Some amine hydrofluorides and amines in organofluorine chemistry

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entitled

SOME AMINE HYDROFLUORIDES AND AMINES IN ORGANOFLUORINE CHEMISTRY

submitted by

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A candidate for the degree of Doctor of Philosophy
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To Mum, Dad and Aly

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MEMORANDUM

The work described in this thesis was carried out in the University of Durham between October 1988 and September 1991. This thesis is the work of the author, except where acknowledged by reference, and has not been submitted for any other degree.

The work has been presented, in part, by the author at:

13th. International Symposium on Fluorine Chemistry, Ruhr Universitat, Bochum, Germany, September 1991.

NOMENCLATURE

Throughout this thesis an "F" in the centre of a ring is used to denote that all bonds are to fluorines.

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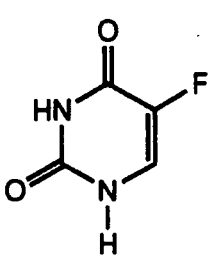
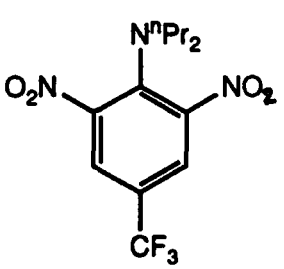
CHAPTER ONE

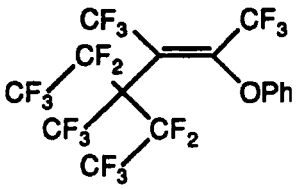
SOURCES OF FLUORIDE ION

1.1 General Introduction

Since the Second World War research in organofluorine chemistry has increased tremendously, motivated by the discovery of the unusual properties acquired by some molecules on the introduction of fluorine or fluorine containing substituents. Organofluorine compounds have been used in an ever widening range of applications from refrigerants to artificial blood (for some examples see Table 1). As fluorine containing compounds are not generally found in nature the area of organofluorine chemistry is entirely synthetic, and consequently a whole new range of reactions and reaction mechanisms may be studied, adding to our understanding of organic chemistry.

Table 1. Some Applications of Fluorine Containing Compounds

Product	Application
CF_2Cl_2	Refrigerant
$CF_3CHBrCl$	Anaesthetic
- $(CF_2)_n$ -	Polymer with high thermal and chemical stability. Non-stick properties
Perfluorodecalin	Artificial blood
Fluoro Steroids	Anti-inflammatory Agent
 5-F-Uracil	Anti-Cancer Drug
 Trifluralin	Plant Protection (Weed control in Maize)



Surfactants

Dyes containing CF_3 groups — Good light fastness

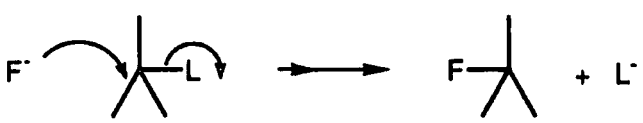
Differences in chemical and physical properties between hydrocarbon and fluorocarbon systems are mainly due to a) electronegativity differences, 2) unshared electron pairs on fluorine, 3) the more easy displacement of fluorine as fluoride ion, and 4) the greater bond strength of C-F.

As the number of fluorine containing compounds grows, the variety of fluorinating reagents and methods of synthesis also increase and intense research continues in the development of new classes of fluorinating reagents. This thesis is concerned with the development of new types of fluoride ion reagent and so a brief description of the chemistry and the sources of fluoride ion follows.

1.2 Formation of C-F Bonds using Fluoride Ion

The introduction of fluorine into an organic molecule via the displacement of a leaving group by fluoride ion in a nucleophilic substitution reaction has proved to be extremely efficient in many cases[1-4]. Nucleophilic substitution reactions at saturated, unsaturated and aromatic carbon are possible and general mechanisms are outlined below[1].

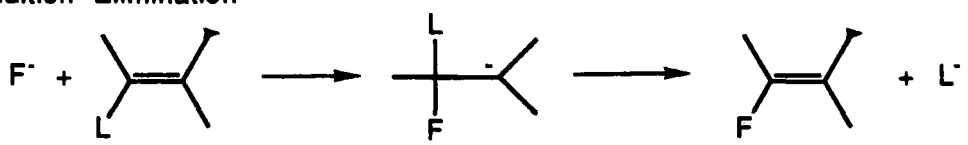
1.2.1 Nucleophilic Substitution at Saturated Carbon



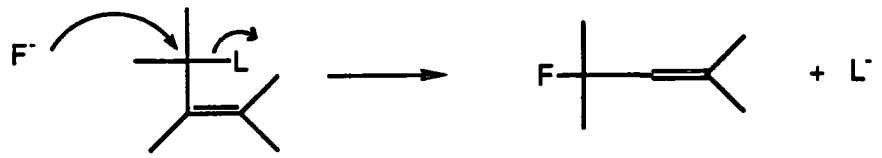
1.2.2 Nucleophilic Substitution Involving Unsaturated Carbon

Three modes of nucleophilic substitution involving fluoride ion can occur in unsaturated systems:-

(i) Addition Elimination

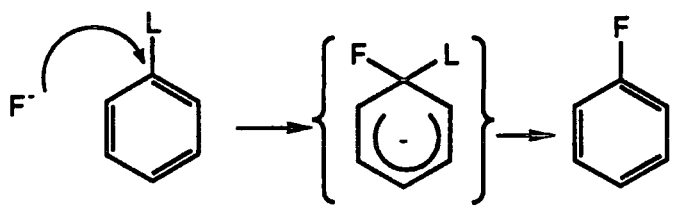


(ii) S_N2



(iii) Substitution with Rearrangement - S_N2'

1.2.3 Nucleophilic Substitution at Aromatic Carbon



Other aspects of fluoride ion chemistry, such as catalysing the oligomerisation of perfluoroalkenes, are discussed at the relevant sections of the following text.

Hence, fluoride ion is a valuable synthetic reagent and a discussion of modern sources of fluoride ion follows.

1.3 Sources of Fluoride Ion

1.3.1 Alkali Metal Fluorides

A general order of reactivity of the alkali metal fluorides is: CsF > KF > NaF, LiF, which may be attributed to the fact that caesium fluoride has the lowest lattice energy. The easy availability of the alkali metal fluorides, KF and CsF, means that these reagents continue to be widely used. However, their low reactivity, low solubility, hygroscopic nature and the harsh reaction conditions required has limited their use in more complex systems. Hence, new sources of fluoride ion, which may introduce fluorine into molecules in greater yield and greater selectivity, continue to be developed. A brief description of the main classes of modern fluoride ion reagents which have been investigated in an attempt to alleviate these problems will be discussed here for completeness, but are reviewed in more detail elsewhere[5].

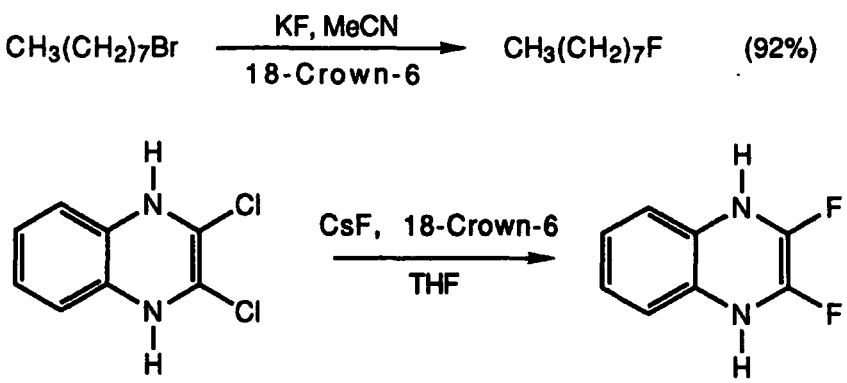
Examples of the use of these modern reagents in synthesis, from the recent literature (1988-1990 where possible), are presented.

The reactivity of the alkali metal fluorides may be improved by either increasing their solubility or by increasing the surface area of the reagent. The following methods have been used to improve the reactivity of the alkali metal fluorides.

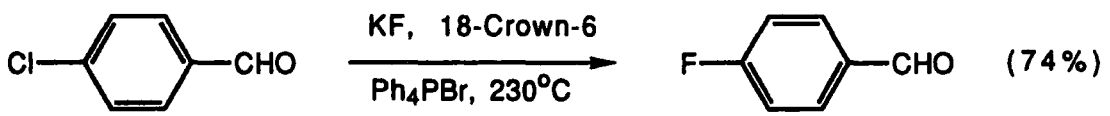
1.3.1.1 Crown Ether Activation

The nucleophilic substitution process is enhanced by the use of a chelating crown ether which selectively complexes with the cation leaving the unsolvated fluoride ion ("naked fluoride") strongly nucleophilic[6]. The addition of a crown ether to KF increases its solubility, thus increasing the concentration of fluoride ion in solution[7]. 18-Crown-6 was found to be the most active catalyst[8] due to its excellent complexing ability with K^+ and Cs^+.

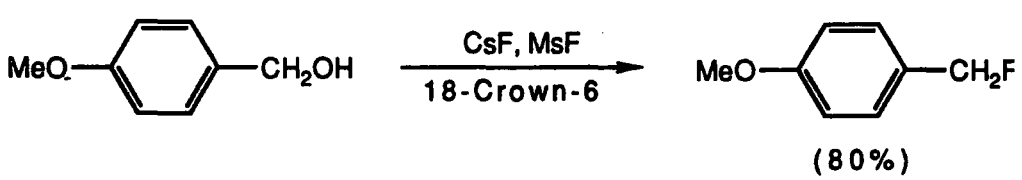
Selected examples of the use of alkali metal fluorides in conjunction with crown ethers are as follows[6,8]:-



KF has been used with a combination of 18-Crown-6 and tetraphenylphosphonium bromide in halex reactions[9].



Primary alcohols are converted to the fluorides by a CsF/18-Crown-6/methanesulphonyl fluoride system[10].



Fluorodestannylation reactions have been performed[11].

1.3.1.2 Phase Transfer Catalysis

The concentration of fluoride ion in the organic phase of a reaction may be increased by using KF in conjunction with a phase transfer catalyst (PTC). Reactions of the following type were studied[12]:-

$$RCl_{(org)} + KF_{(s\ or\ aq)} \xrightarrow{PTC} RF_{(org)} + KCl_{(s\ or\ aq)}$$

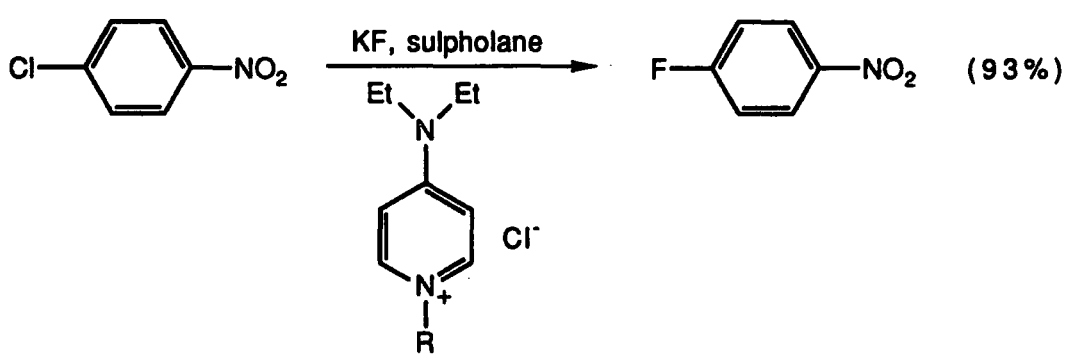
The role of the PTC, usually a tetraalkylammonium halide, may be considered thus:-

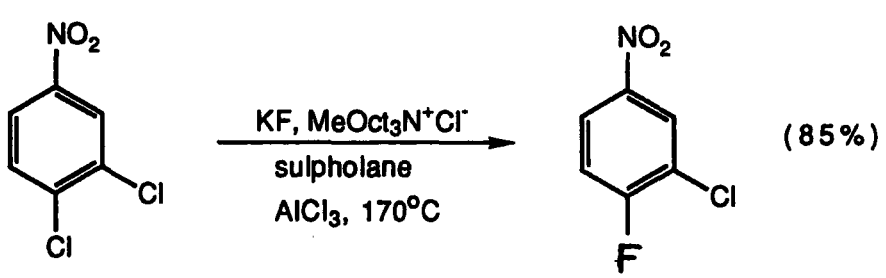
$$KF_{(s\ or\ aq)} + R_4N^+Cl^-_{(org)} \longrightarrow KCl_{(s\ or\ aq)} + R_4N^+F^-_{(org)}$$

Hence, fluoride ion is transferred from the aqueous/solid phase into the organic phase enhancing the reactivity of KF.

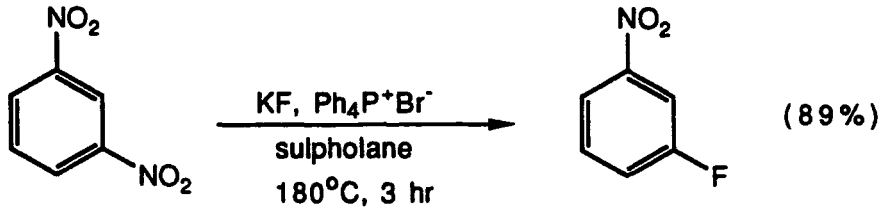
1.3.1.3 Additives to KF

The addition of alkylpyridinium salts[13] and tetraalkylammonium chlorides[14] to KF has been shown to be effective in halogen exchange reactions:-





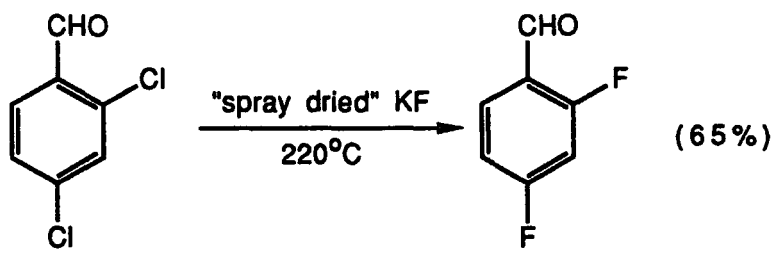
The addition of tetraphenylphosphonium bromide improves the reactivity of KF[15]. Fluorodenitration reactions have been performed using this system[16].



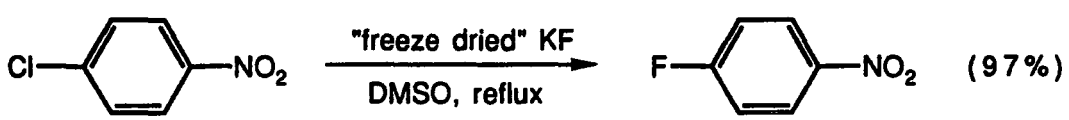
Tetraphenyl phosphonium bromide has been used as an additive supported on a cross-linked styrene/*p*-chloro-methyl styrene copolymer in fluorinations of aromatic chlorides[17].

1.3.1.4 Spray-Dried and Freeze-Dried KF

The surface area of "normal" KF ($0.1 m^2/g$) is much less than that of "spray-dried" KF ($1.3 m^2/g$) and consequently spray-dried KF shows greater reactivity than normal KF[18].

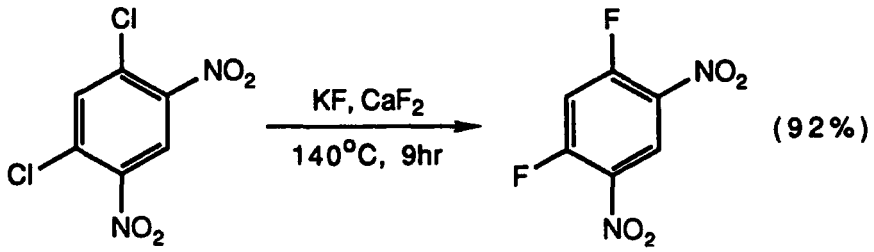


Similarly, "freeze-dried" KF has been investigated, but was originally found to be ineffective for the fluorination of some activated chlorinated compounds[19]. However, renewed interest in this reagent showed that fluorination was possible[20]:-



1.3.1.5 KF on Support Reagents

An alternative to the use of phase transfer catalysis to improve the reactivity of KF is the use of supported reagents which show greater reactivity due to the increased reagent surface area. The reactivity of KF-alumina[21] was seen to be very low due to surface OH-F hydrogen bonding. However, non-surface hydroxylated support materials, such as KF-CaF_2, have been successfully applied as sources of fluoride ion[22,23],as shown below[24].



Inorganic support materials may be surface dehydroxylated prior to use to avoid OH-F interactions[25]. For instance, the surface of alumina is modified by organosilylation of the hydroxyl groups using hexamethyldisilazane. The resultant KF-modified support was used to fluorinate benzyl bromide in 61% yield.

Cross-linked copolymers of divinylbenzene and styrene were used as a support material for KF to good effect. The copolymers contain no surface OH groups and can be synthesized to have specific surface properties[26]:-.

$$PhCOCl \xrightarrow[r.t.,\ 10mins]{KF/polymer} PhCOF \quad (95\%)$$

1.3.1.6 Ion Exchange Resins

Anion exchange resins, such as Amberlite IRA 900 of the form below, have been used as carriers of fluoride ion[27].

$$PhCOCH_2Br \xrightarrow{Amberlite\ F^-} PhCOCH_2F \quad (61\%)$$

The resin may be considered as both a phase transfer catalyst and a support material, acting in the following way:-

$$F^-_{(resin)} + RX \longrightarrow RF + X^-_{(resin)}$$

1.3.2 Alternatives to Alkali Metal Fluorides

Compounds based on elements of Group V (nitrogen, phosphorous) and Group VI (sulphur, selenium) have been studied as sources of fluoride ion and a brief outline of

their use is given here. However, the very hygroscopic nature and high cost of some of these reagents give large grounds for improvement.

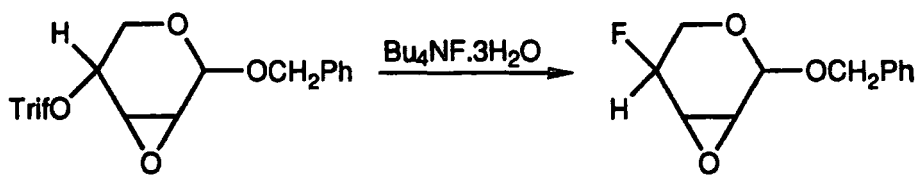
1.3.2.1 Tetraalkyl Ammonium and Phosphonium Salts

Tetraalkylammonium fluorides such as tetrabutylammonium fluoride (TBAF) have received considerable attention over the last few years. "Anhydrous" TBAF is prepared by heating TBAF.$3H_2O$ at 40-45°C under high vacuum for several hours. It must be used immediately due to its hygroscopic nature and has been used in a full range of fluoride ion reactions[28], as shown in Table 2.

Table 2 Reactions using TBAF as source of Fluoride ion

Substrate	Time/hr	Product	Yield/%
CH_2=CH-CH_2Br	0.1	CH_2=CH-CH_2F	85
Ph-CH_2Br	8	Ph-CH_2F	100
$CH_3(CH_2)_7$Br	<1	$CH_3(CH_2)_7$F	48
		CH_2=CH$(CH_2)_5CH_3$	12
		$CH_3(CH_2)_7$OH	40
$CH_3(CH_2)_7$OTos	<1	$CH_3(CH_2)_7$F	98
PhCOCl	<1	PhCOF	81

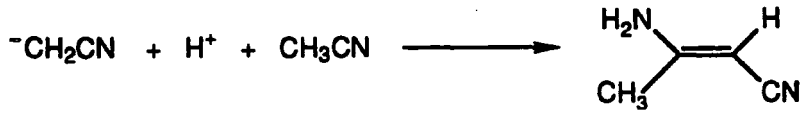
Also, fluorodenitration reactions of aromatic nitro groups have been performed[29] and fluorodeoxy sugars have been prepared from pyranosides[30].



Recently, a method for the preparation of anhydrous and HF_2^- free tetramethylammonium fluoride has been described[31]. $Me_4NF.H_2O$ is first heated under vacuum to remove most of the water and then recrystallised in dry isopropanol as the alcoholate. The solvated alcohol is removed under vacuum at 80°C.

Me_4NF was found to abstract a proton from acetonitrile[32] resulting in the slow formation of HF_2^- and the dimerisation of the acetonitrile:-

$$2F^- + CH_3CN \longrightarrow {}^-CH_2CN + HF_2^-$$



Also, chlorinated solvents such as chloroform undergo halex reactions.

$$CHCl_3 + Me_4NF \longrightarrow CHCl_2F + CHClF_2 + CHF_3 \quad (2:3:1 \text{ Molar Ratio})$$

This shows the remarkable reactivity of the fluoride ion when present as a soluble salt free from HF, HF_2^- and water. Their use in organic synthesis is yet to be investigated but their reactions with solvents may be a problem.

Tetraphenylphosphonium hydrogendifluoride has been used successfully in a variety of halogen exchange reactions[33]. Similarly, tetraamidophosphonium hydrogendifluoride reacts with decyl tosylate and p-chloronitrobenzene to give the corresponding fluorides in 100% and 93% yield respectively[34].

1.3.2.2 Phosphoranes

The salts methyltri-n-butylfluorophosphorane ($(n\text{-}C_4H_9)_3PFCH_3$) and phenyl tetrafluorophosphorane ($C_6H_5PF_4$) have been used in tosyl displacement reactions in the preparation of 2-fluoro alkyl compounds[35].

$$\underset{(-)\text{-}(R)}{C_6H_{13}CH(OTos)CH_3} \xrightarrow{(nC_4H_9)_3PFCH_3} \underset{(+)\text{-}(S)}{C_6H_{13}CHFCH_3} \quad (15\%)$$

1.3.2.3 Amine Hydrofluoride Salts

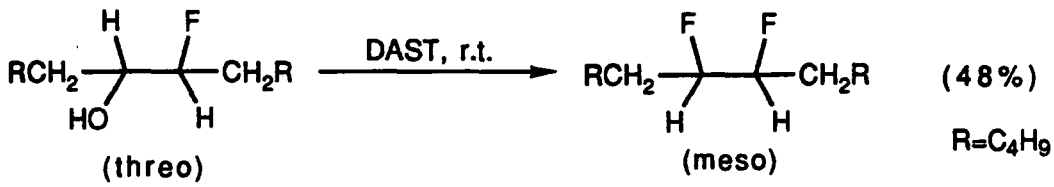
Pyridine/HF mixtures and Triethylamine Trishydrofluoride have been used in a variety of fluorination reactions and will be discussed in detail in sections 1.5 and 1.6.

1.3.2.4 Diethylaminosulphur Trifluoride (DAST) and Tris(dimethylamino)-sulphonium Difluorotrimethylsilicate (TAS-F)

DAST is prepared by reacting diethylaminotrimethylsilane with sulphur tetrafluoride[36]:-

$$Et_2NSi(CH_3)_3 + SF_4 \longrightarrow \underset{\text{DAST}}{Et_2NSF_3} + SiF(CH_3)_3$$

The main synthetic use for DAST is converting alcohols to fluorides[37] and carbonyl groups to geminal difluorides.

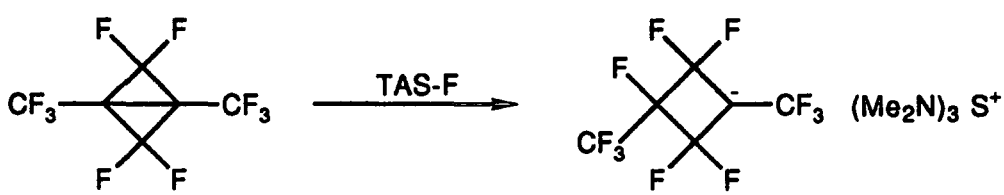


However, DAST is thermally unstable and recently the more stable morpholino sulphur trifluoride has been recommended for fluorinations of alcohols[38].

The more reactive fluoride ion source, TAS-F, is prepared by the reaction of dimethylaminosulphurdifluoride with dimethylaminotrimethylsilane:-

$$(Me_2N)_2SF_2 + Me_2NSi(CH_3)_3 \longrightarrow \underset{\text{TAS-F}}{[(Me_2N)_3S]^+[(CH_3)_3\ SiF_2]^-}$$

TAS-F readily converts even unreactive halides to fluorides under very mild conditions and has been used to form stable perfluorinated carbanion salts[39], in a fluoride promoted C-C bond cleavage reaction.



A comprehensive review on the use and reactions of DAST, TAS-F and related reagents has been published recently[36].

1.3.2.5 Tris(morpholino)selenonium Fluoride

The reaction of $RSiMe_3$ (R=morpholino) with selenium tetrafluoride gives tris(morpholino) selenonium fluoride, which has been used in a few fluorination reactions[40].

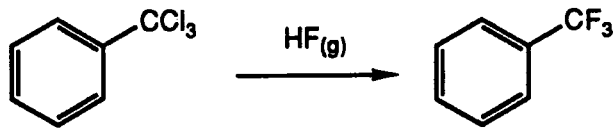
$$PhSO_2Cl \xrightarrow{R_3Se^+F^-} PhSO_2F \quad (82\%)$$

$$Ph_2POCl \xrightarrow{R_3Se^+F^-} Ph_2POF \quad (76\%)$$

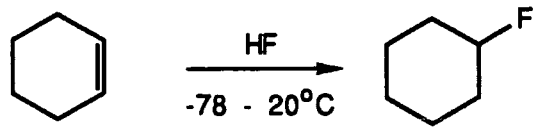
1.4 Hydrogen Fluoride as a Fluorinating Agent

1.4.1 Classical Processes

Anhydrous Hydrogen fluoride (HF) is one of the least expensive fluorinating agents and has been used in a variety of halex and electrophilic addition reactions[2]:-



(95%)



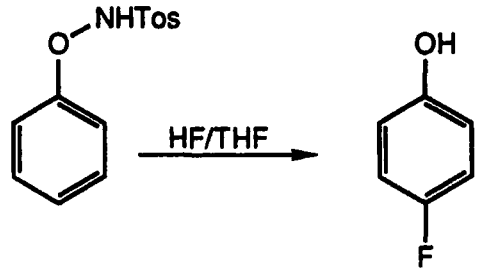
(70%)

However, most reactions using HF are performed under pressure or in the vapour phase due to its low boiling point (19.6°C). The corrosive and harmful nature of HF requires rigorous safety precautions and specialist equipment.

1.4.2 HF used in Conjunction with Lewis Base Co-solvents

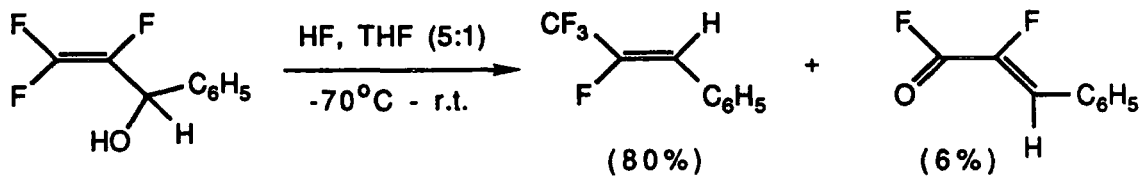
To overcome the high volatility of HF several authors have studied complexes of HF with various Lewis bases as co-solvents.

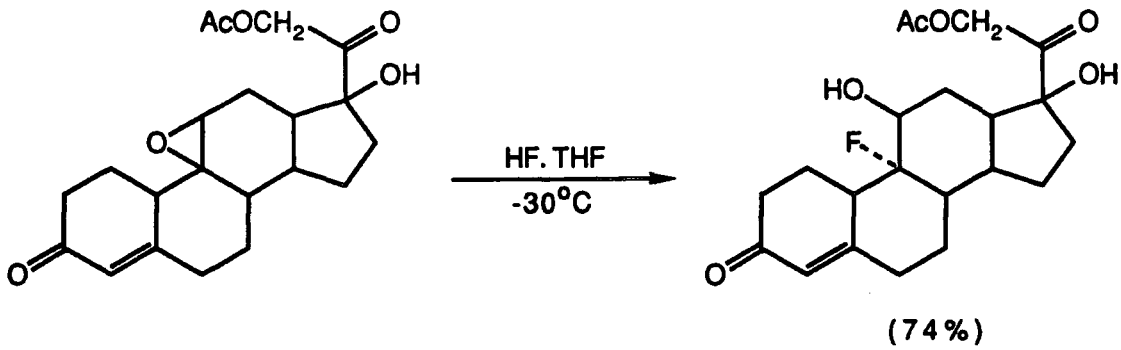
Stable solutions of HF in amides[41] (formation of amide/HF complexes), carbamic acids and esters[42] (hydrofluorination of epoxide rings in steroids), trialkylphosphines[43] (formation of triethyl and triphenyl phosphine/HF complexes) and tetrahydrofuran[44] (ring opening hydrofluorination of epoxides in steroids) were investigated. There has been renewed interest in THF/HF solutions[45,46], the solution formed being a more effective source of fluoride ion than HF and also more acidic than pyridine/HF. Examples of the use of HF/THF solutions are below[44-46]:-



(38%)

- -via an umpolung strategy involving the phenoxonium ion as an intermediate





(74%)

It was not until the introduction of amine/HF complexes, in particular Pyridine/HF, that a general fluorinating agent using HF coupled to a base became widely accepted. These reagents are discussed in detail in the next section.

1.5 Pyridine Poly(Hydrogen Fluoride) - Olah's Reagent

The use of Lewis Base/HF solutions as fluorinating reagents became widely accepted upon the introduction of Pyridine/HF solutions by Olah[47], although pyridine/HF solutions had been used previously in epoxide ring opening hydrofluorination reactions of steroids by Bergstrom[48].

Pyridine forms stable solutions with anhydrous HF. The solution generally used consists of about 9 equivalents of HF to 1 of pyridine (70% w/w HF, 30% w/w pyridine) and is stable to 55°C.

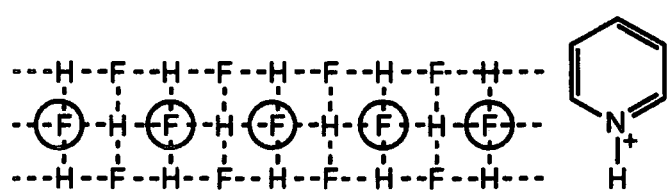
Pyridinium Fluoride can be prepared by the reaction of formyl fluoride with pyridine through the decarbonylation of the intermediate N-formylpyridinium fluoride[49].

$$C_6H_5N + HCOF \longrightarrow (C_6H_5N.H)^+F^- \longrightarrow C_6H_5N.HF + CO$$

However, no spectral data appears in the publication.

1.5.1 Structure of Pyridinium Poly(Hydrogen Fluoride)

The ^1H n.m.r. spectrum for pyridinium poly(hydrogen fluoride) shows a typical pattern for pyridinium ring protons but the ^{19}F n.m.r. spectrum at -60°C shows a quintet (J_{HF}=120 Hz) at 188.1ppm, indicating the presence of a polyhydrogen fluoride species in which each fluorine atom is surrounded by four protons:-



It is unclear whether any exchange occurs between the pyridinium cation and the HF matrix and we would also expect to see n.m.r. peaks due to species such as HF_2^-. The presence of pyridinium hydrogen difluoride in pyridinium poly(hydrogen fluoride) solutions was shown in low temperature X-ray crystallographic work by Mootz[50] (see below). Perhaps, as $PyH^+HF_2^-$ and PyH^+F^- have melting points of -1°C and -31°C respectively, from differential thermal analysis, these species were not seen in the n.m.r. spectrum as they are solid at -60°C (No n.m.r. solvent is indicated in the publication). Hence, at -60°C the only species present in pyridinium poly(hydrogen

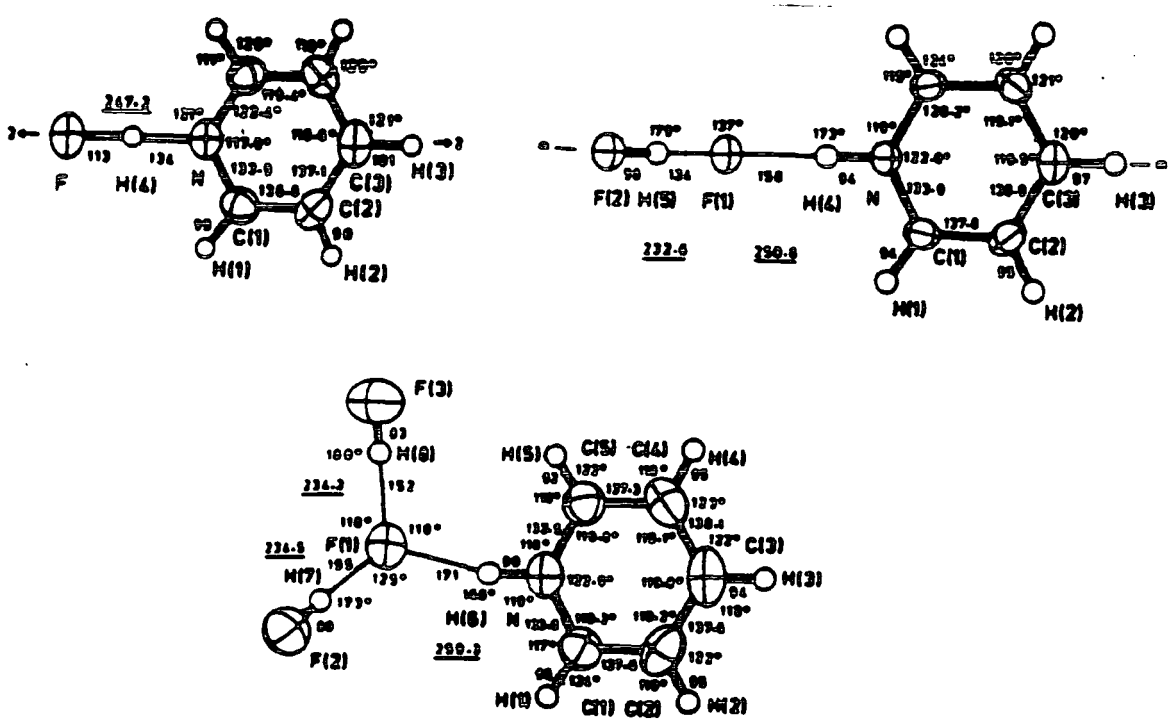
fluoride)solutions are Pyridine.5HF and higher homologues which give rise to the observed quintet.

The pyridine/HF mixture was studied by differential thermal analysis and X-ray crystallography by Mootz[50], who identified 8 intermediary compounds, $C_5H_5N.nHF$ (n=1-8), with melting points between -1 and -124°C. X-ray structures of complexes n=1-4 were obtained. See Fig. 1 for structures of n=1,2.

The following points can be noted from the structures reported:-

1) In complex $C_6H_5N.HF$ (n=1) the hydrogen atom in the NHF hydrogen bond is found much closer to the fluorine atom than to the nitrogen atom suggesting that the hydrogen bond is of the type F-H..N rather than F..H-N, i.e. the base is not protonated by the

Fig 1 X-ray Crystal Structures of Pyridine.nHF Complexes



The structures of $C_5H_5N.nHF$ with n=1, 2, and 3. One formula unit each with interatomic distances (pm) and angles. The N-F and F-F distances in the hydrogen bonds are underlined.

acid. This is the first hydrogen bond of this type reported and the shortest between nitrogen and fluorine.

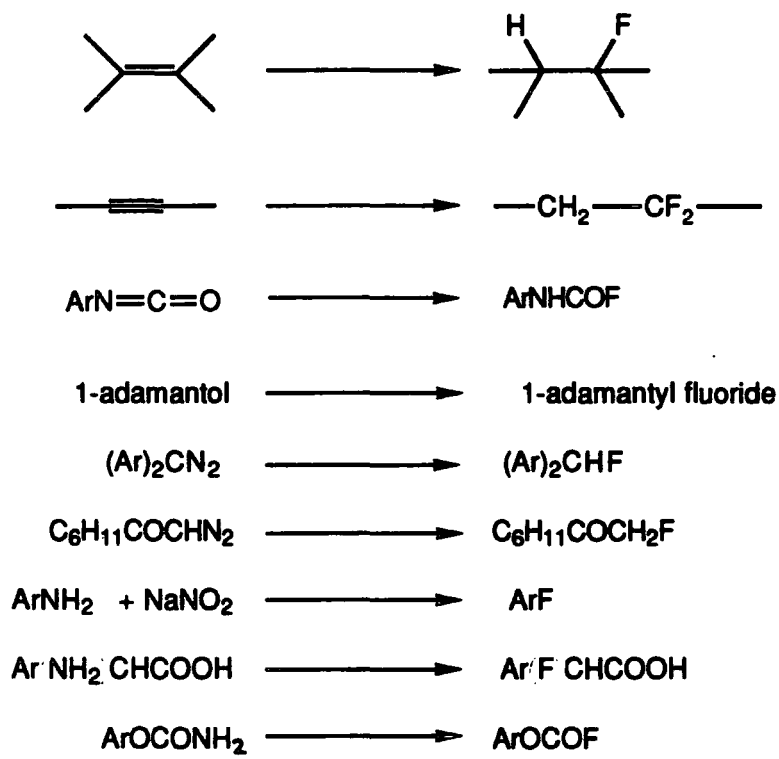
2) Complex $C_6H_5N.2HF$ (n=2), can be reformulated as $C_5H_5NH^+HF_2^-$, pyridinium hydrogendifluoride, with the H atom in an off-centre position.

3) Ionic formulae are also true of the higher pyridine/HF complexes, e.g $C_5H_5NH^+H_2F_3^-$ (n=3), and $C_5H_5NH^+H_3F_4^-$ (n=4).

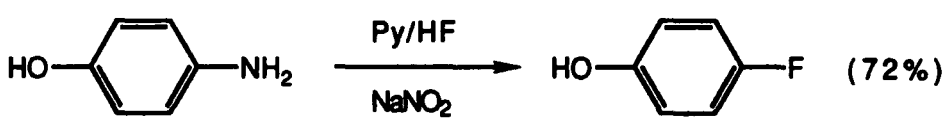
1.5.2 Reactions of Pyridinium poly(hydrogen fluoride)

Pyridinium poly(hydrogen fluoride) was found to be an effective fluorinating agent for various additions to alkenes and alkynes, for deaminative and dediazonative halogenation reactions, for fluorine substitution of hydroxyl groups and halogen exchange reactions[47, 51], as summarised in Table 3.

Table 3. Reactions Performed Using Pyridinium Poly(Hydrogen Fluoride)



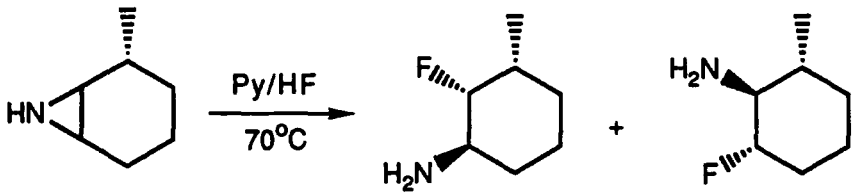
Dediazonative fluorinations of *p*-aminophenols have been performed recently[52,53].

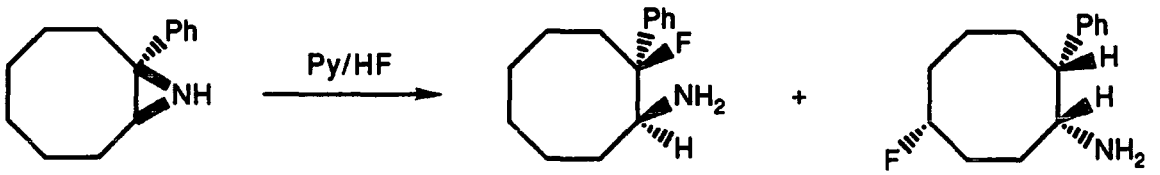


More recently, pyridinium poly(hydrogen fluoride) has been used in ring opening hydrofluorination reactions of aziridines[54,55], azabicycloalkane[56] and cyclopropane[57] ring systems, as summarised in Table 4.

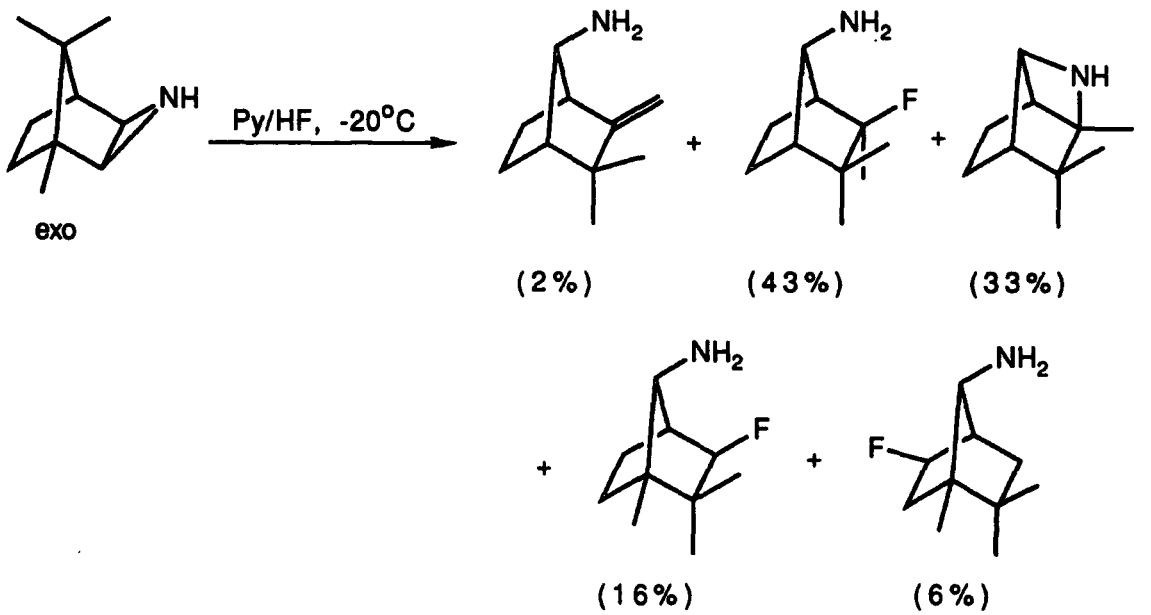
Table 4. Ring Opening Hydrofluorination Reactions using Pyridine Poly(Hydrogen Fluoride)

Aziridines[54, 55]

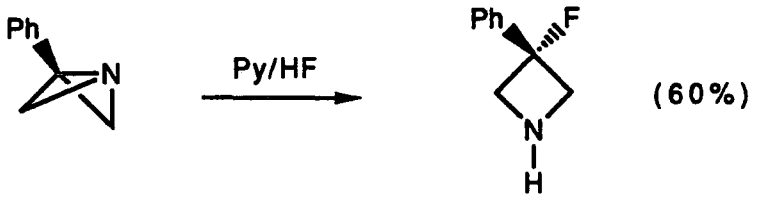


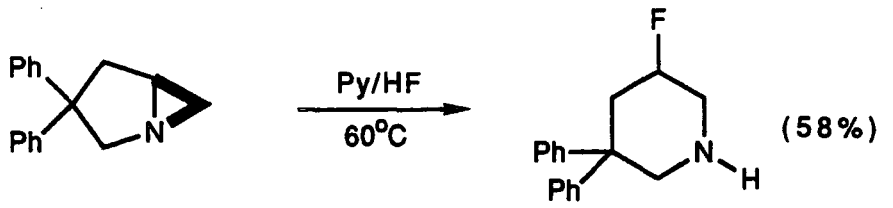


Ring opening hydrofluorination of 3-aza-1,8,8-trimethyl-tricyclo [5.2.1.$0^{2,4}$] octane leads to a variety of products[58].

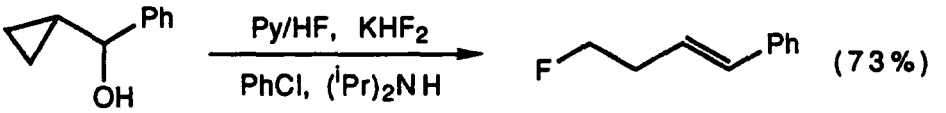


Azabicycloalkanes[56]





Cyclopropanes[57]



Poly-4-vinyl pyridinium poly(hydrogen fluoride), a solid pyridine poly(hydrogen fluoride) has been used in hydrofluorinations and bromofluorinations of alkenes[59].

Most recent publications dealing with Amine/HF systems utilise $Et_3N.3HF$ as the fluorinating agents and it is to these systems that we now turn.

1.6 Amine Hydrofluoride Salts

1.6.1 Introduction

Amine hydrofluoride salts have been known since 1879 when Beamer and Clarke[60] prepared white, crystalline aniline hydrofluoride. A comprehensive study of amine hydrofluorides was carried out by Berliner and Mann[61], who prepared hydrofluoride salts of aromatic, primary, secondary and tertiary amines. They suggested a structure of base.4HF after titration with sodium hydroxide.

The use of amine hydrofluorides as fluorinating agents remained limited to steroids[48] until Franz[62] prepared a series of amine trishydrofluorides, such as $Et_3N.3HF$. These hydrofluoride complexes were found to be stable, distillable under vacuum, could be handled without hazard and did not corrode borosilicate glass. Since then $Et_3N.3HF$ and other amine trishydrofluorides have been used in a range of fluorination reactions (see Section 1.6.3), similar to those carried out using Olah's reagent (Section 1.5.2). Spectroscopic studies of these systems are discussed here followed by their use in synthesis.

1.6.2 Spectroscopy of Amine.HF Systems

The structure of $R_3N.nHF$ systems (R = alkyl) is not very well understood. Unlike the case of pyridine/HF, no crystallographic data of the complexes present in $R_3N.nHF$ mixtures has been published. N.m.r. spectroscopy has been used to investigate these systems in solution and so a discussion of the n.m.r. and also the i.r. of $R_3N.nHF$ and related systems, such as F^-, HF and HF_2^- containing species, follows.

1.6.2.1 Nuclear Magnetic Resonance Spectroscopy

Before we can discuss the n.m.r. spectra of $R_3N.HF$ salts, we need to review the literature data concerning the species that may be involved in solutions of these salts i.e. F^-, HF and HF_2^-

The literature covering the n.m.r. of fluoride ion in solution is very confused; different authors quote different signs for upfield and downfield, references, solvents and concentrations, all of which affect the fluorine shift.The situation was improved on the publication of a review by Hudlicky[63], who repeated some of the n.m.r. experiments.

The following table is taken from that review[63], and shows the variation of fluorine shift for each species as measured by various authors.

Table 5 N.M.R. shifts of F^-, HF and HF_2^- . Chemical shifts are given in negative values of ppm upfield of $CFCl_3$.

Species	F^-	HF	HF_2^-
KF(aq)	-124.8		
KF(aq)	-120.2		
KF(aq)	-117.5		
Pr_4NF	-114.6		
HF(aq)		-204.0	
HF(anhyd)		-196.0	
Bu_4NHF_2			-144.0
Pr_4NHF_2			-149.4

From this table we can make the general assumption that fluoride ion has a shift between -114-125ppm; HF between -160-200ppm and HF_2^- between -144-149ppm.

However, we must note that the shifts for fluoride ion were measured in either aqueous or aqueous organic solutions, and so are not really due to fluoride ion alone because of hydrogen bonding between F^- and water. This was confirmed by Christe[64], who has very recently prepared anhydrous tetramethylammonium fluoride (Me_4NF). ^{19}F n.m.r. of this compound in solution (MeCN) showed a singlet at -73.2ppm, significantly shifted from other values for F^- by about 40ppm! However, Me_4NF was found to react with the acetonitrile[32] to form HF_2^- (section 1.3.2.1), so the fluoride ion is still not "naked" but must hydrogen bond with acetonitrile as F^- is such a strong base.

Christe concluded that the large upfield shifts noted for fluoride ion in aqueous solution was probably due to the presence of HF_2^-, HF or both; the shift of the singlet, broadened by the rapid exchange between these species, depending on the relative molar amounts of each species.

The lowfield shift for anhydrous Me_4NF is supported by solid state measurements on CsF, by Clark[65]. On reducing the water content in CsF samples a downfield shift occurs to the limiting anhydrous CsF case where the shift is -79ppm.

Hence, the amount of water present seems to be a controlling factor on the F^- chemical shift.

Intuitively, we would predict that on going from HF to F^- , thus increasing the electron density on F, an upfield shift would occur, such as in the case of ^{13}C NMR (e.g. an upfield shift is observed on negatively charged carbon atoms in stable fluorinated carbanions[66]). However in this case, on going from HF to F^-, a downfield shift is seen. The change in electron density on F may be negligible due to the small size of the HF molecule.

The shift of F^- in Me_4NF is also dependent on the solvent (e.g. -136.7 in ethanol, -97 in dichloromethane)[64]. This could be attributed to the strength of the hydrogen bonding between the solvent and fluoride ion, but the work of Symons[67] showed that the trends in F^- shift (^{19}F NMR) in a series of different solvents was similar to the trends in the shifts of Xenon (^{129}Xe NMR), as compared to ^{35}Cl NMR data. Xenon would not be expected to hydrogen bond with the solvents, so if the trends in chemical shifts of Xe and F^- are analogous then the controlling factor behind the shifts must be the same, but not the strength of the hydrogen bonding with the solvent. However, the factors which effect the shifts in the Xe case are not stated. The ease of solvation of F^- may be an important factor.

However as a general rule we may observe that F^-, HF and HF_2^- come in the following shift ranges:-

F^- : -75ppm (anhydrous, ion-pair, e.g. $Me_4N^+F^-$)
F^- : -114-125ppm (in presence of HF and HF_2^-, broad due to exchange)
HF_2^- : -144-149ppm (J_{HF}=122 Hz)
HF : -160-200ppm (broad due to exchange)

1.6.2.1.1 $R_3N.nHF$ Systems

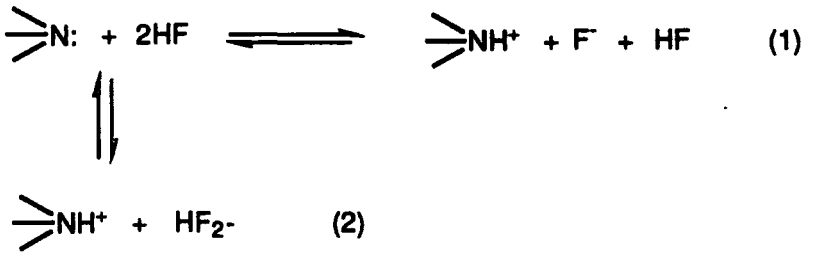
The ^1H and ^{19}F n.m.r. of $R_3N.nHF$ (n=1,1.5,2) systems were studied by Cousseau[68] at room temperature and at -80°C, (Table 6).

Table 6 ^{19}F N.M.R. Spectra of $R_3N.nHF$ Systems

Chemical shifts are quoted as negative values upfield of $CFCl_3$

	Room Temperature	-80°C	
		$\delta_F(F^-)$	$\delta_F(HF_2^-)$
$Et_3N.HF$	-150.5	-123.6	-152.0 (J_{HF}=138Hz)
$Et_3N.1.5HF$	-153.0	not observed	-151.7 (J_{HF}=138Hz)
$Et_3N.2HF$	-158.0		
$Bu_3N.HF$	-151.2	-125.3	-152.0 (J_{HF}=138Hz)
$Bu_3N.2HF$	-159.2		

Hence, we may consider that amine.HF systems are a series of equilibria in solution:-



These assumptions agree with the observed singlet seen in the ^{19}F spectrum at room temperature caused by fast proton and fluorine exchange:-

$$HF + F^- \rightleftharpoons F^- + HF \qquad (3)$$

$$HF + HF_2^- \rightleftharpoons HF_2^- + HF \qquad (4)$$

So, in compounds with no "free HF", i.e. $R_3N.HF$, we see signals due to F^- and HF_2^- as the rates of exchanges (3) and (4) are slowed down due to excess amine. Cousseau concluded that $Bu_3N.HF$ exists in the ionic forms in solution which give rise to both F^- and HF_2^- signals.

Apart from the low temperature n.m.r. of Olah on pyridine/HF systems[47] (no F^- or HF_2^- observed), this appears to be the only n.m.r. study performed on amine.HF complexes.

1.6.2.2 Infra Red Spectroscopy

A short discussion of the infra red data concerning HF and HF_2^- systems appears here, as we need to ascertain later whether Amine.HF salts contain these species.

1.6.2.2.1 Hydrogen Fluoride

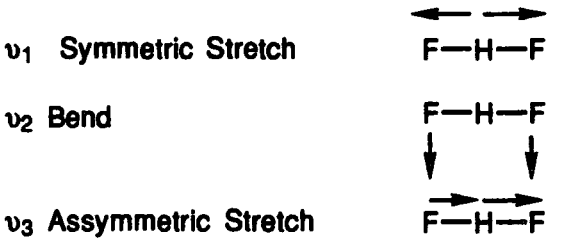
The i.r. spectrum of hydrogen fluoride in the gas phase as well as in solution (CCl_4) was measured[69] and the absorption band found to be at 2.61μ = 3820cm^{-1}.

1.6.2.2.2 Hydrogen Difluoride HF_2^-

The HF_2^- anion, a linear triatomic species, can exist either as a symmetrical (centred H) or an asymmetrical (non-centred H) species, as reviewed by Emsley[70]. Most difluoride species have a centred H, e.g. KHF_2, as shown by X-ray crystallography and i.r. spectroscopy[71,72]. The very short R(F...F) distance was measured to be 225pm. However, not all crystals have a perfectly centred HF_2^- anion. p-Toluidinium hydrogendifluoride forms a secondary hydrogen bond (N-H..F-H-F) which displaces the proton from the central position[73].

The i.r. absorptions for both symmetrical and asymmetrical difluoride anions are shown in Table 7, data from ref. 70.

Table 7. Infra Red absorptions for Hydrogen Difluoride Species



	Geometry	ν_1	ν_2	ν_3
KHF_2	centred	inactive	1225, 1274	1450
Pr_4NHF_2	centred	inactive	1255, 1315	1900
p-Me-C_6H_4-$NH_3^+HF_2^-$	non-centred	450	1080, 1230	1740

All absorptions measured in cm^{-1}.

If the difluoride ion is centred ν_1 is i.r. inactive. The doublet observed for ν_2 in KHF_2 is due to lattice energy effects lifting the degeneracy of this mode, not due to the

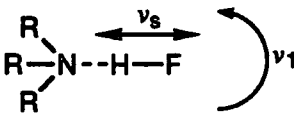
HF_2^- being asymmetric. In asymmetric HF_2^-, the doublet has a separation of $150cm^{-1}$, as in the case of p-toluidinium hydrogendifluoride.

1.6.2.2.3 Trialkylamine Hydrogen Fluoride Systems

The IR spectra of $Me_3N.nHF$ and $Et_3N.nHF$ complexes in solid argon matrices at 10K were measured by Andrews[74]. Fundamental vibration modes for both the 1:1 and 1:2 complexes were measured for both systems.

The vibrational modes for $R_3N.HF$ and $R_3N.2HF$ and the measured absorptions for each system are as follows:-

1:1 Complex



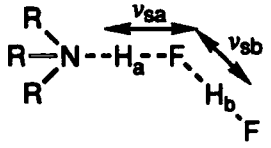
ν_s - HF fundamental stretching vibration

ν_1 - HF librational motion

	ν_s / cm^{-1}	ν_1 / cm^{-1}
$Me_3N.HF$	2589	1030
$Et_3N.HF$	2527	-

The trimethylamine HF complex also shows two distinct perturbated C-N stretching modes.

1:2 Complex



ν_{sa} - H-F stretching mode for H_a-F

ν_{sb} - H-F mode between H_b and fluorine in H_aF

	ν_{sa} / cm^{-1}	ν_{sb} / cm^{-1}
$Me_3N.2HF$	1870	2548
$Et_3N.2HF$	1889	-

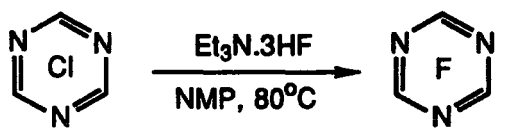
In general the 1:2 complexes were characterised by a strong band near the $1900cm^{-1}$ region of "shared" proton vibrations. The vibrational spectra suggest that H_a is shared between N and the inside F. H_b-F is lengthened but H_b is too close to the terminal F for F..H-F to be considered as an asymmetric difluoride ion.

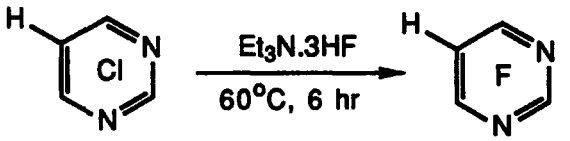
1.6.3 Reactions of Amine Hydrofluorides as Fluorinating Agents

Amine.HF systems, usually $Et_3N.3HF$, have been used to carry out a range of fluorination reactions similar to those performed with pyridine/HF. A comprehensive review of the reactions involving $Et_3N.3HF$, $iPr_2NH.3HF$ and $Me_3N.2HF$ as fluorinating agents is discussed here. Halex, halofluorination, sulphenylation fluorination, ring opening hydrofluorination and oxidative fluorination reactions are presented.

1.6.3.1 Halogen Exchange Reactions (Halex)

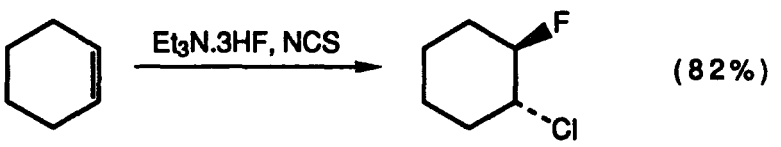
Franz used $Et_3N.3HF$ to prepare fluoroacetone, cyanuric fluoride, difluorophosgene, oxalyl fluoride, and sulphur tetrafluoride[62]. Other fluorinations of activated, chlorinated heterocycles have been performed[75].

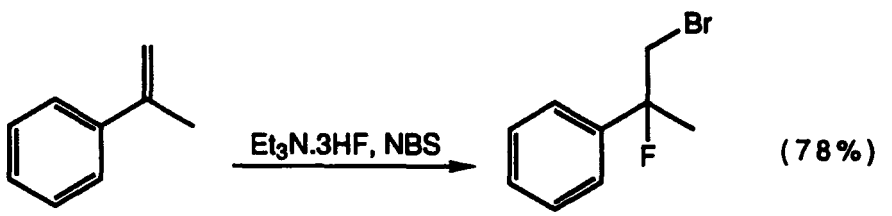




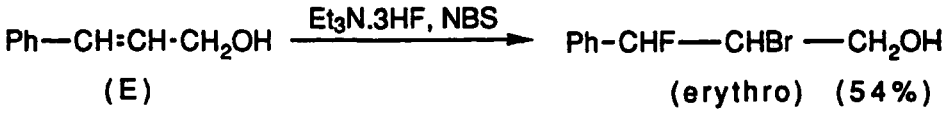
1.6.3.2 Halofluorination

$Et_3N.3HF$ used in conjunction with N-halosuccinimides is a useful reagent for the halofluorination of alkenes[76]. The reactions are stereospecifically anti-additions and for unsymmetrical alkenes the orientation of addition follows Markownikoff's rule.

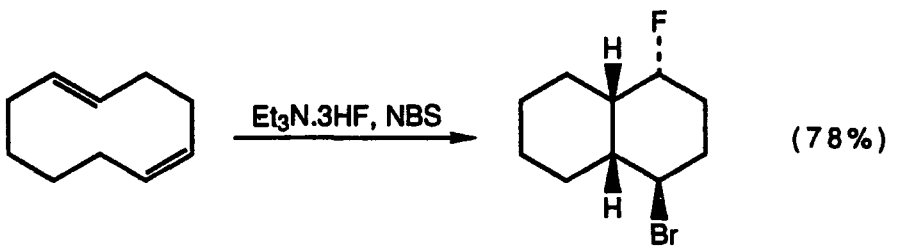




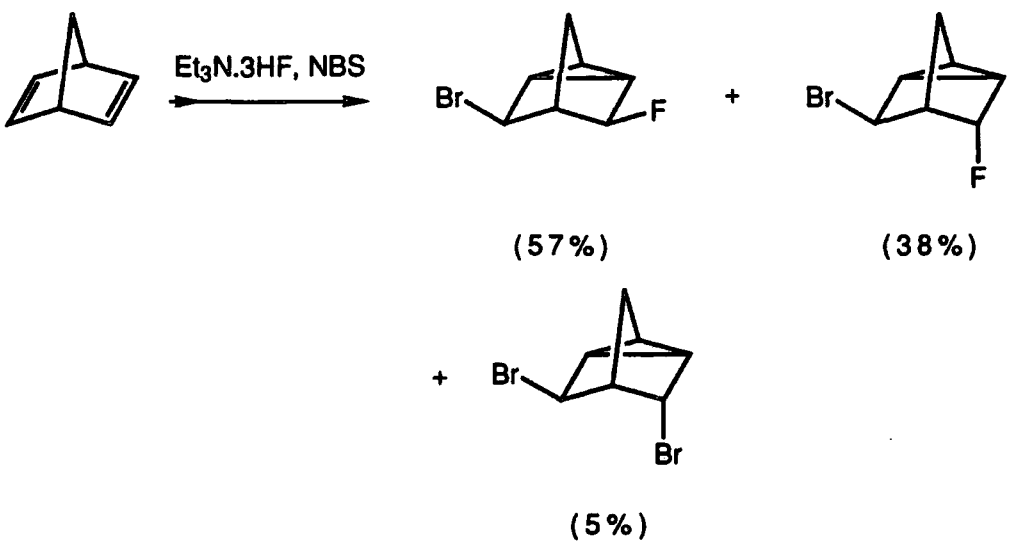
Similarly, bromofluorinations of allylic alcohols have been achieved[77].



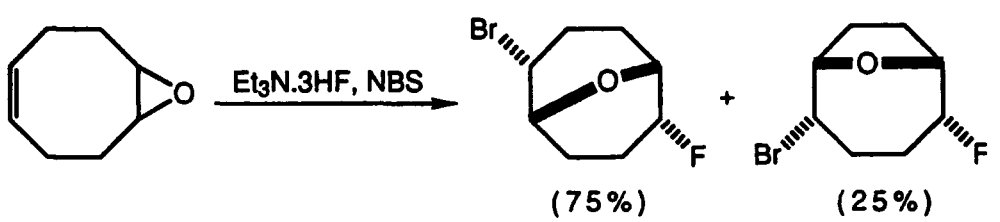
In halofluorinations of cyclic dienes, such as cyclodeca-1,5-diene, transannular π-participation of the second double bond is observed[78].



The same effect is seen in the halofluorination of norbornadiene where a variety of products are obtained[79].

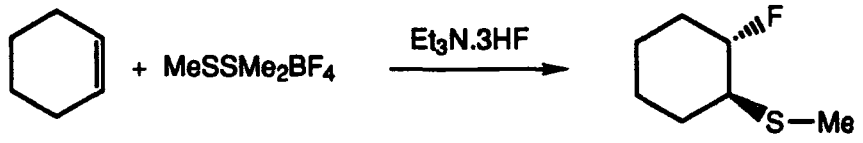


Similarly, transannular oxygen participation is seen in the halofluorination of 9-oxabicyclo[6.1.0]non-4-ene[80].



1.6.3.3 Sulphenylation Fluorination

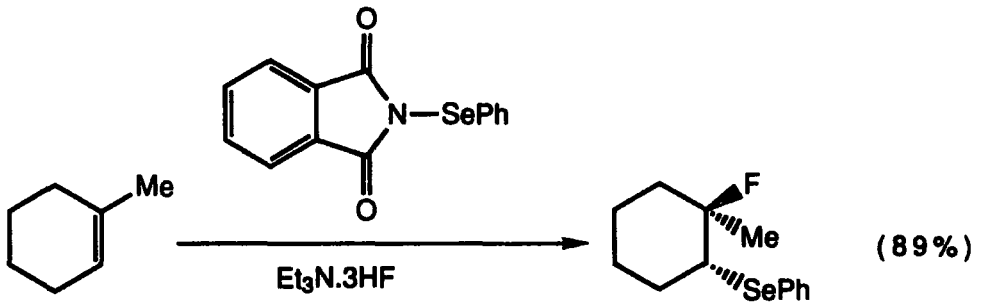
Stereoselective sulphenylation fluorination can be carried out using $(MeSSMe_2)^+ BF_4^-$ with $Et_3N.3HF$ to form β-fluoro thio(methyl)ethers[81, 82].



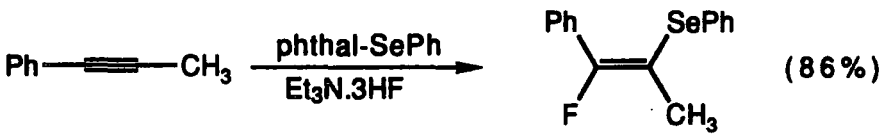
An alternative method of synthesizing β-fluoro thioethers is by first forming the episulphonium chloride by addition of phenylsulphur chloride to the alkene followed by ring cleavage by the fluorinating agent[83].

1.6.3.4 Phenylselenofluorination

β-phenylselenofluorides may be synthesized by the reaction of N-phenylselenophthalimide with alkenes in the presence of $Et_3N.3HF$ in a one-pot reaction[84].



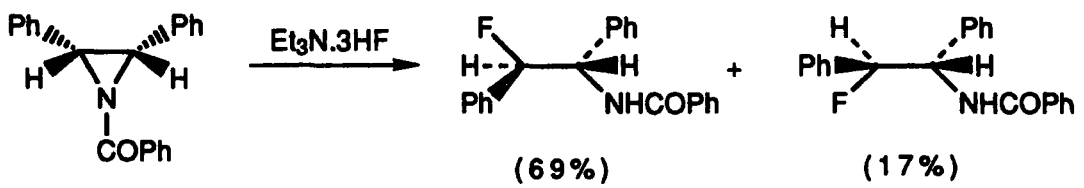
Similar reactions are seen with alkynes[85].



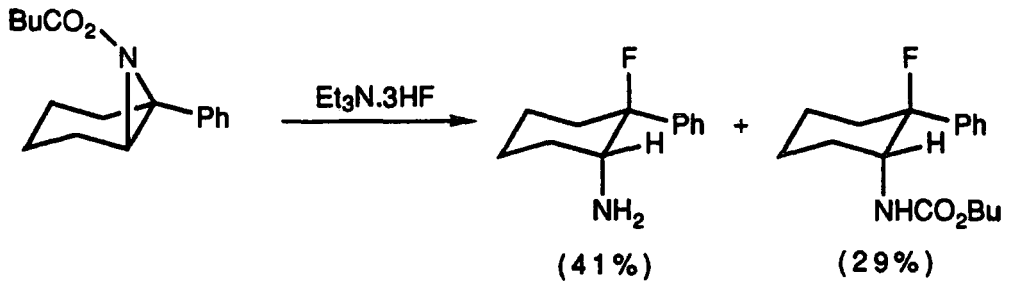
1.6.3.5 Ring Opening Reactions

1.6.3.5.1 Aziridines

α,β-fluoroamines may be prepared by the ring opening of aziridines[86].

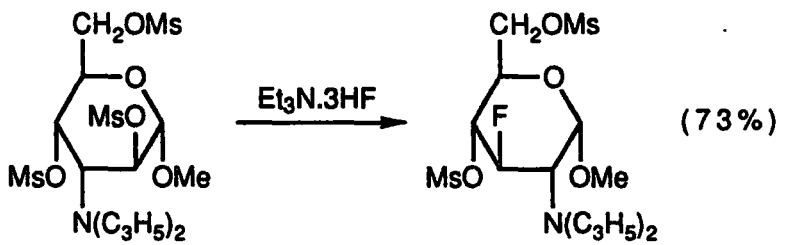


The stereochemical course of the reaction depends on the relative stabilities of the aziridinium ion and the open carbonium ion and the nature of the fluorinating agent (acidity and nucleophilicity). In cyclic systems trans-fluoroamines were obtained by the reaction of N-activated aziridines with $Et_3N.3HF$, whereas the cis compound is obtained with Olah's reagent[86].



1.6.3.5.2 Aziridinium Ion

Fluorodeoxyglucopyranosides have been prepared from altropyranosides bearing N,N-diallylamine and mesylate groups in a trans configuration[87, 88].

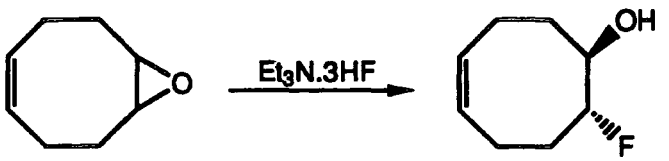


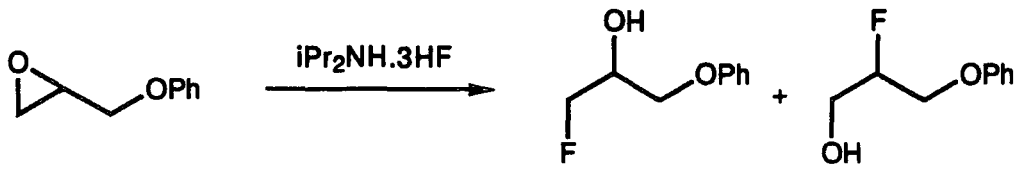
Neighbouring group participation by the diallylamino group produces the aziridinium ion which is ring opened by fluoride ion resulting in a 1,2 shift of the nitrogen atom. The diallylamino group is then reduced using hydrogen on a palladium catalyst. Similar reactions have been carried out using this methodology[89, 90].

Triflate groups may be replaced by fluorine in carbohydrate systems using this idea[91].

1.6.3.5.3 Epoxides

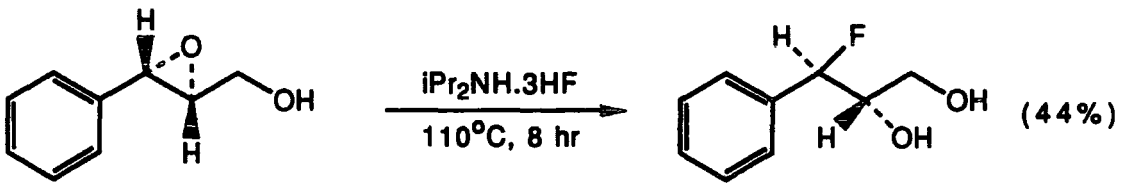
Epoxide ring systems are regioselectively opened with amine.HF complexes to give the corresponding trans-addition products[92, 93].

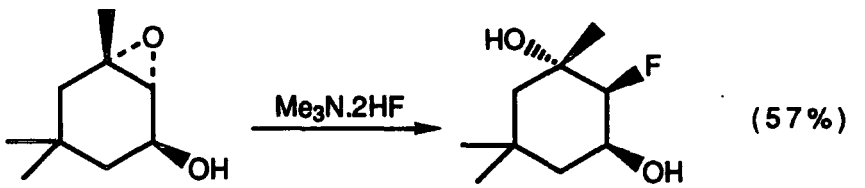




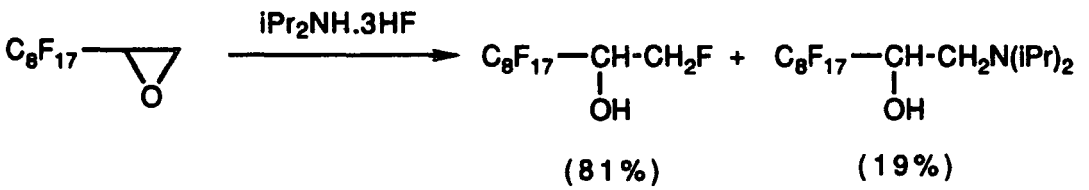
15:1 (75%)

Optically active α,β-fluoroalcohols may be prepared from the corresponding optically active epoxide[94-96].



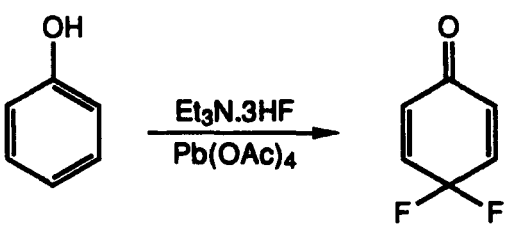


Fluoroalkyl epoxides give similar products[97].



1.6.3.6 Oxidative Fluorinations

Phenols may be oxidatively fluorinated at the anode to form difluorocyclohexadienones using $Et_3N.3HF$ with lead tetra-acetate[98].



1.6.3.7 Other Systems

Mixtures of melamine/HF have been used in hydrofluorination reactions of alkenes[99, 100] (e.g. cyclohexene gives fluorocyclohexane in 98% yield). Recently, amine.HF systems have been used as catalysts in conjunction with chromium chloride impregnated support materials in the fluorination of carbon tetrachloride by HF to give a mixture of chlorofluorocarbons[101].

Since the writing of this chapter, a review covering a similar subject area has been published[102]. This review concentrates on the use of the pyridine/HF system and is not comprehensive with respect to the trialkylamine hydrofluoride systems. Also, no discussion of the structures of hydrofluoride salts is present.

CHAPTER TWO

1,8-Bis(dimethylamino)naphthalene Hydrofluoride (PS/HF) as a Potential Source of Soluble Fluoride Ion

2.1 Introduction

The types of fluoride ion reagent that are currently available have been discussed in Chapter One. However, there remains a need for a source of soluble fluoride ion, as reagents such as the alkali metal fluorides are largely insoluble in organic solvents which limits their use in organic synthesis.

One obvious possibility is the use of amine.HF complexes, as reagents such as $Et_3N.3HF$ have already been used successfully as fluorinating reagents. Thus, we decided to investigate whether amine.HF systems could act as fluoride ion donors in solution.

However, problems associated with amine.HF complexes in solution are that an equilibrium exists between amine.HF, free HF, HF_2^- and the free amine, and the position of equilibrium will affect the reactivity of the amine.HF complex as fluoride ion donors. Factors which may affect this equilibrium are the base strength and the size of the hydrocarbon moiety of the amines. We therefore wanted to determine whether the proton of HF could be effectively "buried" in the hydrocarbon part of the amine thus leaving the fluoride ion free to react with organic substrates.

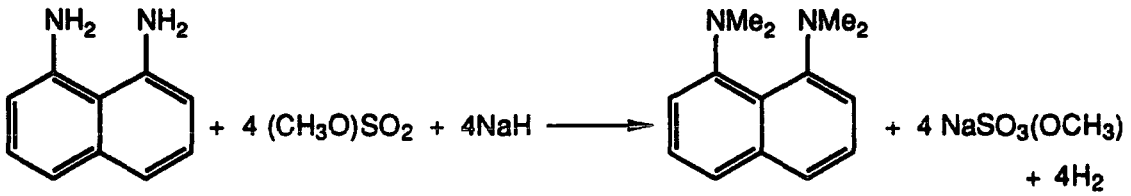
Hence, a series of amine.HF complexes were synthesised and their reactivity as fluoride ion sources monitored. We chose sterically hindered, non-nucleophilic, strong bases as the carriers of HF in order to "bury" the proton as much as possible. The amine.HF complexes were then used as the source of fluoride ion in a range of experiments designed to measure their reactivity as fluoride ion donors. Details of the experiments performed are given in the following discussion.

Initially we investigated the HF complex of Proton Sponge as PS is a very strong base (pK_a of the conjugate acid =12.3), sterically hindered around the basic site and is a large molecule which should aid the solubility of the HF complex in organic solvents. A discussion on the preparation, structure, basicity, spectroscopy and reactions of PS follows.

2.2 1,8-Bis(dimethylamino)Naphthalene (Proton Sponge)

2.2.1 Preparation

1,8-Bis(dimethylamino)naphthalene was first obtained as an oil by Brown[103] who reduced 1,8-dinitronaphthalene by tin chloride/HCl to form the diamine which was then methylated using excess methyl sulphate. Alder obtained the product as a solid (m.p. 47-48°C) by extracting into an aqueous pH 8 solution[104]. An improved synthesis was published in 1972 when the diamine was methylated using excess dimethyl sulphate in the presence of sodium hydride[105]:-



1,8-Bis(dimethylamino)naphthalene is now marketed by Aldrich under the name "Proton Sponge", and will be referred to as PS in the following discussion.

A series of other N,N,N',N'-tetrasubstituted compounds have been prepared from the parent diamine in a similar manner[106].

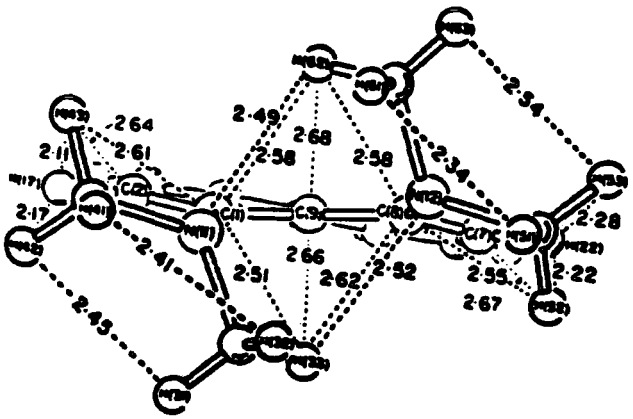
2.2.2 Structure

The structure of PS is especially interesting because of the steric effects that are encountered. The 1,8-naphthalene substituents are said to be *peri* to each other and are much closer to one another than to ortho substituents on the aromatic ring.

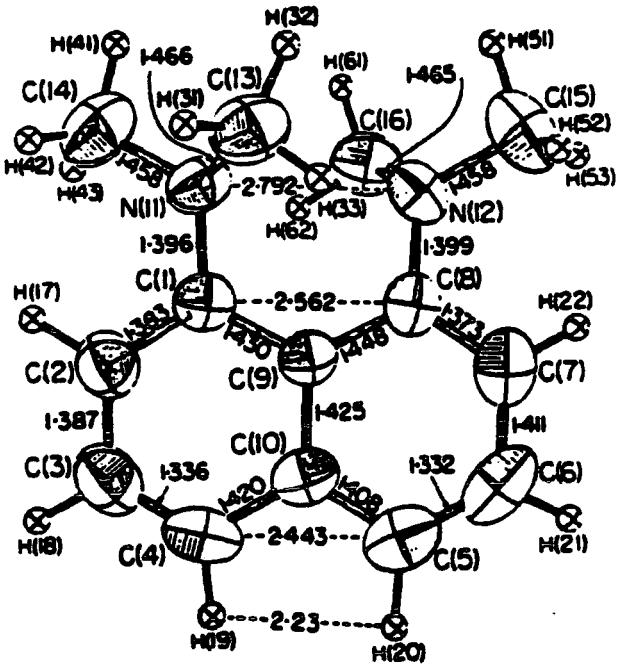
Steric strain of *peri* substituents may be overcome by (1) a stretching of the bonds; (2) in-plane deflection of substituents; (3) out-of-plane deflection; (4) distortion or buckling of the ring. A stretching of the bonds is ruled out because of the high energy required for such a process and so a compromise situation is reached. Other factors in the case of PS are (1) there is no possibility of bringing even one of the dimethylamino groups into the plane of the ring; (2) if the methyl groups are out of each others way then the nitrogen lone pairs will be brought face-to-face; (3) if the nitrogen lone pairs are favourably situated, one pair of the methyl groups will interfere strongly with a nitrogen atom.

Einspahr and Robert carried out an X-ray crystal structure determination (Fig. 2) to investigate these effects[107].

Fig. 2 X-Ray Crystal Structure of 1,8-Bis(dimethylamino)naphthalene



A representation of the molecule viewed along the C(9)–C(10) bond, including selected intramolecular non-bonded distances. E.s.d.'s are about 0·05 Å for the C–H and N–H distances and about 0·07 Å for the H–H distances.



From the structure we can see that the naphthalene ring is non-planar and the molecule has accommodated the bulky *peri* substituents with surprisingly little strain. The C(ring)-N bonds have retained a significant amount of *p*-character, and two of the N-C(methyl) bonds remain in the plane of the ring. Close interlocking of the hydrogen atoms is the key to the molecular conformation, the atoms of the methyl groups being neatly staggered with respect to the ring hydrogen atoms.

2.2.3 Structure of 1,8-Bis(dimethylamino)naphthalene Salts

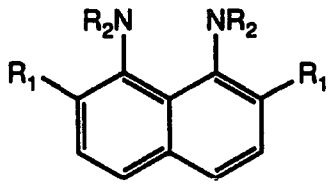
Protonation of PS causes the following modifications to the structure[108]; (1) the N-N distance is shortened as lone pair repulsions are eliminated (this is one contributing factor to the high basicity of PS); (2) the naphthalene ring becomes more planar; (3) in the N-H-N bridge the proton does not exist in a straight line between the nitrogen atoms.

Errors in X-ray crystallography limits the evidence for the proton existing in a symmetric or unsymmetrical N-H-N bridge. N_{1s} ESCA studies[109] on $PSH^+BF_4^-$ show two inequivalent nitrogen atoms which suggests an unsymmetrical N-H-N bridge. This is supported by positive proton NMR isotope effects[110].

2.2.4 Basicity

PS (pK_a of the conjugate acid = 12.3) has a much greater basicity than the parent 1,8-naphthalenediamine (pK_a 4.6) and ten million times greater than that of N,N-dimethylaniline (pK_a 5.1). The reasons for this huge increase in basicity have been of considerable interest. Basicities of some substituted 1,8-diaminonaphthalenes are listed below (Table 8).

Table 8. pK_a Values for Proton Sponge Conjugate Acids and Related Compounds



R	R_1	pK_a
Me	H	12.1
Et	H	12.7
Me	OMe	16.1
Et	OMe	16.3

The high basicity of PS type compounds is considered to be due to the following reasons; (1) relief of lone pair-lone pair repulsions on protonation resulting in a decrease in the steric strain of the system; (2) protonation gives a monocation with a very stable intramolecular hydrogen bond; (3) the naphthalene ring is forced to be more planar on protonation; (4) recent calculations suggest that the basicity is due to the destabilisation of the neutral form of PS because of its inability to form a hydrogen bond between the methyl groups and the nitrogen atoms[111].

The increase in basicity on addition of 2,7-methoxy substituents is attributed to the "buttressing" effect, the methoxy groups forcing the naphthalene ring to adopt a more planar configuration in the free base thus giving a greater relief in strain on protonation[112, 113].

The high basicity of PS is accompanied by very low rates of proton transfer[114] due to the intramolecular hydrogen bond which is stabilised by hydrophobic NMe_2 groups. Proton transfer is considered to be a two step process; the hydrogen bond is broken followed by deprotonation. This low rate of proton transfer means that PS has not found many uses as a base catalyst in organic syntheses (section 2.2.6).

2.2.5 Spectroscopy

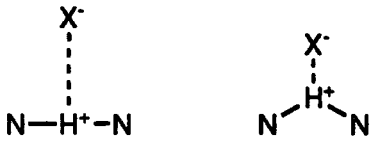
2.2.5.1 Ultraviolet Spectroscopy

The long wavelength band of PS in the UV spectrum appears at 335nm (log ε_{max} 3.96) which is shifted to 285nm (log ε_{max} 3.78) on protonation[104].

2.2.5.2 Infra Red Spectroscopy

The infra red spectra of PS salts have been studied by Polish workers[115-117]. The protonic absorption band due to the protonic vibrations in the potential well between the two nitrogen atoms, i.e. N-H$^+$-N, is found at low frequencies[115], e.g. PS/HBr at 543cm^{-1}. The absorption is dependent on the counter ion which interacts with the N-H-N bridge. A shift to higher frequencies is seen with an increase in the base strength of the anion and the isotopic ratio (ISR), ν_H/ν_D, was found to decrease as the frequency increased. N-H-N stretching absorptions and ISR ratios are listed in Table 9.

Table 9. N-H-N Infra Red Stretching absorptions in Proton Sponge Salts.



Low absorption
High ISR

High absorption
Low ISR

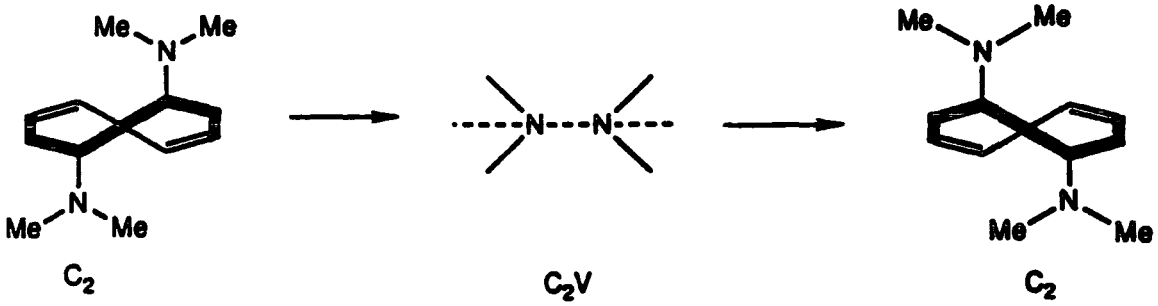
Acid	ν_s / cm^{-1}	ISR
HBF_4	463	1.85
HPF_6	479	2.05
HI	509	2.0
HBr	543	1.7
Pentachlorophenol	590	1.0

The rich structure of this band was due to the coupling with other low frequency, internal vibrations of the naphthalene ring. Except for a narrow band at 1200cm^{-1}, there are no absorptions at a higher frequency that may be due to protonic vibrations.

The IR spectra of the salts in acetonitrile solutions have been investigated[117]. In solution the protonation of PS is seen in the absorptions of the methyl groups. The N-Me bands at 2900-3000cm^{-1} disappear for PS.HBF$_4$ as the base is still fully protonated in solution. Absorptions due to N-Me may still be seen if some free base remains in solution, as is the case for PS.Pentachlorophenol.The absorption at 1576cm^{-1} in the free base due to the asymmetry of the buckled naphthalene ring also decreases in intensity when the base is protonated as protonation causes a flattening of the ring removing the asymmetry. The protonic absorption band is a continua extending from 300-3000cm^{-1}. The interaction of polar solvent molecules cause drastic changes in the bridge geometry and hence the potential shape of the proton motion. For all PS salts the broad continua indicates complete dissociation has taken place.

2.2.5.3 Nuclear Magnetic Resonance Spectroscopy

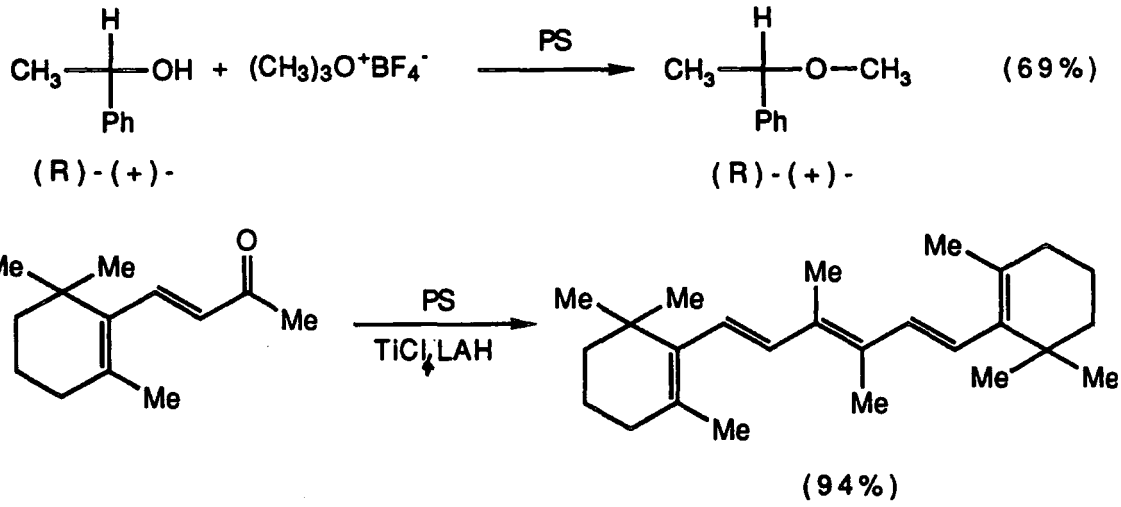
The mode of rotation of the peri NMe_2 groups in the free base is an interesting question because of the steric considerations. At room temperature the methyl protons have a shift of 2.77ppm (singlet) but at -133°C a 1:1 doublet is seen, centred at 2.74ppm (J = 25.6 Hz). The symmetry of the spectral changes suggests that conformational changes are taking place, the naphthalene ring flipping from the most stable C_2 conformer through a C_{2v} transition state to the other C_2 conformer[118].



On protonation, the proton on the nitrogen is extremely deshielded and has a very high shift, e.g. $PSH^+BPh_4^-$ δ_{H+} = 18.46ppm [110], $PSH^+CO_2CF_3^-$ δ_{H+} = 19.5ppm [104].

2.2.6 Reactions

PS is weakly nucleophilic for steric reasons and is recovered unchanged after four days reflux with ethyl iodide[104]. PS has been used in organic synthesis as a strong hindered, non-nucleophilic base in base catalysed reactions[119-120], but the slow rate of proton transfer has limited its use.



Recently, PS has been shown to react with electrophiles in aromatic substitution reactions but these will be discussed in the introduction to Chapter 4.

2.3 The Hydrofluoride Complex of 1,8-Bis(dimethylamino)naphthalene (Proton Sponge)

2.3.1 Preparation of PS/HF

The PS/HF complex (1) is formed by adding the required 1:1 stoichiometric amount of an HF/ether solution to an ethereal solution of the base. The ether was removed to leave a white solid. Elemental analysis showed that the solid was a 1:1 base:HF complex. The PS/HF complex was completely soluble in acetonitrile and sulpholane. NMR, IR and mass spectrometry were obtained for the complex in an attempt to rationalise its structure and prove whether it exists as a simple salt or as a mixture of base, base.HF, baseH$^+$, HF_2^- etc. Spectroscopic data is as follows.

2.3.2 Spectroscopical Studies of PS/HF

2.3.2.1 NMR

^1H and ^{19}F NMR spectra were recorded for the complex (1) dissolved in deuterated acetonitrile at 400MHz. The ^1H spectrum is shown overleaf (Fig 3).

From the ^1H spectrum we can observe the following; (1) two singlets at 2.8 and 3.0ppm; (2) about five peaks in the aromatic region; (3) broad peaks at 13.6 and 18.7ppm. The ^{19}F NMR spectrum consists of a sharp singlet at -169ppm at room temperature.

From the literature we know that the peak at 18.7ppm is due to the protonated PS (N-H$^+$...N) (c.f PSH$^+$. $CF_3CO_2^-$ at 19.5ppm[104]). The origin of the peak at 13.6ppm is uncertain. If it was due to HF_2^- being present in solution we would expect to see a doublet in the ^{19}F spectrum at about -145ppm[63] and this is not the case. Hence the peak at 13.6ppm is probably due to free HF. Thus the complex in solution probably exists as a mixture of base, protonated base in equilibrium with HF, as shown below.

$$PSH^+ + F^- \rightleftharpoons PS/HF \rightleftharpoons PS + HF \rightleftharpoons PSH^+ + HF_2^-$$

The broadened singlets seen at 2.8 and 3.0ppm may be explained as corresponding to PS and to protonated PS. Similarly, five resonances are seen in the aromatic region because of this mixture.

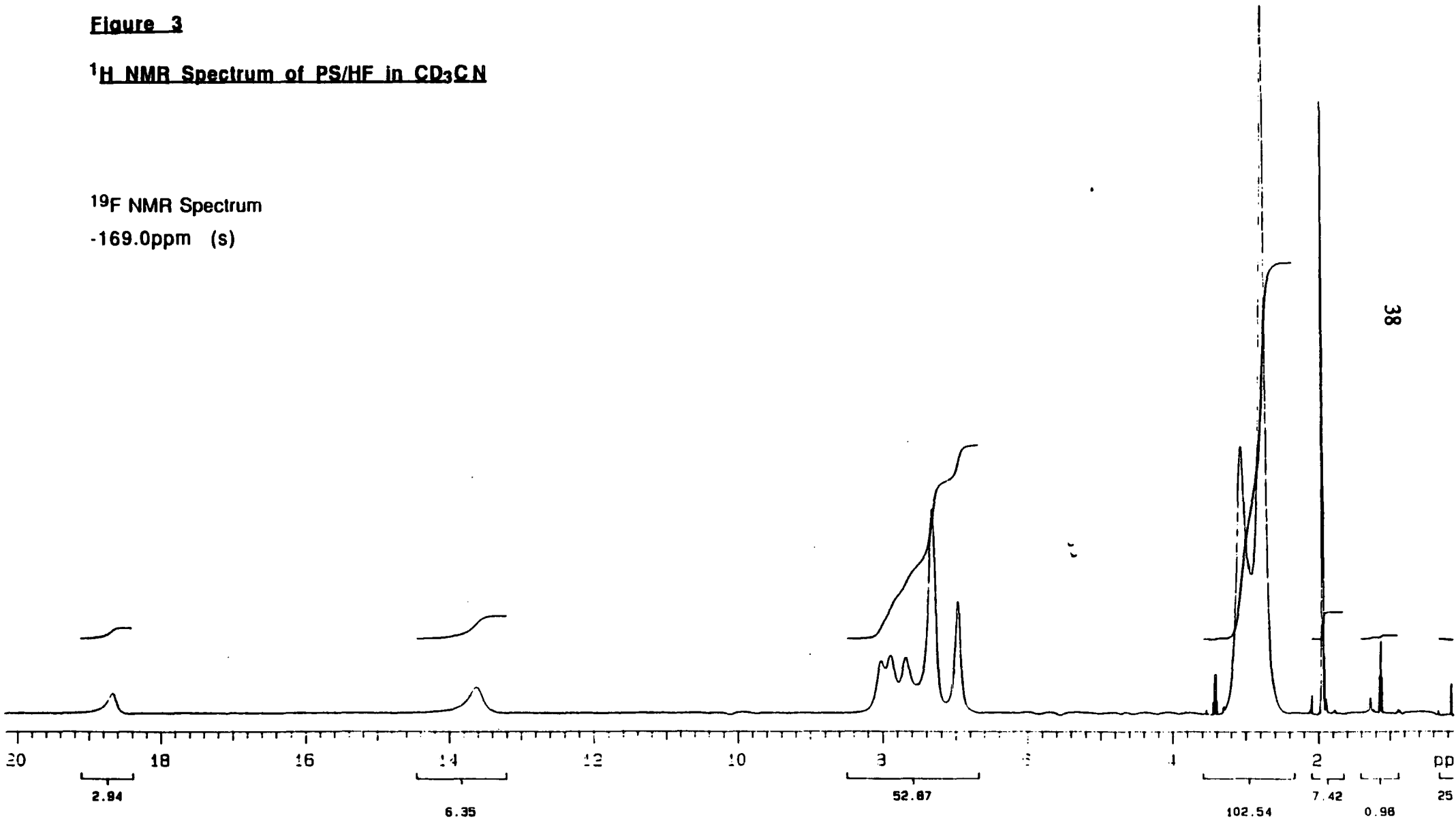
The position of the fluorine resonance at -169ppm is downfield from HF (-180ppm) and upfield from fluoride ion (-112ppm) (from reference 63 and

Figure 3

^{1}H NMR Spectrum of PS/HF in CD_3CN

^{19}F NMR Spectrum

-169.0ppm (s)



established in section 1.6.2.1 for another base.HF system) and indicates an equilibrium between base, HF and fluoride ion.

Low temperature solution state NMR studies were unsuccessful as the solid PS/HF precipitates out of solution at about -20°C.

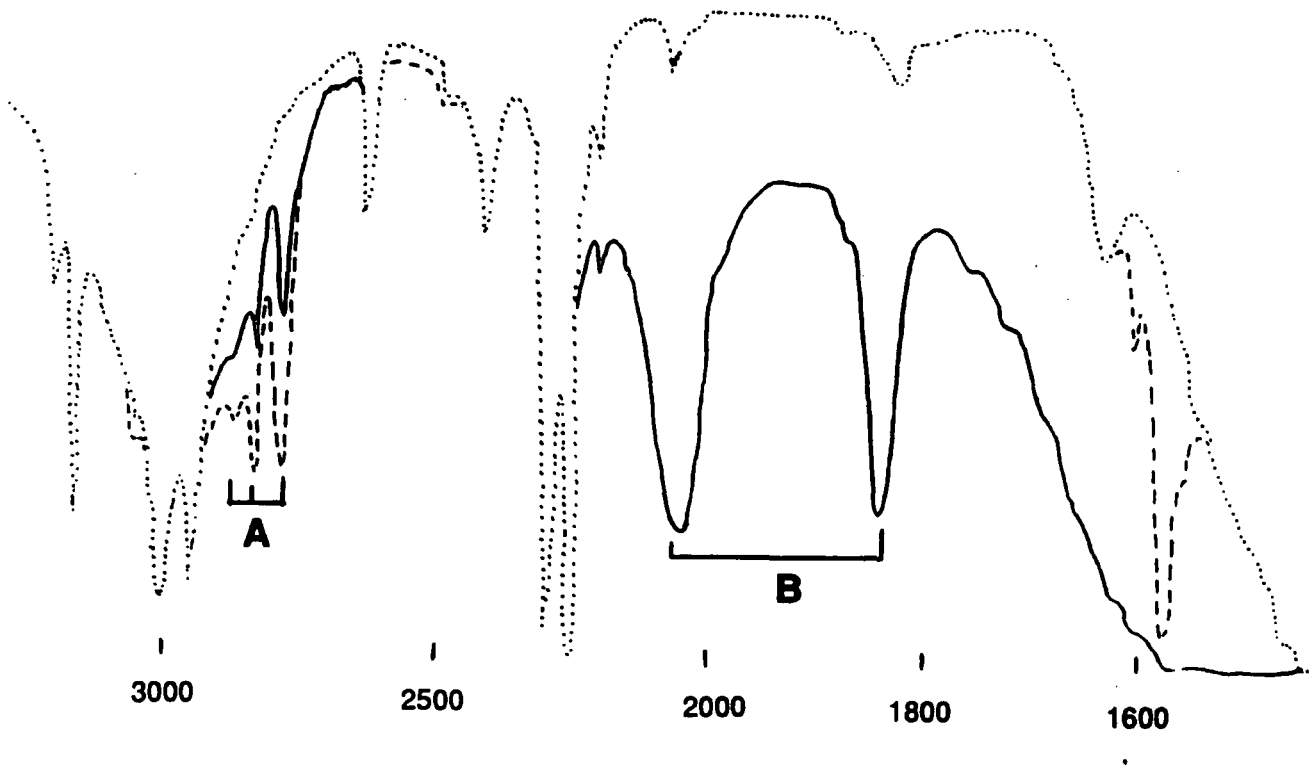
However we can postulate that the PS/HF complex, a 1:1 complex in the solid state, exists as an equilibrium between the free base, protonated base and HF in solution. These exchanges in solution generate fluoride ion which may be used as a source of soluble fluoride ion as discussed in section 2.4.

2.3.2.2 Infra Red

The literature concerning the infra red spectra of related proton sponge salts both in the solid state and in solution have been discussed in section 2.2.5.2.

The infra red spectra of PS and PS/HF complex were recorded in acetonitrile solution at 0.3 mol l^{-1} concentration. The region between 3000 and 1500cm^{-1} is shown below (Fig. 4).

Figure 4
Solution Infra Red Spectra of PS and PS/HF in MeCN



The Bohlmann bands at 2785, 2840, and 2880cm^{-1} (A) (lit[117]. 2780, 2831, and 2869cm^{-1}), are reduced on protonation but do not completely disappear as for fully protonated molecules[117]. Hence we can conclude that there is some free base present in solution which is consistent with the ^{1}H NMR data above.The main difference in the PS/HF spectrum is the appearance of the large broad bands at 1840 and 2050cm^{-1}(B), which are not seen in other PS salts[117]. These must be due to N-H-F vibrations. Free HF occurs[69] at 3820cm^{-1} and so we are observing the effect of the base complexing with the HF. A broad peak is observed at 580cm^{-1} which agrees with results for other salts indicating that the N-H-N bridge has a bent geometry as we would expect.

The IR spectrum of PS/HF in a Nujol mull gives different results. A large broad band is seen at 1800cm^{-1} which must be due to N-H-F vibrations.

2.3.2.3 Mass Spectroscopy

The PS/HF complex is not observed in the mass spectrum, the complex decomposing in the spectrometer even in the FAB mode, the most appropriate method for analysing salts. The peak seen at 215 corresponding to protonated PS is probably due to the free PS being protonated by the FAB matrix (methanol/glycerol). Thus FAB mass spectrometry was unsuccessful in determining the types of species present in the solid state of the PS/HF complex.

2.4 Reactions of PS/HF

A series of experiments were performed using PS/HF as the source of fluoride ion in order to determine whether the complex could act as a fluoride ion donor in solution.

PS/HF was used to catalyse C-C bond forming reactions (oligomerisations, perfluoroalkylations) and in C-F bond forming reactions (nucleophilic substitution reactions with a range of substrates). The results of the reactions performed using PS/HF as the source of fluoride ion are discussed below along with literature results using other sources of fluoride ion for comparison.

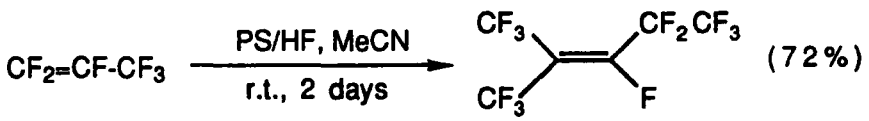
2.4.1 PS/HF as a Catalyst in C-C Bond Forming Reactions

2.4.1.1 Oligomerisation Reactions

It is well established that fluoride ion catalyses the oligomerisation reactions of perfluorinated alkenes[121], cyclic alkenes[122] and alkynes[123]. The source of fluoride ion is usually KF or CsF as heterogeneous catalysts and so a series of analogous reactions was performed using PS/HF as a homogeneous catalyst.

Tetrafluoroethylene was not oligomerised using PS/HF as the catalyst even when the temperature of the reaction was raised to 110°C and the pressure of the TFE in the reaction vessel was raised to 10 bar. (This reaction was performed at the ICI Experimental Site, Widnes).

Hexafluoropropene was dimerised to its thermodynamic dimer (2), as the only product by GC (72% yield, 100% conversion), at room temperature in two days using acetonitrile as the solvent with the hexafluoropropene in a 7:1 molar excess.

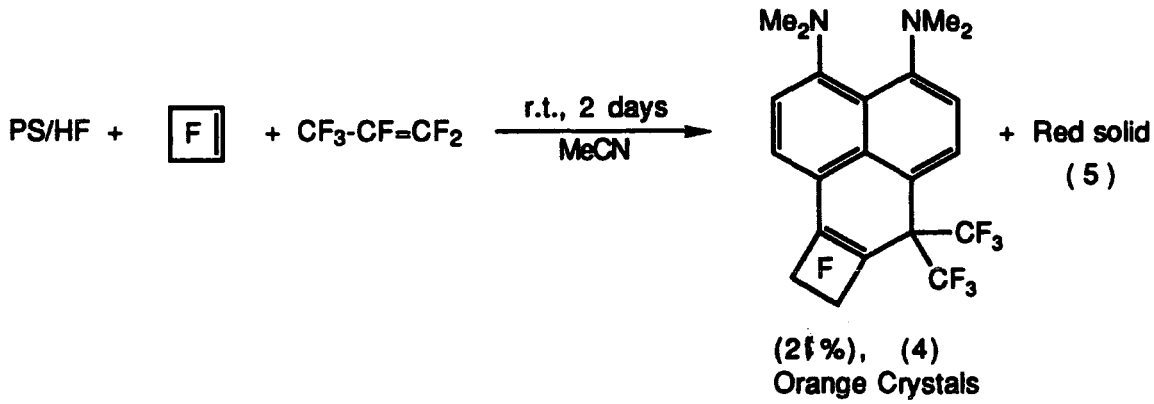


(2)

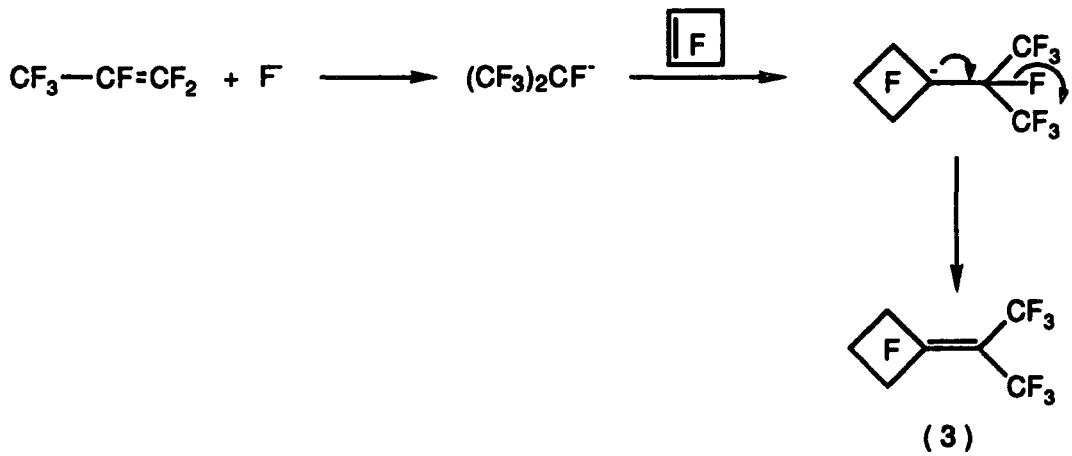
The product dimer separates from the acetonitrile. The solvent layer can then be recharged with hexafluoropropene and the reaction repeated to give the same yield of dimer, demonstrating the catalytic nature of the process. In an analogous reaction hexafluoropropene was dimerised to its thermodynamic dimer (2) in 95% yield under the same conditions when CsF was used as the source of fluoride ion[121].

Oligomers of perfluorocyclobutene[122] could not be isolated from its attempted oligomerisation using PS/HF as the catalyst in various solvents and at elevated temperatures.

The co-dimer (3) of hexafluoropropene and perfluorocyclobutene is formed using PS/HF as the catalyst. However, the alkene (3) so formed reacts with the PS to form the annelation product (4).



The co-dimerisation process may proceed by the following route:-



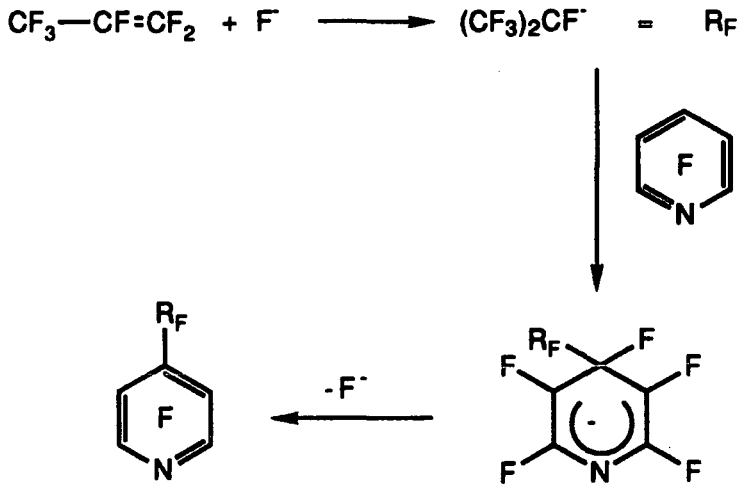
The perfluorinated alkene then reacts further with PS and this reaction is discussed in detail in Chapter 4.

The mechanism of these oligomerisations may not be a simple fluoride ion catalysed process as proton transfer from the HF to the intermediate carbanion may take place.

Attempts to form a stable perfluorinated carbanion, by the reaction of hexafluoropropene dimer (2) and PS/HF, failed. Stable perfluorinated carbanions have been synthesised in reactions between perfluoroalkenes and CsF[66].

2.4.1.2 Perfluoroalkylation Reactions

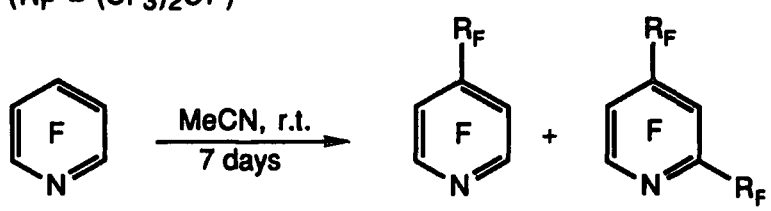
Fluoride ion catalyses perfluoroalkylation reactions of fluorinated heterocycles the carbanion formed on addition of fluoride ion to the fluoroalkene being trapped by the heterocycle , as outlined in the following mechanism.



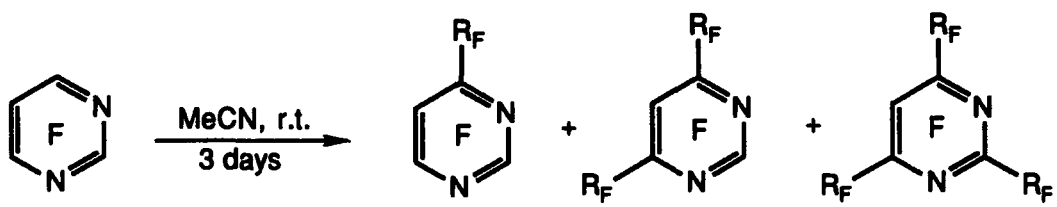
Previously, alkali metal fluorides have been used as the source of fluoride ion in perfluoroalkylation reactions between hexafluoropropene and pentafluoropyridine(6)[124], tetrafluoropyrimidine(9)[125] and trifluoro-s-triazine(13)[126].

A series of perfluoroalkylation reactions of fluorinated nitrogen heterocycles by hexafluoropropene using PS/HF as the catalyst were performed and are tabulated below.

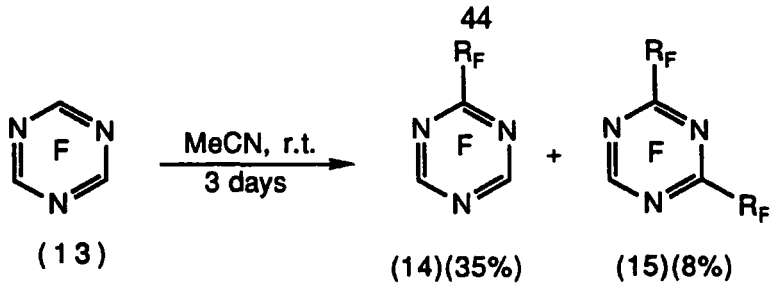
(R_F = $(CF_3)_2CF$)



(6) (7)(44%) (8)(trace)



(9) (10) (27%) (11)(15%) (12)(39%)



(13) (14)(35%) (15)(8%)

All products were identified by g.c./m.s. and ^{19}F NMR as compared to the literature data. Yields were determined by g.c. for accuracy.

In an analogous reaction, (6) was perfluoroalkylated[124] by hexafluoropropene, using KF as the source of fluoride ion, to give (7)(94% yield) and (8)(trace) after heating in sulpholane at 130°C for 12 hr. Similarly, (9) was perfluoroalkylated[125] by hexafluoropropene, using CsF as catalyst, to give (11)(45% yield) and (12)(43%) after heating in sulpholane at 100°C for 16 hr. Also, (13) gave (14)(39% yield), (15)(51%) and the trisubstituted derivative (16)(5%) using CsF as the catalyst after heating in sulpholane at 70°C for 20 hr.

Comparison of perfluoroalkylation reactions using alkali metal fluorides and those using PS/HF as the source of fluoride ion show that much milder conditions are required when PS/HF is used.

2.4.2 The Use of PS/HF in C-F Bond Forming Reactions

A series of reactions designed to form C-F bonds were carried out using PS/HF as the source of fluoride ion in nucleophilic substitution reactions at unsaturated and saturated carbon.

In all the halogen exchange reactions PS/HX (X = Cl, Br, I) precipitates as the reactions proceed as white solids. Hence the PS may be recovered by heating the PS/HX with base.

2.4.2.1 At Unsaturated Carbon

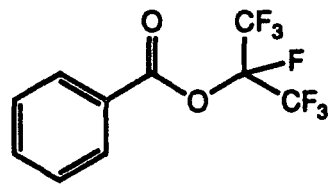
The reaction between PS/HF and benzoyl chloride gave a 76% yield of benzoyl fluoride at room temperature in acetonitrile after 24 hr. The yield was calculated from NMR integration, referenced to a benzotrifluoride marker.

Hexafluoroacetone reacts with KF to form a carbinolate anion which can then be trapped by electrophiles[127]. The KF-hexafluoroacetone complex was not isolated. PS/HF reacts with hexafluoroacetone to form the same type of species (17) which was observed by ^{19}F NMR.

$$PS/HF + (CF_3)_2C{=}O \underset{}{\overset{MeCN,\ r.t.}{\rightleftharpoons}} PSH^+\ (CF_3)_2CFO^-$$

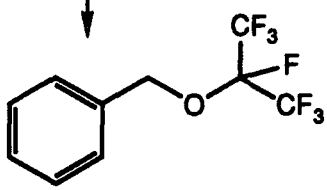
(17)

The shift of the tertiary fluorine was -107.9ppm, deshielded from usual C-F resonances indicating that the fluorine atom is adjacent to an atom bearing a negative charge, as seen in the NMR shifts in perfluorinated carbanions[66]. The complex (17) was trapped by the electrophiles benzoyl chloride and benzyl bromide to give the products (18) and (19) respectively.

$PSH^+\ (CF_3)_2CFO^-$ —PhCOCl, MeCN, r.t.→  + PhCOF

(18)(49%) (51%)

$PhCH_2Br$, MeCN, r.t.



(19)(61%)

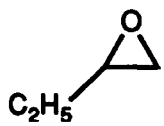
2,4-Dinitrochlorobenzene was fluorinated to 2,4-dinitrofluorobenzene by PS/HF in 45% yield after 48 hrs reflux in acetonitrile.

2.4.2.2 At Saturated Carbon

Reactions between PS/HF and octyl iodide, benzyl bromide and 1,2-epoxybutane were performed and the results are shown below:-

$$CH_3(CH_2)_6CH_2I \xrightarrow[24\ hr]{MeCN,\ reflux} CH_3(CH_2)_6CH_2F \quad (65\%)$$

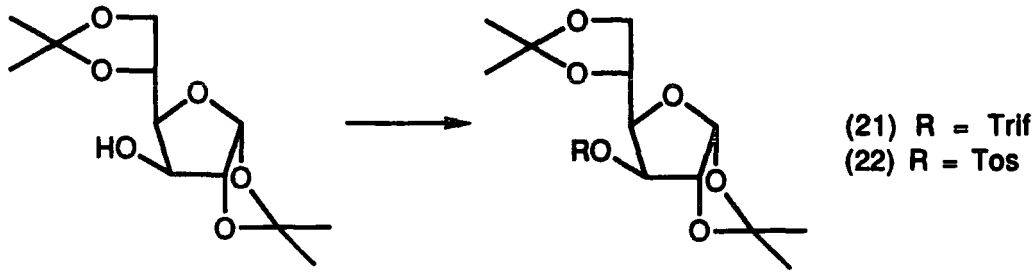
$$PhCH_2Br \xrightarrow[24\ hr]{MeCN,\ reflux} PhCH_2F \quad (72\%)$$

 $\xrightarrow[48\ hr]{MeCN,\ reflux}$ no reaction

Benzyl bromide is the most reactive species towards nucleophilic attack due to resonance stabilisation of the intermediate carbocation.

There is an increasing need for reagents that can introduce fluorine into biologically active molecules. Consequently we attempted to fluorinate the triflate and tosylate derivatives of diacetone-D-glucose (20) which have previously been fluorinated by $Bu_4NF.3H_2O$ [128] and TAS-F[129] respectively.

The triflate (21) and the tosylate (22) were prepared by literature methods[129, 130], as shown below.



(20)

(i) R = Trif, $(CF_3SO_2)_2O$, 0°C, pyridine, CH_2Cl_2

(ii) R = Tos, Tosyl Chloride, r.t., pyridine

There was no fluorination of the tosylate (22) after two days reflux in acetonitrile. The triflate (21) was not fluorinated at room temperature. Refluxing in acetonitrile caused the glucose to decompose and the triflate salt of PS (23) was recovered. No fluorination of the glucose (20) could be detected.

2.5 Summary

We have shown that the PS/HF system is stable, easily prepared, easily handled, does not corrode borosilicate glass and is completely soluble in acetonitrile. and can be used as a source of soluble fluoride ion in a range of reactions. The PS/HF system has been used to catalyse C-C bond forming reactions and in C-F bond forming reactions.

The structure of the PS/HF system in solution is uncertain but probably exists as a mixture of base, base.HF, $baseH^+.HF_2^-$ etc. in an analogous way to the $Bu_3N.HF$ system (Chapter 3). Whatever the structure of PS/HF and its mode of action, the ability of PS to bind with HF to produce a source of soluble fluoride ion is clear.

A feature of the PS/HF system is that the PS/HX (X = Cl, Br, I) salts, formed as products in halogen exchange reactions are insoluble in acetonitrile and precipitate out of the reaction mixture.

e.g.

$$PS/HF + C\text{-}Cl \longrightarrow PS/HCl\downarrow + C\text{-}F$$

The proton sponge free base can then be regenerated by heating these salts with sodium hydroxide solution.

However, the fact that PS/HF reacted with the fluorinated alkene (3) *in situ* restricts the use of the system. We decided to investigate other base.HF systems as sources of soluble fluoride ion to determine the factors which may affect the ability of base.HF complexes acting as fluoride ion donors, as it is clear from the reactions performed using PS/HF as the source of soluble fluoride ion that amine.HF systems can be used as sources of soluble fluoride ion.

CHAPTER THREE

BASE HYDROFLUORIDE COMPLEXES AS POTENTIAL SOURCES OF SOLUBLE FLUORIDE ION

3.1 Introduction

The success of the PS/HF system as a source of soluble fluoride ion prompted us to synthesize a series of sterically hindered base HF complexes. We hoped to determine the factors which governed the reactivity of these systems as fluorinating agents in order to develop the most efficient reagent. We hoped to distinguish between the effect of increasing the steric hindrance around the basic nitrogen atom and base strength.

After preliminary work in this laboratory[5] we chose to compare hydrofluoride complexes of trialkylamines, pentamethylpiperidines and tetramethyiguanidine.

The literature concerning hydrofluoride salts has been reviewed in Chapter One.

3.2 Trialkylamine Hydrofluoride Complexes

The HF complexes of trialkylamines were prepared in the same way as the PS/HF system (section 2.3.1). i.e adding the required 1:1 stoichiometric amount of an HF/ether solution to an ethereal solution of the base.

The following base.HF complexes were prepared:-
$R_3N.HF$: (24) R=Ethyl, (25) R=Butyl, (26) R=Hexyl, (27) R=Octyl, (28) R=Dodecyl.

3.2.1 NMR Spectroscopy

^1H and ^{19}F NMR spectra for each of the $R_3N.HF$ complexes were recorded at room temperature in deuterated acetonitrile. The proton resonance for the H-F proton occurs downfield between 10.8 and 12.7ppm as broad singlets as tabulated below (Table 10). All $R_3N.HF$ complexes give a singlet in the ^{19}F NMR spectrum at room temperature between -154 and -159ppm (Table 10).

Table 10. NMR Chemical Shifts of $R_3N.HF$. ^1H shift for HF and ^{19}F Shifts Only

R	δ_H	δ_F
Et	12.7	-154.8
Bu	12.7	-157.1
Hex	12.5	-157.0
Oct	10.8	-156.6
Dodec	11.6	-159.3

No information about the species that are present in solution can be gained from the NMR spectra at room temperature except to say that the HF has bound to the base as the fluorine shift is downfield from free HF. Consequently a study of the low temperature NMR of $Bu_3N.HF$ complex was carried out and is discussed in the next section.

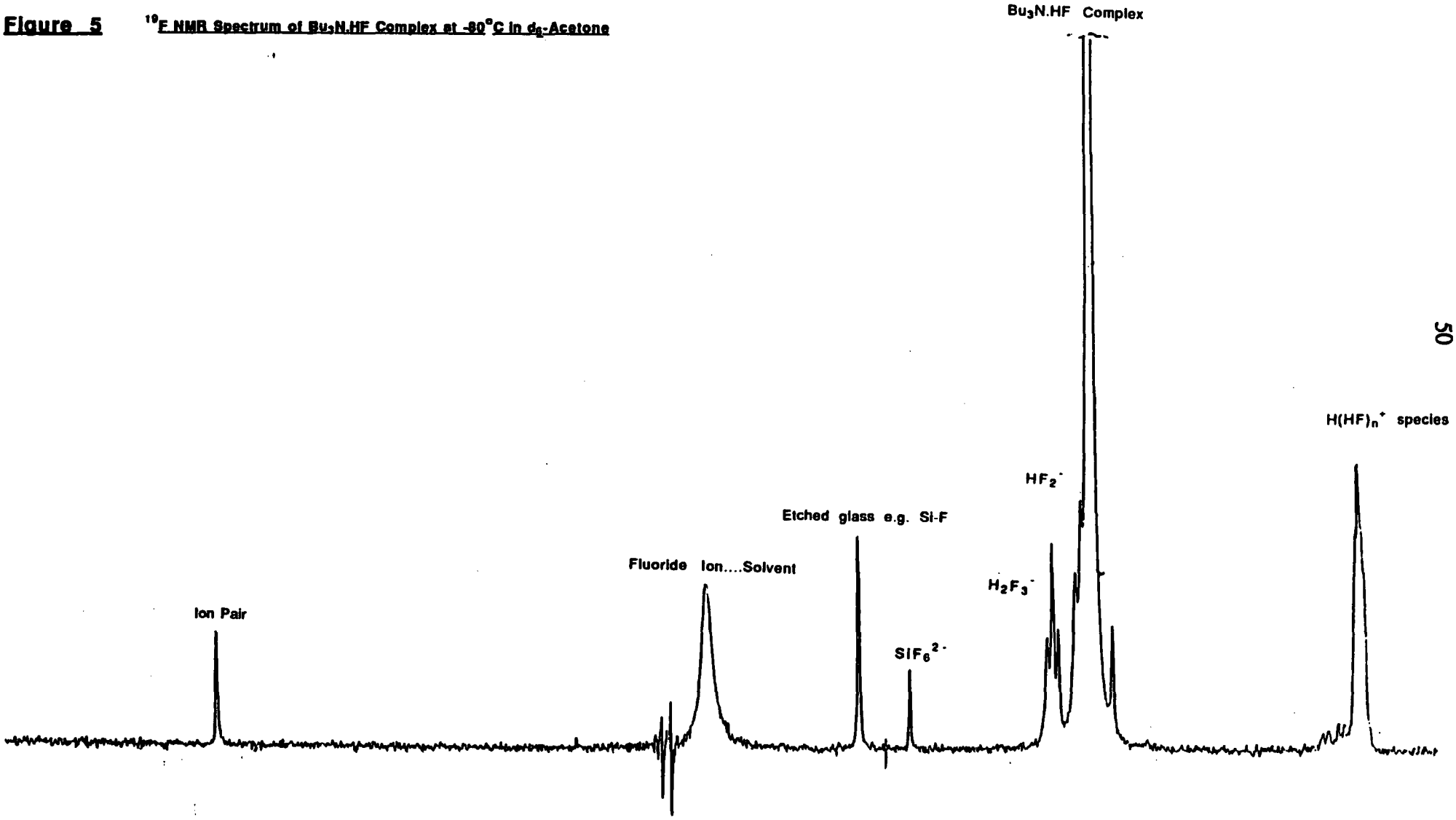
3.2.2 Low Temperature NMR Study of $Bu_3N.HF$

Following the work by Cousseau[68] we investigated the low temperature NMR spectrum of $Bu_3N.HF$ at -80°C in an attempt to ascertain the species that are present in solutions of Base.HF complexes. The spectrum obtained for $Bu_3N.HF$ complex at -80°C is shown overleaf.

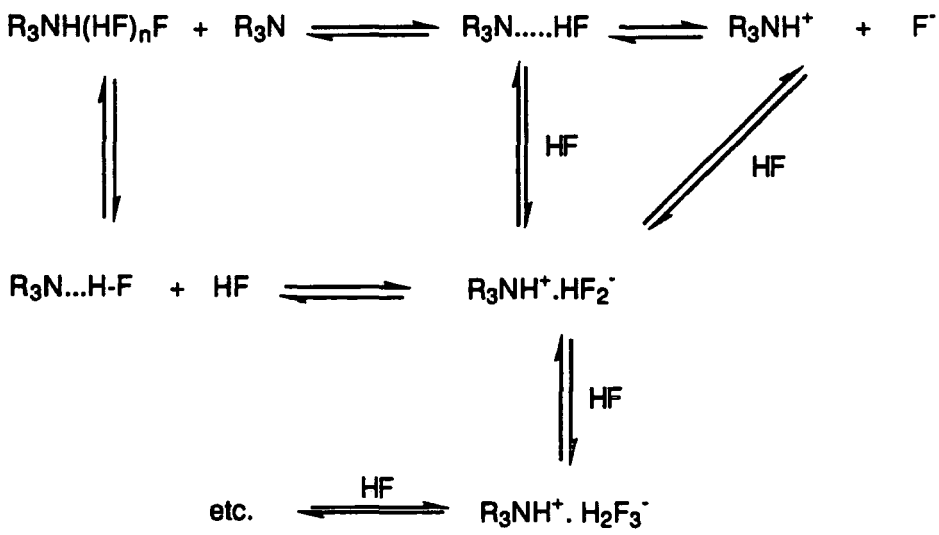
Using the information discussed in Section 1.6.2.1.1 the following assignments may be made:-

Peak		Assignment
-65.38		Ion Pair e.g $Bu_3NH^+F^-$
-111.99		Fluoride Ion F^- hydrogen bonding with the solvent[63]
-126.56		Si-F or B-F from etched NMR tube
-131.42		SiF_6^{2-} from etched NMR tube[64]
-144.97	triplet J_{HF} = 123 Hz	$H_2F_3^-$
-147.82	doublet J_{HF} = 147 Hz	HF_2^- [63]
-148.74		$Bu_3N.HF$ Complex[68]
-150.68		
-174.12		$H(HF)_n^+$ type species[68]

Figure 5 ^{19}F NMR Spectrum of $Bu_3N.HF$ Complex at -80°C in d_8-Acetone



The NMR spectrum at -80°C shows that there are a number of species present in solutions of $Bu_3N.HF$ systems. The peaks at -112 indicating F^-, at -174 indicating $H(HF)_n^+$ species and the smaller triplet and doublet at -144 and -148ppm corresponding to $H_2F_3^-$ and HF_2^- respectively proves that a number of exchange processes must be occurring in $Bu_3N.HF$ solutions which may be summarised as follows:-



The peak at -112ppm is direct evidence for the existence of fluoride ion in $Bu_3N.HF$ solutions. All the exchange processes listed above must be occurring very rapidly for a singlet to result in the ^{19}F NMR spectrum at room temperature.It seems reasonable to assume the same model for all amine.HF systems in solution.

3.2.3 Reactions

Three standard experiments were carried out using each of the Base.HF complexes as the source of soluble fluoride ion. The reactions chosen and conditions are given below:-

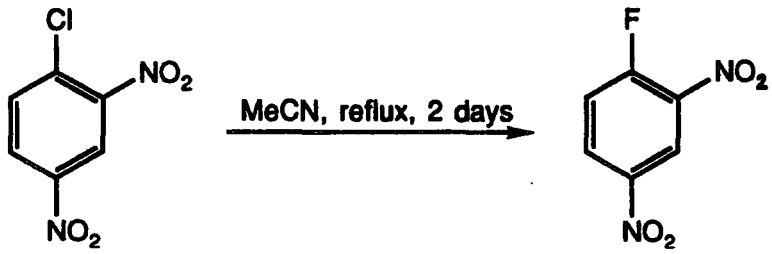
1) Benzoyl Chloride

$$PhCOCl \xrightarrow{MeCN,\ r.t.,\ 1\ day} PHCOF$$

2) Benzyl Bromide

$$PhCH_2Br \xrightarrow{MeCN,\ reflux,\ 1\ day} PhCH_2F$$

3) 2,4-Dinitrochlorobenzene



All reaction yields were calculated by ^{19}F NMR integration on the Bruker AC250 spectrometer operating at 235 MHz with reference to a benzo trifluoride marker. This procedure was adopted to avoid loss of products in reaction work-up and hence provide a more accurate picture of the fluorinating ability of the base.HF salts.

Yields for the three standard reactions using trialkylamine.HF complexes (24)-(28) as sources of fluoride ion are collated in Table 11. In all cases the Base.HX (X=Cl, Br) salts produced do not precipitate from solution unlike the PS case (section 2.4.2).

Table 11. Reaction Yields Using Trialkylamine Hydrofluoride Complexes as Sources of Fluoride Ion

Base.HF	PhCOCl	$PhCH_2Br$	Dinitrochloro-benzene
(24)	91	18	34
(25)	88	12	84
(26)	90	17	77
(27)	68	14	61
(28)	79	11	14

From the table we can make the following general observations:-

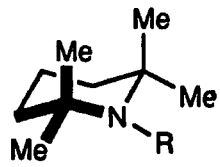
(1) Benzoyl Chloride is easily fluorinated in good yield by all base.HF complexes.

(2) Benzyl bromide did not fluorinate in good yield indicating that these systems are probably not very good reagents for S_N2 processes.

(3) Bu_3N.HF appears to be the most efficient fluorinating agent. The $Dodec_3N$.HF shows less reactivity probably due to its lower solubility.

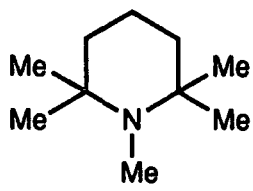
3.3 Tetramethylpiperidinium Hydrofluoride Complexes

2,2,6,6-Tetramethylpiperidine is a very hindered, non-nucleophilic base due to the steric constraints around the nitrogen atom caused by the α-methyl groups. N-alkylation increases this effect.

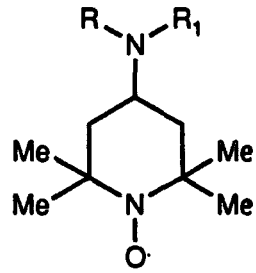


Hence, we synthesized a series of pentaalkylpiperidinium hydrofluoride complexes to determine whether these complexes are convenient sources of soluble fluoride ion.

A large literature exists for tetramethylpiperidine bases and their derivatives as emphasised in a recent review[131]. Most of the work conducted in this field was directed towards the development of anti-ganglionic blocking drugs (29) (relieves hypertension) and in the development of iminoxy radicals for use in ESR (30).



(29)

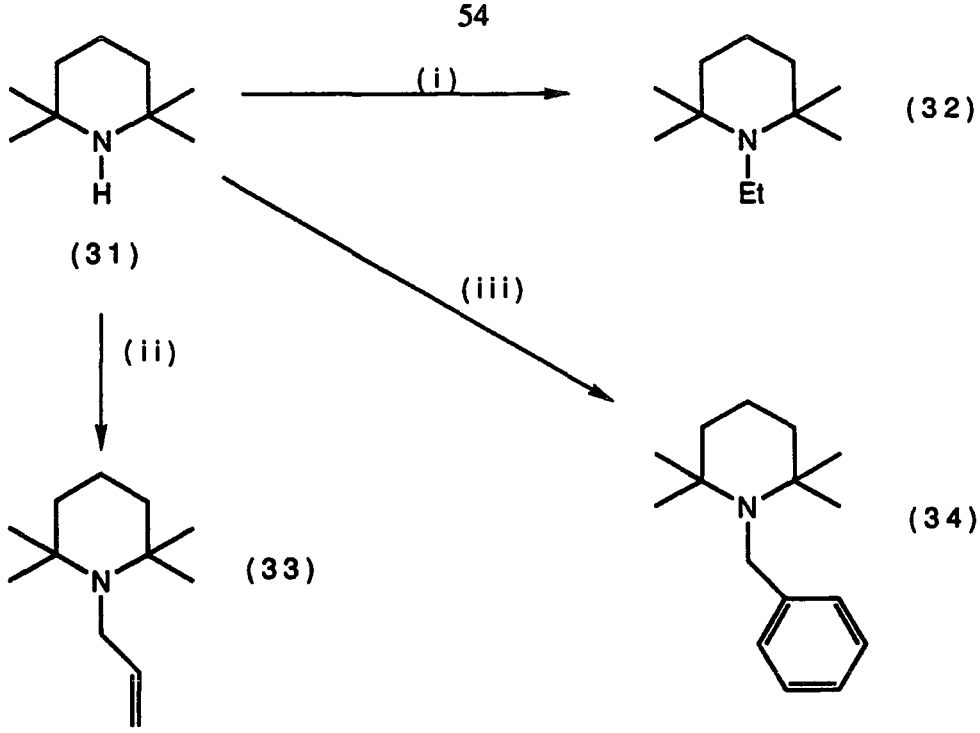


(30)

The pKa's of the conjugate acids of tetramethylpiperidine (31) and pentamethylpiperidine (29) are 11.24 and 11.25 respectively.

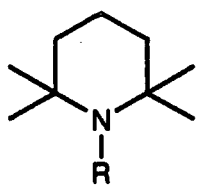
3.3.1 Preparation of Penta-alkylpiperidine Bases and Their Hydrofluoride Complexes

Both 2,2,6,6-Tetramethyl- and 1,2,2,6,6-Pentamethyl-piperidine were obtained commercially (Aldrich). The N-ethyl-, allyl- and benzyl-2,2,6,6-tetramethylpiperidines (32-34) were prepared by reacting the parent piperidine (31) with the appropriate tosylate or bromide as shown below[132].



(i) Et-OTos, 100°C, 24 hr, 21% yield
(ii) allyl bromide, 50°C, 3 days, 24% yield
(iii) benzyl bromide, 100°C, 8 hr, 32% yield

The HF salts of these five tetramethylpiperidine bases were prepared in the same manner as for all other HF complexes. i.e. pipette the required stoichiometric amount of HF/ether solution into an ethereal solution of the base. The following HF complexes (35)-(39) were prepared:-



(35) R = H
(36) R = Me
(37) R = Et
(38) R = allyl
(39) R = benzyl

Each complex was totally soluble in acetonitrile.

3.3.2 NMR Spectroscopy

Both proton and fluorine NMR spectra of each salt (35)-(39) were recorded in deuterated acetonitrile at room temperature. The resonances corresponding to HF in the proton spectra are collated in Table 12 along with the shifts of the singlets seen in the fluorine spectra.

Table 12. NMR Chemical Shifts for Poly-alkylpiperidine.HF Complexes. ^{1}H Shift for HF in Base.HF and ^{19}F shifts Only

Base. HF	δ_{HF}	δ_{F}
(35)	9.30	-135.0
(36)	12.7	-148.9
(37)	11.1	-143.9
(38)	12.1	-146.0
(39)	11.7	-152.4

Again, no information about the nature of the species in solution can been obtained from the NMR spectral data at room temperature except to say that HF has bound to the base to form a complex.

3.3.3 Reactions

The same three standard reactions were performed as described in section 3.2.3 using the piperidine hydrofluoride salts (35)-(39) as the sources of soluble fluoride ion. In all cases the Piperidine. HX (X = Cl, Br) produced in the nucleophilic substitution reactions remain in solution in contrast to the PS/HF system.

Yields of the reactions are collated in Table 13.

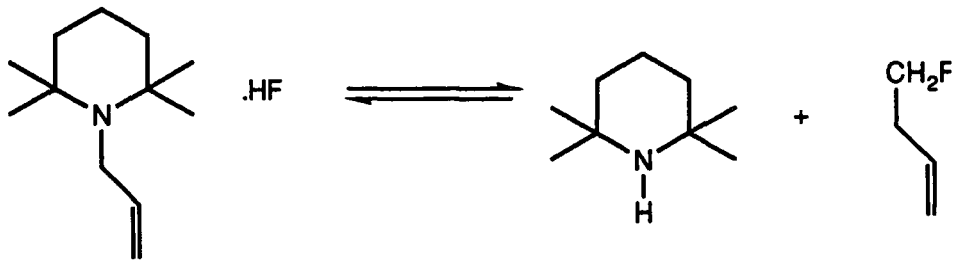
Table 13. Reaction Yields Using Pentaalkylpiperidine Hydrofluoride Complexes (35)-(39) as Sources of Fluoride Ion

Base.HF	PhCOCl	$PhCH_2Br$	Dinitrochloro-benzene
(35)	83	25	49
(36)	64	84	78
(37)	78	38	94
(38)	55	no reaction	31
(39)	42	no reaction	23

From the table we can make the following general observations:-

(1) Both methyl and ethyl tetramethylpiperidine HF complexes are good sources of fluoride ion showing good reactivity. These bases have about the same pK_a as tetramethylpiperidine and so there appears to be increased reactivity with increased steric hindrance around the nitrogen atom in these systems.

(2) Allyl and benzyl tetramethylpiperidine HF complexes show little reactivity as sources of fluoride ion. This is perhaps due to the following exchange processes occuring in solution decreasing the availability of the fluoride ion :-



3.4 Tetramethylguanidine Hydrofluoride Complex

Tetramethylguanidine is a very strong base (pK_a of the conjugate acid = 13.6)[133] and so it seemed a good alternative to PS in forming a hydrofluoride complex to use as a source of soluble fluoride ion. (PS/HF was found to react with certain substrates which limit its use (section 2.4.1.1)).

The HF complex of tetramethylguanidine was prepared in the same way as for other HF complexes and the two reactions were performed using this complex (40) as the source of fluoride ion. Benzoyl chloride gave benzoyl fluoride in 65% yield and dinitrochlorobenzene gave dinitrofluorobenzene in 36% yield.

Attempts to prepare pentamethylguanidine (41) were unsuccessful. The reaction between tetramethylguanidine and methyl iodide gives pentamethylguanidinium hydriodide (42), in agreement with literature results[133]. Attempts to remove the HI to generate pentamethylguanidine resulted in the formation of a mixture of tetramethylguanidine and pentamethylguanidine which could not be separated.

3.5 Conclusions

We have shown that a series of sterically hindered strong bases may be coupled with HF to produce complexes that may be used as sources of soluble fluoride ion in a variety of reactions.

The most effective fluorinating reagents were the complexes of the strongest bases e.g. PS, ethyl-tetramethylpiperidine.

To ascertain why these are the most effective reagents we need to find out the species involved in solutions of these complexes. Low temperature NMR is the best method for doing this but was unfortunately unsuccessful for these systems. However,

a ^{19}F NMR spectrum of $Bu_3N.HF$ complex was obtained at -80°C. From the spectrum we have shown that a series of equilibria are present forming a variety of species.

Thus we can postulate that the success of a reagent as a fluoride ion source depends on the following equilibrium:-

$$R_3N.HF \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_3N.H^+ + F^-$$

For a good fluoride ion source k_1 must be large and k_{-1} small. The equilibrium is improved by increasing the base strength of the base (increases k_1) and the steric hindrance around the basic nitrogen atom (reduces k_{-1}).

However the situation is complicated by the fact that other equilibria are occuring as seen in low temperature NMR.

e.g. $R_3N.HF + HF \rightleftharpoons R_3NH^+.HF_2^-$

Whether the presence of HF_2^- effects the reactivity of these reagents in these types fluorination reactions is unclear, but $Bu_4N^+HF_2^-$ has been shown to be an effective source of fluoride ion in its own right[134].

Comparison of the reactivities of the tetramethylpiperidine HF systems suggests that increasing the steric hindrance around the nitrogen atom causes an increase in fluoride ion reactivity.

These preliminary studies give some idea about the nature of the reactivity of amine.HF complexes as sources of fluoride ion in that amine.HF complexes exist in solution as an equilibrium between numerous species which we have identified by low temperature NMR. Increasing the steric hindrance around the basic site in the amine appears to increase reactivity of the amine.HF systems as sources of fluoride ion.

We have shown that amine.HF complexes can act as fluoride ion donors in solution in several nucleophilic substitution reactions, but the amine.HF systems can not be compared with alkali metal fluorides as their mode of reactivity involves an equilibrium situation.

CHAPTER FOUR

ANNELATION REACTIONS BETWEEN 1,8-BIS(DIMETHYLAMINO)-NAPHTHALENE (PROTON SPONGE) AND FLUORINATED ALKENES

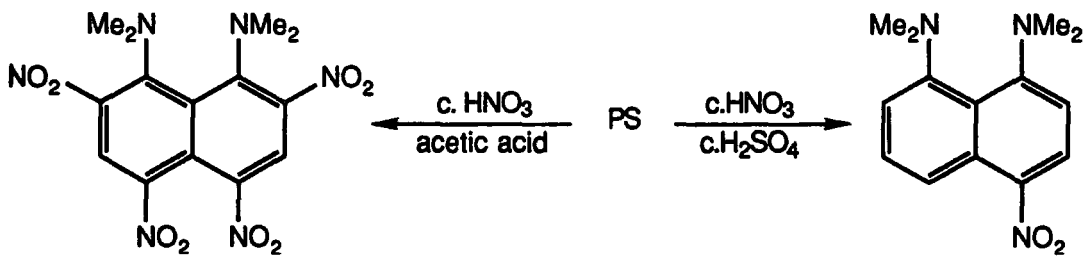
4.1 Introduction

Proton Sponge (PS) was found to react with fluorinated alkenes via the naphthalene ring in electrophilic substitution reactions to form novel products. Reactions of aromatic systems with electrophiles are well known[135] but only a few reactions between PS and electrophiles have been recorded and are reviewed below. Reactions between soft carbon nucleophiles with fluorinated alkenes have not been reported, to our knowledge.

4.2 Electrophilic Substitution Reactions of 1,8-Bis(dimethylamino)-naphthalene (PS)

4.2.1 Nitration

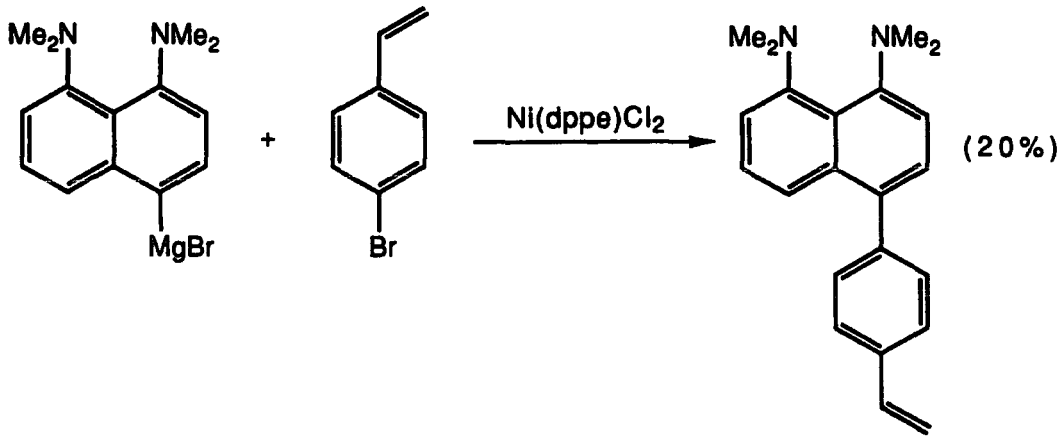
PS is nitrated at the 4 position by a mixture of concentrated nitric and sulphuric acids. However a mixture of nitric and acetic acid produces the 1,4,5,8-tetra nitrated product[136].



4.2.2 Bromination

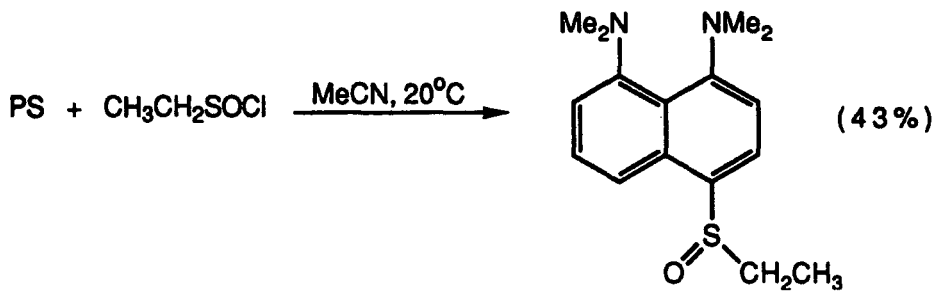
PS is brominated to 4-Bromo-1,8-bis(dimethylamino)naphthalene by using bromine in conjunction with an iron/iron (III) chloride catalyst in 39% yield[137]. The same product is realised in greater yield (80%) on bromination with bromine in sulphuric acid[138].

The Grignard reagent of this 4-bromo derivative may be prepared and may undergo coupling reactions with other aromatic bromides to form potential monomers[137].



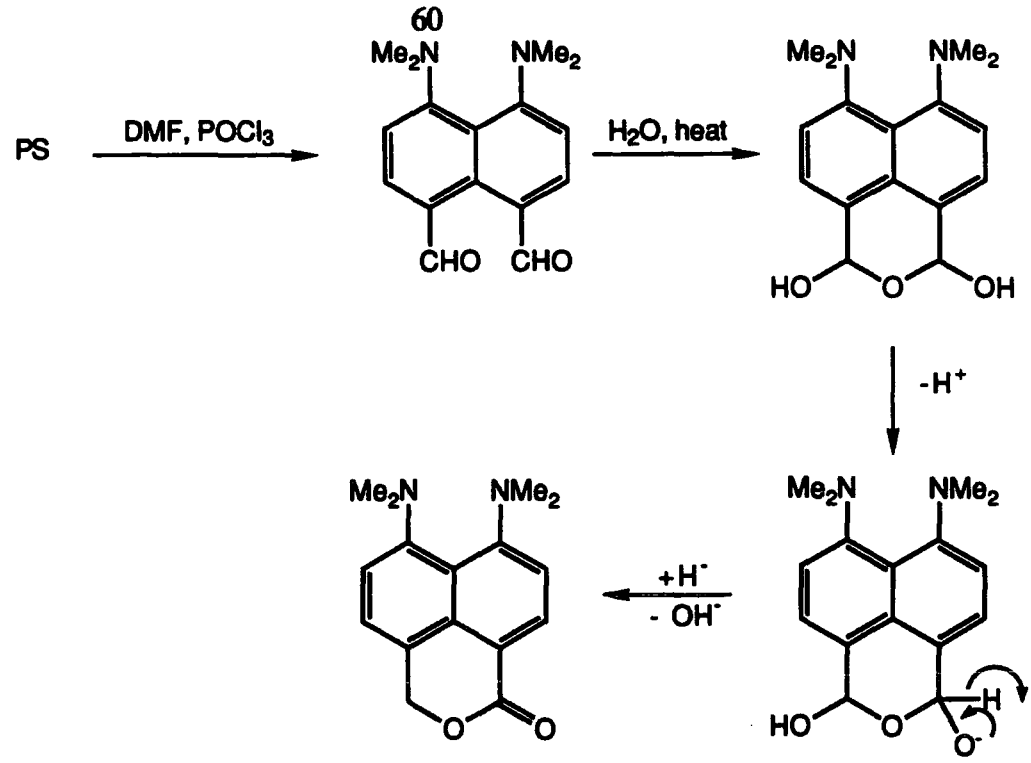
4.2.3 Alkylsulphination

PS is alkylsulphinated in the 4 position[139].



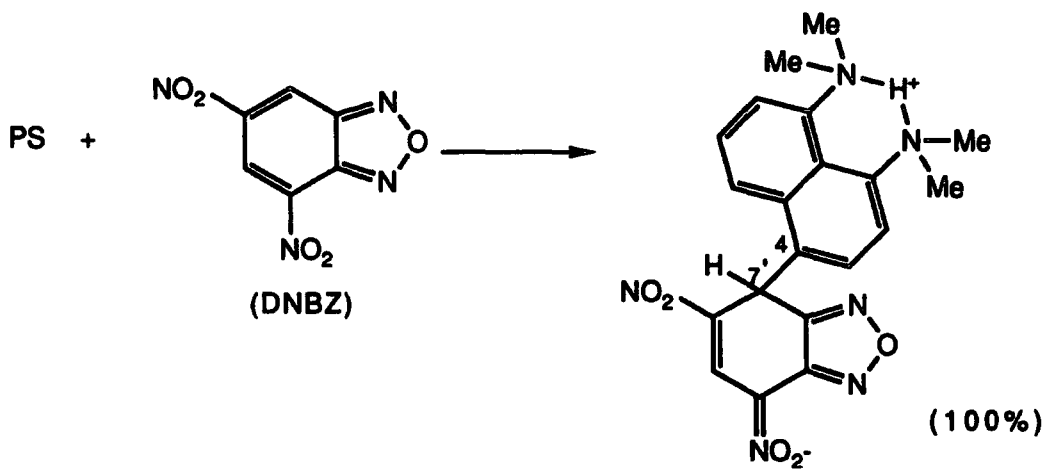
4.2.4 Formylation

PS is formylated using the complex of dimethylformamide and phosphorus oxychloride (the Vilsmeir reagent) as formylating agent[138]. 4,5-diformyl-1,8-bis(dimethylamino)naphthalene is formed which then undergoes an intramolecular Cannizarro reaction to produce a naphthopyranone derivative in 36% yield. This reaction is an example of an annelation reaction involving PS.



4.2.5 Reaction with Dinitrobenzofurazan (DNBZ)

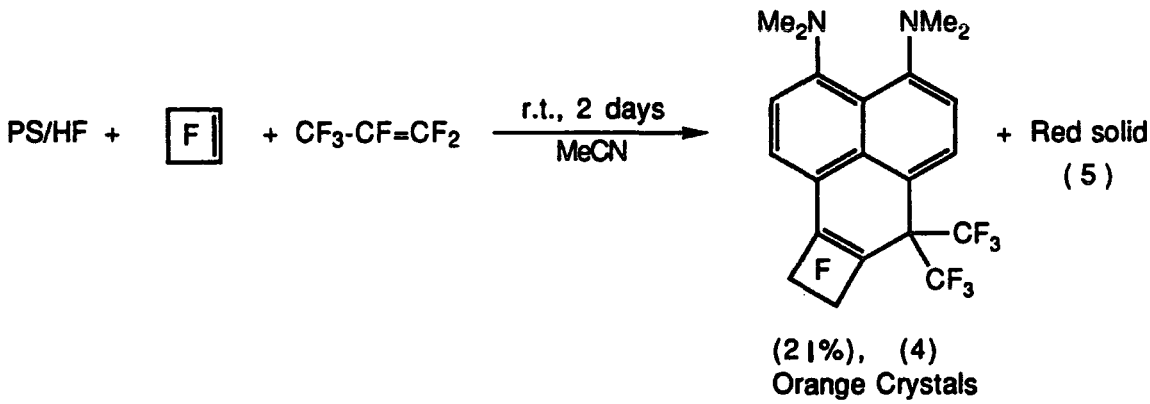
PS reacts with the very strong electrophiles dinitrobenzofuroxan (DNBF) and dinitrobenzofurazan (DNBZ) to form zwitterionic products[140], which exist as two conformers, proved by low temperature n.m.r, with restricted rotation around the C4-C7' bond[141].



4.3 Reactions of 1,8-Bis(dimethylamino)naphthalene with Fluorinated Alkenes (3) and (43)

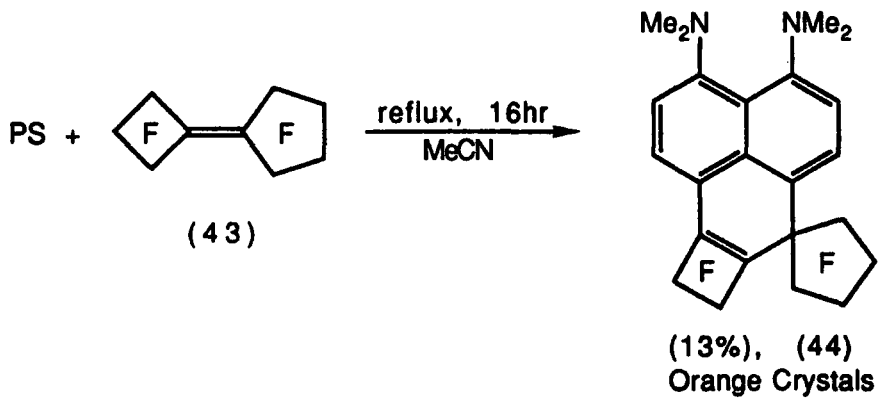
The success of the PS/HF system in catalysing the dimerisation of hexafluoropropene (section 2.4.1.1) prompted us to try to prepare the co-dimer of perfluorocyclobutene and hexafluoropropene using PS/HF as the catalyst.

PS/HF does indeed catalyse the co-dimerisation but the alkene so formed reacts further with the naphthalene ring of PS in an electrophilic substitution reaction to form two solid products which could be separated by column chromatography. The major product, an orange solid (4) was isolated in 21% yield. A red solid (5)(trace) was also isolated but remains unidentified.



This reaction therefore revealed a range of possible reactions between tertiary aromatic amines and perfluorinated alkenes. Thus, the direct reaction between PS and the co-dimer (3) gave the same product (4) in a comparative yield (22%).

Similarly PS reacts with the fluoroalkene (43) to give the annelation product (44), another orange solid , in 13% yield.



4.3.1 Structure Elucidation

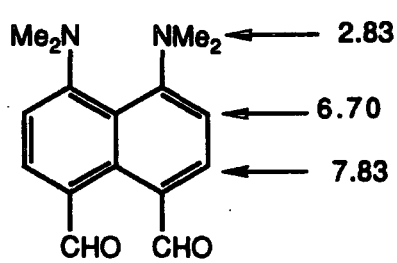
Before any mechanistic considerations (section 4.4) we must prove the structures of (4) and (44), which was done using all available spectroscopic techniques. As (4) and (44) have similar structures we will consider their spectral properties together.

Both (4) and (44) gave satisfactory elemental analyses for $C_{21}H_{16}N_2F_{10}$ and $C_{23}H_{16}N_2F_{12}$ respectively and mass spectra in the Cl^+ and Cl^- modes.

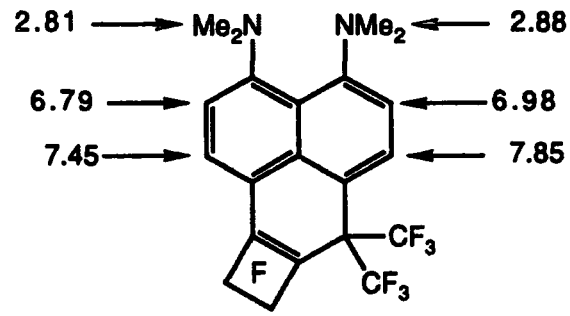
4.3.1.1 NMR Spectra of (4) and (44)

^{1}H NMR - The ^{1}H NMR spectrum of (4) consists of two singlets at 2.81 and 2.88ppm each having a relative intensity of six, corresponding to the NMe_2 groups, and two AX systems in the aromatic region (6.79 - 7.85ppm) each with a relative intensity of two, thus corresponding to four aromatic protons. The two AX systems (J_{AX} = 8.3 and 8.8 Hz) indicate that the naphthalene ring must be a 1,4,5,8-tetrasubstituted derivative.

Similarly, the ^{1}H NMR spectrum of (44) consists of two singlets (2.88, 2.94 ppm) and two AX systems (6.86-7.52ppm, J_{AX} = 8.4 and 8.8Hz).
These results agree with a similar tetrasubstituted PS system (45)[138].



(45)

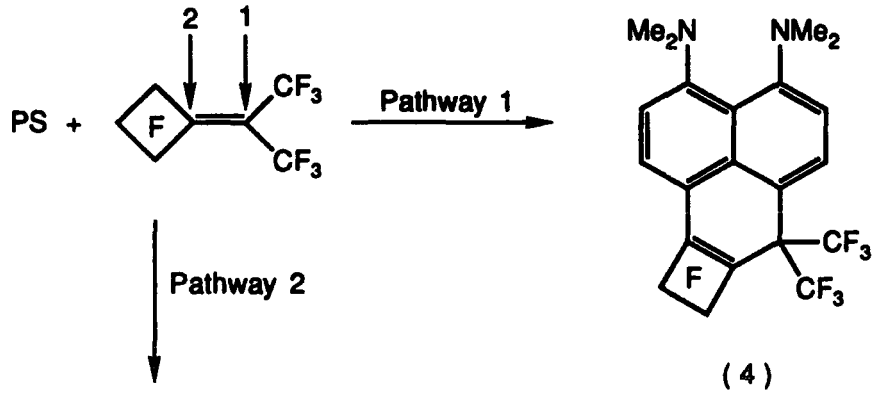


(4) is an unsymmetrical molecule and so the NMe_2 groups each give a singlet. The peak which is further upfield is assigned to the NMe_2 group with the more electronegative substituent on the 4-position of the same benzene ring which gives a deshielding effect, i.e we assume that $(CF_3)_2C$ is a more electron withdrawing group than the cyclobutene ring as more fluorine atoms are present in this substituent. Similarly, the aromatic protons are assigned in this way.

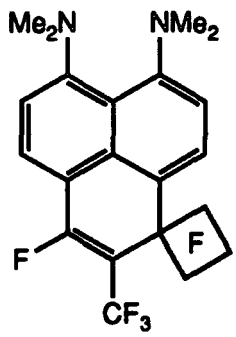
^{19}F NMR - ^{19}F NMR was essential in proving the structures for (4) and (44) and hence the orientation of initial nucleophilic attack by PS on the fluoroalkene.

^{19}F NMR for Annelation Product (4)

There are two possible sites of nucleophilic attack by PS on the fluoroalkene which would produce different products according to the mechanism outlined (section 4.4).



(4)



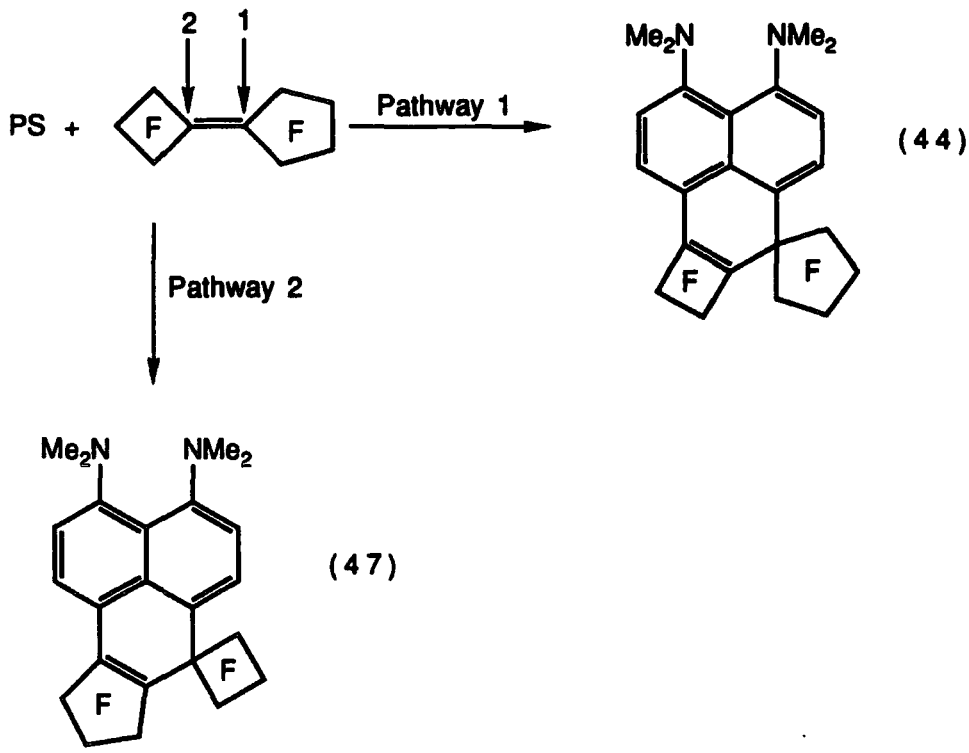
(46)

(^{1}H NMR of (4) and (46) would be similar)
(The red solid (5) isolated in small yield shows two singlets in the ^{19}F NMR spectrum at -68.9 and -110.5ppm, and hence could not be (46). The red solid is most probably a hydrolysed product of (4) as the infra red spectrum reveals a peak at 1790cm-1 which may be a carbonyl group. However, attempts to hydrolyse (4) failed.)

We would expect (4) to give a ^{19}F NMR spectrum consisting of three resonances (CF_3, CF_2, CF_2) of relative intensities 6:2:2, and (46) to give a spectrum consisting of four resonances (F, CF_3, CF_2, CF_2) of relative intensities 1:3:4:2. The spectrum obtained consists of three singlets at -67.2 (6F, $2CF_3$), -105.1 (2F, CF_2) and -112.5 (2F, CF_2) corresponding to structure (4).

^{19}F NMR for Annelation Product (44)

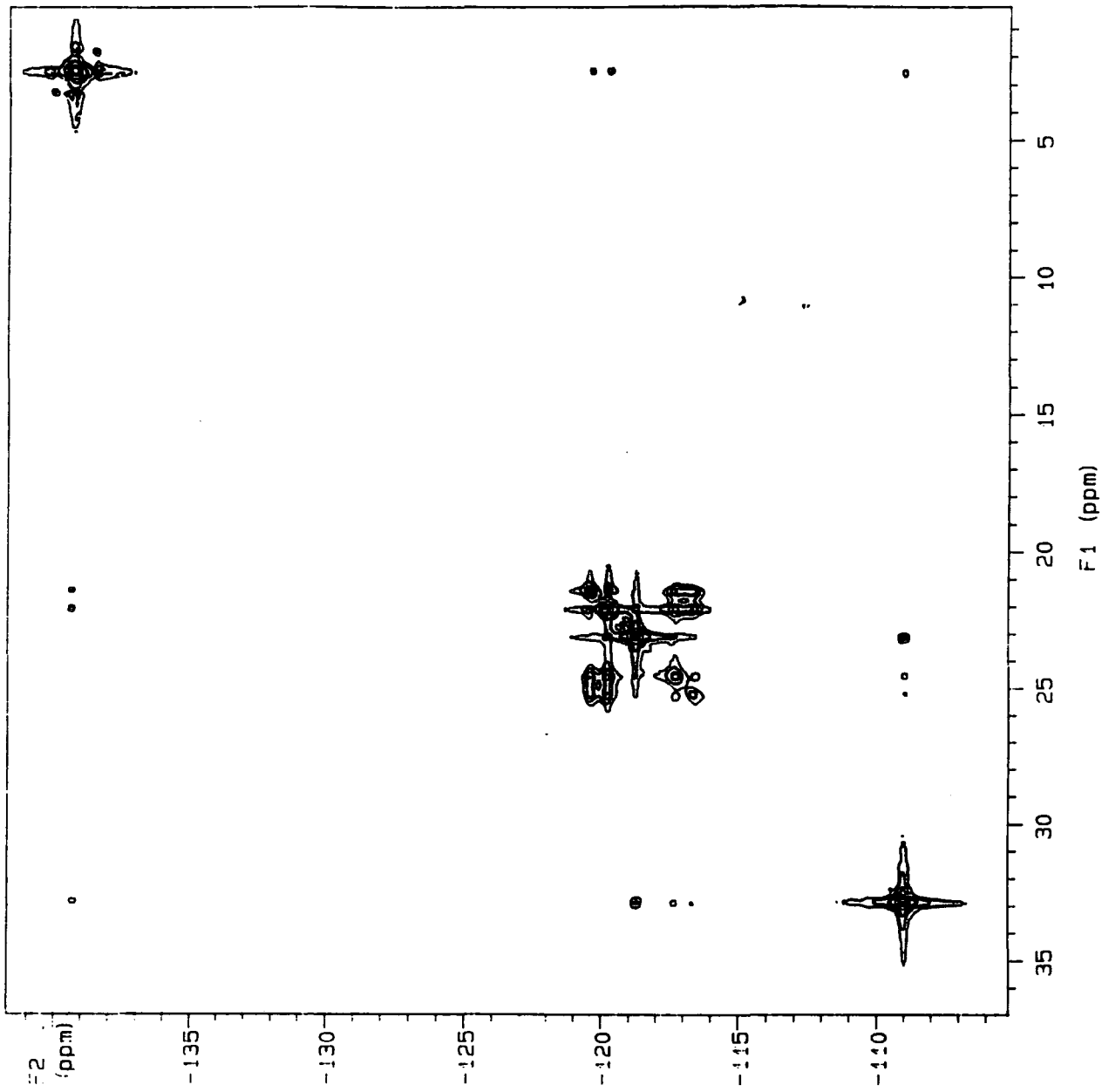
Again two possible products could be envisaged.



For structure (44) we would expect a ^{19}F NMR spectrum consisting of four resonances ($4CF_2$) with relative intensities of 2:2:4:4, and for structure (47) a spectrum consisting of five resonances ($5CF_2$) with relative intensities 2:2:2:4:2. The spectrum obtained consists of four resonances; -104.9 (s, 2F), -114.6 (s, 2F), -135.2 (s, 4F) and -112.8 and -116.0 (AB, J_{AB} = 250Hz, 4F); the spectrum along with the ^{19}F 2-D COSY spectrum is shown overleaf (Fig 6).

In the AB system, the peaks centred at -112.8ppm are broader than those at -116.0ppm which is probably due to long distance F-H coupling. The fact that this is an AB system is proved by the COSY spectrum, indicating that the peaks at -112.8 and -116.0 are indeed coupled. Thus the COSY spectrum confirms that there are three singlets and an AB system with the required relative intensities for structure (44).

Also, the shifts of the CF_2 groups in the cyclobutene ring substructures are similar for structures (4) and (44) as shown below.



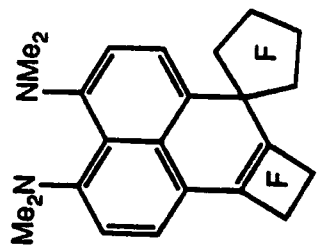
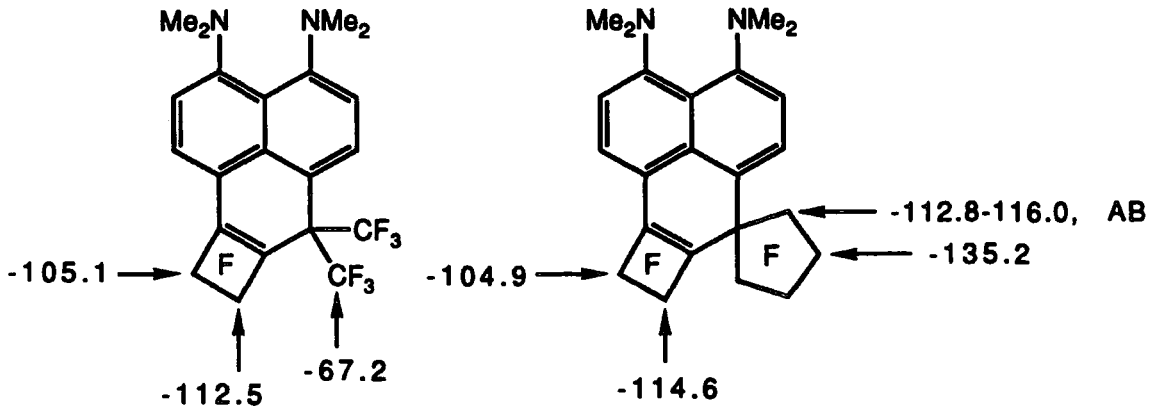


Figure 6

^{19}F 2-D COSY NMR Spectrum

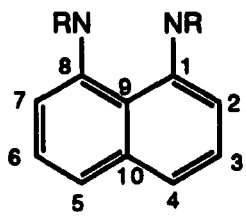


^{13}C NMR - ^{13}C NMR was not very helpful in establishing the structures of (4) and (44) because of the complexity of the spectra between 115 and 120ppm due to C-F coupling. However, peaks may be assigned for the "hydrocarbon half" of the molecules where C-F coupling is absent.

^{13}C spectra were assigned using the chemical shifts for published, unsubstituted compounds as models[106], and are collated in Table 14.

Table 14. ^{13}C NMR Data for 1,8-(bisdimethylamino)naphthalene Compounds (Aromatic Ring only)

The following numbering system has been used for the naphthalene nucleus for both published compounds (48)-(51), (4) and (44). (For (4) and (44) positions 4 and 5 are substituted).



(48) R = Me_2
(49) R = $-CH_2-(CH_2)_2-CH_2-$
(50) R = $-CH_2-(CH_2)_3-CH_2-$
(51) R = $-CH_2-CH_2-O-CH_2-CH_2-$

	C-1 C-8	C-2 C-7	C-3 C-6	C-4 C-5	C-9	C-10	N(CH$_3$)$_2$
(48)	150.7	112.6	125.4	121.7	120.5	137.8	44.4
(49)	147.7	108.2	125.4	119.2	119.2	137.4	-
(50)	151.2	113.0	125.3	123.4	120.8	137.7	-
(51)	149.6	113.2	125.6	123.8	120.0	137.8	-
(4)	156.1	111.5	130.4	107.7	121.4	134.1	43.5
	152.9	108.9	126.9	116.7			
(44)	158.2	111.4	135.8	107.4	unass	134.0	43.0
	154.4	109.4	128.6	unass			

The assignment of the peaks is aided by the fact that non-quaternary carbon atoms, i.e.aromatic C-H, have low relaxation times and hence give large peaks. Thus C-2, C-3, C-6 and C-7 are easily assigned. The shifts are similar to those reported but, of course, C-4 and C-5 substitution would alter their shifts slightly.

For structures (4) and (44) C-2 has a greater shift value than C-7 (C-3 > C-6 etc) as C-4 has the more electronegative substituent ($(CF_3)_2C$) causing a deshielding of that part of the naphthalene ring.

C-1 and C-8 all occur at around 150ppm , as seen in table.14.

A full assignment was not possible due to the complexity of the spectra but the four C_{Ar}-H peaks provide further evidence of a tetrasubstituted naphthalene derivative for structures (4) and (44).

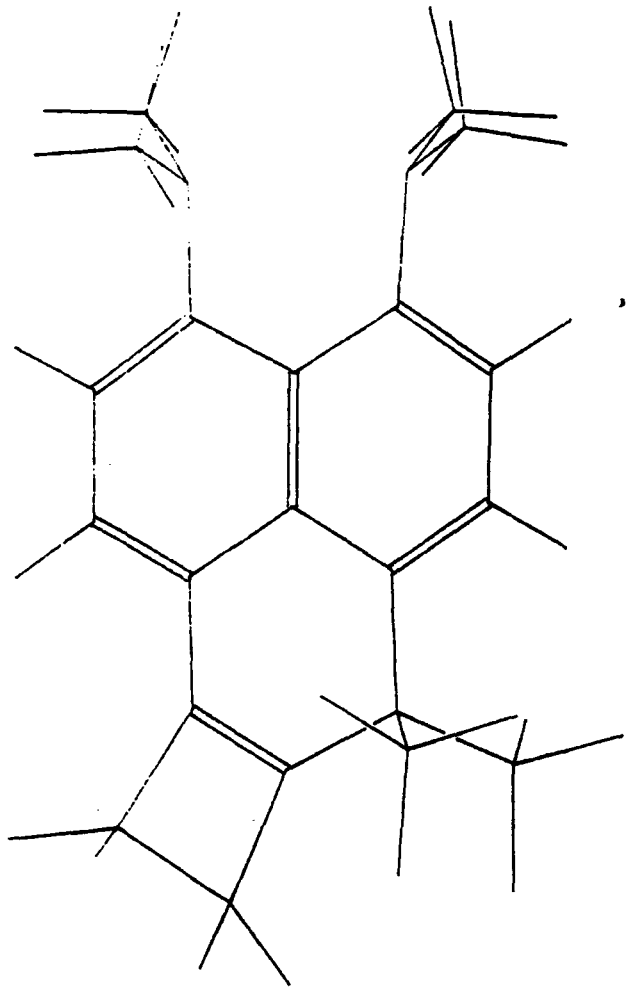
4.3.2 Molecular Modelling of Annelation Product (4)

Molecular modelling studies were carried out by Dr. J. Morley, ICI. and predicted structures are shown overleaf (Fig 7).

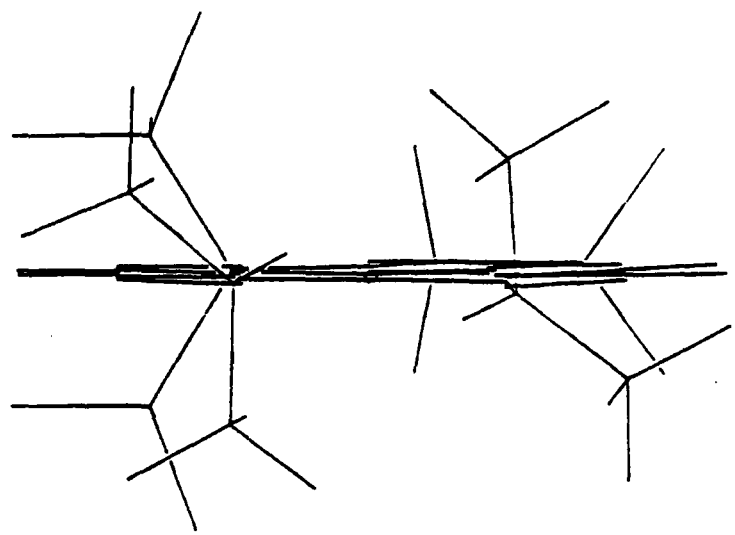
From the diagrams we see that the naphthalene ring is slightly buckled and the lone pairs do not face each other but are parallel, much the same as in PS itself[107]. Hence we would predict that the annelation product (4) to have the same high basicity as PS.

Figure 7

Computer Generated Structure of (4)



(A)



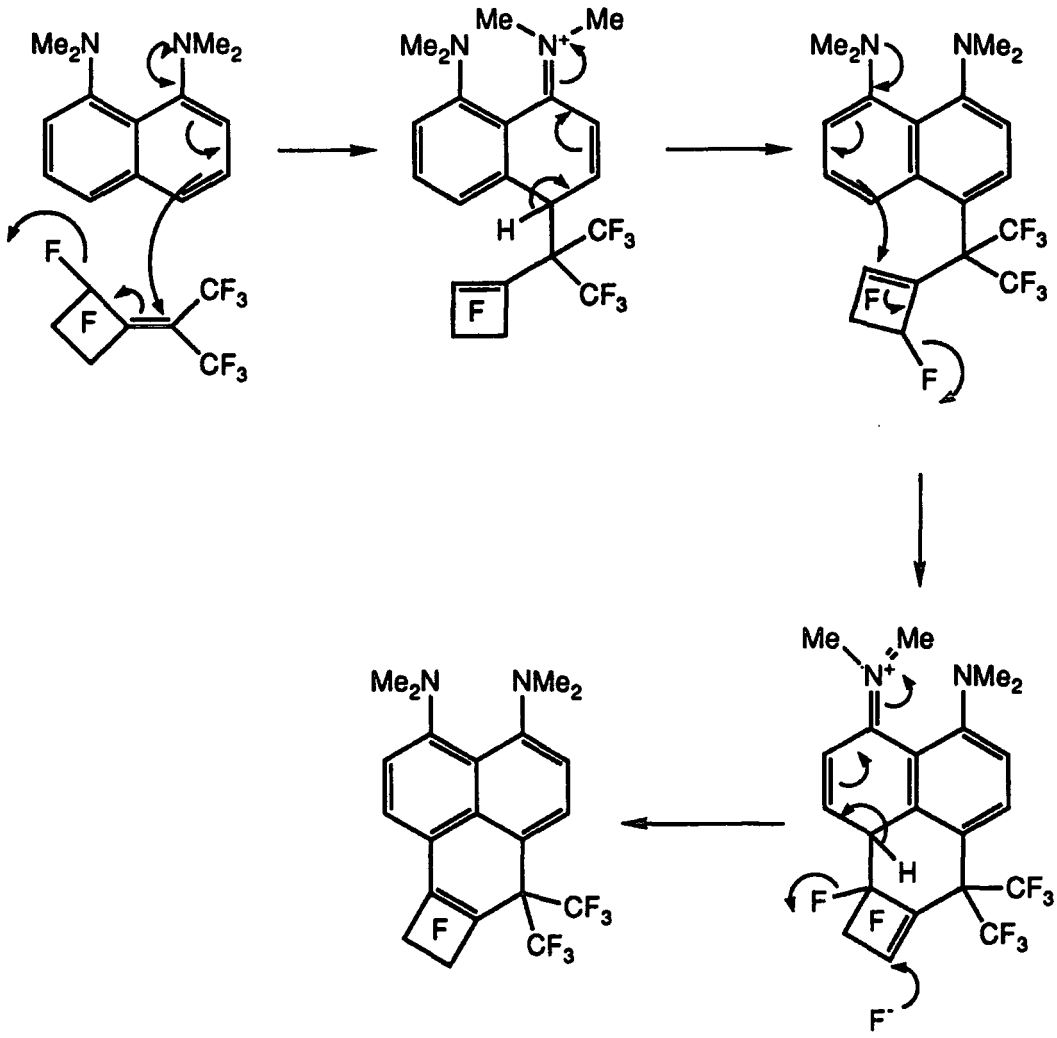
(B)

(A) - Side-on View

(B) - Head-on View - looking along the plane of the Naphthalene Ring from above the Dimethylamino Groups

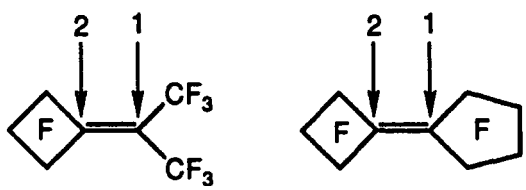
4.4 Mechanism of the Annelation Reaction

The following mechanism has been postulated for the reaction of PS with fluorinated alkenes (shown is formation of product (4)).



4.4.1 Orientation of Initial Nucleophilic Attack

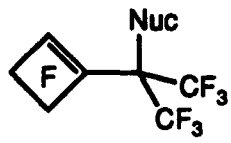
For each fluoroalkene (3) and (43) there are two possible sites for initial nucleophilic attack.



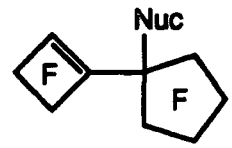
We have proved that pathway (1) is preferred and following is a rationale of these observations.

The potential intermediate species for each pathway are as follows:-

(1)

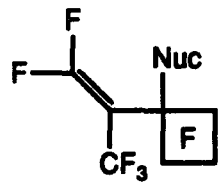


(52A)

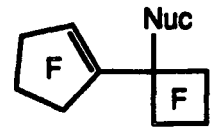


(52B)

(2)



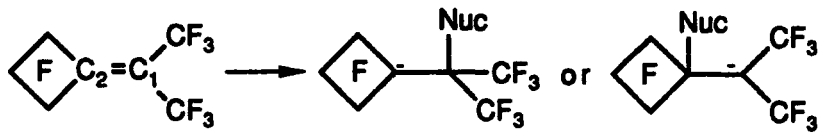
(53A)



(53B)

We would expect the angle strain around the spiro carbon atom in intermediates (52A) and (52B) to be much less than in (53A) and (53B). The formation of intermediates via pathway (1) is more energetically favourable and so the orientation of attack may be controlled by the angle strain in the reaction intermediates.

Also, two intermediate carbanions are possible[142].



(54A) (54B)

When the nucleophile is fluoride ion, (54A) is formed exclusively as shown by the formation of stable perfluorinated carbanions[142]. The stability of perfluorocarbanions is governed by the substituents on the carbanion centre. Essentially, C^--F is destabilising due to electron pair repulsions and C^--C-F is stabilising due to the inductive effect[143]. However for fluoroalkenes (3) and (43) both are of the general formula $(R_F)_2C{=}C(R_F)_2$ and so the stabilising effects on each carbanion are apparently very similar. Also the Frontier Orbitals at each unsaturated carbon atom will have similar coefficients[144]. Therefore we would not expect there to be any selectivity in the direction of nucleophilic attack if the stability of the intermediate carbanions are the controlling factor.

The direction of nucleophilic attack at C_1 rather than C_2 has been attributed to the increased electronegativity of carbon (C_2) in the ring[143]. This may be explained by a consideration of the hybridisation of the orbitals on C_1 and C_2.

sp_2 hybridised orbitals are at 120° angles and sp_3 orbitals are at 109° angles. sp_3 hybridised orbitals have greater p character than sp_2 orbitals, and conversely sp_2 orbitals have greater s character than sp_3 orbitals. Also, s orbitals are more electronegative than p orbitals as s orbitals are closer to the nucleus of the atom.

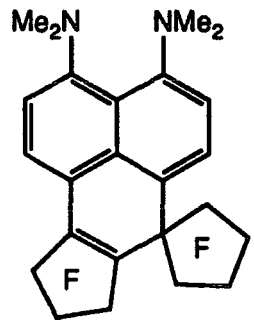
In the case of (54A) the angle of the orbitals forming the bonds in the ring are constrained to being less than 90°. Hence, these orbitals are more like sp_3 orbitals than sp_2 orbitals and so are rich in p character. Thus, the orbital containing the carbanion must be rich in s character. In the case of (54B) the orbitals forming the bonds with the CF_3 groups are at an angle of greater than 90° and are not as rich in p character as in the case of (54A). So, the orbital containing the carbanion in (54B) is not as rich in s character as in (54A). So, the orbital containg the carbanion in (54A) has more s character than in (54B). Orbitals richer in s character are more electronegative and so the carbanion is more stable in orbitals rich in s character. Thus the most stable carbanion is (54A) and hence the most likely reaction intermediate. Thus the nucleophile initially attacks C_1 for the more stable carbanion (54A) to be formed, in accordance with our findings.

4.5 Reaction of 1,8-Bis(dimethylamino)naphthalene with Perfluorobicyclopentylidene (55)

4.5.1 At Low Dilution

When PS and fluoroalkene (55) were stirred overnight at room temperature in acetonitrile a dark olive green solid precipitated which was purified by recrystallisation to give flat, square, dark green crystals (56).

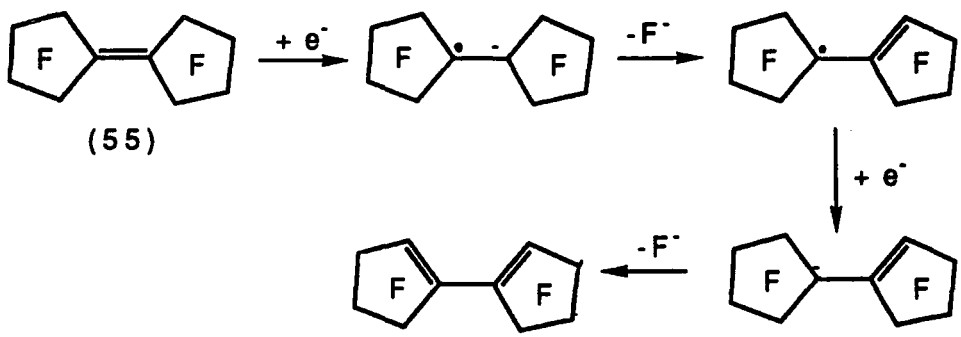
Mass spectrometry and elemental analysis of this product gave a molecular formula of $C_{24}H_{16}N_2F_{12}$ which is two fluorine atoms less than that of the expected annelation product (57).



(57)

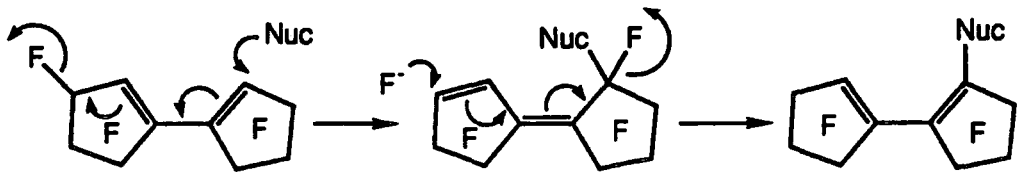
No NMR spectra of the product were obtainable and so the structure of (56) is uncertain. Hence single crystal X-ray Crystallography is being attempted for a structure determination.

The molecular formula of the product indicates that defluorination of the starting alkene has taken place. This can occur by reduction of the alkene in a 1-electron transfer process[145].



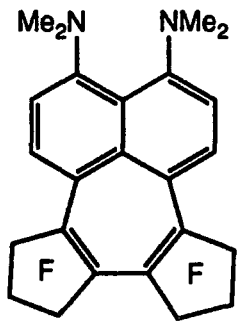
(55) (58)

The diene (58) so formed could then react with PS in the following type of process[145].

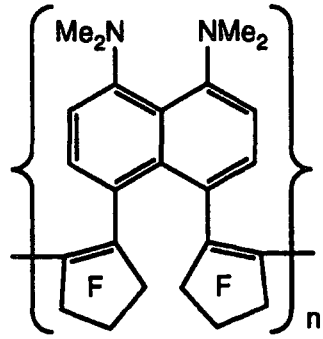


In a separate experiment[146] PS reacted with the diene (58) to give the same product as that obtained between the alkene (55) and PS. The reduction of alkene (55) to the diene (58) has previously been performed using a sodium amalgam route[145], and so this reaction shows the possibility of using tertiary amines as reducing agents (electron donors) in reactions of this type.

The most probable structures are shown below.



(56)



(59)

The structure is most likely to be (56) because of the crystallinity of the product and the formation of molecular ions in the EI^+, CI^+ and CI^- mass spectra. However, an X-ray structure is required.

4.5.2 At High Dilution

Initially we thought that the product arising from the reaction between PS and perfluorobicyclopentylidene (55) gave the polymeric structure (59). Hence we repeated the reaction at high dilution in an attempt to isolate any monomeric products. Three products were isolated by column chromatography, the first compound eluted being (56).The second and third compounds had a remarkable appearance. The second compound eluted was bright green flakes (60) of a metallic lustre which in solution gave a purple colouration and the third compound eluted was purple flakes (61) of a metallic appearance which in solution gave a green colouration! Firstly we must attempt to prove the structures of these fascinating compounds.

4.5.2.1 Green Crystals (60)

Mass spectrometry and elemental analysis suggest a molecular formula of $C_{24}H_{16}N_2F_{12}O$.

^{1}H NMR - The ^{1}H NMR spectrum shows a singlet at 2.16 (12H, NMe_2 groups) and two AX systems in the aromatic region between 6.95 and 7.92ppm.

The broad peak seen between 2.5 and 3.4ppm may be due to complexing between the solvent and the compound. This may explain the change in colour on going from the crystalline form into solution.

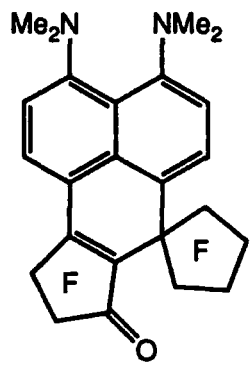
Each AX pattern has additional splitting on the more upfield peaks probably due to long-range proton-fluorine coupling.

However, the singlet at 2.16ppm and the two AX patterns in the aromatic region corresponding to four protons indicate the presence of a 1,4,5,8-tetrasubstituted PS system, as before.

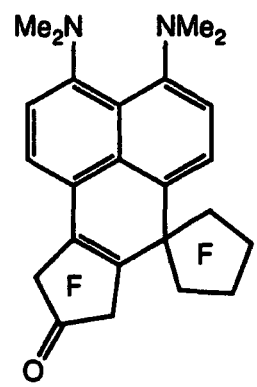
^{19}F NMR - The ^{19}F and ^{19}F 2-D COSY NMR spectra are shown overleaf (fig 8).

The spectrum consists of four resonances; an AB system between -111.0 and -113.4ppm (relative intensity 4), a broadened resonance, essentially a singlet or pseudo AB, at -132.3ppm (4F), and two other singlets (pseudo AB) at -117.8 (2F) and -131.4ppm (2F).

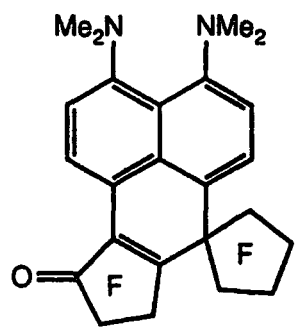
The molecular formula suggests that a structure similar to the expected annelation product (57) is present, with a CF_2 group substituted by a carbonyl group. The infra red spectrum reveals a peak at 1720cm^{-1} which could correspond to the carbonyl group. Possible structures based on this assumption are shown below.



(60)



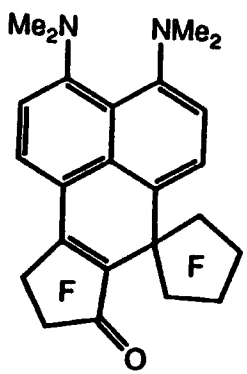
(60A)



(60B)

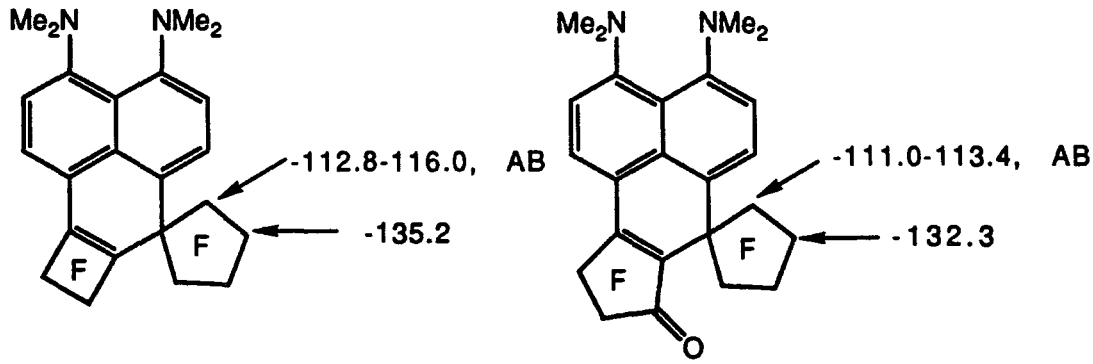
Figure 8

^{19}F 2-D COSY NMR Spectrum

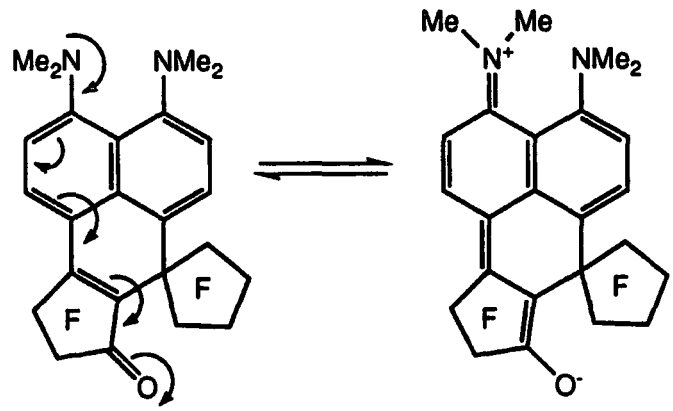


We would expect the CF_2 group adjacent to the C=C double bond to be more easily hydrolysed and so it is unlikely that the structure is (60A).

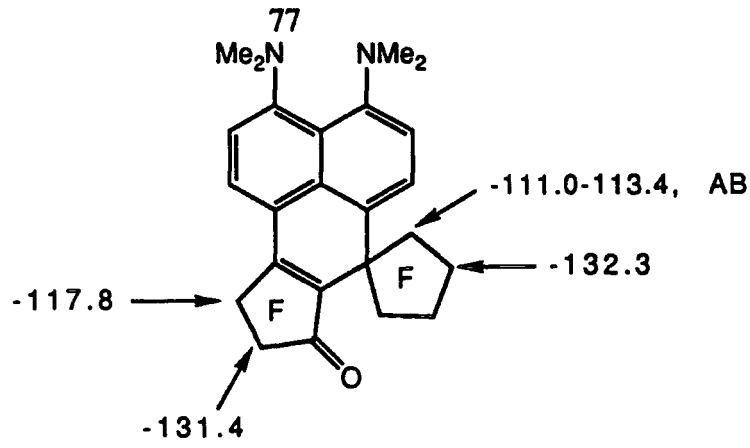
The AB system and singlet at -133ppm are similar to the shifts found for the spiro-cyclopentene substructure in compound (44) and are compared below.



The other two singlets are consistent with all three possible structures (60), (60A) and (60B). However, because of the metallic nature of the compound, structure (60) is favoured as conjugation of the π system is spread throughout the molecule. This structure would give the molecule charge-transfer properties as an electron donor group (NMe_2) is connected via a conjugated π system to an electron acceptor group (C=O). The molecules may then align in a one-dimensional stack, giving the crystalline state a metallic nature[147]. These donor-acceptor properties may also explain the change in colour in going from the crystalline state into solution.



A final assignment of the ^{19}F NMR spectrum is as follows:-



The analysis for (60) is slightly in error. This could be due to complexing with water, which is known for α-fluorocarbonyl compounds. If one molecule of water is present for each of (60) the analysis is correct.

4.5.2.2 Purple Crystals (61)

Mass spectrometry and elemental analysis point to a molecular formula of $C_{24}H_{16}N_2F_{10}O$. Hence we would expect a structure similar to (56).

^{1}H NMR - Again we see a singlet at 2.16ppm corresponding to the NMe_2 groups and two AX systems between 6.4 and 7.4ppm, which point to a 1,4,5,8-tetrasubstituted PS system.

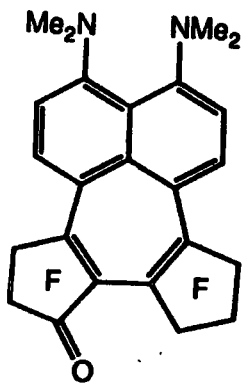
The appearance of the broadened quartet between 2.6 and 3.1ppm may again be due to complexing of the compound with the solvent, which may explain the colour of the compound in solution.The proton decoupled ^{19}F NMR spectrum shows that proton-fluorine coupling does occur and this may explain the added complexity of the AX systems.

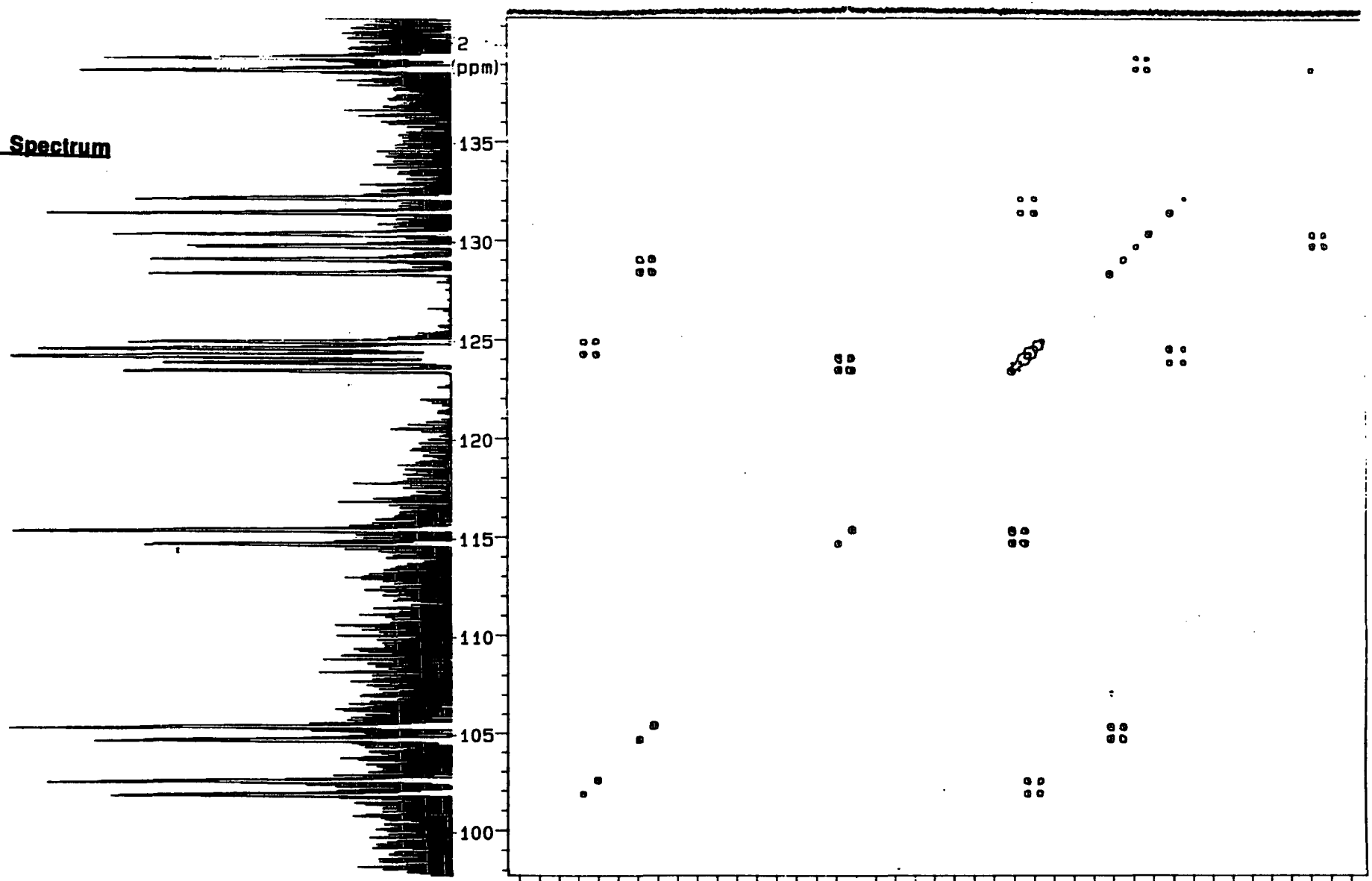
^{19}F NMR - The ^{19}F NMR spectrum is very complex and ^{19}F 2-D COSY spectroscopy was essential in determining which peaks were coupled, and is shown overleaf (fig 9).

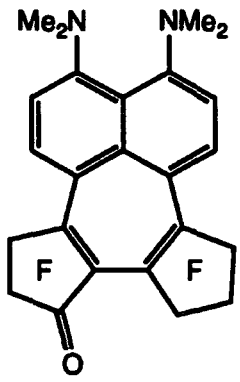
The COSY spectrum clearly shows the presence of five AB systems and the integrations confirm that these correspond to five inequivalent CF_2 groups. The molecular formula suggests a structure similar to (56), so we can suggest the following structures, each having five inequivalent CF_2 groups.

Figure 9

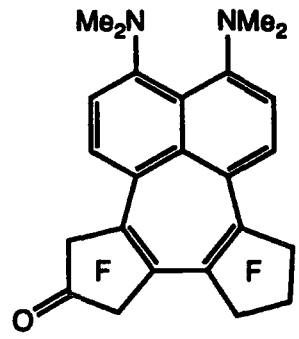
^{19}F 2-D COSY NMR Spectrum



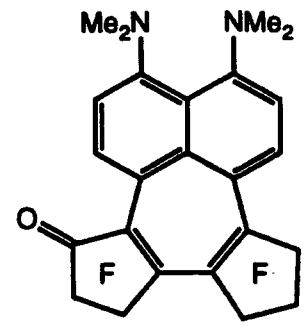




(61)

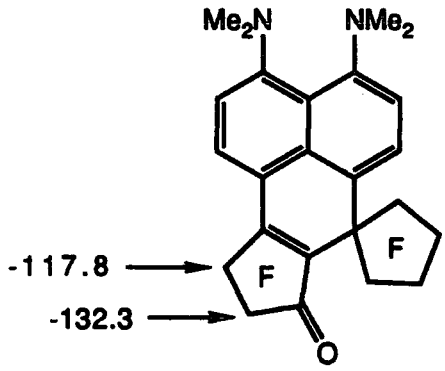


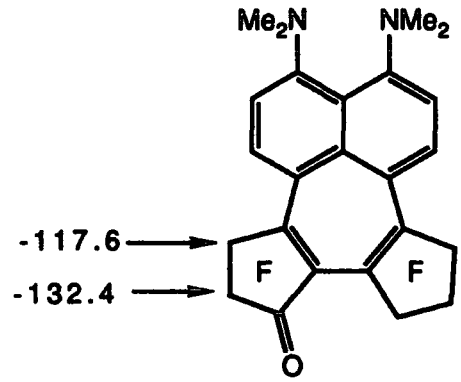
(61A)



(61B)

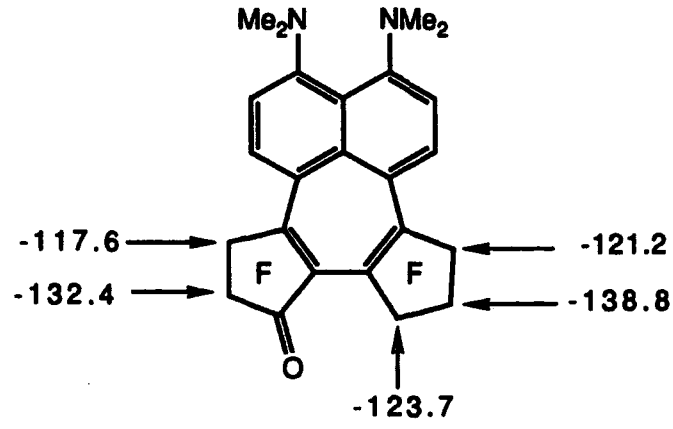
We would expect the chemical shifts of the CF_2 groups in the carbonyl substituted pentene ring to have similar values to those in the green crystals, structure (60). If we take the mid points of the AB systems and compare the shifts with the singlets in structure (61) this is indeed so.





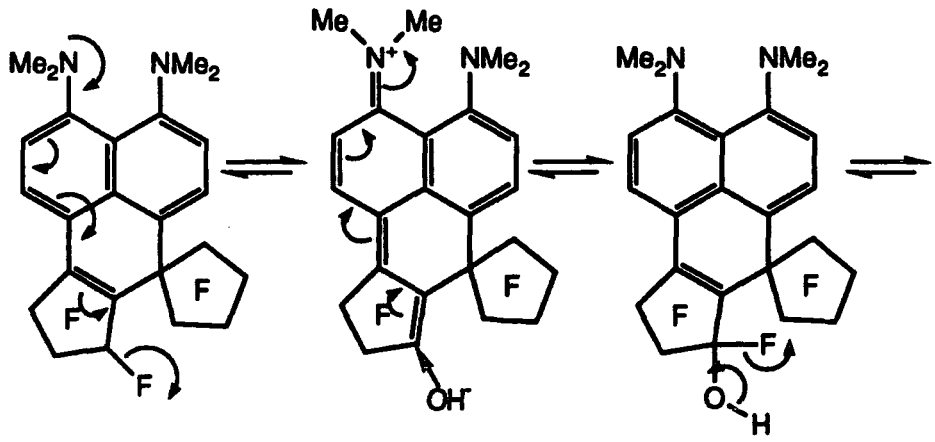
Again structure (61) is prefered because of the charge transfer properties associated with a fully conjugated π system connecting electron donor and acceptor groups.

A final assignment of the ^{19}F NMR spectrum of (61) is below. Shifts coressponding to the mid-points of the AB systems are given.



4.5.2.3 Mechanism of Hydrolysis to form (60) and (61)

Both green (60) and purple (61) crystals are the product of hydrolysis of the expected products via the following proposed mechanism.



(60)

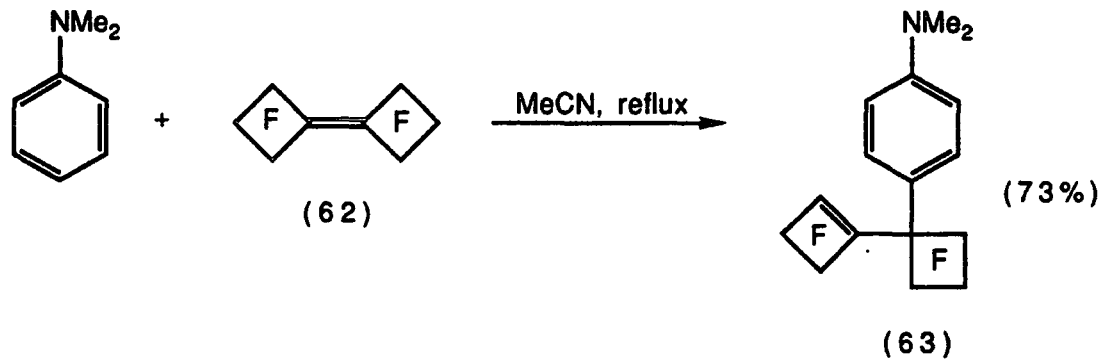
The water may have been present in the solvent or hydroxyl groups on the alumina used in the separation may have caused hydrolysis.

4.6 Reactions of Perfluorobicyclobutylidene (62) with Tertiary Aromatic Amines

It was of interest to know whether fluorinated alkenes would react with single ring systems. Hence, the fluoroalkene (62) was reacted with PS, N,N-dimethylanailine and N-methylindole. Although the reactions with the aniline and indole are not annelation reactions, we feel that it is wise to include them at this point as they are reactions between fluoroalkenes and soft, carbon, aromatic nucleophiles.

4.6.1 Reaction with N,N-Dimethylaniline

N,N-Dimethylaniline reacts with (62) to give the electrophilic substitution product (63) as white crystals in 73% yield.

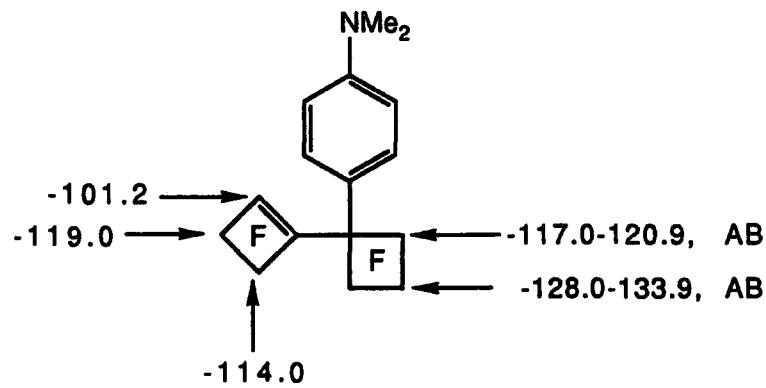


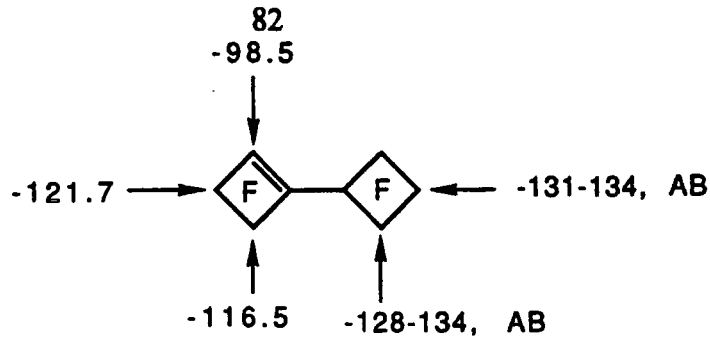
(62)

(63)

The ^{1}H NMR spectrum of (63) shows the familiar AA'XX' splitting pattern between 6.76 and 7.16 ppm (J_{AX}= 8.7 Hz) indicative of a *para*-disubstituted benzene ring and a singlet at corresponding to the NMe_2 group.

The ^{19}F NMR spectrum shows five resonances of relative intensity 1:2:2:4:2 which have been assigned in comparison with a similar unsubstituted fluoroalkene (64), as shown below.



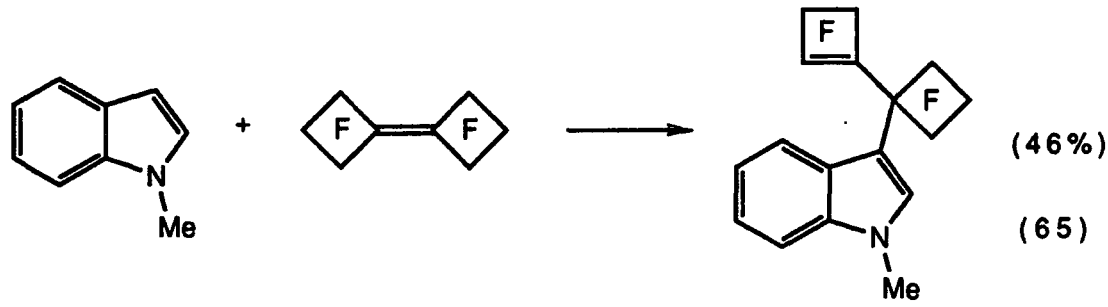


(64)

(63) gives satisfactory elemental analysis and mass spectra.

4.6.2 Reaction with N-Methylindole

Similarly, N-methylindole reacts with fluoroalkene (62) to give the product (65) as white crystals in 46% yield. The orientation of electrophilic substitution in indoles will be discussed in section 5.5.

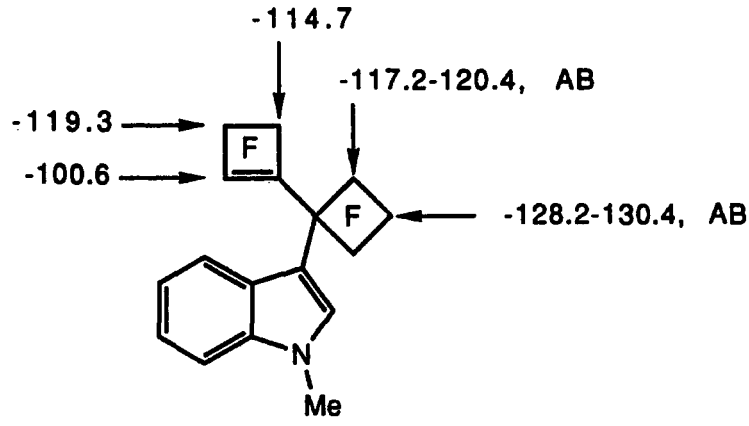


(46%)

(65)

The ^{1}H NMR spectrum of (65) is similar to those of adducts (73)-(75) as discussed in section 5.5.

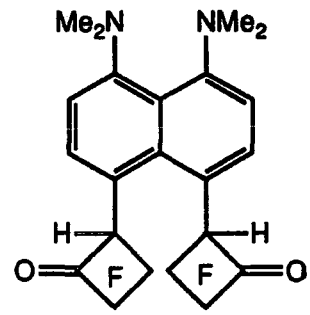
The ^{19}F NMR spectrum is similar to that of product (63). Satisfactory analysis and mass spectra were obtained.



4.6.3 Reaction with PS

PS and perfluorobicyclobutylidene were stirred together in acetonitrile. Addition of water to the reaction mixture gave a white solid, elemental analysis giving a formula of $C_{22}H_{18}N_2F_8O_2$. Clearly hydrolysis of the expected annelation product had taken place.

^{19}F NMR of the product (66) gives two resonances; a singlet at -120.1ppm and an AB system at 129.8 and 133.8ppm with the same relative intensities. This suggests a symmetrical structure and we have tentatively suggested structure (66).

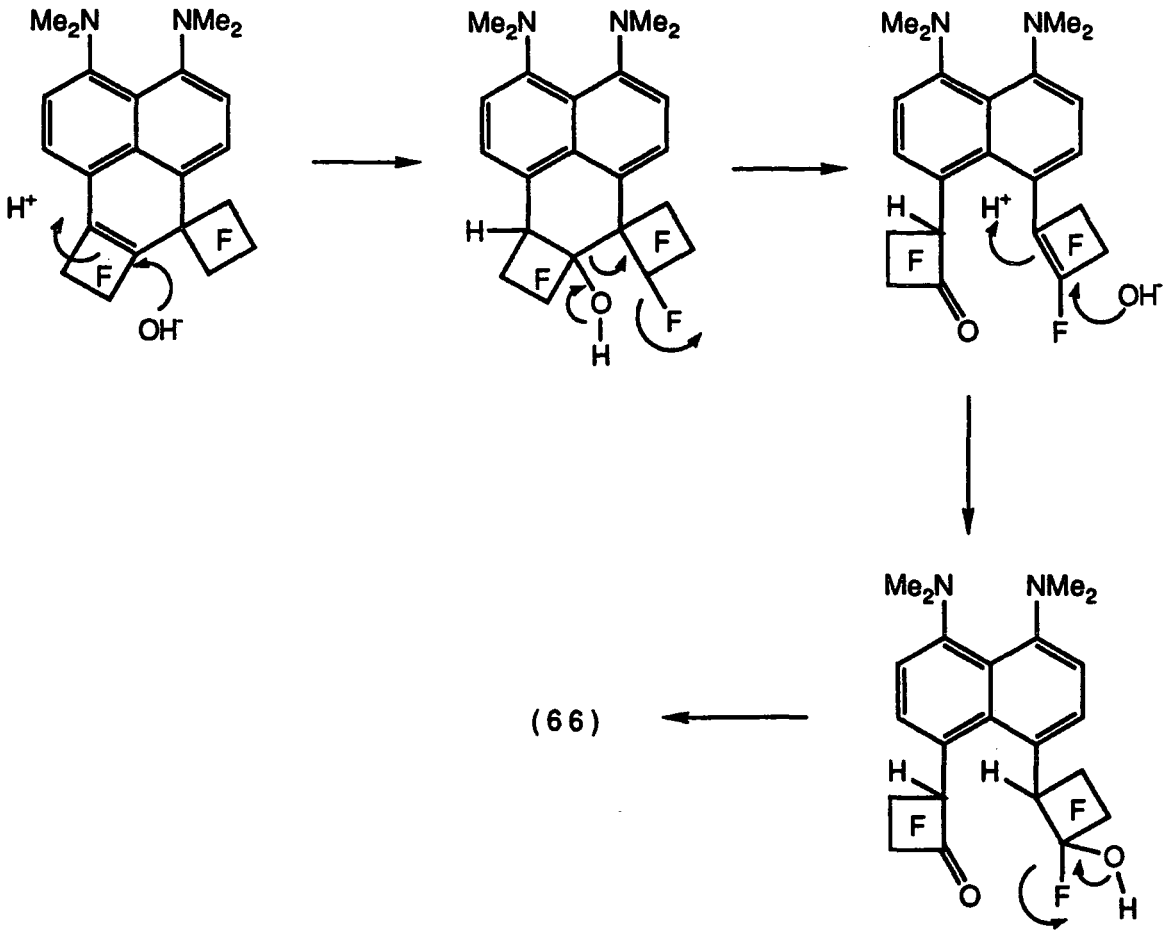


(66)

The singlet at -120.1ppm is assigned to the CF_2 groups adjacent to the carbonyl groups and the AB system to the asymmetric CF_2 groups.

The ^1H spectrum is more complex in the aromatic region compared to (4) and (44) and this may be due to isomeric forms of the product. The product (66) decomposes in the mass spectrometer so no confirmation of the structure is possible. The infra red spectrum shows an absorption at 1770cm^{-1} which could be attributable to the carbonyl bonds.

The product (66) may be formed by the hydrolysis of the expected annelation product, as follows:-



4.7 SUMMARY

We have shown that tertiary aromatic amines can act as carbon nucleophiles in reactions with perfluorinated alkenes. In particular, annelation reactions between 1,8-bis(dimethylamino)naphthalene (PS) and alkenes (3) and (43) have been performed. A mechanism for this reaction has been proposed and reasons for the direction of nucleophilic attack on the fluoroalkene discussed.

The general reaction may be extended to anilines and indoles. Hence we have discovered a general route for the nucleophilic substitution of fluorinated alkenes by soft carbon aromatic nucleophiles which, to our knowledge, has not been reported previously.

CHAPTER FIVE

REACTIONS BETWEEN TERTIARY AROMATIC AMINES ACTING AS SOFT CARBON NUCLEOPHILES WITH FLUORINATED HETEROCYCLES

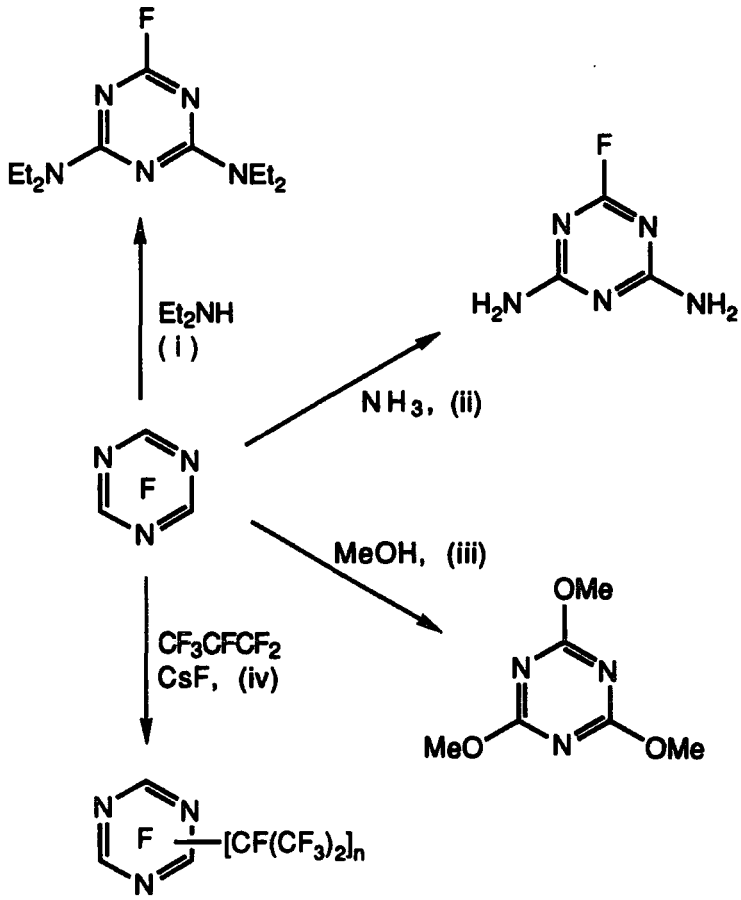
5.1 Introduction

The success of the reaction between tertiary aromatic amines and fluorinated alkenes (Chapter Four) prompted us to try reactions between tertiary aromatic amines and fluorinated heterocyclic systems. The reactivity of perfluoroheterocyclic compounds towards nucleophiles is well known[148].

Reactions between trifluoro-s-triazine and soft, aromatic carbon nucleophiles were performed. Some reactions between trichloro-s-triazine[149] and aromatic carbon nucleophiles have been reported and are reviewed below, but we are unaware of any previous detailed investigations of reactions between trifluoro-s-triazine and aromatic amines acting as carbon nucleophiles. The only comparable example that we have found in the literature is the reaction between trifluoro-s-triazine and N-methylpyrrole[150] (see below).

5.2 Nucleophilic Substitution Reactions of Trifluoro-s-triazine

Trifluoro-s-triazine is very reactive towards nucleophiles and reactions with O, N and perfluorinated carbanion nucleophiles have been well studied[148]. Some examples of nucleophilic substitution reactions of trifluoro-s-triazine are given below which proceed via the mechanism outlined previously in section 2.4.1.2.



Conditions and Yields

(i) r.t., THF, 2 hr, 74%

(ii) 0°C, Ether, 1 hr, 90%

(iii) r.t., THF, K_2CO_3, 2 hr, 77%

(iv) 70°C, sulpholane, 20 hr. n=1, 39%; n=2, 51%; n=3, 5%

5.3 Reactions between Trichloro-s-triazine (Cyanuric Chloride) and Tertiary, Aromatic Amines Acting as Carbon Nucleophiles

5.3.1 With N,N-Dialkylanilines and Toluidines

Reactions between cyanuric chloride and N,N-Dialkylanilines were studied by Shaw[151]. It was found that the aniline acted as a ambident nucleophile to give a mixture of products of types (IIA), (IIIA) and (IVA), as outlined in the following scheme.

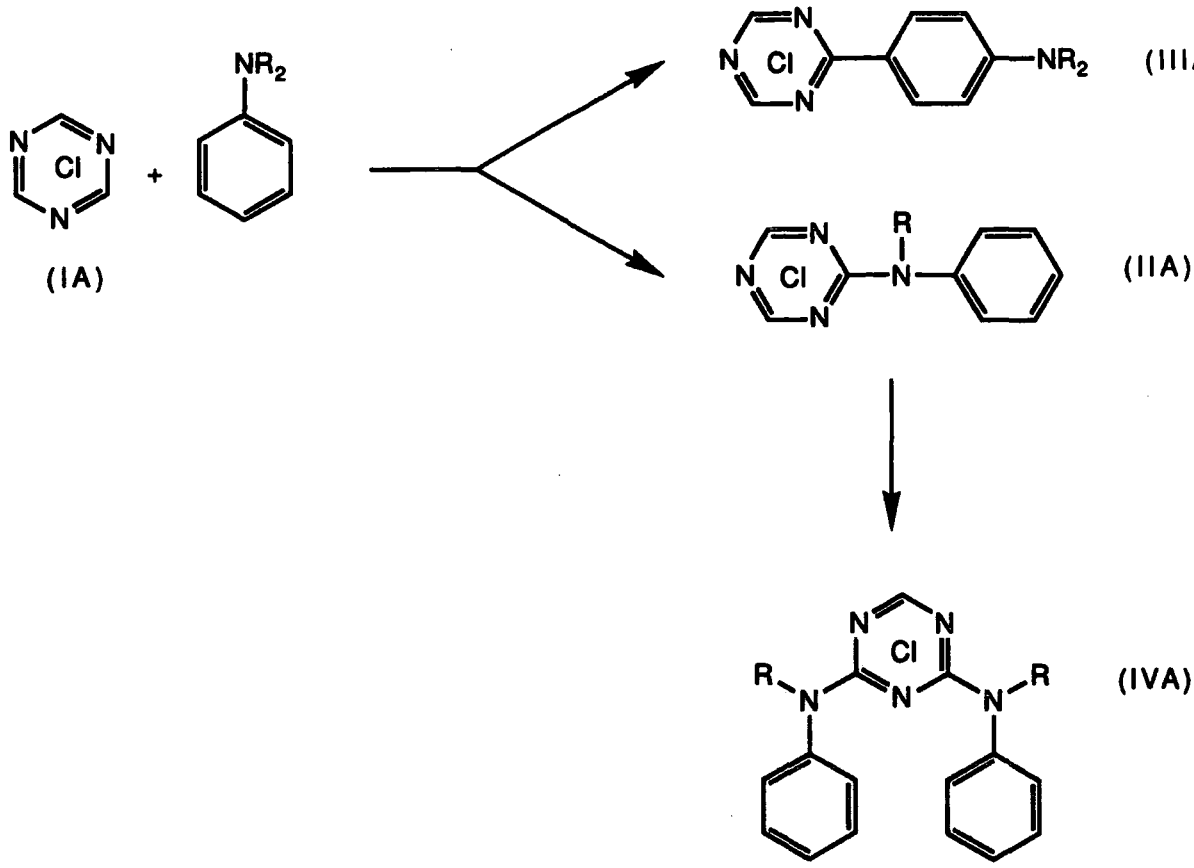
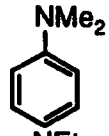
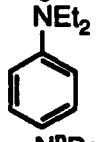
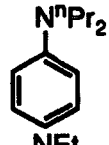
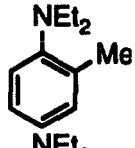
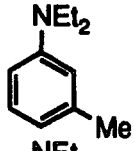
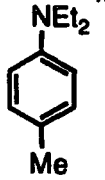


Table 15 is taken from this paper[151] and a discussion of the results follows. All reactions were carried out in the absence of solvent at a temperature of 90°C for 8 hours.

Table 15. Reactions Between Cyanuric Chloride and N,N-Dialkyl Anilines and Toluidines.

Amine	Conversion (%)	(III) (%)	(II) (%)	(IV) (%)
	92	-	55	45
	95.5	30	70	-
	74.5	40	60	-
	38.6	-	100	-
	75.0	55	45	-
	77.5	-	100	-

From the table the following points may be rationalised:-

(1) N,N-Dimethylaniline gives only the nitrogen substituted product (II).

(2) N,N-Diethylaniline gives a 1:2 mixture of carbon substituted product to nitrogen substituted product (II). There is an increase in the amount of carbon substituted product with increasing alkyl chain length on the nitrogen. This was accounted for by the increased steric hindrance around the nitrogen atom and the increasing inductive effects of the alkyl chain making the p-carbon more activated towards electrophilic substitution.

(3) Both the 2- and 4-methyl toluidines yielded only the nitrogen substituted products. For the 4- isomer reaction can only occur at the nitrogen; no ortho-substitution was observed. With the 2- isomer, the 2-methyl group prevents the NEt_2 group from conjugating with the ring and hence decreases activation towards electrophilic attack and so only the nitrogen substituted product is obtained.

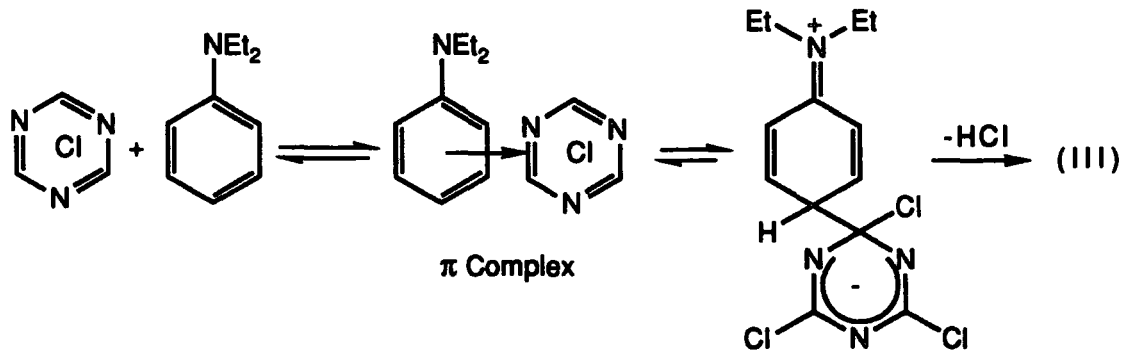
In reactions between N,N-dialkylnaphthylamines and cyanuric chloride the carbon substitution product forms exclusively[152]. This was attributed to the greater activation of the naphthalene ring towards electrophilic attack and steric hindrance of the nitrogen by the peri hydrogen atom.

The carbon substituted compounds (II) have been patented[153].

The UV, IR and ^{1}H NMR spectra of the carbon substituted compounds were presented in a separate paper[154], but details will be included later in the discussion for comparison with our data.

5.3.1.1 Mechanism

A mechanism for the formation of the carbon substituted compounds of cyanuric chloride has been postulated[155], and is shown below. The reaction is claimed to proceed via successive π and σ complexes. The charge transfer complexes may be seen by UV spectroscopy.

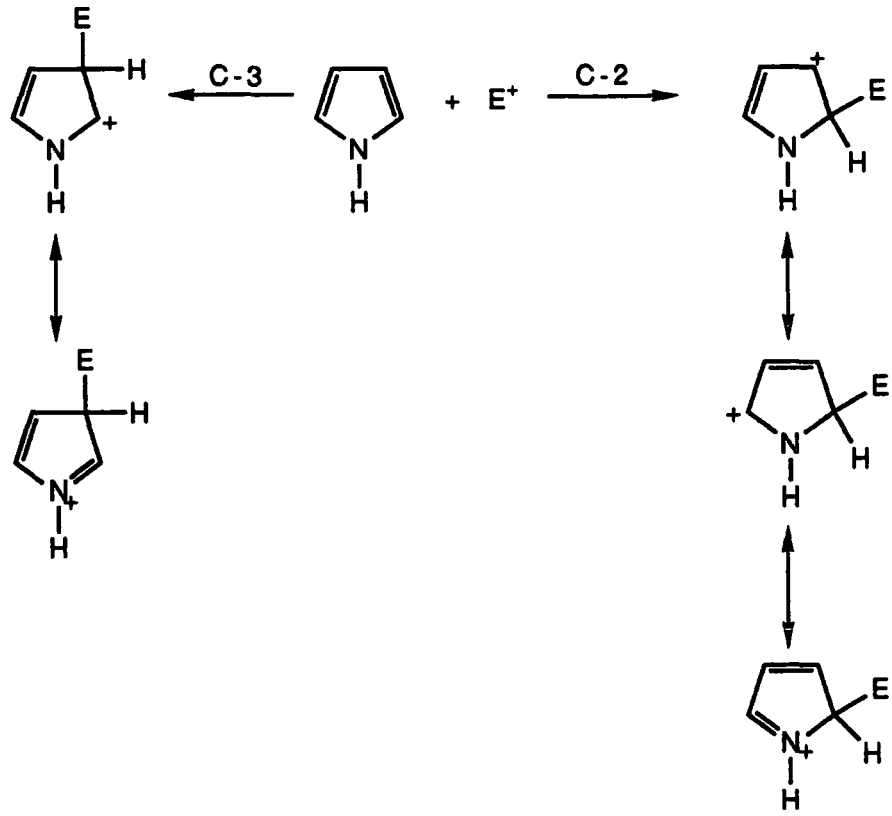


π Complex

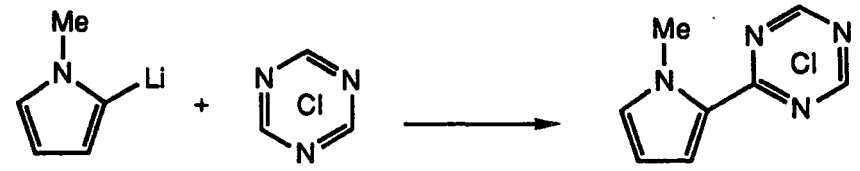
σ Complex

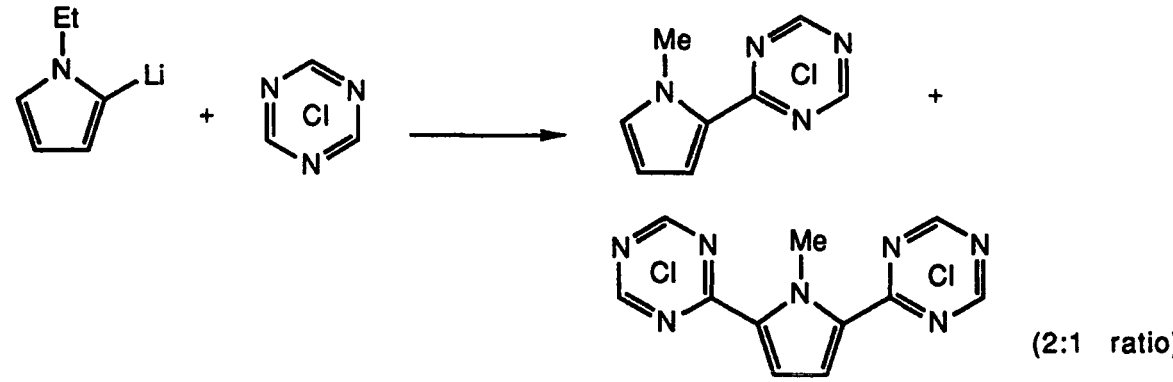
5.3.2 With 5-Membered Heterocyclic Rings

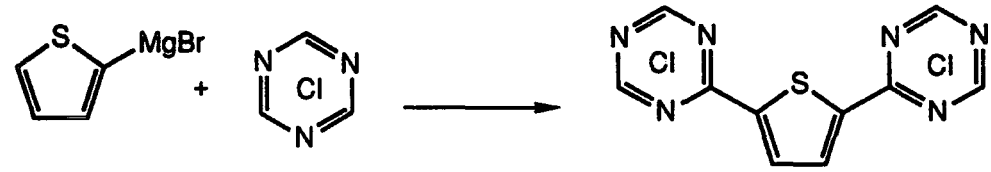
Pyrroles are electron rich heterocycles that react readily with a wide range of electrophiles. Generally, substitution at the 2-position is favoured over the 3-position as the intermediate carbocation formed is more extensively delocalised[156], as shown below.



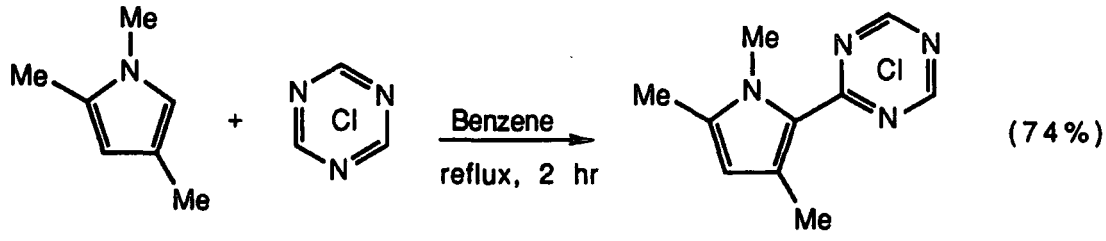
Reactions between cyanuric chloride and furans, pyrroles and thiophenes have been studied in a series of publications by Chakrabarti and Todd for the Lilley Chemical Company. Initially, a metallated derivative of the unsubstituted thiophene or pyrrole was used to couple with the triazine to produce the desired dihalogeno-heteroaryl-s-triazine[157]. The metallation involved either reaction with n-butyl lithium or formation of a Grignard reagent, as shown below.



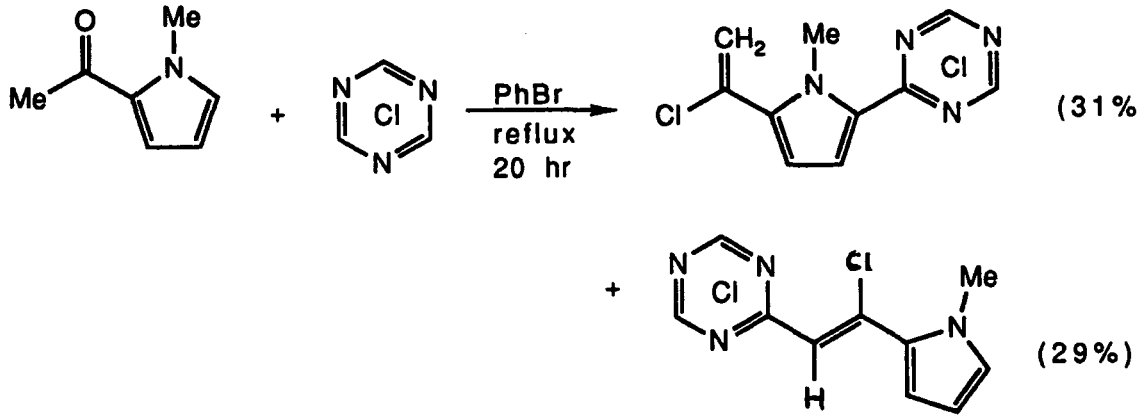




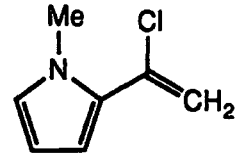
In a subsequent publication[158], the use of a metallated species was found to be unnecessary and a series of pyrrolyl-s-triazines were produced by electrophilic substitution reactions.



Unusually, the reaction of cyanuric chloride with 2-acetyl-1-methylpyrrole gave an equimolar mixture of two products[159].



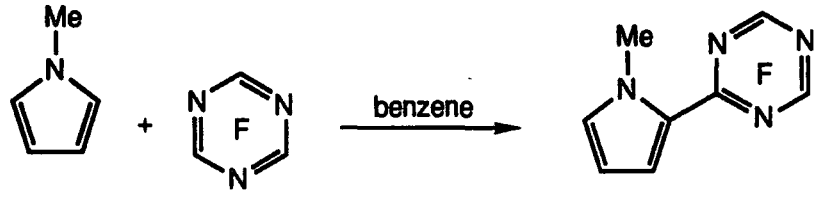
This reaction proceeds via the intermediate (V) which is the likely product of the reaction of cyanuric chloride with an acetyl derivative[160].



(V)

In similar work, Shaw reported the reaction of cyanuric chloride with N-ethyl pyrrole and indole to give carbon substituted electrophilic products[161].

The reaction between trifluoro-s-triazine and N-methylpyrrole was recorded[150].

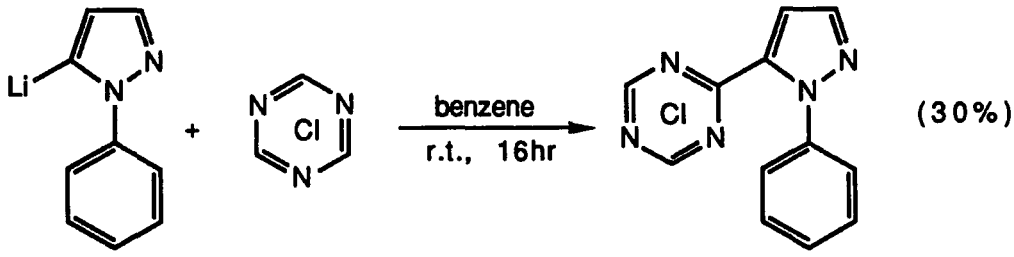


However, no spectral data appears in the publication and no detailed investigation of the reactions of trifluoro-s-triazine appears in the literature.

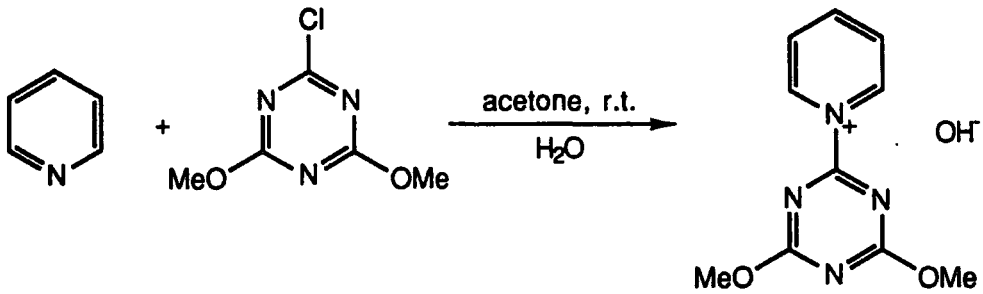
The pyrrolyl-dichloro-s-triazines have been patented as anti parasitic agents[162] and fungicides[163-165], showing biological activity against fungi such as anthracnose (Collectotrichum lagenarium), rice leaf spot disease and grey mold of grapes (Botrytis cinerea), amongst others.

The hydrolysis of (N-methylpyrrol-2-yl)-dichloro-s-triazine was studied[150]. Successive hydrolyses to the triazin-2-one and then to the triazine-2,4-dione by sodium hydroxide in water was found.

Pyrazoles also react nucleophilically with cyanuric chloride via a metallated species[166].



However, reactions with the more basic heterocycles such as imidazoles, thiazoles, benzothiazoles, and pyridines do not give electrophilic substitution products but instead give quaternary salts. For example, pyridine reacts with 2-chloro-4,6-dimethoxy-s-triazine to give the unstable chloride salt which slowly hydrolyses to the hydroxide[166].

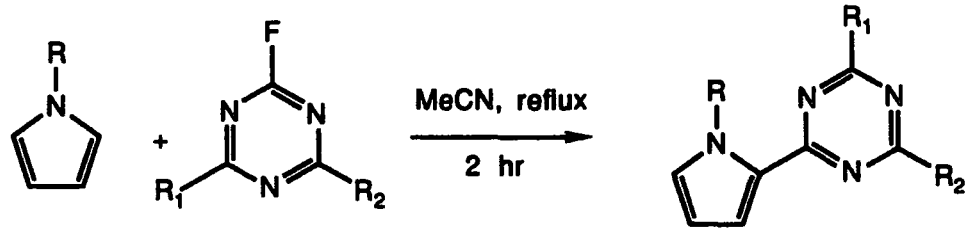


(46%)

RESULTS AND DISCUSSION

5.4 Reactions of Fluorinated Triazines with Pyrroles

Both pyrrole and N-methylpyrrole react with trifluoro-s-triazine (13), perfluoroisopropyl-s-triazine (14) and perfluorodiisopropyl-s-triazine (15) to form electrophilic substitution products (67)-(72), in good yield.



(67) R=H, R_1=F, R_2=F
(68) R=H, R_1=F, R_2=R_F
(69) R=H, R_1=R_F, R_2=R_F
(70) R=Me, R_1=F, R_2=F
(71) R=Me, R_1=F, R_2=R_F
(72) R=Me, R_1=R_F, R_2=R_F

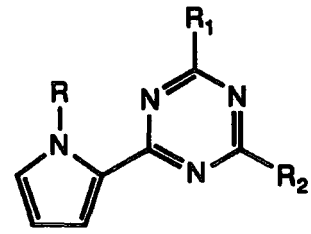
R_F = $(CF_3)_2CF$-

The products were precipitated from the reaction mixture by adding water and then purified by vacuum sublimation.

Electrophilic substitution occurs at the 2-position of the pyrrole ring, as expected, and this is proved by the values of the proton-proton coupling constants (section 5.4.1.1).

Yields, melting points and UV spectral data for compounds (67)-(72) are collated in table 16, below. Satisfactory elemental analyses and mass spectra were recorded for each compound (67)-(72).

Table 16. Yields, melting points and UV spectra of Pyrrolyl-s-triazines



Compound No.	R	R_1	R_2	Yield (%)	m.p. (°C)	λ_{max} (nm) ($log_{10}\varepsilon$)
(67)	H	F	F	65	156-160	310.1 (4.48)
(68)	H	F	R_F	71	112-115	336.0 (4.41)
(69)	H	R_F	R_F	68	64-66	344.8 (4.58)
(70)	Me	F	F	45	117-118	314.6 (4.44)
(71)	Me	F	R_F	54	110-111	324.5 (4.38)
(72)	Me	R_F	R_F	48	88-89	349.4 (4.33)

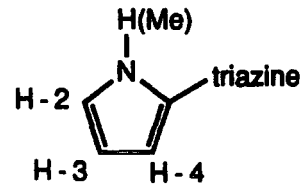
(R_F = $(CF_3)_2CF$-)

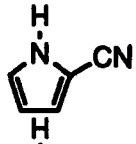
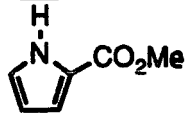
5.4.1 Spectroscopy of Pyrrolyl-s-Triazines

5.4.1.1 ^{1}H NMR

All products (67)-(72) gave similar proton NMR spectra and are collated in table 17. The spectra were assigned with reference to shifts of similar pyrroles bearing electron-withdrawing substituents at the 2-position taken from the literature[167]; two literature compounds are included in table 17, for comparison.

Table 17. ^{1}H NMR Spectra of Pyrrolyl-s-triazines. Chemical Shifts ($J_{H, H}$)



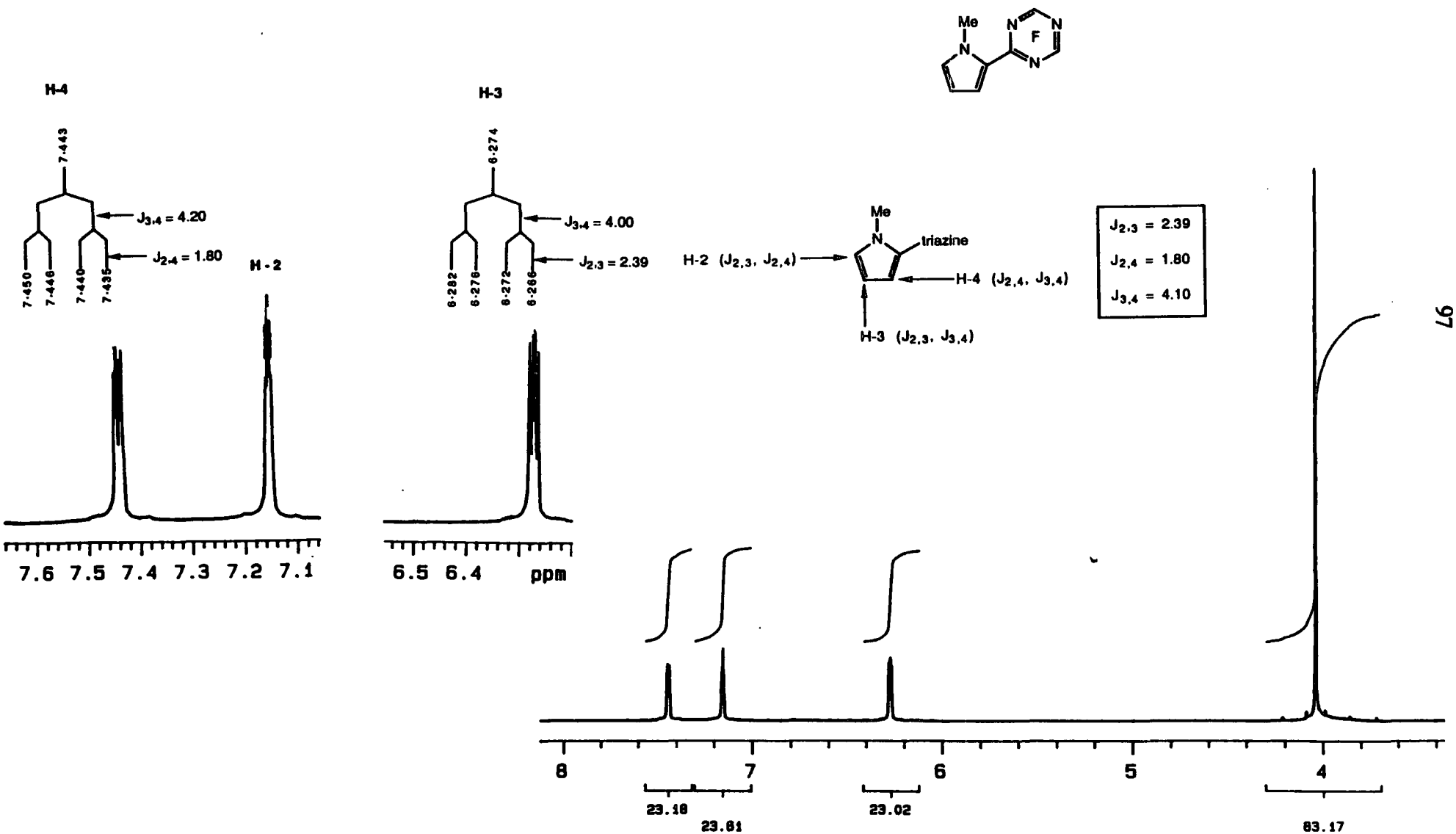
Compound	N-H	N-CH_3	H-2 ($J_{2,3}$)	H-3 ($J_{3,4}$)	H-4 ($J_{2,4}$)
	-	-	6.91	6.03	6.64
			-	-	-
	-	-	6.76	5.90	6.54
			-	-	-
(67)	10.30	-	7.23	6.40	7.34
			(2.3)	(4.0)	(1.6)
(68)	10.62	-	7.27	6.43	7.40
			(2.4)	(4.0)	(1.2)
(69)	9.50	-	7.15	6.31	7.29
			(1.7)	(3.5)	(1.5)
(70)	-	4.04	7.14	6.27	7.44
			(2.4)	(4.0)	(1.8)
(71)	-	4.12	7.35	6.33	7.52
			(2.3)	(4.2)	(1.8)
(72)	-	4.07	7.05	6.32	7.66
			(2.3)	(4.2)	(1.9)

The ring proton coupling constants for pyrroles are diagnostic of the position of substitution. Typical values for the coupling constants in pyrrole rings are as follows[167]:-

$J_{2,4}$ 1.35-1.80 < $J_{2,5}$ 1.95-2.30 < $J_{2,3}$ 2.40-3.10 < $J_{3,4}$ 3.40-3.80

The ^{1}H NMR spectrum of (70) is shown overleaf (Fig. 10), and is typical of the spectra obtained for compounds (67)-(72). From the spectrum we can see that the resonance at 6.27ppm has coupling constants 2.39 and 4.00Hz, and the resonance at 7.43ppm has coupling constants 1.80 and 4.2 Hz. From the list of typical values of coupling constants above we can assign the resonance at 6.27ppm to be H-3, and at 7.43ppm to be H-4. Hence, the pyrrole has undergone substitution at the 2-position, as expected from the electrophilic substitution mechanism outlined in section 5.3.2.

Figure 10 ^{1}H NMR Spectrum of 2-(N-methylpyrrol-2-yl)-4,6-difluoro-s-triazine



5.4.1.2 ^{19}F NMR

The ^{19}F NMR shifts for compounds (67)-(72) are tabulated below (Table 18) along with the shifts of the unsubstituted triazines[126] (13)-(15), for comparison.

Table 18. ^{19}F NMR Shifts for Pyrrolyl-s-Triazines.

Compound	Ring F	CF_3	C-F
(13)	-30.4	-	-
(14)	-30.4	-74.4	-183.8
(15)	-30.5	-74.8	-185.2
(67)	-39.7	-	-
(68)	-39.7	-74.4	-184.5
(69)	-	-74.4	-184.7
(70)	-45.6	-	-
(71)	-38.4	-74.2	-184.3
(72)	-	-75.0	-185.2

The spectra are as expected by comparison with the shifts of the parent triazines (13)-(15).

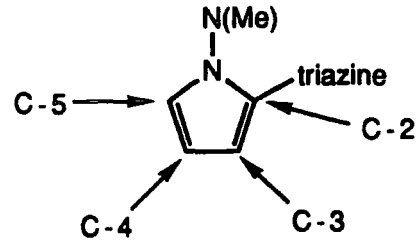
5.4.1.3 ^{13}C NMR

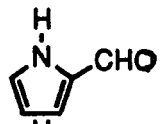
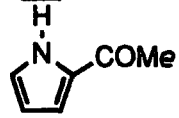
^{13}C spectra were recorded for compounds (68)-(72), (67) being too insoluble for a ^{13}C spectrum to be obtained.

The ^{13}C NMR shifts for the carbon atoms in the pyrrole ring were assigned by comparison with similar literature compounds bearing electron withdrawing groups at the 2-position[167]. Assignment of these peaks is helped by the fact that there is not any C-F coupling and so the peaks are singlets. Also, peaks due to aromatic C-H are large due to their short relaxation time.

^{13}C NMR shifts for the pyrrole ring carbons in the pyrrolyl-s-triazines are collated in table 19. Shifts for two literature compounds are also included for comparison.

Table 19. ^{13}C NMR shifts for Pyrrole Ring Carbon Atoms in Pyrrolyl-s-Triazines (68)-(72)



Compound	N-CH_3	C-2	C-3	C-4	C-5
	-	133.8	121.8	112.3	129.8
	-	133.4	118.5	111.2	127.0
(68)	-	128.5	121.2	114.5	130.5
(69)	-	128.2	121.3	114.3	130.6
(70)	39.2	136.1	123.3	111.1	128.0
(71)	39.3	136.8	123.9	111.5	128.0
(72)	39.1	137.7	124.7	111.9	128.1

The assignment of the peaks for the triazine ring carbon atoms in (68)-(72) is more complex as C-F coupling is present. Typical coupling values for 1 bond C-F coupling ($^1J_{C-F}$), 2 bond ($^2J_{C-F}$), 3 bond ($^3J_{C-F}$) and 4 bond ($^4J_{C-F}$) are as follows[168]:-

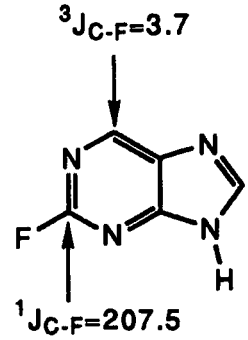
$^1J_{C-F}$ = 158 - 408 Hz

$^2J_{C-F}$ = 0 - 103 Hz

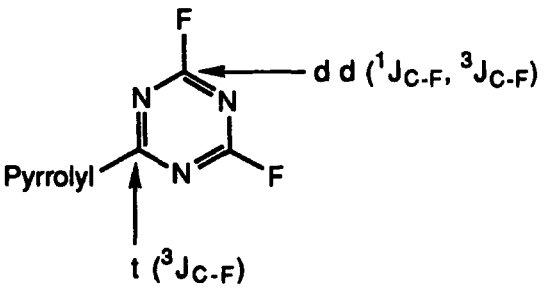
$^3J_{C-F}$ = 0 - 43 Hz

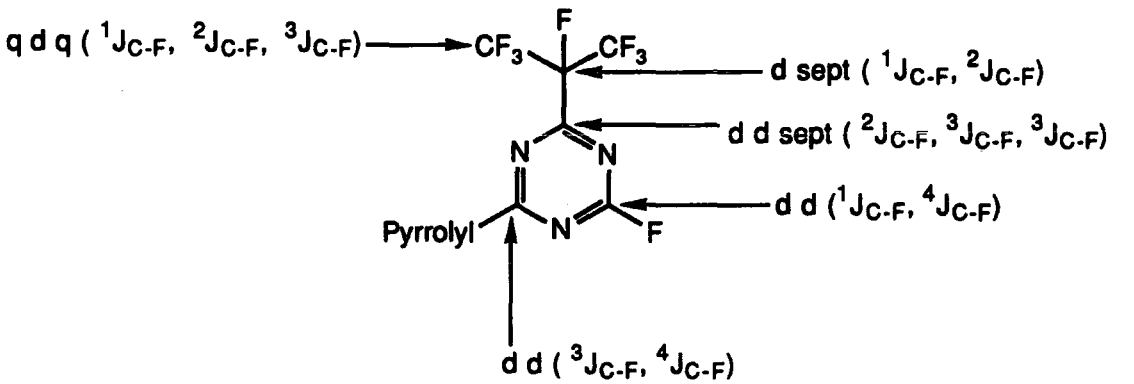
$^4J_{C-F}$ = 0 - 24 Hz

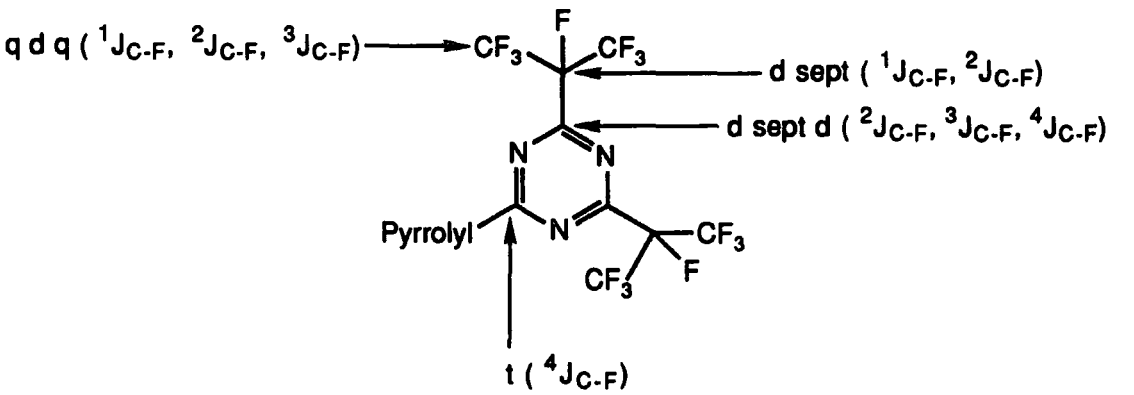
Examples of C-F coupling in a related system are as follows and may be taken as a guide in assigning the spectra of (68)-(72).



For mono-, di- and tri-substituted triazines we would expect the following peaks to be seen in the ^{13}C NMR spectrum, given that carbon couples with fluorine through at least four bonds.



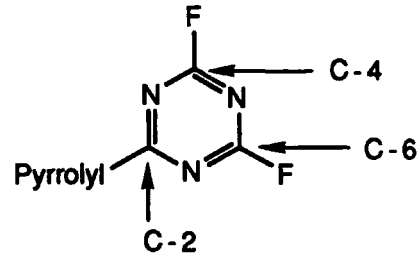




Using these models and expected J_{C-F} values as a guide the ^{13}C NMR spectra for (68)-(72) have been assigned as shown in table 20.

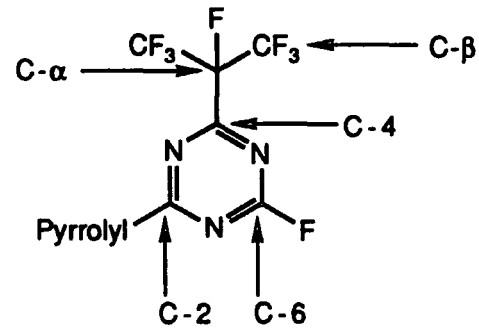
Table 20. ^{13}C NMR shifts for Triazine Ring Carbon Atoms in Pyrrolyl-s-Triazines (68)-(72)

Monosubstituted Triazine (70)



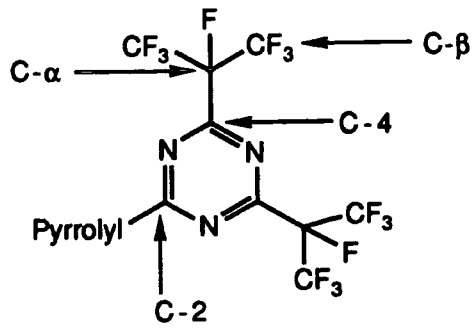
Compound	C-2	C-4
	t (^3J)	d d (^1J, ^3J)
(70)	172.3 (14)	172.0 (226, 19)

Disubstituted Triazines (68) and (71)



Compound	C-2	C-4	C-6	C-α	C-β
	dd	dd	dd	d sept	qd
	(^3J, ^4J)	(^2J, ^3J)	(^1J, ^4J)	(^1J, ^2J)	(^1J, ^2J)
(68)	170.4	169.2	171.2	90.9	121.3
	(13, 3)	(22, 12)	(229, 3)	(211, 33)	(288, 27)
(71)	170.2	168.2	170.3	90.3	120.8
	(13, 3)	(21, 12)	(228, 3)	(211, 35)	(288, 27)

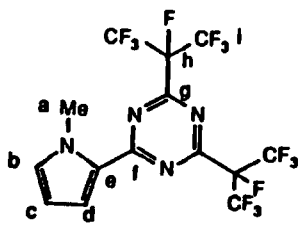
Trisubstituted Triazines (69) and (72)



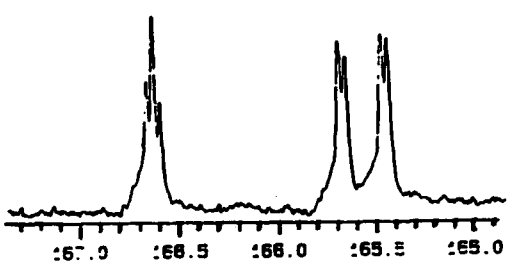
Compound	C-2	C-4	C-α	C-β
	t	dd	d sept	qd
	(^4J)	(^2J, ^3J)	(^1J, ^2J)	(^1J, ^2J)
(69)	166.5	165.9	90.4	120.8
	(3)	(22, 4)	(211, 33)	(288, 27)
(72)	166.6	165.5	90.2	120.7
	(3)	(22, 3)	(218, 33)	(288, 27)

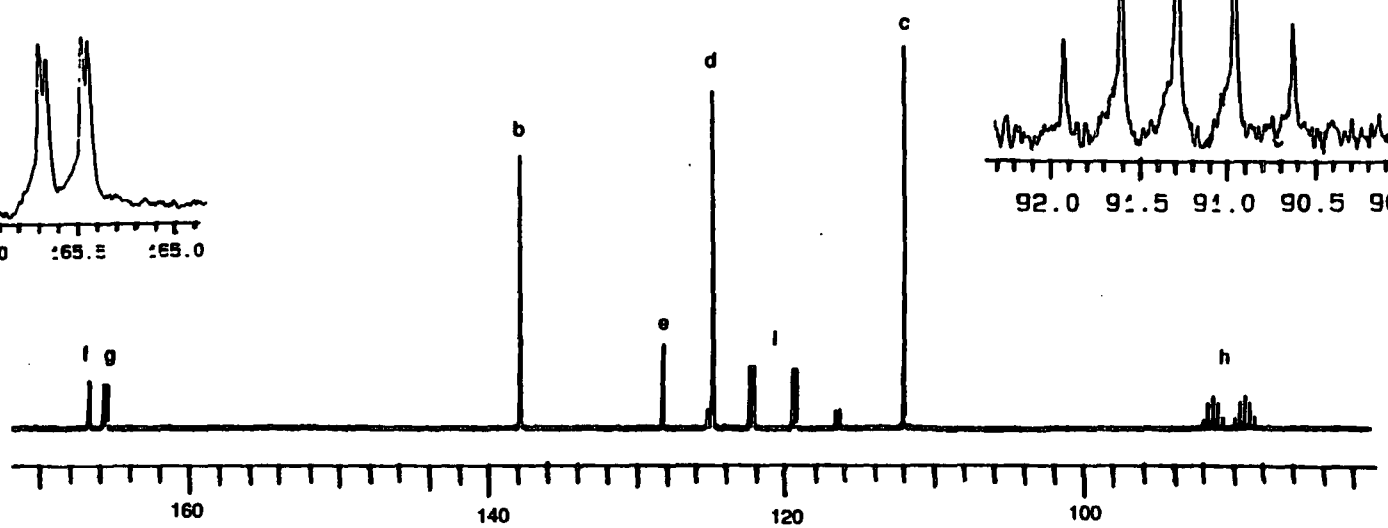
The complete ^{13}C NMR spectrum of compound (72) is shown overleaf (Fig. 11).

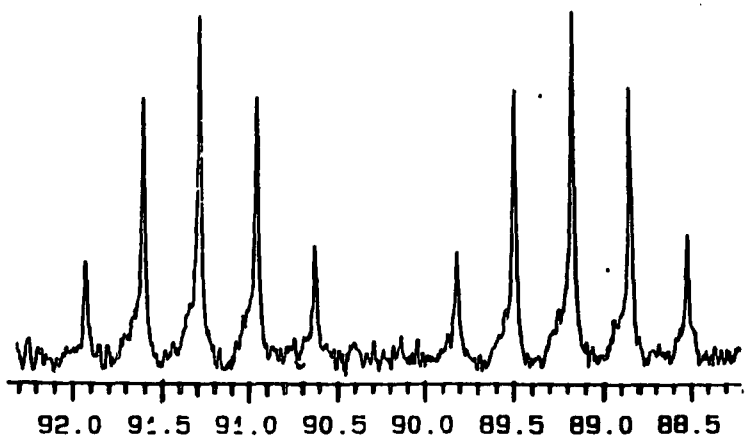
Figure 11 ^{13}C NMR Spectrum of 2-(N-methylpyrrol-2-yl)-4,6-perfluorodi-isopropyl-s-triazine



Chemical Shift (ppm)	Multiplicity Coupling Constants (Hz)	Assignment
39.09	s	a
90.21	d sept 218, 33	h
111.88	s	c
120.73	qd 288, 27	l
124.75	s	d
128.12	s	e
137.67	s	b
165.55	dd 22, 3	g
166.62	t 3	f

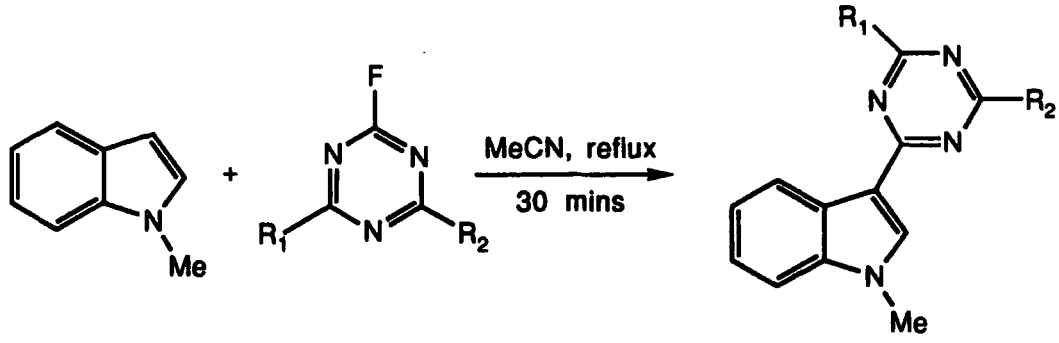






5.5 Reactions of Fluorinated Triazines With N-Methylindole

N-methylindole reacted with the triazines (13)-(15) to give electrophilic substitution products (73)-(75), respectively, in good yield.



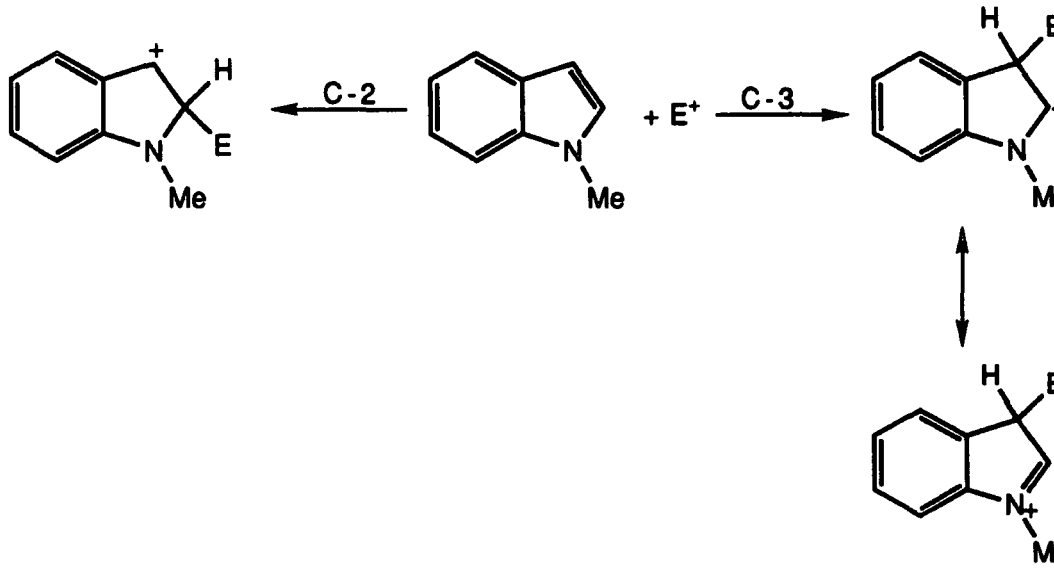
(73) R_1=F, R_2=F

(74) R_1=F, R_2=R_F

(75) R_1=R_F, R_2=R_F

(R_F = $(CF_3)_2CF$-)

Indoles are very nucleophilic heterocycles and react easily with electrophiles. Electrophilic substitution occurs preferentially at the C-3 site rather than at C-2, in contrast to pyrrole systems, because the intermediate cation formed by attack at C-3 is more stable than that formed at C-2 as the positive charge may be delocalised without involving the benzene ring part of the molecule[156].



Yields and melting points for compounds (73)-(75) are collated in table 21, below. Satisfactory elemental analyses and mass spectra were recorded for each compound (73)-(75).

Table 21. Yields and melting points of Indolyl-s-triazines

Compound No.	Yield (%)	m.p. (°C)
(73)	78	244
(74)	90	190-194
(75)	87	205-206

5.5.1 Spectroscopy of Indolyl-s-Triazines

5.5.1.1 ^{1}H NMR

The ^{1}H NMR spectrum of (74) is shown overleaf (Fig 12). From the spectrum we can see five protons in the aromatic region. The four multiplets are due to the indole ring protons and the singlet corresponds to the proton at the 2-position of the indole ring, by comparison with literature data[167]. This singlet proves that the electrophilic substitution has taken place at the 3-position as long range coupling would be seen if the 3-proton was present.

5.5.1.2 ^{19}F NMR

^{19}F NMR spectra for the indolyl-s-triazines were similar to those found for the pyrrolyl-s-triazines and were assigned in the same way. The ^{19}F NMR shifts for the indolyl-s-triazines (73)-(75) are collated in table 22.

Table 22. ^{19}F NMR Shifts for Indolyl-s-Triazines.(73)-(75)

Compound No.	Ring F	CF_3	C-F
(73)	-40.2	-	-
(74)	-39.2	-74.2	-184.2
(75)	-	-74.2	-184.4

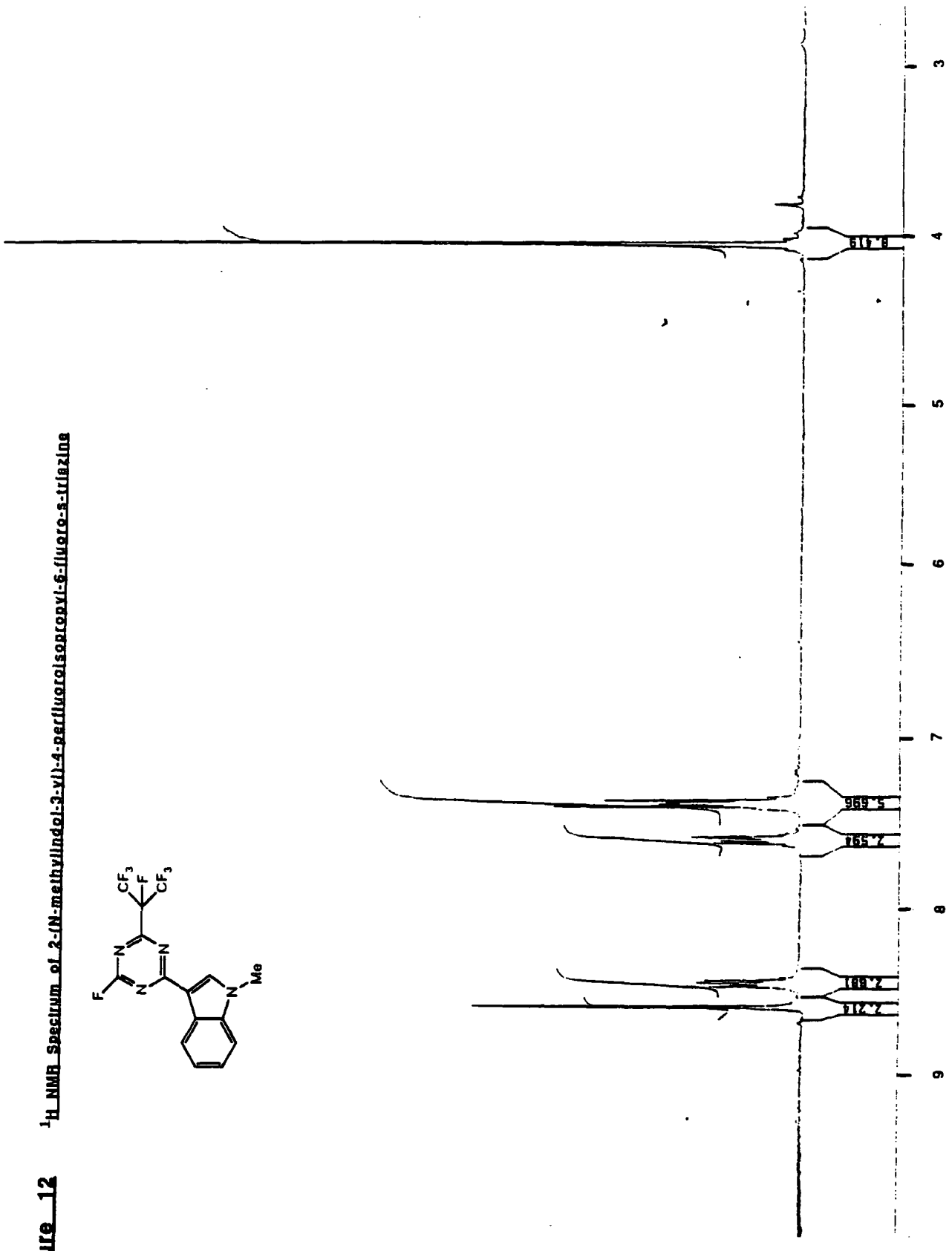


Figure 12 ^{1}H NMR Spectrum of 2-(N-methylindol-3-yl)-4-perfluoroisopropyl-6-fluoro-s-triazine

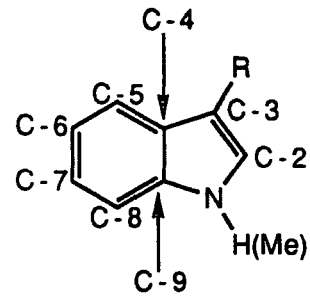
5.5.1.3 ^{13}C NMR

A ^{13}C spectrum was recorded for compound (74), but (73) and (75) are too insoluble for ^{13}C spectra to be obtained.

The ^{13}C NMR shifts for the carbon atoms in the indole ring were assigned by comparison with similar literature compounds bearing electron withdrawing groups at the 3-position[167]. Assignment of these peaks is helped by the fact that there is not any C-F coupling and so the peaks are singlets. Also, peaks due to aromatic C-H are large due to their short relaxation time.

^{13}C NMR shifts for the indole ring carbons in the indolyl-s-triazines are collated in table 23. Shifts for two literature compounds are also included for comparison.

Table 23. ^{13}C NMR shifts for Indole Ring Carbon Atoms in Indolyl-s-Triazines (74)



R	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9
COMe	133.4	116.2	122.0	120.9	120.9	111.4	124.4	135.9
CHO	138.1	118.2	123.3	122.0	120.8	112.3	124.2	137.1
(74)	140.5	111.7	127.2	124.0	123.0	112.0	124.6	139.6

The similar ^{13}C shifts of literature compounds and the product (74) is further proof of the position of substitution at the 3-position.

The ^{13}C NMR shifts for the triazine ring carbon atoms were assigned in the same way as for the pyrrolyl-s-triazines. The shifts for the triazine ring carbons in the pyrrolyl compounds (68), (71) and the indolyl compound (74) are tabulated below (Table 24) for comparison.

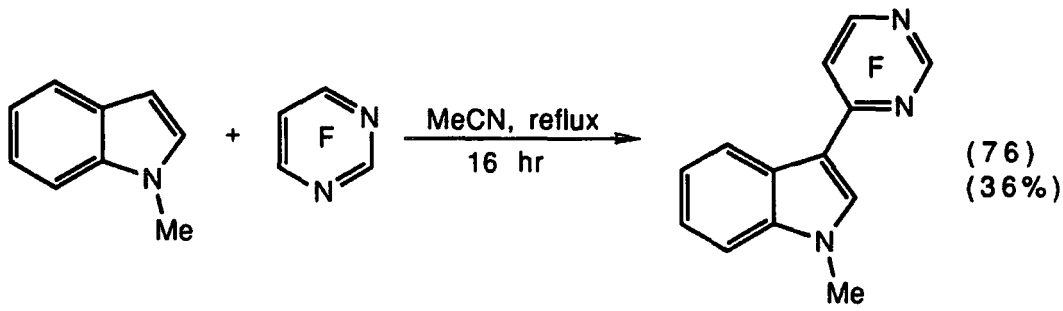
Table 24. ^{13}C NMR shifts for Triazine Ring Carbon Atoms in Indolyl-s-Triazine (74)

(Same nomenclature as in Table 20)

Compound	C-2	C-4	C-6	C-α	C-β
	dd	dd	dd	d sept	qd
	(^3J, ^4J)	(^2J, ^3J)	(^1J, ^4J)	(^1J, ^2J)	(^1J, ^2J)
(68)	170.4	169.2	171.2	90.9	121.3
	(13, 3)	(22, 12)	(229, 3)	(211, 33)	(288, 27)
(71)	170.2	168.2	170.3	90.3	120.8
	(13, 3)	(21, 12)	(228, 3)	(211, 35)	(288, 27)
(74)	175.0	168.1	170.3	90.2	120.8
	(13, 3)	(multiplet)	(229)	(210, 33)	(287, 27)

5.6 Reaction of Tetrafluoropyrimidine With N-Methylindole

N-methylindole also reacts with tetrafluoropyrimidine, which is less activated towards nucleophilic attack than trifluoro-s-triazine, to give a similar electrophilic substitution product (76) as yellow crystals (m.p. 231°C) in 36% yield.



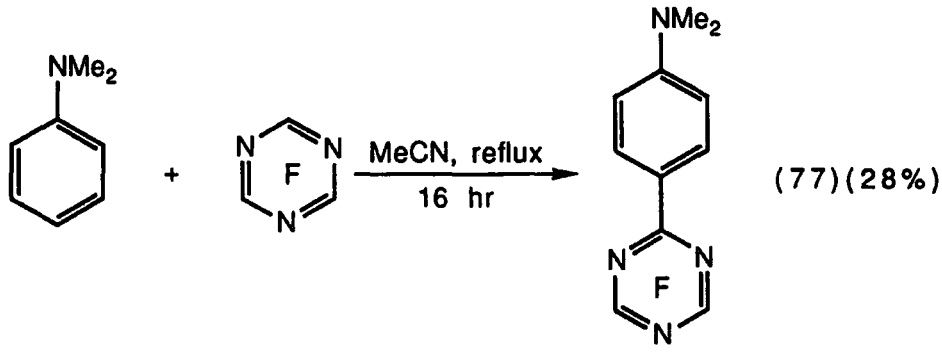
(76)
(36%)

Satisfactory elemental analysis and mass spectra were recorded. The product was too insoluble for NMR spectra to be recorded.

5.7 Reactions of Fluorinated-s-triazine with Anilines

5.7.1 Reaction of Trifluoro-s-triazine with N,N-Dimethylaniline

Trifluoro-s-triazine reacts with N,N-dimethylaniline to give the carbon-substituted product (77) exclusively, as brown-red crystals (m.p. 234-237°C) in 28% yield.



(77)(28%)

The ^1H NMR spectrum proves the carbon-substituted structure (77) as shown. The spectrum shows a singlet at 3.10ppm corresponding to 6 protons and an AA'XX' system in the aromatic region (6.80 and 8.28ppm, J_{AX} = 9.0 Hz), corresponding to 4 protons, as is usual for a 1,4-disubstituted benzene ring. This agrees with ^1H NMR data for an analogous compound produced by Shaw in the reaction between cyanuric chloride and N,N-diethylaniline[154].

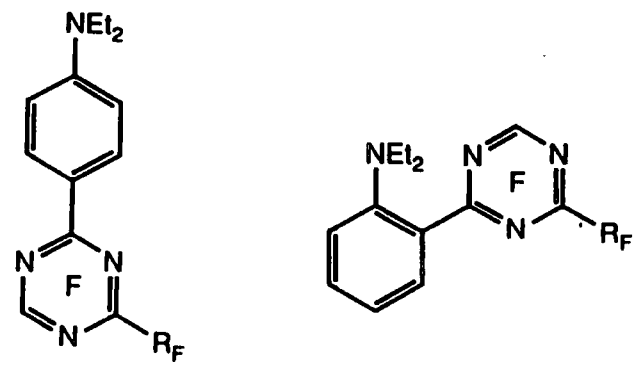
The reaction between cyanuric chloride and N,N-dimethylaniline gave no carbon substituted product[151]. This shows that trifluoro-s-triazine is more susceptible to nucleophilic attack than trichloro-s-triazine.

5.7.2 Reaction of Perfluoroisopropyl-s-triazine (14) with N,N-Dimethyl- and Diethyl-aniline

Similarly perfluoroisopropyl-s-triazine (14) reacts with N,N-dimethylaniline to produce the carbon-substituted product (78) in 36% yield. Again, ^1H NMR proves the structure of (78) and is included in table 25.

However the reaction between N,N-diethylaniline and triazine (14) is not as simple. The same work-up procedure was used to obtain a yellow solid which gave elemental analysis and mass spectra consistent with the formula $C_{16}H_{14}N_4F_8$. ^1H and ^{19}F NMR revealed the presence of two products which must be isomers from the elemental analysis. The ^1H NMR spectrum of this product mixture is shown overleaf.

^{1}H NMR Spectrum of N,N-(Diethylamino)-perfluoroisopropyl-s-Triazine Ortho and Para Isomers



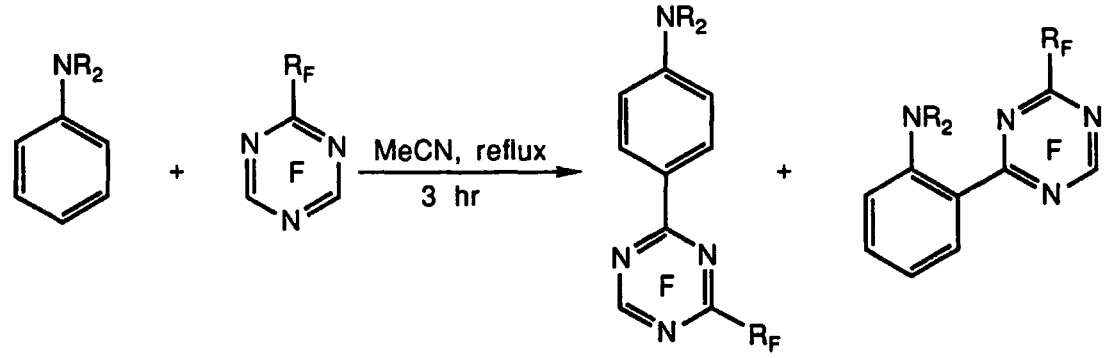
TMS

CD_3CN

9 8 7 6 5 4 3 2 1 ppm

18.53 6.90 10.41 19.65 54.12 36.31 76.10 62.0

The major product seen in the NMR spectra is the expected *para* substituted product (79A) which gives a triplet and a quartet at 1.20 and 3.49ppm respectively and an AA'XX' system at 6.80 and 8.27ppm (J_{AX}=9.6Hz) in the ^{1}H NMR spectrum. The minor product must be the *ortho* substituted isomer (79) as shown below.



(78) R=Me, 36% yield, only A formed.

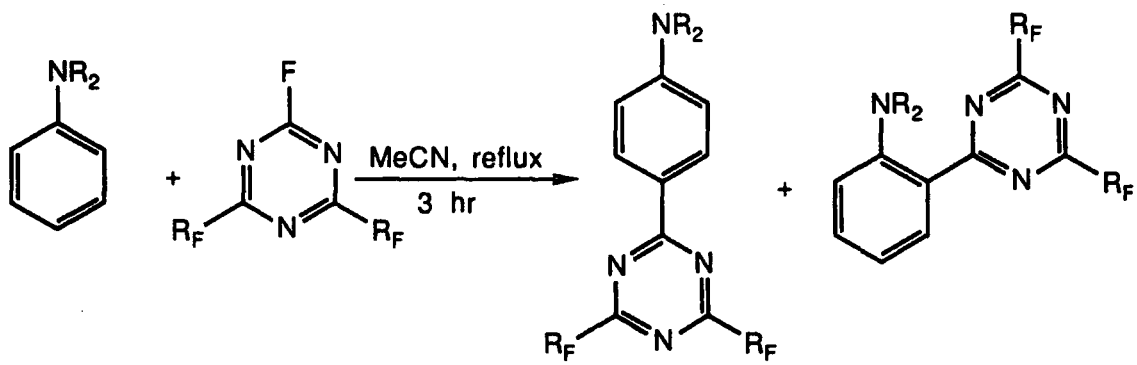
(79) R=Et, 45% yield, A:B = 69:31.

The nitrogen substituted product (80) was prepared directly from N-ethylaniline and triazine (14) as a white solid (section 5.9) for comparison of NMR data.

The formation of *ortho*-substituted products has not been noted before in reactions between cyanuric chloride and anilines[151] (section 5.3.1).

5.7.3 Reaction of Perfluorodiisopropyl-s-triazine (15) with N,N-Dimethyl- and Diethyl-aniline

Reactions between N,N-dimethyl- and diethyl-aniline and triazine (15) both gave a mixture of isomers (81A)-(82B).



(81) R=Me,77% yield, A:B = 44:56

(82) R=Et, 72% yield, A:B = 63:37

5.7.4 Collected NMR Data For Phenyl-s-Triazines (77)-(82)

Although products (77)-(82) could not be separated from their respective *ortho* isomers, the ^{1}H and ^{19}F NMR shifts for these compounds could be assigned from the spectra of the mixtures of isomers (Table 25).

Table 25 ^{1}H NMR Spectra of Phenyl-s-triazines (77)-(82A)

Compound	N-Me	CH_3	CH_2	AA'XX' System	J_{AX} (Hz)
(77)	3.10	-	-	6.80, 8.28	9.0
(78)	3.40	-	-	6.98, 8.65	9.4
(81A)	3.08	-	-	6.67, 8.36	9.2
(79A)	-	1.20	3.49	6.80, 8.27	9.6
(82A)	-	1.18	3.42	6.65, 8.33	9.2

Table 26 ^{19}F NMR Spectra of 4-Phenyl-s-Triazines (77)-(82A)

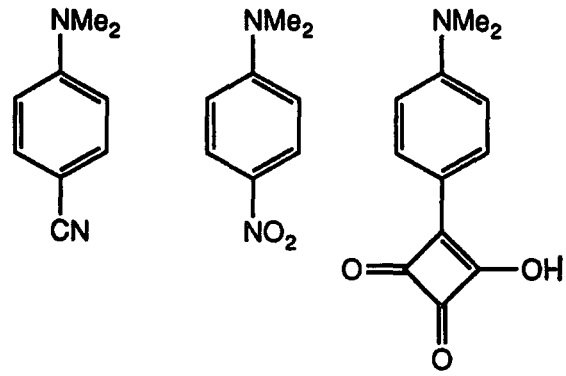
Compound	Ring F	CF_3	C-F
(77)	-40.1	-	-
(78)	-37.2	-74.3	-184.8
(81A)	-	-73.7	-184.0
(79A)	-43.5	-78.1	-188.2
(82A)	-	-73.1	-183.8

The enhanced reactivity of the triazines (14) and (15) must be the reason for the formation of the *ortho* substituted products. All the *ortho* substituted products give complicated ^{1}H NMR spectra each having four aromatic protons. The ^{19}F NMR spectra of the *ortho* substituted compounds are similar to the spectra recorded for the *para* substituted compounds, as expected. ^{1}H and ^{19}F NMR are listed in the appendix.

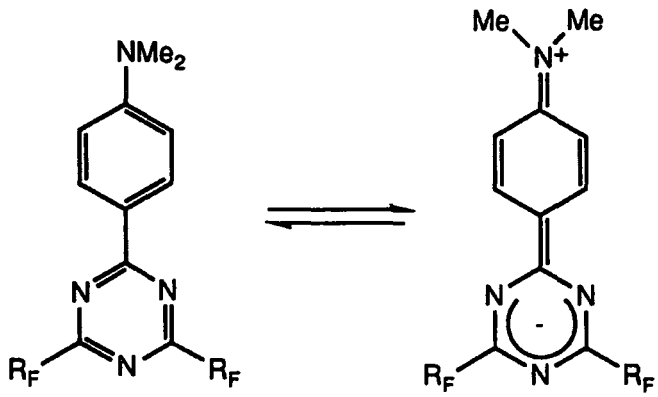
5.7.5 Potential Use of Compounds (77)-(82A) as Non-Linear Optic Molecules.

Organic molecules with an electron donor group connected to an electron acceptor group via a conjugated π system may show charge transfer properties, i.e. electron density transferred from the donor part of the molecule to the acceptor part thus creating charge separation. There is a great amount of interest in using these types of molecules in non-linear optical devices[169]. Their fluorescent properties have

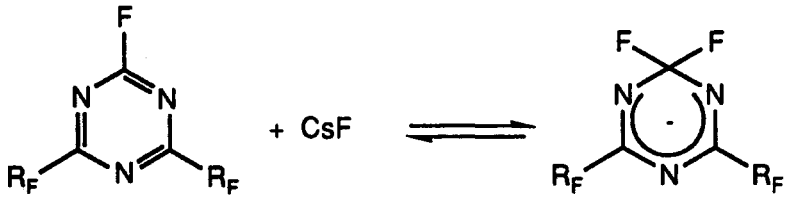
been studied[170]. It is beyond the scope of this thesis to consider the physics of these systems but the following molecules, which all have donor-acceptor structures, exhibit physical properties of interest to non-linear optic theory[171].



We may consider the phenyl-s-triazines to have the following structure:-



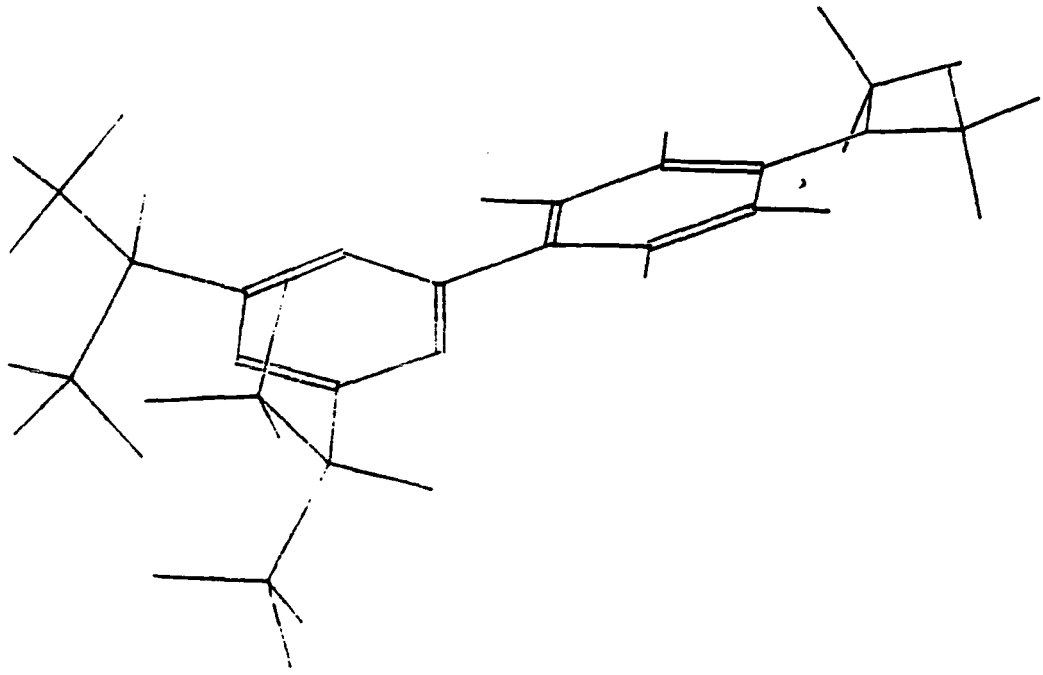
This donor acceptor structure is plausible as fluorinated triazine rings have been shown to be capable of supporting a negative charge in the formation of stable σ complexes[172].



In computer modelling studies (81A) was found to be non-planar, the benzene ring being at an angle to the triazine ring, as shown below (Fig 13).

Figure 13

Computer Generated Structure of (81)

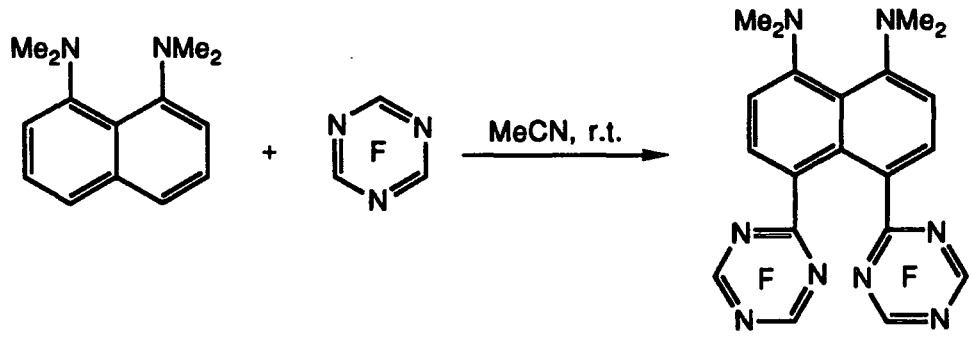


This twisted geometry may give rise to unusual fluorescent properties as seen in molecules of a similar structure. Indeed, the fluorescent properties of 2-(N,N-diethylamino)-4,6-dichloro-s-triazine have been studied[170].

Computer calculations suggest that molecules of the type (77)-(82A) do exhibit non-linear optical behaviour but are no better than more readily available molecules.

5.8 Reaction of 1,8-Bis(dimethylamino)naphthalene with Trifluoro-s-triazine

1,8-Bis(dimethylamino)naphthalene reacts with trifluoro-s-triazine to produce a tetrasubstituted naphthalene derivative (83) as red crystals in 53% yield.

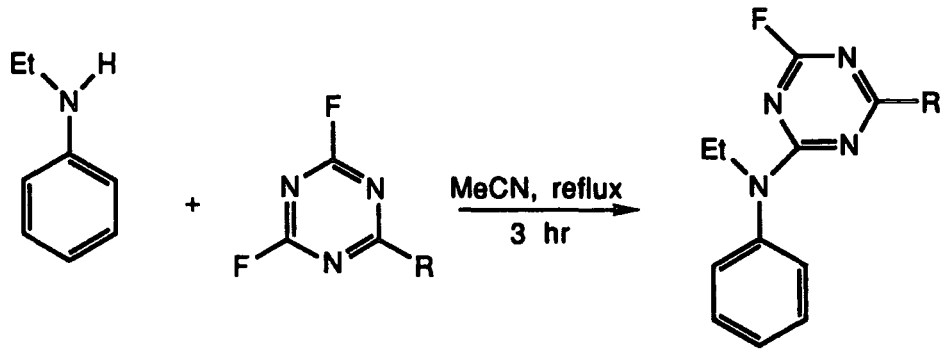


(83)(53%)

^{1}H NMR of the product (83) is similar to those of the annelation products (4) and (44) as discussed in Chapter 4, proving the tetrasubstituted naphthalene structure. Elemental analysis and mass spectra were obtained consistent with the assigned structure.

5.9 Reactions of Fluorinated -s-triazines with N-Ethylaniline

Reactions between trifluoro-s-triazine and secondary amines are well known as outlined in section 5.2. Reactions between N-ethylaniline and the triazines (13) and (14) were performed to ascertain whether any carbon substituted products were formed. We found that only the nitrogen substituted products (84) and (80) were produced in 69 and 89% yield respectively.



(84) R = F

(80) R = $(CF_3)_2CF$

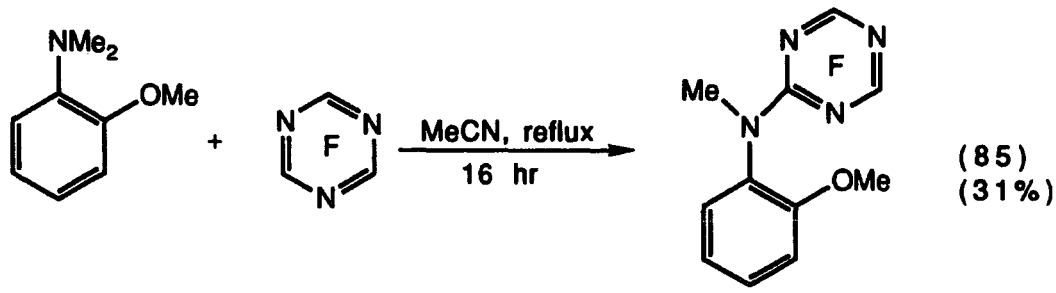
The position of substitution of the triazine ring is proved by the ^{1}H NMR spectra. No N-H resonances are seen indicating that the N-H proton has been substituted. Also, five protons are seen in the aromatic region rather than four protons forming an AB system which we would expect for a carbon-substituted product.

^{19}F NMR, mass spectra, UV spectra, IR spectra and elemental analyses were obtained for (84) and (80) in accordance with the assigned structures.

We may conclude that N-H is a stronger nucleophile than the activated aromatic ring acting as a carbon nucleophile.

5.10 Reaction of Trifluoro-s-triazine with 2-(N,N-Dimethylamino)-Methoxybenzene

Trifluoro-s-triazine reacts with 2-(N,N-dimethylamino)-methoxybenzene to produce the nitrogen substituted product (85) in 31% yield.



(85)
(31%)

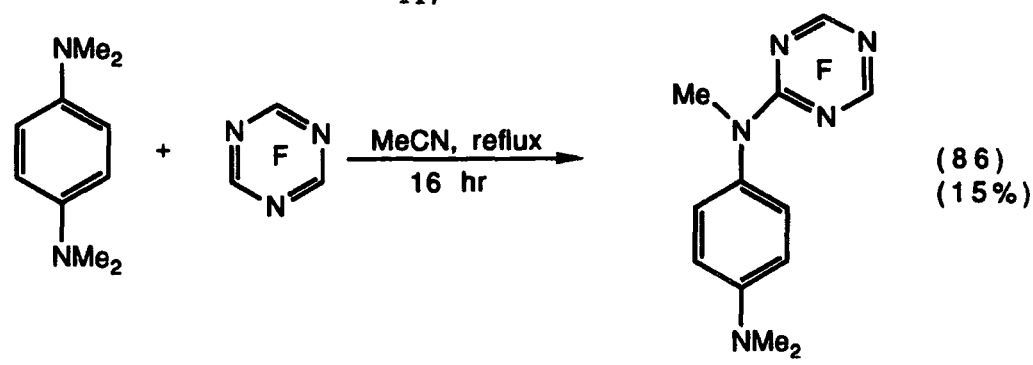
The structure is proved by the ^{1}H NMR spectrum. Four protons are seen in the aromatic region and there are two singlets at 3.47 and 3.84ppm each having a relative intensity of three indicating that one methyl group on the nitrogen atom has been substituted.

^{19}F NMR, mass spectra, UV spectra, IR spectra and elemental analyses were obtained for (85) in accordance with the assigned structure.

This result indicates that the 2-methoxy group prevents the NMe_2 group from conjugating with the ring thus decreasing activation towards electrophilic attack on the ring, in agreement with Shaws' results in reactions between 2-toluidine and cyanuric chloride[151] (section 5.3.1).

5.11 Reaction of Trifluoro-s-triazine with N,N,N',N'-Tetramethyl-1,4-Diaminobenzene

Trifluoro-s-triazine reacts with N,N,N',N'-tetramethyl-1,4-diaminobenzene to produce the nitrogen substituted product (86) in 15% yield.



(86)
(15%)

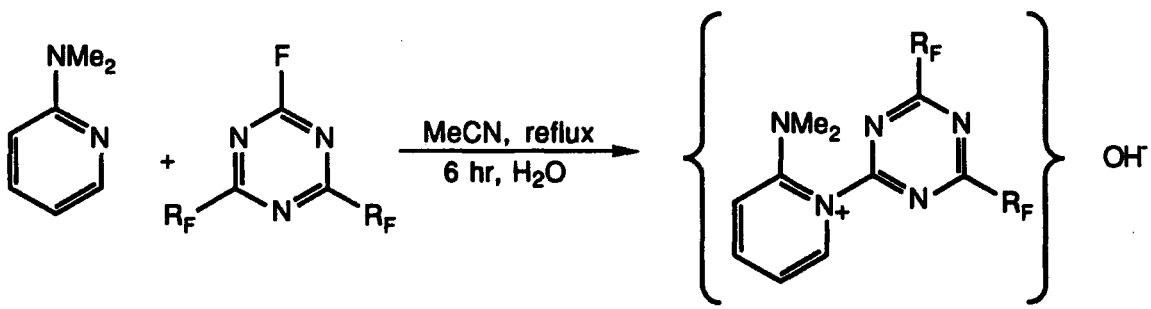
The structure of (86) is proved by the ^{1}H NMR spectrum.Two singlets at 2.97 and 3.50ppm with relative intensities 6 and 3 respectively indicate that one of the methyl groups has been substituted. Also, the AB system (6.78 and 7.17ppm (J_{AB}=8.9Hz)) indicative of a *para*-substituted benzene ring remains.

^{19}F NMR, mass spectra, UV spectra, IR spectra and elemental analyses were obtained for (86) in accordance with the assigned structure.

The nitrogen-substituted product is obtained as the 4-position is blocked. No *ortho* substituted products were obtained, in agreement with Shaws' results in the reaction between 2-toluidine and cyanuric chloride[151] (section 5.3.1).

5.12 Reaction between 2-(N,N-Dimethylamino)-pyridine and Perfluorodi-isopropyl-s-triazine

2-(N,N-Dimethylamino)-pyridine reacts with perfluorodi-isopropyl-s-triazine to give the pyridinium hydroxide salt (87) after the reaction was washed with water.



(47%)

No carbon substituted products were obtained in agreement with Chakrabarti's results[166].

The ^1H NMR spectrum shows a singlet at 3.25ppm corres ponding to the NMe_2 group and four protons in the aromatic region. Elemental analysis is consistent with a molecular formula of $C_{16}H_{11}N_5F_{14}O$.

5.13 Summary

We have shown that pyrroles, indoles and tertiary anilines can act as carbon nucleophiles in reactions with perfluorinated heterocycles in electrophilic substitution reactions.

Pyrroles are substituted at the 2-position, as proved by ^1H NMR coupling constants, whereas indoles undergo substitution at the 3-position, proved by ^1H and ^{13}C NMR, which is in accordance with the literature[167].

Tertiary anilines react via the para carbon atom to form electrophilic substitution products. The reaction is complicated by the formation of the ortho species when the nucleophile is stronger.

EXPERIMENTAL SECTION

INSTRUMENTATION

Gas liquid Chromatography (g.c.) analysis was carried out on a Hewlett Packard 5890A gas chromatograph fitted with a 25m cross-linked methyl silicone capillary column. Preparative g.c. was performed on a Varian Aerograph Model 920 (catharometer detector) gas chromatograph.

Fractional distillation of product mixtures was carried out using a Fischer Spahltrohr MMS 255 small concentric tube apparatus. Boiling points were recorded during distillation. Melting points were carried out at atmospheric pressure and are uncorrected.

Carbon, hydrogen and nitrogen elemental analyses were obtained using a Perkin-Elmer 240 Elemental Analyser or a Carlo Erba 1106 Elemental Analyser. Analysis for halogens were performed as described in the literature.

Ultraviolet spectra were recorded on a Perkin-Elmer Lambda 2 or a Pye-Unicam PU 8720 UV/Vis spectrophotometer.

Infra Red spectra were recorded on either a Perkin-Elmer 457 or 577 Grating Spectrophotometer using conventional techniques.

Proton NMR spectra were recorded on a Hitachi Perkin-Elmer R-24B (60MHz), a Bruker AC250 (250MHz) and a Varian VXR400S(400MHz) NMR spectrometer.

Fluorine NMR spectra were recorded on a Varian EM360l (56.45MHz), a Bruker AC250 (235MHz) and a Varian VXR400S (365MHz) NMR spectrometer.

Carbon NMR were recorded on a Varian VXR400S (100MHz) NMR spectrometer.

Mass Spectra of solid samples were recorded on a VG 7070E spectrometer. G.c. mass spectra were recorded on the VG 7070E spectrometer linked to a Hewlett Packard 5790A gas chromatograph fitted with a 25m cross-linked methyl silicone capillary column.

REAGENTS

In general chemicals were used as received from suppliers (Aldrich, Lancaster, Fluka) and solvents were dried by literature procedures.

CHAPTER SIX

EXPERIMENTAL TO CHAPTER TWO

6.1 Preparation of HF/Ether Solution

Anhydrous Hydrogen Fluoride gas was bubbled through dry diethyl ether (100ml), under anhydrous conditions,which was contained in an ice cooled FEP bottle. Face masks, gloves and an efficient fume hood are essential when handling anhydrous HF. The concentration of HF was determined by titrating an aliquot of the ether solution with a standard solution of sodium hydroxide using phenolphthalein as the indicator. e.g. a 1ml aliquot of HF/ether solution required 5.65ml of 1.192M NaOH solution giving a $0.134g_{HF}$/ml solution.

6.2 Preparation of 1,8-Bis(dimethylamino)naphthalene Hydrogen Fluoride Complex (PS/HF)

1,8-Bis(dimethylamino)naphthalene (Proton Sponge) (1.5g, 7mmol) was dissolved in the minimum amount of dry diethyl ether and the required 1:1 stoichiometric amount of the HF/ether solution ($0.134g_{HF}$/ml) (1.05ml, 7mmol) was added by pipette. A white solid immediately precipitated and the ether was carefully removed under reduced pressure to leave 1,8-Bis(dimethylamino)-naphthalene hydrofluoride (PS/HF) (1)(1.62g, 98%); m.p. 117-118°C; (Found: C, 69.7; H, 8.5; N, 11.5. $C_{14}H_{19}N_2F$ requires C, 71.8; H, 8.1; N, 11.95%); i.r. spectrum 1; n.m.r. spectrum 1; mass spectrum 1.

The preparation was repeated many times as the material was required usually on the 3g scale, but was scaled up to 25g without any problems. In all the following reactions 1,8-Bis(dimethylamino)-naphthalene hydrogen fluoride complex will be referred to as PS/HF.

6.3 Reactions using PS/HF as the Catalyst in C-C Bond Forming Reactions

6.3.1 Attempted Oligomerisation of Tetrafluoroethylene

This experiment was carried out at the ICI Experimental Site, Widnes with Dr. J. Hutchinson and Mr. M. Martin on 30/1/90.

A 0.5l autoclave was charged with PS/HF (23g, 98mmol) in dimethylformamide and α-Pinene (2 drops) was added (to inhibit any free radical reactions). The autoclave was flushed out with dry nitrogen four times and then with

tetrafluoroethylene three times. Then tetrafluoroethylene was added up to a maximum pressure of 10 bar and a maximum temperature of 110°C. No pressure drop was observed on the manometer. Consequently, on cooling, the autoclave was opened to reveal a red solvent layer and no lower fluorocarbon layer.

6.3.2 Dimerisation of Hexafluoropropene

A Carius tube was charged with PS/HF (1.63g, 7mmol) and acetonitrile (35ml), and hexafluoropropene (7.34g, 49mmol) was transferred under vacuum to the tube which was cooled in liquid air. The tube was sealed and allowed to warm to room temperature in a steel casing and then agitated on a rotating arm for 48 hr at room temperature. The tube was opened to reveal a lower fluorocarbon layer which was collected and determined to be the thermodynamic dimer of hexafluoropropene (2)(5.3g, 72%) as the only product by GC; δ_F (60MHz, $CFCl_3$) -60ppm (m, 3F, CF_3), -63 (m, 3F, CF_3), -86 (m, 3F, CF_3), -100.5 (s(br), 1F, CF), -119 (m, 2F, CF_2); m/z (EI^+) 281 (M^+-F, 24%); as compared to the literature data[121] [δ_F= -60.2ppm (m, 3F, CF_3), -62.8 (m, 3F, CF_3), -86.4 (m, 3F, CF_3), -100.1 (s (br), 1F, CF), -119.6 (m, 2F, CF_2); m/z (EI^+) 281 (M^+-F, 27%)].

6.3.3 Attempted Oligomerisation of Perfluorocyclobutene

A Carius tube was charged with PS/HF (1.07g, 5mmol) and acetonitrile (30ml), and perfluorocyclobutene (12.90g, 79mmol) was transferred under vacuum to the tube which was cooled in liquid air. The tube was sealed and allowed to warm to room temperature in a steel casing and then agitated on a rotating arm for 48 hr at room temperature. All volatiles were transferred under vacuum to a trap and analysis by GC/MS and ^{19}F n.m.r. showed no evidence for perfluorocyclobutene oligomers.

The reaction was repeated at 50°C in acetonitrile and using sulpholane as the solvent but no oligomers of perfluorocyclobutene were isolated.

6.3.4 Attempted Formation of a Stable Perfluorinated Carbanion

A flask was charged with hexafluoropropene dimer (2)(1.8g, 6mmol), PS/HF (1.4g, 6mmol) and sulpholane (5ml) under a plume of dry nitrogen and the mixture was stirred for one week at room temperature. ^{19}F NMR of the mixture revealed only start material. The reaction was repeated in tetraglyme and acetonitrile but only start material was observed by ^{19}F NMR.

6.3.5 Perfluoroalkylation of Pentafluoropyridine

A flask was charged with PS/HF (0.75g, 3mmol), pentafluoropyridine (6)(2.20g, 13mmol) and dry sulpholane (20ml) and then cooled in liquid air and evacuated. After warming to room temperature, hexafluoropropene (3.4g, 23mmol) was added via an expandable gas reservoir and the mixture was stirred vigorously for 7 days at room temperature. The volatile products were removed from the reaction mixture by flash distillation (4.8g). GC/MS showed three main products, which were separated using an SE 30 column at 100°C and identified as hexafluoropropene dimer (2)(2%); pentafluoropyridine (6)(49%); perfluoro-4-isopropylpyridine (7)(44%); δ_F (235 MHz, CD_3CN, $CFCl_3$) -75.4 (6F, s, CF_3), -86.7 (2F, s, 2,6-ring F), -135.3, 137.5 (2F, d, 3,5-ring F), -180.5 (1F, m, C-F); m/z (EI^+) 319 (M^+, 41%), 250 (15, M - CF_3), 200 (100, M - C_2F_5), as compared to the literature data[124] (δ_F= -74.3 (6F, s, $2CF_3$), -87.3 (2F, s, 2,6-ring F), -135.1 (2F, s, 3,5-ring F), -178.5 (1F, s, CF); m/e 319 (M)). Trace amounts of perfluorodi-isopropylpyridine (8)(2%); m/z (EI^+) 469 (M^+, 18%); and, perfluorotri-isopropylpyridine (12)(1%); m/z (EI^+) 619 (M^+, 16%); were also observed by GC/MS.

6.3.6 Perfluoroalkylation of Tetrafluoropyrimidine

A flask was charged with PS/HF (1.40g, 6mmol), tetrafluoropyrimidine (9)(2.30g, 15mmol) and dry sulpholane (30ml) and then cooled in liquid air and evacuated. After warming to room temperature, hexafluoropropene (5.23g, 35mmol) was added via an expandable gas reservoir and the mixture was stirred vigorously for 3 days at room temperature. The volatile products were removed from the reaction mixture by flash distillation (6.1g). The product mixture was analysed by GC/MS and ^{19}F n.m.r. and found to consist of perfluoro-4-isopropylpyrimidine (10)(27%); δ_F (235MHz, CD_3CN, $CFCl_3$) -48.7ppm (*2*-ring F), -72 (*6*-ring F), -76.1 (CF_3 groups), -154 (*5*-ring F), -186.9 (CF); m/z (EI^+) 302 (M^+, 35%), 283 (20, M - F), 233 (18, M - CF_3), 183 (51, M - C_2F_5); as compared to the literature data[125] [δ_F= -48.7ppm (*2*-ring F), -72.5 (*6*-ring F), -78.1 (CF_3), -154.5 (*5*-ring F), -188.7 (CF); m/e (EI^+) 302 (M^+, 65%), 283 (36, M-F), 233 (20, M-CF_3), 183 (57, M-C_2F_5)]; perfluoro-2,6-di-isopropylpyrimidine (11)(15%); δ_F (235MHz, CD_3CN, $CFCl_3$) -48.7ppm (*2*-ring F), -76.2 (CF_3), -133.5 (*5*-ring F), -186.9 (CF); m/e (EI^+) 452 (M^+, 22%), 433 (33, M - F), 383 (16, M - CF_3), 333 (40, M - C_2F_5); as compared to the literature data[125] [δ_F= -48.6 (*2*-ring F), -76.5 (CF_3), -132.5 (*5*-ring F), -186.3 (CF); m/e (EI^+) 452 (M^+, 42%), 433 (44, M-F), 383 (22, M-CF_3), 333 (37, M-C_2F_5)]; perfluoro-2,4,6-tri-isopropylpyrimidine (12)(39%); δ_F (235MHz, CD_3CN, $CFCl_3$) -76.2 (CF_3), -

124.1 (5-ring F), -182 (CF), -186.9 (CF); m/e (EI^+) 602 (M^+, 5%), 583 (9, M - F), 533 (4, M - CF_3), 452 (14, M - C_3F_6); as compared to the literature data[125] [δ_F= -76.5ppm (CF_3), -123.1 (5-ring F), -182.1 (CF), -186.3 (CF); m/e (EI^+) 602 (M+, 46%), 583 (50, M-F), 533 (22, M-CF_3)].

6.3.7 Perfluoroalkylation of Trifluoro-s-triazine

A flask was charged with PS/HF (0.70g, 3mmol), trifluoro-s-triazine (13)(1.80g, 13mmol) and dry sulpholane (20ml) and then cooled in liquid air and evacuated. After warming to room temperature, hexafluoropropene (7.5g, 50mmol) was added via an expandable gas reservoir and the mixture was stirred vigorously for 3 days at room temperature. The volatile products were removed from the reaction mixture by flash distillation (8.2g). The product mixture was analysed by ^{19}F n.m.r. and GC/MS and found to consist of two main products; perfluoroisopropyl-s-triazine (14)(35% by GC); m/z (EI^+) 285 (M^+, 100%), 266 (98, M - F), 197 (88, M - FCF_3), 166 (51, M - C_2F_5); perfluorodi-isopropyl-s-triazine (15)(8%); m/z (EI^+) 435 (M^+, 65%), 416 (100, M - F), 347 (38, M - FCF_3), 316 (11, M - C_2F_5). ^{19}F n.m.r. of the product mixture revealed perfluoroalkylation; δ_F (235 MHz, CD_3CN, $CFCl_3$) -33ppm (N=C-F), -73 (CF_3), -183.8 (CF); as compared to the literature data[126] [δ_F= -30.4-30.6ppm (ring F), -74.4-75.4 (CF_3 groups), -183.8-186.5 (CF)].

6.4 Reactions Using PS/HF in C-F Bond Forming Reactions

6.4.1 With Benzoyl Chloride

A mixture containing PS/HF (1.07g, 4.5mmol), benzoyl chloride (0.70g, 5mmol) and acetonitrile was allowed to stand at room temperature for 24 hr. A white solid, 1,8-bis(dimethylamino)naphthalene hydrochloride (PS/HCl), precipitated. The mixture was filtered and benzo trifluoride (0.17g, 1.16mmol) was added as an nmr marker.^{19}F n.m.r. revealed benzoyl fluoride (76% yield by integration); δ_F (235 MHz, CH_3CN, $CFCl_3$) +17.0 (1F, s, CO-F); as compared to the literature data (δ_F=+17.1ppm)[173].

6.4.2 Reaction between Hexafluoroacetone and PS/HF

A Carius tube was charged with PS/HF (5.1g, 22mmol) in acetonitrile (20ml) and hexafluoroacetone (5.3g, 32mmol) was transferred under vacuum to the trap which was cooled in liquid air.The tube was sealed and allowed to stand at room temperature overnight. The solution went pale yellow. The tube was opened and ^{19}F

n.m.r. revealed the desired carbinolate species (17); δ_F (235 MHz, CH_3CN, $CFCl_3$) -80.33 (6F, s, CF_3), -107.88 (1F, s(br), CF). There was no peak at -164ppm indicating that all the PS/HF had reacted, hence the solution contained 22mmol of the carbinolate species. The reaction solution was used in the two following trapping reactions.

6.4.2.1 Preparation of Heptafluoroisopropyl benzoate (18)

Benzoyl chloride (1.7g, 12mmol) was added dropwise to the carbinolate solution prepared above (10ml, 11mmol) and the mixture was stirred overnight. The volatiles were transferred under vacuum and analysed by GC/MS and ^{19}F n.m.r. There were two products; benzoyl fluoride (51%); and, heptafluoroisopropyl benzoate (18) (49%) which was isolated by preparative GC using a 30% SE 30 column at 150°C; δ_F (235 MHz, CH_3CN, $CFCl_3$) -78.1 (6F, s, CF_3), -141.1 (1F, s, CF); m/z (EI^+) 290 (M^+, 22%), 105 (100, Ar-C=O), 77 (60, C_6H_5), 69 (11, CF_3).

6.4.2.2 Preparation of Heptafluoroisopropyl benzyl ether (19)

Benzyl bromide (2.3g, 13mmol) was added dropwise to the carbinolate solution prepared above (10ml, 11mmol) and the mixture was stirred overnight at room temperature. All volatile materials were transferred under vacuum and analysed by GC/MS and ^{19}F n.m.r. There were two components; benzyl bromide (39%) and, heptafluoroisopropyl benzyl ether (19)(61%) which was isolated by preparative scale GC using a 30% SE 30 column at 150°C; υ_{max} 1230cm^{-1} (C-O-C stretch); δ_H (250 MHz, $CDCl_3$, TMS) 5.01 (2H, s, CH_2), 7.42 (5H, m, Ar-H); δ_F (235 MHz, $CDCl_3$, $CFCl_3$) -79.5 (6F, s, CF_3), -142.6 (1F, s, CF); m/z (EI^+) 276 (M^+, 33%), 91 (100, Ar-CH_2); m/z (EI^+) 276 (M^+, 33%), 91 (100, Ar-CH_2).

6.4.3 With 2,4-Dinitrochlorobenzene

A mixture containing PS/HF (3.06g, 13mmol) and 2,4-dinitrochlorobenzene (2.69g, 13mmol) was refluxed in acetonitrile for 2 days. Benzotrifluoride was added as an nmr marker and ^{19}F nmr revealed 2,4-dinitrofluorobenzene (45% yield by integration) at -109ppm, as compared to the literature data (δ_F=-107.7ppm)[173].

6.4.4 With Benzyl Bromide

A mixture containing PS/HF (1.87g, 8mmol), benzyl bromide (1.30g, 8mmol) and acetonitrile ((15ml) was refluxed for 24 hr. A white solid, 1,8-bis(dimethylamino)naphthalene hydrobromide (PS/HBr), precipitated (i.r.

spectrum). The mixture was filtered and benzo trifluoride (0.19g, 1.30mmol) was added as an nmr marker. ^{19}F n.m.r. revealed benzyl fluoride (72% by integration); δ_F (235 MHz, CH_3CN, $CFCl_3$) -206.4 (1F, t, J_{HF}=49 Hz, $-CH_2F$); as compared to the literature data (δ_F=-207ppm)[173].

6.4.5 With Octyl Iodide

A mixture containing PS/HF (1.10g, 4.7mmol), octyl iodide (0.91g, 3.8mmol) and acetonitrile was heated at reflux for 24 hr. On cooling white crystals, 1,8-bis(dimethylamino)naphthalene hydriodide, precipitated (i.r.spectrum). The mixture was filtered and and benzo trifluoride (0.23g, 1.57mmol) was added as an nmr marker. ^{19}F n.m.r. revealed octyl fluoride (65% yield by integration); δ_F (235 MHz, CH_3CN, $CFCl_3$) 218.0 (1F, t, J_{HF}=42 Hz, $-CH_2F$); as compared to the literature data (δ_F= -219ppm)[173].

6.4.6 Attempted Reaction Between PS/HF and 1,2-Epoxybutane

A mixture containing PS/HF (1.54g, 6.6mmol), 1,2-epoxybutane (0.43g, 6.0mmol) and acetonitrile (15ml) was refluxed for 48 hr. ^{19}F n.m.r. of the mixture showed that no reaction had taken place. The reaction was repeated in sulpholane at 130°C for 3 days with no hydrofluorination taking place, by ^{19}F n.m.r.

6.4.7 Preparation of 1,2:5,6-Di-O-isopropylidene-3-O-triflic-α-D-gulofuranose (21)

Diacetone-D-glucose (20)(1.83g, 7mmol) and pyridine (2.5g, 32mmol) were dissolved in dichloromethane (50ml) and the solution, under dry nitrogen, was cooled down to 0°C with an ice/salt bath. Triflic anhydride (5.1g, 18mmol) was added dropwise, with the temperature of the reaction maintained under 5°C. The solution was stirred at 5°C for 30 mins. A white solid was deposited and the solution went pale yellow. The solution was washed sequentially with ice-cold dilute hydrochloric acid and water. The organic layer was dried ($MgSO_4$) and evaporated to leave a solid, the desired triflate (21)(2.17g, 79%); δ_F (60 MHz, $CDCl_3$, $CFCl_3$) -76.0 (3F, s, CF_3); as compared to the literature data[129]; and was used immediately in the next reaction.

6.4.8 Attempted Reaction Between PS/HF and Triflate (21)

A mixture containing triflate (21)(2.17g, 5.5mmol), PS/HF (1.80g, 7.7mmol) and acetonitrile (20ml) was refluxed overnight. The solution went dark brown and a solid precipitated. This solid was collected by filtration and recrystallised

from water as white needles and found to be the salt, 1,8-bis(dimethylamino)-naphthalene hydrotriflate (23); m.p. 215-218°C; (Found: C, 49.7; H, 5.3; N, 7.6. Calc for $C_{15}H_{19}N_2F_3SO_3$: C, 49.5; H, 5.2; N, 7.6%); i.r. spectrum recorded; m/z (EI^+) 214 (naphthalene ion, 40%). ^{19}F n.m.r. of the remaining reaction solution showed no evidence for a fluorinated glucose. The triflate salt may have been produced after decomposition of the triflated glucose.

The reaction was repeated at room temperature but no fluorinated glucose was observed, by ^{19}F n.m.r.

6.4.9 Preparation of 1,2:5,6-Di-O-isopropylidene-3-O-toluene-p-sulphonyl-α-D-allofuranose (22)

Diacetone-D-glucose (20)(3.00g, 11.5mmol) was dissolved in pyridine (40ml) and cooled to 0°C. A solution of tosyl chloride (7.00g, 36.7mmol) in pyridine (20ml) was added dropwise. The solution was stirred at room temperature for two days. Water (4ml) was added and the solution was left to stand for a further 20 mins. It was then poured onto ice/water (300ml) and the crude sulphonate was filtered off and recrystallised from aqueous ethanol to yield the desired tosylate (22)(2.50g, 52%); m.p. 120-122°C (lit.[130], 122-123°C); (Found: C, 54.5; H, 6.2. Calc for $C_{19}H_{26}SO_8$: C, 55.1; H, 6.3%); IR spectrum recorded; δ_H (235 MHz, $CDCl_3$, TMS) 1.15, 1.19, 1.31 and 1.48 (3H, s, acetal groups), 2.46 (3H, s, Ar-CH_3), 3.89-4.06 (4H, m, unassigned 2CH, CH_2), 4.78 (1H, m, H-1), 4.83 (1H, d, $J_{3,4}$=3.6 Hz, H-4), 5.93 (1H, d, $J_{1,2}$=3.6 Hz, H-1), 7.34 and 7.83 (4H, AB, J_{AB}=8.3 Hz, Ar-H); as compared to the literature data[130].

6.4.10 Attempted Reaction Between PS/HF and Tosylate (22)

A mixture containing tosylate (22)(0.80g, 1.9mmol), PS/HF (0.70g, 3mmol) and acetonitrile (5ml) was refluxed overnignt. ^{19}F n.m.r. of the reaction mixture showed unreacted PS/HF and no evidence for a fluorinated glucose.

CHAPTER SEVEN

Experimental to Chapter Three

7.1 Preparation and Reactions of Trialkylamine Hydrofluoride Complexes

7.1.1 Preparation of Trialkylamine Hydrofluoride Complexes (24)-(28)

All bases were used as supplied (Aldrich). The hydrofluoride salts were prepared by adding a stoichiometric amount of a callibrated HF/ether solution to an ethereal solution of the base, followed by evaporation of the solvent to leave the salt, as described previously (Section 6.1).

The following salts were prepared:-

1) Triethylamine Hydrofluoride (24); hygroscopic solid at r.t; i.r. spectrum 2; n.m.r. spectrum 2; mass spectrum 2.

2) Tributylamine Hydrofluoride (25); liquid; i.r. spectrum 3; n.m.r. spectrum 3; mass spectrum 3.

3) Trihexylamine Hydrofluoride (26); liquid; i.r. spectrum 4; n.m.r. spectrum 4; mass spectrum 4.

4) Trioctylamine Hydrofluoride (27); liquid; i.r. spectrum 5; n.m.r. spectrum 5; mass spectrum 5.

5) Tridodecylamine Hydrofluoride (28); liquid; i.r. spectrum 6; n.m.r. spectrum 6; mass spectrum 6.

7.1.2 Methodology for Standard Reactions

Three standard experiments were performed using each amine.HF complex as the source of soluble fluoride ion. The experiments were chosen to provide a range of fluoride ion reactions. i.e. nucleophilic substitution reactions at unsaturated, saturated and aromatic carbon positions. The same methodology was used for each hydrofluoride salt, so general procedures for the three standard reactions appear in this section. The quantities of each reagent used can be found in the tables listed under the appropriate

section. Any deviation from these procedures are listed under the appropriate sections; e.g. solubility of HCl salt formed in the reactions using the piperidine HF salts. All yields quoted are n.m.r. yields of the crude reaction mixtures, not isolated yields. We chose not to work-up the reactions due to their small scale and the fact that crude n.m.r. yields give the true maximun yield as there are no handling losses associated with work-up.

7.1.2.1 Reaction of Base Hydrofluoride Complexes with Benzoyl Chloride

A mixture containing Base/HF, benzoyl chloride and acetonitrile (10ml) was allowed to stand at room temperature for 24 hr. A white solid, the corresponding Base/HCl salt, was precipitated. Benzotrifluoride was added to the reaction mixture which was shaken to ensure homogeneity. The mass, and hence the number of moles of benzotrifluoride provided a marker for n.m.r. integration. ^{19}F n.m.r. of the reaction mixture was recorded; δ_F (235 MHz, CH_3CN, $CFCl_3$); to reveal a peak at +16.7 ppm due to benzoyl fluoride, as compared to the literature data[173]; at -63ppm due to the benzotrifluoride marker and between -150 and -170 ppm due to unreacted Base/HF. The yield of benzoyl fluoride was calculated by comparing the integration of the peak due to the benzotrifluoride marker and that due to benzoyl fluoride.

7.1.2.2 Reaction of Base Hydrofluoride Complexes with Benzyl Bromide

A mixture containing Base/HF, benzyl bromide and acetonitrile (15ml) was refluxed for 24 hr. On cooling, a white solid, the corresponding Base/HBr salt precipitated. Benzotrifluoride was added to the reaction mixture which was shaken to ensure homogeneity. The mass, and hence the number of moles of benzotrifluoride provided a marker for n.m.r. integration. ^{19}F n.m.r. of the reaction mixture was recorded; δ_F (235 MHz, CH_3CN, $CFCl_3$); to reveal a peak at -63 ppm due to the benzotrifluoride marker; a peak between -150 and -170 ppm due to unreacted Base/HF and a peak at -206.4 (t, J_{HF}=49Hz) due to benzyl fluoride, as compared to the literature data[173]. The yield of benzyl fluoride was calculated by comparing the integration of the peak due to the benzotrifluoride marker and that due to benzyl fluoride.

7.1.2.3 Reaction of Base Hydrofluoride Complexes and 2,4-Dinitrochlorobenzene

A mixture containing Base/HF, 2,4-dinitrochlorobenzene and acetonitrile was refluxed for 48 hr. A white solid, the corresponding Base/HCl salt, was precipitated. Benzotrifluoride was added to the reaction mixture which was shaken to ensure

homogeneity. The mass, and hence the number of moles of benzotrifluoride provided a marker for n.m.r. integration. ^{19}F n.m.r. of the reaction mixture was recorded; δ_F (235 MHz, CH_3CN, $CFCl_3$); to reveal a peak at -63 ppm due to the benzotrifluoride marker; at -108.8 ppm due to 2,4-dinitrofluorobenzene, as compared to the literature data[173] and a peak between -150 and -170 ppm due to unreacted Base/HF. The yield of 2,4-dinitrofluorobenzene was calculated by comparing the integration of the peak due to the benzotrifluoride marker and that due to dinitrofluorobenzene.

7.1.3 Reactions of Trialkylamine.HF Complexes

The three standard reactions were performed using the trialkylamine.HF complexes as the source of Fluoride ion. See above for details of the methodology. Hence, in the following tables the HF salt used was $R_3N.HF$, where R = alkyl.

7.1.3.1 Reaction with Benzoyl Chloride

R	HF salt g, mmol	Benzoyl Chloride g, mmol	Benzotrifluoride g, mmol	Yield %
Et	0.89, 7.35	0.86, 6.10	0.20, 1.37	91
But	1.01, 4.93	0.62, 4.41	0.17, 1.16	88
Hex	1.29, 4.46	0.54, 3.84	0.29, 1.99	90
Oct	2.32, 6.22	0.80, 5.69	0.28, 1.92	68
Dodec	0.62, 1.15	0.28, 1.98	0.19, 1.35	79

7.1.3.2 Reaction with Benzyl Bromide

R	HF salt g, mmol	Benzyl Bromide g, mmol	Benzotrifluoride g, mmol	Yield %
Et	0.75, 6.20	0.86, 5.03	0.25, 1.71	18
But	0.90, 4.39	0.72, 4.21	0.25, 1.71	12
Hex	1.91, 6.61	1.01, 5.91	0.29, 1.98	17
Oct	2.22, 5.94	0.95, 5.55	0.23, 1.57	14
Dodec	1.90, 3.50	0.53, 3.09	0.24, 1.64	11

7.1.3.3 Reaction with 2,4-Dinitrochlorobenzene

R	HF salt g, mmol	DNCBenzene g, mmol	Benzotrifluoride g, mmol	Yield %
Et	0.39, 3.22	0.52, 2.57	0.22, 1.50	34
But	0.72, 3.51	0.63, 3.11	0.33, 2.26	84
Hex	1.81, 6.26	1.06, 5.23	0.20, 1.37	77
Oct	1.54, 4.13	0.75, 3.70	0.33, 2.26	61
Dodec	1.02, 1.88	0.36, 1.78	0.21, 1.44	14

7.2 Preparation and Reactions of Polysubstituted Piperidine Hydrofluoride Complexes

7.2.1 Preparation of Pentasubstituted Piperidine Bases

Tetramethylpiperidine (31) and pentamethylpiperidine (29) were used as supplied (Aldrich). The three other piperidine bases were prepared as follows:-

7.2.1.1 Preparation of N-Ethyl-2,2,6,6-Tetramethylpiperidine (32)[132]

A mixture containing tetramethylpiperidine (31)(24.7g, 0.17mol) and ethyl p-toluene sulphonate (18.0g, 0.09mol) was heated at 100°C for 24 hr in a flask fitted with an air condenser. The mixture solidified into a partly browned cake. On cooling, the product mixture was washed thoroughly with diethyl ether to precipitate a white solid which was collected by filtration and identified as the salt, tetramethylpiperidinium tosylate; m.p. 218-222°C (lit.,[132] 219-221°C); IR spectrum recorded; m/z (EI^+)142 (M^+ piperidinium cation, 6.6%). The ether layer was dried and evaporated and the residue was distilled on the Fischer Spahltrohr to yield N-Ethyl-2,2,6,6-tetramethylpiperidine (32)(6.38g, 21%); b.p. 95.6-96°C/24mmHg; (Found: C, 78.1; H, 14.2; N, 8.4. Calc for $C_{11}H_{23}N$: C, 78.1; H, 13.6; N, 8.4%); IR spectrum recorded; δ_H (235MHz, $CDCl_3$, TMS) 1.28 (15H, m, CH_3), 1.62 (4H, m, C-CH_2-N), 1.75 (2H, m, C-CH_2-C), 2.72 (2H, q, J=7.1 Hz, CH_2); m/z (EI^+) 168 (M^+, 3.8%), 154 (M^+-Me group).

7.2.1.2 Preparation of N-Allyl-2,2,6,6-Tetramethylpiperidine (33)[132]

A mixture containing tetramethylpiperidine (31)(30.7g, 0.22mol) and allyl bromide (13.2g, 0.11mol) was heated at 50°C for 3 days. The mixture turned pale yellow. The mixture was washed thoroughly with diethyl ether and filtered. The ether layer was dried and evaporated and the residue was distilled on the Fischer Spahltrohr to yield N-allyl-2,2,6,6-tetramethylpiperidine (33)(9.3g, 24%); b.p. 103-109°C/20mm Hg (pure by GC); (Found: C, 79.5; H, 13.1; N, 7.9. Calc for $C_{12}H_{23}N$: C, 79.5; H, 12.7; N, 7.7%); IR spectrum recorded; δ_H (60MHz, $CDCl_3$, TMS) 1.1 (12H, s, CH_3), 1.5 (6H, s, ring CH_2), 3.2 (2H, m, N-CH_2-Ar), 5.1 (2H, m, C=CH_2), 5.9 (1H, m, -CH=); m/z (EI^+) 181 (M^+, 9.9%), 166 (100%, M^+-Me group).

7.2.1.3 Preparation of N-Benzyl-2,2,6,6-Tetramethylpiperidine (34)[132]

Benzyl bromide (12.2g, 71mmol) was added to tetramethylpiperidine (31)(26.6g, 0.19mol) over 20 mins at 60°C with stirring. The solution was heated at 100°C for 8 hr. On cooling, the reaction mixture was washed thoroughly with diethyl ether and filtered. The ether layer was dried and evaporated and the residue was distilled on the Fischer Spahltrohr to yield N-benzyl-2,2,6,6-tetramethylpiperidine (34)(5.4g, 32%); b.p. 135°C/6mm Hg; m.p. 30-32°C; (Found: C, 83.7; H, 11.1; N, 6.1. Calc for $C_{16}H_{25}N$: C, 83.1; H, 10.8; N, 6.1%); IR spectrum recorded; δ_H (60MHz, $CDCl_3$, TMS) 0.97 (12H, s, CH_3), 1.5 (6H, m, ring CH_2), 3.75 (2H, s, N-CH_2-Ar), 7.25 (5H, m, Ar-H); m/z (EI^+) 231 (M^+, 3.3%), 216 (100%, M^+-Me group).

7.2.2 Preparation of the Hydrofluoride Complexes (35)-(39)

The hydrofluoride salts were prepared by adding a stoichiometric amount of a callibrated HF/ether solution to an ethereal solution of the base, followed by evaporation of the solvent to leave the salt, as described previously (Section 6.1).

The following salts were prepared:-

1) 2,2,6,6-tetramethylpiperidine Hydrofluoride (35); m.p. 76-80°C; (Found: C, 66.5; H, 12.4; N, 7.6. $C_9H_{20}NF$ requires C, 67.1; H, 12.4; N, 8.7%); i.r. spectrum 7; n.m.r. spectrum 7; mass spectrum 7.

2) 1,2,2,6,6-pentamethylpiperidine Hydrofluoride (36); m.p. 122-124°C; i.r. spectrum 8; n.m.r. spectrum 8; mass spectrum 8.

3) N-ethyl-2,2,6,6-tetramethylpiperidine Hydrofluoride (37); m.p. 74-76°C; i.r. spectrum 9; n.m.r. spectrum 9; mass spectrum 9.

4) N-allyl-2,2,6,6-tetramethylpiperidine Hydrofluoride (38); m.p.72-74°C; i.r. spectrum 10; n.m.r. spectrum 10; mass spectrum 10.

5) N-benzyl-2,2,6,6-tetramethylpiperidine Hydrofluoride (39); m.p. 83-86°C; i.r. spectrum 11; n.m.r. spectrum 11; mass spectrum 11.

7.2.3 Reactions of Piperidine.HF Complexes (35)-(39)

The same standard reactions were performed using the piperidine.HF salts as the source of Fluoride ion, under the same conditions as those carried out previously with other salts . See Section 7.1.2 for the methodology. However, in these reactions the hydrochloride/hydrobromide salt produced as a side product does not precipitate but remains in solution. In the following tables R refers to the group attached to the nitrogen atom in the piperidine.HF complex.

7.2.3.1 Reaction with Benzoyl Chloride

R	HF salt g, mmol	Benzoylchloride g, mmol	Benzotrifluoride g, mmol	Yield %
H	0.81, 5.0	0.57, 4.0	0.14, 0.9	83
Me	0.43, 2.46	0.32, 2.28	0.25, 1.71	64
Et	1.05, 5.55	0.70, 4.99	0.22, 1.51	78
Allyl	0.06, 0.29	0.27, 1.95	0.25, 1.71	55
Benzyl	0.49, 1.95	0.27, 1.95	0.17, 1.16	42

7.2.3.2 Reaction with Benzyl Bromide

R	HF salt g, mmol	Benzylbromide g, mmol	Benzotrifluoride g, mmol	Yield %
H	1.35, 8.40	1.40, 8.20	0.14, 0.8	25
Me	0.95, 5.43	0.84, 4.91	0.31, 2.12	84
Et	0.58, 3.07	0.49, 2.86	0.27, 1.85	38
Allyl	0.45, 2.24	0.27, 1.58	0.21, 1.44	n.r.
Benzyl	0.27, 2.08	0.18, 1.05	0.11, 0.64	n.r.

7.2.3.3 Reaction with 2,4-Dinitrochlorobenzene

R	HF salt g, mmol	DNCBenzene g, mmol	Benzotrifluoride g, mmol	Yield %
H	1.12, 6.90	1.31, 6.40	0.44, 3.0	49
Me	0.57, 3.26	0.63, 3.11	0.25, 1.71	78
Et	1.08, 5.71	0.80, 3.95	0.42, 2.88	94
Allyl	0.37, 1.84	0.36, 1.78	0.15, 1.03	31
Benzyl	0.31, 1.23	0.28, 1.38	0.18, 1.23	23

7.3 Preparation and Reactions of Tetramethylguanidine HF Complex

The tetramethylguanidine hydrogen fluoride complex (40) was prepared in the same manner as for the preparation of PS/HF (section 6.1).

Tetramethylguanidine Hydrogen Fluoride Complex (40); m.p. 66-68°C; (Found: C, 41.8; H, 11.1; N, 29.4. $C_5H_{14}N_3F$ requires C, 44.4; H, 10.4; N, 29.4%); i.r. spectrum 12; n.m.r. spectrum 12; mass spectrum 12.

Two reactions were performed as described above (section 7.2.3); quantities used and yields are tabulated below:-

Substrate	Substrate g/mmol	HF complex g/mmol	$PhCF_3$ g/mmol	Yield %
PhCOCl	1.40, 9.9	1.15, 9.0	0.21, 1.4	65
Dinitrochloro-benzene	1.37, 7.0	1.07, 8.0	0.24, 1.6	36

7.3.1 Attempted Preparation of Pentamethylguanidine (41)[133]

Tetramethylguanidine (4.6g, 53mmol) and methyl iodide (7.6g, 54mmol) were stirred in toluene (50ml) at room temperature overnight. A white solid is slowly deposited and this was collected by filtration and identified as pentamethylguanidinium hydriodide (42)(3.2g, 29%); m.p. 137°C (from aq. EtOH) (lit[133], 137°C); (Found: C, 30.0; H, 6.5; N, 14.9. Calc for $C_6H_{16}N_3I.0.5C_2H_5OH$: C, 30.0; H, 6.8; N, 15.0%); δ_H (60MHz, D_2O, TMS) 2.9ppm (s, 4H, N-Me), 4.7 (s, 1H, =N-Me).

Heating the pentamethylguanidinium hydriodide salt with NaOH caused a mixture of tetramethylguanidine and pentamethylguanidine to be produced (gc/ms) which could not be separated by distillation.

CHAPTER 8

EXPERIMENTAL TO CHAPTER 4

8.1 Reaction between PS/HF, Perfluorocyclobutene and Hexafluoropropene

A Carius tube was charged with 1,8-bis(dimethylamino)naphthalene hydrofluoride (1)(2.5g, 10.6mmol) in acetonitrile (20ml) and perfluorocyclobutene (6.7g, 41mmol) and hexafluoropropene (5.0g, 33mmol) were transferred under vacuum to the tube which was cooled in liquid air. After agitating on a rotating arm at room temperature for two days, the tube was opened to reveal a red solvent layer. On adding water (20ml), an orange solid precipitated and was collected by filtration. TLC showed that the solid contained two components. The solid was evaporated onto chromatographic alumina and light petroleum eluted 1,1-Bistrifluoromethyl-(6,7-bisdimethylamino)-2,3-tetrafluoroethano-[1H]-phenalene (4) (1.1g, 21%) as orange crystals; R_F=0.5; m.p. 128°C (from aqueous ethanol); λ_{max} (CH_3CN) 273.6nm ($\log_{10}$ ε 3.78), 367.6 (3.45), 451.2 (3.78); (Found: C, 52.2; H, 3.4; N, 5.6; F, 38.0. $C_{21}H_{16}N_2F_{10}$ requires C, 51.9; H, 3.3; N, 5.8; F, 39.0%). n.m.r. spectrum 13; i.r. spectrum 13; mass spectrum 13.

A red solid (5) was also isolated (0.05g) as yet unidentified; δ_F ($CFCl_3$, CD_3CN, 235MHz) -68.9ppm (s, 6F), -110.5 (s, 2F); i.r. spectrum 14; mass spectrum 14.

8.2 Reaction Between PS and Co-dimer (3)

A mixture containing PS (0.7g, 3.2mmol), co-dimer (3)(1.0g, 3.2mmol) and acetonitrile (10ml) was stirred at room temperature for two days. Water was added to the mixture to precipitate an orange solid.which was collected by filtration. The same proceedure was then carried out as above (section 8.1) to yield pure (4)(0.35g, 22%) as orange crystals; m.p. 128°C; spectral data as above.

8.3 Preparation of Codimer (43)

A Carius tube was charged with pyridine (2.5g, 32mmol) and perfluorocyclobutene (20g, 0.12mol) and perfluorocyclopentene (25g, 0.12mol) were transferred to the tube which was cooled in liquid air. After rotating on a rotating arm for two days the tube was opened and all volatile products were transferred under vacuum to a trap. These were washed with water, dried (P_2O_5) and distilled on the Fischer Spahltrohr to yield perfluorobicyclobutylidene (62)(2.9g, 8%); b.p. 74-

85°C; and, codimer (43) (2.3g, 5%); b.p. 98-100°C; as compared to the literature data[121].

8.4 Reaction between PS and Codimer (43)

A mixture containing PS (0.6g, 2.8mmol) and codimer (43) (1.0g, 2.7mmol) was refluxed overnight in acetonitrile (5ml). The solvent was removed to leave an orange solid which was washed with water, collected and dried. The solid was evaporated onto chromatographic alumina and 40/60 petroleum ether eluted Spiro[octafluorocyclopentane-1,1'-(6,7-bisdimethylamino)-2',3'-tetrafluoroethano-[1H]-phenalene (44)(0.2g, 13%) as orange crystals; m.p. 137-139°C; R_F=0.5; λ_{max} (CH_3CN) 273.6nm ($\log_{10}\varepsilon$ 4.06), 365.6 (3.74), 452.8 (4.10); (Found: C, 50.4; H, 3.9; N, 4.4. $C_{23}H_{16}N_2F_{12}$ requires C, 50.3; H, 2.9; N, 5.1%). Mass required for $C_{23}H_{16}N_2F_{12}$: 548.11219. Found: 548.11762 a.m.u.; n.m.r. spectrum 14; i.r. spectrum 15; mass spectrum 15.

8.5 Reaction between PS and Perfluoro-bicyclopentylidene (55)

8.5.1 At Low Dilution

A mixture containing PS (1.1g, 5.1mmol) and perfluorobicyclopentylidene (55)(1.0g, 2.3mmol) was stirred overnight at room temperature in acetonitrile (5ml). A dark olive green precipitate formed. Water was added to the mixture and the solid was collected by filtration. The solid was absorbed onto chromatographic alumina and light petroleum/dichloromethane (4:1) eluted (7,8)-(9,10)-dihexafluoro-propano-(3,4-bisdimethylamino)-cyclohepta[*d*, *e*]-naphthalene (56)(0.54g, 42%); m.p. 243-45°C (decomp) (from acetonitrile); R_F=0.65; (Found: C, 51.3; H, 2.8; N, 4.9; F, 40.0. $C_{24}H_{16}N_2F_{12}$ requires C, 51.4; H, 2.8; N, 5.0; F, 40.7%). no n.m.r. could be recorded; i.r. spectrum 16; mass spectrum 16.

8.5.2 At High Dilution

A mixture containing PS (0.5g, 2.5mmol) and perfluorobicyclopentylidene (55)(1.0g, 2.3mmol) was stirred overnight at room temperature in acetonitrile (120ml). The solvent was removed under vacuum to leave a solid residue, which was absorbed onto chromatographic alumina and petroleum ether/dichloromethane (4:1) eluted (56)(0.23g, 18%), as above; Spiro-[octafluoro-cyclopentane-1,1'-(6,7-bisdimethylamino)-2',3'-tetrafluoropropan-1''-one-[1H]-phenalene (60)(0.14g, 10%) as bright green metallic looking flakes; m.p. >280°C; R_F=0.45; (Found: C, 48.4; H, 2.75; N, 4.50. $C_{24}H_{16}N_2F_{12}O$ requires C, 50.0; H, 2.75; N, 4.5%.

$C_{24}H_{16}N_2F_{12}O.H_2O$ requires C, 48.5; H, 3.0; N, 4.7%); n.m.r. spectrum 15; i.r. spectrum 17; mass spectrum 17; and, 7,8-propano-9,10-propan-1''-one-cyclohepta-[*d*, *e*]-naphthalene (61)(0.12g, 9%) as bright purple metallic looking flakes; m.p. >280°C; R_F=0.3; (Found: C, 53.2; H, 3.05; N, 4.75. $C_{24}H_{16}N_2F_{10}O$ requires C, 53.5; H, 2.95; N, 5.2%); $C_{24}H_{16}N_2F_{10}O$ requires 538.110295 a.m.u. Found 538.1100900 a.m.u; n.m.r. spectrum 16; i.r. spectrum 18; mass spectrum 18.

8.6 Preparation of Perfluorobicyclobutylidene (62)

A Carius tube was charged with pyridine (1.04g, 13mmol) and perfluorocyclobutene (28.3g, 0.15mol) was transferred to the tube which was cooled in liquid air. After agitating on a rotating arm for two days the tube was opened and all volatiles were transferred under vacuum. These were washed with water and the lower fluorocarbon layer was separated, dried (P_2O_5) and distilled on the Fischer Spahltrohr to yield perfluorobicyclobutylidene (62)(5.2g, 10%); b.p. 74-85°C; as compared to the literature data[121].

8.7 Reaction between N,N-Dimethylaniline and Perfluoro-bicyclobutylidene

A mixture containing N,N-Dimethylaniline (0.5g, 4.1mmol) and perfluorobicyclobutylidene (62)(1.1g, 3.4mmol) was stirred at room temperature overnight in acetonitrile (5ml). Water (15ml) was added to the mixture to precipitate the solid product which was collected by filtration. Recrystallisation from aqueous ethanol and vacuum sublimation yielded Spiro[hexafluorocyclobutane-3,1'-1,2-tetrafluoroethano-1-fluoro-3-(4''-N,N-dimethylaminophenyl)-propene] (63) (1.05g, 73%) as white needles; m.p. 84-85°C; (Found: C, 45.0; H, 2.3; N, 3.2. $C_{16}H_{10}NF_{11}$ requires C, 45.2; H, 2.3; N, 3.3%). n.m.r. spectrum 17; i.r. spectrum 19; mass spectrum 19.

8.8 Reaction of N-methylindole with Perfluorobicyclobutylidene (62)

A mixture containing N-methylindole (0.4g, 3mmol) and perfluoro-bicyclobutylidene (62)(1.0g, 3mmol) was refluxed in acetonitrile (5ml) for 1 hr. On cooling, water (15ml) was added to the reaction mixture to precipitate the solid product which was collected by filtration, dried and purified by vacuum sublimation (oil bath temperature 100°C, <0.1mm Hg) to white crystals and identified as Spiro[hexafluorocyclobutane-3,1'-1,2-tetrafluoroethano-1-fluoro-3-(N-methyl-indol-3''-yl)-propene] (65)(0.60g, 46%); m.p. 59-60°C; (Found: C, 47.25; H,

1.8; N, 3.1. $C_{17}H_8NF_{11}$ requires C, 46.9; H, 1.85; N, 3.2%). n.m.r. spectrum 18; i.r. spectrum 20; mass spectrum 20.

8.9 Reaction between 1,8-Bis(dimethylamino)naphthalene and Perfluoro-bicyclobutylidene

A mixture containing 1,8-bis(dimethylamino)naphthalene (1.16g, 5.4mmol) and perfluorobicyclobutylidene (62)(1.56g, 4.8mmol) was stirred overnight at room temperature in acetonitrile (5ml). An orange solid precipitated which was collected by filtration and washed with water. Recrystallisation from aqueous acetonitrile yielded a white solid which was identified as the substitution product (66) (0.83g, 35%); m.p. 210-215°C (decomp); (Found: C, 53.2; H, 3.6; N, 5.6; F, 29.7. $C_{22}H_{18}N_2F_8O_2$ requires C, 53.4; H, 3.6; N, 5.6; F, 30.7%). n.m.r. spectrum 19; i.r. spectrum 21.

CHAPTER NINE

EXPERIMENTAL TO CHAPTER FIVE

9.1 Preparation of Trifluoro-s-triazine (13)

An autoclave (460ml, No. 14) was charged with trichloro-s-triazine (37g, 0.2mol) and flame dried potassium fluoride (125g, 2mol), evacuated and then heated at 310°C for 16hrs (Furnace No. 3). The volatile products were transferred from the hot autoclave to a trap which was cooled in liquid air. The product, trifluoro-s-triazine (13)(20g, 74%) did not require any further purification and was stored in a rotaflo tube.

9.2 Preparation of Perfluoroisopropyl-s-triazine (14) and Perfluorodiisopropyl-s-triazine (15)

A flask was charged with trifluoro-s-triazine (13)(15.0g, 0.11mol), potassium fluoride (5.0g, 86mmol) and dry sulpholane (100ml). The flask was frozen down in liquid air and evacuated. Hexafluoropropene (17g, 0.11mol) was added via a bladder and the reaction mixture was heated at 70°C for 16hrs with vigourous stirring. All volatile products were removed by transfer under vacuum and then distilled on the Fischer Spahltrohr to yield perfluoroisopropyl-s-triazine (14)(5.8g, 18%); b.p. 105-106°C; m/z (EI^+) 285 (M^+, 43%) and perfluorodi-isopropyl-s-triazine (15)(4.9g, 10%); b.p. 133.7-135.2°C; m/z (EI^+) 435 (M^+, 24.5%); as compared to the literature data[126].

9.3 Reactions of Pyrroles with Fluorinated Triazines

General Procedure - A mixture containing a pyrrole and the corresponding fluorinated triazine was refluxed in acetonitrile (5ml) for two hours. On cooling, water (15ml) was added to the reaction mixture to precipitate the solid product, which was collected by filtration, dried in a desiccator and purified by vacuum sublimation (Oil bath temperature 130°C, <0.1mm Hg). All yields are quoted for pure, isolated products.

9.3.1 Reaction of Pyrrole with perfluoro-s-triazine (13)

Pyrrole (0.5g, 7.4mmol) and perfluoro-s-triazine (13)(1.0g, 7.4mmol) gave 2-(pyrrol-2-yl)-4,6-difluoro-s-triazine (67)(0.87g, 65%) as white crystals; m.p. 156-160°C; (Found: C, 46.0; H, 2.1; N, 30.8. $C_7H_4N_4F_2$ requires C,

46.15; H, 2.2; N, 30.75%); λ_{max} (CH_3CN) 310.1nm ($\log_{10}\varepsilon$ 4.48); n.m.r. spectrum 20; i.r. spectrum 22; mass spectrum 21.

9.3.2 Reaction of Pyrrole with perfluoroisopropyl-s-triazine (14)

Pyrrole (0.80g, 12mmol) and perfluoroisopropyl-s-triazine (14)(2.5g, 9mmol) gave 2-(pyrrol-2-yl)-4-perfluoroisopropyl-6-fluoro-s-triazine (68)(2.05g, 71%) as pale yellow needles; m.p. 112-115°C; (Found: C, 35.7; H, 1.2; N, 16.5; $C_{10}H_4N_4F_8$ requires C, 36.1; H, 1.2; N, 16.85%); λ_{max} (CH_3CN) 336.0nm ($\log_{10}\varepsilon$ 4.41). n.m.r. spectrum 21; i.r. spectrum 23; mass spectrum 22.

9.3.3 Reaction of Pyrrole with Perfluorodi-isopropyl-s-triazine (15)

Pyrrole (0.27g, 4.0mmol) and perfluorodi-isopropyl-s-triazine (15)(1.46g, 3.3mmol) gave 2-(pyrrol-2-yl)-4,6-perfluorodi-isopropyl-s-triazine (69)(1.1g, 68%) as pale yellow needles; m.p. 64-66°C; (Found: C, 32.2; H, 0.75; N, 11.5. $C_{13}H_4N_4F_{14}$ requires C, 32.4; H, 0.8; N, 11.6%); λ_{max} (CH_3CN) 344.8nm ($\log_{10}\varepsilon$ 4.58). n.m.r. spectrum 22; i.r. spectrum 24; mass spectrum 23.

9.3.4 Reaction of N-methylpyrrole with perfluoro-s-triazine (13)

N-methylpyrrole (1.0g, 12mmol) and perfluoro-s-triazine (13)(1.6g, 12mmol) gave 2-(N-methylpyrrol-2-yl)-4,6-difluoro-s-triazine (70)(1.06g, 45%) as pale yellow needles; m.p. 117-118°C; (Found: C, 48.5; H, 3.0; N, 28.4. $C_8H_6N_4F_2$ requires C, 49.0; H, 3.1; N, 28.6%); λ_{max} (CH_3CN) 314.6nm ($\log_{10}\varepsilon$ 4.44) n.m.r. spectrum 23; i.r. spectrum 25; mass spectrum 24.

9.3.5 Reaction of N-methylpyrrole with perfluoroisopropyl-s-triazine (14)

N-methylpyrrole (0.30g, 3.7mmol) and perfluoroisopropyl-s-triazine (14)(1.05g, 3.7mmol) gave 2-(N-methylpyrrol-2-yl)-4-perfluoroisopropyl-6-fluoro-s-triazine (71)(0.69g, 54%) as pale yellow needles; m.p. 110-111°C; (Found: C, 38.2; H, 1.5; N, 15.9; F, 43.4. $C_{11}H_6N_4F_8$ requires C, 38.15; H, 1.7; N, 16.2; F, 43.95%); λ_{max} (CH_3CN) 324.5nm ($\log_{10}\varepsilon$ 4.38). n.m.r. spectrum 24; i.r. spectrum 26; mass spectrum 25.

9.3.6 Reaction of N-methylpyrrole with Perfluorodi-isopropyl-s-triazine (15)

N-methylpyrrole (0.3g, 3.7mmol) and perfluorodi-isopropyl-s-triazine (15)(1.5g, 3.5mol) gave 2-(N-methylpyrrol-2-yl)-4,6-perfluorodi-isopropyl-s-triazine (72)(0.73g, 48%) as pale yellow needles; m.p. 88-89°C; (Found: C, 33.9; H, 1.1; N, 11.3; F, 53.9. $C_{14}H_6N_4F_{14}$ requires C, 33.9; H, 1.2; N, 11.3; F, 53.6%); λ_{max} (CH_3CN) 349.4nm ($\log_{10}\varepsilon$ 4.33). n.m.r. spectrum 25; i.r. spectrum 27; mass spectrum 26.

9.4 Reactions of N-methylindole with Fluorinated Triazines

General Proceedure - A mixture containing N-methylindole and the corresponding fluorinated triazine was refluxed in acetonitrile (5ml) for 30mins. On cooling, water (15ml) was added to precipitate the solid product which was dried and purified by vacuum sublimation (Oil bath temperature 150°C, <0.1mm Hg).

9.4.1 Reaction of N-methylindole with perfluoro-s-triazine (13)

N-methylindole (1.0g,7.6mmol) and perfluoro-s-triazine (13)(1.0g, 7.4mmol) gave 2-(N-methylindol-3-yl)-4,6-difluoro-s-triazine (73)(1.43g, 78%) as white crystals (from acetone); m.p. 244°C; (Found: C, 58.25; H, 3.25; N, 22.6. $C_{12}H_8N_4F_2$ requires C, 58.5; H, 3.25; N, 22.75%). n.m.r. spectrum 26; i.r. spectrum 28; mass spectrum 27.

9.4.2 Reaction of N-methylindole with Perfluoroisopropyl-s-triazine (14)

N-methylindole (0.7g, 5.3mmol) and perfluoroisopropyl-s-triazine (14)(1.5g, 5.3mmol) gave 2-(N-methylindol-3-yl)-4-perfluoroisopropyl-6-fluoro-s-triazine (74)(1.76g, 90%) as pale yellow needles; m.p. 190-194°C; (Found: C, 45.7; H, 2.0; N, 14.2; F, 38.1. $C_{15}H_8N_4F_8$ requires C, 45.45; H, 2.0; N, 14.1; F, 38.4%); λ_{max} (CH_3CN) 262.4nm ($\log_{10}\varepsilon$ 4.12), 355.3 (4.31);. n.m.r. spectrum 27; i.r. spectrum 29; mass spectrum 28.

9.4.3 Reaction of N-methylindole with Perfluorodi-isopropyl-s-triazine (15)

N-methylindole (0.3g, 2.3mmol) and perfluorodi-isopropyl-s-triazine (15)(1.0g, 2.3mmol) gave 2-(N-methylindol-3-yl)-4,6-perfluorodi-isopropyl-

s-triazine (75)(1.1g, 87%) as yellow crystals; m.p. 205-206°C; (Found: C, 39.25; H, 1.45; N, 9.9; F, 48.9. $C_{18}H_8N_4F_{14}$ requires C, 39.55; H, 1.45; N, 10.25; F, 48.7%); λ_{max} (CH_3CN) 213.0nm ($\log_{10}\varepsilon$ 4.56), 246.0 (4.02), 265.0 (4.23), 276.0 (4.14), 365.0 (4.53);. n.m.r. spectrum 28; i.r. spectrum 30; mass spectrum 29.

9.5 Reaction of N-methylindole with Tetrafluoropyrimidine

A mixture containing N-methylindole (0.8g, 6mmol) and tetrafluoropyrimidine (1.0g, 6.5mmol) was refluxed overnight in acetonitrile (5ml). On cooling, water (15ml) was added to the reaction mixture to precipitate the solid product which was collected by filtration, dried, recrystallised from acetone as yellow plates and identified as 6-(N-methylindol-3-yl)-2,4,5-trifluoropyrimidine (76)(0.58g, 36%); m.p. 231°C; (Found: C, 59.35; H, 3.0; N, 15.9; F, 22.0. $C_{13}H_8N_3F_3$ requires C, 59.3; H, 3.05; N, 15.95; F, 21.7%); λ_{max} (CH_3CN) 214.0nm ($\log_{10}\varepsilon$ 4.75), 263.0 (4.35), 344.0 (4.78); i.r. spectrum 31; mass spectrum 30.

9.6 Reactions of Anilines With Fluorinated s-Triazines (13)-(15)

9.6.1 Reaction of N,N-Dimethylaniline with Trifluoro-s-triazine (13)

A mixture containing N,N-Dimethylaniline (1.75g, 14mmol) and trifluoro-s-triazine (13)(2.0g, 15mmol) was refluxed overnight in acetonitrile (5ml). On cooling a red/brown solid precipitated which was collected by filtration, washed with water and recrystallised from acetonitrile to yield pure 2-(4-N,N-dimethylaminophenyl)-4,6-difluoro-s-triazine (77)(0.96g, 28%); m.p. 234-237°C; (Found: C, 55.6; H, 4.05; N, 23.5. $C_{11}H_{10}N_4F_2$ requires C, 55.9; H, 4.25; N, 23.7%); λ_{max} (CH_3CN) 364.0nm ($\log_{10}\varepsilon$ 4.51); $C_{11}H_{10}N_4F_2$ requires 236.08735amu. Found 236.08416amu; n.m.r. spectrum 29; i.r. spectrum 32; mass spectrum 31.

9.6.2 Reaction of N,N-Dimethylaniline with Perfluoroisopropyl-s-triazine (14)

A mixture containing N,N-Dimethylaniline (0.5g, 4.1mmol) and perfluoroisopropyl-s-triazine (1.2g, 4.2mmol) was refluxed in acetonitrile (5ml) for 2 hr. On cooling, water (15ml) was added to precipitate the solid product which was collected by filtration and dried. Vacuum sublimation yielded pure 2-(4-N,N-dimethylaminophenyl)-4-perfluoroisopropyl-6-fluoro-s-triazine (78)(0.62g,

36%) as a yellow solid; m.p. 168-170°C; (Found: C, 42.8; H, 2.5; N, 14.2. $C_{14}H_{10}N_4F_8$ requires C, 43.5; H, 2.6; N, 14.5%); λ_{max} (CH_3CN) 368.8nm ($\log_{10}\varepsilon$ 4.40). n.m.r. spectrum 30; i.r. spectrum 33; mass spectrum 32.

9.6.3 Reaction of N,N-Diethylaniline with Perfluoroisopropyl-s-triazine (14)

A mixture containing N,N-Diethylaniline (0.5g, 3.4mmol) and perfluoroisopropyl-s-triazine (14)(1.0g, 3.5mmol) was refluxed in acetonitrile (5ml) for 2 hr. On cooling, water (15ml) was added to precipitate the solid product which was collected by filtration and dried. Vacuum sublimation yielded a mixture of the two isomers 2-(4-N,N-diethylaminophenyl)-4-perfluoroisopropyl-6-fluoro-s-triazine (79A) and 2-(2-N,N-diethylaminophenyl)-4-perfluoroisopropyl-6-fluoro-s-triazine (79B)(0.63g, 45%) as a yellow solid; (Found: C, 46.0; H, 3.5; N, 13.6. $C_{16}H_{14}N_4F_8$ requires C, 46.35; H, 3.4; N, 13.5%); λ_{max} (CH_3CN) 228.0nm ($\log_{10}\varepsilon$ 3.86), 260.9 (3.93), 405.3 (4.39). n.m.r. spectrum 32; i.r. spectrum 35; mass spectrum 34.

9.6.4 Reaction of N,N-Dimethylaniline with Perfluorodi-isopropyl-s-triazine (15)

A mixture containing N,N-Dimethylaniline (0.5g, 4.1mmol) and perfluorodi-isopropyl-s-triazine (15)(1.5g, 3.4mmol) was refluxed in acetonitrile (5ml) for 3 hr. On cooling, water (15ml) was added to the reaction mixture to precipitate the solid product which was collected by filtration and dried. Vacuum sublimation yielded a mixture of the two isomers 2-(4-N,N-dimethylaminophenyl)-4,6-perfluorodiisopropyl-s-triazine (81A) and 2-(2-N,N-dimethylaminophenyl)-4,6-perfluorodiisopropyl-s-triazine (81B)(0.95g, 77%) as a yellow solid; (Found: C, 37.9; H, 2.0; N, 10.3. $C_{17}H_{10}N_4F_{14}$ requires C, 38.05; H, 1.85; N, 10.45%); λ_{max} (CH_3CN) 412.0nm ($\log_{10}\varepsilon$ 4.28); n.m.r. spectrum 31; i.r. spectrum 34; mass spectrum 33.

9.6.5 Reaction of N,N-Diethylaniline with Perfluorodi-isopropyl-s-triazine (15)

A mixture containing N,N-Diethylaniline (0.6g, 4mmol) and perfluorodi-isopropyl-s-triazine (15)(1.0g, 2.3mmol) was refluxed in acetonitrile (5ml) for 2 hr. On cooling, water (15ml) was added to the reaction mixture to precipitate an orange oil which solidified on standing. This solid was washed repeatedly with water and analysis confirmed the solid to be a mixture of the two isomers 2-(4-N,N-

diethylaminophenyl)-4,6-perfluorodiisopropyl-s-triazine (82A) and 2-(2-N,N-diethylaminophenyl)-4,6-perfluorodiisopropyl-s-triazine (82B)(0.93g, 72%); (Found: C, 40.3; H, 2.7; N, 9.6. $C_{19}H_{14}N_4F_{14}$ requires C, 40.4; H, 2.5; N, 9.9%); λ_{max} (CH_3CN) 419.6nm ($log_{10}\varepsilon$ 4.47); n.m.r. spectrum 33; i.r. spectrum 36; mass spectrum 35.

9.6.6 Reaction between 1,8-(Bisdimethylamino)-naphthalene and Trifluoro-s-triazine (13)

A mixture containing 1,8-(bisdimethylamino)-naphthalene (2.1g, 10mmol) and trifluoro-s-triazine (13)(1.5g, 11mmol) was stirred at room temperature overnight in acetonitrile (5ml). The solution turned orange immediately and gradually red crystals precipitated which were collected by filtration and recrystallised from acetonitrile to yield pure 1,8-(bisdimethylamino)-4,5-(bisdifluoro-s-triaz-1-yl)-naphthalene (83)(2.3g, 53%); m.p. 258-260°C; (Found: C, 53.7; H, 3.6; N, 24.9. $C_{20}H_{16}N_8F_4$ requires C, 54.0; H, 3.6; N, 25.2%). $C_{20}H_{16}N_8F_4$ requires 444.1434amu. Found 444.1272amu; n.m.r. spectrum 34; i.r. spectrum 37; mass spectrum 36.

9.6.7 Reaction of N-ethylaniline with Trifluoro-s-triazine (13)

A mixture containing N-ethylaniline (0.9g, 7.4mmol) and trifluoro-s-triazine (13)(1.0g, 7.4mmol) was refluxed in acetonitrile (5ml) for 3 hr. The solvent was removed under reduced pressure to leave an off-white solid which was washed with water and collected by filtration. Vacuum sublimation yielded pure 2-(ethylphenylamino)-4,6-difluoro-s-triazine (84)(1.2g, 69%) as white needles; m.p. 63.5-64°C; (Found: C, 55.6; H, 4.0; N, 24.0. $C_{11}H_{10}N_4F_2$ requires C, 55.9; H, 4.2; N, 23.7%); λ_{max} (CH_3CN) 236.0nm ($log_{10}\varepsilon$ 4.26). n.m.r. spectrum 35; i.r. spectrum 38; mass spectrum 37.

9.6.8 Reaction of N-ethylaniline with Perfluoroisopropyl-s-triazine (14)

A mixture containing N-ethylaniline (0.63g, 5.2mmol) and perfluoroisopropyl-s-triazine (14)(1.5g, 5.2mmol) was refluxed overnight in acetonitrile (5ml). The solvent was removed under reduced pressure to leave an off-white solid which was washed with water and collected by filtration. Vacuum sublimation yielded pure 2-(ethylphenylamino)-4-perfluoroisopropyl-s-triazine (80)(1.8g, 89%) as white crystals; m.p. 70-72°C; (Found: C, 43.8; H, 2.65; N, 14.8; F, 40.0. $C_{14}H_{10}N_4F_8$ requires C, 43.5; H, 2.6; N, 14.5; F, 39.4%); λ_{max}

(CH_3CN) 239.0nm ($log_{10}\varepsilon$ 4.30);. n.m.r. spectrum 36; i.r. spectrum 39; mass spectrum 38.

9.6.9 Preparation of N,N-Dimethylamino-2-methoxybenzene

A flask was charged with 2-methoxyaniline (20g, 0.16mol) and trimethylphosphite (22g, 0.16mol). The mixture was heated until a fine mist appeared after which the heat source was removed and the reaction allowed to subside. The reaction was then heated at reflux for a further 2 hrs. After cooling to 90°C, sodium hydroxide solution (22g in 170ml water) was added and the aqueous mixture was left to stand for 1.5hrs. The amines were extracted with ether and distilled on the Fischer Spahltrohr to yield N,N-Dimethylamino-2-methoxybenzene (13.0g, 54%); pure by GC; b.p. 81.7-82°C/5mm Hg; IR spectrum recorded; m/z (EI^+) 151 (M^+, 100%).

9.6.10 Reaction of N,N-Dimethylamino-2-methoxybenzene with Trifluoro-s-triazine (13)

A mixture containing N,N-Dimethylamino-2-methoxybenzene (1.0g, 6.6mmol) and trifluoro-s-triazine (13)(1.2g, 8.8mmol) was refluxed overnight in acetonitrile (5ml). Water (15ml) was added to the mixture to precipitate the solid product which was collected by filtration. Vacuum sublimation yielded pure 2-methyl(2-methoxyphenyl)-amino-4,6-difluoro-s-triazine (85)(0.51g, 31%) as white crystals; m.p. 139°C; (Found: C, 52.25; H, 3.85; N, 22.35. $C_{11}H_{10}N_4OF_2$ requires C, 52.4; H, 3.95; N, 22.2%). n.m.r. spectrum 37; i.r. spectrum 40; mass spectrum 39.

9.6.11 Reaction of N,N,N',N'-tetramethyl-1,4-diaminobenzene with trifluoro-s-triazine (13)

A mixture containing N,N,N',N'-tetramethyl-1,4-diaminobenzene (0.6g, 3.6mmol) and trifluoro-s-triazine (13)(0.4g, 3.0mmol) was refluxed overnight in acetonitrile (5ml). Water was added to the mixture to precipitate the solid product which was collected by filtration. Vacuum sublimation yielded pure 2-methyl(4-N,N-dimethylaminophenyl)amino-4,6-difluoro-s-triazine (86) (0.12g, 15%) as white crystals; (Found: C, 54.5; H, 5.1; N, 26.7. $C_{12}H_{13}N_5F_2$ requires C, 54.3; H, 4.9; N, 26.4%). n.m.r. spectrum 38; i.r. spectrum 41; mass spectrum 40.

9.6.12 Reaction between 2-N,N-dimethylamino-pyridine and Perfluorodi-isopropyl-s-triazine (15)

A mixture containing 2-N,N-dimethylaminopyridine (0.5g, 3.5mmol) and perfluorodi-isopropyl-s-triazine (1.5g, 3.4mmol) was refluxed in acetonitrile (5ml) for 6 hr. On cooling, water (15ml) was added to precipitate the solid product which was collected by filtration. Vacuum sublimation yielded the pyridinium salt (87)(0.9g, 47%) as a pale yellow solid; (Found: C, 34.65; H, 1.7; N, 12.8. $C_{16}H_{11}N_5OF_{14}$ requires C, 34.6; H, 2.0; N, 12.6%). n.m.r. spectrum 39; i.r. spectrum 42; mass spectrum 41.

APPENDICES

APPENDIX ONE

NUCLEAR MAGNETIC RESONANCE SPECTRA

1. 1,8-(Bisdimethylamino)-naphthalene Hydrogen Fluoride Complex (PS/HF) (1)
2. Triethylamine Hydrogen Fluoride Complex (24)
3. Tributylamine Hydrogen Fluoride Complex (25)
4. Trihexylamine Hydrogen Fluoride Complex (26)
5. Trioctylamine Hydrogen Fluoride Complex (27)
6. Tridodecylamine Hydrogen Fluoride Complex (28)
7. 2,2,6,6-Tetramethylpiperidine Hydrogen Fluoride Complex (35)
8. N-Methyl-2,2,6,6-Tetramethylpiperidine Hydrogen Fluoride Complex (36)
9. N-Ethyl-2,2,6,6-Tetramethylpiperidine Hydrogen Fluoride Complex (37)
10. N-Allyl-2,2,6,6-Tetramethylpiperidine Hydrogen Fluoride Complex (38)
11. N-Benzyl-2,2,6,6-Tetramethylpiperidine Hydrogen Fluoride Complex (39)
12. Tetramethylguanidine Hydrogen Fluoride Complex (40)
13. 1,1-Bistrifluoromethyl-6,7-bisdimethylamino-2,3-tetrafluoro-ethano-[1H]-phenalene (4)
14. Spiro[octafluorocyclopentane-1,1'-(6,7-bisdimethylamino)-2',3'-tetrafluoroethano-[1H]-phenalene] (44)
15. Spiro[octafluorocyclopentane-1,1'-(6,7-bisdimethylamino)-2',3'-tetrafluoro-propan-1''-one-[1H]-phenalene] (60)
16. 7,8-propano-9,10-propan-1''-one-cyclohepta-[*d,e*]-naphthalene (61)
17. Spiro[hexafluorocyclobutane-3,1'-1,2-tetrafluoroethano-1-fluoro-3-(4''-N,N-dimethylaminophenyl)-propene] (63)
18. Spiro[hexafluorocyclobutane-3,1'-1,2-tetrafluoroethano-1-fluoro-3-(N-methylindol-3''-yl)-propene] (65)
19. White Solid (66)
20. 2-(pyrrol-2-yl)-4,6-difluoro-s-triazine (67)
21. 2-(pyrrol-2-yl)-4-perfluoroisopropyl-6-fluoro-s-triazine (68)
22. 2-(pyrrol-2-yl)-4,6-perfluorodi-isopropyl-s-triazine (69)
23. 2-(N-methylpyrrol-2-yl)-4,6-difluoro-s-triazine (70)
24. 2-(N-methylpyrrol-2-yl)-4-perfluoroisopropyl-6-fluoro-s-triazine (71)
25. 2-(N-methylpyrrol-2-yl)-4,6-perfluorodi-isopropyl-s-triazine (72)
26. 2-(N-methylindol-3-yl)-4,6-difluoro-s-triazine (73)
27. 2-(N-methylindol-3-yl)-4-perfluoroisopropyl-6-fluoro-s-triazine (74)
28. 2-(N-methylindol-3-yl)-4,6-perfluorodi-isopropyl-s-triazine (75)
29. 2-(4-N,N-dimethylaminophenyl)-4,6-difluoro-s-triazine (77)
30. 2-(4-N,N-dimethylaminophenyl)-4-perfluoroisopropyl-6-fluoro-s-triazine (78)

31. 2-(4-N,N-dimethylaminophenyl)-4,6-perfluorodi-isopropyl-s-triazine (81A) and 2-(2-N,N-dimethylaminophenyl)-4,6-perfluorodi-isopropyl-s-triazine (81B)
32. 2-(4-N,N-diethylaminophenyl)-4-perfluoroisopropyl-6-fluoro-s-triazine (79A) and 2-(2-N,N-diethylaminophenyl)-4-perfluoroisopropyl-6-fluoro-s-triazine (79B)
33. 2-(4-N,N-diethylaminophenyl)-4,6-perfluorodi-isopropyl-s-triazine (82A) and 2-(2-N,N-diethylaminophenyl)-4,6-perfluorodi-isopropyl-s-triazine (82B)
34 1,8-(Bisdimethylamino)-4,5-(bisdifluoro-s-triaz-2-yl)-naphthalene (83)
35. 2-(ethylphenylamino)-4,6-difluoro-s-triazine (84)
36. 2-(ethylphenylamino)-4-perfluoroisopropyl-6-fluoro-s-triazine (80)
37. 2-methyl-(2-methoxyphenyl)-amino-4,6-difluoro-s-triazine (85)
38. 2-methyl-(4-N,N-dimethylaminophenyl)-amino-4,6-difluoro-s-triazine (86)
39. Pyridinium Salt (87)

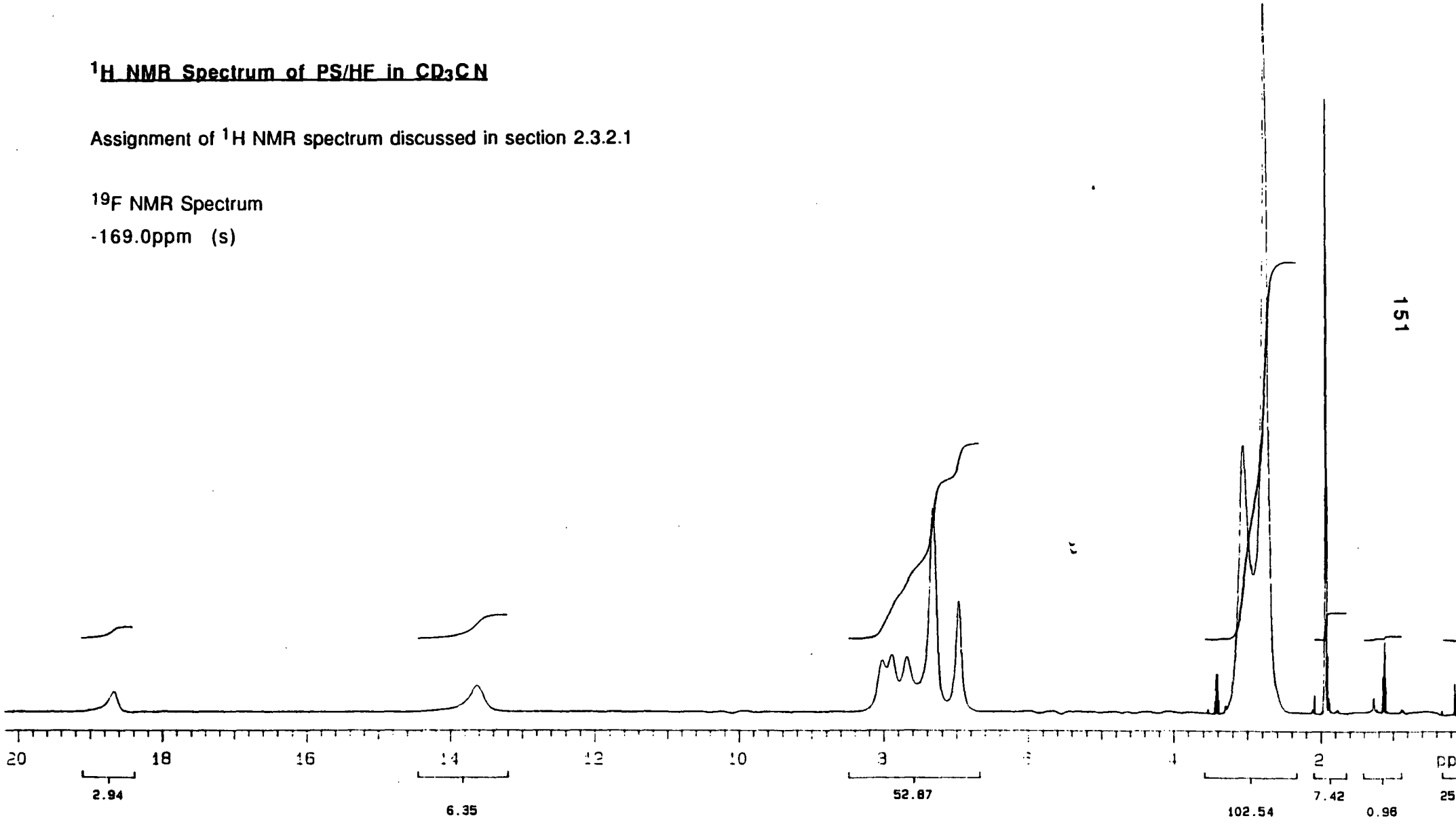
NMR spectra were recorded in d_3-acetonitrile solutions unless otherwise stated. Reference compounds (^1H and ^{13}C - Me_4Si, ^{19}F - $CFCl_3$) were used internally.

^{1}H NMR Spectrum of PS/HF in CD_3CN

Assignment of ^{1}H NMR spectrum discussed in section 2.3.2.1

^{19}F NMR Spectrum

-169.0ppm (s)



No. 2 Triethylamine HF Complex

a b c d
$(CH_3CH_2)_3N \cdot HF$

Chemical Shift (ppm)	Multiplicity Coupling Constants (Hz)	Relative Intensity	Assignment
^1H			
1.21	t $J_{a,b}$=7.3	9H	a
2.96	q	6H	b
12.68	s (br)	1H	c
^{19}F			
-154.81	s		d

No. 3 Tri-n-butylamine HF Complex

a b c d e f
$(CH_3CH_2CH_2CH_2)_3N \cdot HF$

Chemical Shift (ppm)	Multiplicity Coupling Constants (Hz)	Relative Intensity	Assignment
^1H			
1.07	m	9H	a
1.51	m	6H	b
1.78	m	6H	c
3.04	m	6H	d
12.67	s (br)	1H	e
^{19}F			
-157.09	s		f

No. 4 Tri-n-hexylamine HF Complex

a b c d e f g h
$(CH_3CH_2CH_2CH_2CH_2CH_2)_3N \cdot HF$

Chemical Shift (ppm)	Multiplicity Coupling Constants (Hz)	Relative Intensity	Assignment
^1H			
0.99	t $J_{a,b}$=6.6	9H	a
1.41	m	18H	b, c, d
1.69	m	6H	e
2.87	t $J_{e,f}$=7.0	6H	f
12.50	s (br)	1H	g
^{19}F			
-157.04	s		h

No. 5 Tri-n-octylamine HF Complex

a b c d e f g h i j
$(CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2)_3N \cdot HF$

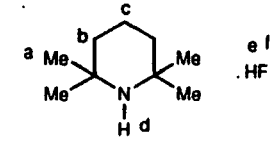
Chemical Shift (ppm)	Multiplicity Coupling Constants (Hz)	Relative Intensity	Assignment
^1H			
1.07	t $J_{a,b}$=6.1	9H	a
1.49-1.78	m	36H	b, c, d, e, f, g
2.96	m	6H	h
10.76	s (br)	1H	i
^{19}F			
-156.6	s		j

No. 6 Tri-n-dodecamine HF Complex

$(CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2)_3\overset{a\ b}{N}\cdot HF$

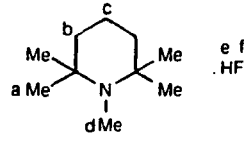
Chemical Shift (ppm)	Multiplicity / Coupling Constants (Hz)	Relative Intensity	Assignment
^1H			
0.4-2.90	m (overlapping peaks)		CH_3, CH_2
11.61	s (br)		a
^{19}F			
-159.30	s		b

No. 7 2,2,6,6-Tetramethylpiperidine Hydrogen Fluoride Complex



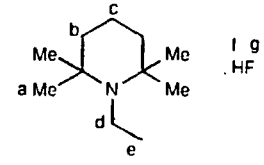
Chemical Shift (ppm)	Multiplicity / Coupling Constants (Hz)	Relative Intensity	Assignment
^1H			
1.21	s	12H	a
1.52	m	4H	b
1.66	m	2H	c
4.90	s (br)	1H	d
9.30	s (br)	1H	e
^{19}F			
-134.96	s (br)		f

No. 8 1,2,2,6,6-Pentamethylpiperidine HF Complex



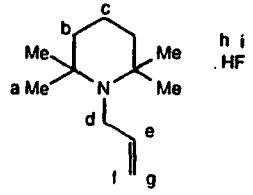
Chemical Shift (ppm)	Multiplicity Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H			
1.27	s	12H	a
1.68	m	6H	b, c
2.48	s	3H	d
12.74	s (br)	1H	e
^{19}F			
-148.9	s (br)		f

No. 9 N-Ethyl-2,2,6,6-Tetramethylpiperidine HF Complex



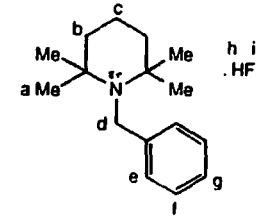
Chemical Shift (ppm)	Multiplicity Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H			
1.32	s	12H	a
1.32	t $J_{d,e}=7.4$	3H	e
1.71	m	2H	c
1.81	m	4H	b
3.00	q	2H	d
11.10	s (br)	1H	f
^{19}F			
-143.9	s (br)		g

No. 10 N-Allyl-2,2,6,6-Tetramethylpiperidine HF Complex



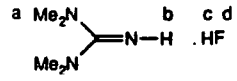
Chemical Shift (ppm)	Multiplicity / Coupling Constants (Hz)		Relative Intensity	Assignment
^{1}H				
1.32	s		12H	a
1.68	m		2H	c
1.73	m		4H	b
3.62	d	$J_{d,\ e}$=6.0	2H	d
5.26	dd	$J_{e,\ f}$=17.0	2H	f, g
6.11	ddt	$J_{e,\ g}$=10.0	1H	e
12.1	s (br)		1H	h
^{19}F				
-146.0				i

No. 11 N-Benzyl-2,2,6,6-Tetramethylpiperidine HF Complex



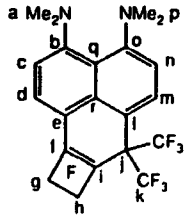
Chemical Shift (ppm)	Multiplicity / Coupling Constants (Hz)		Relative Intensity	Assignment
^{1}H				
1.23	s		12H	a
1.71	m		6H	b, c
4.11	s		2H	d
7.25	t	$J_{f,\ g}$=7.3	1H	g
7.30	t	$J_{e,\ f}$=7.6	2H	f
7.54	d		2H	e
11.7	s (br)		1H	h
^{19}F				
-152.4	s (br)			

No. 12 Tetramethylguanidine Hydrogen Fluoride Complex



Chemical Shift (ppm)	Multiplicity Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H			
2.71	s	12H	a
3.63	s	1H	b
8.63	s (br)	1H	c
^{19}F			
-142.97			d

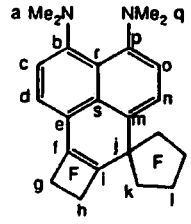
No. 13 **1,1-Bistrifluoromethyl-6,7-bisdimethylamino-2,3-tetrafluoro-ethano-[1H]-phenalene**



Chemical Shift (ppm)	Multiplicity / Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H			
2.81	s	6H	a
2.88	s	6H	p
6.79	AX J_{AX}=8.3	1H	c
7.45	AX J_{AX}=8.3	1H	d
6.98	AX J_{AX}=8.8	1H	n
7.85	AX J_{AX}=8.8	1H	m
^{19}F			
-67.23	s	6F	k
-105.10	s	2F	g
-112.55	s	2F	h
^{13}C			
43.5	s (br)		a, p
107.7	s		l
108.9	s		c
111.5	s		n
115-120	many overlapping peaks		CF_2 and CF_3 g,h,k
116.7	s		e
121.4	s		q
123.7	s		f
126.0	s		i
126.9	s		d
130.4	s		m
134.1	s		r
152.9	s		b
153.0	m		j
156.1	s		o

The complexity of the ^{13}C spectrum prevents a full assignment, especially for peaks in the region of 115-125ppm.

No. 14 Spiro[octafluorocyclopentane-1,1'-(6,7-bisdimethylamino)-2',3'-tetrafluoroethano -[1H]-phenalene]

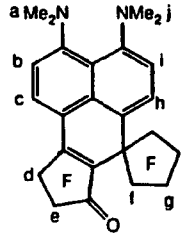


Chemical Shift (ppm)	Multiplicity / Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H			
2.88	s	6H	a
2.94	s	6H	q
6.86	AX, J_{AX} = 8.4	1H	c
7.33		1H	d
7.04	AX, J_{AX} = 8.8	1H	o
7.52		1H	n
^{19}F			
-104.9	s	2F	g
-112.8	AB, J_{AB} = 249.1	4F	k
-116.0			
-114.6	s	2F	h
-135.2	s	4F	l

^{19}F 2-D COSY spectrum also recorded.

^{13}C		
43.0	s (br)	a, q
105.6	s	
107.4		
109.4	s	c
111.4	s	o
115.4	s	r
115-120	many overlapping peaks	g, h, k, l
128.6	s	d
134.0	s	s
135.8	s	n
151.9	m	j
154.4	s	b
158.2	s	p

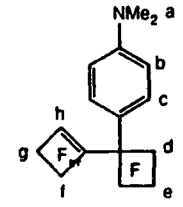
No. 15 Spiro[octafluorocyclopentane-1,1'-(6,7-bisdimethylamino)-2',3'-tetrafluoropropan-2''-one-[1H]-phenalene]



Chemical Shift (ppm)	Multiplicity / Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H			
2.16	s	12H	a, j
6.95	AX, J_{AX} = 8.8	1H	b
7.25	AX, J_{AX} = 8.8	1H	c
7.05	AX, J_{AX} = 8.8	1H	i
7.92	AX, J_{AX} = 8.8	1H	j
^{19}F			
-111.0	AB, J_{AB} = 246.7	4F	f
-113.4	AB, J_{AB} = 246.7	4F	f
-117.8	s (pseudo AB)	2F	d
-131.4	s (pseudo AB)	2F	e
-132.3	s (pseudo AB)	4F	g

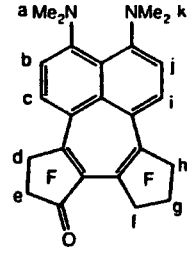
^{19}F 2-D COSY spectrum also recorded.

No. 17 Spiro-[hexafluorocyclobutane-3,1'-1,2-tetrafluoroethano-1-fluoro-3-(4''-N,N-Dimethylaminophenyl)-propene



Chemical Shift (ppm)	Multiplicity / Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H			
2.96	s	6H	a
6.76	AB, J_{AB}=8.7	2H	b
7.16	AB, J_{AB}=8.7	2H	c
^{19}F			
-101.22	s	1F	h
-114.04	s	2F	f
-119.04	s	2F	g
-117.05	AB, J_{AB}=214	4F	d
-120.93	AB, J_{AB}=214	4F	d
-127.99	AB, J_{AB}=222	2F	e
-133.89	AB, J_{AB}=222	2F	e

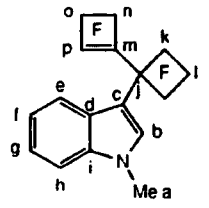
No. 16 7.8-Propano-9.10-propan-2''-one-cyclo-hepta-[*d.e*]-naphthalene



Chemical Shift (ppm)	Multiplicity / Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H			
2.16	s	12H	a, k
6.49	AX J_{AX} = 8.8	1H	j
6.92		1H	i
6.51	AX J_{AX} = 8.8	1H	b
7.33		1H	c
^{19}F			
-106.5	AB J_{AB} = 278	2F	d
-128.8			
-109.3	AB J_{AB} = 262	2F	h
-133.1			
-119.4	AB J_{AB} = 260	2F	f
-128.0			
-128.8	AB J_{AB} = 283	2F	e
-136.0			
-133.4	AB J_{AB} = 240	2F	g
-143.4			

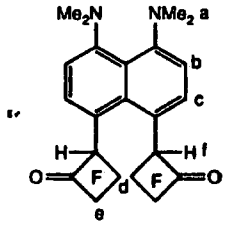
^{19}F 2-D COSY spectrum also recorded. The midpoints of the AB systems are -117.6, -121.2, -123.7, -132.4 and -138.8ppm.

No. 18 Spiro-(hexafluorocyclobutane-3,1'-1,2-tetrafluoroethano-1-fluoro-3-(N-Methylindol-3-yl)-propene



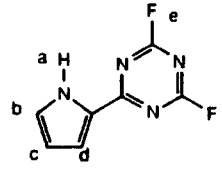
Chemical Shift (ppm)	Multiplicity	Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H				
3.85	s		3H	a
7.20	t	7.6	1H	f or g
7.33	t	7.6	1H	f or g
7.39	d	8.0	1H	h
7.51	d	8.3	1H	e
7.56	s (br)		1H	b
^{19}F				
-100.63	s		1F	p
-114.70	s		2F	n
-119.30	s		2F	o
-117.22 / -120.45	AB	J_{AB}=215	4F	k
-128.22 / -130.37	AB	J_{AB}=221	2F	l

No. 19 White Solid (*)



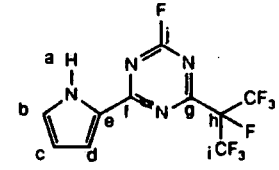
Chemical Shift (ppm)	Multiplicity	Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H				
2.19	s		2H	f
3.12	s		12H	a
7.82-8.40			4H	b, c
^{19}F				
-120.14	s		4F	e
-130.40 / -133.89	AB	J_{AB}=215	4F	d

No. 20 2-(pyrrol-2-yl)-4,6-difluoro-s-triazine



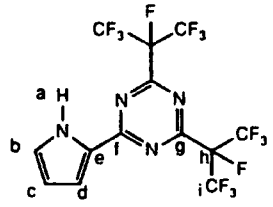
Chemical Shift (ppm)	Multiplicity	Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H				
6.40	dd	$J_{c,d}$=4.0	1H	c
7.23	m	$J_{b,c}$=2.3	1H	b
7.34	dd	$J_{b,d}$=1.6	1H	d
10.30	s (broad)		1H	a
^{19}F				
-39.68	s			e

No. 21 2-(pyrrol-2-yl)-4-fluoro-6-perfluoroisopropyl-s-triazine



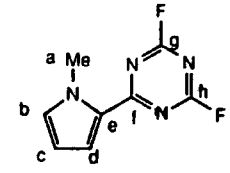
Chemical Shift (ppm)	Multiplicity	Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H				
6.43	m	$J_{c,d}$=4.0	1H	c
7.27	m	$J_{b,c}$=2.4	1H	b
7.40	m	$J_{b,d}$=1.2	1H	d
10.62	s (br)		1H	a
^{19}F				
-39.68	s		1F	j
-74.43	s		6F	i
-184.47	s		1F	h
^{13}C				
90.9	d sept	211, 33		h
114.5	s			c
121.2	s			d
121.3	qd	288, 27		i
128.5	s			e
130.5	s			b
169.2	dd	22, 12		g
170.4	dd	13, 3		f
171.2	dd	229, 3		j

No. 22 2-(pyrrol-2-yl)-4,6-perfluorodi-isopropyl-s-triazine



Chemical Shift (ppm)	Multiplicity	Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H				
6.31	dd	$J_{c,d}$=3.5	1H	c
7.15	m	$J_{b,c}$=1.7	1H	b
7.29	dd	$J_{b,d}$=1.5	1H	d
9.50	s (br)		1H	a
^{19}F				
-74.42	s		6F	i
-184.72	s		1F	h
^{13}C				
90.4	d sept	211, 33		h
114.3	s			c
120.8	qd	288, 27		i
121.3	s			d
128.2	s			e
130.6	s			b
165.9	dd	22, 4		g
166.5	t	3		f

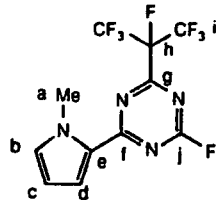
No. 23 2-(N-methylpyrrol-2-yl)-4,6-difluoro-s-triazine



Chemical Shift (ppm)	Multiplicity	Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H				
4.04	s		3H	a
6.27	dd	$J_{c,d}$=4.0	1H	c
7.15	m	$J_{b,c}$=2.4	1H	b
7.44	dd	$J_{b,d}$=1.8	1H	d
^{19}F				
-45.60	s (broad)			g,h
^{13}C				
39.21	s			a
111.09	s			c
123.34	s			d
128.0	s			e
136.13	s			b
172.03	dd	226, 19		g, h
172.35	t	14		f

For ^{13}C spectra, it is important to have the proton decoupler on during acquisition but off during delay. This prevents artificial nuclear overhouser enhancement of peaks with low relaxation times (e.g. non-substituted aromatic carbons), hence giving greater resolution for peaks with a longer relaxation time (e.g. C-F carbons). However, a much longer acquisition time is necessary.

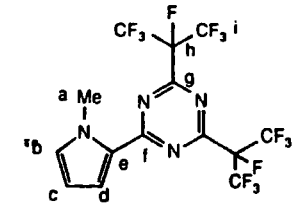
No. 24 2-(N-methylpyrrol-2-yl)-4-perfluoroisopropyl-6-fluoro-s-triazine



Chemical Shift (ppm)	Multiplicity	Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H				
4.12	s		3H	a
6.33	dd	$J_{c,d}$=4.2	1H	c
7.35	m	$J_{b,c}$=2.3	1H	b
7.52	dd	$J_{b,d}$=1.8	1H	d
^{19}F				
-38.4	s		1F	j
-74.2	s		6F	i
-184.3	s		1F	h
^{13}C				
39.28	s			a
90.28	d sept	211, 35		h
111.55	s			c
120.76	qd	288, 27		i
123.95	s			d
128.06	s			e
136.85	s			b
168.18	dd	21, 12		g
170.21	dd	13, 3		f
170.27	dd	228, 3		j

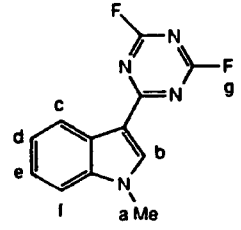
^{13}C acquisition time 17.5 hr

No. 25 2-(N-methylpyrrol-2-yl)-4,6-perfluorodi-isopropyl-s-triazine



Chemical Shift (ppm)	Multiplicity	Coupling Constants (Hz)	Relative Intensity	Assignment
Spectra recorded in d_6-acetone				
^{1}H				
4.07	s		3H	a
6.32	dd	$J_{c,d}$=4.2	1H	c
7.05	m	$J_{b,c}$=2.3	1H	b
7.66	dd	$J_{b,d}$=1.9	1H	d
^{19}F				
-74.96	s		6F	i
-185.19	s		1F	h
^{13}C				
39.09	s			a
90.21	d sept	218, 33		h
111.88	s			c
120.73	qd	288, 27		i
124.75	s			d
128.12	s			e
137.67	s			b
165.55	dd	22, 3		g
166.62	t	3		f

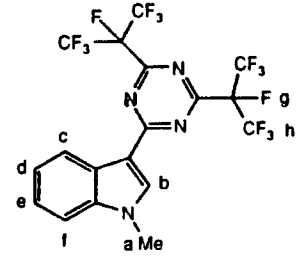
No. 26 2-(N-methylindol-3-yl)-4,6-difluoro-s-triazine



Chemical Shift (ppm)	Multiplicity Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H			
4.1	s	3H	a
7.4	m	2H	d, e
7.7	m	1H	f
8.6	m	1H	c
8.7	s	1H	b
^{19}F			
-40.2	s		g

Resolution of ^{1}H spectrum is poor due to the low solubility of the product

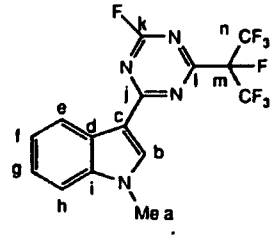
No. 28 2-(N-methylindol-3-yl)-4,6-perfluorodi-isopropyl-s-triazine



Chemical Shift (ppm)	Multiplicity Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H			
3.97	s	3H	a
7.43	m	2H	d, e
7.59	m	1H	f
8.44	m	1H	c
8.56	s	1H	b
^{19}F			
-74.17	s	6F	h
-184.44	s	1F	g

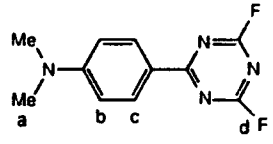
Resolution on ^{1}H spectrum poor due to the low solubility of the product

No. 27 2-(N-methylindol-3-yl)-4-perfluoroisopropyl-6-fluoro-s-triazine



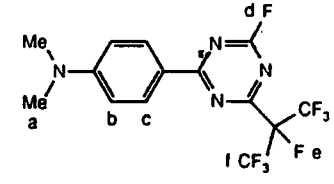
Chemical Shift (ppm)	Multiplicity	Coupling Constants (Hz)	Relative Intensity	Assignment
Spectra recorded in d_6-acetone				
^{1}H				
4.04	s		3H	a
7.36	m		2H	f, g
7.67	dd	$J_{g,h}$=6 $J_{f,h}$=2	1H	h
8.45	dd	$J_{e,f}$=6.5 $J_{e,g}$=3	1H	e
8.59	s		1H	b
^{19}F				
-39.2	s		1F	k
-74.2	s		6F	n
-184.2	s		1F	m
^{13}C				
34.23	s			a
90.17	d sept	210, 33		m
111.72	d	1.9		c
111.98	s			g
120.77	dq	287, 27		n
122.98	s			f
123.98	s			e
124.63	s			h
127.16	s			d
139.65	s			i
140.53	s			b
168.14	m (br)			l
170.29	dm	229		k
175.02	dd	13, 3		j

No 29 2-(N,N-dimethylaminophenyl)-4,6-difluoro-s-triazine



Chemical Shift (ppm)	Multiplicity	Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H				
3.10	s		6H	a
6.80	AX	J_{AX}=9.0	2H	b
8.28	AX	J_{AX}=9.0	2H	c
^{19}F				
-40.13	s			d

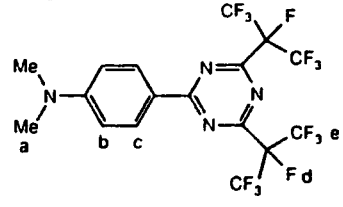
No. 30 2-(4-N,N-Dimethylaminophenyl)-4-perfluoro-isopropyl-6-fluoro-s-triazine



Chemical Shift (ppm)	Multiplicity	Coupling Constants (Hz)	Relative Intensity	Assignment
Spectra recorded in $CDCl_3$				
^{1}H				
3.40	s		6H	a
6.98	AX	J_{AX}=9.4	2H	b
8.65	AX	J_{AX}=9.4	2H	c
^{19}F				
-37.25	s		1F	d
-74.27	d	7.5	6F	f
-184.82	sept	7.5	1F	e

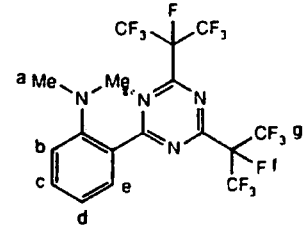
No. 31 2-(4-N,N-Dimethylaminophenyl)-4,6-perfluorodi-isopropyl-s-triazine

Para Isomer



Chemical Shift (ppm)	Multiplicity	Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H				
3.08	s		6H	a
6.67	AX	J_{AX}=9.2	2H	b
8.36	AX	J_{AX}=9.2	2H	c
^{19}F				
-73.66	d	7.2	6F	f
-184.00	sept	7.2	1F	e

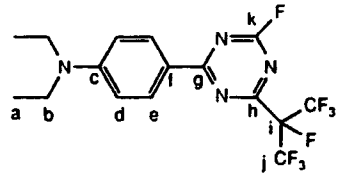
Ortho Isomer



Chemical Shift (ppm)	Multiplicity	Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H				
3.11	s		6H	a
7.40-8.90			4H	b, c, d, e
^{19}F				
-73.48	d	6.8	6F	g
-184.13	sept	6.8	1F	f

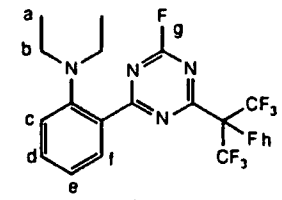
No 32 2-(N,N-diethylaminophenyl)-4-perfluoroisopropyl-6-fluoro-s-triazine

Para isomer



Chemical Shift (ppm)	Multiplicity	Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H				
1.20	t	7	6H	a
3.49	q	7	4H	b
6.80	AX	J_{AX}=9.6	2H	c
8.27	AX	J_{AX}=9.6	2H	d
^{19}F				
-43.50	s		1F	e
-78.09	d	6.8	6F	g
-188.17	sept	6.8	1F	f
^{13}C				
12.5	s			a
44.8	s			b
89.3	d sept	213, 33		i
111.16	s			d
119.74	qdq	288, 27		j
130.30	s			f
132.74	s			e
153.14	s			c
167.95	dd	21.9, 11.5		h
169.79	d	234		k
176.00	d	12.5		g

Ortho Isomer

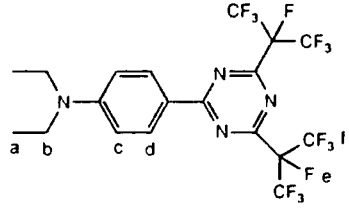


Chemical Shift (ppm)	Multiplicity	Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H				
1.07	t	7.1	6H	a
3.51	q	7.1	4H	b
7.16-7.48			4H	c, d, e, f
^{19}F				
-43.50	s		1F	g
-78.03	d	6.4	6F	i
-187.09	sept	6.8	1F	h

The resonances corresponding to the ortho isomer in the ^{13}C spectrum cannot be resolved due to the small concentration of this isomer. However, line broadening of the spectrum indicates the presence of the ortho isomer.

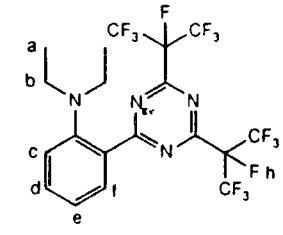
No. 33 2-(4-N,N-Diethylaminophenyl)-4,6-perfluorodiisopropyl-s-triazine

Para Isomer



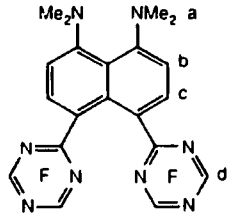
Chemical Shift (ppm)	Multiplicity	Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H				
1.18	t	7.2	6H	a
3.42	q	7.2	4H	b
6.65	AX	J_{AX}=9.2	2H	c
8.33	AX	J_{AX}=9.2	2H	d
^{19}F				
-73.15	d	7.1	12F	f
-183.78	sept	7.1	2F	e

Ortho Isomer



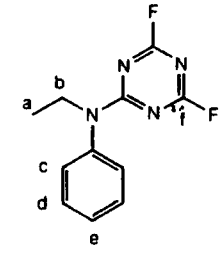
Chemical Shift (ppm)	Multiplicity	Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H				
1.05	t	7.2	6H	a
3.42	q	7.2	4H	b
7.34-7.60			4H	c, d, e, f
^{19}F				
-73.33	d	7.5	6F	i
-183.60	sept	7.2	1F	h

No. 34 1,8-(Bisdimethylamino)-4,5-(bisdifluorotriaz-1-yl)-naphthalene



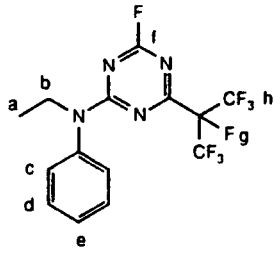
Chemical Shift (ppm)	Multiplicity	Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H				
3.09	s		6H	a
7.02	AX	J_{AX}=8.6		b
8.36	AX	J_{AX}=8.6		c
^{19}F				
-40.2				d

No. 35 2-(ethylphenylamino)-4,6-difluoro-s-triazine



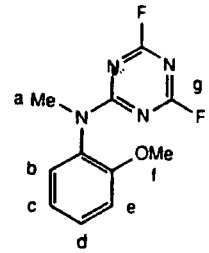
Chemical Shift (ppm)	Multiplicity	Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H				
1.26	t	7.2	3H	a
4.03	q		2H	b
7.21	d	8.1	2H	c
7.45	m		3H	d, e
^{19}F				
-37.32	s		1F	f
-37.88	s		1F	f

No 36 2-(ethylphenyl)amino-4-perfluoroisopropyl-s-triazine



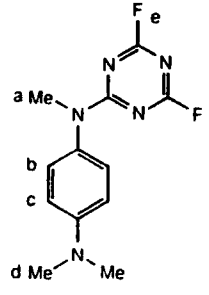
Chemical Shift (ppm)	Multiplicity	Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H				
1.24	t	7.2	3H	a
4.76	q	7.2	2H	b
7.29	t	7.2	2H	d
7.48	m		3H	c, e
^{19}F				
-39.9	s		1F	f
-74.45	s		6F	h
-184.65	s		1F	g

No. 37 2-(methyl-(2-methoxy-phenyl)amino-4,6-difluoro-s-triazine



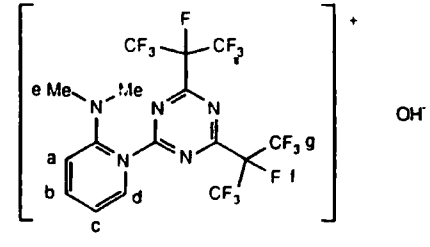
Chemical Shift (ppm)	Multiplicity	Coupling Constants (Hz)	Relative Intensity	Assignment
Spectra recorded in d_6-acetone				
^{1}H				
3.47	s		3H	a or f
3.84	s		3H	a or f
7.06	t	7.0	1H	c or d
7.18	d	8.1	1H	b or e
7.33	d	7.5	iH	b or e
7.39	t	7.6	1H	c or d
^{19}F				
-40.33	s		1F	g
-41.14	s		1F	g

No 38 2-(methyl(N,N-dimethylamino)phenyl)-4,6-difluoro-s-triazine



Chemical Shift (ppm)	Multiplicity / Coupling Constants (Hz)	Relative Intensity	Assignment
Spectra recorded in d_6-acetone			
^{1}H			
2.97	s	6H	d
3.50	s	3H	a
6.78	AB J_{AB}=8.9	2H	b
7.17		2H	c
^{19}F			
-40.6	s	1F	e
-41.1	s	1F	e

No. 39 Pyridine Salt



Chemical Shift (ppm)	Multiplicity / Coupling Constants (Hz)	Relative Intensity	Assignment
^{1}H			
3.25	s	6H	e
6.84	ddd $J_{c,d}$=6.4	1H	c
7.06	ddd $J_{a,b}$=9 $J_{a,c}$=0.8 $J_{a,d}$=0.8	1H	a
7.91	ddd $J_{b,c}$=7 $J_{b,d}$=1.9	1H	b
8.06	ddd	1H	d
^{19}F			
-74.95	s	6F	g
-185.30	s	1F	f

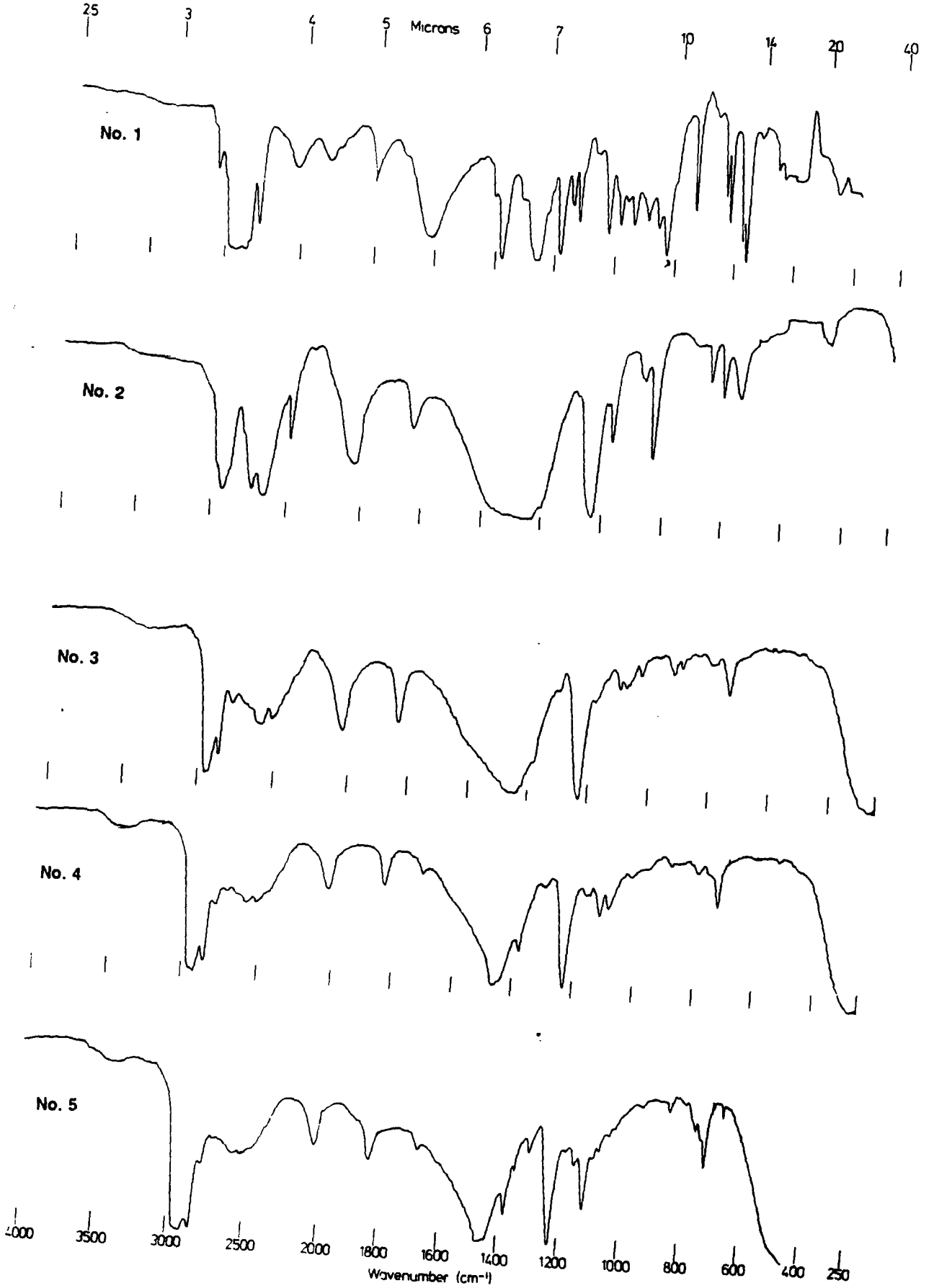
APPENDIX TWO

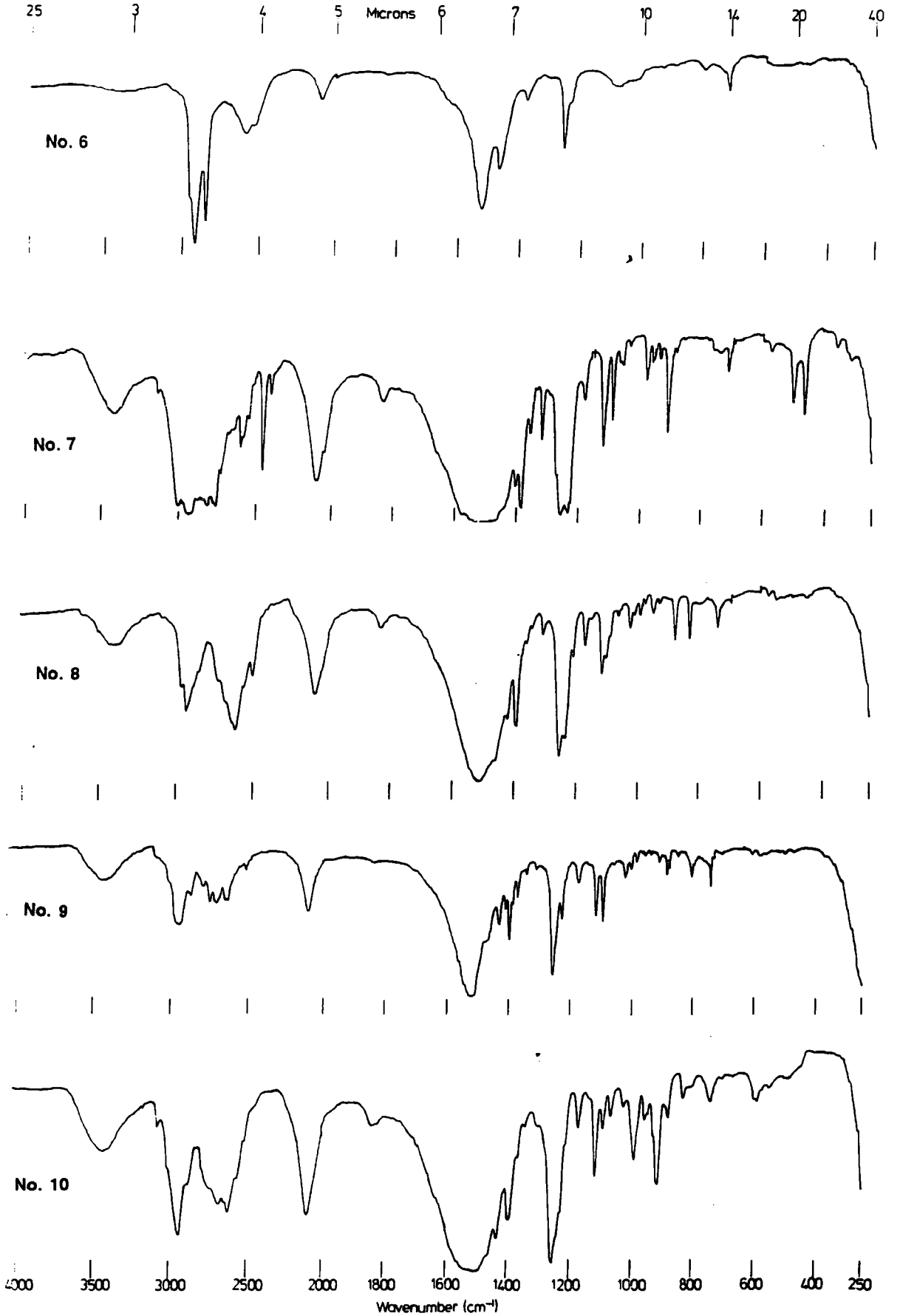
INFRA RED SPECTRA

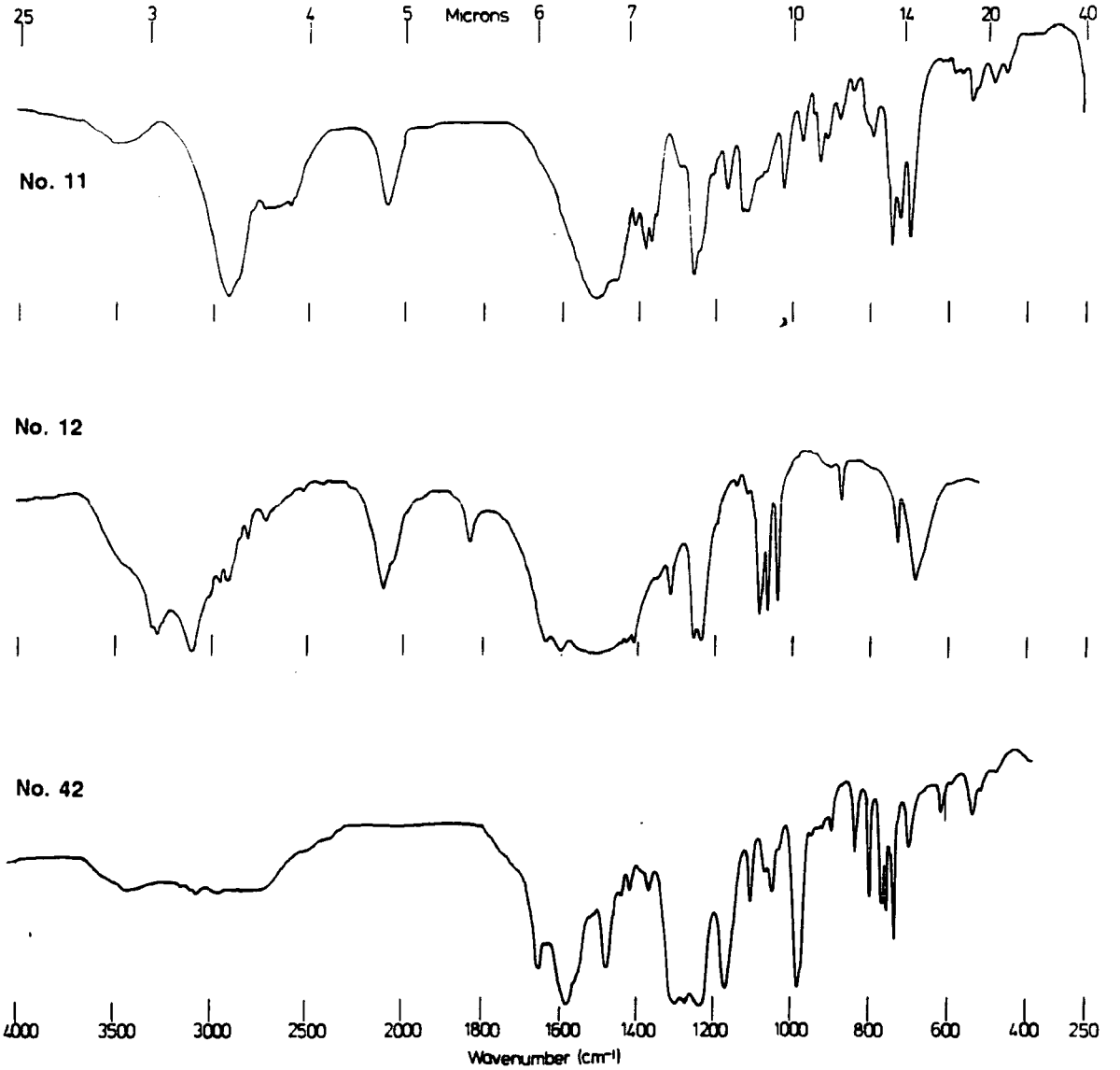
1. 1,8-(Bisdimethylamino)-naphthalene Hydrogen Fluoride Complex (PS/HF) (1)(Nujol mull)
2. Triethylamine Hydrogen Fluoride Complex (24)
3. Tributylamine Hydrogen Fluoride Complex (25)
4. Trihexylamine Hydrogen Fluoride Complex (26)
5. Trioctylamine Hydrogen Fluoride Complex (27)
6. Tridodecylamine Hydrogen Fluoride Complex (28)
7. 2,2,6,6-Tetramethylpiperidine Hydrogen Fluoride Complex (35)
8. N-Methyl-2,2,6,6-Tetramethylpiperidine Hydrogen Fluoride Complex (36)
9. N-Ethyl-2,2,6,6-Tetramethylpiperidine Hydrogen Fluoride Complex (37)
10. N-Allyl-2,2,6,6-Tetramethylpiperidine Hydrogen Fluoride Complex (38)
11. N-Benzyl-2,2,6,6-Tetramethylpiperidine Hydrogen Fluoride Complex (39)
12. Tetramethylguanidine Hydrogen Fluoride Complex (40)
13. 1,1-Bistrifluoromethyl-6,7-bisdimethylamino-2,3-tetrafluoro-ethano-[1H]-phenalene (4)
14. Unidentified Red Solid (5)
15. Spiro[octafluorocyclopentane-1,1'-(6,7-bisdimethylamino)-2',3'-tetrafluoroethano-[1H]-phenalene] (44)
16. (7,8)-(9,10)-dihexafluoropropano-3,4-bisdimethylamino-cyclohepta-[*d,e*]-naphthalene (56)
17. Spiro[octafluorocyclopentane-1,1'-(6,7-bisdimethylamino)-2',3'-tetrafluoropropan-2"one-[1H]-phenalene] (60)
18. 7,8-propano-9,10-propan-2"-one-cyclohepta-[*d,e*]-naphthalene (61)
19. Spiro[hexafluorocyclobutane-3,1'-1,2-tetrafluoroethano-1-fluoro-3-(4"-N,N-dimethylaminophenyl)-propene] (63)
20. Spiro[hexafluorocyclobutane-3,1'-1,2-tetrafluoroethano-1-fluoro-3-(N-methylindol-3"-yl)-propene] (65)
21. White Solid (66)
22. 2-(pyrrol-2-yl)-4,6-difluoro-s-triazine (67)
23. 2-(pyrrol-2-yl)-4-perfluoroisopropyl-6-fluoro-s-triazine (68)
24. 2-(pyrrol-2-yl)-4,6-perfluorodi-isopropyl-s-triazine (69)
25. 2-(N-methylpyrrol-2-yl)-4,6-difluoro-s-triazine (70)
26. 2-(N-methylpyrrol-2-yl)-4-perfluoroisopropyl-6-fluoro-s-triazine (71)
27. 2-(N-methylpyrrol-2-yl)-4,6-perfluorodi-isopropyl-s-triazine (72)
28. 2-(N-methylindol-3-yl)-4,6-difluoro-s-triazine (73)
29. 2-(N-methylindol-3-yl)-4-perfluoroisopropyl-6-fluoro-s-triazine (74)

30. 2-(N-methylindol-3-yl)-4,6-perfluorodi-isopropyl-s-triazine (75)
31. 6-(N-methylindol-3-yl)-2,4,5-trifluoro-pyrimidine (76)
32. 2-(4-N,N-dimethylaminophenyl)-4,6-difluoro-s-triazine (77)
33. 2-(4-N,N-dimethylaminophenyl)-4-perfluoroisopropyl-6-fluoro-s-triazine (78)
34. 2-(4-N,N-dimethylaminophenyl)-4,6-perfluorodi-isopropyl-s-triazine (81A) and 2-(2-N,N-dimethylaminophenyl)-4,6-perfluorodi-isopropyl-s-triazine (81B)
35. 2-(4-N,N-diethylaminophenyl)-4-perfluoroisopropyl-6-fluoro-s-triazine (79A) and 2-(2-N,N-diethylaminophenyl)-4-perfluoroisopropyl-6-fluoro-s-triazine (79B)
36. 2-(4-N,N-diethylaminophenyl)-4,6-perfluorodi-isopropyl-s-triazine (82A) and 2-(2-N,N-diethylaminophenyl)-4,6-perfluorodi-isopropyl-s-triazine (82B)
37. 1,8-(Bisdimethylamino)-4,5-(bisdifluoro-s-triaz-2-yl)-naphthalene (83)
38. 2-(ethylphenylamino)-4,6-difluoro-s-triazine (84)
39. 2-(ethylphenylamino)-4-perfluoroisopropyl-6-fluoro-s-triazine (80)
40. 2-methyl-(2-methoxyphenyl)-amino-4,6-difluoro-s-triazine (85)
41. 2-methyl-(4-N,N-dimethylaminophenyl)-amino-4,6-difluoro-s-triazine (86)
42. Pyridinium Salt (87)

All solids were recorded as KBr discs unless otherwise stated. All liquids were run as thin films between KBr plates


25
3
4
5
Microns
6
7
10
14
20
40
No. 1
No. 2
No. 3
No. 4
No. 5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250
Wavenumber (cm⁻¹)


25
3
4
5
Microns
6
7
10
14
20
40
No. 6
No. 7
No. 8
No. 9
No. 10
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250
Wavenumber (cm⁻¹)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3
4
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Microns
6
7
10
14
20
40
No. 11
No. 12
No. 42
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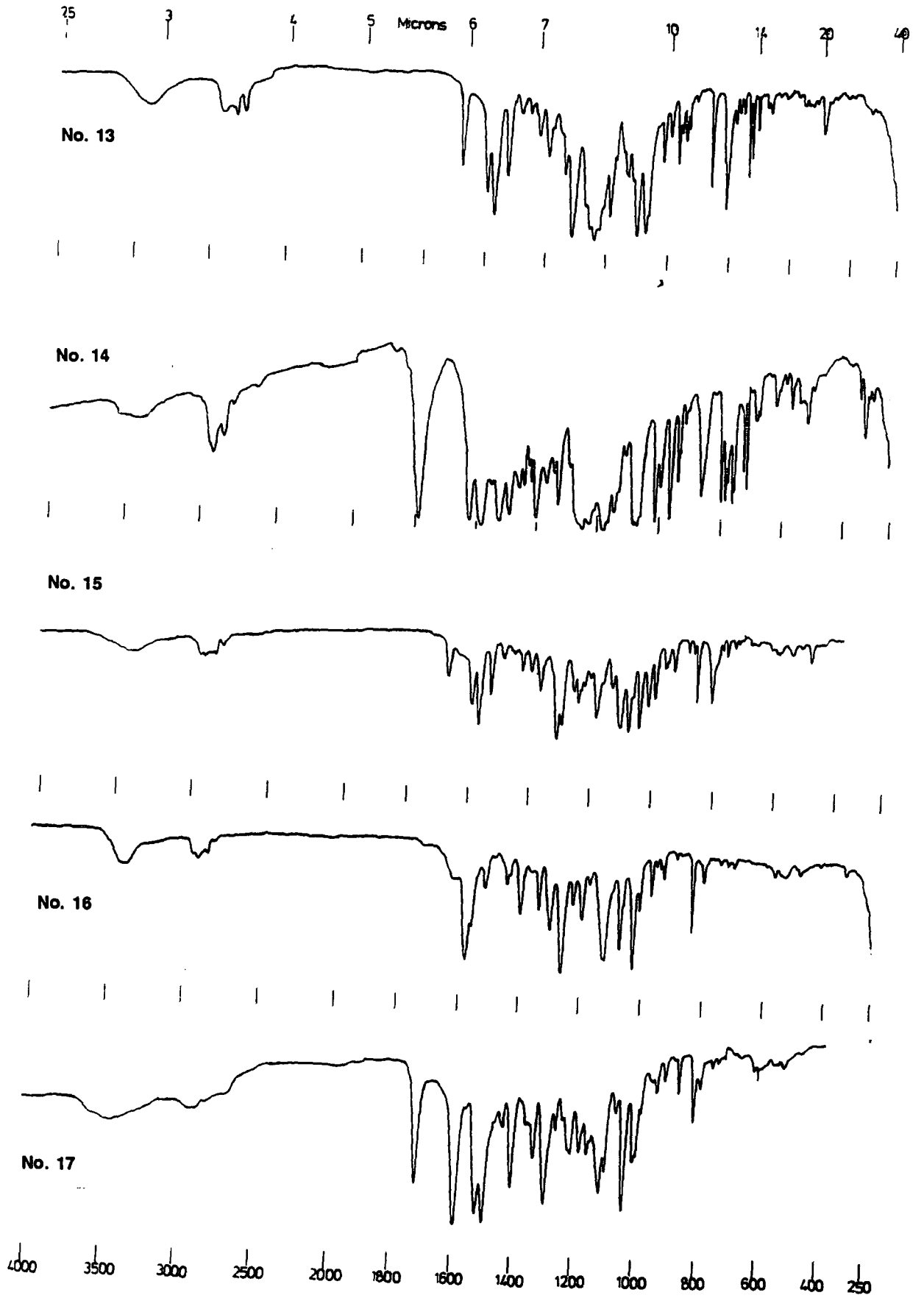
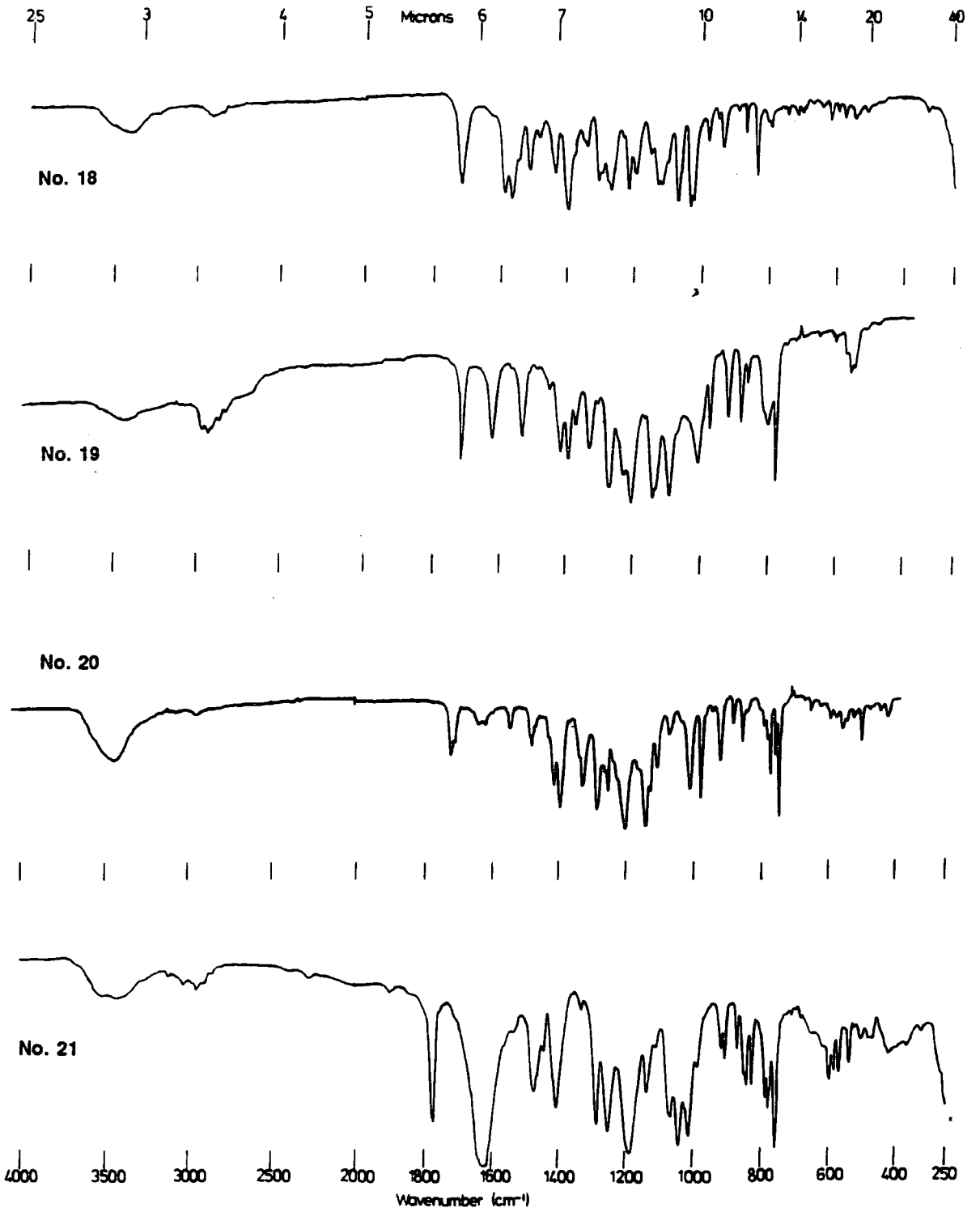
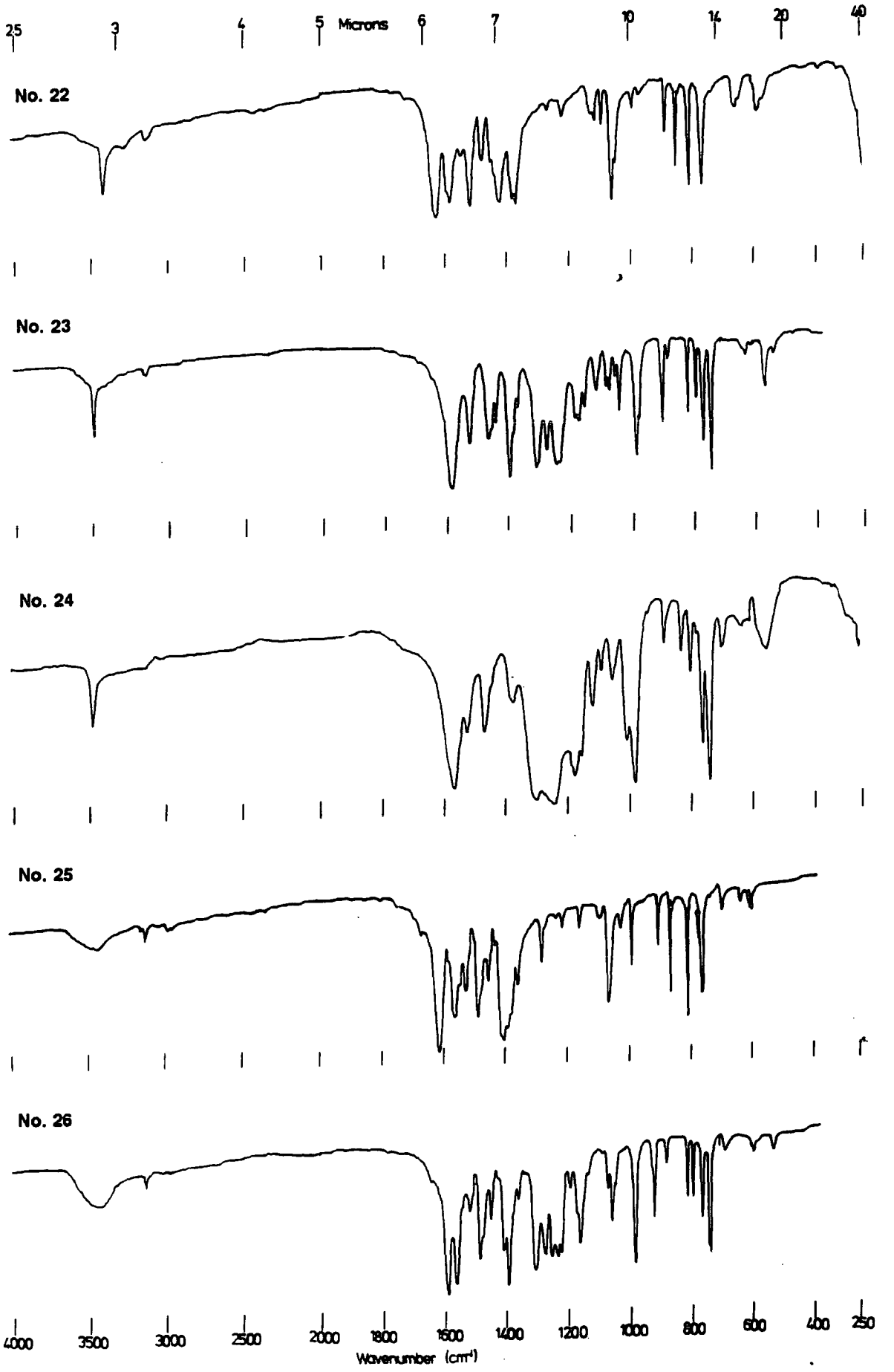
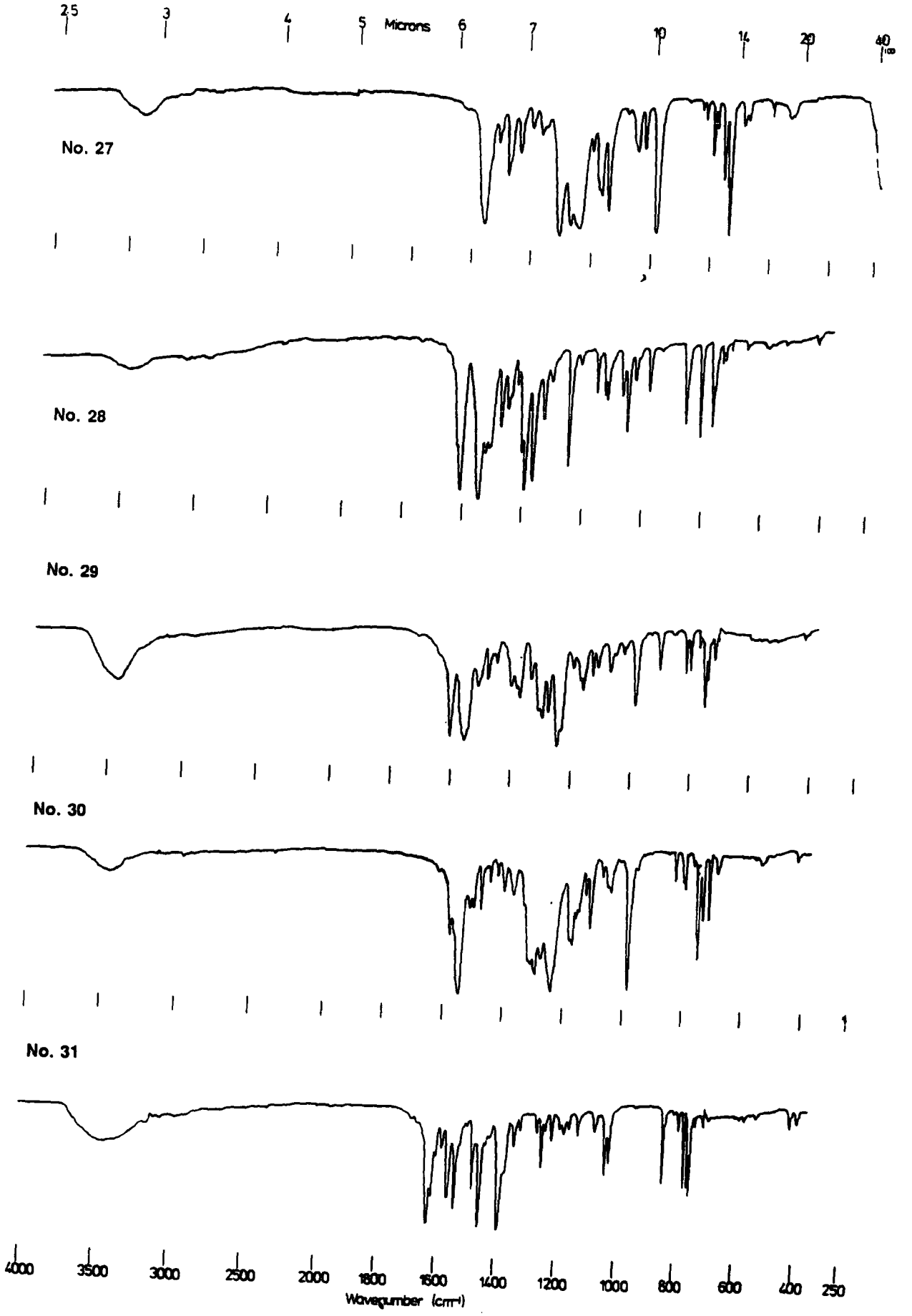
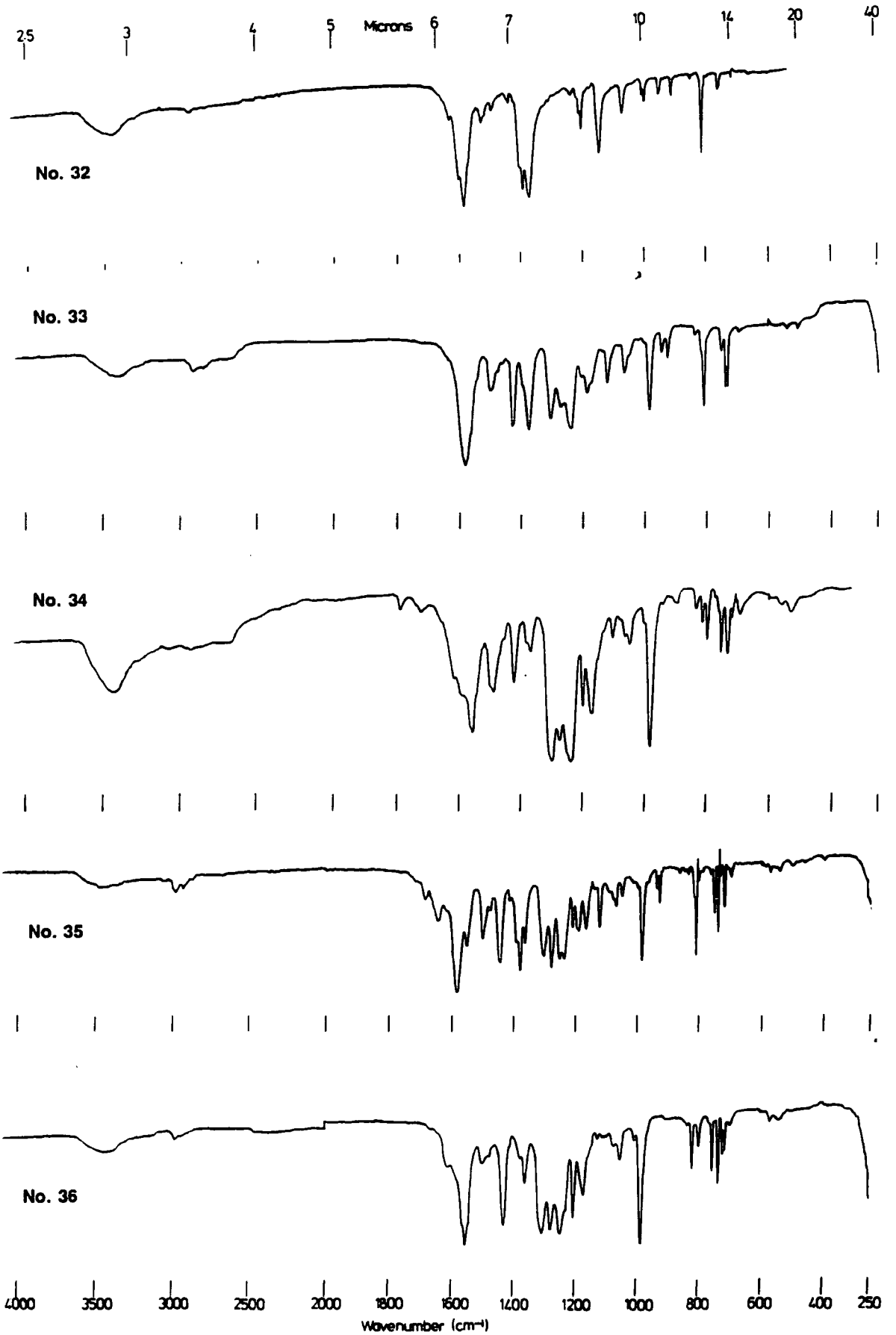
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250
Wavenumber (cm⁻¹)

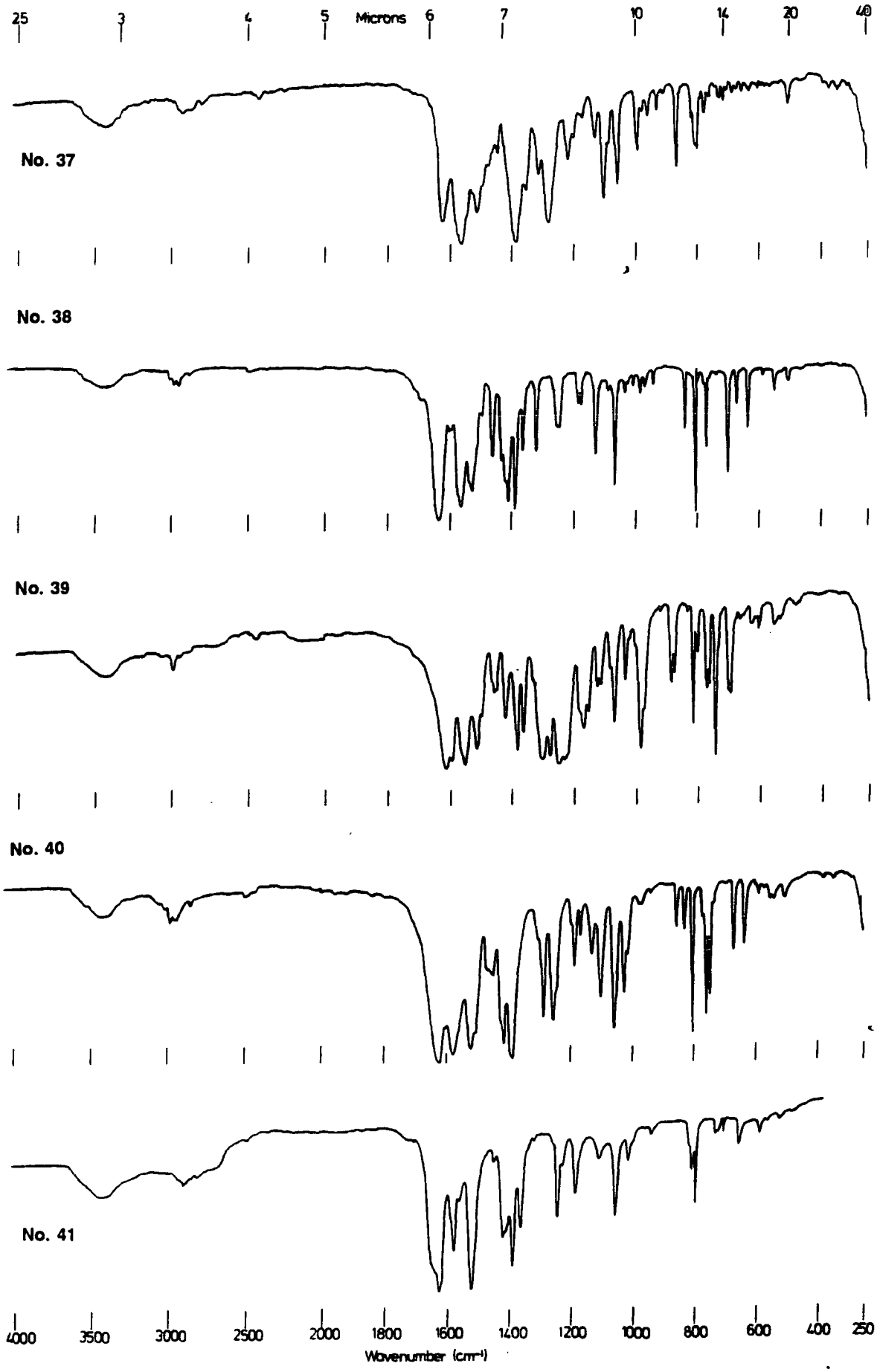

2.5
3
4
5
Microns
6
7
10
14
20
40
No. 13
No. 14
No. 15
No. 16
No. 17
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250


25
3
4
5
Microns
6
7
10
14
20
40
No. 18
No. 19
No. 20
No. 21
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250
Wavenumber (cm⁻¹)


25
3
4
5
Microns
6
7
10
14
20
40
No. 22
No. 23
No. 24
No. 25
No. 26
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250
Wavenumber (cm⁻¹)


2.5
3
4
5
Microns
6
7
10
14
20
40
100
No. 27
No. 28
No. 29
No. 30
No. 31
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250
Wavenumber (cm⁻¹)


2.5
3
4
5
Microns
6
7
10
14
20
40
No. 32
No. 33
No. 34
No. 35
No. 36
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250
Wavenumber (cm⁻¹)


25
3
4
5
Microns
6
7
10
14
20
40
No. 37
No. 38
No. 39
No. 40
No. 41
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250
Wavenumber (cm⁻¹)

APPENDIX THREE

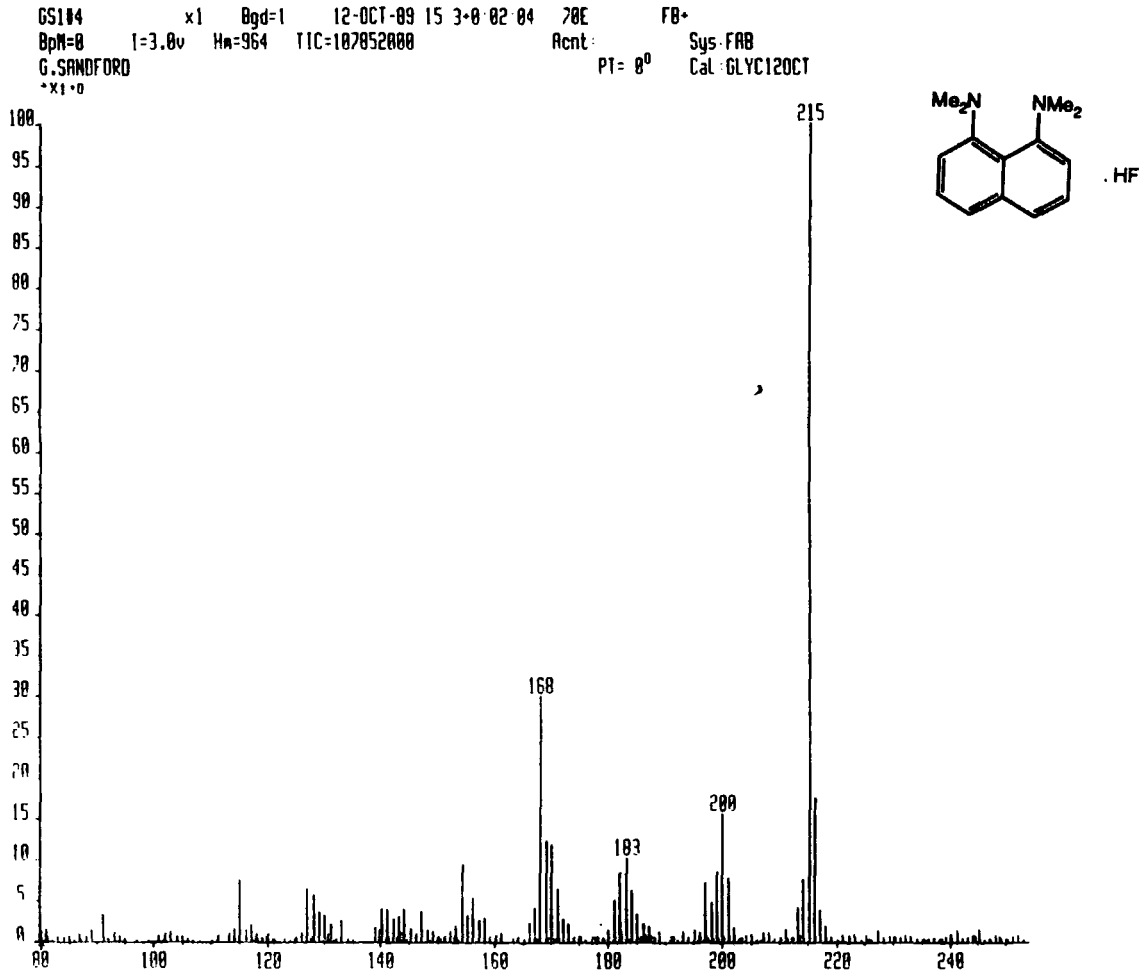
MASS SPECTRA

1. 1,8-(Bisdimethylamino)-naphthalene Hydrogen Fluoride Complex (PS/HF) (1)
2. Triethylamine Hydrogen Fluoride Complex (24)
3. Tributylamine Hydrogen Fluoride Complex (25)
4. Trihexylamine Hydrogen Fluoride Complex (26)
5. Trioctylamine Hydrogen Fluoride Complex (27)
6. Tridodecylamine Hydrogen Fluoride Complex (28)
7. 2,2,6,6-Tetramethylpiperidine Hydrogen Fluoride Complex (35)
8. N-Methyl-2,2,6,6-Tetramethylpiperidine Hydrogen Fluoride Complex (36)
9. N-Ethyl-2,2,6,6-Tetramethylpiperidine Hydrogen Fluoride Complex (37)
10. N-Allyl-2,2,6,6-Tetramethylpiperidine Hydrogen Fluoride Complex (38)
11. N-Benzyl-2,2,6,6-Tetramethylpiperidine Hydrogen Fluoride Complex (39)
12. Tetramethylguanidine Hydrogen Fluoride Complex (40)
13. 1,1-Bistrifluoromethyl-6,7-bisdimethylamino-2,3-tetrafluoro-ethano-[1H]-phenalene (4)
14. Unidentified Red Solid (5)
15. Spiro[octafluorocyclopentane-1,1'-(6,7-bisdimethylamino)-2',3'-tetrafluoroethano-[1H]-phenalene] (44)
16. (7,8)-(9,10)-dihexafluoropropano-3,4-bisdimethylamino-cyclohepta-[*d,e*]-naphthalene (56)
17. Spiro[octafluorocyclopentane-1,1'-(6,7-bisdimethylamino)-2',3'-tetrafluoropropan-2"one-[1H]-phenalene] (60)
18. 7,8-propano-9,10-propan-2"-one-cyclohepta-[*d,e*]-naphthalene (61)
19. Spiro[hexafluorocyclobutane-3,1'-1,2-tetrafluoroethano-1-fluoro-3-(4"-N,N-dimethylaminophenyl)-propene] (63)
20. Spiro[hexafluorocyclobutane-3,1'-1,2-tetrafluoroethano-1-fluoro-3-(N-methylindol-3"-yl)-propene] (65)
21. 2-(pyrrol-2-yl)-4,6-difluoro-s-triazine (67)
22. 2-(pyrrol-2-yl)-4-perfluoroisopropyl-6-fluoro-s-triazine (68)
23. 2-(pyrrol-2-yl)-4,6-perfluorodi-isopropyl-s-triazine (69)
24. 2-(N-methylpyrrol-2-yl)-4,6-difluoro-s-triazine (70)
25. 2-(N-methylpyrrol-2-yl)-4-perfluoroisopropyl-6-fluoro-s-triazine (71)
26. 2-(N-methylpyrrol-2-yl)-4,6-perfluorodi-isopropyl-s-triazine (72)
27. 2-(N-methylindol-3-yl)-4,6-difluoro-s-triazine (73)
28. 2-(N-methylindol-3-yl)-4-perfluoroisopropyl-6-fluoro-s-triazine (74)
29. 2-(N-methylindol-3-yl)-4,6-perfluorodi-isopropyl-s-triazine (75)
30. 6-(N-methylindol-3-yl)-2,4,5-trifluoro-pyrimidine (76)

31. 2-(4-N,N-dimethylaminophenyl)-4,6-difluoro-s-triazine (77)
32. 2-(4-N,N-dimethylaminophenyl)-4-perfluoroisopropyl-6-fluoro-s-triazin(78)
33. 2-(4-N,N-dimethylaminophenyl)-4,6-perfluorodi-isopropyl-s-triazine (81A) and 2-(2-N,N-dimethylaminophenyl)-4,6-perfluorodi-isopropyl-s-triazine (81B)
34. 2-(4-N,N-diethylaminophenyl)-4-perfluoroisopropyl-6-fluoro-s-triazine (79A) and 2-(2-N,N-diethylaminophenyl)-4-perfluoroisopropyl-6-fluoro-s-triazine (79B)
35. 2-(4-N,N-diethylaminophenyl)-4,6-perfluorodi-isopropyl-s-triazine (82A) and 2-(2-N,N-diethylaminophenyl)-4,6-perfluorodi-isopropyl-s-triazine (82B)
36. 1,8-(Bisdimethylamino)-4,5-(bisdifluoro-s-triaz-2-yl)-naphthalene (83)
37. 2-(ethylphenylamino)-4,6-difluoro-s-triazine (84)
38. 2-(ethylphenylamino)-4-perfluoroisopropyl-6-fluoro-s-triazine (80)
39. 2-methyl-(2-methoxyphenyl)-amino-4,6-difluoro-s-triazine (85)
40. 2-methyl-(4-N,N-dimethylaminophenyl)-amino-4,6-difluoro-s-triazine (86)
41. Pyridinium Salt (87)

No.1

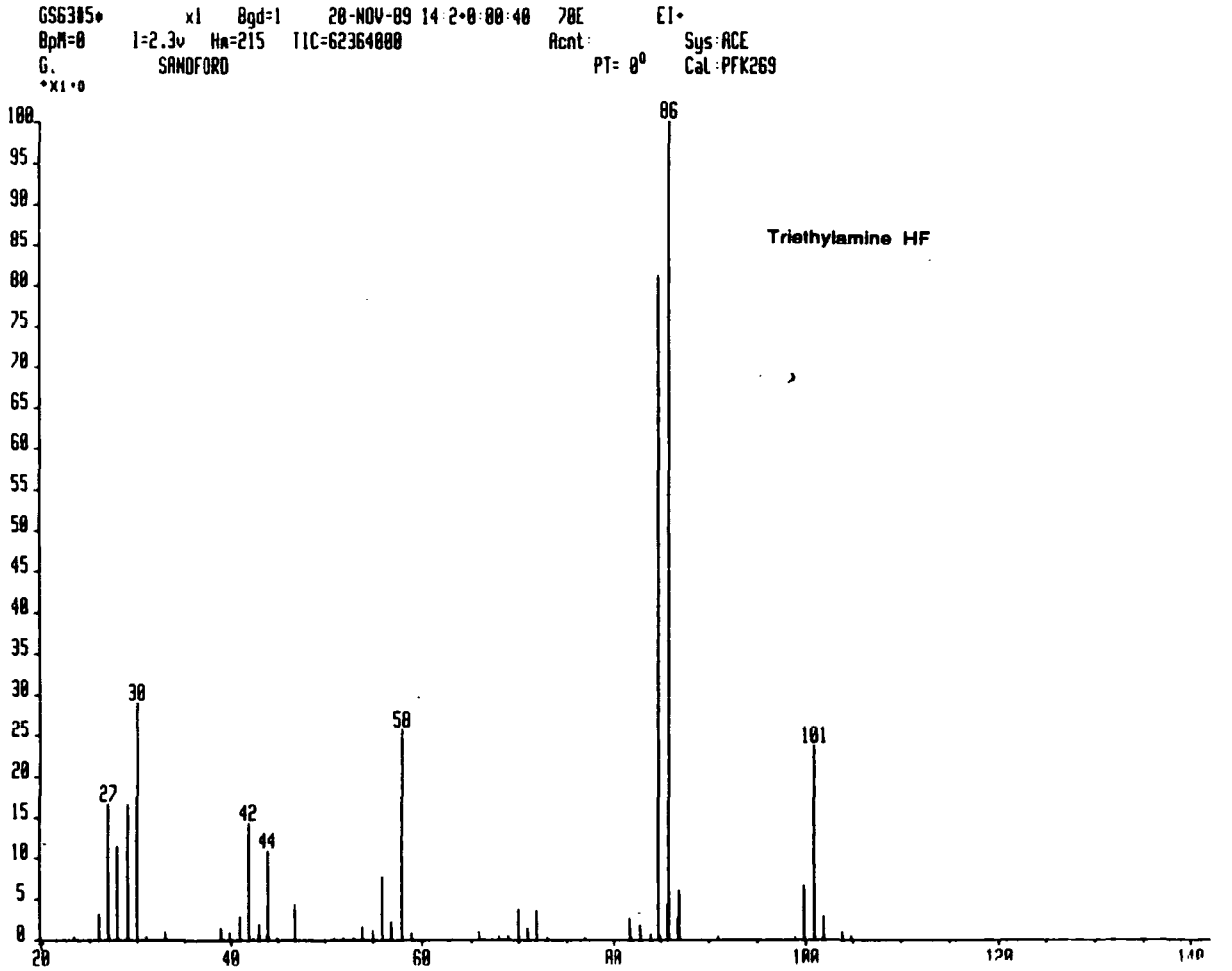
FAB+



Mass	% Base
167.09	4.11
167.21	0.29
167.58	0.31
167.61	0.28
168.09	30.07
169.09	12.20
169.68	0.40
170.10	11.82
170.45	0.34
170.88	0.25
170.93	0.28
171.11	6.37
171.45	0.36
172.12	2.79
173.13	2.15
174.09	0.44
174.92	0.41
178.98	0.39
180.08	1.32
181.09	5.05
182.09	3.28
182.31	1.29
183.10	10.11
183.65	0.23
184.10	6.26
185.11	3.38
185.56	0.29
185.82	0.66
186.11	2.06
196.81	0.24
197.10	1.19
197.33	0.53
197.51	0.31
198.11	4.65
198.50	0.23
199.12	8.53
199.36	0.33
200.12	15.61
200.27	0.49
201.13	1.74
202.11	1.73
203.03	0.34
208.07	0.99
209.08	0.34
210.09	0.49
211.10	1.49
211.33	0.33
212.05	0.44
212.14	0.51
213.13	4.16
213.59	0.69
214.15	7.57
215.15	100.00
216.16	17.55
217.15	3.80
218.08	1.89
219.02	0.39
221.10	0.75
222.08	0.74
223.15	0.87
225.04	0.63

No. 2

EI+

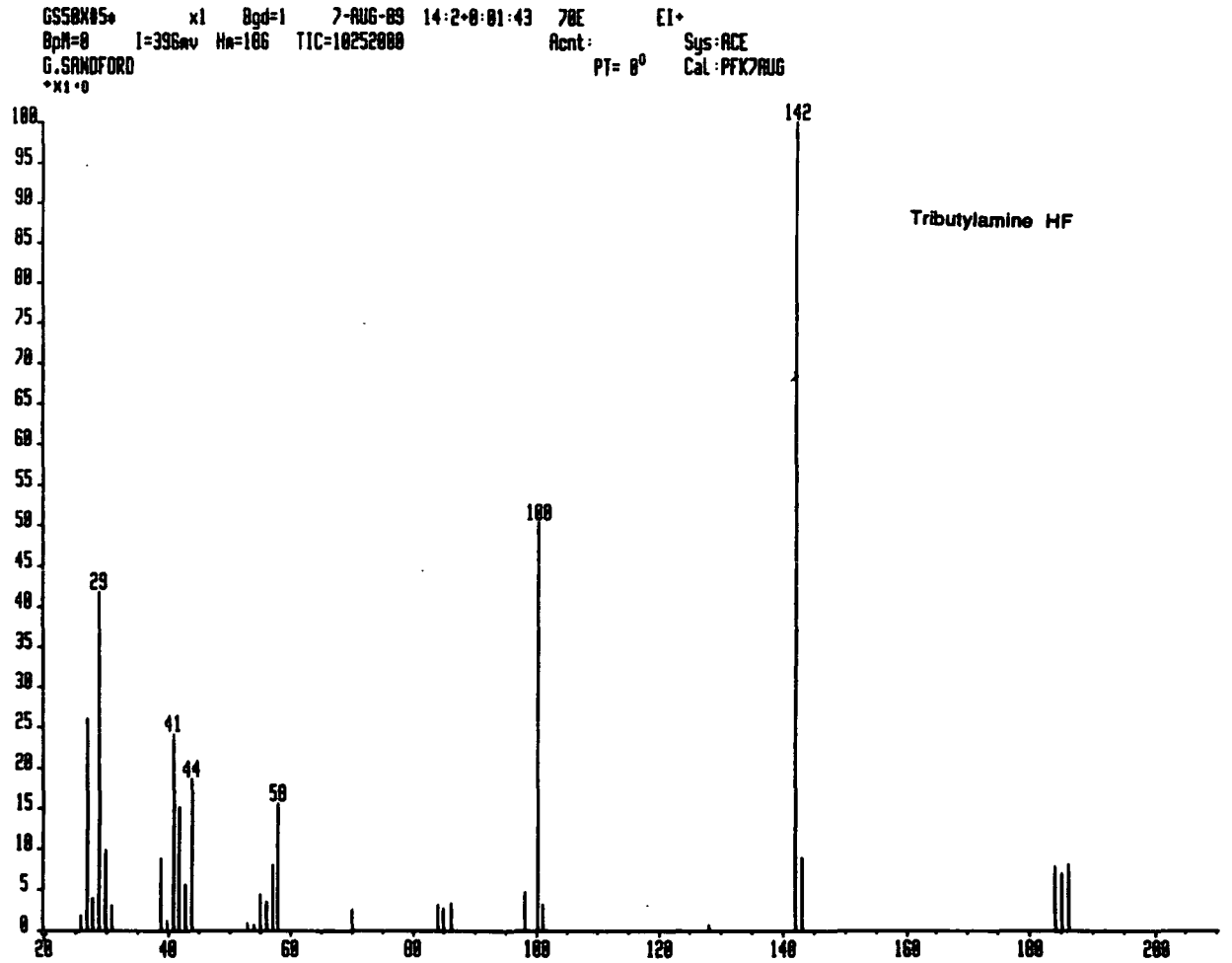


EI+ Data

Mass	% Base		Mass	% Base
23.41	0.31		82.82	1.60
25.94	3.08		83.93	0.60
26.95	16.50		84.81	81.17
27.90	2.92		84.93	0.23
27.94	11.18	F	85.82	4.21
27.95	3.56	F	85.94	100.00
28.96	16.44		86.81	2.52
29.95	28.87		86.94	5.85
30.96	0.23		90.89	0.23
32.90	0.94		99.94	6.56
38.93	1.30		100.95	23.58
39.93	0.77		101.95	2.69
40.94	2.77		103.80	0.90
41.94	14.30		104.80	0.35
42.39	0.22		148.81	0.83
42.92	0.44			
42.95	1.76			
43.89	0.40			
43.95	10.73			
46.87	4.18			
51.91	0.21			
53.92	1.54			
54.93	1.03			
55.93	7.65			
56.94	2.07			
57.94	25.66			
58.94	0.78			
65.83	0.98			
67.91	0.31			
68.92	0.32			
69.92	3.62			
70.92	1.37			
71.93	3.55			
81.84	2.50			

No. 3

EI+

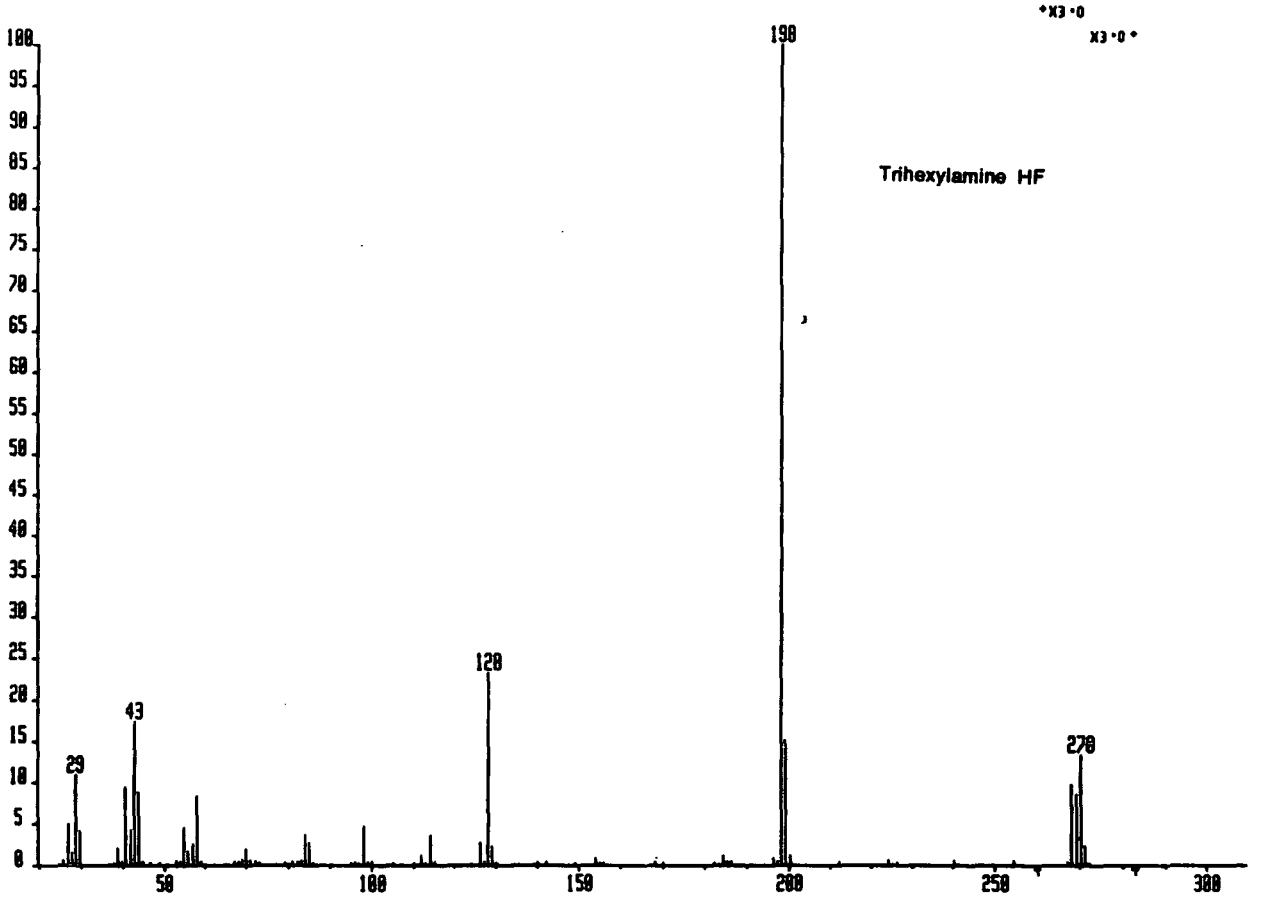


Mass	% Base
40.88	24.03
41.88	15.07
42.90	5.42
43.90	18.49
52.94	0.69
53.95	0.62
54.97	4.31
55.97	3.38
56.99	7.92
57.99	15.46
70.05	2.50
84.09	3.00
84.98	2.58
86.10	3.19
98.11	4.50
100.12	50.37
101.13	2.96
128.12	0.65
142.17	100.00
+143.18	8.73
*184.20	7.77
185.21	6.81
186.22	8.04

No. 4

EI^+

GS40X85e x1 Bgd=1 7-AUG-89 14:2+0:00:30 70E EI+
BpM=0 I=7.2v Hm=312 TIC=127377000 Acnt: Sys:ACE
G.SANDFORD PT= 0° Cal:PFK7AUG

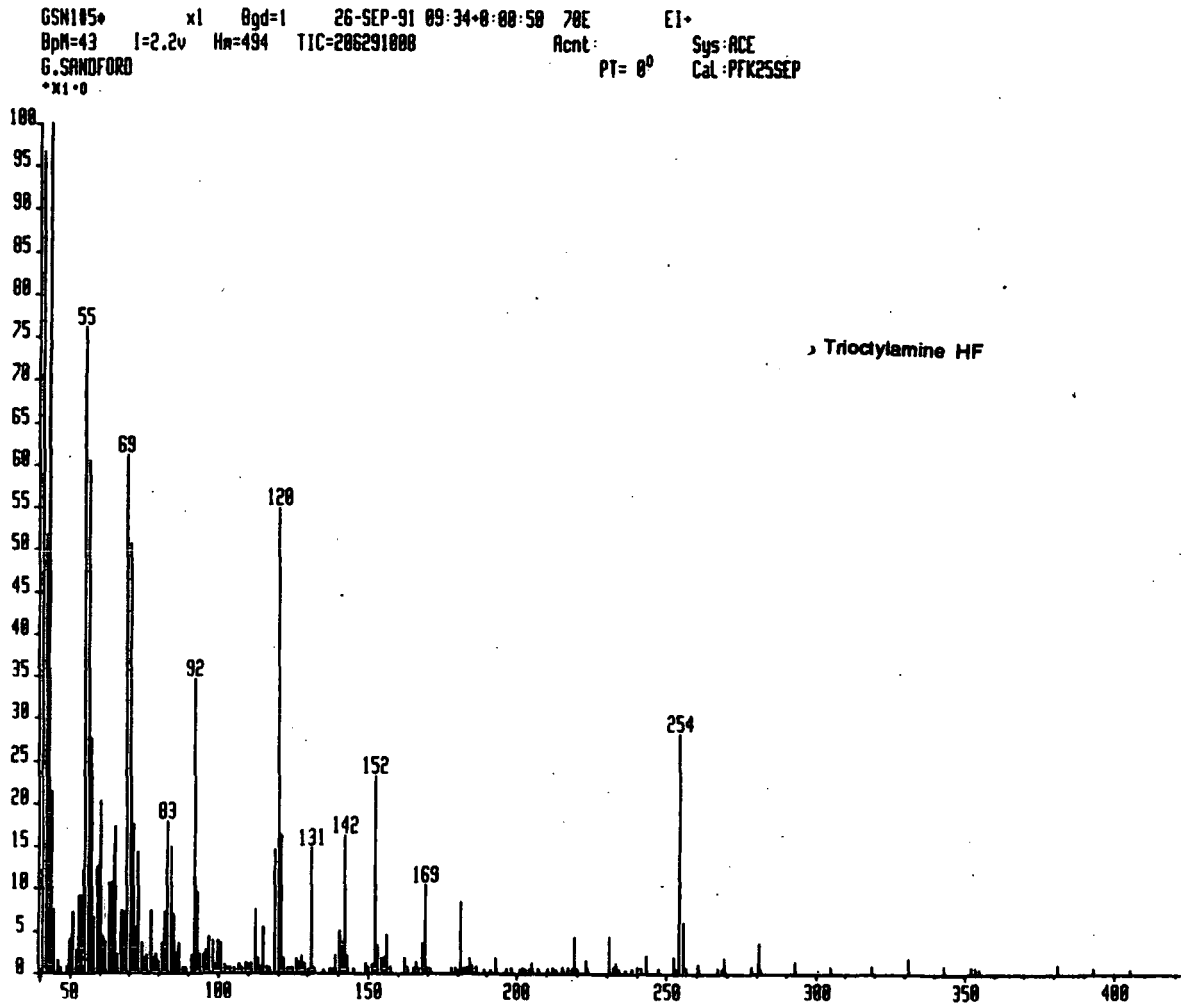


EI^+ Data

Mass	% Base
40.87	9.19
41.87	4.06
42.89	17.32
43.89	8.62
44.90	0.23
52.93	0.47
53.94	0.29
54.96	4.43
55.96	1.59
56.97	2.47
57.98	8.24
58.99	0.27
67.01	0.35
68.01	0.28
69.04	0.61
70.03	1.75
71.04	0.50
72.05	0.26
81.06	0.24
82.06	0.37
83.07	0.49
84.07	3.53
84.96	2.53
85.08	0.55
96.07	0.23
98.09	4.59
99.09	0.35
100.10	0.36
112.10	1.05
114.10	3.47
115.10	0.28
126.08	2.52
127.09	0.26
128.09	23.13
129.10	2.10
140.12	0.28
142.14	0.23
154.13	0.78
156.14	0.21
168.12	0.32
184.16	1.08
185.17	0.27
186.18	0.30
196.18	0.70
197.18	0.26
198.19	100.00
199.20	14.96
200.20	1.05
212.20	0.31
224.22	0.42
240.24	0.49
254.26	0.39
268.28	3.22
269.28	2.83
270.29	4.45
271.29	0.78

No. 5

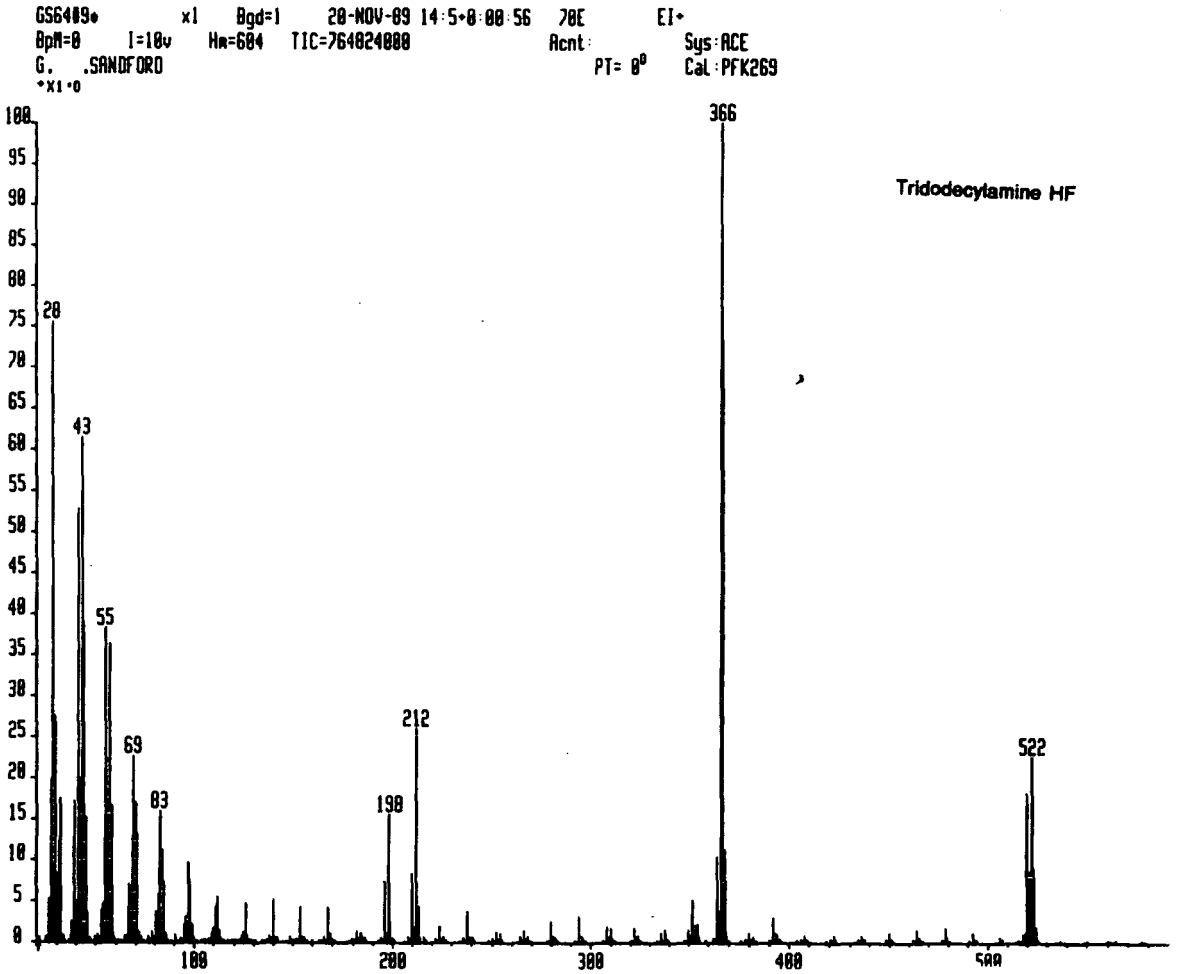
EI+



Mass	% Base
119.03	14.66
120.05	54.90
121.06	16.40
122.08	1.78
123.11	0.53
124.10	0.61
125.14	0.57
126.16	1.78
127.12	1.34
128.12	2.05
129.11	1.20
130.12	0.38
131.03	14.69
132.04	0.56
135.11	0.36
137.08	0.51
138.14	0.42
139.11	2.03
140.16	4.99
141.12	3.58
* 142.19	16.20
* 143.13	2.05
145.16	0.46
149.07	1.23
150.04	0.74
151.05	0.96
152.08	23.17
153.10	3.16
154.18	1.78
155.10	1.91
156.20	4.49
157.16	0.70
162.03	1.78
163.05	0.74
165.15	0.54
166.18	1.34
167.14	0.58
168.14	3.56
169.04	10.30
170.14	0.60
171.16	0.39
243.08	2.03
247.17	0.38
252.33	1.94
253.34	0.41
254.35	28.16
255.31	5.93
256.36	0.63
260.15	1.04
267.06	0.54
268.36	0.41
269.05	1.81
278.16	0.71
280.37	1.10
281.06	3.56

No. 6

EI+



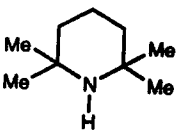
EI+ Data

Mass	% Base		Mass	% Base
353.14	2.04		478.31	1.64
354.15	2.19		479.31	0.61
355.16	0.55		492.33	1.00
362.12	0.51		493.33	0.38
363.13	0.28		506.35	0.61
364.13	10.32	F	507.35	0.24
365.09	3.60	F	518.35	1.07
366.14	100.00	FO	519.36	1.17
367.16	73.26	F	520.36	18.16
368.16	11.24		521.37	8.44
369.17	1.26		522.39	22.54
378.16	0.33		523.39	8.95
380.17	1.08		524.40	1.85
381.18	0.36		525.40	0.21
382.17	0.54			
392.18	2.94			
393.17	1.00			
394.19	0.90			
395.19	0.25			
406.20	0.29			
408.21	0.72			
409.22	0.26			
420.22	0.25			
422.23	0.79			
423.24	0.26			
434.23	0.28			
436.25	0.82			
437.25	0.27			
448.26	0.31			
450.27	1.05			
451.28	0.30			
462.27	0.24			
464.29	1.57			
465.30	0.58			
476.30	0.28			

No.7

Cl^+

GS3688♦ x1 Bgd=6 27-APR-89 14:3♦:00:51 70E Cl+
BpM=0 I=10v Hm=539 TIC=103458000 Acnt: Sys:ACE
G.SANDFORD PT= 0° Cal:PFK26APR



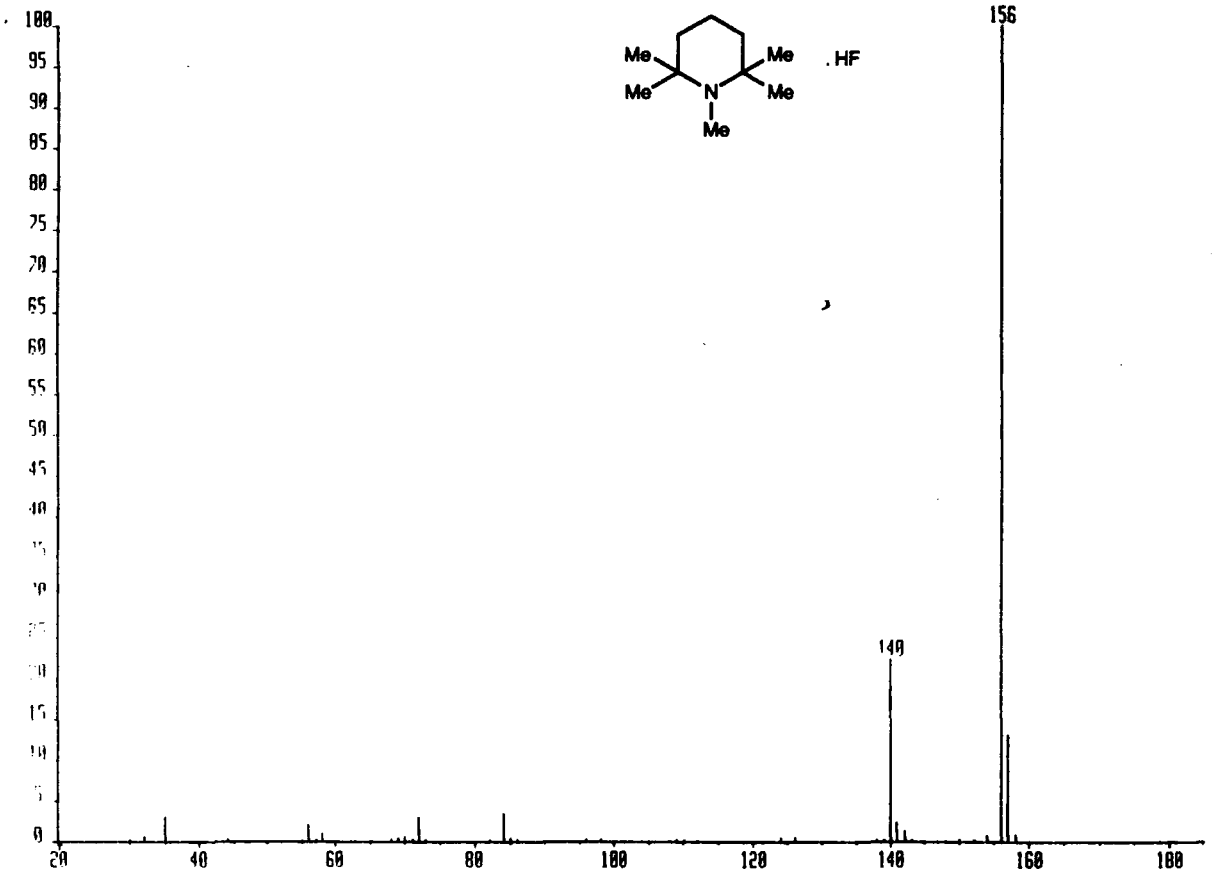
.HF

Mass	% Base			
44.04	1.10	140.14	0.27	
58.06	12.84	140.47	0.03	
70.06	4.55	140.51	0.03	
98.09	1.36	140.55	0.04	
113.11	1.01	140.60	0.05	
120.08	0.05	140.67	0.03	
121.11	0.04	142.24	100.00	FO
122.07	0.19	143.17	31.60	F
123.10	0.11	143.69	0.04	
124.01	0.03	143.74	0.04	
124.11	0.27	143.76	0.04	
125.12	0.23	143.83	0.05	
125.61	0.03	143.90	0.04	
125.68	0.04	143.93	0.05	
125.73	0.04	144.17	1.62	
126.13	21.79			
126.42	0.04			
127.14	2.03			
128.14	0.18			
129.10	0.04			
130.08	0.05			
130.12	0.04			
131.08	0.07			
132.07	0.02			
♦132.11	0.04			
♦133.09	0.20			
134.07	0.06			
134.12	0.04			
135.09	0.07			
136.08	0.04			
136.11	0.04			
137.06	0.05			
137.08	0.04			
137.14	0.06			
138.13	0.79			
139.03	0.07			
139.13	0.19			

No.8

Cl^+

GS41#23◆ x1 Bgd=6 8-JUN-89 16:3◆:01:52 70E Cl◆
BpM=0 I=10v Hm=150 TIC=103024000 Acnt: Sys:ACE
G.SANDFORD PT= 0° Cat:PFK19MAY
*x1*0

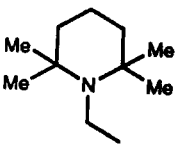


Mass	% Base	
56.03	1.96	
58.05	0.92	
70.04	0.43	
72.08	2.91	
84.05	3.39	
124.06	0.31	
126.07	0.52	
140.09	22.20	
141.08	2.32	
142.09	1.26	
154.08	0.66	
156.13	100.00	FO
157.10	13.02	F
158.11	1.69	

No.9

CI+

GS52126+ x1 Bgd=6 15-AUG-89 11:5+0:02:04 78E CI+
BpM=0 I=2.8v Hm=448 TIC=73872000 Acnt: Sys:RCE
G.SANDFORD PT= 0° Cal:PFK7AUG
*x1*0



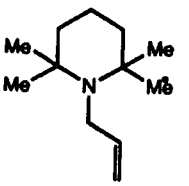
. HF

Mass	% Base	Mass	% Base
121.14	0.43	162.21	0.48
122.15	0.65	163.22	0.52
123.15	0.71	164.21	0.53
124.15	0.83	165.20	0.27
125.17	0.44	165.27	0.20
126.18	5.58	166.23	0.47
127.18	0.60	167.21	0.22
128.19	0.48	168.25	0.57
132.15	0.31	169.26	0.84
133.15	0.41	170.28	100.00
134.16	0.41	171.28	12.32
135.17	0.35	172.26	0.97
136.17	0.42	173.20	0.28
137.19	0.38	174.21	0.24
138.21	0.98	175.22	0.33
139.20	0.39	176.23	0.28
140.24	0.59	177.20	0.29
141.18	0.22	178.24	0.31
142.26	16.61	179.25	0.24
143.27	1.47	180.26	0.28
144.21	0.30	182.26	0.32
145.17	0.28	183.23	0.22
146.20	0.29	184.25	0.23
147.19	0.54		
*148.20	0.36		
149.21	0.40		
150.22	0.36		
151.21	0.28		
152.22	0.52		
153.23	0.46		
154.26	33.71		
155.26	3.88		
156.26	0.69		
158.20	0.26		
159.20	0.23		
160.20	0.24		
161.20	0.34		

No. 10

EI+

GS66814 x1 Bgd=1 20-NOV-89 16:2+0:01:15 70E EI+
BpM=0 I=10v Hm=367 TIC=452894816 Rcnt: Sys:ACE
G. SANOFORD PT= 0° Cal:PFK269
+x1+u

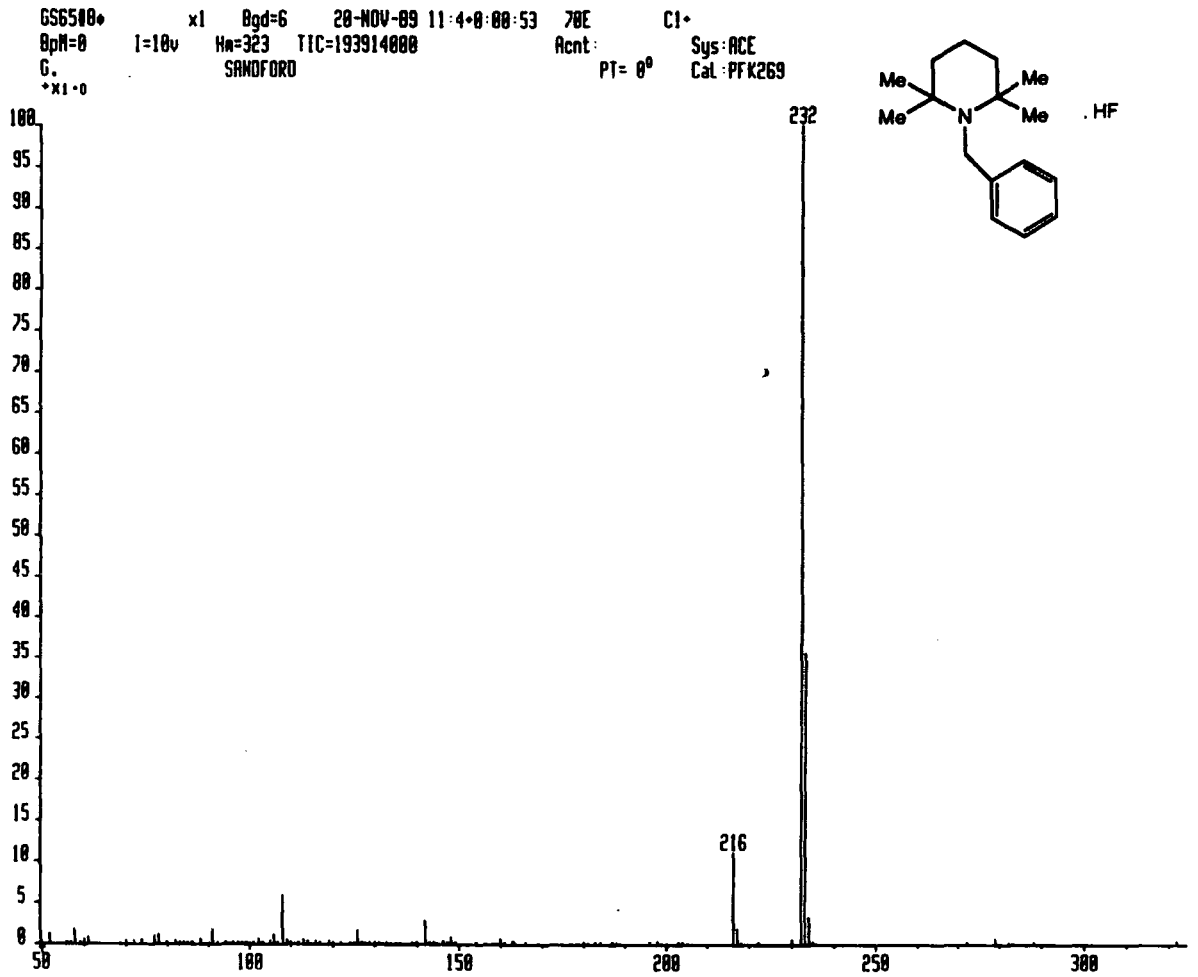


.HF

Mass	% Base				
20.95	1.09	77.90	0.25	180.97	16.41
24.94	0.32	78.91	1.77	181.98	20.27
25.94	2.70	79.91	2.27	182.98	2.67
26.95	12.93	80.92	4.79	366.19	0.36
27.95	4.73 F	81.92	17.97		
27.96	4.15 F	82.93	2.42		
28.97	11.69	83.94	2.47		
29.96	8.57	92.92	1.36		
36.92	0.65	93.91	2.62		
37.93	1.37	94.92	1.81		
38.94	24.74	95.93	6.97		
39.94	4.43	96.93	5.26		
40.95	71.83	97.94	32.55		
41.95	22.71	98.94	2.20		
42.96	4.47	107.92	3.23		
43.96	1.14	108.93	5.30		
44.94	0.47	109.93	72.91		
49.91	0.49	110.93	6.55		
50.92	0.96	111.94	1.05		
51.92	0.57	119.90	0.23		
52.93	5.72	121.91	1.73		
53.93	4.40	122.92	0.68		
54.94	13.23	123.93	2.40		
* 55.94	13.73	124.93	2.79		
* 56.95	2.31	125.94	4.20		
57.95	11.95	149.93	7.55		
58.95	0.37	150.93	0.90		
64.91	1.10	151.95	1.16		
65.91	0.67	153.96	2.27		
66.92	6.54	154.96	0.33		
67.91	3.77	163.94	1.23		
68.93	32.98	164.94	5.69 F		
69.93	6.47	165.97	100.00 F0		
70.93	1.11	166.96	40.71 F		
71.94	1.00	167.96	2.55		
76.90	0.86	179.96	3.98		

No.11

Cl^+

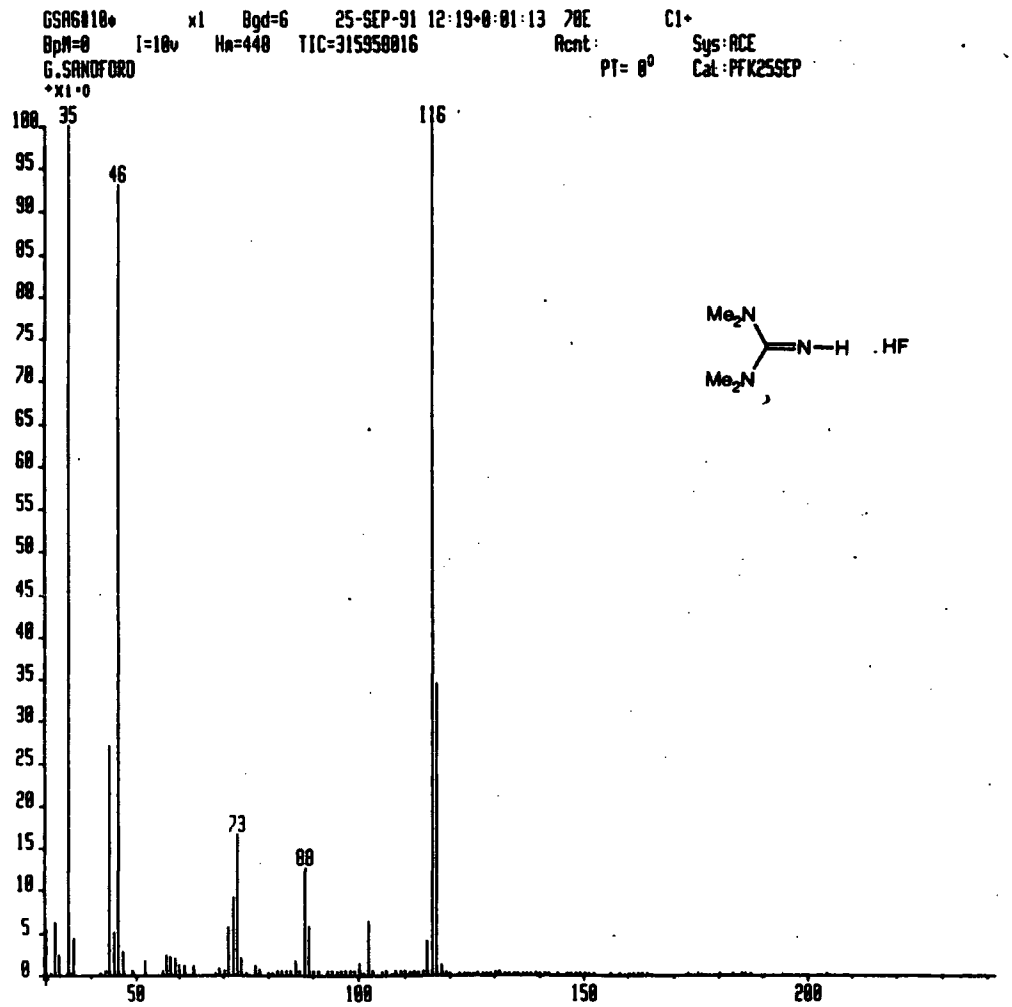


Cl^+ Data

Mass	% Base		Mass	% Base	
29.98	0.24		159.99	0.53	
31.98	1.16		162.85	0.23	
32.99	0.45		198.01	0.27	
35.01	100.00	0	203.04	0.21	
36.00	2.53		216.05	11.14	
43.98	1.12		217.06	1.86	
44.98	0.25		230.07	0.47	
46.00	0.24		232.12	100.00	0
52.01	1.12		233.10	35.66	
57.98	1.68		234.10	3.23	
59.96	0.45		279.05	0.60	
60.95	0.75		322.17	0.25	
69.97	0.29				
71.98	0.30				
73.96	0.43				
76.98	0.95				
77.97	1.02				
79.95	0.20				
81.97	0.32				
87.98	0.56				
90.96	1.62				
98.98	0.21				
101.99	0.56				
105.00	0.37				
105.96	1.11				
107.98	5.75				
108.98	0.51				
112.99	0.42				
113.98	0.27				
115.99	0.31				
119.00	0.26				
126.01	1.51				
138.98	0.21				
142.04	2.75				
145.98	0.28				
147.99	0.70				

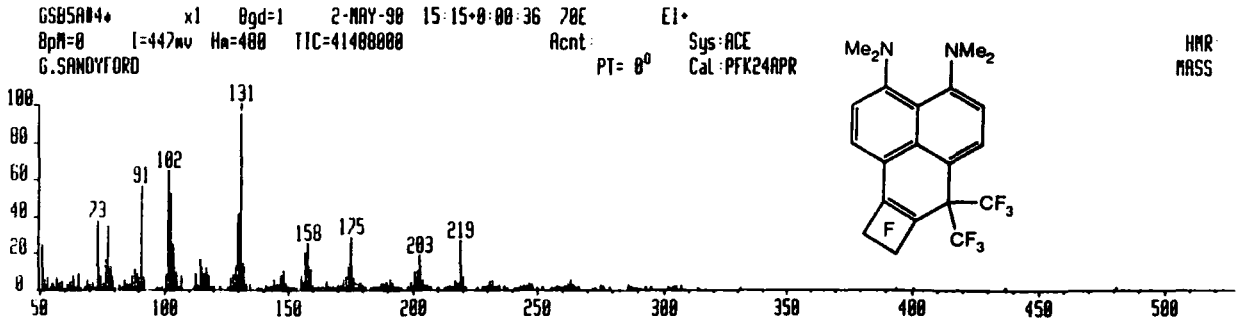
No.12

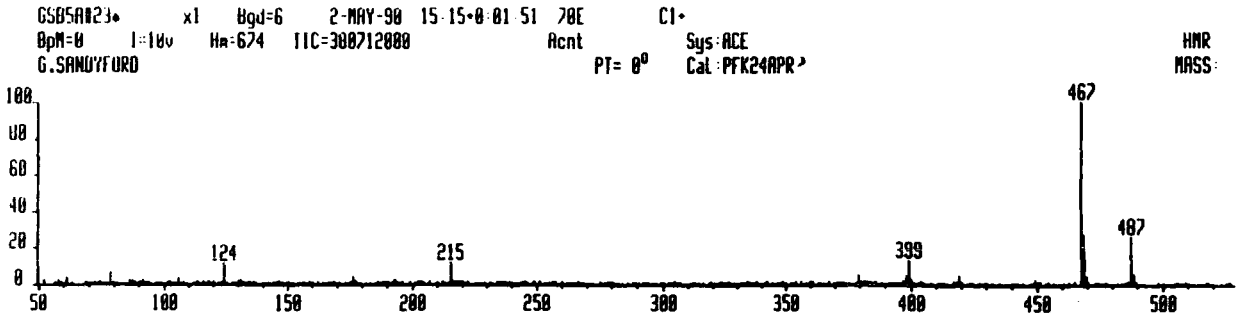
Cl^+

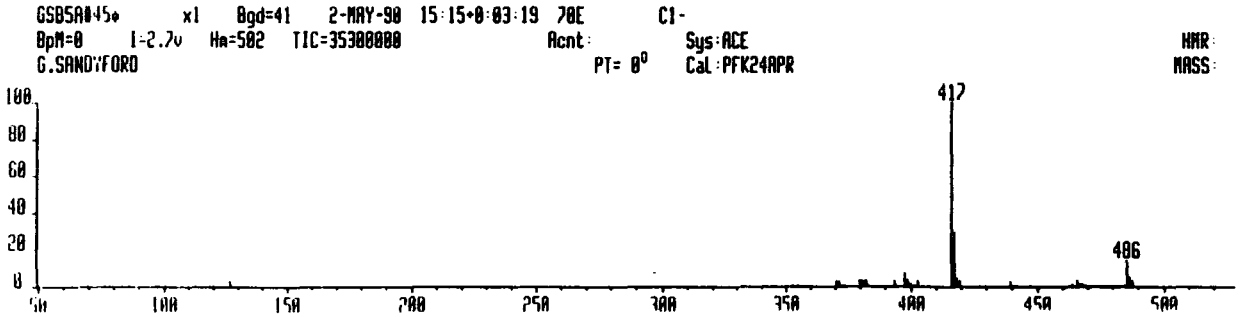


Mass	% Base		Mass	% Base	
43.06	0.47		94.11	0.39	
44.07	26.97		96.12	0.45	
45.08	5.00		97.13	0.38	
46.09	93.00		98.14	0.50	
47.09	2.56		99.13	0.39	
49.10	0.39		100.14	1.36	
52.12	1.64		102.15	6.35	
56.09	0.40		103.16	0.47	
57.08	2.34		106.14	0.38	
58.10	2.11		108.13	0.39	
59.10	1.86		109.14	0.39	
60.08	1.13	F	110.14	0.41	
60.12	1.19	F	112.15	0.39	
61.07	1.02	F	114.17	0.45	
61.12	0.54	F	115.11	3.88	F
63.13	0.98		116.20	100.00	F0
69.09	0.80		117.18	34.42	F
70.10	0.43		118.18	1.17	
71.10	5.48		119.17	0.32	
72.11	9.07		126.17	0.34	
73.12	16.54		131.19	0.39	
74.11	1.84				
77.11	0.97				
78.11	0.52				
82.11	0.43				
83.10	0.43				
84.12	0.49				
85.12	0.40				
86.13	1.54				
87.14	0.41				
88.13	12.58				
89.12	5.73				
90.12	0.37				
91.13	0.39				
93.10	0.45				

No.13 M.Wt. 486 CI^+/CI^-





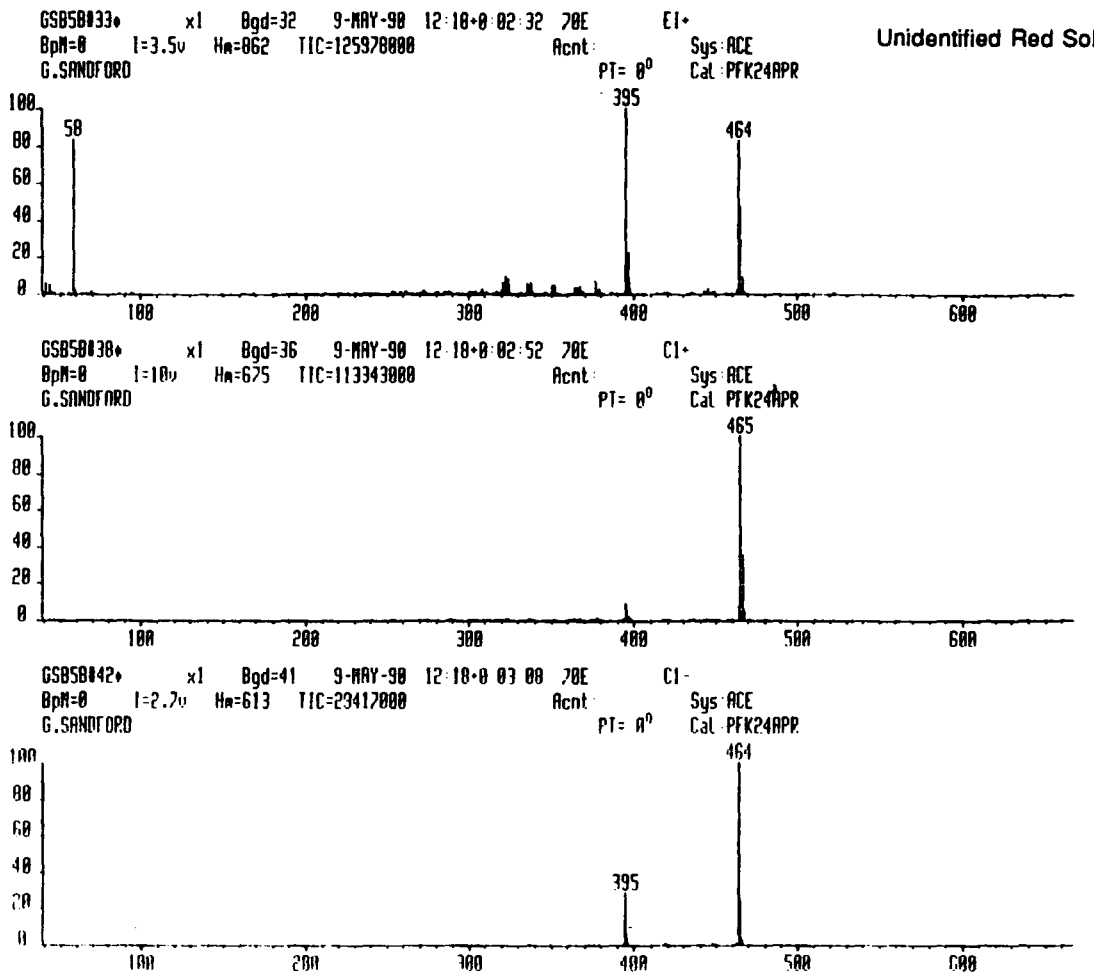


CI^+ Data

Mass	% Base	
397.20	1.42	
398.17	3.70	F
399.18	10.05	F
400.19	2.18	
401.20	0.57	
402.21	0.80	
403.17	0 79	
404.17	0.82	
408.21	0.73	
411.25	0.73	
412.25	0.73	
413.17	0.72	
414.21	0.72	
417.18	1.59	
418.19	1.26	
419.19	3.85	
420.20	1.09	
464.84	1.19	F
467.14	78.65	F
468.16	21.04	F
469.17	3.24	F
470.15	1.04	
474.21	0.72	
477.20	0.72	
485.17	0.76	
486.14	1.17	F
487.14	20.32	F
488.16	4.46	F
489.16	1.12	
498.21	0.70	

No.14 M.Wt. 464 $EI^+/CI^+/CI^-$

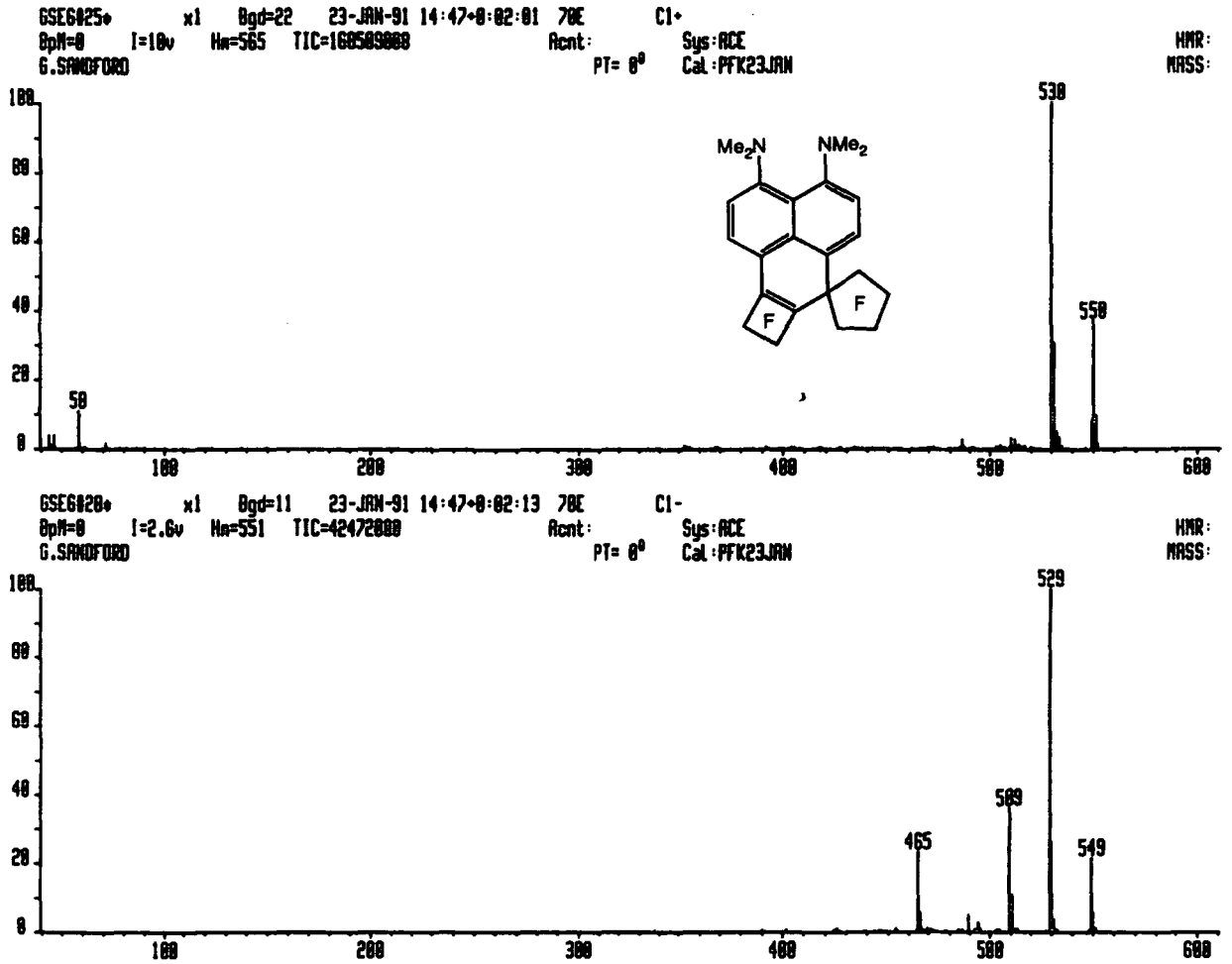
Unidentified Red Solid



EI^+ Data

Mass	% Base
41.99	5.09
44.01	4.95
58.08	82.98
59.09	2.72
308.24	2.47
321.24	6.03
322.25	9.69
323.26	2.90
324.27	7.88
335.25	5.48
336.26	4.96
337.27	6.07
350.24	4.96
351.26	5.00
352.26	4.69
364.27	3.47
365.27	3.13
367.32	4.19
376.31	6.78
377.32	2.35
379.28	2.78
395.32	100.00
396.32	22.62
397.32	2.67
445.33	2.59
• 450.21	0.33
• 455.35	0.07
456.37	0.07
457.34	0.22
458.34	0.23
459.35	0.08
463.31	2.32
463.74	0.05
464.32	82.73
464.86	0.06
465.33	46.51
466.33	9.10
467.34	0.96
468.34	0.08

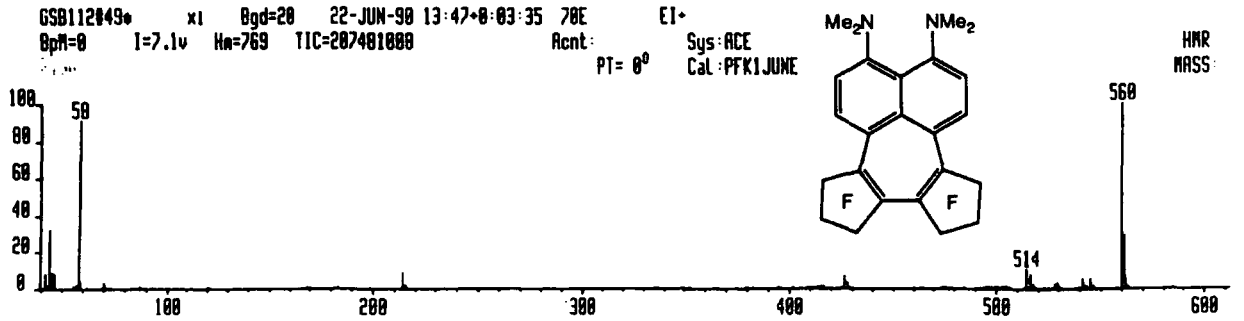
No. 15 M.Wt. 548 CI^+/CI^-

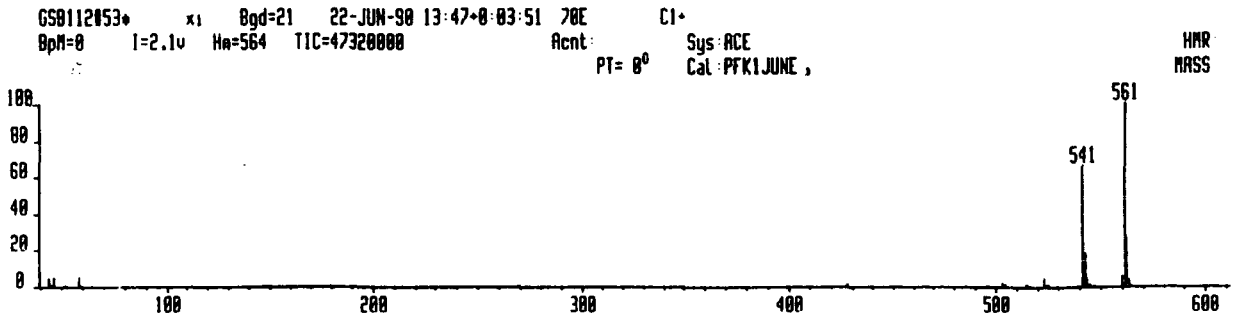


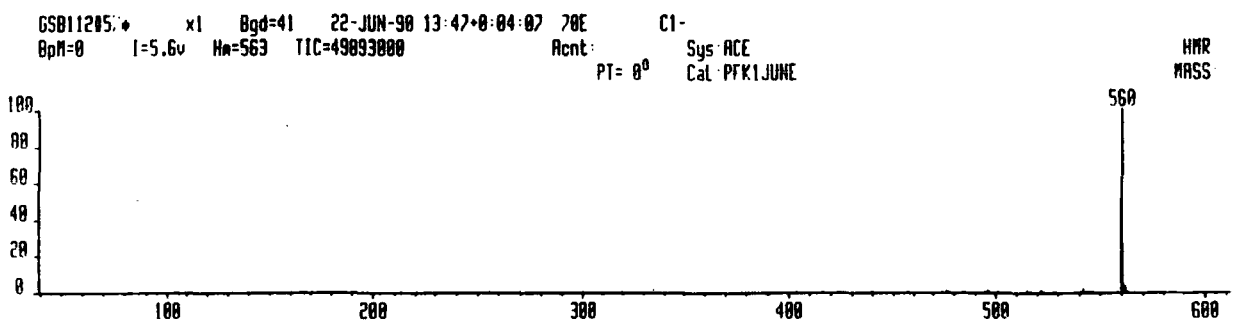
CI^+ Data

Mass	% Base		Mass	% Base	
43.95	3.69		530.23	100.00	FO
44.96	0.67		531.12	30.69	F
45.98	3.52		532.28	5.15	F
58.06	10.89		534.09	3.22	F
59.06	0.47		535.38	0.80	F
71.14	1.26		549.22	7.85	F
72.15	0.39		550.20	36.89	F
352.82	0.60		551.20	9.39	F
353.84	0.44		552.29	1.27	F
367.61	0.44				
368.62	0.39				
391.67	0.41				
403.72	0.39				
404.73	0.39				
417.74	0.39				
426.77	0.35				
433.84	0.40				
471.93	0.39				
484.92	0.39				
485.92	2.34				
486.93	0.65				
490.95	0.39				
491.99	0.39				
502.95	0.61				
503.97	0.39				
504.97	1.23				
505.98	0.39				
506.99	0.31				
510.00	2.91	F			
511.01	0.81	F			
512.05	2.34	F			
513.05	0.59				
514.01	0.92				
515.00	0.30				
516.00	0.39				
517.06	0.78				

No.16 M.Wt. 560 $EI^+/CI^+/CI^-$



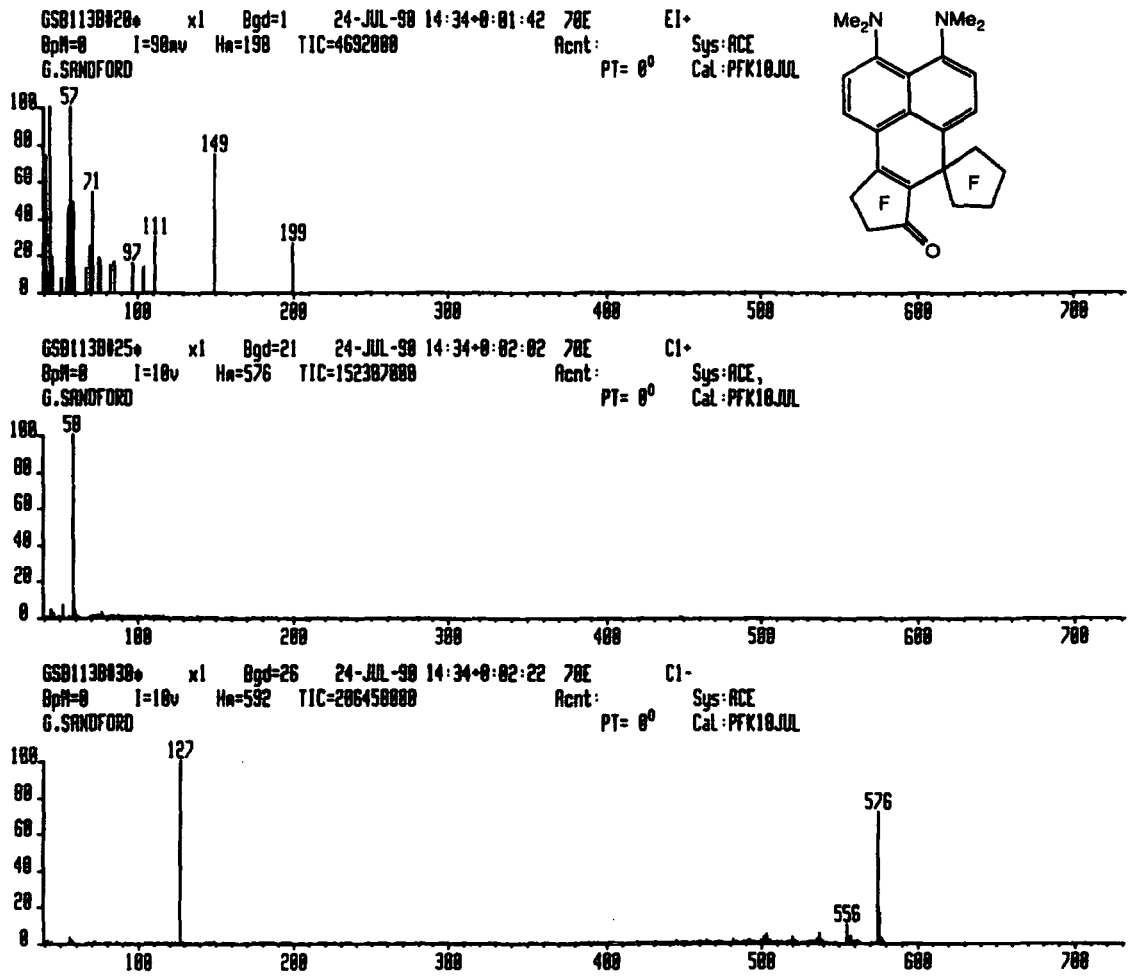




EI^+ Data

Mass	% Base		Mass	% Base	
41.93	7.45		546.29	1.62	
42.95	1.35		547.30	0.16	
43.95	31.78		557.71	0.04	
44.97	7.97		558.01	0.05	
45.98	7.41		558.11	0.10	
57.01	1.62		558.27	0.04	
58.02	90.75		560.12	64.24	F
59.02	3.05		560.37	100.00	F
70.06	2.42		561.32	28.08	F
71.07	0 78		562.33	4.58	
214.14	8.08				
215.15	1.66				
514.20	10.04				
515.10	4.47	F			
515.29	4.95	F			
516.22	7.49				
517.22	1.82				
518.23	0.79				
519.15	0.16				
519.33	0.15				
522.29	0.24				
523.24	0.07				
525.13	0.07				
525.31	0.19				
527.20	0.17				
528.20	2.34				
529.21	2.57				
530.20	1.05				
531.24	0.24				
538.29	0.15				
539.25	0.17				
540.35	0.11				
541.29	4.91				
542.31	1.37				
543.28	0.53				
544.29	0.22				
545.27	4.43				

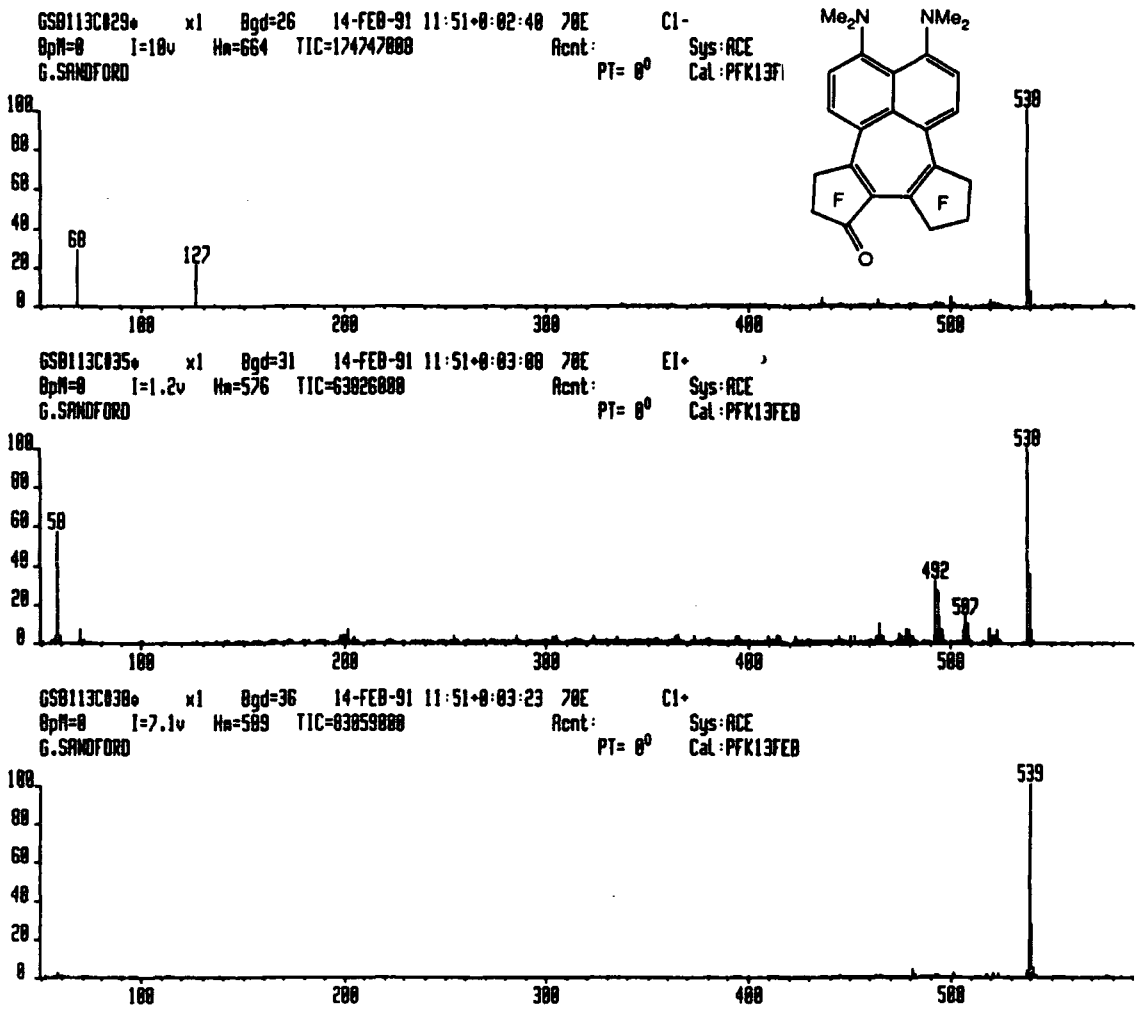
No.17 M.Wt. 576 $EI^+/CI^+/CI^-$



CI^- Data

Mass	% Base	
40.95	0.49	
41.93	1.21	
43.94	0.47	
55.97	3.49	
56.96	1.12	
57.95	1.17	
71.95	0.53	
85.95	0.42	
126.76	100.00	O
127.88	0.42	
147.82	0.51	
169.81	0.34	
419.62	0.56	
421.65	0.32	
431.62	0.36	
530.52	0.51	
532.53	0.55	
533.57	0.34	
535.58	1.86	
536.54	2.39	F
537.55	5.57	F
538.54	1.89	
539.56	1.36	
555.54	10.10	
556.54	3.25	
557.55	4.24	
558.55	0.84	
559.52	1.07	
560.48	0.51	
561.51	1.03	
575.52	71.71	F
576.54	17.57	F
577.54	2.93	
578.54	0.50	
591.56	0.32	

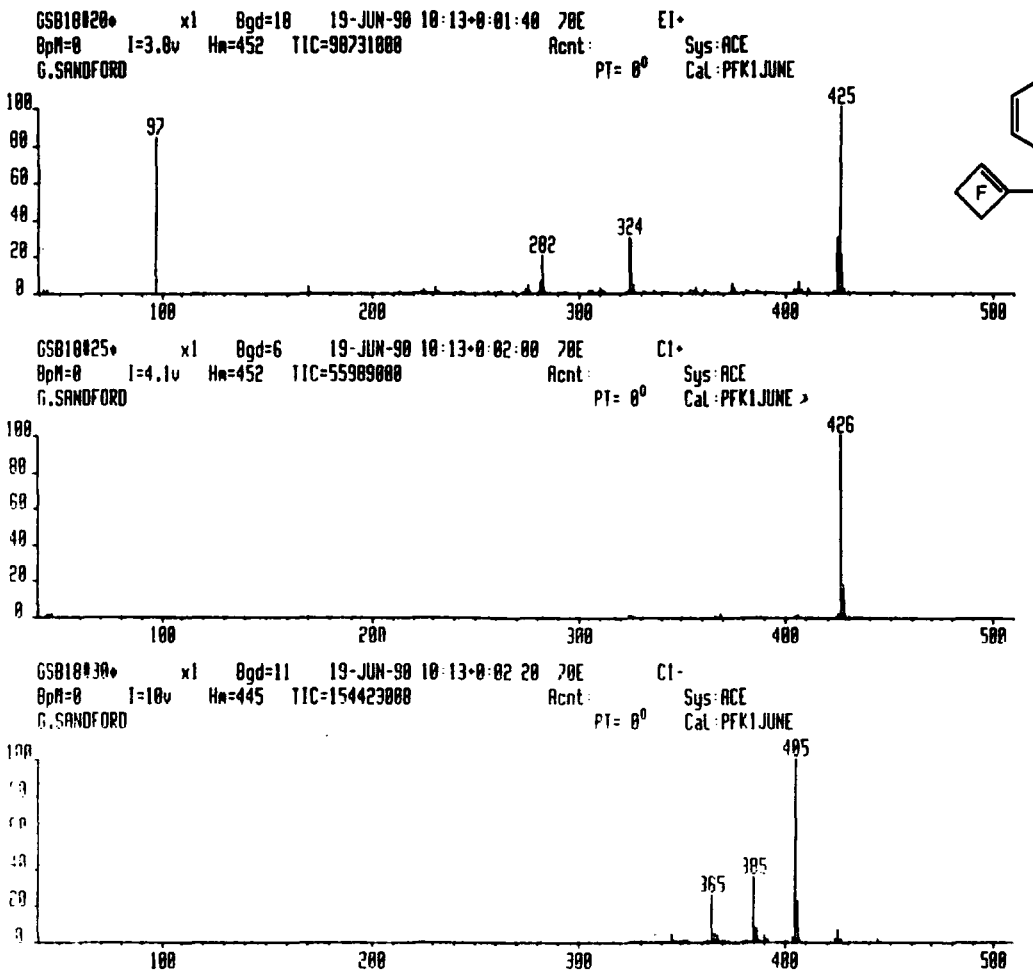
No.18 M.Wt. 538 $EI^+/CI^+/CI^-$



CI^+ Data

Mass	% Base	
43.89	7.11	
44.89	0.80	
45.90	8.41	
48.90	0.48	
51.91	0.55	
57.87	1.68	
59.88	0.55	
69.84	0.31	
445.10	0.55	
463.11	0.45	
465.11	0.58	
481.05	3.75	F
482.59	1.09	F
492.04	0.40	
493.05	0.55	
501.13	1.64	
518.23	1.09	F
521.12	1.74	F
523.98	1.64	F
538.08	3.00	F
539.13	100.00	F
540.13	27.20	F
541.14	4.25	F
542.82	0.55	F
577.16	0.55	

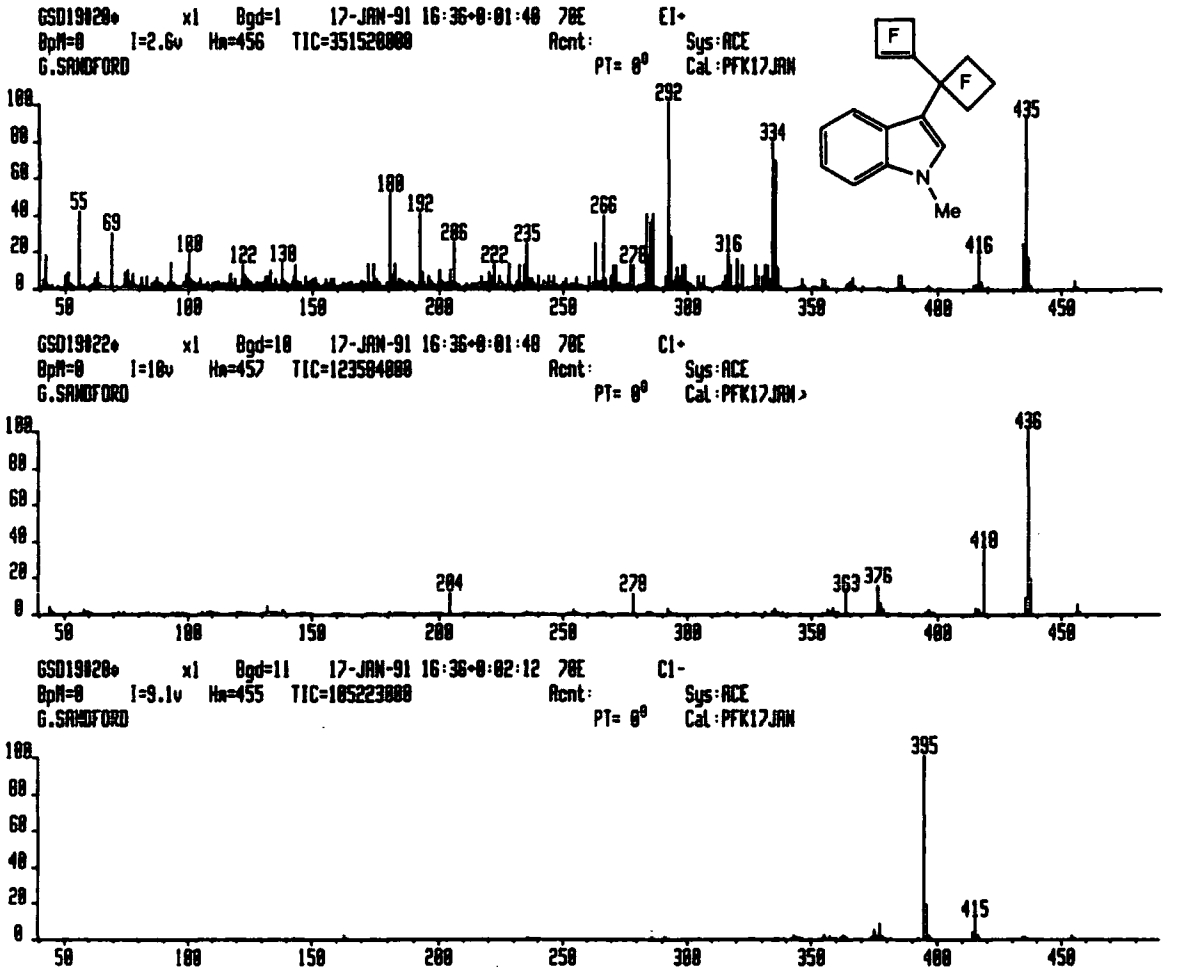
No.19 M.Wt. 425 $EI^+/CI^+/CI^-$



EI^+ Data

Mass	% Base
41.97	1.20
43.99	1.16
97.40	93.87
170.22	3.59
224.26	0.92
225.26	1.34
231.22	2.57
232.26	0.72
256.30	0.81
268.28	0.89
274.29	2.03
275.30	4.18
281.26	6.41
282.31	19.95
283.32	2.65
293.28	0.55
304.32	0.93
305.33	1.18
306.34	1.44
309.31	0.54
310.32	2.59
311.31	1.04
312.30	0.86
323.31	0.50
324.32	29.64
325.33	28.28
326.33	4.05
331.32	0.84
336.37	0.59
354.37	1.36
355.38	0.92
356.39	2.58
361.34	1.07
374.40	4.46
375.41	2.23
381.37	0.70
386.42	0.55
404.42	1.52
405.44	1.30
406.44	5.64
407.45	1.07
410.42	1.94
422.44	0.82
423.44	0.58
424.44	29.80
425.45	100.00
426.46	20.55
427.47	1.98
451.52	0.77

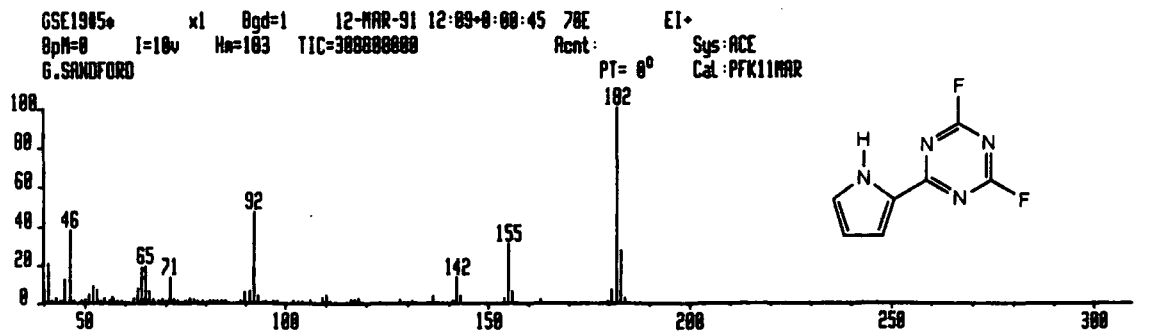
No. 20 M.Wt. 435 $EI^+/CI^+/CI^-$

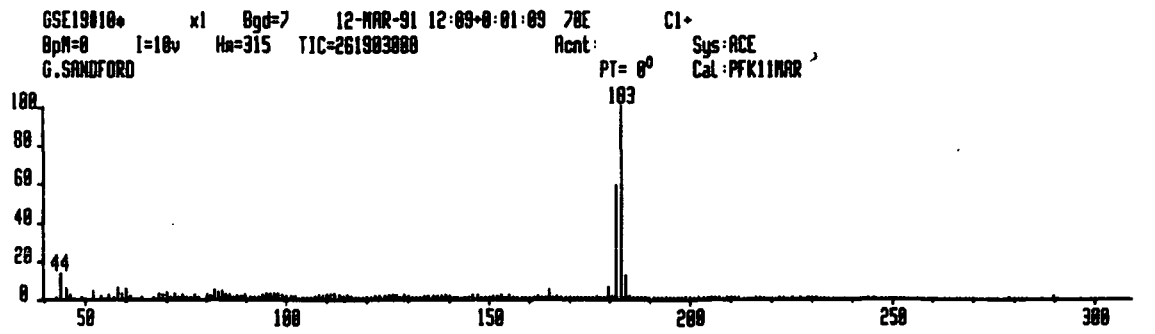


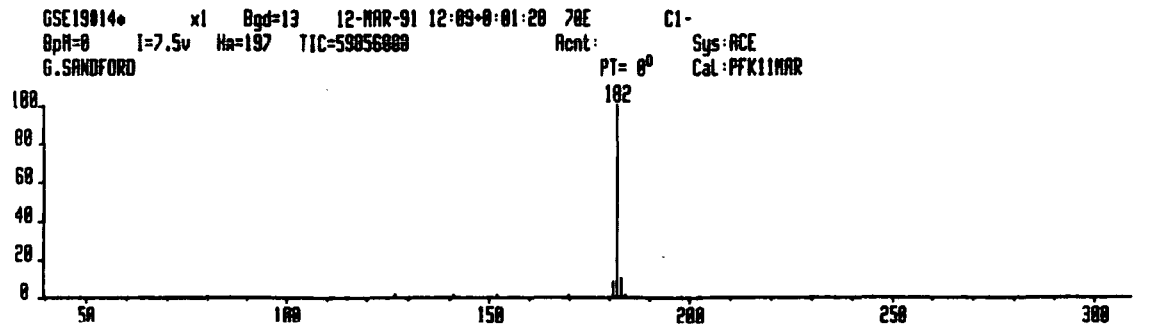
CI^+ Data

Mass	% Base	
43.96	0.90	
44.96	0.39	
58.03	0.50	
132.14	1.19	
138.17	0.55	
204.22	3.05	
254.20	0.51	
278.28	3.05	
292.25	0.78	
334.29	0.43	
335.29	0.79	
356.28	0.59	
358.30	0.71	
363.36	3.07	
376.32	4.34	
377.33	1.54	
378.34	0.60	
396.37	0.55	
415.38	0.68	
416.38	0.58	
418.36	10.08	
435.31	2.48	F
436.42	28.55	F
437.50	5.48	F
456.46	1.40	

No.21 M.Wt. 182 $EI^+/CI^+/CI^-$



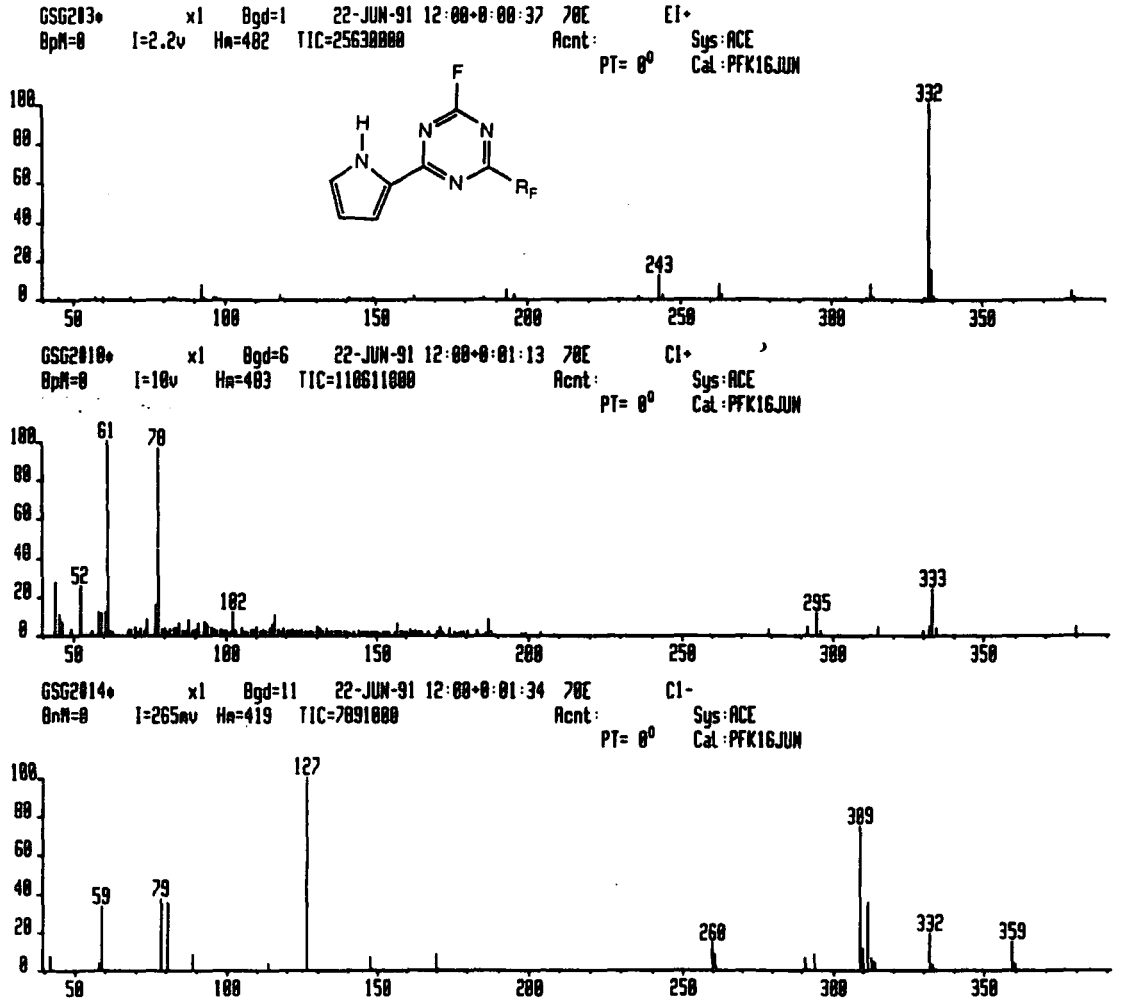




EI^+ Data

Mass	% Base	
40.01	6.66	
41.01	19.60	
43.04	2.15	F
44.98	11.51	F
45.02	2.00	F
45.99	36.95	
50.99	3.73	
52.00	8.63	
52.99	6.63	
55.03	2.06	F
56.98	2.49	F
61.98	2.01	
62.98	6.81	
63.99	18.09	
65.00	18.39	
66.00	5.53	
70.97	13.05	
89.95	5.34	
90.97	5.85	
91.99	46.90	
92.99	3.38	
108.97	2.77	
109.97	3.60	
135.95	3.38	
141.94	12.81	
142.94	2.98	
153.93	2.18	
154.94	30.42	
155.94	5.60	
180.93	6.68	
181.94	100.00	0
182.94	26.61	
183.94	1.81	

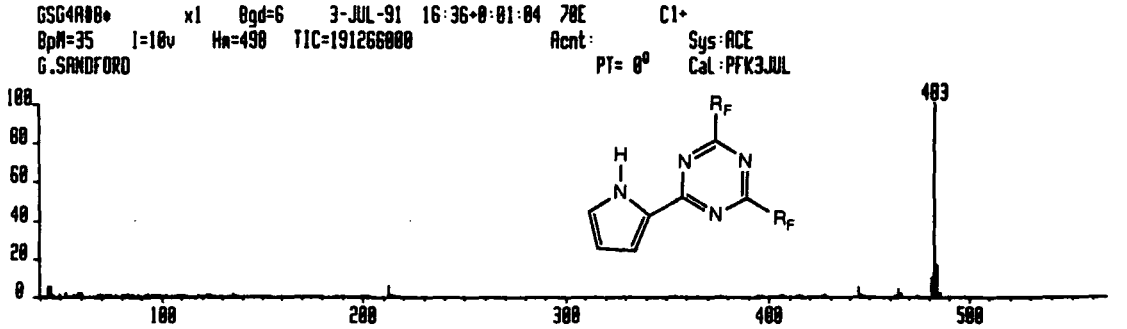
No. 22 M.Wt. 332 $EI^+/CI^+/CI^-$

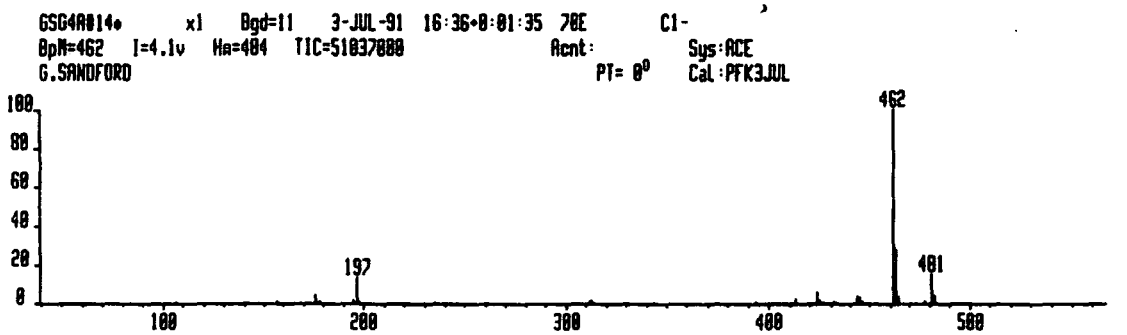


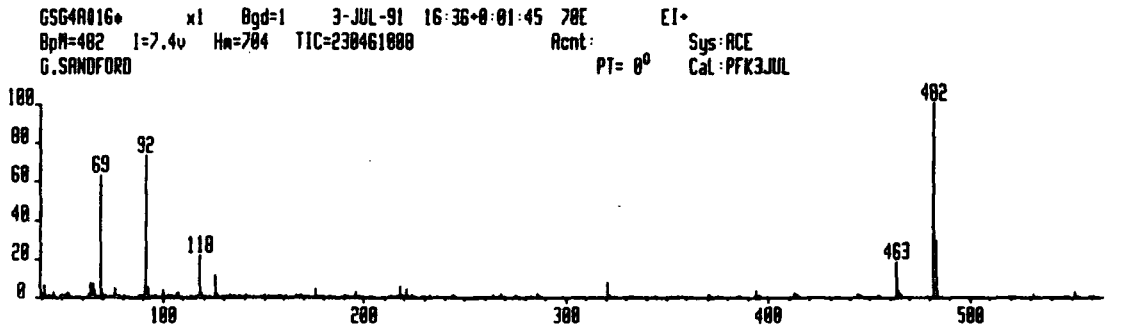
EI^+ Data

Mass	% Base
45.02	0.59
57.06	0.52
60.02	0.46
69.05	0.37
81.91	0.39
83.06	0.39
92.01	6.99
93.02	0.89
96.06	0.38
97.07	0.39
118.01	2.02
119.01	0.32
141.00	0.39
149.00	0.92
163.01	1.01
185.97	0.62
192.99	4.18
195.96	1.64
235.98	0.54
236.19	0.55
243.00	11.60
244.00	2.12
263.01	6.90
264.01	1.77
*304.98	0.45
312.03	0.62
313.02	7.04
314.04	0.68
331.01	0.42
332.02	100.00
333.03	15.01
334.03	1.23
379.08	4.06
380.09	0.75
424.09	1.58
439.14	0.52
482.06	1.61

No. 23 M.Wt. 482 $EI^+/CI^+/CI^-$



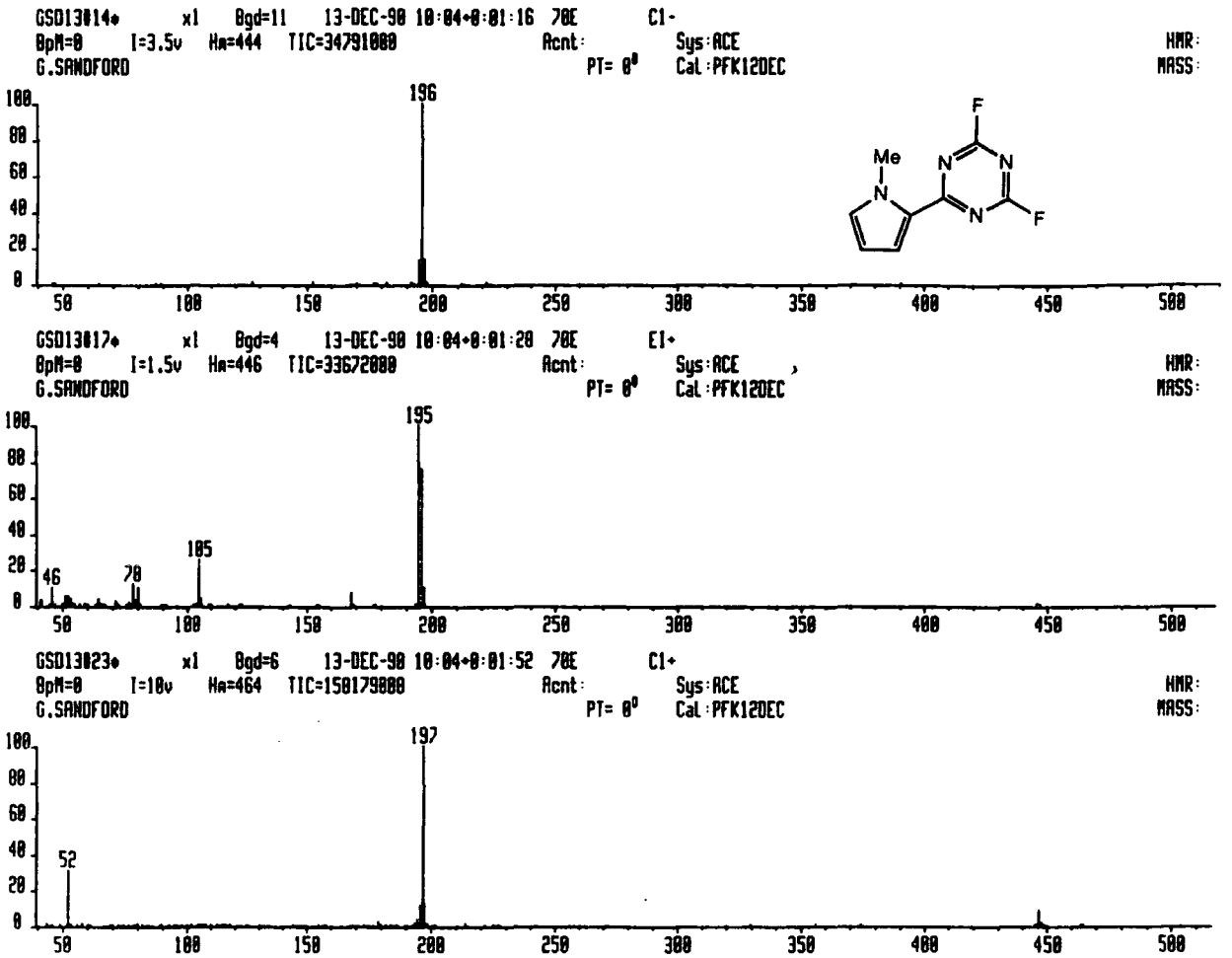




EI^+ Data

Mass	% Base		Mass	% Base	
40.03	1.65		413.11	1.62	
41.03	5.75		414.11	1.16	
46.01	2.49		415.13	0 25	
52.02	2.18		425.09	0.09	
53.01	1.94		433.05	0.16	
63.01	1.66		434.06	0.13	
64.02	7.11		444.11	1.17	
65.02	6.75		445.11	0.39	
66.03	3.45		446.12	0.14	
68.99	62.68		454.09	0.47	
70.00	1.62		455.09	0.09	
76.00	4.35		463.11	18.03	F
91.03	4.21		464.15	3.46	F
92.04	73.22		465.15	1.37	
93.03	5.09		466.16	0.27	
99.99	3.23		478.72	0.06	
107.00	2.19		482.08	100.00	F
108.01	1.62		483.11	29.01	F
118.05	21.36		484.24	3.33	F
119.03	1.87		486.04	0.06	
126.00	10.71				
127.01	1.00				
133.01	1.06				
176.01	3.78				
196.02	2.71				
218.06	5.29				
221.02	3.78				
268.07	1.52				
286.07	1.60				
321.05	7.26				
371.04	1.49				
394.10	3.07				
412.09	0.08				

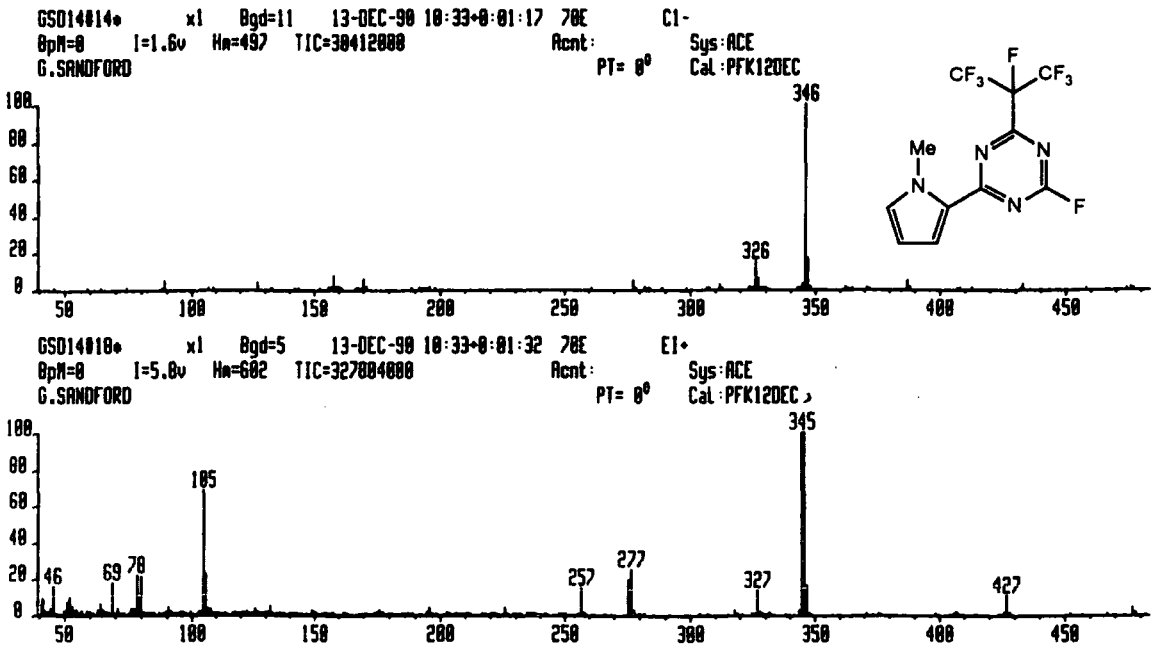
No. 24 M.Wt. 196 $EI^+/CI^+/CI^-$



EI^+ Data

Mass	% Base		
25.73	1.02	80.97	0.50
26.74	2.77	89.92	0.44
27.74	3.02	90.92	0.81
30.73	1.34	91.93	0.51
36.77	1.22	95.94	0.32
37.78	2.56	102.92	0.80
38.79	5.38	103.92	0.76
39.79	0.98	104.94	25.58
40.81	2.63	105.94	3.88
41.82	3.55	108.91	0.59
44.80	0.51	109.92	0.54
45.81	10.35	116.86	0.58
46.82	0.37	116.90	0.63
49.84	1.60	121.89	0.40
50.85	5.12	122.93	0.47
51.86	5.25	142.89	0.49
52.87	4.19	153.85	0.86
53.88	1.43	154.84	0.34
54.89	0.89	154.88	0.66
56.85	0.46	167.87	7.68
58.88	1.09	168.88	0.68
59.89	0.55	176.85	0.39
62.89	0.69	176.91	0.48
* 63.90	4.16	193.87	1.07
64.92	1.21	194.20	0.39
65.92	0.71	194.62	0.36
66.92	0.41	194.84	100.00
66.93	0.38	195.85	75.37
70.91	2.56	196.86	10.43
71.93	0.65	197.85	0.61
74.92	0.75	445.73	1.18
75.93	1.83	446.72	0.41
76.94	1.00		
77.95	12.18		
78.95	3.24		
79.97	10.24		

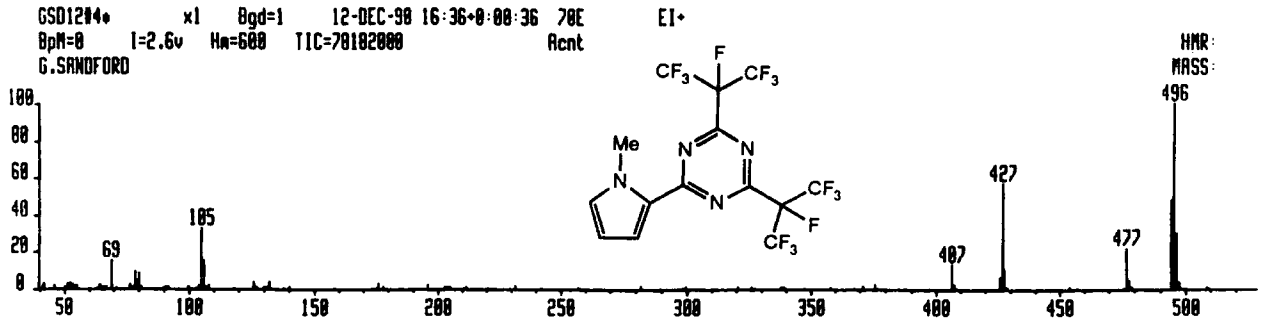
No.25 M.Wt. 346 EI^+/Cl^-

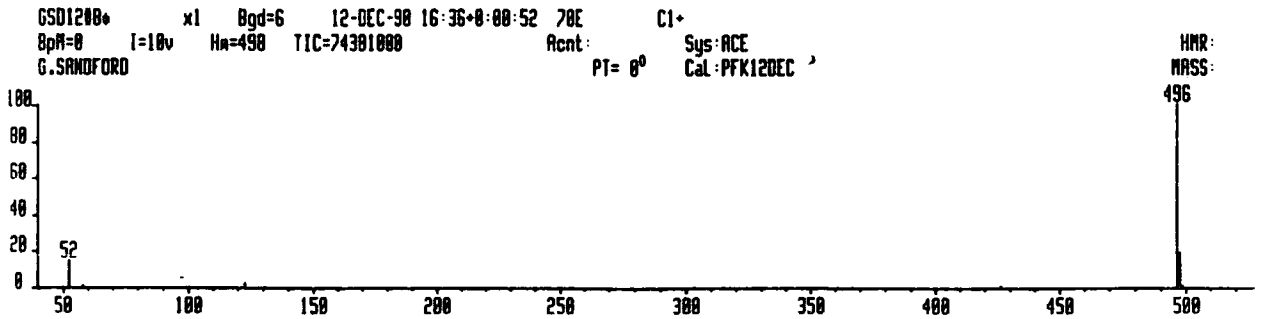


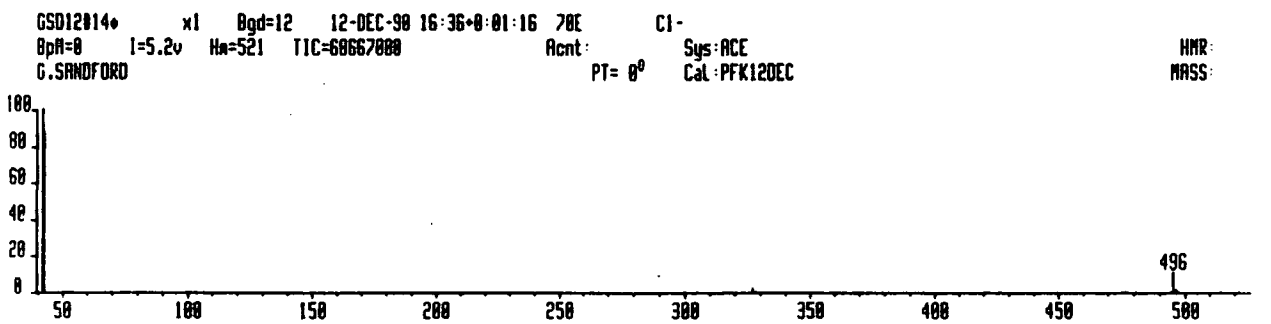
Cl^- Data

Mass	% Base		Mass	% Base
25.71	2.95		361.93	1.62
45.81	0.70		362.88	0.76
58.89	0.36		364.69	0.90
63.86	0.50		370.93	0.75
73.95	0.41		371.92	0.32
88.00	0.50		386.87	4.89
88.96	4.89			
106.94	0.80			
108.96	0.38			
126.82	3.70			
126.92	0.52			
132.89	0.41			
141.94	0.72			
143.89	0.58			
151.86	0.54			
155.89	1.35			
156.88	0.97			
156.92	1.29			
157.90	7.34			
158.90	1.32			
323.84	0.86			
323.98	1.24			
324.78	0.78			
325.81	15.10	F		
325.96	11.19	F		
326.12	0.50			
326.87	6.06			
327.85	0.71			
328.00	0.70			
328.92	0.63			
329.01	0.41			
329.88	0.71			
342.83	0.50			
343.27	0.44			
343.78	0.73			
344.82	2.46			
345.85	100.00			
346.36	0.46			
346.77	17.13	F		
346.95	14.91	F		
347.71	0.97			
347.87	1.01			
348.01	1.02			

No. 26 M.Wt. 496 $EI^+/CI^+/CI^-$







EI^+ Data

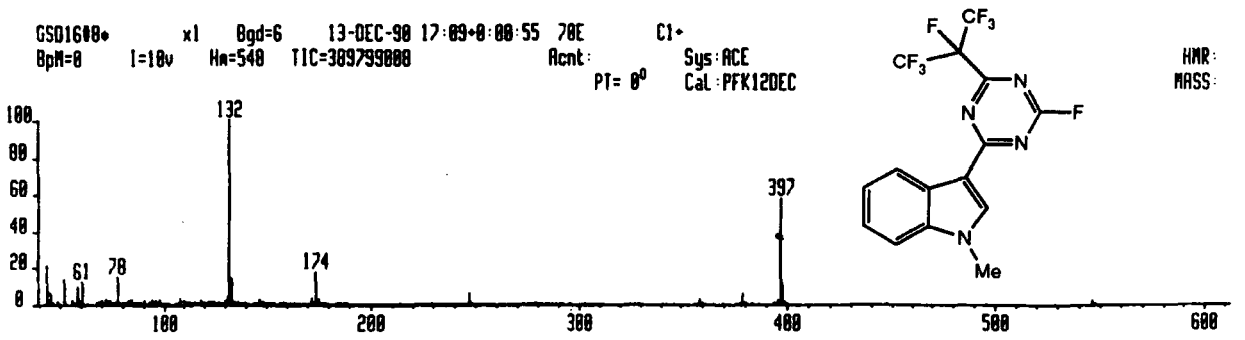
Mass	% Base
26.75	1.32
27.75	1.62
37.79	0.66
38.80	3.80
40.82	1.14
41.83	2.98
45.82	1.49
49.85	0.49
50.86	2.38
51.87	3.02
52.89	1.77
53.89	0.71
54.90	1.49
63.91	2.26
64.92	0.83
65.94	0.86
66.94	0.56
68.91	14.92
75.94	1.85
76.96	0.82
77.96	8.61
78.97	3.94
79.98	7.92
80.99	0.45
90.95	0.52
91.96	0.66
99.91	0.94
103.95	1.49
104.95	32.11
105.96	14.98
106.95	0.91
107.92	1.02
125.89	3.25
126.91	0.51
129.93	0.65
130.94	0.70
131.94	3.30
132.93	0.33
139.90	0.60
175.85	2.98
177.89	0.63
195.84	2.04
202.86	0.44
203.88	0.55
204.87	0.48
210.89	0.32
211.87	0.91
231.86	1.57
241.84	0.31
256.85	0.47
281.80	1.07
298.80	0.31
299.79	0.50
320.81	0.79
325.82	0.75
326.81	0.32
337.77	0.75
338.79	0.40
357.76	0.51
370.67	1.52
375.73	1.90
406.71	12.52
407.72	2.25
425.68	5.96
426.69	56.89
427.70	10.01
428.69	0.62
453.72	0.49
456.72	0.32
476.66	21.93
477.68	4.13
478.68	0.78
494.60	47.88 F
495.64	100.00 F
496.64	29.81
497.64	3.25

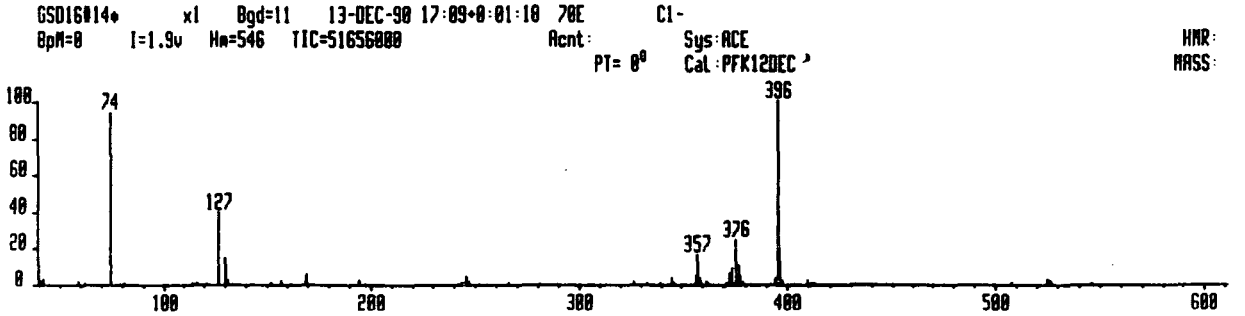
No.27 M.Wt. 246 EI^+/CI^+

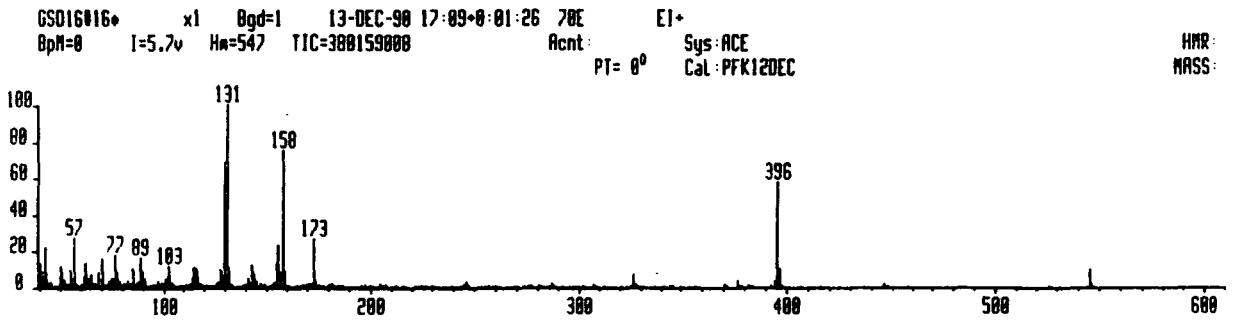
CI^+ Data

Mass	% Base	
45.86	0.39	
117.75	0.78	
129.73	0.78	
130.72	0.39	
154.71	1.17	
158.75	0.39	
169.75	0.79	
183.75	0.78	
201.77	0.77	
203.71	0.40	
204.70	0.45	
217.64	0.78	
224.69	1.56	
226.74	0.41	
228.68	0.79	
239.70	2.54	
242.06	2.55	F
243.74	0.78	F
244.69	2.58	F
245.72	25.24	F
246.74	100.00	FO
247.76	17.23	F
248.94	1.56	F
261.78	0.39	
288.78	0.39	

No. 28 M.Wt. 396 $EI^+/CI^+/CI^-$



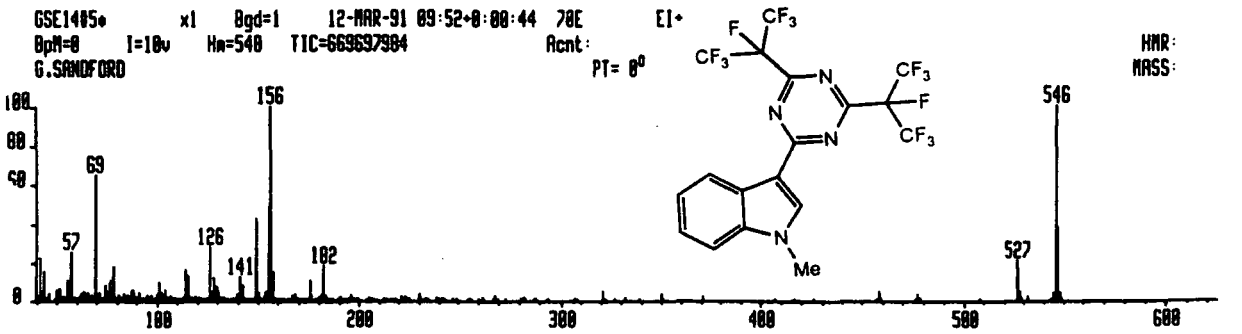


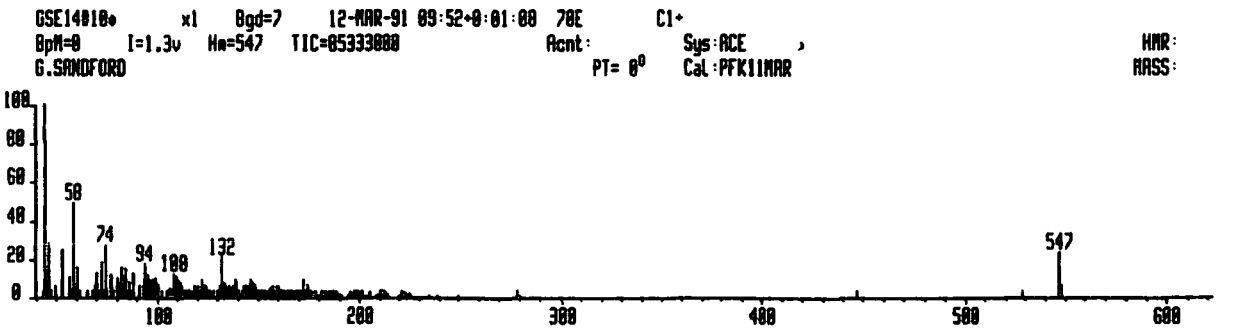


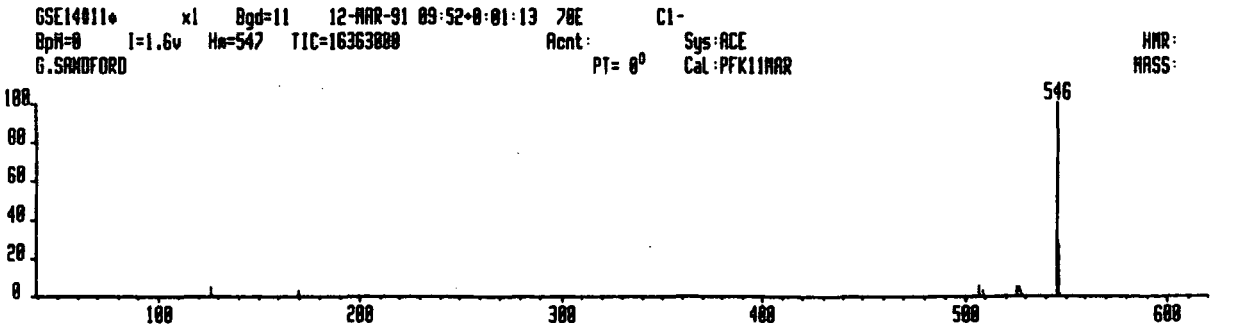
EI^+ Data

Mass	% Base		Mass	% Base		Mass	% Base	
68.89	8.41	F	99.91	1.25		171.92	2.06	
68.97	5.84	F	100.42	1.29		172.93	26.19	
69.97	3.77		100.92	4.59		173.93	3.66	
70.98	15.43		101.93	6.00		174.92	0.50	
71.44	0.80		102.94	11.31		226.83	0.49	
71.96	0.98		103.94	2.75		229.83	0.75	
72.45	1.07		112.97	2.19		230.86	0.30	
72.94	1.38		113.92	5.60		238.99	0.31	
73.92	3.64		114.93	10.60		244.82	1.07	
74.93	5.03		115.93	9.98		245.82	3.00	
75.93	4.84		116.93	5.29		326.78	6.72	
76.95	17.50		117.93	2.08		327.76	1.13	
77.44	0.90		125.90	2.08		344.70	0.42	
77.95	8.08		126.91	2.45	F	345.71	0.55	
78.45	1.78		127.01	1.61	F	370.67	1.38	
78.96	3.65		127.92	9.44		376.69	3.59	
79.97	0.69		128.93	6.32	F	377.70	0.95	
80.98	2.06		129.93	68.03	F	381.66	0.60	
81.99	1.67		130.94	100.00		392.70	0.39	
83.00	3.70		131.93	10.57		394.48	3.27	F
84.00	2.14		132.92	1.18		395.67	57.42	F
85.01	10.22		136.98	0.33		396.69	10.27	F
85.46	0.46		138.93	0.54		397.69	0.87	
85.95	1.45		139.91	1.67		445.77	1.14	
86.46	0.90		140.92	4.61				
86.93	2.82		141.91	2.87				
87.93	3.63		142.92	12.08				
88.94	15.95		143.92	6.75				
89.94	9.10		144.92	3.24				
90.95	4.58		153.90	2.46				
91.95	0.73		154.89	12.88				
92.96	0.73		155.90	23.03				
93.96	0.39		156.91	7.79				
94.97	1.15		157.92	75.31				
95.97	1.10		158.92	9.35				
96.99	3.07							
97.97	1.24							
98.99	2.95							

No. 29 M.Wt. 546 $EI^+/CI^+/CI^-$



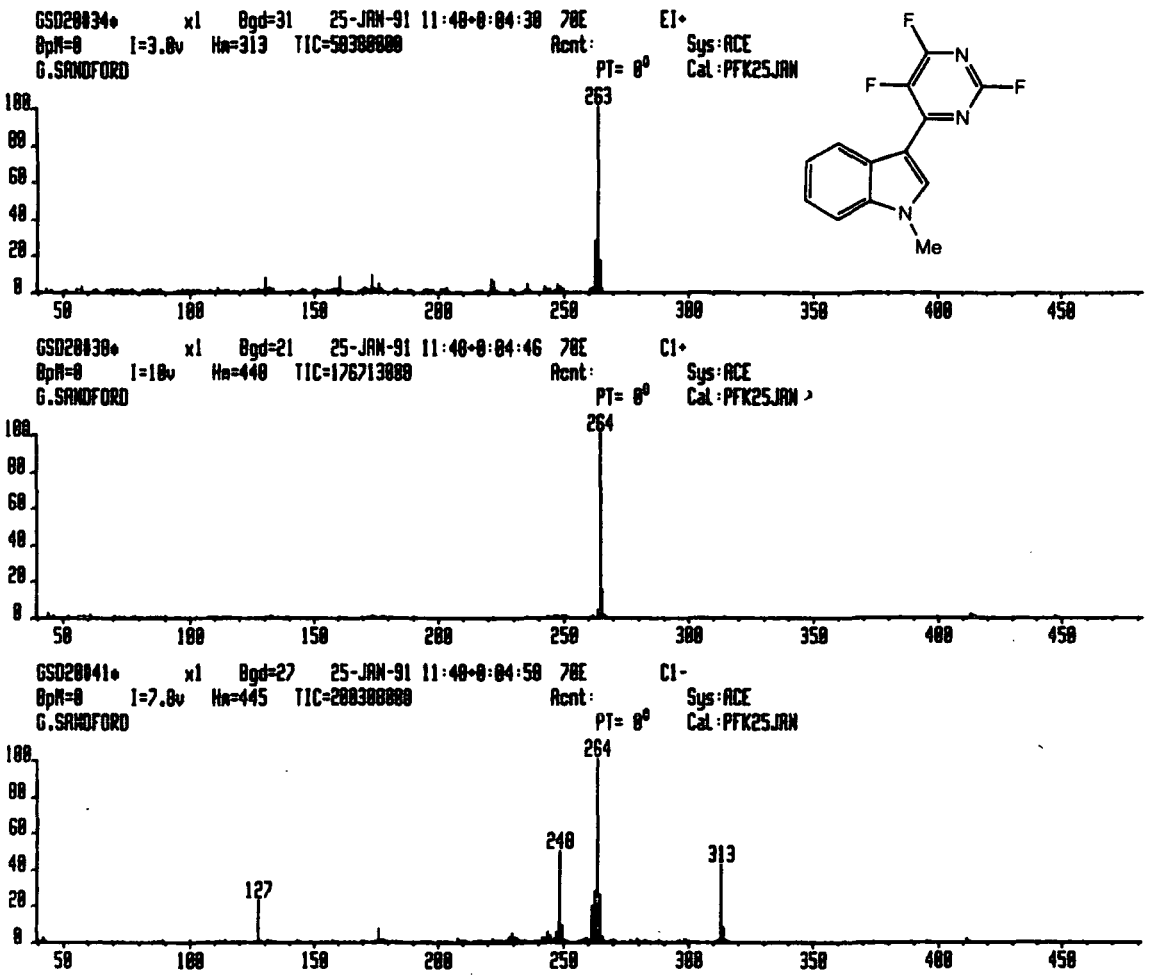




EI^+ Data

Mass	% Base		Mass	% Base		Mass	% Base	
68.97	64.44	F	103.01	2.73		156.01	100.00	0
69.06	5.74	F	103.99	5.78		157.02	14.66	
69.98	1.06	F	105.01	1.61		158.01	1.17	
70.06	2.34	F	106.95	2.35	F	166.99	2.79	
70.98	1.56	F	107.98	1.58		168.02	3.13	
71.07	4.10	F	109.07	1.43		168.92	1.19	F
73.02	1.56		111.08	1.48		175.48	10.43	
74.01	7.70		112.98	1.97	F	175.96	2.69	
75.00	4.19		113.99	16.03		180.00	1.98	
75.97	8.90	F	115.00	12.78		181.00	3.11	
76.01	7.44	F	116.00	1.87		182.01	17.91	
77.01	10.43		117.02	1.15		183.01	2.27	
77.51	1.17		118.95	1.88	F	457.95	4.40	
78.01	17.21		119.05	1.92	F	458.94	1.17	
78.51	1.99		120.98	1.17	F	476.95	3.34	
79.03	1.56		125.96	27.39		477.96	1.17	
81.04	2.39	F	126.98	4.69	F	507.94	0.61	
82.03	1.56		128.01	11.51		526.94	20.64	
83.06	3.02		129.01	6.78		527.94	4.78	
84.06	1.23		130.03	5.24		528.95	1.56	
85.06	2.78	F	130.94	1.97	F	531.93	1.91	
87.00	5.30		131.03	1.19	F	543.88	0.78	F
87.99	5.26		132.00	1.17		544.80	3.91	F
89.00	2.12		139.01	1.03		545.90	100.00	F0
91.01	3.93		139.99	2.97		546.93	37.54	F
93.00	1.56		141.00	12.03		547.94	3.60	
95.04	2.29		142.02	7.42		548.95	0.39	
96.06	1.23		143.03	1.22				
97.06	2.73		148.98	42.34				
98.98	1.05	F	149.98	3.93				
99.97	3.39		152.99	2.73				
101.00	9.72		153.96	4.27	F			
102.00	4.81		154.18	1.17	F			
			154.99	49.01	F			

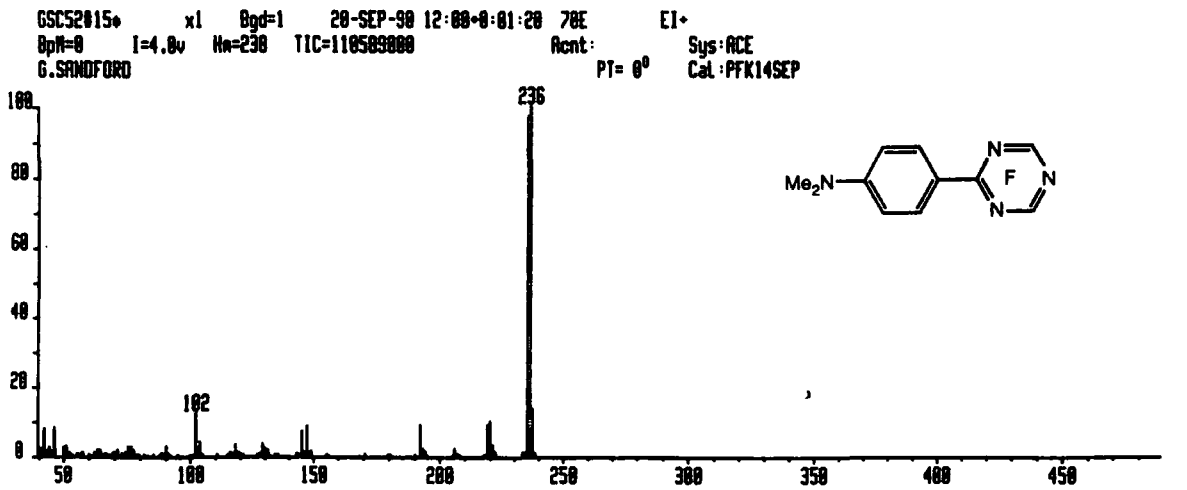
No.30 M.Wt. 263 $EI^+/CI^+/CI^-$

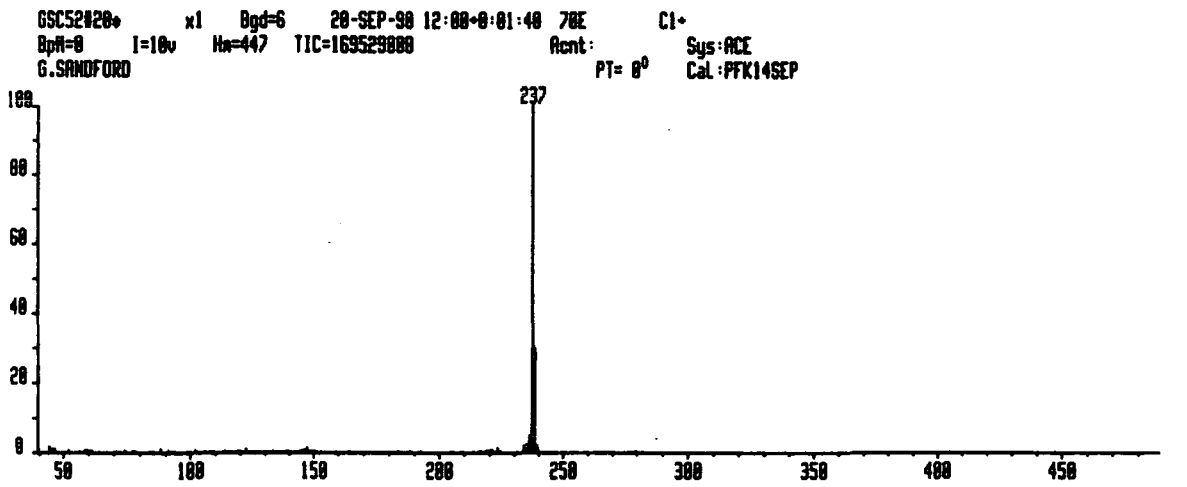


EI^+ Data

Mass	% Base		
151.28	0.44	217.32	0.64
152.29	0.52	220.29	0.32
155.31	0.38	221.30	6.49
156.30	0.52	222.30	5.73
157.28	1.30	223.31	0.85
158.29	1.30	228.31	1.30
159.31	1.03	229.32	0.61
160.32	7.79	234.32	0.40
161.33	0.67	235.32	3.90
163.28	0.33	236.33	0.49
168.28	0.38	242.33	2.93
169.27	0.38	243.33	1.30
170.30	2.09	244.34	1.30
171.29	1.30	246.33	0.44
172.30	0.49	247.31	3.90
173.33	9.00	248.32	2.72
174.33	1.30	249.32	1.30
175.28	0.60	260.32	1.30
176.28	3.91	261.37	1.78
177.29	1.30	262.33	27.62
182.28	0.47	263.35	100.00
183.29	1.30	264.35	16.63
188.28	0.64	265.35	1.30
189.29	0.51		
190.30	0.30		
194.27	0.65		
195.28	1.66		
196.29	0.49		
197.30	0.49		
198.30	0.51		
201.28	1.30		
202.29	1.30		
203.30	1.70		
215.31	0.71		
216.31	0.34		

No. 31 M.Wt. 236 EI^+/CI^+

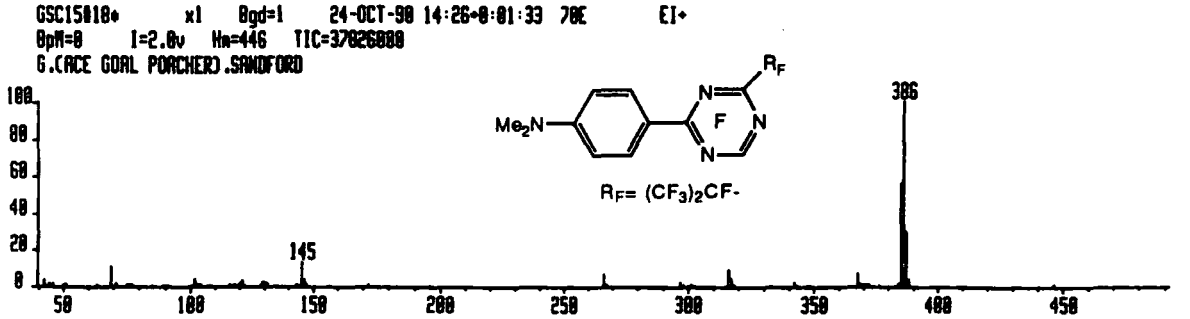


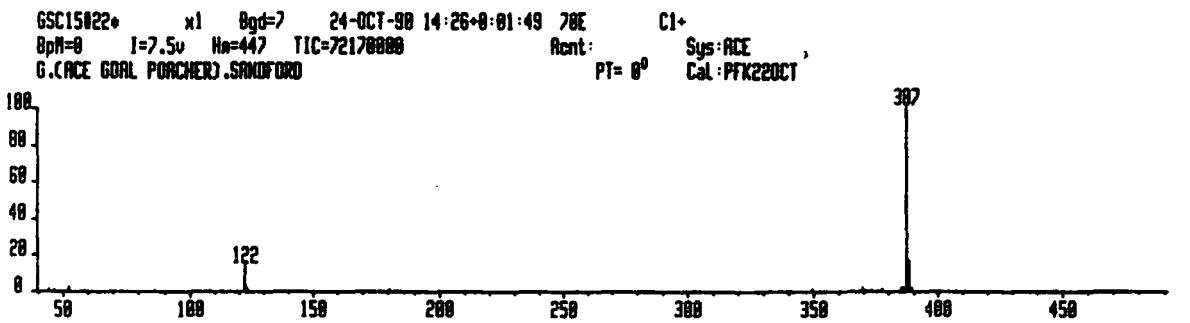


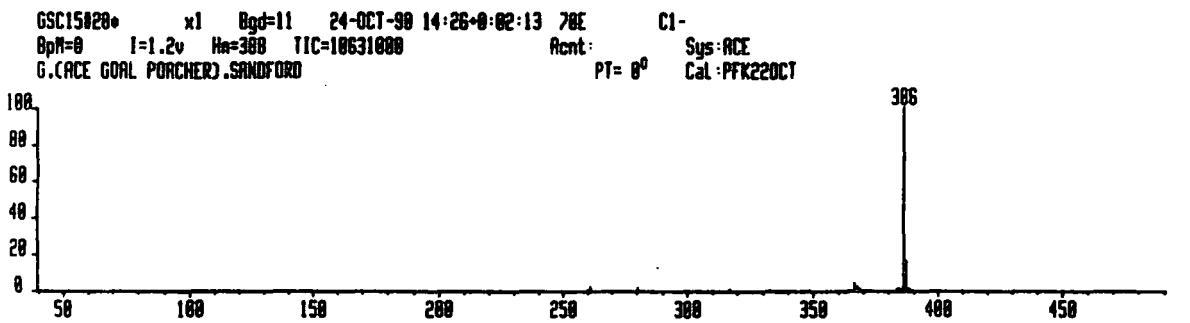
EI^+ Data

Mass	% Base				
40.04	1.18	105.13	0.38	235.27	97.22
41.06	2.24	110.62	0.36	236.28	100.00
42.06	7.72	115.12	0.36	237.28	13.70
43.07	1.29	116.13	1.10	238.29	0.89
44.08	2.48	117.14	0.60		
45.03	1.34	118.15	3.28		
46.04	8.33	119.16	1.00		
50.05	2.57	120.17	0.71		
51.06	2.81	127.13	0.37		
52.06	0.99	128.14	0.77		
55.09	0.59	129.14	3.46		
56.10	0.35	130.15	2.30		
57.11	1.12	131.16	1.63		
60.06	0.31	143.17	0.75		
62.06	1.13	144.18	0.40		
63.06	1.93	145.19	7.30		
64.06	1.95	146.19	1.25		
65.07	0.38	147.15	8.58		
66.08	0.73	148.16	0.67		
69.11	1.13	149.14	1.45		
71.05	1.71	170.21	0.70		
71.13	0.47	179.17	0.39		
72.58	0.56	192.19	9.07		
74.07	0.90	193.19	1.98		
75.07	2.87	194.21	1.58		
76.08	2.93	195.22	0.49		
77.09	1.81	205.20	0.35		
78.09	0.49	206.21	2.05		
81.13	0.34	207.22	0.84		
88.08	0.55	208.23	0.38		
89.10	0.84	219.23	9.05		
90.08	2.82	220.24	9.83		
91.09	0.79	221.24	3.37		
95.10	0.38	222.25	0.92		
101.10	0.47	233.25	0.91		
102.11	12.05	234.28	1.02		
103.12	2.37				
104.12	3.92				

No. 32 M.Wt. 386 $EI^+/CI^+/CI^-$



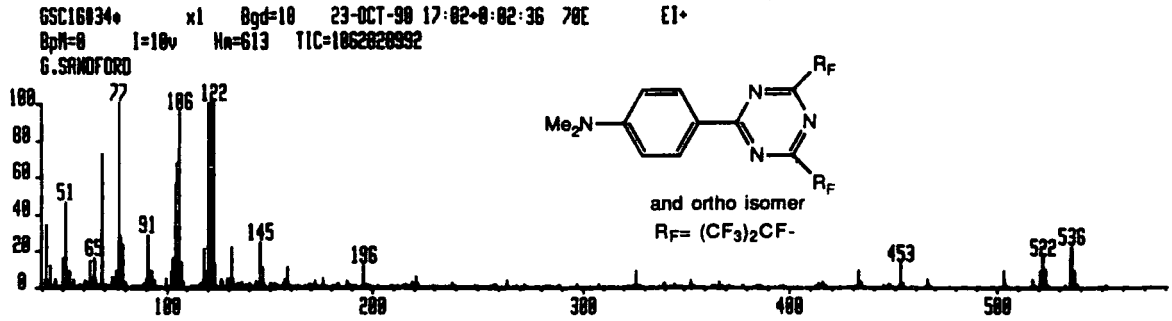


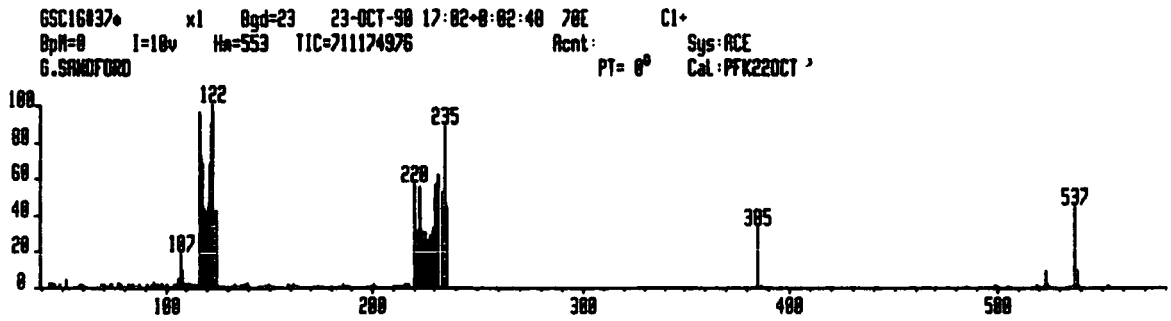


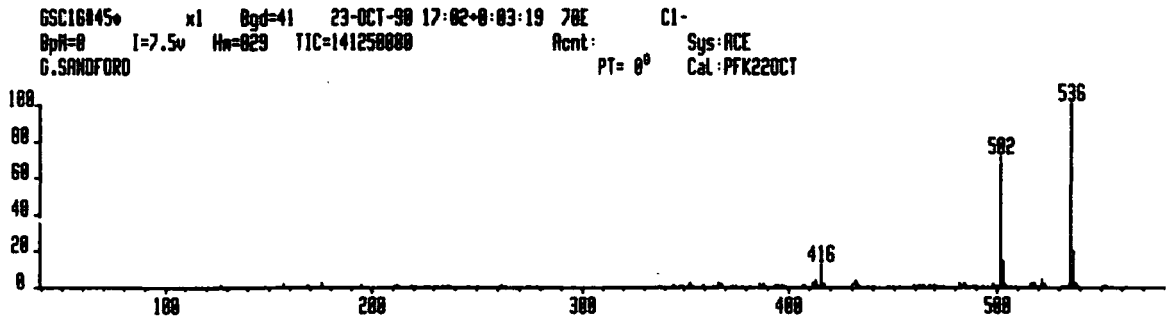
EI^+ Data

Mass	% Base	Mass	% Base
42.03	3.10	342.09	1.82
43.04	0.31	367.19	6.87
44.05	1.20	368.19	1.25
46.01	1.09	369.15	0.55
50.02	0.41	370.15	0.65
51.03	0.86	371.17	0.74
63.03	0.49	372.17	0.41
69.00	9.87	384.19	1.16
71.00	1.27	385.19	56.36
75.02	0.84	386.19	100.00
76.01	0.77	387.20	29.80
77.04	0.83	388.21	3.35
90.04	0.31	446.33	0.57
102.04	3.60		
103.05	0.94		
104.05	0.96		
116.05	0.64		
117.06	0.34		
118.07	0.60		
120.09	1.20		
121.09	2.55		
129.06	2.31		
130.06	1.84		
131.07	1.28		
143.07	0.42		
145.09	12.59		
146.09	3.32		
147.05	1.22		
172.10	0.41		
266.13	6.25		
267.13	0.91		
297.15	2.10		
298.17	0.96		
301.12	0.45		
316.15	9.12		
317.15	4.05		
318.16	0.58		

No. 33 M.Wt. 536 $EI^+/CI^+/CI^-$



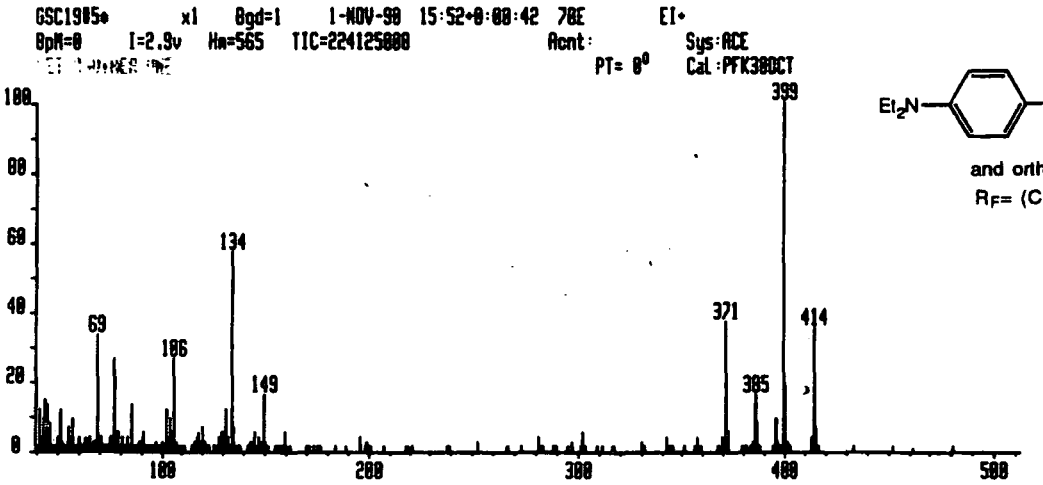




CI^- Data

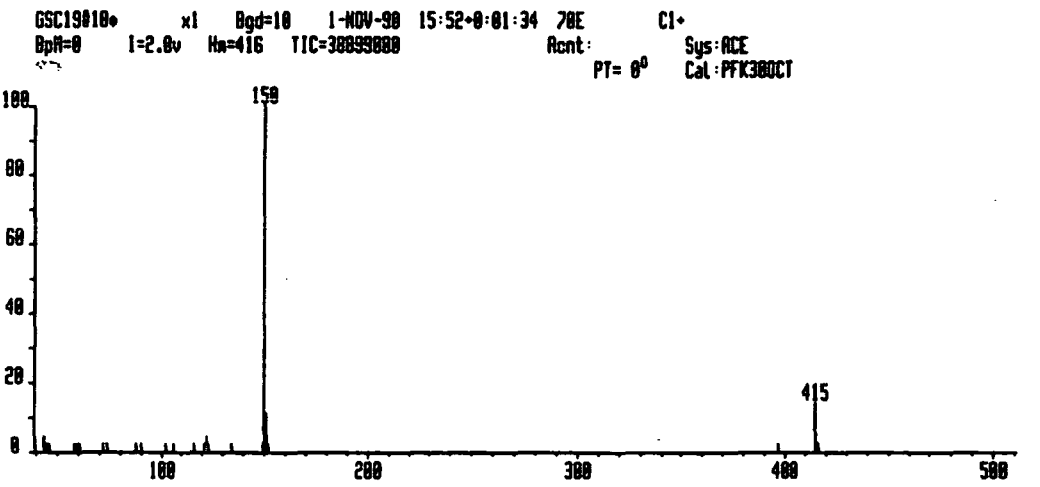
Mass	% Base			
126.83	0.97	497.98	1.06	
156.91	1.26	501.95	71.22	F
168.90	0.40	502.97	14.00	F
175.90	1.85	503.98	1.38	
194.89	0.99	516.00	1.37	
211.86	0.56	517.00	1.69	
261.94	0.95	518.02	1.73	
344.90	0.95	519.01	0.32	
351.95	0.39	520.96	0.30	
352.96	2.01	522.00	4.11	
353.97	0.30	523.02	1.02	
358.96	0.91	534.85	1.29	F
366.95	1.80	536.00	100.00	F
367.97	1.17	537.01	19.45	F
385.97	1.50	538.02	2.15	
387.89	1.63	552.03	0.62	
393.89	0.34			
394.90	0.46			
396.89	0.40			
406.90	0.58			
407.23	0.95			
411.89	1.97			
412.88	3.53			
413.88	0.48			
415.88	11.93			
416.89	1.45			
429.90	0.63			
430.90	1.60			
431.89	3.12			
432.90	2.01			
459.96	0.36			
462.02	0.96			
463.95	0.68			
466.97	0.71			
469.94	0.56			
481.95	2.02			
482.96	0.50			
483.97	1.87			
484.97	0.41			

No. 34 M.Wt. 414 EI^+/CI^+



and ortho isomer

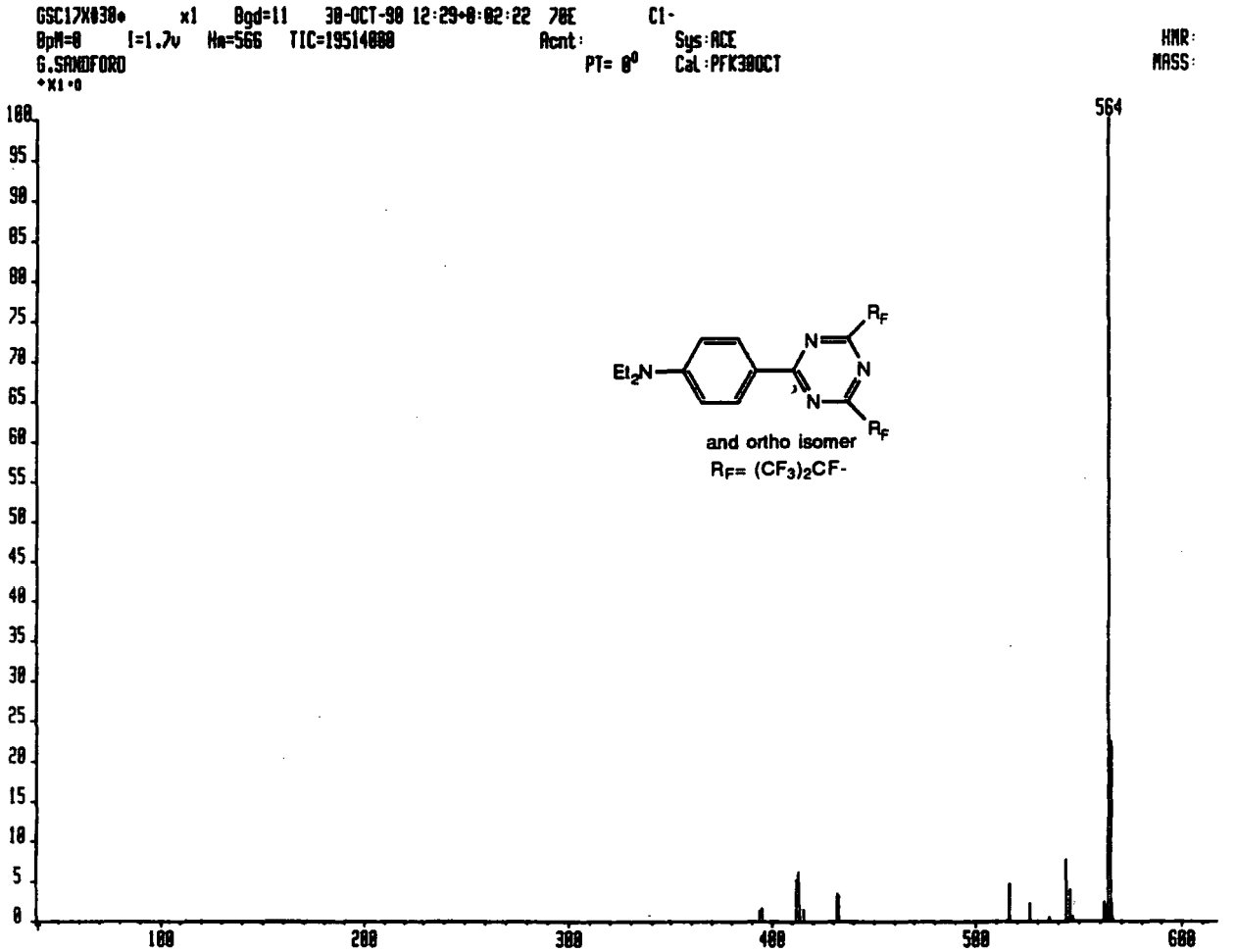
$R_F = (CF_3)_2CF-$



CI^+ Data

Mass	% Base
44.04	3.92
44.08	1.96
45.02	1.96
45.04	1.96
46.04	1.96
46.06	1.96
46.07	1.96
58.05	1.96
58.08	1.96
59.05	1.49
60.04	1.96
61.03	1.96
72.07	1.96
74.05	1.96
88.06	1.96
90.02	1.96
102.02	1.96
102.08	1.96
106.03	1.96
106.08	1.96
116.06	1.96
121.03	1.96
122.06	3.92
123.03	1.96
134.06	2.02
149.08	1.96
150.08	91.74
150.34	1.96
151.09	10.11
152.04	1.96
397.06	1.96
415.12	12.89
416.15	2.18

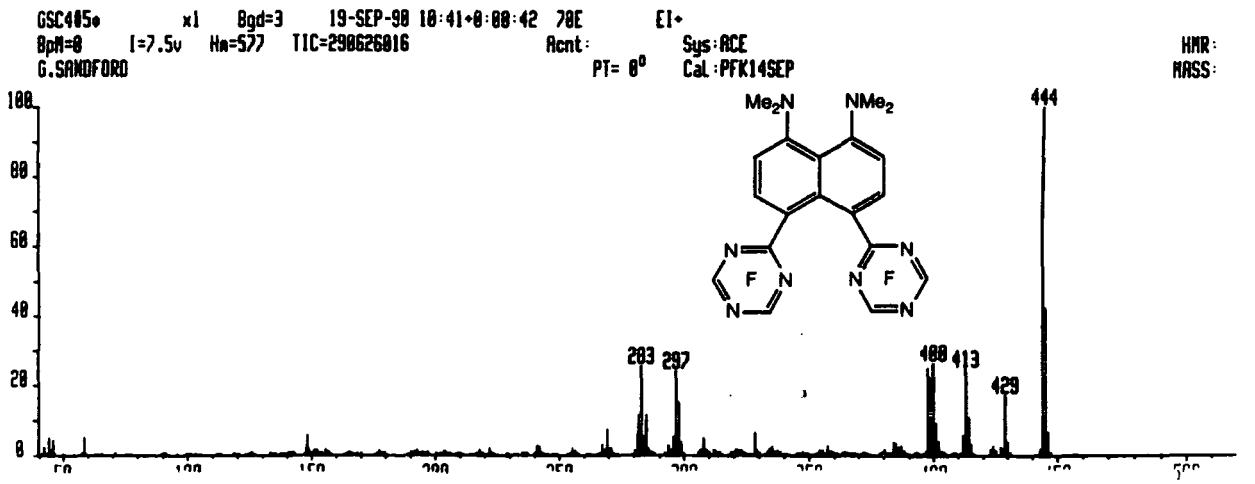
No. 35 M.Wt. 564 Cl^-

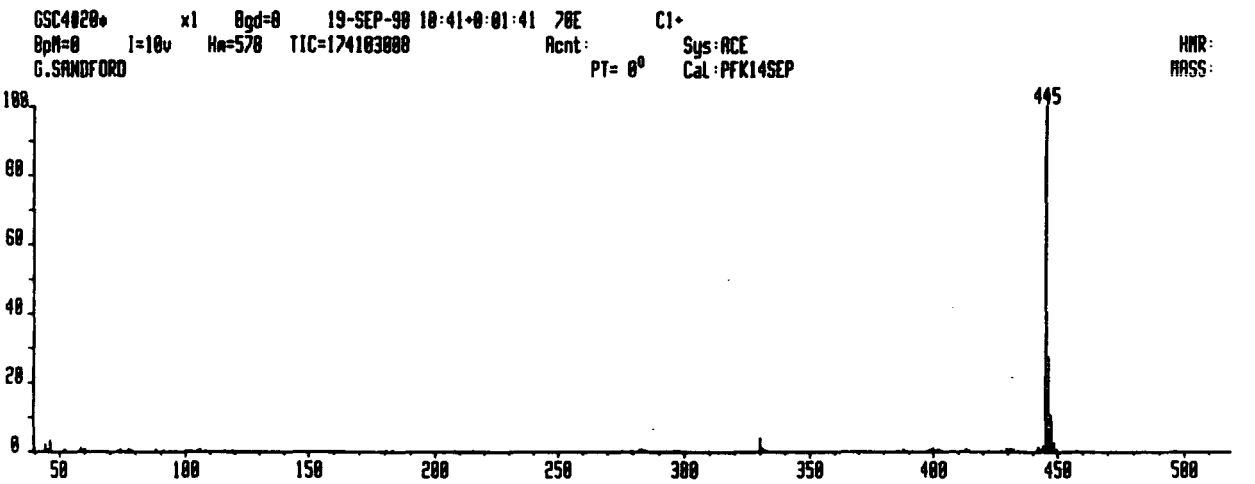


Cl^- Data

Mass	% Base
393.93	1.22
395.02	1.47
411.92	4.95
412.92	6.07
413.99	1.81
415.89	1.33
431.90	3.34
432.90	3.05
515.98	4.60
516.98	0.32
526.02	2.13
536.02	0.46
544.01	7.56
545.01	3.47
546.03	3.81
547.05	0.49
562.01	2.27
563.04	1.86
564.02	100.00
565.02	22.30
566.01	2.07

No. 36 M.Wt. 444 EI^+/CI^+

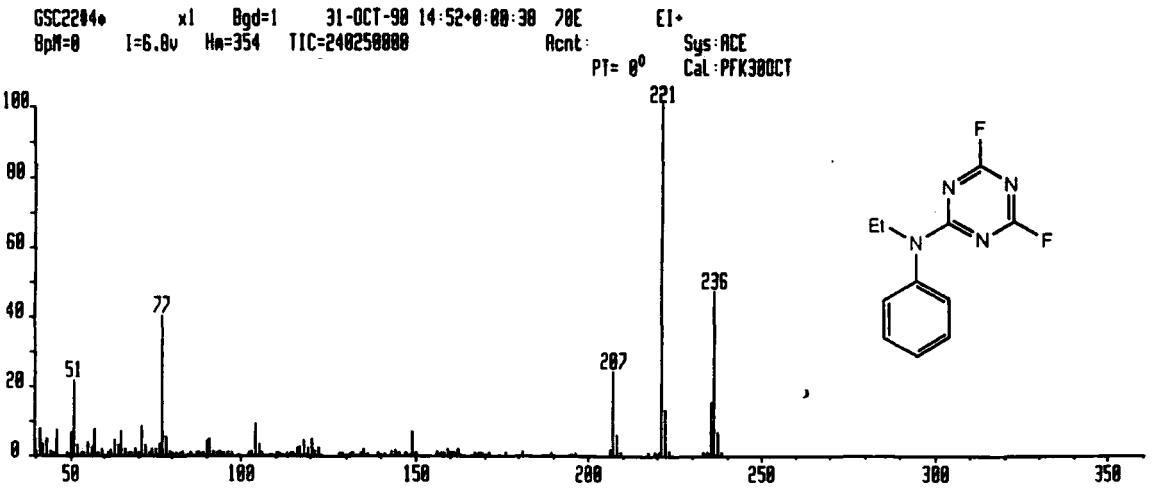


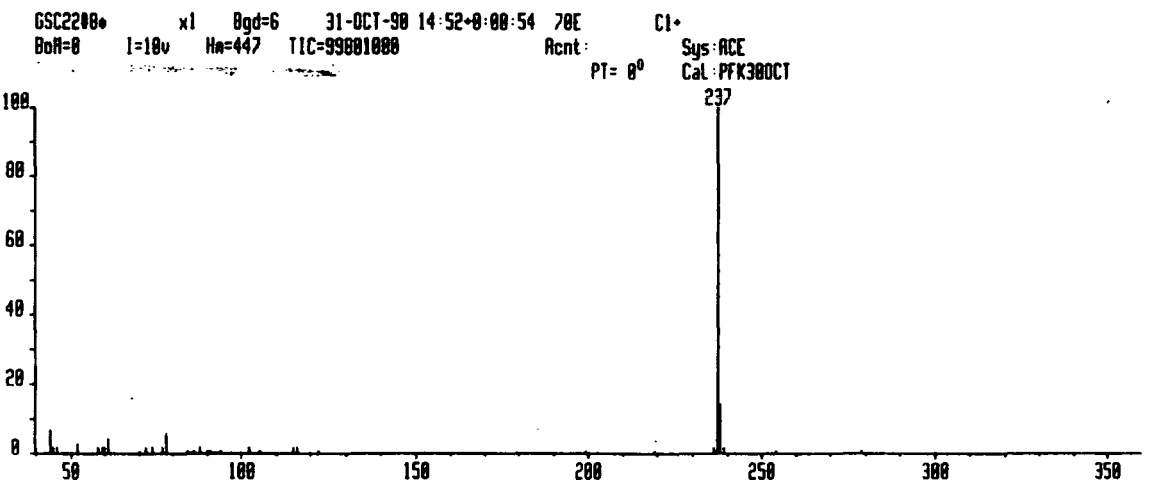


CI^+ Data

Mass	% Base	
44.06	1.67	
46.08	2.74	
58.08	0.76	
88.10	0.38	
330.30	3.45	
331.30	0.71	
400.27	0.58	
402.28	0.32	
413.27	0.33	
429.30	0.60	
431.32	0.86	
442.36	0.96	
443.35	0.34	
444.29	1.52	F
445.31	100.00	F0
446.33	27.20	F
447.34	10.34	
448.34	2.51	
449.35	0.41	

No. 37 M.Wt. 236 EI^+/CI^+

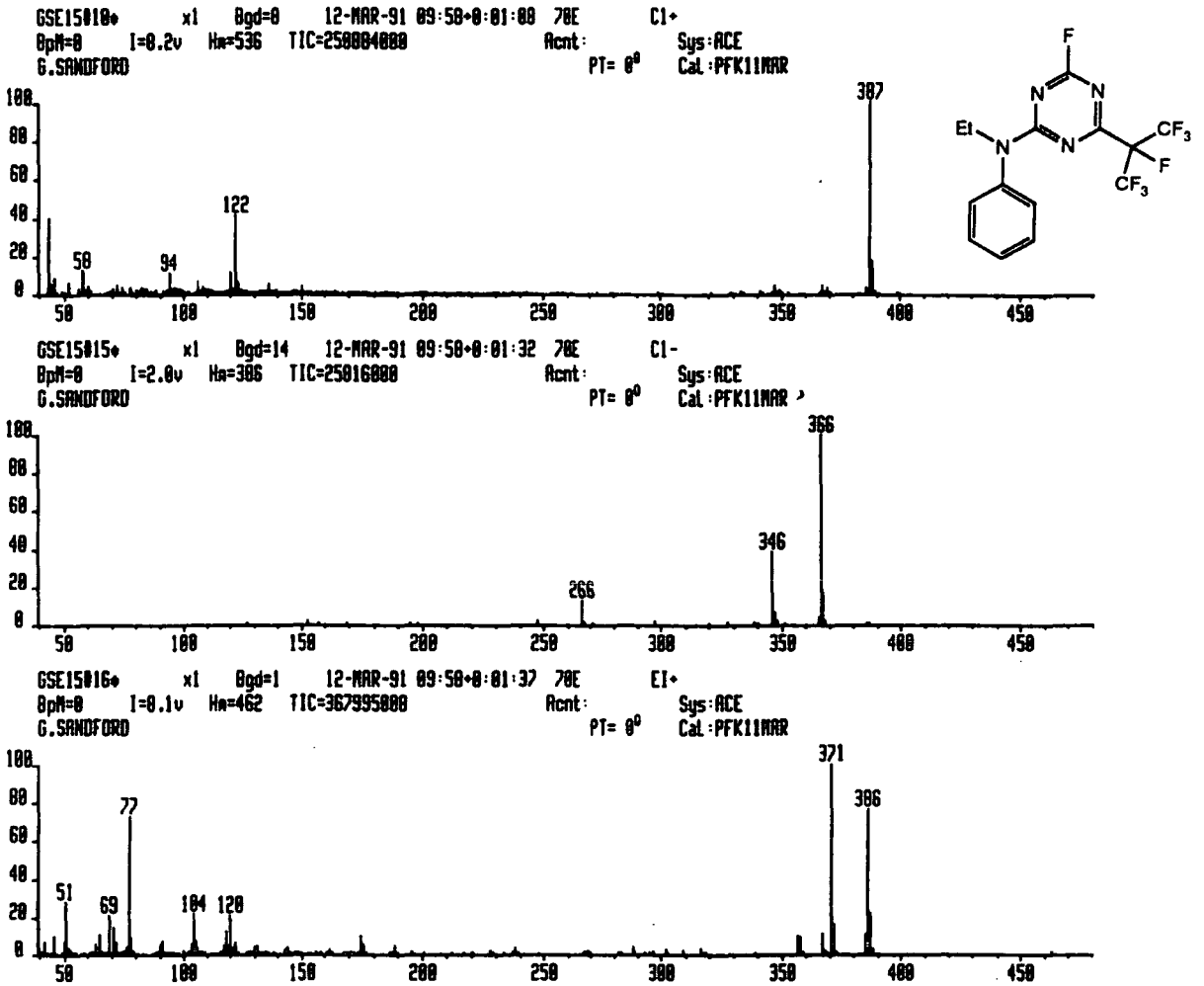




EI^+ Data

mass	% base						
69.00	0.58		104.08	0.88		161.07	0.58
69.07	1.73		105.08	2.91		162.07	1.77
70.09	0.58		106.08	0.58		167.07	0.58
71.01	8.08	F	110.05	0.58		168.07	0.58
71.10	1.36	F	110.55	0.58		169.08	0.58
72.03	2.88		111.14	0.49		171.10	0.58
73.05	0.58		113.08	0.58		176.09	0.58
74.03	1.73		114.10	0.58		181.09	1.15
75.03	1.73		115.05	0.58		189.09	0.58
76.04	3.04		115.08	0.58		196.12	0.58
77.05	39.99		116.04	2.30		206.08	1.36
78.05	5.39		117.05	2.50		207.08	24.10
79.07	1.15		118.07	4.26		208.09	5.80
80.07	0.58		119.09	2.03		209.10	0.60
81.09	0.82		120.11	4.81		217.12	0.58
82.08	0.58		121.09	1.15		219.09	0.58
83.10	1.15		122.07	2.06		220.09	0.58
85.12	0.70		128.08	0.82		221.10	100.00
87.06	0.58		129.08	0.81		222.11	12.80
88.04	0.58		131.09	0.58		223.13	1.15
89.05	0.65		132.05	0.58		233.13	0.58
90.05	4.04		134.06	0.58		234.16	0.58
91.06	4.61		135.06	1.73		235.13	14.98
92.06	1.17		136.07	0.39		236.14	46.86
93.06	0.64		139.07	0.64		237.15	6.33
94.06	1.15		143.06	1.23		238.16	0.58
95.08	0.58		144.08	1.33			
96.05	0.58		145.07	0.58			
97.12	0.58		147.06	0.72			
102.05	0.58		149.05	6.68			
103.07	1.25		150.06	0.58			
			156.09	0.90			
			157.07	0.58			
			158.08	0.58			
			159.07	1.73			
			160.06	0.58			

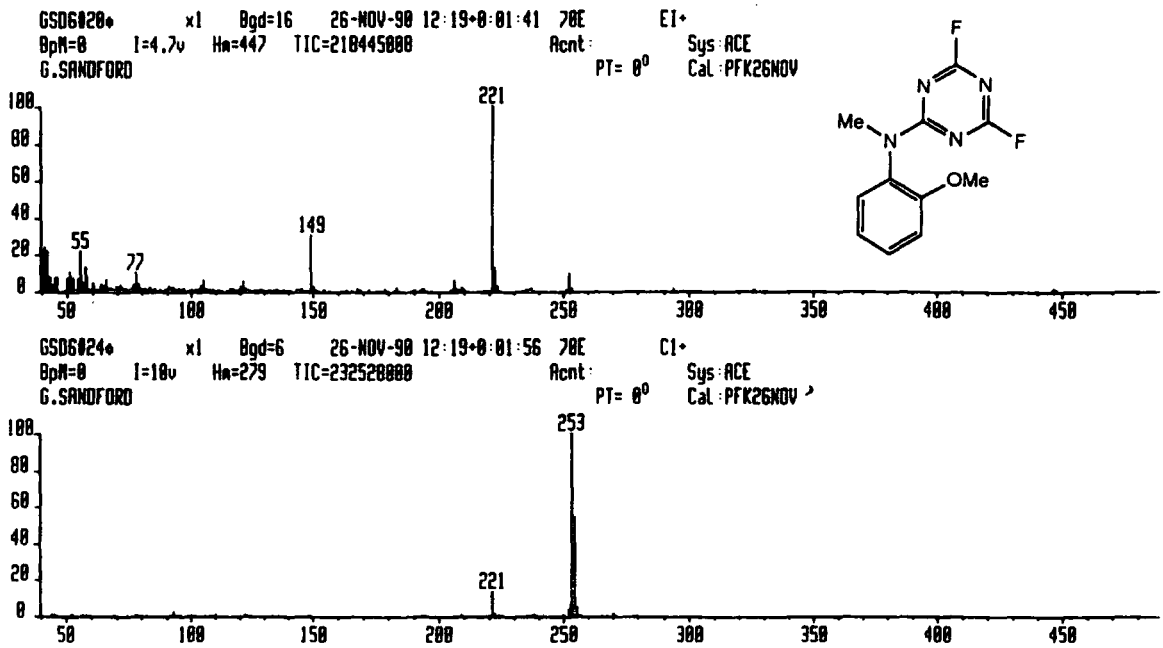
No. 38 M.Wt. 386 $EI^+/CI^+/CI^-$



EI^+ Data

Mass	% Base				
41.03	1.33	120.02	20.65	385.91	76.16 F
42.03	6.38	121.02	3.40	386.93	21.57 F
46.00	9.77	121.98	5.53	387.93	2.45
50.00	6.32	127.98	1.20	462.98	1.47
51.01	27.25	128.98	1.59		
52.01	2.93	129.98	3.87		
53.01	2.07	130.99	4.52		
62.00	1.44	134.97	1.49		
63.00	5.31	142.98	2.77		
64.01	3.50	143.98	4.04		
65.02	9.99	144.99	1.09		
66.02	1.44	155.97	1.25		
68.97	20.25 F	161.96	2.41		
69.02	2.17 F	174.96	9.66		
70.98	13.87	175.96	4.96		
71.99	6.44	187.95	1.37		
73.99	1.52	188.96	4.26		
74.99	1.94	195.90	1.34		
75.99	3.67	227.89	2.16		
77.01	72.27	237.92	3.40		
78.01	8.73	266.88	1.44		
79.01	1.88	267.90	1.04		
88.99	1.01	268.91	2.14		
89.99	5.20	287.90	3.97		
91.00	7.36	288.90	1.97		
92.00	1.54	298.93	1.44		
94.00	1.19	301.92	2.88		
99.98	1.61	308.90	2.04		
101.98	1.03	316.94	3.39		
102.99	4.87	356.73	9.38 F		
104.00	20.93	357.89	9.24 F		
105.01	6.75	358.90	1.44		
106.01	2.93	366.93	10.78		
107.96	1.25	367.93	1.92		
115.98	1.54	370.88	100.00 F		
116.98	4.31	371.91	15.93 F		
118.00	12.42	372.91	1.27		
119.00	4.77	384.84	10.38 F		

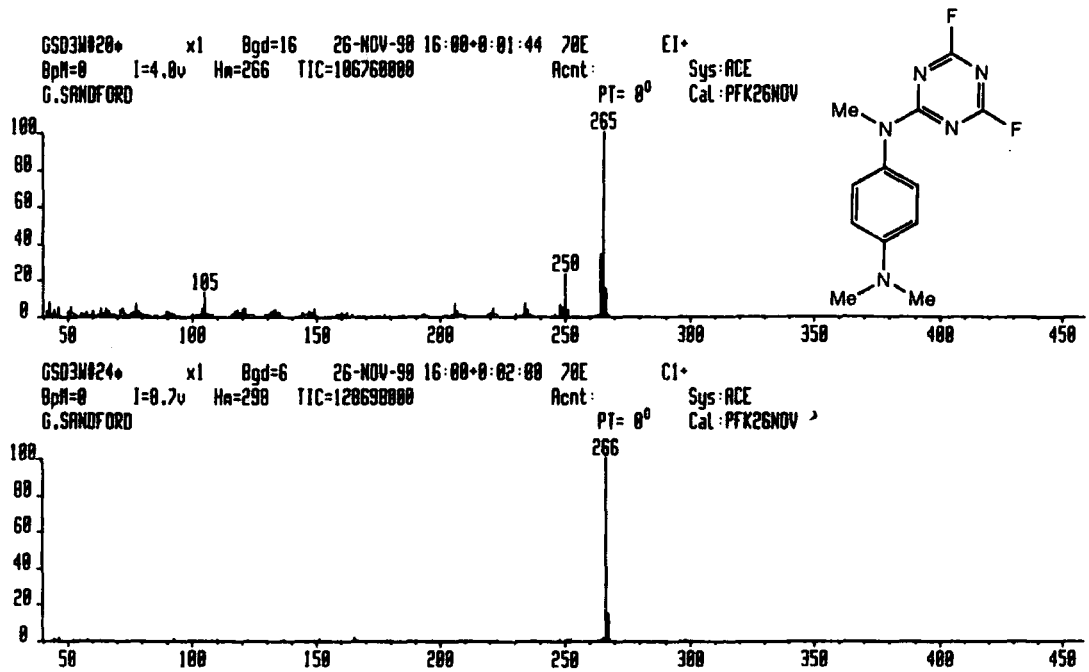
No. 39 M.Wt. 252 EI^+/CI^+



EI^+ Data

Mass	% Base		Mass	% Base		Mass	% Base
69.06	2.76		115.04	0.33		235.02	0.66
70.07	1.14		116.00	1.21		236.03	0.84
70.99	3.64	F	117.01	1.33		237.04	1.07
71.07	2.07	F	118.01	0.44		251.05	0.48
72.00	1.29		119.05	0.43		252.06	9.30
73.02	1.11		120.03	2.95		253.07	1.34
74.01	0.91		121.01	5.74		293.96	1.30
75.01	1.05		122.02	1.47		325.94	0.36
76.02	3.35		123.02	0.64		446.17	1.49
77.03	10.28		128.02	0.51		447.18	0.49
78.03	4.28		129.04	0.57			
79.03	1.27		132.01	0.70			
80.05	0.36		134.03	0.53			
81.06	1.30		135.04	1.16			
82.07	0.95		137.98	0.59			
83.02	1.97	F	143.00	0.59			
83.07	1.70	F	144.04	0.70			
84.08	0.49		145.02	1.02			
85.09	1.26		149.00	30.23			
86.02	0.31		150.01	2.64			
86.96	0.94		151.01	0.88			
87.03	0.33		154.02	0.42			
89.03	0.39		161.02	0.30			
90.02	1.45		162.96	0.57			
91.04	2.51		167.01	1.32			
92.03	1.71		168.02	0.85			
93.02	2.01		172.03	0.84			
94.05	0.47		178.06	1.36			
95.06	1.52		182.96	2.12			
96.08	0.59		190.00	0.52			
97.08	1.68		193.02	0.90			
99.99	0.44		194.02	1.19			
102.02	0.56		205.06	0.53			
103.02	0.90		206.02	5.98			
104.02	2.63		207.03	1.56			
105.02	6.36		208.03	0.49			
106.03	1.15		209.04	1.92			
107.04	0.65		210.04	0.40			
108.04	0.49		221.04	100.00			
109.08	0.68		222.05	12.97			
111.10	0.89		223.07	2.59			
			233.06	0.33			

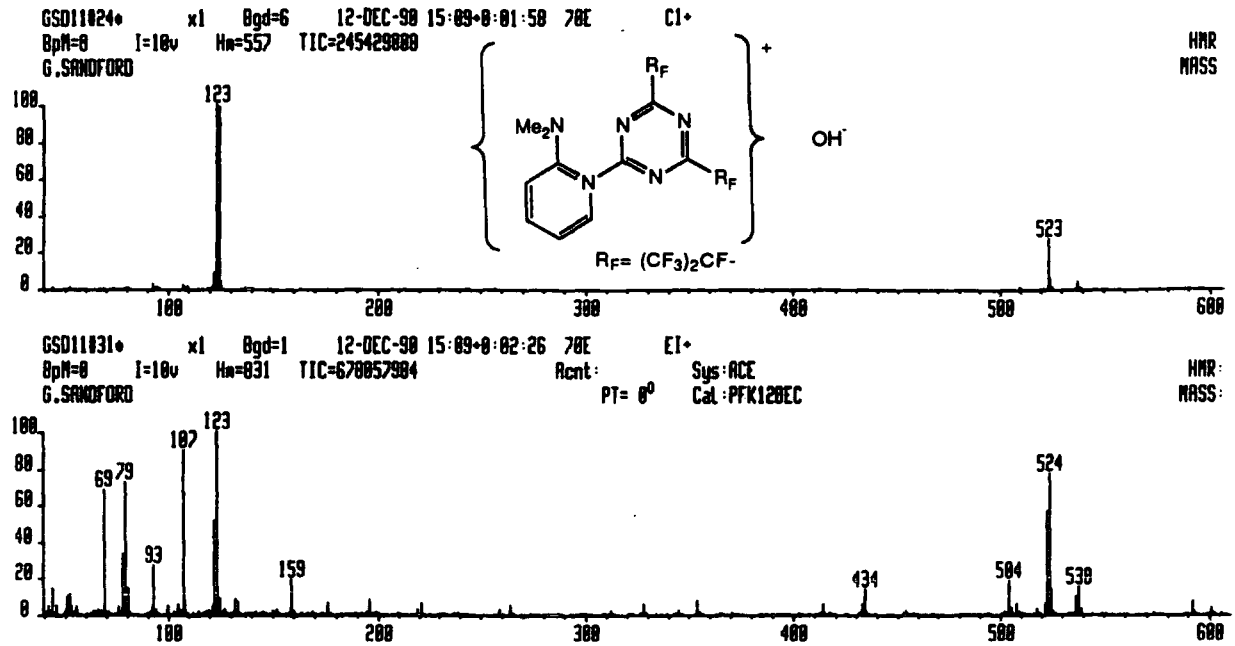
No.40 M.Wt. 265 EI+/CI+



EI+ Data

Mass	% Base					
69.04	0.99	123.47	0.43		222.97	0.34
70.97	3.42	124.48	0.73		229.97	0.56
71.05	0.45	128.98	0.50		232.93	0.59
71.97	3.75	129.98	0.69		233.94	6.87
73.01	1.21	130.99	2.02		234.95	3.64
74.00	0.73	131.48	2.31		235.96	0.59
74.99	1.15	131.99	2.64		245.99	0.35
75.99	1.97	132.49	3.44		247.95	6.13
77.00	6.87	133.00	3.06		248.96	4.58
78.00	2.95	134.02	1.86		249.96	22.67
79.01	1.24	135.01	2.03		250.97	3.53
79.89	0.36	143.98	1.89		261.96	0.32
81.03	0.40	144.98	0.98		262.98	0.77
81.88	0.39	146.00	0.43		263.95	33.96
82.01	0.38	147.01	2.68		264.96	100.00
87.98	0.32	148.02	1.75		265.96	14.67
88.99	0.55	148.95	3.80	F	266.99	0.90
89.99	2.66	149.03	2.00	F		
91.00	2.13	157.99	0.51			
92.00	1.61	159.00	0.45			
93.00	1.52	160.00	2.28			
100.00	0.55	160.99	0.41			
101.98	1.00	162.04	1.75			
102.98	0.65	164.05	0.58			
103.99	4.17	177.06	0.51			
104.98	12.87	184.99	0.40			
106.00	1.56	192.94	0.56			
107.02	0.87	193.94	0.64			
108.02	0.98	204.93	0.39			
115.96	1.31	205.94	6.61			
116.96	2.95	206.94	2.48			
118.00	3.52	207.95	0.56			
119.00	2.17	218.94	0.40			
120.02	4.21	219.94	1.31			
121.02	3.80	220.95	4.04			
122.03	0.83	221.96	0.59			

No. 41 M.Wt. 538 EI^+/CI^+



EI^+ Data

68.91	68.33	157.90	1.22	
69.92	1.21	158.92	19.15	
70.92	1.32	159.92	2.08	
75.93	4.24	432.63	5.22	
76.95	1.57	433.65	13.70	
77.96	33.24	434.66	1.59	
78.97	72.30	438.69	0.33	
79.97	14.15	444.66	0.31	
80.96	1.20	452.73	0.87	
87.92	0.30	453.74	2.18	
89.94	0.50	454.75	0.46	
90.94	1.17	457.68	0.54	
91.94	4.00	493.63	0.39	
92.97	27.22	501.59	1.17	
93.95	2.87	502.59	0.53	
94.95	0.64	503.62	18.41	
99.90	4.84	504.61	3.66	
102.94	1.56	505.63	0.42	
103.94	1.68	507.61	5.63	
104.95	5.69	508.62	1.42	
105.95	1.79	509.62	0.78	
106.97	90.01	510.60	0.53	
107.95	7.42	517.65	2.73	
108.96	0.48	518.64	0.64	
111.90	0.58	521.58	5.94	F
113.91	1.39	522.61	56.13	F
116.94	0.55	523.60	77.24	F
117.95	1.61	524.62	13.28	F
118.92	1.77	525.60	1.37	
119.95	0.78	535.64	0.86	
120.96	4.41	536.64	9.59	F
121.97	51.54	537.66	14.64	F
122.99	100.00	538.66	2.55	
123.98	8.63	573.65	0.64	
124.98	0.32	574.63	0.34	
125.89	1.99			
126.89	2.86			
127.90	0.42			
129.93	0.59			
130.89	1.29			
131.94	7.81			
132.93	6.74			

APPENDIX FOUR

The Board of Studies in Chemistry requires that each postgraduate research thesis contains an appendix listing:-

(1) all research colloquia, seminars and lectures arranged by the Department of Chemistry during the period of the author's residence as a postgraduate student;

(2) lectures organised by Durham University Chemical Society;

(3) all research conferences attended and papers presented by the author during the period when research for the thesis was carried out;

(4) details of the postgraduate induction course.

COLLOQUIA, LECTURES AND SEMINARS GIVEN BY INVITED SPEAKERS, OCTOBER 1988 - SEPTEMBER 1991

(Those attended are marked *)

18.10.88 Dr. J. Dingwall (Ciba Geigy)
Phosphorous Containing Amino Acids: Biologically Active Natural and Unnatural Products

24.11.88 Drs. R.R. Baldwin and R.W. Walker (Hull University)
Combustion: Some Burning Problems

12.88 Dr. G. Hardgrove (St. Olaf College, USA)
Polymers in the Physical Chemistry Laboratory

25.1.89 Dr. L. Harwood (Oxford University)
Synthetic Approaches to Phorbols Via Intramolecular Furan Diels-Alder Reactions: Chemistry Under Pressure

2.2.89 Prof. L.D. Hall (Addenbrooke's Hospital, Cambridge)
* *NMR - A Window to the Human Body*

9.2.89 Prof. J.E. Baldwin (Oxford University)
* *Recent Advances in the Bioorganic Chemistry of Penicillin Biosynthesis*

15.2.89 Dr. A.R. Butler (St. Andrews University)
* *Cancer in Linxiam: The Chemical Dimension*

16.2.89 Prof. B.J. Aylett (Queen Mary College, London)
Silicon Based Chips: The Chemist's Contribution

1.3.89 Dr. R.J. Errington (Newcastle University)
Polymetalate Assembly in Organic Solvents

15.3.89 Dr. R. Aveyard (Hull University)
Surfactants at your Surface

20.4.89 Dr. M. Casey (Salford University)
Sulphoxides in Stereoselective Synthesis

27.4.89 Dr. D. Crich (University College, London)
Some Novel Uses of Free Radicals in Organic Synthesis

11.5.89 Dr. J. Frey (Southampton University)
Spectroscopy of the Reaction Path: Photodissociation Raman Spectra of NOCl

10.11.89 Prof. J.I.G. Cadogan (B.P.)
From Pure Science to Profit

17.10.89 Dr. F. Palmer (Nottingham University)
* *Thunder and Lightning*

25.10.89 Prof. C. Floriani (Lausanne University, Switzerland)
Molecular Aggregates - A Bridge Between Homogeneous and Heterogeneous Systems

1.11.89 Dr. J.P.S. Badyal (Durham University)
Breakthroughs in Heterogeneous Catalysis

9.11.89 Prof. N.N. Greenwood (Leeds University)
Novel Cluster Geometries in Metalloborane Chemistry

10.11.89 Prof. J.E. Bercaw (California Institute of Technology)
* *Synthetic and Mechanistic Approaches to Ziegler-Natta Polymerisation of Olefins.*

13.11.89 Dr. J. Becher (Odense University)
* *Synthesis of New Macrocyclic Systems using Heterocyclic Building Blocks*

16.11.89 Dr. D. Parker (Durham University)
* *Macrocycles, Drugs and Rock 'n' Roll*

29.11.89 Prof. D.J. Cole-Hamilton (St. Andrews University)
New Polymers from Homogeneous Catalysis

30.11.89 Dr. M.N. Hughes (King's College, London)
* *A Bug's Eye View of the Periodic Table*

4.12.89 Dr. D. Graham (B.P. Research Centre)
How Proteins Absorb on Interfaces

6.12.89 Dr. R.L. Powell (ICI)
* *The Development of CFC Replacements*

7.12.89 Dr. A. Butler (St. Andrews University)
* *The Discovery of Penicillin: Facts and Fancies*

13.12.89 Dr. J. Klinowski (Cambridge University)
Solid State NMR Studies of Zeolite Cages

15.12.89 Prof. R. Huisgen (Universitat Munchen)
* *Recent Mechanistic Studies of [2+2] Additions*

24.1.90 Dr. R.N. Perutz (York University)
Plotting the Course of C-H Activations with Organometallics

31.1.90 Dr. U. Dyer (Glaxo)
* *Synthesis and Conformation of C-Glycosides*

1.2.90 Prof. J.H. Holloway (Leicester University)
* *Noble Gas Chemistry*

7.2.90 Dr. D.P. Thompson (Newcastle University)
The role of Nitrogen in Extending Silicate Crystal Chemistry

8.2.90 Rev. R. Lancaster (Kimbolton Fireworks)
* *Fireworks - Principles and Practice*

12.2.90 Prof. L. Lunazzi (University of Bologna)
Application of Dynamic NMR to the Study of Conformational Isomerism

14.2.90 Prof. D. Sutton (Simon Fraser University, Vancouver B.C.)
Synthesis and Applications of Dinitrogen and Diazo Compounds of Rhenium and Iridium

15.2.90 Prof. L. Crombie (Nottingham University)
The Chemistry of Cannabis and Khat

21.2.90 Dr. C. Bleasdale (Newcastle University)
The Mode of Action of some Anti-tumour Agents

22.2.90 Prof. D.T. Clark (ICI Wilton)
* *Spatially Resolved Chemistry using Nature's Paradigm in the Advanced Materials Area*

28.2.90 Dr. R.K. Thomas (Oxford University)
Neutron Reflectometry from Surfaces

1.3.90 Dr. J.F. Stoddart (Sheffield University)
* *Molecular Lego*

8.3.90 Dr. A.K. Cheetham (Oxford University)
* *Chemistry of Zeolite Cages*

21.3.90 Dr. I. Powis (Nottingham University)
Spinning off in a huff: Photodissociation of Methyl Iodide

23.3.90 Prof. J.M. Bowman (Emory University)
Fitting Experiment with Theory in Ar-OH

9.7.90 Prof. L.S. German (USSR Academy of Sciences - Moscow)
* *New Syntheses in Fluoroaliphatic Chemistry: Recent Advances in the Chemistry of Fluorinated Oxiranes*

9.7.90 Prof. V.E. Platonov (USSR Academy of Sciences - Novosibirsk)
* *Polyfluoroindanes: Synthesis and Transformation*

9.7.90 Prof. I.N. Rozhkov (USSR Academy of Sciences - Moscow)
* *Reactivity of Perfluoroalkyl Bromides*

11.10.90 Dr. W.A. MacDonald (ICI Wilton)
* *Materials for the Space Age*

24.10.90 Dr. M. Bochmann (U.E.A.)
Synthesis, Reactions and Catalytic Activity of Cationic Titanium Alkyls

26.10.90 Prof. R. Soulen (South Western University, Texas)
* *Chemistry of some Fluorinated Cyclobutenes*

31.10.90 Dr. R. Jackson (Newcastle University)
* *New Synthetic Methods: α-aminoacids and Small Rings*

1.11.90 Dr. N. Logan (Nottingham University)
Rocket Propellants

6.11.90 Dr. P. Kocovsky (Uppsala)
* *Stereo-controlled Reactions Mediated by Transition and Non-Transition Metals*

7.11.90 Dr. D. Gerrard (B.P.)
Raman Spectroscopy for Industrial Analysis

7.11.90 Dr. W. Dolbier (Gainsville, Florida)
* *Rearrangements of bis CF_3 Vinyl Aromatics: a Route to 1,3,5-Hexatrienes*

8.11.91 Dr. S.K. Scott (Leeds University)
* *Clocks, Oscillations and Chaos*

14.11.90 Prof. T. Bell (SUNY, Stony Brook)
* *Functional Molecular Architicture and Molecular Recognition*

21.11.90 Prof. J. Pritchard (Queen Mary and Westfield College, London)
Copper Surfaces and Catalysts

28.11.90 Dr. B.J. Whitaker (Leeds University)
Two-dimensional Velocity Imaging of State-selected Reaction Products

29.11.90 Prof. D. Crout (Warwick University)
Enzymes in Organic Synthesis

5.12.90 Dr. P.G. Pringle (Bristol University)
* *Metal Complexes with Functionalised Phosphines*

13.12.90 Prof. A.H. Cowley (University of Texas)
New Organometallic Routes to Electronic Materials

15.1.91 Dr. B.J. Alder (Lawrence Livermore Labs., California)
Hydrogen in all its Glory

17.1.91 Dr. P. Sarre (Nottingham University)
Comet Chemistry

23.1.91 Prof. J.S. Higgins (Imperial College, London)
Rheology and Molecular Structure of Ionomer Solutions

24.1.91 Dr. P.J. Sadler (Birkbeck College, London)
Design of Inorganic Drugs: Precious Metals, Hypertension and HIV

30.1.91 Prof. E. Sinn (Hull University)
New Results in High T_C Superconductivity

31.1.91 Dr. D. Lacey (Hull University)
* *Liquid Crystals*

6.2.91 Dr. R. Bushby (Leeds University)
* *Biradicals and Organic Magnets*

14.2.91 Dr. M.C. Petty (Durham University)
* *Molecular Electronics*

20.2.91 Prof. B.L. Shaw (Leeds University)
* *New Chemistry with Transition Metal Multihydrides*

28.2.91 Dr. J. Brown (Oxford University)

Can Chemistry Provide Catalysts Superior to Enzymes?

6.3.91 Dr. C.M. Dobson (Oxford University)
NMR Studies of Dynamics in Molecular Crystals

7.3.91 Dr. J. Markam (ICI Pharmaceuticals)
* *DNA Fingerprinting*

24.4.91 Prof. R.R. Schrock (MIT)
* *Metal-ligand Multiple Bonds and Metathesis Initiators*

25.4.91 Prof. T. Hudlicky (Virginia Polytechnic Institute)
Biocatalysis and Symmetry Based Approaches to the Efficient Synthesis of Complex Natural Products

20.6.91 Prof. M.S. Brookhart (University of North Carolina)
Olefin Polymerisations, Oligomerisations and Dimerisations Using Electrophilic Late Transition Metal Catalysts

29.7.91 Dr. M.A. Brimble (Massey University, New Zealand)
* *Synthetic Studies Towards the Antibiotic Griseusin-A*

Research Conferences Attended

Dec 88 Royal Society of Chemistry Perkin Division, One Day Meeting,York University.

April 1989 North East Graduate Symposium, Durham University.

5.7.89 Royal Society of Chemistry Heterocyclic Group, Postgraduate Heterocyclic Symposium, Sheffield University.

Aug. 89 European Symposium on Fluorine Chemistry, Leicester University.

13.12.89 Modern Aspects of Stereochemistry, One Day Meeting, Sheffield University

15.12.89 Royal Society of Chemistry Perkin Division, One Day Meeting, Durham University.

7.3.90 SCI Graduate Symposium, York University.

2.4.90 North East Graduate Symposium, Newcastle University.

Sept 91 13th International Symposium on Fluorine Chemistry, Ruhr Universität, Bochum, Germany.

FIRST YEAR INDUCTION COURSE

This course consists of a series of one hour lectures on the services available in the department.

Departmental Organisation - Dr. E.J.F. Ross
Safety Matters - Dr. M.R. Crampton
Electrical Appliances - Mr. B.T. Barker
Chromatography and Microanalysis - Mr. T.F. Holmes
Atomic Absorptiometry and Inorganic Analysis - Mr. R. Coult
Library Facilities - Mr. R.B. Woodward
Mass Spectroscopy - Dr. M. Jones
Nuclear Magnetic Resonance Spectroscopy - Dr. R.S. Matthews
Glass-blowing Techniques - Mr. R. Hart and Mr. G. Haswell

REFERENCES

1. R.D. Chambers, *"Fluorine in Organic Chemistry"*, John Wiley and Sons, New York, 1973.
2. M.R.C. Gerstenberger and A. Haas, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 647.
3. S. Rozen and R. Filler, *Tetrahedron*, 1985, **41**, 1111.
4. J. Mann, *Chem. Soc. Rev.*, 1987, **16**, 381.
5. J. Emsley, *M. Sc. Thesis*, University of Durham, 1988.
6. C.L. Liotta and H.P. Harris, *J. Am. Chem. Soc.*, 1974, **96**, 2250.
7. G.C. Yakobson, *J. Fluorine Chem.*, 1985, **28**, 73.
8. K. Makuo and H. Yoshioka, *J. Fluorine Chem.*, 1987, **35**, 677.
9. Y. Yoshida and Y. Kimura, *Chem. Lett.*, 1988, 1355.
10. K. Makino and H. Yoshioka, *J. Fluorine Chem.*, 1987, **35**, 677.
11. M. Gingras and D.N. Harpp, *Tetrahedron Lett.*, 1988, **37**, 4669.
12. S. Dermiek and Y. Sason, *J. Org. Chem.*, 1985, **50**, 879.
13. G.L Cantrell, U.S. Patent No. 4 849 552 (1989). *C. Abstr.* **112**: 118436f.
14. E. Kysela and R. Braden, German Patent DE 3 827 436 (1990). *C. Abstr.* **113**: 40127e.
15. J.H. Clark and D.J. MacQuarrie, *Tetrahedron Lett.*, 1987, **28**, 111.
16. N. Yazawa, H. Suzuki, Y. Yoshida, O. Furusawa, and Y. Kimura, *Chem. Lett.*, 1989, 2213.
17. Y. Yoshida, Y. Kimura, and M. Tomoi, *Chem. Lett.*, 1990, 769.
18. N. Ishikawa, T Kitazume, T. Yamazaki, Y. Mochida, and T. Tatsuio, *Chem. Lett.*, 1981, 761.
19. N. Ishikawa, T. Kitazune, and M. Nakabayashi, *Chem. Lett.*, 1980, 1089.
20. Y. Kimura and H. Suzuki, *Tetrahedron Lett.*, 1989, **30**, 1271.
21. A. McKillop and D.W. Young, *Synthesis*, 1979, **401**, 481.
22. J.H. Clark, A.J. Hyde, and D.K. Smith, *J. Chem. Soc., Chem. Commun.*, 1986, 791.
23. J. Ichihara, T. Matsuo, T. Hanafusa, and T. Ando, *J. Chem. Soc., Chem. Commun.*, 1986, 793.
24. K. Takemoto, J. Ichihara, A. Hanabusa, and T. Ando, Japanese Patent 62 114 939 (1987).
25. H. Liu, H. Lu, P. Wang, P. Sun, and F. Zhang, *J. Chem. Soc., Perkin Trans. I*, 1990, 2624.
26. H. Liu, P. Wang, and P. Sun, *J. Fluorine Chem.*,1989, **43**, 429.
27. J Cousseau and P. Albert, *J. Org. Chem.*, 1989, **54**, 5380.
28. D.P. Cox, J. Terpinski, and W. Lawrynowicz, *J. Org. Chem.*, 1984, **49**, 3216.
29. J.H. Clark and D.K. Smith, *Tetrahedron Lett.*, 1985, **26**, 2233.
30. I. Latif, A. Malik, and W. Voelter, *Liebigs Ann. Chem.*, 1987, 617.
31. K.O. Christe, *Inorg Chem, in press*

32. K.O. Christe and W.W. Wilson, *J. Fluorine Chem.*, 1990, **47**, 117.
33. S.J. Brown and J.H. Clark, *J. Chem. Soc., Chem. Commun.*, 1985, 672.
34. A.A. Kolomeitsev, Y.L Yagupol'skii, G.N. Koidan, A.P. Marchenko, and A.M. Pinchuk, *Zh. Org. Chim.*, 1990, **26**, 1143.
35. J. Leroy, E. Hebert, and C. Wakselman, *J. Org. Chem.*, 1979, **44**, 3406.
36. M. Hudlicky, *"Organic Reactions"*, Vol 35, John Wiley and Sons, New York, 1986.
37. T. Hamatani, S. Matsubara, H. Matsuda, and M. Schlosser, *Tetrahedron*, 1988, **44**, 2875.
38. P.A. Messina, K.C. Mange, and W.J. Middleton, *J. Fluorine Chem.*, 1989, **42**, 137.
39. W.B. Farnham, D.A. Dixon, and J.C. Calabrese, *J. Am. Chem. Soc.*, 1988, **110**, 2607.
40. L.N. Markovskii, V.L Tovstenko, E.G. Martynyuk, V.E. Pashinnik, Y.V. Shermolovich, and S.V. Iksanova, *Zh. Org. Chim.*, 1990, **26**, 1372.
41. S.S. Hecht and E.S. Rothman, *J. Org. Chem.*, 1973, **38**, 395.
42. French Patent 1 374 591 (1964), Ciba Ltd: *C. Abstr.*, **62**: P9212a.
43. M. van der Akken and F. Jellinek, *Recl. Trav. Chim. Pays-Bas*, 1967, **86**, 275.
44. R.F. Hirschmann, R. Miller, J. Wood, and R.E. Jones, *J. Am. Chem. Soc.*, 1956, **78**, 4956.
45. W.R. Dolbier, T.A. Gray, and K. Ohnishi, *Synthesis*, 1987, 956.
46. W.R. Dolbier, L. Celewicz, and K. Ohnishi, *Tetrahedron Lett.*, 1989, **30**, 4929.
47. G.A. Olah, J.T Welch, Y.D. Vankar, M. Nojima, I. Kerekes, and J.A. Olah, *J. Org. Chem.*, 1979, **44**, 3872.
48. C.G. Bergstrom, R.T Nicholson, and R.M Dodson, *J. Org. Chem.*, 1963, **28**, 2633.
49. G.A. Olah and S.J. Kuhn, *J. Am. Chem. Soc.*, 1960, **82**, 2380.
50. D. Boenigk and D. Mootz, *J. Am. Chem. Soc.*, 1988, **110**, 2135.
51. G.A. Olah, *Acc. Chem. Res.*, 1980, **13**, 330.
52. T. Fukuhara, S. Sasaki, N. Yoneda, and A. Suzuki, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 2058.
53. T. Fukuhara, N. Yoneda, K. Takamara, and A. Suzuki, *J. Fluorine Chem.*, 1991, **51**, 299.
54. Y. Girault, S. Geribaldi, M. Rouillard, and M. Azzaro, *Tetrahedron*, 1987, **43**, 2485.
55. G. Haufe, S. Lacombe, A. Laurent, and C. Rousset, *Tetrahedron Lett.*, 1983, **24**, 5877.
56. G. Alvernhe, A. Laurent, K. Touhami, R. Bartnik, and G. Mloston, *J. Fluorine Chem.*, 1985, **29**, 363.
57 S. Kanemoto, M. Shimizu, and H. Yoshioka, *Tetrahedron Lett.*, 1987, **28**, 663.
58. Y. Girault, M. Rouillard, M. Decouzan, and S. Geribaldi, *J. Fluorine Chem.*, 1990, **49**, 231.

59. G.A Olah and X.Y. Li, *Synlett.*, 1990, 267.
60. A. Beamer and W. Clarke, *Ber.*, 1879, **12**, 1067.
61. J.F.T. Berliner and R.M. Mann, *J. Phys. Chem.*, 1928, **32**, 1142.
62. R. Franz, *J. Fluorine Chem.*, 1980, **15**, 423.
63. M. Hudlicky, *J. Fluorine Chem.*, 1985, **28**, 461.
64. K.O. Christe and W.W. Wilson, *J. Fluorine Chem.*, 1990, **46**, 339.
65. J.H. Clark, E.M. Goodman, D.K. Smith, S.J. Brown, and J.M. Miller, *J. Chem. Soc., Chem. Commun.*, 1986, 657.
66. A.E. Bayliff and R.D. Chambers, *J. Chem. Soc., Perkin Trans. I*, 1988, 201.
67. C. Carmona, G. Eaton, and M.C.R Symons, *J. Chem. Soc., Chem. Commun.*, 1987, 873.
68. L. Gouin, J. Cousseau, and J.A.S. Smith, *J. Chem. Soc., Faraday Trans. II*, 1977, **73**, 1878.
69. A.M. Buswell, R.L. Maycock, and W. H. Rodebush, *J. Chem. Phys.*, 1940, **8**, 362.
70. J. Emsley, *Chem. Soc. Rev.*, 1980, 91.
71. S.W. Peterson and H. A. Levy, *J. Chem. Phys.*, 1952, **20**, 704.
72. K.M. Harmon, S.L. Madeira, and R.W. Carling, *Inorg. Chem.*, 1974, **13**, 1260.
73. I. Gennick, K.M. Harmon, and M.M. Potvin, *Inorg. Chem.*, 1977, **16**, 2033.
74. L. Andrews, S.R. Davis, and G.L. Johnson, *J. Phys. Chem.*, 1986, **90**, 4273.
75. M. Bimmler, M. Von Janta-Lipinski, P. Langen, and H. Plaul, East German Patent DD 221, 736.
76. G. Alvernhe, A. Laurent, and G. Haufe, *Synthesis*, 1987, 562.
77. I. Chehidi, M.M. Chaabouni, and A. Baklouti, *Tetrahedron Lett.*, 1989, **30**, 3167.
78. G. Haufe, G. Alvernhe, and A. Laurent, *Tetrahedron Lett.*, 1986, **27**, 4449.
79. G. Alvernhe, D. Anker, A. Laurent, G. Haufe, and C. Beguin, *Tetrahedron*, 1988, **44**, 3551.
80. G. Haufe, G. Alvernhe, and A. Laurent, *J. Fluorine Chem.*, 1990, **46**, 83.
81. G. Alvernhe, A. Laurent, and G. Haufe, French Patent, 2 616 145 (1988); *C. Abstr.* **112**: 20544q.
82. G. Haufe, G. Alvernhe, D. Anker, A. Laurent, and C. Saluzzo, *Tetrahedron Lett.*, 1988, **29**, 2311.
83. C. Saluzzo, G. Alvernhe, and D. Anker, *J. Fluorine Chem.*, 1990, **47**, 467.
84. C. Saluzzo, G. Alvernhe, D. Anker, and G. Haufe, *Tetrahedron Lett.*, 1990, **31**, 663.
85. C. Saluzzo, G. Alvernhe, D. Anker, and G. Haufe, *Tetrahedron Lett.*, 1990, **31**, 2127.
86. G. Alvernhe, C.M. Ennakoua, S.M. Lacombe, and A.J. Laurent, *J. Org. Chem.*, 1981, **46**, 4938.
87. D. Picq, D. Anker, C. Rousset, and A. Laurent, *Tetrahedron Lett.*, 1983, **24**, 5619.

88. D. Picq, I. Drivas, G. Carret, D. Anker, and M. Abou-Assali, *Tetrahedron*, 1985, **41**, 2681.
89. P. Nebois, D. Picq, and D. Anker, *J. Carbohydr. Chem.*, 1990, **9**, 359.
90. D. Picq and D. Anker, *Carbohydr. Res.*, 1987, **166**, 309.
91. D. Picq and D. Anker, *J. Carbohydr. Chem.*, 1985, **4**, 113.
92. G. Alvernhe, A. Laurent, and G. Haufe, *J. Fluorine Chem.*, 1986, **34**, 147.
93. M. Muehlbacher and C.D. Poulter, *J. Org. Chem.*, 1988, **53**, 1026.
94. S. Takano, M. Yanase, and K. Ogasawara, *Chemistry Lett.*, 1989, 1689.
95. H. Amri and M.M. El Gaieo, *J. Fluorine Chem.*, 1990, **46**, 75.
96. J. Umezawa and K. Furuhashi, Japanese Patent JP 02, 167, 240 (1990).
97. M.M. Chaabouni and A. Baklouti, *Bull. Chim. Soc. Fr.*, 1989, 549.
98. J.H. Meurs, D.W. Sopher, and W. Eilenberg, *Angew. Chem., Int. Ed. Eng.*, 1989, **28**, 927.
99. N. Yoneda, T. Abe, T. Fukuhara, and A. Suzuki, *Chem. Lett.*, 1983, **7**, 1135.
100. N. Yoneda, S. Nagata, T. Fukuhara, and A. Suzuki, *Chem. Lett.*, 1984, 1241.
101. D. Haas, E. Kemnitz, M. Roennebeck, U. Schmidt, R. Kaden, and C. Henke, Patent Ger. (East) DD 268 170 (1989). *C. Abstr.*, **111**: P216313u.
102. N. Yoneda, *Tetrahedron*, 1991, **47**, 5329.
103. W.G. Brown and N.J. Letang, *J. Am. Chem. Soc.*, 1941, **63**, 358.
104. R.W. Alder, P.S. Bowmann, W.R.S. Steele, and D.R. Winterman, *J. Chem. Soc., Chem. Commun.*, 1968, 723.
105. H. Quast, W. Risler, and G. Dollscher, *Synthesis*, 1972, 558.
106. R.W. Alder, M.R. Bryce, N.C. Goode, N. Miller, and J. Owen, *J. Chem Soc., Perkin Trans I*, 1981, 2840.
107. H. Einspahr, J.-B. Robert, R.E. Marsh, and J.D. Roberts, *Acta. Crystallogr., Sect. B*, **29**, 1611.
108. M.R. Truker and B.L. Vickery, *J. Chem. Soc., Dalton Trans.*, 1972, 395.
109. E. Haselbach, A. Henriksson, F. Jachimowicz, and J. Wirz, *Helv. Chim. Acta.*, 1972, **55**, 167.
110. L.J. Altman, D. Laungani, G. Gunnarsson, H. Winnerstrom, and S. Forsen, *J. Am. Chem. Soc.*, 1978, **100**, 8264.
111. S.S. Pachkovskii and A.A. Voityuk, *Z. Fiz. Khim.*, 1990, **64**, 1592.
112. H.A. Staab and T. Saupe, *Angew. Chem. Int. Ed. Eng.*, 1988, **27**, 865.
113. R.W. Alder, *Chem. Rev.*, 1989, **89**, 1215.
114. F. Hibbert, *Acc. Chem. Res.*, 1984, **17**, 115.
115. E. Grech, Z. Malarski, and L. Sobczyk, *Chem. Phys. Lett.*, 1986, **128**, 259.
116. E. Grech, Z. Malarski, and L. Sobczyk, *J. Mol. Struct.*, 1985, **129**, 35.
117. B. Brzezinski, E. Grech, Z. Malarski, and L. Sobczyk, *J. Chem. Soc. Faraday Trans.*, 1990, **86**, 1777.
118. R.W. Alder and J.E. Anderson, *J. Chem. Soc., Perkin Trans. II*, 1973, 2086.

119. M.J Diem, D.F. Burow, and J.L. Fry, *J. Org. Chem.*, 1977, **42**, 1801.

120. A. Ishida and T. Mukaiyama, *Chem. Lett.*, 1976, 1127.

121. A. Bayliff, *Ph. D., Thesis*, Durham University, 1986.

122. R.D. Chambers, G. Taylor, and R.L. Powell, *J. Chem. Soc., Perkin Trans. I*, 1980, 426.

123. R.D. Chambers, S. Partington, and D.B. Speight, *J. Chem. Soc., Perkin Trans. I*, 1974, 2673.

124. R.D. Chambers, J.A. Jackson, and R.A Storey, *J. Chem. Soc., (C)*, 1968, 2221.

125. C.J. Drayton, W.T. Flowers, and R.N. Hazeldine, *J. Chem. Soc., (C)*, 1971, 2750.

126. R.L. Dressler and J.A. Young, *J. Org. Chem.*, 1967, **32**, 2004.

127. A.G. Pittman, D.L. Sharp, and R.E. Lundin, *J. Polymer Sci., A11*, 1966, **4**, 2637.

128. J.S. Brimacombe, A.B. Foster, R. Hems, J.H. Westwood, and L.D. Hall, *Can. J. Chem.*, 1970, **48**, 3946.

129. W.A. Szarek, G.W. Hay, and B. Doboszewski, *J. Chem. Soc., Chem. Commun.*, 1985, 663.

130. J.S. Brimacombe, P.A. Gent, and M. Stacey, *J. Chem. Soc. (C).*, 1968, 567.

131. L.N. Yakhontov, *Russ. Chem. Rev.*, 1984, **53**, 757.

132. I.B. Simon and V.P. Vvedenskii, *Zh. Obs. Khim.*, 1964, **34**, 4037.

133. S.J. Angyal and W.K. Warburton, *J. Chem. Soc.*, 1951, 2492.

134. P. Bosch, F. Camps, E. Chamarro, V. Gasol, and A. Guerroro, *Tetrahedron Lett.*, 1987, **28**, 4733.

135. J. March, *"Advanced Organic Chemistry"*, John Wiley and Sons, New York, 1985.

136. V. Kurasov, Zh. Org. Khim., 1983, 19, 590.

137. M.L. Hallensleben and H. Kansy, *Makromol. Chem.*, 1989, **190**, 231.

138. N.V. Vistorobskii and A.F. Pozharskii, *Z. Org. Chim.*, 1989, **25**, 2154.

139. G. Opitz, K. Rieth, and G. Rimmler, *Tetrahedron Lett.*, 1986, **27**, 167.

140. F. Terrier, J-C. Halle, M-J. Pouet, and M-P. Simonnin, *J. Org. Chem.*, 1986, **51**, 409.

141. M-P. Simonnin, J-C. Halle, M-J. Pouet, F. Terrier, and D. Davoust, *Can. J. Chem.*, 1986, **64**, 404.

142. R.D. Chambers, R.S. Matthews, G. Taylor, and R.L. Powell, *J. Chem. Soc., Perkin Trans. I*, 1980, 435.

143. R.D. Chambers and M.R. Bryce in *"Comprehensive Carbanion Chemistry"*, eds. E. Buncel and T. Durst, Elsevier, Amsterdam, 1987, ch. 5, p. 293.

144. M.R. Bryce, R.D. Chambers, and G. Taylor, *J. Chem. Soc., Perkin Trans. I, 1984, 509.*

145. M.W. Briscoe, R.D. Chambers, S.J. Mullins, T. Nakamura, and F.G. Drakesmith, *J. Chem. Soc., Chem. Commun.*, 1990, 1127.

146. T. Nakamura, these laboratories.

147. D.J. Cowley and I. Pasha, *J. Chem. Soc., Perkin Trans. 2.*, 1981, 918.

148. R.D Chambers, *Adv. Heterocycl. Chem.*, 1981, **28**, 1.

149. J.M.E. Quirke, in *"Comprehensive Heterocyclic Chemistry"*, Eds. A.J. Boulton and A McKillop, Pergamon, Oxford, 1984.

150. J.K. Chakrabarti, A.F. Cockerill, G.L.O. Davies, T.M. Hotten, D.M. Rackham, and D.E. Tupper, *J. Chem. Soc., Perkin Trans II*, 1974, 861.

151. R.A. Shaw and P. Ward, *J. Chem. Soc.*, 1965, 5446.

152. R.A. Shaw and P Ward, *J. Chem. Soc. (B)*, 1968, 1431.

153. R.A. Shaw and P. Ward, Brit. Pat., 1, 119, 824 (1968). *C. Abstr.*, **69**: P87024.

154. R.A. Shaw and P. Ward, *J. Chem. Soc., (B)*, 1967, 123.

155. R.A. Shaw and P. Ward, *J. Chem. Soc. (B)*, 1969, 596.

156. T.L. Gilchrist, *"Heterocyclic Chemistry"*, Pitman, London, 1985.

157. J.K. Chakrabarti, R.W. Goulding, and A. Todd, *J. Chem. Soc. Perkin Trans I*, 1973, 2499.

158. J.K. Chakrabarti and D.E. Tupper, *J. Het. Chem.*, 1974, **11**, 417.

159. J.K. Chakrabarti and D.E. Tupper, *J. Org. Chem.*, 1975, **40**, 958.

160. J.R. Sandler, *J. Org. Chem.*, 1970, **35**, 3967.

161. R.A. Shaw and P. Ward, *J. Chem. Soc., Perkin Trans II*, 1973, 2075.

162. J.K. Chakrabarti and A. Todd, *Eur. J. Chem.-Chim. Ther.*, 1974, **9**, 146.

163. J.K. Chakrabarti and A. Todd, U.S. Pat., 3, 830, 915 (1974). *C. Abstr.*, **81**: P164750t.

164. J.K. Chakrabarti and A. Todd, Ger. Pat., 2, 117, 100 (1971). *C. Abstr.*, **76**: P46220u.

165. J.K. Chakrabarti and A. Todd, Brit. Pat., 1, 353, 581 (1970). *C. Abstr.*, **81**: P63688y.

166. J.K. Chakrabarti and D.E. Tupper, *Tetrahedron*, 1975, **31**, 1879.

167. D.J. Chadwick, in *"Comprehensive Heterocyclic Chemistry"*, Eds. C.W. Bird and G.W.H. Cheeseman, Pergamon, Oxford, 1984.

168. H-O. Kalinowski, S. Berger, and S. Braun, *"^{13}C NMR Spectroscopy"*, John Wiley and Sons, New York, 1988.

169. D.J. Williams, *Angew. Chem. Int. Ed. Engl.*, 1984, **23**, 690.

170. W. Rettig, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 971.

171. L.S. Pu, *J. Chem. Soc., Chem. Commun.*, 1991, 429.

172. R.D. Chambers, P.D. Philpot, and P.L. Russell, *J. Chem. Soc., Perkin Trans. I*, 1977, 1605.

173. C.H. Dungan and J.R. Van Wazer, *"Compilation of Reported ^{19}F NMR Chemical Shifts"*, Wiley-Interscience, New York, 1970.