Hasson, Samia J. (1983) *Preparation and complexation reactions of some sulfur compounds.* PhD thesis.

A Thesis

entitled

PREPARATION AND COMPLEXATION REACTIONS OF SOME SULFUR COMPOUNDS

submitted to the

UNIVERSITY OF GLASGOW

in fulfilment of the
requirements for the
degree of

DOCTOR OF PHILOSOPHY

by

Samia J. HASSON, B.Sc. (Baghdad)

Department of Chemistry,
University of Glasgow,
Glasgow G12 8QQ.

August 1983

ACKNOWLEDGEMENT

I wish to thank my supervisor, Professor D.W.A. Sharp, for his valued advice and encouragement during the course of this work. I am especially indebted to Dr. D.S. Rycroft who spent much time and patience in supervising the NMR work. My thanks go to Mr. T. Boyle for technical assistance. Thanks are also due to the members of staff of Chemistry Department who were always willing to help with any problems, in particular the Inorganic and Organic groups.

I would like to thank the members of my family for their support, financial and otherwise, over the past few years, especially my husband KHazzal and my children Adel and Ebtehal, and to my fellow research students.

The financial support by IRAQI Government and University of Basrah is gratefully acknowledged.

Abstract

The aim of this work was to prepare metal complexes of organothiolate derivatives.

General chemistry of sulfur, in particular new sulfur compounds, is reviewed. The reaction of α-β-dibromobis(pentafluorophenyl)ethane with copper phenylthiolate, copper methylthiolate and sodium methylthiolate in different polar solvents e.g., ammonia and dimethylformamide, and of α-β-dibromobis(pentafluorophenyl)ethene with copper methylthiolate resulted in both debromination and nucleophilic displacement of para fluorine atoms in the ring. The type of nucleophilic displacement depends on the solvent employed and on the amount of the reagent. The reaction using $NaSMe/NH_3$ give methanethiolate derivatives as products in good yield.

In the reactions using copper methylthiolate in dimethylformamide, products were predominantly those corresponding to nucleophilic substitution of dimethylamino groups into the aromatic rings. Bis(4-dimethylaminotetrafluorophenyl)ethyne interacts with cobalt carbonyl and iron carbonyl to give derivatives with complexing through the triple bond.

Infrared, mass and n.m.r. spectra have been recorded and discussed for all products.

Bis(alkylthio)alkanes and alkylthio ethenes have been prepared by photochemical reactions e.g.

$$CH_3SH + PhC{\equiv}CH \xrightarrow{h\nu} CH_3SCHPhCH_2SCH_3$$

The photolytic reactions are considered to proceed via sulfur-containing radicals. The isomers formed in these reactions are discussed. Interactions of bis(alkylthio)alkanes and alkylthio — ethenes with palladium(II) dichloride and tetrachloroplatinates(II) afforded new complexes of the type LMX_2 and L_2MX_2 in which the ligands may be bonded in a bidentate or monodentate mode. Co-ordination is generally from the CH_3S grouping.

In solution all complexes containing five-membered chelate rings exhibit the presence of isomers due to inversion of configuration at sulfur and the relative position of methylene substituents. Thus for the compounds containing $CH_3SCH(R)CH_2SCH_3$ and $CH_3SCH(R)CH(R)SCH_3$ ligands with planar MX_2 4 and 6 isomers are possible. Isomers can be identified by spectroscopy and by consideration of steric effects in the complexes. ^{195}Pt nmr studies have shown the existence of all possible isomers for the first time in such complexes.

CONTENTS

CHAPTER 1

SULFUR

CHAPTER 1

SULFUR

History and occurrence

Sulfur is one of the most versatile and essential elements on this planet. It is one of the chemical industry's most widely used raw material as sulfuric acid is one of the biggest tonnage chemicals.

Although sulfur has been known and used by man for thousands of years, it was considered a strange earth until Lavoisier proved that it is an element.

Prehistoric man used sulfur to colour his cave drawings and supposedly ate sulfur as a spring tonic to purify his blood. Man discovered that the strange yellow rock would burn with an ethereal blue flame to give off a sharp pungent odour.

This seemingly supernatural power led him to believe that the burning sulfur could be used to ward off evil spirits.

Historians report that some twenty centuries before the birth of Christ, high priests used the same qualities of sulfur to add mysticism to temple sacrifices and purification rites.

About 1600 BC the Egyptians discovered that sulfur dioxide from the burning of sulfur had practical value as a bleach for cotton and linen. Egyptian artists at the same time used various sulfur compounds as colour additions for paints.

In 1000 BC Homer said that Odysseus burned sulfur in his home presumably as a fumigant after he had slain his wife's suitors.

In 500 BC when the Chinese invented gun-powder, they used sulfur as an ingredient. Free sulfur deposits are located in volcanic regions, such as Sicily, Iceland, Mexico, Spain and Japan. In Louisiana and Texas underground deposits of free sulfur exists which probably had been formed through the reduction of sulfates.[1]

The first commercial sulfur was produced in Sicily early in the fifteenth century. There was much competition for control of the Sicilian sulfur deposits.

In 1735 there was commercial development of a process to manufacture sulfuric acid from sulfur and sulfur production became Sicily's chief industry. A French company realising the potential value of sulfur gained control of the Sicilian deposits in 1839 and subsequently raised the price of sulfur. Other countries, particularly England and the United States, undertook the development of their own sources. They soon learned that sulfuric acid could be made from sulfur dioxide derived from the roasting of iron pyrites.

Frasch conceived the idea of the melting elementary sulfur underground by injecting superheated water into the formation and then lifting the sulfur to the surface with a sucker-rod pump (The Frasch process) Fig. (1).

Frasch proceeded with his scheme and in December 1864 pumped the first flow of molten sulfur from the Calcasien Parish deposit.

The Calcasien Parish deposit was buried hundreds of feet beneath successive strata of clay, gravel and quicksand which contained hydrogen sulfide.

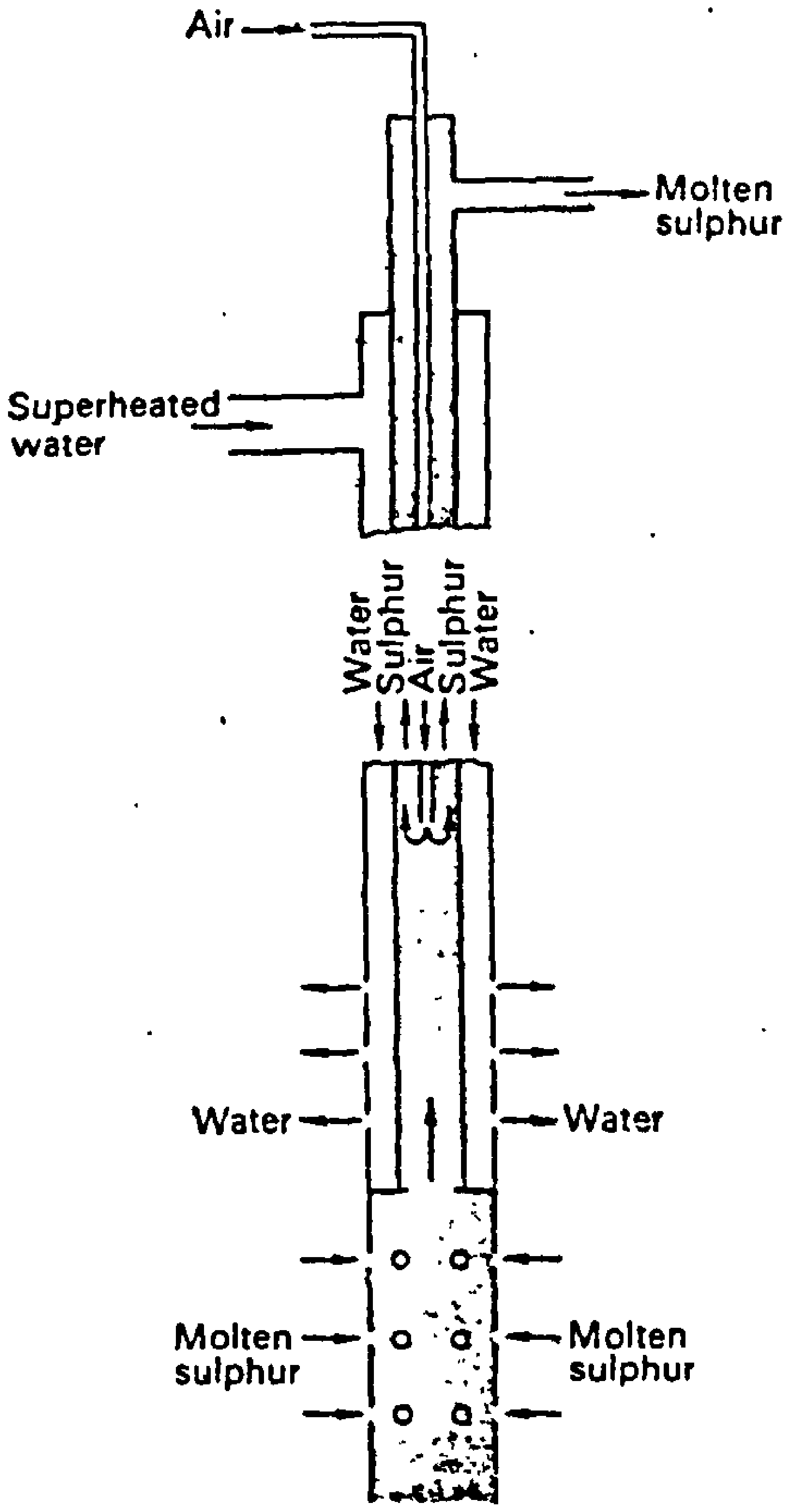


Figure (1) - The Frasch Process

Eight years later, after a succession of setbacks, the French process was established as a commercial success. In the 1890's Frasch developed a process for removing sulfur from crude oil. The sulfur is normally from hydrogen sulfide in the crude oil. Petroleum and coal have become very large resources and their use has grown rapidly. Other sources include metal sulfides (such as pyrites and sulfate minerals [gypsum, $CaSO_4$]). Sulfur also occurs in the vast Athabasca Tar Sands of Canada as sulfur compounds.[2]

Sulfur is called Schwefel in Germany, Soufre in France, Solfo or Zolho in Italy, Zufre in Spain and Kebreet كبريت in Arab countries.

Sulfur is normally one of the most recession-resistant products in the entire chemical industry, but in the recent recession over the last two years has joined the pack of industrial chemicals where supply outstrips demand. Sulfur, most of which is converted to sulfuric acid, is one of the true workhorse materials of the chemical industry. But during the last few years the horse has gone lame.

Thus in 1982 sulfur has suffered badly from declining demand topped off by a round of lower posted prices as the fourth quarter opened. This year (1983) especially in the second half, the grass may be greener and sulfur demands could improve. However full recovery to 1981 levels won't happen very soon.[3]

Production/Capacity

Millions of Long Tons

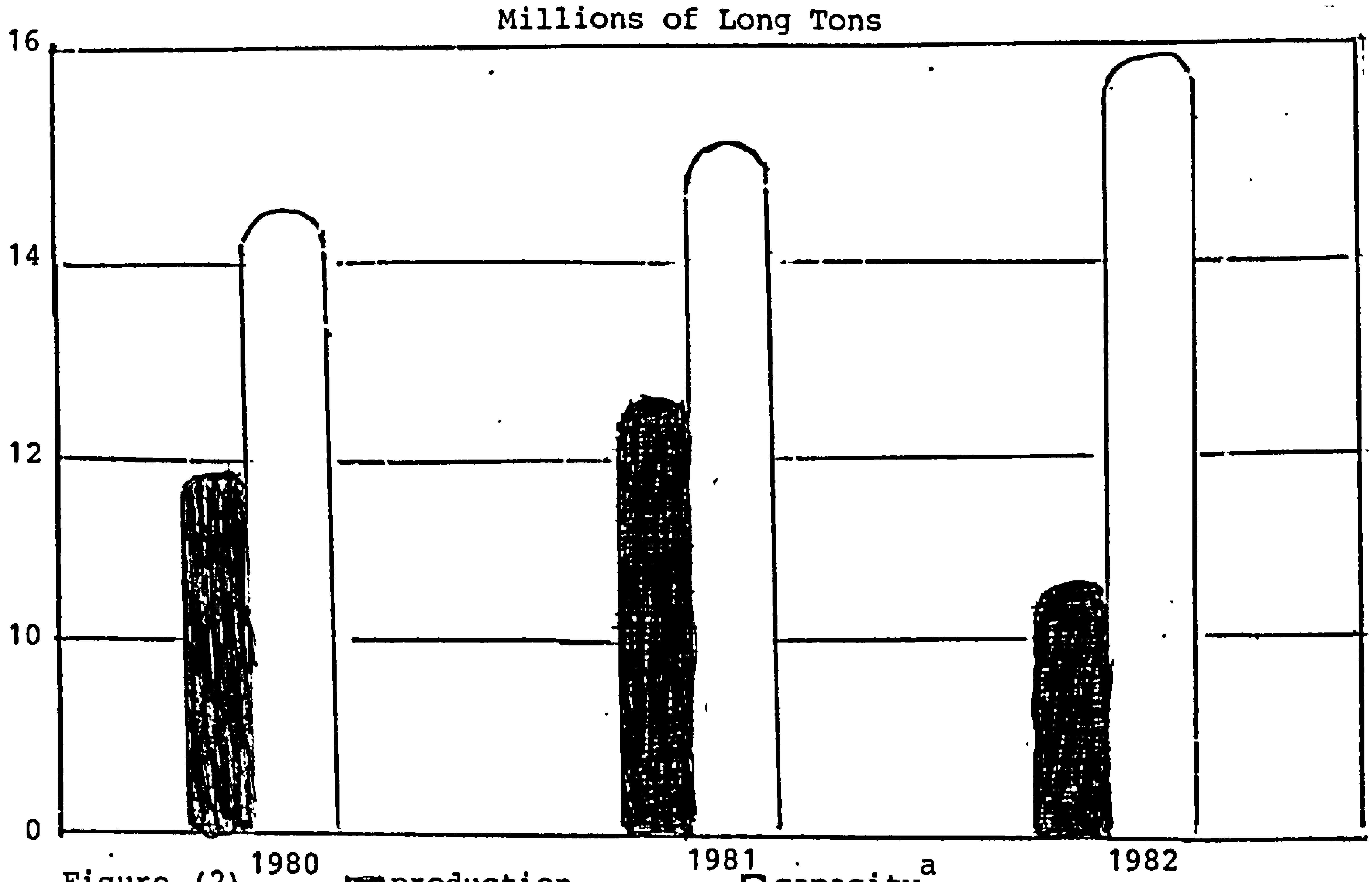


Figure (2). ▨production, ☐capacity[a]

a) All sources as of first quarter; excludes standby capacity of about 5 million long tons at recovery plants and smelters.

Uses

Sulfur is used directly or indirectly in the manufacture of such a diversity of products that a nation's sulfur consumption is considered to be a barometer of its economic activity.[2]

The largest single use for sulfur is in the production of sulfuric acid, which is then used in many other manufacturing processes. Therefore, the uses for sulfur are usually classified as either sulfuric acid uses or non-acid uses.

Sulfuric acid is used primarily for the manufacture of fertilizers, organic and inorganic chemicals, pigments, steel, rayon, petroleum products and explosives, all of which use sulfuric acid.

Sulfur is used in highway marking in its plastic form mixed with a dye and reflecting beads. It is sprayed on the surface of the highway with a conventional type of paint sprayer. The paint adheres very well both to asphalt and concrete surfaces without prior preparation and is apparently very wear resistant

Health and safety factors

Solid elemental sulfur in itself is virtually non-toxic and can be taken internally without injury. Although the inhalation of sulfur dust is not known to be harmful, when sulfur burns in air it forms sulfur dioxide, an irritant gas which affects the eyes and respiratory tract.

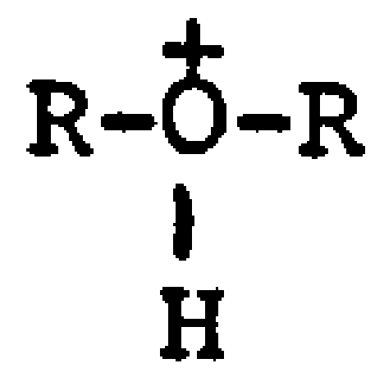
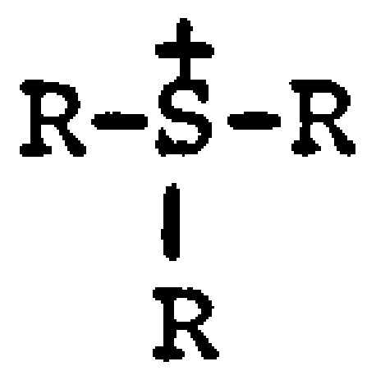
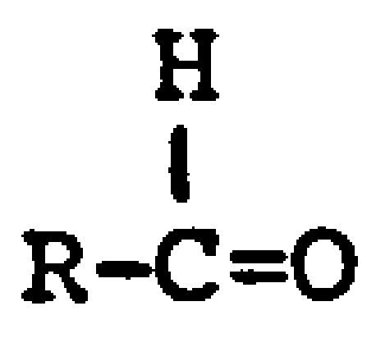
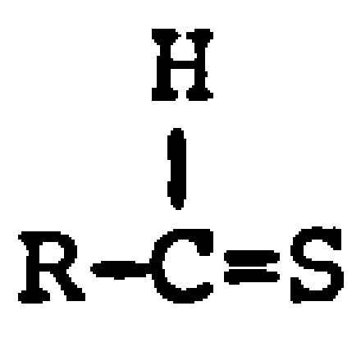
Because of the low ignition temperature of sulfur and its tendency to develop static charges, sulfur dust presents a fire and explosion hazard. Sulfur liquifies at 160°C.

The primary hazards to be recognised when handling liquid sulfur include its relatively low ignition point, the possible presence of hydrogen sulfide and the fact that it is a hot liquid capable of producing severe burns.[4,5]

Sulfur compounds

A key feature of the industrial chemistry of sulfur is that sulfur is abundant and inexpensive. It has therefore attracted much effort by industrial and academic research workers. Sulfur chemistry has traditionally been considered in terms of organic and inorganic divisions. A knowledge of both the organic and inorganic aspects is essential for understanding the full scope of sulfur chemistry and the artificial separation between organic and inorganic of sulfur chemistry is not desirable. Many sulfur compounds are formally analogous to oxygen compounds as may be expected from the periodic table with oxygen and sulfur as the first and second members of the sixth main group One major difference between sulfur and oxygen is the ability of sulfur to show higher oxidation states such as 4^+ and 6^+, e.g. (SF_4, SF_6, $H_2C{=}SF_4$).

Table (1) lists some compounds of sulfur which are formal analogues of oxygen compounds

Oxygen group	Sulfur group
alcohol, ROH	thioalcohol, RSH also called thiol or mercaptan
phenols, ArOH	thiophenols, ArSH
peroxides, ROOR	disulfides, RSSR
cyanates, ROCN	thiocyanates, RSCN
isocyanates, RN=C=O	isothiocyanates, RN=C=S
oxonium ion  $R-\underset{H}{\overset{+}{O}}-R$	sulfonium ions,  $R-\underset{R}{\overset{+}{S}}-R$
aldehydes,  $R-\overset{H}{C}{=}O$	thioaldehydes,  $R-\overset{H}{C}{=}S$
ketones, $R_2C{=}O$	thioketones, $R_2C{=}S$

Electronegativity and orbital ionisation potentials

Electronegativity is defined as the ability of an atom in a molecule to attract electrons to itself.

Ionisation potential is the energy required to remove an electron from a gaseous atom, leaving both the electron and the resulting ion without kinetic energy.

Electron affinity is the energy of the converse process to ionisation, that is the energy when a gaseous species gains an electron. Mulliken's definition of the electronegativity x of element is

$$x = \frac{1}{2}(I_\nu + E_\nu)$$

I_ν = ionisation potential of the valence state and E_ν is the electron affinity.

The most electronegative elements occur in the top-right corner of the Periodic Table and electronegativity falls on going down and to the left along a period towards the alkali metals. The electronegativity of the element decreases with rise in oxidation state and depends also on the other atoms attached to it. Thus carbon in CH_3-X is less electronegative than carbon in F_3C-X, as the highly electronegative fluorine atoms in the trifluoromethyl compound remove more electron density from the carbon in the C-F bond than the hydrogen atom in the C-H bonds. The carbon atom in F_3C-X has more tendency to attract the electron in the C-X bond than has the carbon atom in H_3C-X. This fact is important in our work [page 69].

The values of electronegativity are O 3.5, S 2.44 and Se 2.48.

Isotopes of sulfur

There are ten isotopes of sulfur, four of which are stable whilst the remaining six are radioactive. As found in nature, sulfur has a mean atomic weight of 32.064 with approximate distribution,[8,9] between the four stable isotopes ^{32}S, 95%; ^{33}S, 0.76%; ^{34}S, 4.22% and ^{36}S, 0.02%.[10] The best known radioactive isotope is ^{35}S, which has fairly good characteristics for tracer studies. For example, it has been used to study,[11] sulfur and sulfide ion exchange in polysulfide solutions and also to study S^{2-} and SO_4^{2-}, SO_3^{2-} and SO_4^{2-}, H_2SO_3 and HSO_4^- exchange even at 100°C.

As an example of the use of radioactive sulfur traces, if radioactive sulfur is reacted with inactive SO_3^{2-} to form $S_2O_3^{2-}$ and then the sulfur removed with acid, the H_2SO_3 regenerated is inactive, therefore the two sulfur atoms in thiosulfate are not equivalent. The ions $S_2O_3^{2-}$ and SO_3^{2-} exchange only very slowly at room temperature, but exchange sulfur fairly rapidly at 100°C. Extensive tracer studies have been made for sulfur compounds in the agricultural and biological fields.[13]

Elementary forms of sulfur

Sulfur exists in the gaseous liquid and solid phases and the relationships between the various phases are exceedingly complex.[14] Fig. (3) shows the phase diagram of sulfur with P plotted against T.[15] Four phases are involved, an orthorhombic solid, a monoclinic solid and vapour.

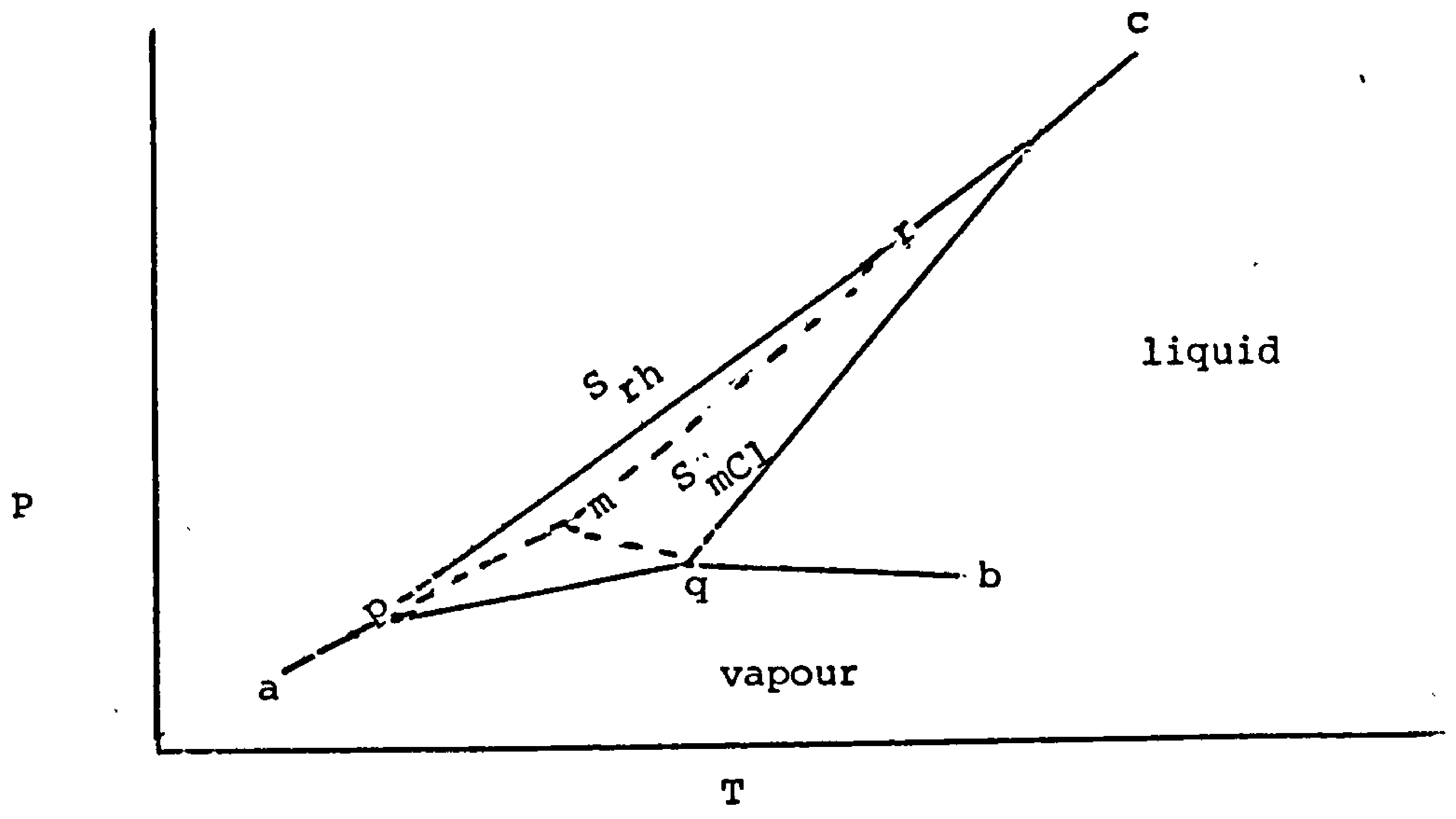


Figure (3)*

---

* Coordinates are not given on the pressure and temperature axes because this phase diagram cannot conveniently be drawn quantitatively. The three invariant points p, q, m lie rather close together on the p-axis at low pressures while the invariant point r lies at very much higher pressure. The phase diagram Fig. (3) is simply schematic.

Phase diagram for sulfur

The solid lines represent equilibria between stable phases; broken lines represent metastable equilibria in the stability field of monoclinic sulfur, i.e. mr is a metastable extension of rc, pm of ap, mq of qb, which correspond respectively to $S_{rh} \rightleftharpoons$ vapour $\rightleftharpoons$ liquid $\rightleftharpoons$ vapour (S_{rh} = orthorhombic sulfur; S_{mCl} = monoclinic sulfur. In the solid state the following phases have been established (note that many of these phases are metastable and do not appear in the above phase diagram.)

1) Solid State

In the solid state sulfur has phases containing cyclic polymers S_n when n varies from 6 to 20. There are also chain forms.

A. Cyclo hexasulfur formed pure from the following reaction in ether. $S_2C\ell_2 + H_2S_4 \longrightarrow S_6 + HC\ell$ or by addition of concentrated $HC\ell$ to an aqueous solution of $Na_2S_2O_3$ at -10°C, extraction of the precipitate with benzene followed by crystallization to give orange crystals.[16] It decomposes quite rapidly and is chemically more reactive than S_8 probably because the ring is more strained.

B. Cyclooctasulfur S_8

There are three main allotropes, S_α, S_β, S_γ. Normal commercial sulfur contains eight-membered ring cyclic molecules crystallizing in the orthorhombic system:- Figure (4).

Figure (4) - Orthorhombic system

The structures of S_8 [17,18]

On heating, orthorhombic cycloocta-S is converted into monoclinic cycloocta-S. The monoclinic $S_{(\beta)}$ is stable between 95°C and the melting point.

Whenever sulfur crystallizes from solutions or melts, monoclinic sulfur crystals are formed within the temperature range of 95°C to about 119°C.

S_γ:- is also cycloocta sulfur - it transforms slowly into S_β and/or S_α on standing and is stable between 95-115°C[19] up to the melting point.

The eight-membered rings should be stable in different conformations but only the crown shape is known.[20,21,22,23]

The ring conformation is a result of the gauche interactions in the S-S-S systems

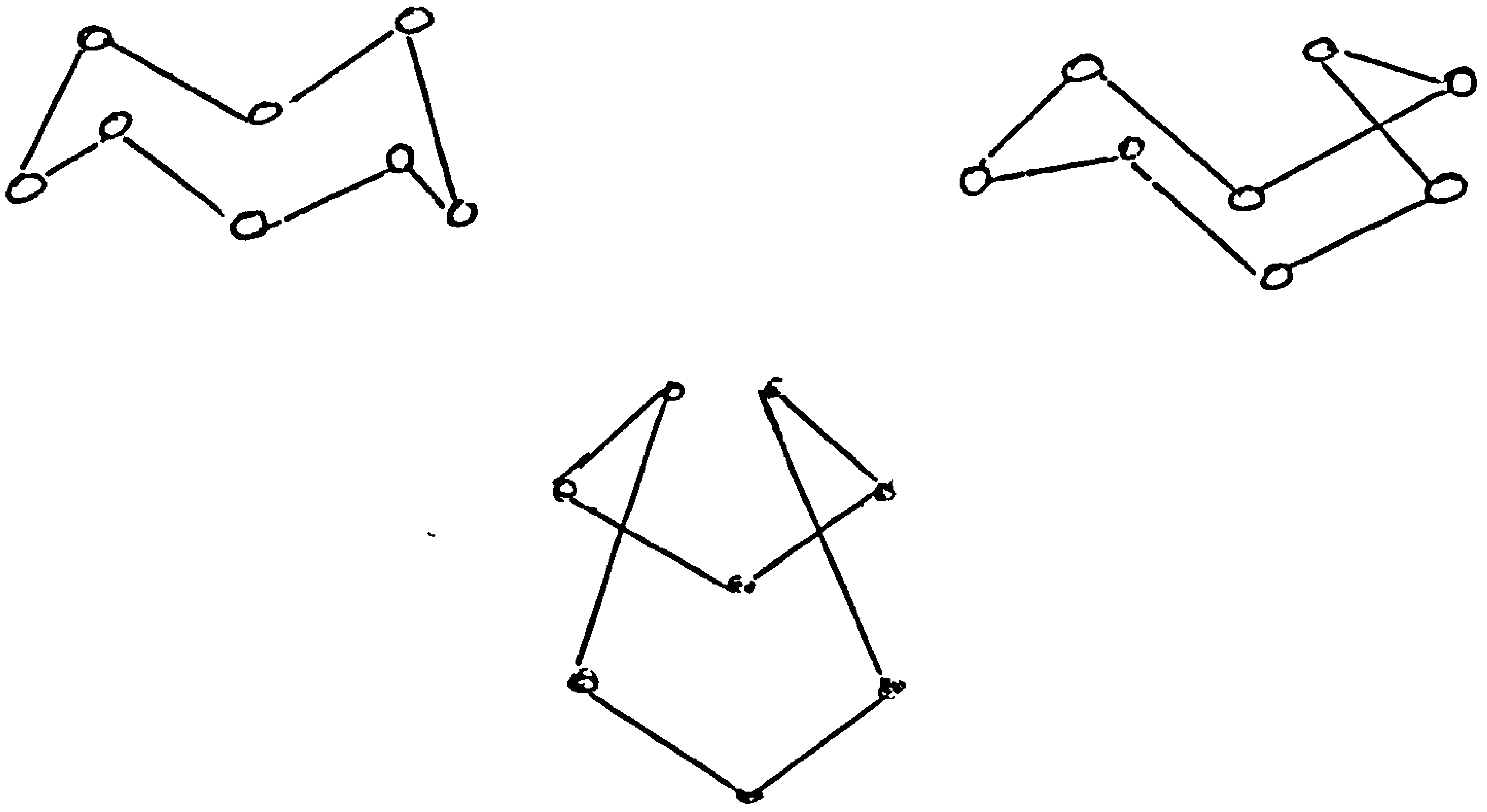


Figure (5) - Crown shape of eight-membered rings

Other forms of sulfur known include e.g. S_{10}:- an olive green solid prepared by slow reaction of

H_2S_6 + $S_4C\ell_2$ in dry ether in the dark[24]

S_{12}:- is unexpectedly stable. It crystallizes in pale yellow lamellae (m.p. = 146-148°C). The bond distance is 2.050 ± 0.05Å. The bond angles 106.8 ± 1°; and the torsion angle 107.5 ± 1°. S_6 and S_{12} are prepared by reaction of bis(cyclopentadienyl)titanium(IV)pentasulfide with $\mathrm{SC\ell_2}$[26]

$$\begin{aligned}(\mathrm{C_5H_5})_2\mathrm{TiS_5} \quad &+ \ \mathrm{SC\ell_2} \longrightarrow (\mathrm{C_5H_5})_2\mathrm{TiC\ell_2} + \mathrm{S_5} + \mathrm{S_{12}}\\ &+ \ \mathrm{S_2C\ell_2} \longrightarrow \mathrm{S_7}\\ &+ \ \mathrm{S_4C\ell_2} \longrightarrow \mathrm{S_9}\\ &+ \ \mathrm{SO_2C\ell_2} \longrightarrow (\mathrm{S_5}) \longrightarrow 1/2\ \mathrm{S_{10}}\end{aligned}$$

This procedure is a general method also suitable for the preparation of S_7, S_9 and S_{10}

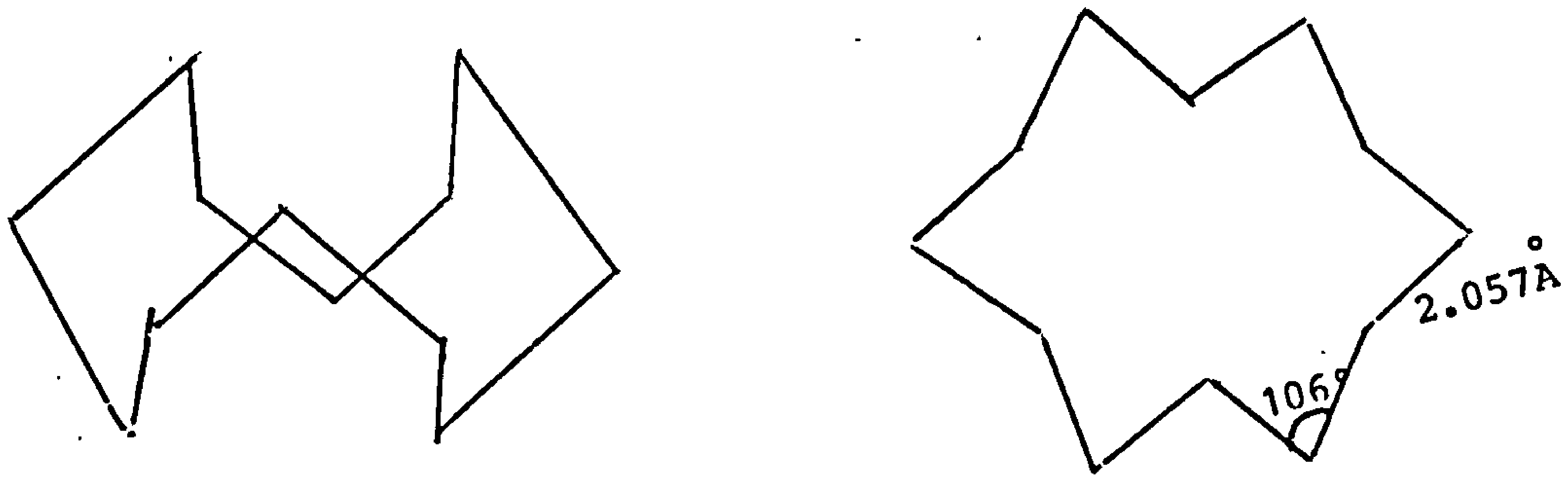


Figure (6) - S_{12}

B. Meyer, Chem. Rev., 1976, 76, 367.

S_{12} is more stable than S_6 and can be kept. S_6 and S_7 have been studied by R. Steudel and Hans-Joachim Mäusle. Since the IR and Raman spectra of S_6,[27] S_7,[28a] S_8,[29] S_{10},[28b] and S_{12}[30] rings and of the chain shaped polysulfide ions S_n^{2-} (n=3 to 8)[31] are known, it should be possible to carry out qualitative analysis of sulfur melts by vibrational spectroscopy.

S_6, IR:- 313; Raman 265, 203 cm^{-1}

S_7, IR:- 516, 481, 400, 270 Raman 518, 481, 402, 360, 239 cm^{-1}

The seven-membered ring in S_7 has an unusually long S-S bond 2.18Å c.f. normal Ca. 2.06Å, The cyclosulfurs S_{18} (decompose 126°) and S_{20} (decompose 121°) are quite stable, but other cyclosulfurs are thermodynamically unstable and sensitive to light and air, although they can be preserved at low temperatures.

Catenasulfur

When molten sulfur is poured into ice water, so-called plastic sulfur is obtained. Normally this has S_8 inclusions and can be obtained as long fibres by heating S_α in nitrogen at 300°C for 5 minutes followed by quenching a thin stream in ice water. These fibres can be stretched under water and appear to contain helical chains of sulfur atoms with about 3.5 atoms per turn. Unlike the other sulfur allotropes catenasulfur is insoluble in CS_2; it transforms to S_α[32] on heating.

Liquid sulfur

On melting, cyclooctasulfur first gives a yellow, transparent mobile liquid, which becomes brown and increasingly viscous above about 160°C. The viscosity reaches a maximum at about 200°C and thereafter falls until at boiling point 444.60°C the sulfur is again a rather mobile, dark red liquid. Together with this viscosity change the specific heat, the density, the electric conductivity, the velocity of sound and almost all physical properties show a discontinuity[33] around 160°C. The physical properties of liquid sulfur are so unusual that they are familiar demonstrations to school students. The phenomena are related to equilibrium polymerization of sulfur initiated by ring scission.[34]

Sulfur vapor

In addition to S_8 sulfur vapor contains S_3, S_4, S_5, S_7 and probably other S_n species, in temperature dependent equilibrium. S_2 molecules predominate at higher temperatures above 2200°C and at pressures below 10^{-7} cm/Hg sulfur atoms predominate and can be condensed to give highly coloured solids, unstable above -80°C, which contain S_2 molecules. These have two unpaired electrons as does O_2.

Stereochemistry of sulfur

Sulfur shows very marked tendencies to form rings and chains of linked sulfur atoms as in elemental sulfur. π-bonding is however often important particularly for S=O groups in compounds such as the sulfoxide R_2SO. The π-bonds between two atoms are formed by sideways overlap of atomic orbitals of suitable symmetry. In the case of sulfoxides the bonds are formed from sp^3 hybrids on the sulfur atom using all 3p orbitals on the sulfur. The π-bond requires the use of a suitable sulfur 3d orbital to overlap with a p orbital of the oxygen. This bond is shown in figure (7) which also shows the lone pair and the d-p π-orbital. π-bond affects the bond order and angles.

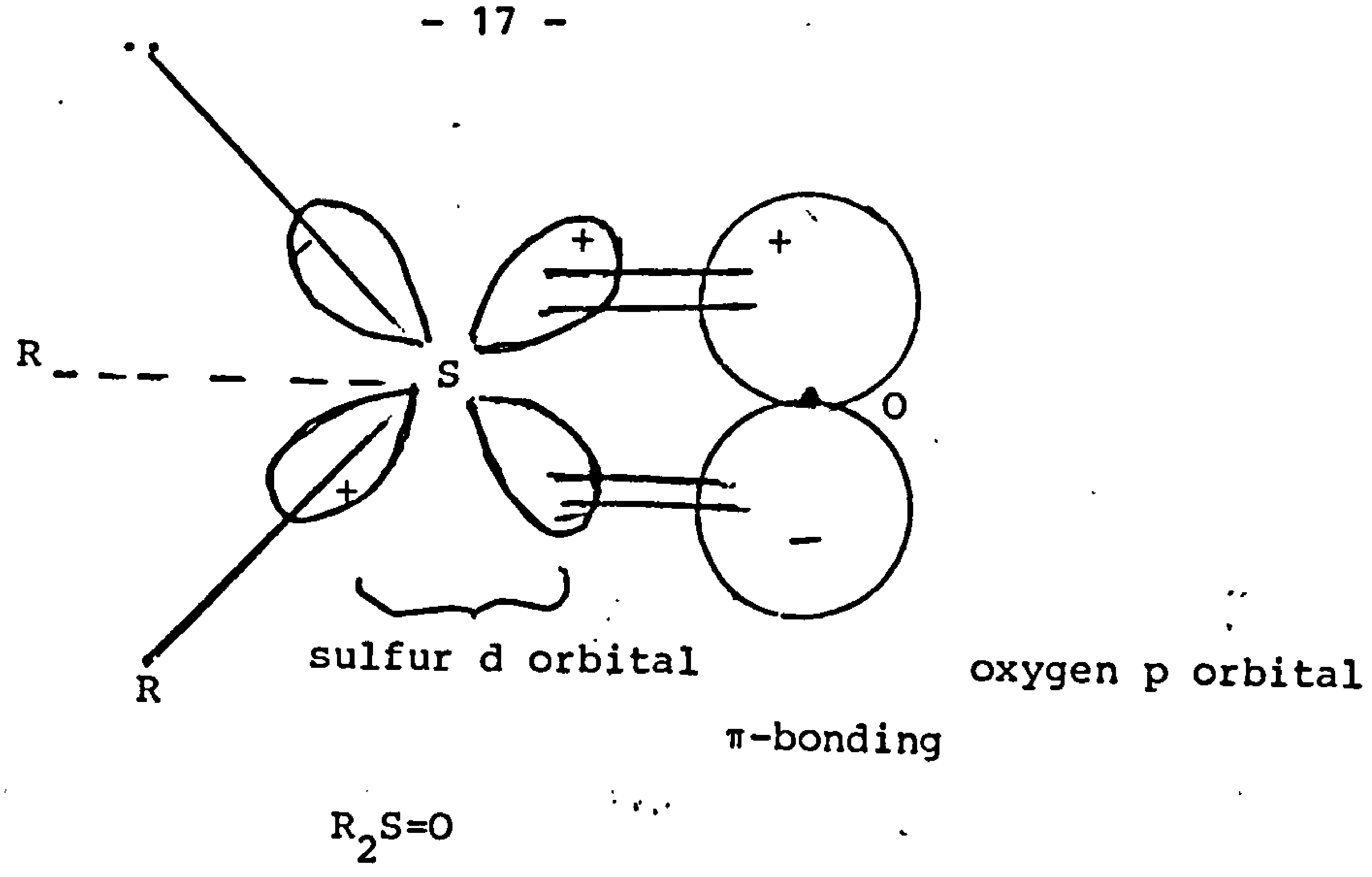


Figure (7) - Localised π-bonds in a sulfoxide

The tendency of sulfur to act as a donor atom also has a profound effect on its stereochemistry.

For the purposes of this discussion we will use a system based on the coordination number of the element rather than on the hybridisation scheme. For each coordination number the different hybridisation possibilities are discussed and hence the different stereochemical arrangements. Coordination of sulfur is conventionally formulated as considering a central atom surrounded by a set [usually 2 to 6] of other atoms, ions or small molecules, the latter being called ligands. We shall discuss briefly each coordination number.

Coordination number (2)

The majority of sulfur compounds with coordination number 2 have their geometry explained in terms of sp^3 hybridisation with two lone pairs. It is however also necessary to consider effects introduced by multiple bonding, particularly of the pπ-pπ type, as in SO_2 which formally has sp^2 hybridisation. It is also important to consider electron pair repulsions. The literature contains a large number of investigations of compounds in which S is bonded to two other atoms and it is convenient to distinguish between the case of S bonded in chains and in cyclic system; the latter case is particularly important in our work.

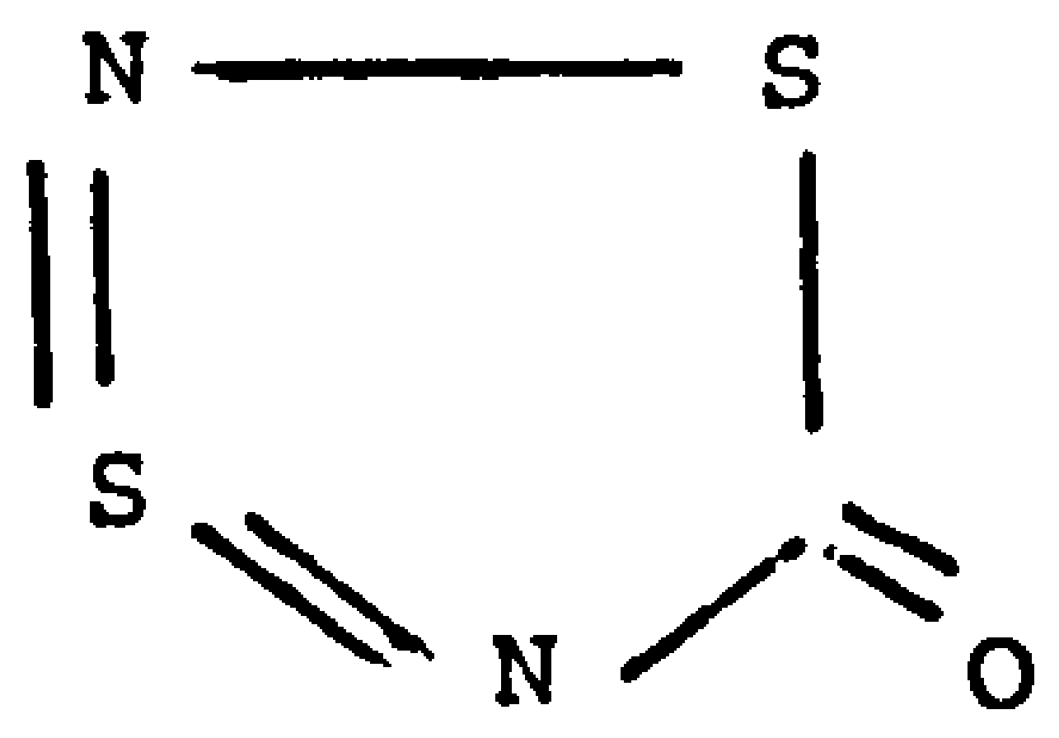
There are two hybridisation schemes leading to a simple σ-bond description for this coordination number.

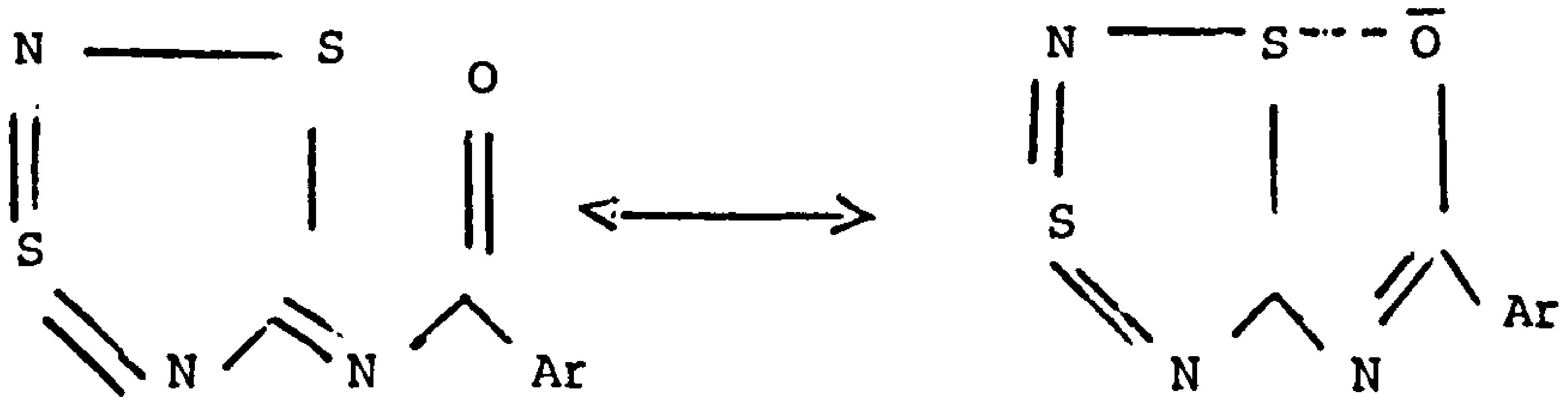
i) Formal sp^2 hybridisation with one lone pair, sulfur in oxidation state four. The hybridised orbitals are formed by one s and three p orbitals. These are directed towards the corners of trigonal pyramidal. The resultant bond angles are thus about 120°.

ii) Formal sp^3 hybridisation with two lone pairs (bond angle 109°) such as RSR, formal oxidation state two. The hybridised orbitals are formed by one s and three p orbitals. These are directed towards the corners of a tetrahedron. The resultant bond angles are 109° but will be altered by π-bonding, i.e. different R groups.

Examples of these systems are:

Sulfurdi-imides - these are useful key substances in heterocyclic synthesis by reaction of sulfurdi-imides with bifunctional acid chlorides and afford novel heterocycles as follows.[35,36,37,38]





39

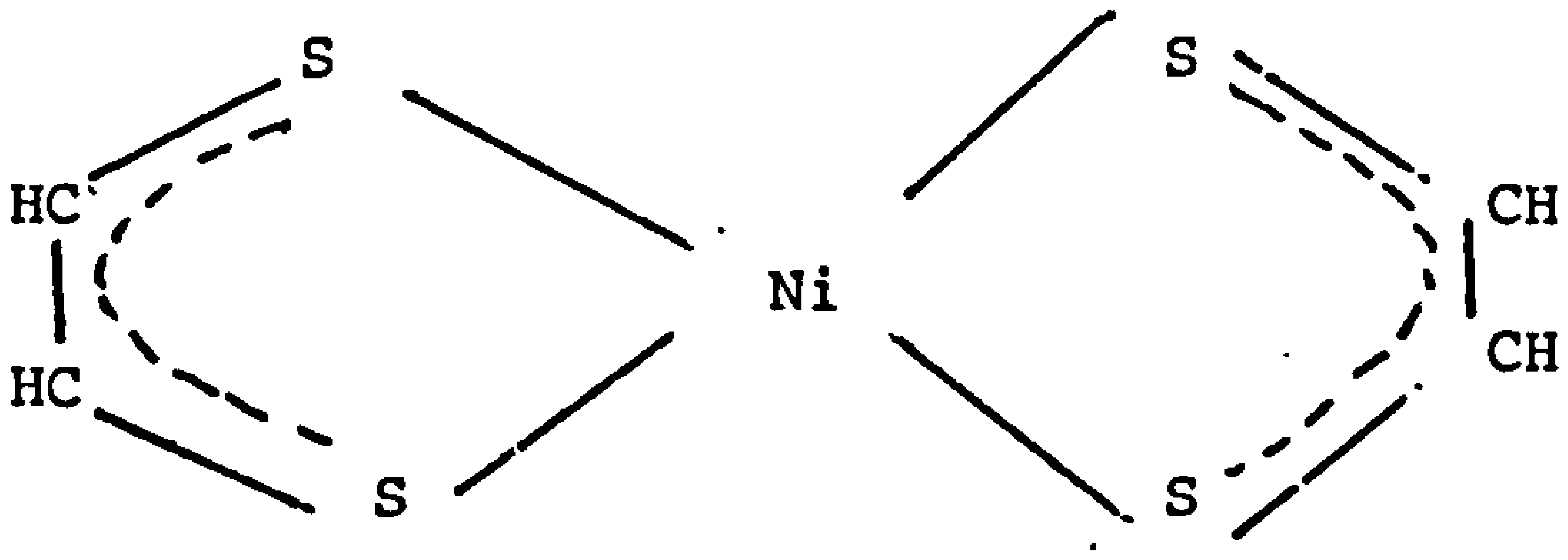
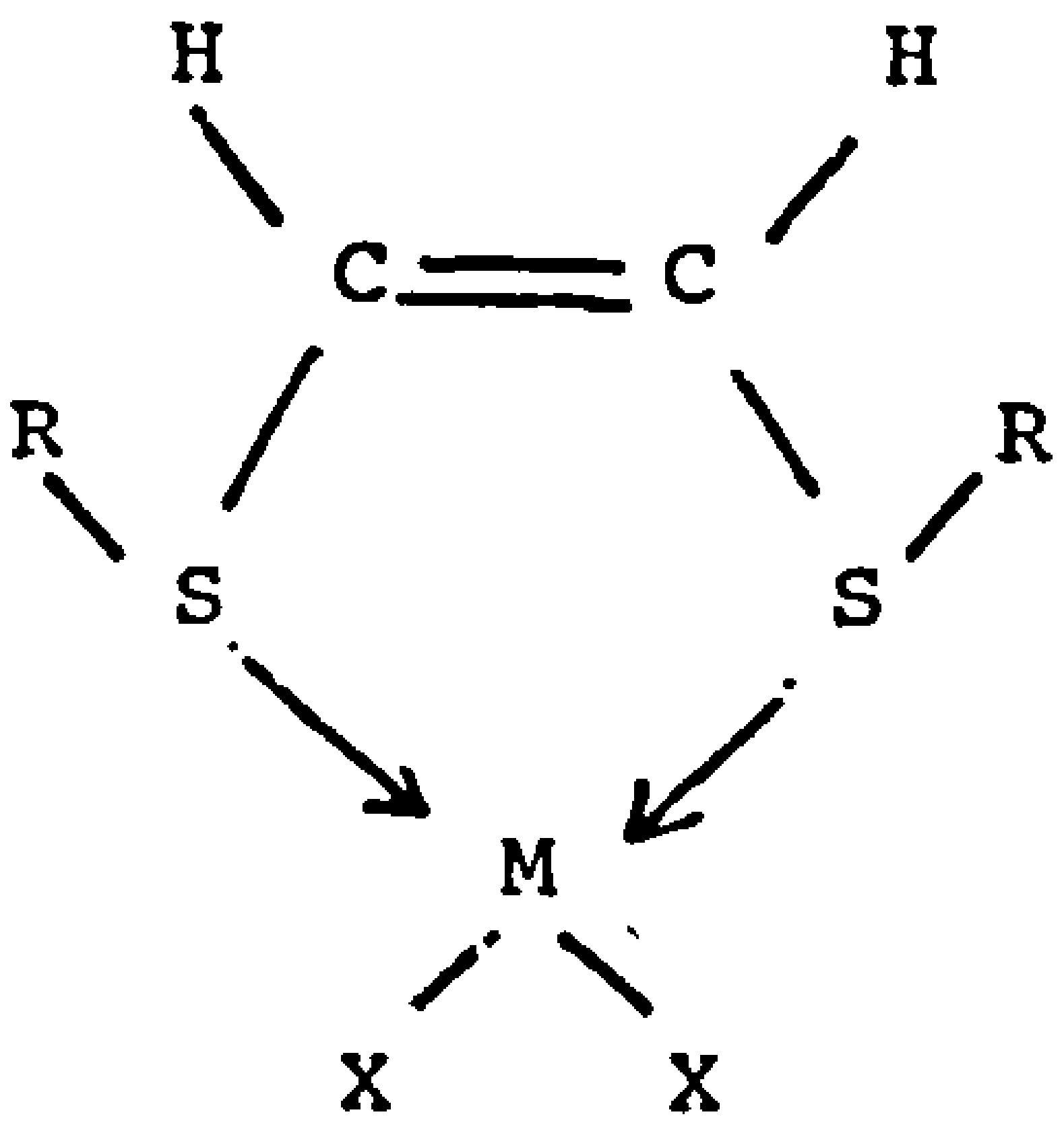


Figure (8) - Heterocyclic system

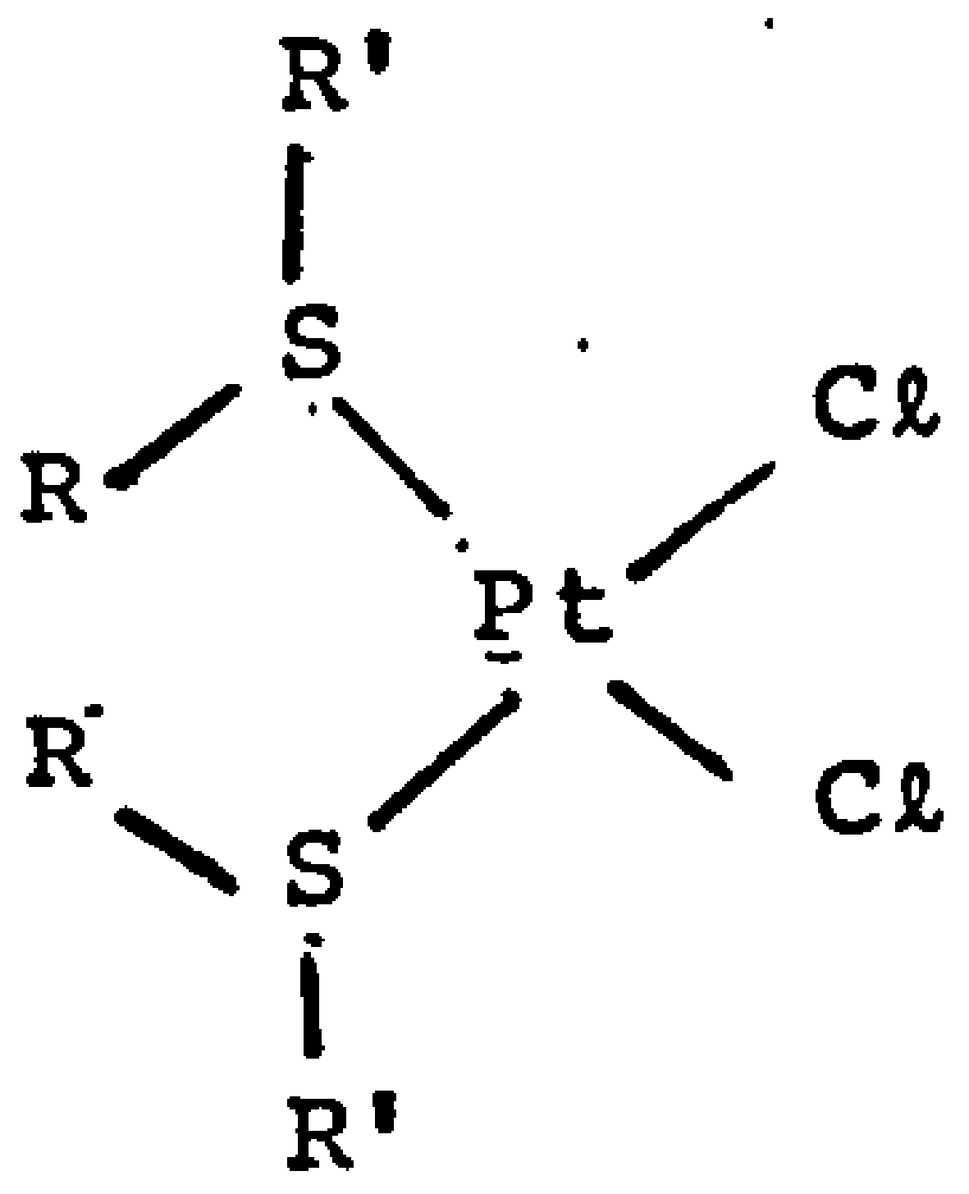
Coordination number (3)

For sulfur with this coordination number it is usual to recognise two main types of compounds:

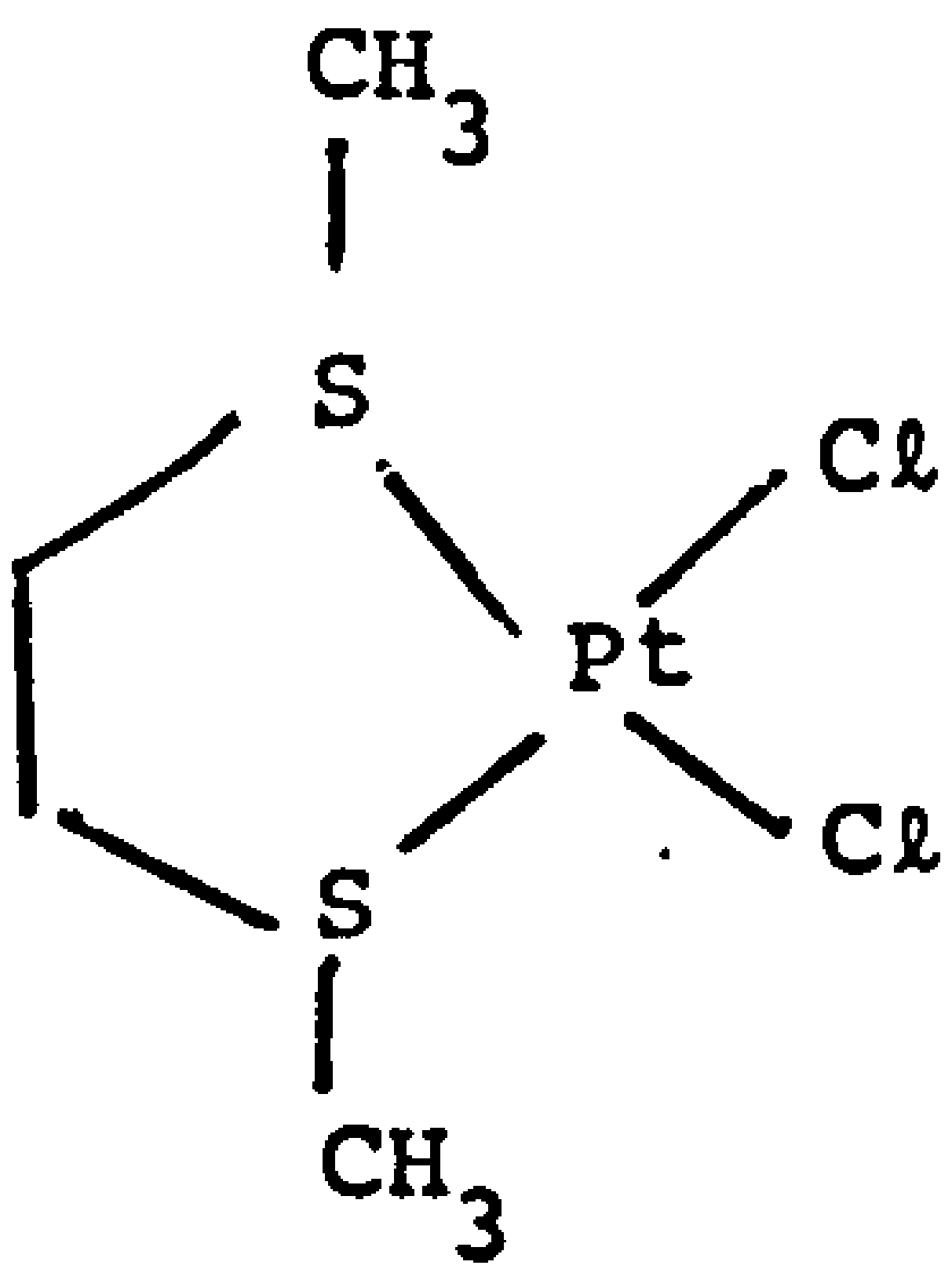
i) Those containing sulfur in formal sp^3 hybridisation with pyramidal geometry, one of the four positions being occupied by a lone pair. This type of three coordinate sulfur occurs in a number of metal complexes in which a sulfur atom bonded to two other atoms functions as a donor atom complex.[40]



41



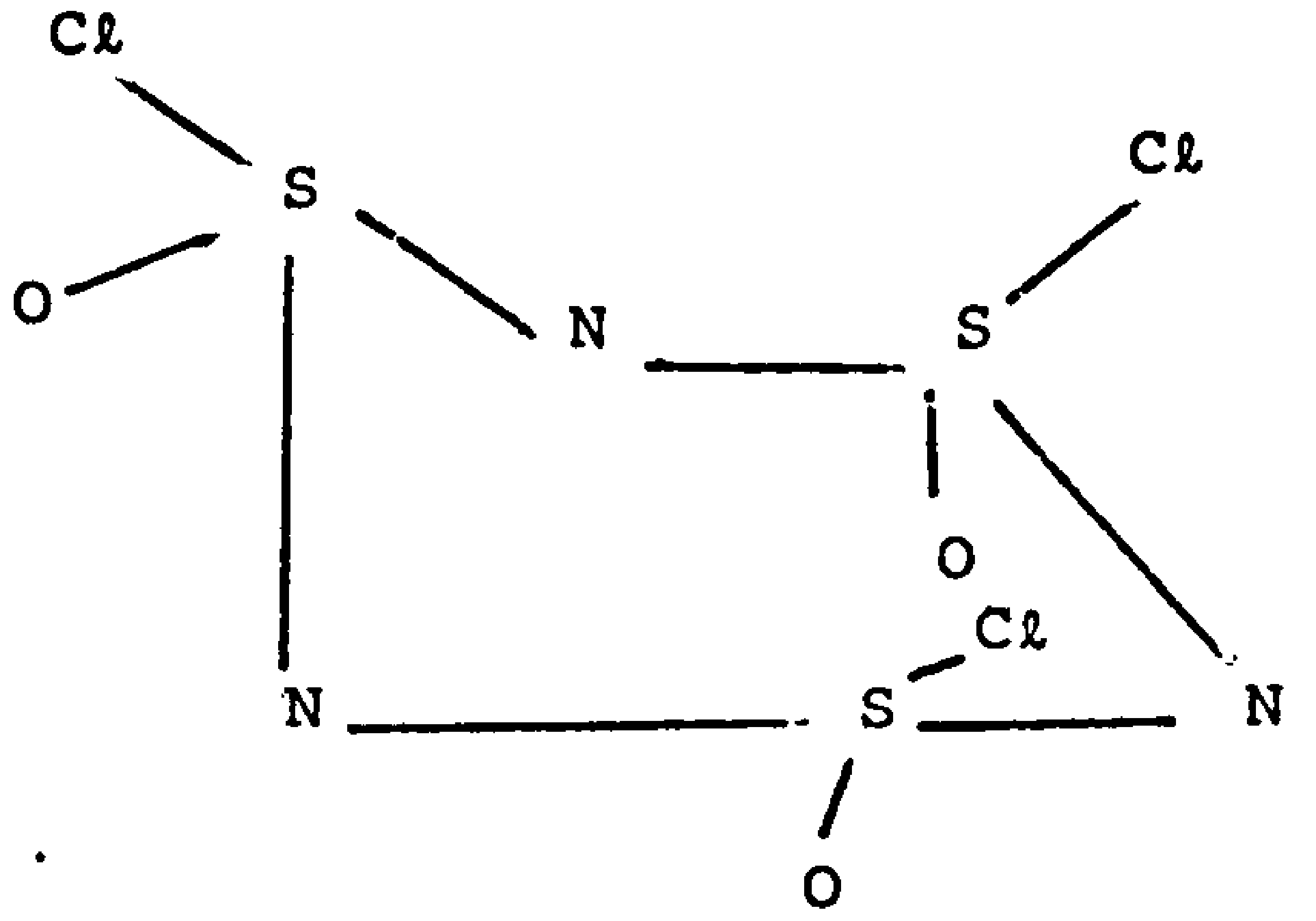
42



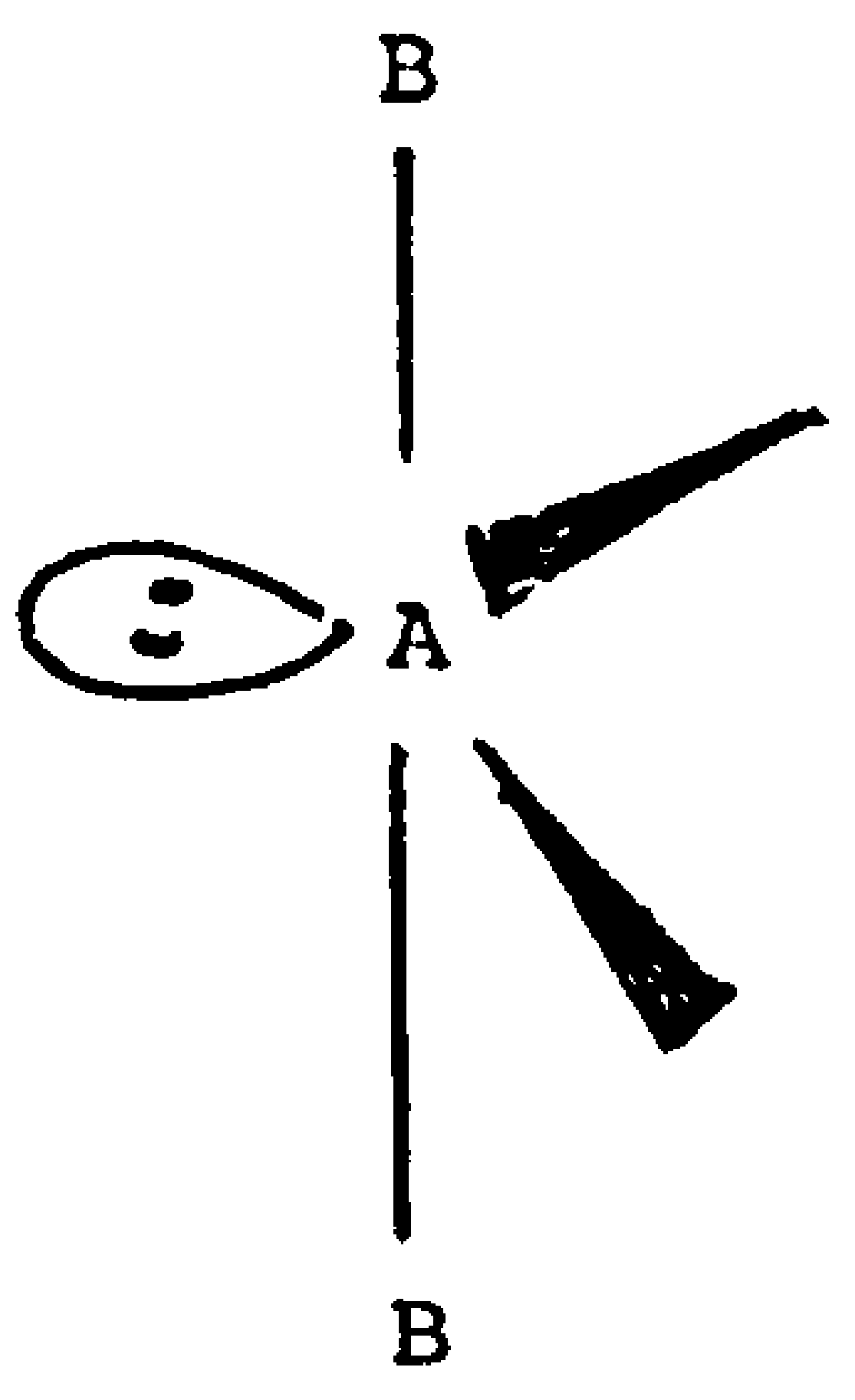
ii) Those molecules containing sulfur in a formal sp^2 hybridisation; the molecule being trigonal planar. The best known example of trigonal planar stereochemistry of sulfur is gaseous SO_3.

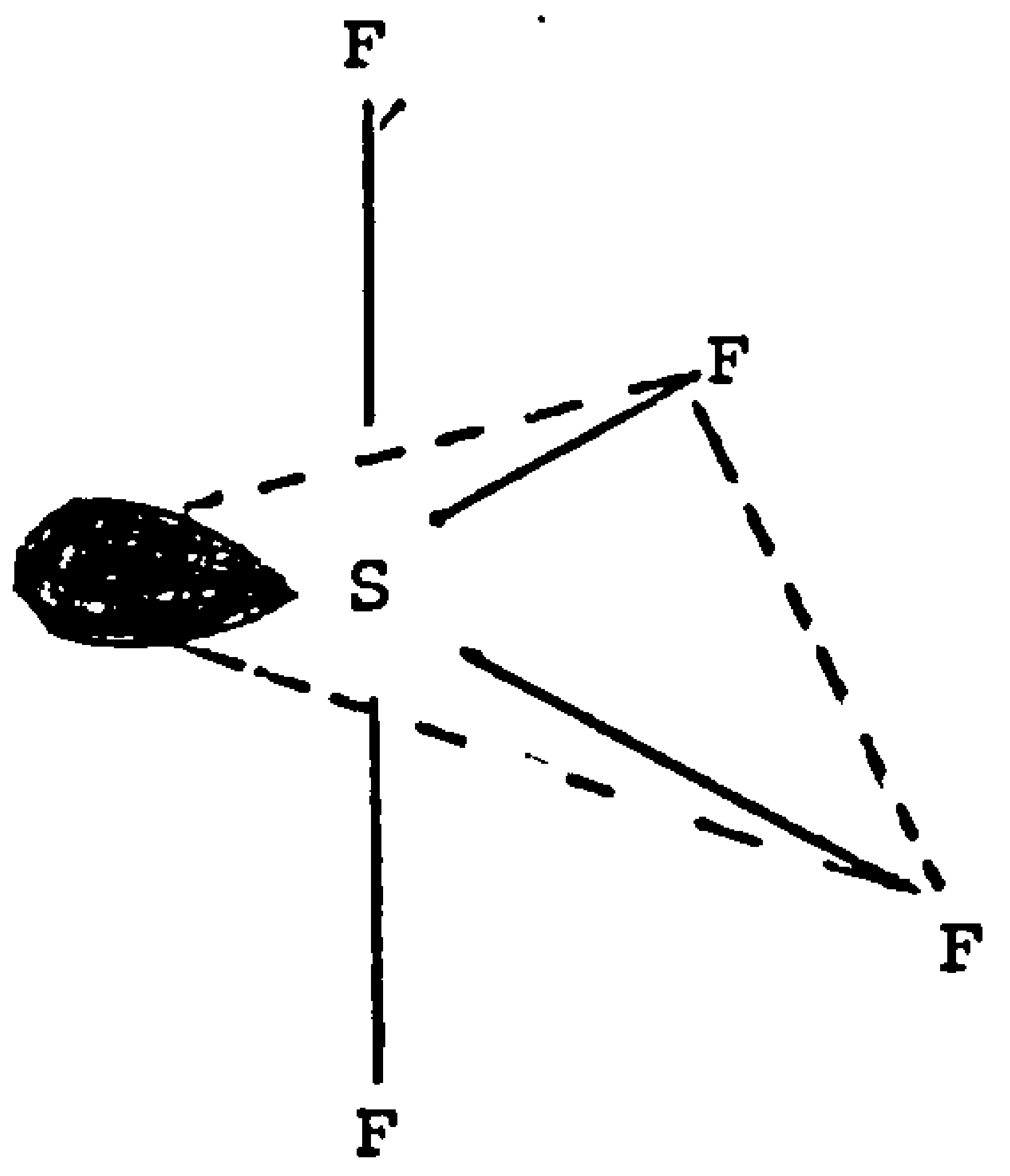
Coordination number (4)

It is possible to recognise two fundamental types of stereochemistry associated with coordination number (4). (i) Tetrahedral bond distribution with formal sp^3 hybridisation. Distortions will be introduced by lone pair repulsions associated with the different combinations of atoms to which sulfur is bonded, and by different bond lengths. This stereochemical arrangement for sulfur is most common and occurs in a wide range of molecular compounds, chain compounds, cyclic compounds and complexes containing four-coordinate sulfur, for example sulfur-nitrogen ring compounds are known with rings containing tetrahedral sulfur atoms.[43]



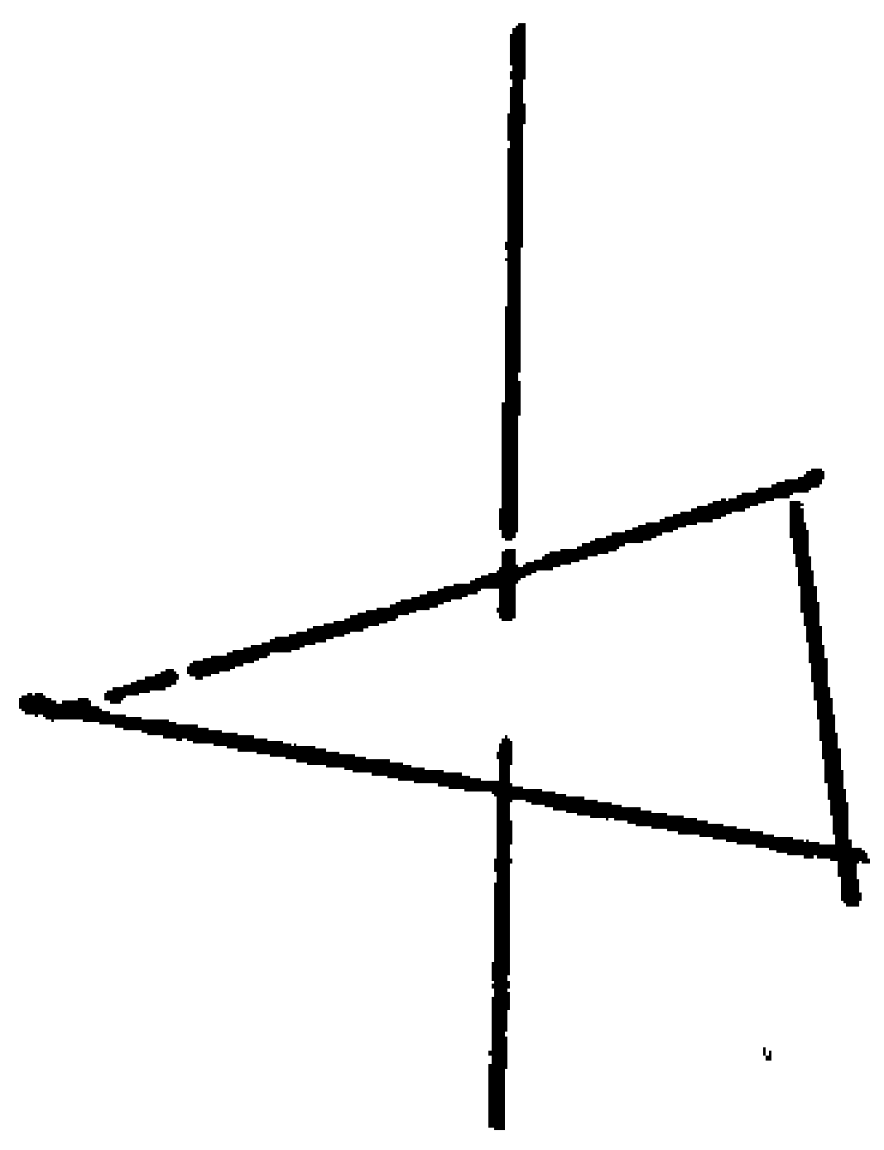
(ii) Distorted trigonal bipyramidal distribution, based on a formal dsp^3 hybridisation, one of the positions being occupied by a lone pair of electrons. An example is SF_4[44] with the irregular arrangement

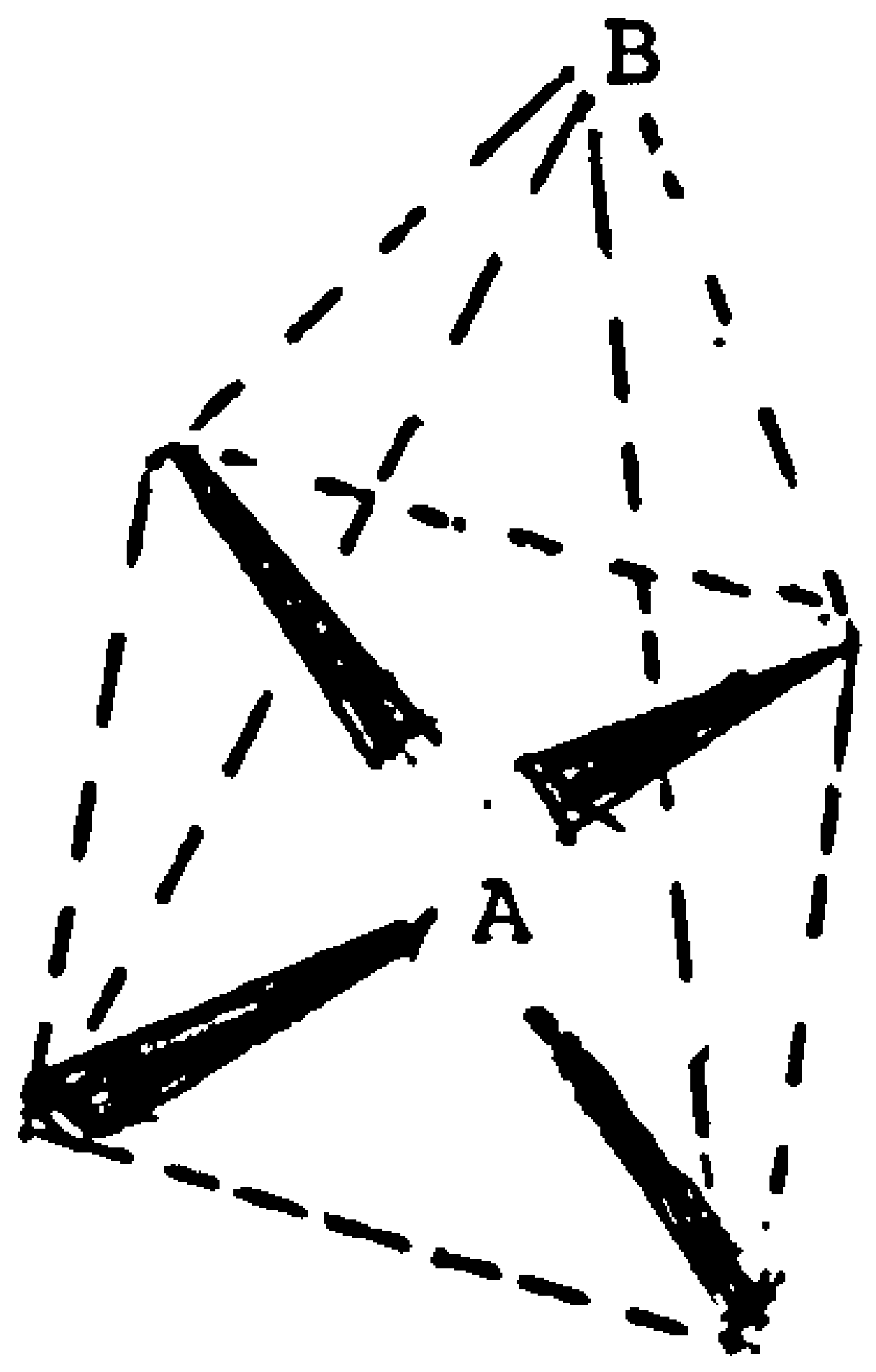




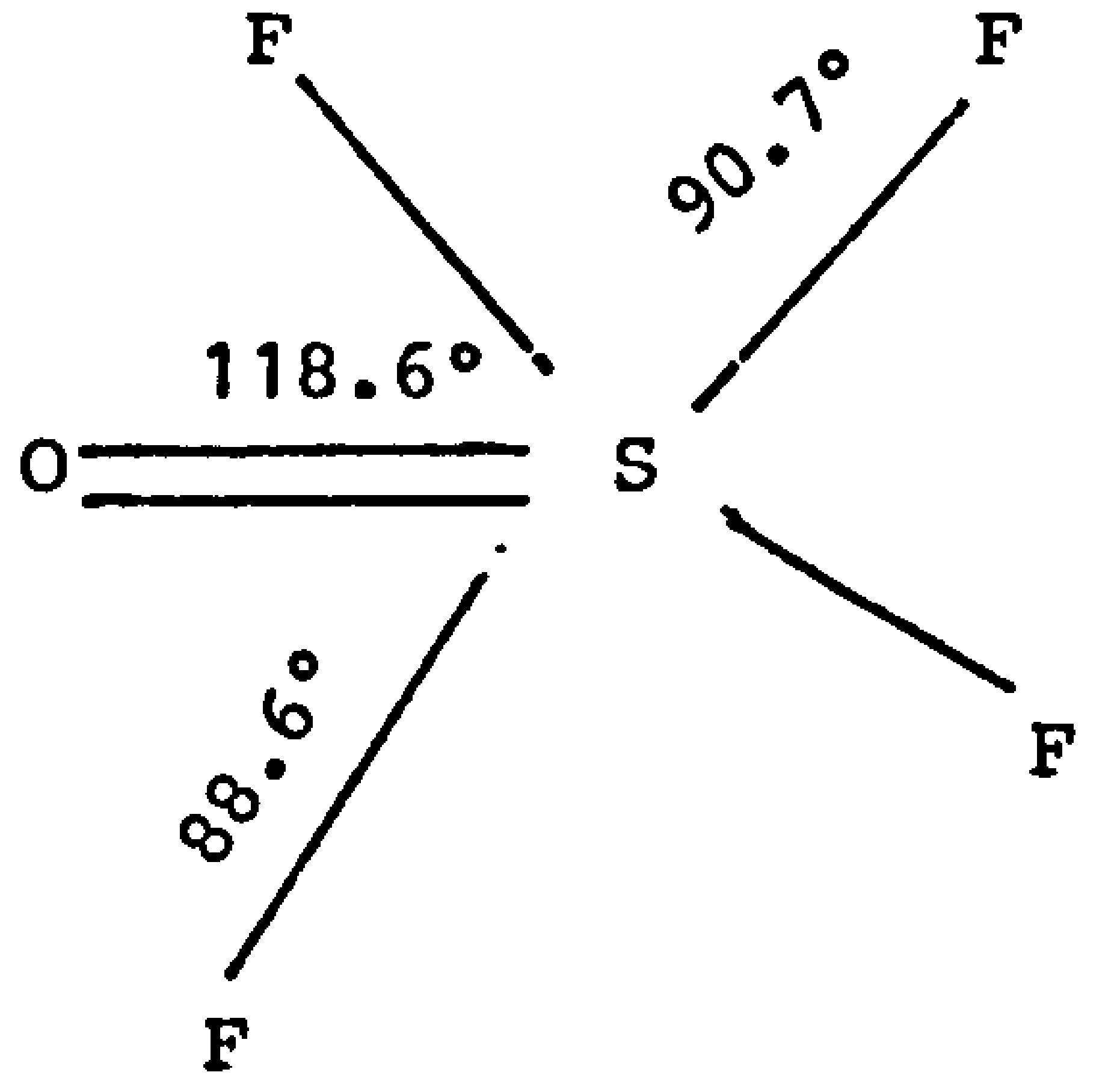
Coordination number (5)

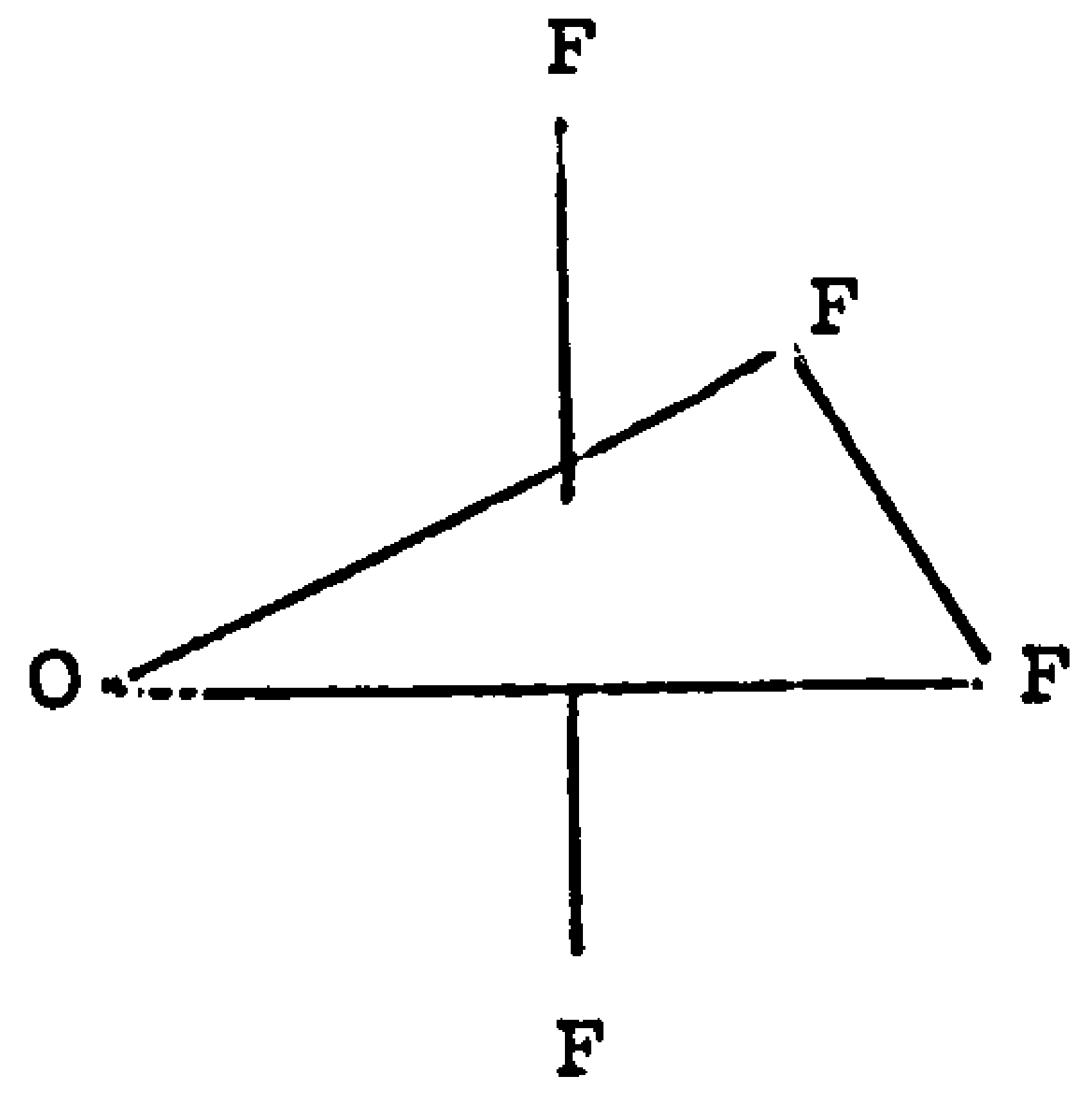
There are only few examples of this coordination number known for sulfur with both of the theoretically possible stereochemical arrangements (square pyramidal and trigonal bipyramidal).



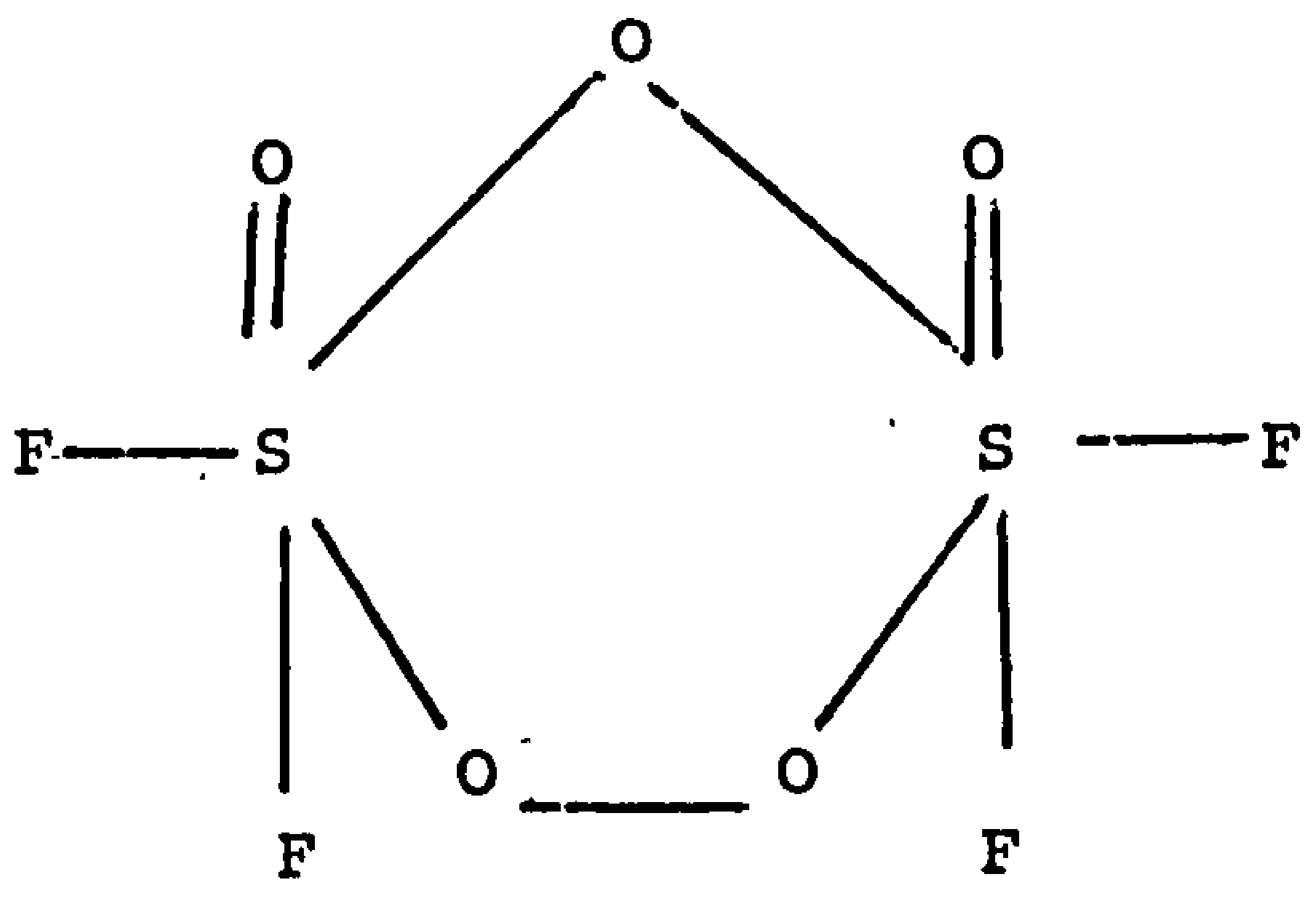


i) It has been suggested that[45] the ion $[SF_5]^-$ occurs in the compound $(CH_3)_4N.SF_5$ and the structure seems likely to be square pyramidal.
ii) There have been a number of investigations[46,47,48] of SOF_4 and it is now concluded that SOF_4 is bonded in a trigonal bipyramid with the oxygen in an equatorial position sp^3d (trigonal bipyramidal).



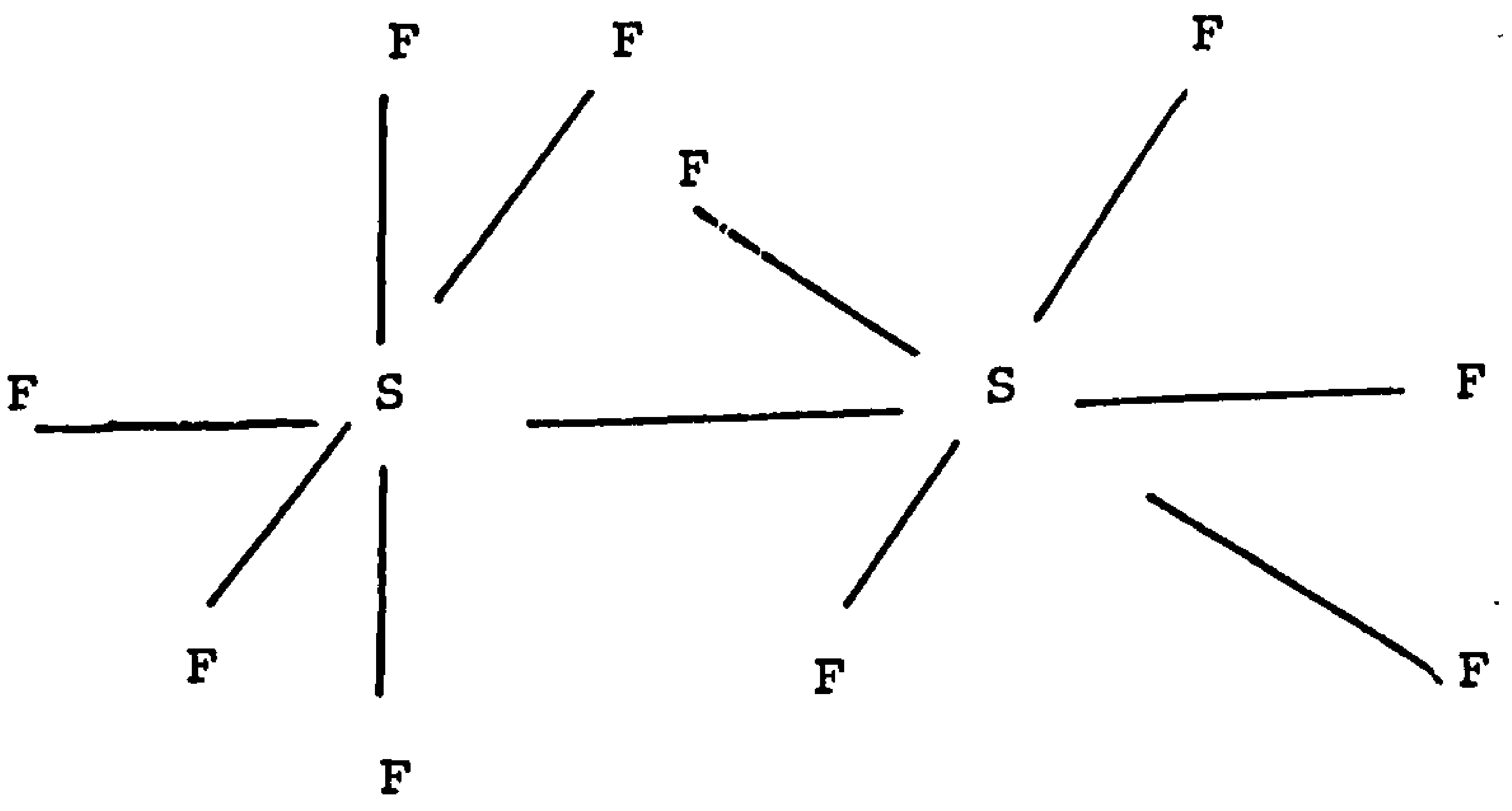


It has also been suggested that the structure of monoperoxytetrafluorodisulfur(VI)oxide $S_2O_5F_4$ is as shown.[49]



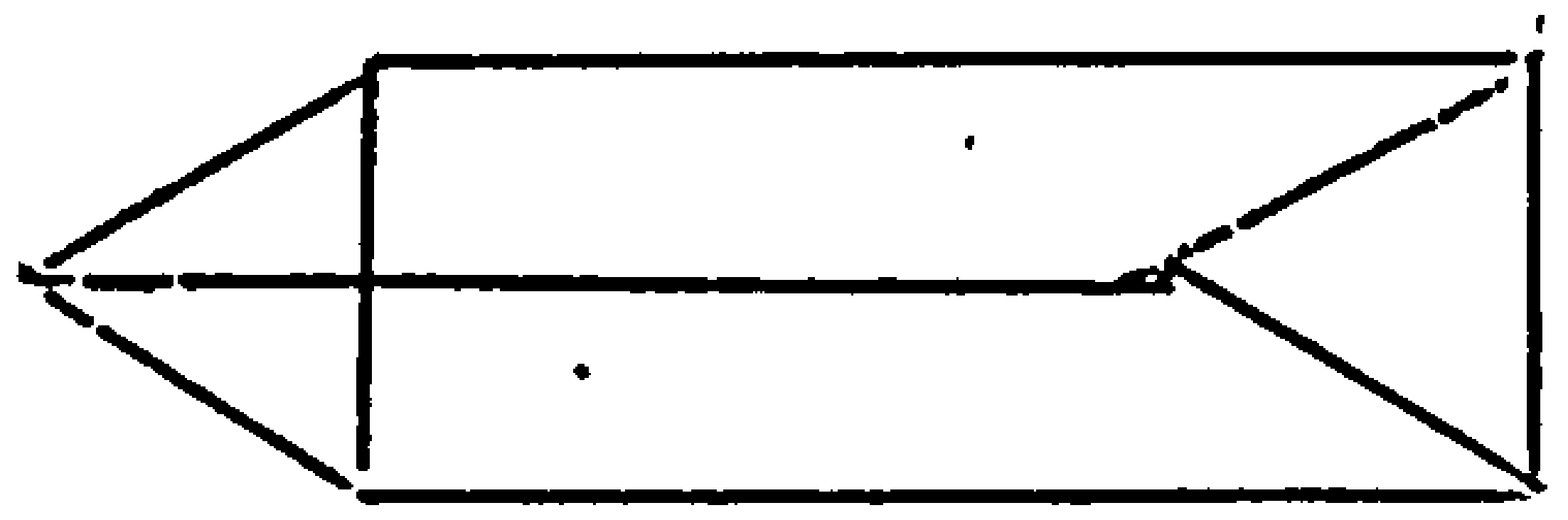
Coordination number (6)

The problem of the stereochemistry of this coordination number in relation to the Group VIB element has been studied and discussed by Gillespie and Nyholm.[50] In practice it is found that all six-coordinate molecular compounds so far studied have octahedral coordination. The binary halides which show octahedral stereochemistry are SF_6, S_2F_{10}, SF_5Cl and SF_5Br.[51,52,53] However, S_2F_{10} has an interesting structure which has been studied by infra-red[54,55] and Raman spectroscopy[56] and n.m.r. The molecule consists of two SF_5 units joined by an S-S bond to give a staggered octahedral bond distribution about each S atom as shown.



The structure of disulfur decafluoride S_2F_{10}.

Another type of six-coordination geometry, much rarer but nevertheless important, is that in which the ligands lie at the vertices of a trigonal prism. Figure (8).

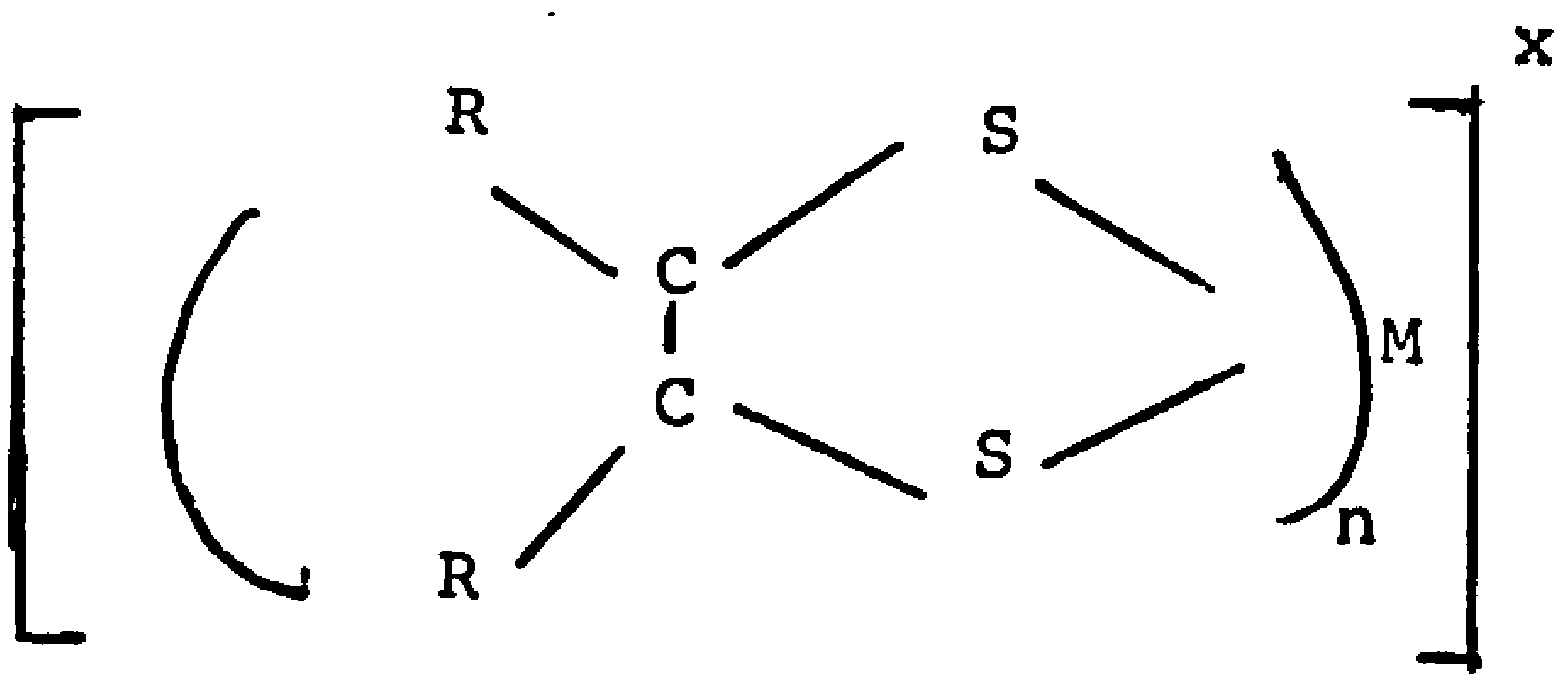


This arrangement has been observed for sulfur in complexes with chelating ligands and in a few metal sulfides, namely WS_2 and MoS_2. These heavy metals were coordinated in crystal lattices.[57] Trigonal prismatic complexes of ligands of the type $R_2C_2S_2$ have been fully characterized with rhenium, molybdenum, tungsten, vanadium, and suggested for other metals.[58] The 1,2-dithiolenes are a class of ligand that form a wide variety of compounds with metals in apparently many different oxidation states,[60,59] many of which are in a trigonal prismatic coordination about the metal.

R = H, alkyl, C_6H_5, CF_3, CN

n = 2; X = 0, -1, -2

n = 3; X = 0, -1, -2, -3



CHAPTER 2

CHAPTER 2

Introduction

Although most thiol reactions are nucleophilic additions and nucleophilic substitutions, the propensity of thiols to form thiyl radicals by homolysis of the S-H bond forms the basis of a significant group of reactions, including the formation of oxidation products (disulfides and sulfur oxyacids and their derivatives). Scheme (2-1) displays interconversions which may be brought about between the sulfur functional groups, indicating a key position for thiols as starting materials for the preparation of the other organic sulfur compounds.[61]

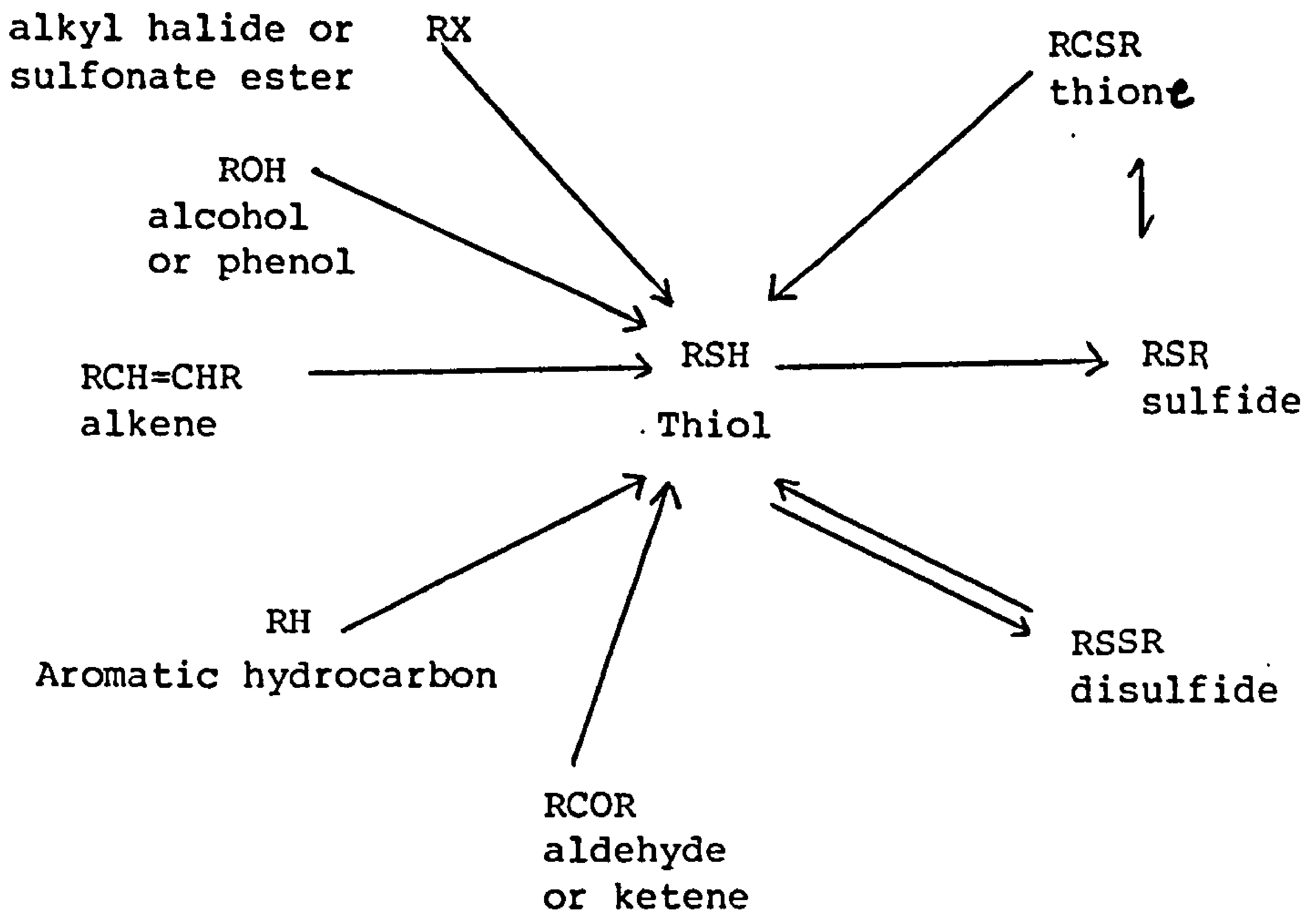


Figure (2-1)

Thiols

Thiols are the sulfur (or thio) analogues of alcohols as we described in table (1). They were formerly known as mercaptans and this name is still in wide use particularly in commerce, and it was applied by Zeise to ethanethiol because of its bad odour. Mercaptan was derived from the Latin mercurium captans (seizing mercury) because of its ability to remove mercury from solution as crystalline precipitates. It has also been accepted as a descriptive name for most organic compounds containing the -SH group, some of which do not smell. The name mercaptan and adoption of the term were recommended by a Commission of the International Union of Chemistry in 1930. Thiols are important not only for their use in the synthesis of other organosulfur compounds but also for their roles in cell biochemistry. For these reasons a large number of laboratories have contributed in recent years to the development of reliable methods of synthesis of thiols[61,62,63] and to the investigation of their properties. Compounds containing the sulfhydryl (-SH) group and the related disulfide (-S-S-) linkage may have animal or vegetable origin, and play important roles in biological processes.[61]

Physical properties of thiols

Thiols or mercaptans are characterized by their extraordinarily unpleasant odours. The physical properties of thiols will be compared with those of their oxygen analogues.

A. Dissociation energies

Table 2-1

Bond dissociation energies of thiols and their oxygen analogues[64-66]

Compound	Bond Dissociation Energy kcal/mol	
	X=S	X=O
HX-H	89	116
CH_3X-H	89	100
C_2H_5X-H	87	63.5
CH_3-XH	67	90
C_2H_5-XH	63.5	90
$PhCH_2$-XH	53	73

The dissociation energies in the above table relate to the bonds marked -.

Apparently the S-H(C-S) bond energy is less than that of O-H(C-O). The ease of hydrogen abstraction from S-H to give free radicals as compared with the ease of formation of oxygen containing radicals from O-H bonds is accounted for by this fact. It is interesting to note that the bond dissociation energy of H-Br, which is also a good hydrogen donor, is 87.5 kcal/mol. This is consistent with the description that the bonding orbitals on sulfur atoms have more p-character than those on oxygen atoms. The weaker bonds to hydrogen in thiols in comparison with those between oxygen and hydrogen make thiols more acidic than the corresponding alcohol. The pKa values of thiols and alcohols are given in table (2-2).[67-73]

Table 2-2

Acidities of thiols and alcohols at 25°C

Compound	pKa	
	X=S	X=O
H_2X	7.24[a], 14.92[b]	14
C_2H_5XH	10.60	18
$n\text{-}C_4H_9XH$	11.51	16
C_6H_5XH	8.3	9.94

[a] First ionisation constant

[b] Second ionisation constant

Bond length

Table 2-3

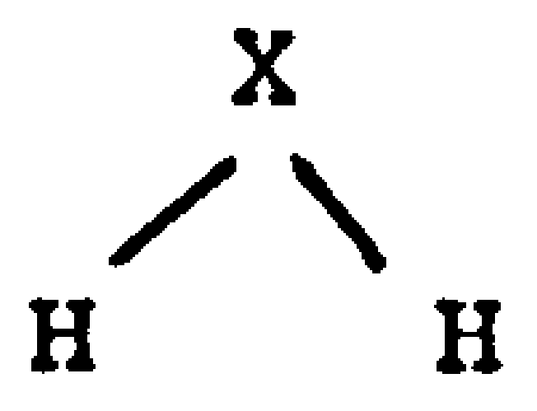
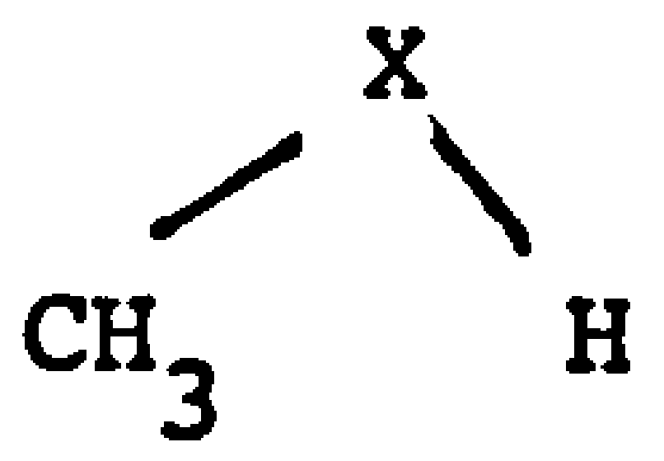
Selected bond lengths of some simple compounds containing S-H functional groups[74]

	Bond length
S-H	1.35Å
HS-H	1.328Å
CH_3S-H	1.329Å

Bond angle

Table 2-4

Bond angles in thiols and alcohols

Compound	Bond angle degree	
	X=S	X=O
	92.2 ± 0.10	104.45 ± 0.10
	100.3 ± 0.2	108 ± 2

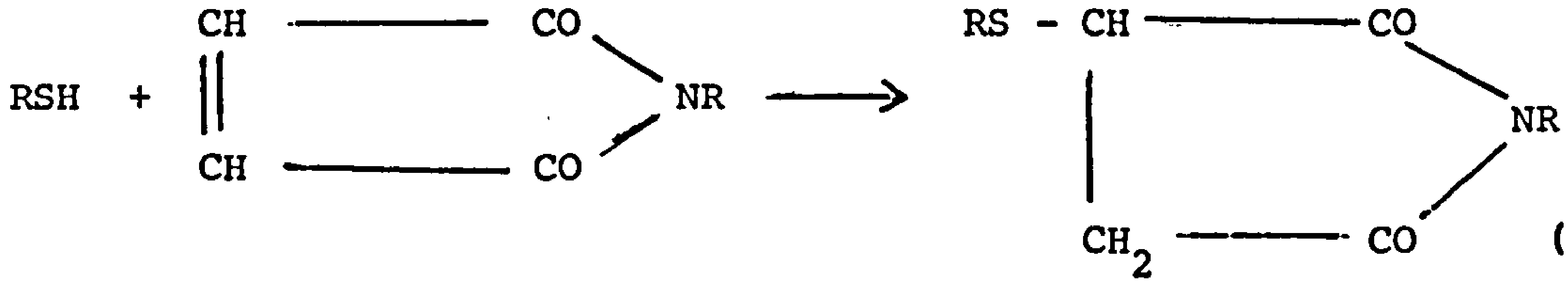
Bond angles around the sulfur atom in thiols are smaller than those around the oxygen atom in corresponding oxygen analogues.[75,76]

Chemical properties

1. Replacement of hydrogen

Thiols show the characteristic reaction of nucleophiles by displacement at a saturated carbon center. The high nucleophilicity together with low basicity shown by metal thiolates has been used in organic synthesis.

As a simple example, sodium thiophenoxide, PhSNa is a weaker base than NaOEt or PhONa, but has higher nucleophilicity than the oxygen compound and is used to replace benzoate groups, e.g.


(1)

The reason for this appeared to be much greater accessibility of carbon attached to bivalent sulfur.

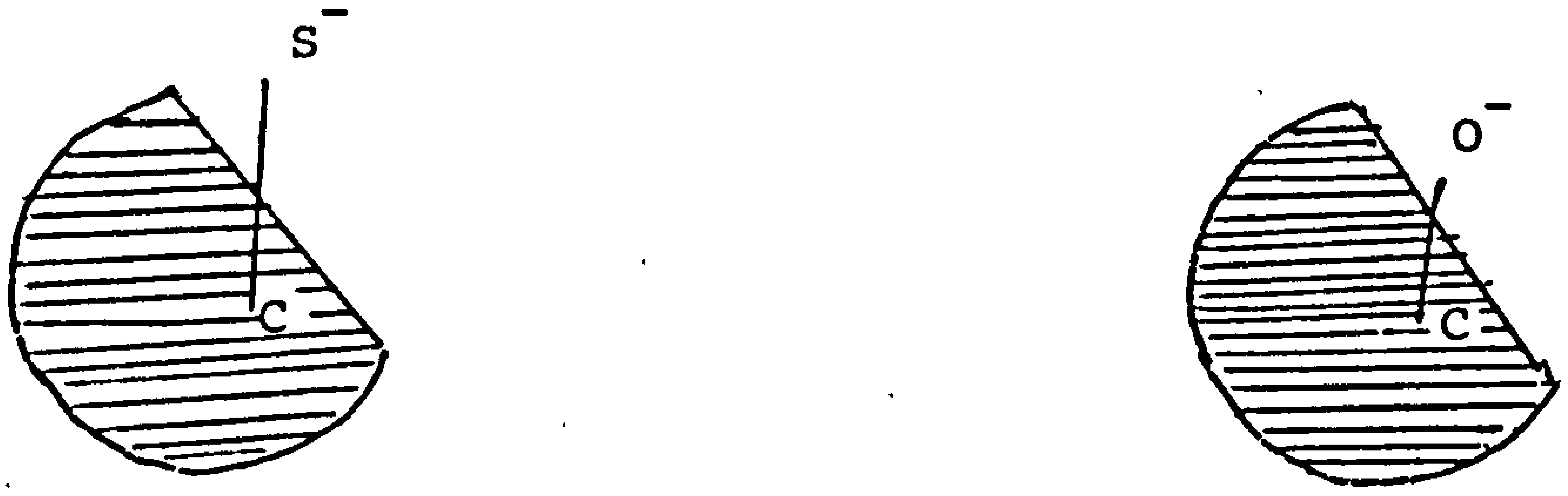
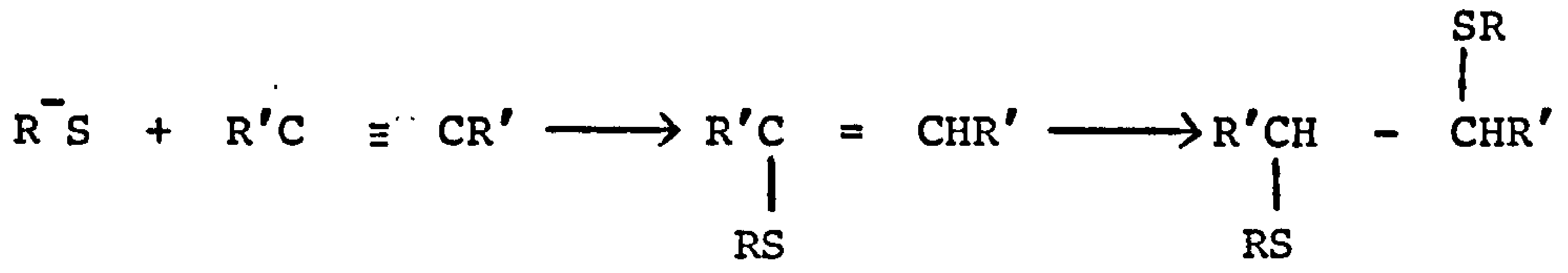


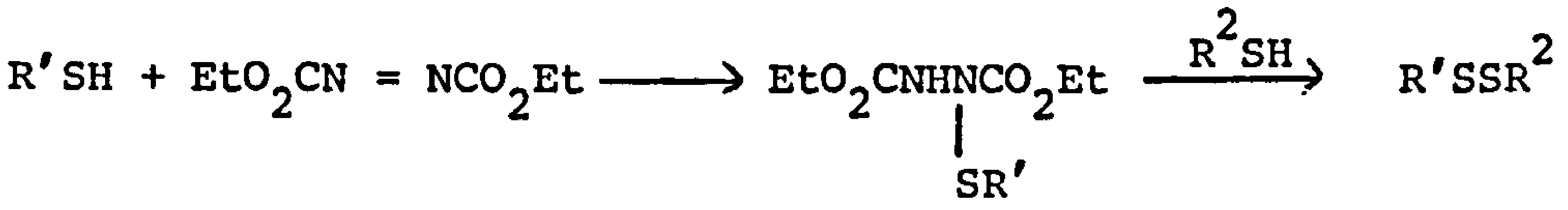
Figure (2-2) - Accessibility of bicovalent sulfur and oxygen. Van der Waals radius of CH_2 drawn to scale as compared to C-S and C-O bond lengths.

Another example is of nucleophilic addition to unsaturated systems.


$$R^{-}S + R'C \equiv CR' \longrightarrow \underset{\displaystyle RS}{R'C} = CHR' \longrightarrow \underset{\displaystyle RS}{R'CH} - \overset{\displaystyle SR}{CHR'} \quad (2)$$

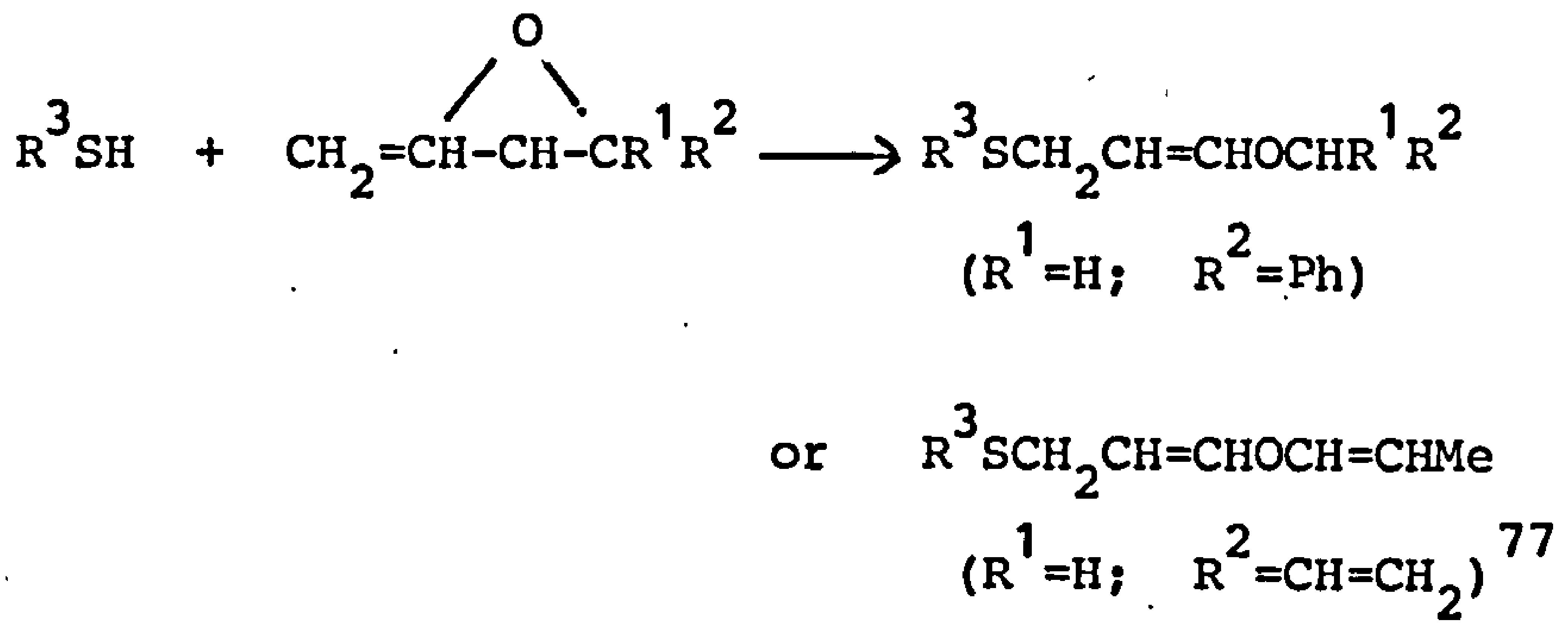
$R' = CO_2H$

$$RSH + CH_2 = C = O \longrightarrow RSCOCH_3 \quad (3)$$


$$R'SH + EtO_2CN = NCO_2Et \longrightarrow \underset{\displaystyle SR'}{EtO_2CNHNCO_2Et} \xrightarrow{R^2SH} R'SSR^2 \quad (4)$$

2. Free radical additions

Free radical addition of thiols to alkenes is more common in the absence of bases and leads to an anti-Markownikov adduct, as shown below, which is an example of the reaction of thiyl radicals [RS•]

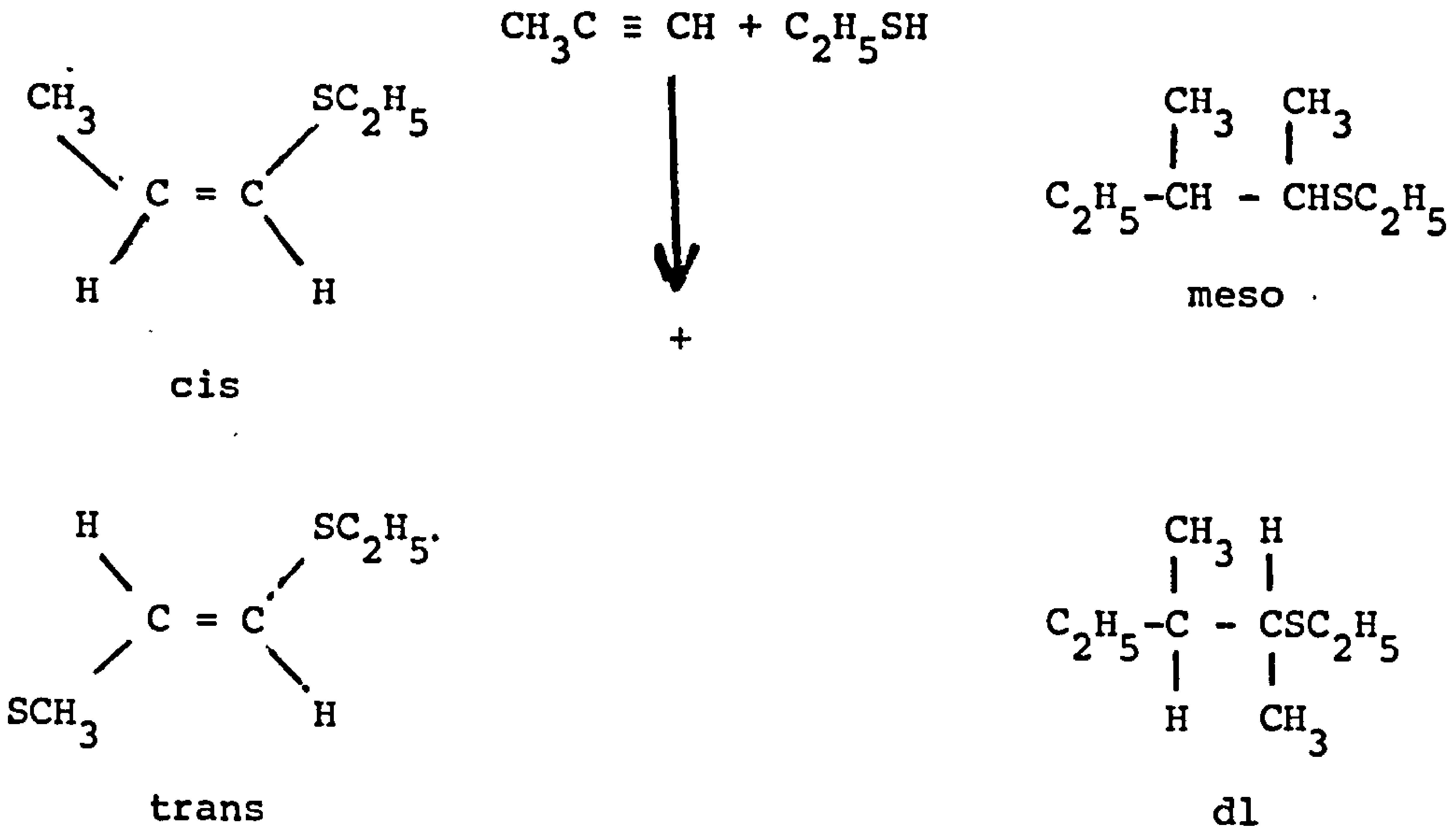


$$R^3SH + CH_2=CH-\overset{O}{CH-CR^1R^2} \longrightarrow R^3SCH_2CH=CHOCHR^1R^2 \quad (R^1=H;\ R^2=Ph)$$

$$\text{or} \quad R^3SCH_2CH=CHOCH=CHMe \quad (R^1=H;\ R^2=CH=CH_2)^{77}$$

(5)

Reaction of thiols with alkylacetylenes generally gives the anti-Markownikov monoadduct and the 1,2 diadduct, e.g. 1-ethylthiopropene(cis-trans mixture) and 1,2 bis(ethylthio)propane are obtained from the reaction of methanethiol with propyne in the presence of azobisisobutyronitrile as free radical initiator.[78]



(6) (7)

With phenyl acetylene mono addition of toluenthiol occurs more readily in one instance even without addition of an initiator.[79]

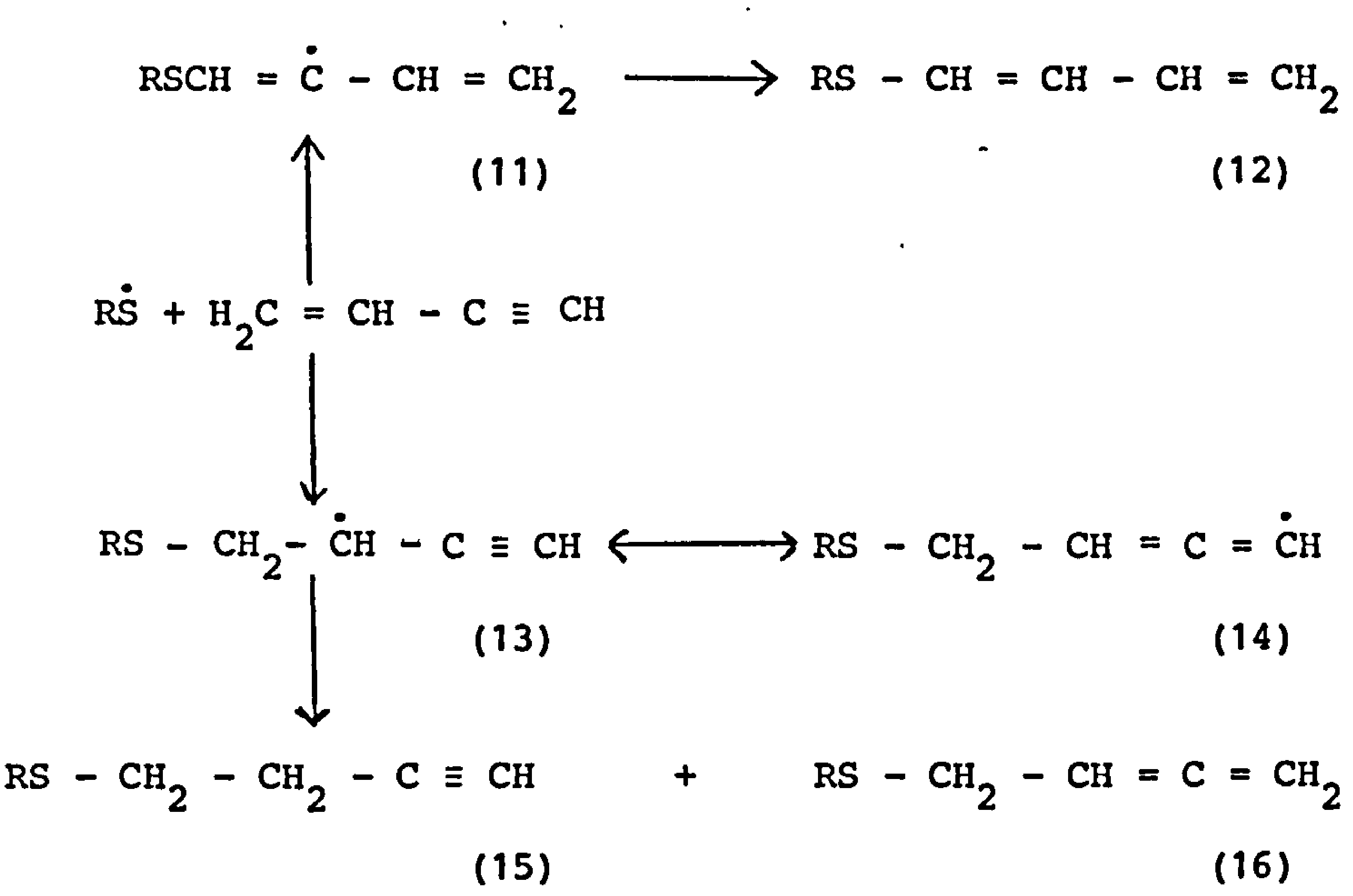
$$CH_3C_6H_4SH + C_6H_5C{\equiv}CH \longrightarrow C_6H_5CH{=}CHSC_6H_4CH_3 \qquad (8)$$

Reaction with excess ethanethiol under extended ultraviolet irradiation gives the diadducts; the geminal diaddition is attributed to the stability of the intermediate benzyl radical $C_6H_5CH{\cdot}CH(SC_2H_5)_2$.[79]

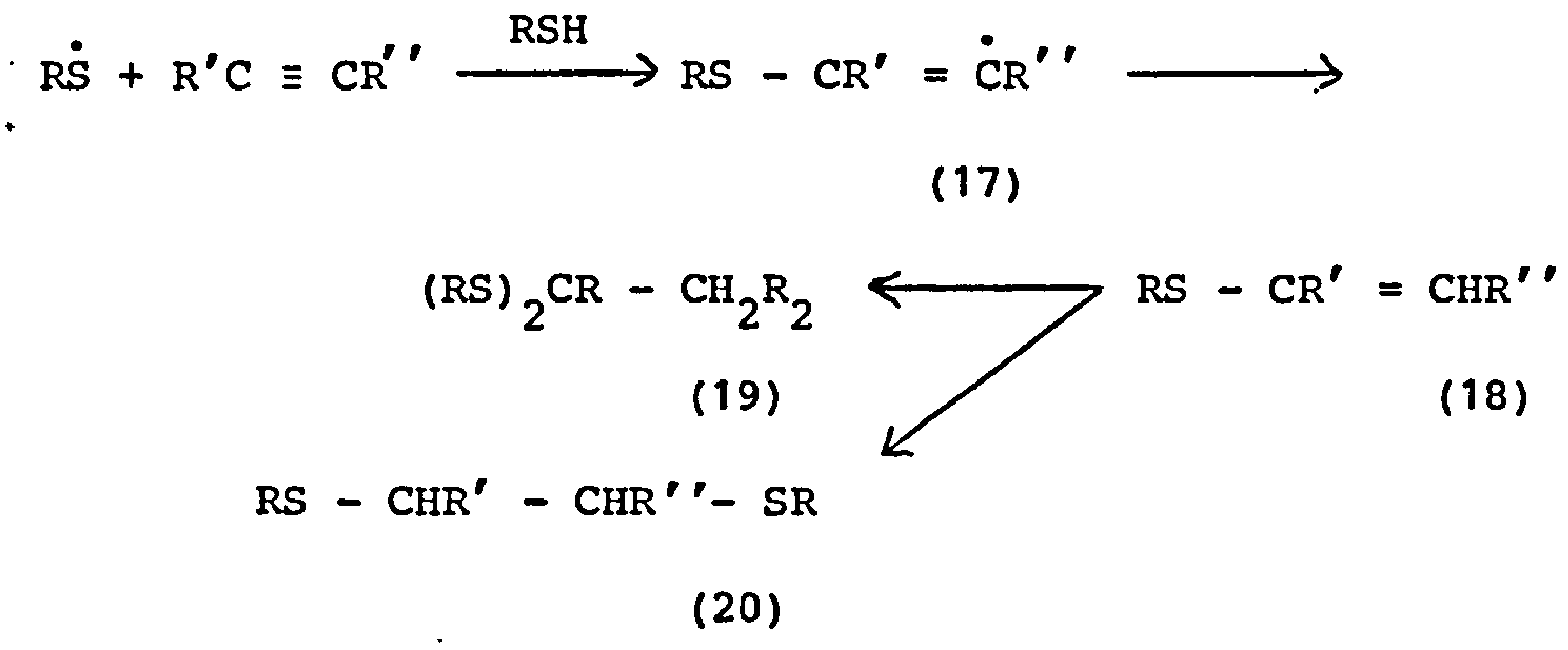
$$2\ C_2H_5SH + C_6H_5C{\equiv}CH \longrightarrow C_6H_5CH_2CH(SC_2H_5)_2 \qquad (9)$$

$$3\ C_2H_5SH + 2CH_3C{\equiv}CH \longrightarrow CH_3CH{=}CHSC_2H_5 \qquad (10)$$

The course of free radical addition of thiols to alkynes is basically similar to addition to alkenes, as was mentioned on page [32]. The few comparative studies so far published have shown, however, that alkenes react more rapidly than the analogous alkynes. For example, in an equimolar mixture of propene and propyne, the propene reacts about 1.2 times as rapidly as the propyne with $R\dot{S}$.[80] This difference is still more pronounced in reactions of vinylacetylene which, depending on the thiol, gives between 10 and 100% of the product from addition to the double bond with little addition to the triple bond. See equations[81]



The high selectivity in this case may, however, also be due to the fact that the radical (13) can be stabilized by resonance[82] whereas the vinyl radical (11) would require the loss of conjugation. Addition to the triple bond would lead via the vinyl radical (14) to cis and trans isomeric vinyl sulfide monoadducts (15) which could then add a further molecule of thiol more or less selectively and rapidly, depending on the substituents R, R′ and R′′, and depending on the wavelength of irradiation [see page 94].



Thus the most important problems in such additions are: The orientation in the second addition step and the relative rates of the reactions leading to products (19) and (20), mono alkylacetylenes generally give vicinal diadducts [(20) where R′=H] whilst monoaryl acetylenes give diadducts [(19) where R′=H]. Since the vinyl sulfides or vinyl thiols formed in the first addition step are generally more reactive than the alkynes from which they are derived, most thiol additions to alkynes are accompanied by at least partial diaddition. Exceptions to this rule are addition to aryl substituted acetylenes, in which, owing to the stability of the intermediate benzyl radical (21) the addition of the second thiyl radical is strongly reversible and thus reduces the extent of the diaddition

$$RS - CH = CH - C_6H_5 \underset{\text{fast}}{\overset{R\dot{S}}{\rightleftharpoons}} (RS)_2CH - \dot{C}H - C_6H_5$$

$$(RS)_2CH - CH_2C_6H_5 \longleftarrow \qquad (21)$$

<u>The stereochemistry of the addition of thiols to acetylenes</u>

Investigation of the photochemical decomposition of thiols dates back to 1938 and the work of Thompson and coworkers.[83,84] The mechanism tentatively proposed at that time for the photolysis of methanethiol consisted of the following three steps:

SCHEME (1)

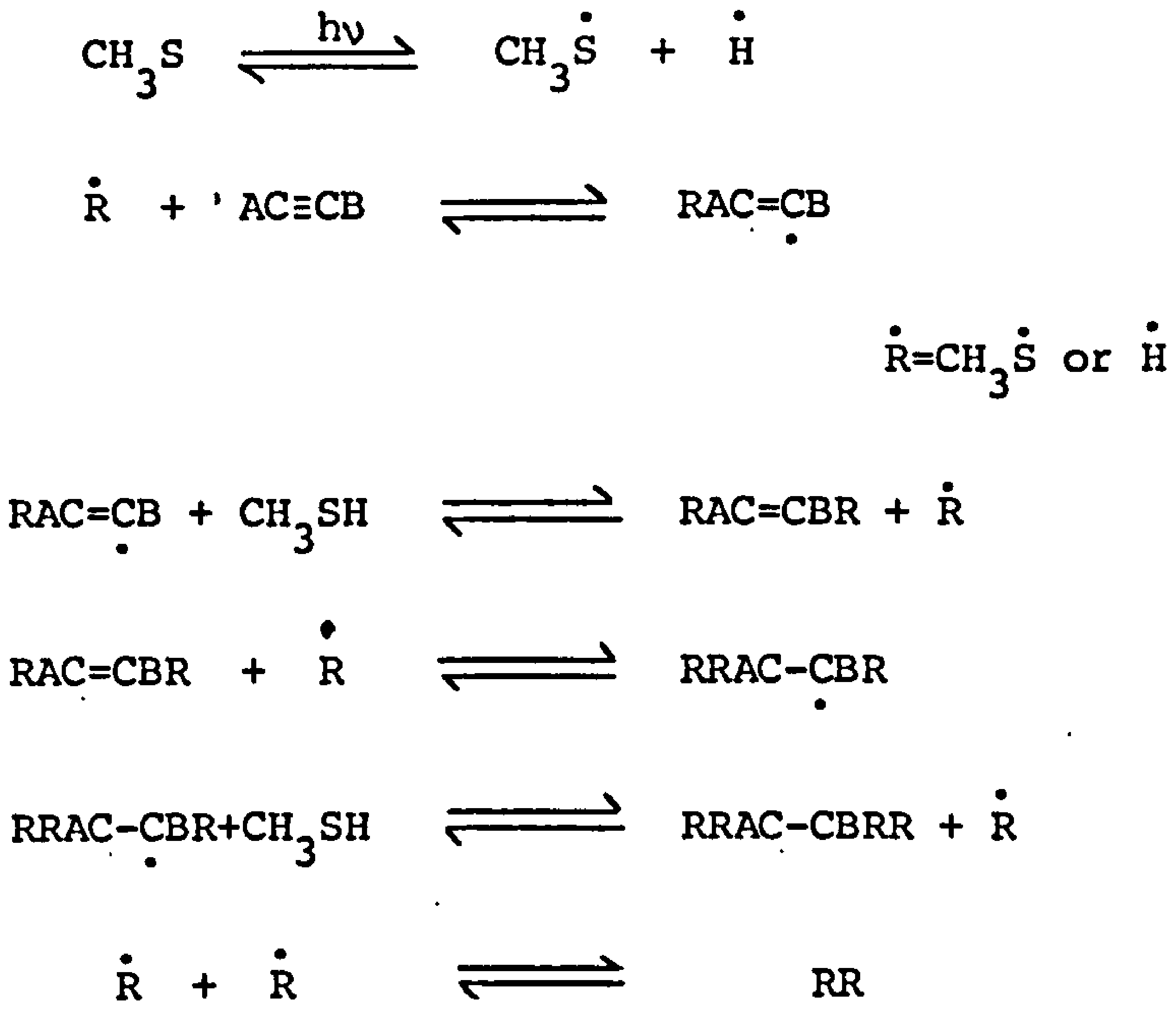
$$CH_3SH + h\nu \longrightarrow CH_3\dot{S} + \dot{H} \qquad (1)$$

$$\dot{H} + CH_3SH \longrightarrow CH_3\dot{S} + H_2 \qquad (2)$$

$$2CH_3\dot{S} \longrightarrow CH_3SSCH_3 \qquad (3)$$

The reaction can be conveniently described in terms of the following scheme (2) showing the reaction between the methylthiyl radical and hydrogen atoms (radicals) with acetylenes.[85]

SCHEME (2)



$$CH_3S \xrightleftharpoons{h\nu} CH_3\dot{S} + \dot{H}$$

$$\dot{R} + AC{\equiv}CB \rightleftharpoons RAC{=}\underset{\bullet}{C}B$$

$$\dot{R}{=}CH_3\dot{S} \text{ or } \dot{H}$$

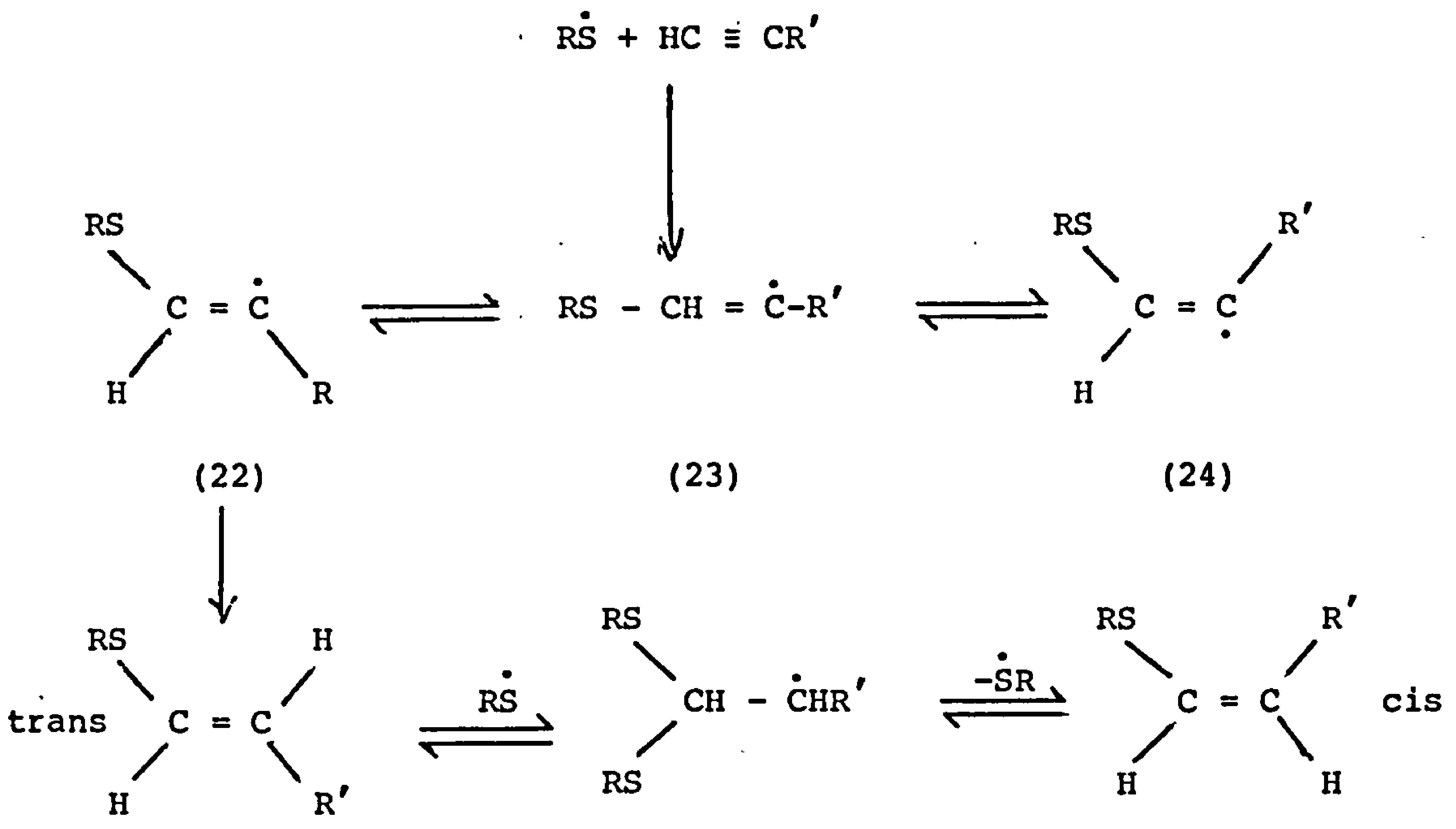
$$RAC{=}\underset{\bullet}{C}B + CH_3SH \rightleftharpoons RAC{=}CBR + \dot{R}$$

$$RAC{=}CBR + \dot{R} \rightleftharpoons RRAC{-}\underset{\bullet}{C}BR$$

$$RRAC{-}\underset{\bullet}{C}BR + CH_3SH \rightleftharpoons RRAC{-}CBRR + \dot{R}$$

$$\dot{R} + \dot{R} \rightleftharpoons RR$$

The stereochemistry of the addition has been studied in detail for phenyl acetylene[86] and 1-hexyne.[87] The stereoselectivity was strongly dependent on the molar ratio of the reactants, particularly for the addition to phenylacetylene with excess thiol, the ratio of isomers (22) and (23) corresponded to that of the thermodynamic equilibrium



(22) (23) (24)

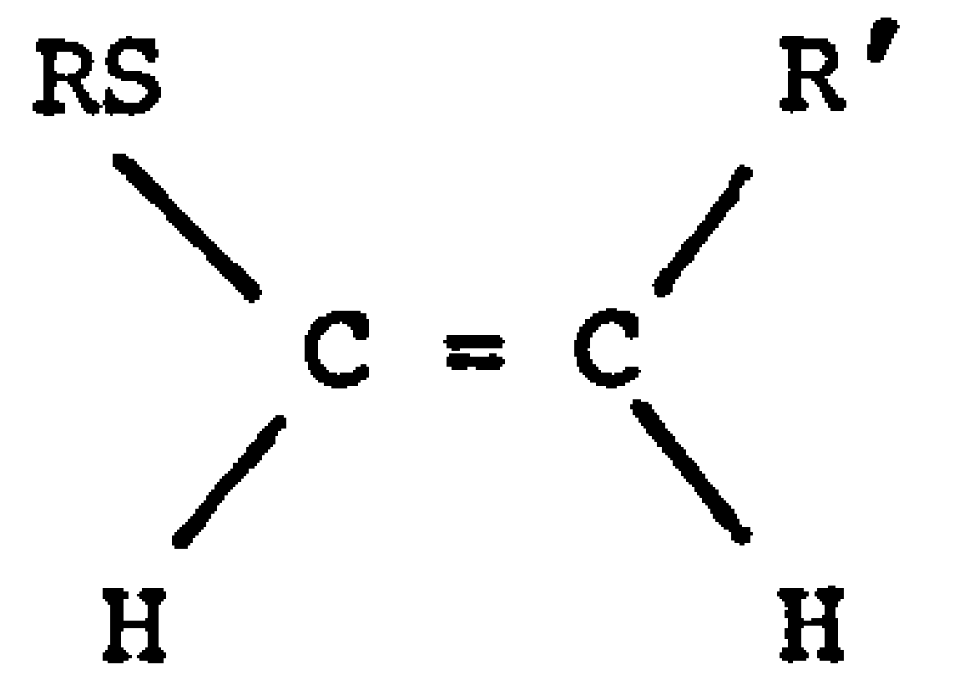
If, on the other hand, equimolar quantities or an excess of the alkyne were used, the cis  adducts could be obtained with very high selectivities in some cases.

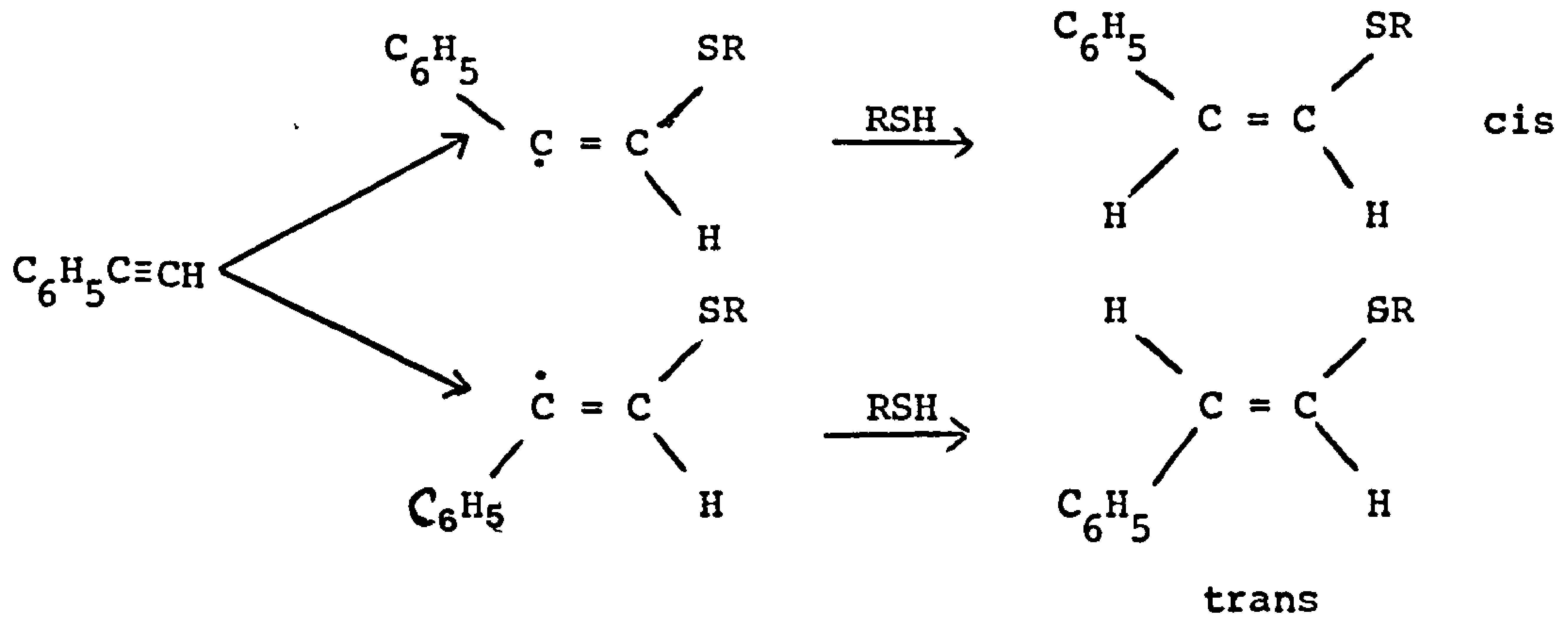
Table (2-5) shows the dependence of the stereochemical course of the addition to alkynes on the relative concentrations of the reactants.

Table 2-5

Thiol	Alkyne	Thiol:Alkyne	Ratio cis:trans	Ref.
C_6H_5SH	$C_6H_5C{\equiv}CH$	20:1	16:84	86
C_6H_5SH	$C_6H_5C{\equiv}CH$	1:1	56:46	86
C_6H_5SH	$C_6H_5C{\equiv}CH$	0.05:1	>95:<5	86
CH_3SH	$C_6H_5C{\equiv}CH$	1:1	84:16	86
CH_3COSH	$C_4H_9C{\equiv}CH$	1:1	73:27	87
CH_3COSH	$C_4H_9C{\equiv}CH$	0.002:1	83:17	87

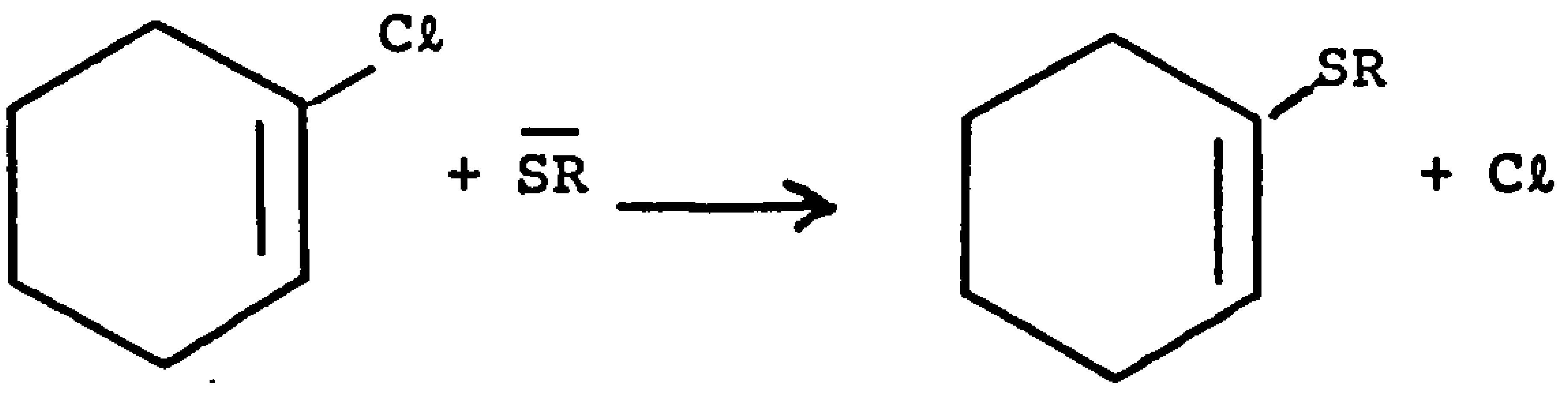
Thus the free radical addition of thiols to acetylenes proceeds readily to give monoadducts, diadducts, or both, depending on the relative proportions of the starting materials.[88,89] The cis/trans ratio of the monoadduct also depends on the ratio of [thiol]/[acetylene] and the reaction time. The cis isomer predominates when an excess of acetylene is used, while the trans isomer tends to predominate when the amount of thiol is increased.[87]

SCHEME (3)



Thiols as nucleophiles

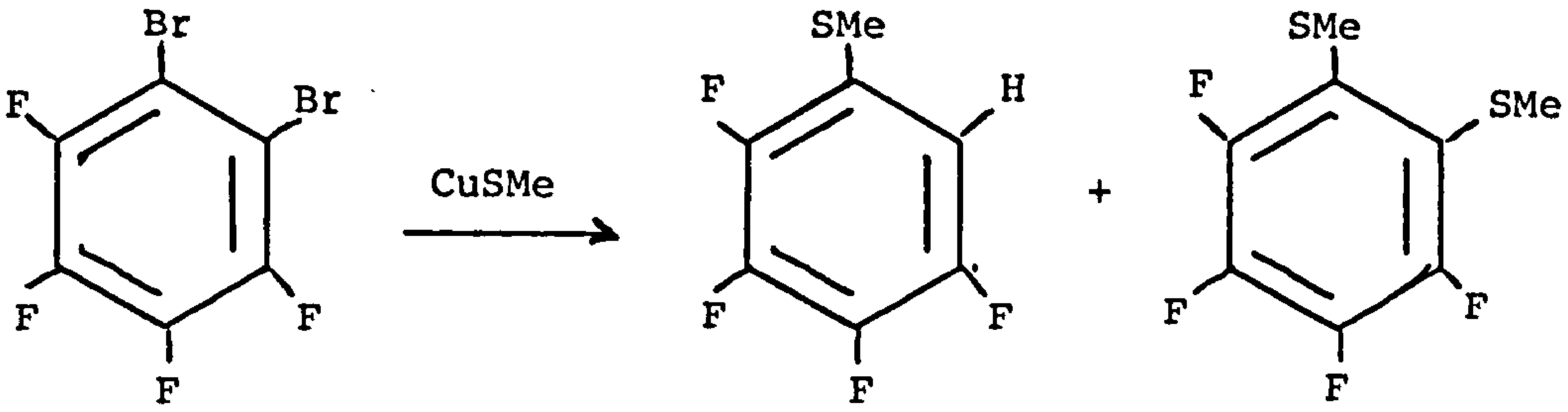
The substitution reactions to be discussed will be restricted primarily to reactions involving the thiolate anion, $\overline{RS}$ acting as a nucleophile. Thiolate anion reactions with ethylenic substrates have recently been reviewed. The simplest example of substitution in a vinyl halide is the preparation of thiol derivatives of 1-cyclohexene from the thiol and sodamide in THF with chloro-1-cyclohexane, equation (25).[90]



(1)

(25)

Vinyl bromides react with copper(I) thiolates, both aliphatic and aromatic to give vinyl sulfides (thio ethers)[91] equation (26) as do aryl bromides.



(I)

(II)

(26)

The vinyl bromides studied included β-bromostyrene and 1-bromo-2-methyl-1-propene. This method of synthesis of thio ethers is claimed to be superior to that using sodium thiolate and most other reported methods.[92]

1,2 dibromoethylene gives a yield of a mixture of cis 18% and trans 42% 1,2 diphenylthioethylene with copper(I) benzenethiolate, but copper(I) ethynethiolate ethylthioacetylene is formed with the elimination of hydrogen bromide,[92] equation (27).

$$\mathrm{BrHC{=}CHBr + CuSEt \longrightarrow HC{\equiv}CSEt + HBr + CuBr} \tag{27}$$

When substitution occurs in an ethylene derivative, it is of interest to observe whether the original configuration is retained. Several reactions of ethylene derivatives where configuration is retained, have been reported, e.g.

$$\mathrm{Ha\ell CH{=}CHCO_2Et + Et\bar{S} \longrightarrow EtSCH{=}CHCO_2Et}\;[93] \tag{28}$$

$$(\mathrm{Ha\ell = C\ell, Br, I})$$

In the reactions

$$\mathrm{(PhSO_2)HC{=}CFH + Ph\bar{S} \longrightarrow (PhSO_2)HC{=}C(SPh)H + \bar{F}} \tag{29}$$

the trans reactant gives the trans product, but the cis reactant gives cis and trans products in a 3:1 ratio.[94] When several halogens are present, as in trifluorochloroethylene, replacement of a fluoride with thiolate occurs with the sodium thiolate.

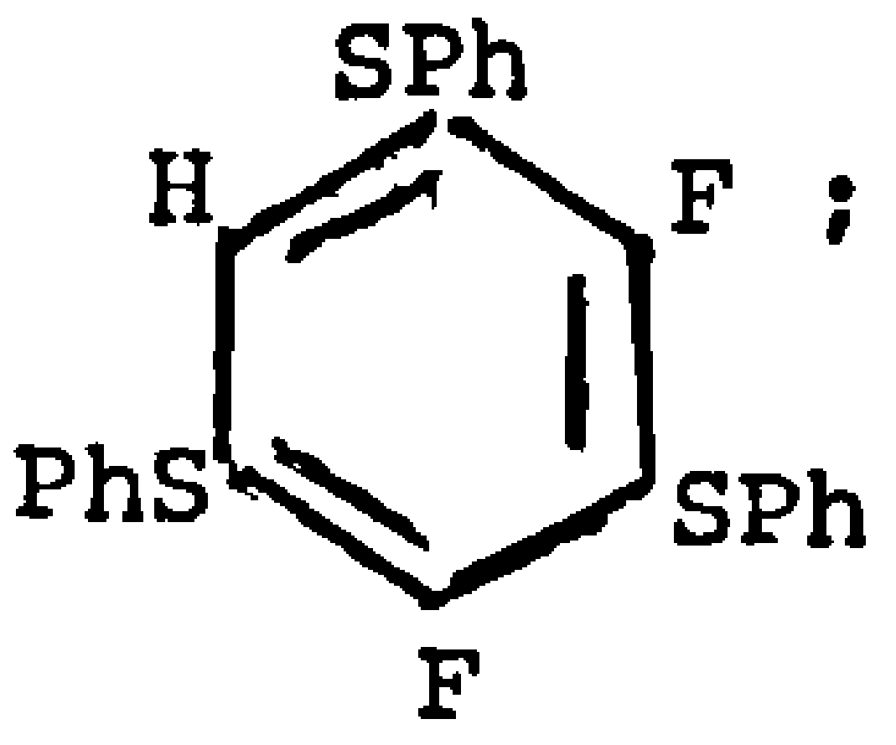
$$\mathrm{CF_2{=}CFC\ell + PhSNa \longrightarrow (PhS)CF{=}CFC\ell + NaF} \tag{30}$$

Butanethiol reacts similarly with $\mathrm{CF_2{=}CFHa\ell}$ ($\mathrm{Ha\ell = C\ell, Br}$) and $\mathrm{CF_2 = CC\ell_2}$ forming $\mathrm{BuSCF{=}CF\ Ha\ell}$ and $\mathrm{BuSCF{=}CC\ell_2}$ respectively.[95] Aromatic nucleophilic substitution with thiolate anions can be represented as

$$ArX + \overline{RS} \longrightarrow ArSR + \overline{X} \qquad (31)$$

where $\overline{X}$ is usually a stable ion such as a halide. For the series of monosubstituted halopentafluorobenzenes, C_6F_5 Haℓ, it is of interest to observe which halogen is replaced initially. Bis(pentafluorophenyl)-sulfide, $(C_6F_5)_2S$ may be prepared from bromopentafluorobenzene and copper(I) pentafluorobenzenethiolate in DMF.[96] The nucleophilic activity is PhS > MeS for the reaction with 1-iodo-2,4-dinitrobenzene, but MeS > PhS for p-fluoronitrobenzene[97]. The copper assisted nucleophilic displacement reactions of halopentafluorobenzenes have been studied.[98] The reaction of CuSBu with C_6F_5Br gave two products

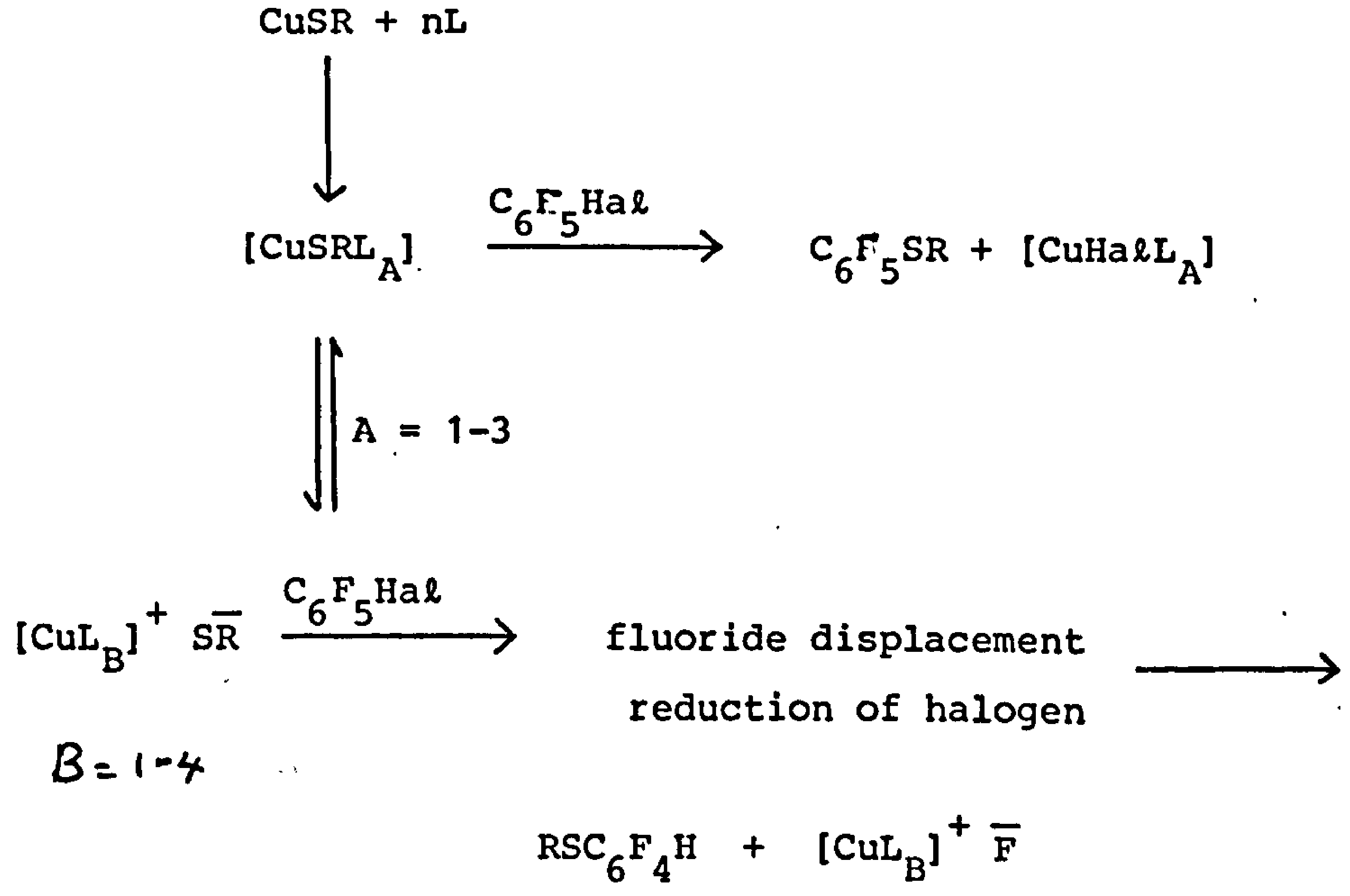
$$\underset{}{C_6F_5Br} + CuSBu \longrightarrow \underset{(1)}{C_6F_5SBu} + \underset{(2)}{BuSC_6F_4H} \qquad (32)$$

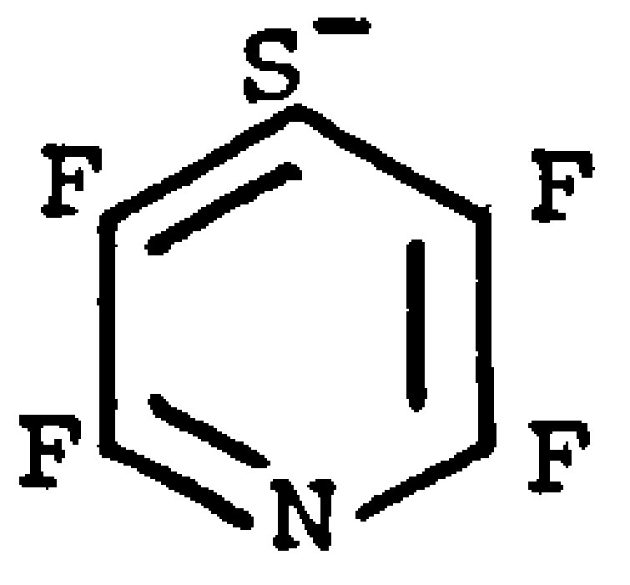
The ratio of the products depends on the solvent employed. In DMF product (1) was formed exclusively whereas product (2) involving halogen reduction was formed in various solvents in the presence of thiourea, although thiourea alone does not react with bromopentafluorobenzene. With these results in mind Tatlow and his coworkers[98] have investigated the effects of solvents and the addition of thiourea on copper-assisted nucleophilic displacement (c.a.n.d.) reactions of pentafluorohalogenobenzene, i.e. those reactions which take place with copper(I) species and probably involve the coordination sphere of the metal atoms. With iodopentafluorobenzene and copper(I) benzenethiolate and thiourea, rapid reduction of the iodide occurred together with multiple fluorine replacement, resulting in the formation of 2,4-difluoro-1,3,5-tris(phenylthio)benzene 

; pentafluorobenzene gave essentially the same products under the same conditions.

The formation of product (1) (C_6F_5SBu) (equation 32), without further substitution, suggests that the species such as $C_6F_5(Br)(SBut)$ may be complexed to the copper. A reaction scheme has been postulated involving the participation of the solvent and thiolate anion acting as reducing agent.

SCHEME (4)

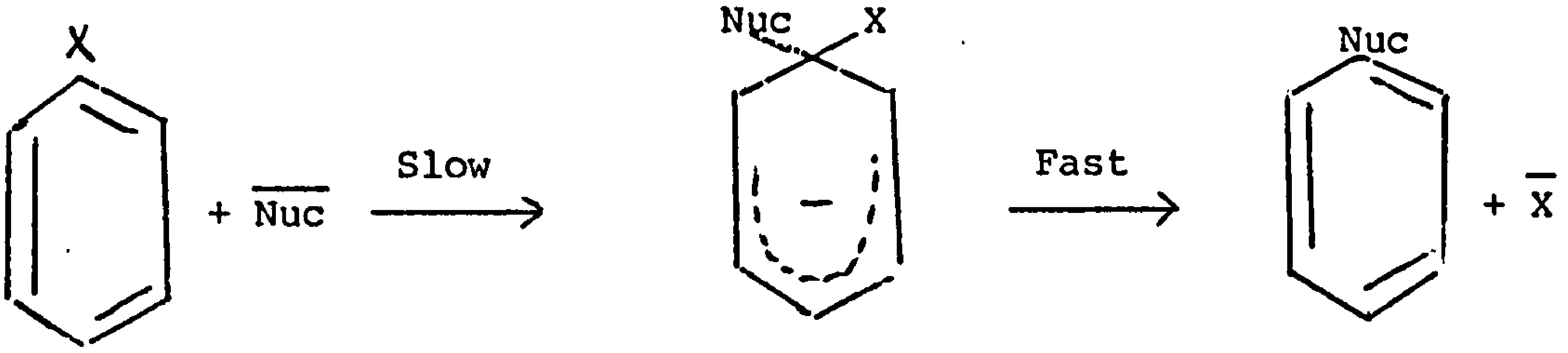


The reaction of nitro- and amino-fluorobromobenzenes of the type o-XC_6F_4Br and o-XC_6F_4Br where X = NO_2 or NH_2 with copper(I) pentafluorobenzenethiolate, result in the replacement of the bromine.[99] The pentafluorobenzenethiolate anion or the anion of 2,3,5,6-tetrafluoro-4-mercaptopyridine,  replaced the fluorine ortho or para to the nitro group. Para substitution only occurred in solvents of high dielectric constant, such as DMF and acetonitrile, whereas in solvents of low dielectric constant, such as ether, mixed replacement of ortho and para fluorine was observed.[99,100] The solvent plays an important role in determining the relative amounts of ortho- and para-substitution. Increasing ionisation of thiol is postulated to cause predominantly para substitution. Solvents with dielectric constant lower than about 30 cause some ortho substitution, whereas solvents of dielectric constant greater than 30 give almost exclusive para substitution. This has been attributed to increasing ionic dissociation of the thiolate in the higher dielectric constant solvents.[99,100] Presumably the formation of meta substituted products in the solvents of low dielectric constant does not involve the formation of the thiolate anion as the active entity. Thiolates can also cause dehalogenation of various halogen compounds, such as 2-bromo-3-nitrothiophene and 4-halo-napthol.[101,102]

Addition-elimination in fluoroaromatic rings

Nucleophilic displacements of halogen from activated systems most commonly occur via a two-step addition-elimination mechanism.[103]

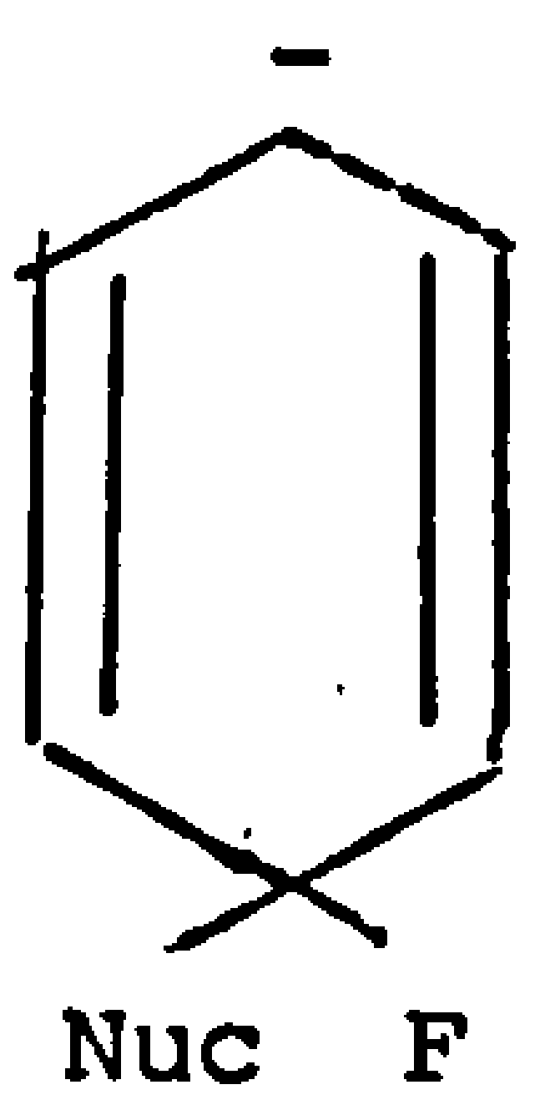
The first step in the reaction is usually but not always,



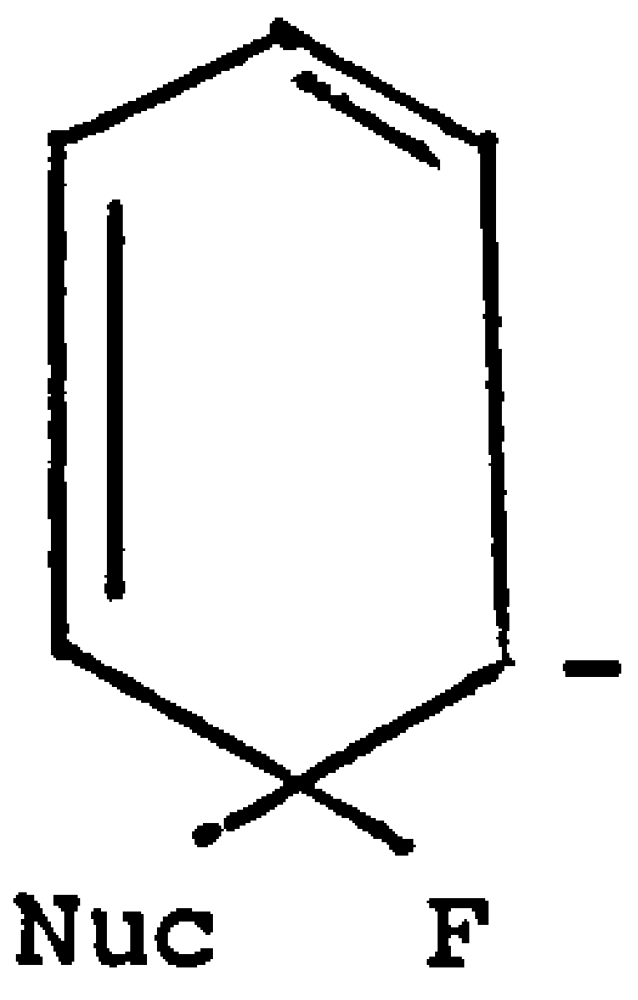
rate determining. Some of the most convincing evidence for this is that the mobility order of the halogens, established by the classic work of Bunnett and his co-workers,[104] is F >> Cl, Br, I. Since the carbon-fluorine bond is the strongest of the series then there can be little bond breaking in the rate-determining step in systems where this order is observed. However, we must explain why the fluoro derivatives should be so much more reactive than the other halogen derivatives. It has been argued that carbon-fluorine bond polarity $\overset{\delta+}{C} - \overset{\delta-}{F}$ is mainly responsible for this mobility order, i.e. making the carbon atom under attack more electrophilic in character, although the different steric requirements of the halogens probably make some contribution to the mobility order.

Orientation and reactivity in nucleophilic displacement reactions

A detailed study of orientation and reactivity in the nucleophilic replacement reaction of aromatic polyhalo compounds has been published.[105] It involves study of the stability of the Wheland type intermediates (1) and (2)



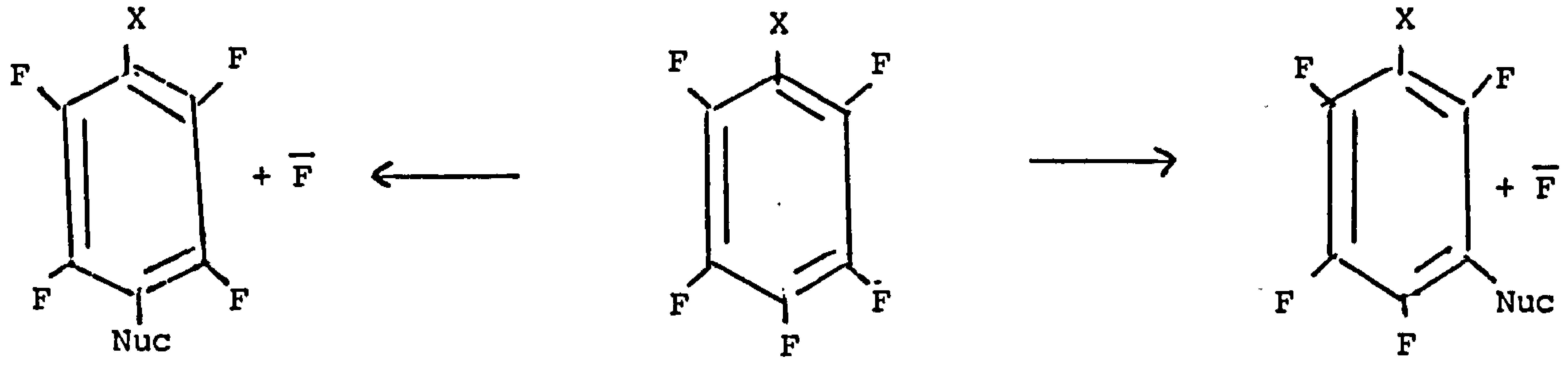
(1)



(2)

($\overline{Nuc}$ is nucleophilic)

Most activating groups cause primarily para substitution but some ortho substitution may also occur. The formation of meta products from a nucleophile may be rationalised by a scheme involving carbonium intermediates.[106] It is only with highly halogenated systems that problems arise about orientation of substitution, and these are analogous to the classical orientation problems of electrophilic aromatic substitution. The orientation of substitution and reactivity of polyhaloaromatic compounds has been the subject of much discussion and only in 1977 has a clear picture emerged.[107,108]



(e.g. X=H, Me, CF_3)

X=NH_2, $\overline{O}$

In most cases for substitution in perfluorobenzenes C_6F_5X, the main product (>90%) arises from displacement of a fluorine atom para to the substituents X (for example) where X = H, Me, SMe, CF_3, NMe_2, NO_2, etc. [109,105] In a few cases (X=NH_2, R) replacement in the meta position predominates. The effect of substituents on rate constants is, however, in the direction expected for nucleophilic aromatic substitution in that, electron-donating groups deactivate, for example $C_6F_5NH_2$ and $C_6F_5\overline{O}$ are strongly deactivated while withdrawing groups activate.

Some relative rate constants[110] are shown below, illustrating that the great range of rate constants depends upon the electrophile.

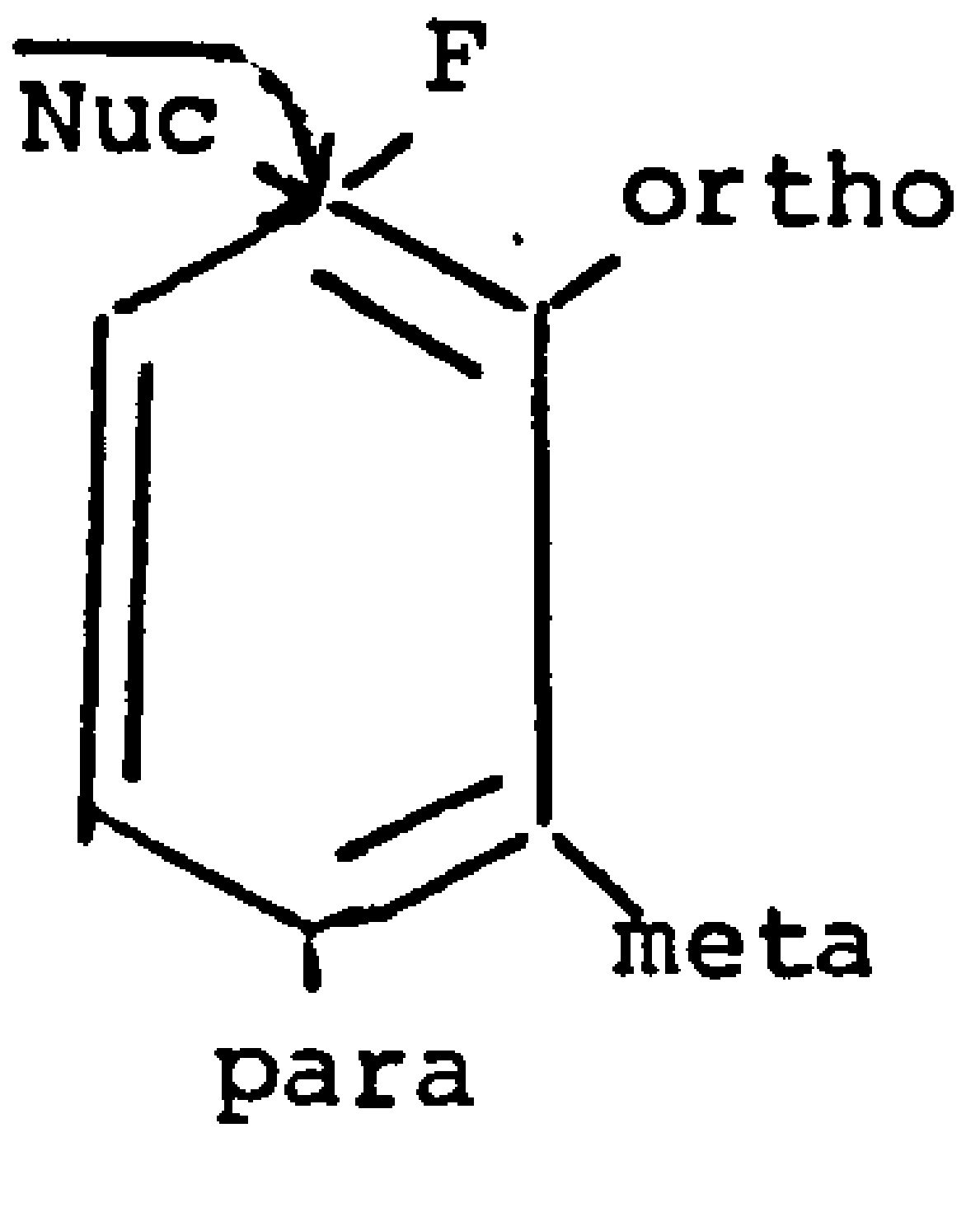
By contrast the orientation pattern is relatively insensitive to the substituent.

Table 2-6

Relative rate constants for reaction with $NaOC_6F_5$ at 106°C in N,N-Dimethylacetamide with C_6F_5X

X	K_{rel}
CF_3	2.4×10^4
CO_2Et	2.9×10^3
C_6F_5	7.3×10^2
Br	39
Cl	32
H	1
F	0.91

The basis of the unusual orientation effect of the halogens is the different activating influence of fluorine atoms which are ortho, meta and para to the point of nucleophilic attack on the ring.



activating influence of F, meta > ortho >> para.

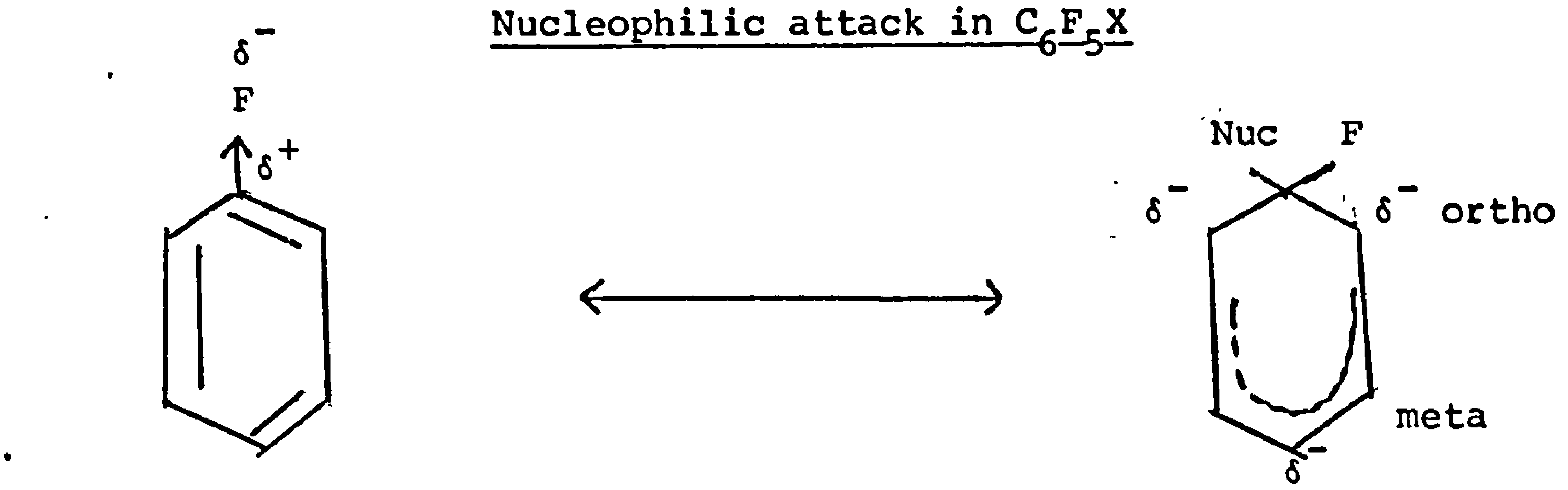
These separate activating influences have been established for reactions with methoxide in methanol.[108]

The effect of fluorine para to the reaction center is little different to that of hydrogen at the same site, whereas ortho and meta fluorines are strongly activating.

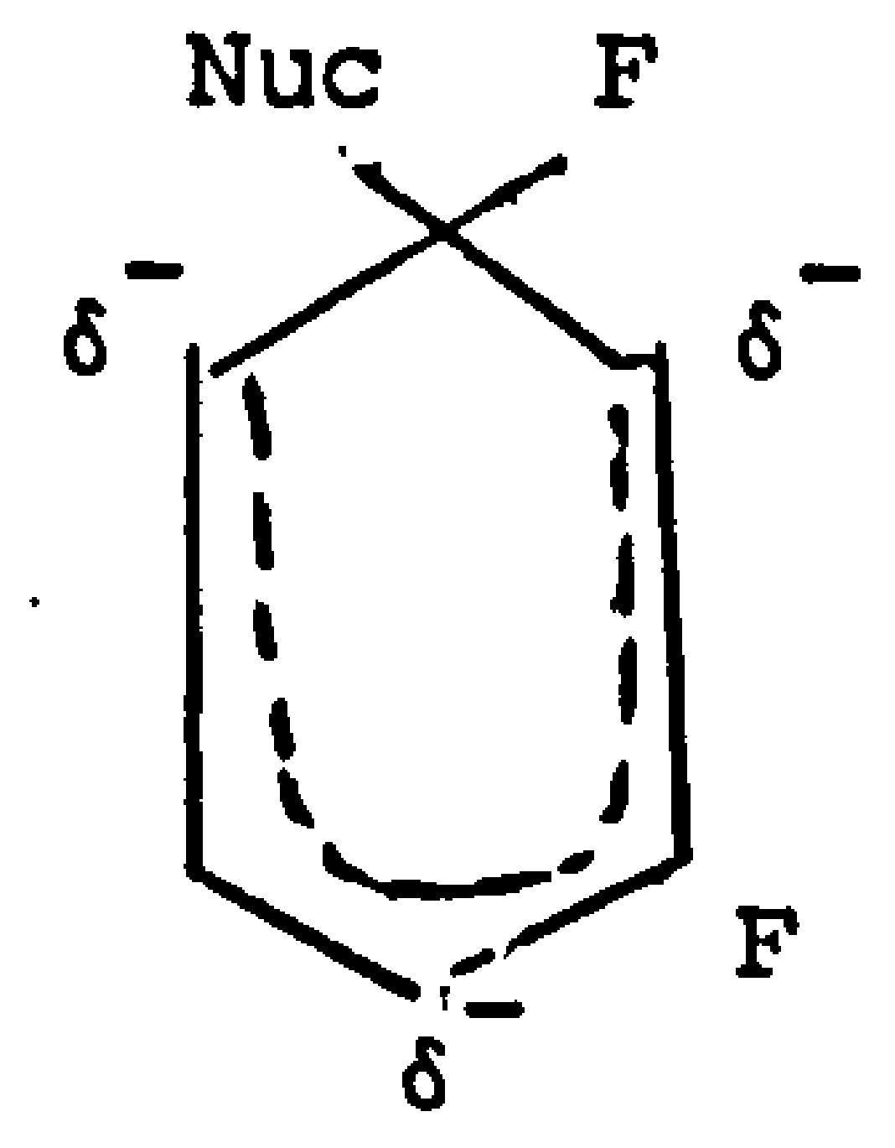
An explanation of these effects has been advanced based on (1) as model for the transition state of the rate determining step.[107,108]

SCHEME 5

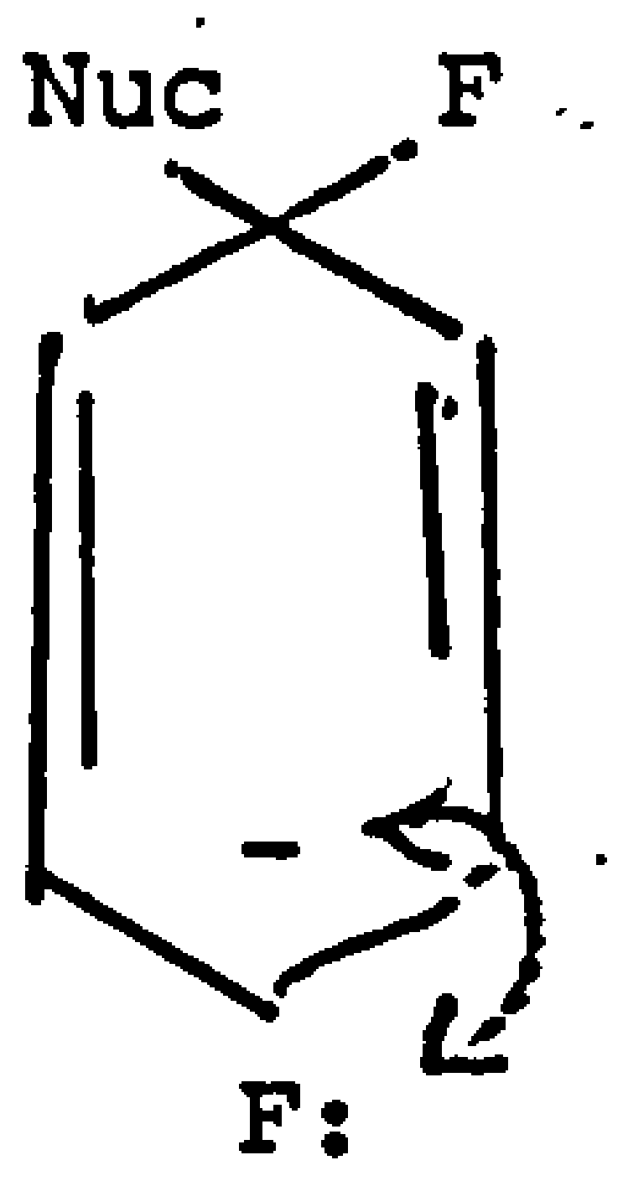
Nucleophilic attack in C_6F_5X



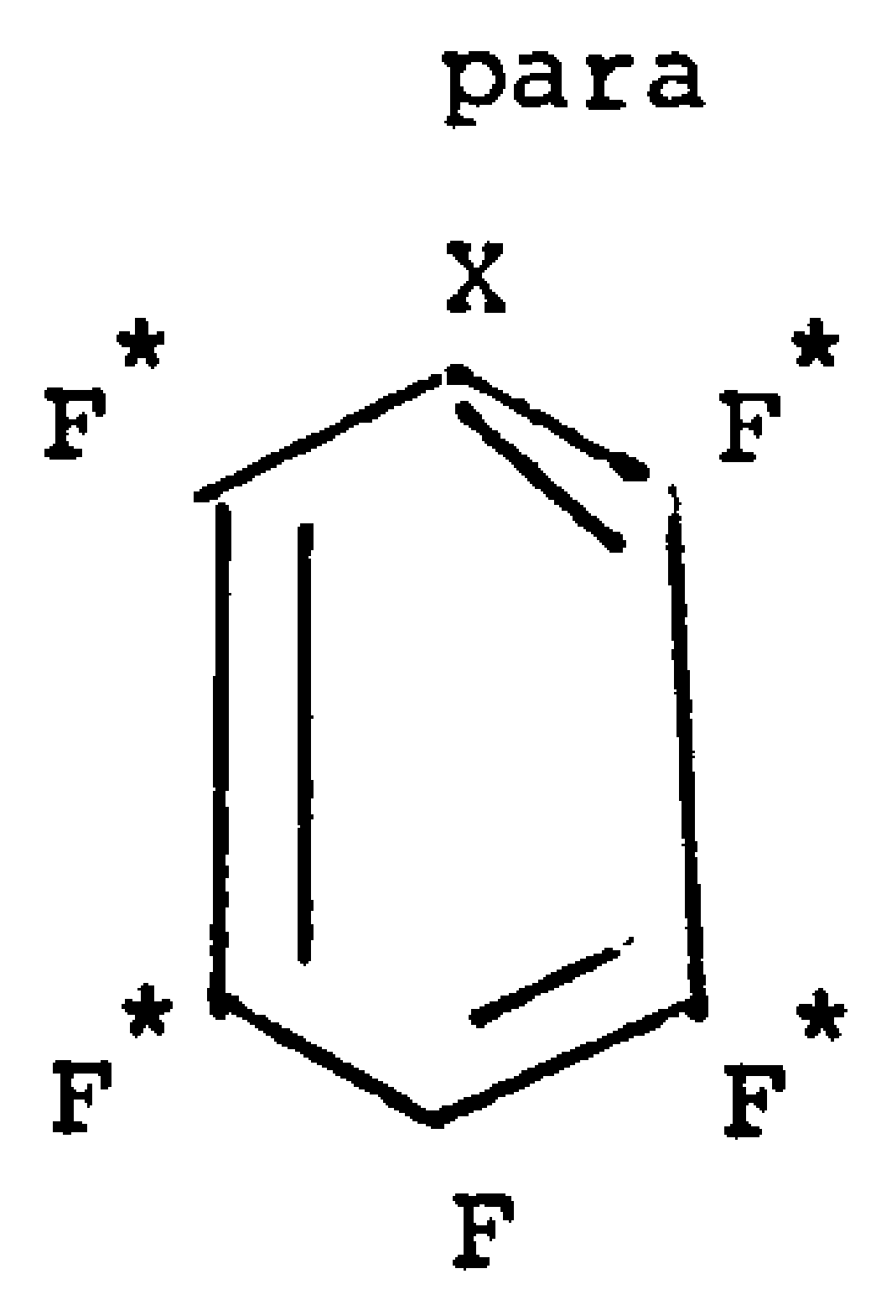
(1a) (1b)



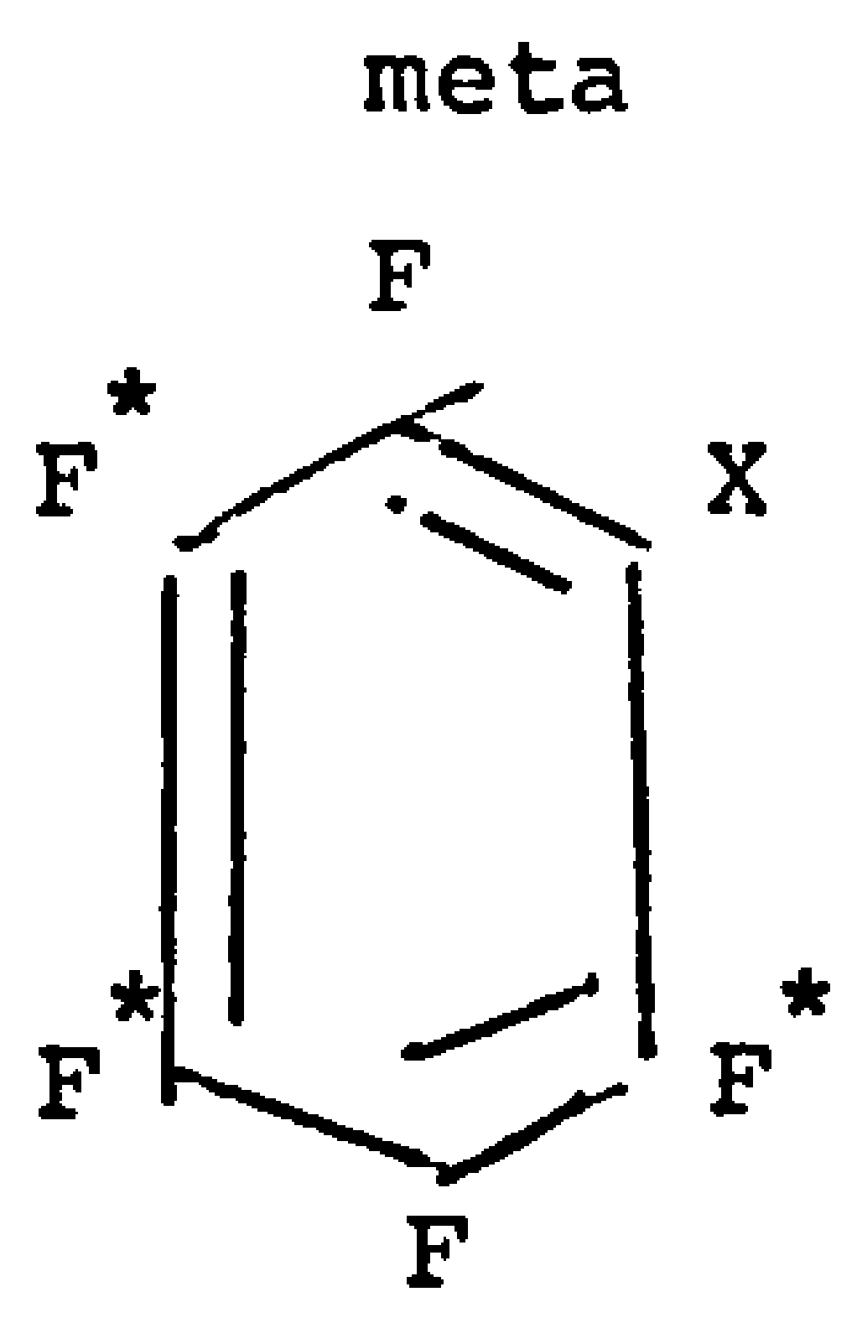
(2)



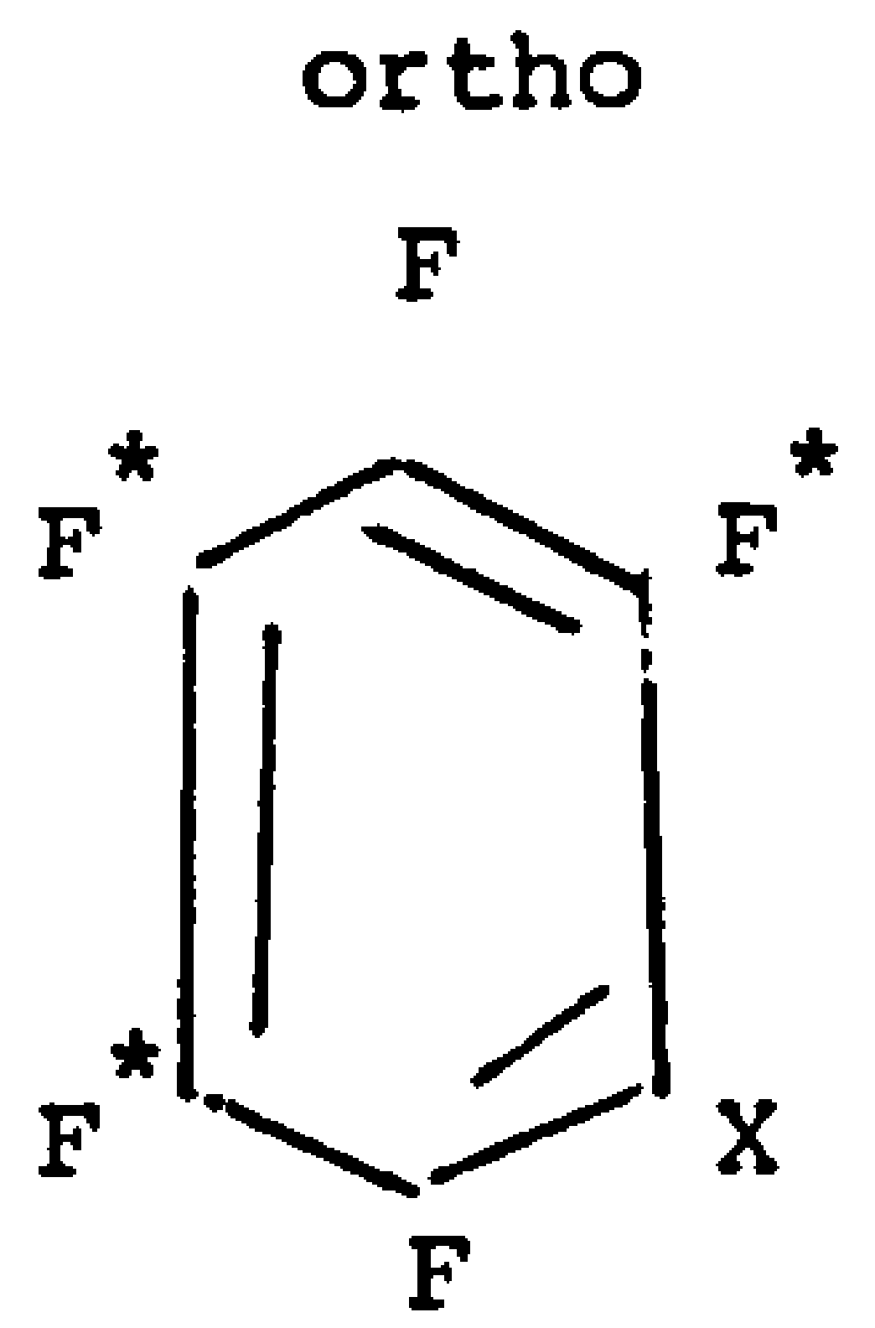
(3)



Four activating F



Three activating F



Three activating F

The activating influence of the meta fluorine is shown in (2). Likewise the minor effect of para fluorine is a consequence of competing inductive withdrawal and electron-pair repulsion (3). However, the significant activating influence of ortho fluorine is more difficult to account for since transition state (1b) would only imply similar effects for both ortho and para fluorines. It is probable, therefore, that the ortho fluorine atom activates by enhancing the already electrophilic nature of the carbon atom under attack in the initial-state contribution (1a).

Nevertheless, regardless of the basis of these activating effects for fluorine substituents, it is quite clear that nucleophilic attack usually occurs in C_6F_5X predominantly para to the substituents because this maximises the activation of fluorine atom.

CHAPTER 3

CHAPTER 3

Introduction

The preparation of hydrocarbon dithioethers is well documented[111-117] and for a large number of compounds it involves simple, straightforward reactions[117] such as in figure (3.1)

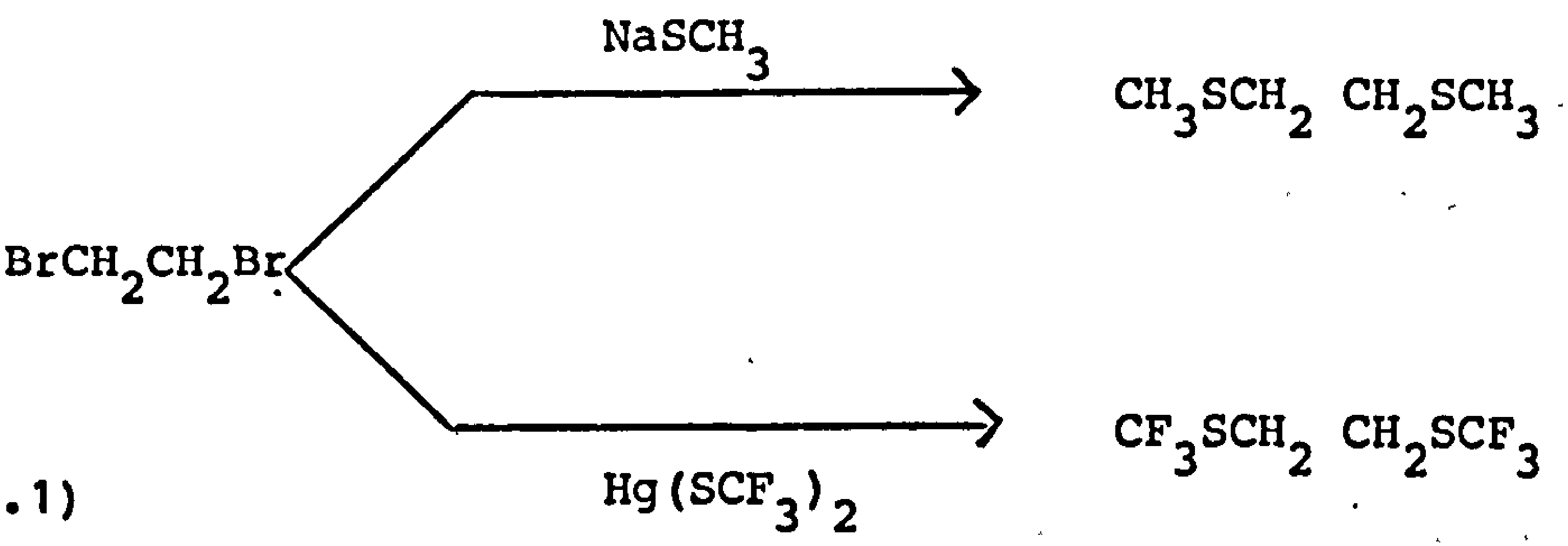


Figure (3.1)

When similar reactions are used to obtain fluorinated analogues, however, these reactions often fail to produce the desired compound and alternative routes have to be devised. The method used by H. Torrens to obtain symmetric dithioethers involves the reaction of a suitable alkyl dihalide, normally a bromide with sodium or potassium thiolates. The reaction generally proceeds in good yield. Figure 3.2

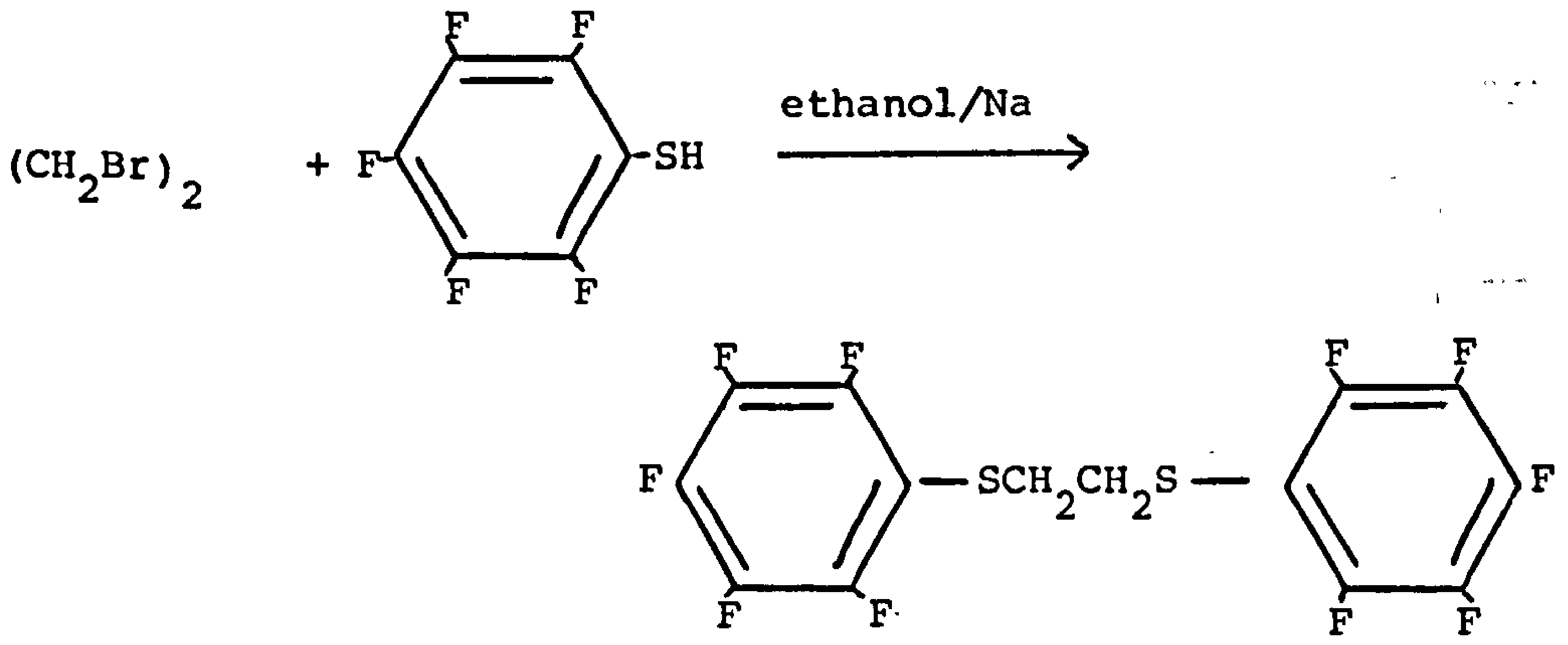
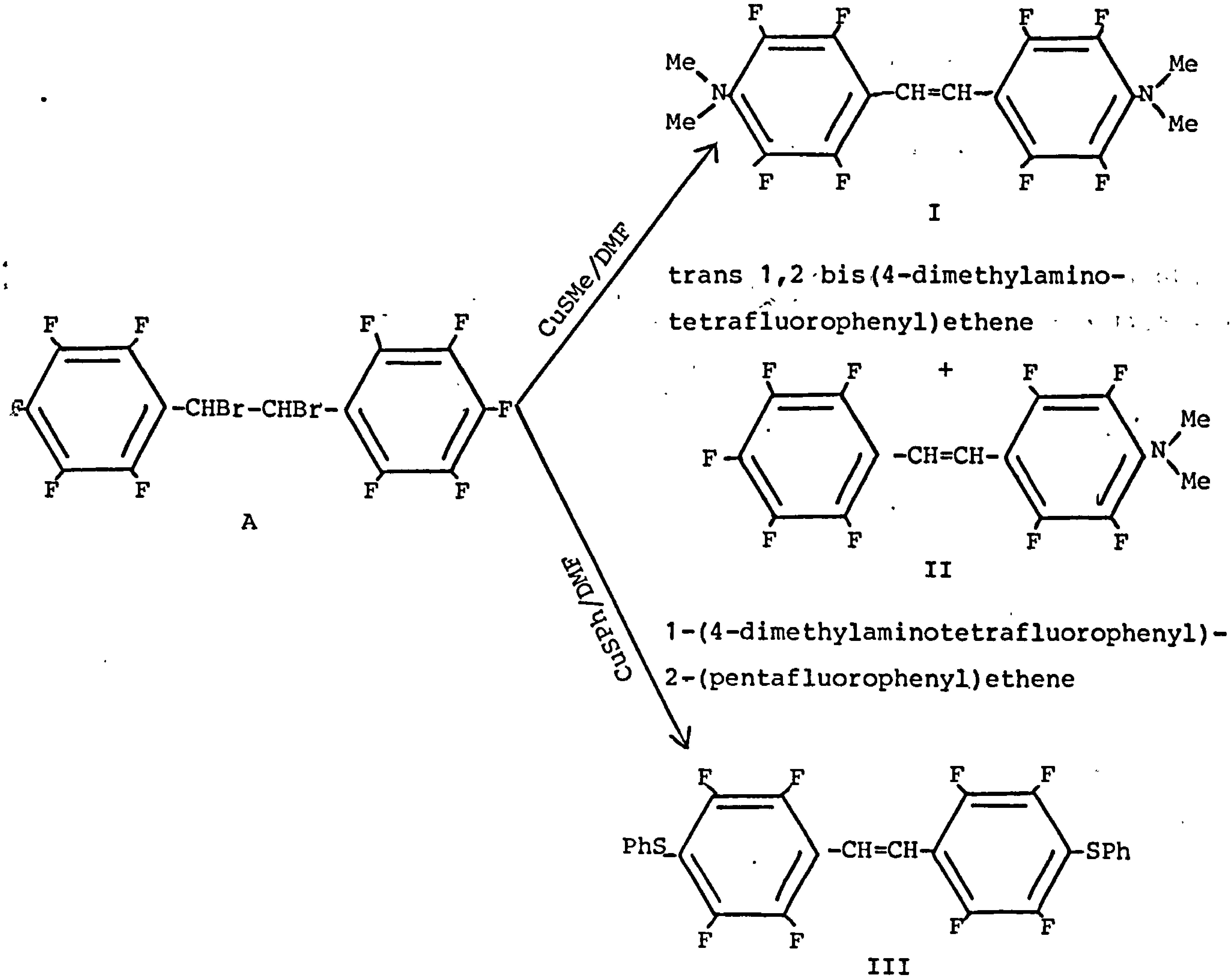


Figure (3.2)

Very recently in 1982 and after we had carried out our own reactions, M.E. Peach obtained similar products in low yield from the reaction of $(CH_2Br)_2$ with copper(I) thiolates in dimethylformamide. In our work we used both methods. The following reactions have been used to obtain symmetrical and unsymmetrical fluorinated derivatives.

Results

The reactions in figure (3.3) were carried out



A

I

trans 1,2 bis(4-dimethylamino-tetrafluorophenyl)ethene

+

II

1-(4-dimethylaminotetrafluorophenyl)-2-(pentafluorophenyl)ethene

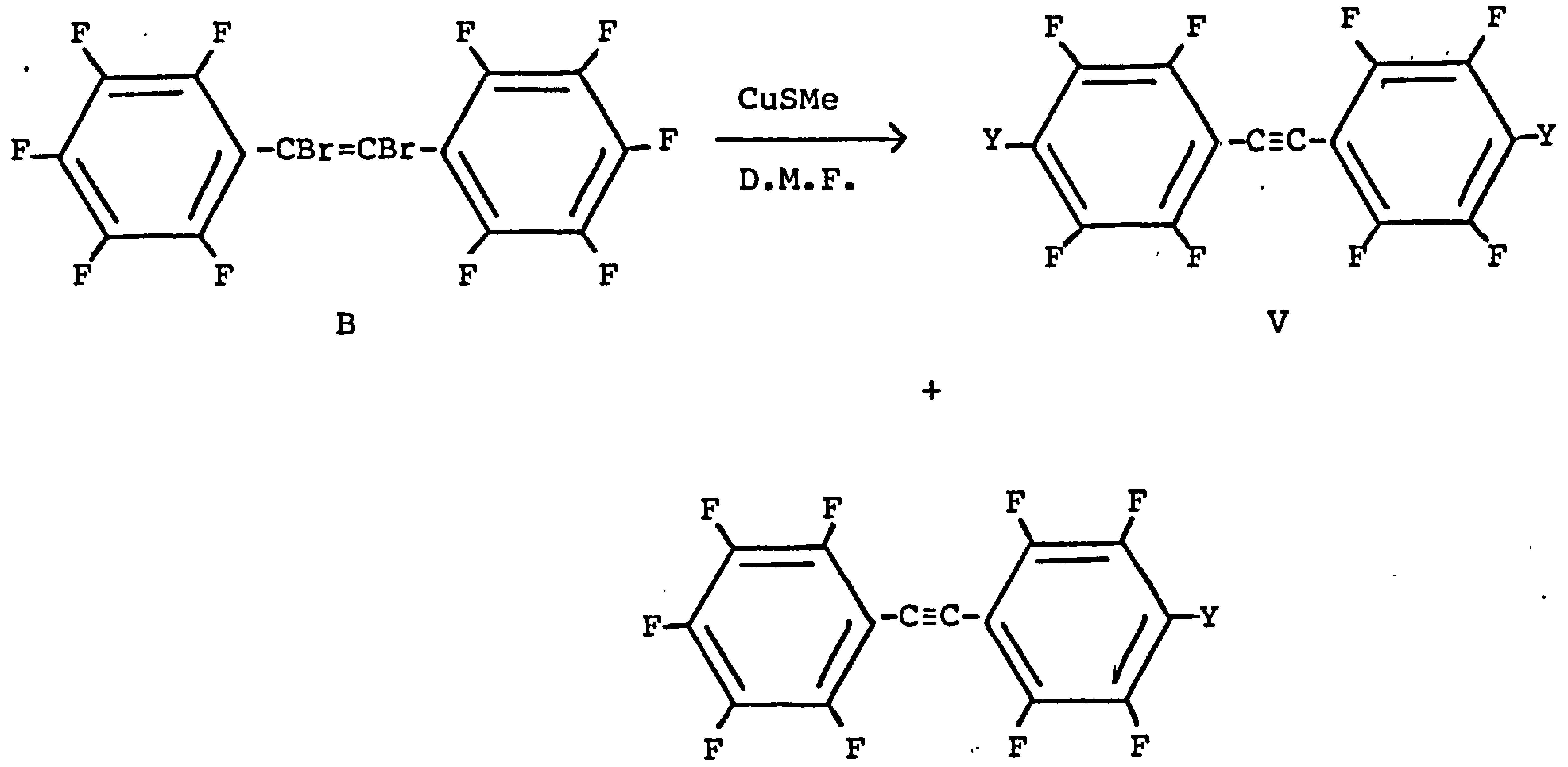
III

1,2bis(4-phenylthiotetrafluoro phenyl)ethene

+

$C_{14}F_6(SPh)_4$ + PhS-SPh

IV

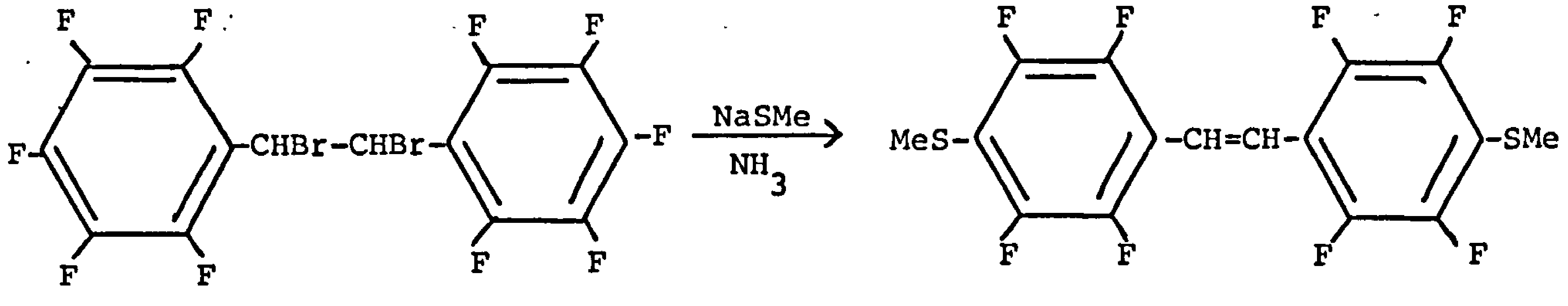


B

V

VI

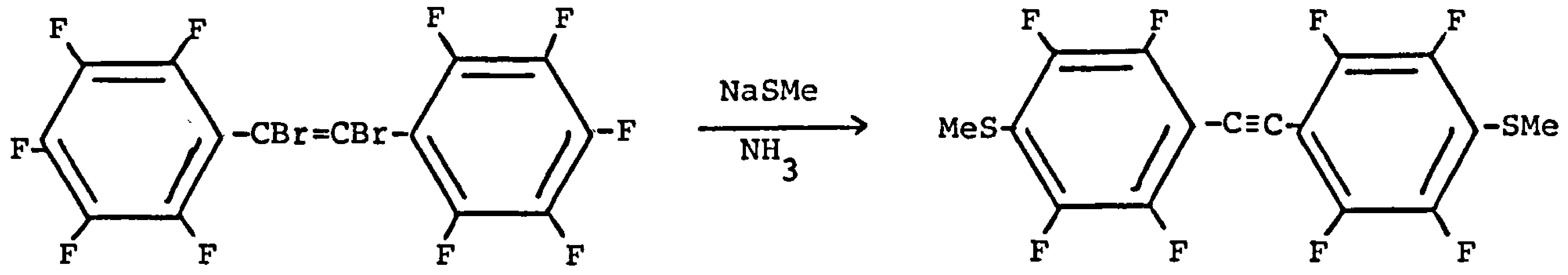
Y is NMe_2 or SMe



C

VII

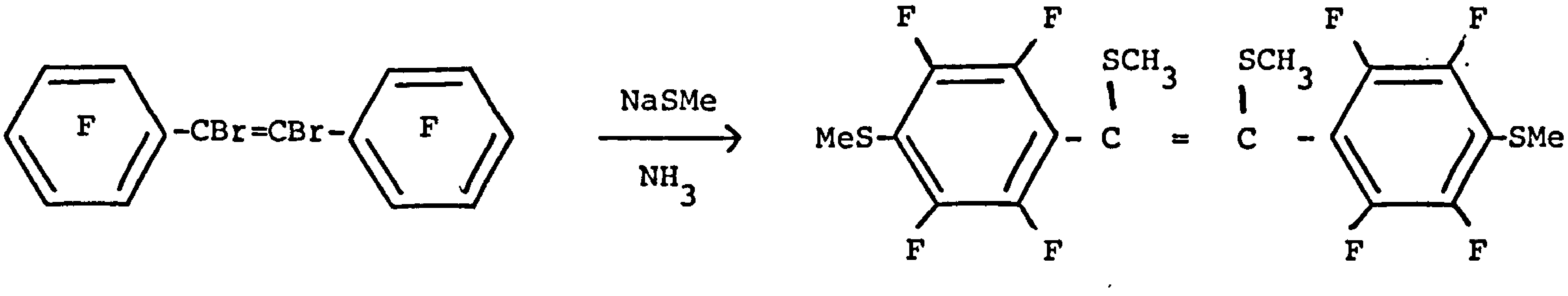
1,2bis(4-methylthiotetrafluorophenyl)ethene



VIII

1,2bis(4-methylthiotetrafluorophenyl)ethyne

We should note that in the above reactions, in addition to substitution of halides by the aryl groups, there is debromination to give alkenes and alkynes. There is also para substitution of fluorine.



E

two isomers

IX

1,2bis(4-methylthiotetrafluorophenyl)-1,2bis(methylthio)ethene

In the above reactions all of those using NaSM/NH_3 give methanethiolate derivatives as products in a good yield. In the reactions using CuSMe in dimethylformamide products are predominantly those corresponding to nucleophilic substitution of $-NMe_2$ groups into the aromatic ring. (also in reaction (B) there is some nucleophilic substitution of $-NMe_2$ groups and also of MeS- groups so that a mixture results of the two series of compounds.)

In all cases the pure methanethiolate derivatives were obtained from the reactions using sodium methanethiolate, as shown above. When $\bar{S}Ph$ is used, the products correspond to $\bar{S}Ph$ substitution into the aromatic ring but debromination also results.

The reagents CuSMe[91] and CuSPh were prepared from the thiols and copper(II) acetate. The preparations of $C_6F_5CHBrCHBrC_6F_5$ and $C_6F_5BrC{=}CBrC_6F_5$ as used in reactions A, B, C, D and E are discussed in Chapter (7). The crude products of the reactions were examined by thin layer chromatography and by column chromatography. Fractions were isolated by use of the Chromatron. The reactions of α-β-dibromobis(pentafluorophenyl)ethane (A and C) with CuSPh, CuSMe and NaSMe in different polar solvents, e.g. (NH_3 and dimethylformamide), and of α-β-dibromobis(pentafluorophenyl)ethene (B and D) with CuSMe resulted in debromination and nucleophilic displacement of para fluorine atoms in the rings. The type of nucleophilic displacement depends on the solvent employed[119] and on the amount of reagent.

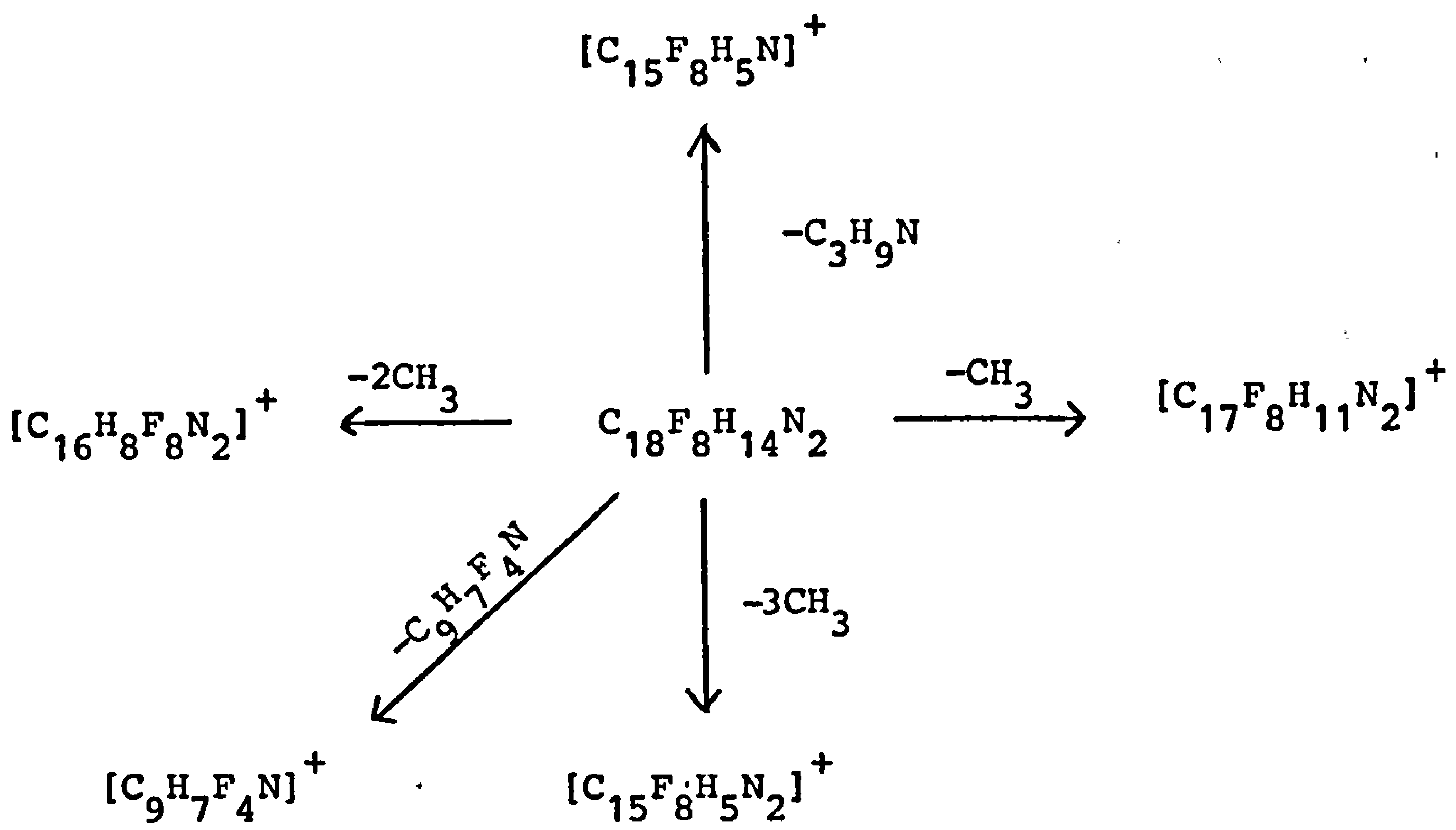
The products were characterised by various methods. Microanalysis of compounds I, II, V and VII indicated the presence of nitrogen and this is confirmed by other spectroscopic measurements.

Mass spectroscopy of products I, II, V and VI reveals parent ions at m/e = 410, 385, 408 and 383, corresponding to $C_{14}F_8H_2[N(CH_3)_2]_2$, $C_{14}F_9H_2NMe_2$, $C_{14}F_8(NMe_2)_2$ and $C_{14}F_9NMe_2$ respectively.

There is a 3 a.m.u. (atomic molecular unit) difference between an SMe group (47) and NMe_2 group (44). In general, even when we know from other evidence that mixtures are present, we did not detect parent ions corresponding to sulfur species. We assume that this is due to lower volatility or higher ionisation energies or both for the sulfur compounds.

We note that Peach et al 1974 have studied mass spectra of methanethiolate derivatives and comment that breakdown in the mass spectrometer can take place by loss of hydrogen for the compound $C_6F_5SCH_3$. It is possible however that the sample used in this mass spectrometric determination was actually $C_6F_5NMe_2$. We have been unable to check the method used in the preparation of the $C_6F_5SCH_3$, but we note that Peach et al 1979 do use CuSMe/DMF in their reactions.

Some initial fragmentation modes for (I) are shown in Scheme (1).



Scheme (1) - Fragmentation modes for $C_{18}F_8H_{14}N_2$ 1,2bis(dimethylamino-tetrafluorophenyl)ethene.

Other spectra of product I have been examined to confirm the structure. The infrared spectra show bands at 2941-2870 cm^{-1} for C-H stretches at 1480 (v.s.) cm^{-1} and at 1450 (s) cm^{-1} for ring vibrations and at 975, 965, 850 (s) for (C-F).

The NMR spectra shown in table (1) were valuable in assigning the structure. A proton NMR signal at 2.99 ppm is split into a triplet due to coupling with the fluorines ortho to it (JH-F 2.1 Hz).[120,121] Thus the compound $C_{14}F_8H_2(NMe_2)_2$ (I) is confirmed as having para substitution. The ethylenic proton signal occurs at 7.2 ppm (ratio 6:1) whilst the ^{13}C NMR spectrum indicates a trans configuration JC-H 17 Hz,[122] the trans structure is further confirmed by the presence of a doublet, indicating that there is electron delocalisation between the 4-4 positions, at 2.92 ppm, which is similar to that found in trans stilbene derivatives[123] (see page 75].

^{19}F NMR spectra show two multiplets for ortho and meta fluorines at 145 ppm and 153.5 ppm respectively. This, together with the lack of observation of a para-fluorine, further confirms that the nucleophilic substitution of NMe_2 has taken place at the para position with respect to the ethylenic group. All of the above spectroscopic data are consistent with the structure

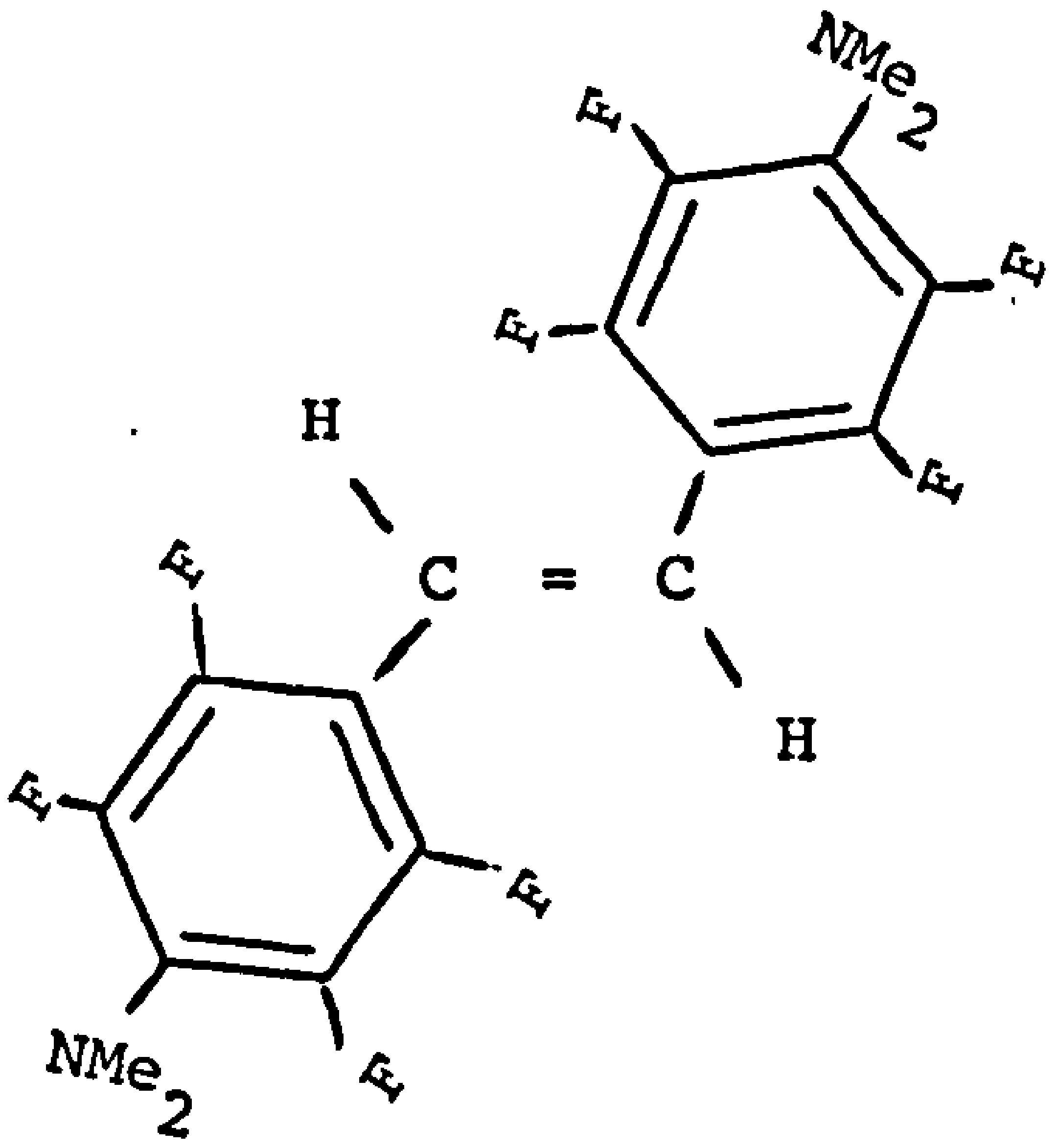
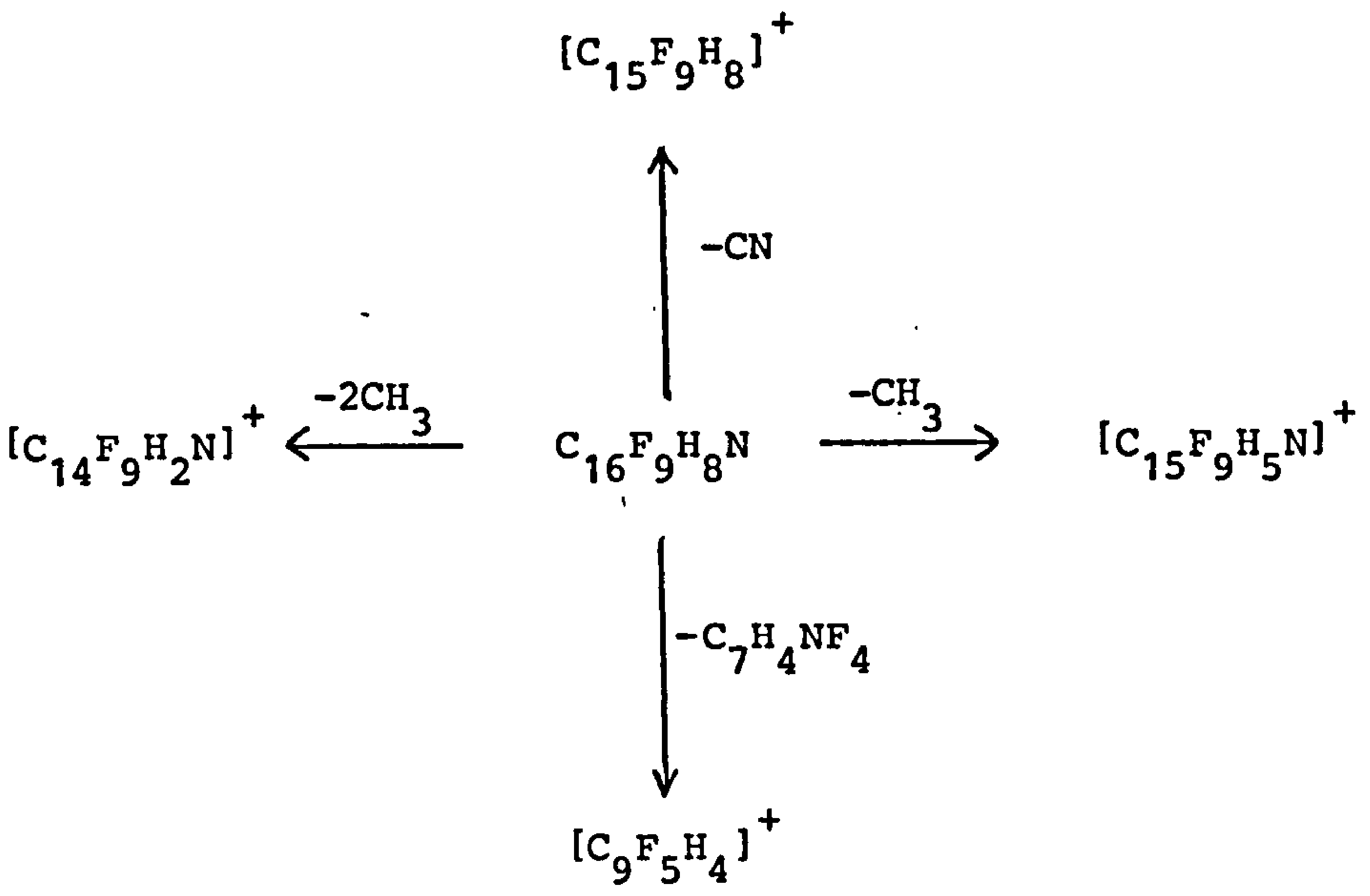


Figure (3.4) - trans-1,2bis(4-dimethylaminotetrafluorophenyl)ethene.

The minor product (II) was examined by mass spectroscopy which showed a parent ion m/e = 385 corresponding to $C_{16}H_8F_9N^+$, the monosubstituted derivative. The breakdown of (II) in the mass spectrometer can be illustrated by Scheme (2)



Scheme (2) - initial fragmentation of 1-dimethylaminotetrafluorophenyl)-2-(pentafluorophenyl)ethene.

The infrared spectra of this compound in carbon tetrachloride show bands at 2942-2871 (m) cm^{-1} for C-H stretches of CH_3 groups and C-H groups, at 1479 (v.s.) cm^{-1} and at 1450 (s) cm^{-1} for ring vibrations and 975 (v.s.) cm^{-1}, 962 cm^{-1}, 852 and 735 (v.s.) cm^{-1} for C-F modes. See figure (3.5).

The ^1H and ^{19}F nmr spectra are consistent with the above data. The measured shifts are ^1H at 2.94 $[N(CH_3)_2]$ ppm and 5.12 ppm [=CH], ratio 6:2. The methyl protons are coupled to the fluorines ortho to it (JHF 2.2 Hz).[125,122] The ^{19}F spectra show second order effects. The chemical shifts observed for the fluorine are consistent with the literature[125] showing ortho peaks at ca 143 ppm, para peaks at ca 155 ppm and for para ca 162 ppm for ring A. Ring B shows multiplets for ortho and meta at 145 ppm and 151.8 ppm respectively.[125]

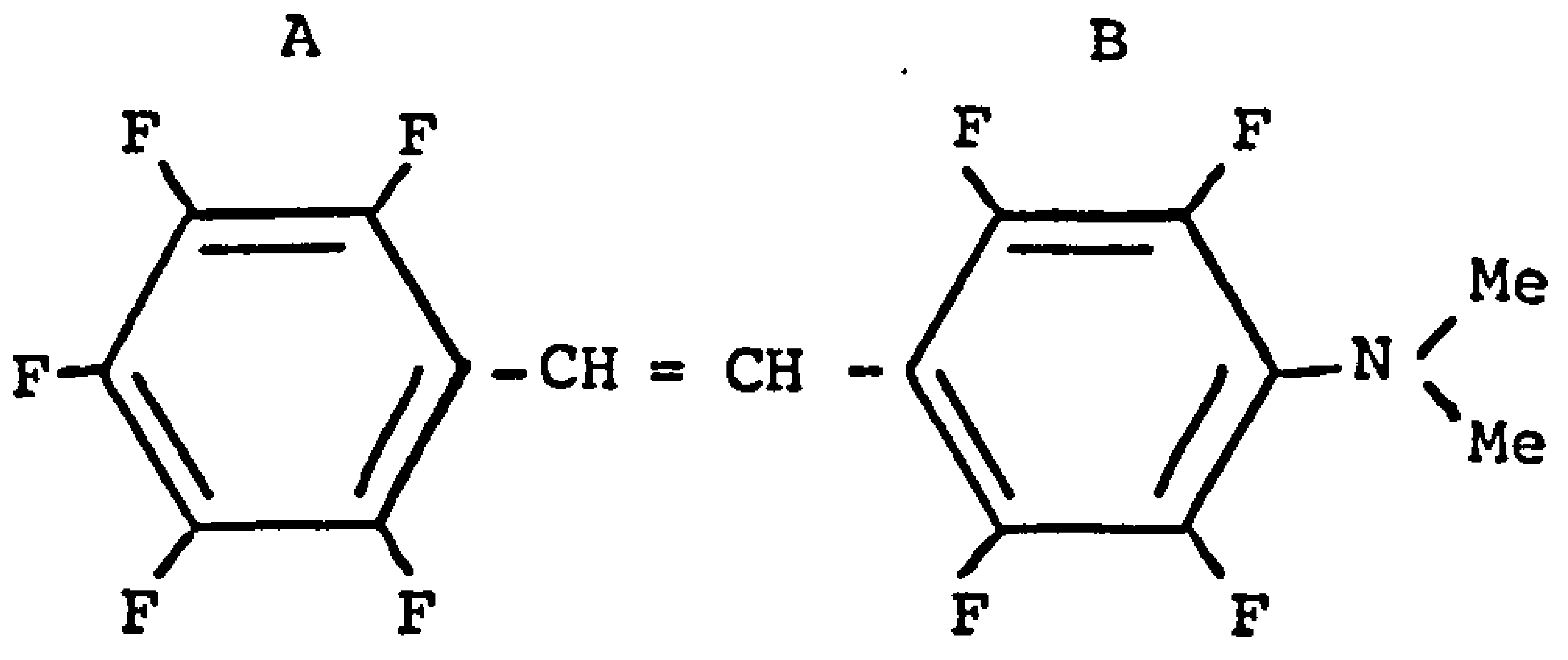


Figure (3.5) - 1 -(dimethylaminotetrafluorophenyl)2-(pentafluorophenyl)ethene.

Both ^{1}H and ^{19}F nmr spectra indicated that this product exists as one isomer only.

^{1}H NMR spectra shows a signal at 2.94 ppm as the expected triplet from coupling to ortho fluorines J_{HF} 2.2 Hz, the ethylenic protons give a broad signal at 5.2 ppm.

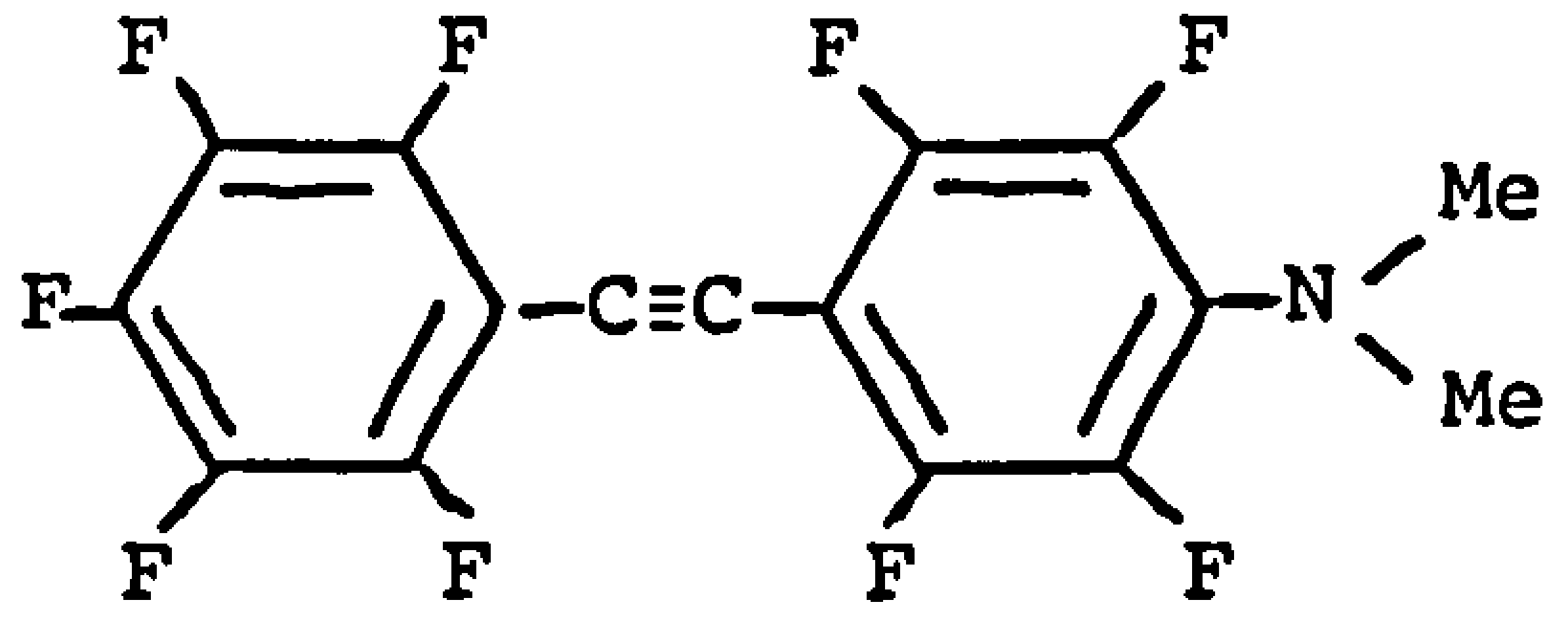
The mass spectra of product V show a parent ion at m/e = 408 corresponding to $C_{14}F_8(NMe_2)_2$. The mode of breakdown in the mass spectrometer is shown in Scheme (3).

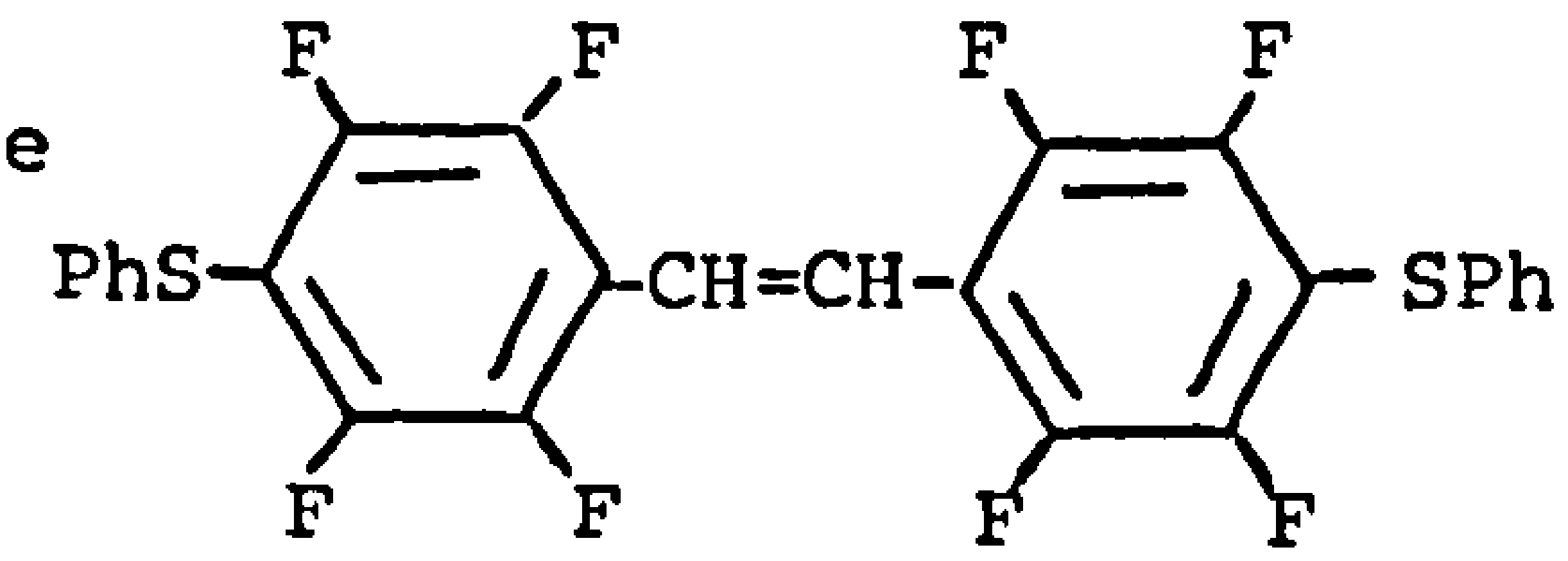
$$\begin{tikzcd}
C_{13}F_{7} & C_{14}F_{8} \arrow[l, "-CF"'] & C_{17}F_{8}H_{12}N \arrow[l, "C_{3}H_{9}N"'] \arrow[r, "-CH_{3}"] & C_{16}F_{8}H_{9}N \\
 & C_{8}F_{4}NH_{6} & C_{18}F_{8}N_{2}H_{12} \arrow[l, "C_{10}F_{4}NH_{6}"'] \arrow[u, "-CN"'] \arrow[r, "-CH_{3}"] & C_{17}F_{8}N_{2}H_{9}
\end{tikzcd}$$

Scheme (3) - Fragmentation of $C_{18}F_8N_2H_{12}$ 1,2(4-dimethylaminofluorophenyl)ethyne.

Infrared spectra of this compound show bands at 2980-2820 (m) cm^{-1}, 2810 (m) cm^{-1} for C-H vibrations, at 1715 (s) cm^{-1}, at 1640 (m) cm^{-1} for C=C stretch. No band is observed due to the C≡C stretch between 2500 and 1900 cm^{-1} as this is a symmetrical acetylene. Other bands are seen between 1585-1428 (s) cm^{-1} for ring vibrations, at 1020 (m) cm^{-1}, 980 (v.s.) cm^{-1} for C-F stretches.

^{1}H NMR spectra show a broad signal at 3.1 ppm for the CH_3 groups. The ^{19}F NMR spectrum of this compound is complicated and second order.

The structure of compound VI  is indicated by the presence of one proton signal at 3.09 ppm. The infrared spectrum shows peaks at 2938-2815 cm^{-1} for C-H vibration of CH_3 groups. A peak at 2230 cm^{-1} for the C≡C stretch indicates an unsymmetric acetylene, see figure (3.6). There are also very strong absorptions at 1020 and 985 cm^{-1} (C-F) stretches. Insufficient material was available to run ^{19}F nmr spectra.

The infrared spectrum of 1,2bis(4-phenylthiotetrafluorophenyl)-ethene  taken in a KBr disc shows a weak band at 3070-3500 cm^{-1}, attributable to the phenyl C-H vibration bands,at 2940-2870 (m) cm^{-1} due to C-H modes, bands at 1575 (m) cm^{-1}, at 1475 (v.s.) and at 1455 (s) cm^{-1} at 960 (v.s.) cm^{-1} for C-F vibrations, at 850 (s) cm^{-1} and at 740 (v.s.) cm^{-1} from phenyl C-H stretching modes. The mass spectrum showed a parent ion at m/e = 540. The melting point of the mixture of isomers is 205°C. The ^{1}H spectrum contains a multiplet at δ7.3 ppm for

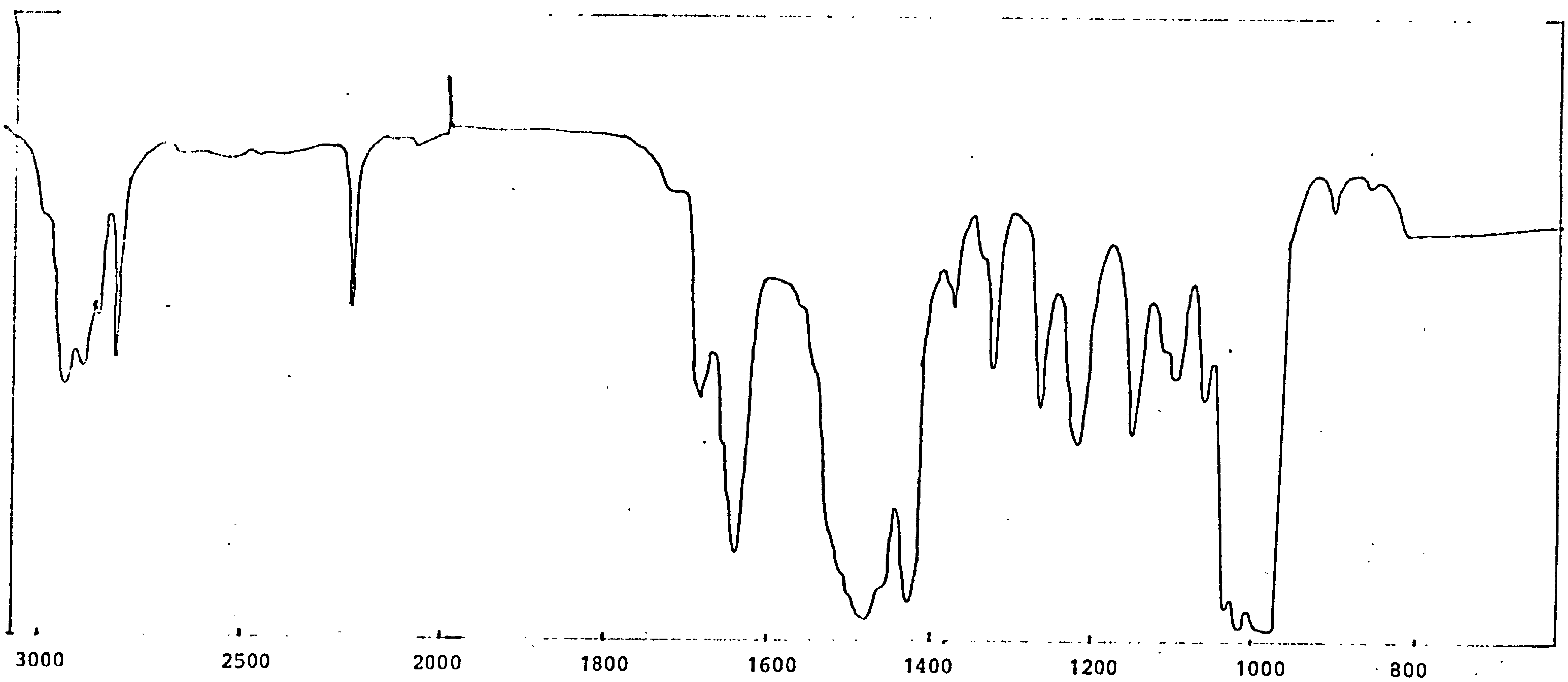
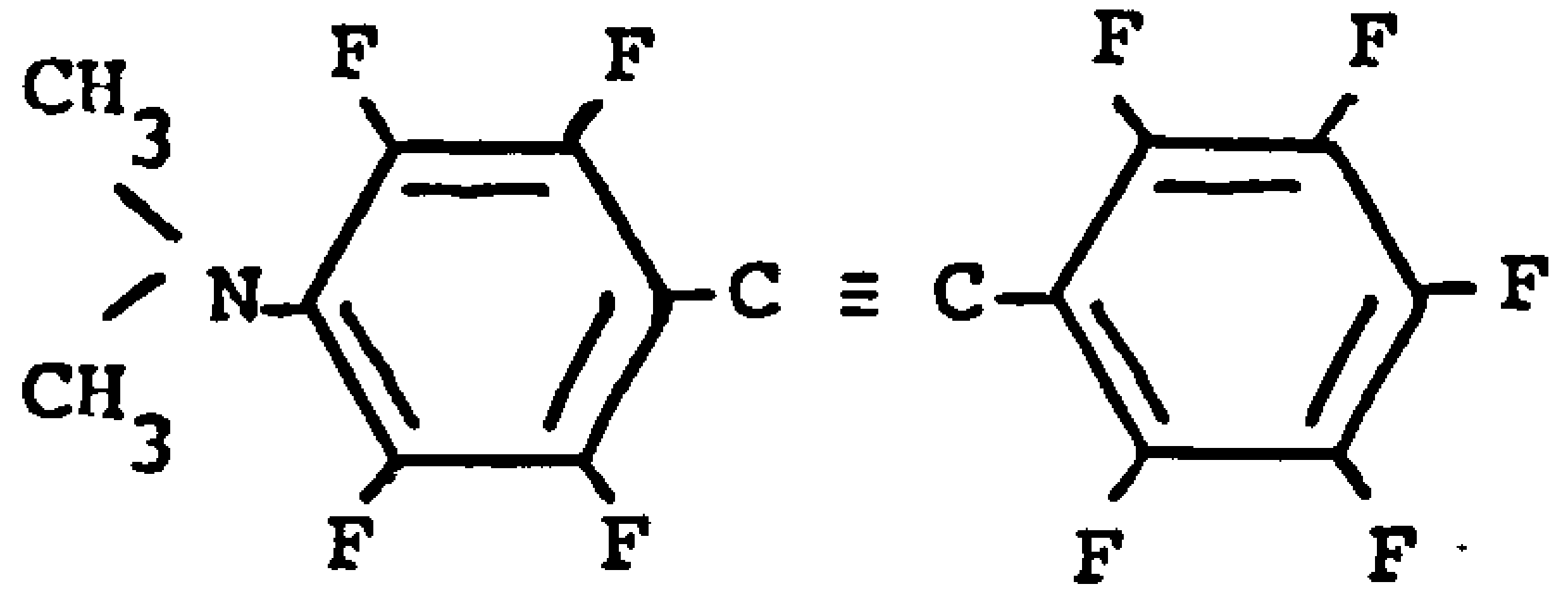


Figure (3.6) - Infra red spectrum of



the phenyl groups and the ethylenic proton =C-H is at 6.2 ppm. The ethylenic shift is unusual since the normal ethylenic proton occurs at 4.0-5.0 ppm. The presence of a thiophenyl substituent in the para position of the fluorinated phenyl ring shields the ethylenic proton in this type of compound and gives unusual chemical shifts as we will describe further in page [75] where we will also discuss steric effects.

R.N. Haszeldine found the chemical shift of the ethenylic proton for cis-decafluorostilbene at 6.9 ppm and for the trans-derivative at 7.4 ppm. We found the chemical shift of the cis isomer at 6.74 ppm (see Table 2). The $^{19}F-\{H\}$ chemical shifts of the first isomer which we have prepared are [134.12 ppm (F_1)] and [141.70 ppm (F_2)] and the chemical shifts of the second isomer are [134.13 ppm (F_1)] and [141.96 ppm (F_2)]. All are second order multiplets from AA'BB' systems.[130] These patterns plus the fact that the signals which could arise from para-fluorines are absent indicate that substitution has taken place in the para position. The spectra of the phenylthio and methylthio derivatives VII and III were very similar and are as predicted for 4,4-substituted octafluorobiphenyl derivatives $RSC_6F_4C_6F_4SR$,[127] figure (3.7) R=SPh, SMe. The structure III was studied further by reaction with bromine in carbon tetrachloride at -5°C where there was addition to the double bond. This reaction gives 1,2-dibromo-1,2bis(4-phenylthio-(tetrafluorophenyl)ethane which has a melting point of 168-170°C. The ^1H nmr shows signals with chemical shift of 6.1 ppm and the ^{19}F nmr spectrum is very complex and indicates a ABCD second order spectrum, see figure (3.10).

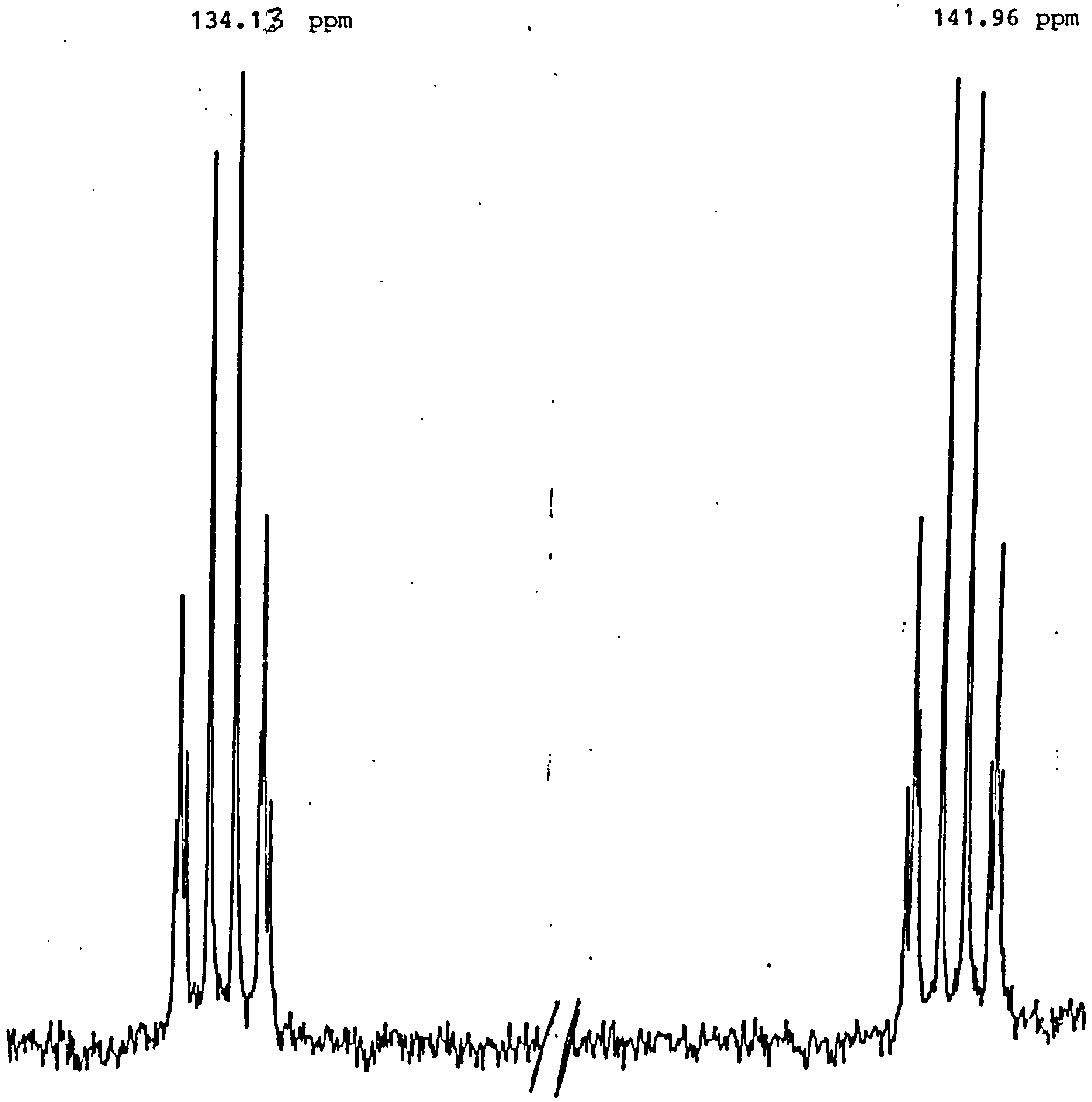
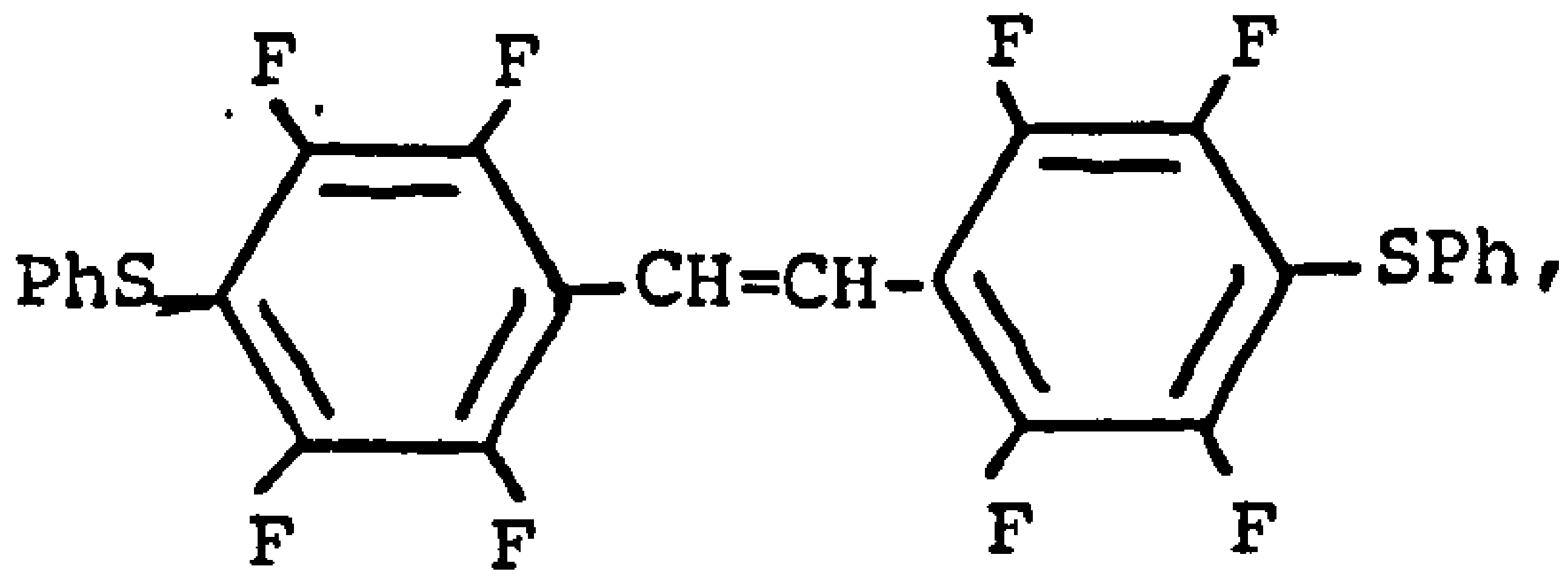


Figure (3.7) - ^{19}F nmr spectrum of  , AA'BB' system δA = -132.1

δB = -132.4

δC = -139.1

δC = -141.5

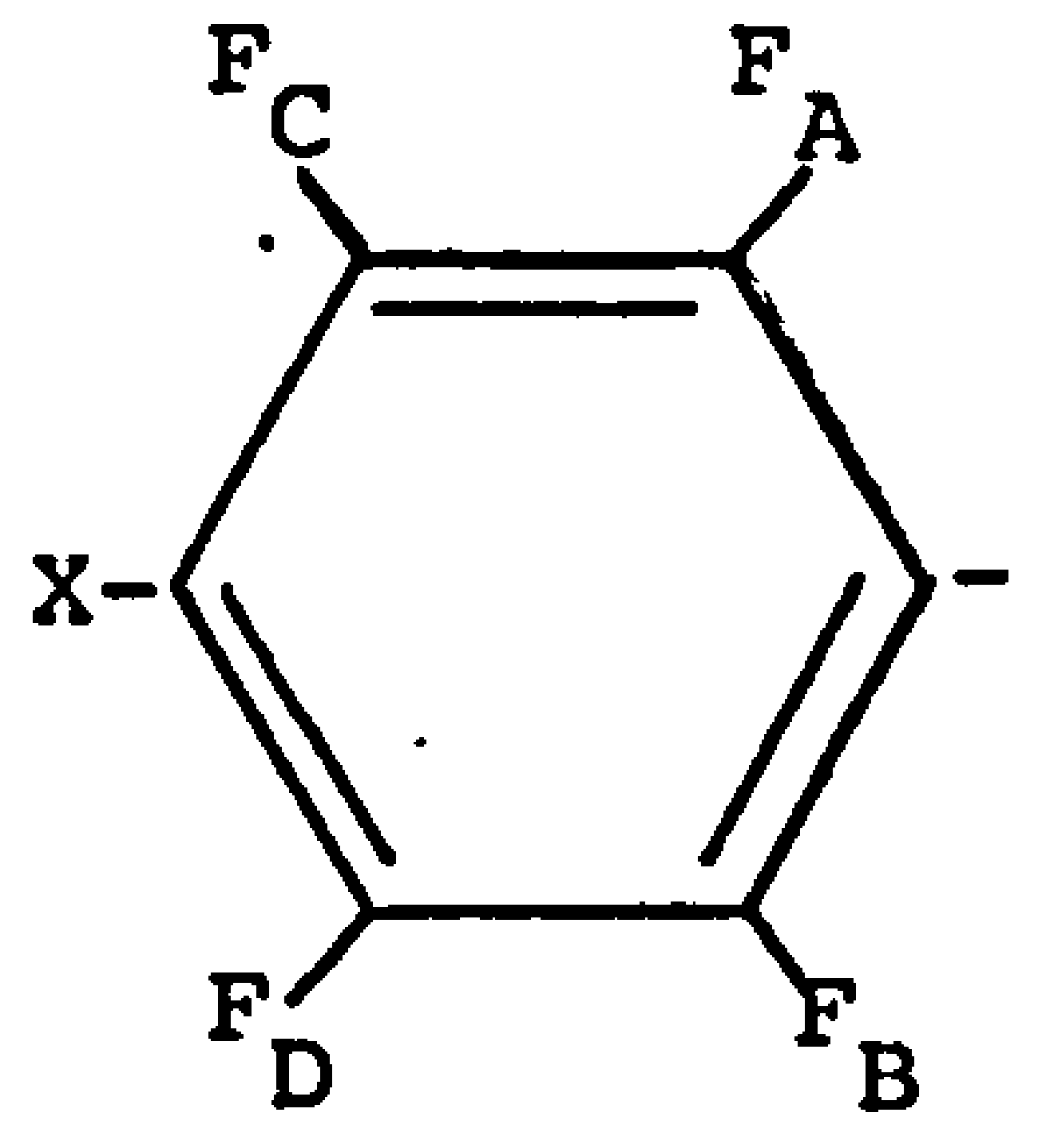


Figure (3.8) - Chemical shift of 1,2bis(4-phenylthiotetrafluorophenyl)ethene

X = SPh

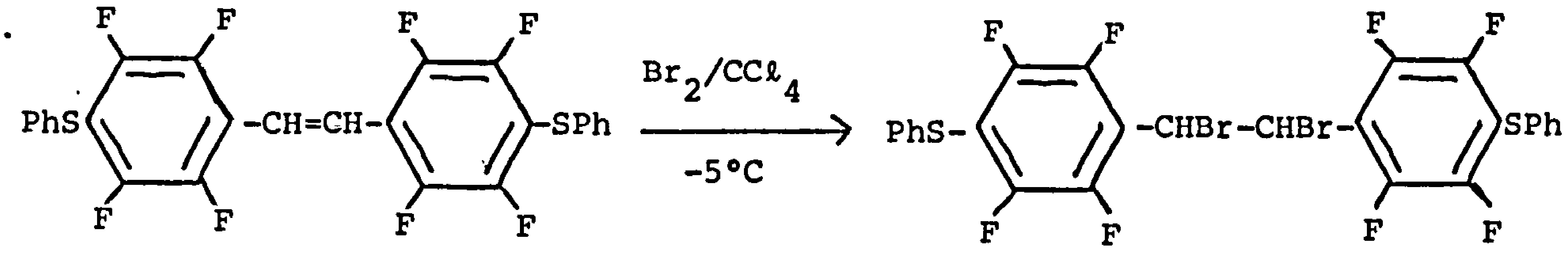


Figure (3.9) - Preparation of 1,2-dibromo-1,2-bis(4-phenylthiotetrafluorophenyl)ethane.

These spectra were explained in terms of steric effects, on page (82).

The reaction of 1,2-dibromo-1,2-bis(pentafluorophenyl)ethane and 1,2-dibromo-1,2-bis(pentafluorophenyl)ethene in reactions C and D with NaSMe in liquid ammonia resulted in debromination and nucleophilic displacement of para fluorine atoms in the rings. The extent of replacement by the thiolate anion depends on the amount of the reagent and the solvent employed.[128] The products were characterised by various methods. Mass spectra of VII, VIII reveal parent ions m/e = 416 and 414 respectively, corresponding to $C_{14}F_8H_2(SMe)_2$ and $C_{14}F_8(SMe)_2$. The fragmentation scheme in the mass spectrometer is

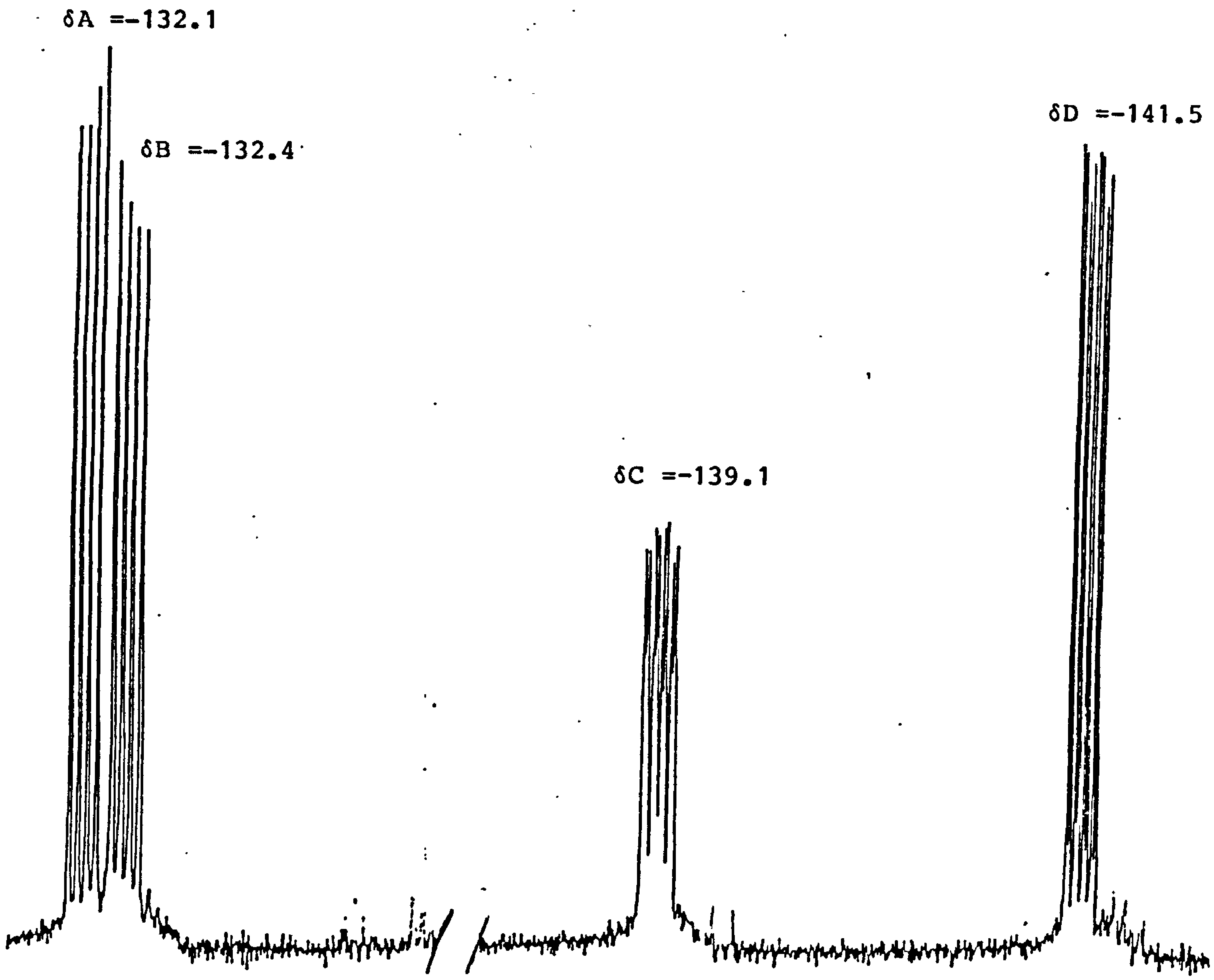
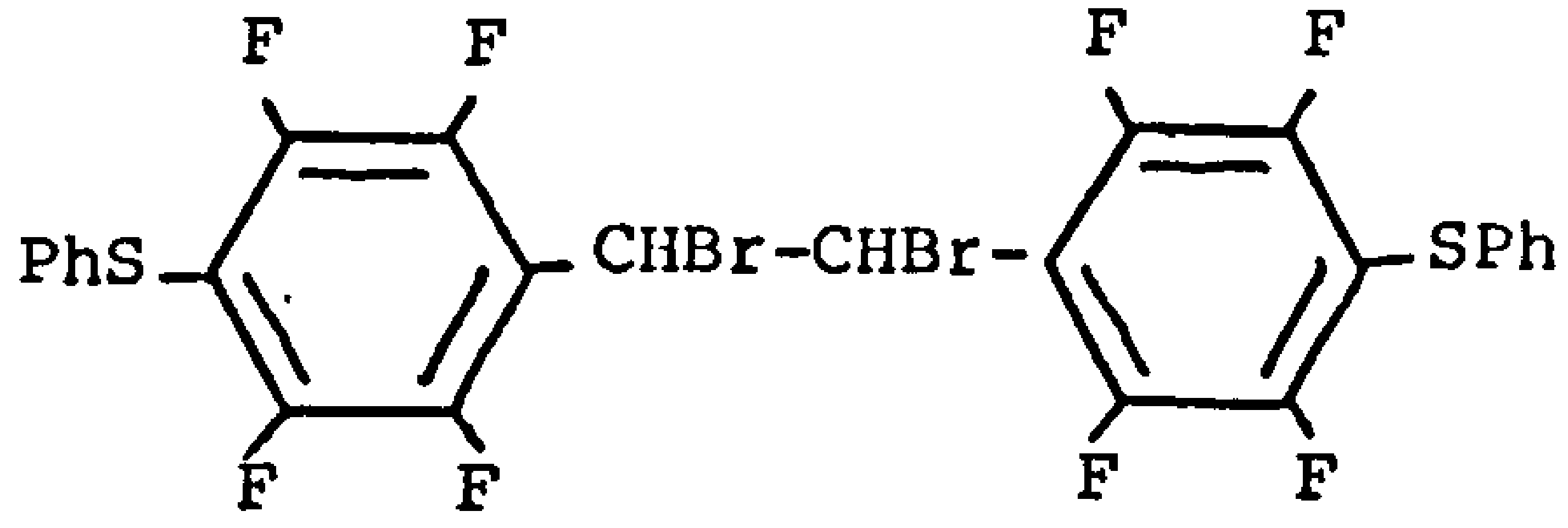
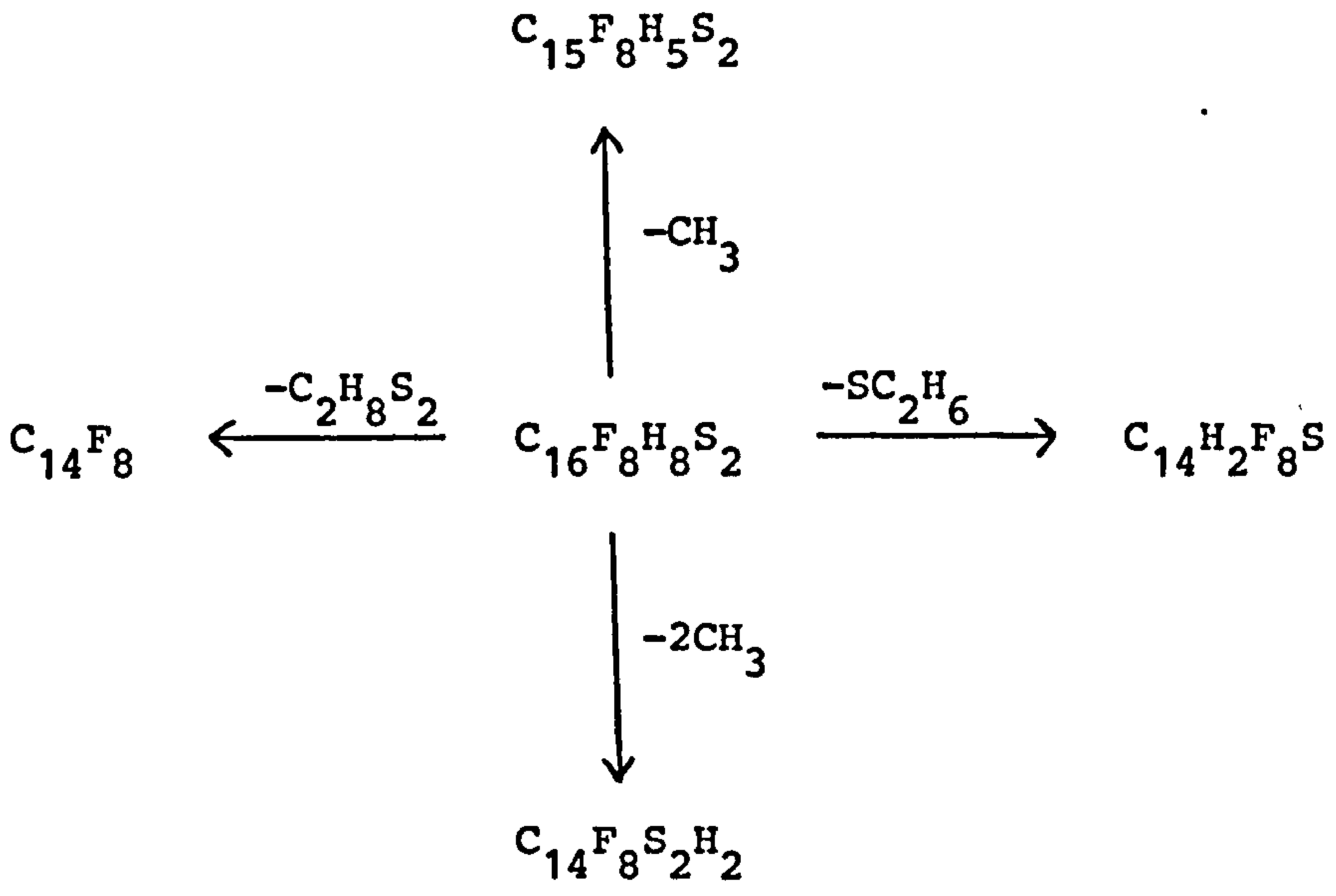


Figure (3.10) - ^{19}F nmr spectrum of

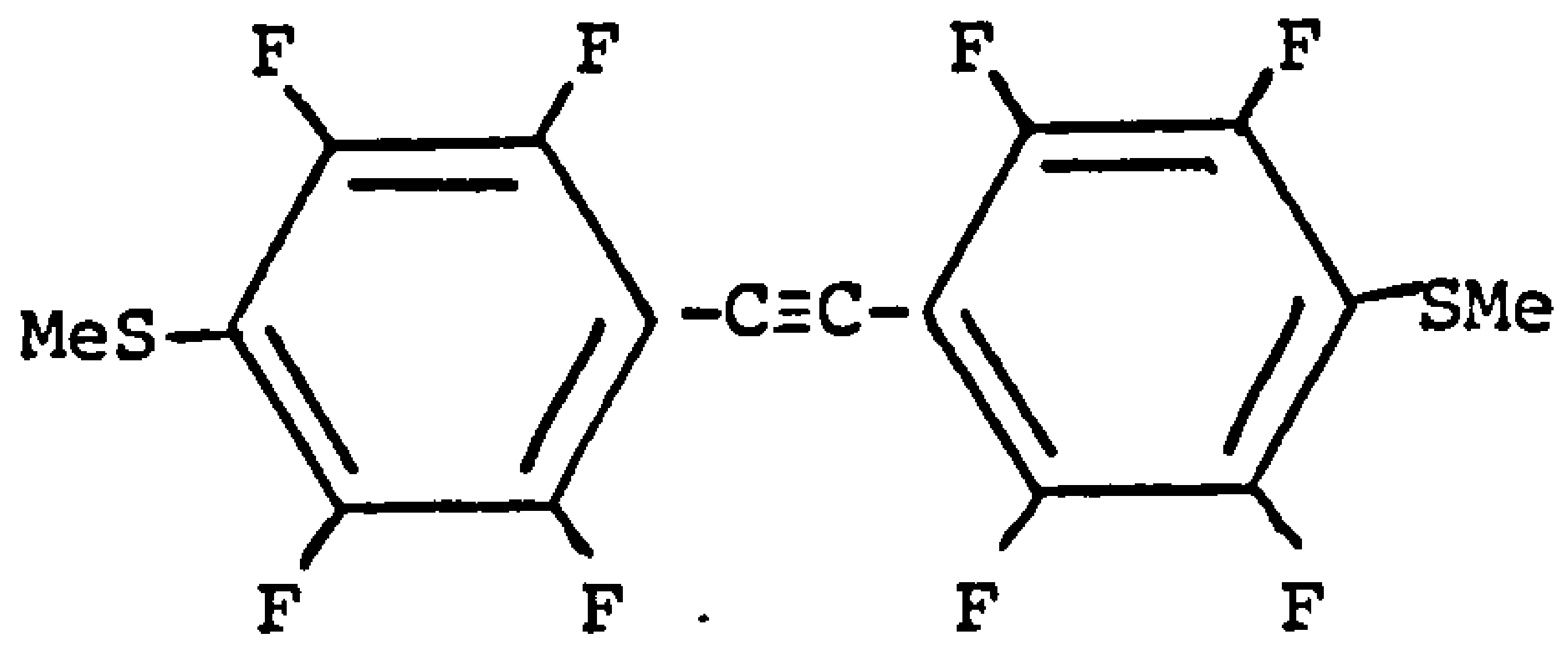




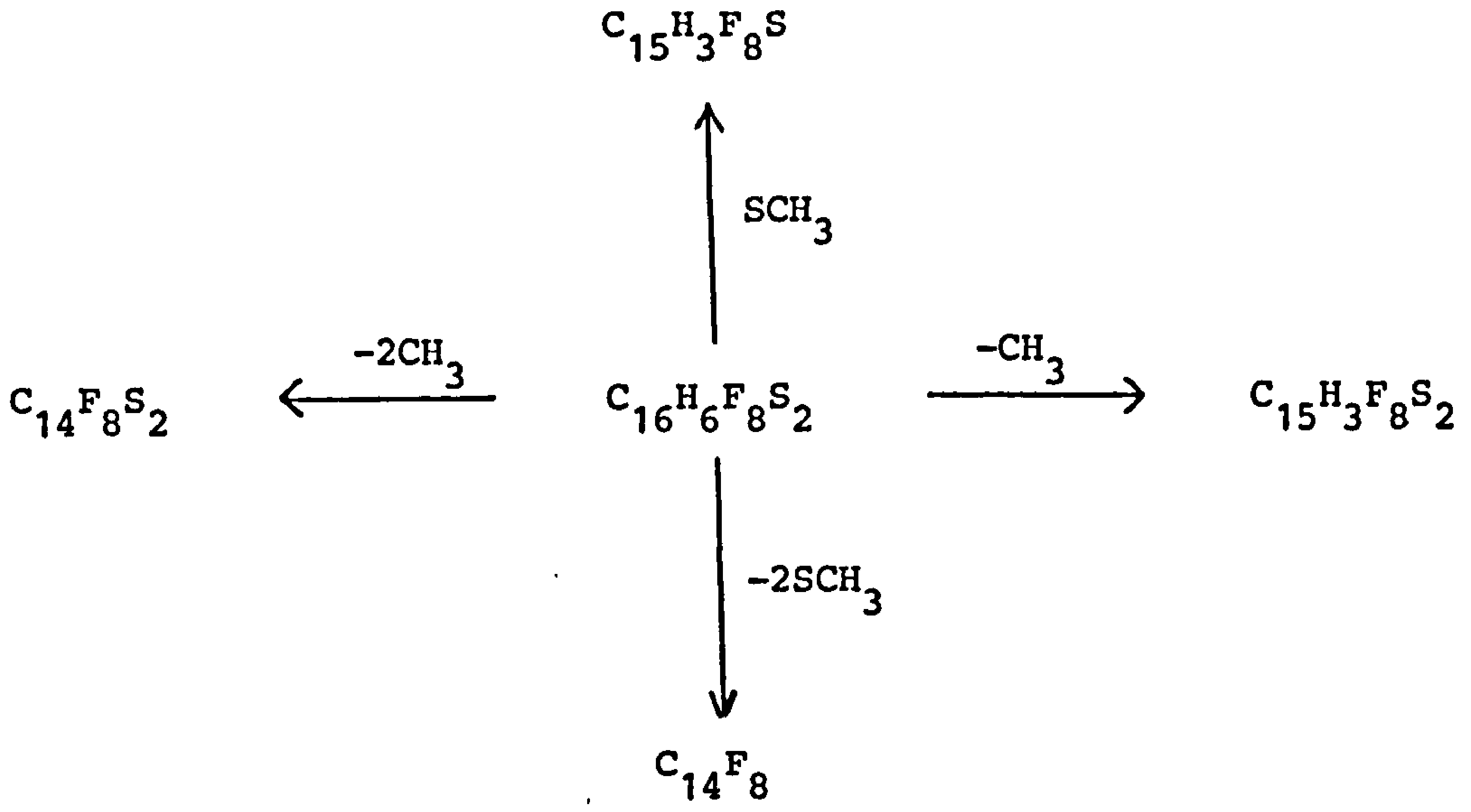
Scheme (4) - Initial fragmentation of 1,2-bis(4-methylthiotetrafluorophenyl)ethyne.

^{1}H nmr spectra of product VII show two signals at δ3.01 for the SCH_3 protons and 7.4 ppm for δ=C-H protons. ^{19}F nmr spectra show only one isomer with an AA′BB′ system,[130] a similar spectrum to the phenylthiol derivative, see figure (3.7).

The product VII was indicated as

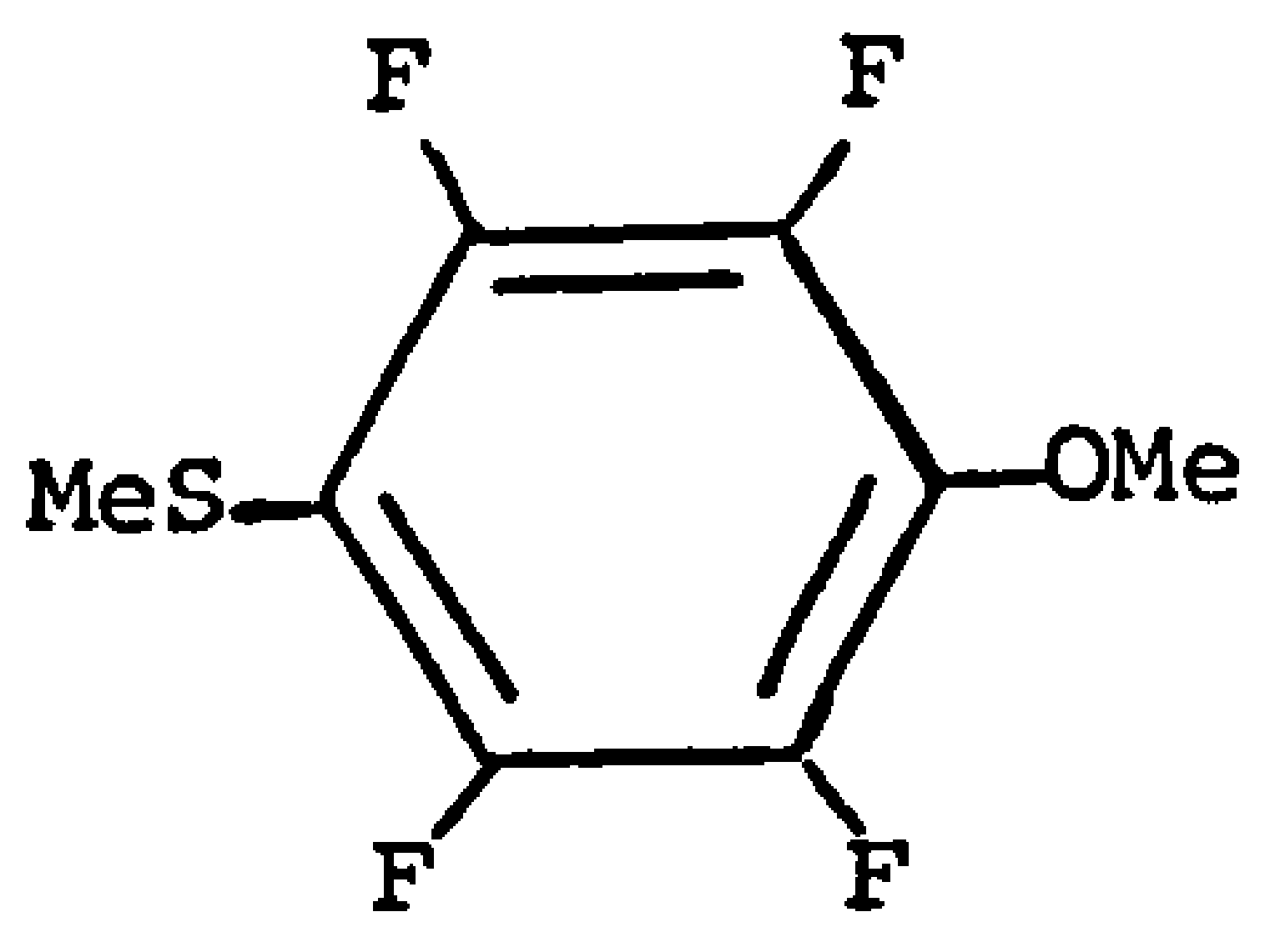


Mass spectroscopy of this compound showed a parent ion at m/e = 414, corresponding to $C_{16}H_6F_8S_2$. The initial fragmentation pattern is shown in Scheme (5).



Scheme (5) - Initial fragmentation of 1,2-bis(4-methylthiotetrafluorophenyl)ethyne.

IR spectroscopy indicates that this compound is a symmetrical acetylene derivative from the lack of absorption peaks in the region between 3000-2000 cm^{-1}. ^{1}H nmr spectra show one sharp signal at 3.01 ppm for the SCH_3 protons. ^{19}F nmr spectra show second order AA'BB' spectra for the ortho and meta fluorines at about 133 ppm and 137 ppm respectively. These spectra are similar to those of ^{130}(see figure (3.11)).



We were very interested to substitute methylthiolate in the bridge so we reacted 1,2-dibromo-1,2-bis(pentafluorophenyl)ethene and sodium methylthiolate in the presence of liquid ammonia. It seems that the first reaction is in the para position of the perfluoroaryl group and the

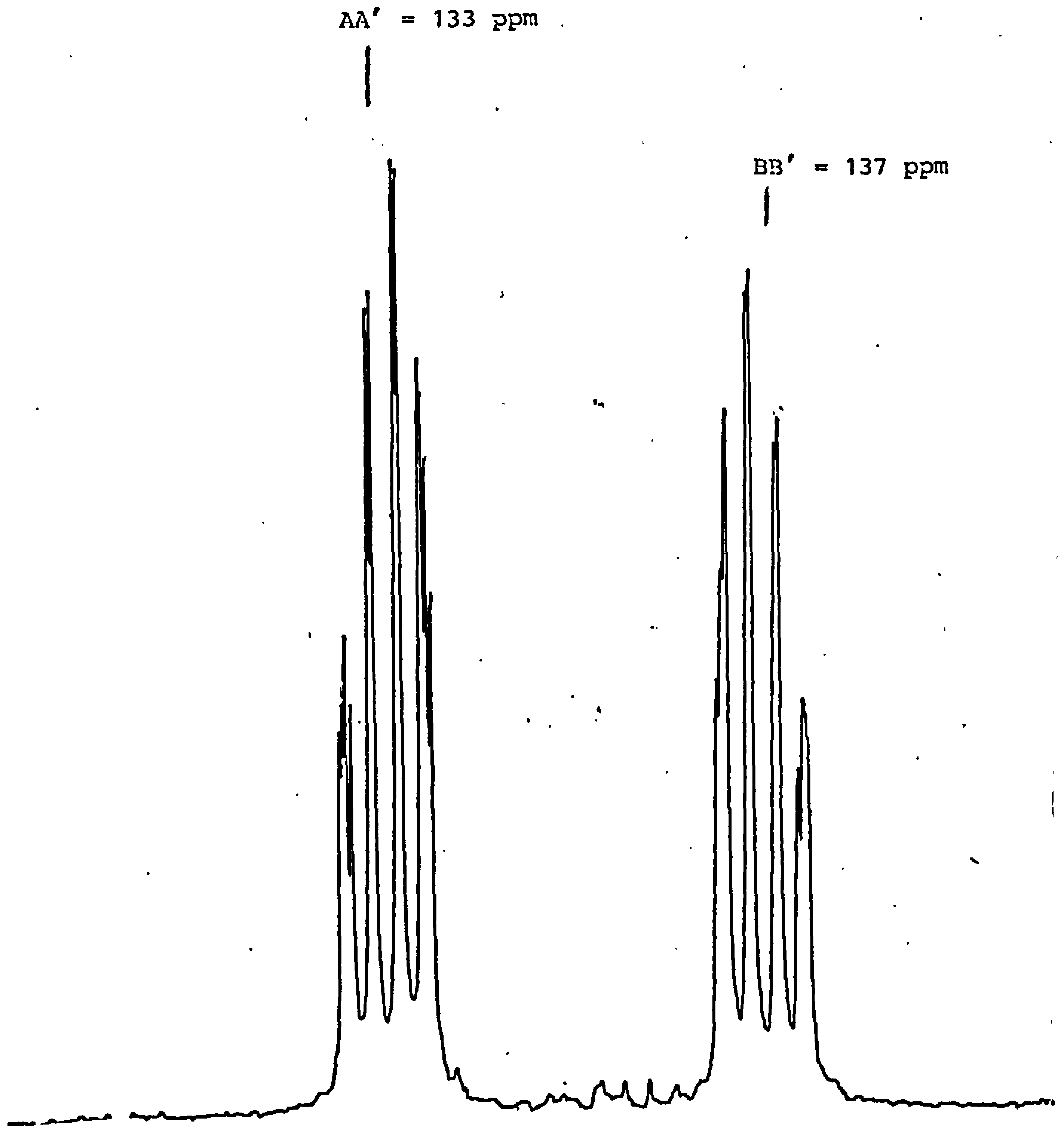
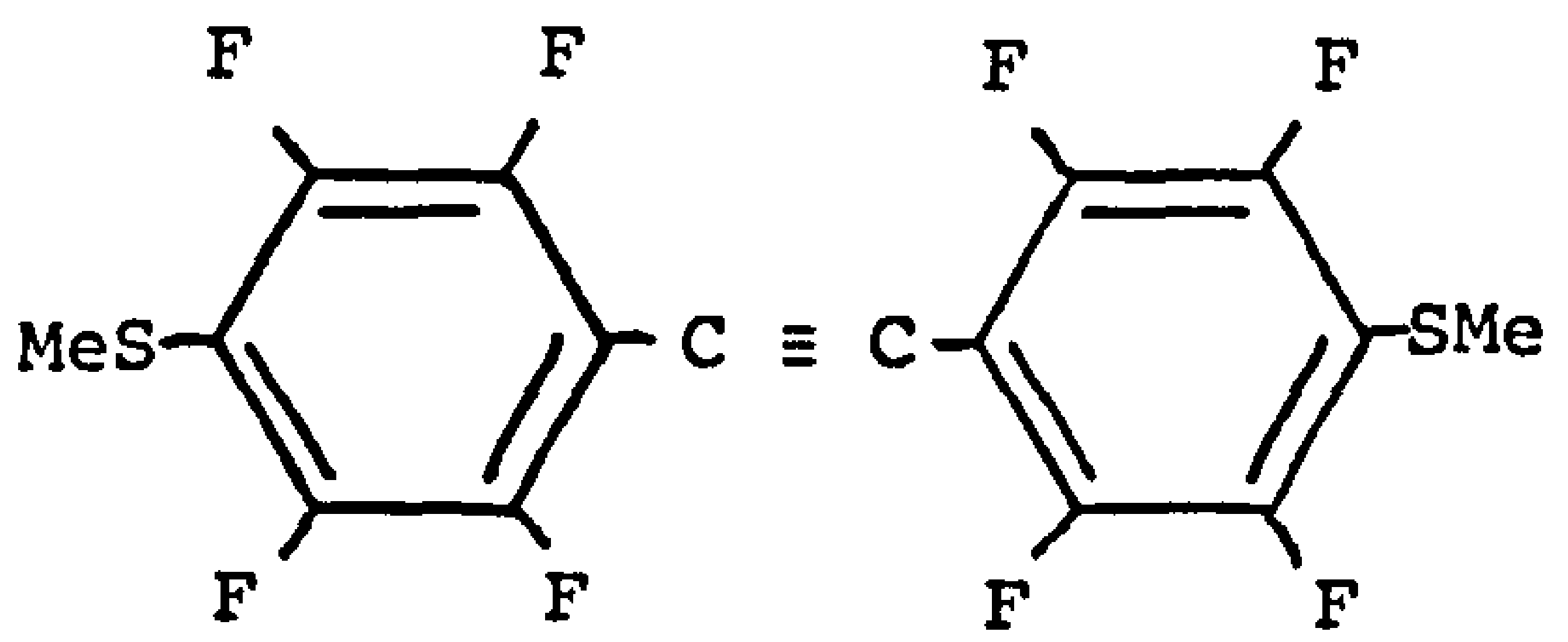


Figure (3.11) - ^{19}F nmr spectrum of  , AA′BB′ system second reaction was in the bridge. The product of this reaction was a mixture of two isomers. Mass spectroscopy shows an ion of highest m/e at 508. This corresponds to the parent ion of $C_{18}H_{12}F_5S_4$. The ^1H nmr spectrum shows two signals at 3.0 ppm and 2.5 ppm. The presence of two isomers was very clearly indicated by ^{19}F nmr which showed two ABCD systems, see table (4). Thus the reaction which had occurred was

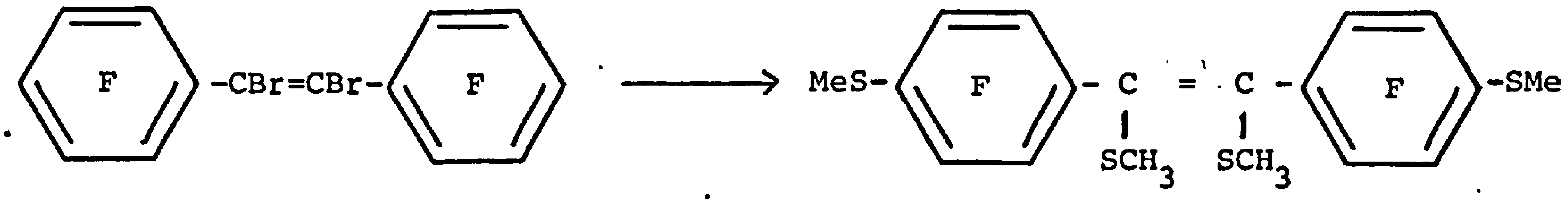
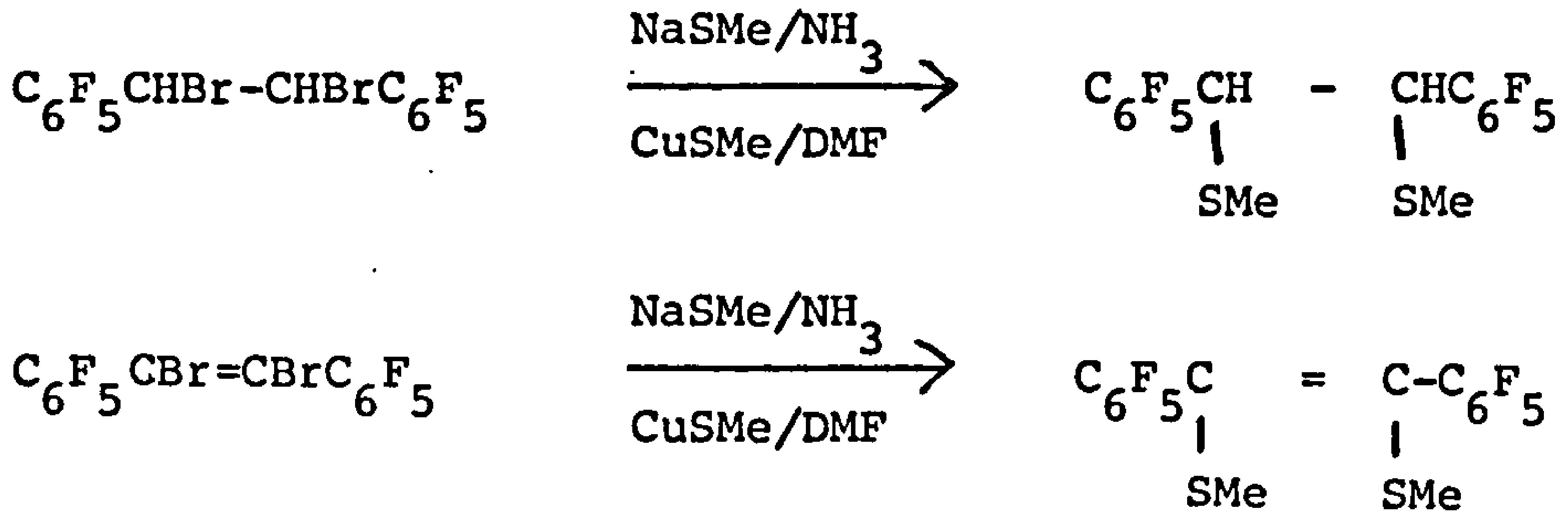


Figure (3.12) - Preparation of 1,2-di(methylthio)-1,2-bis(4-methylthiotetrafluorophenyl)ethene

Mechanisms of Reactions

The first fluorinated bis(alkylthio)alkanes were reported in 1961 by Harris and Stacey[131] from the reaction of fluoroalkanethiols and hexafluoropropene. Later Sharp et al.[116,132] employing photochemical addition of thiols and disulfides, and Peach using fluorinated thiols, greatly extended the range of these compounds. Similarly fluorinated substituents at the sulfur atom have been incorporated by reaction of a hydrocarbon halide with a suitable metal thiolate.[133,134]

These methods are illustrated by the reactions in Figure (3.1) page (50). During the course of the present work, attempts were made to prepare fluorinated dithioethers by reacting fluorinated arylalkylbromides with $NaSCH_3$ or copper(I) thiolate, Figure (3.13).



$$C_6F_5CHBr\text{-}CHBrC_6F_5 \xrightarrow[CuSMe/DMF]{NaSMe/NH_3} C_6F_5\underset{\substack{|\\SMe}}{CH} - \underset{\substack{|\\SMe}}{CH}C_6F_5$$

$$C_6F_5CBr{=}CBrC_6F_5 \xrightarrow[CuSMe/DMF]{NaSMe/NH_3} C_6F_5\underset{\substack{|\\SMe}}{C} = \underset{\substack{|\\SMe}}{C}\text{-}C_6F_5$$

Figure (3.13)

However, the reaction often failed to produce the desired products and there is extensive substitution of aromatic fluorine and also debromination as has been shown in fig. [3.2 and 3.3].

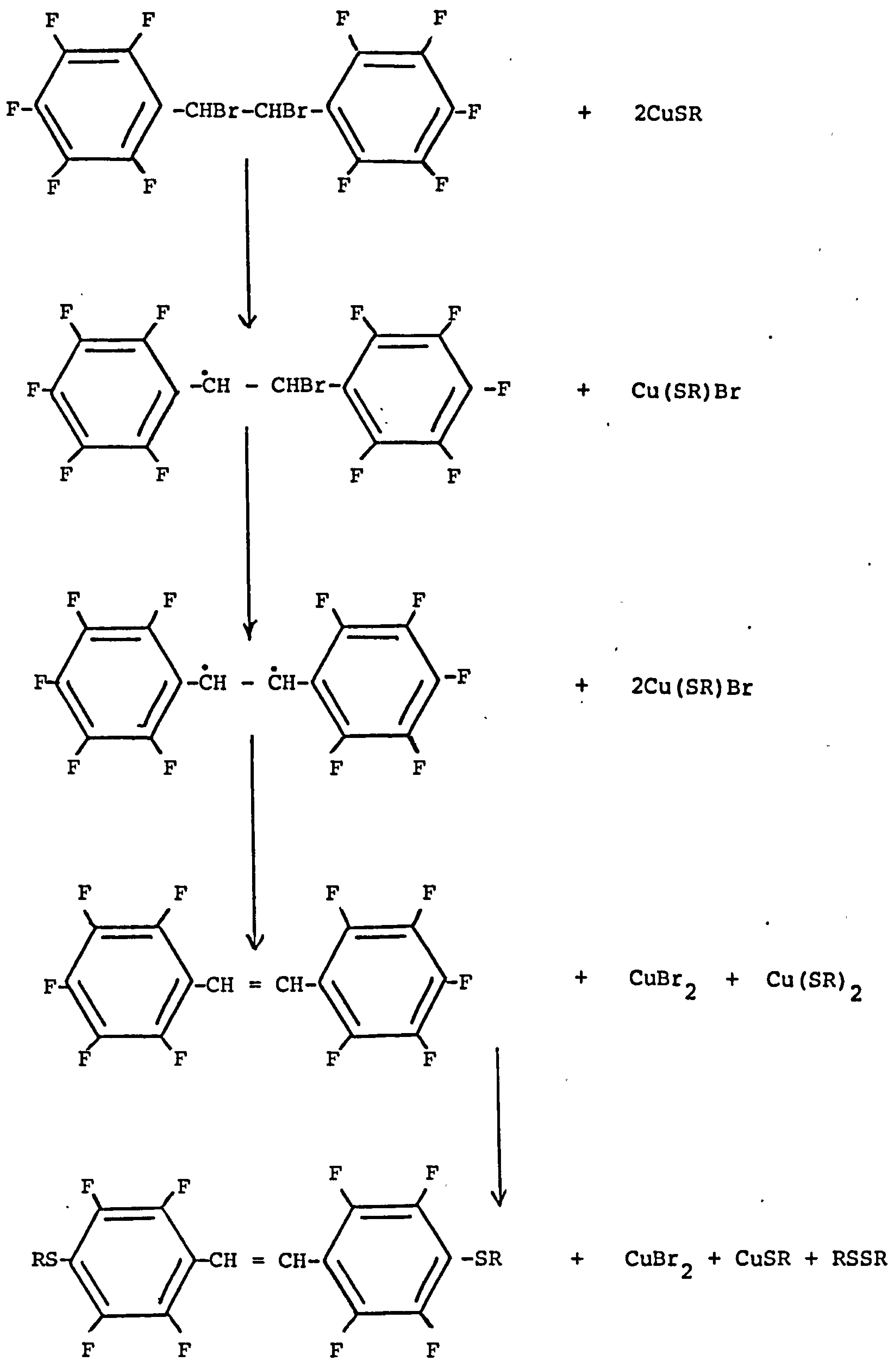
The presence of fluorine in a molecule changes the polarity of carbon halogen bonds as compared with the situation when fluorine is absent. Thus trifluoroiodomethane (b.p. - 22.5°C) is quite different in properties from methyl iodide (b.p. 42.5°C). The three fluorine atoms shield the carbon atom from nucleophilic attack and through their inductive effect cause the C-I bond to be polarized in the opposite direction to that found in methyl iodide[135] Figure (3.14).

Fig. (3.14) - The presence of fluorine in a molecule changes the polarity of carbon halogen bonds.

Reasoning similar to that used above for trifluoroiodomethane can be employed to explain why perfluorobromo-alkanes or perfluorobromo-alkenes resist nucleophilic substitution of bromine on carbon. This order makes it difficult, if not impossible, to substitute the iodine in CF_3-I or the bromine in our compounds by nucleophilic substitution mechanisms and substitution has to take place by some other mechanism (radical transfer).

We thought it possible that copper(I) species in dimethylformamide as a solvent would induce such reactions. With these results in mind we have investigated the effect of copper (I) species on the reaction of [fig. 3.13].

From the results on Page [51] there seem to be two types of reactions occurring between 1,2-dibromo-1,2-bis(pentafluorophenyl)ethane and copper(I) species. It seems that the reaction occurs in two steps by, firstly, removal of halogen atoms (bromine), so that copper(I) is oxidised to copper(II) and the dehalogenated molecule (diradical) rearranges to form an olefine.[136-138] The mechanism involves a homolytic mechanism, shown in scheme (6). The initial debromination is followed by nucleophilic attack of $SR^{\ominus}$ on the para position of the pentafluorophenyl ring. This type of substitution reaction in halogenated aromatic nuclei has been widely studied.[139] We do not have real information on sequence of the debromination and ring substitution steps.



Scheme (6) - Homolytic mechanism:debrominated molecule (diradical) rearranges to form an olefine followed by nucleophilic attack of SR^- on the para position of the pentafluorophenyl ring.

Dimethylformamide, $HCONMe_2$, is a very good solvent for polar and non-polar compounds as it has a high dielectric constant and is a good complexing agent for cations. It is hydrolysed slowly by water, rapidly by acid and more rapidly by alkalies. It also reacts with nucleophiles and this can give rise to NMe^{-}_{2} groups which can subsequently react as nucleophiles themselves. In hydrolysis Y is $\overline{OH}$, in our reaction it is $\overline{SR}$.

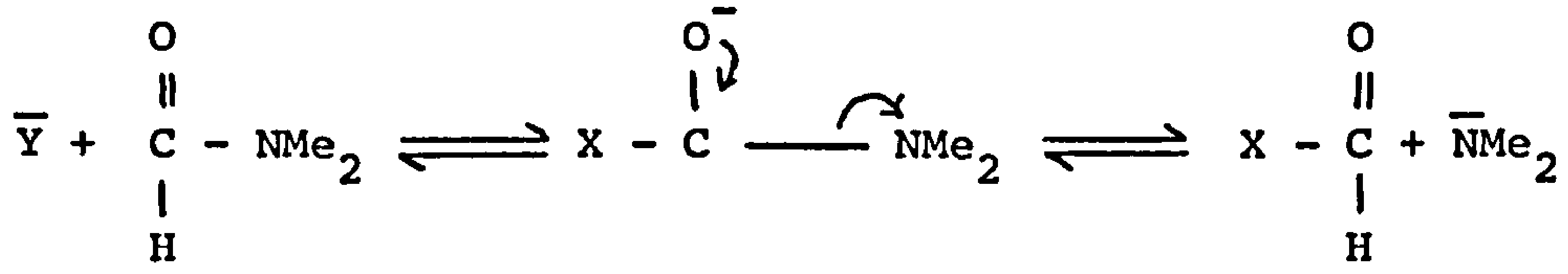
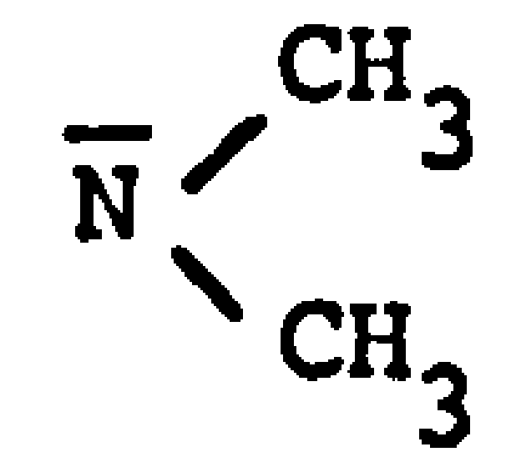


Figure (3.15) - Hydrolysis of dimethylformamide.

The reaction of 1,2-dibromo-1,2-bis(pentafluorophenyl)ethane and 1,2-dibromo-1,2-bis(pentafluorophenyl)ethene with copper(I) methylthiolate in dimethylformamide resulted in debromination and  $\bar{N}(CH_3)_2$ groups replaced the para fluorines in the perfluoro-aromatic rings. It seems that the reaction occurs in two steps by firstly, removal of halogen atoms (bromide) so that copper(I) is oxidised to copper(II) and the dehalogenated molecule (diradical) rearranges to form an olefine. This is followed by nucleophilic attack of $\overline{N}Me_2$. It seems that $\overline{N}Me_2$ is more reactive than $\overline{S}Me$ for attack on the para position of the pentafluorophenyl ring and $Ph\overline{S}$ is more reactive than $Me\overline{S}$, see (page 44) in chapter (2).

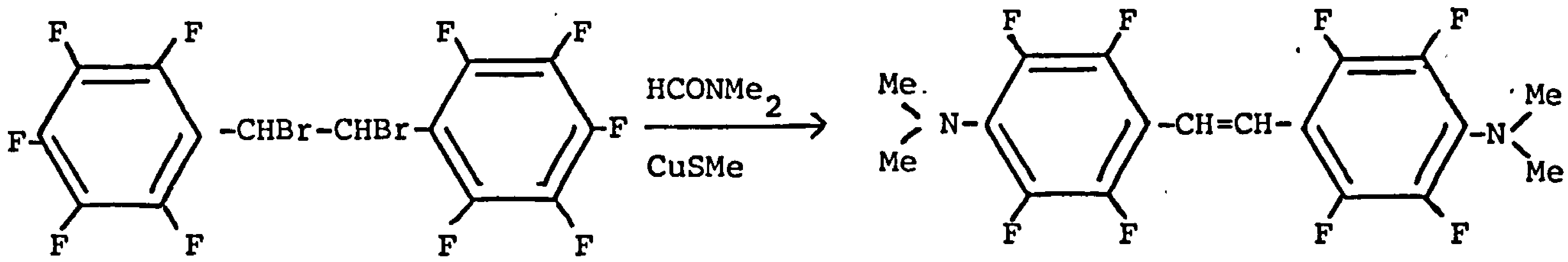
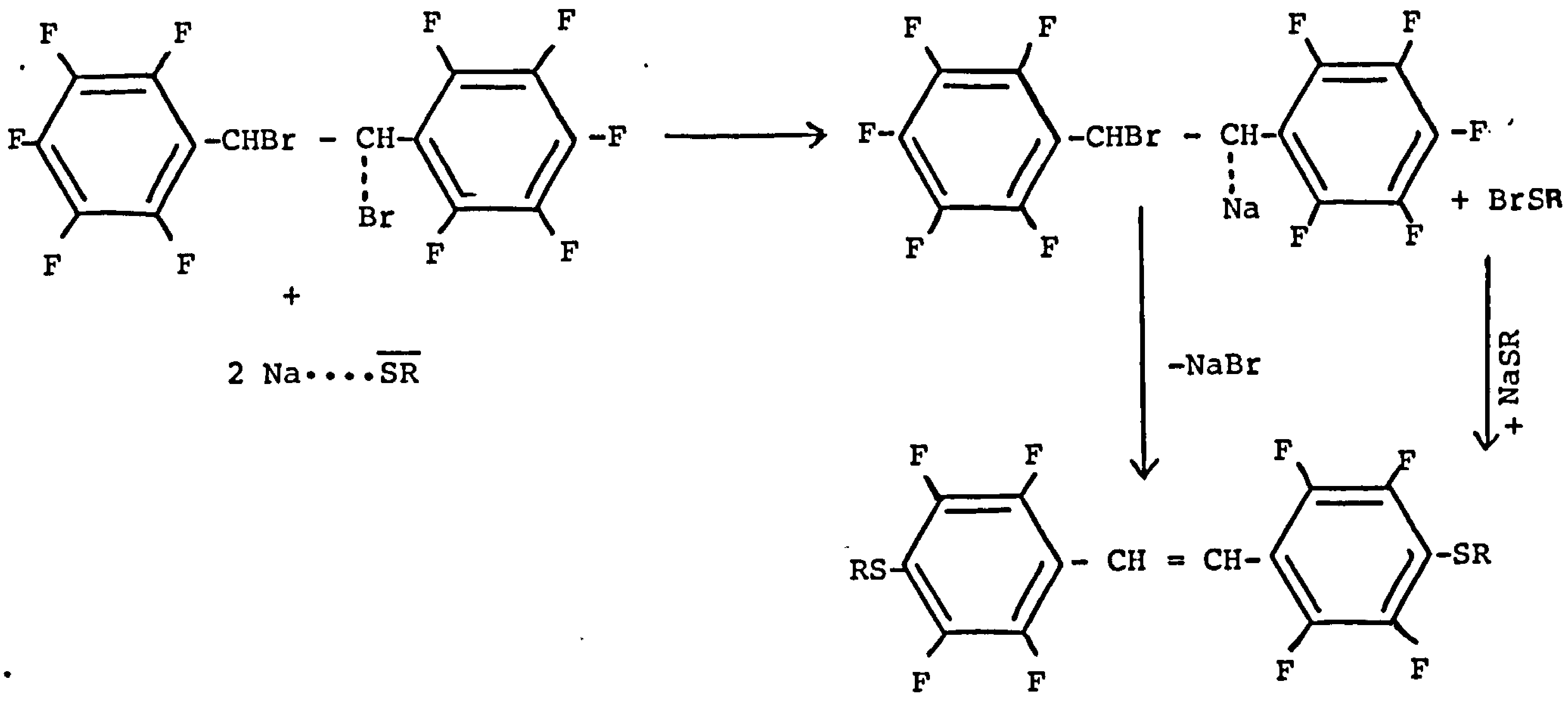


Figure (3.16) - Trans-1,2-bis(dimethylaminotetrafluorophenyl)ethene.

The substitution is exclusively into the para position as described in chapter (2) (page 46).

We used $NaSCH_3$ to effect substitution. The reaction was carried out using liquid ammonia as solvent. In this reaction the products correspond to substitution of $\overline{S}Me$ groups into the perfluoroaromatic rings. No products corresponding to substitution of $\overline{N}H_2$ groups (from the solvent) were identified. However, the mechanism must be completely different from that postulated above because we do not have the possibility of the redox reaction Cu(I) ⟶ Cu(II) to explain the debromination step. We therefore, postulate the mechanism shown below for this reaction scheme (7). We believe that in liquid ammonia the sodium thiolate is almost completely ionised. We suggest intermediate formation of unstable BrSR species which break down to form RSSR. The final solution shows a red colour consistent with the presence of bromine and the disulfides were identified in the solution.



SCHEME (7)

It must be emphasised that experimental evidence for this pathway[117] has also come from work done by Torrens in 1978[117] when he reacted $BrCF_2CF_2Br$ with $NaSCH_3$. The reaction produced $CF_2=CF_2$ without nucleophilic substitution. Further evidence for a scheme of the present type is the sensitivity of alkyl reactivity to the nature of the substituted species.[140,141]

Evidently the possibility of electrophilic displacement by the fluoroalkyl group has been partly reduced by the fluorine substituents and, according to the products obtained, it appears to act as a nucleophile with reversal in the polarity of carbon-halogen bond, allowing initial attack on the electron deficient halide. This has been previously suggested[142-144], to explain the reaction of fluorocarbon halides with bases and it is probably equally important in the present reaction.
It is relevant that the participation of $C\ell SCH_3$ has been previously postulated[142] in the reaction of the type

$$R - C\ell + CH_3SK \longrightarrow CH_3SR + CH_3SSCH_3$$

R = alkyl

Steric effects in 1,2-bis(pentafluoroaryl)ethene derivatives. NMR spectra; the effect of bulky electronegative substituents

The trans stilbene molecule is almost planar[145] and the conjugation between the ethylenic bond and the phenyl ring is large

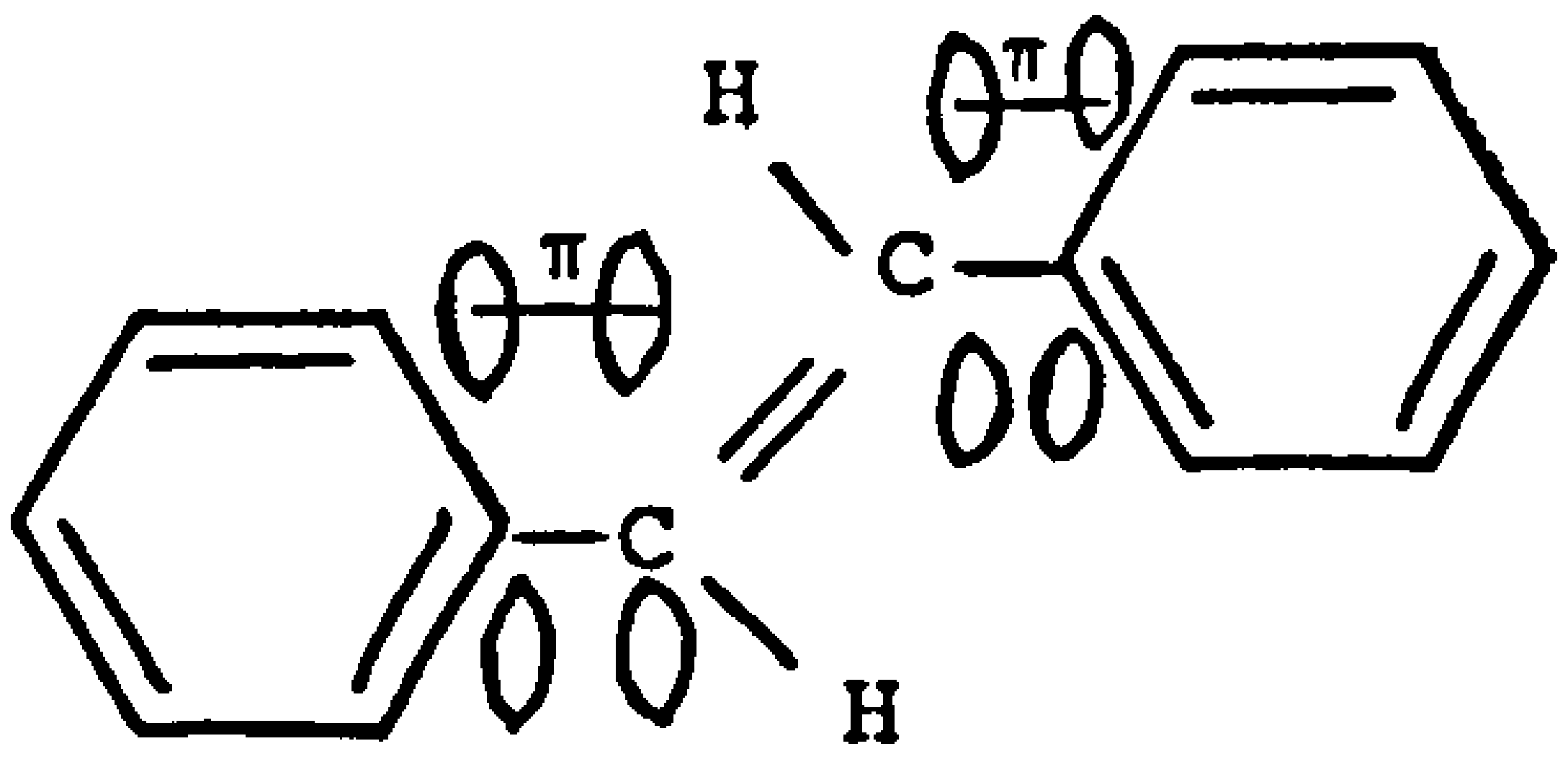
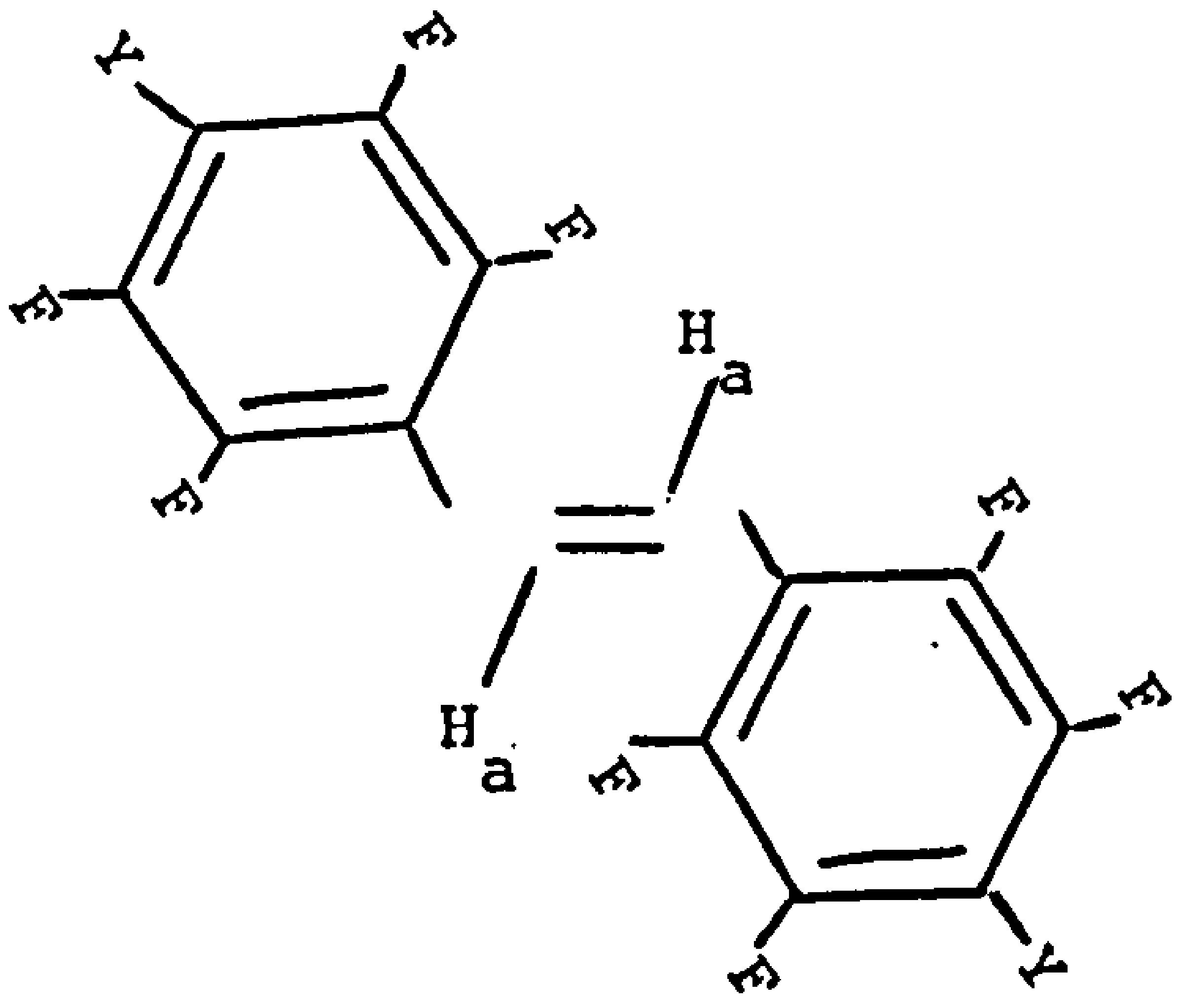


Figure (3.17) - trans stilbene

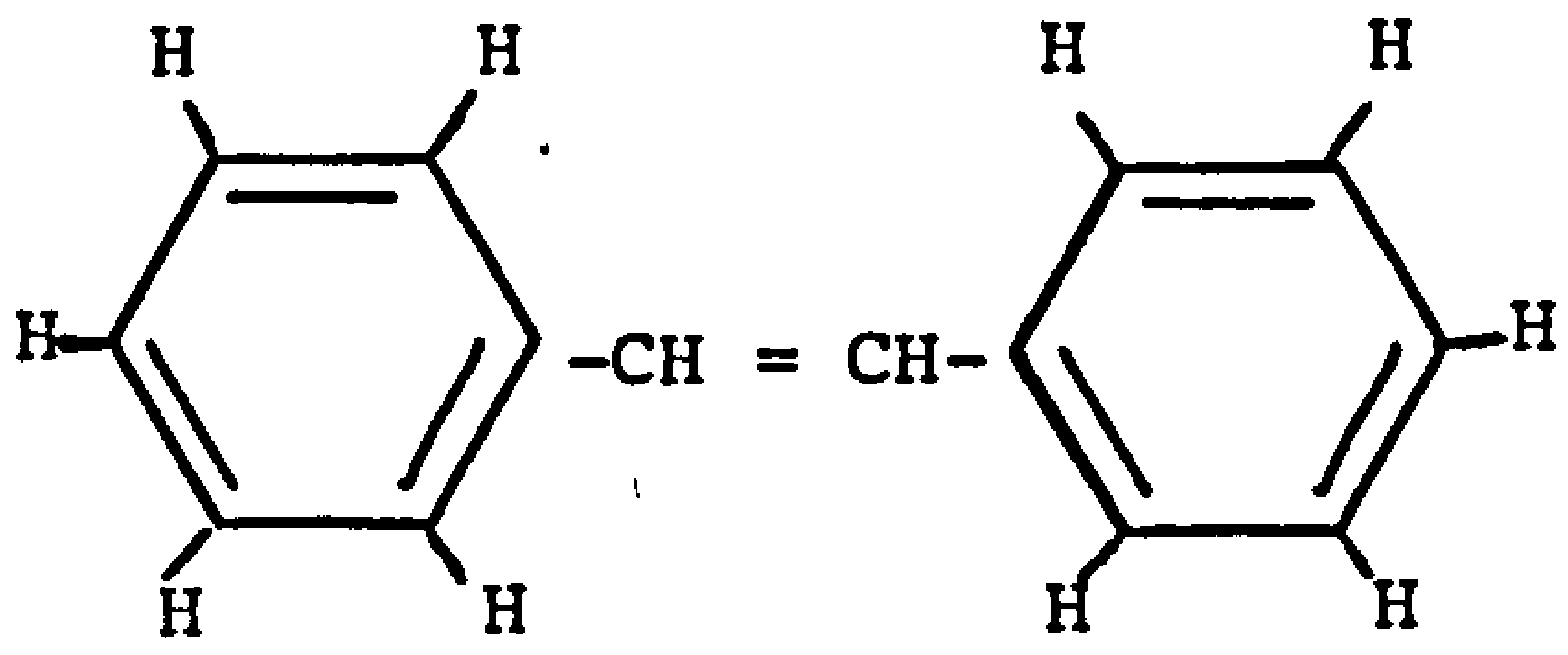
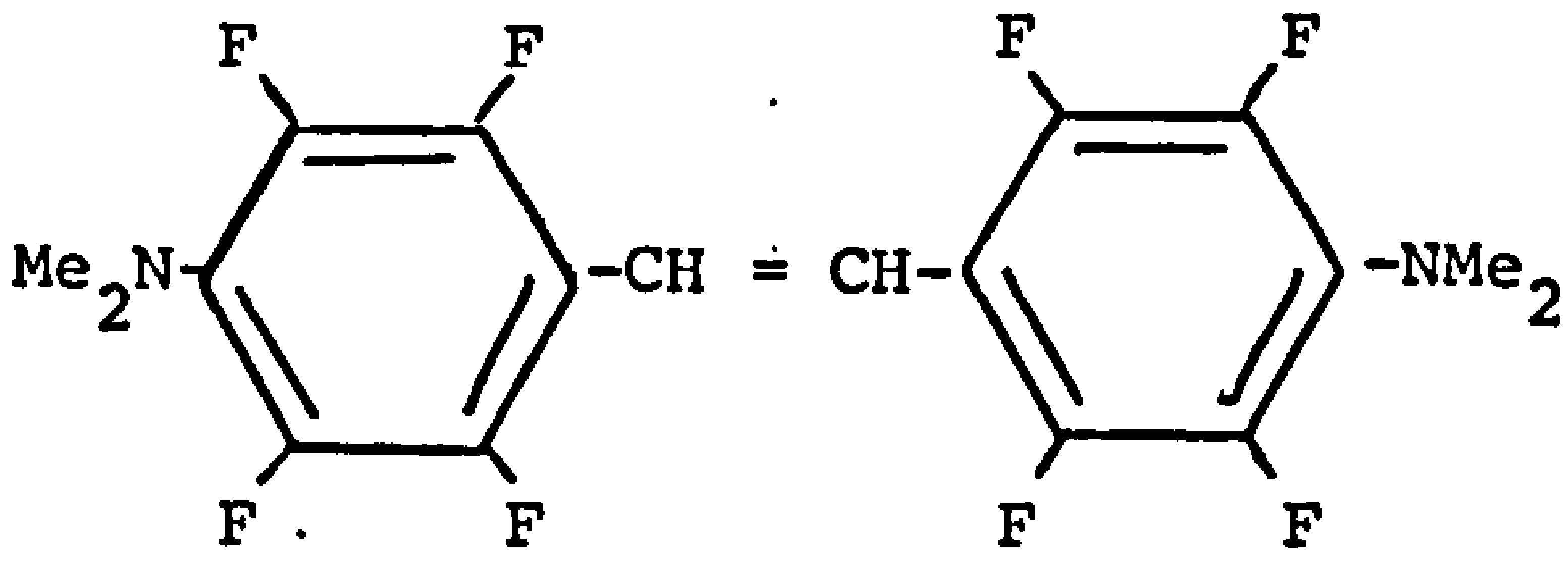
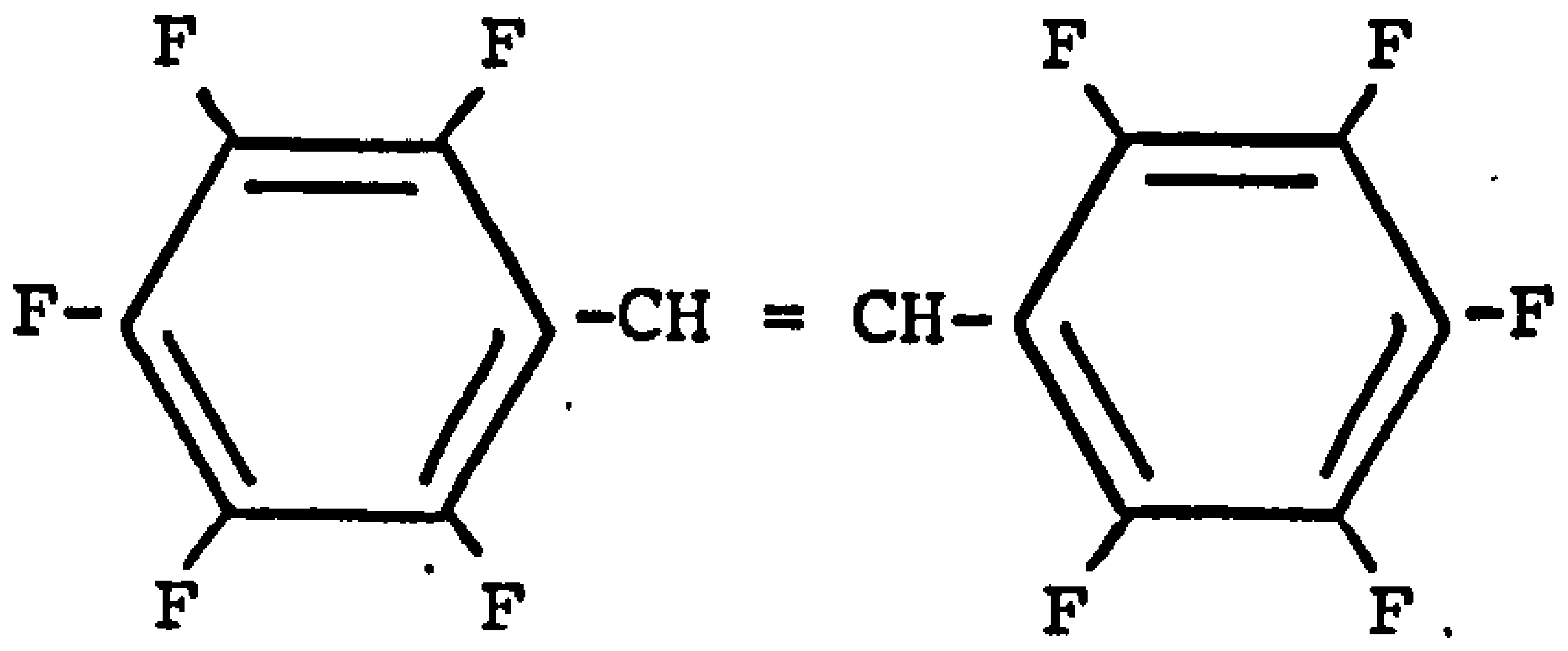
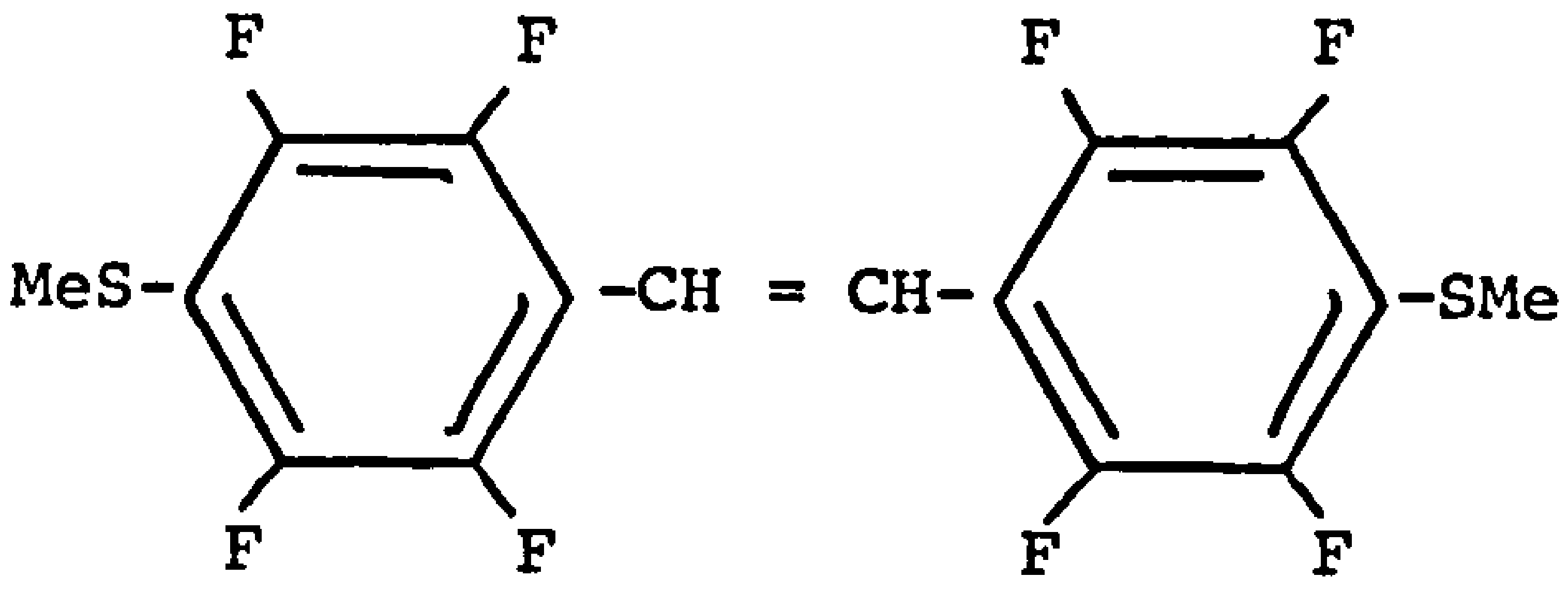
The π electron system makes the ethylenic protons more shielded through ring current effects so that the ^1H nmr signal occurs at low field at 6.99 ppm[146] in $CC\ell_4$, and 7.4 ppm for 1,2-bis(4-methylthiotetrafluorophenyl)ethene, and 7.4 ppm for 1,2-bis(pentafluorophenyl)ethene,[126] and 7.2 ppm for 1,2-bis(4-dimethylaminotetrafluorophenyl)ethene, see table (1).



Y = F,SMe,NMe_2

Figure (3.18) - trans derivative

TABLE (1)

Substituted trans stilbenes	Chemical shift of ethylenic protons
	Ref. 146 6.99 ppm ($CC\ell_4$)
	7.2 ppm ($CC\ell_4$)
	Ref. 126 7.4 ppm (T.H.F.)
	7.4 ppm ($CC\ell_4$)

From the above table we observe that the ethylenic protons are more shielded in the perfluorophenyl cases and thus these derivatives give signals at lower fields than for the phenyl derivatives. The order of shifts corresponding to the aryl groups are $C_6F_5 \approx C_6F_4SMe > C_6F_4NMe_2 > C_6H_5$. The shift parameters are very different from those of analogous alkyl derivatives.

In cis-stilbenes, however, a planar arrangement would be sterically crowded, particularly if there are other substituents in the aryl rings. Therefore in cis-derivatives it is likely that both phenyl rings would be turned through a considerable angle to the plane of the ethylenic bond in order to avoid steric strain. This twisting of the aromatic rings will lead to an inhibition of the conjugation through the extended π-system.

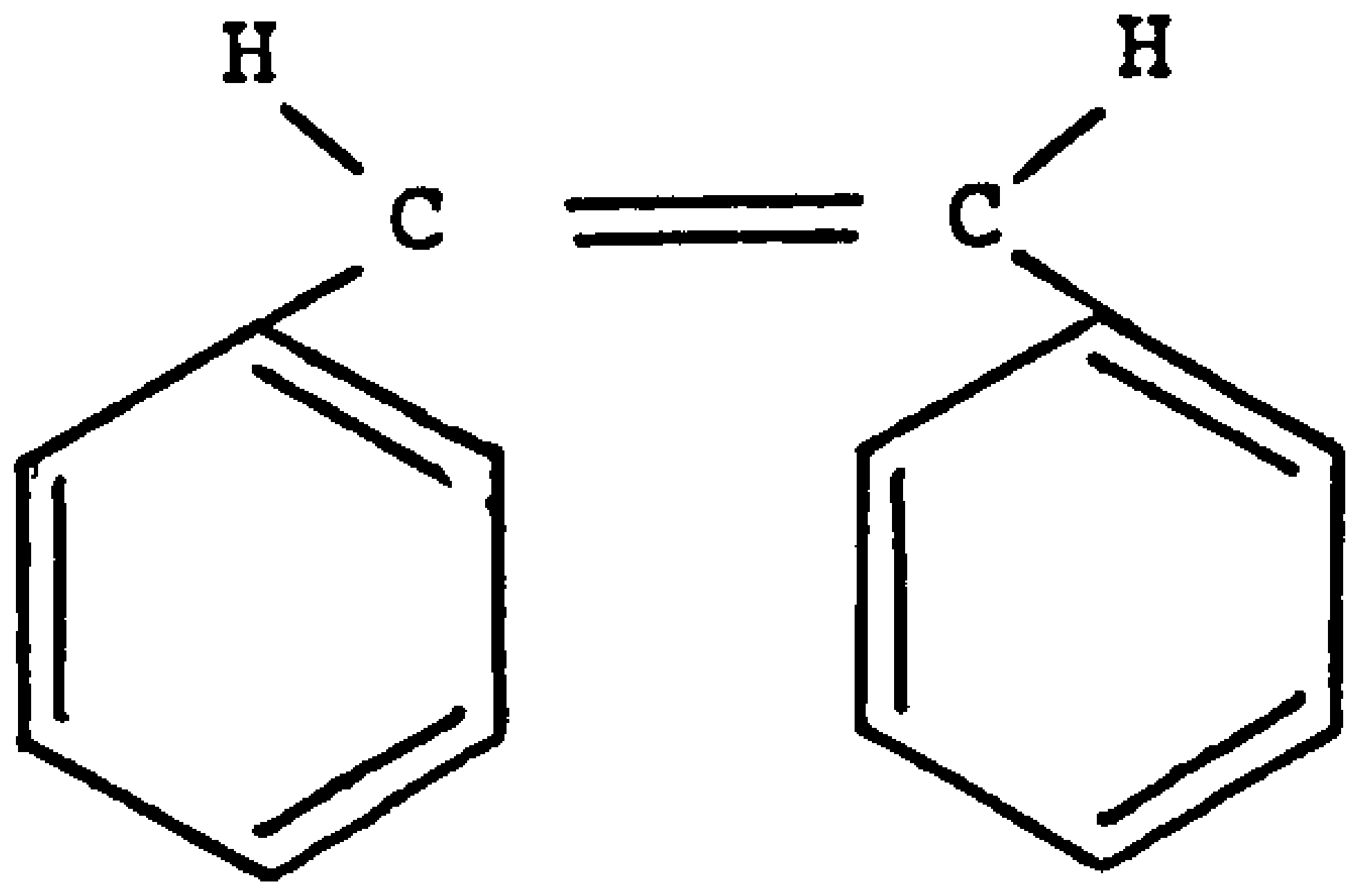
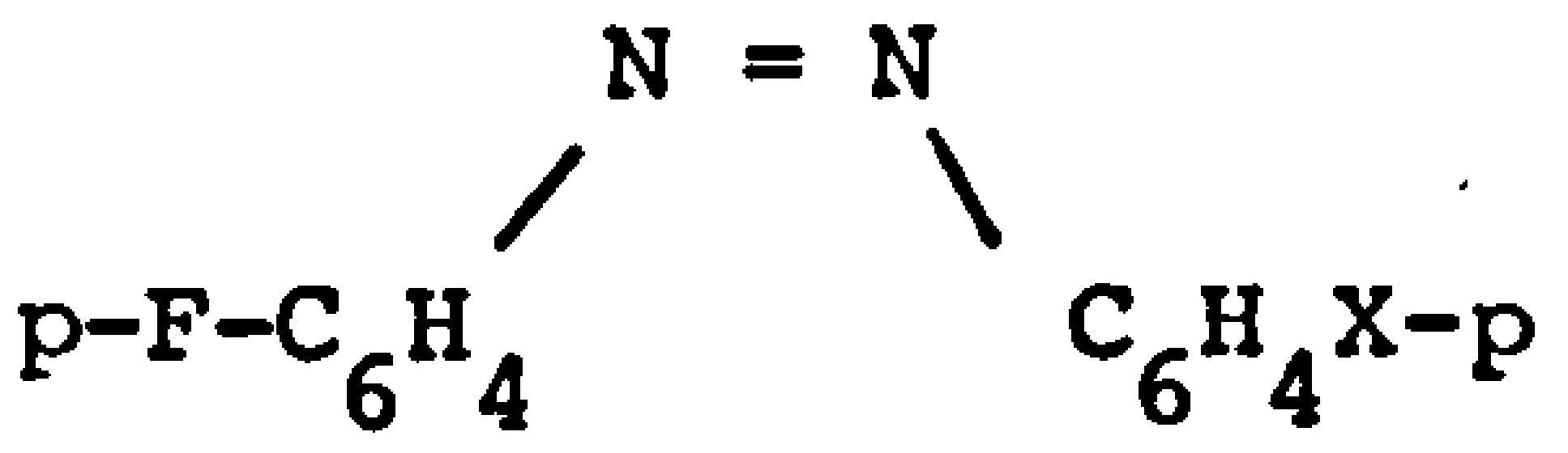
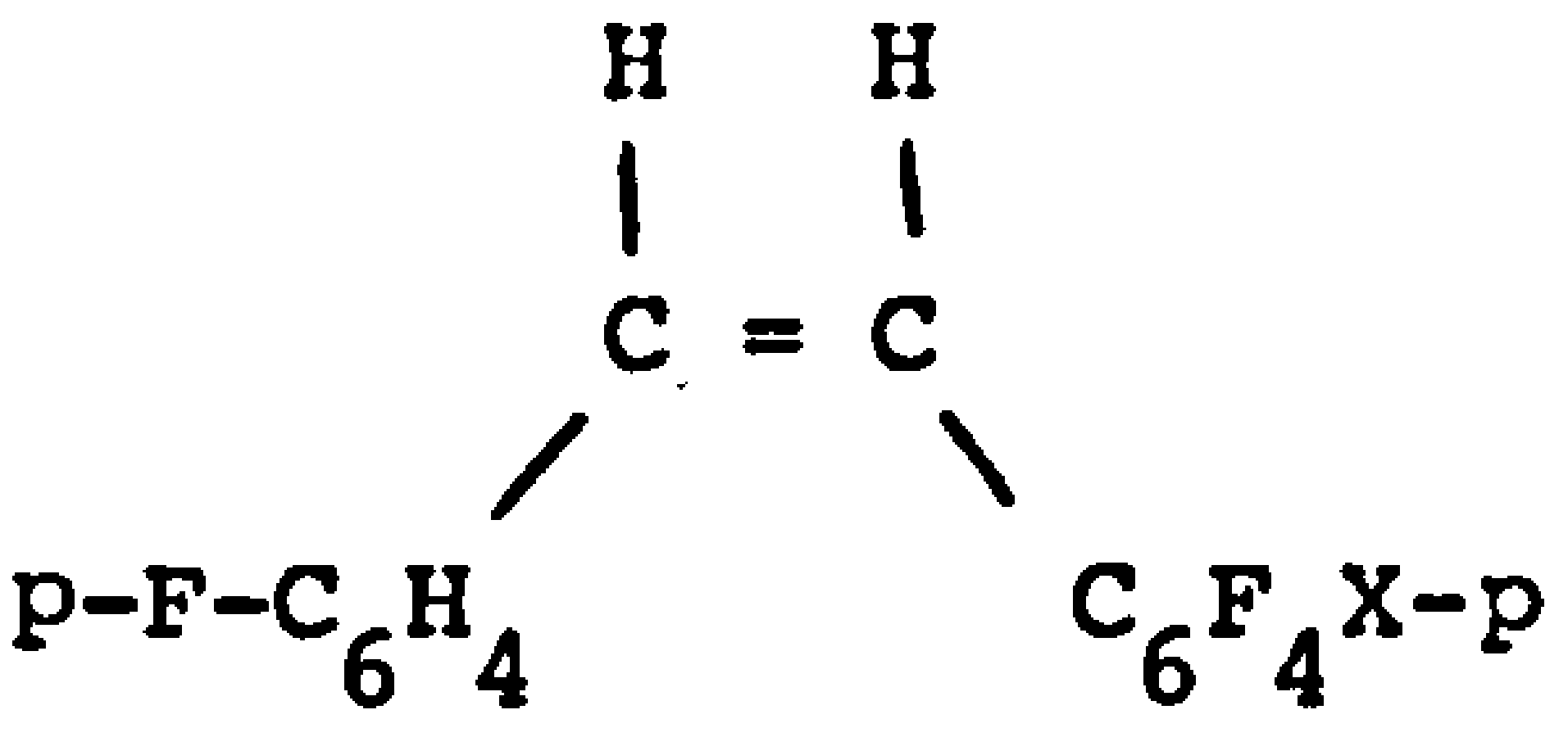


Figure (3.19) - Cis-stilbene

The effect of such inhibition of conjugation may be observed in analogous compounds e.g. in the electronic spectra of the cis-azobenzenes.[147]

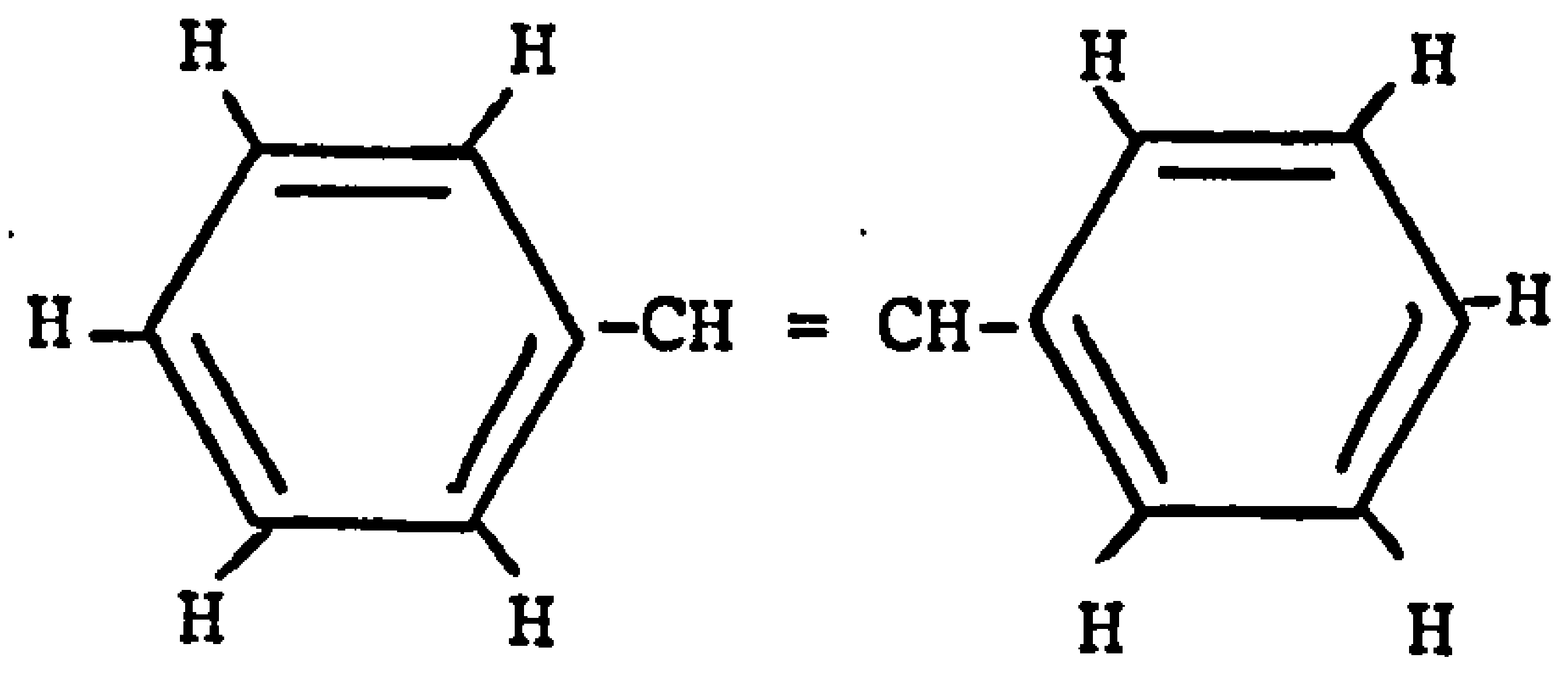
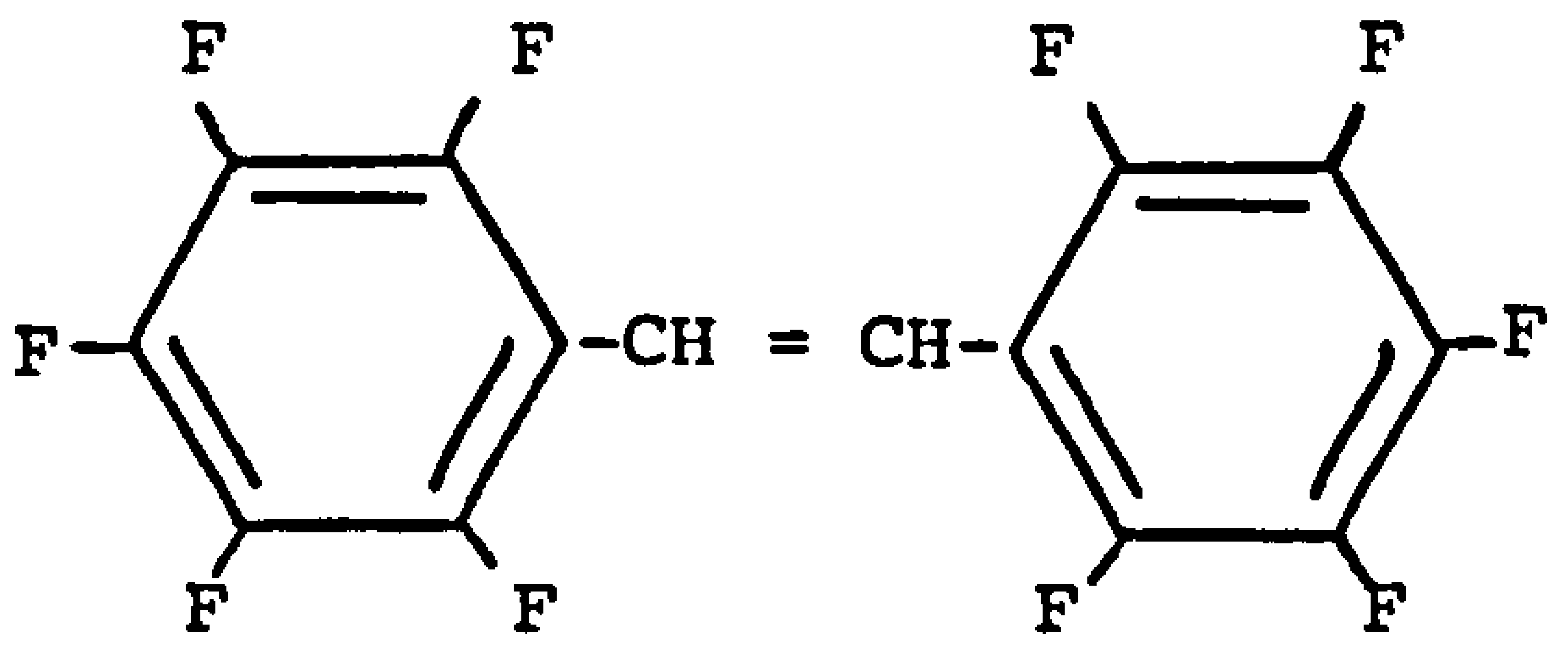


and

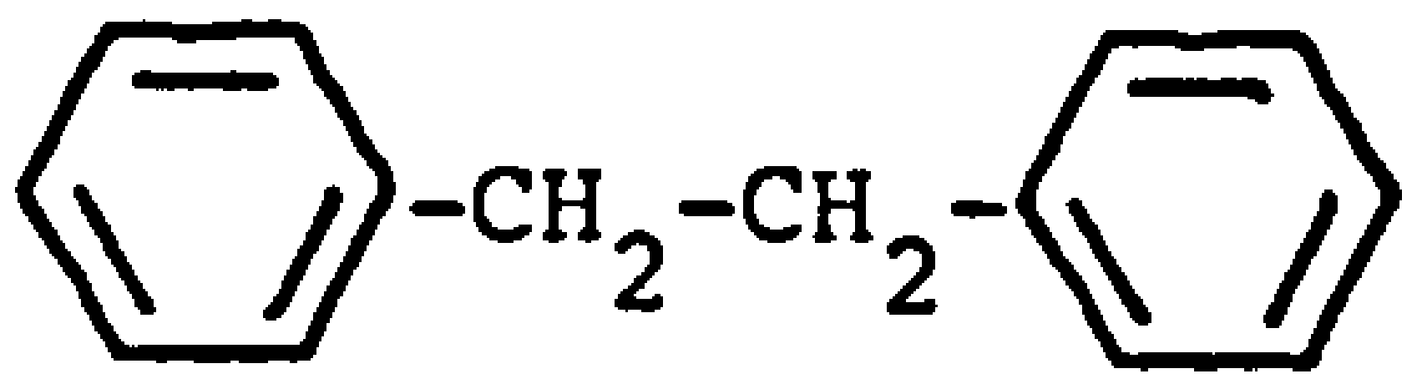


In cis-stilbene derivatives the inhibition of conjugation and the twisting of the aryl rings inhibits ring current effects so that the chemical shift of the ethylenic protons occurs at much lower field than in the trans derivatives. However the product VII $MeSC_6F_4CH{=}CHC_6F_4SMe$ is likely to be trans, not cis.

TABLE (2)

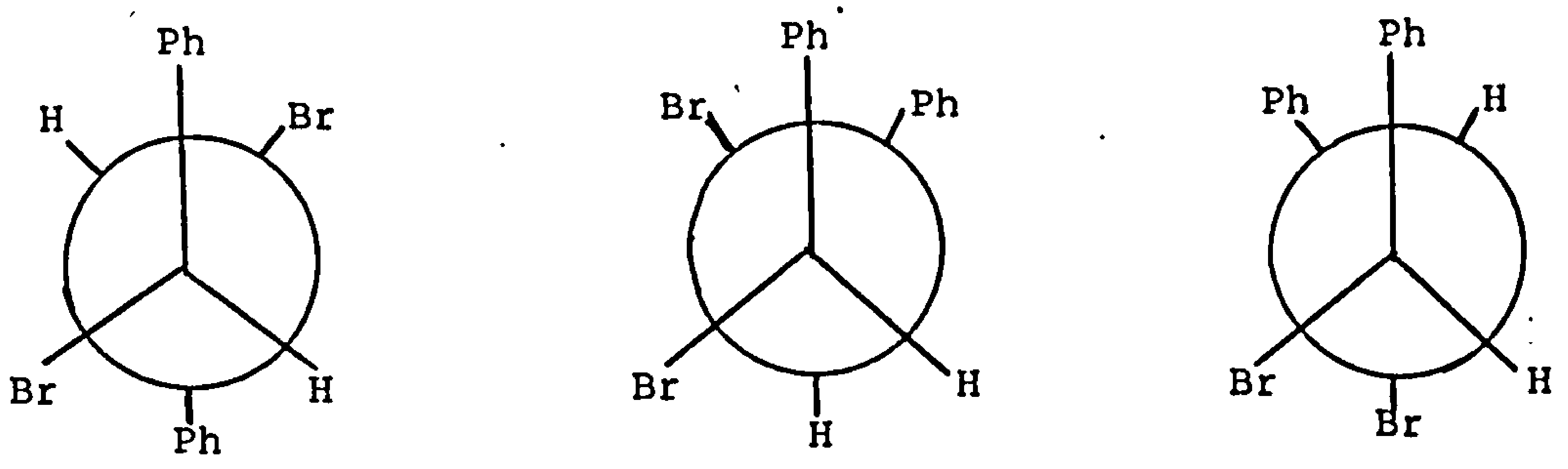
Cis stilbene	Chemical shift of ethylenic proton
	Ref. 146 6.55 ppm ($CHC\ell_3$)
	Ref. 126 6.9,6.7 ppm ($CC\ell_4$)

Steric effects in 1,2-bis(polyfluoroaryl)ethanes

A suitable introduction to a discussion of steric effects in ethane derivatives can come from discussion of dibenzyl . X-ray diffraction[148] indicates that in the crystalline state the phenyl rings are anti to one another and the central C-C bond is inclined at 70° to the planes of the rings, which are parallel but not coplanar. In this conformation steric repulsions between the phenyl rings are minimised and because this interaction must be the most destabilising aspect of the structure, it is likely that this conformation will persist in solution.

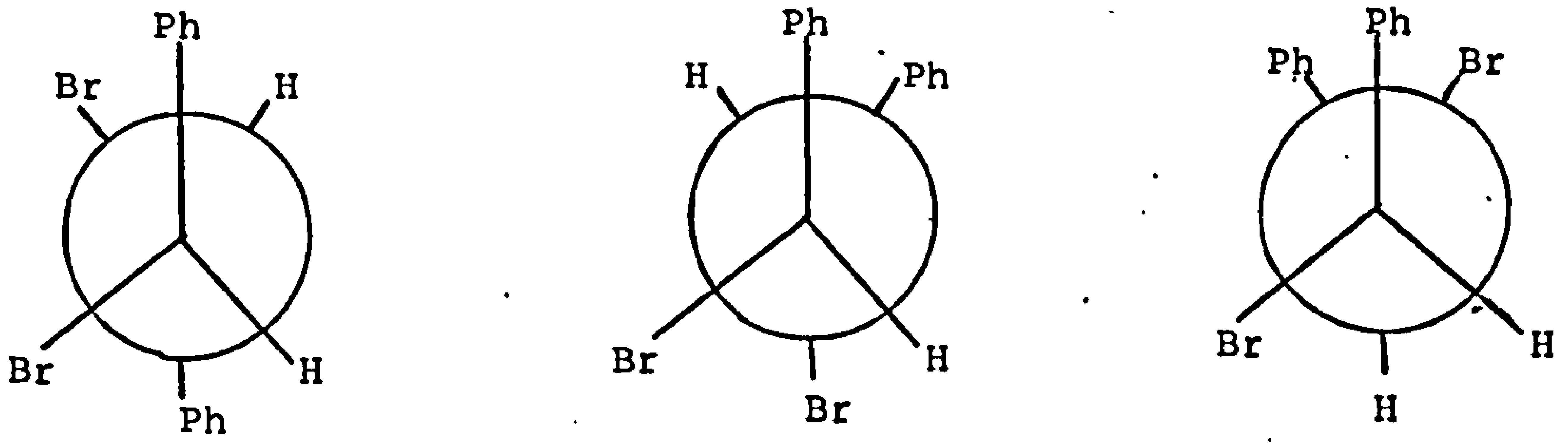
Although the C-H bonds in the connecting groups are not as close to orthogonality with the phenyl rings as those in cis-stilbene, they are still favourably oriented to engage in some interaction with the π-system. Such an interaction will be influenced by the nature of the substituent in the para position of the rings and its effect will be transmitted to the bridge by modification of the repulsive interaction between them. In this case, however, the C-H bonds are not syn, but gauche to one another.

In order to assess further the effect of conformation upon transmission of substituent effects we compared the properties of two series of enantiomeric compounds namely, meso and $d\ell$-1,2-dibromo-1,2-bis(pentafluorophenyl)ethane with meso and dl-dibromobibenzyls.[123]



I II III

meso



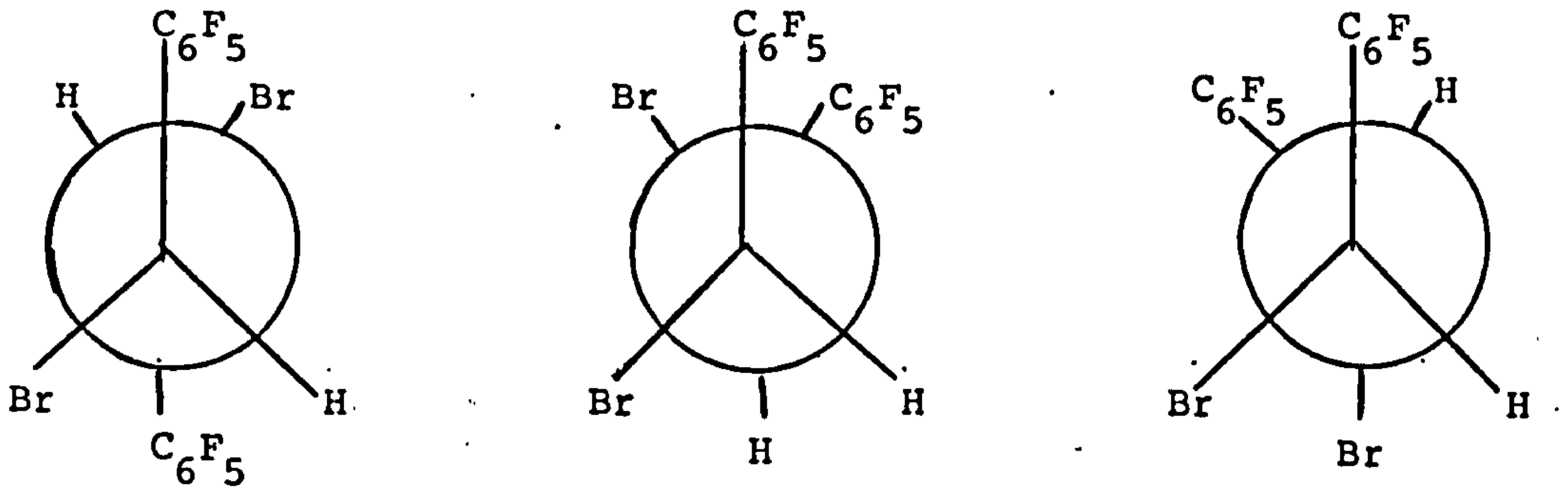
IV V VI

dℓ-

Figure (3.20) - Conformations of meso and dℓ-dibromobibenzyl[123]

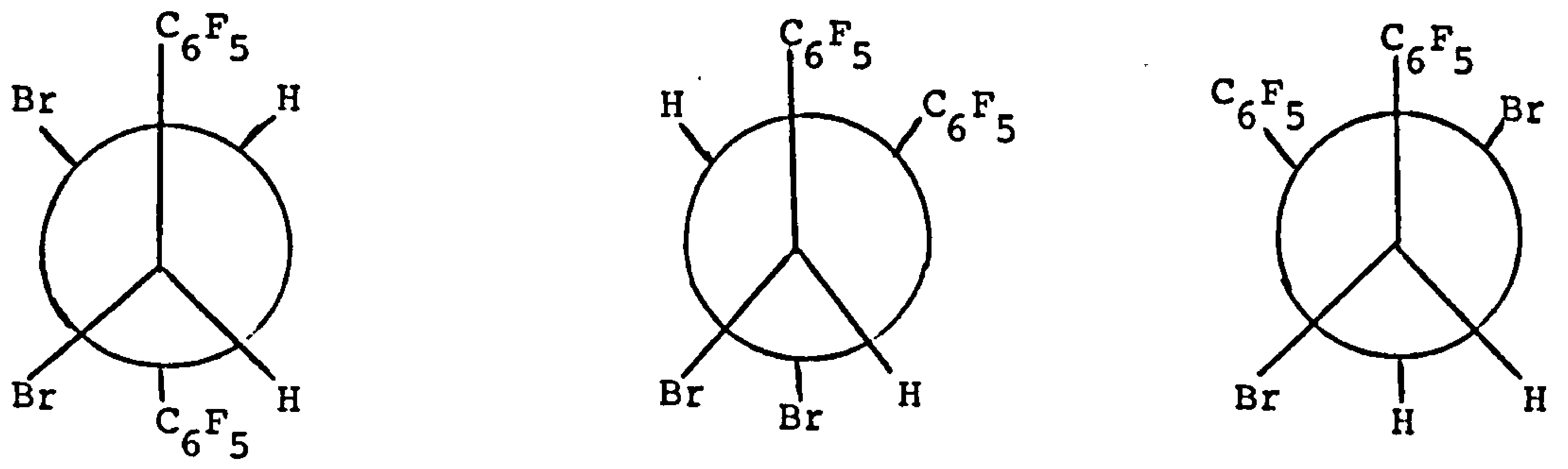
The preferred conformations of representative molecules in the crystalline state have been determined by X-ray analysis,[149] the possible conformations being illustrated in Figure (3.20). Crystallographic studies have shown that the meso-form crystallises with conformation I where both the phenyl groups and bromines are anti (bromine-bromine distance 4.50Å) so that both steric and dipolar repulsions are at a minimum; the dℓ-form, however, crystallises in conformation IV in which the bromines are approximately gauche-(Br-Br distance 3.85Å) equal to the sum of the combined Van der Waals radii and in which the steric and dipolar repulsions of the C-Br bond are not minimised. The conformers which are found in the solid state are those which would be predicted to minimise steric effects.

To consider our own perfluorophenyl derivatives, it is likely that similar effects will predominate. The different intermolecular interaction in the two isomers (meso- and dℓ-) leads to observed differences in properties.



(1) (2) (3)

meso



(4) (5) (6)

dℓ

Figure (3.21) - Conformations of meso and dℓ-1,2-dibromo-1,2-bis(pentafluorophenyl)ethane.

^{19}F {-H} nmr spectra of the products from the preparation of $C_6F_5CHBr.CHBrC_6F_5$ isomers showed a single ABCDE system, thus there is only isomer present. The spectra may be rationalised by consideration of the likely preferred conformations. In the ±dℓ form (4), the repulsive interaction between vicinal bonds of the CHBr.CHBr group is probably larger than in the meso gauche form because the bromine atoms are very close to one another, and as we mentioned before, the phenyl rings are anti to one another. This makes rotation around the C-C bond centre difficult and puts the pairs of ortho and meta fluorine atoms in different environments giving rise to an ABCDE system. Thus the presence of fluorine, which is larger than hydrogen, has given rise to an ABCDE pattern. The fluorine has a greater steric effect than hydrogen and also because fluorine chemical shifts are larger than those of hydrogen, the molecule gives a pattern which cannot be observed in the hydrocarbon derivative. Further, the proton spectra are less well separated and the spin-system cannot be identified fully. It is not possible to identify which conformer is present from the nmr spectra. See figure (3.23).

When the aromatic rings have para-phenyl thio substituents these may give even greater steric effects, and in fact an ABCD pattern is observed for these compounds. The steric interaction in this molecule has been demonstrated by molecular models

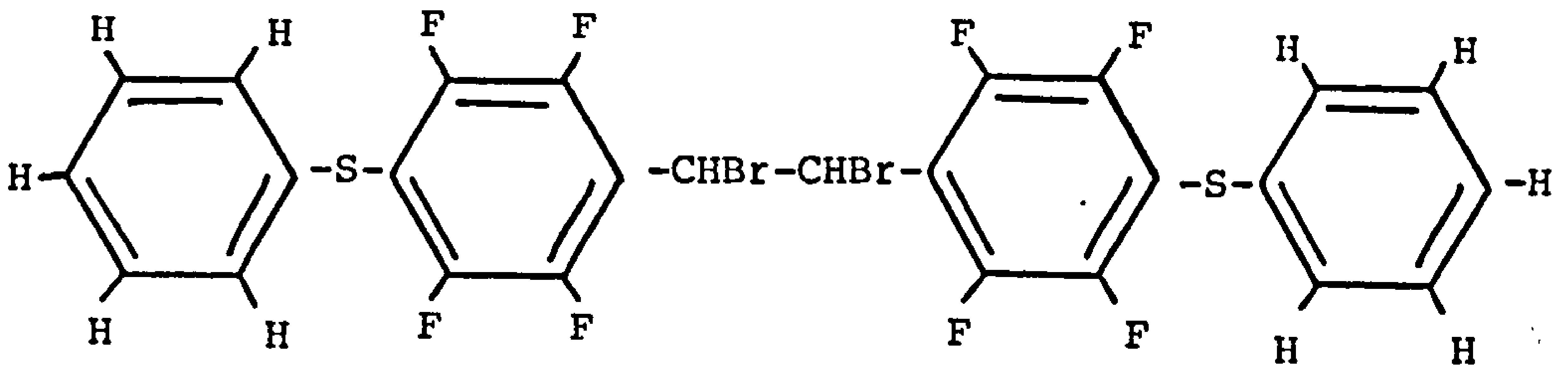


Figure (3.22) - 1,2-dibromo-1,2 (4-phenylthiotetrafluorophenyl)ethane.

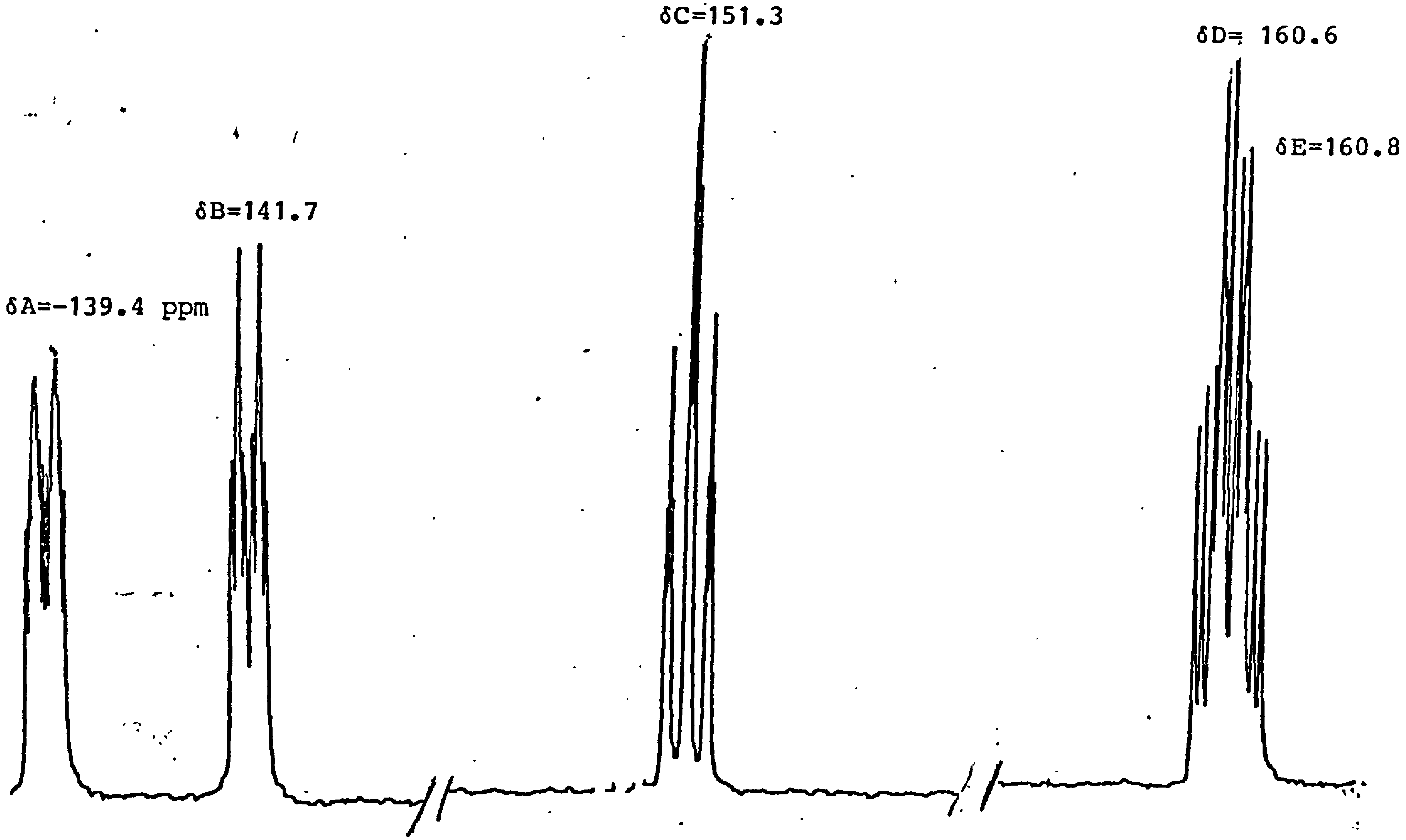


Figure (3.23) - ^{19}F nmr spectrum of

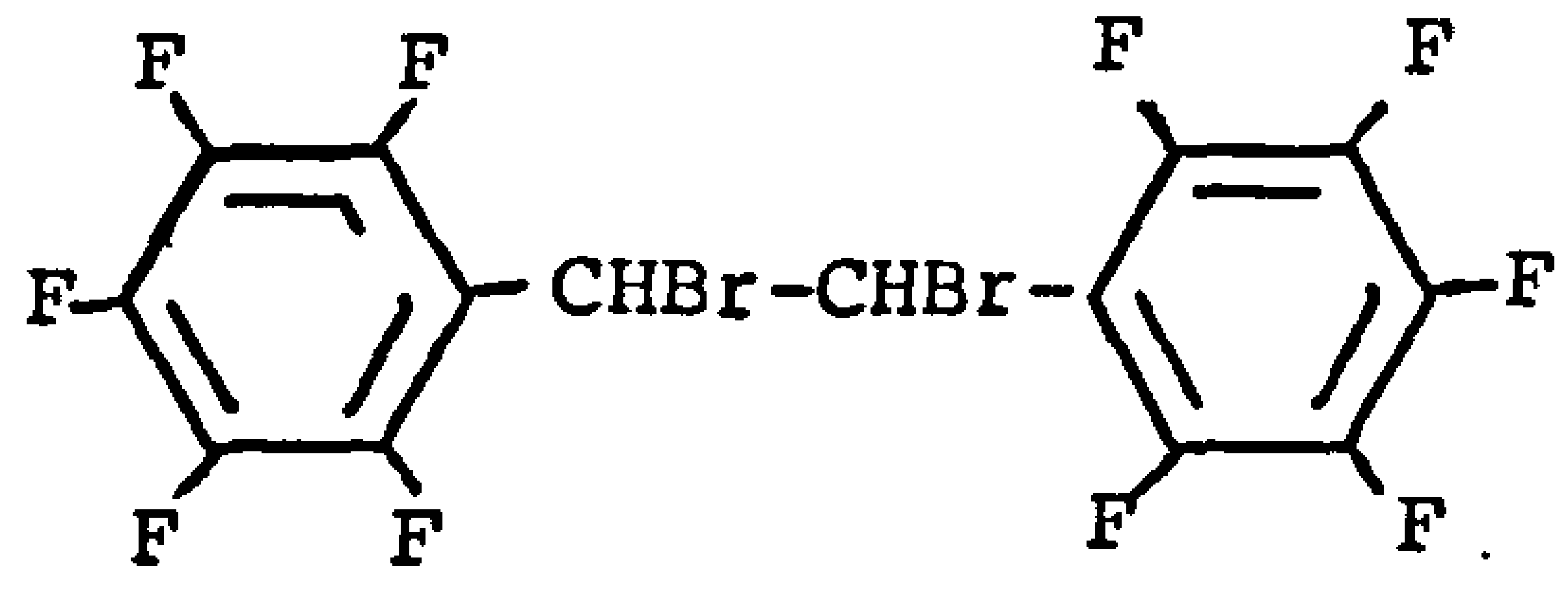


TABLE (3)

^{1}H nmr spectra

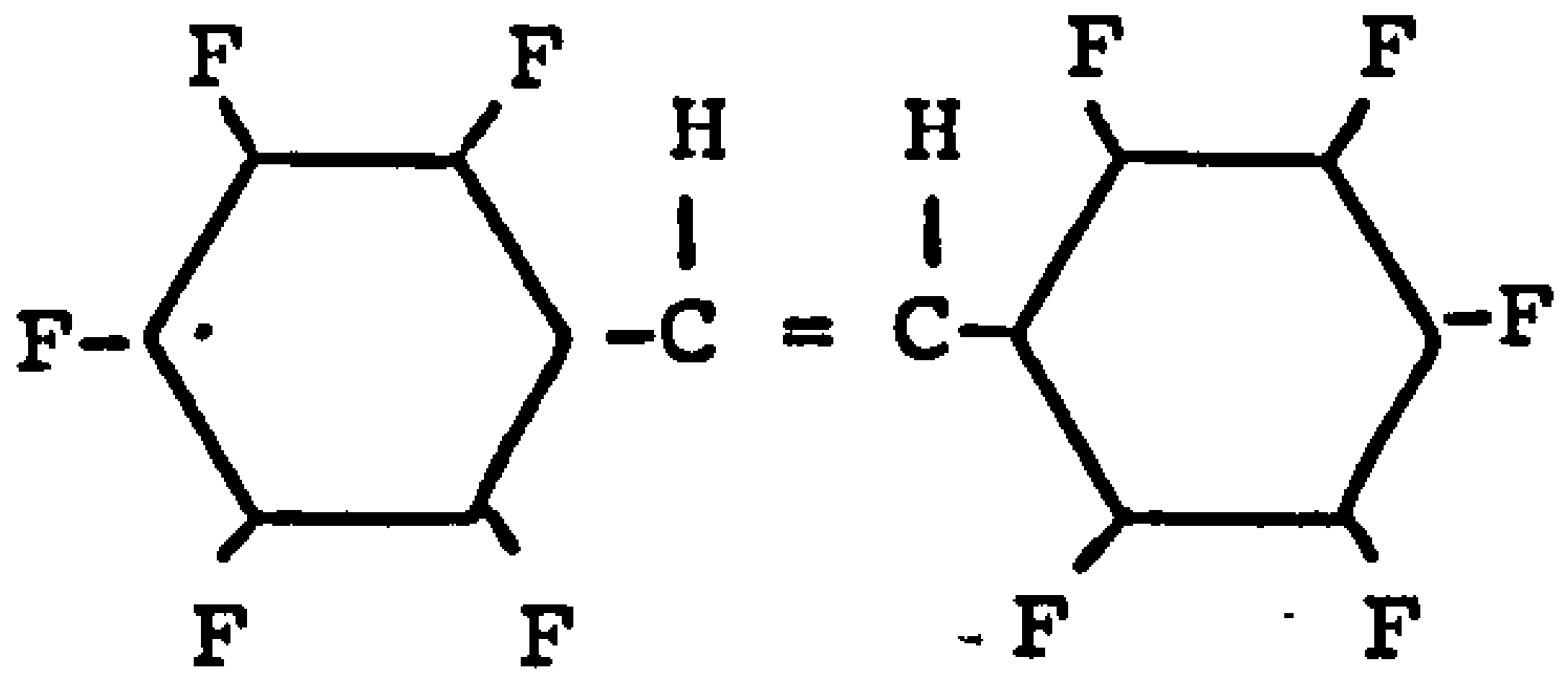
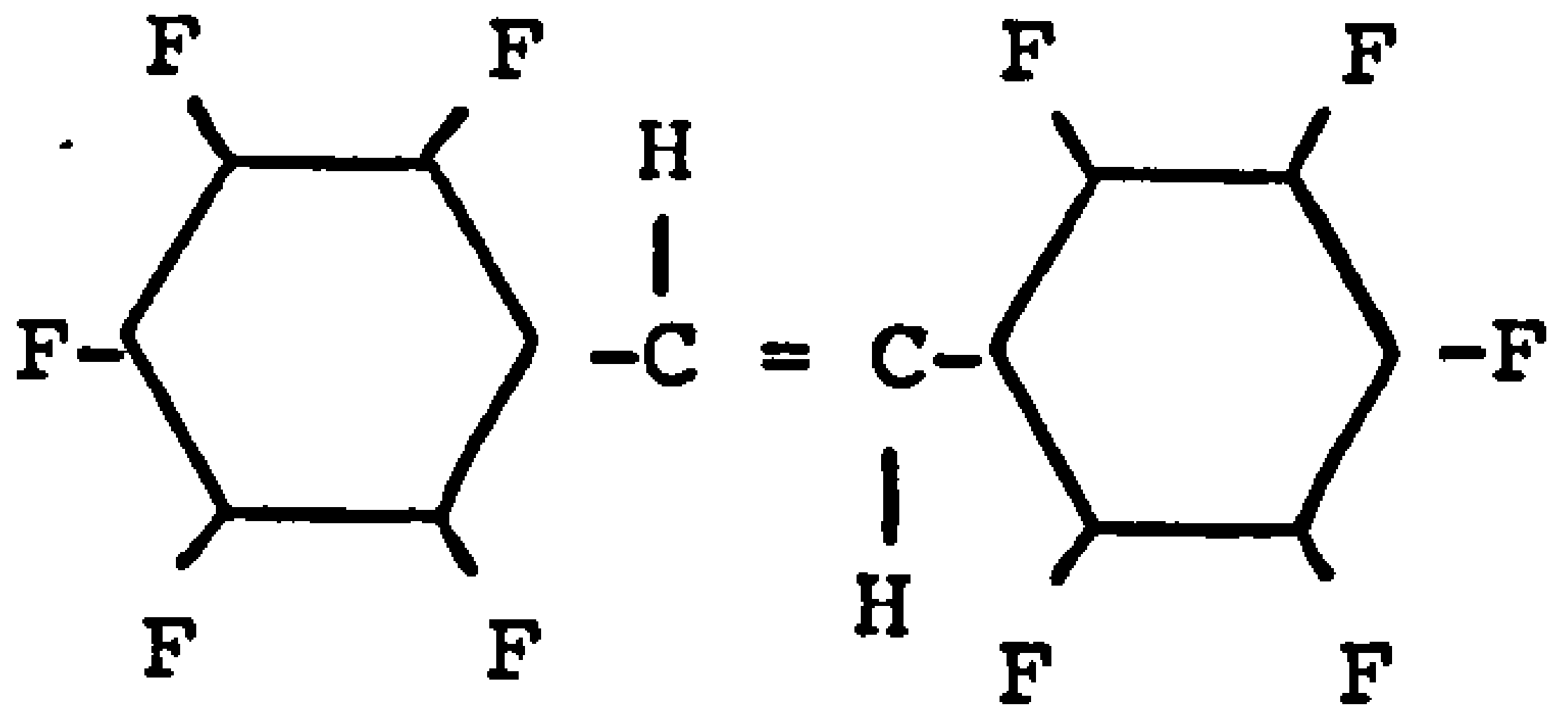
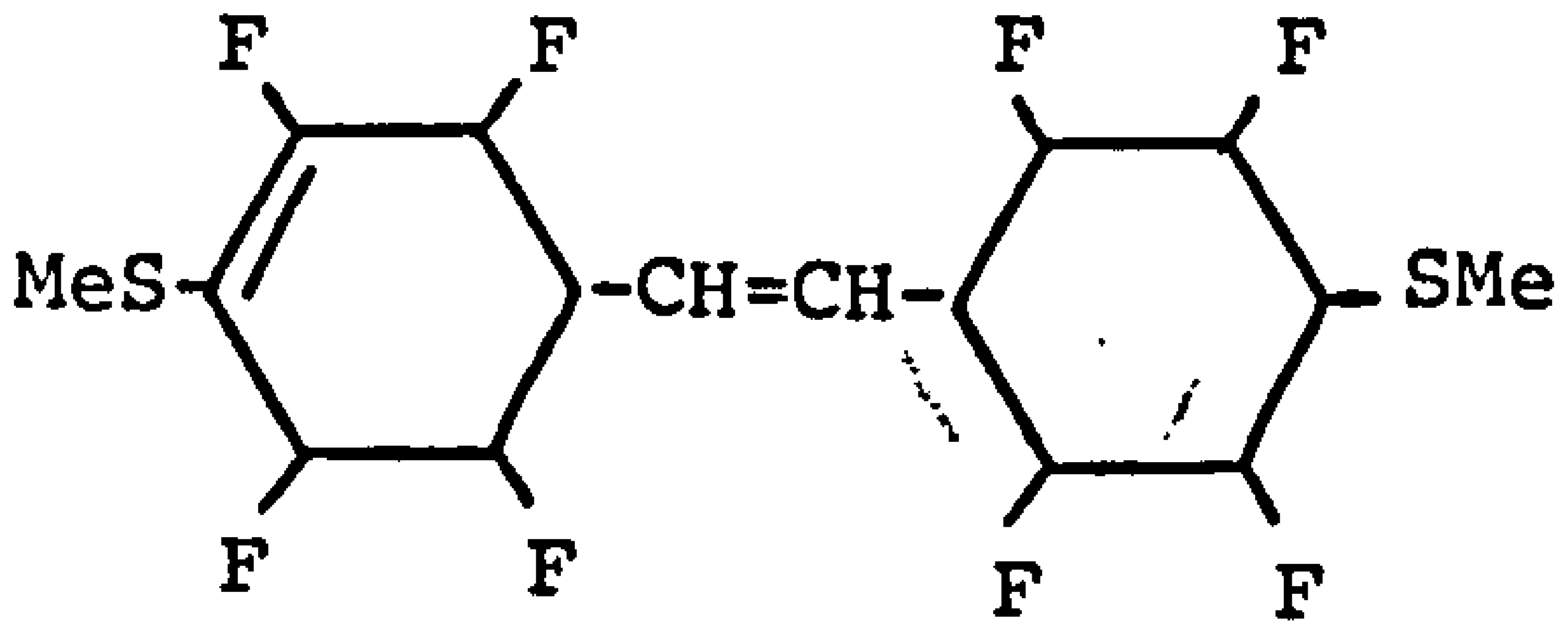
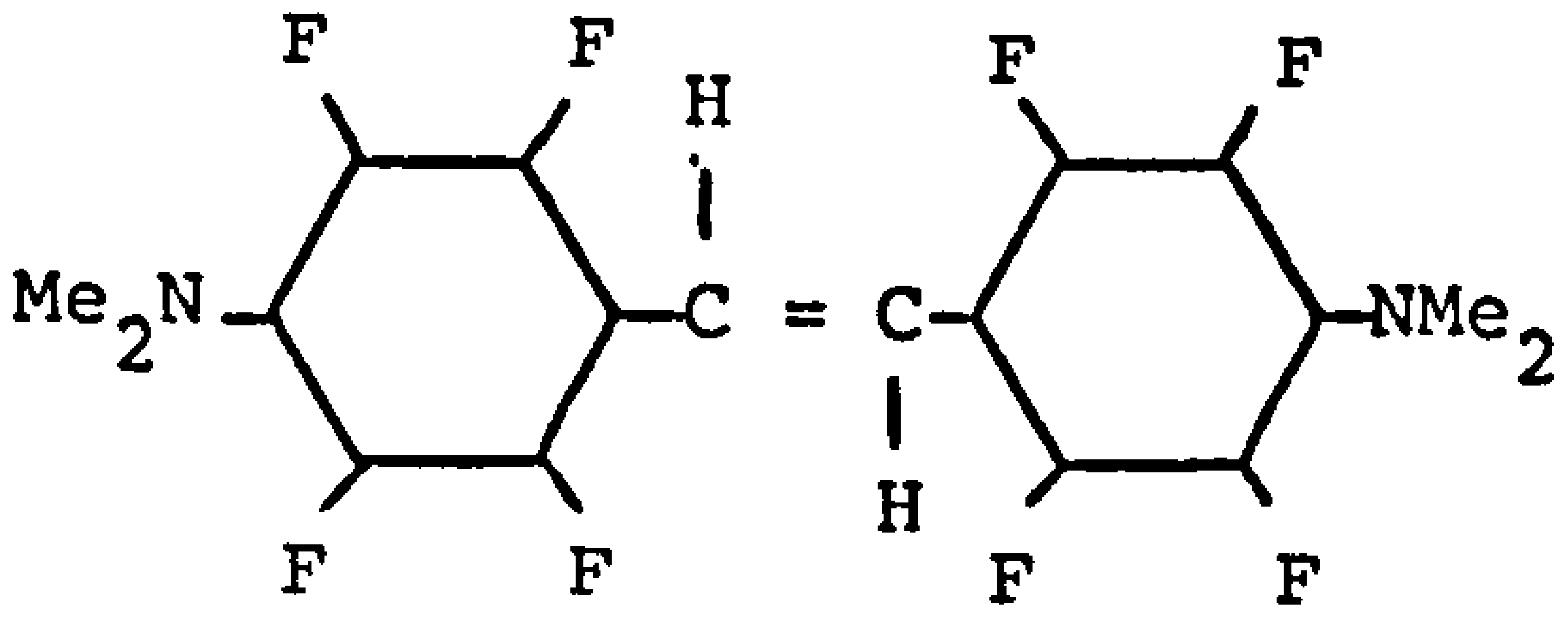
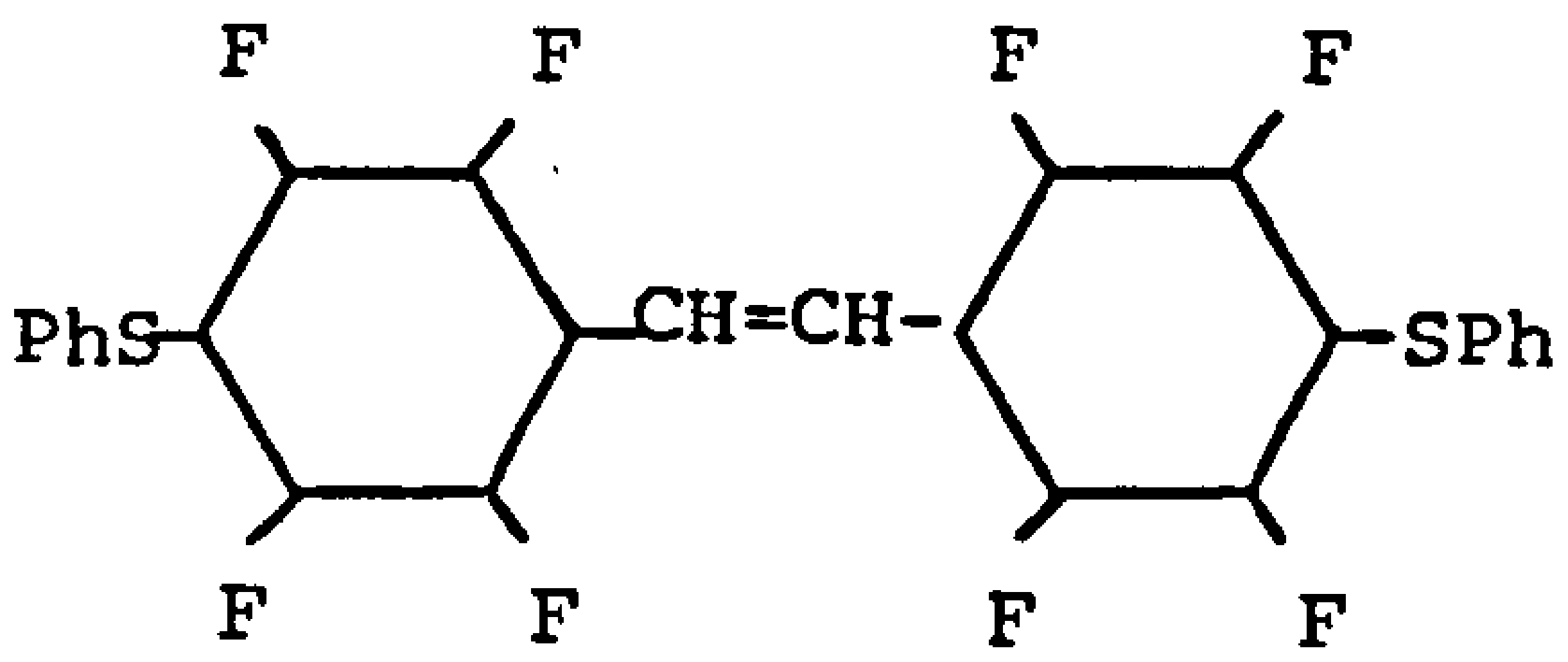
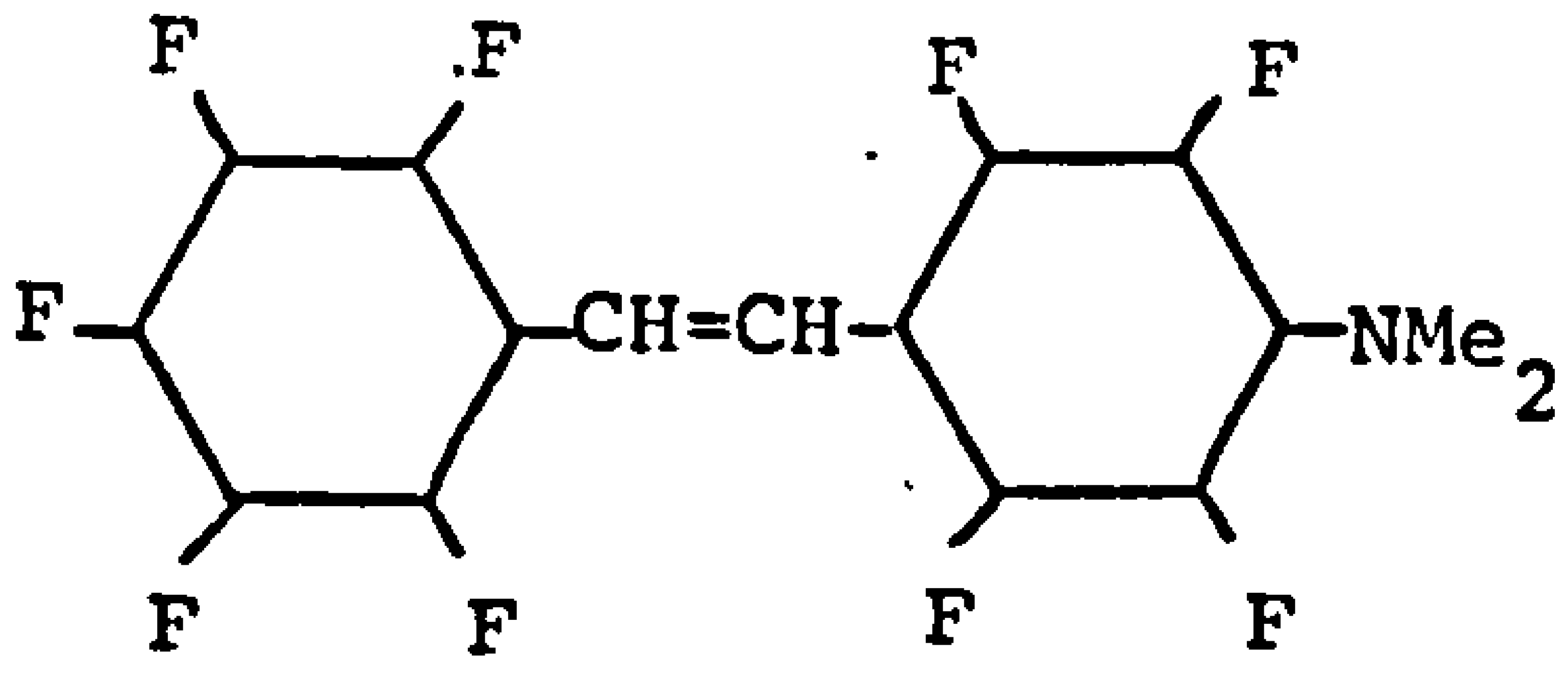
Compound	Solvent	Chemical Shift (w.r.t. Me_4Si)		
		δCH	δSCH_3: $\delta N(CH_3)_2$	SPh
	carbon tetra-chloride	6.71 6.9	-	-
	tetrahydrofuran	7.4	-	-
	chloroform	7.4	2.54	-
	chloroform	7.29	2.99	-
	chloroform	6.2	-	7.2
	$CDC\ell_3$	5.2	2.94	-

TABLE (3) contd.

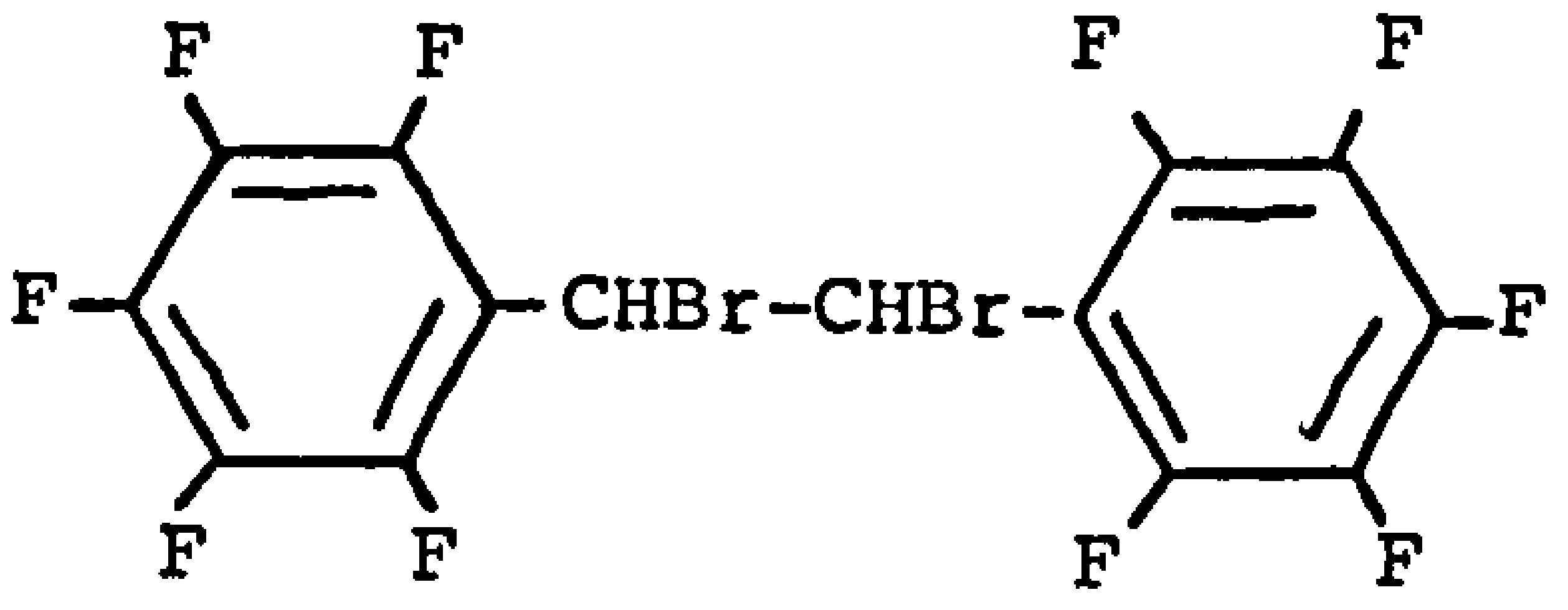
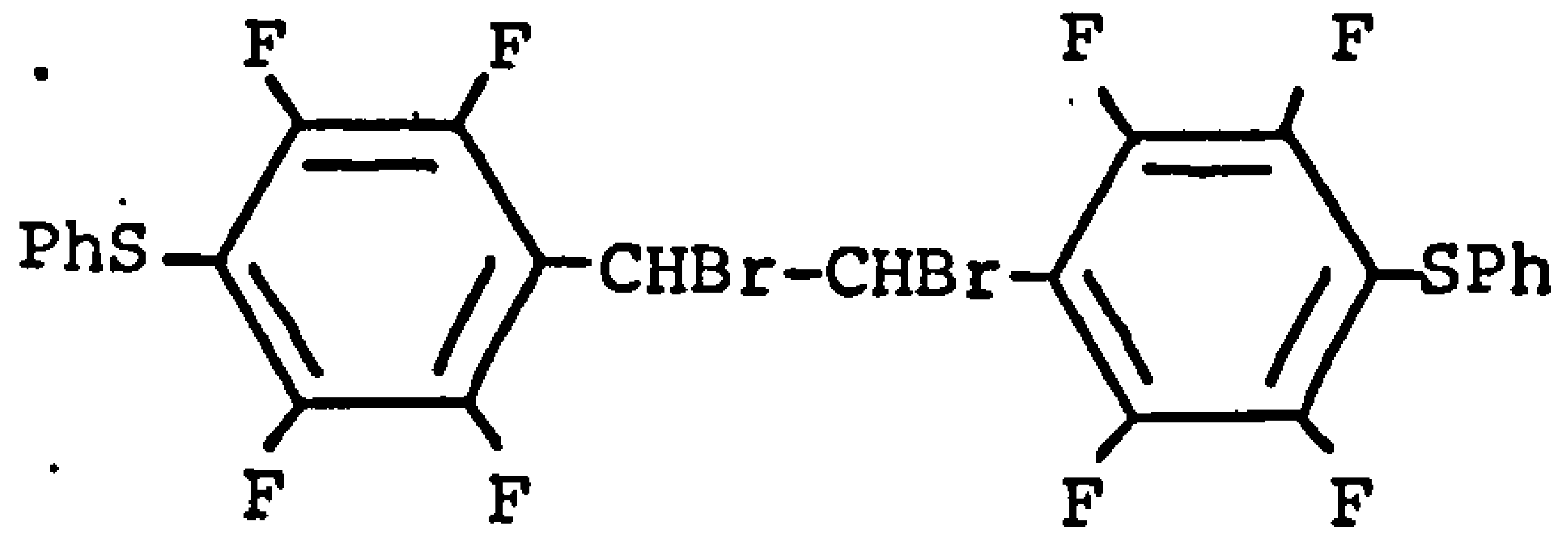
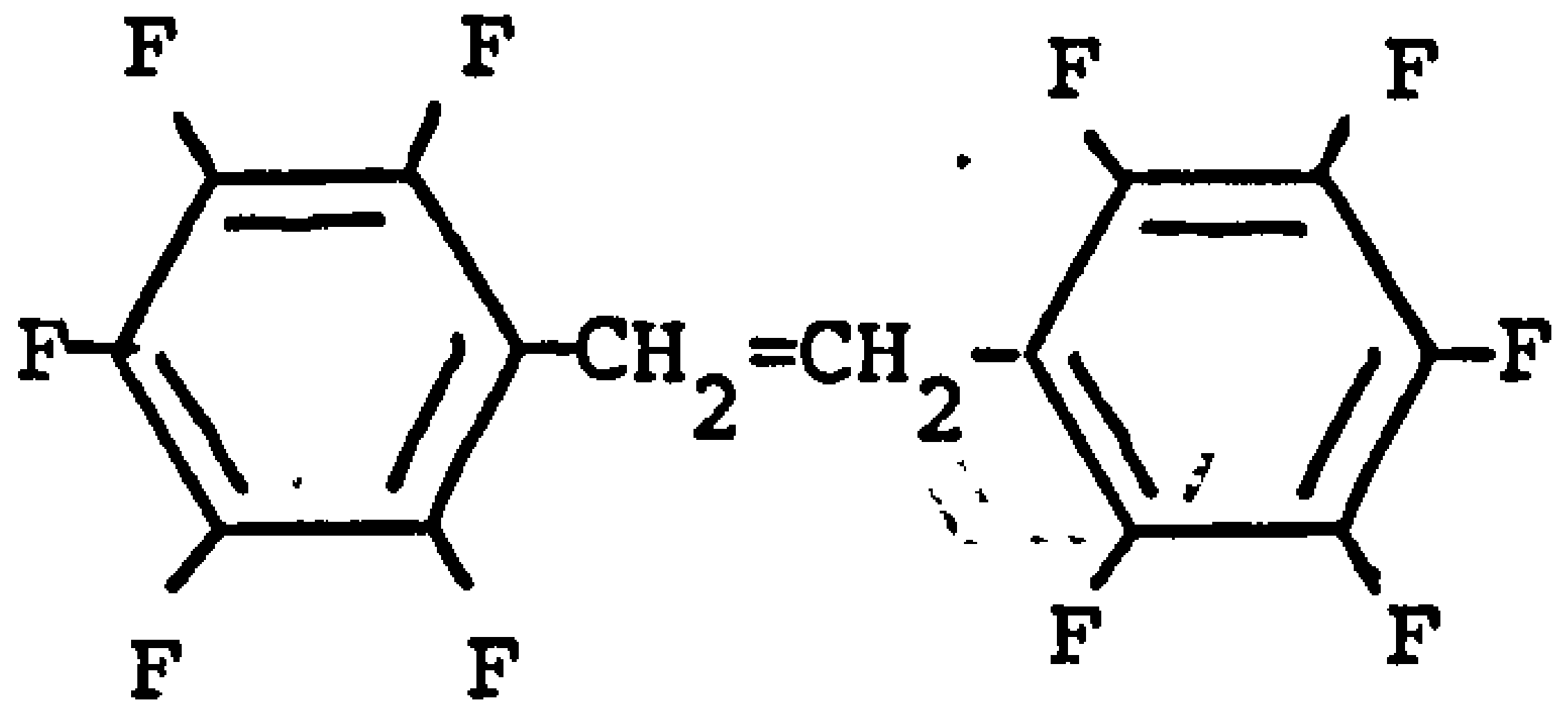
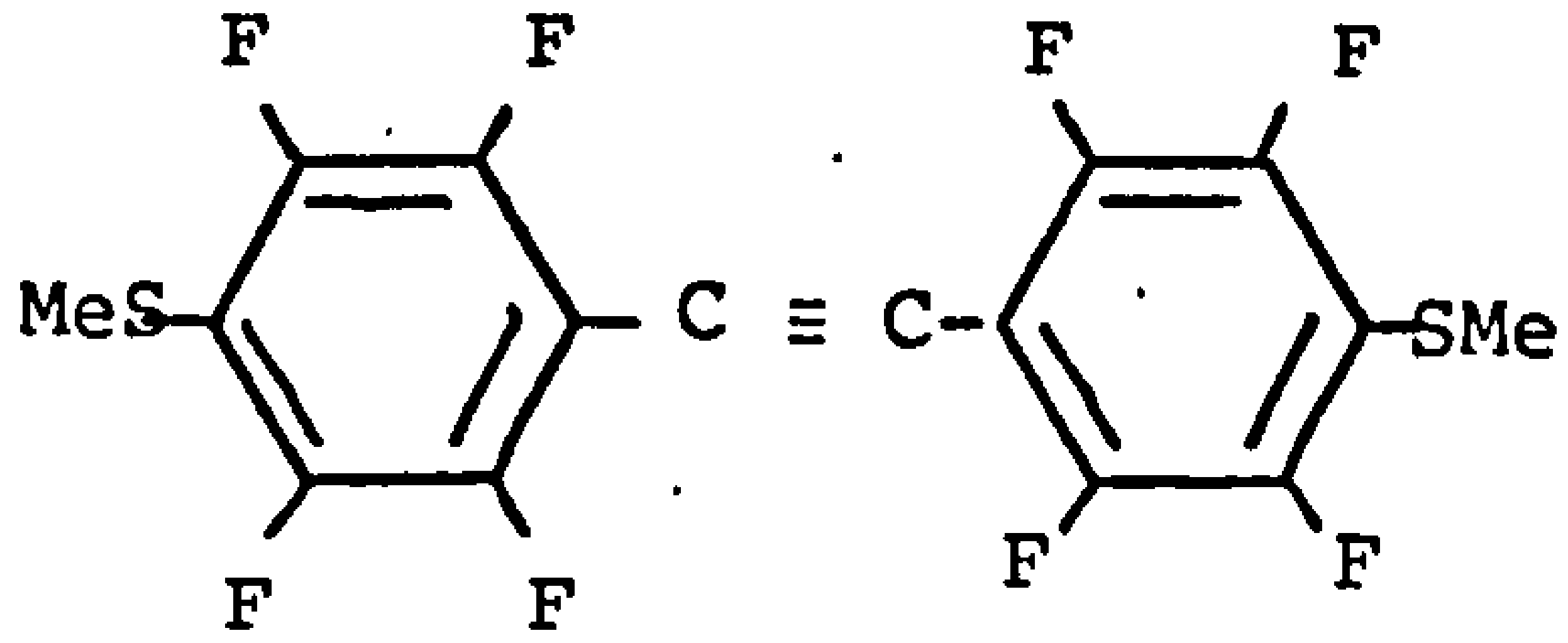
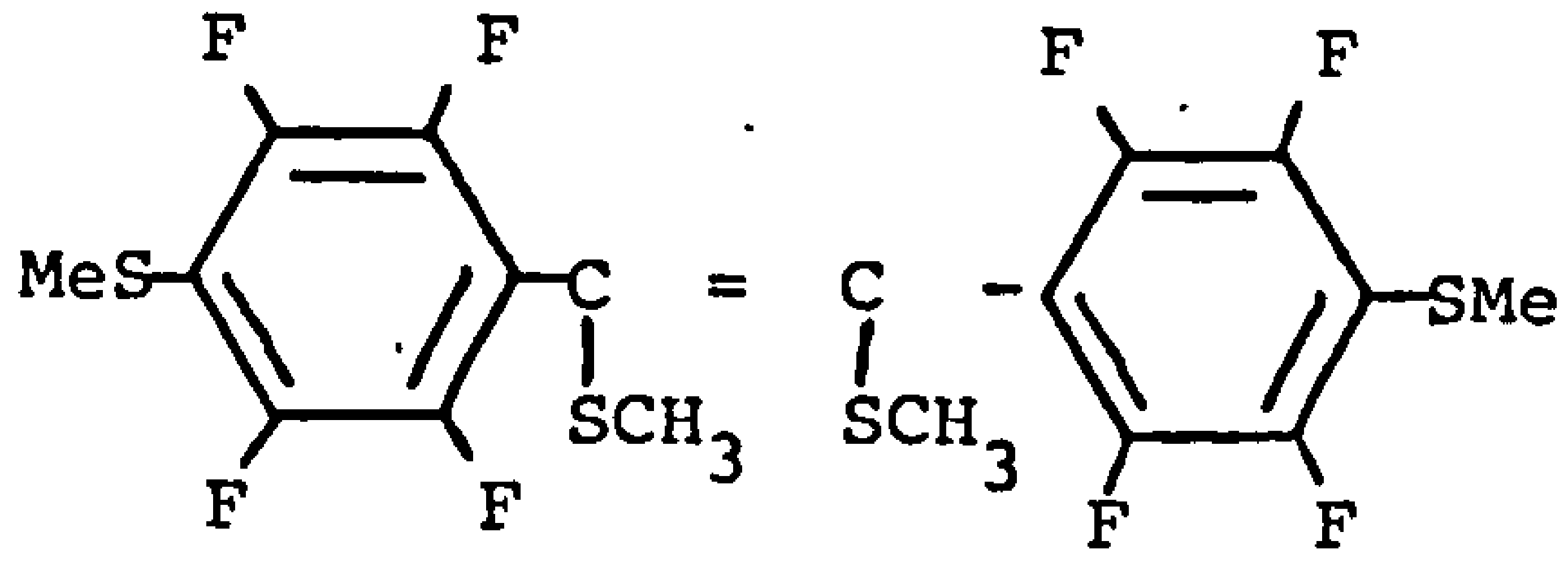
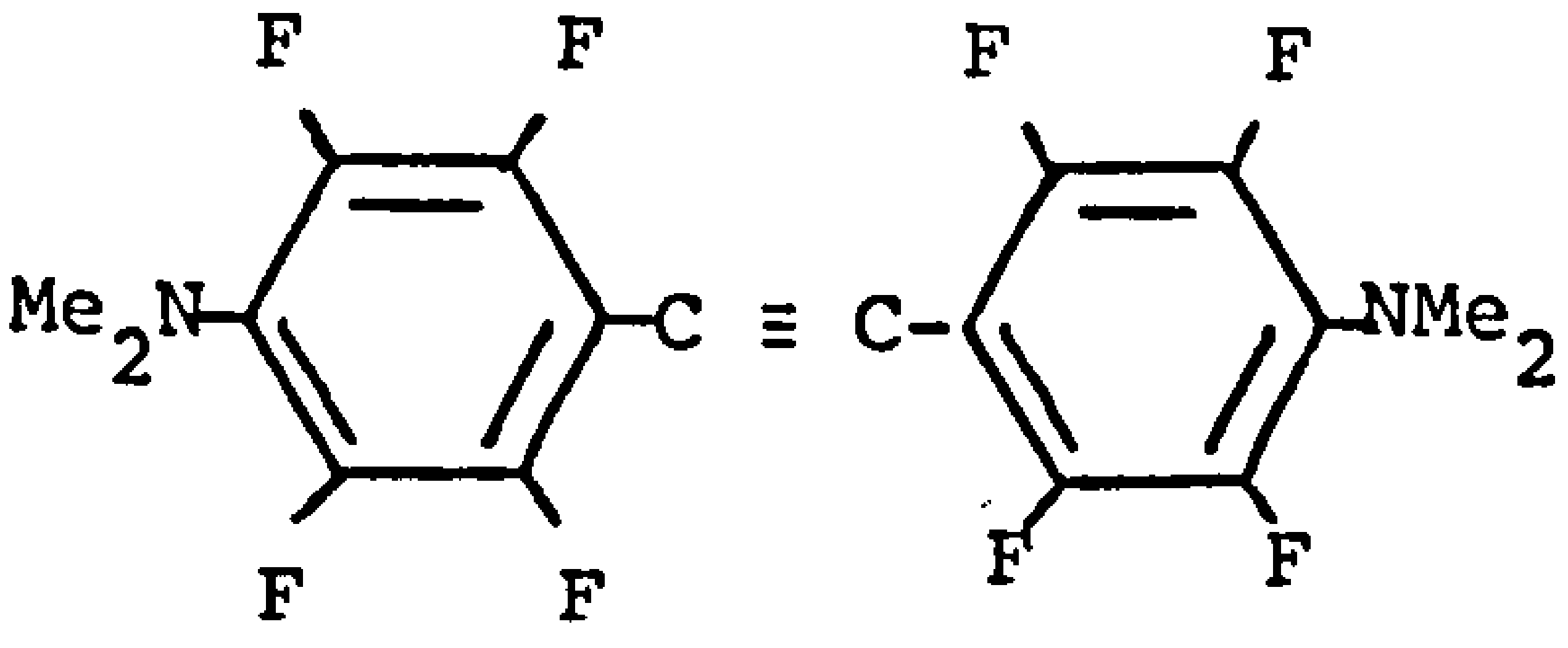
	$CHCl_3$	6.02	-	-
	chloroform	6.10	-	7.30
	CCl_4	3.00	-	-
		-	3.01	-
		-	2.5 3.02	-
		-	3.09	-

TABLE (4)

^{19}F nuclear magnetic resonance spectra (shifts w.r.t. $CFCl_3$)

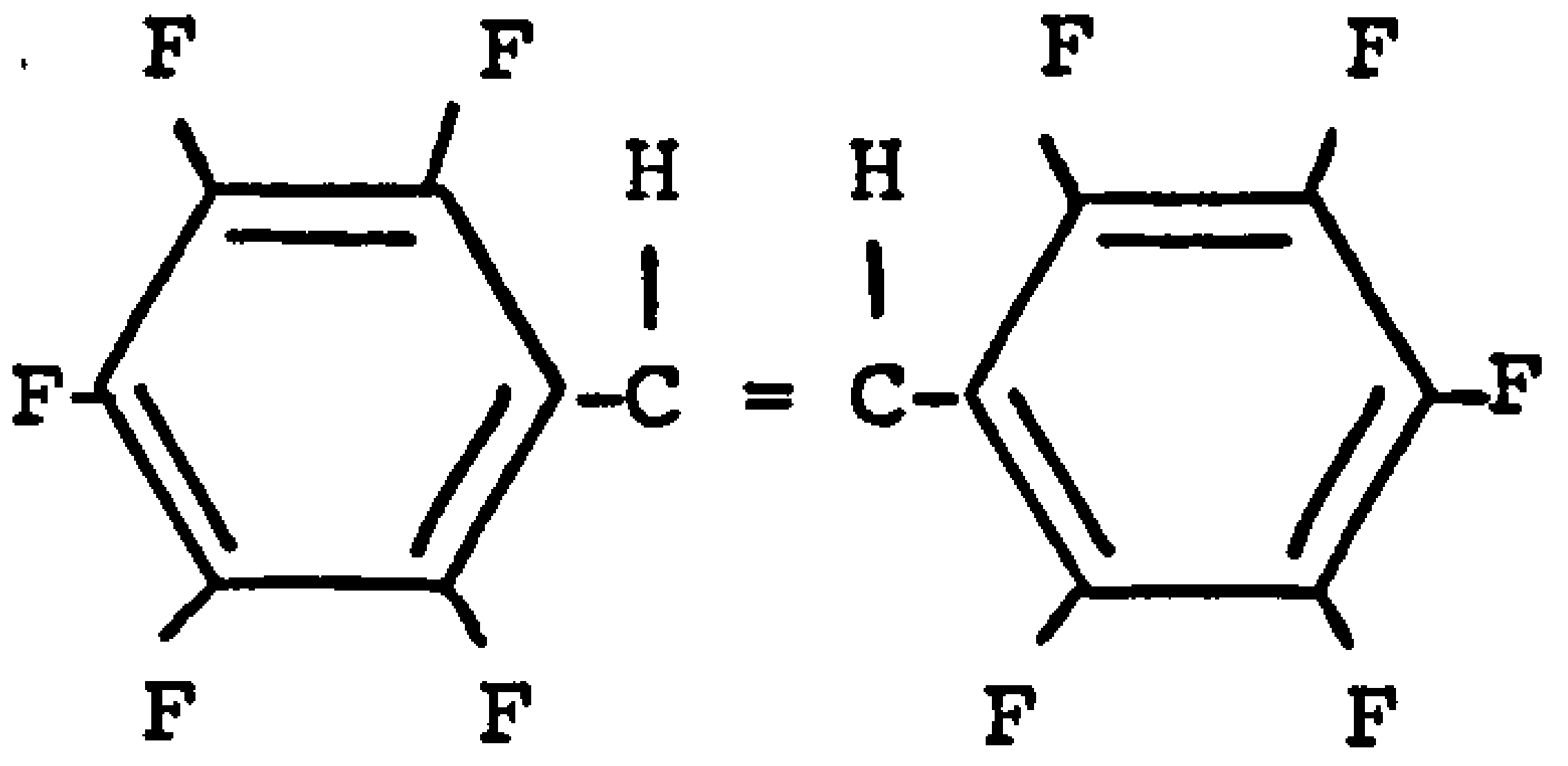
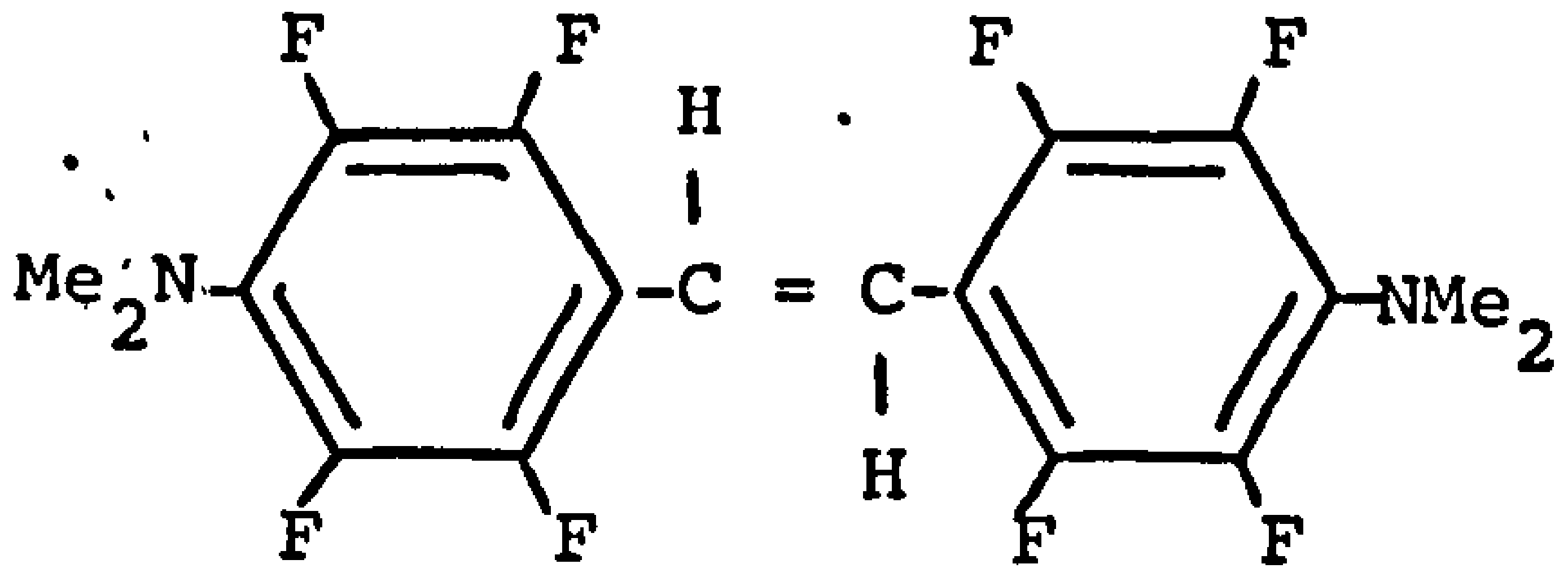
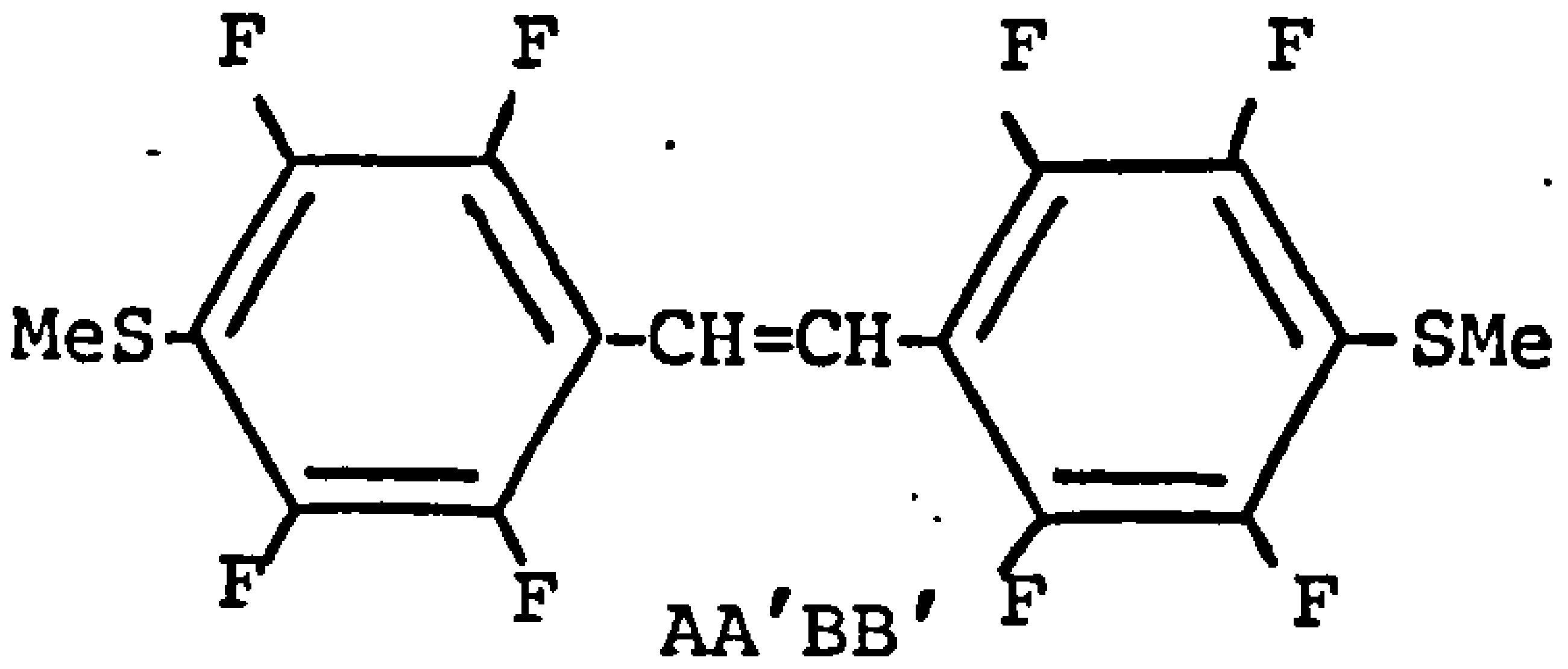
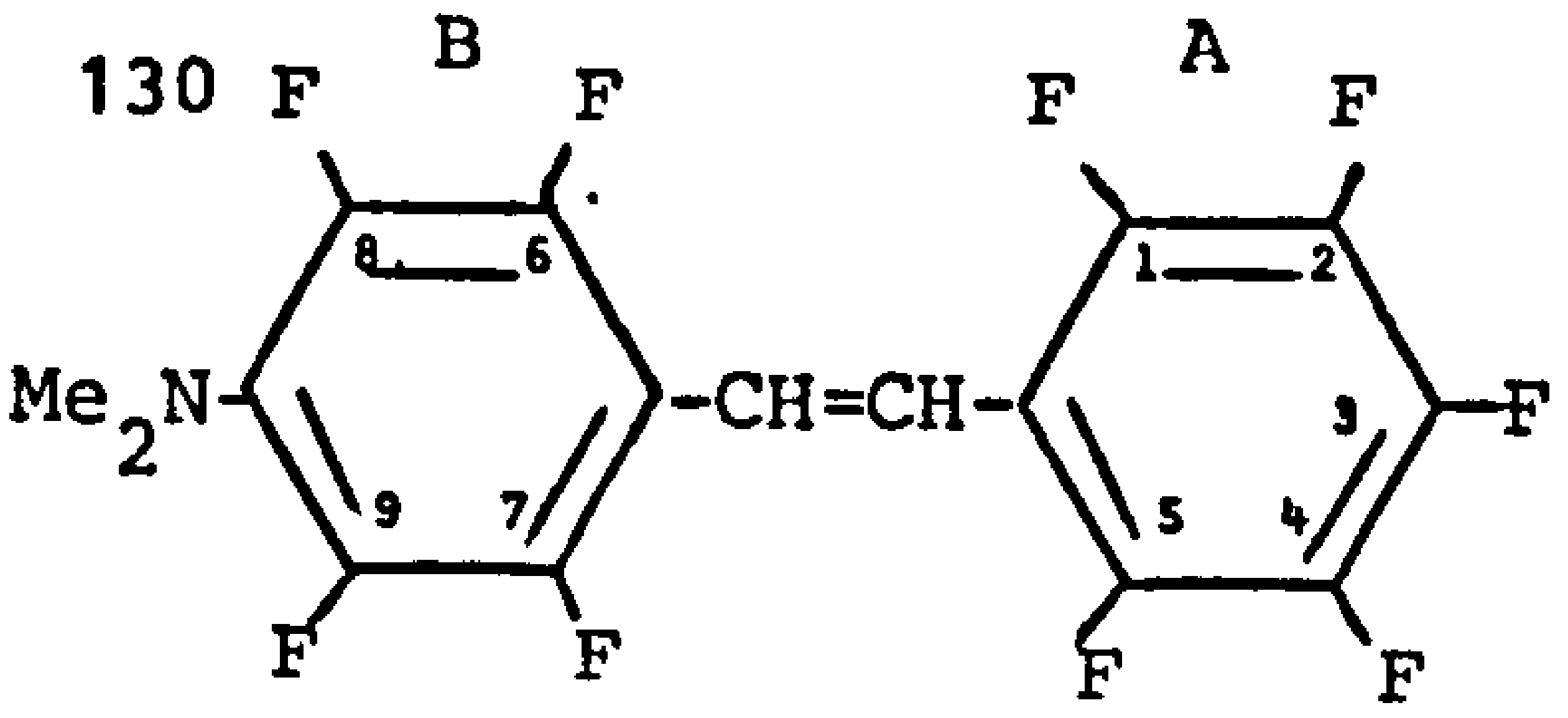
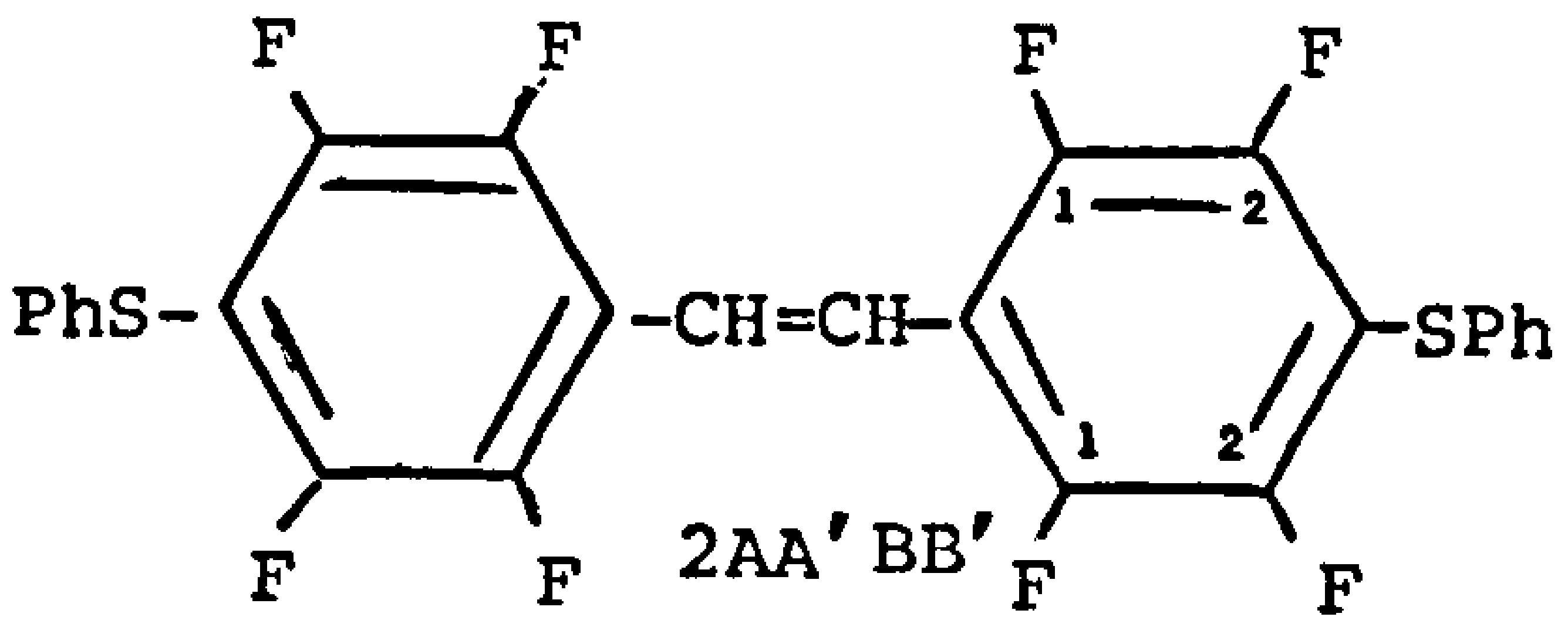
Compound	Solvent	Chemical Shift ortho	 para	 meta
	$CDCl_3$	140.09	153.1	162.36
 AA'BB'	$CDCl_3$	145.5	-	153.5
 AA'BB'	$CDCl_3$	136.54	-	142.89
130 	$CDCl_3$	F1-5=142.7 F6-7=145.0	F3=155.3	F2-4=162.1 F8-9=151.8
	1st isomer 2nd isomer	134.12 134.12		141.78 141.86

TABLE (4) contd.

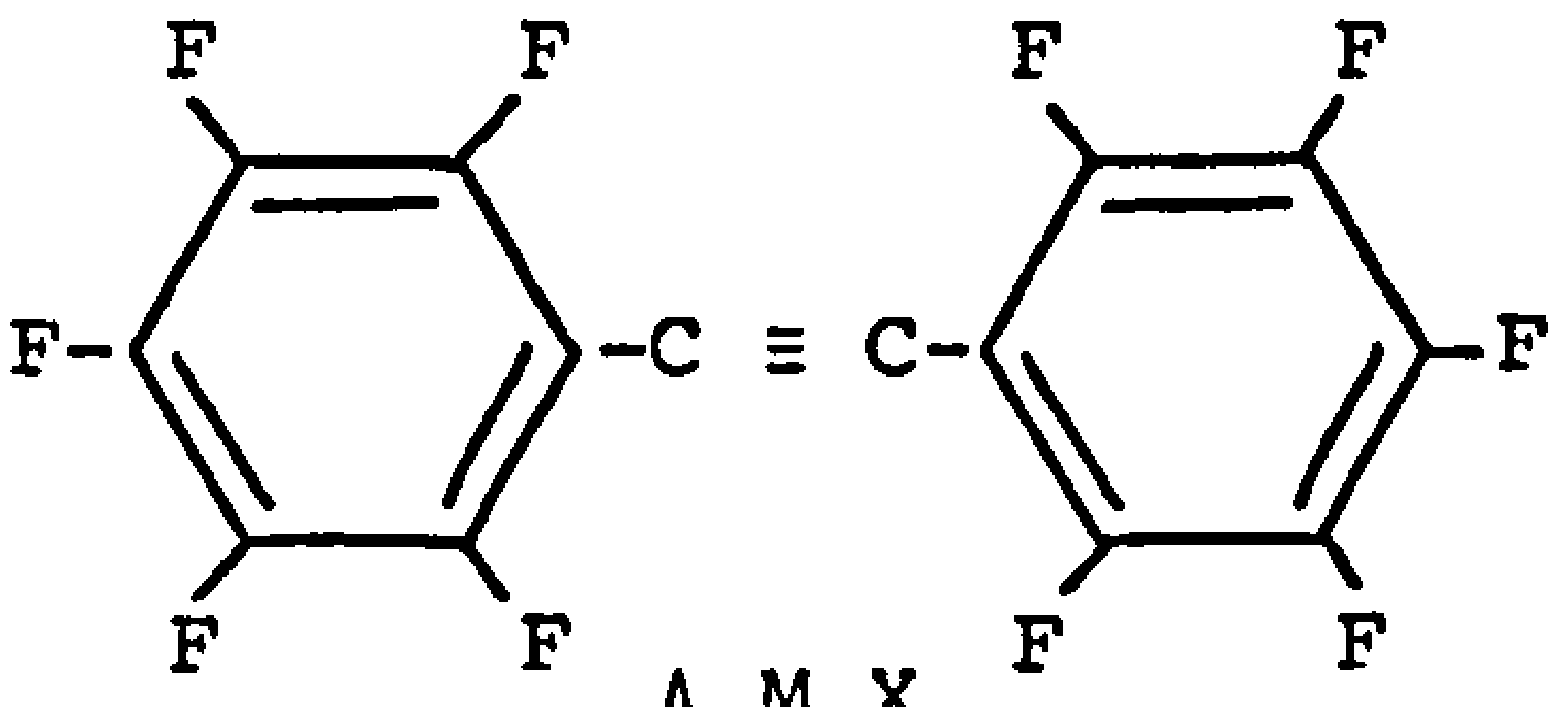
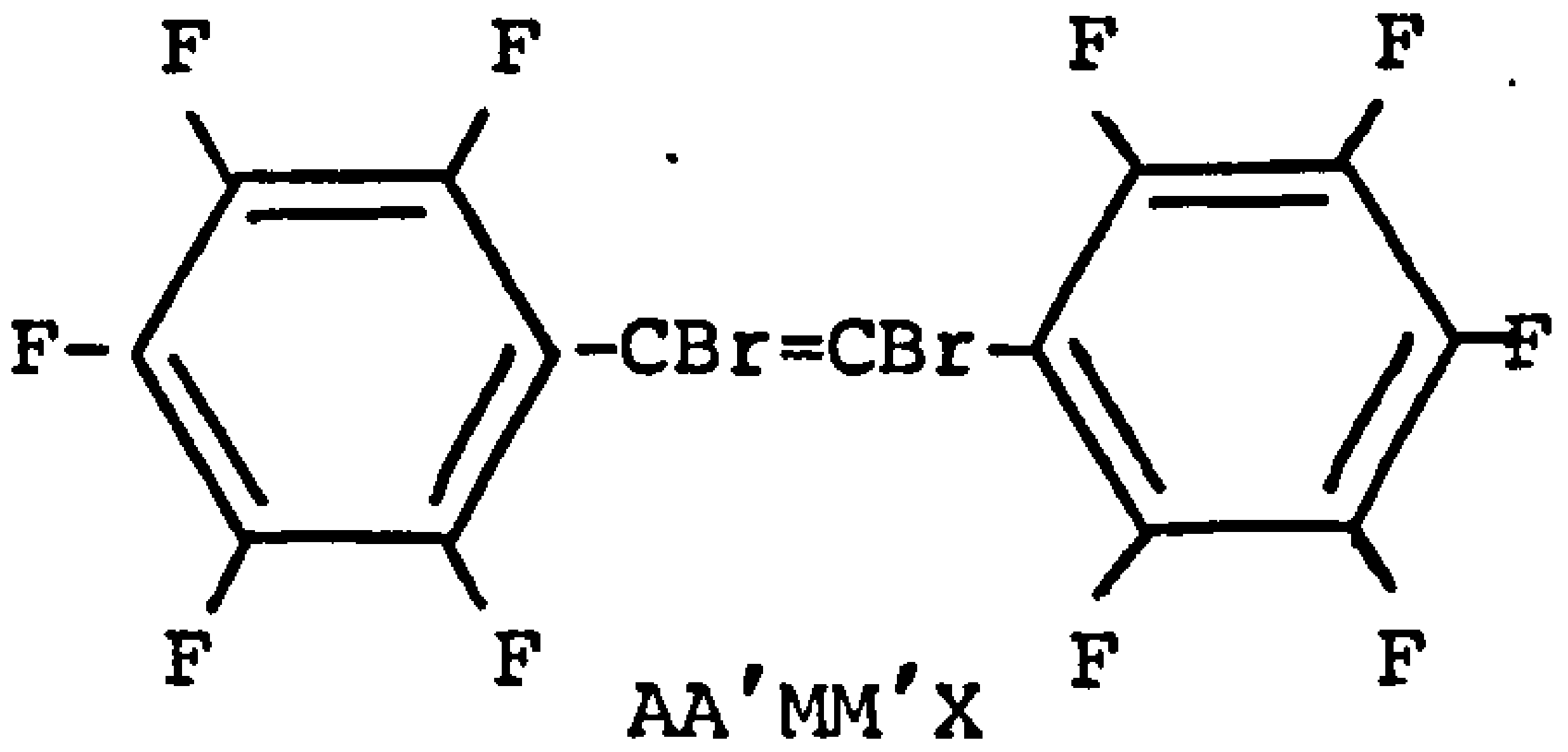
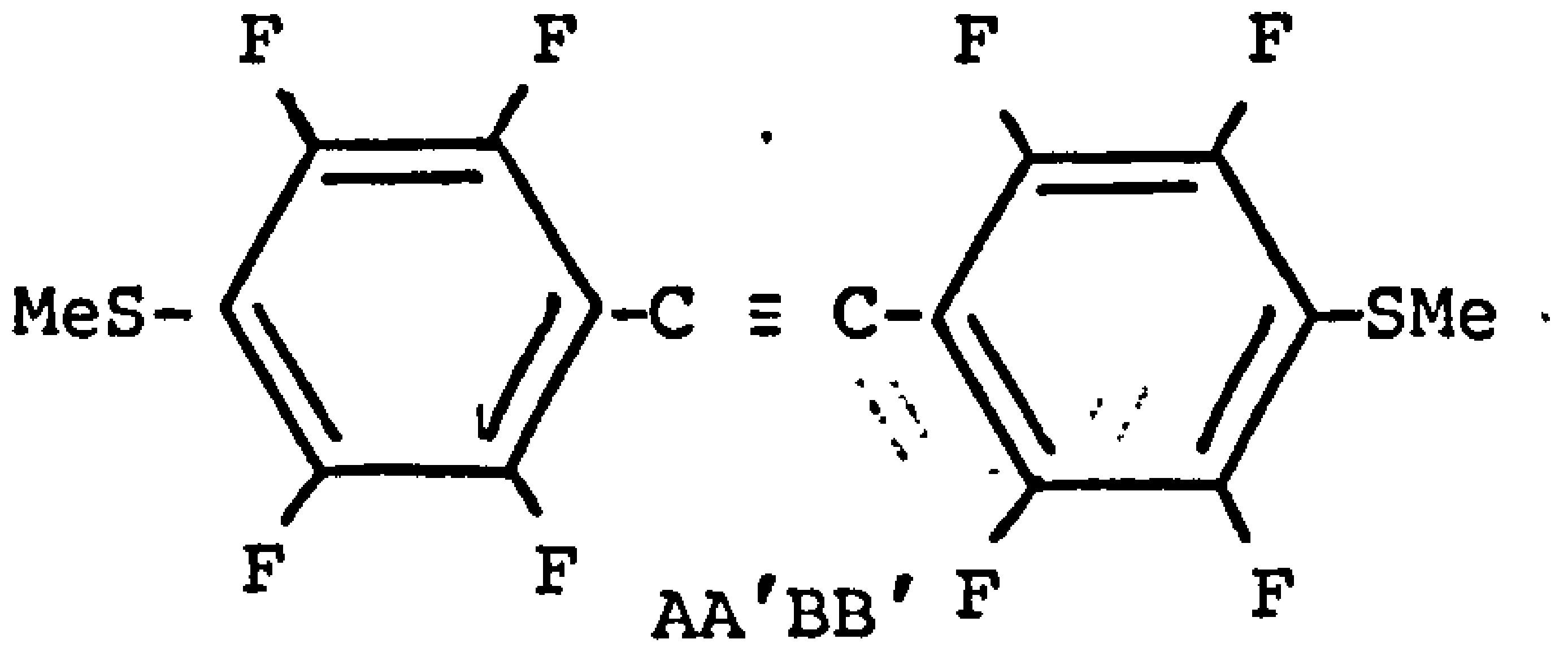
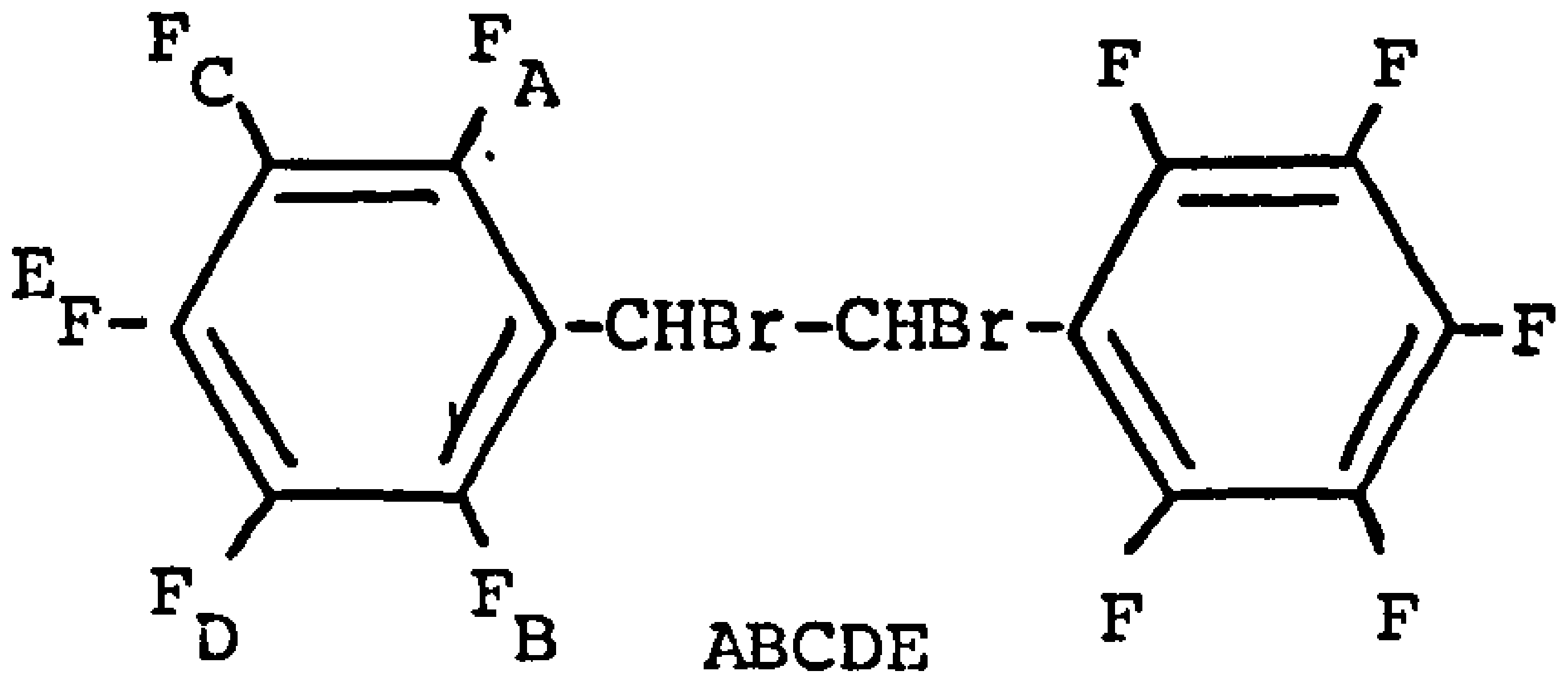
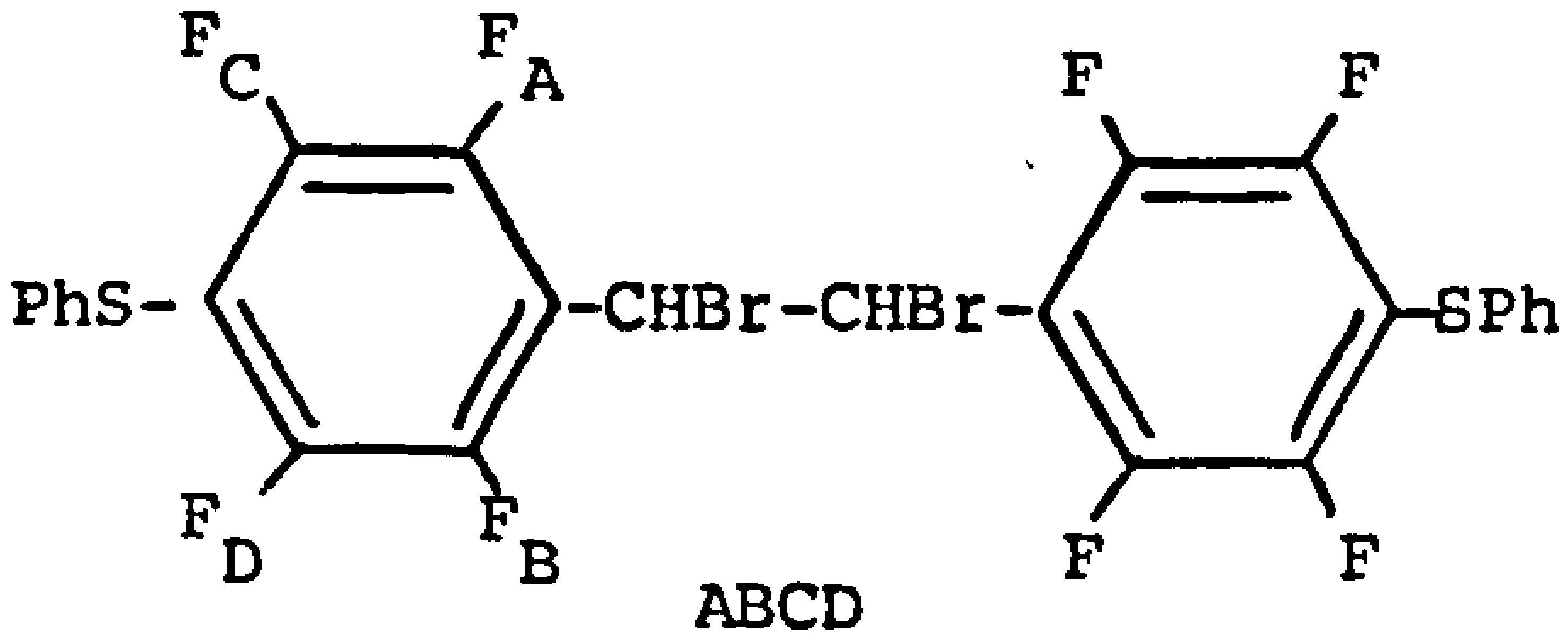
Compound	ortho	meta	para
 A_2M_2X	135.15 m	161.42 m	150.17 t
 AA'MM'X	139.75	161.28	151.25
 AA'BB'	135.59	137.17	
 ABCDE	A=139.4 B=141.7	C=151.3 D=-160.6	E=160.8
 ABCD	A=-132.1 B=-132.4	C=-139.1 D=-141.5	

TABLE (4) contd.

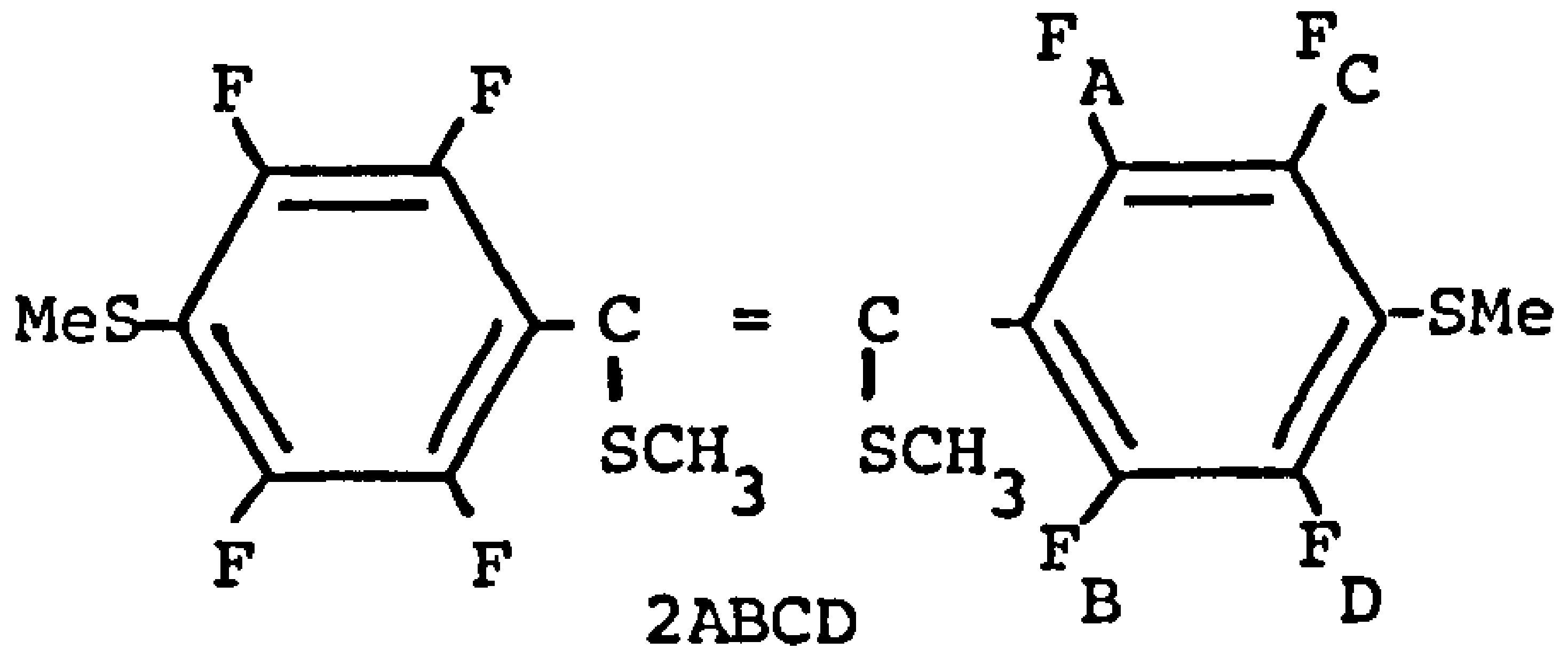
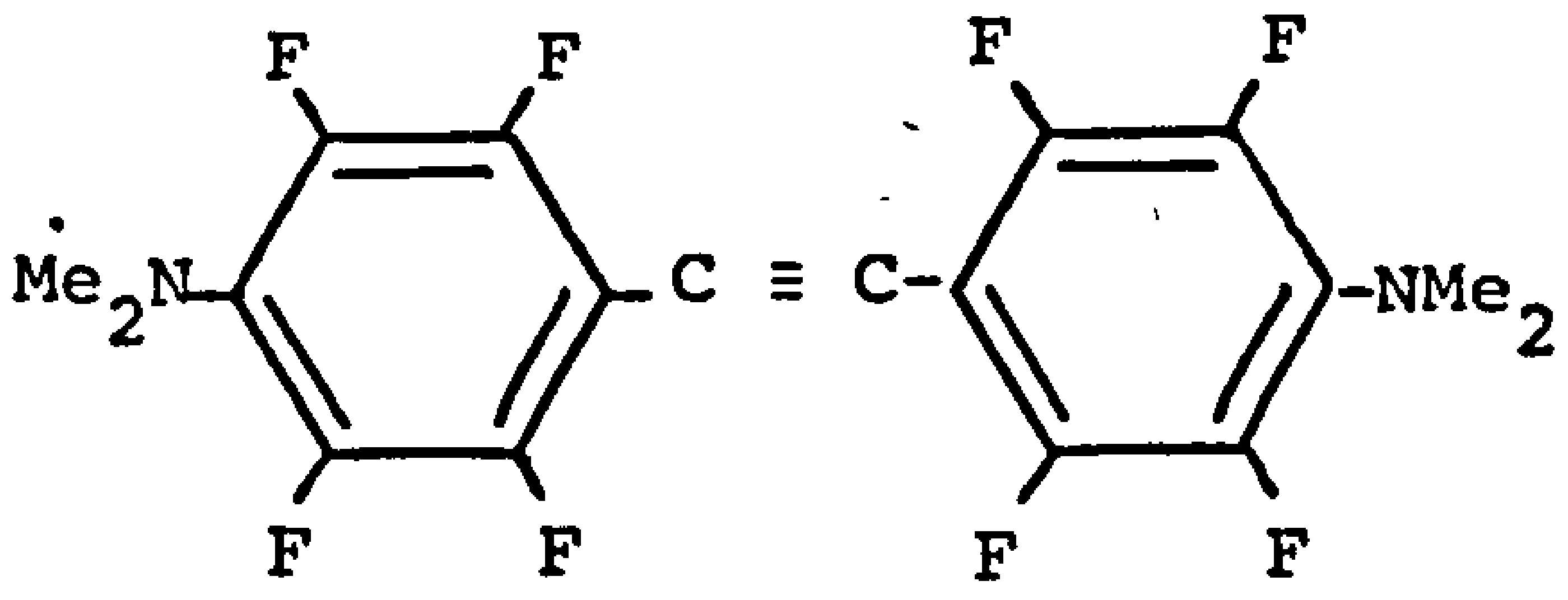
Compound	1st isomer	2nd isomer
	A = -135.1 B = 135.2 C = 138.4 D = 140.8	A = 136.1 B = 136.2 C = 137.5 D = 141.6
	- see text -	

TABLE (5)

Coupling constants of fluorinated derivatives

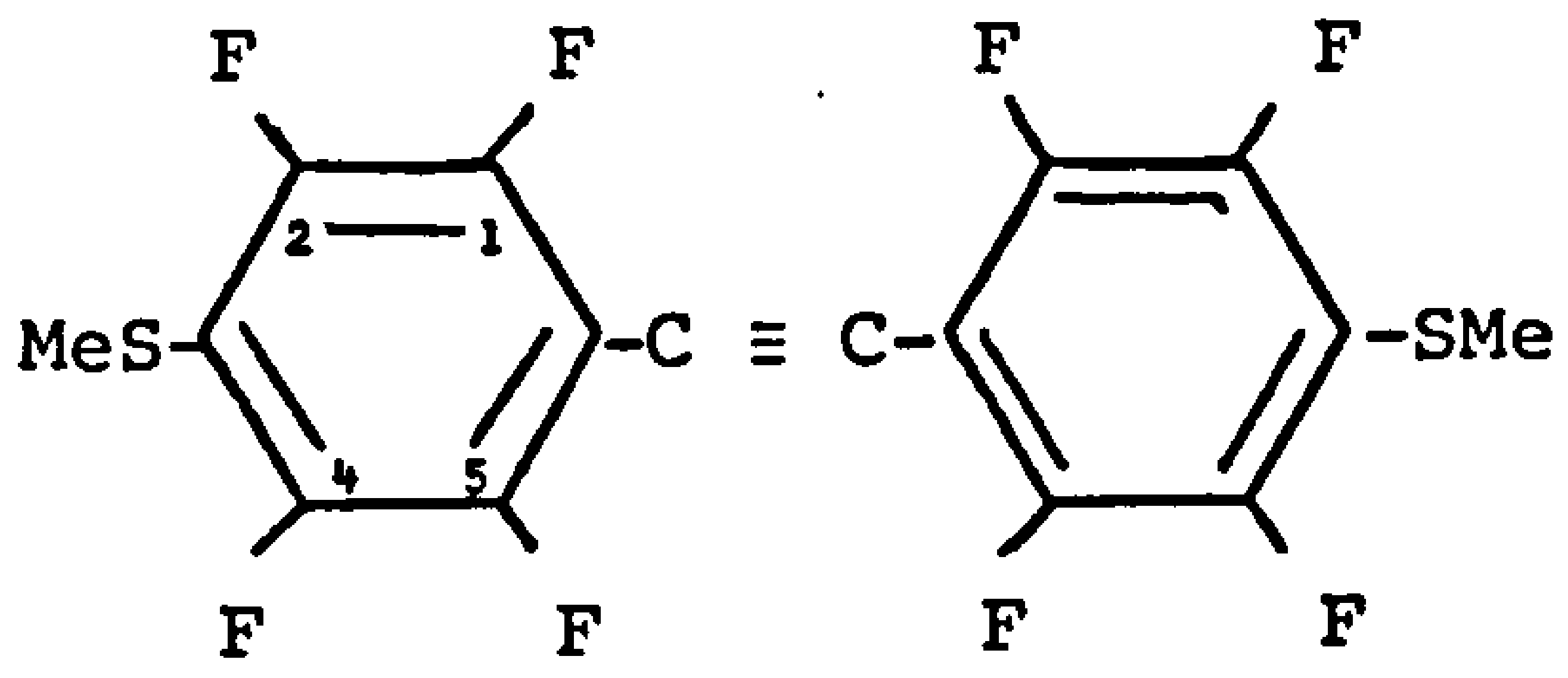
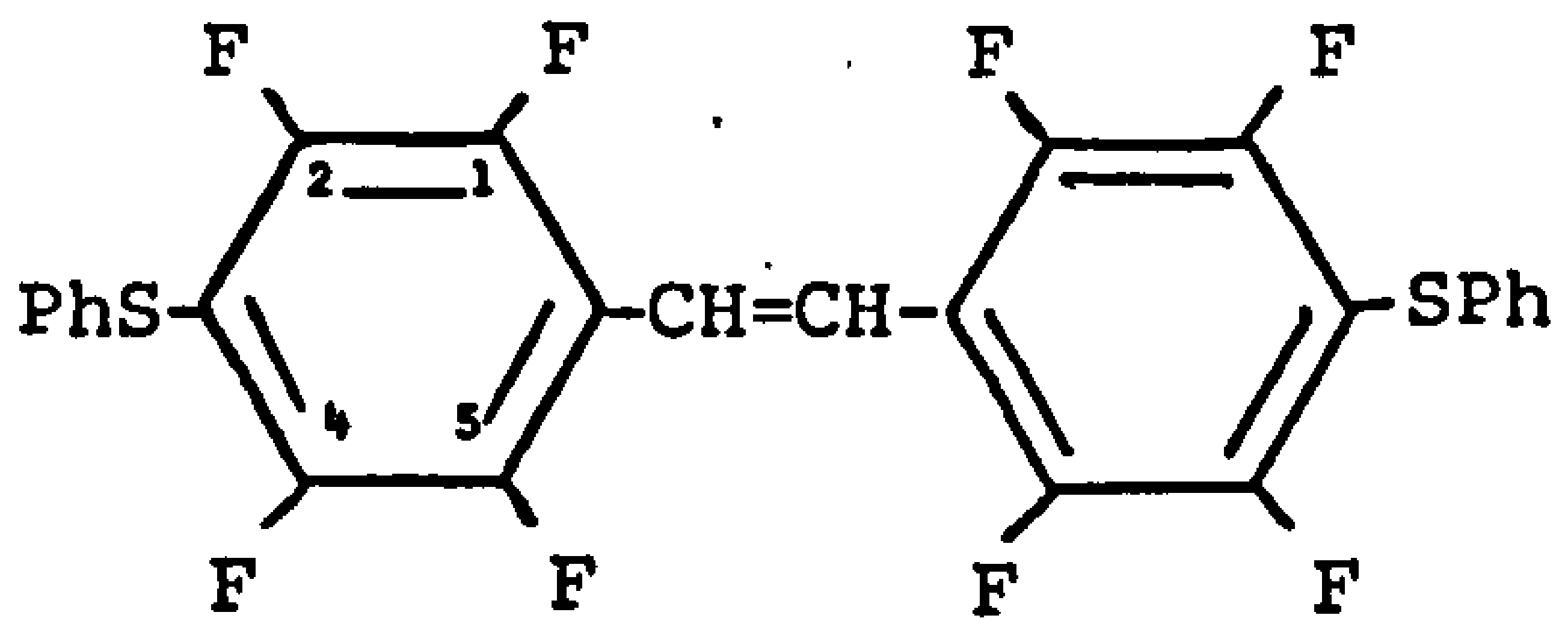
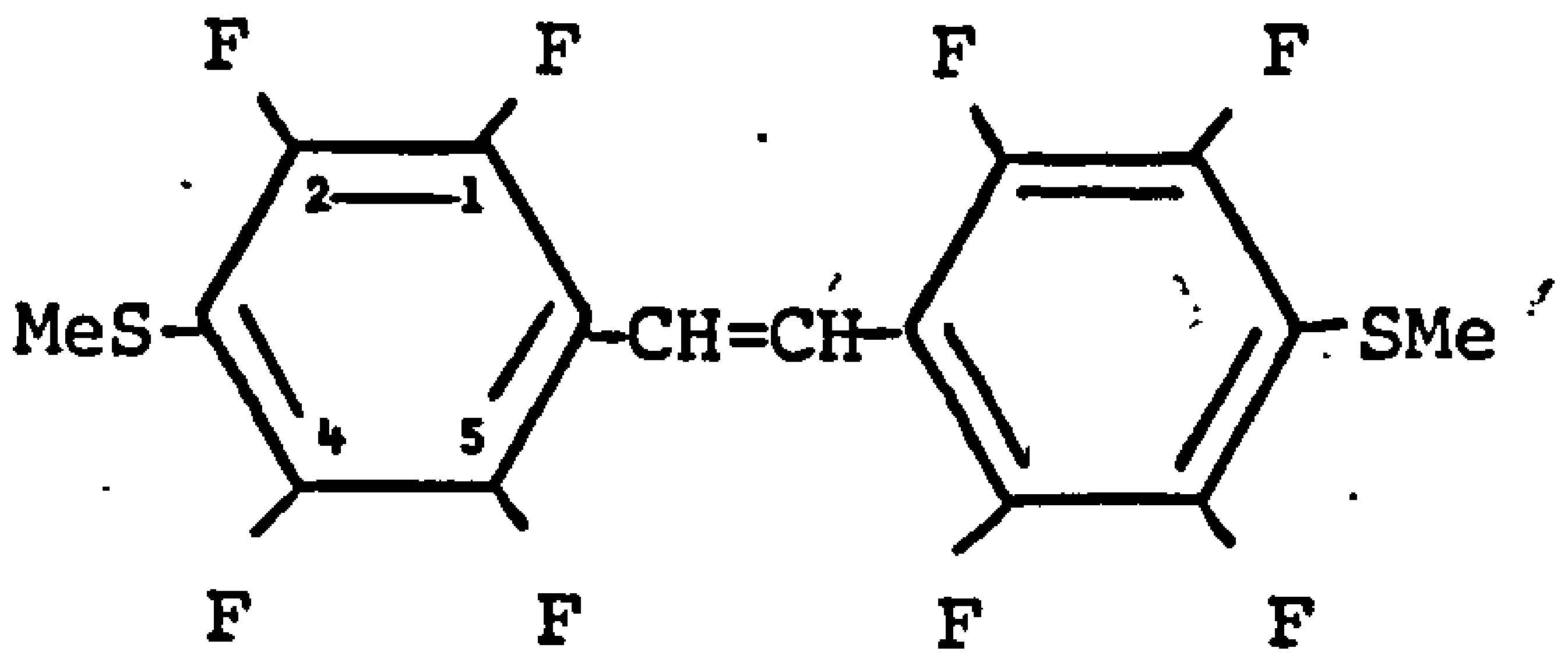
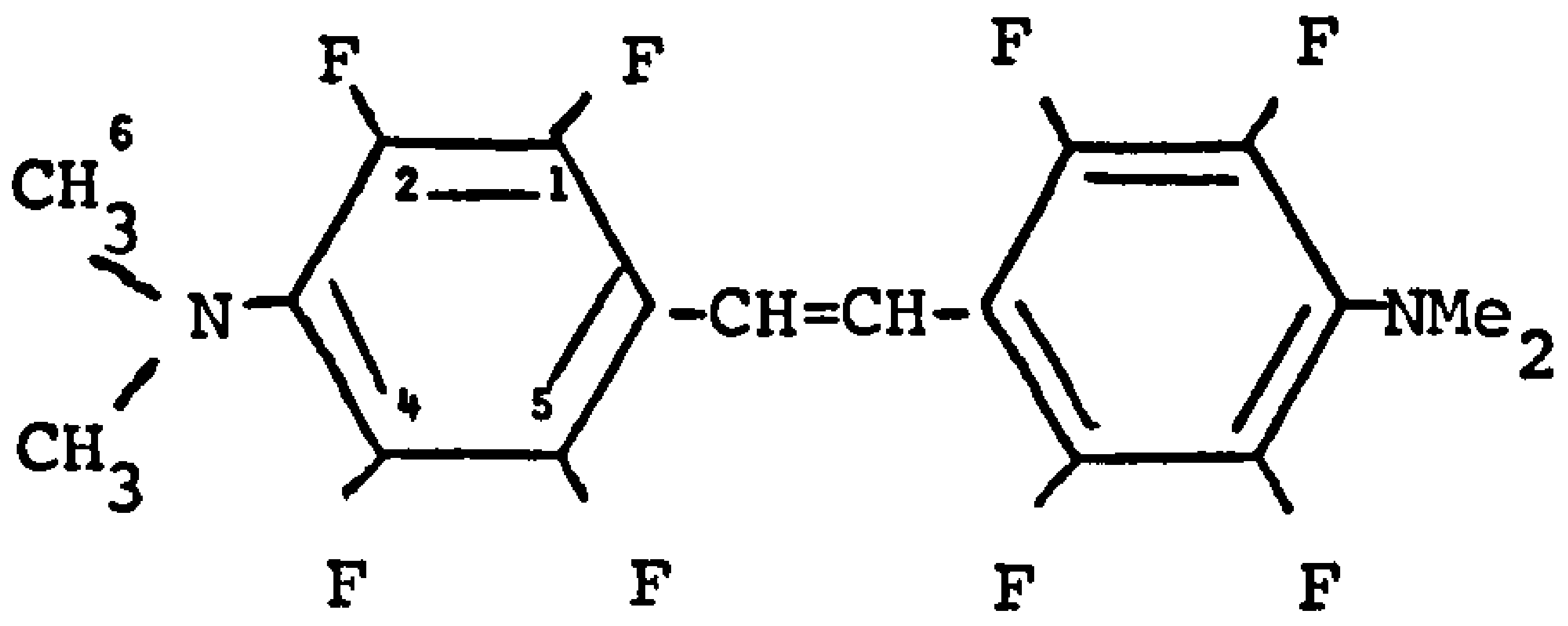
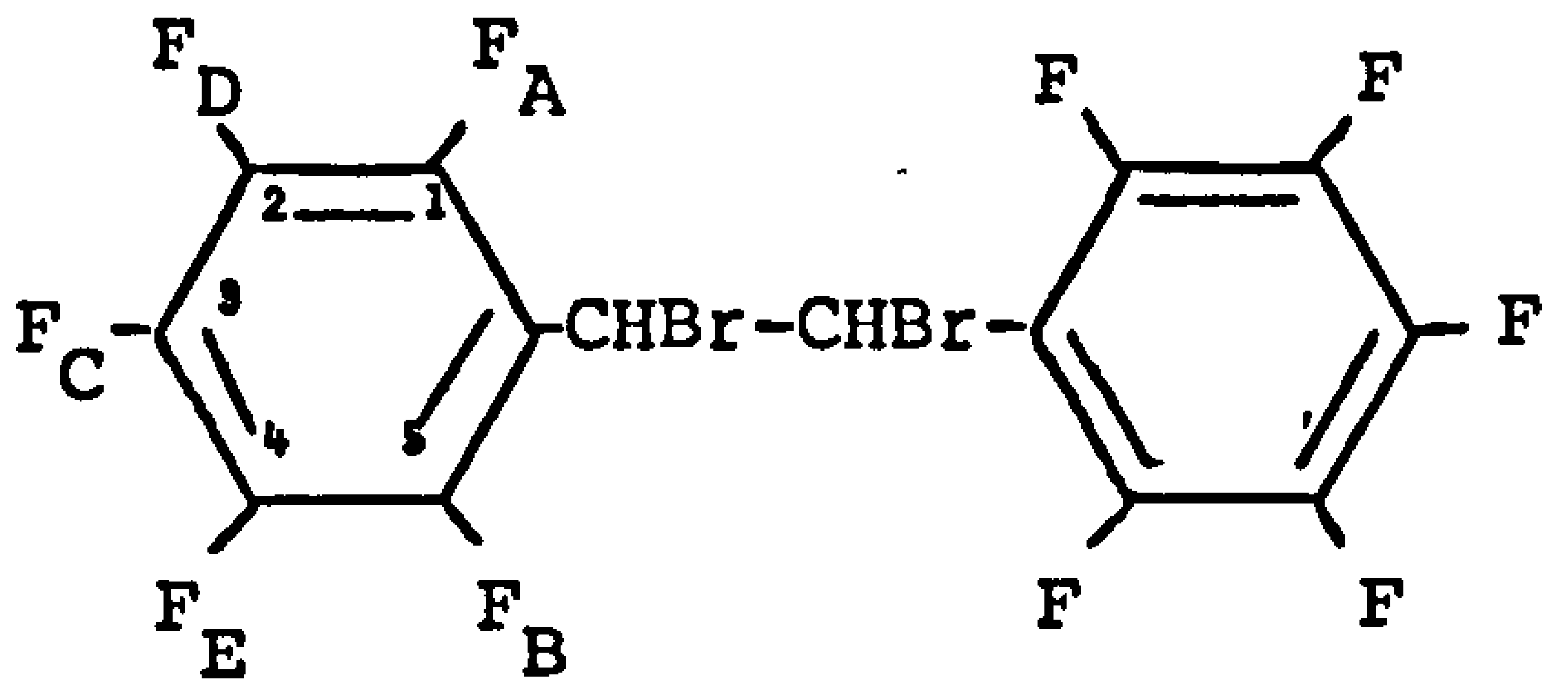
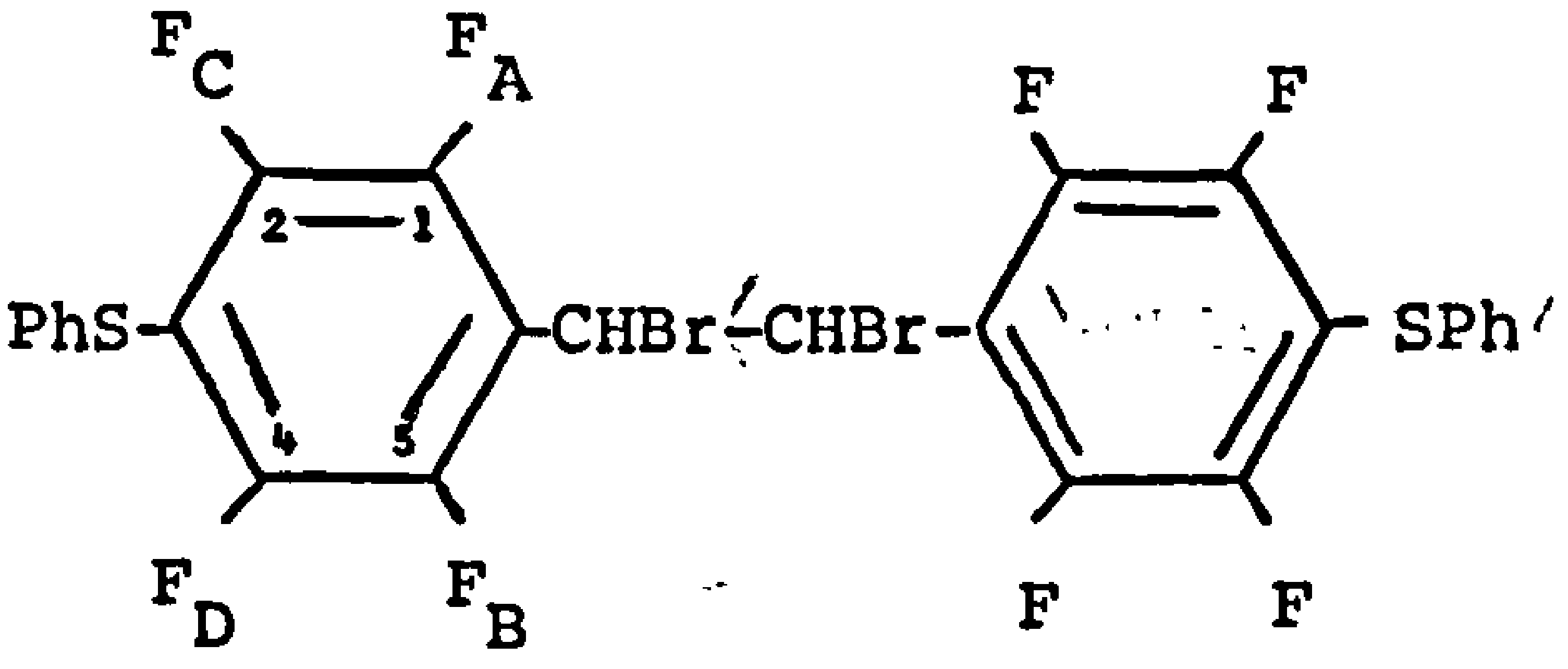
Compound	Coupling constant Hz
	J(1-5) 3.1 J(2-4) 0.6 J(1-2) 23.6 J(1-4) 10.6
	J(1-5) 2.3 J(2-4) 2.3 J(1-2) 22.8 J(1-4) 12.1
	J(1-5) 1.9 J(2-4) 1.9 J(1-2) 21.9 J(1-4) 11.4
	J(1-5) 2.4 J(2-4) 2.4 J(1-2) 19.4 J(1-4) 8.7 J(2-6) 2.1

TABLE (5) contd.



J(1-5)	6.3
J(2-3)	20.9
J(4-5)	22.4
J(1-4)	8.2
J(3-5)	2.8
J(1-2)	21.8
J(2-4)	1.1
J(2-5)	7.9
J(1-3)	3.6



J(1-5)	2.0
J(1-4)	14.5
J(1-2)	12.2
J(2-5)	23.3
J(4-5)	12.1
J(2-4)	5.0

CHAPTER 4

PRODUCTS FROM THE FREE RADICAL ADDITION OF THIOLS TO ACETYLENES

CHAPTER 4

PRODUCTS FROM THE FREE RADICAL ADDITION OF THIOLS TO ACETYLENES

Free radical addition of thiols to acetylenes has received very little attention[150] compared with reactions with olefines.[88,151,152] Addition of thiols to acetylenes has been known for more than 50 years.[79] One of the first examples of such addition of thiols to an acetylene was by Köhler and Potter in 1935 who added p-thiocresol to phenylacetylene giving a quantitative yield of a mixture of an equal amount of cis- and trans-isomers of p-tolyl-β-styryl sulfide. Twenty five years later Truce

$$p - CH_3C_6H_4SH + PhC{\equiv}CH \longrightarrow C_6H_5CH{=}CHSC_6H_4CH_3$$

and co-workers[153] showed by carrying out the same reaction in the presence of a peroxide catalyst, that the addition took place by a chain mechanism probably involving free radicals. However, it was not possible to decide whether the equal amount of the two isomeric monoadducts is a result of the addition or of post isomerisation. Both groups of authors had their reaction mixture at about 80°C. Indeed, Köhler and Potter[79] mention that the higher melting cis compound is slowly isomerized to the trans isomer by distillation. In 1950, Smith and Davis [154] added benzenethiol to phenylacetylene at 0°C without a catalyst, probably by a radical mechanism. By distillation in vacuo, which may have caused isomerization, they obtained a 70% mixture of the cis- and trans- monoadducts as liquids.

$$C_6H_5SH + C_6H_5C{\equiv}CH \longrightarrow C_6H_5SCH{=}CHC_6H_5$$

Blomquist and Wolinsky[155] reacted ethanethiol with a series of acetylenic compounds under ultraviolet irradiation. However in most cases they identified only the corresponding diadducts as a result of the long irradiation period (2 weeks) and the excess of the ethanethiol used. Because of the ease of post isomerization in this system, the isomer ratios of cis- and trans-monoadducts were determined at room temperature by nuclear magnetic resonance (n.m.r.)[156,157,158] and infra-red spectroscopy (i.r.)[158]

Methanethiol has been reported to react with acetylene and carbon monoxide under the influence of a peroxide catalyst and pressure to give $CH_3SCH{=}CHCHO$ and $CH_3SCH_2CH_2SCH_3$[159]

$$RSH + CO + HC{\equiv}CH \longrightarrow RSCH_2CH_2SR + RSCH{=}CHCHO$$

With $HC{\equiv}CCH_2OH$, under similar conditions, it reacts to give $CH_3SCH_2CH(SCH_3)CH_2OH$,[160] under uv irradiation and in the presence of a catalyst and with $CH_3C{\equiv}CH$ to afford $CH_3SCH(CH_3)CH_2SCH_3$.[161,117] No reactions were reported between fluorinated acetylenes and CH_3SH prior to 1978.[117] However, addition across the triple bond of these compounds has been previously studied for several systems[162,163,164] including H_2S,[165] alcohols[166], phosphines,[167,168] arsines,[168-169] and

$$CH_3C{\equiv}CH + H_2S \longrightarrow CH_3CH{=}CHSH + CH_3CHSHCH_2SH$$

amines.[166]

In 1978 Torrens reacted methylthiol with fluorinated acetylenes to produce diadducts[117] (Figure 4.1)

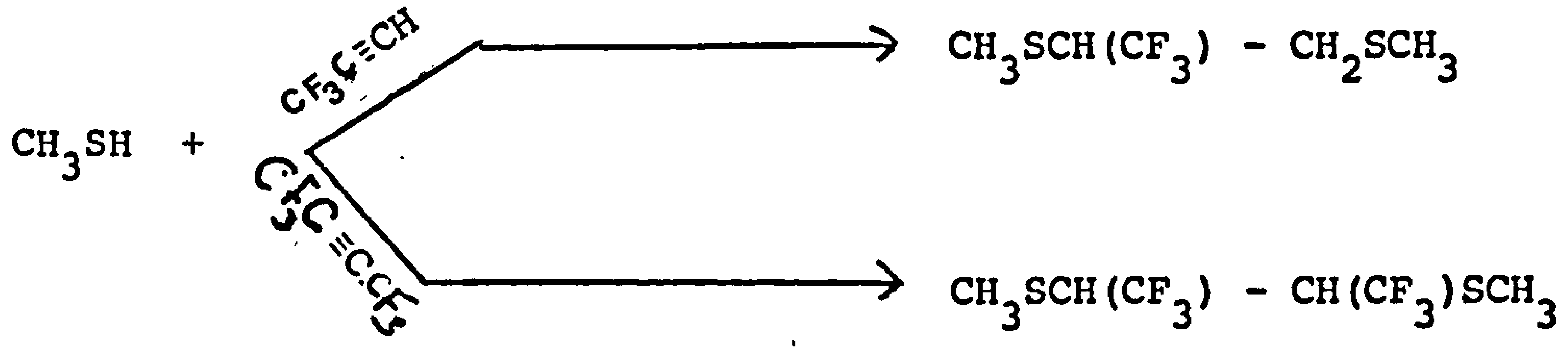


Figure (4.1) - Reactions of methylthiol with the acetylenes.

In general we obtained the products expected from anti-Markownikoff addition to the alkynes and secondary addition to the resulting olefine. The actual products obtained are given in Figure (4.1). We must emphasize that the product formed depends on the ratio of reagents and the u.v. lamp used rather than the time of irradiation. All the products were characterized by infrared spectroscopy, microanalysis, ^1H, ^{19}F n.m.r. spectroscopy and mass spectroscopy.

The IR spectrum of product I ($CH_3SCHPh-CH_2SCH_3$) revealed a very strong band between (3080-3020) cm^{-1} (CH vibration of phenyl group) between 2980-2910) (v.s.) cm^{-1} (C-H vibrations of SCH_3, CH_2 and CH groups), between 2845-2825 (br,s) cm^{-1} (C-H vibrations), bands at 1600 (s) cm^{-1}, (s), 1470, at 1450-1420 (v.s.) cm^{-1}, between 1315-1030 (s) cm^{-1}, at 695 (v.s.) cm^{-1} (all phenyl vibrations). Mass spectroscopy showed a parent ion at m/e = 198, corresponding to the parent ion $[C_{10}H_{14}S_2]^+$.

^1H n.m.r. spectroscopy indicated the structure of this compound and showed peaks corresponding to those expected for a rapid interconversion of rotamers.[170]

In the present work it was found that on u.v. irradiation in quartz apparatus in the presence of acetylenes and thiols CH_3SH or Bu^tSH undergo the addition reactions as shown below (Table 4-1).

TABLE (4-1)

Photochemical Addition of CH_3SH or Bu^tSH to acetylene

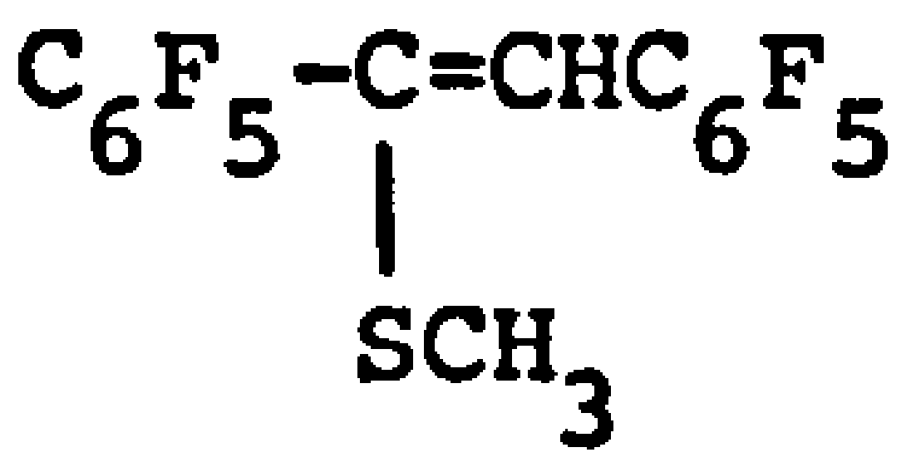
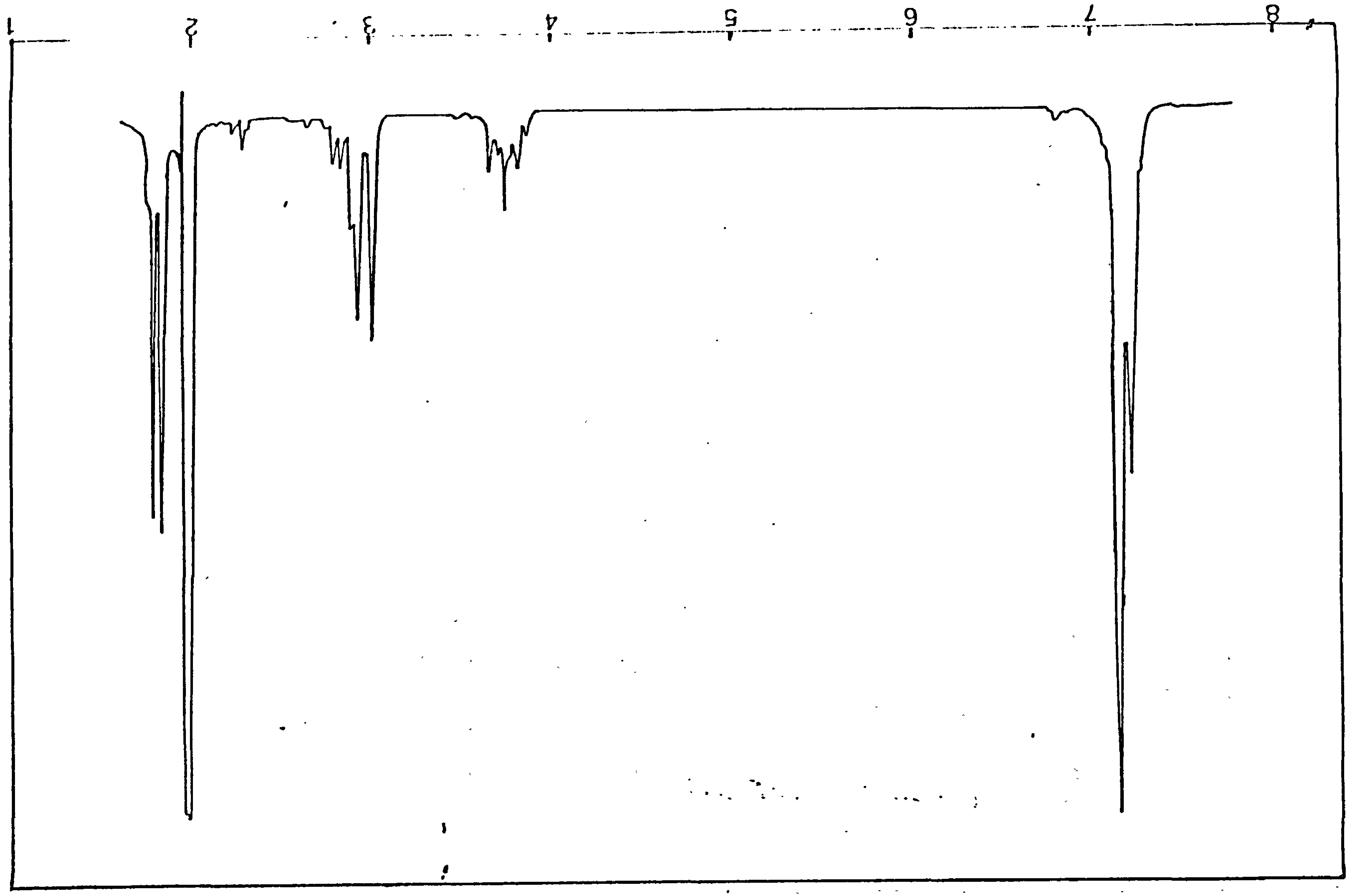
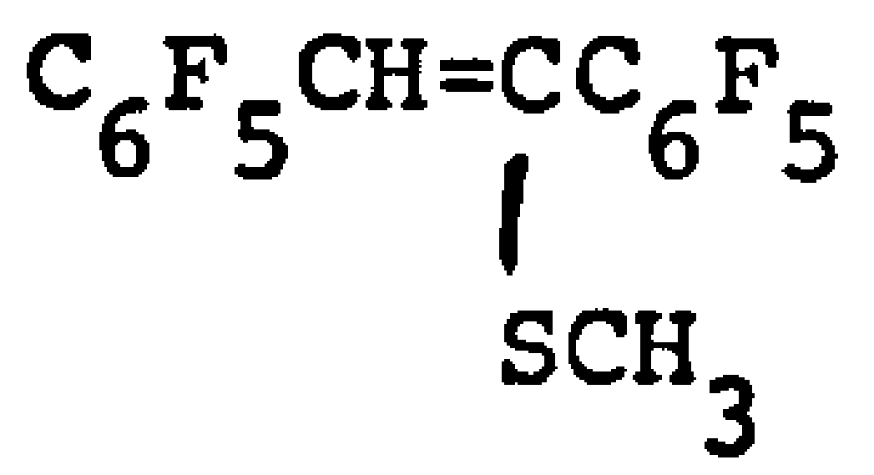
Alkyne		Product
$PhC\equiv CH$		$CH_3SCHPhCH_2SCH_3$ (I)
$PhC\equiv Ph$		$(CH_3S)_2CPh\text{-}CHPhSCH_3$ (II) +
	$\xrightarrow[h\nu]{CH_3SH}$	$CH_3SCHPh\text{-}CHPhSCH_3$ (III)
$PhC\equiv CPh$		$CH_3SCPh{=}CHPh$ (IV)
$C_6F_5C\equiv CC_6F_5$		 $C_6F_5\text{-}C(SCH_3){=}CHC_6F_5$ (V)
$CF_3C\equiv CCF_3$		$Bu^tS(CF_3)C{=}CH(CF_3)$ (VI)
	$\xrightarrow[h\nu]{Bu^tSH}$	$Bu^tS(CF_3)CH\text{-}CH(CF_3)SBu^t$ (VII)
$CF_3C\equiv CH$		$Bu^tSCH(CF_3)\text{-}CH_2SBu^t$ $Bu^tSCH{=}CH(CF_3)$ $Bu^tSC(CF_3){=}CH_2$

Figure (4.2) - ^{1}H nmr spectrum of ($CH_3SCH_2CHPhSCH_3$)

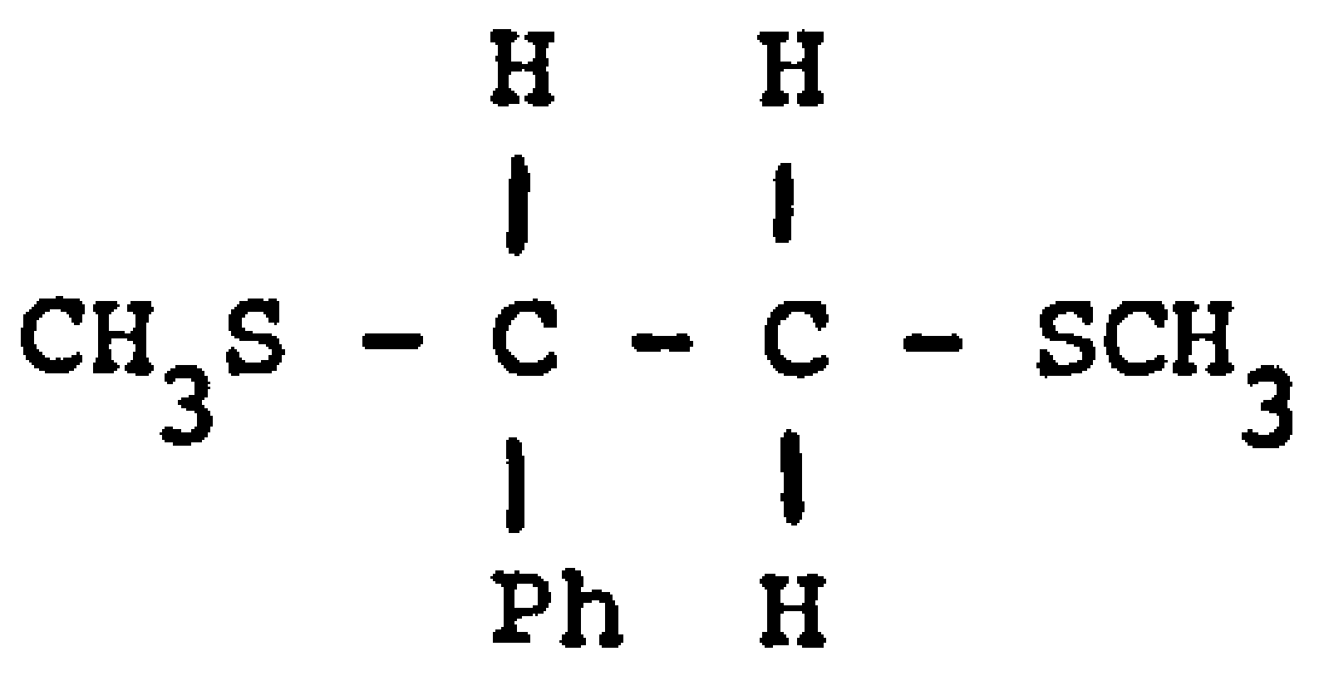


Conditions for Reactions in Table (4-2)

Acetylene	Time	Thiol	Conversion	Products
PhC≡CH	2 weeks	CH_3SH	85%	$CH_3SCHPhCH_2SCH_3$ (I)
PhC≡CPh	1 week	CH_3SH	5%	$(CH_3S)_2CPh-CHPhSCH_3$ (II) +
			90%	$CH_3SCHPh-CHPhSCH_3$ (III)
PhC≡CPh	2 weeks	CH_3SH	80%	$CH_3SCPh=CHPh$ (IV)
$C_6F_5C≡CC_6F_5$	4 weeks	CH_3SH	12%	 $C_6F_5CH=C(SCH_3)C_6F_5$ (V)
$CF_3C≡CCF_3$	10 days	Bu^tSH	15%	$Bu^tSC(CF_3)=CH(CF_3)$ (VI)
$CF_3C≡CCF_3$	3 days	Bu^tSH	10%	$Bu^tSCH(CF_3)-CH(CF_3)SBu^t$ (VII)
$CF_3C≡CH$	3 days	Bu^tSH	13%	$Bu^tSCH(CF_3)-CH_2SBu^t$ (VIII) + $Bu^tSCH=CHCF_3$[a] (IV) + $Bu^tSC(CF_3)=CH_2$[a]

[a] Not isolated

The chemical shift of phenyl C$\underline{\underline{H}}$ is at 7.26 ppm. The methylene group adjacent to an asymmetric centre has non-equivalent protons. i.e. in different environments, and each proton couples with the other



$$\mathrm{CH_3S-\overset{H}{\underset{Ph}{C}}-\overset{H}{\underset{H}{C}}-SCH_3}$$

[The methylene protons are non-equivalent even assuming fast rotation around the central C-C bond]. The spectra of this compound were simple and first order, see Figure (4-2).

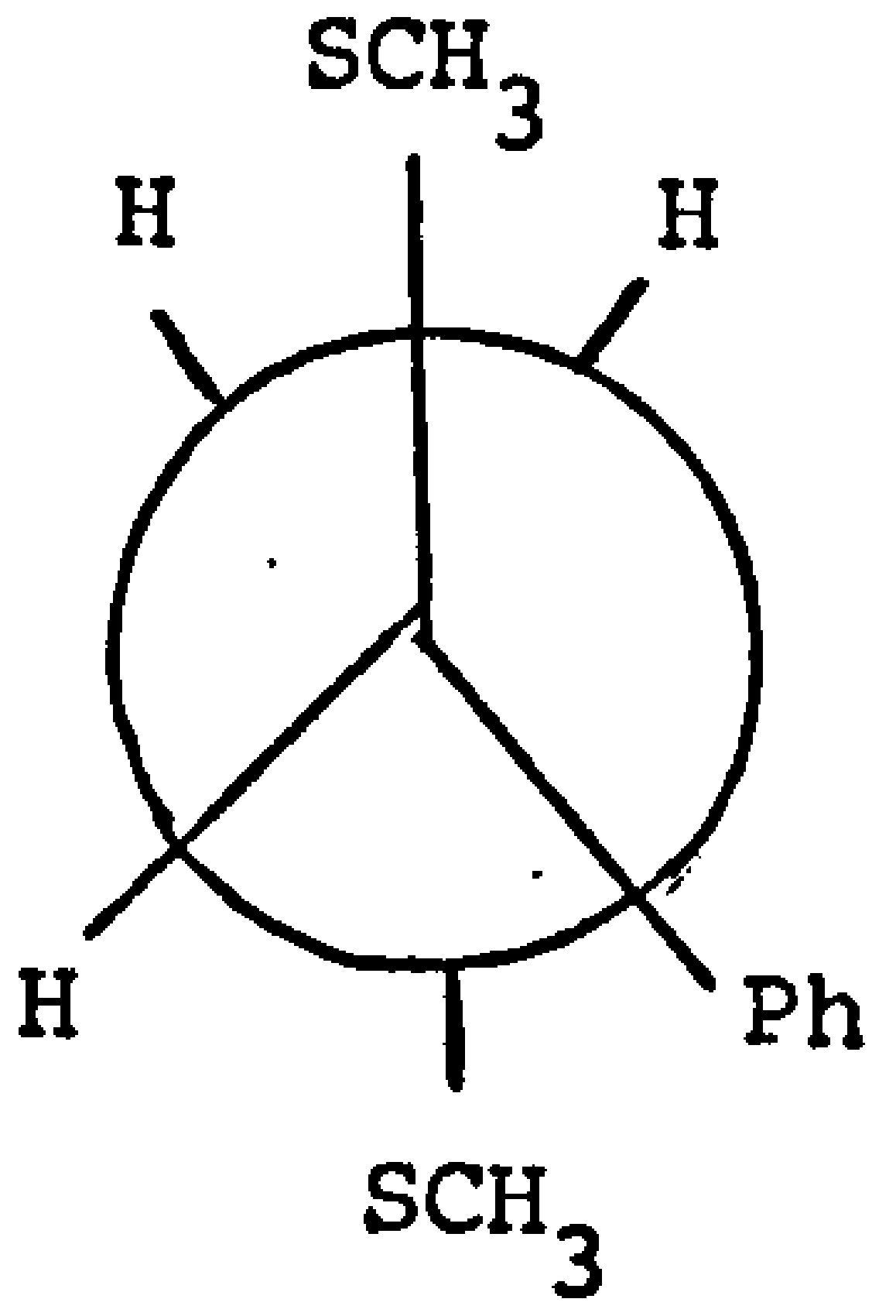


Figure (4-3) - Newman diagram for $CH_3SCH_2CHPhSCH_3$.

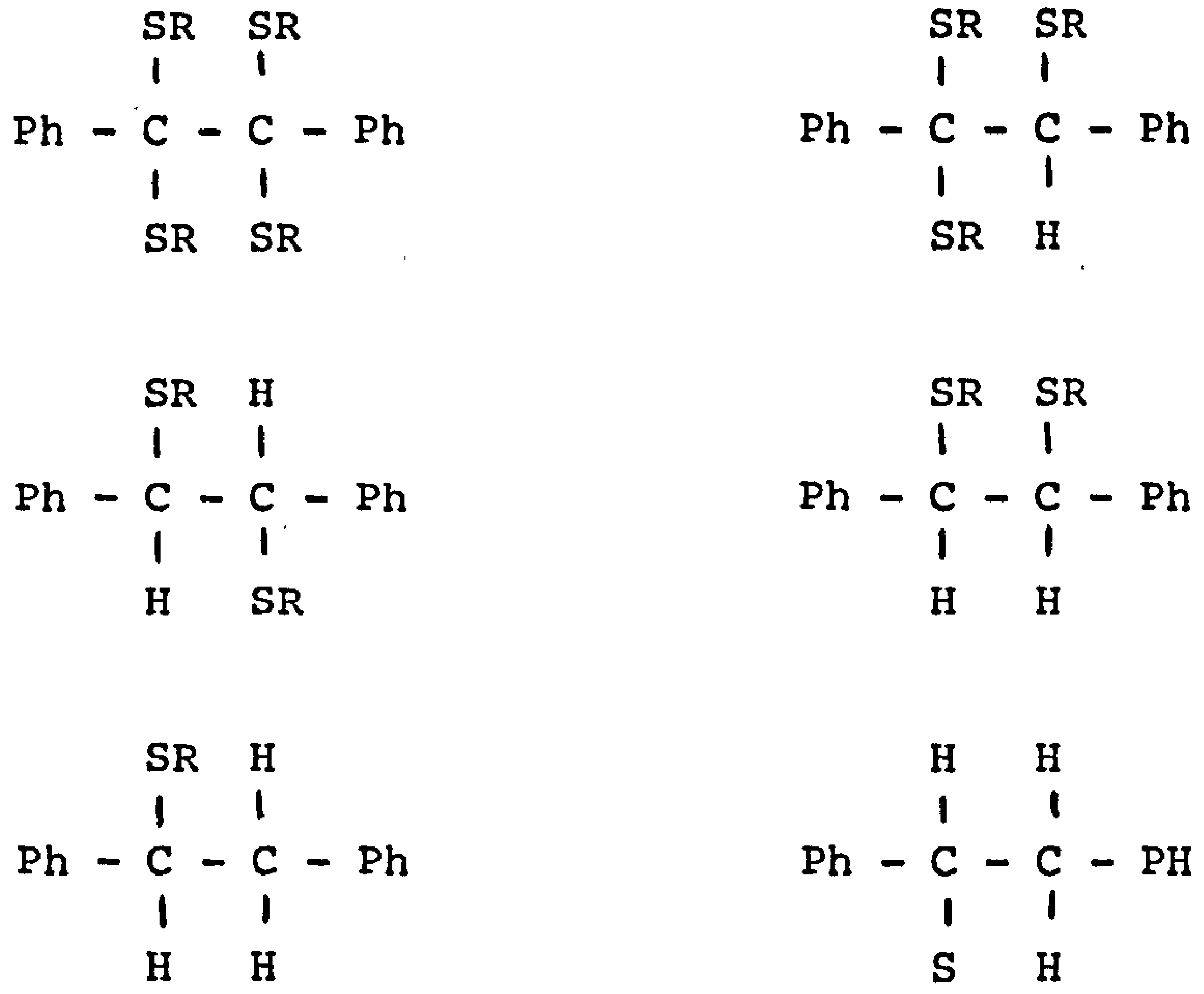
TABLE (4-3)

N.m.r. Parameters of $CH_3SCH(R)CH(R)SCH_3$, R=H, CH_3, CF_3, Ph

Compound	δSCH_3	SCH	SPh	δCH_2	Ref.
(1) (2) $CH_3SCH(CH_3)CH_2SCH_3$	2.52 (1)	3.12	-	-	117
	2.54 (2)				
(1) (2) $CH_3CH(CF_3)CH_2SCH_3$	2.77 (1)	3.87m	-	3.46	117
	2.71 (2)				
(1) (2) $CH_3SCHPhCH_2SCH_3$	1.81 (1)	3.74^b	7.3	$2.95m^b$	-
	1.95 (2)				

[b] Approximate shift of the multiplet.

According to Scheme (2) Chapter (2) six different saturated products are possible when thiols RSH are added to the symmetric acetylene AC=CA, as illustrated below, Figure (4-4).



Experimentally products $(CH_3S)_2CPh\text{-}CHPhSCH_3$ and $(CH_3S)CHPhCHPh(SCH_3)$ were detected by mass spectroscopy and ^1H spectroscopy. $(CH_3S)_2CPh\text{-}CHPh(SCH_3)$ was isolated as colourless crystals with melting point 157°C. Mass spectra showed m/e = 273 corresponding to $[C_{17}H_{20}S_3]^+$, that is the parent ion with loss of $[SCH_3]^+$. This compound is further identified by the appearance of the fragment $[(CH_3S)_2CPh]^+$ m/e = 183 in the mass spectrum. ^1H n.m.r. spectra showed peaks at 3.95 for C-H protons and at 1.6 ppm and 1.23 ppm for SCH_3 protons corresponding to non-equivalent SCH_3 groups. The proportion of the compound just described is very small, about 5%; the proportion of the symmetric compound $CH_3SCHPhCHPhSCH_3$ produced was greater than 90%.

The mass spectra of $(CH_3SCHPh\text{-}CHPhSCH_3)$ shows a peak at m/e = 226 corresponding to the ion $(C_{16}H_{18}S_2]^+$ which is the parent ion less a (SCH_3) group. IR spectra of this compound have bands at 3029 (s) cm^{-1} (C-H vibration of phenyl groups), at 2950-2860 (v.s.) cm^{-1} (C-H vibration of CH_3 groups and C-H groups), at 1590 and 1340-920 (m) cm^{-1} (aromatic vibrations).

$CH_3SCHPhCH(Ph)SCH_3$ having two asymmetric carbon atoms should adopt meso and (±) isomeric structures as shown in the figure below

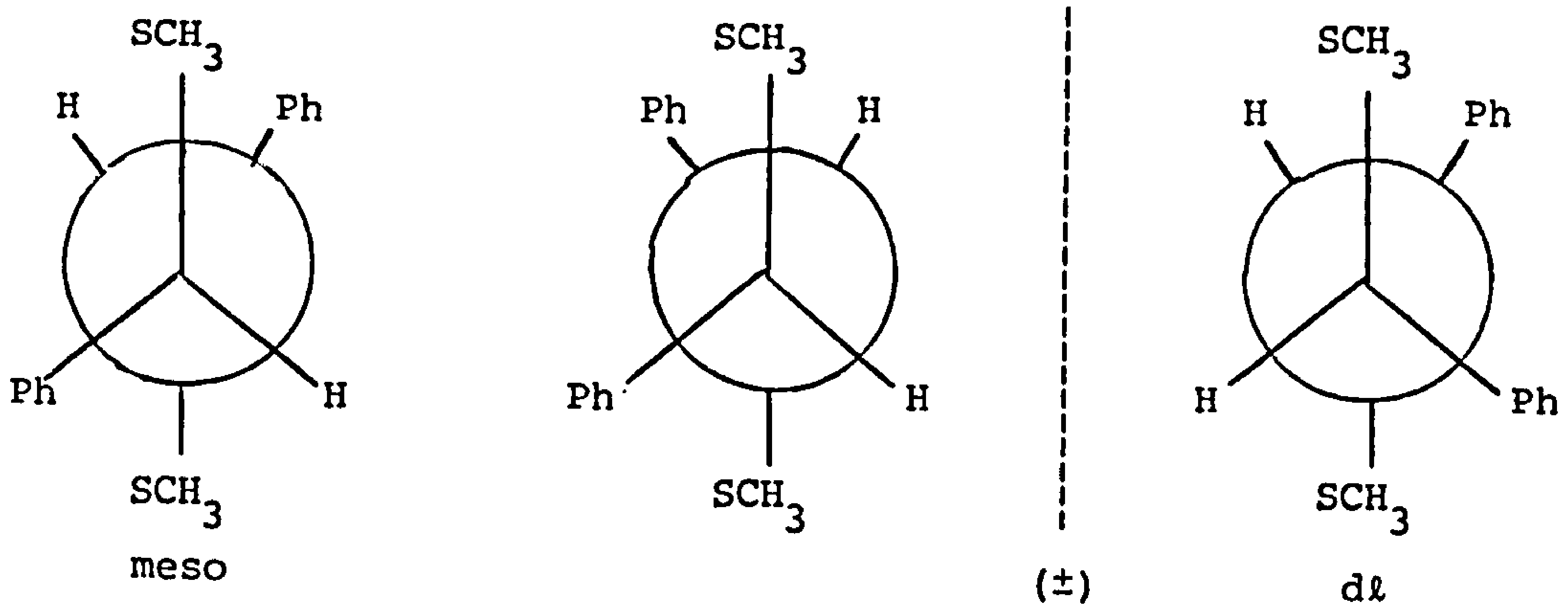


Figure (4:5) - meso and dℓ in 1,2-bis(methylthio)-1,2-diphenyl)ethene.

TABLE (4-4)

N.m.r. parameters of $CH_3SCH(R)CH(R)SCH_3$, R = CH_3, CF_3, Ph

Chemical Shifts[a]

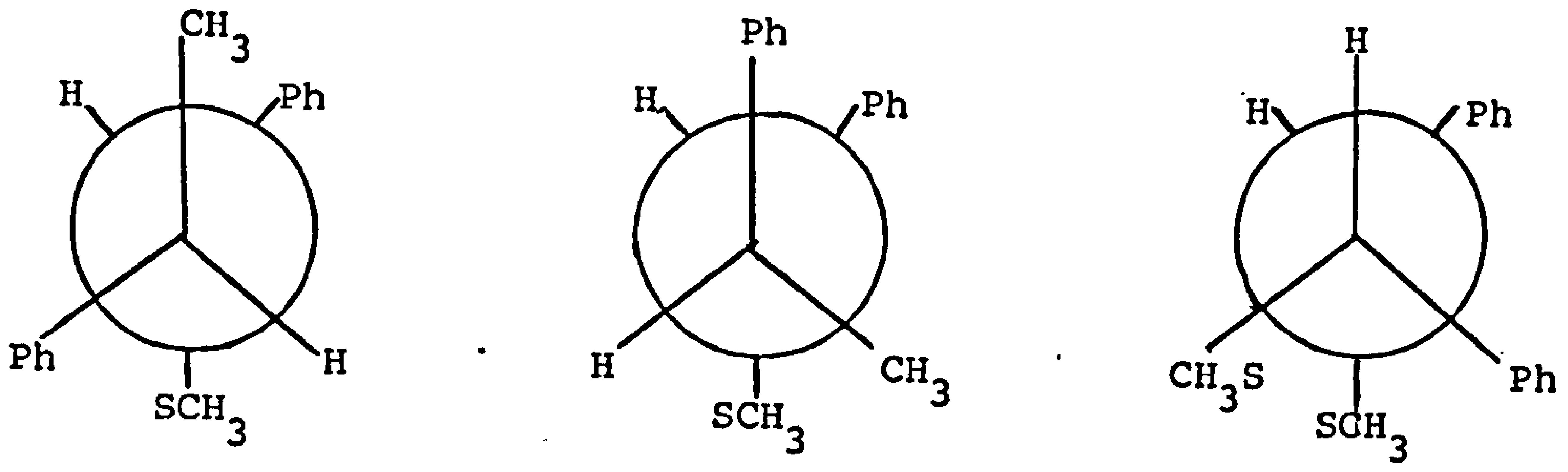
Compound	δCH_3S	δ^b CH-CH_n	δCH_3	SPh	δCF_3
$CH_3SCH(CH_3)CH(CH_3)SCH_3$[117]	meso 2.31	3.00	1.56	-	-
	(±) 1.90	-	1.43	-	-
$CH_3SCH(CF_3)CH(CF_3)SCH_3$[117]	meso 2.88	4.17	-	-	-73.5
	(±) 2.83	-	-		-78.2
$(CH_3)SCHPhCHPhSCH_3$	br 2.07	3.37	-	7.2	-
$(CH_3S)_2CPh-CHPhSCH_3$	1.23	3.95	-	7.25	-
	1.60	-	-	-	-

---

[a] Values of ^1H in ppm from external TMS. Values of ^{19}F positive to low field of external $CC\ell_3F$.

[b] Approximate shift of the multiplet.

Corresponding groups in the (±) isomer are magnetically equivalent in any rotamer and form ($2A_3 + 2(N_2X_5)$) systems where A = SCH_3, N = H and X = C_6H_5. Groups in the meso isomer are magnetically non-equivalent in the two possible gauche conformations and equivalent in the trans



meso gauche gauche

Figure (4:6)

rotamer. Equivalence of these groups is achieved by rapid rotation about the carbon-carbon bond and the proton spectra show a broad absorption with a shoulder at 7.2 ppm from the phenyl groups. The CH group resonates at 3.37 ppm as a singlet with a shoulder at 2.07 ppm for the SCH_3 group.

Product $CH_3SCHPh{=}CHPh$, is a monoadduct of CH_3SH and PhC≡CPh. It is a colourless liquid with a bad smell. The mass spectrum shows a parent ion at m/e = 226 corresponding to $C_{15}H_{14}S^+$, the parent ion. Infrared spectroscopy shows both cis and trans isomers. The trans isomer can be readily recognised[129] by the presence of a very strong absorption peak from CH= deformation modes in the region of a 955 cm^{-1}. The cis isomer, however, exhibited no characteristic peak. The out of plane ethylenic proton deformation of the trans-benzene thiol adduct absorbed at 955 cm^{-1}, the trans-alkylmercaptan adducts at 930 cm^{-1}. The vibrations of symmetrically disubstituted trans-ethylenes usually occur at frequencies between 980 and 960 cm^{-1} [129(b)]. However, this absorption could be expected at a somewhat lower frequency because of the effect of the phenyl group. In the case of our trans-adduct the absorption occurs in the frequency range 950-880 cm^{-1}. The mixture of isomers shows absorption in the 1640-1600 cm^{-1} region due to aromatic C=C skeletal vibrations.

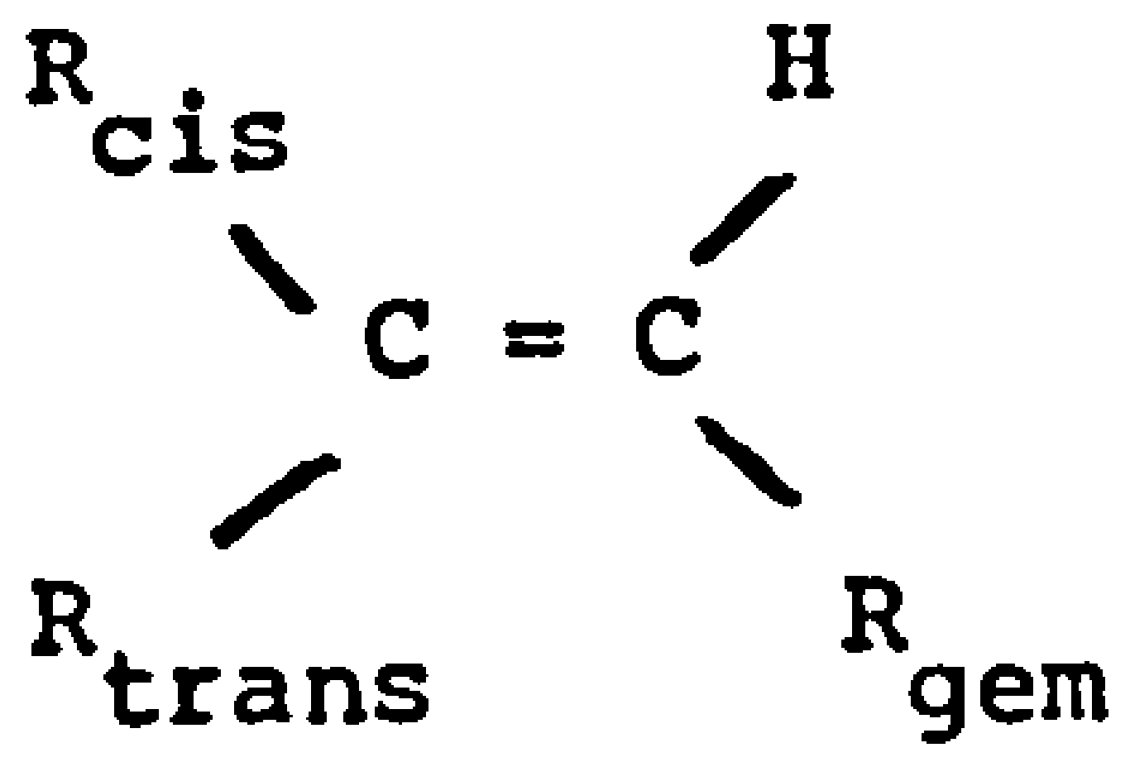
Proton nmr spectroscopy of the monoadduct $CH_3SCPh{=}CHPh$ indicated the presence of two isomers presumably of cis- and trans-forms. The chemical shifts of the ethylenic proton in the cis- and trans-forms were determined by calculation[171] and comparison with experimental results. The ratio of isomers was 1:1 trans to cis. A ^{195}Pt nmr spectrum on complexes prepared from this ligand [p.171] showed that the complexes contained some derivatives derived from the 2:1 adducts. It is clear from these results that the ligand was not pure.

Theoretical Calculation

The equation used is

$$\delta \underset{\substack{\backslash \\ H}}{C{=}C} = 5.25 + Z_{gem} + Z_{cis} + Z_{trans} \quad (171)$$

TABLE (4-5)



	Z for R (ppm)		
-R	Z_{gem}	Z_{cis}	Z_{trans}
Aromatic	1.38	0.36	- 0.07
SR	1.11	-0.29	- 0.13

Theoretical		Experimental
cis	6.27	6.4
trans	6.86	6.7

Product $CH_3SC(C_6F_5)=CHC_6F_5$ is a monoadduct of CH_3SH and $C_6F_5C\equiv CC_6F_5$. It is a colourless crystalline solid with melting point 107°C. The mass spectrum shows a parent ion at m/e = 406 corresponding to $[C_{15}H_4F_{10}S]^+$. Infrared spectroscopy shows a peak at 3026-2920 (m) cm^{-1} (C-H vibration) and 1635-1660 cm^{-1} (-C=C-). Identities were further established by nmr spectroscopy. ^1H nmr spectra showed peaks at 6.25 and 6.30 for the ethylenic protons in the cis- and trans-isomers. The chemical shifts of the SCH_3 protons were 2.00 and 2.01 ppm.

^{19}F nmr spectra show AA′XX′ systems for the two isomers

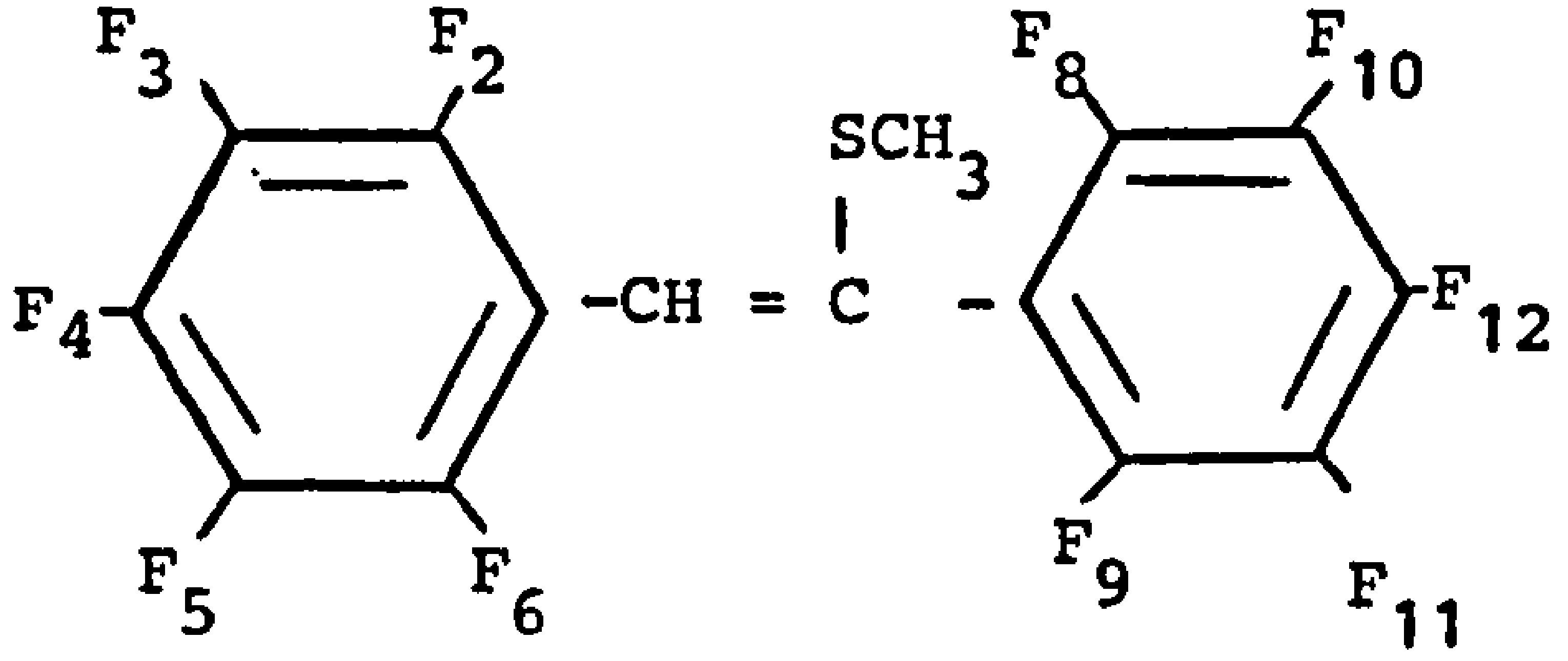


Figure (4:7) - 1,methylthioethane-1,2-(pentafluorophenyl).

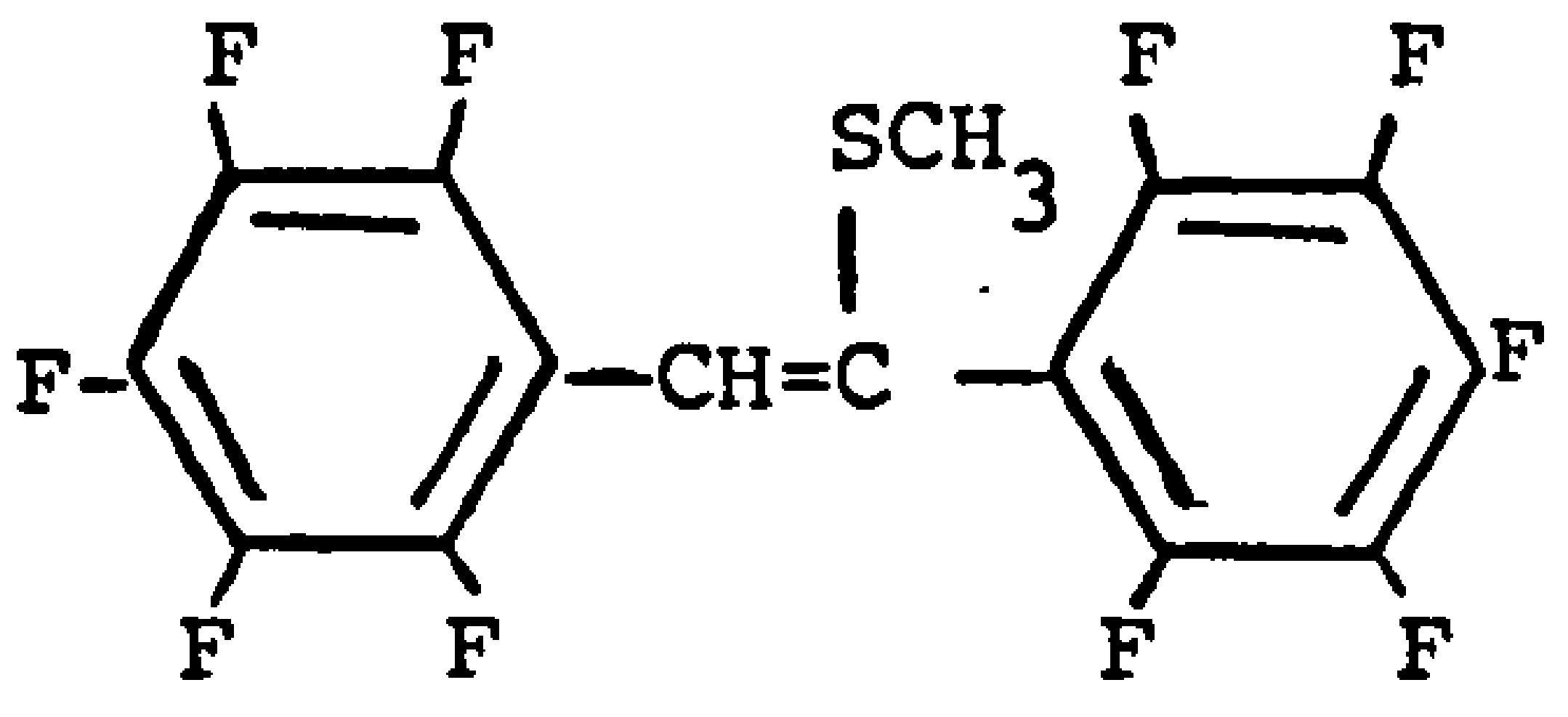
(TABLE (4-6)

^{19}F Chemical Shifts

	ortho	para	meta
$C_6F_5CH{=}CSCH_3C_6F_5$			
1st isomer	(2-6) 138.1	151.8(12)	(3-5) 161.2
	(8-9) 139.7	152.5(4)	(10-11) 162.9
2nd isomer	(2-6) 140.6	(4)153.4	(3-5) 162.4
	(8-9) 141.0	(12)154.9	(10-11) 163.1

TABLE (4-7)

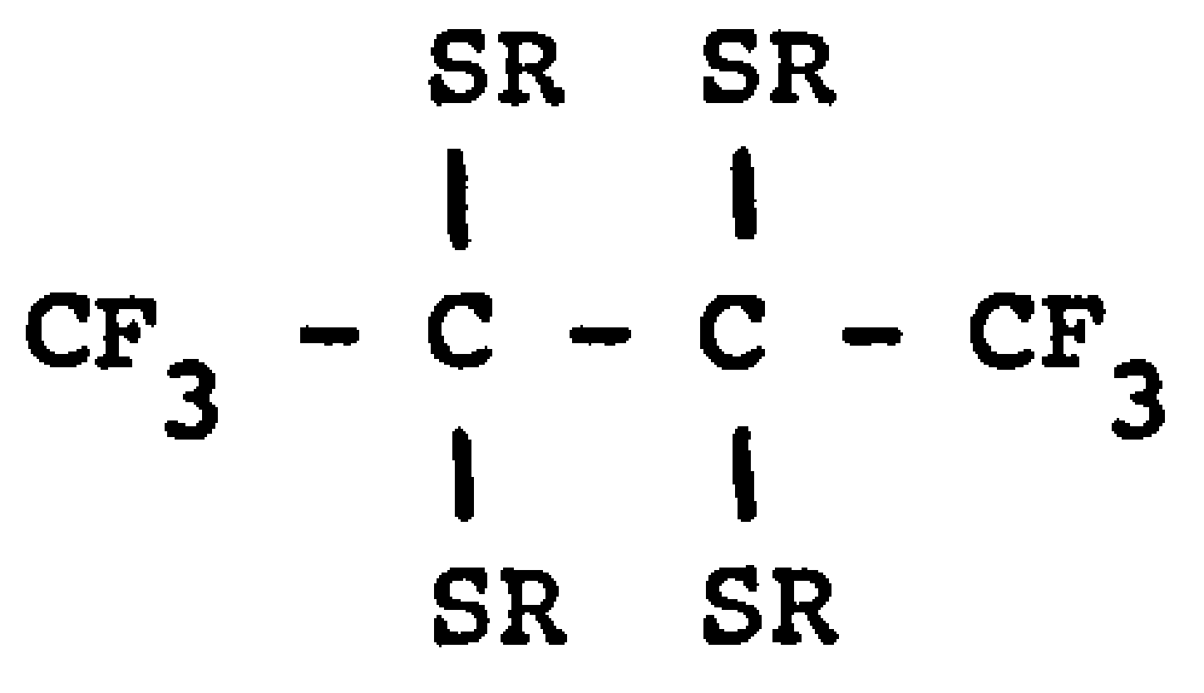
The chemical shifts of methyl thio derivatives

Compound	δSCH_3	δCH_2[b]	δ=CH-	δC-H[b]	δPh
$CH_3SCHPhCH_2SCH_3$	1.81(1)d 1.95(5)s	2.95	-	3.74	7.26
$CH_3SCHPhCHPhSCH_3$	2.07	-	-	3.37	7.2
$(CH_3S)_2CPh{-}CHPhSCH_3$	1.6	-	-	-	-
	1.23	-	-	3.95	7.3
$CH_3SCPh{=}CHPh$ trans	1.78	-	6.7	-	-
cis	1.92	-	6.4	-	-
	2.00		6.25		
	2.01		6.30		

b - Average position of signals

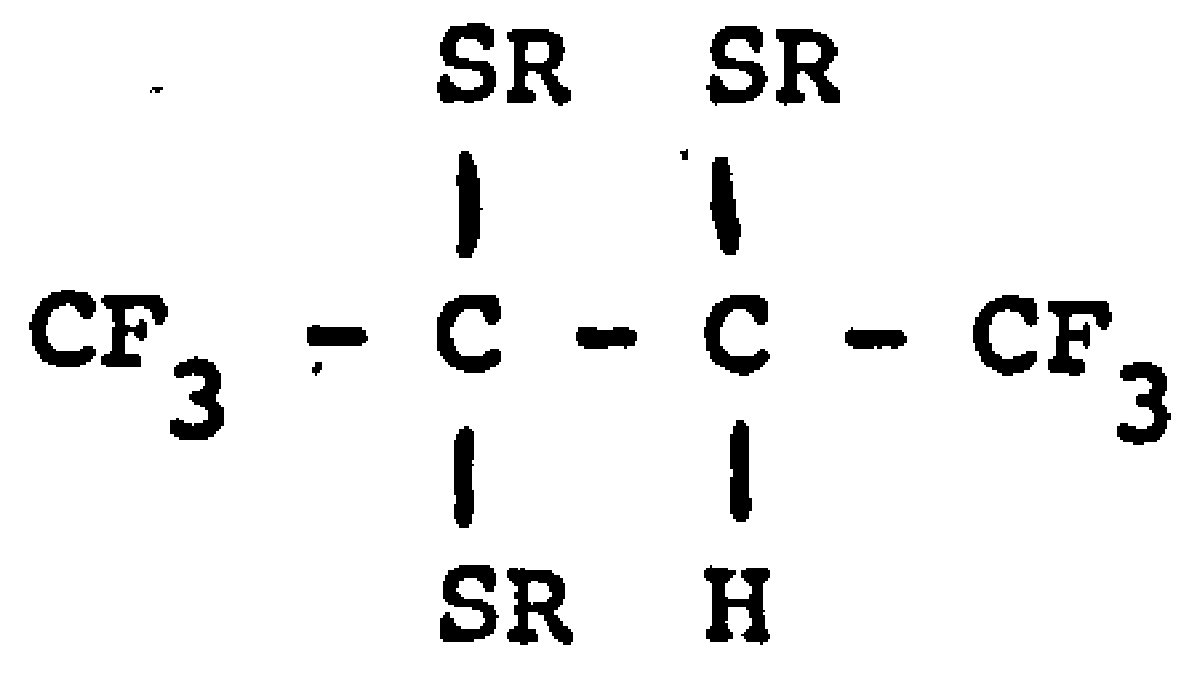
The addition of Bu^tSH to $CF_3C{\equiv}CCF_3$ and $CF_3C{\equiv}CH$ under irradiation

These reactions are similar to those involving olefines in the gas phase that we have described previously.[172-175] The relative proportion of reactants had a major effect on the observed products which were a mixture of compounds (13)% saturated and (15)% unsaturated as expected from a general reaction of acetylenes with alkyl thiols.[117,165] The results can arise from a fast reaction of the alkyne with the thiols followed by slow reaction of the excess thiol with the resultant olefine. A high reactivity of olefinic monoadducts towards alkyl thiols has been previously observed.[165] The reactions take place according to the scheme (2) in Chapter (2). Six or nine different saturated products are possible from each reaction depending on whether the acetylene $AC{\equiv}CB$ is symmetric (A=B) or asymmetric (A≠B). For example if $A=B=CF_3$ the following six products are possible:



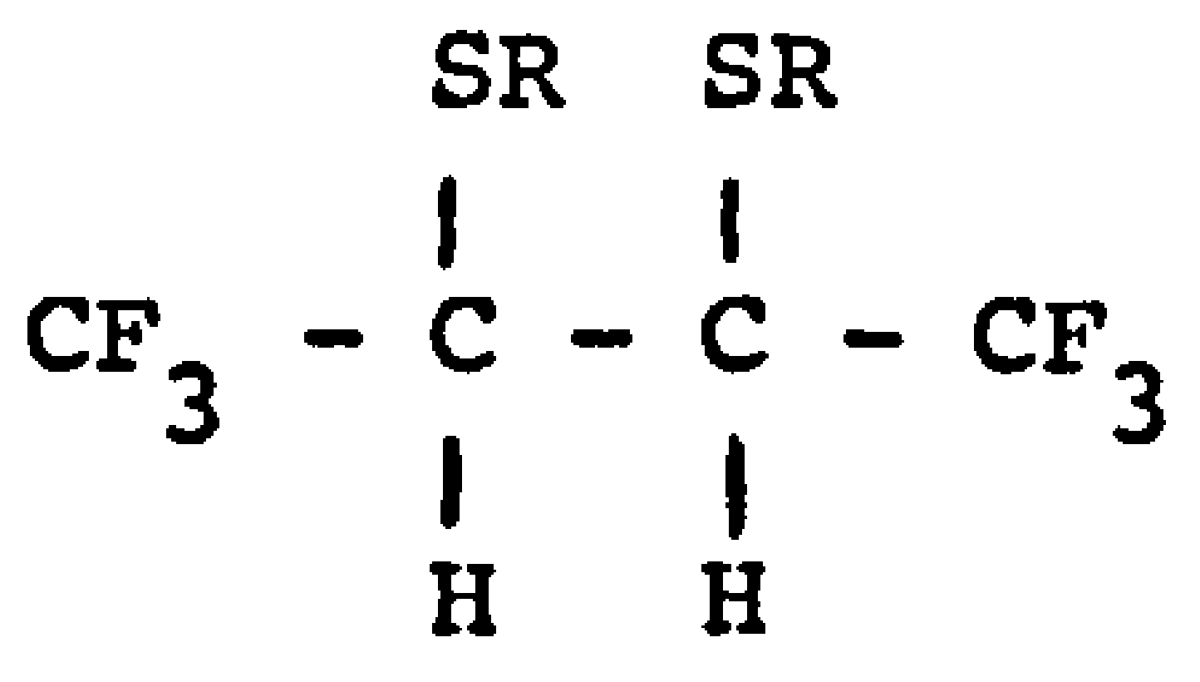
$$CF_3-\overset{SR}{\underset{SR}{C}}-\overset{SR}{\underset{SR}{C}}-CF_3$$

I



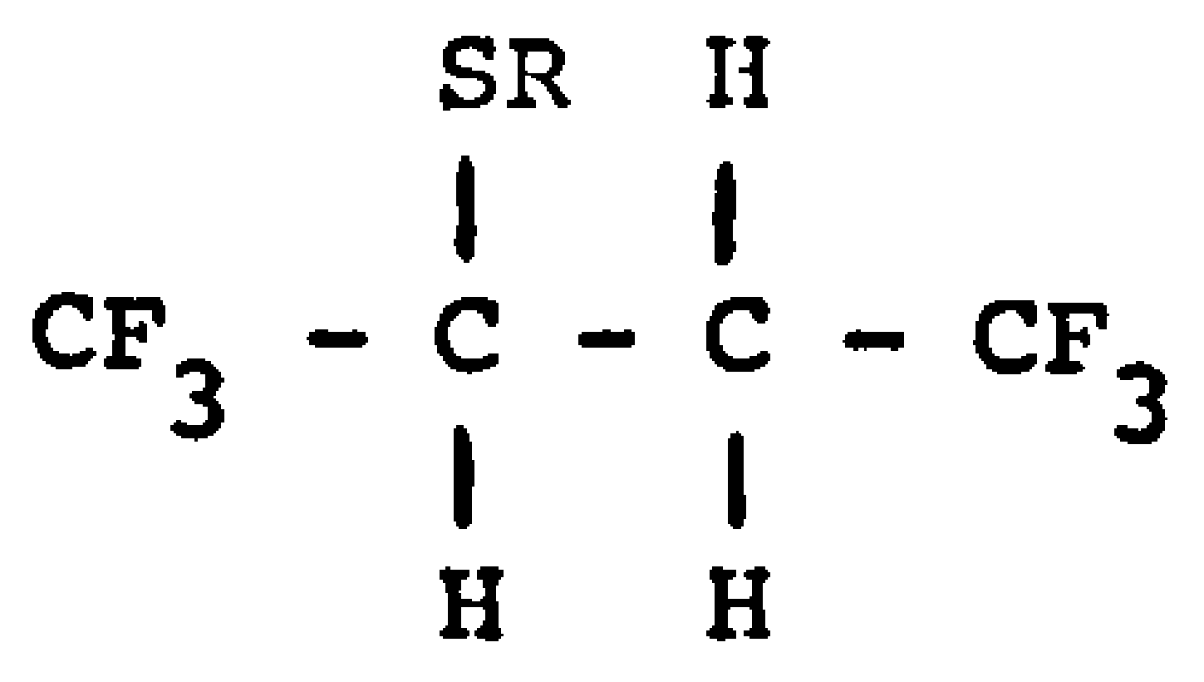
$$CF_3-\overset{SR}{\underset{SR}{C}}-\overset{SR}{\underset{H}{C}}-CF_3$$

II



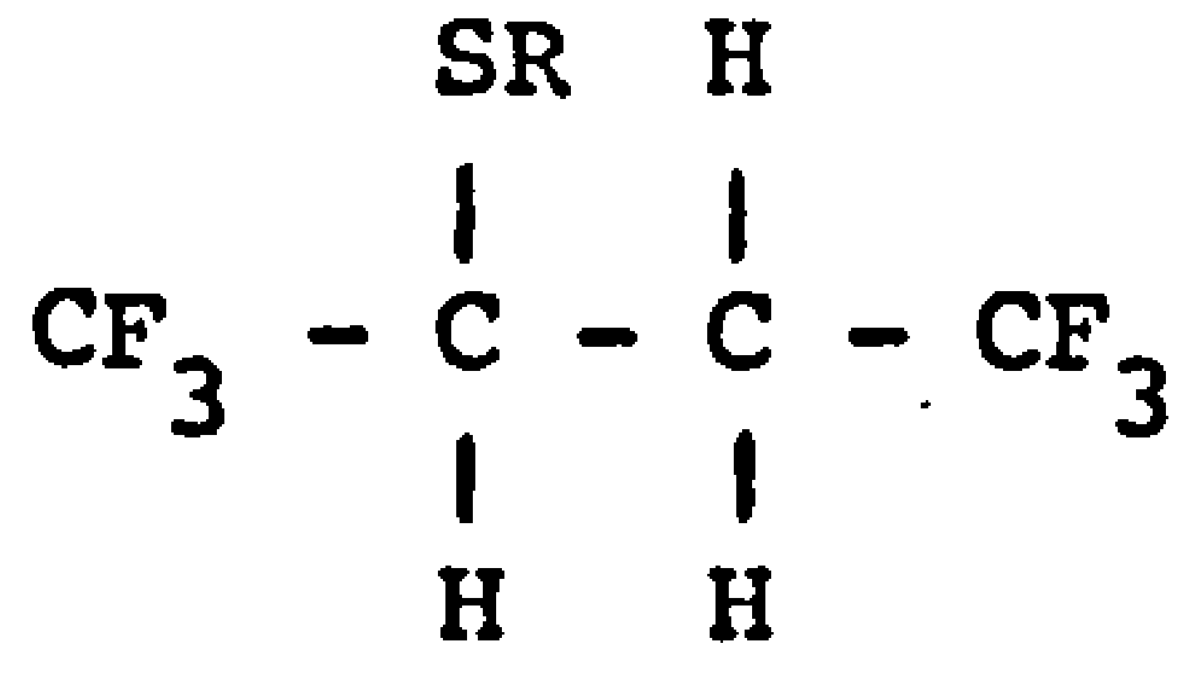
$$CF_3-\overset{SR}{\underset{H}{C}}-\overset{SR}{\underset{H}{C}}-CF_3$$

III



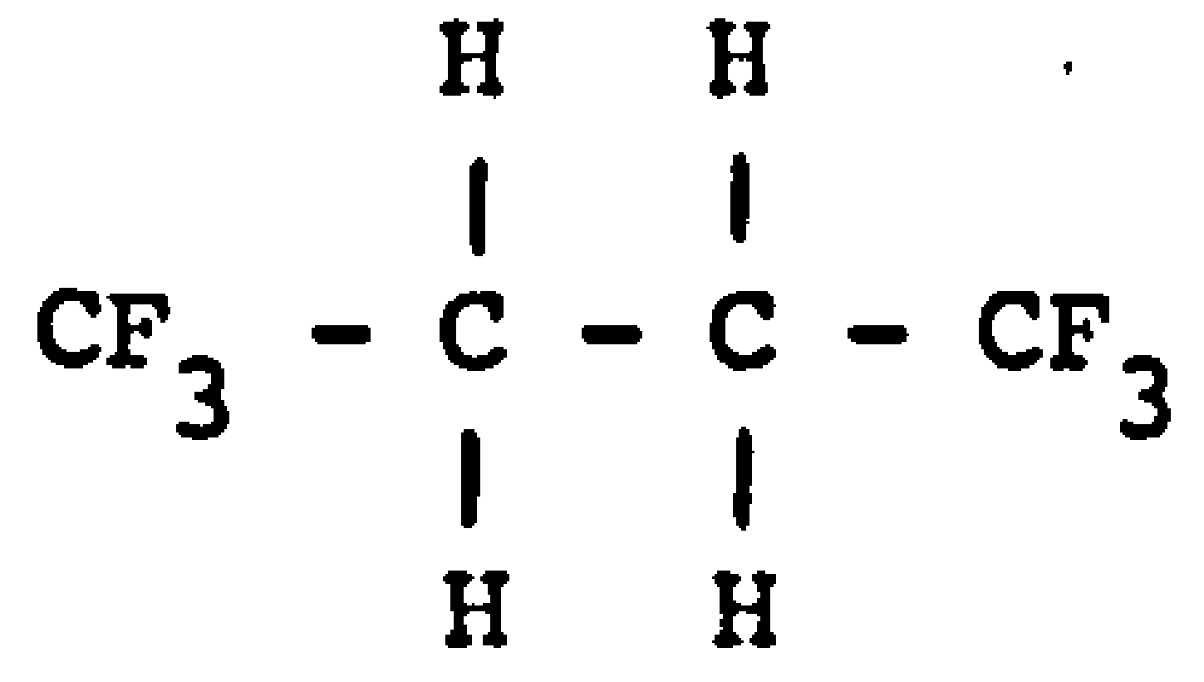
$$CF_3-\overset{SR}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-CF_3$$

IV



$$CF_3-\overset{SR}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-CF_3$$

V



$$CF_3-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-CF_3$$

VI

Figure (4:8)

The presence of two saturated[117] isomers III and IV was shown by ^{19}F -{^1H} nmr spectroscopy. One of them is the meso form and one the dℓ-isomer.

The mass spectra of the reaction products from the reaction of Bu^tSH with $CF_3C{\equiv}CCF_3$ shows the ions of highest molecular mass m/e = 342 corresponding to the parent ion $[C_{12}H_{20}F_6S_2]^+$. $Bu^tSCH(CF_3)CH(CF_3)SBu^t$ and the analogous $CH_3SCH(CF_3)CH(CF_3)SCH_3$[117] have two chiral centres and the proportion of meso to (±) is approximately 2:1 as determined by nmr intensity measurements. The product shows infrared peaks at 998-950 cm^{-1} for (C-F). The ^{19}F-{H} nmr spectrum shows two signals at 60.33 ppm and 63.04 ppm for $Bu^tSCH(CF_3)$-$CH(CF_3)SBu^t$, indicating that all fluorines were magnetically equivalent.[117]

The addition of Bu^tSH to $CF_3C{\equiv}CCF_3$ under irradiation with a low strength u.v. lamp but using a longer reaction time, produced as a major product the olefine[165] $Bu^tSCCF_3{=}CH(CF_3)$ which showed in its mass spectrum a peak at m/e = 252 corresponding to $[C_8H_{10}F_6S]^+$ that is the parent ion. ^{19}F-{H} nmr spectroscopy showed the presence of cis- and trans-adducts[177] the same as the vinyl thiol $HSC(CH_3){=}CHCF_3$. One isomer absorbed in the region (64.64) and (71.45) ppm. The other isomer which is probably the trans showed an AB splitting pattern at (64.84,q) ppm and (71.7,q) ppm with coupling constant 0.58 Hz. The infrared spectra[183] of the mixture had a peak at 1640 cm^{-1} for -C=C- absorption and in the 1005-995 and 1146-1110 cm^{-1} regions for C-F vibrations. The possible reason for the preferential formation of one isomer requires that the radical attack on the primary olefinic adduct produces an intermediate capable of undergoing carbon-carbon rotation. This is normally assumed in photochemical initiated mechanisms[178] and the final product will then be established via the most stable, probably the least crowded, intermediate as shown in Figure (4:9)

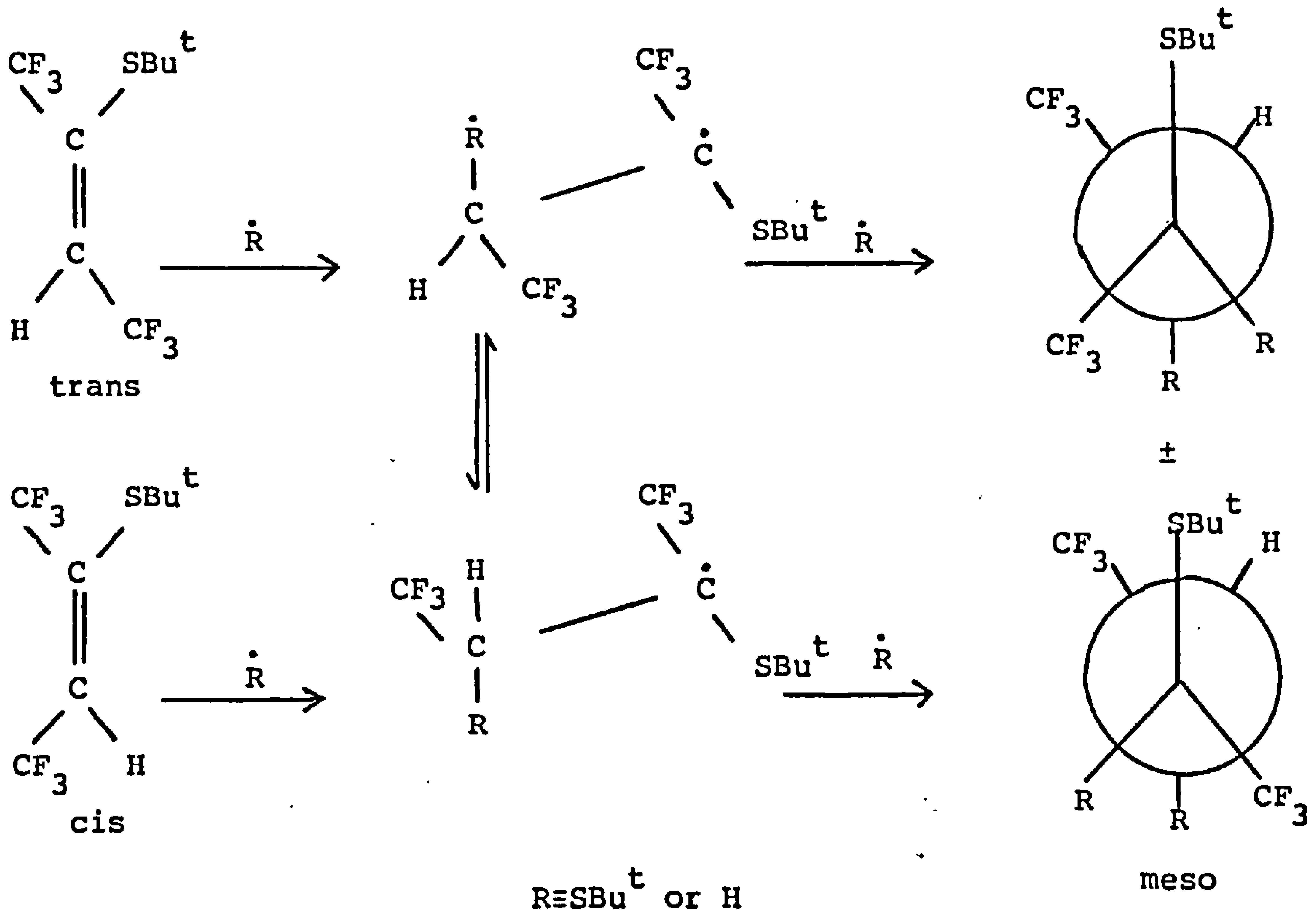


Figure (4:9) - Free radical addition of Bu^{t}SH to Bu^{t}SC$(CF_3)=CH(CF_3)$.

The reaction mixture obtained from 3,3,3-trifluoropropyne and t-butyl thiol also contains both saturated and unsaturated products. The mass spectrum shows the highest peak at m/e = 274 corresponding to the molecule $[C_{11}H_{21}F_2S_2]^+$ Bu^{t}SCH(CF_3)-CH$_2$Bu^t. ^{19}F-{H} nmr spectroscopy of the mixture of products which was produced shows the presence of Bu^{t}SCHCF$_3$-CH$_2$SBu^t and three isomeric olefines the cis-and trans-forms of Bu^{t}SCH=CH(CF_3)[179] and Bu^{t}S$(CF_3)C=CH_2$, see table (4.8).

TABLE (4-8)

NMR Parameters

^{1}H Chemical shift values relative to Me_4Si

^{19}F Chemical shift values relative to $CFCl_3$,

ppm positive to low field of standard.

Compound	$\delta Bu^{t}S$	δCH_2	$\delta{=}CH_2$	δCH	$\delta{=}CH$	δCF_3
$Bu^{t}SCH(CF_3)CH(CF_3)SBu^{t}$	0.99	-	-	4.25	-	60.33 meso 63.040 t
$Bu^{t}SC(CF_3)=CH(CF_3)$	1.2	-	-	-	6.39	(q)64.859) (q)71.79) cis
					6.42	(s)64.64) (s)71.4) trans
$\overset{i}{Bu^{t}}SCH(CF_3)CH_2\overset{ii}{SBu^{t}}$	(i)1.4 (s) (ii)1.08(t)	2.96(s)	-	3.5(9)		52.26
$Bu^{t}SCH=CH(CF_3)$	1.5	-	-	-	6.1	60.395 cis 64.083 trans
$Bu^{t}SC(CF_3)=CH_2$	1.42	-	4.5	-	-	67.30

s - singlet; t - triplet - q - quartet.

TABLE (4-9)

Fluorinated Compounds

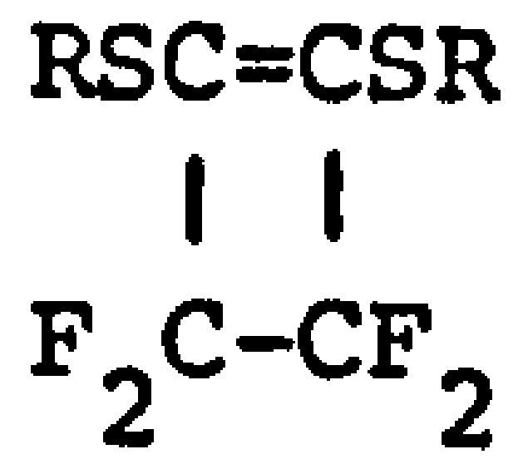
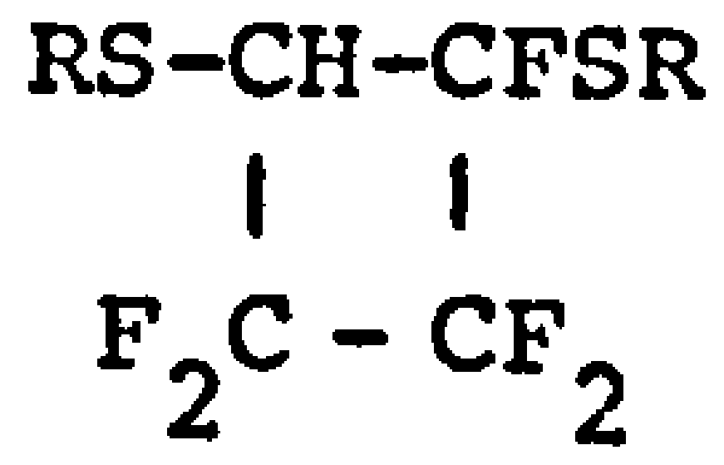
No. of fluorine atoms	Compound	Preparation	Ref.
2	$CH_3SCF_2CH_2SCH_3$	A,E	117
3	$CF_3SCH_2CH_2SCH_3$	E	117
	$CH_3SCHCF_3CH_2SCH_3$	B	117
	$Bu^tC(CF_3)=CH_2$	B	this work
	$Bu^tSCH_2\text{-}CHCF_3SBu^t$	B	this work
	$Bu^tCH=CHCF_3$	B	this work
4	$C_6F_4(SPh)_2$	E	127
	$CH_3SCF_2CF_2SCH_3$	F	181
	$(MeS)_3C_6F_2\cdot C_6F_2(SMe)_3$	E	127
	 $\begin{array}{l}RSC{=}CSR\\ \ \vert \quad \vert\\ F_2C{-}CF_2\end{array}$ $R=C_4H_9$ $=CH_2COOH$	C	182
5	 $\begin{array}{l}RS{-}CH{-}CFSR\\ \quad \vert \quad \vert\\ \ F_2C-CF_2\end{array}$ $R=C_4H_9$	C	182
	$C_6F_5CH_2CH_2SCH_3$	E	117
	$C_6F_5SCH_3$	E	118
6	$C_{14}F_6(SPh)_4$	E	this work
	$CF_3SCH_2CH_2SCF_3$	A,E	116,134
	$Bu^tSCF_3CHCHCF_3SBu^t$	B	this work
	$CF_3SCH(CH_3)CH_2SCF_3$	A	116
	$CH_3SC(CF_3)=C(CF_3)SCH_3$	E	183
	$Bu^tSCF_3C=CHCF_3$	B	this work

TABLE (4-9) contd.

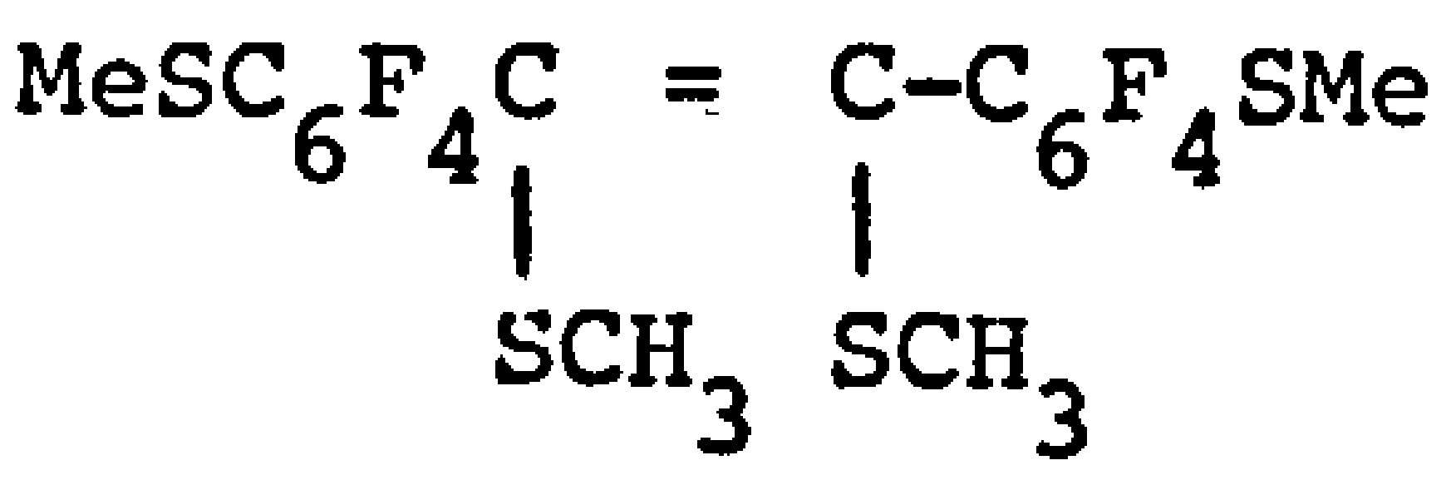
No. of fluorine atoms	Compound	Preparation	Ref.
6	$CH_3SCH(CF_3)CH(CF_3)SCH_3$	B	117
	$(CF_3S)_2CHCH_3$	E	134
	$CF_3S(CH_2CH_2)_nSCF_3$ n=1-3	E	134
	$CF_3SCHBrCH_2SCF_3$	F	134
	$CF_3SCHBrCHBrSCF_3$	F	134
	$CF_3SCBr_2CH_2SCF_3$	F	134
	$CF_3SCH{=}CH_2SCF_3$	F	134
	$C_4F_6S_2$	G	187
8	$CF_3CF_2CH_2SCF_3$	A	116
	$CH_3S(CF_2CF_2)_2SCH_3$	F	143
	$MeSC_6F_4CH{=}CHC_6F_4SMe$	E	this work
	$PhSC_6F_4CH{=}CHC_6F_4SPh$	E	this work
	$MeSC_6F_4C{\equiv}CC_6F_4SMe$	E	this work
	$EtSC_6F_4.C_6F_4SEt$	E	127
	$PhSC_6F_4.C_6F_4SPh$	E	127
	$PhSC_6F_4CHBrCHBrC_6F_4SPh$	E	this work
	 $MeSC_6F_4C(SCH_3){=}C(SCH_3){-}C_6F_4SMe$	E	this work

TABLE (4-9) contd.

No. of fluorine atoms	Compound	Preparation	Ref.
9	$CF_3CF_2CHFSCF_3$	A	116
	$CF_3SCF_2CFC\ell SCF_3$	A	116
	$(CF_3S)_2CHCH_2SCF_3$	E	134
	$MeSC_6F_4C{\equiv}CC_6F_5$	E	this work
	$MeSC_6F_4CH{=}CHC_6F_5$	E	this work
10	$CF_3S(CF_2CH_2)_2SCF_3$	A	116,184
	$CF_3SCF_2CF_2SCF_3$	A	184
	$C_6F_5SCH_2CH_2SC_6F_5$	E	117,118
	$C_6F_5CHBr{-}CHBrC_6F_5$	E	this work
	$C_6F_5CBr{=}CBrC_6F_5$	E	126
	$C_6F_5CH{=}CSCH_3{-}C_6F_5$	B	this work
12	$CF_3S(CF_2CH_2)_3SCF_3$	A	116
	$CF_3S(CF_2CHF)_2SCF_3$	A	116
	$CF_3SCF(CF_3)CF_2SCF_3$	A,F	116,184,185
	$CF_3S(CF_2CFC\ell)_2SCF_3$	A	116,184
	$CF_3S(CF_2CFBr)_2SCF_3$	A	184
	$C_8F_{12}S$	G	187
14	$CF_3S(CF_2CH_2)_4SCF_3$	A	116
	$CF_3S(CF_2CF_2)_2SCF_3$	A	116,184

TABLE (4-9) contd.

No. of fluorine atoms	Compound	Preparation	Ref.
15	$CF_3S(CF_2CHF)_3SCF_3$	A	116
	$CF_3S(CF_2CFC\ell)_3SCF_3$	A	116,184
	$CF_3S(CF_2CFBr)_3SCF_3$	A	184
16	$CF_3S(CF_2CH_2)_5SCF_3$	A	116
18	$CF_3S(CF_2CH_2)_6SCF_3$	A	116
	$CF_3S(CF_2CHF)_4SCF_3$	A	116
	$CF_3S(CF(CF_3)CF_2)SCF_3$	A,F	116,131
	$C_{12}F_{18}S_4$	D	187
20	$C_{28}F_{20}S_2$	G	this work
	$C_{28}F_{20}S$	G	this work
21	$CF_3S(CF_2CHF)_5SCF_3$	A	116
24	$CF_3S(CF_2CHF)_6SCF_3$	A	116
27	$CF_3S(CF_2CHF)_7SCF_3$	A	116
30	$C_{42}F_{30}S_3$	G	this work
40	$CH_3(CF_2CF_2)_{10}SCH_3$	D	186

TABLE (4 9) contd.

A) Photochemical addition to olefine

B) Photochemical addition to acetylene

C) Base catalysed addition to olefine

D) Thermal addition to olefine

E) Metathetical reactions

G) Reaction of sulfur with acetylene at high temperature

F) Other reactions.

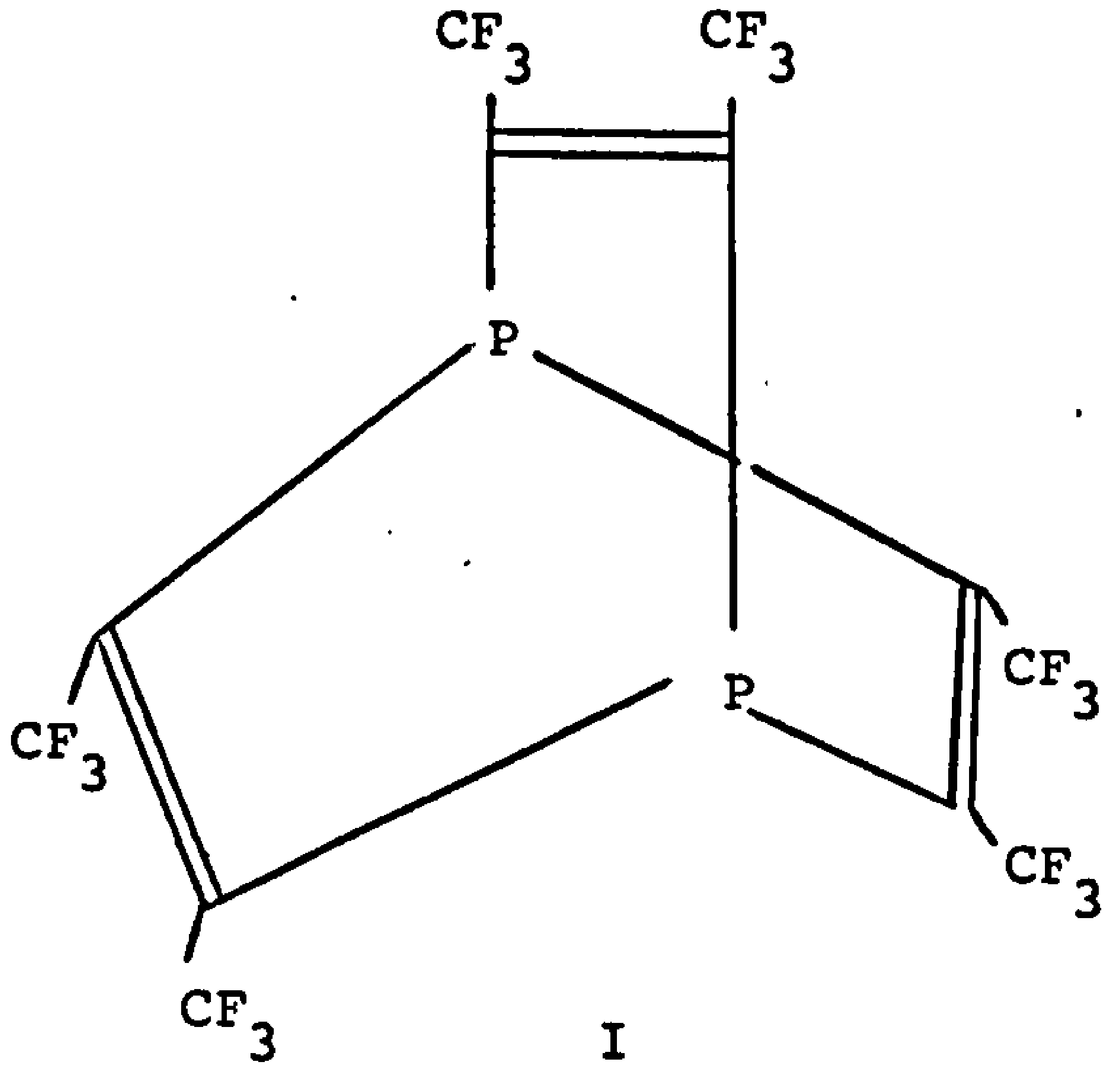
CHAPTER 5

REACTIONS BETWEEN SULFUR AND PERFLUOROALKYNES

CHAPTER 5

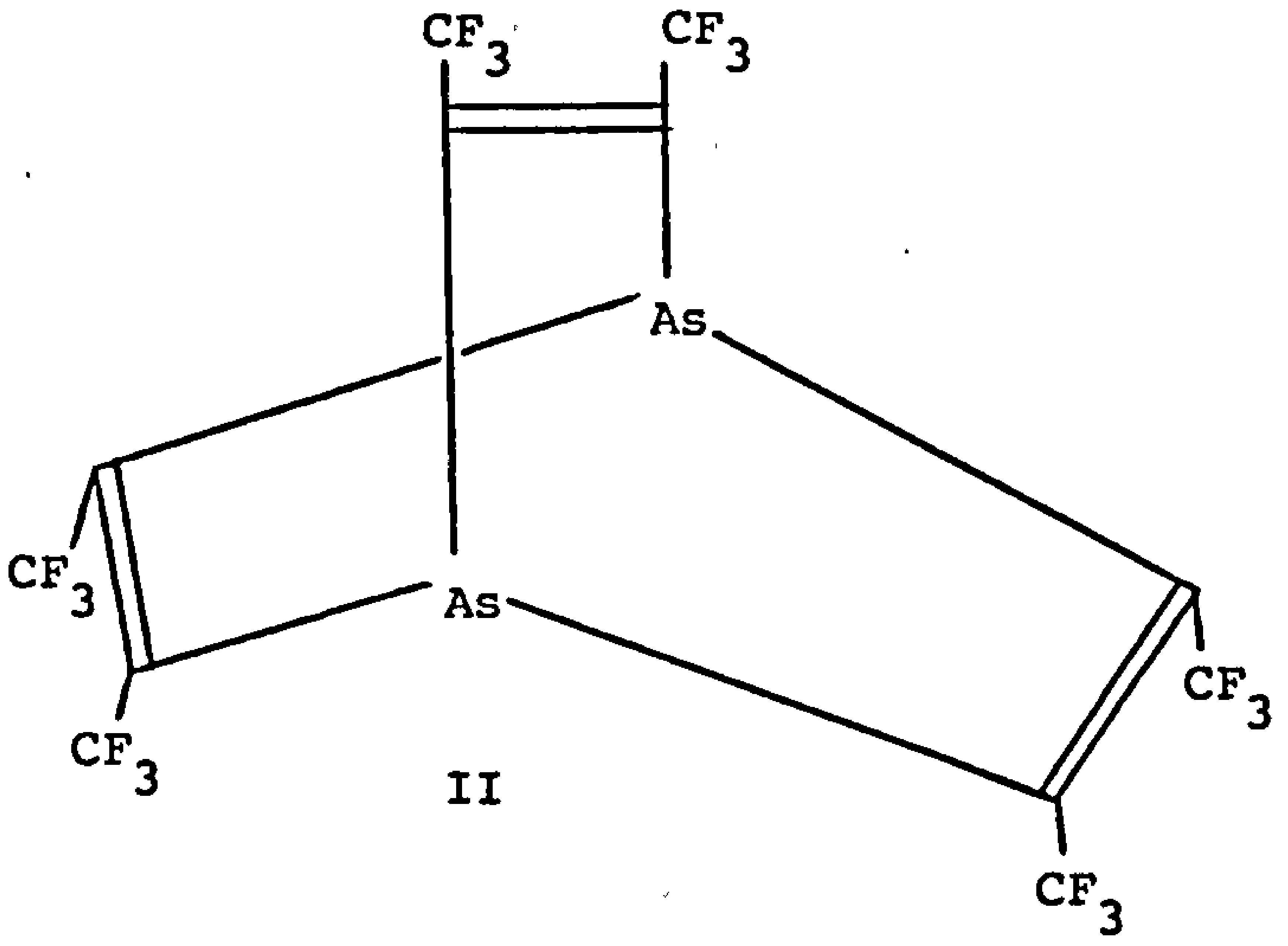
REACTIONS BETWEEN SULFUR AND PERFLUOROALKYNES

Several novel heterocyclic compounds have been prepared from perfluorobut-2-yne by reaction with e.g. phosphorus. Thus when this acetylene is heated at 200°C under pressure with red phosphorus and a catalytic amount of iodine 2,3,5,6,7,8-hexakistrifluoromethyl-1,4-diphosphabicyclo-octatriene(I) is obtained in 43% yield.



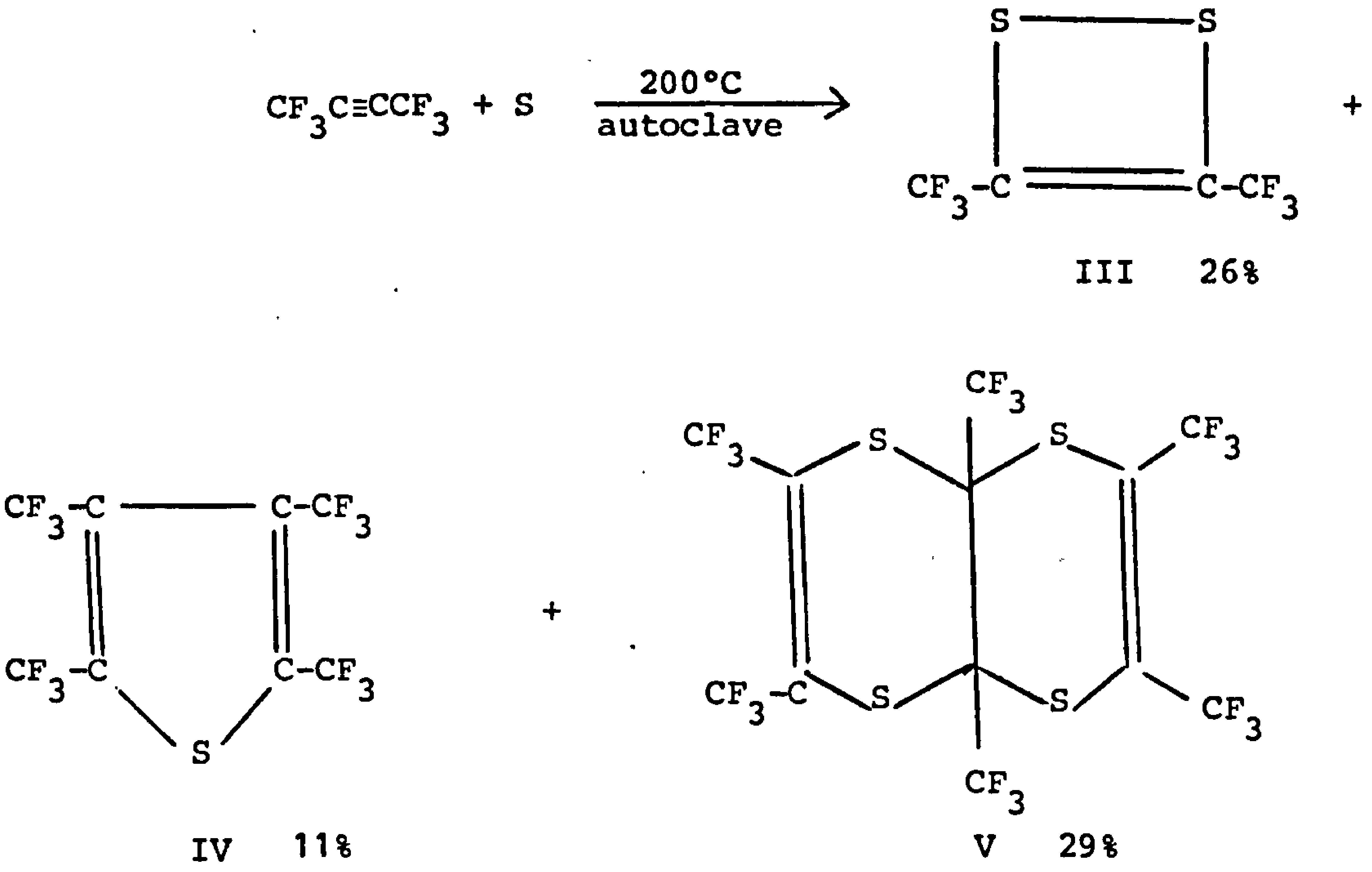
I

The analogous diarsine(II) can be prepared in a similar fashion and a better yield is obtained from arsenic and 2,3-diiodohexafluorobut-2-ene (the latter is made from perfluorobut-2-yne and iodine at 200°C).[188]



II

3,4-bis(trifluoromethyl-1,2-dithietene(III)[187,189] is formed in 80% yield when perfluorobut-2-yne is passed through the vapours of boiling sulfur at atmospheric pressure. Reaction at 200°C under pressure in the presence of iodine also produces tetrakistrifluoromethylthiophen(IV) and a compound that has been formulated as a p-dithiino-p-dithiin(V)

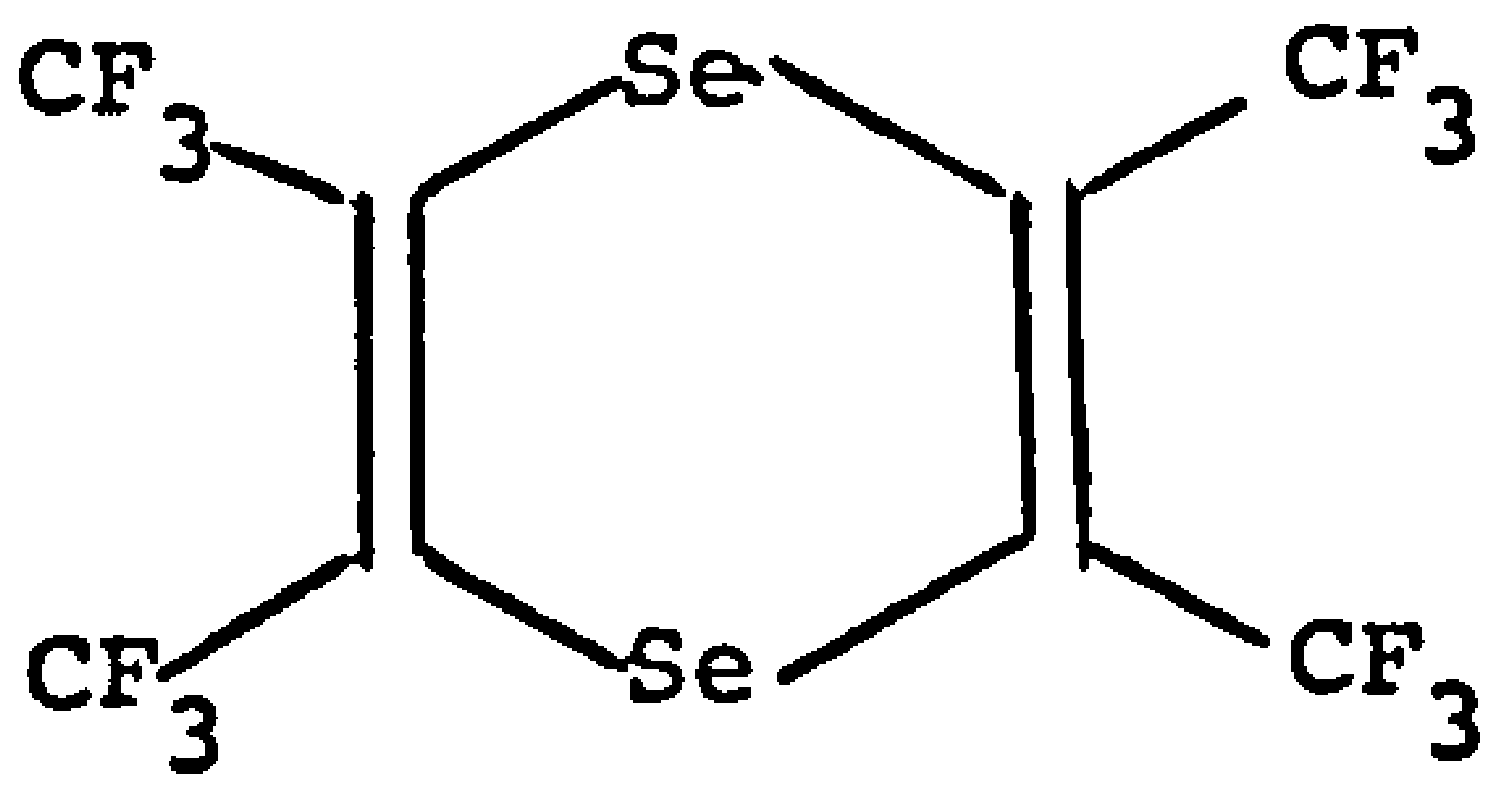


III 26%

IV 11%

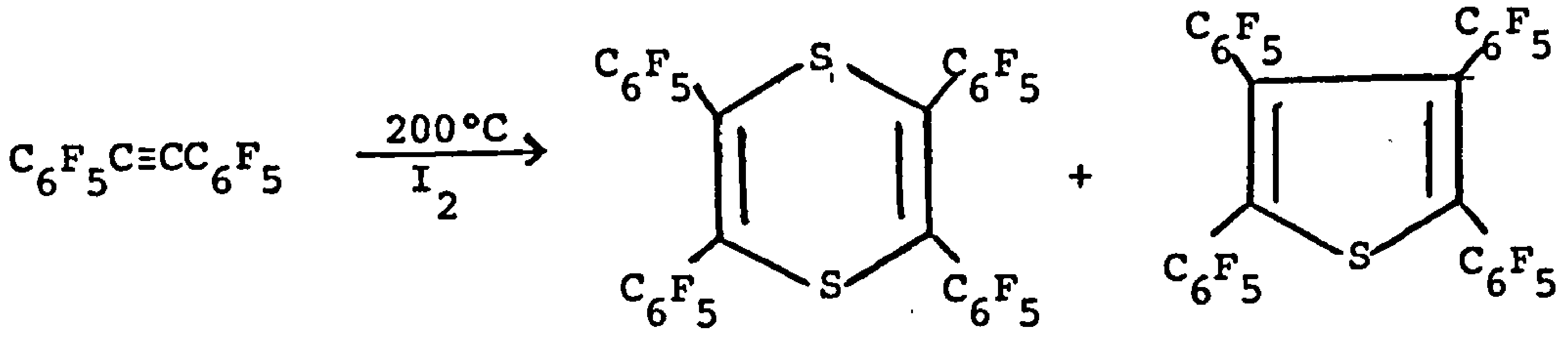
V 29%

Tetrakistrifluoromethyl-p-diselenobenzene(VI) is obtained in low yield (8%) when 2,3,di-iodohexafluorobut-2-ene is heated at 180°C under pressure with selenium.[187]

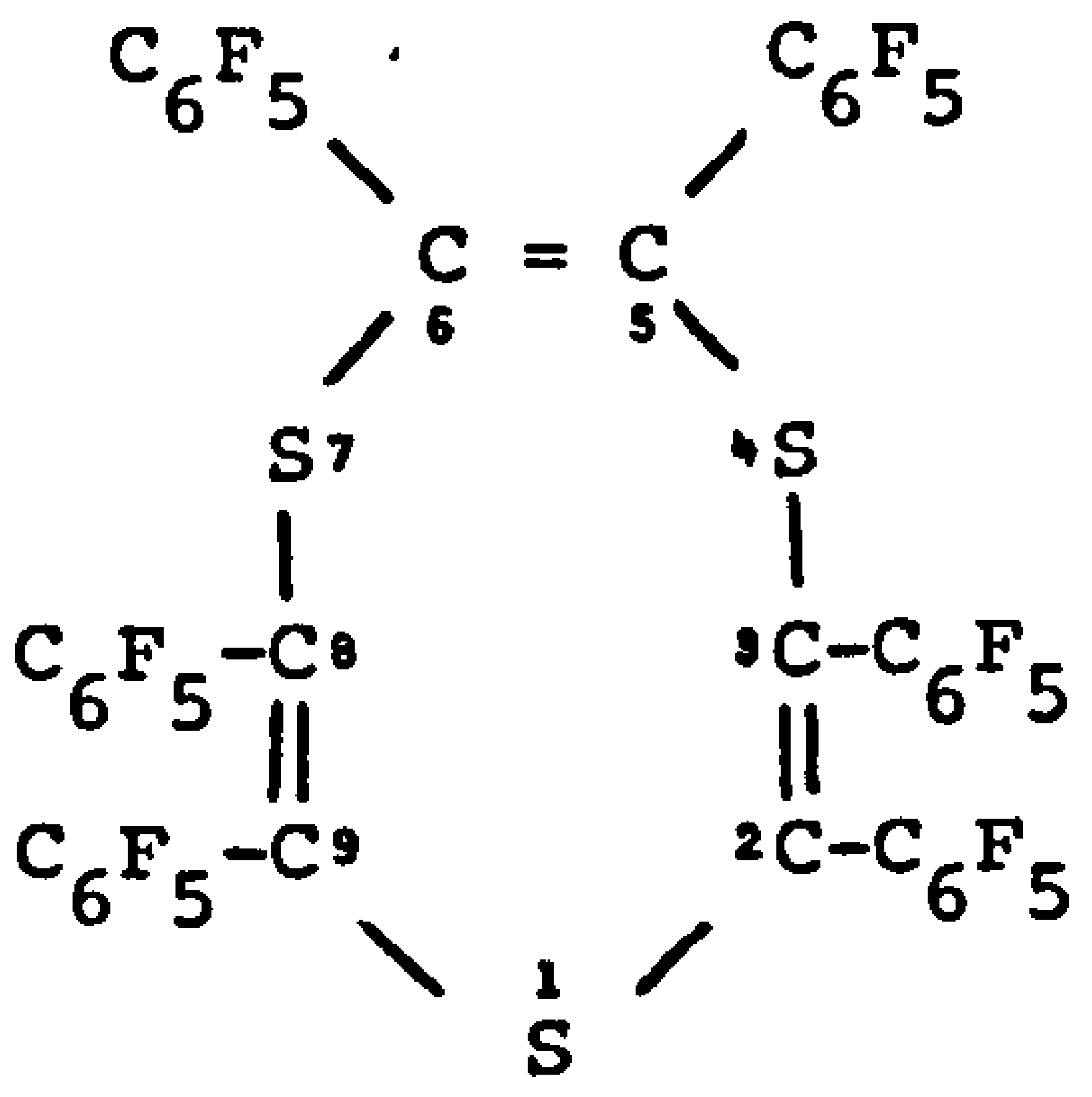


VI

The initial studies have been followed by recent work on hexafluorobut-2-yne which has been shown to yield many cyclic derivatives, including cyclooctatriene[190] derivatives by oligomerisation reactions. Some similar reactions are known for non-fluorinated aromatic derivatives. We have attempted to extend these reactions to fluoroarylalkynes. We found that the reaction of decafluorotolan, $C_6F_5C\equiv CC_6F_5$, with sulfur in the presence of I_2 at 200°C under pressure in a nickel bomb formed 20% of 2,3,5,6-tetrakis(pentafluorophenyl)p-disulfobenzene(VII), 11% of 2,3,4,5-tetrakis(pentafluorophenyl)thiophene(VIII) and 30% of 2,3,5,6,8,9-hexakis(pentafluorophenyl)-1,4,7-trisulfur-nano-2,5,8-triene. Iodine was used to catalyse the reactions. Hexafluorobut-2-yne and sulfur alone form analogous products at 225°C under pressure.



VII 20% VIII 11%



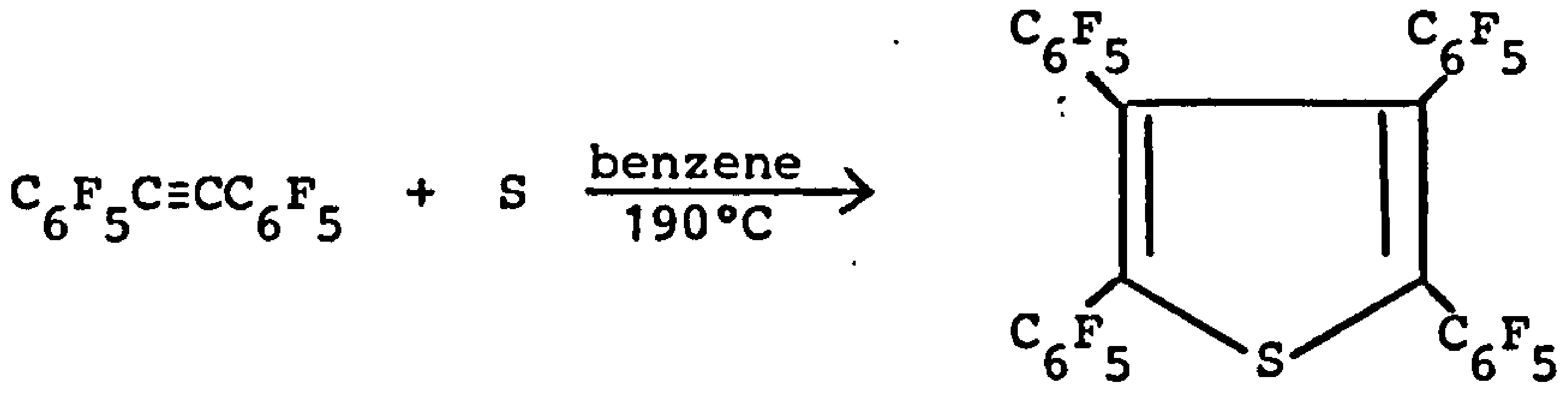
IX 30%

The mixture of products was examined by g.l.c. and separated by use of the Chromatron, followed by purification of each fraction by recrystallisation from 40-60 petroleum ether.

The mass spectrum of product VII showed a parent ion at m/e = 780 corresponding to $C_{28}F_{20}S_2$. The infrared spectrum of compound VII shows the presence of double bonds by a band at 1635-1655 (m) cm^{1} for the C=C bond[165] although the aromatic rings,also the perfluoro aromatic rings,show bands between 1465-1505 (v.s.) m^{-1} and between 900-1010 (v.s.) cm^{-1} for C-F vibrations. There is a weak band from the (C-S) bond near 700 cm^{-1}. The ^{19}F n.m.r. spectrum shows the expected 3 peaks due to ortho, meta, and para fluorines in symmetrical products. The melting point of (VII) is 95°C.

The mass spectrum of product VIII shows a parent ion at m/e = 748 corresponding to $C_{28}F_{30}S$, which has m.p. = 180.5-181°C. The infrared spectrum shows the characteristic fluoroaromatic ring absorptions[191] at 1490 (v.s.) cm^{-1}, 1653 (m) cm^{-1}, together with a very strong C-F band at

988 cm^{-1}. A strong band at 873 and 1515 cm^{-1} probably arises from skeletal vibrations in the thiophene ring.[192] The ^{19}F nmr spectrum shows the presence of two magnetically different types of pentafluorophenyl rings. Ortho 135.3, 135.9 ppm, meta 161.2, 161.7 ppm and para 149.9, 150 ppm. This compound VIII was previously prepared in 1967 by Haszeldine who used the direct reaction of decafluorotolan with sulfur in benzene heated in a sealed tube at 190°C for 14 hrs.



(72% yield)

2,3,4,5-tetrakis(pentafluorophenyl)thiophene

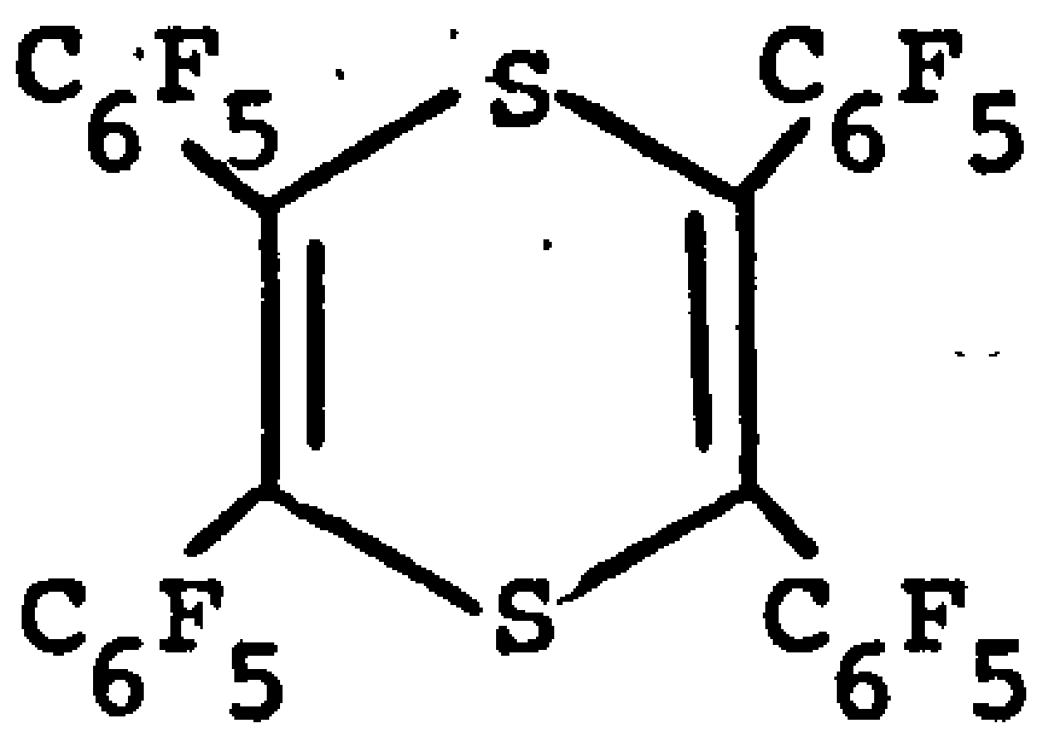
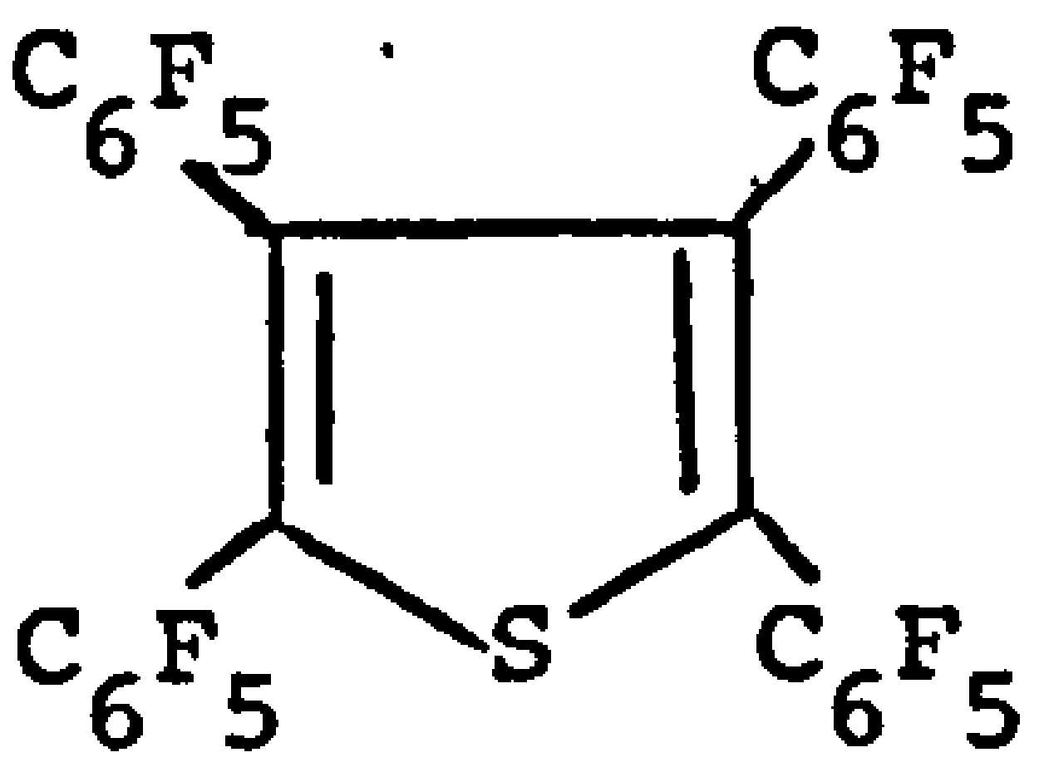
Assuming the product VII  to be a primary product of the original reaction under condition consideration the other product  can form by elimination of one sulfur to form thiophene (mass spectrum shows the reversal of this, Scheme (1)); a reaction previously noted with fluorinated and non-fluorinated p-dithiin[187,193,194] which reacts with product VII to form product IX which has melting point 115°C. The mass spectrum of this compound shows a parent peak at m/e = 1170 corresponding to $[C_{42}F_{30}S_3]^+$. The infrared spectrum of this compound [$C_{42}F_{30}S_3$] shows absorption at 1510 and 1530 cm^{-1} characteristic of the pentafluorophenyl ring.[191] A number of bands attributed to C-F vibrations appear in the region 900-1350 cm^{-1}. The ^{19}F nmr spectrum, Table (1) has three multiplets of relative intensity[126] 2:1:2, attributable to the ortho, para and meta fluorine atoms of six equivalent pentafluorophenyl groups.

TABLE (1)

^{19}F Nuclear magnetic resonance spectra

Compound	Solvent	Chemical shift		
		ortho	para	meta
2,3,5,6-tetrakis(pentafluorophenyl)-p-disulfobenzene (VII)	CCl_4	134.4	149.8	160.9
2,3,4,5-tetrakis(pentafluorophenyl)thiophene (VIII)	CCl_4	135.3 135.9	149.9 150.0	161.2 161.7
2,3,5,6,8,9-hexakis(pentafluorophenyl)-1,4,7-trisulfur-nano-2,5,8-triene (IX)	CCl_4	134.7	149.7	161.0

TABLE (2)

Mass spectrometric data

Compound	m/e	Relative intensity	Assignment
$C_{28}F_{20}S_2$ (VII)	780	40%	$C_{28}F_{20}S_2^+$
	748	16%	$C_{28}F_{20}S^+$
	716	16%	$C_{28}F_{20}^+$
	517	7%	$C_{14}F_{15}S_2^+$
	422	8%	$C_{14}F_{10}S_2^+$
	390	70%	$C_{14}F_{10}S^+$
	358	100%	$C_{14}F_{10}^+$

$$\begin{tikzcd}
C_{28}F_{20}^+ & C_{28}F_{20}S_2 \arrow[l, "-2S"'] \arrow[r, "-S"] \arrow[d, "-C_{14}F_{10}"] & C_{28}F_{20}S^+ \\
C_{14}F_{10}^+ & C_{14}F_{10}S_2^+ \arrow[l, "-2S"'] \arrow[r, "-S"] & C_{14}F_{10}S^+
\end{tikzcd}$$

Scheme (1) - Initial fragmentation pattern of

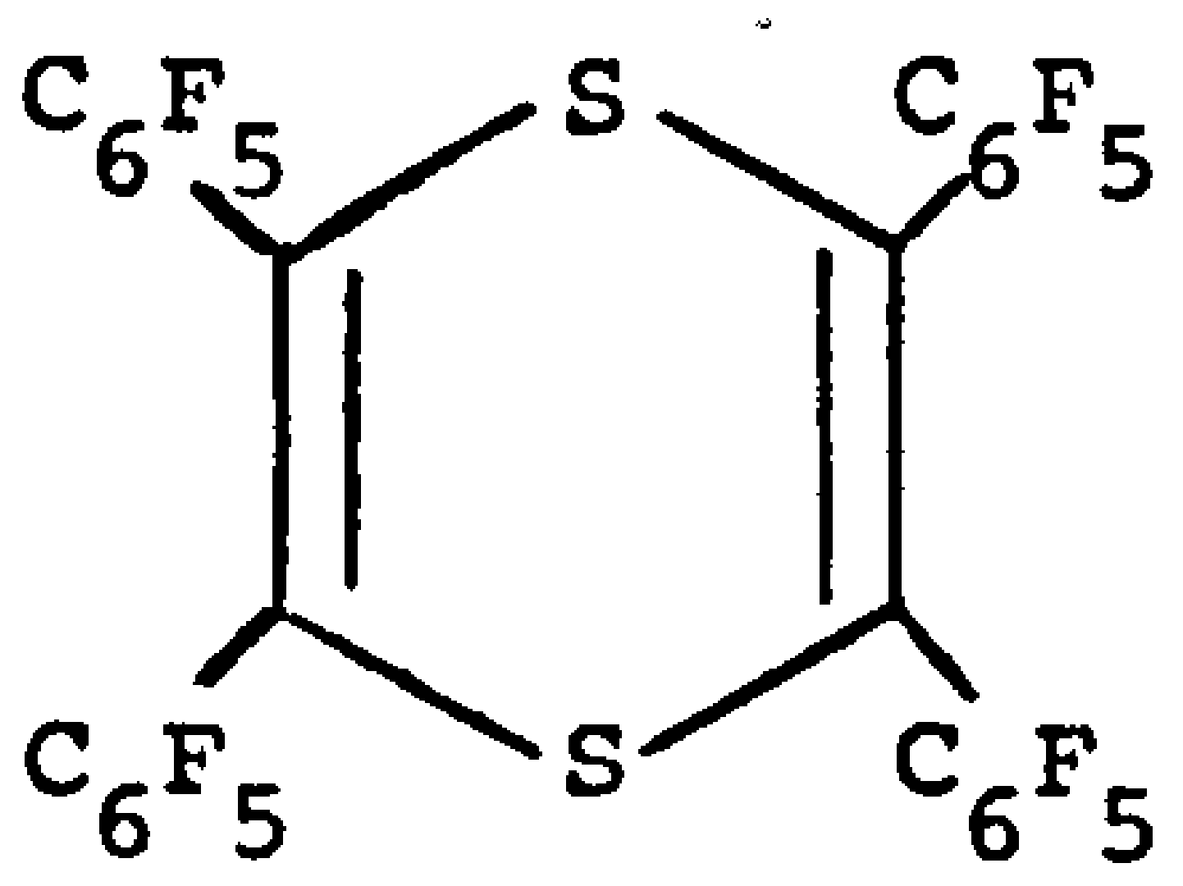


TABLE (3)

Mass spectrometric data

Compound	m/e	Relative intensity	Assignment
$C_{28}F_{20}S$ (VIII)	748	50%	$C_{28}F_{20}S^+$
	716	18%	$C_{28}F_{20}^+$
	611	7%	$C_{24}F_{17}^+$
	390	90%	$C_{14}F_{10}S^+$
	358	100%	$C_{14}F_{10}^+$

$$\begin{tikzcd}
{[C_{14}F_{10}S^+]} \arrow[dr, "-S"'] & {[C_{28}F_{20}S^+]} \arrow[l, "-C_{14}F_{10}"'] \arrow[r, "-S"] \arrow[d, "-C_{14}F_{10}S"] & {[C_{28}F_{20}^+]} \arrow[dl, "-C_{14}F_{10}"] \\
 & {[C_{14}F_{10}^+]} &
\end{tikzcd}$$

Scheme (2) - Initial fragmentation pattern of

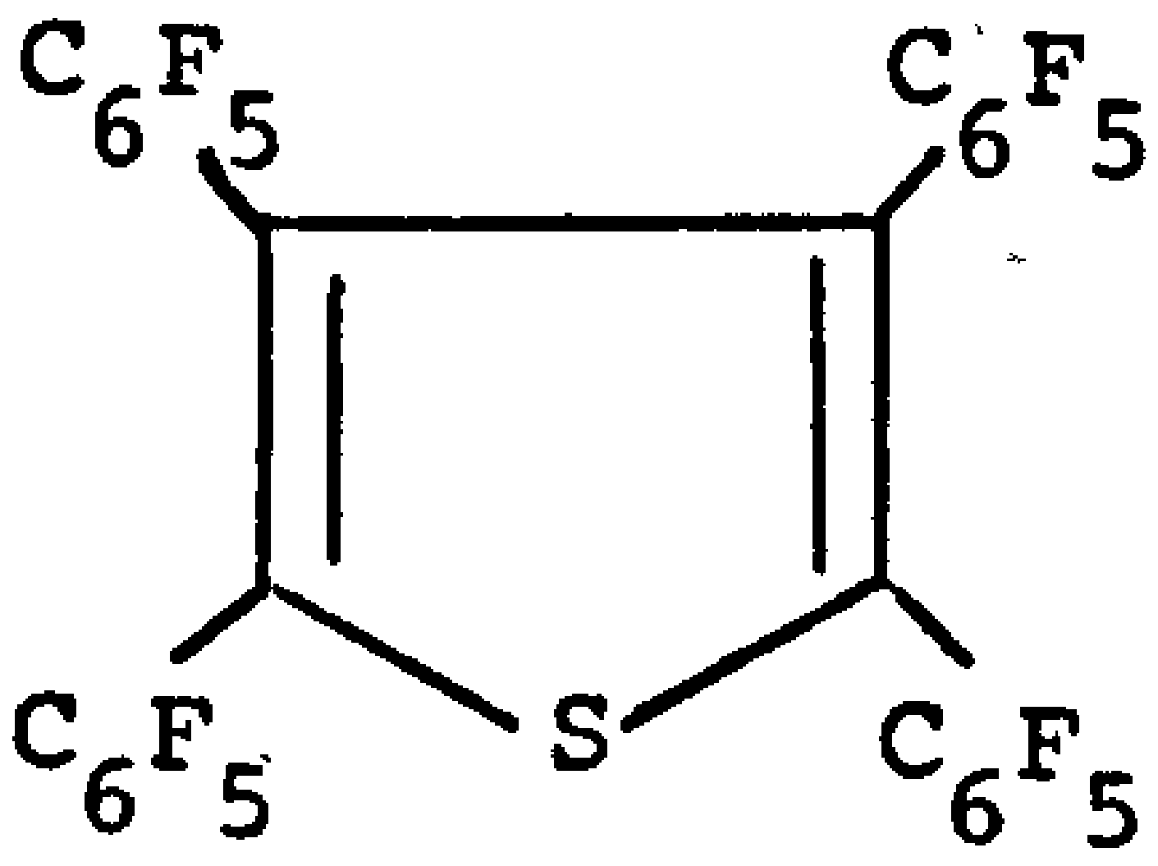


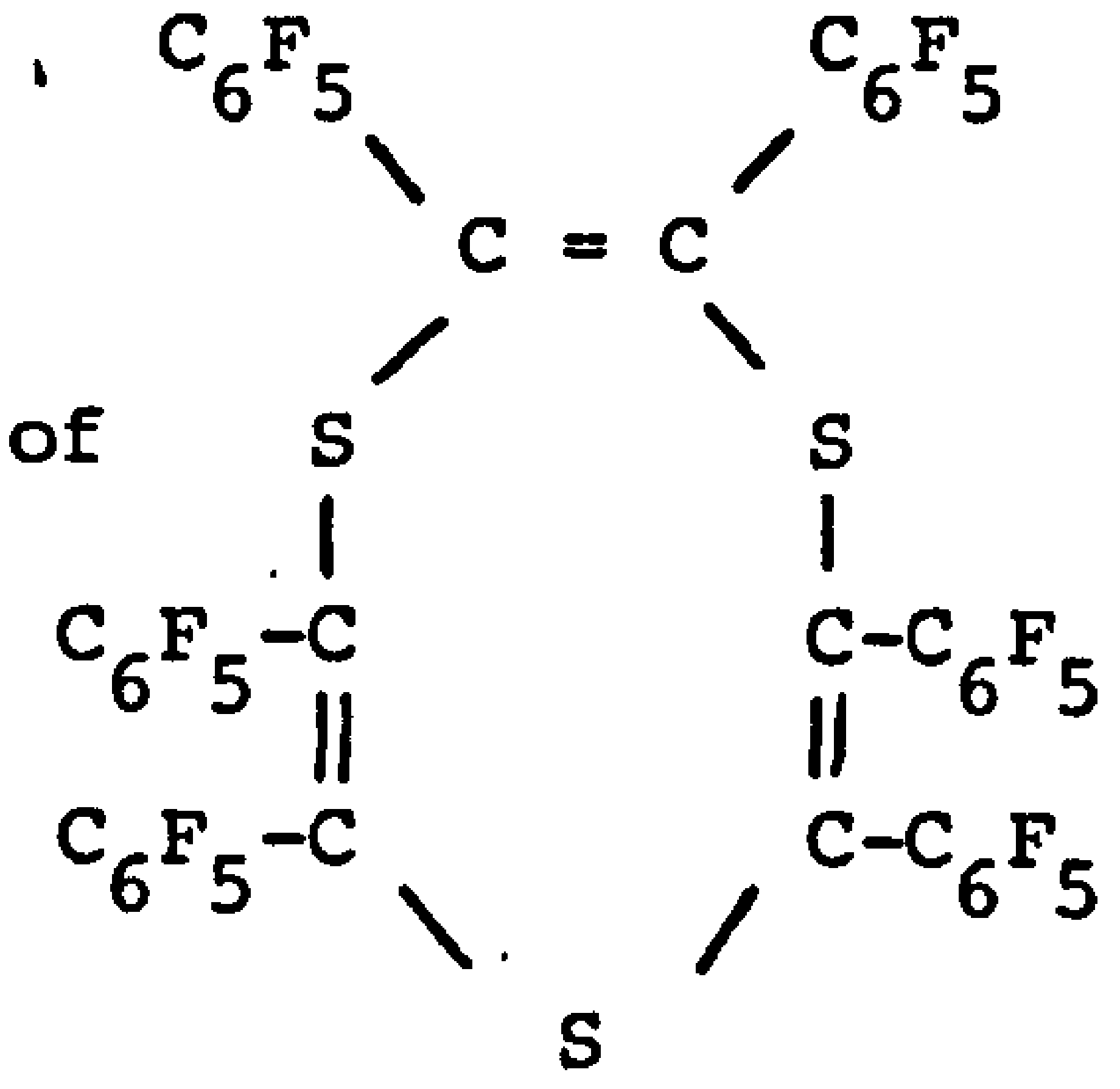
TABLE (4)

Mass spectrometric data

Compound	m/e	Relative intensity	Assignment
$C_{42}F_{30}S_3$ (IX)	1170	20%	$C_{42}F_{30}S_3^+$
	1138	50%	$C_{42}F_{30}S_2^+$
	1100	40%	$C_{42}F_{28}S_2^+$
	1064	20%	$C_{38}F_{27}S_3^+$
	1032	10%	$C_{38}F_{27}S_2^+$
	1000	15%	$C_{38}F_{27}S^+$
	780	30%	$C_{28}F_{20}S_2^+$
	748	40%	$C_{28}F_{20}S^+$
	716	10%	$C_{28}F_{20}^+$
	517	5%	$C_{14}F_{15}S_2^+$
	453	3%	$C_{14}F_{15}$
	422	10%	$C_{14}F_{10}S_2^+$
	390	80%	$C_{14}F_{10}S^+$
	358	100%	$C_{14}F_{10}$

$$\begin{tikzcd}
 & {[C_{28}F_{20}^{+}]} \arrow[dl, "-C_{14}F_{10}"'] & {[C_{28}F_{20}S_2^{+}]} \arrow[l, "-2S"'] \arrow[r, "-S"] & {[C_{28}F_{20}S^{+}]} \\
C_{14}F_{10} & & & \\
 & C_{42}F_{30}S \arrow[ul, "-C_{28}F_{30}S"] & C_{42}F_{30}S_3 \arrow[l, "-2S"'] \arrow[r, "-S"] \arrow[uu, "-C_{14}F_{10}S"'] & C_{42}F_{30}S_2 \arrow[uu, "-C_{28}F_{10}S"']
\end{tikzcd}$$

Scheme (3) - Initial fragmentation pattern of



CHAPTER 6

PLATINUM, PALLADIUM
[IRON, COBALT, CARBONYL]
COMPLEXES OF
SULFUR AND AMINO
LIGANDS

CHAPTER 6

PLATINUM AND PALLADIUM COMPLEXES OF SULFUR LIGANDS

Bonding and structure

Introduction: The chemistry of platinum and palladium consists almost entirely of co-ordination compounds and in this respect is like that of the heavy metals that are at both sides of them in the Periodic Table.

Transition Elements

Mn	Fe	Co	Ni	Cu	Zn
Tc	Ru	Rh	Pd	Ag	Cd
Re	Os	Ir	Pt	Au	Hg

Figure (6.1) - Transition elements showing the position of platinum and palladium in the Periodic Table.

The chemistry of platinum and palladium has recently been reviewed.[195,196] Co-ordination compounds of platinum are known in the oxidation states 0, 2+, 4+, 5+ and 6+ although the latter two states are not important in these studies. Platinum(II) compounds are diamagnetic and generally have square planar co-ordination. Valence bond theory for the complexes assumes a d^8 electronic configuration and uses 5d orbitals.

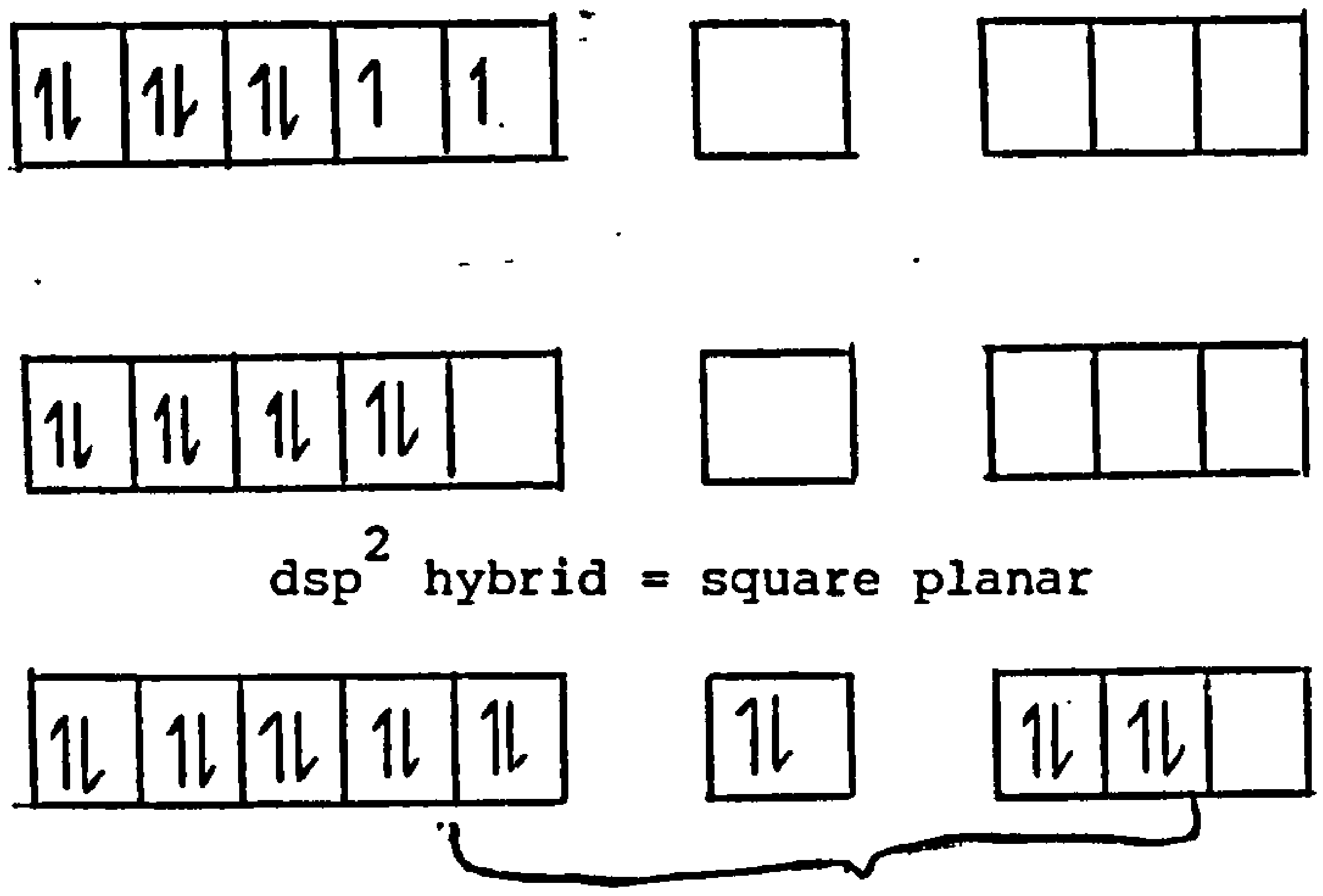
Nine orbitals are available for bonding in these elements assuming that the f-orbitals do not contribute to the bonding in platinum compounds. Those used to form σ bonds are from symmetry requirements $5dx^2-y^2$, $5dz^2$, 6px, 6py and 6s.[197] The remaining orbitals (i.e. 5dxy, 5dxz, 5dyz and 6pz) will be available to form π molecular orbitals with ligand orbitals of appropriate symmetry. The combination of the orbitals in terms of valence bond theory gives dsp^2 hybridization[198] for the square planar complexes.

In terms of valence bond theory square planar co-ordination can be described as follows:

Pt = [Xe] $5d^8$ $6s^2$ $6p^0$ Ground state atom

Pt^{+2} = [Xe] $5d^8$ $6s^0$ $6p^0$ Ground state ion

$PtCl_4^{2-}$



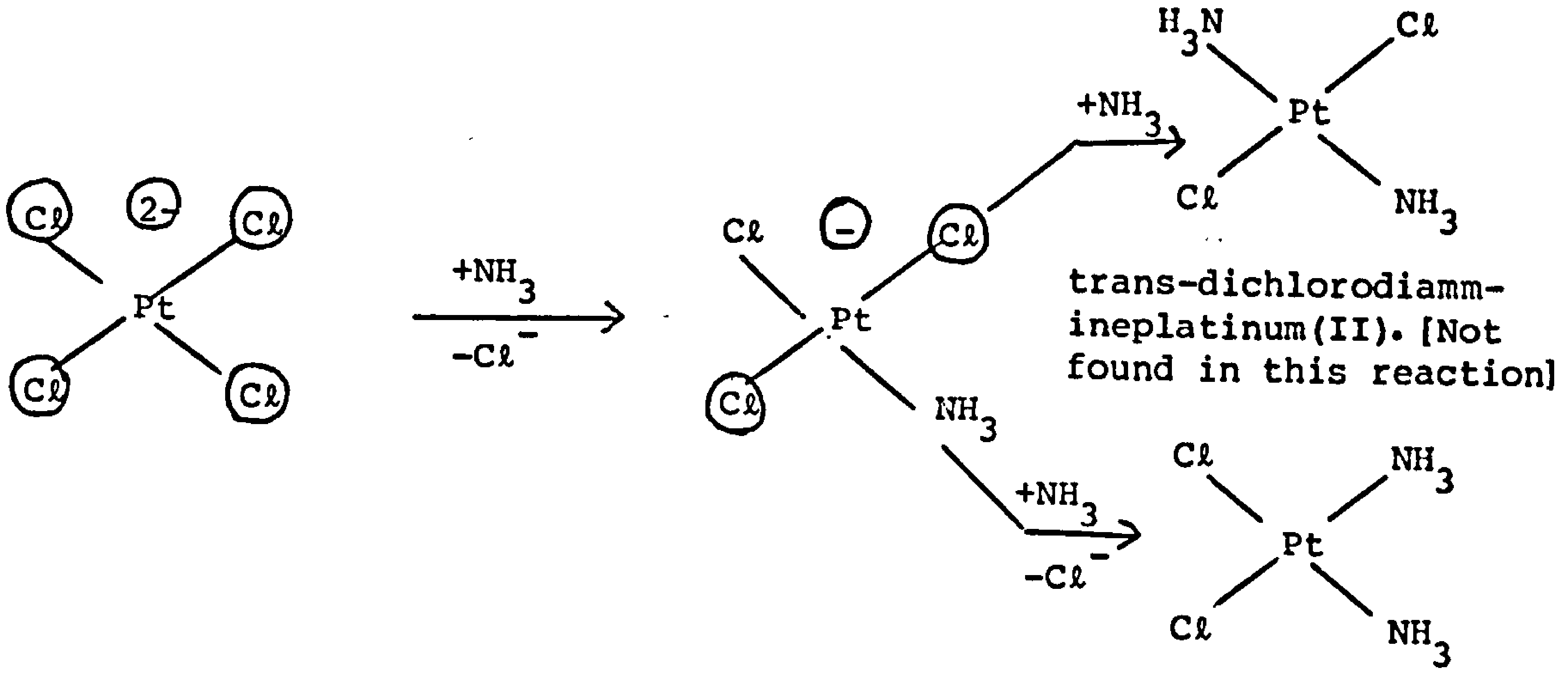
Co-ordination by 4 ligands

In valence bond theory the ligand donates two electrons to the metal and makes up the dative bond through a σ (sigma) bond, this leading to an increase in the formal negative charge on the metal. Simultaneously the metal can direct or redirect part of its electron density to the empty orbitals of the ligand. This latter effect has been called back donation or back bonding. We will use this theory to explain the trans effect and trans influence in a square planar platinum(II) complex and we will now discuss each of these in turn.

Trans effect and trans influence

The trans effect in square planar platinum(II) complexes is the effect of one co-ordination group (e.g. R_2S) upon the rate of substitution of the ligands opposite (trans) to it.[199] The "trans influence" is defined as the extent to which a ligand weakens the bond trans to itself in the equilibrium state.[197] It is important to separate these two effects, although the earlier literature made little attempt to distinguish between them. The trans effect must be kinetically controlled since it refers to rate and the thermodynamically most stable isomer is not always produced. As an example it generally is possible to form two different isomers e.g. [eqs. (1) and (2)]

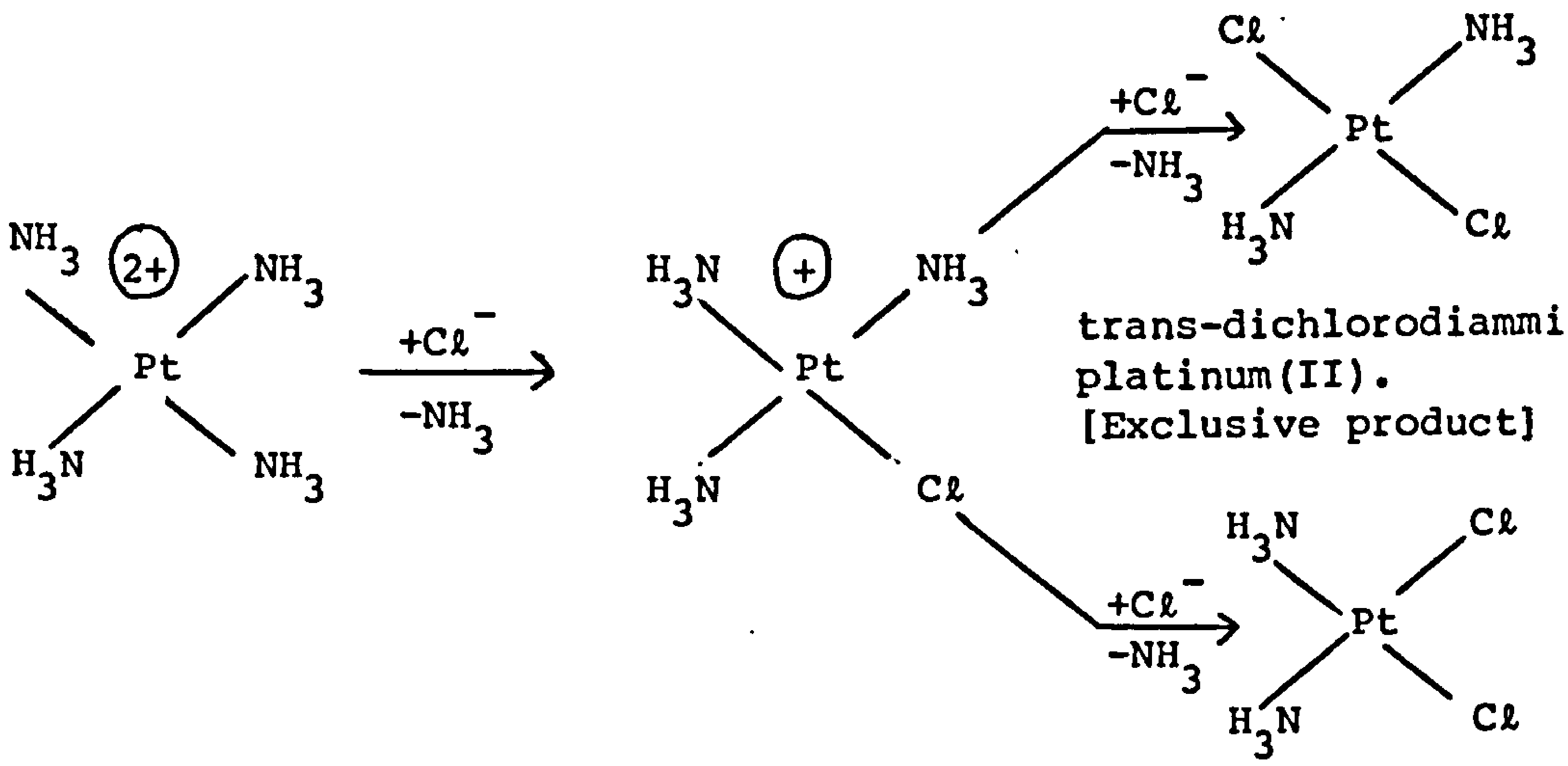
(1)



trans-dichlorodiammineplatinum(II). [Not found in this reaction]

cis-dichlorodiammineplatinum(II). [Exclusive product]

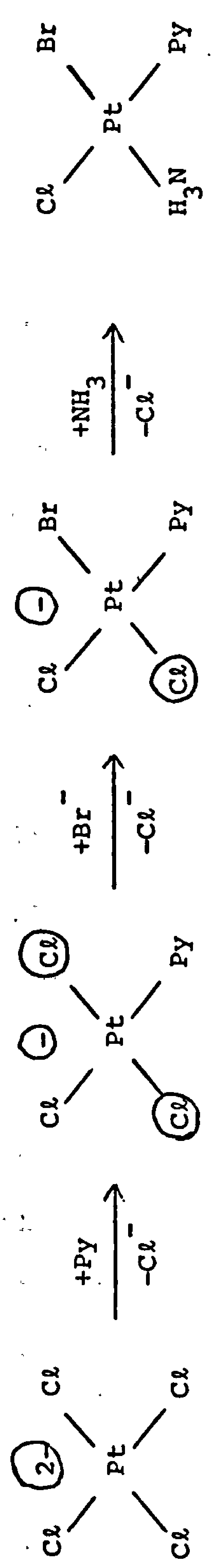
(2)



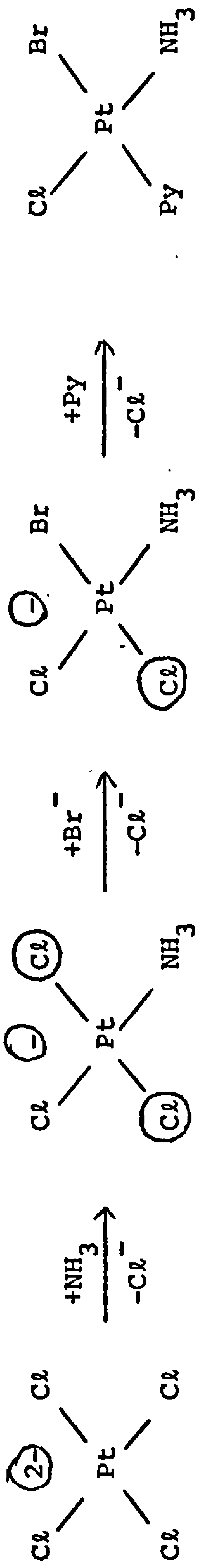
trans-dichlorodiammine-platinum(II). [Exclusive product]

cis-dichlorodiammine-platinum(II). [Not found in this reaction]

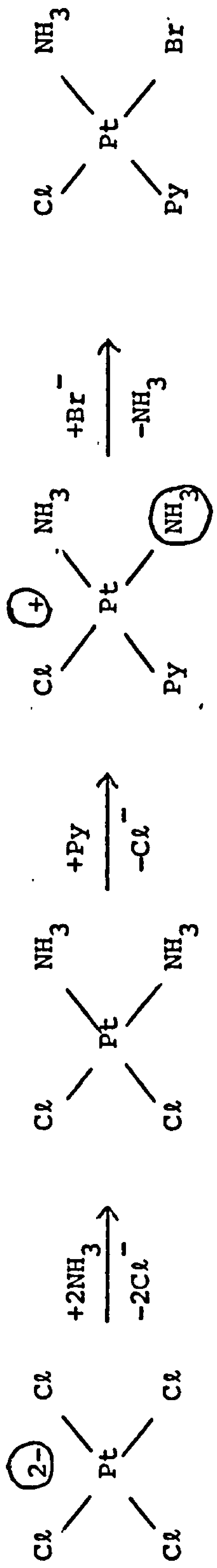
or three different isomers (eqs. (3), (4) and (5)) depending upon the reaction sequence and only one of the isomers can be the most stable in the thermodynamic sense. Furthermore, we observe that the best trans directors (T) are also those that are the best π bonders. Hence in the formation of bis isomers of the sort $[PtC\ell_2T_2]$ from $[PtC\ell_4]^{-2}$ the trans isomer is always observed (eq. 6) even though, in general, the cis isomers are favoured thermodynamically. Such kinetically controlled reactions are common in both organic and inorganic chemistry and represent examples of reactions in which the energy of activation of the activated complex is more important in determining the course of reaction than the energy of the products.



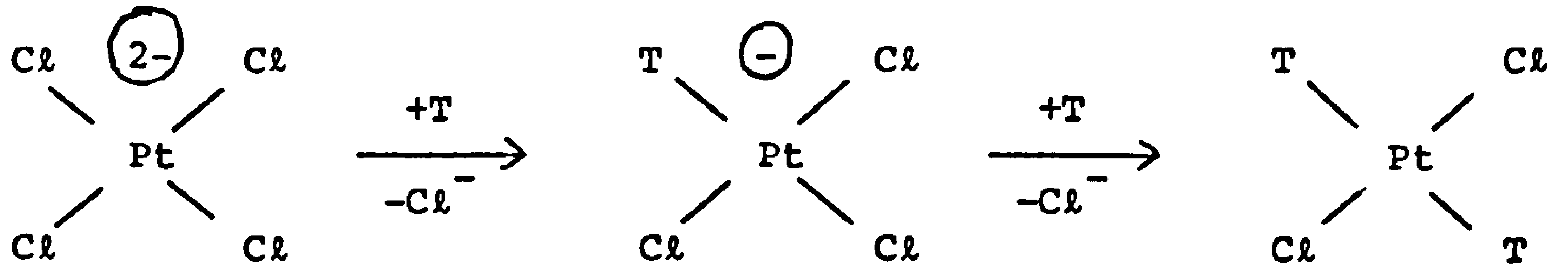
(3)



(4)



(5)



(6)

There are two points to be explained for any mechanism of the trans effect. The first must emphasize the weakening of the trans bond, the second must emphasize the lowering of the activation energy for the trans replacement. The theories that explain the trans effect in transition metal complexes will now be considered.

The earliest theory that still has current application is the polarization theory, the simplest representation of trans influence using σ-sigma bonds.[198] Polarization theory suggests that in complexes such as $[PtC\ell_4]^{-2}$ i.e. a Pt^{2+} ion surrounded by four equivalent chloride ligands, the metal-ligand dipoles will all be identical. If (x), a ligand which is more polarizing, is introduced for Cℓ and thus induces an uncompensated dipole at the metal, this induced dipole on the metal will oppose the natural dipole of the ligand to the polarizing ligand weakening the trans ligand-metal bond. As the ligand x which is more polarizing and the metal attract each other this will strengthen the ligand x-metal bond and weaken the trans bond. Polarization theory indicates that the large and polarizable metal atoms will show greatest trans influence, i.e. the order of a given ligand with different metals is $Pt^{2+} > Pd^{2+} > Ni^{2+}$ because of the relative size of the metal species. It must be noted that polarization theory emphasizes the role of the inductive effect and thus it can be very important in the fluorinated compounds which are part of our work.

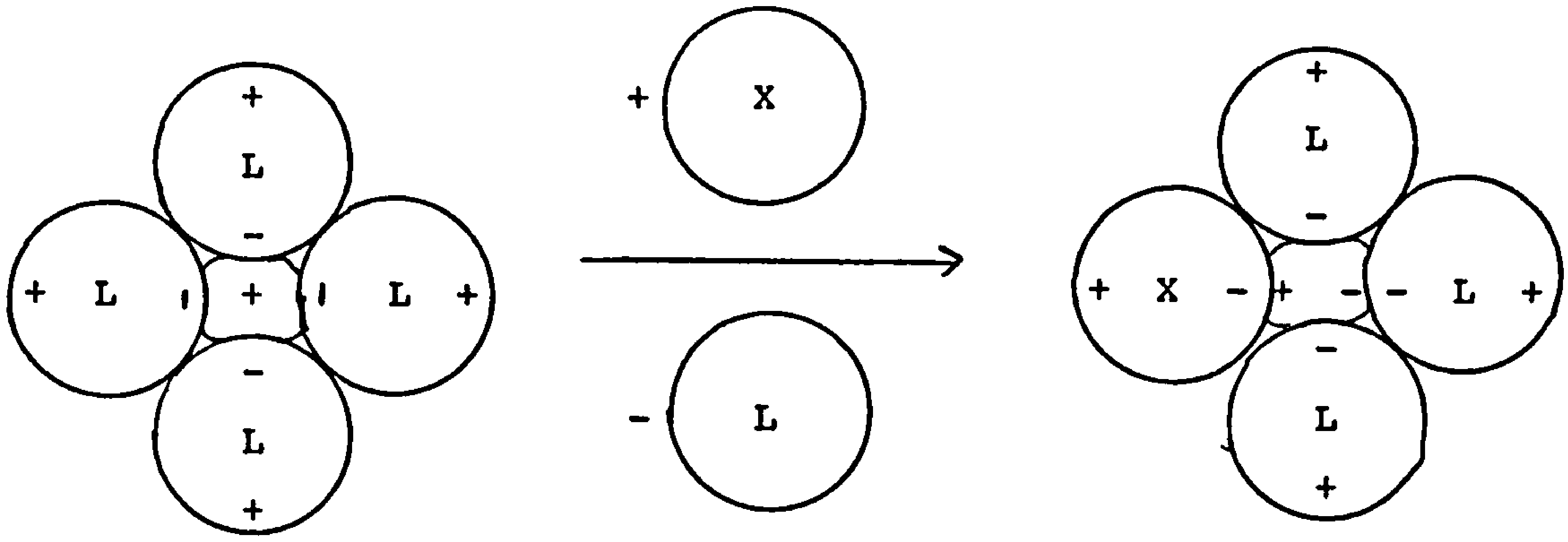
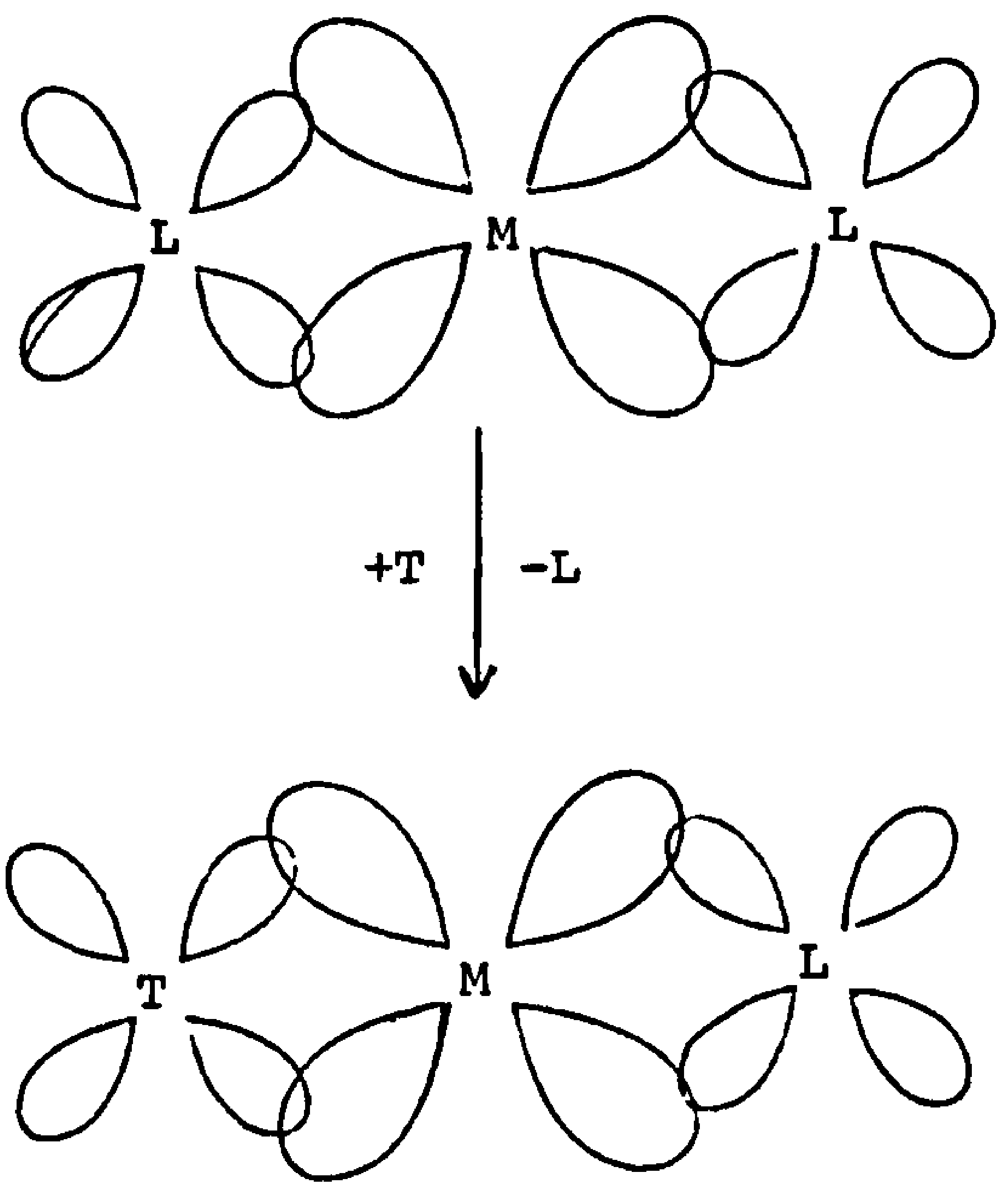


Figure (6. 2) - Grinberg (polarizing) model of trans influence.

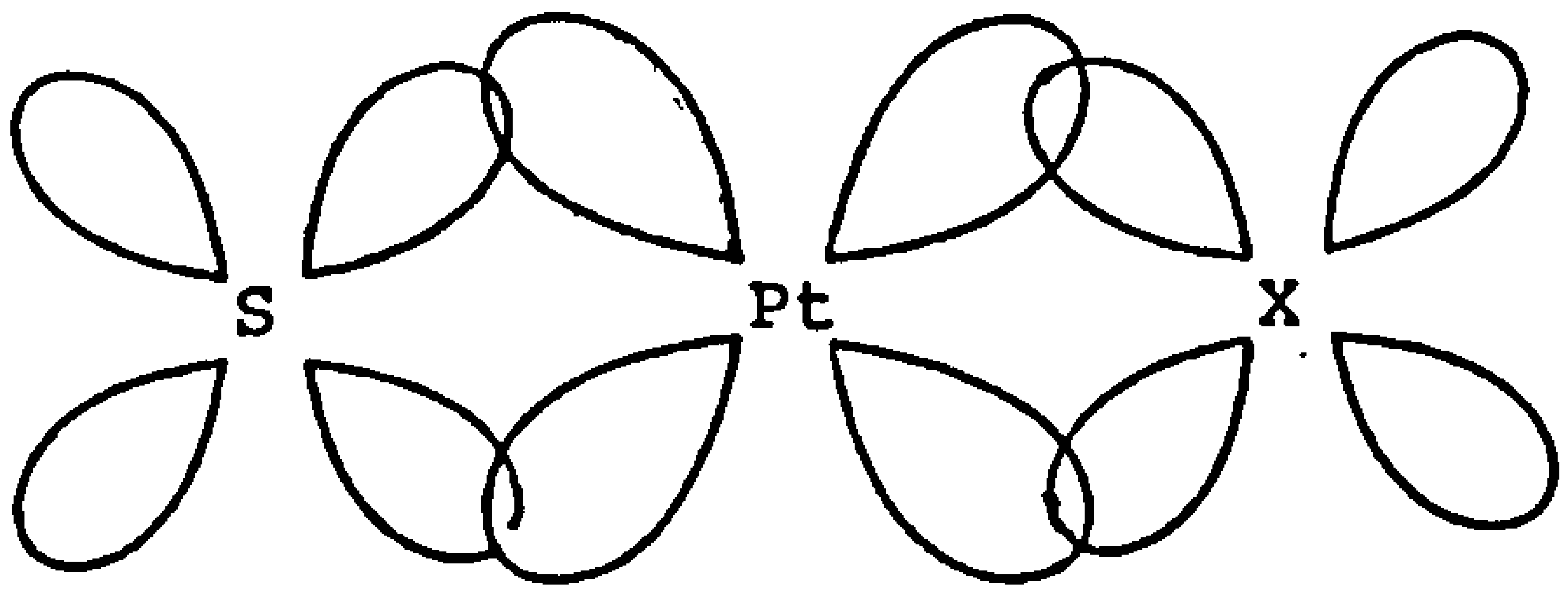
Another theory for the trans effect assumes static π-bonding which weakens the trans bond. It assumes that two π-bonding ligands competing for the d-electrons of the metal will tend to labilize each other and that the strongest π-bonder will dominate thus weakening the bonding of the group trans to it. It is assumed that cis ligands do not compete[260] for electron density from a common d-orbital since they each use different d-orbitals although cis ligands could be considered to share a dxy orbital.



T = Trans Director ligand

Figure (6.3) - Postulated effect of a <u>trans</u> director ligand on the dπ-dπ bonding.

Trans influence is measured by the weakening of bonds. It is often investigated by studies of spin-spin coupling constants[201-203] and i.r. frequencies.[204-206]



Empty S
d-orbital

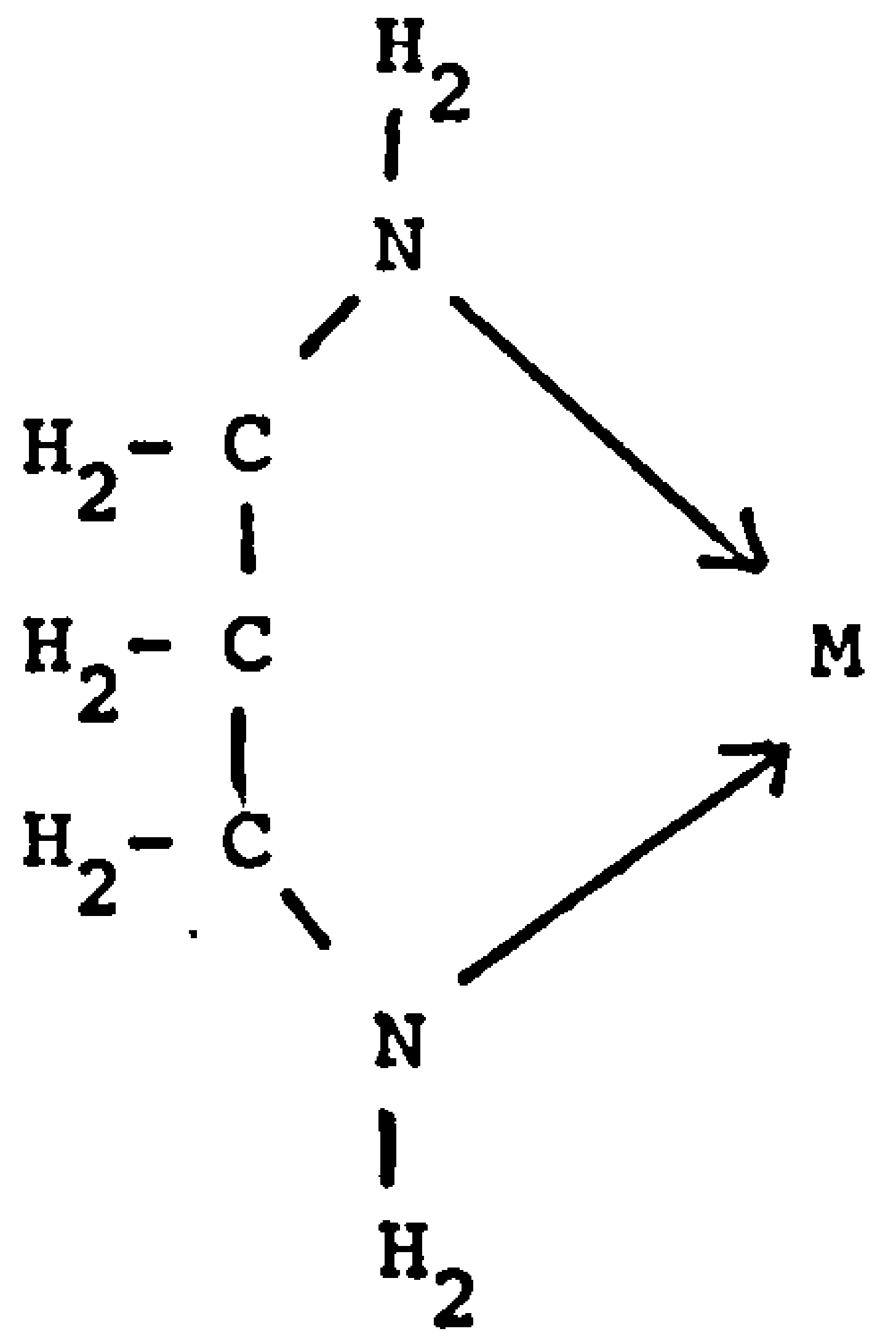
Full Pt
d-orbital

The Figure (6.4) shows dπ-dπ bonding between the ligand and metal S-Pt-X.

Chelate effect

The chelate effect is that ligands which contain more than one donor atom and thus may co-ordinate to more than one position on the acceptor form more stable complexes than the corresponding monodentate ligands.

In 1952 Schwarzenbach[207-209] showed that the stability of metal complexes containing a chelate ring is considerably greater than that of an analogous compound which contains fewer or no chelate rings. This extra stability is termed the chelate effect. There is no unique explanation for the effect, in fact the enhanced stability of complexes containing chelated rings has been attributed to a large variety of factors and even doubted at times although it is now clear that there is extra enhanced stability of such compounds. Resonance stabilization is thought to be responsible for the particular stability of the six-membered rings of 1,3-propanediamine complexes.[210]



Rigid chelated ligands like olefinic diphosphines form more stable complexes than the corresponding saturated diphosphines, presumably because of the greater rotational freedom of the latter ligands encouraging partial dissociation.[211,212] It has also been pointed out[213] that the more favourable enthalpies of formation of metal chelate compounds compared to enthalpies observed in similar complexes without chelate rings can be interpreted as a result of repulsive forces between the polar groups bound to the metal. In simple complexes inter-ligand repulsions can be of great importance, whereas in chelating ligands the bridge between these dipoles holds the donor groups together in opposition to the repulsive forces. Thus the formation of a metal chelate involves a more favourable heat of reaction because it is not necessary to bring together ions or dipoles with like charges.

The effects just described depend on the specific system studied. In addition to these effects there is an entropy factor common to all chelate compounds which is normally regarded as the origin of the chelate effect.[214]

Considering the differences in the dissociation processes of the mono and bidentate ligands shown in Figure (6.5) it is clear that if a metal ligand bond is broken in chelated and non-chelated compounds the probability of the now free monodentate ligand to reform the bond is less than that of the dissociated donor atom in the chelating ligand atom which has been retained near the metal atom bonding the other end of the molecule.

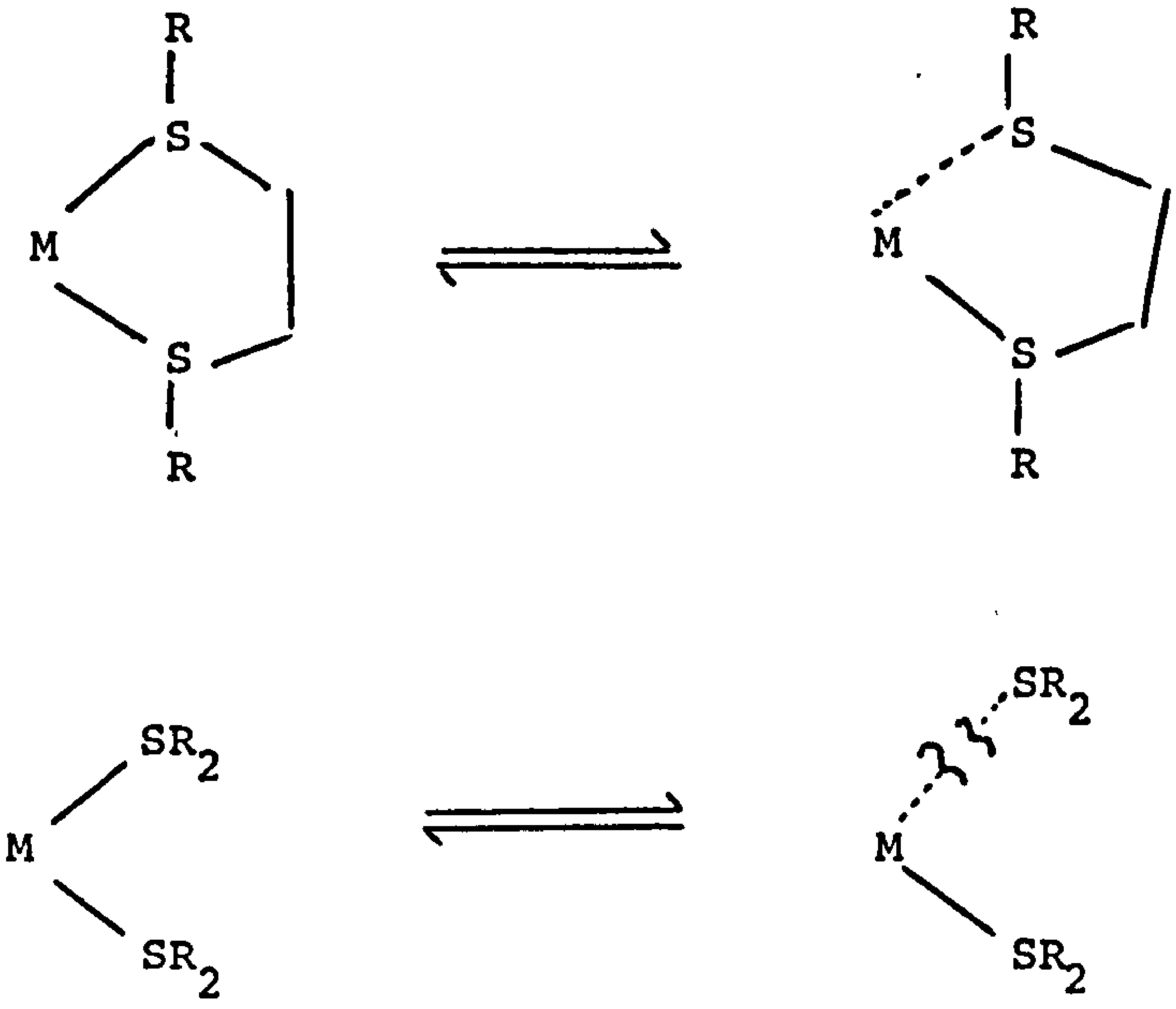
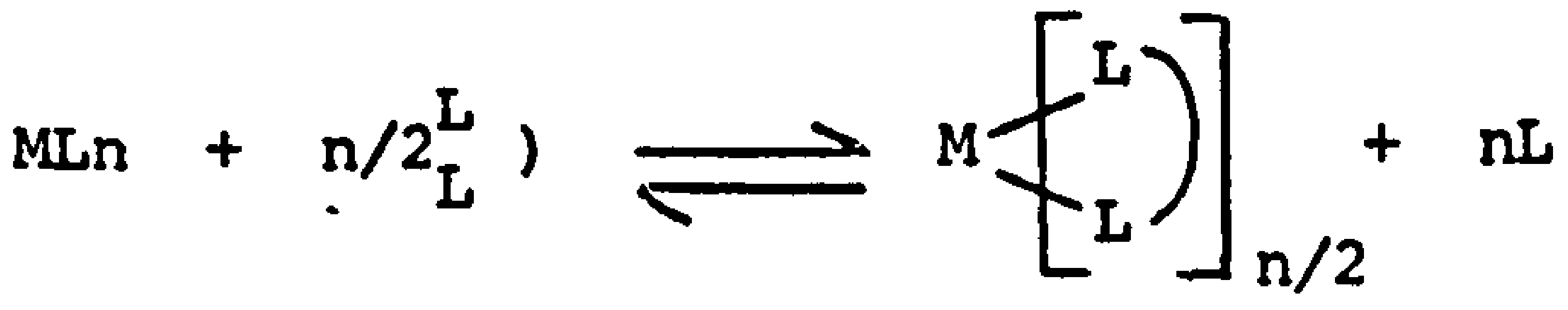


Figure (6.5) - Dissociation of monodentate and bidentate ligands.

Experimentally the above equilibrium has been studied



$$\mathrm{MLn} + n/2\overset{\mathrm{L}}{\underset{\mathrm{L}}{\ }}) \rightleftharpoons \mathrm{M}\left[\overset{\mathrm{L}}{\underset{\mathrm{L}}{)}}\right]_{n/2} + n\mathrm{L} \qquad (I)$$

with a large variety of ligands[215-217] particularly with ammonia and amines.[218,219] The change in entropy for reaction (I) will be proportional to the difference in the number of molecules present in the system.

Platinum and palladium complexes of organic sulphides

Platinum and palladium complexes of organic sulfides[220] and selenides have been the subject of many recent publications, and the pyramidal environment about S and Se in these complexes is now well established. Evidence includes X-ray crystal structural analysis of $[(Et_2S)_2HgC\ell_2]$,[221] $[(EtS)_2Ni]_6$[224]. $[PtC\ell_2(CH_3SCH_2CHCF_3SCH_3)]$[222] and $[PtC\ell_2(CF_3SCHMeCH_2SCF_3)]$[223], $[(Et_2Se)_2PdC\ell_2]$[225], $[(Pr^iSC_2H_4SPr^i)PtC\ell_2]$[226].

The rings in the chelate complexes are not planar but show the effect of tetrahedral co-ordination about sulfur and carbon.

The ^1H NMR spectra of $(MeSC_2H_4SMe)MC\ell_2$ [M=Pd or Pt][227] and $(R_2S)_2PtC\ell_2$[228] $[R_2=(PhCH_2)_2$, Et_2, Me_2 or $PhCH_2$, Me] suggest that the pyramidal conformation about sulfur is retained in solution.

In 1966 Abel[227] reported the proton nmr spectra of $[(MeSC_2H_4SMe)PtC\ell_2]$ showing the presence of two resonances for the methyl groups which are formally equivalent, interpreted as arising from two distinct pairs of equivalent methyl substituents which, on increasing the temperature, converged and eventually coalesced to a sharp signal in a reversible process. These results were explained by the presence in solution of two different isomers shown in figure (6.6a)

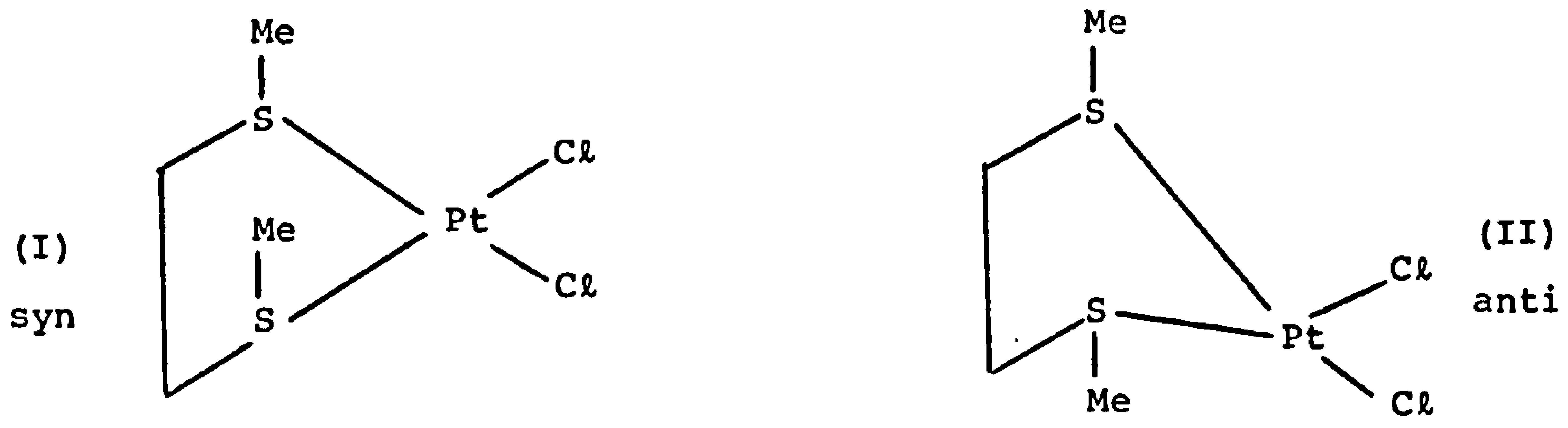


Figure (6.6a) - Stereoisomers of $(MeSC_2H_4SMe)PtCl_2$.

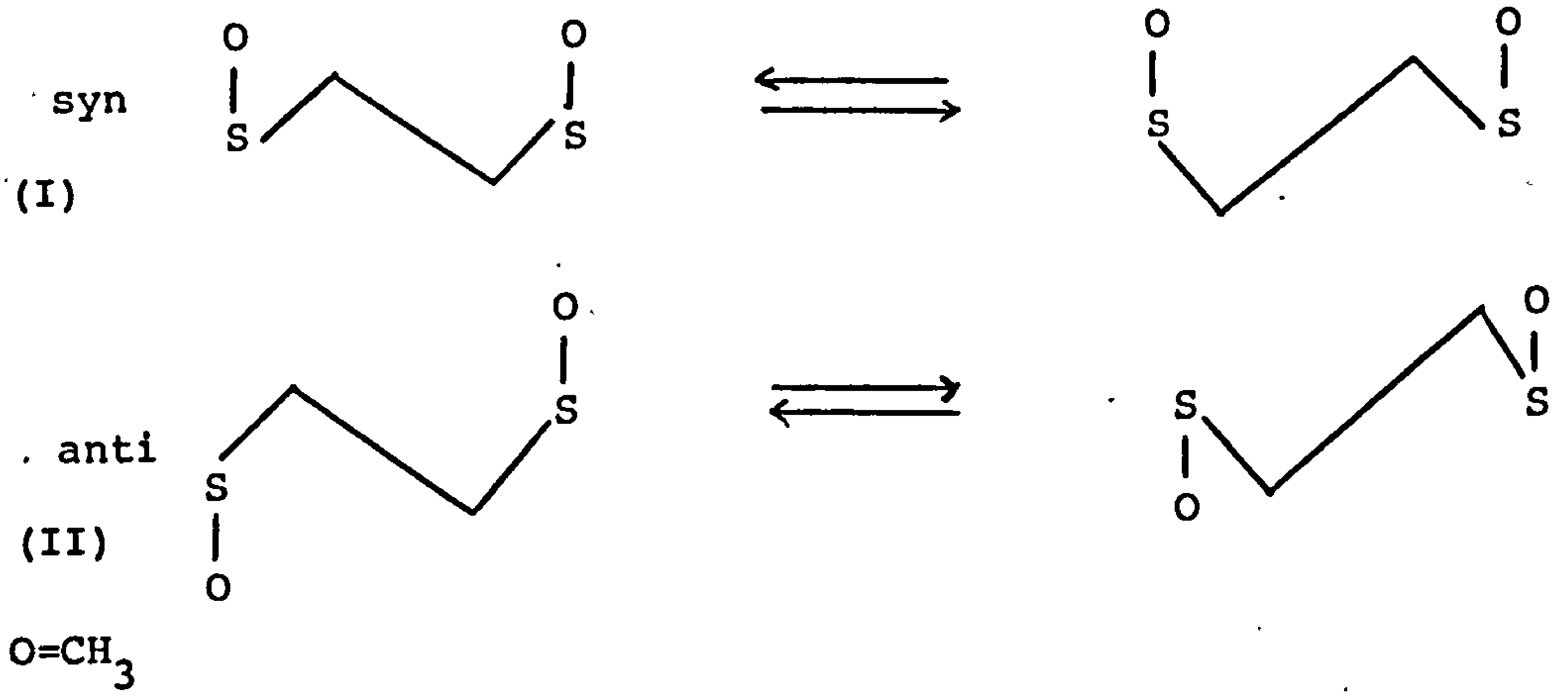


Figure (6.6b) - Isomers of $(MeSCH_2CH_2SMe)PtCl_2$.

In the above and subsequent diagrams the platinum co-ordination plane lies normal to the plane of the paper.

At high temperatures the inversion about sulfur becomes rapid on the NMR timescale so that it is not possible to differentiate between the different environments and a single resonance is observed. In the distinct structures I and II Fig. (6.6a) different molecular environments exist for the methyl groups in the two isomers and two absorptions are generated. At the same time the chemical equivalence of the methyl substituents within each isomer is maintained and both absorptions appear as singlets (ignoring coupling to the ring substituent atoms). It should be noted that ring inversion in the above complexes is very rapid on the nmr time scale and only in the case where bulky substituents have been introduced into the ring is the inversion slowed so that ring inversion processes can be observed in the nmr spectra at low temperatures.[236]

Since the first report, several studies on the possible mechanisms for isomeric inter conversion have been carried out and measurements of the barriers to inversion have been carried out for a large series of closely related dithio[229,230,228,231] and diselenoether[232-235] complexes. Most of these studies are conducted in solution where generally a mixture of isomers is obtained. Surprisingly, however, very little is known about which specific structures are the origin of a given set of spectroscopic parameters obtained from solutions. In general the studies have not been of equilibrium mixtures but the mixture of isomers found in the preparations. It would be of interest to warm up the mixture so that there was rapid interconversion of isomers and then allow the solution to cool. Provided that the complex stayed in solution this would give an equilibrium mixture of isomers. The ratio of isomers could then be compared with that as prepared and would indicate whether the method of preparation favours particular isomers. It is found that the barrier to sulfur inversion is larger for the fluorinated complex $(CF_3SCH_2CH_2SCF_3)PtC\ell_2$[236] than for the hydrocarbon derivative. The factors affecting this barrier are not completely understood, but the information available indicates that the rate of inversion is controlled by (a) the metallic centre[229,237], the inversion barrier rising as the atomic number increases, (b) steric factors[238,239] and (c) factors related to electronic changes at the donor atom during inversion.[240-243]

Sulfur inversion is sensitive to steric factors, particularly when bulky groups in the molecule cause it to adopt a configuration which minimizes steric interactions. On the other hand, the electronic charge at the centre of inversion depends on the substituents at the donor atom and on the other ligands present.

The mass spectra of the chelate complexes of ligands containing trifluoromethylthio derivative have been described[244] and fluorine-containing diselenoethers and their platinum(II) and palladium complexes have recently been published.[245]

Mechanisms

Two mechanisms have been suggested to rationalize the interconversion of isomers resulting from the environment about sulfur.[217] In 1967, Haake and Turley[217] suggested the mechanism depicted below

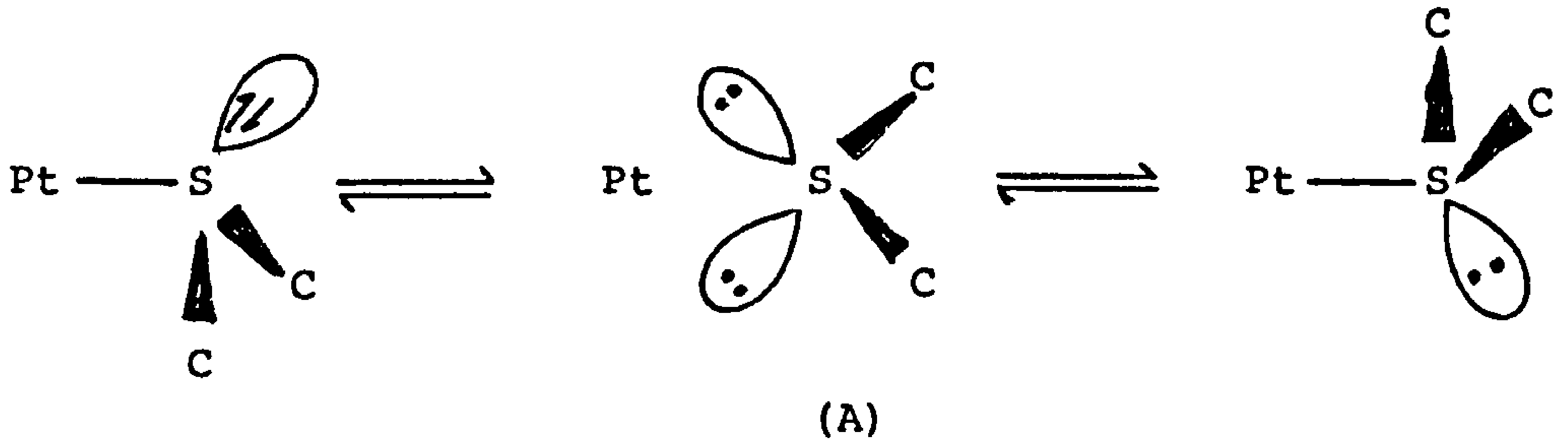


Figure (6.7) - Turley-Haake mechanism for sulfur inversion.

The inversion process is described as an internal displacement of one lone pair by another and in this sense it is an intramolecular displacement process rather than a true inversion of configuration.

In structure (A) Pt, S and both carbons are coplanar and therefore the sulfur atom retains tetrahedral configuration during the process. Alternatively a more widely accepted mechanism,[230,246,247] similar to that suggested for inversion at nitrogen[248] and sulphoxides,[249] is shown in figure (6.8).

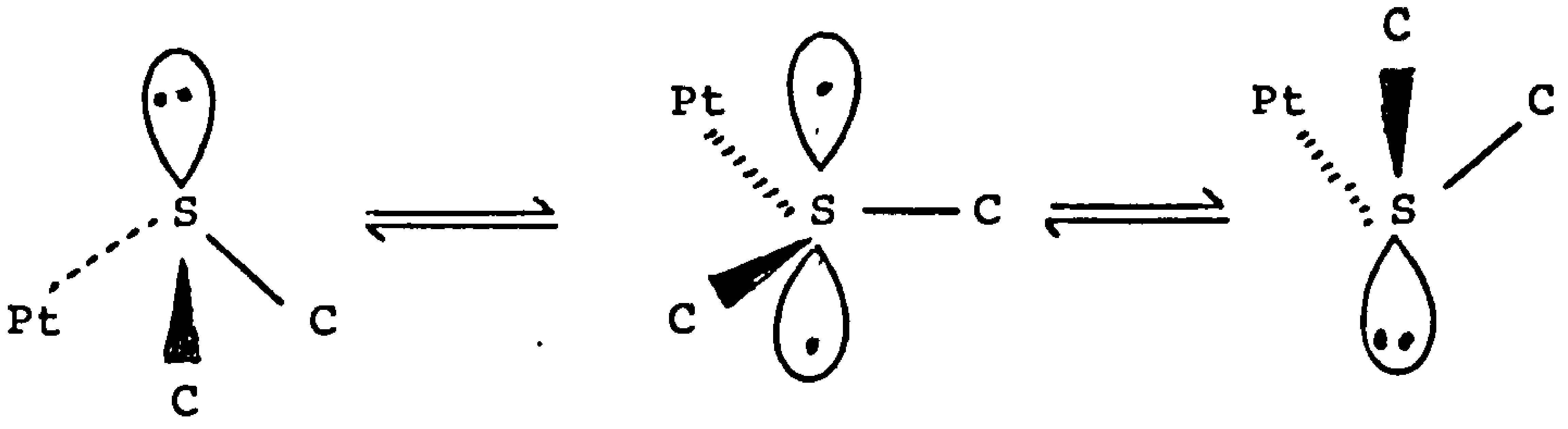


Figure (6.8) - Classical mechanism for sulfur inversion.

This involves the passage through a transition state in which the lone pair has pure p-character. Inversion of configuration occurs through a coplanar, or nearly coplanar, arrangement of substituents around the central sulfur atom in which the bonds of the donor atom approximate to a sp^2 hybridization.[250]

Recently Abel and co-workers,[230,247] have suggested that the distinction between a) both sulfur lone pairs bonding simultaneously to the metal (Haake-Turley mechanism) and b) a σ-bond with the remaining lone pair in a pure p-orbital at sulfur (classical mechanism), has no physical significance and therefore both mechanisms could be regarded as static representations of the same process. The equivalence of both mechanisms is perhaps clearer if the electronic localization in the transition state is avoided as in figure (6.9).

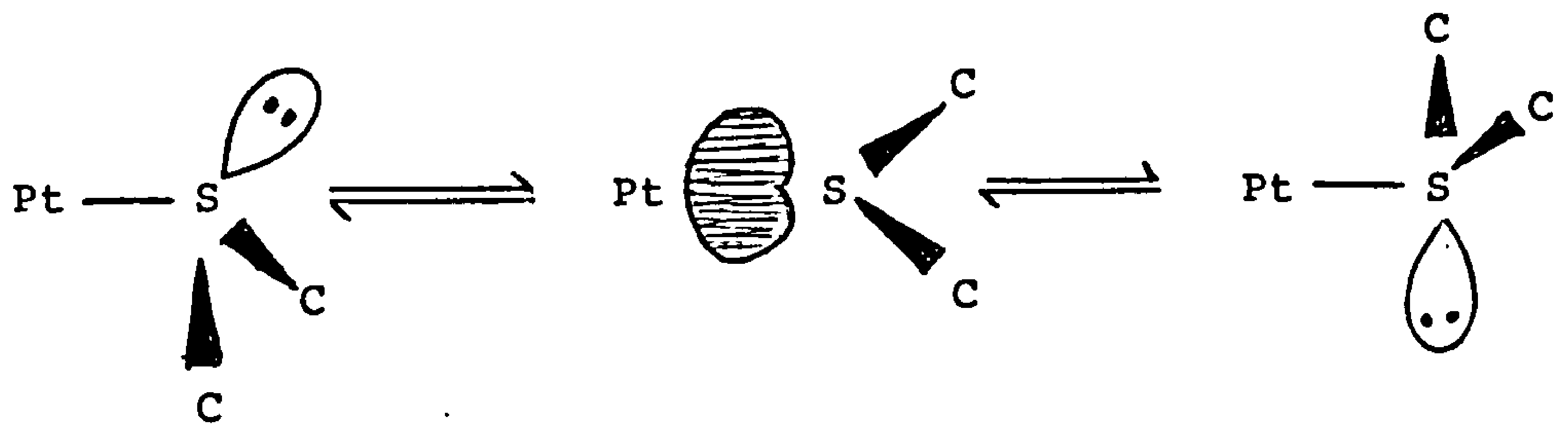


Figure (6.9) - Mechanism for sulfur inversion.

A strong σ-electron donor may exert a weakening effect on the trans Pt-S bond, and a strong π-acceptor ligand will remove electron density from Pt, thus encouraging nucleophilic attack at the trans position. Both processes would enhance the rate of inversion at a sulfur bonded to platinum by the mechanisms we have described. Some evidence of this effect can be derived from observations[217] that inversion is more rapid in trans-$(R_2S)_2PtC\ell_2$ than in cis complexes. Sulfides have much greater trans-influence than chloride.[228]

Discussion

The chelated 1:1 complexes prepared during the course of the present work are indicated in table (1)

TABLE (6.1)

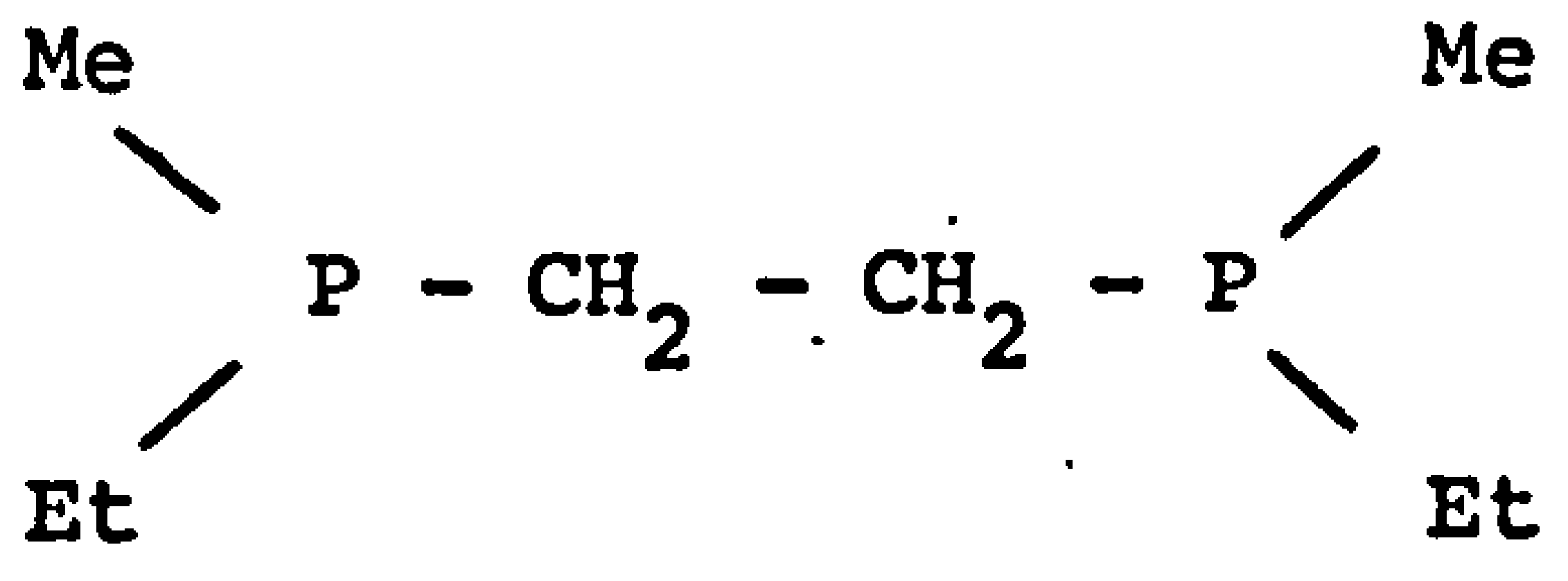
Ligand	1:1 platinum(II) dichloride complexes	1:1 palladium dichloride complexes
$CH_3SCH_2CHPhSCH_3$	yellow	orange
$CH_3SCHPhCHPhSCH_3$	yellow	orange
$CH_3SCPh{=}CHPh$	yellow	orange

All synthesis of complexes were carried out in a very similar manner by reaction of the ligand with a suitable metallic salt (generally N_2MX_4, where N = K, M = Pt, X = Cℓ, and $PdC\ell_2$) in a solvent system which depended on the relative solubilities of both ligand and metal salt. All complexes were obtained from aqueous ethanol solution. The complexes were crystallized from chloroform on standing for varying periods.

The formation of hydrocarbon dithioether complexes of platinum(II) and palladium(II) of the type $[MX_2L]$ generally proceeds[251] through intermediate ionic species of type $[ML_2][MX_4]$ although in the reaction between chlorometallates(II) and dithioethers containing polyfluorinated substituents no such intermediates were observed.[236] The precipitation and crystallization of the complexes PtX_2L was slow and intermediate ionic species cannot be ruled out. Many complexes of 1,2-bis(alkylthio)ethanes are known[252,227,233,253] and in some formally square-planar platinum(II) and palladium(II) derivatives it has been shown that dithioether is chelated to the metal and that in solution at room temperature there are isomers present which arise because of relative positions of the sulfur substituents with respect to the plane of the metal co-ordination. The ring is puckered at the carbon atoms (see page 138). The preparation of some platinum(II) complexes of dithioethers containing phenyl groups on the bridging methylene groups will be described.

The first compound to be considered is $(CH_3SCHPhCH_2SCH_3)PtC\ell_2$ which was shown by n.m.r. spectroscopy to exist as a mixture of isomers. In order to determine the configurational distribution of asymmetric compounds in solution the compounds $(CH_3SCHPhCH_2SCH_3)PtC\ell_2$, M = Pt, Pd were studied.

Some complexes containing an asymmetric chelating dioether group and also diphosphines and diarsines are known.[236,254,255,256] For five-membered ring complexes with group V donor atoms the bridge substituent seems to determine the favoured conformer adopted by these compounds in solution.[255-257] Dithioethers differ from diphosphines and diarsines so that in the latter compounds there is no change in the number of isomers regardless of whether the bridge is symmetric or asymmetric because isomers are present because of the relative position of the substituents in the sulfur whereas this cannot occur for diphosphines unless there are two different substituents present in the phosphorus e.g. for



For dithioethers dissimilar substituents on the bridge change the possible number of isomers in solution.

The complex $[PtC\ell_2(CH_3SCHPhCH_2SCH_3)]$ should exist as four isomers. Figure (6.10) shows the possible isomers.

All of the spectroscopic properties of the present complex suggest the presence of molecular species with square-planar co-ordination about the metal.

The infrared spectra of the complex above are virtually identical to those of the free ligands except that two extra bands assigned to metal chlorine stretching[258] modes are seen near to 300 cm^{-1} and the presence of two Pt–Cℓ modes is consistent with a cis-$PtC\ell_2$ grouping.

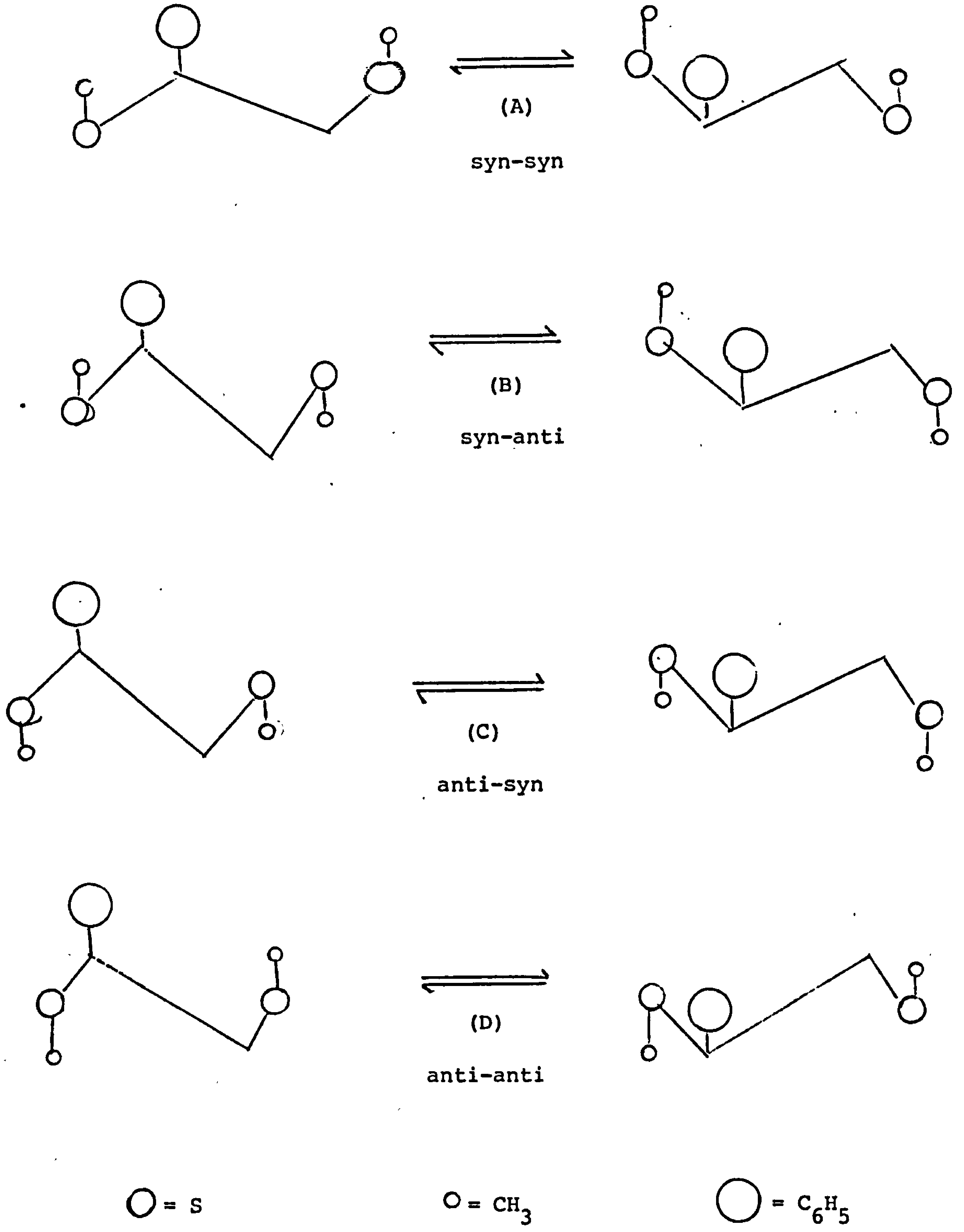
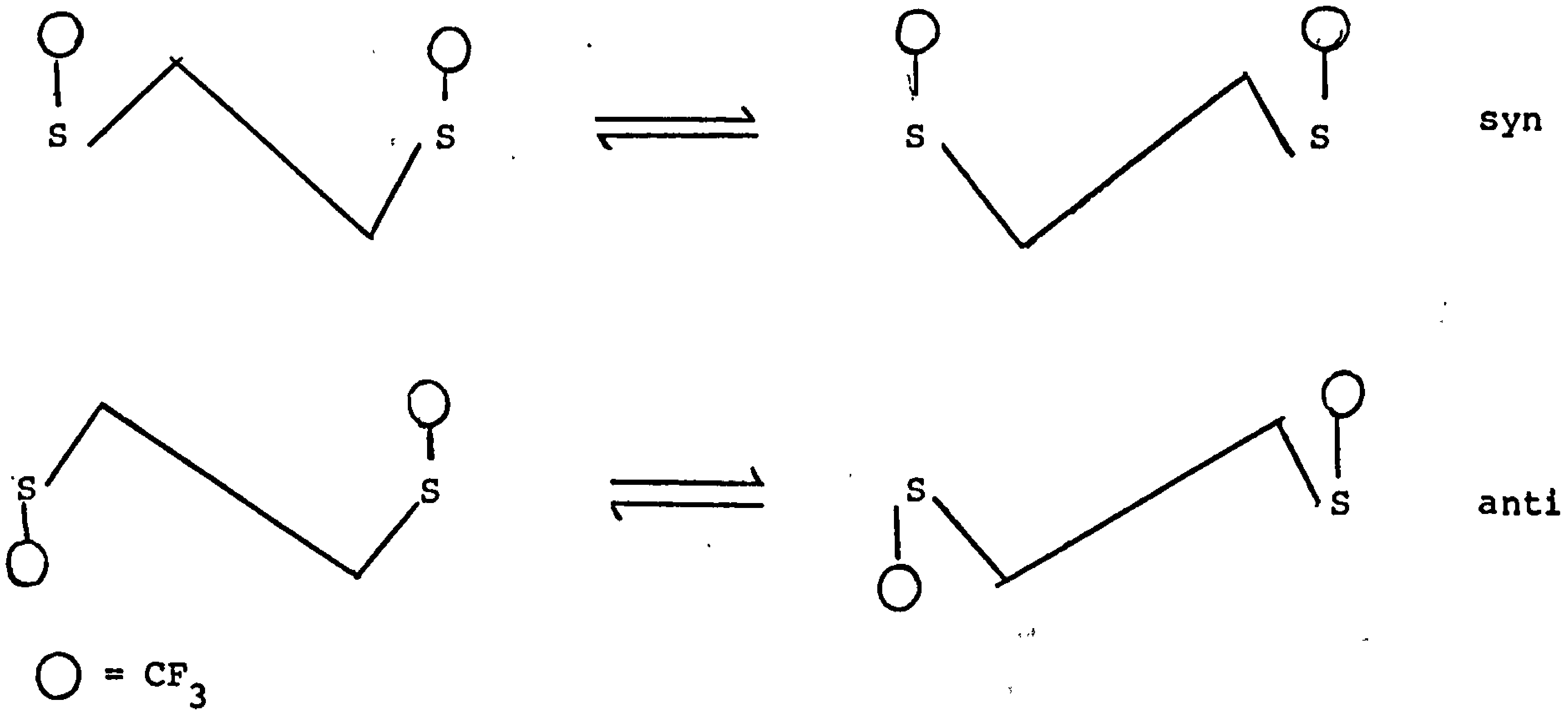


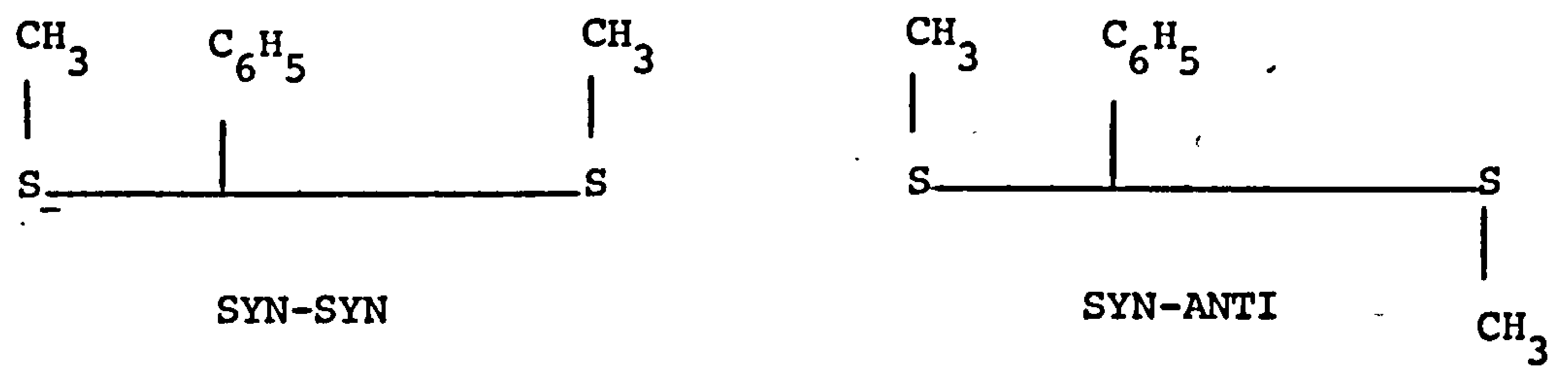
Figure (6.10) - Four pairs of isomers of $[(CH_3SCHPhCH_2SCH_3)PtCl_2]$

In order to identify each arrangement with a simple nomenclature the relative orientation of the bridge substituent and the adjacent sulfur substituent will be referred to as *syn* or *anti* followed by the reference to the relative orientation between both sulfur substituents, also as syn or anti as illustrated in figure (6.10).

In 1982 Hunter was able to identify the isomers of polyfluoroalkyldithioethane platinum complexes by crystallography and n.m.r. spectroscopy. He found for the complex $[PtC\ell_2(CF_3SCH_2CH_2SCF_3)]$



(following the work of Torrens) that proton-decoupled ^{19}F NMR signals show two isomers in the ratio 35:65, the signal at high field shows quartets as a result of $^{19}F-^{19}F$ coupling between the two CF_3 groups which are rendered non-equivalent by the presence of one ^{13}C nucleus. The $J(^{19}F-^{19}F)$ value of 4 Hz was considered too large to represent spin-spin coupling through six bonds.[259] The signal showing $^{19}F-^{19}F$ coupling is assigned to the *syn* isomer where CF_3 groups are on the same side of the $S_2PtC\ell_2$ plane. On the basis of molecular modes, Cross et al.[236] came to the conclusion that the syn conformation would have greater steric interactions than the anti isomer supporting the identification from NMR measurements.


SYN-SYN

SYN-ANTI

Figure (6.11) - Nomenclature for complexes containing a bridge substituent.

The ^{1}H nmr spectrum of $(CH_3SCH_2CHPhSCH_3)PtC\ell_2$ is insufficiently resolved to allow identification of isomers. Torrens used molecular models to determine the relative steric hindrance in the various isomers and hence predicted structures for the isomers in terms of the relative amounts present as determined by nmr spectroscopy. Subsequently he showed that the structure of isomers predicted on this basis were generally in agreement with structures found from nmr evidence , thus for example

TABLE (6.2)

	Isomer			
	syn-syn	syn-anti	anti-syn	anti-anti
	(A)	(B)	(C)	(D)
$[PtC\ell_2(CF_3CHMeCH_2SCF_3)]$				
Relative abundance (%)	4	6	78	12
J(FF)	4.6	0	4.6	0
$\delta(^{19}F)$	-38.5	-37.9	-44.0	-42.1
	-45.1	-43.9	-44.4	-43.7
$[PtC\ell_2\{CH_3SCH(CF_3)CH_2SCH_3\}]$				
Relative abundance (%)	4	8	57	31
$\delta(^{19}F)$	-62.6	-62.6	-66.0	-66.0

TABLE (6.3)

^{1}H Nuclear Magnetic Resonance Parameters

Compound	Relative %	δSCH_3
$[(CH_3SCH_2CHPhSCH_3)PtC\ell_2]$		
Isomer A	4	2.15
		2.2
Isomer B	19	2.06
		2.01
Isomer C	56	2.07
		2.09
Isomer D	21	2.25
		2.3
$[(CH_3SCH_2CHPhSCH_3)PdC\ell_2]$	(broad	
	signal)	2.05
		2.07
		2.09
		2.1

Hunter[222] has determined the x-ray structures of crystals picked from a sample of $[PtC\ell_2(CH_3CH_2CH(CF_3)SCH_3)]$. The ^{19}F NMR spectrum was consistent with the presence of all four possible isomers and the X-ray structure revealed isomer C, previously considered the most abundant isomer.

No direct nmr evidence for the structure corresponding to each nmr resonance is available for any of the complexes formed by $CH_3SCHCF_3CH_2SCH_3$[236] and $(CH_3SCH_2CHCH_3SCH_3)$.[260] The assignment of structures to isomers from the nmr parameters must therefore be made by comparison with the structural assignments of Torrens by considering substitution of methyl or trifluoromethyl groups in the bridge by phenyl groups. This substitution should only result in a small change in nmr parametersaffected by the size and electronic effects of the phenyl group.

The ^1H nmr spectra of the platinum complexes prepared in the present work will now be discussed in detail. The palladium complexes gave broadly similar spectra to the platinum complexes (but without coupling to palladium). With the exception of the complexes of $CH_3SCHPhCHPhSCH_3$ the number of isomers detected at ambient temperature can be explained simply in terms of the relative orientation of the sulfur and methyl substituents assuming rapid conformational exchange of the rings and slow configurational exchange of the sulfur substituents.

As described in Chapter (4) page (100) $CH_3SCHPhCHPhSCH_3$ having two chiral carbon atoms in the bridge has two possible isomeric forms, meso and (±) shown in Figure (6.12)

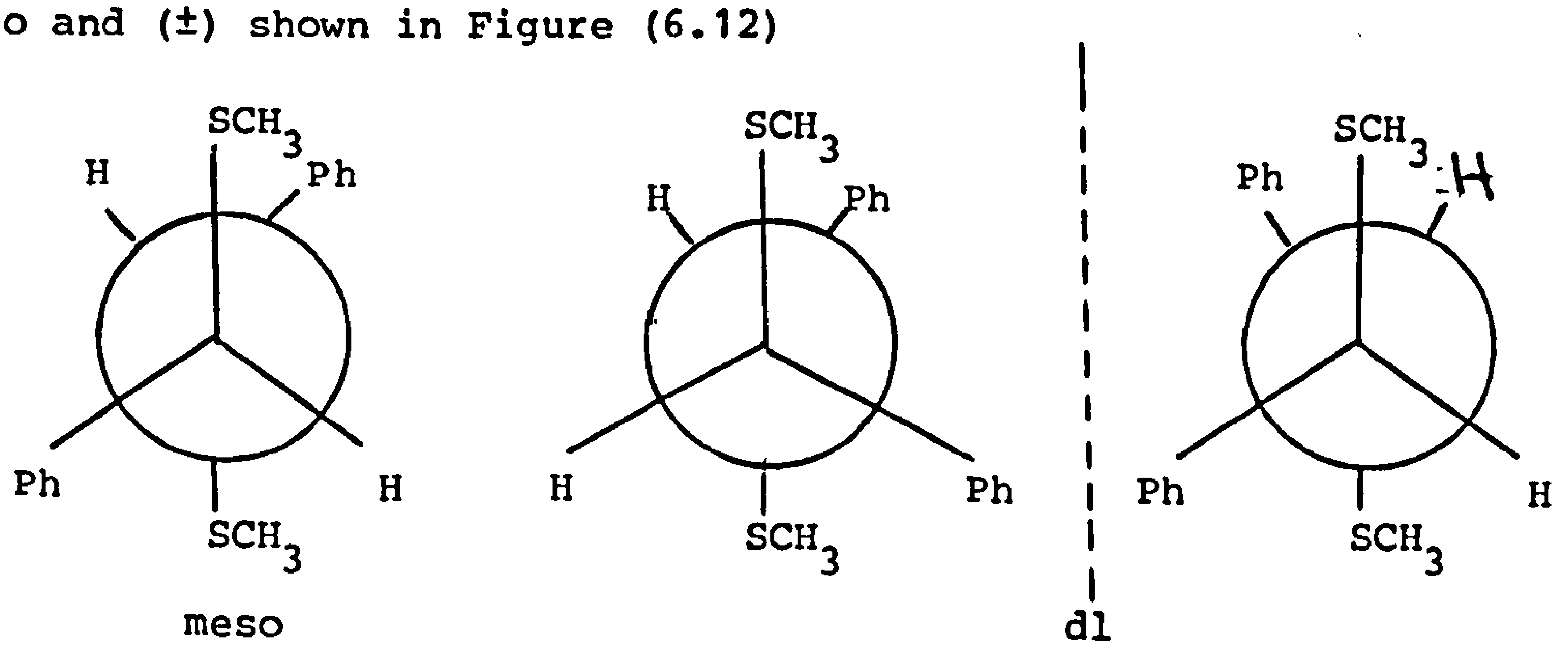
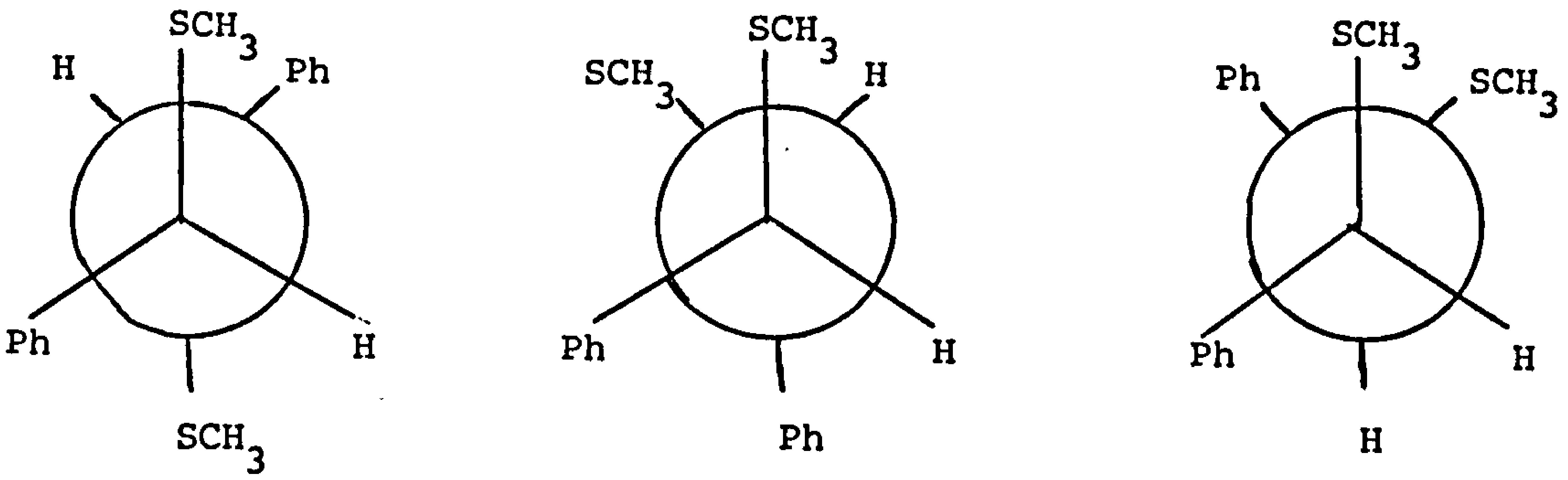


Figure (6.12) - Isomers of $CH_3SCHPhCHPhSCH_3$.

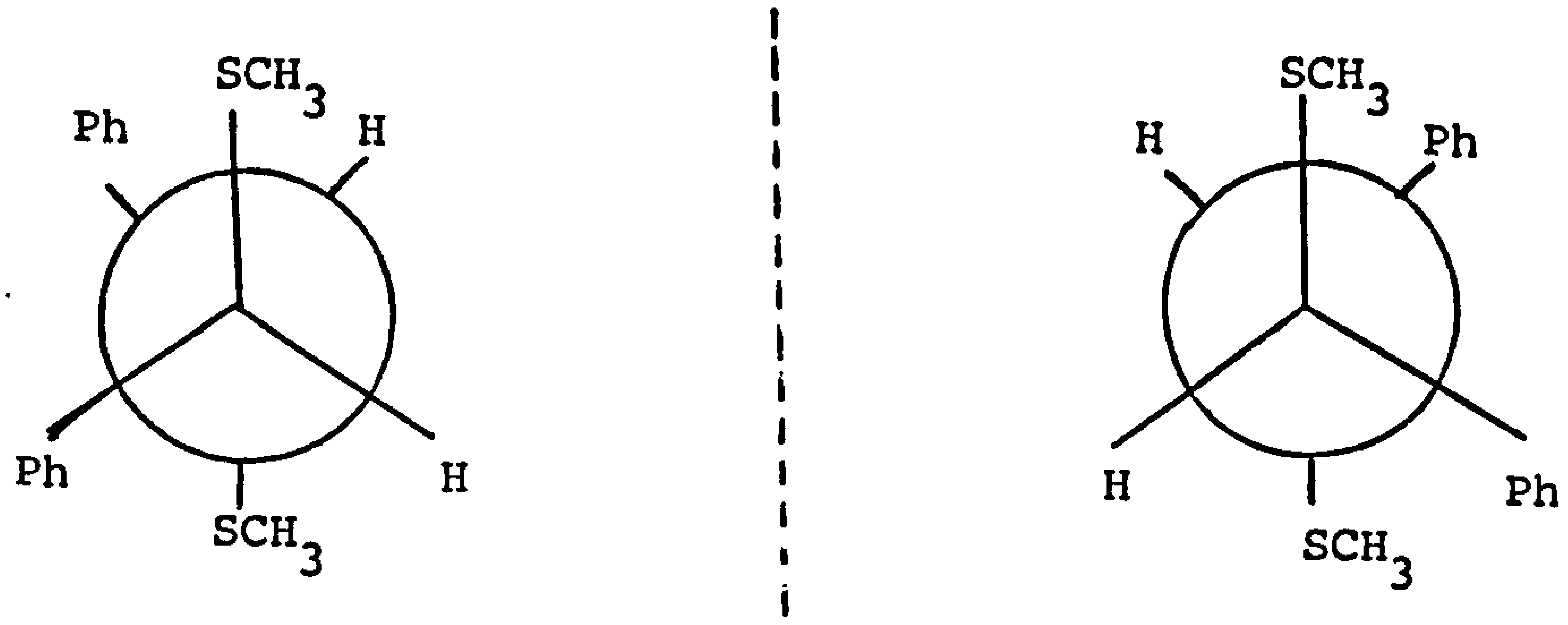
Rotation about the central carbon-carbon bond will produce additional spatial arrangements of the isomers. These conformational isomeric structures IA, IB, IIA and IIB in the figures (6.13) and (6.14) represent three pairs of mirror images.



I meso   IA   IB

Figure (6.13) - Enantiomers of the meso form.

The pair of enantiomers IIA and IIB are chemically different.



II

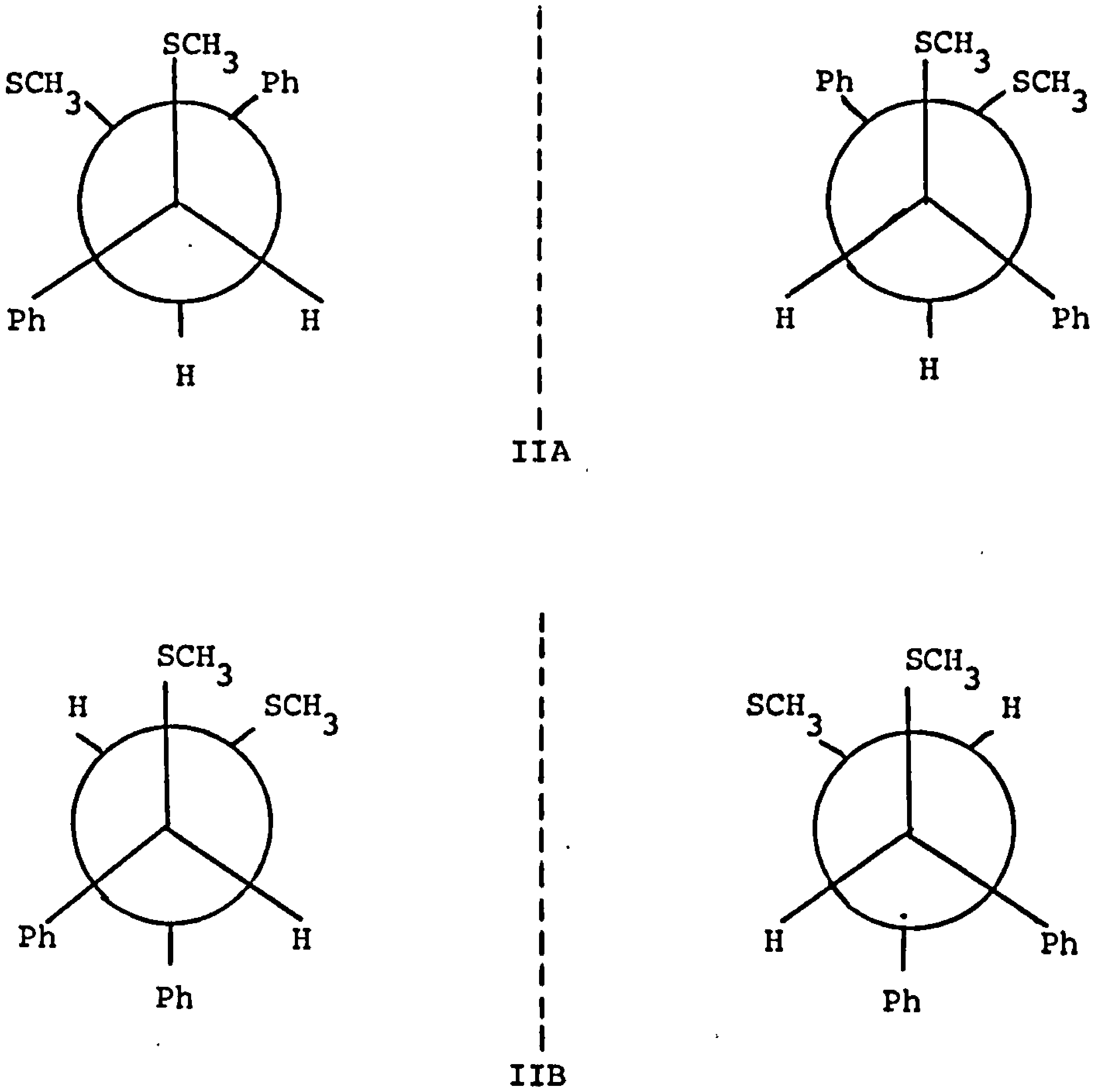
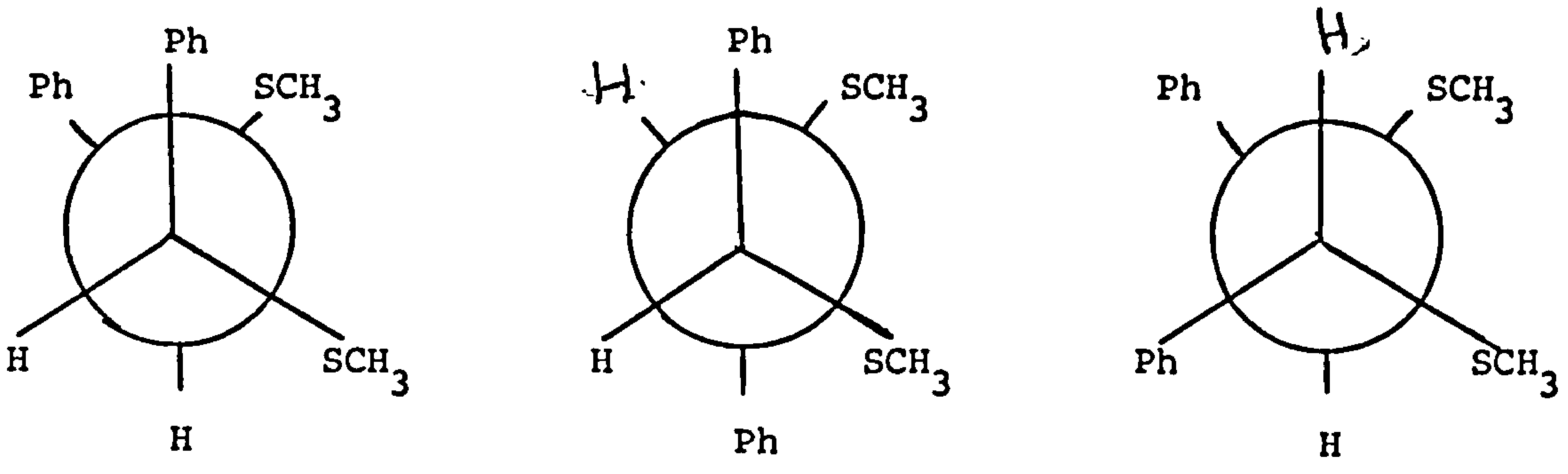


Figure (6.14) - Enantiomers of the (±) form.

The structures which can form complexes are shown in figure (6.15) and clearly show the fact that we can eliminate non-gauche ligand structures from complexes

The analysis does not imply that any of the conformers can exist as isolable species at room temperature.



meso

Figure (5.15) - Gauche forms of meso and (±) isomers.

Individual enantiomers are indistinguishable by nmr spectroscopy. Furthermore rapid rotation about the carbon-carbon bonds as found for the free ligand cannot be maintained after formation of chelated metal complexes. However, in formation of the complexes there are additional possibilities of isomers because of the relative interchange (axial and equatorial positions) in the chelating ring which can result in an averaged signal.

Complexation imposes a restriction on the rotation of the $CH_3\underline{S}-\underline{C}$ bond, fixing two possible orientations of the S-methyl substituents in the same way as found for other dithioether complexes.

The relative position of the sulfur substituents and the possible meso and (±) orientations of the bridge substituents (referring to the isomers of the free ligand) give rise to three isomeric structures A, B and C derived from the meso form in figure (6.16) and three (±) isomeric structures D, E and F derived from the (±) form. In the diagrams used in figure (6.16) the S-Pt-S plane is perpendicular to the plane of the paper with the platinum atom behind the diagram.

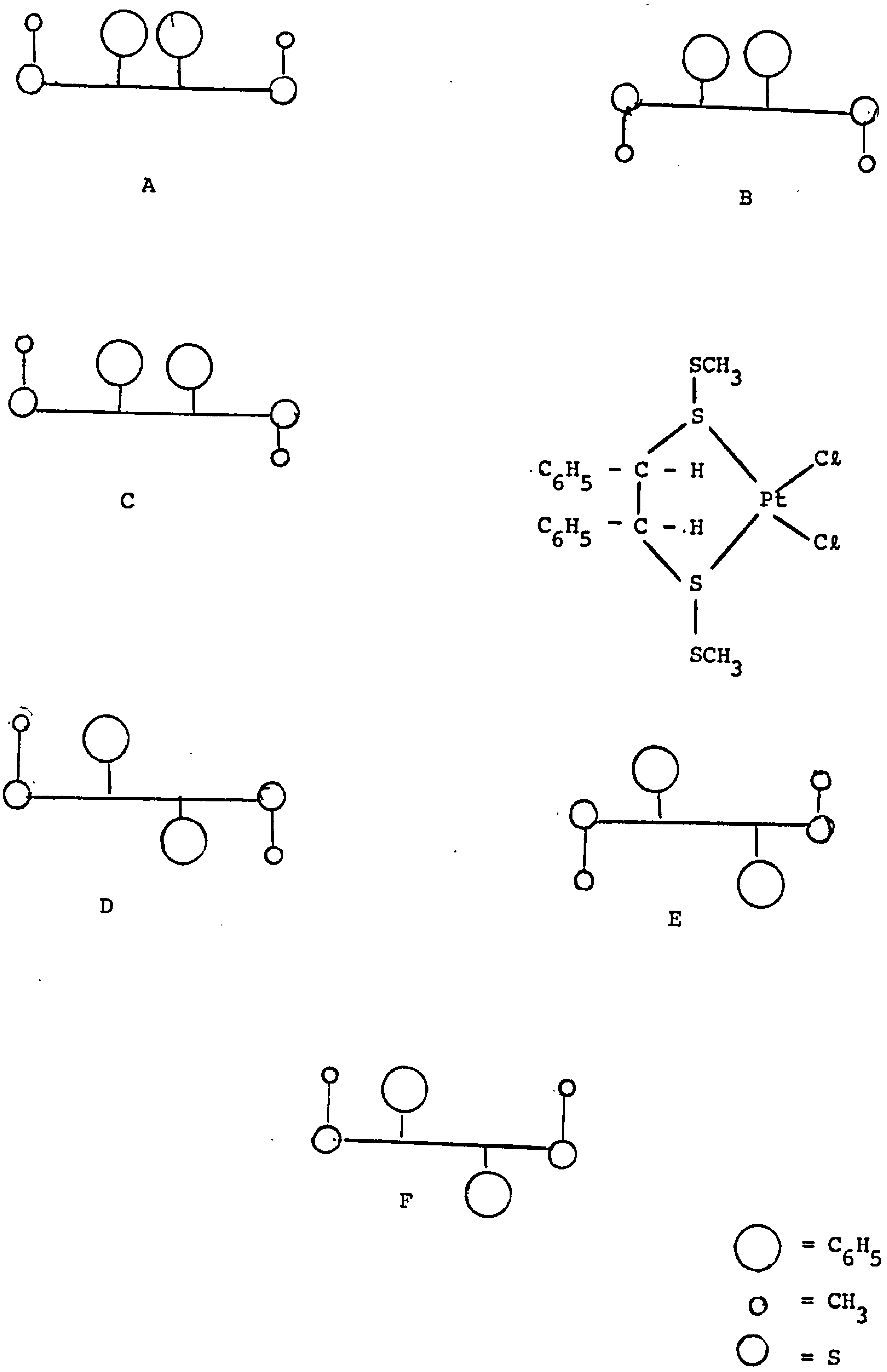


Figure (6.16) - Possible structures of $[(CH_3SCHPhCHPhSCH_3)PtC\ell_2$

TABLE (6.5)

Nuclear Magnetic Resonance Parameters

Compound	δSCH_3
$[(CH_3SCHPhCHPhSCH_3)PtC\ell_2]$	
1st isomer	2.06
2nd isomer	2.29
3rd isomer	1.98
4th isomer	2.48
5th isomer	1.93
6th isomer	1.96
$[(CH_3SCHPhCHPhSCH_3)PdC\ell_2$	
1st isomer	2.10
2nd isomer	2.52
3rd isomer	2.72
4th isomer	2.78
5th isomer	2.91
6th isomer	2.95

The two sets (from meso and dl) are not interconvertible. Within each set, however, each structure can undergo a change of configuration by inverting the orientation of the methyl substituents. This fact can give some indication of the relative proportion of <u>meso</u> and (±) isomers present and since their ratio depends on the relative proportion of meso and (±) isomers in the ligand mixture originally used provided that both forms give complexes of similar stability. To investigate whether both isomers of the ligand had similar tendencies to complexation, the formation of the Pt(II) complexes was followed by nmr spectroscopy. The reaction studied was:

$$mL(EtOH) \; + \; nK_2PtC\ell_4(EtOH) \longrightarrow nLPtC\ell_2 + m - nL + 2KC\ell$$

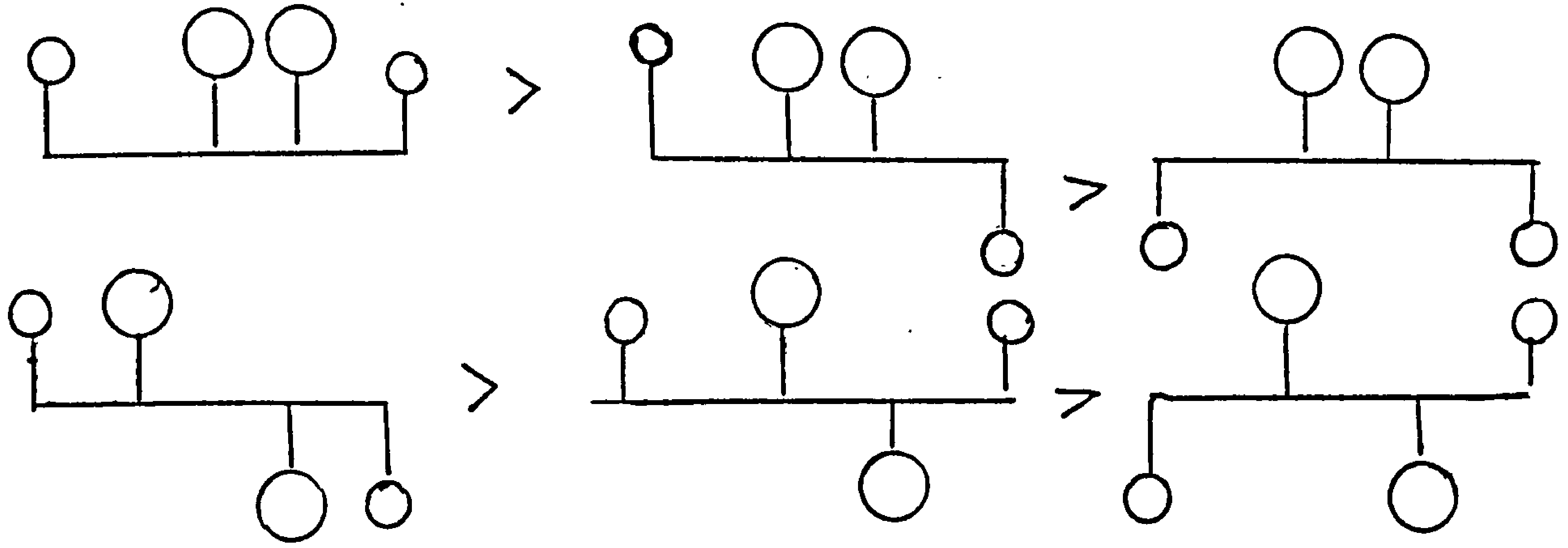
where L = $CH_3SCHPhCHPhSCH_3$ and m > n.

The experiment showed that the relative proportion of meso and (±) isomers in the ligand was maintained throughout the complex formation. The composition of the excess ligand remaining after the reaction was complete showed the same proportion of meso to (±) isomers found initially for the ligand.

It should be noticed from the structures in figure (6.16) that two different types of nmr resonance will be produced depending on the relative positions of the sulfur and bridge substituents. Phenyl groups are equivalent in isomers A, B, D and E and therefore their resonance will be distinct from those arising from isomers C or F in which both phenyl groups are non-equivalent. At this point the information on individual structure is still ambiguous. A more precise identification of the structure from studying the steric hindrance in structural models and further information was obtained by studying IR, mass spectra and microanalysis (see Tables 9, 10 and 11 in Chapter 7).

Steric Interaction

From molecular models, increased steric interaction resulting from the relative orientation of sulfur and ring substituents would be found in the following order:



○ = CH_3 ◯ = Ph

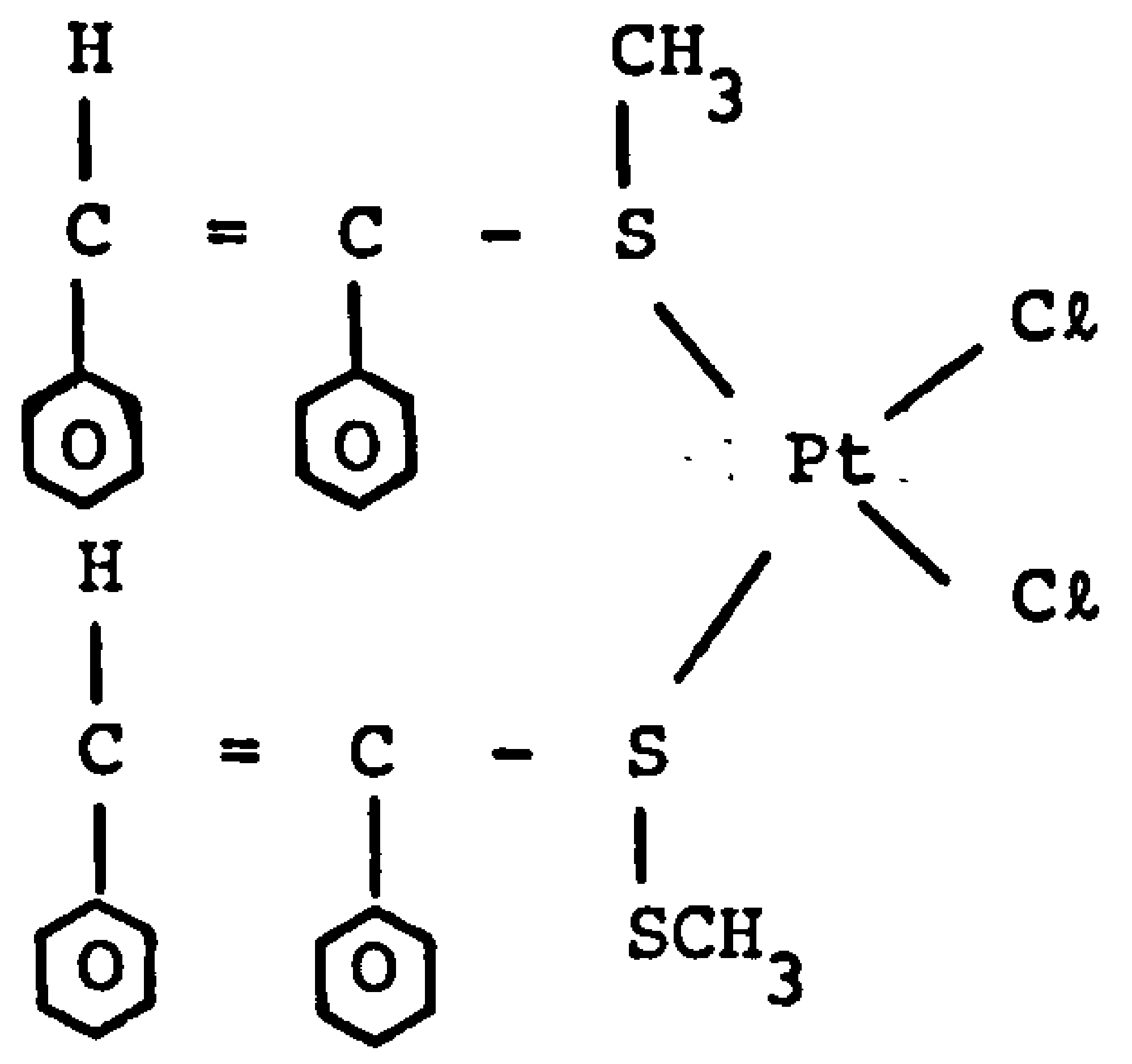
Figure (6.17) - Order of steric interaction.

In terms of steric factors, meso isomers appear to have greater interaction between bridge substituents than those for (±) forms. The ratio of meso to (±) isomers of the complex reflects the ratio of meso to (±) isomers of the ligand. The experimental results could be interpreted by a large preponderance of the meso isomer A in figure (6.17) which shows the larger barrier to ring inversion. The remaining nmr resonances will then be due to the ± isomers in which nmr intensities probably reflect the order shown in figure (6.17).

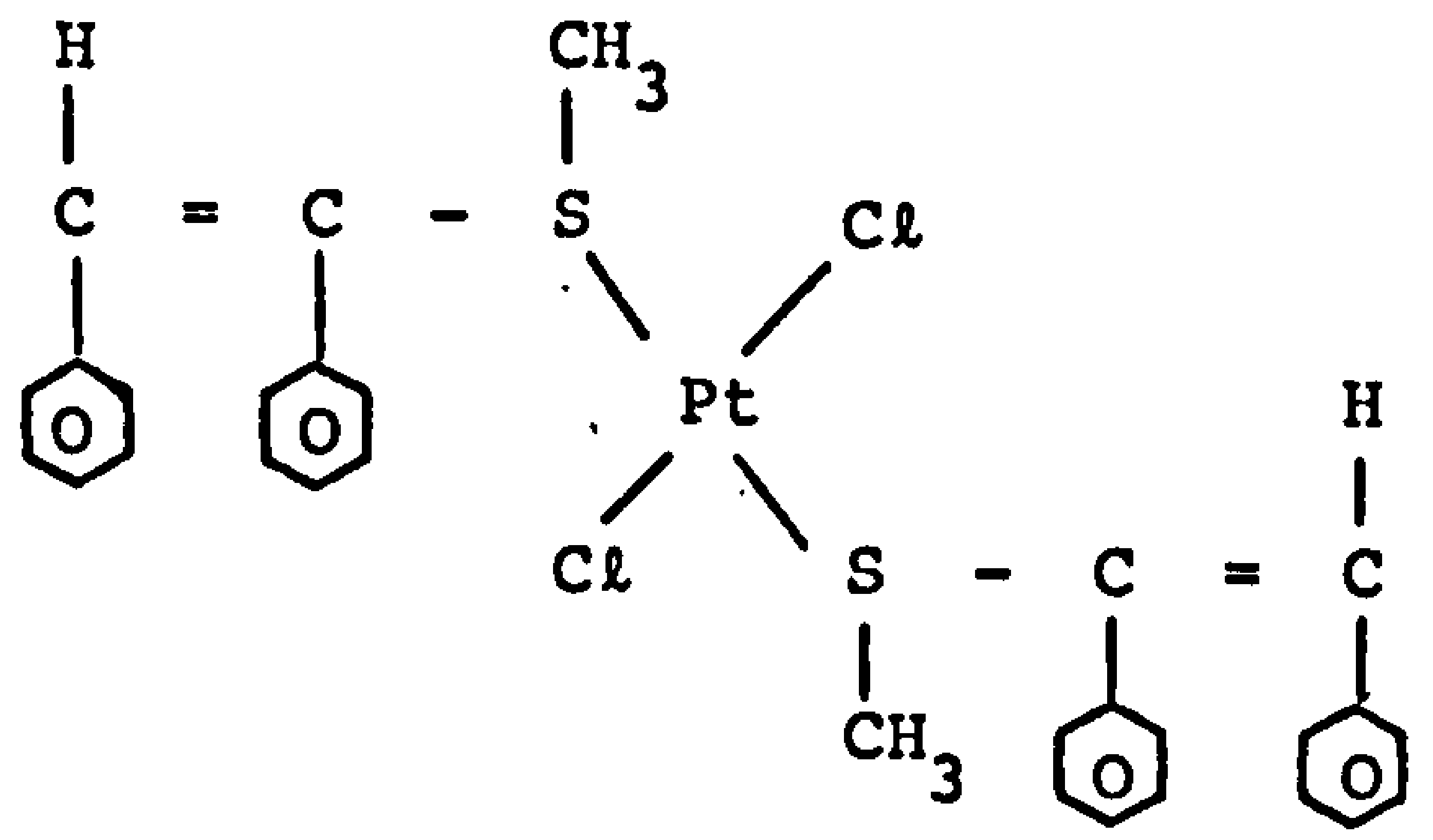
The possible structures of the 2:1 complex formed by $CH_3SCPh=CHPh$ with platinum dichloride are as shown below.

The possible co-ordinating groups are sulfur and the double bond could be chelated, but this is unlikely because of the difficulty for this bond to be in the right position for co-ordination. The sulfur and the double bond could form bridges between two platinum atoms.

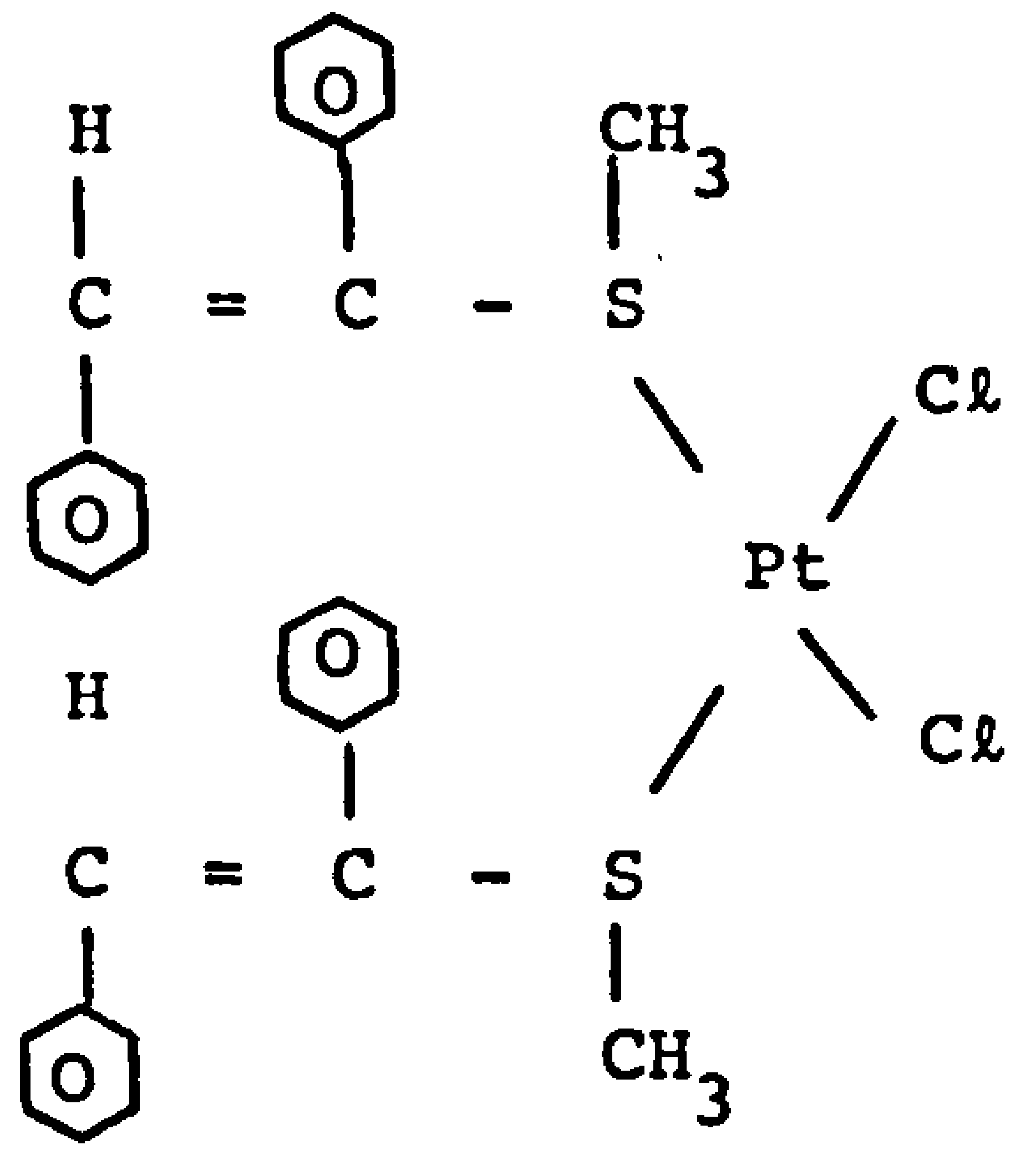
Most platinum(II) compounds are 4-co-ordinate square planar and bonding from sulfur is generally stronger than from a double bond. We therefore believe that the ligands are bonded through sulfur. The two possibilities are for cis and trans co-ordination and also the possibility of cis and trans-ligands. Possible structures are, therefore,



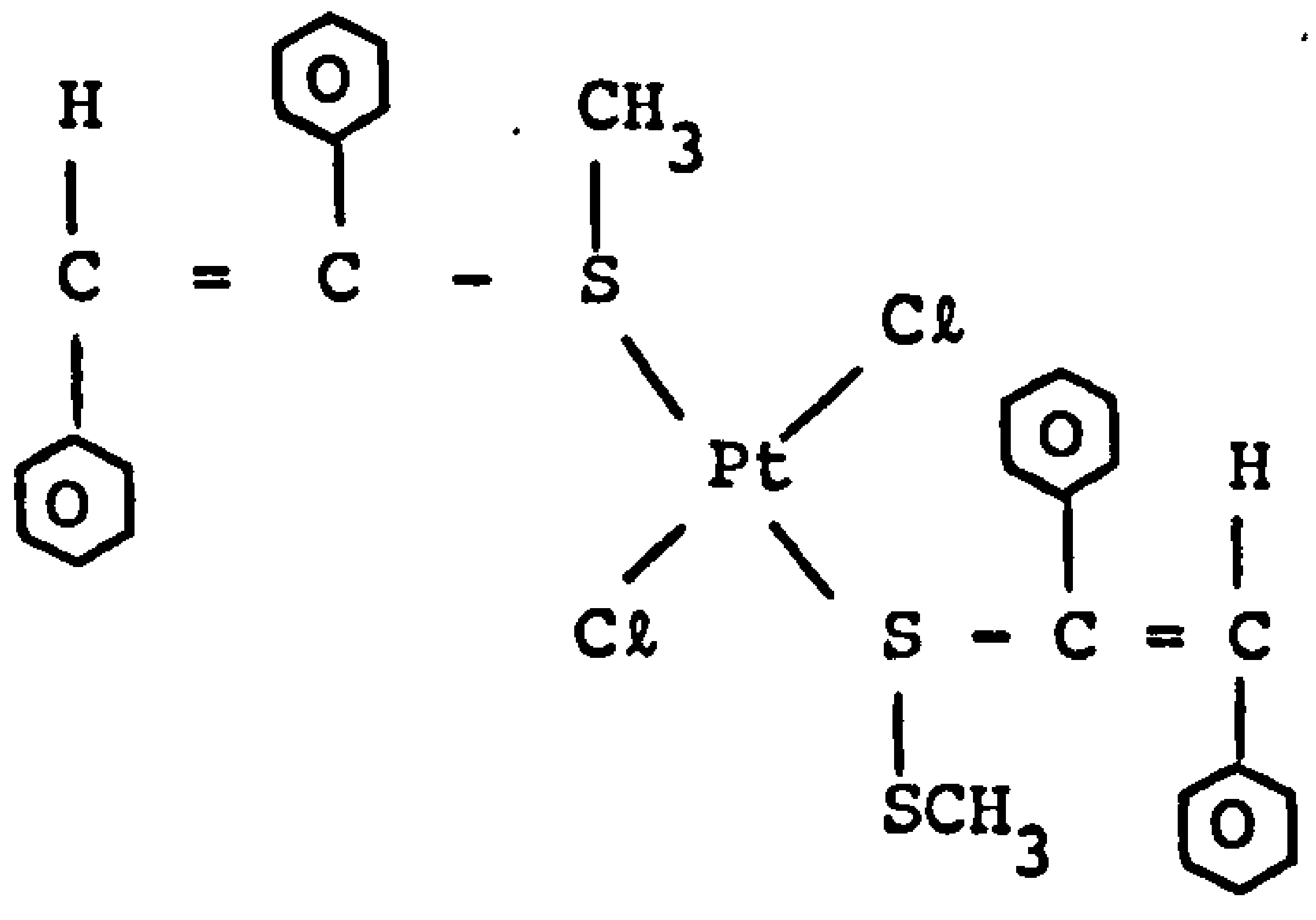
I



II



III



IV

Figure (6.18) - The possible isomers of $[(CH_3SCPh{=}CHPh)_2PtCl_2]$.

TABLE (6.5)

^{1}H Nuclear Magnetic Resonance Parameters

Compound	δSCH_3
$[PtC\ell_2(CH_3PhC=CHPh)_2]$	
1st isomer	3.36
2nd isomer	2.82
$[PdC\ell_2(CH_3SPhC=CHPh)_2]$	
1st isomer	3.32
2nd isomer	2.70

The IR spectrum of this complex shows strong peaks at 308 cm^{-1} and 295 cm^{-1} for Pt-Cℓ vibrations. (^{195}Pt nmr spectra - see page 171).

Platinum chemical shift

Although the direct observation of Pt^{195} resonances was first reported by Proctor and Yu,[283] in 1958, the potential of platinum chemical shifts as an investigative tool in the study of both structural and electronic bonding features was not demonstrated until 1968 when McFarlan,[284] Pidcock et al.,[197] and Von Zelewsky[285] showed that Pt chemical shifts cover a wide range of values, being sensitive not only to the ligands present around the metal atom but also to their arrangement.

The relative low sensitivity of platinum, (9.94×10^{-3} for an equal number of protons at constant field) originally restricted direct measurements to spectrometers not commonly available but Fourier Transform N.M.R. techniques[286] and heteronuclear multiple resonance methods[287] made it possible to obtain Pt measurements with readily accessible equipment and by July 1983 more than 400 platinum chemical shifts had been reported.[288,197,283-285,289-300,236,301,222,223] The information, although extremely small by comparison with ^{1}H or ^{19}F data, has already been successfully applied to practical problems; there are systematic trends that can be used to predict chemical shifts for compounds which have previously been studied[300] and erroneous structural assignments have been discovered from the position of their platinum resonances.[290] Torrens in 1982 studied the ^{195}Pt chemical shifts of a series of dithioether complexes. It is generally considered that the shifts are influenced by several inter-related parameters which are poorly understood and despite the efforts in the last decade, theoretical interpretations have had very limited success[197,292].

In view of this situation, we will compare our results, which are obtained by direct measurements using F.T. n.m.r. techniques with data previously reported.[299] We shall compare our results with those of Torrens who used indirect methods for measuring platinum chemical shifts. An arbitrary reference system is used through this work; Torrens (1982)[299] used cis-$(Me_2S)_2PtC\ell_2$ as reference taken as having Ξ (^{195}Pt) -21 420 980 ± 10 Hz.[291] Conversion between scales used in the literature is in most cases trivial and for other scales, Goodfellow et al.,[290] have given adequate correction factors. $\delta^{195}Pt$ are taken as positive to high frequencies.

We shall start by considering the ^{195}Pt spectra of the series of isomers of $[(CH_3SCHPhCH_2SCH_3)PtC\ell_2]$. For such a complex we expect four isomers analogues of those observed by Torrens for

$[(CF_3SCH(CH_3)CH_2SCF_3)PtC\ell_2]$, $[(CH_3SCH(CF_3)CH_2SCH_3)PtC\ell_2]$, $[(CH_3SCH(CH_3)CH_2SCH_3)PtBr_2]$ and $[(CH_3SCH(CF_3)CH_2SCH_3)PtI_2]$.

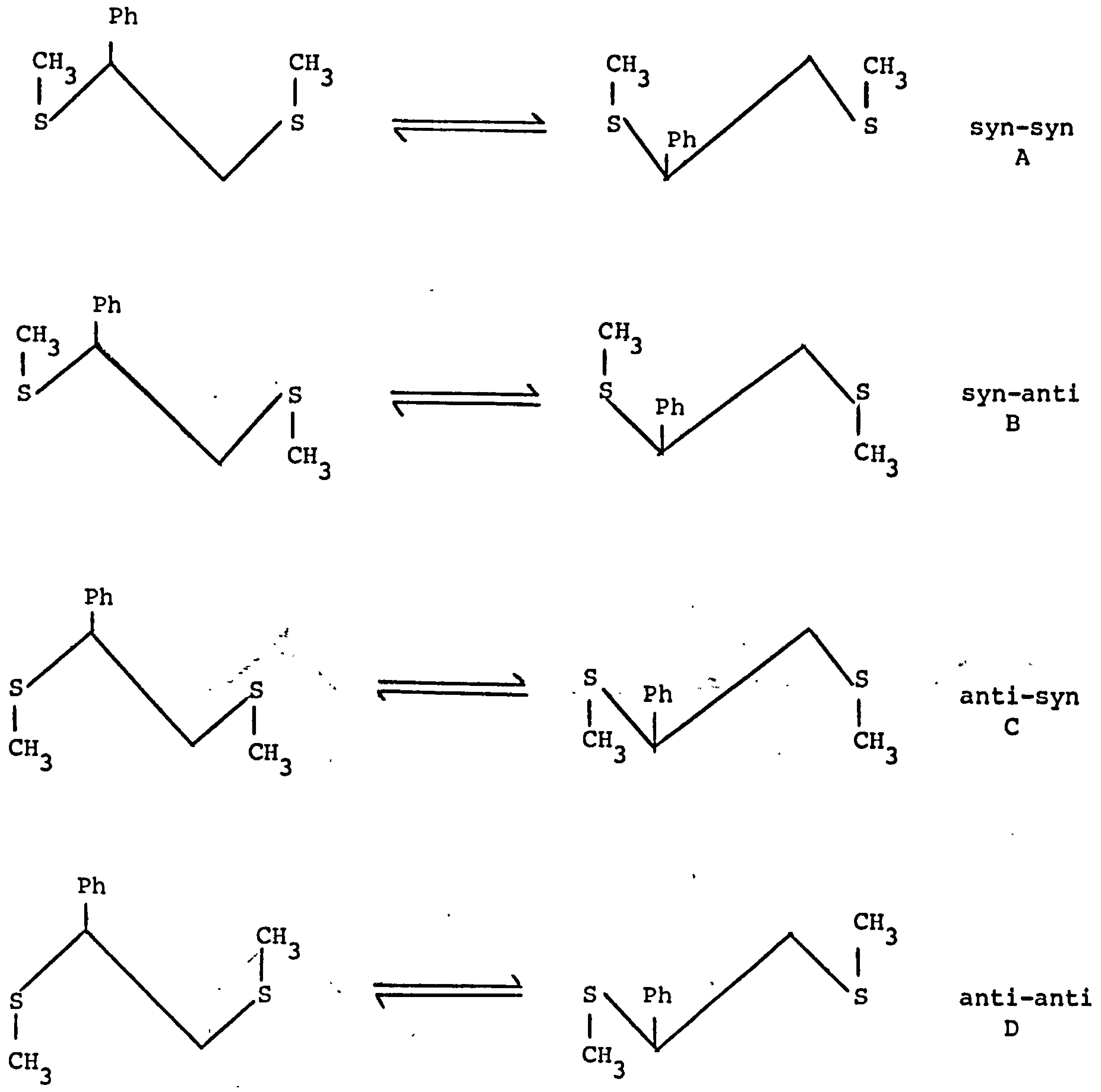


Figure (6.19) - Possible isomers of $[PtC\ell_2(CH_3SCHPhCH_2SCH_3)]$.

By examining the F-F coupling constant (≈ 4Hz in isomers A and C for $[(CF_3SCH(CH_3)CH_2SCF_3)PtC\ell_2]$ and by considering steric interactions Torrens (Thesis) assigned structures to the isomers of all of the above complexes. All of the spectroscopic data was consistent with the assignments. Subsequently Muir and Hunter confirmed these structural assignments by X-ray crystallocraphy on $[(CF_3SCH(CH_3)CH_2SCF_3)PtC\ell_2$ and $[(CH_3SCH(CF_3)CH_2SCH_2)PtC\ell_2]$. In table (6.7) which is taken from Torrens thesis

TABLE (6.7)

Structural assignments for $(RSCH(R)CH_2SR)PtX_2$

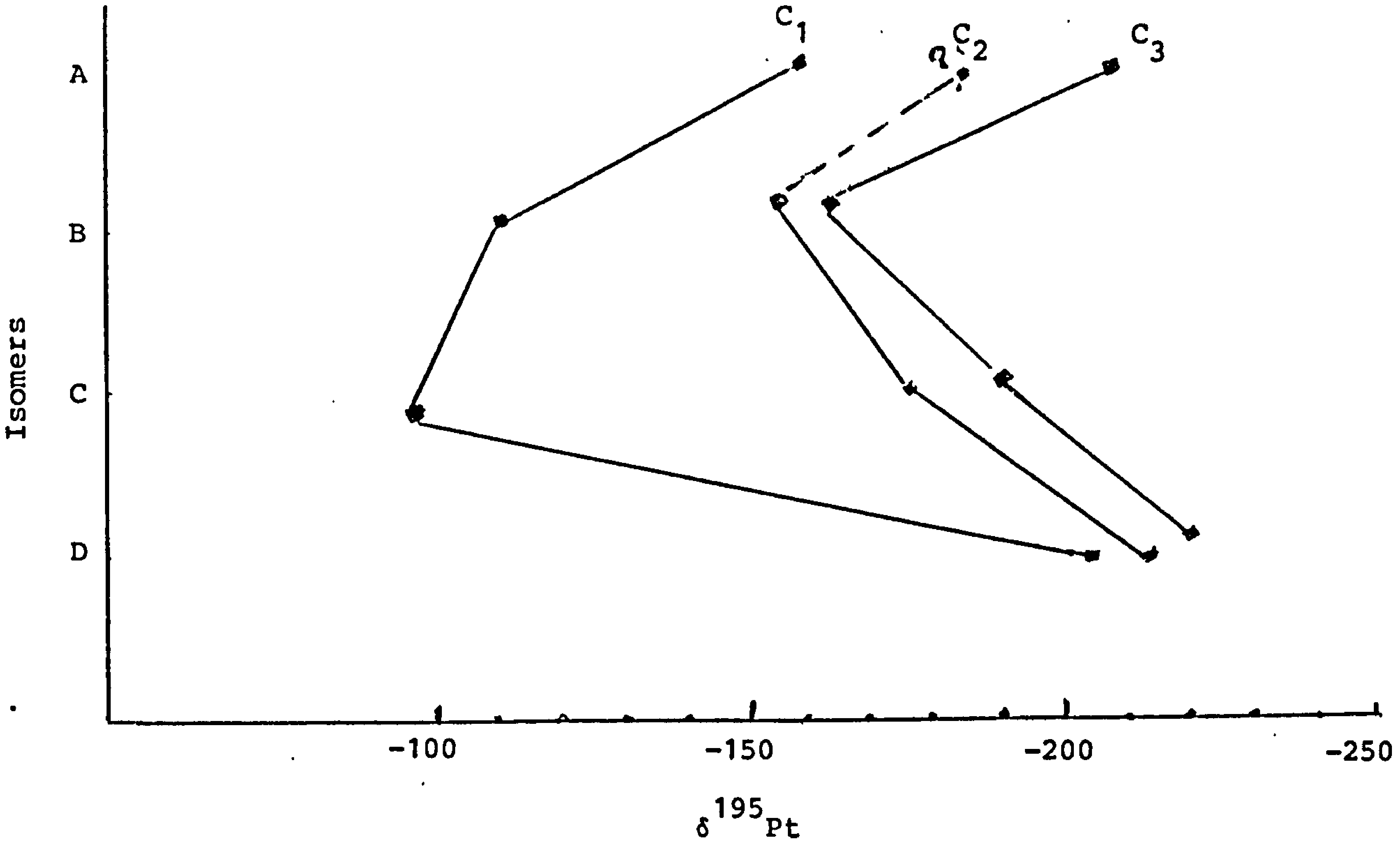
	STRUCTURE			
Compounds	syn-syn	syn-anti	anti-syn	anti-anti
$[(CF_3SCH(CH_3)CH_2SCF_3)PtC\ell_2$				
relative %	4	6	78	12
$\delta^{195}Pt$	-100.5	-154.7	-98.3	-202.3
$[(CH_3SCH(CF_3)CH_2SCH_3)PtC\ell_2]$				
relative %	4	8	57	31
$\delta^{195}Pt$	-195	-165	-192.8	-219.4
$[(CH_3SCH(CF_3)CH_2SCH_3)PtBr_2]$				
relative %	6	13	53	28
$\delta^{195}Pt$	-580.8	-554.8	-580.4	-618.9
$[(CH_3SCH(CF_3)CH_2SCH_3)PtI_2]$				
relative %	5	13	52	24
$\delta^{195}Pt$	-1399.3	-137.4	-1397.9	-1427.3

TABLE (6.7) contd.

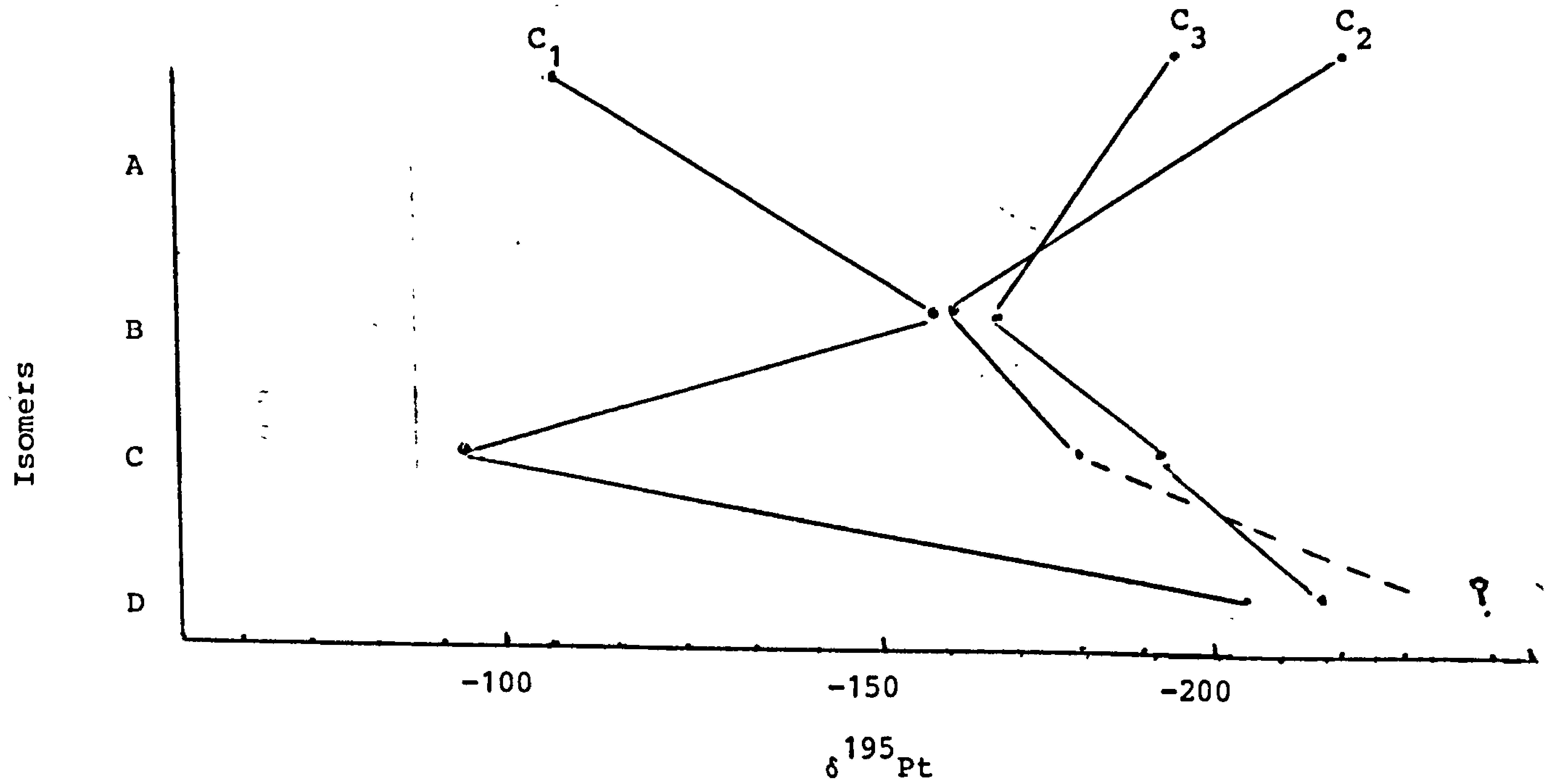
	STRUCTURE			
Compound	syn-syn	syn-anti	anti-syn	anti-anti
$[(CH_3SCH(CH_3)CH_2SCH_3)PtCl_2)$				
$\delta^{195}Pt$	-215.5	-160.6	-179.2	ND[c]

[c] Insufficiently resolved to be determined.

we note the ^{195}Pt shifts. For each complex the most abundant isomer (anti-syn) has a shift close to that of the least abundant (syn-syn). This is taken to indicate that the conformation at the ligand atoms - syn in each case - is a predominant factor in determining the ^{195}Pt chemical shift. Further the anti-anti isomer always has the most negative chemical shift. We shall see similar trends in the ^{195}Pt spectra of $[(CH_3SCHPhCH_2SCH_3)PtCl_2]$. However, before we consider this we should look further into the pattern of shifts observed by Torrens. Figure (6.20) represents the diagram taken from his Thesis and is the same as in his paper (1982).[299]



The diagram was wrong in both cases because of the labelling of the isomers. If we redraw this diagram using his observed chemical shifts and labelling the isomers A, B, C and D according to the table (6.7) we get for this figure (6.20).



C_1 = $[(CF_3SCH(CH_3)CH_2SCF_3)PtC\ell_2]$

C_2 = $[(CH_3SCH(CH_3)CH_2SCH_3)PtC\ell_2]$

C_3 = $[(CH_3SCH(CF_3)CH_2SCH_3)PtC\ell_2]$

Figure (6.20) - Values of platinum chemical shift. Observations of Torrens replotted in this work.

The figure emphasises the points made earlier that the isomers A and C have very similar ^{195}Pt shifts and the isomers D have the largest negative shift.

According to the above description we observed that the complex $[(CH_3SCHPhCH_2SCH_3PtC\ell_2]$ has four isomers from the ^{195}Pt nmr spectrum and also but not very clearly from the proton spectrum (p148).

TABLE (6.8)

Structural assignments for [(CH$_3$SCHPhCH$_2$SCH$_3$)PtCℓ$_2$]

Compound	isomers	%	δ^{195}Pt
[(CH$_3$SCHPhCH$_2$SCH$_3$)PtCℓ$_2$]	(A) syn-syn	4	810.4
	(B) syn-anti	19	783.2
	(C) anti-syn	56	811.7
	(D) anti-anti	21	843.7

The ^{195}Pt nmr spectrum shows two isomers with very similar chemical shift (see fig. 6.21) and these are therefore assigned to isomers with syn-methyl group (A and C). Further, one of these signals corresponds to the most abundant isomer which on steric grounds should be C with the anti-syn conformation. The remaining two isomers have very similar abundances to each other; this pattern is similar to that observed for the various isomers of [PtX$_2$(CF$_3$SCHMeCH$_2$SCH$_3$)].

For the complex [(CH$_3$SCHPhCHPhSCH$_3$)PtCℓ$_2$] the possible isomers are presented in figure (6.22)

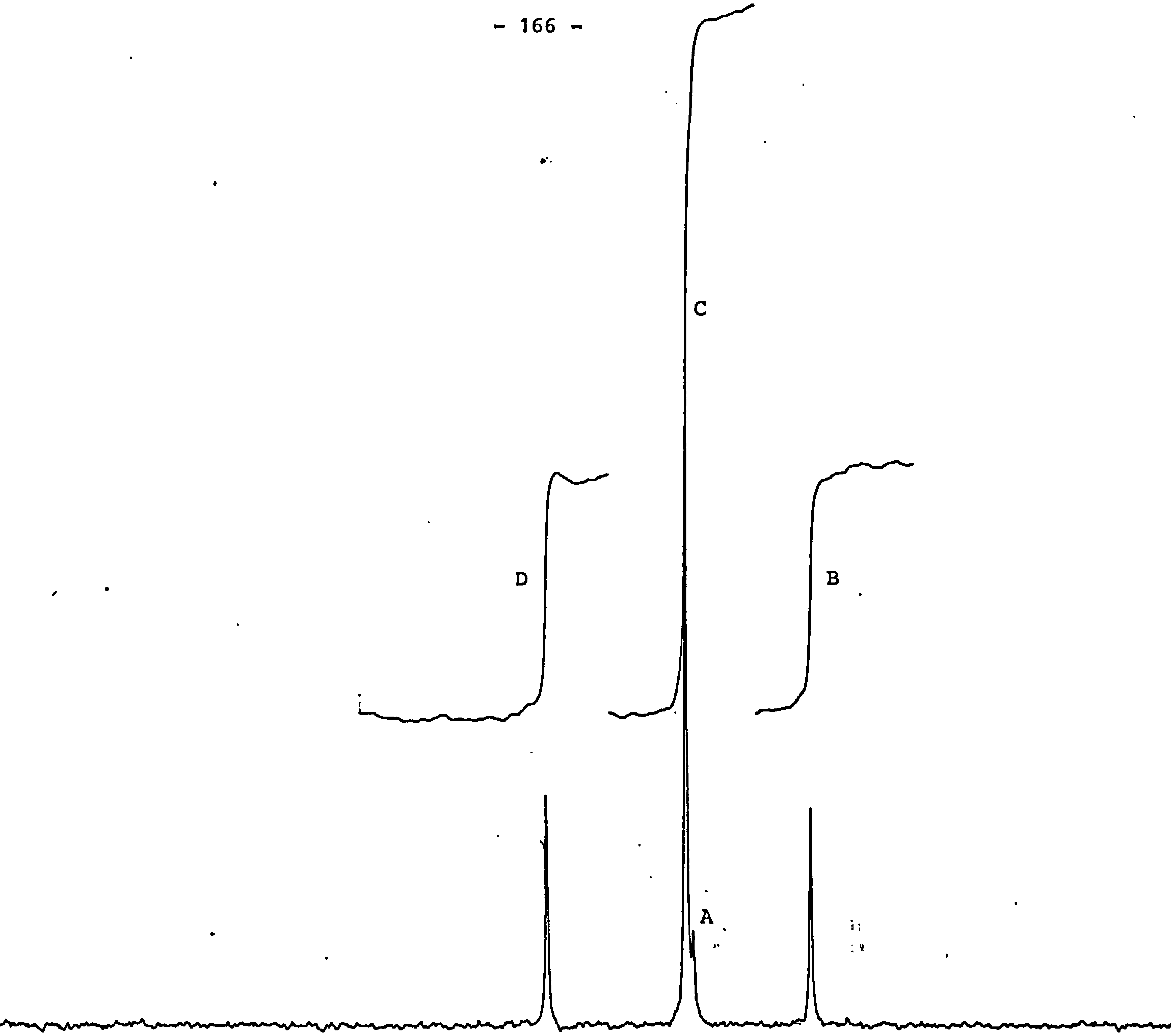
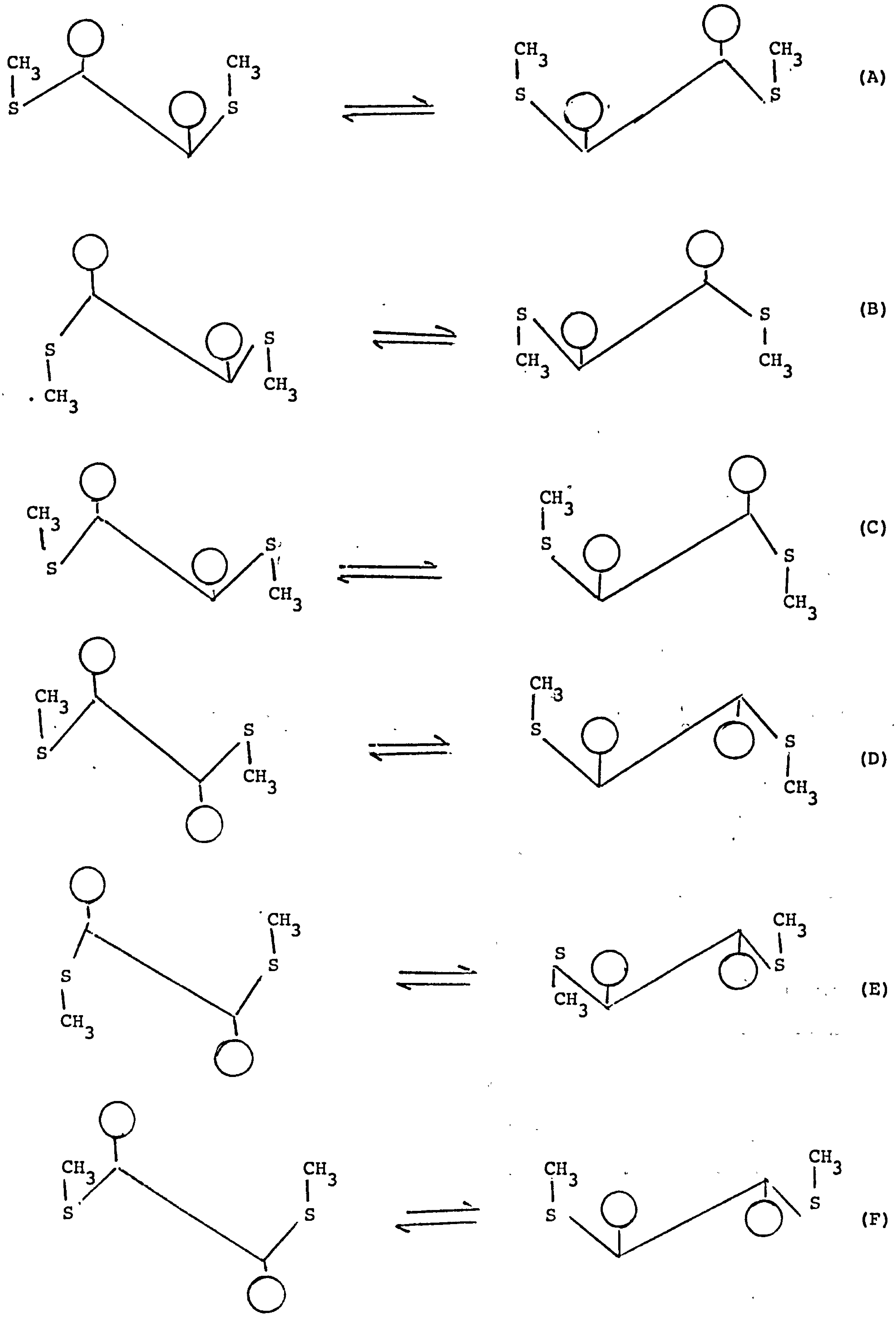


Figure (6.21) - ^{195}Pt spectrum of $[PtCl_2(CH_3SCH_2CHPhSCH_3)]$

Figure (6.22) - Possible isomers of [PtCℓ_2(CH$_3$SCHPhCHPhSCH$_3$)]



The ligand exists in two forms, meso or (±). Isomers A, B, C are derived from the meso form, isomers D, E, F from the (±) form. The meso and (±) forms are not interchangeable but inversion at sulfur means that A, B, C are interconvertible as are D, E and F. Molecular models (our work, Torrens, W. Hunter) indicate steric interactions decreasing in the meso form such that A > C > B, and in the racemic form such that D > F > E.

At room temperature the ^{195}Pt spectrum shows six isomers as singlets, four of them broad and two sharp. The broadening is presumably due to exchange processes. Torrens investigated $[(CH_3SCH(CF_3)CH(CF_3)SCH_3)PtX_2]$ [X = Cℓ, Br, I]. He observed four isomers for the chloride and four for the iodide and five for the bromide. Based on steric interactions, F-F coupling, and variable temperature nmr, Torrens identified his isomers as in table (6.9).

In our ^{195}Pt spectra we observed the expected full six isomers (fig. 6.23), thus confirming the mode of attachment of the ligand to the metal and resolving the problems with the $CH_3SCH(CF_3)CH(CF_3)SCH_3$ complexes when the full expected set of isomers was not observed and therefore there must always be same ambiguity in assignment. Torrens used ^{19}F nmr spectra for study of his complexes and these spectra should be more sensitive than ^{195}Pt nmr spectra.

Torrens assigned the structure of the most abundant isomer of the $[CH_3SCH(CF_3)CH(CF_3)SCH_3PtX_2]$ series as B which is an isomer derived from a meso form of the ligand (the most abundant isomer of the ligand). By analogy with the result of Torrens the isomer with ^{195}Pt chemical shift (1092.3 ppm) abundance 45% is very likely to have this structure,

TABLE (6.9)

NMR parameters of $(CH_3SCH(CF_3)CH(CF_3)SCH_3)PtX_2]$

X	isomer	%	^{195}Pt	$\delta^{19}F$ [a]	J(F-F) [b]	J(Pt-F) [b]
Cℓ	C	20	-231.2	-65.5	0	6.1
	F^c	13	-200.8	-64.1	9.5	5.0
				-59.8		
	B	64	-204.1	-61.25	0	5.3
	A	3	-201.2	-60.11	0	10.6
Br	C	18	-628.4	-65.97	0	Ca_7
	F^c	11		-64.13		
				-59.76	Ca_9	
	D^c	18		-61.15	Ca_9	
				-60.9		
	B	51	-596.4	-61.2	0	4.3
	A	2	-594.1	-59.95	0	9.6
I	C	13	-1469.8	-66.2	0	3.5
	F^c	9	-1424.0	-63.9	9	
				-59.5		
	D	0		0	0	0
	B	73	-1425.9	-61.1	0	
	A	5	-1415.7	-59.5	0	7.0

[a] ppm positive to low field of external $CCℓ_3F$

[b] Hz

[c] values of SCH_3 for two chemical distinct CF_3 groups.

Figure (6.23) - ^{195}Pt spectrum of [PtCl$_2$(CH$_3$SCHPhCHPhSCH$_3$)]

also being derived from the meso form of the ligand. The other nuclei in our complexes are not so sensitive for structural determination as the ^{19}F nuclei in the $CH_3SCH(CF_3)CH(CF_3)SCH_3$ complexes and it is not possible to assign structures to the other isomers.

TABLE (6.10)

^{195}Pt NMR spectrum of $[(CH_3SCHPhCHPhSCH_3)PtC\ell_2]$

Compound	isomer	%	$\delta^{195}Pt^a$
$CH_3SCHPhCHPhSCH_3$	1	2	1091.4
	B=2	54	1092.3
	3	20	1132.3
	4	10	807.6
	5	4	822.6
	6	15	1139.4

[a] ppm positive to low field of external (arbitrary ref.)

The last complex studied by ^{195}Pt nmr spectroscopy was $[(CH_3SPhC{=}CHPh)_2PtC\ell_2]$ where the ligand was formed by mono-addition of CH_3SH to $PhC{\equiv}CPh$. ^{195}Pt nmr spectroscopy has shown 4 signals but two of these signals are those of $[(CH_3SCHPhCHPhSCH_3)PtC\ell_2]$ which must have been present as impurity and only two signals at 775 ppm and 773 ppm can be definitely assigned to this complex. The information available is insufficient to allow assignment of the structure.

TABLE (6.11)

^{195}Pt NMR parameters for [(CH$_3$SPhC=CHPh)$_2$PtCℓ_2]

Compound	isomer	%	δ^{195}Pt [a]
[(CH$_3$SPhC=CHPh)$_2$PtCℓ_2]	1st	90	775.3
	2nd	10	773.2

[a] ppm positive to low field of external (arbitrary ref.)

Complexes between alkyne derivatives and cobalt carbonyl

Compounds of the type [Co$_2$(CO)$_6$(RC$_2$R')] have been previously prepared[126,261-263] by reaction of a large variety of alkynes with dicobalt octacarbonyl, and in addition to those compounds listed in table (6.12), with infrared absorption bands, many other examples are known.

The compounds [Co$_2$(CO)$_6$(RC$_2$R')] are light red to dark violet substances. The compounds can be purified by chromatography on silica gel, alumina or florisil and a wide variety of functional groups (R) can be present in the compounds [Co$_2$(CO)$_6$(RC$_2$R')] including alkoxy, alkoxycarbonyl, amino[262,263] and halogen.

Under high resolution, five fundamental carbonyl stretching frequencies can be observed in the infrared spectra but often one or two of these frequencies are weak.

The absorbtion frequencies are higher for compounds in which the electronegativity of R and R' is high.[263] X-ray structural investigations of several (alkyne)(hexa carbonyl)dicobalt compounds establish that

TABLE (6.12)

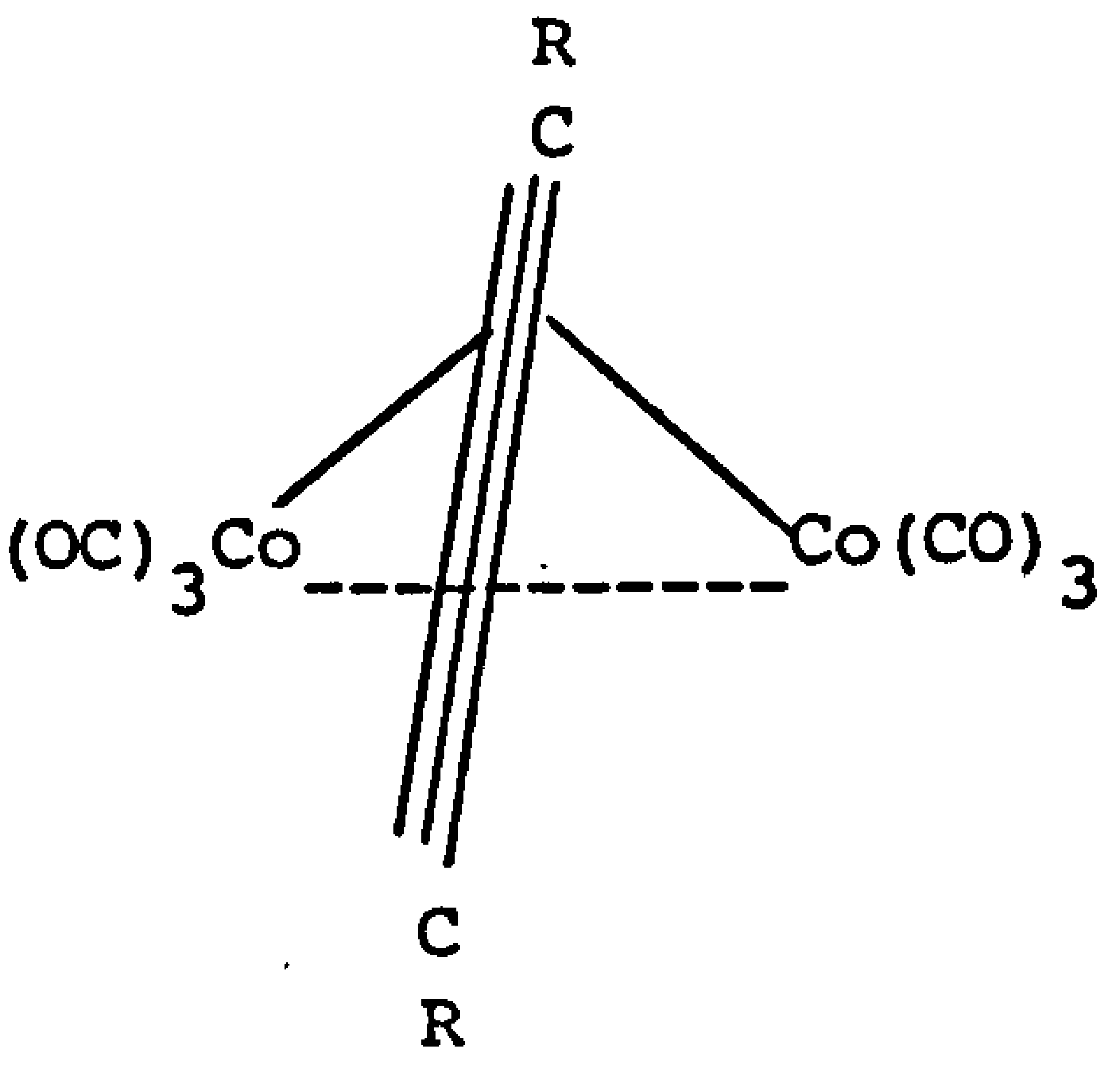
Compound	Origin	IR absorption bands (cm^{-1})				
$Co_2(CO)_6C_{14}F_{10}$ [126]	C=O	2105(s)	2075(vs)	2060(sh)	2049(vs)	2039(s)
						2000(sh)
	(C_6F_5)ring	1643(w)	1516(s)	1495(vs)		
	C-F	990(s)				
$Co_2(CO)_6C_{14}H_{10}$ [268]	C=O	2099(m)	2059(s)	2034(s)	2028(s)	2017(m)
$Co_2(CO)_6C_{14}F_8(OMe)_2$ [126]	C=O	2096(vs)	2062(vs)	2037(s)		
	(C_6F_4OMe)ring	1634(w)	1497(sh)	1479(vs)		
	C-F	994(s)				
$Co_2(CO)_6C_{14}F_8(NMe_2)_2$	C=O	2080(s)	2045(s)	2015(vs)		
	($C_6F_4NMe_2$)ring	1635(w)	1520(s)	1485(s)		
	C-F	995(vs)				

(w) = weak (s) = strong (sh) = shoulder

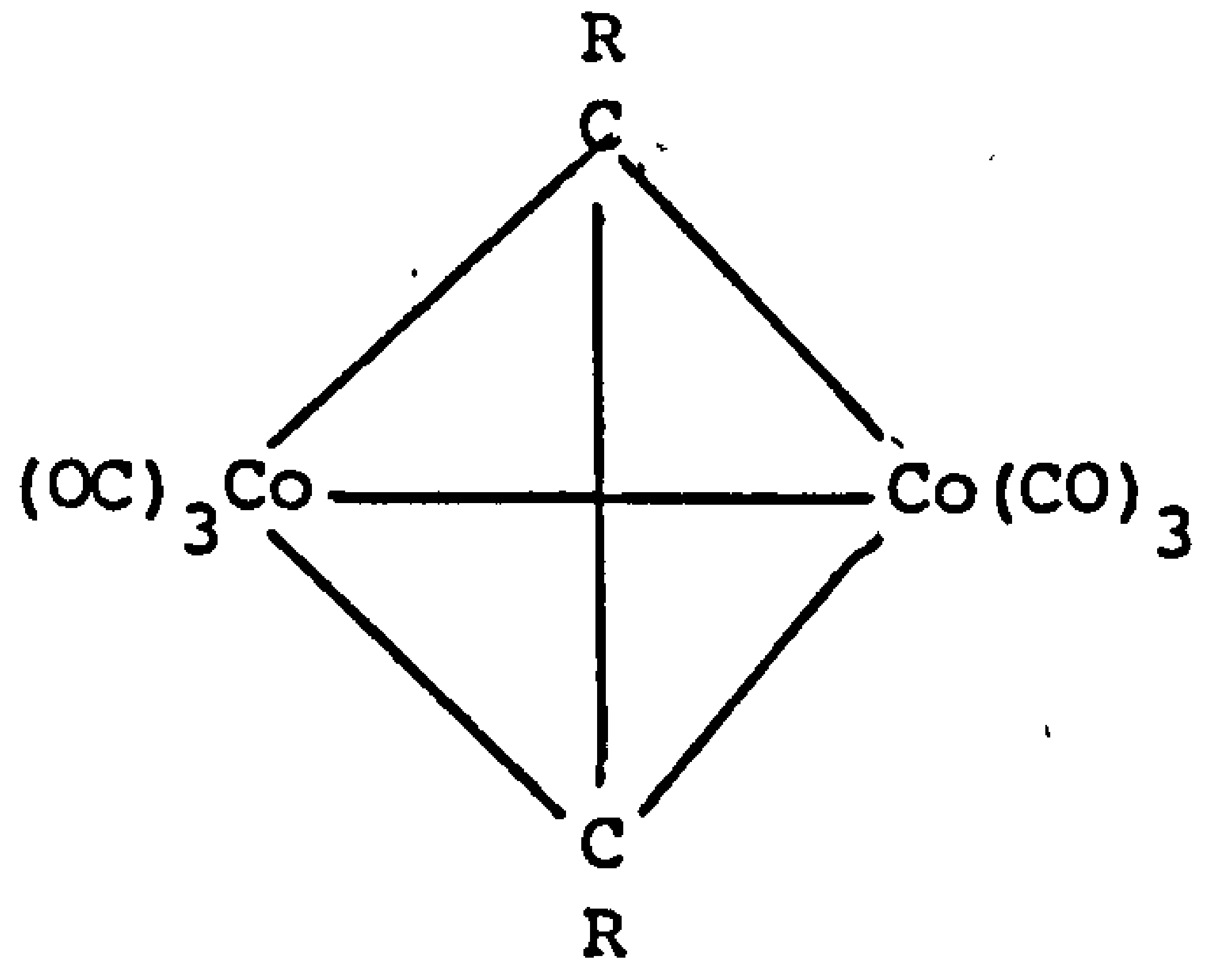
(m) = medium (vs) = very strong

the structure of each compound is derived from that of the parent carbonyl [$Co_2(CO)_8$] by replacement of the two bridging carbonyl ligands by the alkyne.

The co-ordinated alkyne is perpendicular to and lies above the Co-Co axis. The compounds are diamagnetic and the Co-Co distances found in the compounds are in the range 2.45-2.49Å which is less than the Co-Co distance of 2.52Å found for [$Co_2(CO)_8$]. The structures of these compounds have been discussed in terms of the two representations (1) and (2):[263,266]



(1)

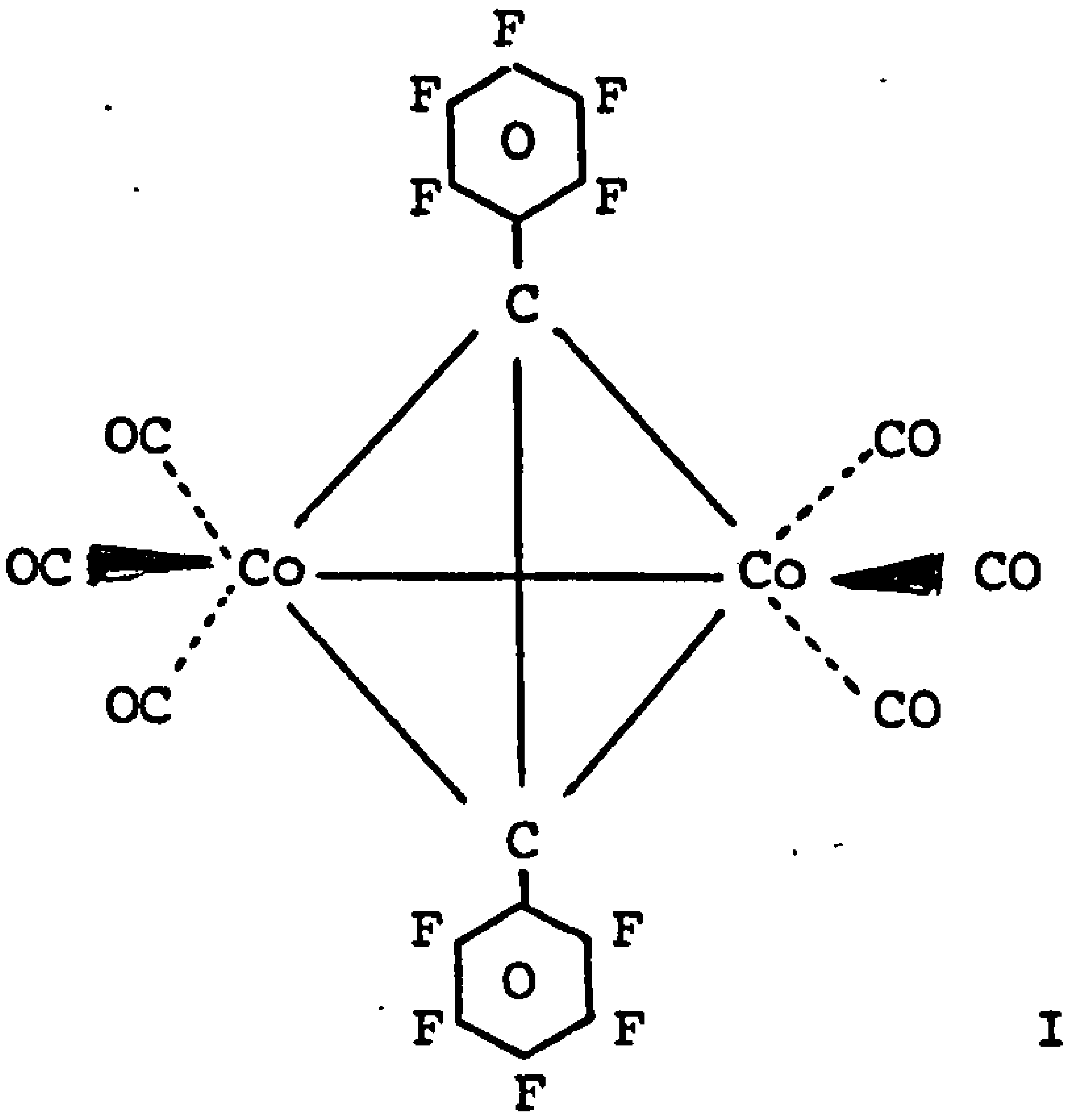


(2)

In (1) the geometry about each cobalt atom is essentially trigonal bipyramidal with one axial and two equatorial carbonyl ligands. One of the sp^2 hybrid orbitals is directed within the trigonal plane to the mid-point of the C≡C bond resulting in two orthogonal localized μ-bonds from alkyne to each cobalt atom. The co-ordinated alkyne will have approximately double bond character according to this description consistent with the observed carbon-carbon distances which fall in the range 1.32-1.31Å. The overall geometry of the co-ordinated alkyne is similar to the cis-bent excited state of acetylene.

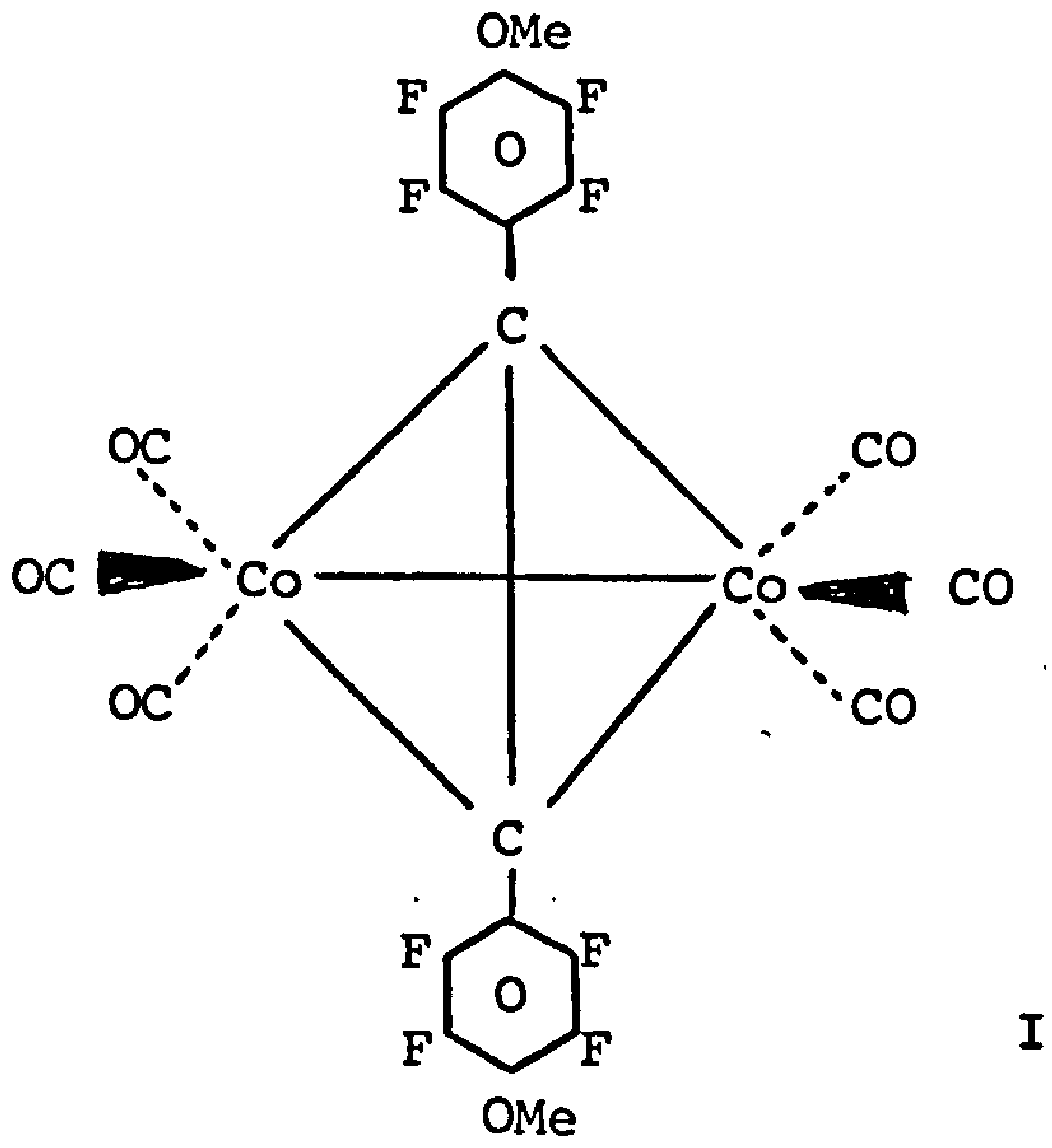
In the structure (2) there is considered to be distorted octahedral geometry about each cobalt atom, the two carbons and two cobalts forming a tetrahedral unit with a carbon-carbon single bond.[263] The Co_2C_2 unit has been compared with the Co_3C unit in the cluster $[Co_3CR(CO)_9]$ and there are some similarities in a few of the reactions of these species. For example, $[Co_2(CO)_6(HC_2H)]$ can be converted to a mixture of $[Co_2(CO)_6(PhC_2H)]$ and $[Co_2(CO)_6(PhC_2Ph)]$ by reaction with diphenyl mercury in a reaction analogous to the phenylation of $[Co_3CH(CO)_9]$ by this reagent.[266]

It has previously been found that cobalt octacarbonyl reacts readily with decafluorotolan in benzene at room temperature; 2 mole of carbon monoxide are evolved, and hexacarbonyl(decafluorotolan)dicobalt(0)[126] is produced as deep red crystals.



I

The complex is soluble in most organic solvents and gives a deep red air stable solution. Its ^{19}F nmr spectrum has three sharply defined bands, indicating the diamagnetism of the complex and attributed to the ortho-, meta-, and para-fluorine atoms of the two equivalent pentafluoro phenyl groups. A similar complex, hexacarbonyl(octafluoro-4,4′-dimethoxytolan)-dicobalt(0)[126] has been shown to be formed by dimethoxyacetylene.



II

We extended this work to prepare hexacarbonyl 1,2-bis(4-dimethylaminotetrafluorophenyl) ethynedicobalt(0)

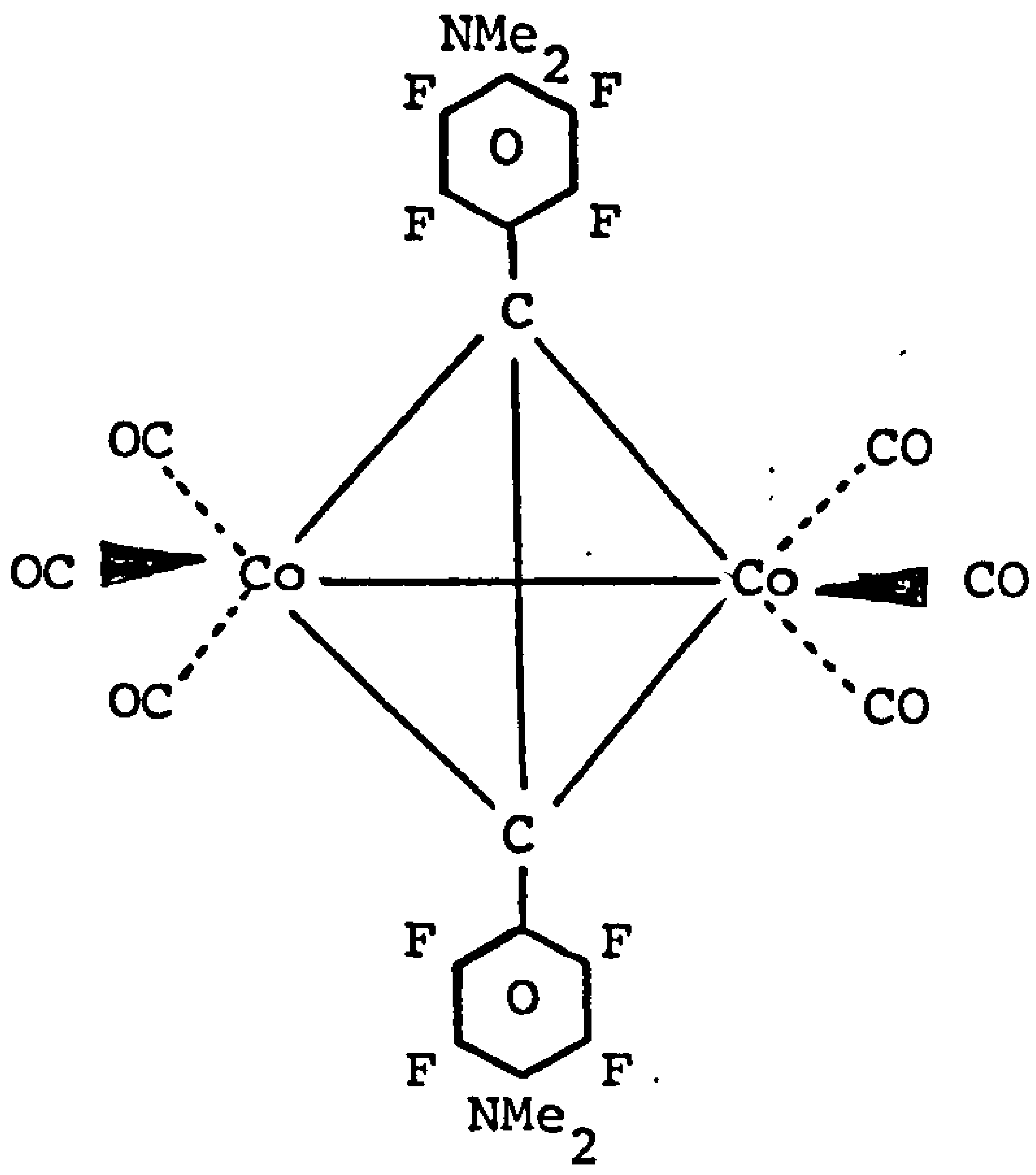


Figure (5.23) - Infrared spectrum of cobalt complex $[Co_2(CO)_6C_{14}F_8(NMe_2)_2]$.

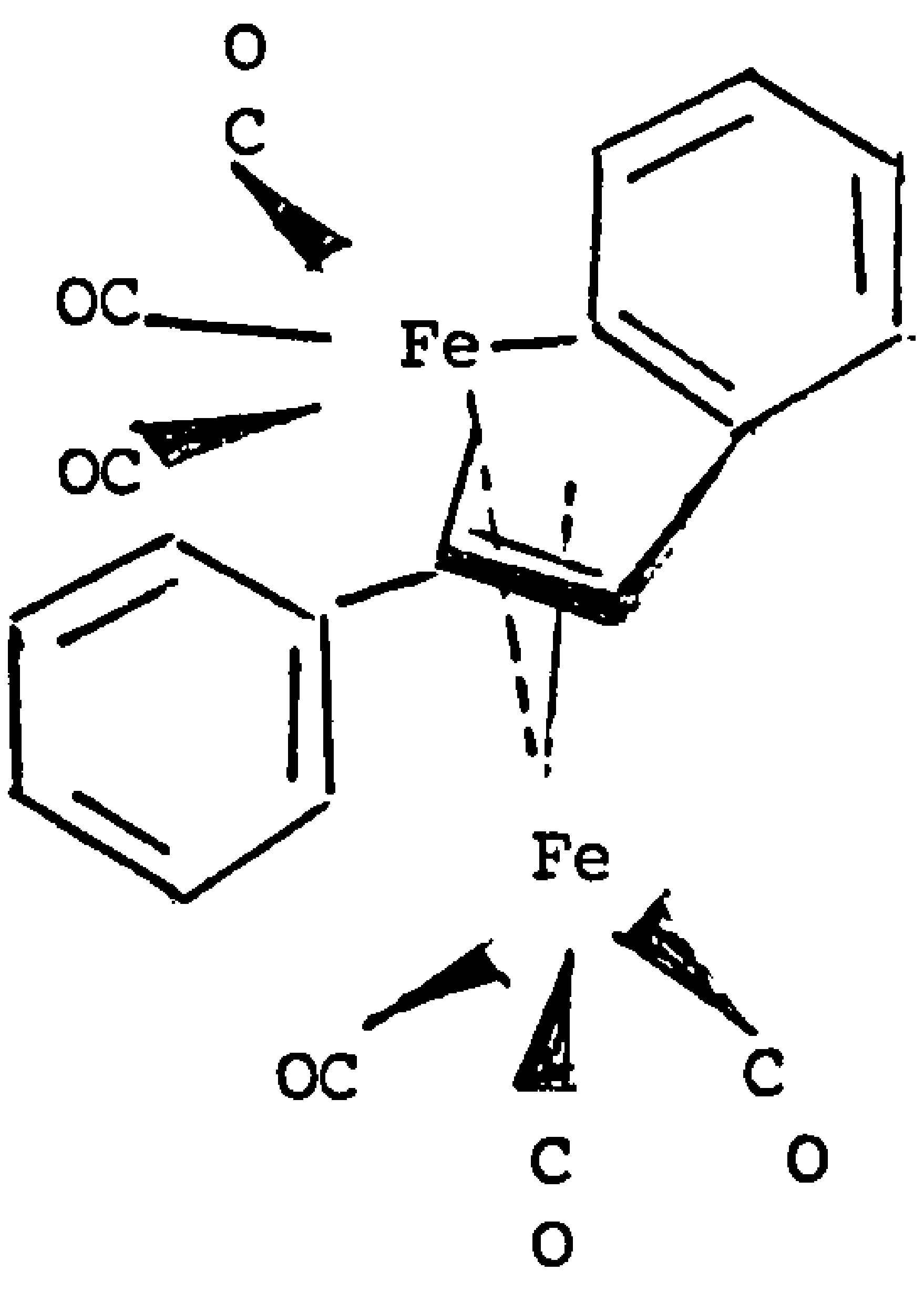
The i.r. spectrum has three bands in the terminal carbonyl region (1900-2150) cm^{-1} but no absorption in the bridging region (1800-1900) cm^{-1}[267]. The absorption pattern is closely similar to that of hexacarbonyl(octafluoro-4,4′-dimethoxytolan)dicobalt(O). The i.r. carbonyl frequencies of this complex lie between those of the fluorocarbon and hydrocarbon complexes (see figure (6.23)). ^{1}H nmr spectra give a sharp signal at 3.03 ppm indicating the diamagnetism of the complex. ^{19}F nmr spectra gave a broad signals at 138.44 (ortho) and 139.56 (meta) ppm.

This ligand could bond to the metal atoms through the nitrogen atoms or through the triple bond. In view of the very close similarity between the infrared spectra of the complex and the infrared spectra of the decafluorotolan complex which must have bonding from the alkyne group to the metals we are sure that in our compound the nitrogen atoms are unco-ordinated. A similar situation holds in the methoxy derivatives where co-ordination is also from the alkyne group. Apparently the bonds from the alkyne group are stronger than any potential bond from N or O; this effect also holds in the non-fluorinated derivatives.

Reaction of iron carbonyls with alkynes

Iron carbonyl reacts with alkynes to give a wide variety of products including compounds such as:

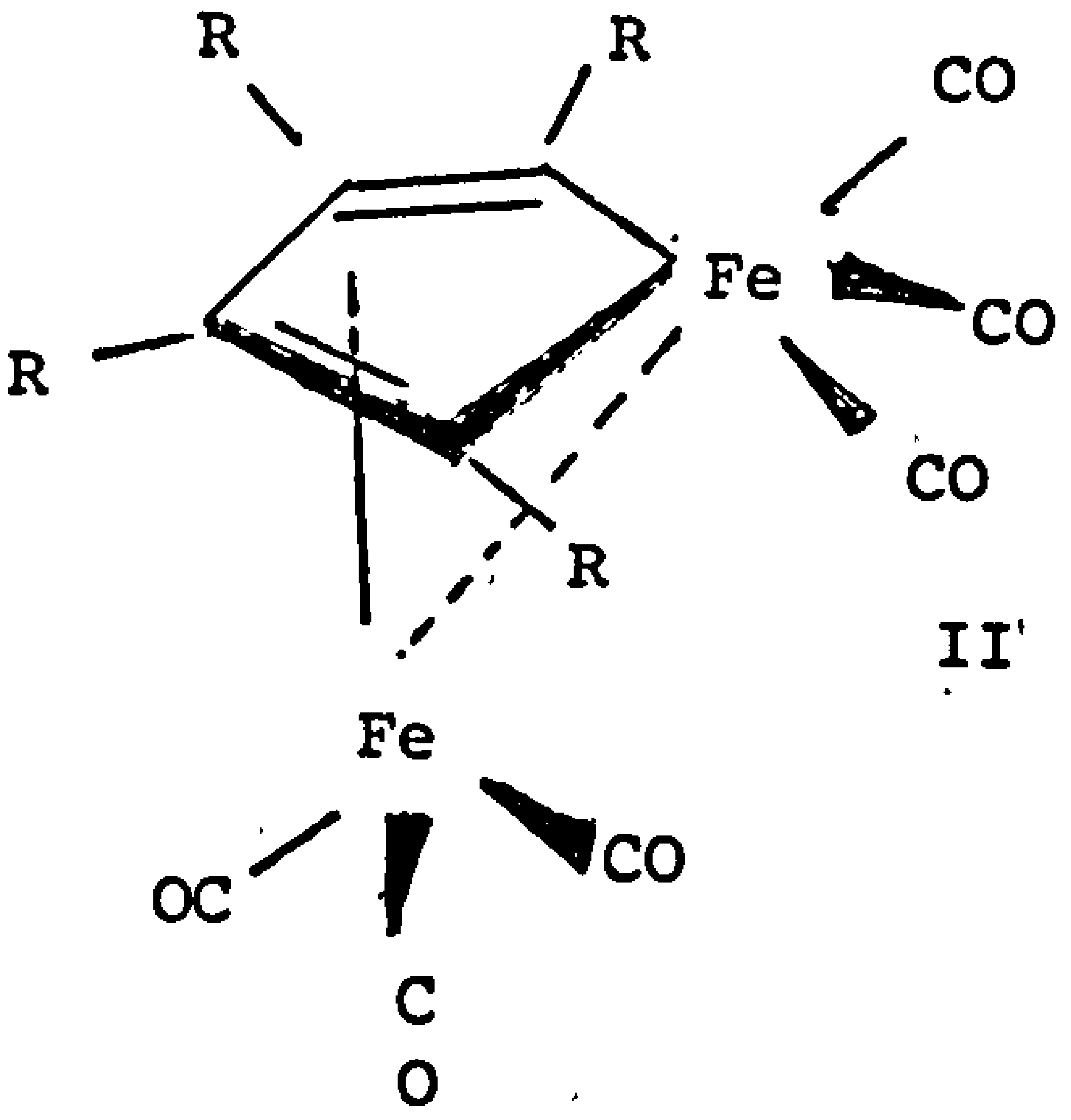
1) $Fe_2(CO)_6(PhC_2Ph)$[268,269]



I

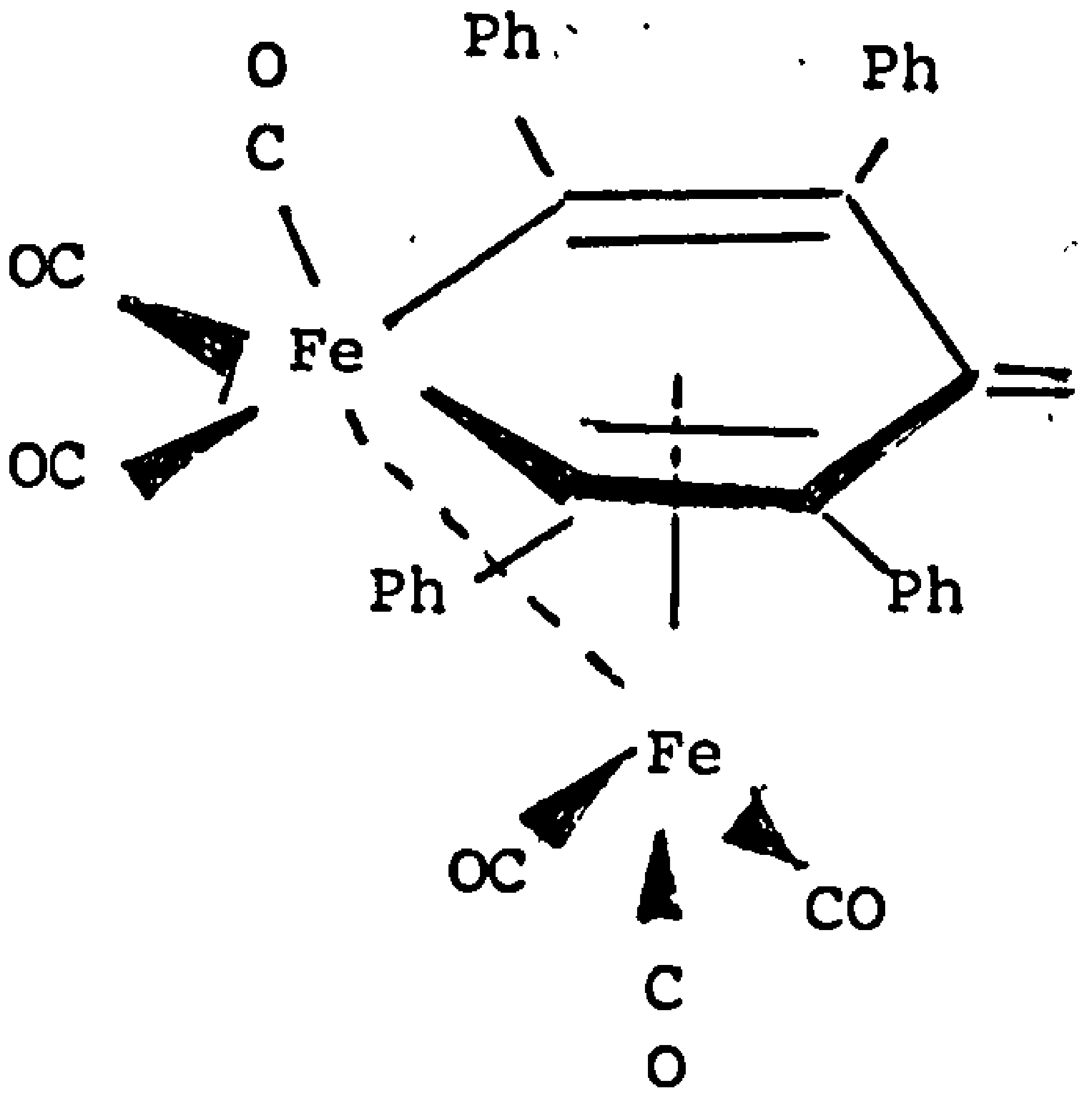
This complex was originally incorrectly formulated[268] as an analogue of the cobalt complexes $Co_2(CO)_6(ac)$. An X-ray study however showed the iron complex to have the structure shown (I,R=H). The ferraindene ligand appears to be formed as a result of hydrogen migration from the aromatic nucleus to one of the original, acetylenic carbon atoms.

2) $Fe_2(CO)_6(PhC_2Ph)_2$[268]



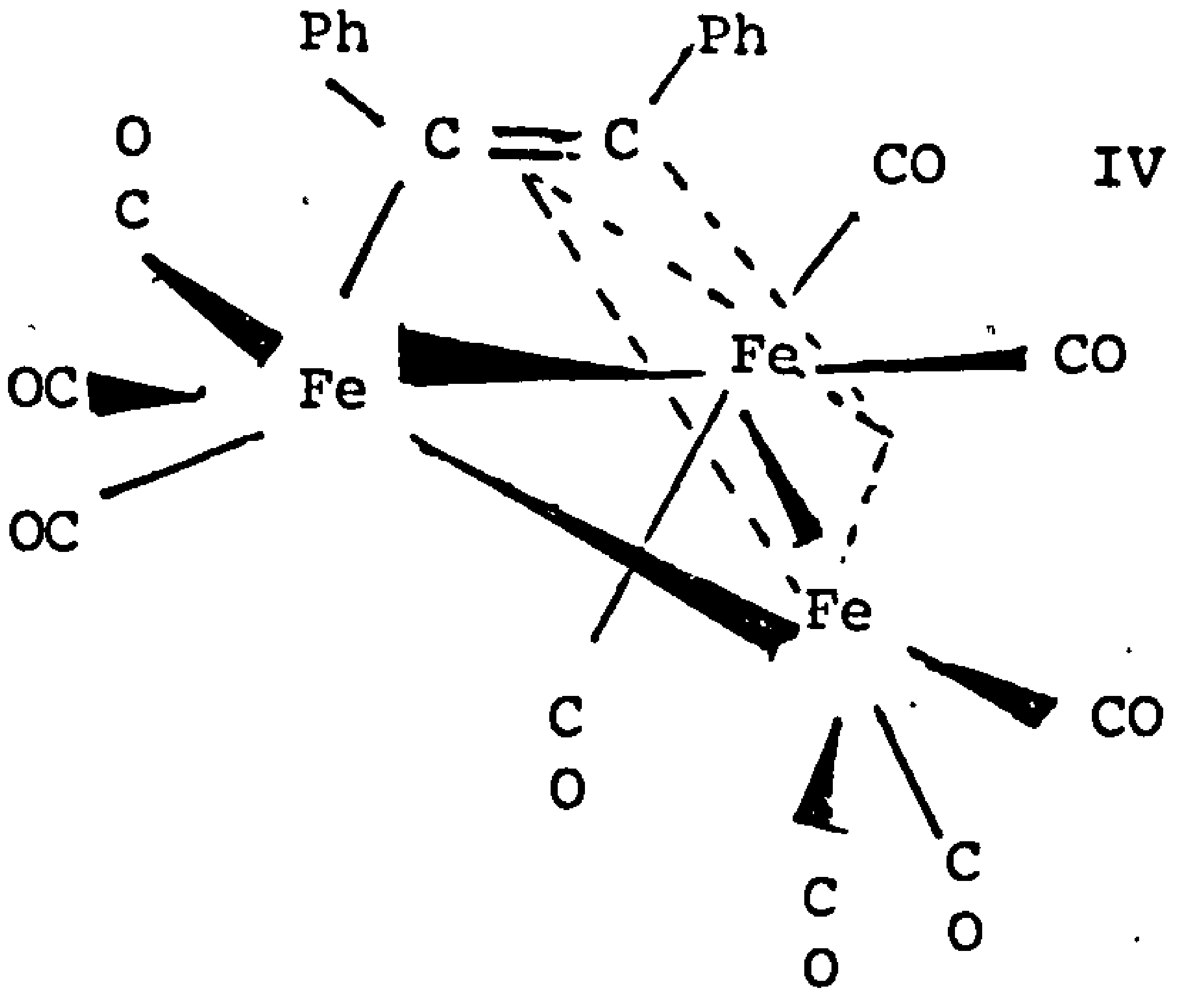
II

3) $Fe_2(CO)_7(PhC_2Ph)_2$[268]

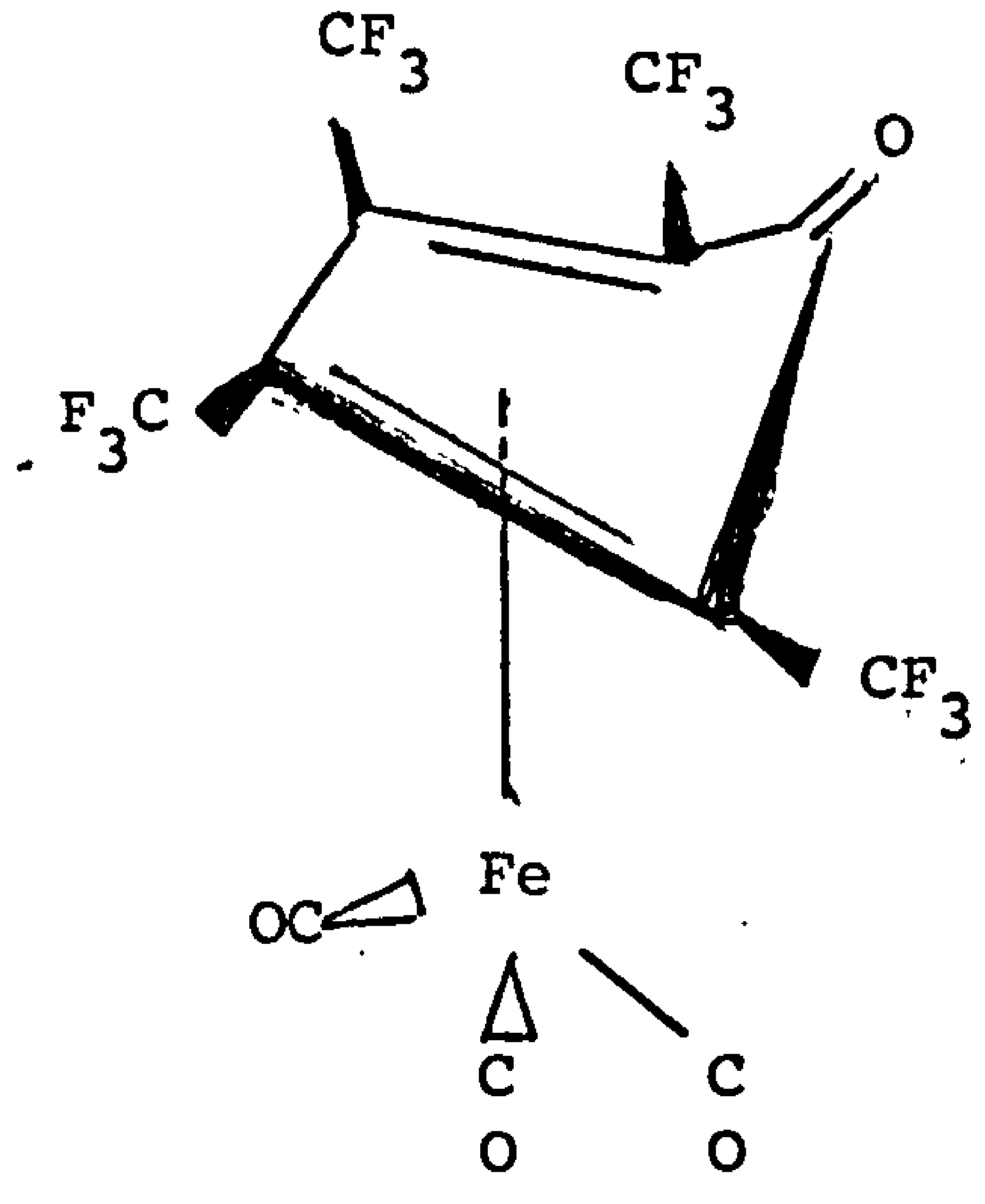


III

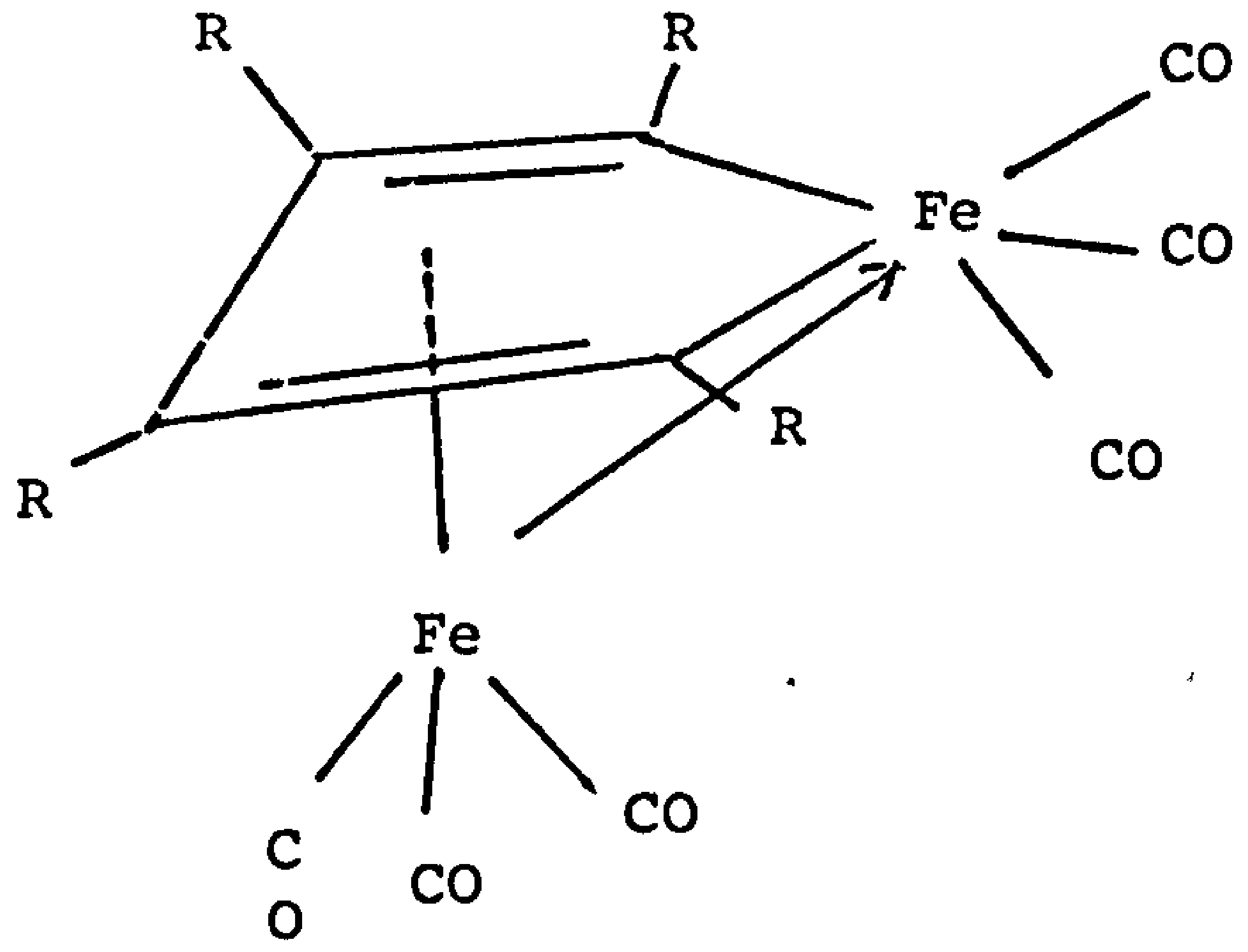
4) $Fe_3(CO)_9PhC_2Ph)$[268,270,271]



IV



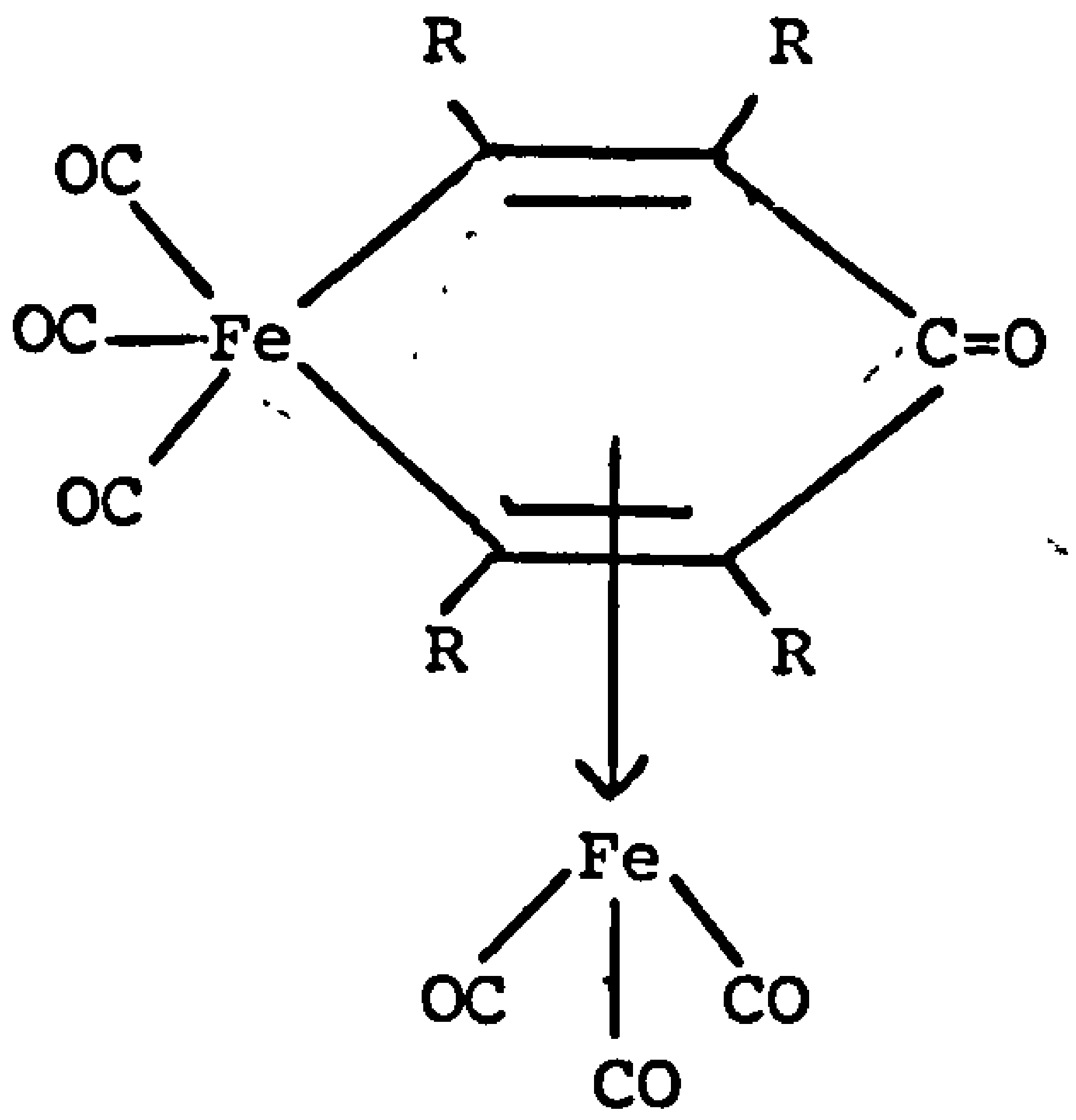
(I)



(II)

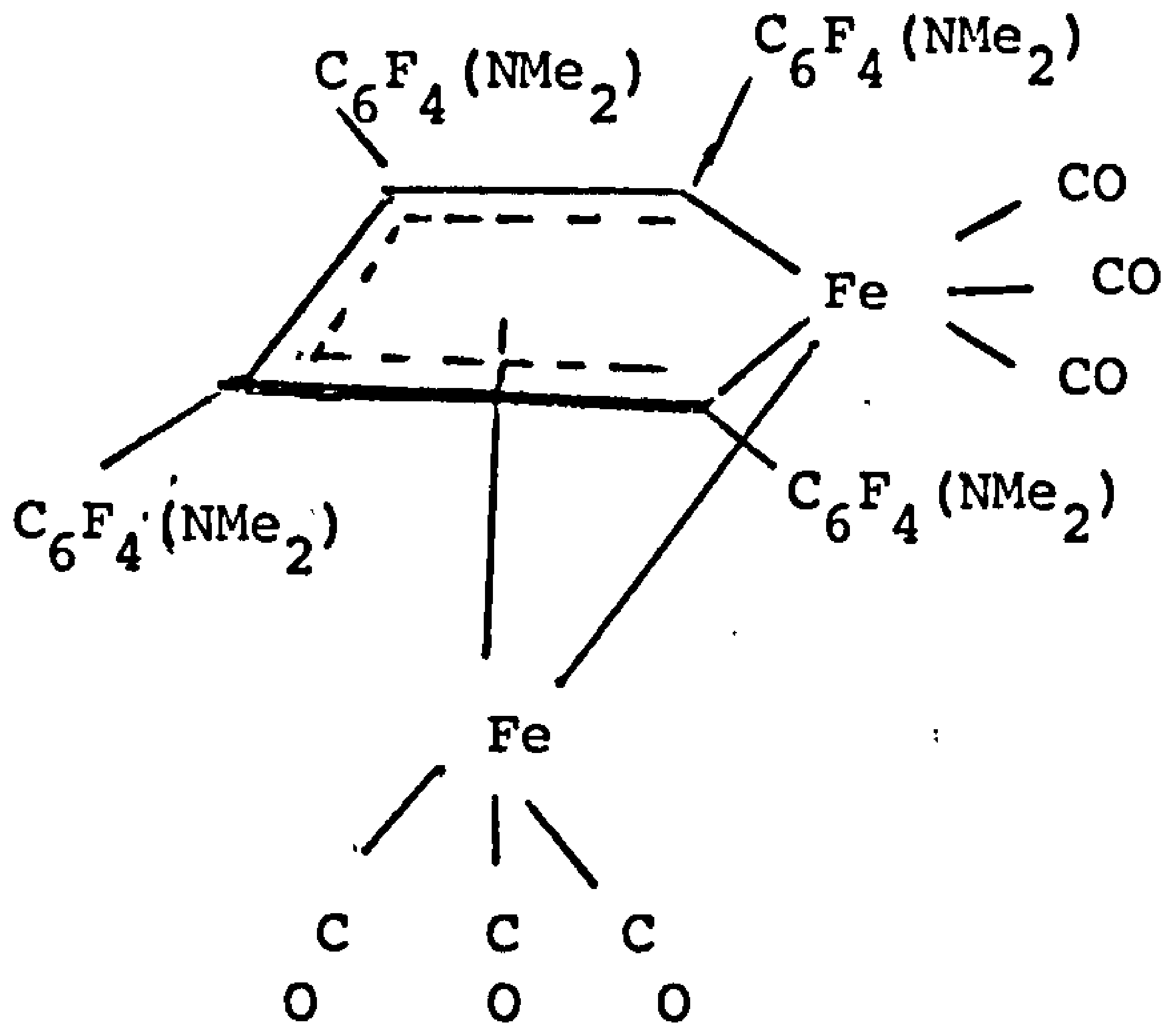
The reaction of the acetylenes $CF_3C{\equiv}CCF_3$,[272], $CF_3C{\equiv}CH$[273] and $C_6F_5C{\equiv}CH$[274] with iron carbonyls gives, in all cases, cyclopentadienone iron tricarbonyl complexes $Fe(CO)_3[C_4R_4CO)]$ (I). The reaction of $Fe_3(CO)_{12}$ with $C_6F_5C{\equiv}CC_6F_5$ gives $Fe_2(CO)_6(C_6F_5C_2C_6F_5)_2$ (II) which, according to spectroscopic data, contains a ferracyclopentadiene ring. This is in contrast to the reaction of iron carbonyls with acetylenes bearing alkyl and aryl groups which yields a large variety of products.[275,276] However these products were usually isolated in low yield from large scale reaction whereas the fluoro-acetylene reactions have been carried out on a small scale due to the relative inaccessibility of the acetylenes, so that a direct comparison is perhaps not valid. This suggestion appears to be substantiated by the report[277] that $PhC{\equiv}CC_6F_4C\ell$ reacts with $Fe_3(CO)_{12}$ to give a complex mixture containing at least twelve products although only three of these could be isolated in sufficient quantity for characterisation. Those isolated were $Fe_2(CO)_6(PhC_2C_6F_4C\ell)_2$, $Fe_2(CO)_2(PhC_2C_6F_4C\ell)_2Co$ and $Fe(CO_3)(PhC_2C_6F_4C\ell)_2$, all of which have analogues produced for dialkyl and diaryl acetylenes.

A complex mixture of two products is obtained when 1,2bis-(4-dimethylaminotetrafluorophenyl)ethene is refluxed in benzene with tri-iron dodeca-carbonyl which is slightly air-sensitive. The main product, formed as about 70% of the total isolable products, will be described on page (182). The other product was only found in sufficient quantities for identification by mass spectroscopy and ir spectroscopy. Mass spectroscopy shows the parent ion m/e = 1124 corresponding to $C_{43}F_6H_{24}N_4O_7Fe_2$. There seems little doubt that this is an analogue of $(Ph_2C_2)_2Fe_2(CO)_7$ reported by Hubel and Braye.



The infrared spectrum showed three terminal co-stretching frequencies around 2000 cm^{-1} and an absorption at 1683 cm^{-1} due to the C=O group.[277]

4,4'-dimethylthiooctafluorotolan, like decafluorotolan itself[126] gives a variety of products with iron dodeca-carbonyl depending on the reaction conditions. The major product produced was a deep red crystalline solid which was unstable in solution, but whose mass spectrum showed a parent ion at m/e 1096 corresponding to $C_{42}F_{16}H_{24}N_4O_6Fe_2$. The ^1H nmr spectrum has a sharp peak at 3.03 ppm indicating that the compound is diamagnetic. The ir spectrum of the complex shows three terminal carbonyl absorptions (see figure (6.24), very similar to the corresponding fluorinated complex $C_{34}F_{20}Fe_2O_6$. Thus we consider that the structure of the complex is



similar to that of the analogous decafluorotolan complex[126] (VI)

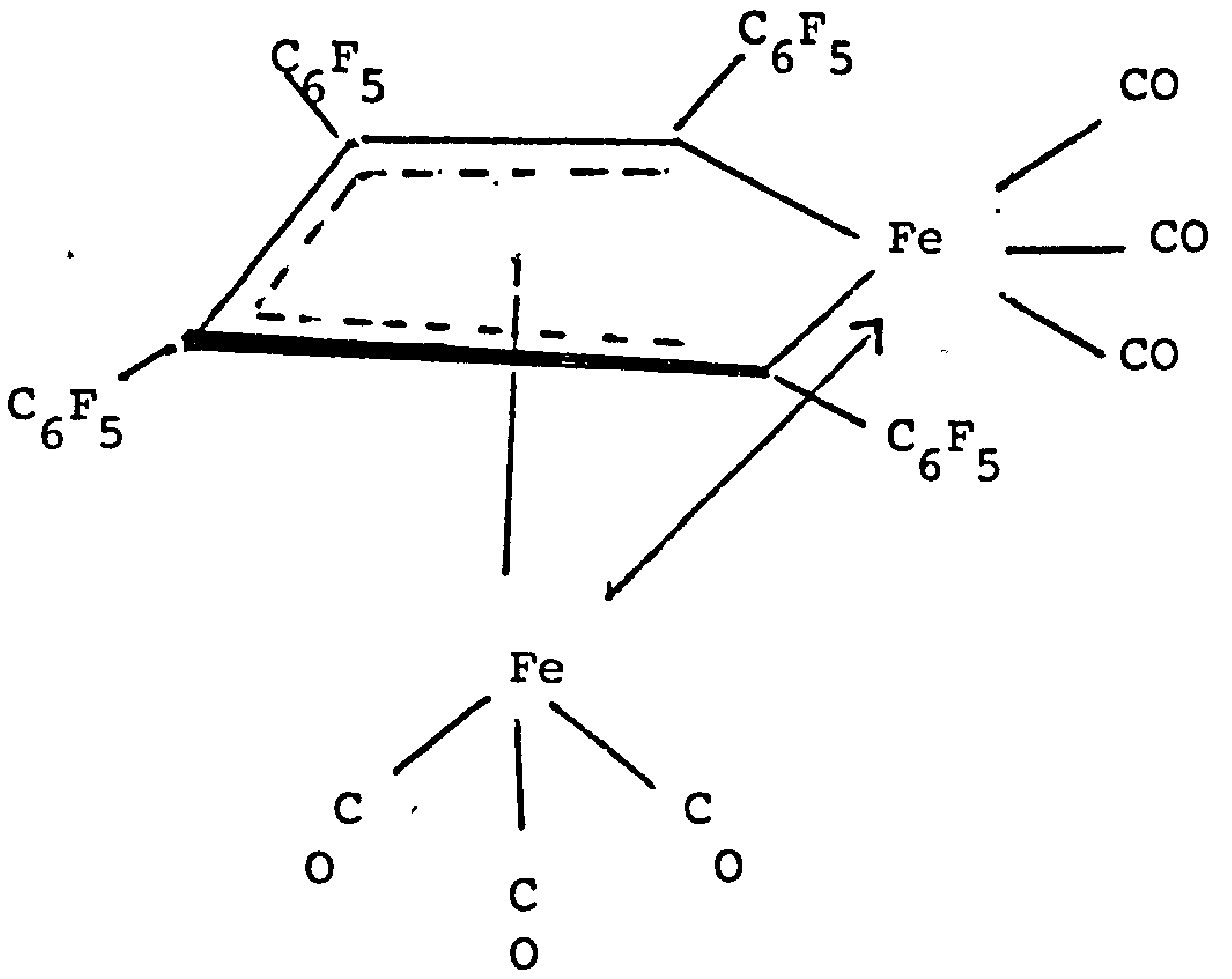


Figure (6.24) - Infra red of iron complex $[Fe_2(CO)_6\{C_{14}F_8(NMe_2)_2\}_2]$.

Table (6.13)

Characteristic infrared absorption bands

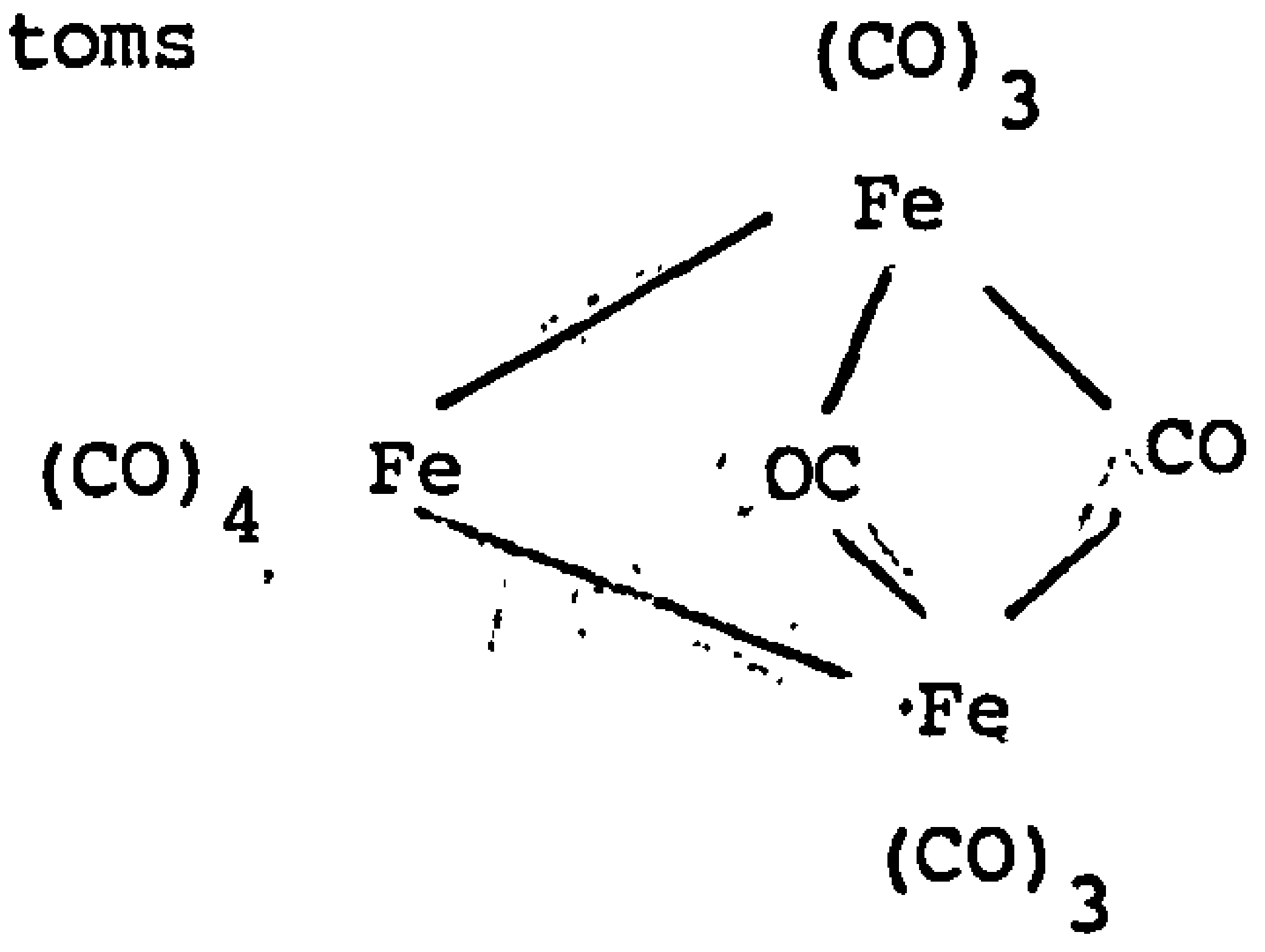
Compound	Origin	IR absorption bands (cm^{-1})				
$[Fe_2(CO)_6\{C_{14}F_8(NMe_2)_2\}_2]$	C=O	2000(vs)	2018(vs)	2050(vs)	2080(s)	
	$[C_6F_4(NMe_2)]$ring	1630(vw)	1535(s)	1483(vs)		
	C-F	995(s)	980(s)			
$[Fe_2(CO)_7\{C_{14}F_8(NMe_2)_2\}_2]$	C=O	2020(vs)	2052(vs)	2078(s)		
	$[C_6F_4(NMe_2)]$ring	1629(vw)	1530(vs)	1480(vs)		
	C-F	990(vs)				
$Fe_2(CO)_6(C_{14}F_{10})_2$ 126	C=O	2100(s)	2066(vs)	2045(vs)	2024(vs)	2012(vs) 1969(s)
	(C_6F_5)ring	1650(m)	1529(vs)	1497(vs)		
	C-F	991(vs)				
$Fe_2(CO)_6C_{14}(H_{10})_2$ 268	C=O	2075(s)	2024(s)	1992	1976(s)	1927(s)

(w) = weak (s) = strong (sh) = shoulder

(m) = medium (vs) = very strong

Structure of $Fe_3(CO)_{12}$

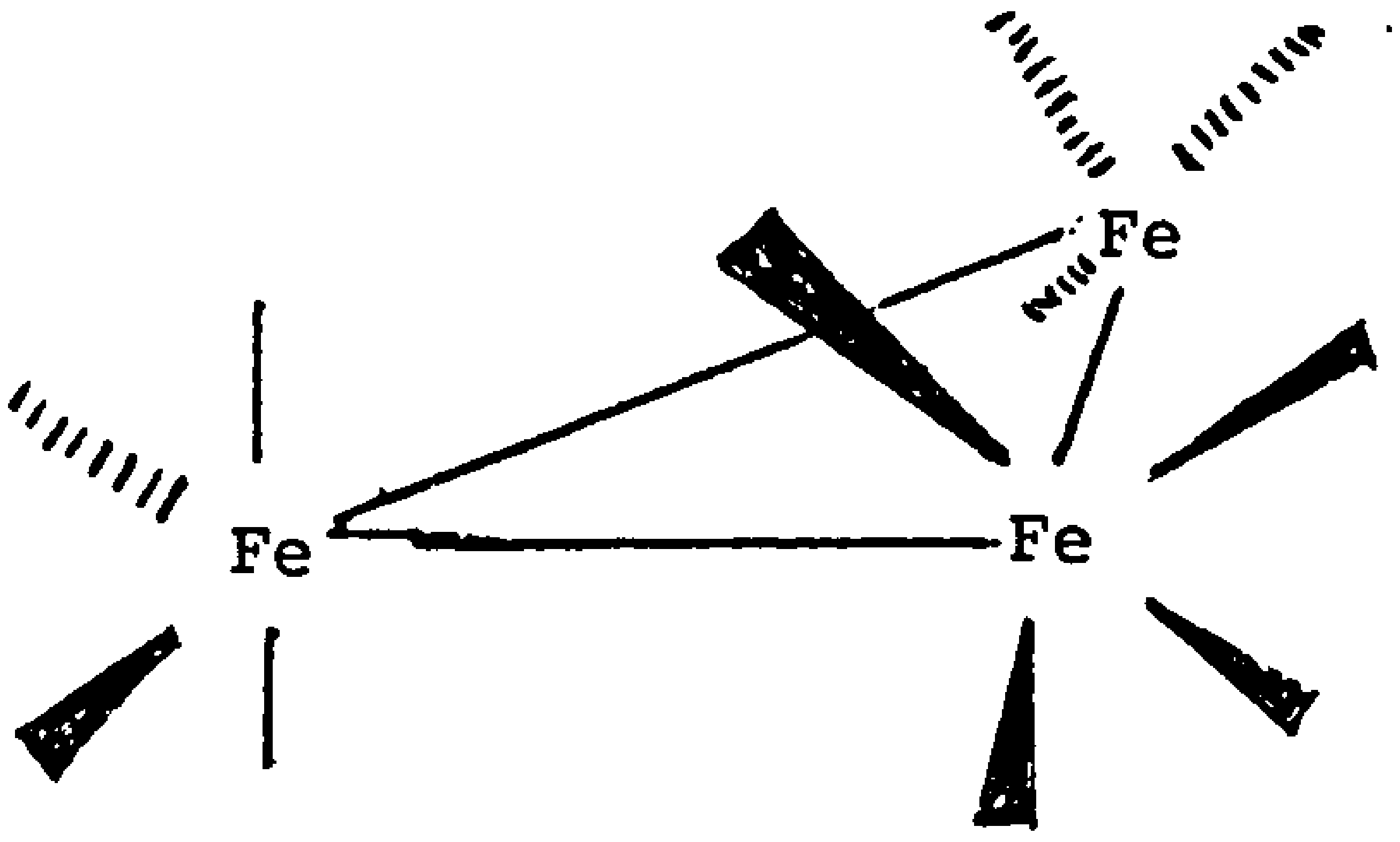
The basic structure of the molecule $Fe_3(CO)_{12}$ has been determined by X-ray crystallography.[278] The structure which is shown in formula (1) has a triangle of Fe atoms



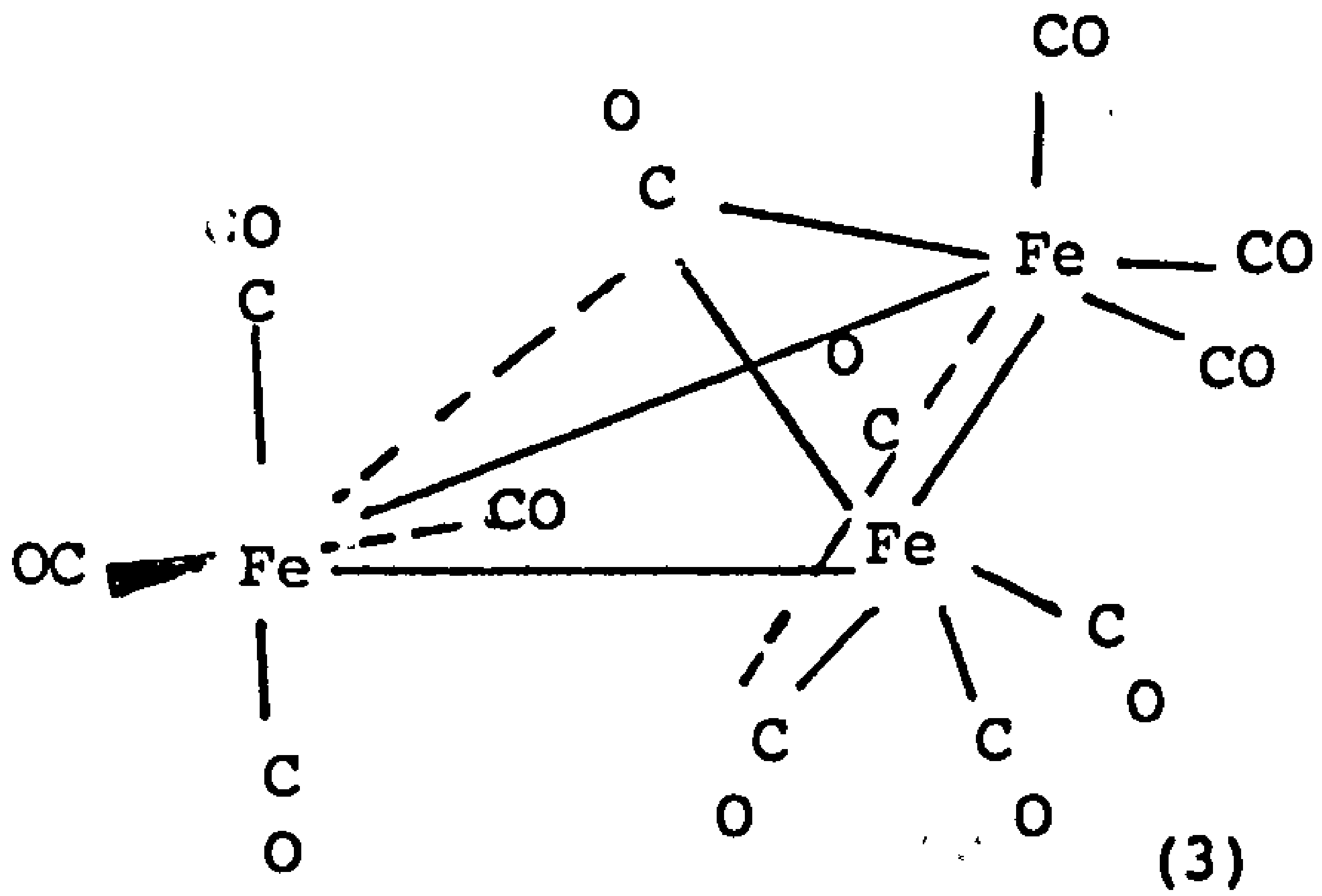
I

Two of the sides consist of Fe-Fe bonds unsupported by CO bridges. The CO bridges appear to be asymmetric.

The ir spectrum for $Fe_3(CO)_{12}$ in hexane solution consists of a strong band at 2046 cm^{-1}, a medium feature at 2023 cm^{-1}, a shoulder at 2013 cm^{-1} in the terminal CO stretching region, and weak broad bands at 1867 and 1835 cm^{-1} arising from the stretching vibration of the bridging CO ligand.[279] This is quite unlike the spectrum of $Fe_3(CO)_{12}$ in an inert gas matrix at 20K, which can be interpreted in terms of the structure of the molecule in the crystalline solid.[280] Therefore it is inferred that the structure in the solid state is not the same as in solution or in the gas phase. The ^{13}C NMR of $Fe_3(CO)_{12}$ consists of a single line down to the lowest temperature so far studied, -150°C at 25 MHz.[282] This is explained by rapid structural rearrangements between the intermediates shown in (I), formula (2) and formula (3). Another way of viewing this process is that the 12 CO ligands are disposed in an icosahedral array,



(2)



(3)

which rotates about the central triangular core of iron atoms with the configurations in (I), (2) and (3) being three limiting structures which arise in this process.

Almost all the transition metals form compounds in which carbon monoxide acts as a ligand. There are three points of interest with respect to these compounds.

(1) Carbon monoxide is not ordinarily considered to be a very strong Lewis base and yet it forms strong bonds to the metals in these complexes.

(2) The metal is in a low oxidation state, most often formally in an oxidation state of zero, therefore the metal atom itself has a relatively high electron density.

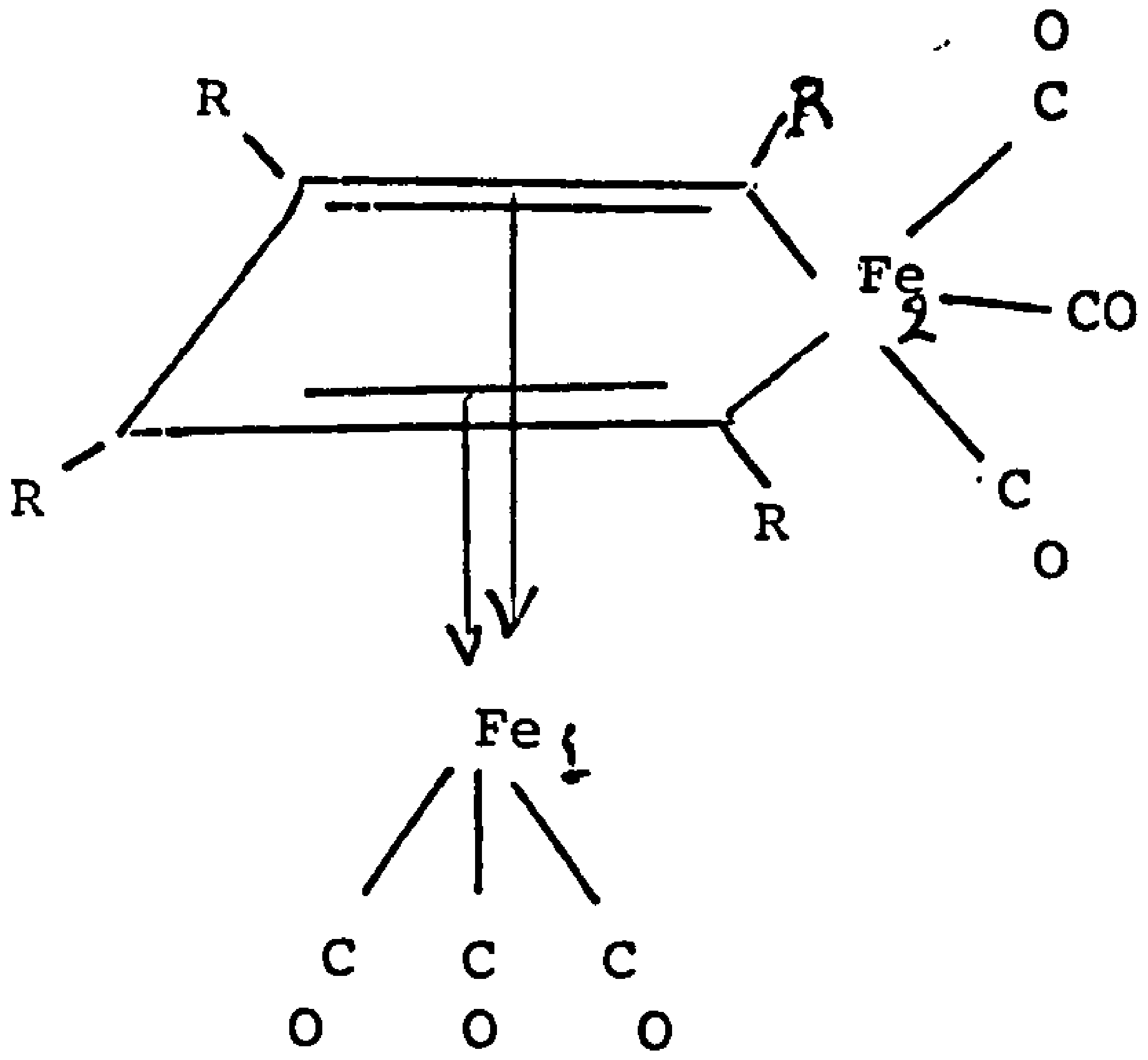
(3) The effective atomic number (EAN) rule is obeyed with remarkable frequency ~~perhaps 99% of the time~~. Thus $Fe_3(CO)_2$ obeys the EAN rule

3Fe	=	78e$^-$
12CO	=	24e$^-$
$Fe_3(CO)_{12}$	=	102e$^-$
EAN	=	34e$^-$/Fe

An EAN of 34 requires two metal-metal bonds on each iron, hence a trimer for the dodeca-carbonyl.

Discussion of bonding of the complex (diiron-acetylene)

In order to obtain a suitable bonding description of our diiron-acetylene complex we count electrons around each iron atom in the following way. Fe_1 has eight electrons s^2p^6 of its own, acquires six more from the three CO groups and four more from the double bonds; this gives it eighteen electrons. Fe_2 has eight electrons of its own, plus six from the three CO groups and only two more from the two Fe-C bonds; this gives it only sixteen electrons. If each metal atom is to have an eighteen-electron valence shell, the Fe-Fe bond must be considered as a dative bond and written as $\overset{+}{Fe}_1 - \overset{-}{Fe}_2$ or $Fe_1 \rightarrow Fe_2$ with resultant separation of charges.



CHAPTER 7

EXPERIMENTAL PROCEDURES

CHAPTER (7)

Experimental Procedures

General Information

Reagents

The commercially available reagents used in this work and their suppliers are listed below. Purity was checked against data reported in the reference following the formula of the reagent. When purification was judged to be necessary, the method employed is also listed.

Reagent	Supplier
$CF_3C{\equiv}CCF_3$[302]	Fluorochem Ltd.
$CF_3C{\equiv}CH$[303]	" "
CH_3SH[304]	Matheson Co. Ltd.
Bu^tSH[304]	Koch-Light Laboratories Ltd.
CH_3SSCH_3	Fluka A.G.
$PhC{\equiv}CH$	Koch-Light Laboratories Ltd.
$PhC{\equiv}CPh$	" " "
Br_2	B.D.H. Chemicals Ltd.
C_6F_5Br	Imperial Smelting Corp. (N.S.C.) Ltd.

Other intermediates were prepared according to published procedures as follows. $C_6F_5C{\equiv}CC_6F_5$[126], C_2I_2[305], $C_6F_5CH{=}CHC_6F_5$[126], $C_6F_5BrC{=}CBrC_6F_5$[126], CuSMe.[92]

Hydrocarbon solvents were dried over sodium and distilled under nitrogen before use. Other solvents were purified and dried by standard methods.[306]

Experimental methods

Volatile materials were transferred by conventional high vacuum techniques using a Pyrex glass vacuum line.

Vacuum distillations were performed with continuous pumping.

Photolytic reactions were carried out in quartz reaction vessels and irradiated by a Hanovia medium pressure mercury lamp[307] emitting predominantly 254 mμ, 265 mμ, 297 mμ, 313 mμ and 366 mμ wavelengths.

All other reactions were carried out under an atmosphere of oxygen-free nitrogen.

Elemental analyses

These were carried out in the Chemistry Department, Glasgow University or Bernhardt Laboratories in West Germany.

Infrared spectra were recorded on Perkin-Elmer PE255 and PE577 spectrophotometers. The samples were investigated as KBr discs, or in $CC\ell_4$ solutions depending on the physical properties of the material. The ^1H NMR spectra were recorded on a Perkin-Elmer R32 spectrometer at 90 MHz; ^{19}F spectra were obtained using a Varian XL100 F.T. spectrometer. Samples were recorded in a number of deuteriosolvents and where comparisons were required, the same solvent was employed. $CFC\ell_3$ and $Si(CH_3)_4$ were used as references for ^{19}F and ^1H spectra respectively. ^{195}Pt NMR spectra were recorded on a Bruker WP 200 SY spectrometer.

Mass spectra were obtained on a VG/Kratos MS12 spectrometer.

Preparation of diiodoacetylene, C_2I_2[305]

25 gm of iodine were placed in a 100 ml beaker and the bottom of the beaker cooled by immersion in a dish of -33°C dry ice-methylene chloride. After standing for one minute 250 ml ammonia was added as

rapidly as possible. Acetylene from a Prestolite cylinder was bubbled through the solution at a constant rate. The contents of the beaker were mechanically stirred. After two and a half to three hours the solution became perfectly clear, indicating the end of the reaction. The beaker was covered with a watch glass and placed at room temperature to evaporate the ammonia. When the volume had been reduced to about half volume 75-50 ml, 100 ml of water was slowly added to precipitate the diiodoacetylene. The precipitate was filtered and pressed as dry as possible by means of a sheet of filter paper.

The product weighed 15-17 gm. The moist diiodoacetylene was dissolved in 75 ml of petroleum ether and treated with 5 gm $CaC\ell_2$. After standing overnight the solution was decanted from the calcium chloride in a beaker which was immersed in liquid ammonia. The diiodoacetylene which crystallized was filtered off in a cold funnel. A yield of 8-8.5 gm was found.

WARNING

If you notice that a black precipitate has formed, immediately stop passage of acetylene and treat the ammonia solution with sulfur dioxide. The black precipitate is a nitrogen iodide which is very explosive when it is dry.

Preparation of decafluorotolan, $C_6F_5C{\equiv}CC_6F_5$[126]

Cobalt(II) chloride (dried in vacuo at 150°C) (0.93 gm; 7.2 mmoles) was added to a cooled (-20°C) solution of pentafluorophenyl magnesium bromide [prepared from bromopentafluorobenzene (24.7 gm; 100 mmoles) and magnesium (2.46 gm; 101 mg-atoms) in anhydrous ether

(200 ml)]. The mixture was stirred vigorously and diiodoacetylene (13.9g; 50.0 mmoles) in anhydrous ether (100 ml) was added dropwise. The temperature was maintained at -20°C ± 5°C throughout the addition (30 min) and for a further 2hr, after which time the mixture was allowed to warm to room temperature. The mixture was acidified with aqueous 20% acetic acid, washed with water (4 x 100 ml), dried ($MgSO_4$) and evaporated in vacuo at room temperature to give a dark brown solid which crystallized from light petroleum (b.p. 60-80°) as white platelets of decafluorotolan (10.1 gm, 56%). M.p. found 121.5°C, literature m.p. 121°C.

Hydrogenation[126] of decafluorotolan, [to cis-1,2-bis-(pentafluorophenyl)ethene, (decafluorostilbene)

A suspension of decafluorotolan (3.65 gm; 10.2 mmoles) in petroleum-ether (40°60°) (400 ml) containing Raney nickel (0.5 gm) was hydrogenated at 1 atmosphere in a standard hydrogenation apparatus until 10.1 mmoles of hydrogen had been absorbed. Filtration of the reaction mixture followed by evaporation of the filtrate yielded a white solid, which was crystallized from petroleum-ether (40-60°) and shown by n.m.r. spectroscopy to be a mixture of decafluoro-cis-stilbene (2.53g; 69%) and decafluorobibenzyl (0.45g; 12%). Repeated recrystallization from light petroleum gave the pure cis-stilbene with m.p. = 53°C.

The Raney nickel catalyst, W_8[308] was prepared as follows. 15 ml of NaOH was dissolved in 75 ml of distilled water in a 500 ml beaker which was cooled to 0°C by dry-ice-methylene chloride , 15 gm Raney nickel was added in small portions, the base was rapidly stirred and the alloy added at such a rate that the temperature of the mixture remained at 0°C. After addition of the alloy the temperature was raised to 100°C using an oil bath and the mixture was digested under reflux until hydrogen evolution had ceased. After digestion the catalyst was washed by decantation with distilled water and transferred to a 100 ml measuring cylinder. The cylinder was placed in a sink and fitted with a glass stirrer. Distilled wash water was added from a reservoir held above the cylinder, the water being supplied through a glass tube extending to the bottom of the cylinder. The stirring was at such a rate that the catalyst was partly in suspension but this caused some of the catalyst to be lost and it was found better to stir by hand each half an hour. After 10hr. the wash water was found to be neutral. 5ℓ of distilled water was found sufficient for washing.

1,2-Dibromo-1,2-bis-(pentafluorophenyl)ethene, $C_6F_5CBr=CBrC_6F_5$ [126]

A solution of decafluorotolan (0.64 gm; 1.79 mmoles) and bromine (1.2 ml) in glacial acetic acid (50 ml) was shaken at room temperature for 20 hr. Water (50 ml) and sodium pyrosulphite (2 gm) were then added and the precipitated solid was filtered off, washed with water, dried in vacuo (P_4O_{10}), and sublimed at 80°C/0.1 mm on to a probe cooled to -78°C. The white sublimate was 1,2-dibromo-1,2-bis-(pentafluorophenyl)ethene 67% m.p. = 106°C (literature m.p. 106°C).

1,2-Dibromo-1,2-bis-(pentafluorophenyl)ethane, $C_6F_5CHBr-CHBrC_6F_5$

Method (A)

1.55 gm (4.3 mmole) of decafluorostilbene ($C_6F_5CH=CHC_6F_5$) was dissolved in 20 ml of cold carbon tetrachloride (-5°C) and (0.688 gm 4.3 mmole) of Br_2 was dissolved in 5 ml of CCl_4 and added slowly with stirring at a rate to keep the temperature of the solution below 0°C.

After the addition was complete the flask was warmed to room temperature and after about half an hour, half of the solvent was removed by distillation. The remaining solvent was removed by distillation under reduced pressure to give crystals of $C_6F_5CHBrCHBrC_6F_5$ 1.84 gm (80% yield). The crystals were recrystallized from petroleum ether (40-60°) at low temperatures to give colourless crystals with m.p. = 132°C.

1,2-Dibromo-1,2-bis-(pentafluorophenyl)ethane, $C_6F_5CHBr-CHBrC_6F_5$

Method (B)

(0.74, 2.05 mmole) of decafluorostilbene was dissolved in 50 ml of glacial acetic acid and 1.2 ml of bromine was added and the solution was shaken for 20hr. Water 50 ml and sodium pyrosulfite 2g $Na_2S_2O_5$ was added. A white precipitate was formed and was filtered off and washed with water, dried in vacuo (P_4O_{16}) overnight and purified by recrystallization from ethanol to give a white crystalline mixture of starting material and the product which recrystallized from methanol to give crystals (75%) of $C_6F_5CHBr-CHBrC_6F_5$ m.p. = 132°C.

trans-1,2-bis-(4-methylthiotetrafluorophenyl)ethene, $MeSC_6F_4CH=CHC_6F_4SMe$

2-3 ml of ammonia was distilled into an ampoule which contained (0.115 gm, 5 mmols) of sodium under vacuum. The ampoule was warmed to -60°C when the colour of the solution was blue. 2.3 gm, 2.5mmole of CH_3SSCH_3 was added to the ampoule containing the blue solution and warmed to -75°C. The reaction was exothermic, bubbling started and a dark red liquid was formed. After the reaction had stopped the ampoule was opened and 1.3 gm, 2.5 mmole of $C_{14}F_{10}H_2Br_2$ in CCl_4 was added. The solution was now yellow. The reaction was allowed to remain at -20°C overnight until no more NaSMe was left when the solution turned to a red colour.

Ammonia was removed and 10 ml of water.was added and 20 ml of ether. This gave two layers which were separated and the etheral layer was distilled to give the final product which was recrystallized from petroleum ether (b.p. 40-60°C) to give colourless crystals 68% yield with m.p. = 152°C.

1,2-bis-(4-methylthiotetrafluorophenyl)ethyne, $MeSC_6F_4C{\equiv}CC_6F_4SMe$

0.8526 gm of $C_6F_5CBr{=}CBrC_6F_5$[126] (1.63 mmole) was dissolved in carbon tetrachloride and added to NaSMe (3.26 mmoles) solution which was prepared as described on page (194) at -75°C. The mixture was warmed to -20°C and left overnight when the solution turned from yellow to red. Ammonia, solvent and excess of CH_3SSCH_3 were distilled on a vacuum pump, the solid product was dissolved in ether and 10 ml of water was added to form two layers. The ethereal layer was taken and ether was pumped away to leave a pale yellow crystalline solid which was recrystallized from petroleum-ether followed by acetone to give odourless crystals of $MeSC_6F_4C{\equiv}CC_6F_4SMe$ yield 78% with melting point 144°C.

1,2-bis-(methylthio)-1,2-bis-(4-methylthiotetrafluorophenyl)ethene

This compound was prepared as above from $C_6F_5BrC{=}CBrC_6F_5$[126] (1 mole) and NaSMe (4 moles) in ammonia and was formed in a 60% yield with m.p. 63°C

Preparation of copper(I) thiolate[92]

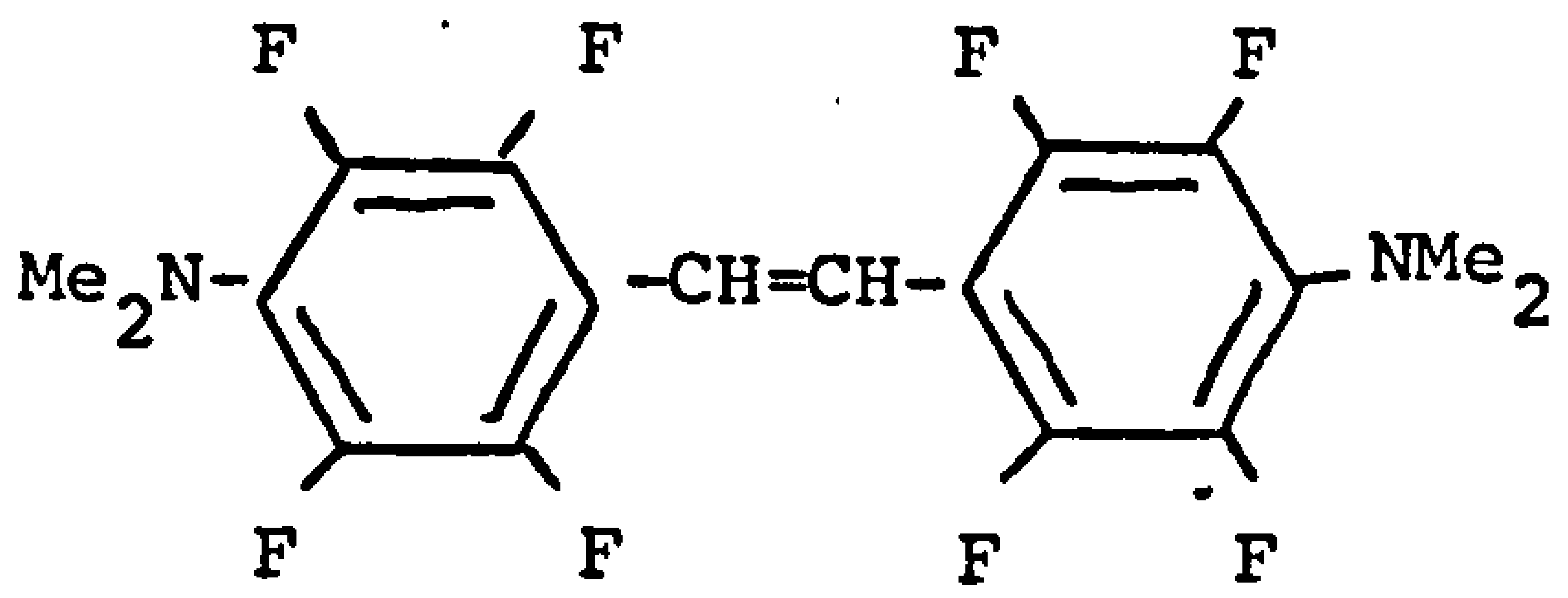
Copper(I) methanethiolate was prepared by bubbling MeSH through an acetone solution of copper(II)acetate when yellow CuSMe precipitated. The CuSMe was air dried and used immediately.

Preparation of copper(I) phenylthiolate

Copper(I) phenylthiolate was prepared by adding PhSH to an acetone solution of copper(II)acetate and the mixture was left for 2 hours with stirring. A yellow precipate was formed. The acetone was decanted off and the precipitate, CuSPh, was air dried and used immediately.

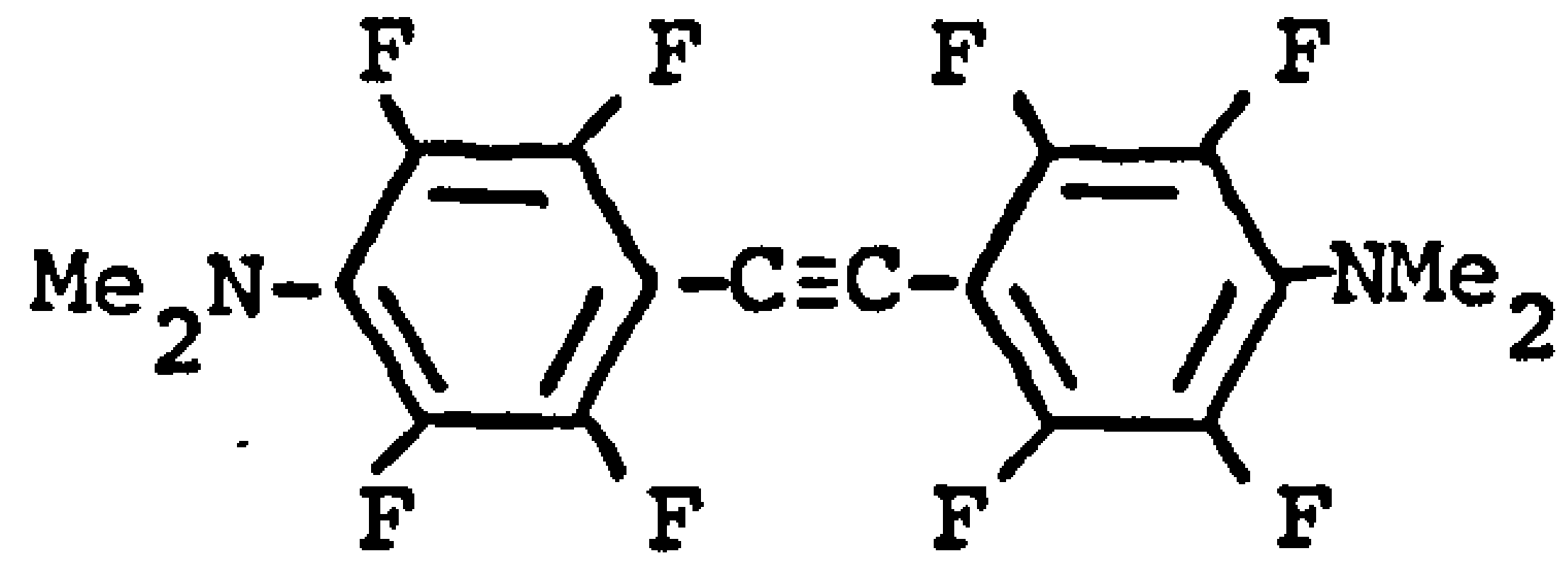
1,2-bis-(dimethylaminotetrafluorophenyl)ethene

3.8 mmole, 0.426 gm of freshly prepared CuSMe was dissolved in 50 ml of dimethylformamide and 0.4 gm, 0.76 mmole of 1,2-dibromo-1,2-bis(pentafluorophenyl)ethene, $C_{14}F_{10}H_2Br_2$ was refluxed for 24 hr. The mixture was poured onto an ice-acid mixture (100 ml 12 MHCℓ and 50 gm of ice) and the product extracted with ether. Considerable difficulty was encountered in the separation of the reaction products. The crude product was cleaned up by column chromatography (silica gel) and dried over $MgSO_4$, then crystallized from petroleum-ether b.p. 40-60°C and shown by ^{19}F n.m.r. spectroscopy to be a mixture of 1,2-bis-(4-dimethylaminotetrafluorophenyl)-ethene and 1-(4-dimethylaminotetrafluorophenyl)-2-(pentafluorophenyl)ethene. Repeated recrystallization and separation on the Chromatron gave pure



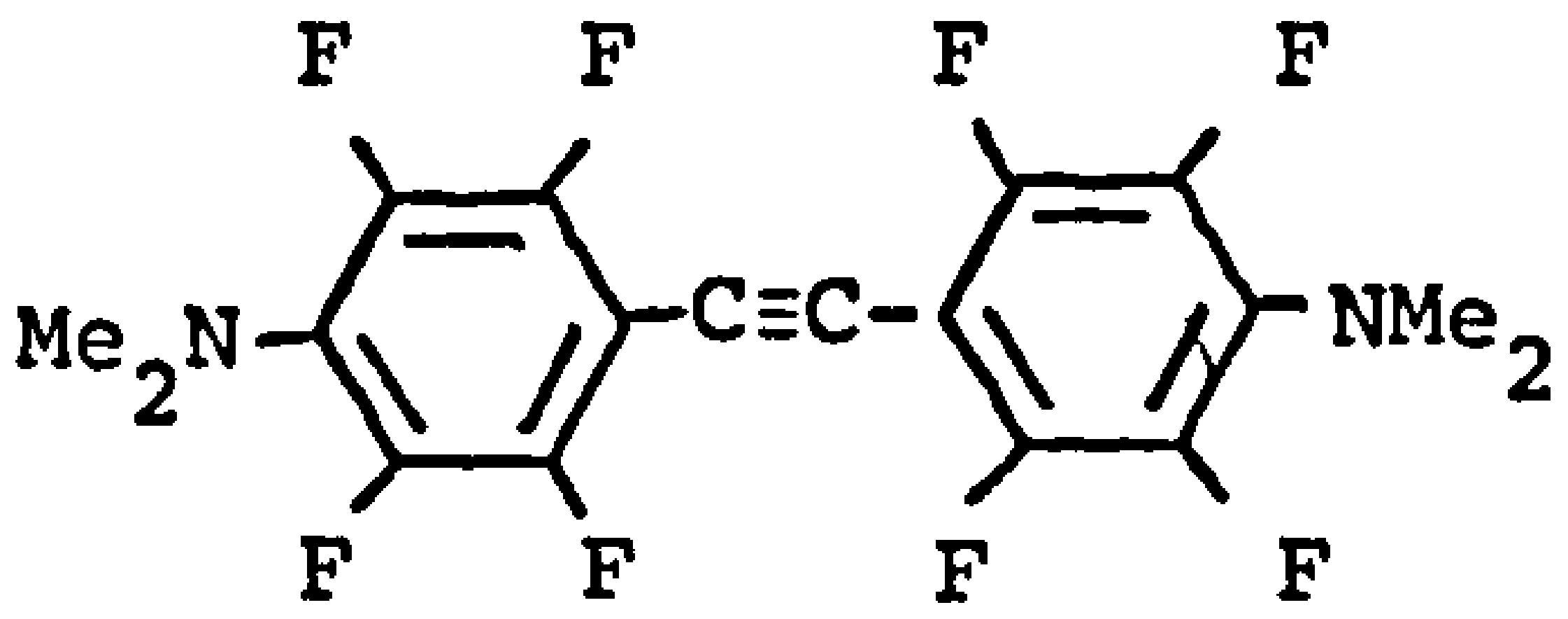
with m.p. = 95° as the major product.

Preparation of

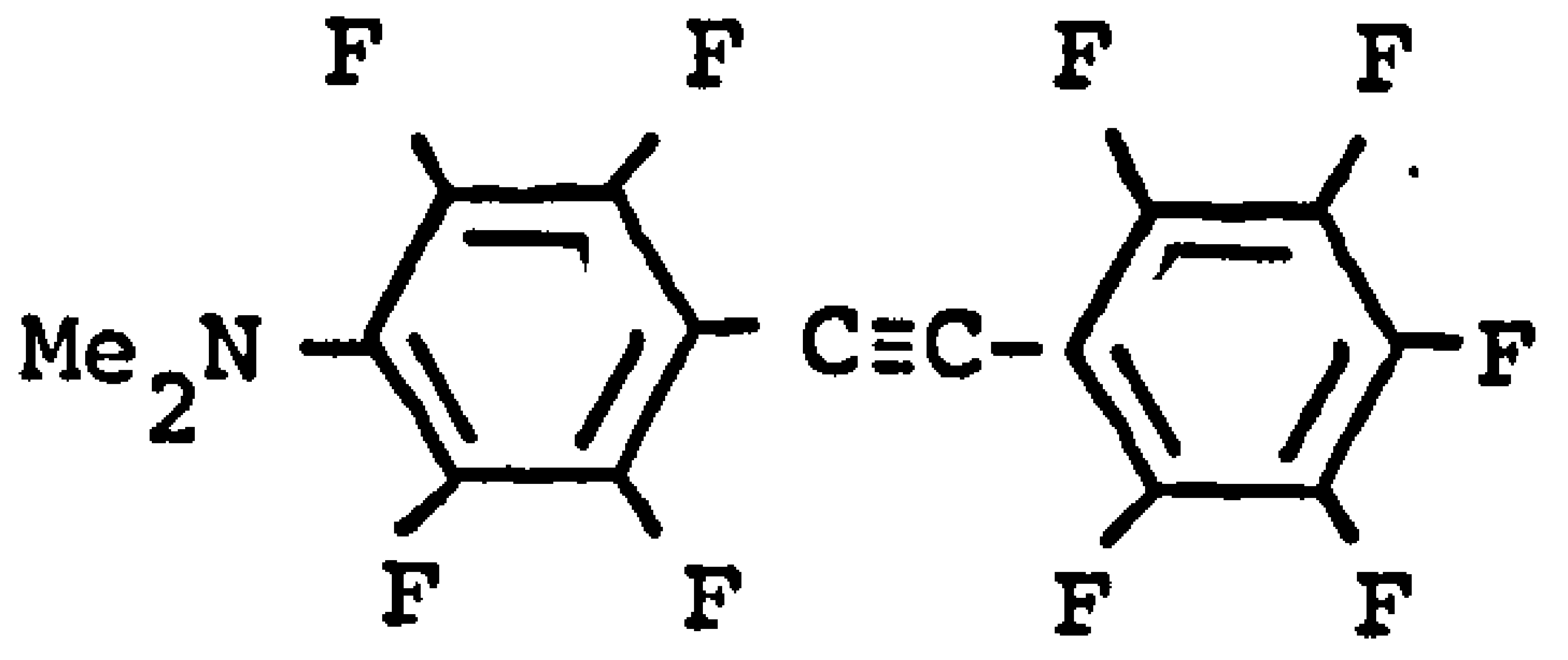


1,2-bis(4-dimethylaminotetrafluorophenyl)ethyne

0.39 gm, 0.74 mmole of 1,2-dibromo-1,2-bis(pentafluorophenyl)-ethene $C_{14}F_{10}Br_2$[126] was added to a solution of 3.8 mmole, 0.426 gm of CuSMe (molar ratio 1:5) and the mixture was refluxed for 24 hr. The mixture was poured on to ice-acid (100 ml HCℓ and 50 gm of ice) and the product extracted with ether. The solution was concentrated and then dried over $MgSO_4$. The crude product was cleaned up by column chromatography on silica gel using $CCℓ_4$ as solvent. The ir spectrum indicated the two products $Me_2NC_6F_4C{\equiv}CC_6F_4NMe_2$ and $Me_2NC_6F_4C{\equiv}CC_6F_5$ with a medium peak at 2230 cm^{-1} for the unsymmetric acetylene. Repeated recrystallization from petroleum-ether (b.p. 40-60°C) gave pure



12% and



3%

m.p.=154°C

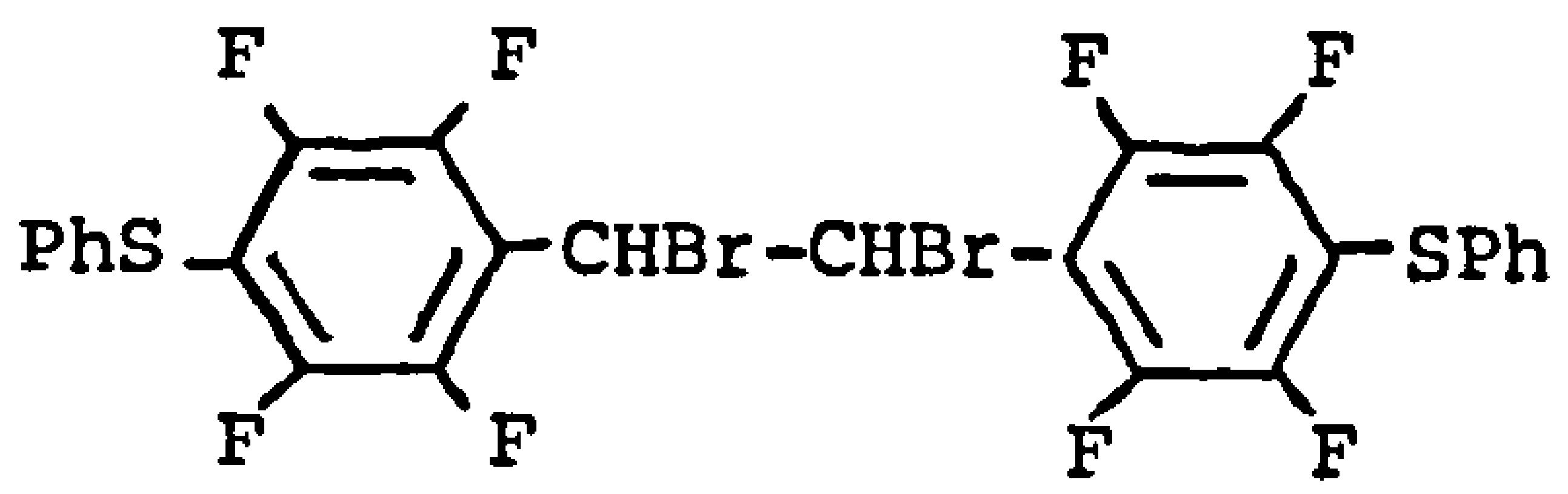
m.p.=60°C

Preparation of 1,2-bis(4-phenylthiotetrafluorophenyl)ethene

0.597 gm (1.15 mmole) of 1,2-dibromo-1,2-bis(pentafluorophenyl)-ethane $C_{14}F_{10}H_2Br_2$[126] was dissolved in dimethylformamide and refluxed for 24 hr. at atmospheric pressure with 5.7 mmole 0.99 gm of CuSPh (ratio of reactants 1:4). We found that CuSPh was suspended in the solution but that at the end of the reaction after 24 hours of refluxing the colour of the solution had changed from yellow to deep red or brown-red. The mixture was poured on to the ice-mixture (100 ml 12 M HCℓ and 50 gm of ice). The product was extracted with ether (53 ml) and a pale yellow precipitate was isolated which was decanted from the two layers and dissolved in chloroform, and dried overnight with $MgSO_4$, followed by recrystallization from chloroform. The white crystals were a mixture of $PhSC_6F_4CH{=}CHC_6F_4SPh$ and $C_{14}F_6H_2(SPh)_4$ (see discussion) which were separated by crystallization to give two isomers of 1,2-bis(4-phenylthiotetrafluorophenyl)ethene $PhSC_6F_4CH{=}CHC_6F_4SPh$ which were isolated by their different solubilities in chloroform. The isomers do not dissolve well in any organic solvent; the best solvent was chloroform. The melting point of the mixture of isomers was 205°C and the yield 25%, 0.12 gm.

The etheral layer was separated from the water layer by use of a separating funnel, the ethereal layer dried by $MgSO_4$ overnight, decanted and evaporated to give an orange oil which is dissolved in petroleum-ether 40-60°C and concentrated, cooled at -76°C to give pale yellow crystals with melting point 64°C. The mass spectrum of this compound showed a parent ion at 218 corresponding to PhSSCH (66% yield).

Preparation of 1,2-dibromo-1,2-bis-(4-phenylthiotetrafluorophenyl)ethane



0.0346 gm (0.064 mmole) of the mixture of isomers of $PhSC_6F_4CH{=}CH{-}C_6F_4SPh$ was dissolved in 5 ml of chloroform and cooled to -5°C. 0.0102 gm of bromine (0.064 mmole) was dissolved in 2 ml of chloroform and added dropwise to the cooled solution with stirring at a rate so that the temperature did not rise above 0°C. The solution turned to an orange colour after each addition. The flask was warmed to room temperature in about half an hour. Half of the solvent was removed by simple distillation when the colour of the solution turned to pale yellow. The other half was evaporated by use of a vacuum pump to give a pale yellow crystalline solid, recrystallized from $CC\ell_4$ to give $PhSC_6F_4CHBr-CHBrC_6F_4SPh$ (yield 0.028 gm 63%) with melting point 173°C.

Addition of thiols to acetylenes

The reactions of CH_3SH and Bu^tSH with $CF_3C\equiv CCF_3$, $CF_3C\equiv CH$, $CH\equiv CPh$, $PhC\equiv CPh$, and $C_6F_5\equiv CC_6F_5$ were all carried out similarly. A 3:1 excess of thiols with the appropriate acetylene were condensed in a quartz vessel and a few drops of di-tert-butyl peroxide added as catalyst. The solution was then irradiated. The periods of irradiation are shown below.

Time of irradiation and yield for the reaction of thiols and acetylenes

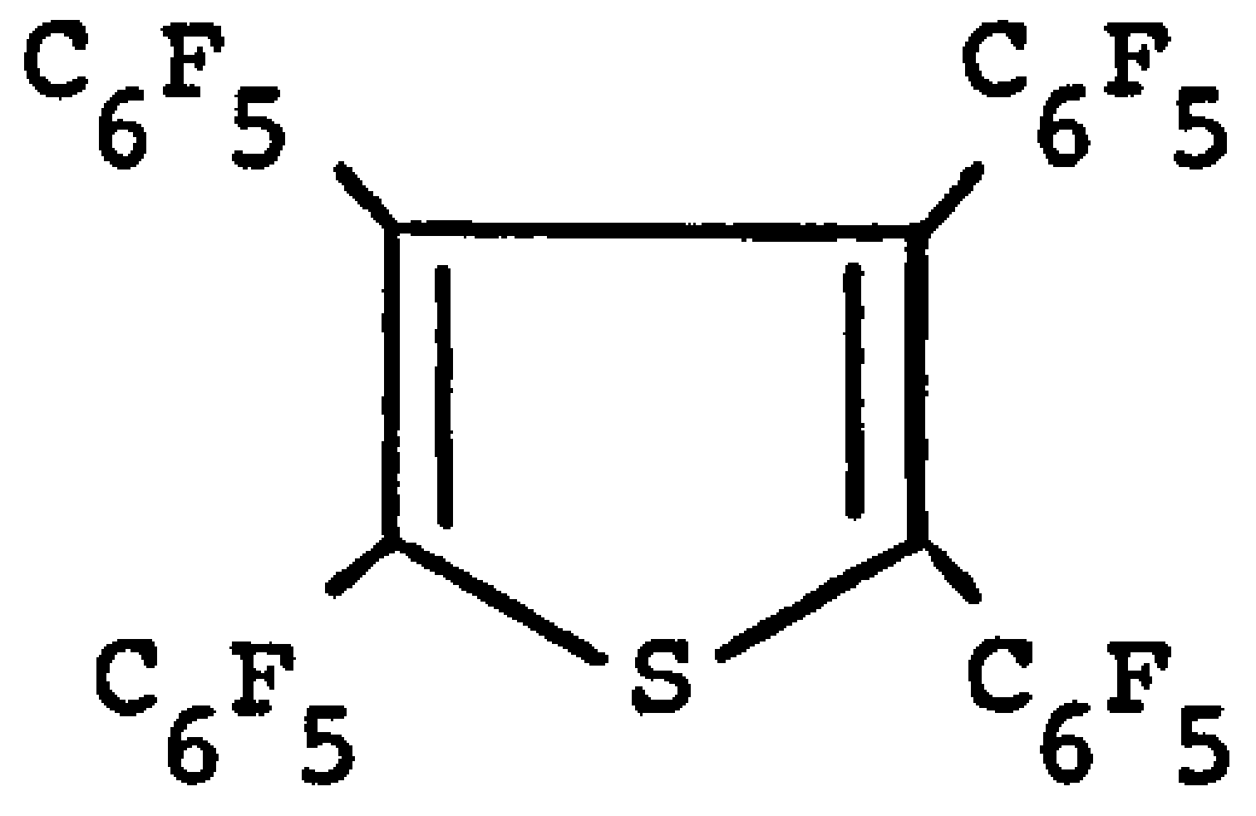
Acetylene	Time of reaction	Thiol	Yield	%
PhC≡CH	2 weeks	CH_3SH	$CH_3SCH_2CHPhSCH_3$	85
PhC≡CPh	2 weeks	CH_3SH	$CH_3SCPh{=}CHPh$	80
PhC≡CPh	1 week	CH_3SH	$CH_3SCHPhCHPhSCH_3$	90
			$(CH_3S)_2CPh\text{-}CHPhSCH_3$	5
$C_6F_5C{\equiv}CC_6F_5$	4 weeks	CH_3SH	$C_6F_5CH{=}C(SCH_3)C_6F_5$	12
$(CF_3)C{\equiv}C(CF_3)$	3 days	Bu^tSH	$Bu^tSCH(CF_3)\text{-}CH(CF_3)SBu^t$	10
$(CF_3)C{\equiv}C(CF_3)$	10 days	Bu^tSH	$Bu^tSC(CF_3){=}CH(CF_3)$	15
$(CF_3)C{\equiv}CH$	3 days	Bu^tSH	$Bu^tSCH(CF_3)\text{-}CH_2SBu^t$ + $Bu^tSCH = CH(CF_3)$ + $Bu^tSC(CF_3) = CH_2$	13

Volatiles were pumped off from the reaction vessel which was cooled to -10°C and the remaining liquids distilled under vacuum.

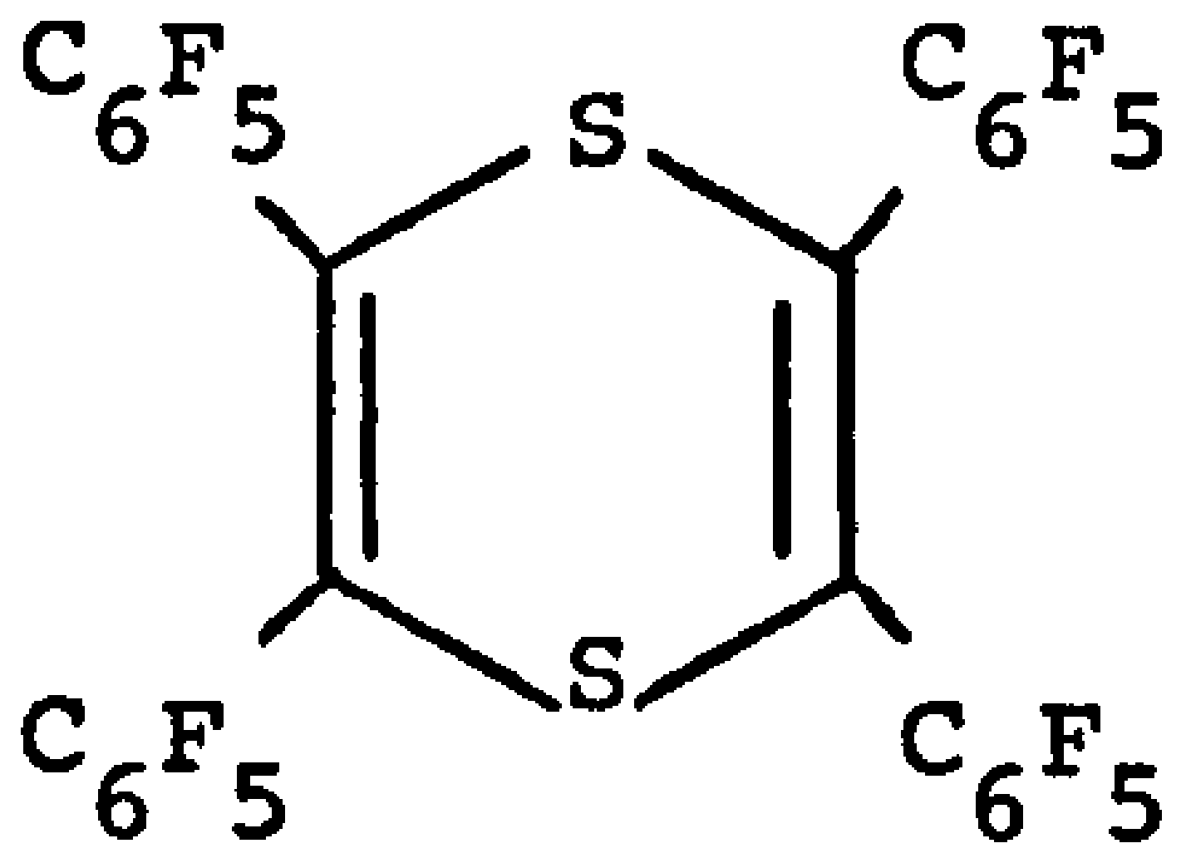
Preparation of cyclic compounds

0.64 gm (0.02 moles) of sulfur, 1.3 gm (0.005 moles) of iodine and 7.00 gm (0.02 mole) of decafluorotolan were placed in a nickel bomb and heated for about 6 hours under pressure to give four products as shown by g.l.c. The products were cleaned up by column chromatography to give

(1)



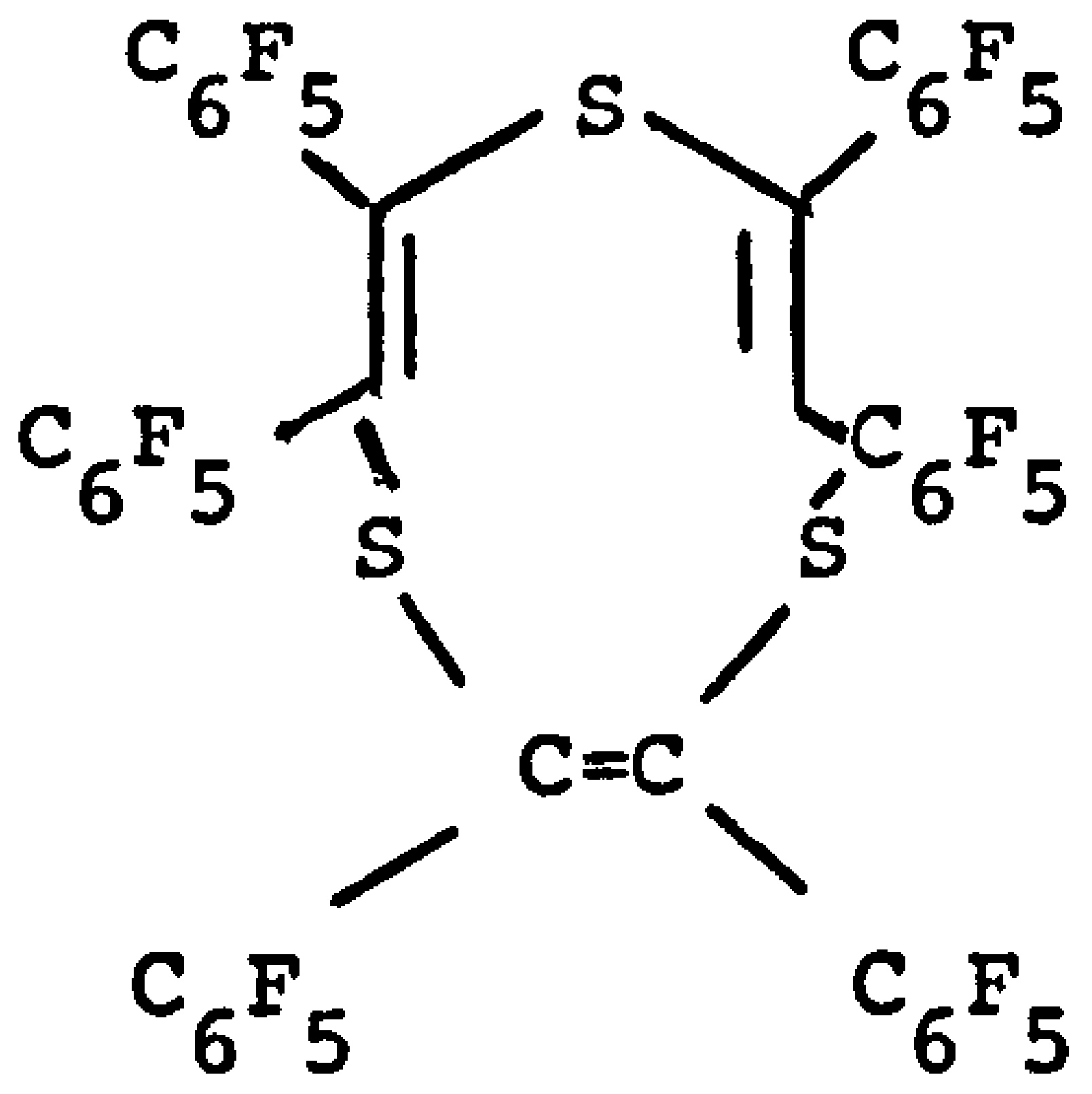
11%



(2)

26%

and



(3)

30%

The other product could only be characterised by spectroscopy. These compounds were isolated by use of the Chromatron, followed by recrystallization from petroleum-ether (b.p. = 40-60°C).

Microanalyses

Compound	Element	Found (%)	Calculated (%)
$CH_3SCHPh-CH_2SCH_3$	C	60.59	60.60
	H	7.08	7.07
	S	32.32	32.32
$C_6F_5CHBrCHBrC_6F_5$	C	32.29	32.30
	H	0.385	0.384
	F	36.55	36.53
	Br	30.74	30.76
$CH_3SCHPh-CHPhSCH_3$	C	70.07	70.07
	H	6.55	6.56
	S	23.36	23.35
$CH_3SCPh=CHPh$	C	79.63	79.64
	H	6.20	6.19
	S	14.13	14.15
$MeSC_6F_4CH=CHC_6F_4SMe$	C	46.18	46.15
	H	1.93	1.92
	S	15.38	15.38
	F	36.55	36.53
$C_{14}F_8H_2(SPh)_2Br_2$	C	44.59	44.58
	H	1.27	1.25
	F	21.97	21.94
	Br	22.98	22.97
	S	9.4	9.4

Compound	Element	Found (%)	Calculated (%)
$CH_3SC_6F_4C{\equiv}CC_6F_4SCH_3$	C	46.37	46.38
	F	36.72	36.71
	H	1.43	1.44
	S	15.47	15.46
$PhSCC_6F_4CH{=}CHC_6F_4SPh$	C	57.79	57.77
	H	2.24	2.22
	F	28.14	28.14
	S	11.84	11.85
$C_{42}F_{30}S_3$	C	43.05	43.07
	F	48.69	48. 7
	S	8.3	8.205
$C_{28}F_{20}S_2$	C	43.08	43.07
	F	48.73	48.71
	S	8.20	8.20
$C_{28}F_{20}S$	C	44.8	44.9
	F	51.1	50.8
	S	4.6	4.3
$Bu^tSCF_3C{=}CHCF_3$	C	38.07	38.09
	H	3.95	3.96
	S	12.70	12.69
	F	45.22	45.23

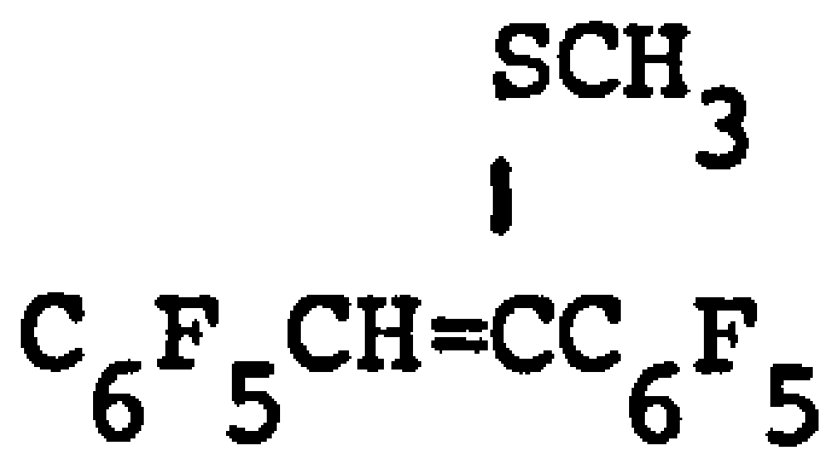
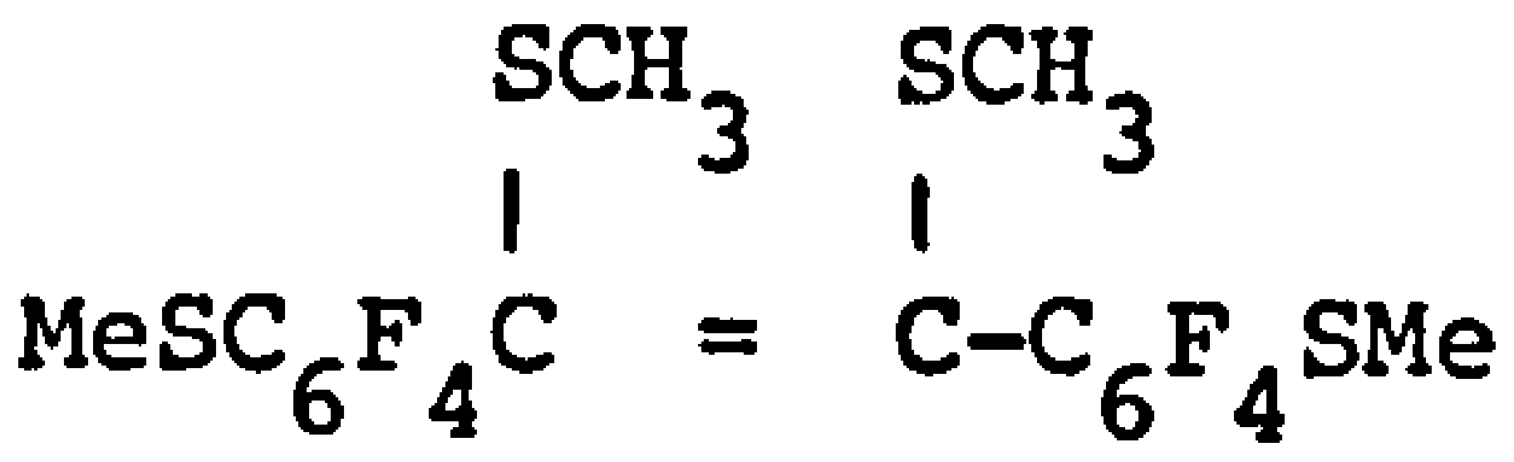
Compound	Element	Found (%)	Calculated (%)
$Bu^tS(CF_3)C=CH_2$	C	45.64	45.65
	H	5.98	5.97
	F	30.95	30.97
$Bu^tS(CF_3)CHCH_2SBu^t$	C	48.18	48.18
	H	7.67	7.66
	S	23.33	23.35
	F	20.79	20.80
$Bu^tS(CF_3)CH-CHCF_3SBu^t$	C	42.11	42.11
	H	5.82	5.84
	F	33.34	33.33
	S	18.70	18.71
 $C_6F_5CH=\overset{SCH_3}{C}C_6F_5$	C	44.30	44.33
	F	46.71	46.79
	H	0.93	0.98
	S	7.90	7.88
 $MeSC_6F_4\overset{SCH_3}{C}=\overset{SCH_3}{C}-C_6F_4SMe$	C	42.39	42.50
	H	2.38	2.40
	F	29.89	29.92
	S	25.21	25.20

TABLE (3)

Infrared data (cm^{-1})

Compound				
$C_6F_5C{\equiv}CC_6F_4NMe_2$	2938,m;	2895,m;	2835,m;	2815,m;
	2230,m;	1685,m;	1660,s;	1650,s;
	1640,s;	1505,vs;	1495,vs;	1485,vs;
	1405,vs;	1430,vs;	1375,m;	1325,m;
	1265,m;	1215,m;	1150,m;	1095,m;
	1060,m;	1035,vs;	1020,vs;	985,vs;
$Me_2NC_6F_4CH{=}CHC_6F_4NMe_2$	2930,s;	2890,s;	2840,s;	2800,s;
	2920,w;	1640,s;	1510,vs;	1495,s;
	1475,s;	1424,m;	1390,w;	1330,m;
	1300,m;	1195,m;	1145,m;	1130,m;
	985,vs;	960,vs;		
$PhSC_6F_4CH{=}CHC_6F_4SPh$	3070,w;	3050,w;	2920,w;	2840,w;
	1575,w;	1475,vs;	1455,s;	1435,m;
	1385,m;	1325,m;	1310,m;	1265,m;
	1145,w;	1065,m;	1020,m;	995,w;
	970,s;	960,vs;	850,s;	740,vs;
	695,m;	685,s;		
$Bu^tS(CF_3)C{=}CHCF_3$	2960,s;	2940,m;	2900,m;	2870,m;
	1455,m;	1430,w;	1380,w;	1365,w;
	1310,m;	1260,s;	1245,s;	1150,vs;
	1110,s;	960,s;	925,m;	845,m;
	715,m;	665,m;		

TABLE (3) contd.

$Bu^tS(CF_3)CH{-}CH(CF_3)SBu^t$	2985,vs;	2940,s;	2900,s;	2860,s;
	1500,s;	1490,s;	1470,s;	1455,s;
	1365,vs;	1200,m;	1175,m;	1160,s;
	1125,s;	1110,s;	990,vs;	
$MeSC_6F_4CH{=}CHC_6F_4SMe$	2932,s;	2897,s;	2845,s;	2805,s;
	2920,w;	1643,s;	1515,vs;	1495,s;
	1480,s;	1424,m;	1395,w;	1335,m;
	1305,m;	1190,m;	1145,m;	1130,m;
	990,vs;	965,vs;		
$C_6F_5CHBr{-}CHBrC_6F_5$	2950,s;	2920,s;	2860,s;	1650,m;
	1510,s;	1500,s;	1435,m;	1328,m;
	1295,m;	1145,m;	1130,s;	995,vs;
	968,s;	670,m;	700,m;	
$PhSC_6F_4CHBr{-}CHBrC_6F_4SPh$	3080,m;	3060,m;	2940,m;	2850,m;
	1725,m;	1690,m;	1650,vs;	1578,s;
	1475,vs;	1440,vs;	1400,m;	1380,vs;
	1325,w;	1295,w	1255,w;	1145,w;
	995,vs;	970,s;	675,m;	705,m;
$MeSC_6F_4C{\equiv}CC_6F_4SMe$	2930,m;	2850,m;	1648,w;	1520,s;
	1505,s;	1480,vs;	1440,m;	1395,m;
	1325,m;	1155,m;	1125,m;	1060,m;
	1060,m;	1035,m;	1010,m;	995,vs;
	915,s;	865,s;		

TABLE (3) contd.

$CH_3SPhC=CHPh$	3060,s;	3020,s;	2950,vs;	2910,vs;
	2850,vs;	1945,w;	1875,w;	1795,w;
	1595,m;	1568,m;	1555,m;	1485,m;
	1460,s;	1450,s;	1440,vs;	1435,vs;
	1420,m;	1370,m;	1355,m;	1305,m;
	1170,m;	1150,m;	1065,m;	1025,m;
	960,vs;	940,vs;	910,m;	685,vs;
	668,vs;			
$CH_3SCHPh-CH_2SCH_3$	3090,m;	3070,m;	3030,s;	2978,s;
	2918,vs;	2855,m;	2830,m;	1940,w;
	1860,w;	1795,w;	1600,m;	1580,w;
	1490,m;	1450,s;	1435,s;	1420,s;
	1315,w;	1250,w;	1195,w;	1175,w;
	1145,w;	1075,m;	1030,m;	955,m;
	925,w;	875,w;	710,m;	690,vs;
	610,w;			
$C_{14}F_6(SPh)_4$	3075,w;	3050,w;	2920,w;	2840,w;
	1575,w;	1475,vs;	1455,s;	1430,m;
	1380,m;	1325,m;	1315,m;	1310,m;
	1065,m;	1020,m;	995,w;	970,s;
	960,vs;	850,s;	745,vs;	695,m;
	685,s;			

TABLE (3) contd.

$CH_3SCHPh-CHPhSCH_3$	3065,s;	3015,s;	2955,vs;	2915,vs;
	2835,vs;	1590,m;	1570,m;	1560,m;
	1490,m;	1465,s;	1455,s;	1435,vs;
	1430,vs;	1420,m;	1375,m;	1360,m;
	1300,m;	1175,m;	1155,m;	1030,m;
	940,m;	910,m;	680,vs;	670,vs;
$Bu^tSCH(CF_3)-CH_2SBu^t$	2981,m;	2920,s;	2837,w;	1620,w;
	1567,w;	1424,s;	1330,vs;	1320,vs;
	1276,vs;	1242,vs;	1205,s;	1170,vs;
	1138,vs;	1101,vs;	1045,m;	978,s;
	960,s;	890,m;	851,w;	838,m;
	769,w;	742,w;	705,w;	695,w;
	660,s;			
$Bu^tSCCF_3=CH_2$	2985,m;	2925,s;	2840,w;	1630,w;
	1570,w;	1430,s;	1335,vs;	1325,vs;
	1270,vs;	1240,vs;	1210,s;	1175,vs;
	1140,vs;	1105,vs;	1045,m;	980,s;
	965,s;	895,m;		
$C_{28}F_{20}S_2$	1655,w;	1645,w;	1635,m;	1505,s;
	1500,vs;	1430,w;	1320,m;	1310,w;
	1150,m;	1120,w;	1035,w;	1020,w;
	993,vs;	700,w;		

TABLE (3) contd.

$C_{42}F_{30}S_3$	1655,w;	1645,w;	1630,w;	1515,s;
	1495,vs;	1430,m;	1375,w;	1320,m;
	1308,w;	1255,m;	1150,m;	1120,w;
	1080,s;	1035,w;	1020,w;	993,vs;
	715,s;			
$C_{28}F_{20}S$	1657,m;	1640,w;	1637,m;	1507,s;
	1505,vs;	1430,w;	1325,m;	1310,w;
	1150,m;	1121,m;	1038,w;	1022,w;
	995,vs;	705,s.		

TABLE (4)

Mass spectral data (m/e in a.m.u.)

Compound	m/e	Relative intensity	Assignment
$MeSC_6F_4C{\equiv}CC_6F_4SMe$	$C_{16}F_8H_6S_2 = 414$		P^+
	$C_{15}F_8H_3S_2 = 399$		P^+-CH_3
	$C_{14}F_8S_2 = 384$		$P^+-C_2H_6$
	$C_{15}F_8H_3S = 367$		P^+-SCH_3
	$C_{14}F_8 = 320$		$P^+-S_2C_2H_6$
$C_{15}H_{14}S$	$C_{15}H_{14}S = 226$	63%	P^+
$CH_3SCPh{=}CHPh$	$C_{14}H_{11}S = 211$	39%	P^+-CH_3
	$C_{14}H_{10} = 178$	100%	P^+-SCH_4
	$C_{12}H_8 = 152$	14%	$P^+-SC_3H_6$
	$C_8H_7S = 135$	6%	$P^+-C_7H_7$
	$C_7H_5 = 89$	8%	$P^+-SC_8H_9$
$C_{10}H_{14}S_2$	$C_{10}H_{14}S_2 = 198$	10%	P^+
$CH_3SCHPh-CH_2SCH_3$	$C_9H_{10}S = 150$	33%	P^+-SCH_4
	$C_8H_7S = 135$	33%	$P^+-SC_2H_7$
	$C_8H_7 = 103$	41%	$P^+-S_2C_2H_7$
	$C_7H_7 = 91$	41%	$P^+-S_2C_3H_7$
	$C_6H_6 = 78$	28%	$P^+-S_2C_4H_8$
	$C_5H_4 = 64$	17%	$P^+-S_2C_5H_{10}$
	$C_4H_2 = 50$	100%	$P^+-S_2C_6H_{12}$

TABLE (4) contd.

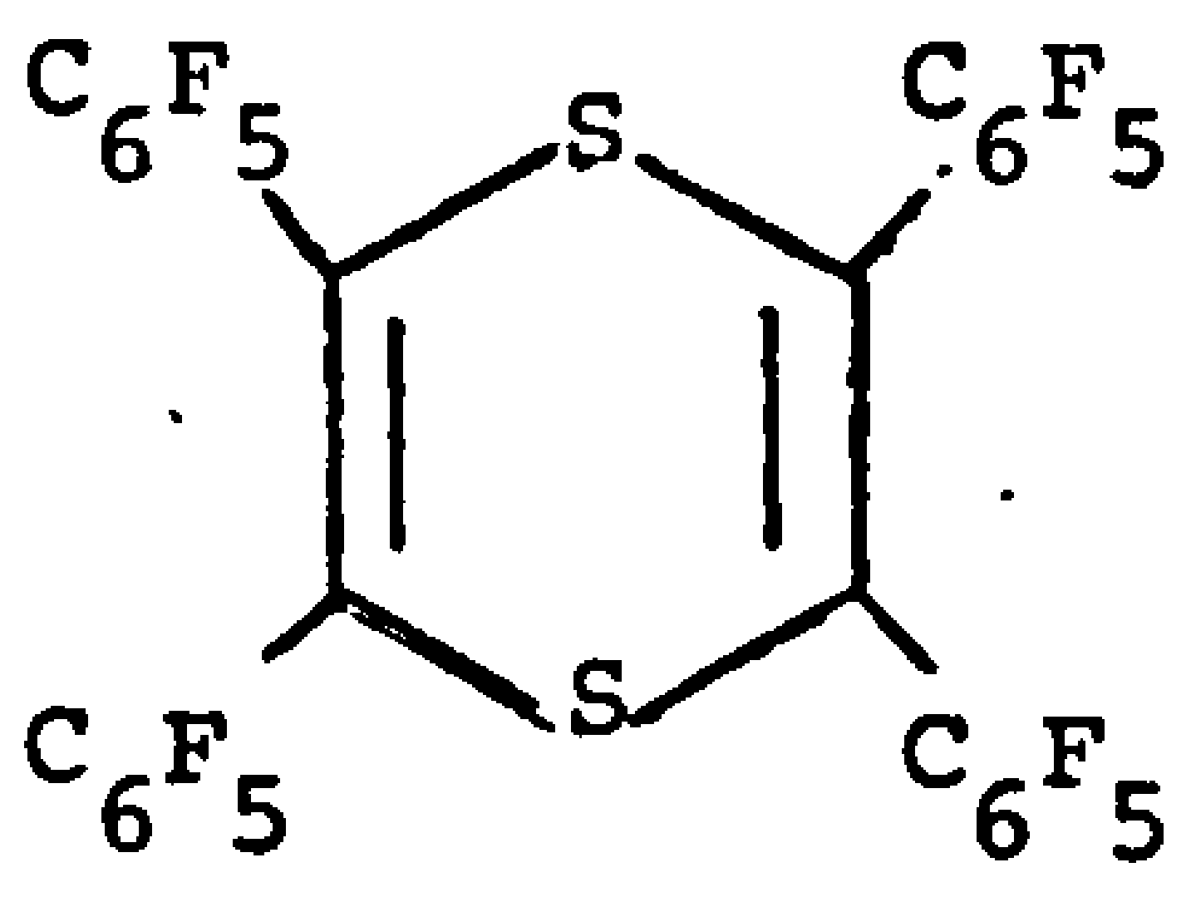
Compound	m/e	Relative intensity	Assignment
$C_{16}H_{18}S_2$	$C_{16}H_{18}S_2$ = 274	33%	P^+
$CH_3SCHPhCHPhSCH_3$	$C_{16}H_{14}S$ = 238	10%	P^+-SH_4
	$C_{15}H_{14}S$ = 226	63%	P^+-SCH_4
	$C_{14}H_{11}S$ = 211	13%	$P^+SC_2H_7$
	$C_{14}H_{10}$ = 178	100%	$P^+-S_2C_2H_6$
$MeSC_6F_4CH{=}CHC_6F_4SMe$	$C_{16}F_8H_8S_2$ = 416		P^+
	$C_{15}F_8H_5S_2$ = 401		P^+-CH_3
	$C_{14}F_8H_2S_2$ = 386		$P^+-C_2H_6$
	$C_{15}F_8H_5S$ = 369		P^+-SCH_3
	$C_{14}F_8$ = 320		$P^+-S_2C_2H_8$
$(CH_3S)_2CPh-CHPhSCH_3$	$C_{17}H_{20}S_3$ = 320	5%	P^+
	$C_{16}H_{17}S_2$ = 273	30%	P^+-SCH_3
	$C_{15}H_{14}S$ = 226	100%	$P^+-S_2C_2H_6$
	$C_{14}H_{11}S$ = 211	13%	$P^+-S_2C_3H_{10}$
	$C_{14}H_{10}$ = 178	50%	$P^+-S_3C_3H_{10}$
$C_{28}F_{20}S_2$	$C_{28}F_{20}S_2$ = 780	40%	P^+
	$C_{28}F_{20}S$ = 748	16%	P^+-S
	$C_{28}F_{20}$ = 716	16%	P^+-S_2
	$C_{24}F_{11}$ = 497	14%	$P^+-C_4F_9S_2$
	$C_{23}F_{11}$ = 485	5%	$P^+-C_5F_9S_2$
	$C_{14}F_{10}S_2$ = 422	8%	$P^+-C_{14}S_{10}$
	$C_{14}F_{10}S$ = 390		$P^+-C_{14}F_{10}S$
	$C_{14}F_{10}$ = 338	100%	$P^+C_{14}F_{10}S_2$

TABLE (4) contd.

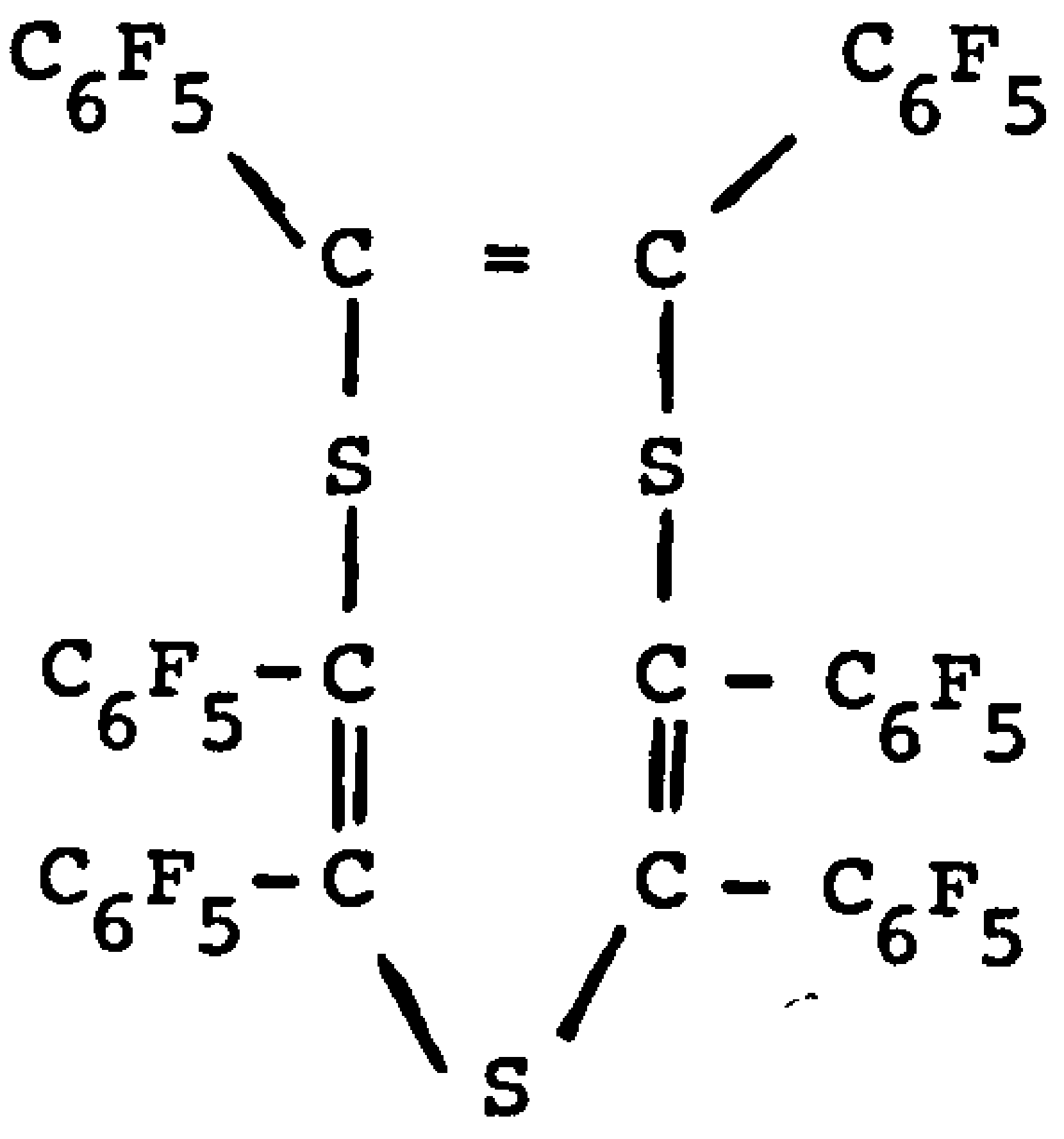
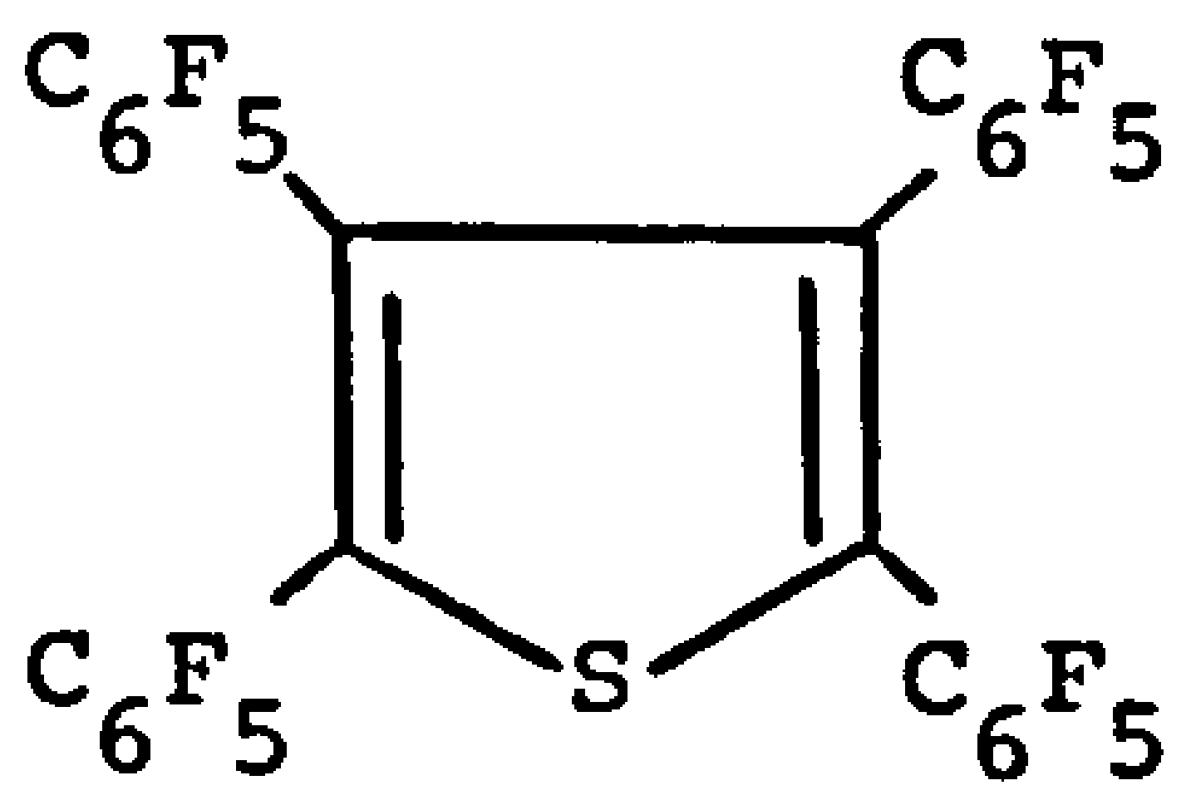
Compound	m/e Relative intensity	Assignment
$C_{42}F_{30}S_3$	$C_{42}F_{30}S_3$ = 1170	P^+
	$C_{42}F_{30}S_2$ = 1130	P^+-S
	$C_{42}F_{28}S_2$ = 1110	$P^+-C_2F_2S$
	$C_{28}F_{27}S_3$ = 1065	$P^+-C_4F_3$
	$C_{38}F_{27}S_2$ = 1033	$P^+-C_4F_3S$
	$C_{38}F_{27}S$ = 1001	$P^+-C_4F_3S_2$
	$C_{28}F_{20}S_2$ = 780	$P^+-C_{14}F_{10}S$
	$C_{28}F_{20}S$ = 748	$P^+-C_{14}F_{10}S_2$
	$C_{28}F_{20}$ = 716	$P^+-C_{14}F_{10}S_3$
	$C_{24}F_{17}$ = 611	$P^+-C_{18}F_{13}S_3$
	$C_{24}F_{11}$ = 497	$P^+-C_{18}F_{19}S_3$
	$C_{23}F_{11}$ = 485	$P^+-C_{18}F_{17}S_3$
	$C_{14}F_{19}S_2$ = 422	$P^+-F_{28}F_{20}S$
	$C_{14}F_{10}S$ = 390	$P^+-F_{28}F_{20}S_2$
	$C_{14}F_{10}$ = 358	$P^+-F_{28}F_{20}S_3$
$C_{28}F_{20}S$	$C_{28}F_{20}S$ = 748	P^+
	$C_{28}F_{20}$ = 716	P^+-S
	$C_{24}F_{17}$ = 611	$P^+-C_4F_3S$
	$C_{24}F_{11}$ = 497	$P^+-C_4F_9S$
	$C_{23}F_{11}$ = 485	$P^+-C_5F_9S$
	$C_{14}F_{10}S$ = 390	$P^+-C_{14}F_{10}$
	$C_{14}F_{10}$ = 358	$P^+-C_{14}F_{10}S$

TABLE (4) contd.

Compound	m/e	Relative intensity	Assignment
$C_{15}H_4F_{10}$	$C_{15}H_4F_{10}S$ = 406		P^+
$C_6F_5CH{=}C(SCH_3)C_6F_5$	$C_{14}H\ F_{10}S$ = 391		P^+-CH_3
	$C_{15}H_3F_{10}$ = 373		P^+-SH
	$C_{14}F_{10}H_4$ = 362		P^+-CS
	$C_{14}F_{10}$ = 358		P^+-CH_4S
$C_{14}F_6H_2(SPh)_4$	$C_{14}F_6H_2(SPh)_4$=720		P^+
	$C_{14}F_6H_2(SPh)_3$=611		P^+-C_6H_5S
	$C_{14}F_6H_2(SPh)_2$=502		P^+-$C_{12}H_{10}S_2$
	$C_{14}F_6H_2(SPh)$ =393		P^+-$C_{19}H_{15}S_3$
	$C_7F_3H(SPH)_2$ =360		P^+-$C_{19}F_3H_{11}S_2$
	$C_7F_3H(SPh)$ =251		P^+-$C_{25}H_{16}F_3S_3$
$PhSC_6F_4CH{=}CHC_6F_4SPh$	$C_{26}F_8H_{12}S_2$ = 252		P^+
	$C_{20}F_8H_7S$ = 431		P^+-$C_{16}H_5S$
	$C_{13}F_4H_6S$ = 270		
$Bu^tS(CF_3)C{=}CH(CF_3)$	$C_8H_{10}F_6S$ = 252	100%	P^+
	$C_8H_{10}F_6$ = 220	5%	P^+-S
	$C_7H_{10}F_6S$ = 183	5%	P^+-CF_3
	C_6H_9S = 113	33%	P^+-C_2F_6H
$MeNC_6F_4C{\equiv}CC_6F_5$	$C_{16}F_9NH_6$ = 383	100%	P^+
	$C_{16}F_9$ = 339	10%	P^+-NMe_2
	C_8F_5 = 191		P^+-C_8F_4
	C_6F_4 = 148		P^+-$C_{10}F_5NH_6$

TABLE (4) contd.

Compound	m/e	Relative intensity	Assignment
$C_{16}F_{10}H_2Br_2$	$C_{16}F_{10}H_2Br_2$ = 518	100%	P^+
$C_6F_5CHBrCHBrC_6F_5$	$C_{16}F_{10}H_2Br$ = 439	39%	P^+-Br
	$C_{14}F_{10}H_2$ = 360	100%	P^+-Br_2
	$C_{13}F_7H$ = 290	50%	$P^+-C_3F_3HBr_2$
	C_7F_5 = 179	3%	$P^+-C_9H_2F_5Br_2$
$Me_2NC_6F_4CH=CHC_6F_4NMe_2$	$C_{18}F_8N_2H_{14}$ = 410	100%	P^+
	$C_{17}F_8N_2H_{11}$ = 395	2%	P^+-CH_3
	$C_{16}F_8N_2H_8$ = 380	7%	$P^+-C_2H_6$
	$C_{16}F_8N\ H_8$ = 366	10%	$P^+-NC_2H_6$
	$C_9F_4N\ H_7$ = 205	50%	$P^+-C_9F_4NH_7$
$Me_2NC_6F_4C\equiv CC_6F_4NMe_2$	$C_{18}F_8N_2H_{12}$ = 408	100%	P^+
	$C_{17}F_8N_2H_9$ = 493	5%	P^+-CH_3
	$C_{16}F_8N_2H_6$ = 378	10%	$P^+-C_2H_6$
	$C_{16}F_8N\ H_6$ = 364	18%	$P^+-NC_2H_6$
	$C_9F_4N\ H_6$ = 203	50%	$P^+-C_9F_4NH_6$

TABLE (5)

Nuclear Magnetic Resonance Parameters

^{1}H Chemical Shifts, Multiplicity:- (a)

s - singlet

d - doublet

t - triplet

m - multiplet

br- broad

$\underline{CH}_3S$ ——	$C\underline{H}Ph$ ——	$CH\underline{Ph}\text{-}SCH_3$
2.07	3.37	7.25
br	s	br

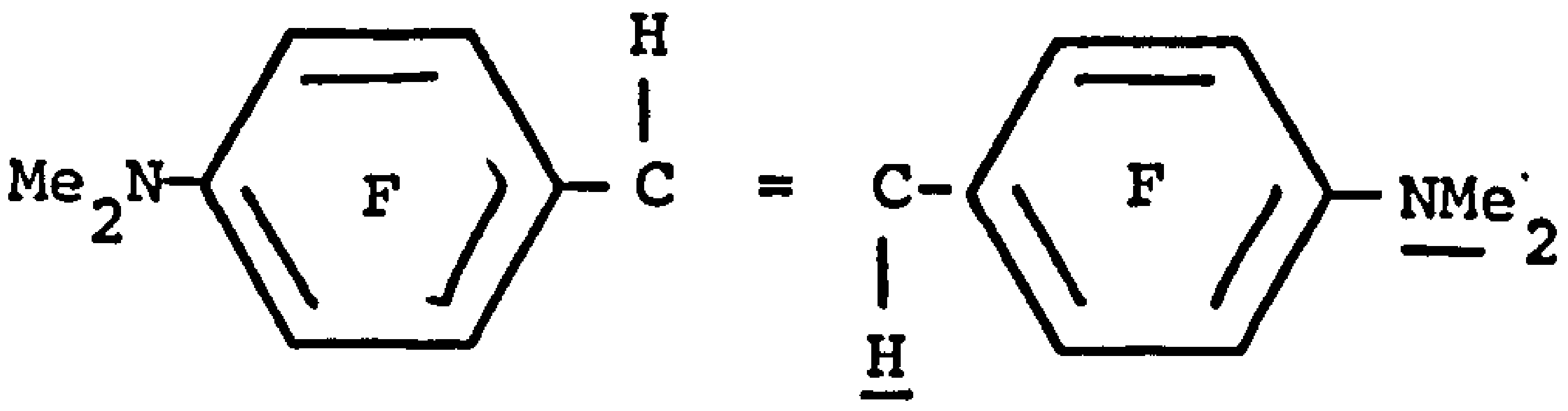
$\underline{CH}_3S$ —	$\underline{CH}_2$ —	$\underline{CH}$ —	$\underline{Ph}$ —	$S\underline{CH}_3$
1.95	2.95	3.74	7.3	1.81
s	m	m		d

	$\underline{CH}_3SCPh$ =	$C\underline{H}Ph$
trans	1.78	6.7
cis	1.92	6.4

$(\underline{CH}_3S)_2$	$C\underline{Ph}$ —	$\underline{CH}$	$\underline{Ph}$	$S\underline{CH}_3$
1.6	7.2	3.95	7.25	1.23
s	m	s	m	br

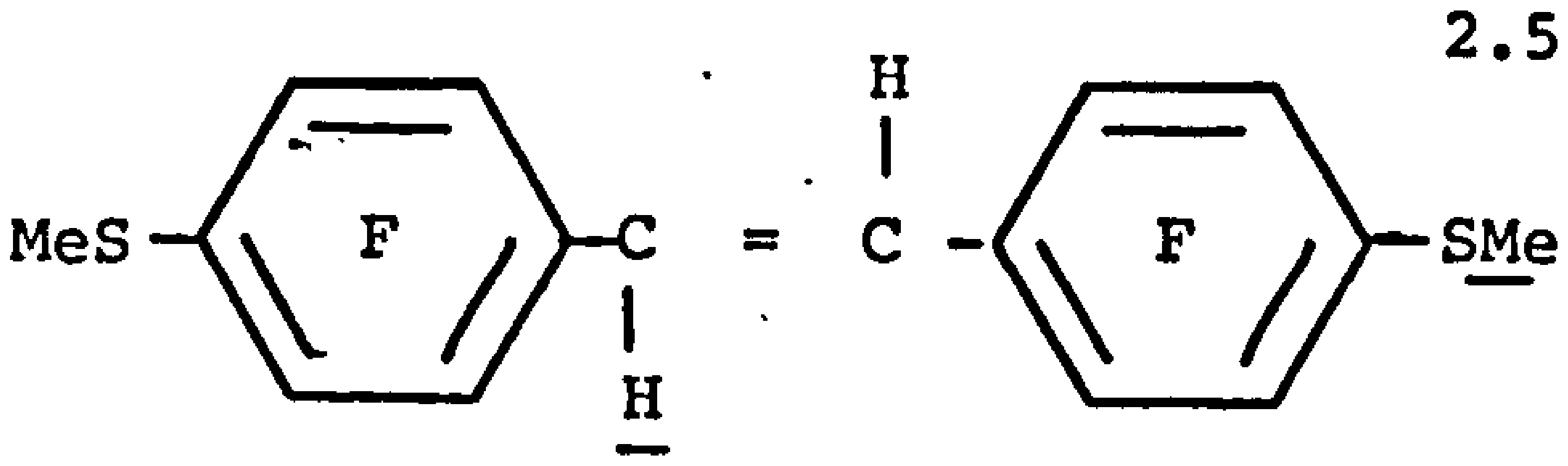
TABLE (5) contd.

3.01

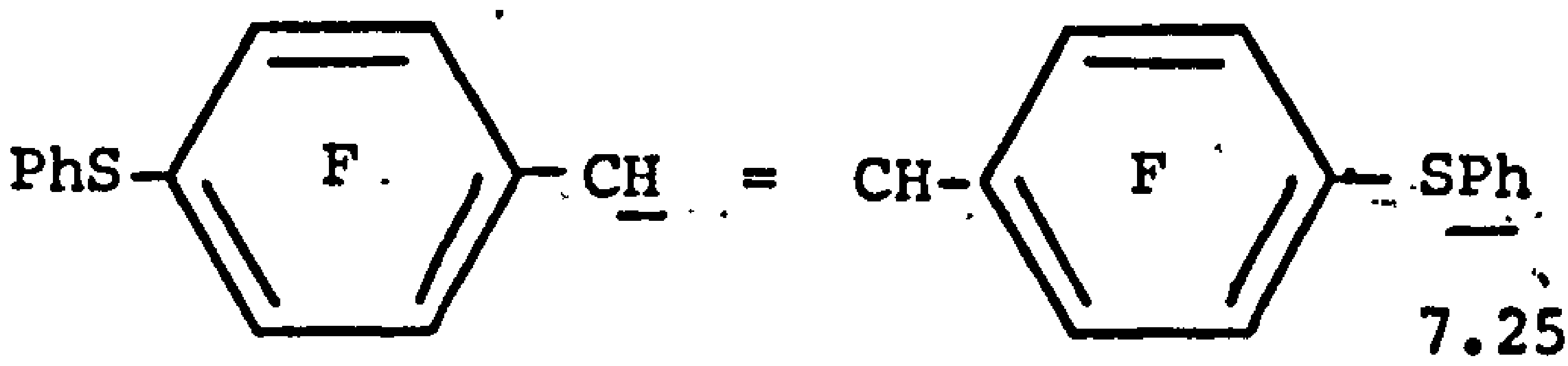


7.2

2.5



7.4

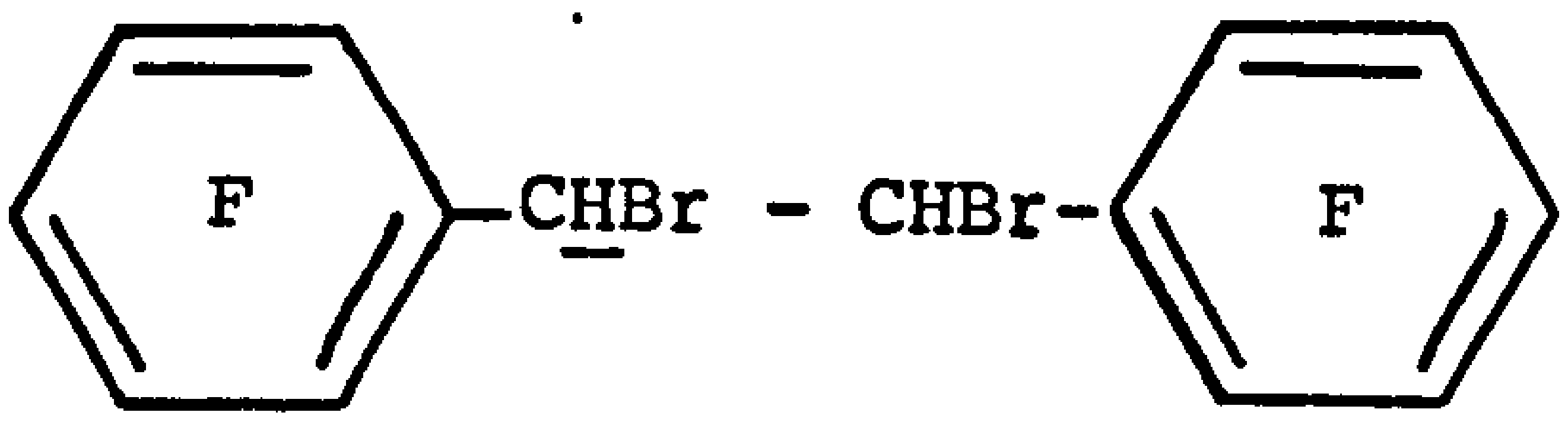


7.25

trans 6.2 s

7.30

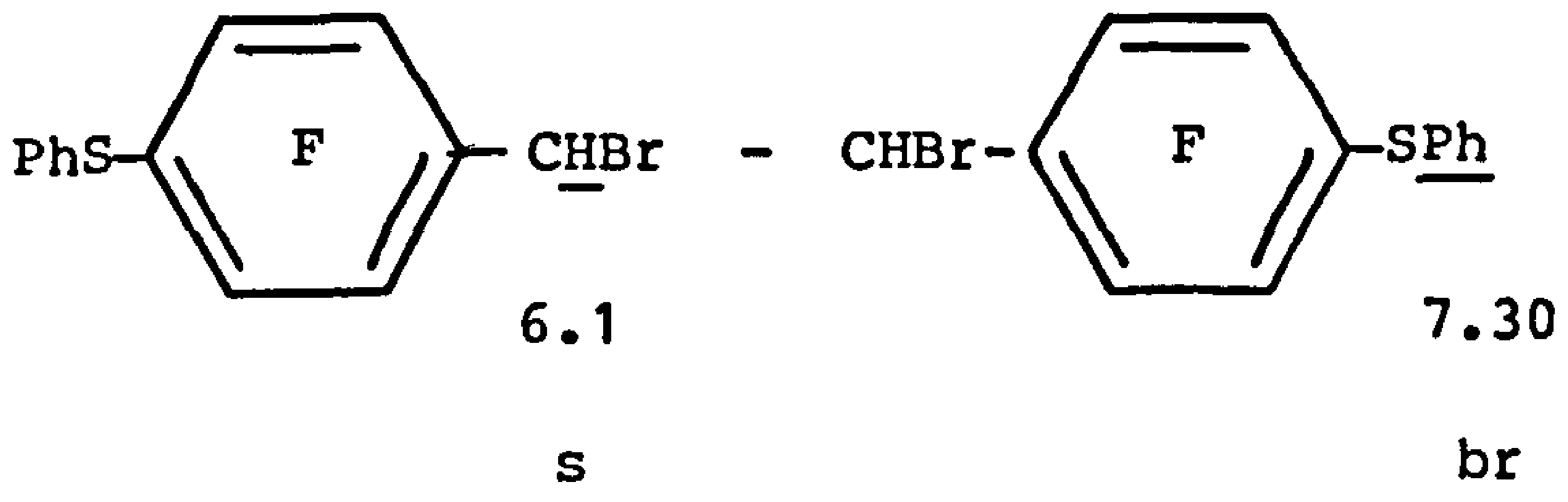
cis 6.25s

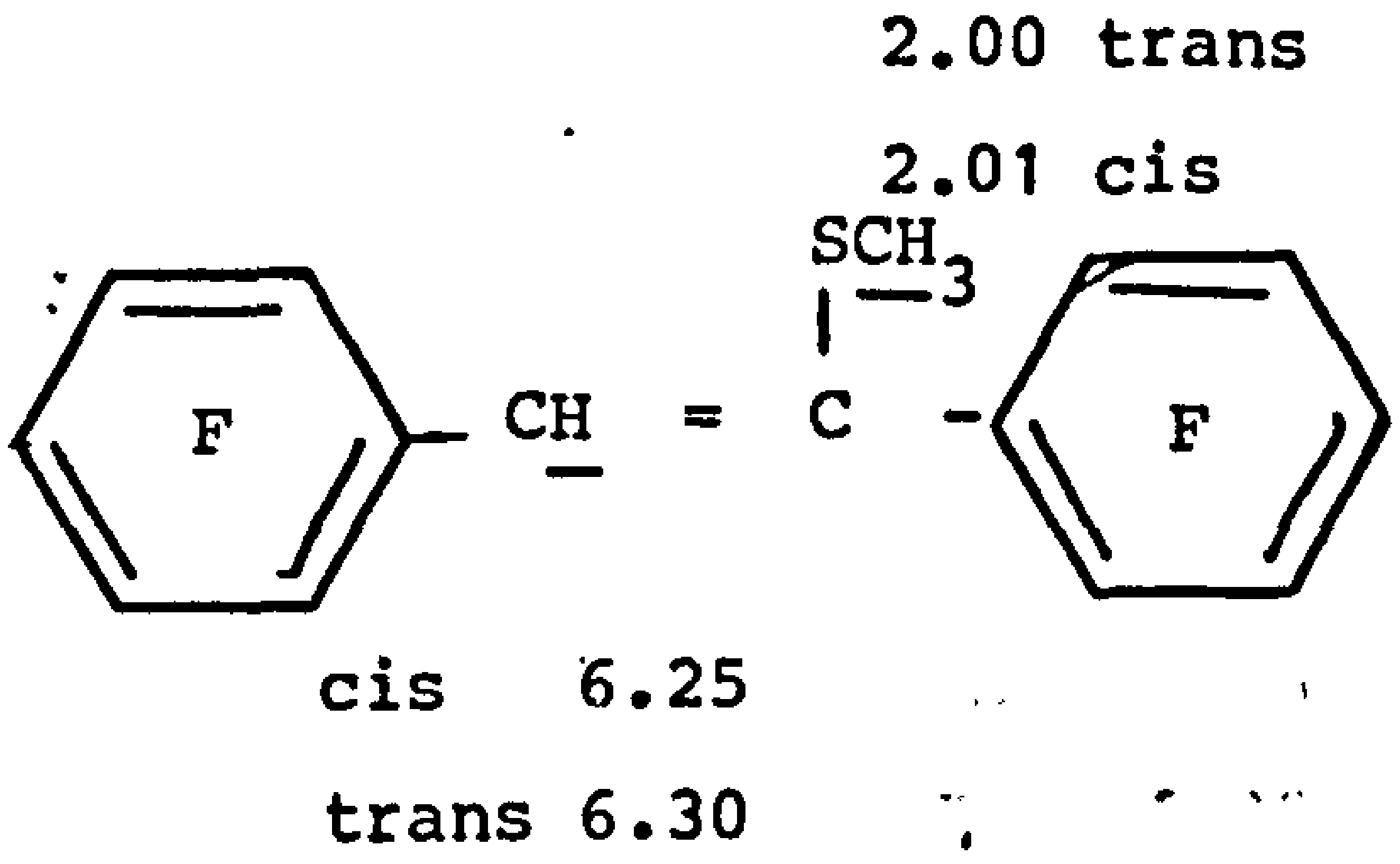


6.02

br

TABLE (5) contd.





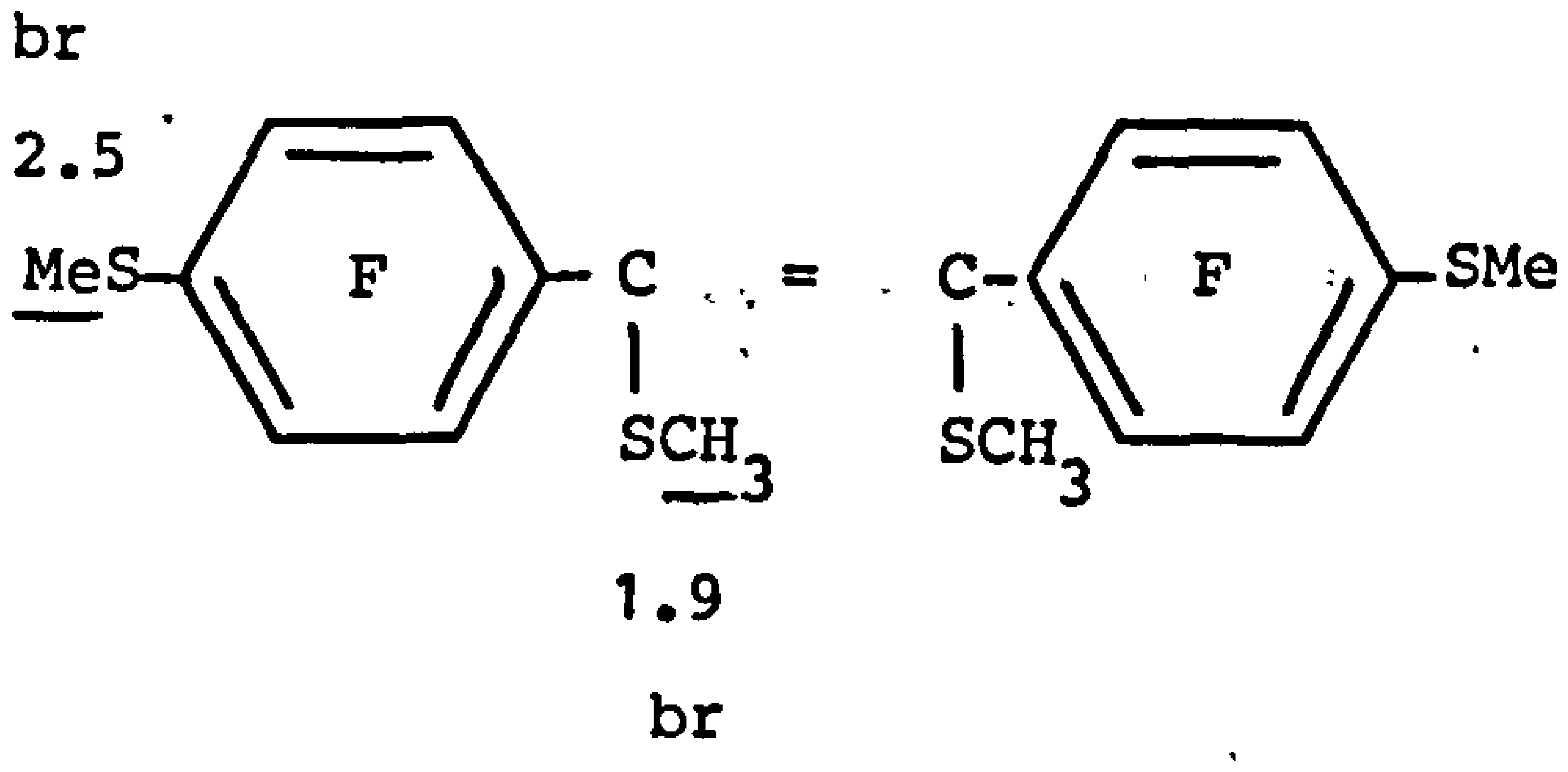


TABLE (5) contd.

$\underline{\mathrm{Bu}}^{t}\mathrm{SC(CF_3)} = \underline{\mathrm{CH}}\mathrm{(CF_3)}$

1.2 6.4

$\underline{\mathrm{Bu}}^{t}\mathrm{CH(CF_3)} - \underline{\mathrm{CH}}\mathrm{(CF_3)SBu}^{t}$

0.99 4.25

$\underline{\mathrm{Bu}}^{t}\ \underline{\mathrm{CH_2}} - \underline{\mathrm{CH}}\mathrm{(CF_3)SBu}^{t}$

1.08 2.96 3.35 [illegible] 1.4 s

t (q) (q)

$\underline{\mathrm{Bu}}^{t}\mathrm{SCH} = \underline{\mathrm{CH}}\mathrm{(CF_3)}$

1.5 6.1

$\underline{\mathrm{Bu}^{t}\mathrm{S}}\mathrm{C(CF_3)} = \underline{\mathrm{CH_2}}$

1.42 4.5

(a) ppm from external TMS.

TABLE (6)

Nuclear Magnetic Resonance Parameters

^{19}F Chemical Shift$^{(a)}$/Multiplicity

s - singlet

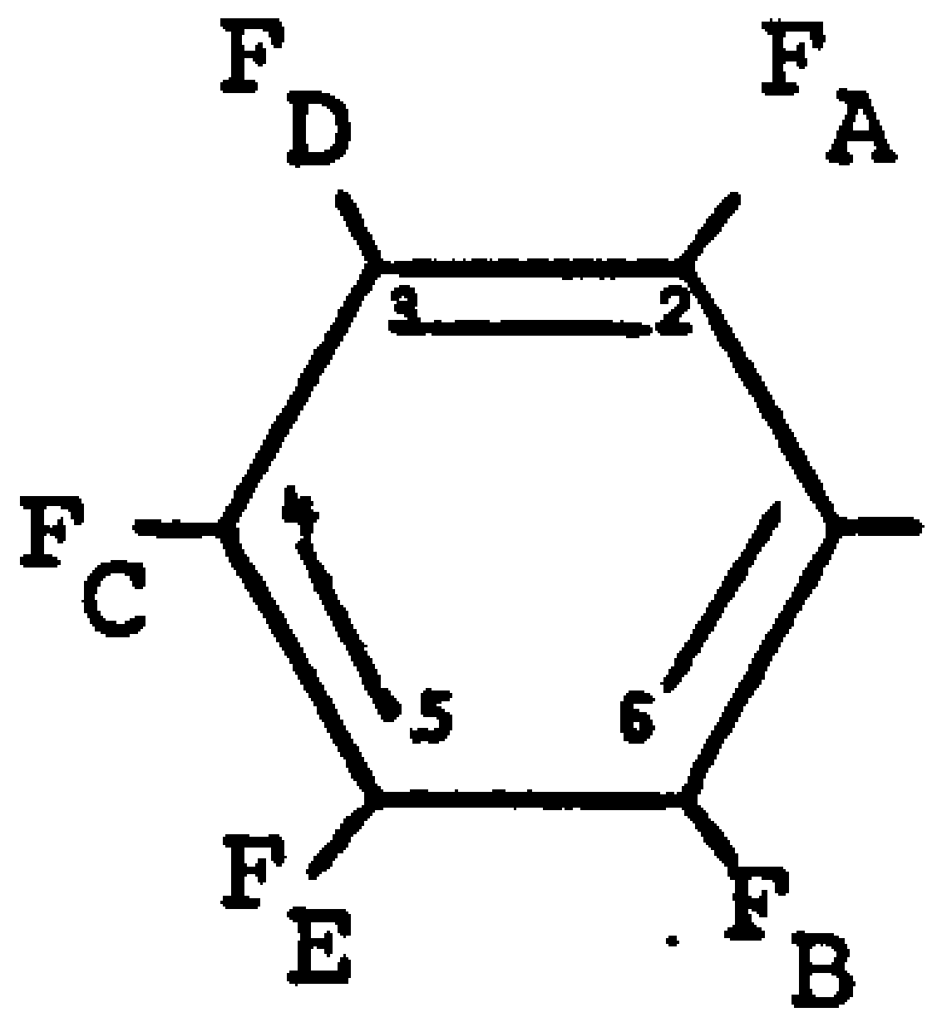
d - doublet

t - triplet

m - multiplet

b - broad

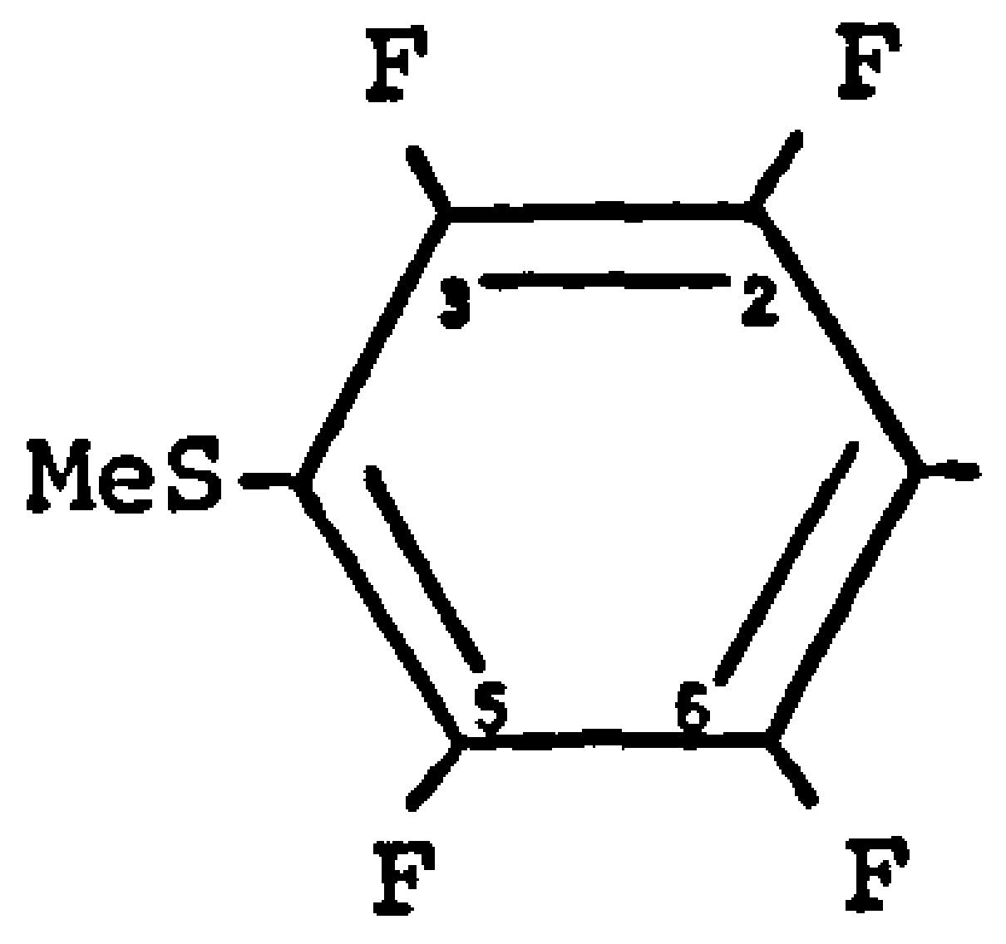
C_6F_5 ——————— $CHBrCHBrC_6F_5$



F(2)	-139.4	m
F(6)	-141.7	m
F(4)	-151.3	m
F(3)	-160.6	m
F(5)	-160.8	m

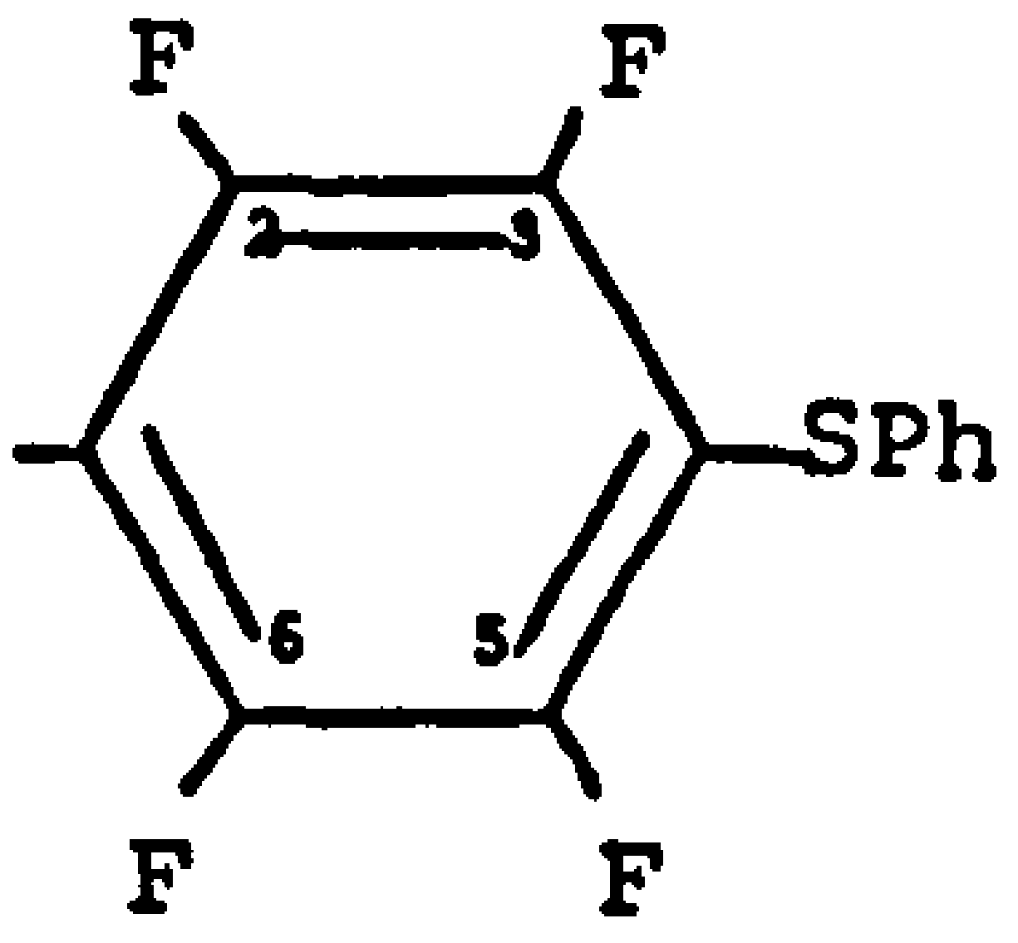
TABLE (6) contd.

$MeSC_6F_4$ ———————— $CH{=}CHC_6F_4SMe$



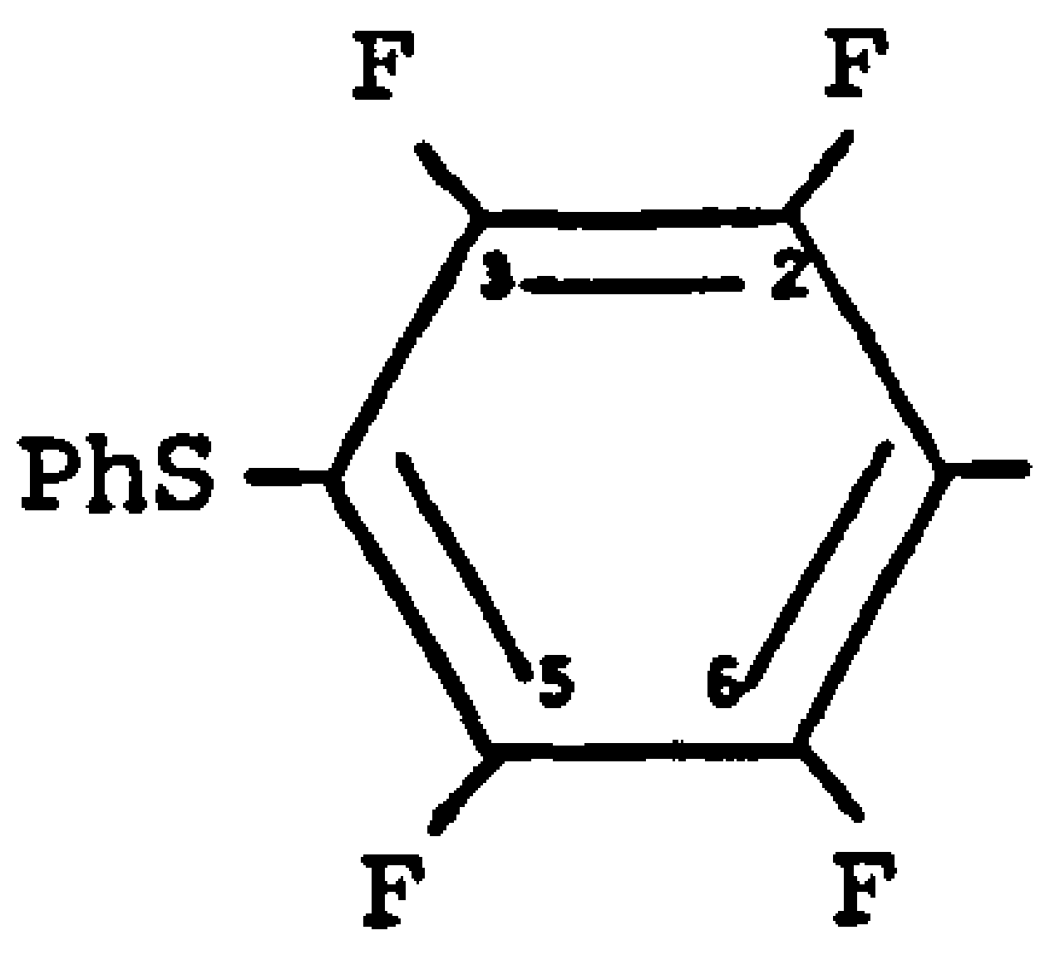
F(2-6)	-136.50	m
F(3-5)	-142.9	

$PhSC_6F_4CH{=}CH$ ———————— C_6F_4SPh



1st Isomer	F(2-6)	-134.12
	F(3-5)	-141.78
2nd Isomer	F(2-6)	-134.13
	F(3-5)	-141.86

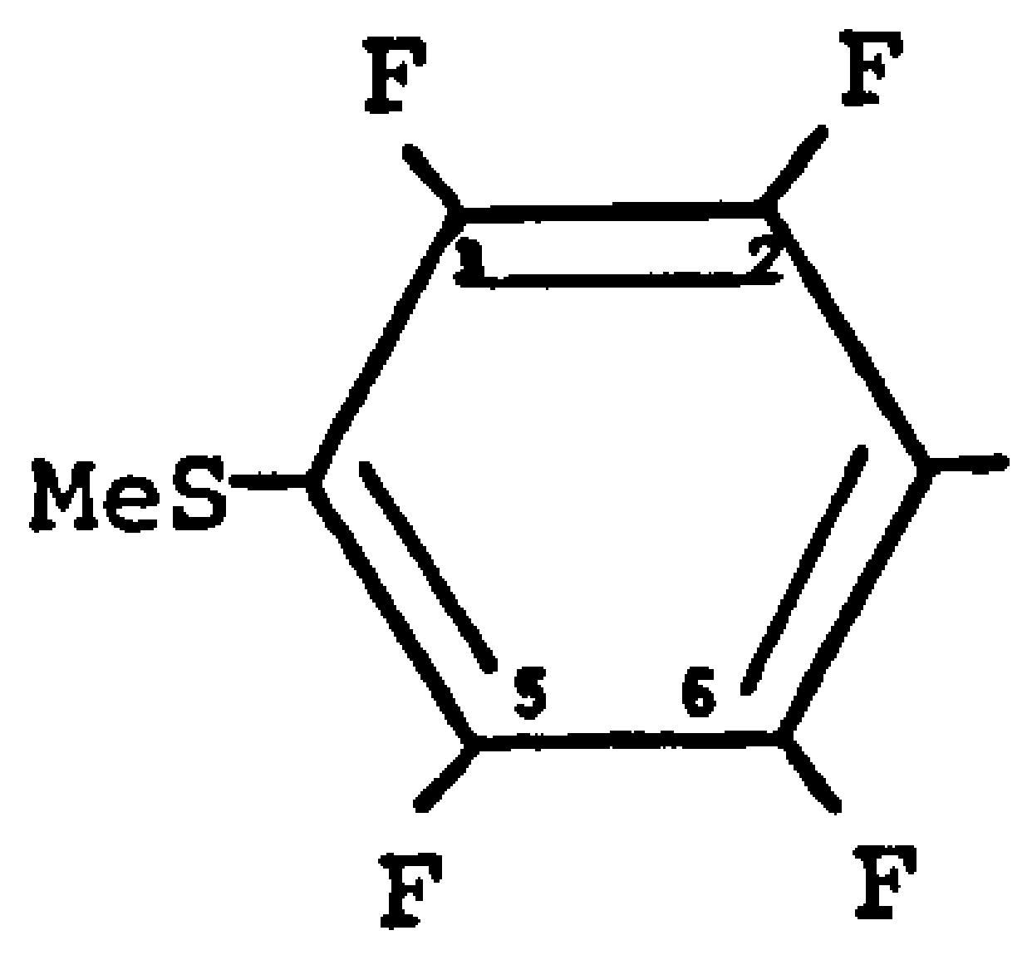
$PhSC_6F_4$ ———————— $CHBrCHBr{-}C_6F_4SPh$



F(2)	-132.1	m
F(6)	-132.4	m
F(3)	-139.1	m
F(5)	-141.5	m

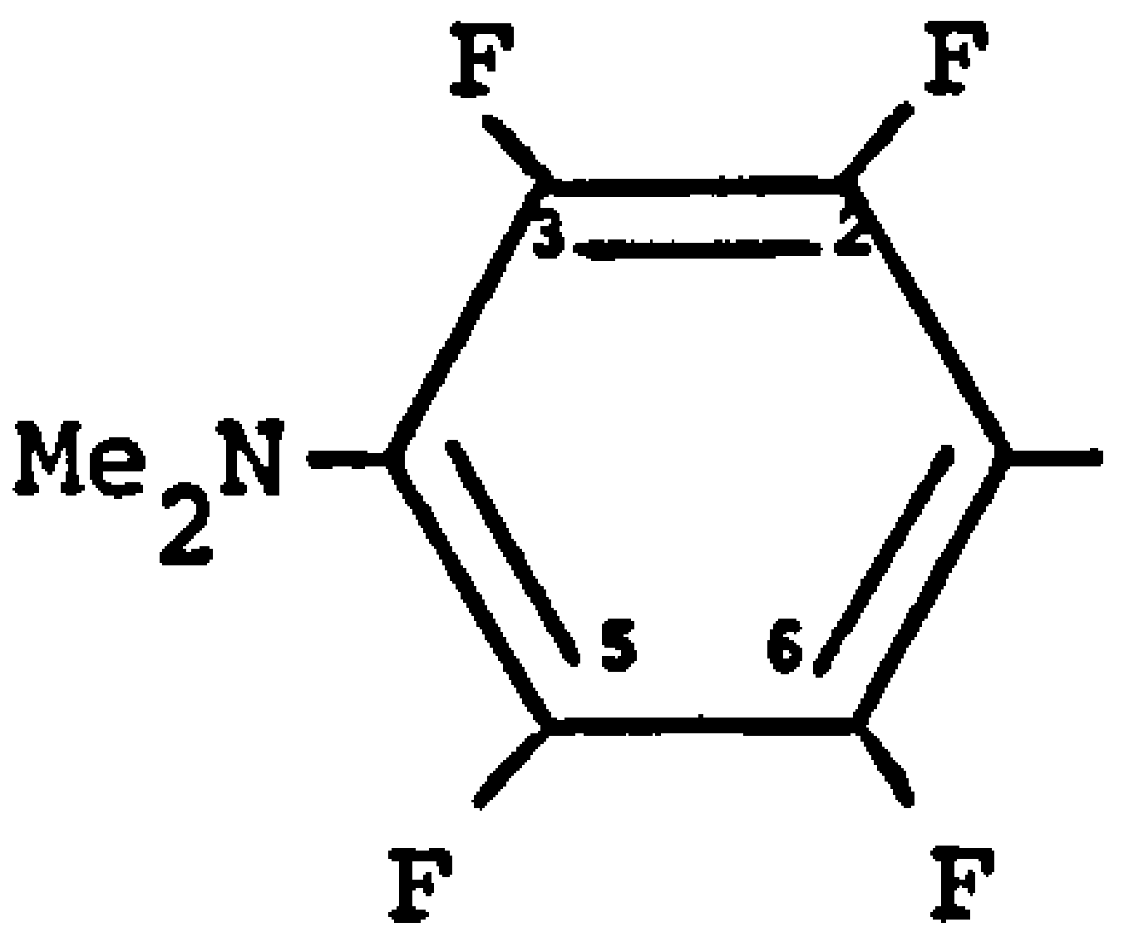
TABLE (6) contd.

$MeSC_6F_4$ ——— $C{\equiv}CC_6F_4SMe$



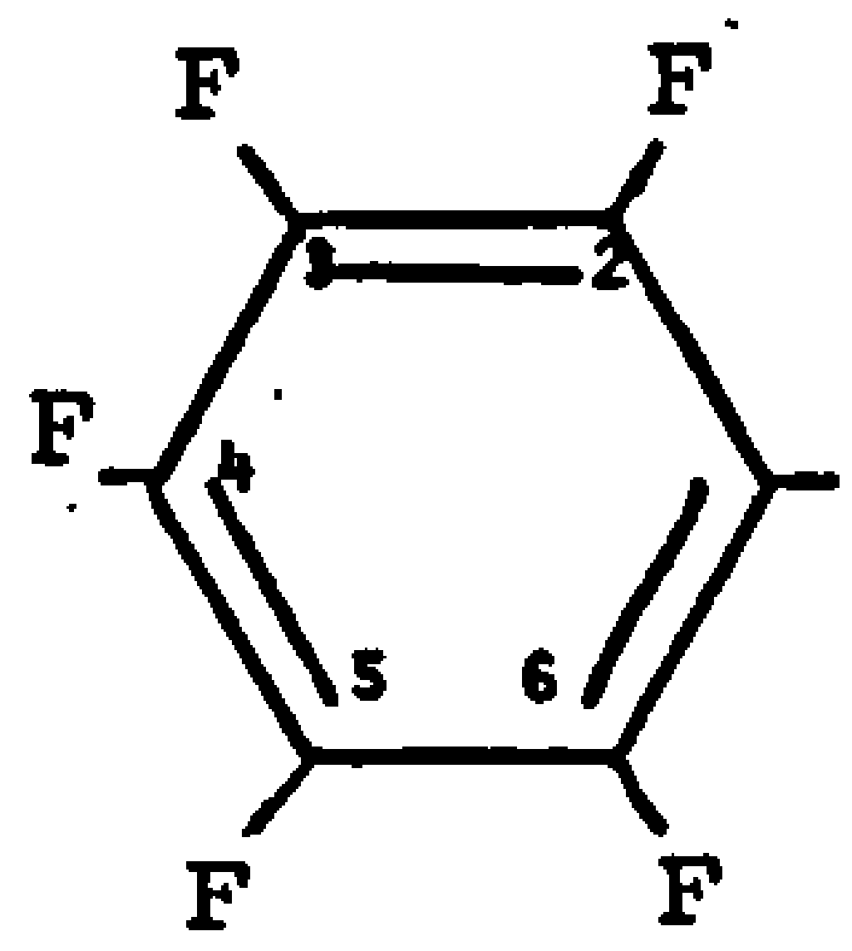
F(2-6)	-135.597 m
F(3-5)	-137.178 m

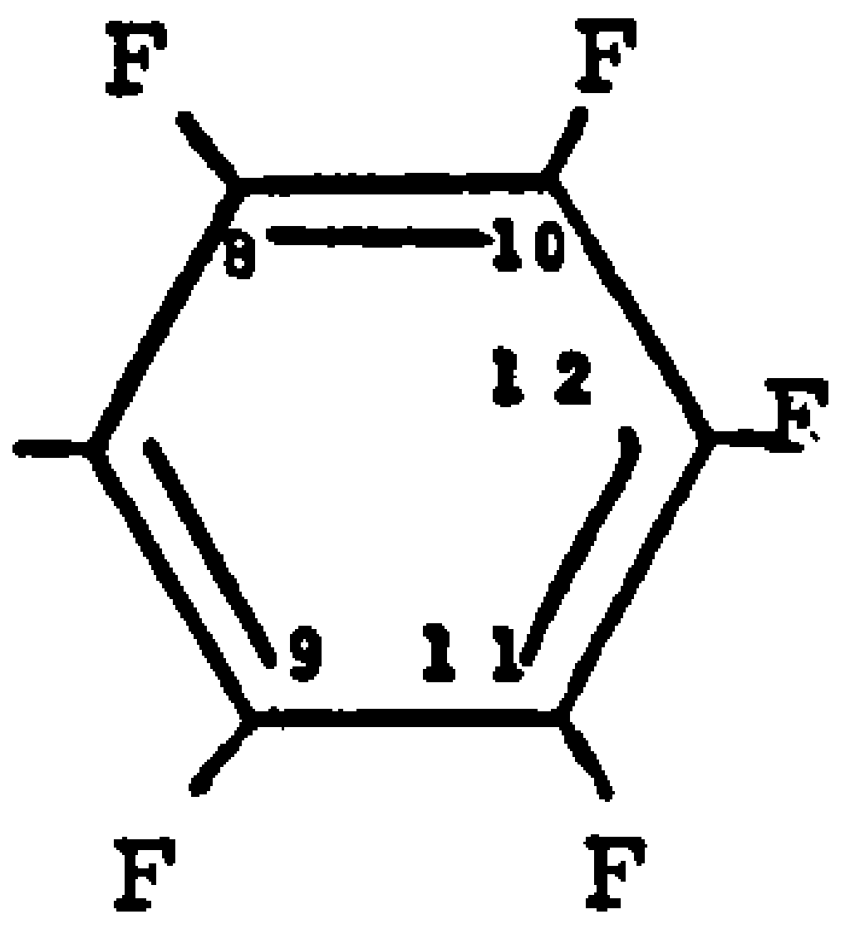
$Me_2NC_6F_4$ ——— $CH{=}CHC_6F_4NMe_2$



F(2-6)	-145.5
F(3-5)	-153.5

C_6F_5 ——— $CH{=}CSCH_3$ ——— C_6F_5

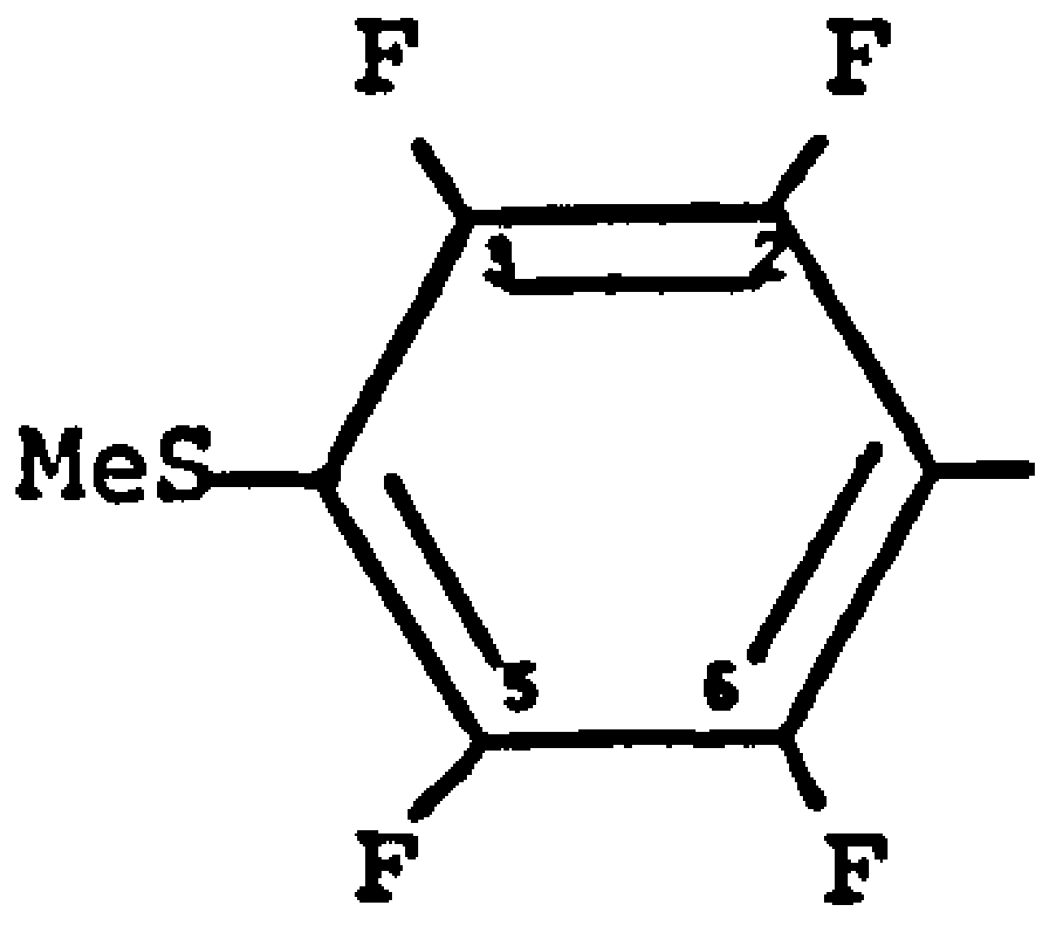




1st isomer	F_2	-138.10	F_8	-139.7
	F_3	-161.20	F_{10}	-162.9
	F_4	-152.5	F_{12}	-154.8
2nd isomer	F_2	-140.59	F_8	-141.01
	F_3	-162.4	F_{10}	-163.1
	F_4	-153.4	F_{12}	-154.9

TABLE (6) contd.

$MeSC_6F_4$ ———— $CSCH_3{=}CSCH_3$ ———— C_6F_4SMe



1st isomer		2nd isomer	
F(2)	-135.1	F(2)	-136.1
F(6)	-135.2	F(6)	-136.2
F(3)	-138.4	F(3)	-137.5
F(5)	-140.8	F(5)	-141.6

Bu^tSC - $(\underline{CF_3})$ = $CH(\underline{CF_3})$

	$(\underline{CF_3})$	$CH(\underline{CF_3})$
	64.64	71.4
	s	s
	64.85	71.79
	q	q

Bu^tS $CH-(\underline{CF_3})-$ CH - $(CF_3)SBu^t$

meso 60.33

+ dl 63.04

Bu^tS CH_2 - $CH(\underline{CF_3})$ SBu^t

52.26

a) ppm positive to low field of external CCl_3F.

TABLE (7)

Nuclear Magnetic Resonance Spectra

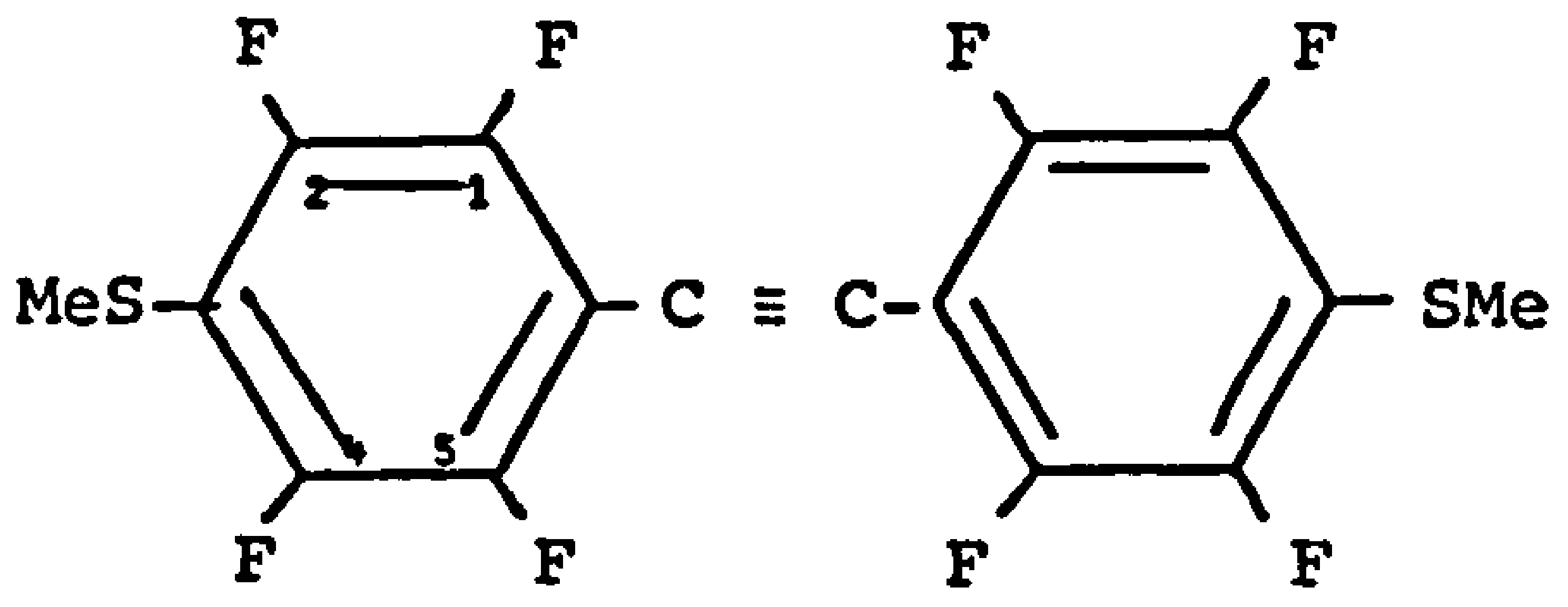
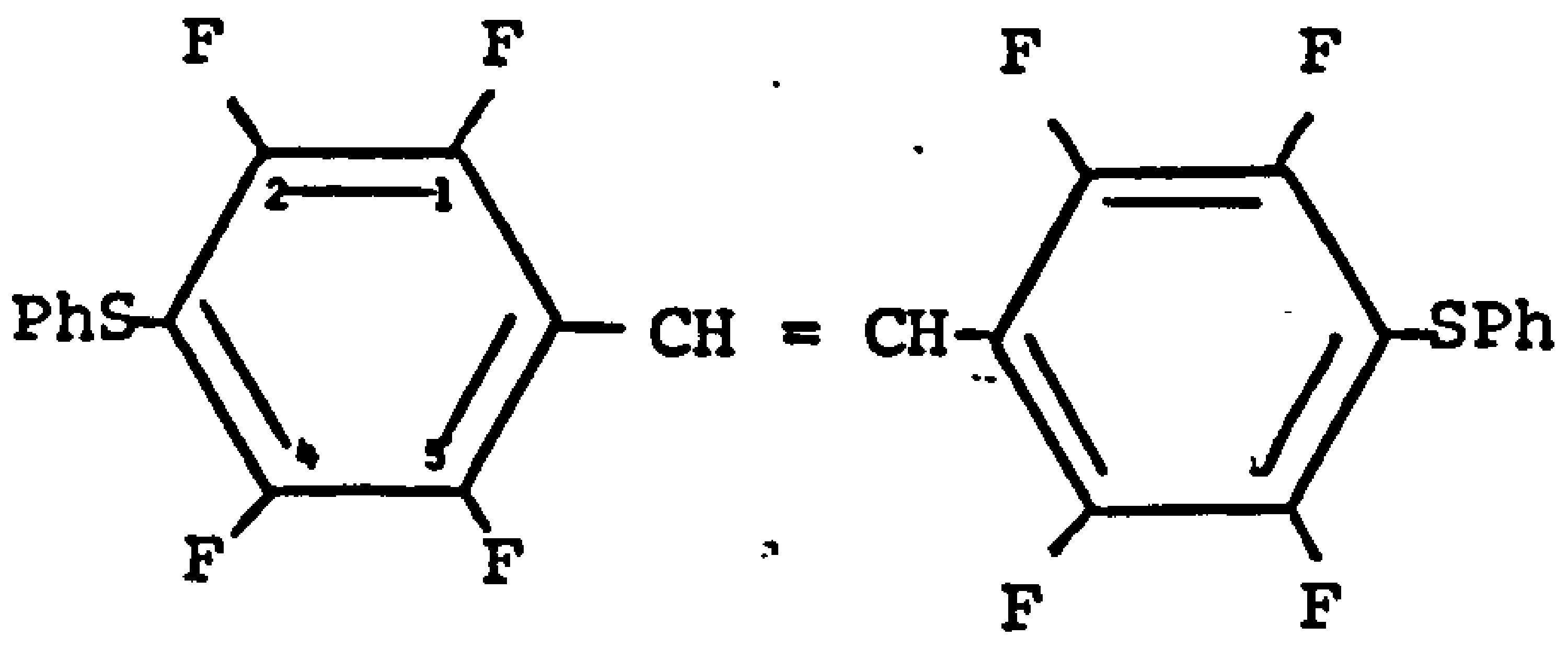
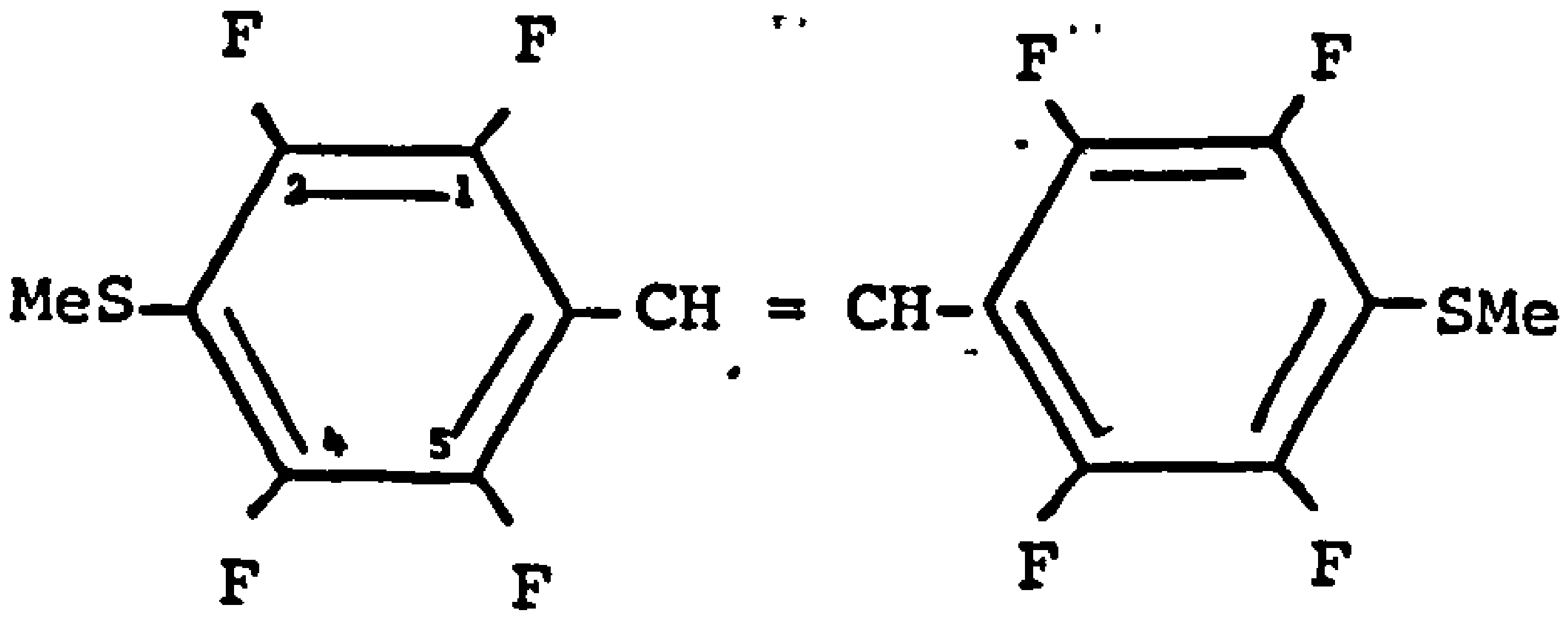
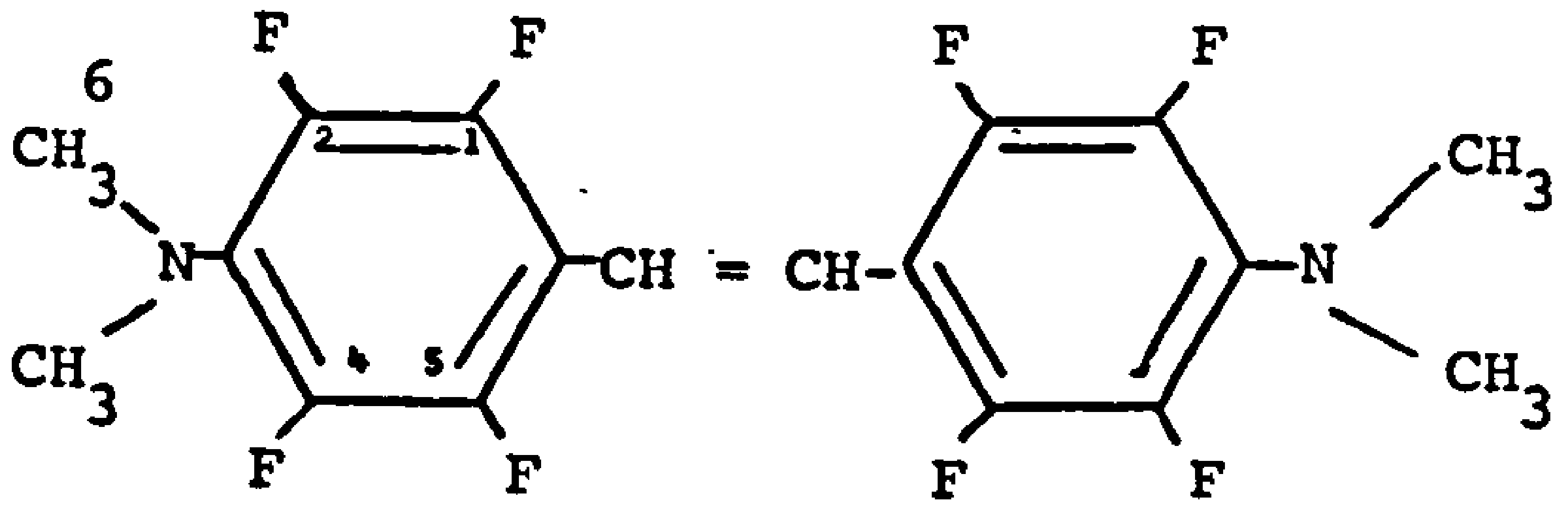
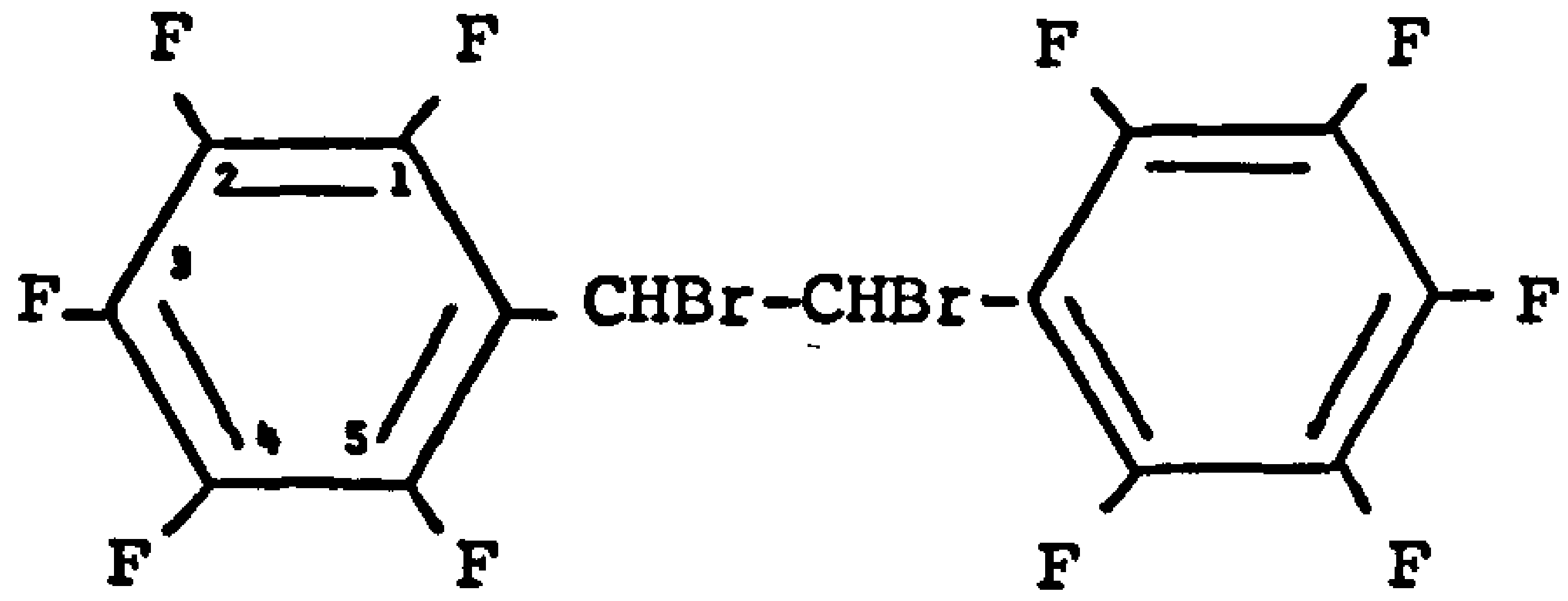
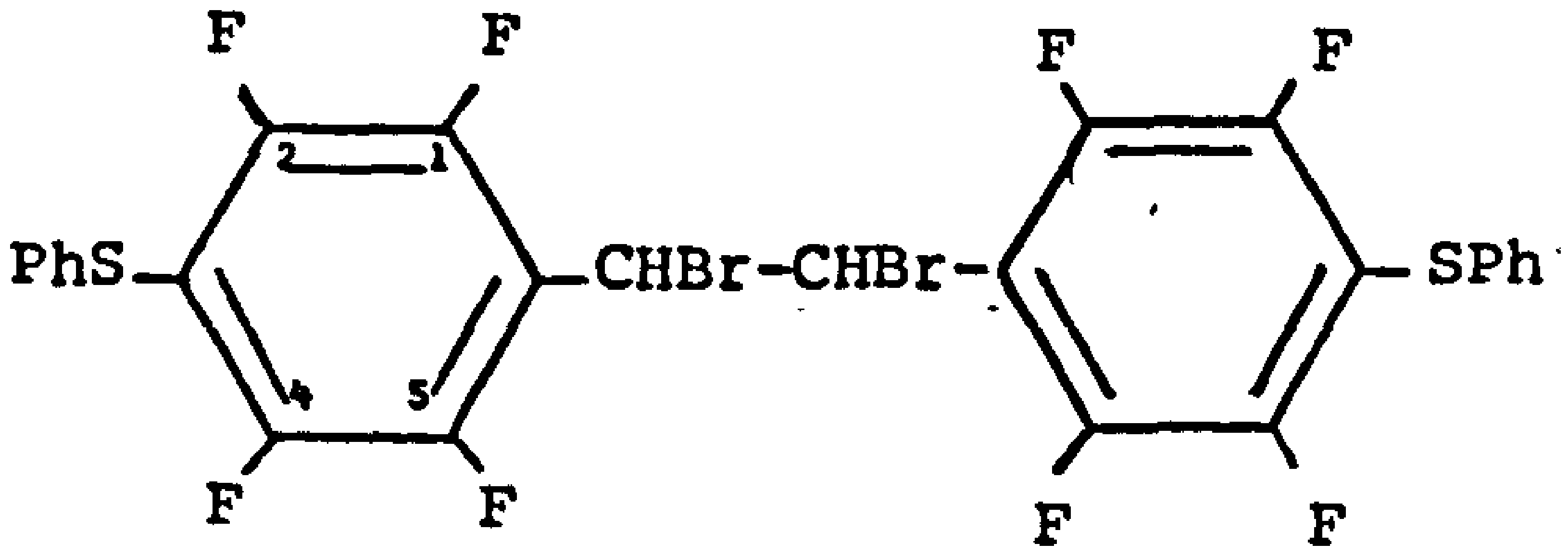
Compound	Coupling constants Hz
	J(1-5) 3.05 J(2-4) 0.65 J(1-2) 23.6 J(1-4) 10.6
	J(1-5) 2.25 J(2-4) 2.25 J(1-2) 22.8 J(1-4) 12.1
	J(1-5) 1.9 J(2-4) 1.9 J(1-2) 21.9 J(1-4) 11.4
	J(1-5) 2.4 J(2-4) 2.4 J(1-2) 19.4 J(1-4) 8.7 J(2-6) 2.1

TABLE (7) contd.

Compound	Coupling constants Hz	
	J(1-5)	6.3
	J(2-3)	20.9
	J(4-5)	22.4
	J(1-4)	8.2
	J(3-5)	2.8
	J(1-2)	21.8
	J(2-4)	1.1
	J(2-5)	7.9
	J(1-3)	3.6
	J(1-5)	2.0
	J(1-4)	14.5
	J(1-2)	12.2
	J(2-5)	23.3
	J(4-5)	12.1
	J(2-4)	5.0

Preparation of Platinum and Palladium Complexes

Reagent

K_2PtCl_4 and $PdCl_2$ obtained from Johnson Matthey and Co., were used as supplied. Dithioethers used as ligands were prepared as described in the previous section.

Experimental methods

Were described in the preceding section.

Preparation of complexes

The preparation of all complexes was very similar, differing only in the solvents, relative proportion of reactants and temperatures. The complexes were found to be stable to oxidation and hydrolysis under ambient conditions and most preparations were carried out using K_2PtCl_4 and $PdCl_2$ and aqueous-ethanolic solution which produce highest yield. A typical example is described below and conditions for other reactions are listed in table (7).

Preparation of $[CH_3SCH_2CHPhSCH_3)PtCl_2$

K_2PtCl_4 (2.1 gm, 5 mmole) was dissolved in 25 ml of water and 20 ml of ethanol was added. $(CH_3SCH_2CHPhSCH_3)$ (0.99 gm, 5 mmole) in 5 ml of ethanol was added to the solution. Immediate reaction occurred and the colour of the solution changed from red to yellow with deposition of crystals. After 24 hours bright yellow crystals of $[(CH_3SCH_2CHPhSCH_3)PtCl_2]$ (1.8 gm, 78%) yield were filtered and washed with cold ethanol and dried under vacuum at room temperature for 6 hrs. The complex obtained gave a satisfactory analysis without further purification.

TABLE (8)

$K_2PtC\ell_4$ solvent	m mol/gm ml	ligand solvent	m mol/gm ml	condition	product/yield
$K_2PtC\ell_4$ C_2H_5OH/H_2O	5/2.1 20/25	$CH_3SCH_2CHPhSCH_3$ C_2H_5OH	5/0.99 5	standing 24 hrs.	$[(CH_3SCH_2CHPhSCH_3)PtC\ell_2]$ 78% 1.8 gm
$K_2PtC\ell_4$ C_2H_5OH/H_2O	1.2/0.5 20/25	$CH_3SCPh{=}CHPh$ C_2H_5OH	2.4/0.56 5	standing 24 hrs.	cis & trans $[(CH_3SCPh{=}CHPh)_2PtC\ell_2]$ 45% 0.4 gm
$K_2PtC\ell_4$ C_2H_5OH/H_2O	0.8/0.3 20/25	$CH_3SCHPhCHPhSCH_3$ C_2H_5OH	0.8/0.22 5	standing 24 hrs.	$[(CH_3SCHPhCHPhSCH_3)PtC\ell_2]$ 58% 0.25 gm
$PdC\ell_2$ C_2H_5OH/H_2O	2/0.35 20/25	$CH_3SCH_2CHPhSCH_3$ C_2H_5OH	2/0.4 5	standing 24 hrs.	$[(CH_3SCH_2CHPh)PdC\ell_2]$ 73% 0.55 gm

TABLE (8) contd.

$K_2PtC\ell_4$ solvent	m mol/gm ml	ligand solvent	m mol/gm ml	condition	product/yield
$PdC\ell_2$ C_2H_5OH/H_2O	1.09/0.192 20/25	$CH_3SCPh{=}CHPh$ C_2H_5OH	2.1/0.46 5	standing 24 hrs.	$[(CH_3SCPh{=}CPhH)_2PdC\ell_2]$ 60% 0.25 gm
$PdC\ell_2$ C_2H_5OH/H_2O	1.5/0.26 20/25	$CH_3SCHPhCHPh$ C_2H_5OH	1.5/0.41 5	standing 24 hrs.	$[(CH_3SCPhH{-}CHPhSCH_3)PdC\ell_2$ 60% 0.30 gm

TABLE (9)

Compound	Colour	Analyses (%) Found/Calculated			
		C	H	S	Cℓ
$(CH_3SCH_2CHPhSCH_3)-PtC\ell_2$	yellow	25.70	3.02	13.90	15.03
		25.90	3.10	13.80	15.10
$-PdC\ell_2$	orange	32.10	3.65	17.08	18.72
		32.05	3.70	17.10	18.69
$(CH_3SCPh{=}CHPh)_2$ $-PtC\ell_2$	yellow	50.30	3.75	8.83	9.71
		50.20	3.90	8.90	9.70
$-PdC\ell_2$	orange	58.15	4.35	10.20	11.15
		58.20	4.50	10.30	11.30
$(CH_3SCHPhCHPhSCH_3)-PtC\ell_2$	yellow	36.85	3.43	12.21	13.29
		36.99	3.46	12.30	13.40
$-PdC\ell_2$	orange	42.55	3.97	14.19	15.52
		42.60	3.99	14.20	15.54

TABLE (10)

Infrared data (cm^{-1})

Compound				
$(CH_3SCH_2CHPhSCH_3)PtC\ell_2$	2970,w;	2910,w;	1750,m;	1410,s;
	1305,w;	1225,w;	968,s;	885,w;
	759,w;	686,w;	664,m;	300,s;
$(CH_3SCH_2CHPhSCH_3)PdC\ell_2$	2965,w,br;	1960,w;	1485,w;	1405,s;
	1348,s;	1316,w;	1279,s;	1251,vs;
	1238,vs;	945,vs;	695,vs;	768,s;
	500,m;	300,m;		
$(CH_3SCPh{=}CHPh)_2PtC\ell_2$	3060,m;	3030,m;	3000,m;	2920,m;
	1490,s;	1450,s;	1440,s;	1410,vs;
	1310,m,br;	1175,m;	965,s;	795,m;
	765,m;	700,vs;	685,vs;	307,vs;
	295,vs;			
$(CH_3SCPh{=}CHPh)_2PdC\ell_2$	3062,m;	3035,m;	3010,m;	2922,m;
	1495,s;	1455,s;	1442,s;	1415,vs;
	1312,m;	1170,m;	962,s;	790,m;
	770,m;	795,vs;	680,vs;	305,vs;
	300,vs;			

TABLE (10) contd.

Compound				
$(CH_3SPhCH{-}CHPhSCH_3)PtC\ell_2$	3060,m;	3030,m;	3010,m;	2920,m;
	1625,m;	1600,m;	1498,s;	1455,s;
	1455,s;	1415,vs;	1310,m;	1080,m;
	1030,m;	960,vs;	770,m;	760,m;
	700,vs;	560,m;	325,s,br;	
$(CH_3SPhCH{-}CHPhSCH_3)PdC\ell_2$	3055,m;	3035,m;	3015,m;	2925,m;
	1630,m;	1610,m;	1495,s;	1450,s;
	1448,s;	1420,vs;	1315,m;	1085,m;
	1035,m;	965,vs;	772,m;	765,m;
	710,vs;	565,m;	320,s;	325,s.

TABLE (11)

Mass spectral data

Compound			m/e	Relative intensity
$(CH_3SCH_2CHPhSCH_3)PtC\ell_2$	$(C_{10}H_{14}S_2)PtC\ell_2$	=	463	11%
	$(C_{10}H_{14}S_2)PtC\ell$	=	428	8%
	$(C_9H_{11}S)PtC\ell_2$	=	416	9%
	$(C_9H_{11}S_2)PtC\ell$	=	413	9%
	$(C_8H_8S_2)PtC\ell$	=	398	3%
	$(C_{10}H_{14}S_2)Pt$	=	393	7%
	$(C_8H_8S)Pt$	=	331	5%
	$(CH_3S)PtC\ell_2$	=	312	5%
	$(C_8H_7)Pt$	=	298	7%
	$(C_2H_6S_2)Pt$	=	289	40%
	$(CH_3S)Pt$	=	242	100%
$(CH_3SCH_2CHPhSCH_3)PdC\ell_2$	$(C_{10}H_{14}S_2)PdC\ell_2$	=	376	32%
	$(C_9H_{11}S_2)PdC\ell_2$	=	361	17%
	$(C_{10}H_{14}S_2)PdC\ell$	=	341	100%
	$(C_{10}H_{14}S)Pd$	=	306	49%
	$(C_8H_{19}S)Pd$	=	245	18%
	$(C_{10}H_{14}S_2)$	=	198	14%

TABLE (11) contd.

Compound			m/e	Relative intensity
$(CH_3SCHPhCHPhSCH_3)PtC\ell_2$	$(C_{14}H_{18}S_2)PtC\ell_2$	=	539	100%
	$(C_{14}H_{18}S_2)PtC\ell$	=	504	13%
	$(C_{14}H_{18}S_2)Pt$	=	469	18%
	$(C_{13}H_{15}S_2)PtC\ell$	=	449	5%
	$(C_7H_9S)PtC\ell_2$	=	402	7%
	$(C_3H_5S_2)Pt$	=	310	8%
	$C_{14}H_{18}S_2$	=	274	15%
	SPt	=	227	35%
	$C_{14}H_{16}$	=	178	100%
	$C_{10}H_{12}S$	=	164	12%
	C_8H_9S	=	137	27%
	$C_9H_{10}S$	=	150	35%
$(CH_3SCHPhCHPhSCH_3)PdC\ell_2$	$(C_{16}H_{18}S_2)PdC\ell_2$	=	459	8%
	$(C_{16}H_{18}S_2)PdC\ell$	=	424	15%
	$(C_{15}H_{15}S_2)PdC\ell$	=	409	9%
	$(C_{16}H_{18}S_2)Pd$	=	389	18%
	$(C_{14}H_{12})PdC\ell_2$	=	365	10%
	$(C_8H_9S_2)Pd$	=	275	90%
	$C_{14}H_{16}S_2$	=	248	3%
	$C_{14}H_{11}S$	=	211	5%
	$C_{14}H_{10}$	=	178	100%
	$C_{12}H_8$	=	152	18%
	$C_{10}H_{15}$	=	135	7%
	C_7H_7	=	91	13%

TABLE (11) contd.

Compound			m/e	Relative intensity
$(CH_3SCPh{=}CPh)_2PtC\ell_2$	$(C_{30}H_{28}S_2)PtC\ell_2$	=	717	30%
	$(C_{30}H_{28}S_2)PtC\ell$	=	682	15%
	$(C_{29}H_{25}S)PtC\ell_2$	=	670	10%
	$(C_{30}H_{28}S_2)Pt$	=	647	20%
	$(C_{15}H_{14}S)PtC\ell_2$	=	402	70%
	$(C_{15}H_{14}S)PtC\ell$	=	377	14%
	$(C_{14}H_{12})PtC\ell_2$	=	355	3%
	$(C_{15}H_{14}S)Pt$	=	342	5%
	$C_{15}H_{14}S$	=	226	50%
	$C_{14}H_{10}$	=	178	60%
$(CH_3SCPh{=}CHPh)_2PdC\ell_2$	$(C_{30}H_{28}S_2)PdC\ell_2$	=	628	15%
	$(C_{30}H_{28}S_2)PdC\ell$	=	573	5%
	$(C_{27}H_{25}S)PdC\ell_2$	=	581	13%
	$(C_{30}H_{28}S_2)Pd$	=	558	9%
	$(C_{16}H_{17}S_2)PdC\ell_2$	=	441	7%
	$(C_{15}H_{14})PdC\ell_2$	=	402	9%
	$(C_{15}H_{14})PdC\ell$	=	367	2%
	$(C_{14}H_{10})Pd$	=	354	43%
	$(C_{15}H_{14})Pd$	=	332	6%
	$(C_{14}H_{11})PdC\ell_2$	=	325	8%

TABLE (12)

^{1}H Nuclear Magnetic Resonance Parameters

Compound	Relative proportion	δSCH_3
$[(CH_3SCH_2CHPhSCH_3)PtC\ell_2]$		
A	4	2.15
		2.2
B	19	2.00
		2.01
C	56	2.07
		2.09
D	21	2.25
		2.3
$[(CH_3SCH_2CHPhSCH_3)PdC\ell_2]$		
		2.05
		2.07
		2.09
		2.1
$[(CH_3SCHPhCHPhSCH_3)PtC\ell_2]$		
1st Isomer		2.06
2nd Isomer		2.29
3rd Isomer		1.98
4th Isomer		2.48
5th Isomer		1.93
6th Isomer		1.96

TABLE (12) contd.

Compound	Relative proportion	δSCH_3
$[(CH_3SCHPhCHPhSCH_3)PdC\ell_2]$		
1st Isomer		2.1
2nd Isomer		2.52
3rd Isomer		2.72
4th Isomer		2.78
5th Isomer		2.91
6th Isomer		2.95
$[(CH_3SPhC{=}CHPh)_2PtC\ell_2]$		
1st Isomer	90	3.36
2nd Isomer	10	2.82
$[(CH_3SPhC{=}CHPh)_2PdC\ell_2]$		
1st Isomer		3.32
2nd Isomer		2.70

TABLE (13)

^{195}Pt NMR Parameters of the Complexes

Compound	Isomer	Relative proportion	$\delta\,^{195}Pt^{a}$
$[(CH_3SCHPhCHPhSCH_3)PtC\ell_2]$	1	2	1091.4
	2=B	54	1092.3
	3	20	1132.3
	4	10	807.6
	5	4	822.6
	6	15	1139.4
$[(CH_3SCHPhCH_2SCH_3)PtC\ell_2$	(A) syn-syn	4	810.4
	(B) syn-anti	19	783.2
	(C) anti-syn	56	811.7
	(D) anti-anti	21	843.7
$[(CH_3SCPh{=}CHPh)_2PtC\ell_2]$	1	90	775.3
	2	16	773.2

[a] ppm positive to low field of external (arbitrary ref.).

Hexacarbonyl[1,2-bis(4-dimethylaminotetrafluorophenyl)ethene]dicobalt(O)

Octafluoro-4,4′-dimethylaminotolan (0.2125 gm, 0.4 mmoles), dicobalt octacarbonyl (0.1368 gm, 0.4 mmoles) and dry benzene (25 ml), were shaken at room temperature in 3 neck round bottomed flask under nitrogen for two hours. The solution was filtered and the filtrate was evaporated to leave a dark purple residue, 0.30 gm (83% yield), which was recrystallized from light petroleum (b.p. 40-60°C) at -78°C to give hexacarbonyl(octafluoro(dimethylamino)tolan dicobalt(O).

Hexacarbonylbis[1,2-bis(4-dimethylaminotetrafluorophenyl)ethene]diiron(O)

(0.2 gm, 0.48 mmole) of $C_{14}F_8(NMe_2)_2$ was dissolved in 25 ml benzene and heated under reflux with (0.24 gm, 0.48 mmoles) of triiron dodecacarbonyl for six hours. The colour changed from green to dark red-brown. The products were chromatographed on neutral alumina (Woelm), with light petroleum (b.p. 60-80°C) ether, and methanol as eluents. The light petroleum fraction was 4,4′-dimethyl(aminooctafluorotolan) 0.02 gm with melting point 140.5°C. The solid residue was recrystallized from light petroleum (b.p. 100-120°C) to yield crystals of the iron complex, 0.15 gm (24% yield) with m/e = 1202 (mass spectra). The ether fraction contained red crystals of the cyclopentadienone with m/e = 1230 (mass spectra) which was identified by i.r. spectroscopy.

References

1. Comprehensive Inorganic Chemistry, Robert C. Brasted, Editor. Vol. 8 (1961) p.7.
2. Encyclopedia of Technical Technology (1969) Kirk-Othmer, John Wiley & Sons, Inc., Second Edition, Vol. 19 p.7.
3. Chemical and Engineering News, 25, 1982 (11).
4. Manufacturing Chemists Association. "Properties and Essential Information for safe handling and use of sulfur." Chem. Safety Data Sheet 50-74 (1959).
5. National Fire Protection Association; Sulfur Fires and Explosions, National Fire Code NE PA NO 655 (1959).
6. R.S. Milliken, J. Chem. Phys., 1934, 2, 782.
7. A.L. Allred, J. Inorg. Nuclear Chem., 1958, 5, 264.
8. H.G. Tohode, J. Macnamara and C.B. Couins, Can. J. Res. B.27, (1947) 361.
9. W.N. Teller (Ed.) "The Sulfur Data Book", McGraw Hill, London, 1954.
10. "Handbook of Chemistry and Physics", 61st Edition, 1980-1981.
11. W.J. Whitehouse and J.L. Putman, 1st Edition, 1958, p.274.
12. D.D. Dziewiatkowski, Radioisotopes, Bone Symposium, Princeton, N.J., 1960 (Pub. 1962) p.277.
13. V.F. Moiseichenko, Fiziol. Biokim, Osnovi Pidvishchennya Produ Ktivnosti Roslin, Derzhgil Gospuiday UKR, RSR, Kiev, 1963, p.113.
14. S.W. Benson, Chem. Rev., 1978, 78, 23; J. Kao and N.L. Allinger, Inorganic Chem., 1977, 16, 35; B. Meyer, Chem. Rev., 1976, 76, 367; Adv. Inorg. Chem. Radiochem., 1976, 18, 287; M. Schmidt, Angew Chem. Int. Ed., 1973, 12, 445; T. Chivers and I. Drummond, Chem. Soc. Rev., 1973, 2, 233.

15. D. McKie and C. Mikie, "Crystalline Solids", Thomas Nelson, 1974, p.509.

16. M. Schmidt and E. Wilhelm, Inorg. Nucl. Chem. Letters, 1965, 1, 39a; M. Schmidt and E. Wilhelm, Angew. Chem., 1966, 78, 1020.

17. B. Meyer, Chem. Rev., 1976, 76, 367.

18. R. Steudel, H.J. Mausle, Angew. Chem., 1977, 89, 114; Angew Chem. Int. Ed. Engl., 1977, 16, 112.

19. L.K. Templeton, D.H. Templeton and A. Zalkin, Inorg. Chem., 1976, 15, 1999.

20. B. Meyer, Chem. Rev., 1964, 46, 429; B. Meyer,"Elemental Sulfur" Interscience, New York, 1965.

21. M. Schmidt, Chemie in Unserer Zeit, 1973, 7, 11.

22. B. Meyer, Elemental Sulfur. G. Nickless (Editor), "Inorganic Sulfur Chemistry", Elsevier, Amsterdam, London, New York, 1968, 240.

23. J. Donohue, "The Structures of Elemental Sulfur", N. Kharasch (Editor), "Organic Sulfur Compounds", O.U.P., London, New York, Paris, Vol. I (1961).

24. M. Schmidt and B. Meyer (Eds.) "Elemental Sulfur Chemistry and Physics", Interscience, New York, 1965, 327.

25. M. Schmidt, G. Kippschild and E. Wilhelm, Chem. Ber., 1968, 101, 381; A. Kutoglu and E. Hellner, Angew. Chem., 1966, 78, 1021; J. Buchler, Angew. Chem., 1966, 78, 1021.

26. M. Schmidt, H. Block, H.D. Block, H. Köpf and E. Wilhelm, Angew. Chem., 1968, 80, 660.

27. J. Berkowiz, W.A. Chupka, E. Bromels and R.L. Belford, J. Chem. Phys., 1967, 47, 4320; L.A. Alimon, V.D. Neff, R.E. Cantley and R.O. Buttlar, J. Mol. Spectrosc., 22, 105 (1967); 26, 175 (1968).

28a. M. Gardner, and A. Rogstad, J. Chem. Soc. Dalton, 1973, 599.

b. R. Steudel and F. Schuster, unpublished work, F. Schuster, Diplomarbeit, Technische Universität Berlin (1976).

29. D.W. Scott, J.M. McCullough and F.H. Kruse, J. Mol. Spectrosc., 1964, 13, 313; G.W. Chantry, A. Anderson, H.A. Gebbie, Spectrochim. Acta, 1964, 20, 1223.

30. R. Steudel and M. Rebsch, J. Mol. Spectrosc., 1974, 51, 189; R. Steudel and D.F. Eggers, Spectrochim. Acta., 1975, 31A, 879.

31. R. Steudel, J. Phys. Chem., 1976, 80, 1516.

32. R. Reinhardt, R. Steudel and F. Schuster, Angew. Chem., Int. Ed., 1978, 17, 57; M. Schmidt, E. Wilhelm, T. Debaerdemaeker, E. Hellner and A. Kutoglu, Z. anorg. Chem., 1974, 405, 153.

33. J.A. Poulis and C.H. Massen, B. Meyer (Editor); "Elemental Sulfur Chemistry and Physics", Interscience, New York, 1965, 109.

34. A.V. Tobolsky and W.J. MacKnight, B. Meyer (Editor); "Elemental Sulfur Chemistry and Physics", Interscience, New York, 1965, 195. A.V. Tobolsky and W.J. MacKnight, "Polymeric Sulfur and Related Polymers", Interscience, New York, 1965.

35. R. Neidlein, P. Leinberger, A. Gieren and B. Dederer, Chem. Ber., 1978, 111, 698.

36. R. Neidlein and P. Leinberger, Chem. Ztg., 1977, 101, 35.

37. K. Neidlein, P. Leinberger, A. Gieren and B. Dederer, Chem., Ber., 1977, 110, 3149.

38. R. Niedlein and P. Leinberger, Synthesis, 1977, 63.

39. G.N. Schrauzer and U.P. Mayweg, J. Amer. Chem. Soc., 1965, 87.

40. F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Wiley, New York, 1980.

41. P.C. Turley and P. Haake, J. Amer. Chem. Soc., 1967, 89, 4617.

42. R.J. Cross, I.G. Dalgleish, G.J. Smith and R. Wordle, J. Chem. Soc. Dalton, 1972, 992.

43. A. Vandi, T. Moeller and T.L. Brown, Inorganic Chem., 1963, 2, 899.

44. F.A. Cotton, J.W. George and J.S. Waugh, J. Chem. Phys., 1958, 28, 994.

45. R. Tunder and B. Siegel, J. Inorg. Nucl. Chem. Phys., 1963, 25, 1097.

46. K. Kimura and S.H. Bauer, J. Chem. Phys., 1963, 39, 3172.

47. F.B. Dudley, J.N. Shoolery and G.H. Cady, J. Amer. Chem. Soc., 1956, 78, 568.

48. P.L. Goggin, H.L. Roberts and L.A. Woodward, Trans. Faraday Soc., 1961, 57, 877.

49. R.J. Gillespie, J. Chem. Soc., 1963, 4672.

50. R.J. Gillespie and R.S. Nyholm, Quart. Rev., Chem. Soc., 1957, 11 339.

51. L.O. Brockway, Rev. Mod. Phys., 1936, 8, 231.

52. H. Braune and S. Knoke, Z. Phys. Chem., 1933, B21, 297.

53. L.R. Maxwell, J. Opt. Soc. Am., 1940, 30, 374.

54. D. Edelson, J. Amer. Chem. Soc., 1952, 74, 262.

55. J.K. Wilmhurst and H.J. Bernstein, Can. J. Chem., 1957, 35, 191.

56. R.E. Dodd, L.A. Woodward and W.L. Roberts, Trans. Faraday Soc., 1957, 53, 1545.

57. A.F. Wells, "Structural Inorganic Chemistry", 3rd ed. Oxford University Press, London, 1962, 520.

58. A.E. Smith, G.N. Schrauzer, U.P. Mayweg and W. Heinrich, J. Amer. Chem. Soc., 1965, 87, 5798; R. Eisenberg, E.I. Stiefel, R.C. Rosenberg and H.R. Gray, J. Amer. Chem. Soc., 1966, 88, 2874.

59. A.A. Diamantis, M.R. Snow and J.A. Vanzo, J. Chem. Soc., Chem. Comm., 1976, 264.

60. J.A. McCleverty, Prog. Inorg. Chem., 1968, 10, 49; R. Eisenberg, Prog. Inorg. Chem., 1970, 12, 295; D. Doucouvanis, Prog. Inorg. Chem., 1970, 11, 233; R.J.H. Clark and P.C. Turtle, J. Chem. Soc. Dalton, 1977, 2142; B.K. Teo and P.A.S. Robinson, Inorg. Chem., 1979, 18, 1490.

61. G. Gapozzi and G. Modena, "The Chemistry of the Thiol Group", ed. S. Patai, Wiley, New York, 1974, 785.

62. A. Ohno and S. Oae, "Inorganic Chemistry of Sulfur", ed. S. Oae, Plenum, New York, 1976.

63. G.C. Barrett, "Inorganic Compounds of Sulfur, Selenium and Tellurium"; The Chemical Society, London, 1970, Vol. 1, p.49; 1973. Vol. 2, p.1; 1975, Vol. 3, p.1; 1977, Vol. 4, p.1.

64. T.L. Cottrell, "The Strength of the Chemical Bond", New York, 1954.

65. J.L. Franklin and H.E. Lumpkin, J. Amer. Chem. Soc., 1952, 74, 1023.

66. L.E. Sutton, Ed., Interatomic Distances, Special Publication No. 11; The Chemical Society, London, 1958.

67. W.H. Fletcher, J. Amer. Chem. Soc., 1940, 68, 2726.

68. J. Maurin and P.A. Paris, Compt. Rend., 1951, 232, 2482.

69. H. Lumbroso, J. Chem. Phys., 1952, 49, 394.

70. L.P. Hammett, "Physical Organic Chemistry", McGraw-Hill, New York, 1940, 50.

71. G.R. Sprengling and C.W. Lewis, J. Amer. Chem. Soc., 1949, 71, 2624.

72. H.L. Loy and D.M. Himmelblau, J. Phys. Chem., 1961, 65, 264.

73. M.M. Kreevoy, E.T. Harper, R.E. Duvall, H.S. Wilgus III and L.T. Ditsch, J. Amer. Chem. Soc., 1960, 82, 4899.

74. G. Csizmadia, "The Chemistry of the Thiol Group", ed. S. Patai, J. Wiley, New York, 1974, 7.

75. L. Pauling, "The Nature of Chemical Bond", Cornell Univ. Press, Ithaca, N.Y., 1960, 110.

76. M. Kotake, Ed., "Constants of Organic Compounds", Asakura Pub. Co., Tokyo, Japan, 1963, 511.

77. R.J. Ferrier and R.H. Furneaux, J. Chem. Soc., Chem. Comm., 1977, 332.

78. T.L. Jacobs and G.E. Illingworth, J. Org. Chem., 1963, 28, 2692.

79. E.P. Kohler and H. Potter, J. Amer. Chem. Soc., 1935, 57, 1316.

80. E.A. Haiba and R.M. Dessau, J. Org. Chem., 1967, 23, 3837.

81. I.G. Sulimov and A.A. Petrov, Z. Organ. Khim., 1965, 2, 767.

82. M.M. Martin and E.B. Sanders, J. Amer. Chem. Soc., 1967, 89, 3777.

83. M. Meissner and H.W. Thompson, Trans. Faraday Soc., 1938, 34, 1238.

84. N.P. Skerrett and H.W. Thompson, Trans. Faraday Soc., 1941, 37, 81.

85. A.P. Steer, B.L. Katra and A.R. Knight, J. Phys. Chem., 1967, 71, 783.

86. A.A. Oswald, K. Griesbaum, B.E. Hudson Jr. and J.M. Bregman, J. Amer. Chem. Soc., 1964, 86, 2877.

87. J.A. Kampmerier and G. Chen, J. Amer. Chem. Soc., 1965, 87, 2608.

88. F.W. Stacey and J.F. Harris Jr., Organic Reaction. John Wiley, New York, 1963, Vol. 13, 150.

89. G. Brindell and S.J. Cristol, N. Kharasch (Editor), "Organic Sulfur Compounds", J. Wiley, New York, 1961, Vol. I.

90. P. Caubere and J.J. Brunet, Bull. Soc. Chim. Fr., 1970, 2418.

91. W.J. Frazee and M.E. Peach, J. Fluor. Chem., 1979, 13, 225.

92. R. Adam and A. Ferretti, J. Amer. Chem. Soc., 1959, 81, 4927.

93. J. Biougne and F. Theron, C.R. Acad. Sci., 1971, 272C, 858.

94. G. Marchese and F. Naso, Chim. Ind. Milan, 1970, 53, 760; Chem. Abstr., 1971, 75, 98077.

95. R. Sauvetre and J.F. Normont, Bull. Soc. Chim. Fr., 1972, 3202.

96. L.J. Beif, M.W. Buxton and G. Fuller, J. Chem. Soc., 1965, 3372.

97. J. Miller, "Aromatic Nucleophilic Substitution", Elsevier, Amsterdam, 1968.

98. J. Burdon, P.L. Coe, C.R. Marsh and J.C. Tatlow, J. Chem. Soc., Perkin Trans. 1972, 1, 763.

99. G.G. Yakobson, G.G. Furin, L.S. Kobrina and N.N. Vorozhtsov, J. Gen. Chem. USSR, 1967, 37 1221.

100. L.S. Kobrina, G.G. Furin and G.G. Yakobson, J. Gen. Chem. USSR, 1968, 38, 505.

101. G. Guanti, C. Dell' Erba and D. Spinelli, Gazz. Chim. Ital., 1970, 100, 184; Chem. Abstr., 1970, 73, 13939.

102. M. Bosco, U. Calos, F. Cirminale, L. Forlani, L. Lopez, N. Efiso and P.E. Todesco, Gazz. Chim. Ital., 1971, 101, 685; Chem. Abst., 1972, 76, 58649.

103. J. Miller, "Aromatic Nucleophilic Substitution", Elsevier, Amsterdam, 1968.

104. J.F. Bunnett and R.E. Zahler, Chem. Rev., 1951, 49, 273; J.F. Bunnett, Quart. Rev., 1958, 12, 1.

105. J. Burdon, Tetrahedron, 1965, 21, 3374.

106. W. Pritzkow, Z. Chemie, 1970, 10, 330.

107. R.D. Chambers, W.K.R. Musgrave, J.S. Waterhouse, D.L.H. Williams, J. Burdon, W.B. Hollyhead and J.C. Tatlow, J. Chem. Soc. Chem. Comm., 1974, 239.

108. R.D. Chambers, J.S. Waterhouse and D.L.H. Williams, J. Chem. Soc. Perkin II, 1977, 585.

109. J.C. Tatlow, Endeavour, 1963, 22, 89.

110. R.J. de Pasquale and C. Tamborski, J. Org. Chem., 1967, 32, 3163.

111. M.E. Peach, "The Chemistry of the Thiol Group", S. Patai, Ed. Part 2, J. Wiley, 1974, 721.

112. F. Feher and K. Vogelbruch, Chem. Ber., 1958, 91, 996.

113. E.V. Bell and G.M. Bennett, J. Chem. Soc., 1928, 3190.

114. G.J. Morgan, S.R. Garter and W.F. Harrison, J. Chem. Soc., 1925, 1917.

115. S. Mathias, Bols. F.F.C.; U. Sao, Paulo. Quimica, 1941, 14, 75, C.A. 40, 2792.

116. G. Haran and D.W.A. Sharp, J.C.S. Perkin I, 1972, 34.

117. D.W.A. Sharp and H. Torrens (1978) (cited from ref. 236).

118. M.E. Peach and A.M. Ritcey, J. Fluor. Chem., 1982, 21, 401.

119. P. Camber, Bull. Soc. Chim. Fr., 1967, 3451.

120. J. Burdon, Tetrahedron, 1965, 21, 1101.

121. J. Burdon, P.L. Coe, C.R. Marsh and J.C. Tatlow, Tetrahedron, 1960, 22, 1183.

122. L.M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd Edition. Pergamon Press, London, 1969, p302.

123. J.M. Gascoyne, P.J. Mitchell and L. Philips, J.C.S. Perkin II, 1977, 1051.

124. W.J. Frazee, M.E. Peach and J.R. Sweet, J. Fluor. Chem., 1977, 9, 377.

125. K. Koppang, J. Fluor. Chem., 1976, 8, 389.

126. J.M. Birchall, F.L. Bowden, R.N. Haszeldine and A.B.P. Lever, J. Chem. Soc. A, 1967, 747.

127. K.R. Langille and M.E. Peach, J. Fluor. Chem., 1971/2, I, 407.

128. P. Camber, Bull. Soc. Chim. Fr., 1967, 3451.

129. L.J. Bellamy, "The Infra-red Spectra of Complex Molecules", 2nd Ed. J. Wiley Inc., New York, 1958, 59(a), 45(b).

130. B.C. Musial and M.E. Peach, J. Fluor. Chem., 1976, 7, 459; G.A. Webb, Annual Report on NMR Spectroscopy, 1980, 10B, 344.

131. F.W. Stacey and J.F. Harris, Jr., J. Amer. Chem. Soc., 1961, 83, 840.

132. G. Haran, Ph.D. Thesis, University of Glasgow, 1972.

133. M.E. Peach and H.G. Spinney, Can. J. Chem., 1971, 49, 644.

134. J.F. Harris, Jun., J. Org. Chem., 1967, 32, 2063.

135. R.E. Banks, "Fluorocarbons and their Derivatives", Macdonald & Co. (Publishers) Ltd., Second edition, 1970, 82.

136. A.I. Scott, Quart. Rev., 1965, 19, 1.

137. R.G.R. Bacon and H.A.O. Hill, Quart. Rev., 1965, 19, 95.

138. P.E. Panta, Chem. Rev., 1946, 38, 139; 1964, 64, 613; A.H. Lewin and T. Cohen, Tetrahedron Lett., 1965, 4531.

139. R.D. Chambers and D.J. Spring, Tetrahedron, 1971, 27, 669.

140. R.D. Chambers, "Fluorine in Organic Chemistry", J. Wiley, N.Y., 1973, 6.

141. G. Modena and G. Scorrano, "The Chemistry of the Carbon-Halogen Bond". S. Patai, Ed., J. Wiley

142. R.N. Haszeldine and B.O. West, J. Chem. Soc., 1956, 3631.

143. B. Haley, R.N. Haszeldine and R.E. Tipping, J. Chem. Soc. Perkin I, 1976, 525.

144. E.L. Eliel and S.A. Evans, Jun., J. Amer. Chem. Soc., 1972, 94, 8588.

145. C.F. Finder, M.G. Newton and A.L. Allinger, Acta Cryst., 1974, B30, 411.

146. R.M. Silverstein, C.G. Bassler and T.C. Norrill, "Spectrometric Identification of Organic Compounds", 3rd edition. John Wiley Inc., New York, 1974, p.224.

147. P.J. Mitchell and L. Phillips, J.C.S. Perkin II, 1974, 109.

148. G.A. Jeffrey, Proc. Roy. Soc., 1947, 188, 222.

149. J.D. McCullough, J. Amer. Chem. Soc., 1940, 62, 480.

150. A. Behzadi and L.N. Owen, J. Chem. Soc. Perkin I, 1974, 25.

151. C. Walling, "Free Radicals in Solution". J. Wiley, N.Y., 1957, p.313.

152. K. Griesbaum, Angew. Chem. Int. Ed., 1970, 9, 373.

153. W.E. Trace, H.G. Klein and R.B. Kruse, J. Amer. Chem. Soc., 1961, 83, 4636.

154. L.I. Smith and H.R. Davis, Jr., J. Org. Chem., 1950, 15, 824.

155. A.T. Blomquist and J. Wolinsky, J. Org. Chem., 1935, 23, 551.

156. J.A. Pople, W.G. Schneider and H.J. Bernstein, "High Resolution Nuclear Magnetic Resonance". McGraw-Hill Book Co., N.Y., 1951, Chapter (I).

157. S. Alexander, J. Chem. Phys., 1958, 28, 358.

158. W.E. Trace and B. Groten, J. Org. Chem., 1962, 27, 128.

159. A. Sauer, J. Amer. Chem. Soc., 1957, 79, 5314.

160. V.K. Yamagishi, T. Tanaka and T. Hoshino, Bull. Chem. Soc. Japan, 1956, 29, 447.

161. K. Griesbaum, A.A. Oswald, E.R. Quiran and W. Naegel, J. Org. Chem., 1963, 28, 1952.

162. A.L. Henne and W.G. Finnegan, J. Amer. Chem. Soc., 1949, 71, 278.

163. A.L. Henne, J.V. Schmitz and W.G. Finnegan, J. Amer. Chem. Soc., 1950, 72, 4195.

164. J.B. Wilford and F.G.A. Stone, Inorg. Chem., 1965, 4, 93.

165. F.W. Stacey and J.F. Harris, J. Amer. Chem. Soc., 1963, 85, 963.

166. R.N. Haszeldine, J. Chem. Soc., 1952, 3491.

167. W. Mahler, J. Amer. Chem. Soc., 1964, 86, 2306.

168. W.R. Cullen, D.S. Dawson and G.E. Styan, Can. J. Chem., 1965, 43, 3392.

169. W.R. Cullen and N.K. Hota, Can. J. Chem., 1964, 42, 1124.

170. J.A. Pople, W.G. Schneider and H.J. Bernstein, "High Resolution Nuclear Magnetic Resonance". McGraw-Hill, N.Y. 1959, 379.

171. D.H. Williams and I. Fleming, "Spectroscopic Methods in Organic Chemistry", 2nd Ed. McGraw-Hill, London, 1973, 137.

172. C.W. Tullock and D.D. Coffman, J. Org. Chem., 1960, 25, 2016.

173. L.M. Yagupolskii and B.E. Gruz, J. Gen. Chem. USSR, 1961, 31, 1219.

174. E.A. Noddiff, S. Lipschutz, P.N. Craig and M. Gordon, J. Org. Chem., 1960, 25, 60.

175. Fr. Patent 2 192 896, 1972 (C.A. 1973, 78, 124021n).

176. M.F. Shostakovskii, E.P. Gracheva and N.N. Kulbovskaya, Zh. Obshei Khim., 1960, 30, 383.

177. D.J. Burton, R.L. Johnson and R.T. Bogan, Canad. J. Chem., 1966, 44, 635.

178. B.A. Bohm and P.I. Abell, Chem. Rev., 1962, 62, 599.

179. C.J. Brookes, P.L. Coe, A.E. Pedler and J.C. Tatlow, J. Chem. Soc. Perkin I, 1978, 202.

180. S.D. Morse, K.A. Laurence, G.H. Sprenger and J.M. Shreeve, J. Fluor. Chem., 1978, 11, 327.

181. R.N. Haszeldine, R.B. Rigby and A.E. Tipping, J. Chem. Soc. Perkin I, 1972, 2438.

182. K.E. Rapp, R.L. Pruett, J.T. Barr, C.T. Bahner, J.D. Gibson and R.H. Lafferty, J. Amer. Chem. Soc., 1950, 72, 3642.

183. C.G. Krespan and B.C. McKusick, J. Amer. Chem. Soc., 1961, 83, 3438.

184. R.E.A. Dear and E.E. Gilbert, J. Fluor. Chem., 1974, 4, 107.

185. J.F. Harris, Jun., J. Amer. Chem. Soc., 1962, 84, 3148.

186. W.E. Hanford, U.S. Patent 2, 443, 603, 1948 (C.A. 42, 6841, 1948).

187. C.G. Krespan, J. Amer. Chem. Soc., 1961, 83, 3434.

188. C.G. Krespan, J. Amer. Chem. Soc., 1961, 83, 3432.

189. C.G. Krespan and B.C. McKusick, J. Amer. Chem. Soc., 1961, 83, 3434.

190. A. Davison and F.T. Shawl, Chem. Comm., 1967, 670.

191. J.M. Birchall and R.N. Haszeldine, J. Chem. Soc. (C), 1961, 3719.

192. A.R. Katritzky and A.J. Boulton, J. Chem. Soc., 1959, 3500; A.R. Katritzky, Quart. Rev., 1959, 13, 362.

193. W.E. Parham and V.J. Traynelis, J. Amer. Chem. Soc., 1955, 77, 68.

194. W.E. Parham, G.L.D. Mayo and B. Gadsby, J. Amer. Chem. Soc., 1959, 81, 5993.

195. F.R. Hartley, "The Chemistry of Platinum and Palladium". Applied Science Publishers, 1973; D.M. Roundhill, Adv. Organomet. Chem., 1975, 13, 274; P.M. Henry, Adv. Organomet. Chem., 1975, 13, 363; P.M. Maitlis, "The Organic Chemistry of Palladium", Vol. 1, 2. Academic Press, 1971; U. Belluco, "Organometallic and Co-ordination Chemistry of Platinum", Academic Press, 1974; "Platinum Group Metals and Compounds", ACS, Advances in Chemistry Series No. 98.

196. S.T. Ahrland, J. Chatt and N.R. Davies, Quart. Rev., 1958, 12.

197. A. Pidcock, R.E. Richards and L.M. Venanzi, J. Chem. Soc. A, 1966, 1707; Proc. Chem. Soc., 1962, 184.

198. A.A. Grinberg, Acta Physicochim, USSR, 1935, 3, 573.

199. F. Basolo and R.G. Pearson, Progr. Inorganic Chem., 1962, 4, 381.

200. I.B. Bersuker, J. Struct. Chem., 1963, 4, 419.

201. J. Chatt, C. Eaborn, S.I. Bekwe and P.N. Kappor, J. Chem. Soc. A, 1970, 1343.

202. D.A. Duddell, P.L. Goggin, R.L. Goodfellow, M.G. Norton and J.G. Smith, J. Chem. Soc. A, 1970, 545.

203. W.J. Cherwinski, H.C. Clark and L.E. Manzer, Inorg. Chem., 1972, 11, 1511.

204. T.G. Appleton and J.R. Hall, Inorg. Chem., 1971, 10, 1717.

205. M.H. Chisholm, H.C. Clark, L.E. Manzer and J.B. Stothers, J. Amer. Chem. Soc., 1972, 94, 5087.

206. R.D.W. Kemmitt and R.D. Moor, J. Chem. Soc. A, 1971, 2472.

207. G. Schwarzenbach, Helv. Chem. Acta, 1952, 35, 2344.

208. G. Schwarzenbach in "Chemical Specificity and Biological Interaction". F.R.N. Gurd, Ed., Academic Press, N.Y., 1954.

209. G. Schwarzenbach, Adv. Inorg. Radiochem., 1961, 3, 257.

210. M.V. Veidis, G.H. Schreiber, T.E. Gough and G.J. Palenik, J. Amer. Chem. Soc., 1969, 91, 1859.

211. R.B. King and C.A. Eggert, Inorg. Chim. Acta, 1968, 2, 33.

212. R.B. King, J. Coord. Chem., 1971, 1, 67.

213. I.I. Chernyaev, N.N. Zheligovskay, V. Let. Ken and D.V. Kurganouich, Russ. J. Inorg. Chem., 1964, 9, 313.

214. D. Munro, Chem. Brit., 1977, 13, 100.

215. L. Cattalini and M. Martelli, J. Amer. Chem. Soc., 1961, 91, 312.

216. U. Belluco, Coord. Chem. Rev., 1966, 1, 111.

217. P.C. Turley and P. Haake, J. Amer. Chem. Soc., 1967, 89, 4617.

218. G.G. Spike and R.W. Parry, J. Amer. Chem. Soc., 1953, 75, 2726.

219. L. Cattalini, M. Martelli and G. Marangoni, Inorg. Chim. Acta, 1968, 2, 405.

220. C.I. Branden, Arkiv. Kemi, 1964, 22, 83.

221. P. Woodward, L.F. Dahl, E.W. Abel and B.C. Crosse, J. Amer. Chem. Soc., 1965, 87, 5251.

222. W.N. Hunter, K.W. Muir and D.W.A. Sharp, J. Fluor. Chem. Soc., 1982, 21, 19.

223. R.J. Cross, L.M. Muir, K.W. Muir, D.S. Rycroft, D.W.A. Sharp, T. Solomun and H. Torrens, J.C.S. Chem. Comm., 1976, 291.

224. P.E. Skakke and S.E. Rasmussen, Acta Chem. Scand., 1970, 24, 2634.

225. H.J. Whitfield, J. Chem. Soc. (A), 1970, 113.

226. R.A. Walton, J. Chem. Soc. (A), 1967

227. E.W. Abel, R.P. Bush, F.J. Hopton and C.R. Jenkins, Chem. Comm., 1966, 58.

228. P.C. Turley and P. Haake, J. Amer. Chem. Soc., 1967, 89, 4611.

229. R.J. Cross, I.G. Dalgleish, G.J. Smith and R. Wardle, J. Chem. Soc. Dalton, 1972, 992.

230. E.W. Abel, G.W. Farrow, K.G. Orrell and V. Sik, J. Chem. Soc. Dalton, 1977, 42.

231. R.J. Cross, G. Hunter and R.C. Massey, J. Chem. Soc. Dalton, 1976, 2015.

232. R. Donaldson, G. Hunter and R.C. Massey, J. Chem. Soc. Dalton, 1974, 288.

233. G. Hunter and R.C. Massey, J. Chem. Soc. Dalton, 1976, 2007.

234. E.W. Abel and G.V. Huston, J. Inorg. Nucl. Chem., 1969, 31, 3335.

235. N.N. Greenwood and G. Hunter, J. Chem. Soc. A, 1962, 1520.

236. R.J. Cross, D.S. Rycroft, D.W.A. Sharp and H. Torrens, J. Chem. Soc. Dalton, 1980, 2434.

237. R.D. Baechler, J.P. Gasey, R.H. Gook, G.H. Senkler and K. Mislow, J. Amer. Chem. Soc., 1972, 94, 2859.

238. J.M. Lehn and J. Wagner, Chem. Comm., 1968, 1298.

239. W.N. Speckamp, V.K. Pandit, P.K. Korner, P.J. Van der Haak and H.O. Huismann, Tetrahedron, 1966, 22, 2413.

240. H.A. Bent, Chem. Rev., 1961, 61, 12.

241. J.D. Readio and R.A. Falk, J. Org. Chem., 1970, 35, 927.

242. F.A.L. Anet and J.M. Osyany, J. Amer. Chem. Soc., 1967, 89, 352.

243. W. Egan, R. Tang, G. Zon and K. Mislow, J. Amer. Chem. Soc., 1970, 92, 1442.

244. D.W.A. Sharp and H. Torrens, Rev. Soc. Quim. Mexico, 1979, 23, 183.

245. K.K. Bhasin, R.J. Cross, D.S. Rycroft and D.W.A. Sharp, J. Fluor. Chem., 1979, 14, 111.

246. T.H. Green, Ph.D. Thesis, University of Glasgow, 1975.

247. E.W. Abel, A.K. Shamsiddin Ahmed, G.W. Farrow, K.G. Orrell and U. Sik, J. Chem. Soc. Dalton, 1977, 47.

248. J.B. Lamber, "Topics in Stereochemistry", Vol. 6, J. Wiley, N.Y., 1971.

249. D.R. Rayner, A.J. Gordon and K. Mislow, J. Amer. Chem. Soc., 1968, 90, 4854.

250. A. Rauk, L.C. Allen and K. Mislow, Angew Chem., Inter. Ed., 1970. 9, 400.

251. H.D.K. Drew, G.H. Preston, W. Wardlaw and G.H. Wyatt, J. Chem. Soc., 1933, 1294; E.G. Cox, H. Saenger and W. Wardlaw, J. Chem. Soc. Dalton, 1934, 182.

252. B.E. Mann, P.M. Bailey and P.M. Maitlis, J. Amer. Chem. Soc., 1975, 97, 1275.

253. R.J. Cross, G. Hunter and R.C. Massey, J.C.S. Dalton, 1980, 2615.

254. D.L. Bobois, W.H. Myers and D.W. Meek, J. Chem. Soc. Dalton, 1975, 1011.

255. S.O. Grim, J.D. Gaudio, R.P. Molenda, C.A. Tolman and J.P. Jensson, J. Amer. Chem. Soc., 1974, 96, 3416.

256. R.B. King, J.A. Zinich and J.C. Cloyel, Jun., Inorg. Chem., 1975, 14, 1554.

257. W.R. Cullen, L.D. Hall and J.E.H. Ward, J. Amer. Chem. Soc., 1974, 96, 3442.

258. D.M. Adams, J. Chatt, J. Gerratt and A.D. Westland, J. Chem. Soc., 1964, 734; S. Mizugshima, I. Ichishima, I. Nakagawa and J.V. Quagliano, J. Phys. Chem., 1955, 59, 293.

259. J. Hilton and L.H. Sutcliffe, Prog. NMR Spec., 1975, 1, 27.

260. H. Torrens, Ph.D. Thesis, University of Glasgow, 1977.

261. G. Bor, Chem. Ber., 1963, 69, 2644.

262. K.M. Nicholas, M.O. Nestle and D. Seyferth in "Transition Metal Organometallics in Organic Synthesis", ed. H. Alper, Academic Press, New York, 1978, Vol. 2.

263. R.S. Dickson and P.J. Fraser, Adv. Organomet. Chem., 1974, 12, 323.

264. G. Vàradi and G. Pàlgi, Inorg. Chem. Acta, 1976, 20, 233.

265. G. Vàradi and G. Pàlgi, Chem. Abstr., 1977, 87, 201, 727.

266. A.B. Anderson, Inorg. Chem., 1976, 15, 2598.

267. E.W. Abel, Quart. Rev., 1963, 17, 142.

268. W. Hübel and E.H. Braye, J. Inorg. Nucl. Chem., 1959, 10, 250.

269. M. van Meershe, Ind. Chem. Belges, 1963, 28, 507.

270. J.F. Blount, L.F. Dahl, C. Hoogzand and W. Hübel, J. Amer. Chem. Soc., 1966, 88, 262.

271. R.P. Dodge and U. Schomaker, J. Organometal. Chem., 1965, 3, 274.

272. J.L. Boston, D.W.A. Sharp and G. Wilkinson, J. Chem. Soc., 1962, 3488.

273. R.S. Dickson and D.B.W. Yawney, Aust. J. Chem., 1967, 20, 77.

274. R.S. Dickson and D.B.W. Yawney, Aust. J. Chem., 1968, 21, 97.

275. W. Hübel, "Organic Syntheses via Metal Carbonyls", Vol. I. Eds. I. Wender and P. Pino, Interscience, New York, 1968, p.273.

276. F.L. Bowden and A.B.P. Lever, Organometal. Chem. Rev., 1968, 3, 227.

277. M.R. Wiles and A.G. Massey, J. Organometal. Chem., 1973, 47, 423.

278. C.H. Wei and C.F. Dahl, J. Chem. Soc., 1969, 91, 1351.

279. J. Knight and M.J. Mays, Chem. Comm., 1970, 1006.

280. M. Poliakoff and J.J. Turner, Chem. Comm., 1970, 1008.

281. F.A. Cotton and J.M. Troup, J. Amer. Chem. Soc., 1974, 96, 4155.

282. F.A. Cotton and D.L. Hunter, Inorg. Chim. Acta, 1974, 11, 119.

283. W.G. Proctor and F.C. Yu, Phys. Rev., 1951, 81, 20.

284. W. McFarlane, Chem. Comm., 1968, 393.

285. A. Von Zelewsky, Helv. Chim. Acta, 1968, 51, 803.

286. D.G. Gillies and D. Shaw, Ann. Rep. NMR Spectroscopy, 1972, 5, 557.

287. W. McFarlane, Ann. Rep. NMR Spectroscopy, 1972, 5, 353.

288. M. Green, J.A.K. Howard, A. Laguna, M. Murray, J.L. Spencer and F.G.A. Stone, J. Chem. Soc. Chem. Comm., 1975, 451.

289. W. McFarlane and R.F.M. White, Chem. Comm., 1969, 439.

290. P.L. Goggin, R.J. Goodfellow, S.R. Haddock, B.F. Taylor and L.R.H. Marshall, J. Chem. Soc. Dalton, 1976, 459.

291. W. McFarlane, J. Chem. Soc. Dalton, 1974, 324.

292. R.R. Dean and J.G. Green, J. Chem. Soc., A, 1968, 3047.

293. W. Freeman, P.S. Pregosin, S.N. Sze and L.M. Venanzi, J. Magnetic Resonance, 1976, 22, 473.

294. J.J. Pesek and W.R. Mason, J. Magnetic Resonance, 1977, 25, 519.

295. D.W.W. Anderson, E.A.V. Ebsworth and D.W.H. Rankin, J. Chem. Soc. Dalton, 1973, 2370.

296. S.J. Anderson, P.L. Goggin and R.J. Goodfellow, J. Chem. Soc. Dalton, 1976, 1959.

297. S.J. Anderson and R.J. Goodfellow, J. Chem. Soc. Dalton, 1977, 1683.

298. C. Brown, B.T. Heaton, P. Chini, A. Fumagalli and G. Longoni, J. Chem. Soc. Chem. Comm., 1977, 309.

299. D.S. Ryecroft, D.W.A. Sharp and H. Torrens, Rev. Soc. Quim. Mex., 1982, 26, 118.

300. J.A. Pople, Proc. Roy. Soc., 1957, A239, 341.

301. L.Manojlović-Muir, K.W. Muir and T. Solomun, Inorg. Chim. Acta, 1977, 22, 69.

302. A.L. Henne and W.G. Finnegan, J. Amer. Chem. Soc., 1949, 71, 298.

303. A.L. Henne and M. Nager, J. Amer. Chem. Soc., 1951, 73, 1042.

304. I.F. Totter and H.W. Thompson, J. Chem. Soc., 1946, 481.

305. T.H. Vaughn and J.A. Nieuwland, J. Amer. Chem. Soc., 1932, 54, 787.

306. D.D. Perrin, W.L.F. Armarego and D.R. Perrin, "Purification of Laboratory Chemicals". Pergamon, London, 1966.

307. Hanovia Photochemical Reactor Manual, Engelhard, Hanovia Lamps, 8.

308. R.L. Augustin, "Catalytic Hydrogenation", Marcel Dekker, Inc., New York, 1965, p148.