SYNTHESIS AND CHARACTERIZATION OF MOLECULES TO STUDY THE CONFORMATIONAL BARRIERS IN FLUOROCARBON CHAINS

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Fluorocarbons are known to be stiffer than their hydrocarbon analogues, a property that underlines the extensive industrial application of fluorocarbon materials. Although there has been previous studies on the rotational barrier of molecules having fluorocarbon centers, a detailed systematic study is necessary to quantify flurocarbon stiffness. The molecules, Pyrene-$(CF_2)_n$-Pyrene, Pyrene-$(CF_2)_n$-F, Pyrene-$(CH_2)_n$-Pyrene and Pyrene-$(CH_2)_n$-H were therefore synthesized to enable the determination of the barrier to rotation of the carbon backbone in fluorocarbons. Conformational studies will be completed with steady-state and time-dependent emission spectroscopy.

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I. INTRODUCTION

The extensive commercial development of fluoropolymers has been motivated by the physical and chemical properties of these materials. Fluorine being the most electronegative element and amongst the smallest elements, forms the strongest single bonds to carbon (bond dissociation energy is 485 kJ/mol) encountered in carbon chemistry. This strong covalent bond is accompanied by weak intermolecular forces in perfluorocarbons, as expected from the high ionization potential for fluorine and the low polarizability. Aliphatic carbon-carbon bonds are usually strengthened by fluorination and the carbon-fluorine bond lengths decrease progressively with accumulation of fluorines.

While the fluorine atom is smaller than carbon and very nearly isosteric with oxygen, the van der Waals radius for fluorine is more than 20% bigger than for hydrogen, so steric interactions between adjacent fluorines occur in perfluoroalkyl chains. The repulsive interactions between fluorines inhibit free rotation about the backbone carbon-carbon bonds. This last mentioned property of fluorocarbons is of active research interest and motivated this work. Conformational rigidity is manifested in bulk properties of materials, such as the glass transition temperature (T_g). The glass transition temperature is the temperature at which solid, glassy polymeric materials begin to soften and flow. It has been shown[1] that, at the same values of steric factor, the glass transition temperature values of fluoropolymers are higher than those of other polymers. A research program was initiated to study these repulsive interactions in terms of the flexibility of short simple perfluoroalkyl chains using steady-state and time-resolved emission spectroscopy. My contribution in this project was the syntheses of the molecules necessary for this study.

I.1 CONFORMATIONAL ANALYSIS

Van't Hoff was of the opinion that free rotation could occur around carbon–carbon single bonds owing to the lack of rotational isomers in compounds such as $ClCH_2CH_2Cl$ (**1**). The first chemist[2] to propose restricted rotation was Bischoff, who in 1890 suggested that the rotation was not free in ethane (**2**) and that ethane assumed a staggered conformation. In a 1930's paper studying dipole moments of stilbene dichlorides (**3**),[3] it was suggested that rotation about single bonds (other than biphenyl[4] bonds) was not free. This conclusion was supported by several other early 1930's investigations[5] of physical properties which led to speculation about the energy barrier to rotation about carbon-carbon single bonds. Kemp and Pitzer suggested in 1936 that there is a barrier to rotation in ethane[6] (**2**) on the order of 3 kcal/mol, which was in agreement with the calculations[7] of heat capacity and entropy based on statistical mechanics. In ethane, the transformation of a S_3 to a C_3 symmetry axis in attaining the eclipsed geometry induces a quadrupole polarization of the density in the C–C bond, causing it to lengthen. This lengthening leads to a decrease in the magnitude of the attractive interaction of each carbon nucleus for the electronic charge basin of the other carbon atom, and this is thought to be the origin of the barrier.[8]

Studies of β- substituted ethyl radicals[9] and of methylsilane[10] (**4**) provide evidence that, for molecules with small barriers, the hindered rotation may be due to variation in zero-point energy. Interactions between the non-bonded atoms of a molecule play an important role in determining conformational energies and geometries as well as barriers to internal rotation. The physical origins of such electromagnetic forces are:

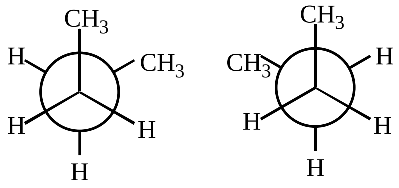
1) electrostatic contributions;

2) induction contributions;

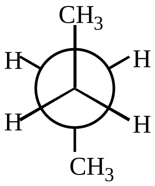
3) dispersion contributions.

Van der Waals[11] suggested that the potential energy function for the interaction between two rare gas atoms had a short range repulsive term arising partly from electron – electron repulsions and partly from the incompletely screened nuclei, and a long range attractive term arising from London dispersive forces. Energy of molecules that contain permanent charges or local dipole moments on the other hand depend on the interaction of these charges or dipoles with other charges or dipoles in the same molecule or in surrounding molecules. Thus, the effect of these electrostatic interactions depend on the conformation of the molecule as well as on the medium. The solvent dependence of conformational energies originates from the electrostatic contribution and a variation in the internal solvent pressure.

n–Butane (**5**) can have two staggered conformations, gauche and anti. The gauche methyl groups repel each other and therefore in butane the anti conformer is more stable by 0.97 kcal/mol,[12] with a barrier height of 3.3-3.6 kcal/mol.



gauche butanes



anti butane

The effects of fluoro substitution[13] in ethane (**2**) and methylsilane (**4**) have been shown, through use of the electrostatic model,[14] to be consistent with inductive transfer of electronic charge. Substitution of the first fluorine in ethane is postulated to produce a fixed-end transition density which, compared to that in ethane, is somewhat diffused about the protons and concentrated about the fluorine. In other words, the rotating protons see two unusually positive hydrogens and one unusually negative fluorine, leading to an increased barrier (4 kcal/mol). Upon substitution of the second fluorine, the rotating protons see one unusually positive hydrogen and two somewhat negative fluorines producing a lower barrier (1 kcal/mole).

Ethane fragments with electron pairs or polar bonds on adjacent carbons show a tendency to adopt the conformation with the maximum number of gauche interactions between the electron pairs and/or the polar bonds ---- an effect known as the gauche effect.[15] The enhanced gauche stability of 1,2-difluoroethane (**6**) (by 0.8 kcal/mol with a barrier of 3.0 kcal/mol) has been explained in terms of hyperconjugation,[16] or correlation effects.[17] The presence of two or more halogen atoms in the molecule make the conformational equilibria appreciably medium dependent as a result of electrostatic attractions.[18]

Conceptually, the energy with respect to rotation of any two groups of atoms A and B attached to the same framework is composed of three contributions[19] related to their orientation ω:

$$E\ (\omega_A,\omega_B)=E_A\ (\omega_A)+E_B\ (\omega_B)+E_{AB}\ (\omega_A\omega_B) \qquad (1)$$

E_A (ω_A) and E_B (ω_B) represent the interaction of the rotors A and B with the framework, whereas, E_{AB} ($\omega_A\omega_B$) is the through space-interaction between A and B.

Molecular Orbital Theory calculations[20] have shown that the potential function of internal rotation can be rationalized on the basis of three principal effects:

1) staggered arrangements of bonds are preferred;

2) the axis of a lone pair of orbital prefers to be coplanar with an adjacent electron-withdrawing polar bond or orthogonal to an adjacent lone pair orbital;

3) dipole moment components perpendicular to the internal rotation axis prefer to be opposed.

I.2 Conformational Studies on Hydrocarbons and Fluorocarbons

Although many of the fundamental ideas of conformations of molecules were developed in the 1920s and the 1930s, the real turning point in the application of modern experimental technology to the interrelationship between chain conformation and cyclization began in 1965, with the quantitative analysis of cyclization in poly (dimethylsiloxane)[21] (**7**). It was only in the 1970s that quantitative advances were made in understanding the factors affecting chain cyclization. These took the form of accurate measurement of ring closure reaction kinetics by Sisido[22] and by Mandolini and Illuminati, [23,24,25] application of photochemical and luminescent techniques by Winnik,[26] analysis of ring-chain polymerization equilibria by Semlyen,[27] and ESR studies by Shimada and Szwarc.[28,29,30] Conformational analysis of medium- and large-ring cycloalkanes was developed, essentially by the NMR studies of Anet[31] and the molecular mechanics calculations of Dale.[32] In the 1970s the field of cyclization dynamics originated with the work of Wilmenski and Fixman.[33]

In 1948 Pace and Aston reported their calorimetric and spectroscopic investigations on perfluoroethane[34] (**8**), motivated by the discovery of a rotational barrier in 1,1,1- trifluoroethane[35] (**9**) and 1,1,1- trichloroethane[36] (**10**) on the order of 3 kcal/mol, which raised serious doubts about the previously accepted theory explaining the rotational barriers as a function of the number of hydrogen atoms. Assuming a C−F bond distance of 1.35 Å and C−C bond distance as 1.45 Å,[37] a symmetry number of six for the molecule, they calculated the entropy due to translation and external rotation from

$$S_{t+r} = 4.575(3/2 \log M + 4\log T + 1/2 \log I_x I_y I_z - \log 6) + 265.289 \qquad (2)$$

The entropy contribution for the degree of freedom corresponding to the free rotation of the CF_3 group was obtained from

$$S_t = 4.575\,(1/2 \log T + ½ \log I_{red}.10^{-40} - \log n) - 1.540;\ n=3 \qquad (3)$$

Because of the presence of restricted rotation, the contribution S_f was reduced by an amount ($S_f - S$) as given by Pitzer's tables.[38] They obtained a potential barrier of 4350 calories per mole restricting the free rotation of the CF_3 group in hexafluoroethane (**11**).

They also observed only seven lines in the Raman spectra, indicating that the rotation was restricted.

In 1968, Weigert and Roberts reported ^{19}F NMR[21] studies to determine the effect of trifluoromethyl groups in the conformational populations and barriers to rotation in bis (trifluoromethyl)–tetrachloroethane (**12**). Using variable temperature NMR techniques, they demonstrated the slow rotation about a trifluoromethyl–carbon bond in a saturated compound.

In 1983 Ted Schaefer *et al*. had reported temperature dependent ^{19}F NMR studies on 2,6-difluoroisopropyl benzene[39] (**13**). They found that relative to hydrogen the fluorine substituents cause substantial increase in the barrier to internal rotation. They determined the signs of the stereospecific couplings, $^{4}J_{0}^{F, CH}$ using this method.

In a recent vibrational spectroscopic study of the temperature dependence of conformational properties on freon-122 (1,1-difluoro-1,2,2-trichloroethane)[40] (**14**) it was found that in both the gas and the liquid phases, the trans conformer was more stable by 330 ±70 and 320 ± 90 cal/mol. The first three coefficients in the Fourier expansion of the potential function for internal rotation were obtained by combining the vibrational frequency data with the conformational energy difference. The trans→ gauche barrier was 8.3 kcal/mol and the trans → trans was 5.1 kcal/mol.

I.3 Pyrene excimer mediated conformational studies

An excimer as defined by Birks[41]is a dimer which is associated in the electronic excited state and which is dissociative in its ground state. The formation of a pyrene excimer requires encounter of an electronically excited pyrene with a second pyrene in its ground state. According to this definition the two pyrenes must be sufficiently far apart, so that the incident radiation can cause 'localized excitation'. These locally excited molecules can give rise to 'monomer' emission. The observation of excimer emission indicates that diffusive encounters between pyrenes have occurred.

There are instances where excimer emission is observed although there are no evidence that the pyrenes are separated in the ground state. These excited species are sometimes referred to as 'static excimers' while those that obey Birks' definition are termed 'dynamic excimers'. Under normal conditions the distinction between static and dynamic excimers is that one can observe, in time-resolved experiments the growth of dynamic excimers while that of static excimers can't be observed. The (pre) associated pyrenes, as distinct from the pyrene excimers, are sufficiently close to exhibit perturbed absorption and excitation spectra.

Quantum mechanical calculations predict the resonance hybrid:[42]

$$\underset{(ER1)}{A^{*}A} \leftrightarrow \underset{(ER2)}{AA^{*}} \leftrightarrow \underset{(CR1)}{A^{+}A^{-}} \leftrightarrow \underset{(CR2)}{A^{-}A^{+}}$$

as a general formulation of the excimer state. Depending on the particular case either the neutral or the ionic configuration may predominate. Most of the calculations give only the excitation energy of the excimer as a function of its geometrical configuration. The latter itself and particularly the equilibrium distance between the planes of the two excimer compounds, can only be deduced from the agreement of calculated and experimental values for the position of the excimer band. Values around 3.24 Å were obtained in every pyrene case studied.

The charge resonance interaction (CR1- CR2) is usually treated as nearly isotropic and only moderately dependent on the distance, while the exciton resonance (ER1- ER2) interaction is polarized and has strong distance dependence. The exciton interaction is predominant in all aromatic excimers except benzene and its derivatives. Both interactions favor the sandwich structure of excimers since they yield the smallest distance between molecular centers.[43,44]

The emission characteristics of the excimers can either be studied in the steady-state, or in the time-resolved mode. In the steady-state analysis, the emission structure of the excimer is obtained after excitation at an absorption maxima for the species. The steady-state emission spectrum provides two parameters, the ratio, I_E/I_M, of the intensities of the excimer emission to that of the monomer emission, and λ_E, the wavelength corresponding to the maximum of excimer emission. In the time-resolved mode on the other hand, the evolution of the excited state is analyzed, by exciting the sample with an extremely short duration light flash. The excimer fluorescence intensity $i_E(t)$ is described in general terms by eq.18 (*vide infra*).

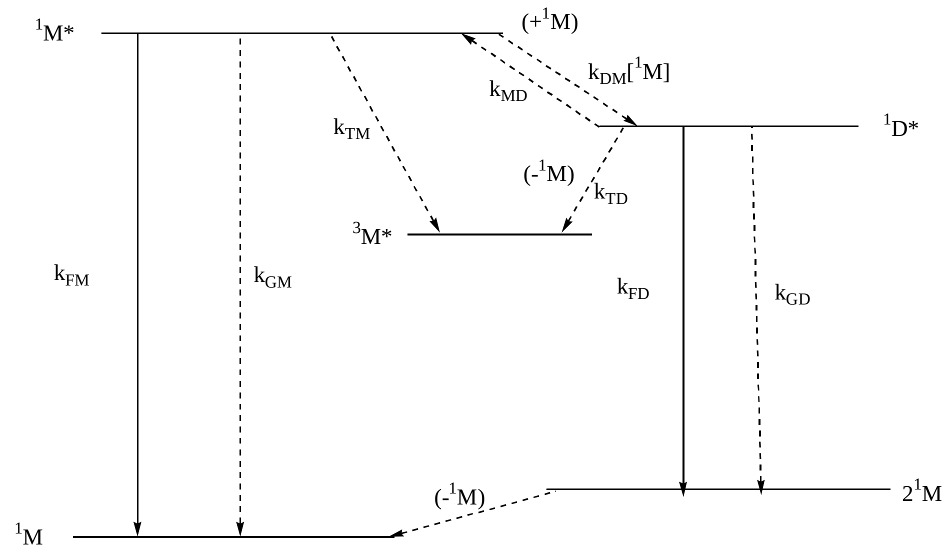


Figure1.1 Rate processes in monomer/excimer system.Solid lines indicate radiative processes; broken lines indicate radiationless processes.

If excimer formation proceeds via Birk's mechanism (fig. 1.1), when t=0 the excimer concentration is equal to 0. Therefore the excimer time-dependent emission profile will present a rising component, and a decaying component and the ratio of the pre-exponential factors in these two components will take a value of 1.0. The ratio deviates from unity when ground state-dimer formation is involved. In figure 1.1, depicting the excimer formation and dissociation processes, k_{FM} and k_{FD} are the fluorescence rates of the $^1M^*$ and the $^1D^*$ states respectively. The values k_{GM} and k_{GD} are the internal conversion rates to the ground state from the $^1M^*$ and the $^1D^*$ states. k_{TM} and k_{TD} are the respective intersystem crossing rates; k_{MD} is the dissociation to $^1M^*$ and the ^1M states of $^1D^*$ while $k_{DM}[^1M^*]$ is the rate of formation of $^1D^*$ from the $^1M^*$ and the ^1M states. Defining the following parameters simplifies the rate equations:

$k_M = k_{FM} + k_{TM} + k_{GM} = k_{FM}/q_{FM} = 1/\tau_M$ (4)

$k_D = k_{FD} + k_{TD} + k_{GD} = k_{FD}/ q_{FD} = 1/ \tau_D$ (5)

$X = k_M + k_{DM}[^1M]$ (6)

$Y = k_D + k_{MD}$ (7)

Where q_{FM} is the molecular fluorescence efficiency, defined as the ratio of the number of photons emitted by a system of molecules in dilute solution to the number of molecules excited into the first excited state, and may also be defined as:

$$q_{FM} = \int_0^\infty F(\nu)d\nu \tag{8}$$

F(ν) is the molecular fluorescence spectrum defined as the relative fluorescence quantum intensity at frequency ν. τ_M and τ_D are the radiative lifetimes of the molecular and the excimer species, defined as the reciprocal of the radiative transition probability k_M and k_D (in s^{-1}). For steady-state excitation with light of intensity I_0 einsteins l^{-1} s^{-1}, the rate equations are:

$$\frac{d[^1M^*]}{dt} = I_0 - (k_M + k_{DM}[^1M])[^1M^*] + k_{DM}[^1D^*] \tag{9}$$

$$\frac{d[^1D^*]}{dt} = k_{DM}[^1M^*][^1M] - (k_D + k_{MD})[^1D^*] \tag{10}$$

and under photostationary conditions $d[^1M^*]/dt = d[^1D^*]/dt = 0$, we have

$$\frac{[^1D^*]}{[^1M^*][^1M]} = \frac{k_{DM}}{(k_{MD} + k_D)} = K_e \tag{11}$$

and

$$\Phi_{FM} = \frac{k_{FM}[^1M^*]}{I_0} = \frac{q_{FM}}{1 + [^1M^*]/[^1M]_h} \tag{12}$$

$$\Phi_{FD} = \frac{k_{FD}[^1D^*]}{I_0} = \frac{q_{FD}}{1 + [^1M]_h/[^1M]} \tag{13}$$

$$K = 1/[^1M]_h = (k_D/k_M)K_e \tag{14}$$

$$\frac{\Phi_{FD}}{\Phi_{FM}} = \frac{k_{FD}}{k_{FM}} K_e[^1M] = K_1[^1M] \tag{15}$$

$[^1M]_h$ is the half value concentration at which $\Phi_{FM} = 0.5q_{FM}$. The parameter K is known as the Stern-Volmer coefficient of concentration quenching. In the pulse fluorometric technique of measuring the fluorescence lifetimes, the sample is excited by a δ-function light flash at $t = 0$, which generates an initial molar concentration $[^1M^*]_0$ of excited molecules; at a subsequent time t, the quantum intensity of molecular fluorescence is given by the molecular fluorescence response function i(t):

$$i_M(t) = k_{FM}[^1M^*] / [^1M^*]_0$$

$$= \{k_{FM}(\lambda_2 - X) / (\lambda_2 - \lambda_1)\}(e^{-\lambda_1 t} + A\, e^{-\lambda_2 t}) ; \tag{16}$$

$$A = (X - \lambda_1)/(\lambda_2 - X) \tag{17}$$

and the excimer fluorescence response function is:

$$i_D(t) = k_{FD}[^1D^*]/^1M^*]_0$$

$$=\{k_{FD}k_{DM}[^1M] / (\lambda_2 - \lambda_1)\}(e^{-\lambda_1 t} - e^{-\lambda_2 t}) \qquad (18)$$

where, $\lambda_{1,2} = ½[X+Y\mp\{(Y-X)^2 + 4k_{MD}[^1M]\}^{1/2}]$

The finite frequency response of a photomultiplier detector modifies the exciting light function p(t), to give the instrumental response function I(t). The response[41] $f_M(t)$ and $f_D(t)$ of a molecular system of fluorescence function $i_M(t)$ and the excimer response $i_D(t)$, excited by p(t) and observed by the same detector, is given by

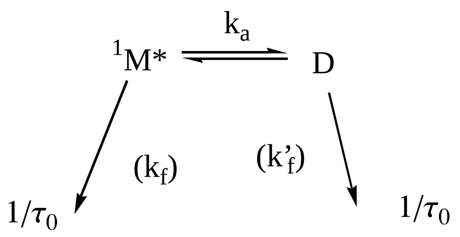
$$f_{M,D}(t) = \int_0^t I(t')\, i_{M,D}(t - t')dt' \qquad (19)$$

Since the initial report of Hirayama[45] in 1965, excimer formation in bichromophoric molecules and intramolecular exciplex formation between different groups at the end of short-chain molecules,[46] have been investigated at length to explore how the stereochemical constraints of the chain affect excimer and exciplex spectroscopies and, to derive conformational properties from changes in the excimer and exciplex spectra.

The most important experimental studies in the field of using the pyrene excimer formation to study end-to-end cyclization in polymers and terminally substituted alkanes was first developed by Zachariasse[47] and by Cuniberti and Perico.[48] Zachariasse examined intramolecular excimer formation in the molecules: pyrene- $(CH_2)_m$-pyrene (**I**), m=2-16, 22, 32. These molecules when electronically excited give the characteristic structured blue fluorescence of the locally excited pyrene chromophore. In this class of molecules (**I**), Zachariasse *et al.* did not observe any ground state interactions. In addition, they show the broad green structureless emission of pyrene excimer due to end-to-end cyclization. In the lowest energy configuration of the pyrene excimer, the two pyrene rings lie face-to-face in parallel planes. Distortion from this geometry destabilizes the excimer and results in hyposochromic (blue) shift of the excimer emission. Cuniberti and Perico[48] have used this technique to study cyclization dynamics (k_{cy}) of poly(ethylene oxide) (**15**).

Subsequent experiments by Cheung and Winnik have demonstrated that for poly(ethyleneoxide) (**15**), k_{cy} is inversely proportional to solvent viscosity as expected from the theory of diffusion controlled kinetics. Winnik[49] and co-workers have demonstrated that poly(ethyleneoxide) (**15**) chains and poly(dimethylsiloxane) (**7**) chains, comparable in length to those of polystyrene (**16**), cyclize faster. This emphasizes that k_{cy} measure the dynamic flexibility of polymer chains.

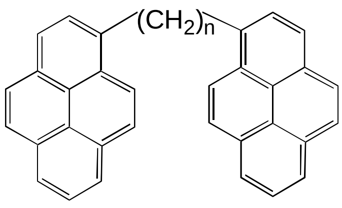
In their further investigations Zachariasse *et al*.[50] found that the fluorescence response functions of 1,3-di(2-pyrenyl)propane (**17**) in methyl cyclohexane can be fitted with two exponential decays having the same decay parameters for the monomer and the excimer. Further, in their studies with the corresponding 1-pyrenyl systems (**I**) they



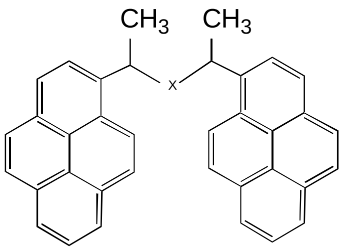
Scheme III

found that three exponentials were required to fit the data. They conclude that the different conformers of the propane chain act as a single kinetically uniform group in forming excimers. This signifies that the kinetic scheme[47] applicable to intermolecular excimer formation (SchemeIII) also explains intramolecular excimer formations.

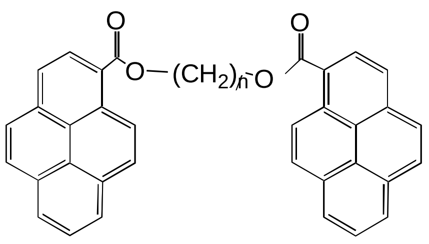
Excimer properties of a number of other short flexible chains linking two pyrenyl chromophores has been studied. When two identical chromophores are linked by three or more sp^3-carbons or by a C-O-C bond (**I**,[51] **II**,[52] **III**[53]) the conformational change of the



I

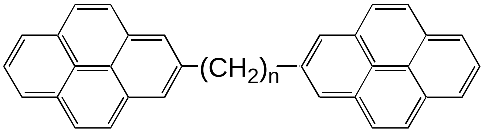


II

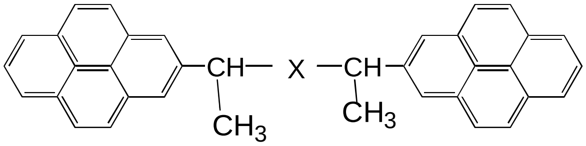


III

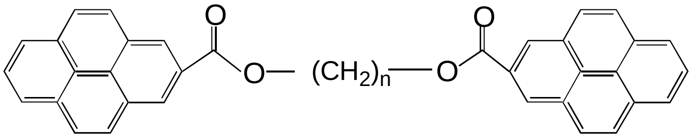
backbone chain is always faster than the excimer-forming step. Nonsymmetrically



IV

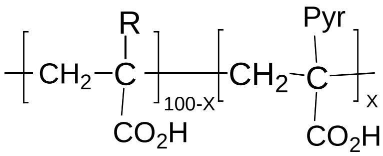


V



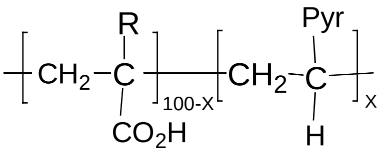
VI

substituted 1-pyrenyl derivatives exist in more than one rotamers and therefore can form more than one excimer. For the symmetrical 2-pyrenyl derivatives (**IV**,[46] **V**,[54] **VI**,[53]) all the rotamers are equivalent, forming spectroscopically indistinguishable excimers. Pyrene excimer formation studies have been developed into a very useful handle to study pH behaviour (**VII**,[55] **VIII**,[56] **IX**[57]) and cyclization kinetics (**X**,[58] **IX**[59]) of polymers.



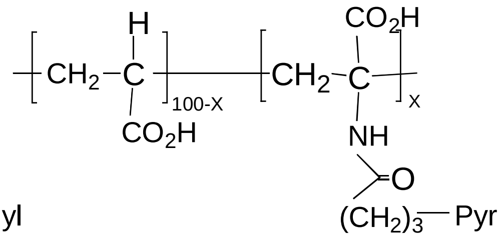
$$-\left[CH_2-\overset{R}{\underset{CO_2H}{C}}\right]_{100-X}\left[CH_2-\overset{Pyr}{\underset{CO_2H}{C}}\right]_X-$$

VII



$$-\left[CH_2-\overset{R}{\underset{CO_2H}{C}}\right]_{100-X}\left[CH_2-\overset{Pyr}{\underset{H}{C}}\right]_X-$$

IX

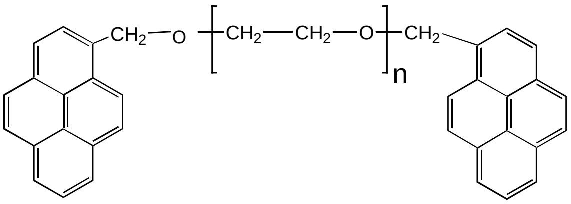


$$-\left[CH_2-\overset{H}{\underset{CO_2H}{C}}\right]_{100-X}\left[CH_2-\overset{CO_2H}{\underset{NH-C(=O)-(CH_2)_3-Pyr}{C}}\right]_X-$$

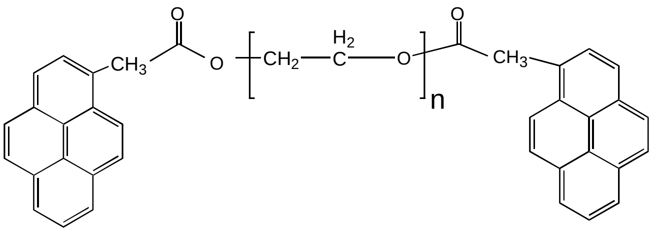
R = H, CH_3

Pyr = 1-Pyrenyl

VIII



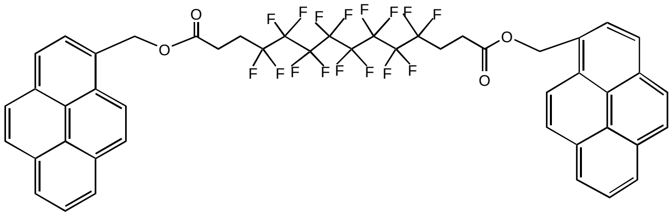
X



XI

Comparing the ^{1}H NMR chemical shift of the aromatic protons of 1,n-bis(2-pyrenylcarboxy)alkanes (**VI**) with n=1-16, 22 and 32, and that of 2-pyrenecarboxylic acid (**18**), Zachariasse *et al.*[50] were able to conclude that a ground state dimer was present for n=3-16, 22 and 32, a sandwich dimer for n>8, and a shifted symmetric dimer for n=3-8. With 1,n-bis(1-pyrenylcarboxy)alkanes, they found dimer formation for n=3-16, predominantly an asymmetric dimer, next to a symmetric one. They confirmed their conclusions by time resolved (picosecond) excimer fluorescence measurements. Measuring the relevant coupling constants they conclude that in pyrenylcarboxy as well as the dipyrenylalkanes, mutual through bond interactions exist up to n=8.

In 1990 Eaton and Smart, reported their studies on a perfluorooctane[60] (**19**) shown



(**19**)

above and its corresponding hydrocarbon (**20**). They observed both, the pyrene monomer as well as the excimer emission in the temperature range -10 °C to +50 °C. They did not observe any ground state interactions in either the hydrocarbon (**20**) or the fluorocarbon (**19**) over the concentration range 1×10^{-6} to 5×10^{-4} M. Further the total emission quantum yields and the first to third vibrionic emission bands were equal for the hydrocarbon (**20**) and the fluorocarbon (**19**). This led the authors to conclude that there were no unusual intramolecular effects due to the fluorocarbon chains' influence on the probe. Further the relative intensities of the excimer emission from the fluorocarbons was always weaker than the hydrocarbons.

Kinetics were compared at room temperature to show that the fluorinated compound (**19**) cyclized slower than the hydrocarbon models in various solvents. In addition, from the temperature dependence data of the monomer and the excimer emission, they determined that the activation barrier to cyclization for the hydrocarbons is 4.3 kcal/mol and for the fluororcarbon is 6.8 kcal/mol. Their data indicate that the rate constant and the kinetic barrier for end-to-end cyclization are significantly different for the partially fluorinated molecule (**19**) and its hydrocarbon analogue (**20**). The activation barrier difference was determined to be about 2.5 kcal/mol. The corresponding value for the perfluorethane (**11**) and ethane (**6**) in the gas phase is known to be 1.0 kcal/mole. The values for the higher homologues were not available for comparison. It was also observed that on increasing the solvent polarity, the rates of cyclization of the fluorocarbon (**19**) increased. This fact could not be explained satisfactorily due to lack of experimental data for the higher homologues of the perfluoroalkanes.

I.4 Studies on Perfluoroalkane chains using the Pyrene excimer emission properties.

Interest in fluorocarbon materials originate from their industrial use as high temperature resistant lubricants[61] and insulators.[62] These properties of fluorocarbons are thought to be due to the rotational barrier of the C-C bonds.[34] Whereas poly(ethylene) (**21**) adopts an extended zigzag conformation, poly(tetrafluoroethylene) (**22**) adopts a helical conformation[63] with a twist angle of 13-15° per C-C bond. All previous work on the conformational properties of fluorocarbons had studied the C-C bond rotation in molecules with one or more non-fluorine containing groups. Since the rotational barrier in fluorocarbons is thought to be considerably different from those in hydrocarbons, studying pure –CF_2– interactions in a perfluoroalkane chain would be extremely informative. Furthermore, the dynamic properties of chain conformation are of interest because that would influence the bulk properties of fluorocarbon materials. This is another aspect that has not been investigated in the earlier literature.

The current research objective is to study the conformational properties in perfluoroalkane chains comparing directly with the corresponding hydrocarbons. For this purpose, I synthesized the fluorophores of the general formula: **Pyr-(CF_2)$_n$-Pyr** (**XII**), with n=4, 6; **Pyr-(CH_2)$_n$-Pyr** (**I**), with n=2, 3; **Pyr-(CF_2)$_n$-F** (**XIII**), with n=4, 6; **Pyr-(CH_2)$_n$-H** (**XIV**), with n=2,4,6. Dimers **Pyr-(CF_2)$_n$-Pyr** (**XII**), with n=2,3 are currently being prepared in our group. Steady-state and time-resolved light emission measurements on the excimers of these di-pyrenyl (**XII**) systems as a function of the chain length n, solvent, and temperature will provide data to determine the barriers to rotation in the fluorocarbon chains. The corresponding fluorocarbon monomers (**XIII**) and the hydrocarbon analogues (**I**) and (**XIV**) are being studied as control compounds. At sufficiently low concentrations,[41] it can be assumed that intramolecular excimer formation is the major event taking place in the solution.

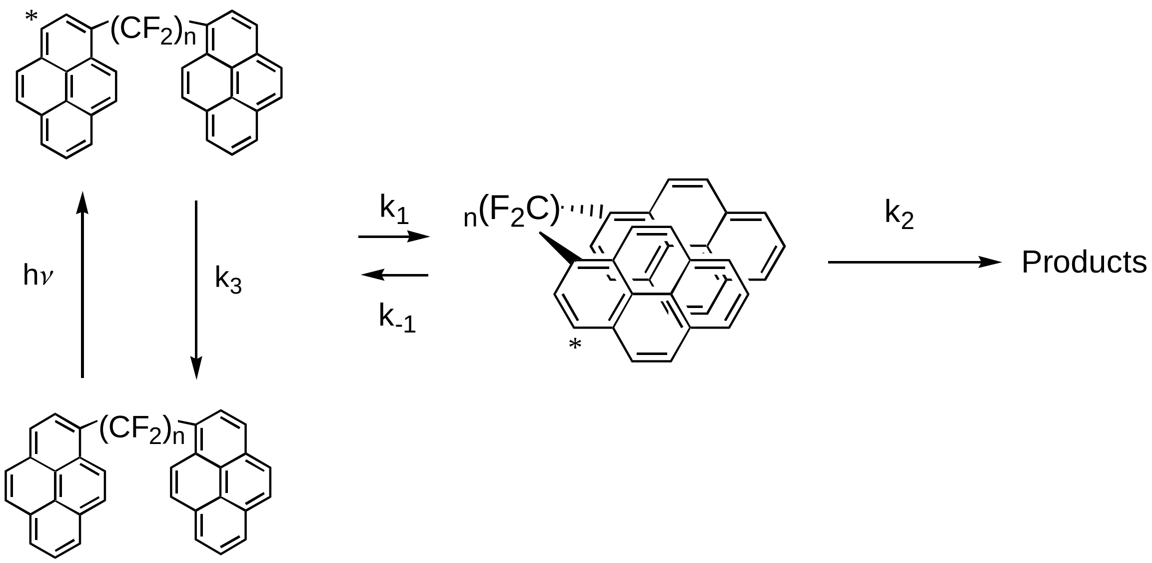


Figure I.2 Schematic of the cyclization kinetic process of (**XII**).

Low temperature NMR studies on these molecules (**1**) will also produce information about the conformational properties of fluorocarbons. Under transient conditions, the excimer formation kinetics of the di-pyrenyl systems (**XII**) can be represented as in figure I.2 above. If the excited state species decays as the sum of two exponentials with decay constants λ_1 and λ_2 when k_{-1} and k_2 are comparable in magnitude, and if k_3 is the sum of first order rate constants for decay of the excited species that does not lead to cyclization, then,

$$\lambda_{1,2} = \frac{1}{2} \{(X+Y) \mp [(Y-X)^2 - 4k_1k_{-1}]^{1/2}\} \qquad (20)$$

where, $X = (k_1 + k_3)$ and $Y = (k_{-1} + k_2)$

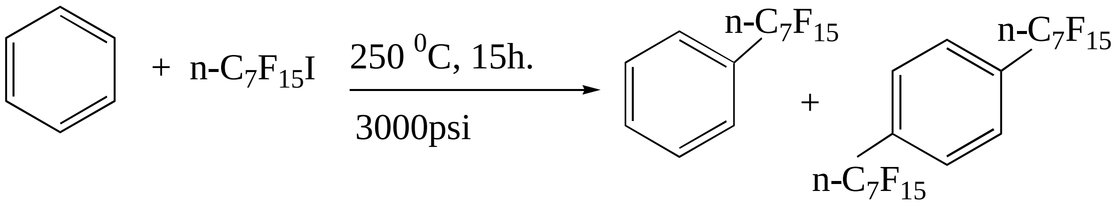
The reaction is diffusion controlled when $4k_1k_{-1}$ is much smaller than $(Y\text{-}X)^2$. This occurs when k_{-1} is small.

The excimer kinetics of a pyrene-perfluoroalkane-pyrene unit (**XII**) will depend to a very large extent on the perfluoroalkane chain's flexibility, since their conformation will dictate the rate at which the two pyrene moeities will be able to achieve the plane-parallel configuration. The $F_2C–CF_2$ bonds will have to rotate to attain the required conformation for the excimers to form and the required rotational angle per $–CF_2–$ decreases as the chain length increases. Therefore, studying an increasing number of $–CF_2–$ units linked between two 1-pyrenyl units, the excimer lifetime can be correlated to the number of $–CF_2–$ units and therefore deduce the rotational barrier introduced by each $–CF_2–$ group.

I.5 BACKGROUND OF THE SYNTHESES

With a few exceptions, fluorocarbon compounds do not occur in nature. Therefore the chemistry of fluorocarbons is almost entirely synthetic. However, selective functionalization of specific hydrogens remains challenging. Although there are a number of strategies for perfluoroalkylating an aromatic ring, the process also replaces all the ring hydrogens by fluorine. The fluoride-ion-induced nucleophilic polyfluoroalkylations on the other hand are facile only with activated polyfluoroaromatic systems. Thus, the real challenge lies in the controlled perfluoroalkylation of the aromatic rings.

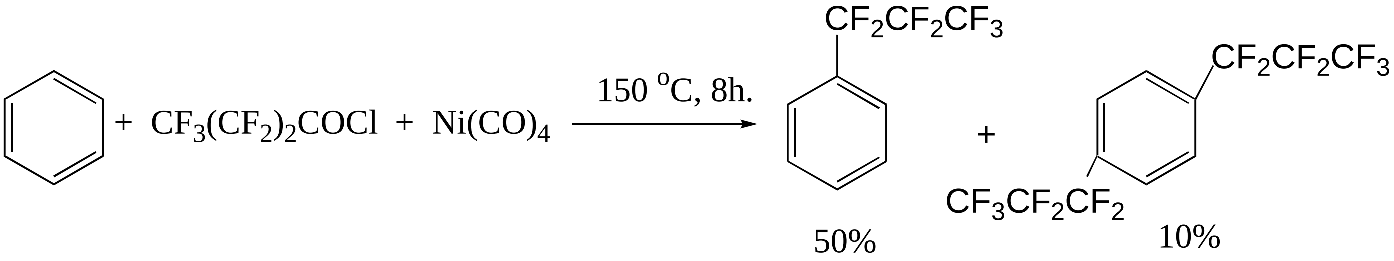
In the 1960s, several thermal procedures for incorporating perfluoroalkyl groups in aromatic systems evolved. The free-radical[64] processes of heating the aryl iodides and fluoroalkanes proved to be versatile. The following class of reactions was studied:



62% (**23**)   26% (**24**)

The scope of free-radical substitution of aromatic hydrogens are limited only by the stability of the aromatic compound under the reaction conditions. The yield in di-substitution was about 25%. Benzene, toluene, naphthalene, halobenzenes, perfluoroalkyl benzenes, benzonitriles, phathalic anhydride and organic dyes have been perfluorinated using this procedure. Using twice the amount of benzene, di-substitution was reduced to 8%, but mono-substitution was not improved concomitantly.

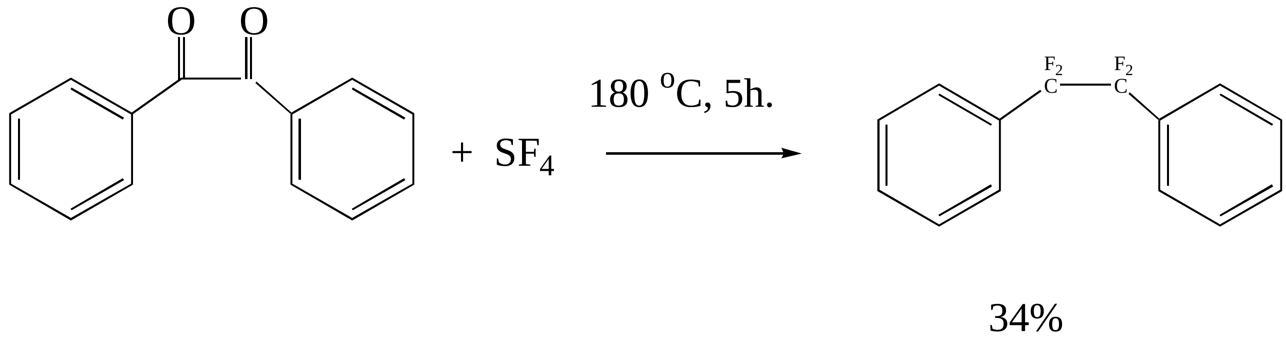
Drysdale and Coffman in 1960 reported a nickel carbonyl[65] catalyzed reaction of polyfluoroacyl chlorides with aromatic compounds. When polyfluoroacyl chlorides were heated with stoichiometric amounts of nickel carbonyl at the decarbonylation temperature (150 °C) of acyl groups, in an aromatic hydrocarbon medium, polyfluoroalkyl-substituted aromatic compounds were formed. Two moles of polyfluoroacyl chloride



(**25**) (**26**)

were consumed for each mole of fluoroalkyl product formed. Perfluoropropionyl chloride however gave heptafluoropropane as a co-product. Benzene, toluene, benzotrifluoride and bromobenzene were perfluorinated by this procedure. Yields varied from 30-80% upon varying the polyfluoroacyl group.

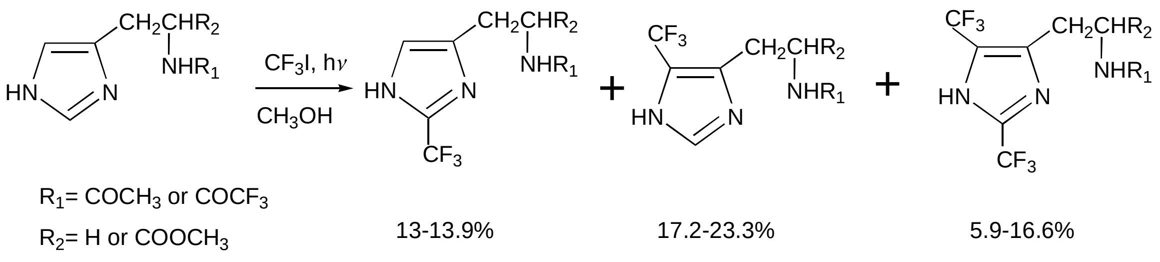
Engelhardt *et al.* in the same year found SF_4 to be an effective agent[66] for the selective replacement of carbonyl oxygen with fluorine. AsF_3, PF_5, TiF_4, BF_3 were found to catalyze the reaction efficiently by coordinating with the carbonyl oxygen thereby polarizing the carbonyl-oxygen bond. Ketones with α-hydrogens gave high yields. Acetone gave a 60% yield of 2,2-difluoro propane. Benzophenone was resistant to the uncatalyzed reaction, probably due to steric reasons, but gave diphenyl difluoromethane in the presence of catalytic amounts of BF_3, AsF_3 or TiF_4. Vicinal diketones, and polyketones, could also be used as substrates:



(27)

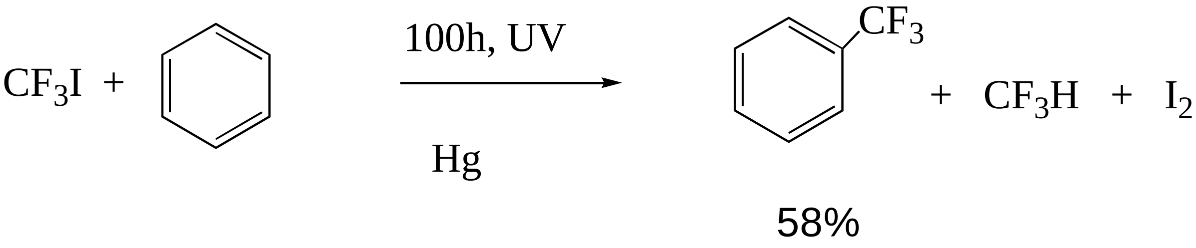
Phenylsulfur trifluoride,[67] a ligand that is easier to handle than the gaseous SF_4, has since been found also to fluorinate carbonyl derivatives.

Photochemical[68] and electrochemical[69] techniques of substitution have also been reported. Cohen *et al* reported[70] trifluoromethyl radical substitution on N-acyl histamines and N-acyl histidine esters. The trifluoromethyl radical generated by UV radiation in methanol effects ring substitution at C-2 and at C-4. Small amounts of the 2,4-bis products were also obtained:



(28) **(29)** **(30)**

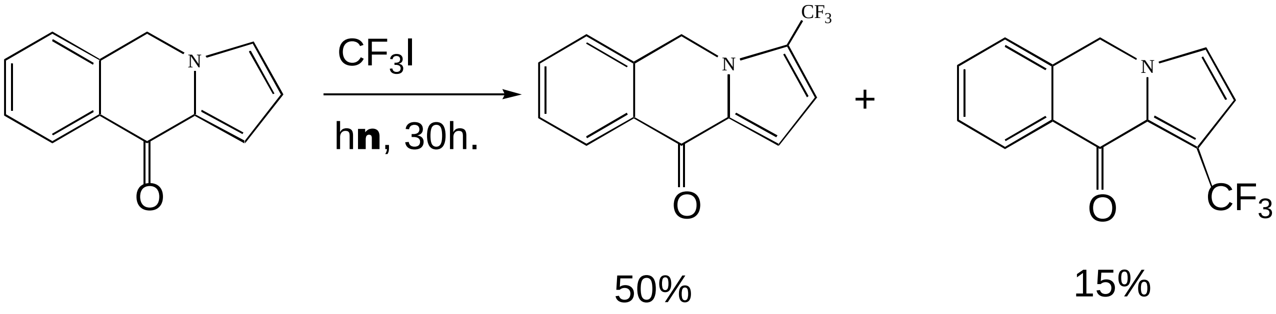
Another photochemical radical process has been reported[71] by Birchall *et al.* Irradiation of a 1:1 mixture of trifluoroiodomethane and benzene with UV light leads to a very slow reaction; fluoroform 39% and benzotrifluoride 58% are formed, the CF_3 radical is believed to be involved.



(**31**)

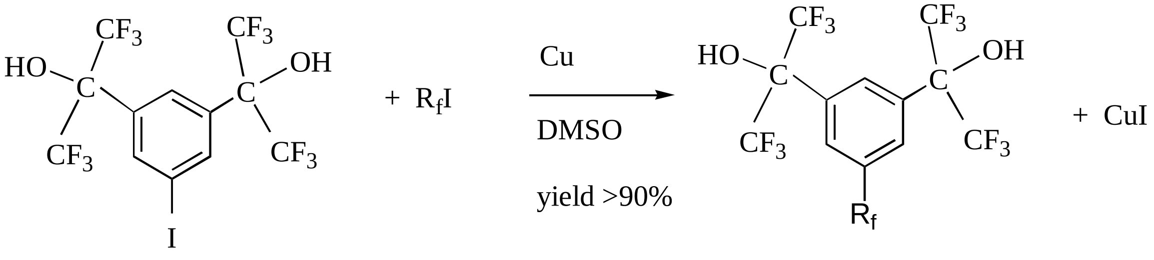
Recombination of the trifluoromethyl and iodo radicals, formed from the fission of the carbon-iodine bond gives rise to the low availability of CF_3 radical. Carrying out the reaction in Hg, effectively removed the iodide radical and lead to a much more convenient rate of generation of CF_3 radical.

Atkinson *et al.* in 1983 used the photochemical[72] method to introduce trifluoromethyl groups into a pyrrole ring by a very mild and general method:



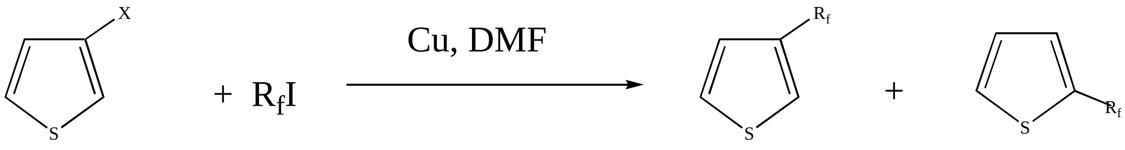
(**32**) (**33**)

Perhaps the best known method to prepare fluoroalkyl-substituted aromatic compounds is a copper-catalyzed[73] reaction between aryliodides and the iodofluoroalkanes. Soulen *et al.* used the reaction for the perfluoroalkylation[74] of substituted phenyls.



R_f : $CF_3CF_2CF_2$- (**35**), $CF_3(CF_2)_4CF_2$- (**36**), $CF_3(CF_2)_5CF_2$- (**37**), $CF_3(CF_2)_6CF_2$- (**38**), C_6F_5- (**39**).

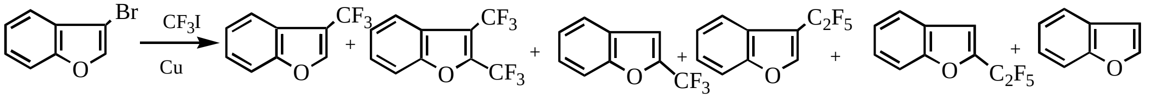
Leroy successfully employed the technique to perfluoroalkylate iodo-thiophenes.[75] When $R_f = CF_3$ and X= Br, no coupling product was obtained. The rearrangement of the product could be controlled by varying the leaving aryl halogen.



X = Br, I

$R_f =$ CF_3 (**40**) yield 17%
= n -C_4F_9 (**41**) 30%
= n - C_8F_{17} (**42**) 50%

Kobayashi *et al.* reported in 1980 their studies on the reaction of CF_3I and 3-bromobenzofuran using the copper-catalysis[76] method. They observed trifluoromethylation at positions without the Br. They postulated that the trifluoromethylation starts with the simultaneous attack by trifluoromethyl anion on the



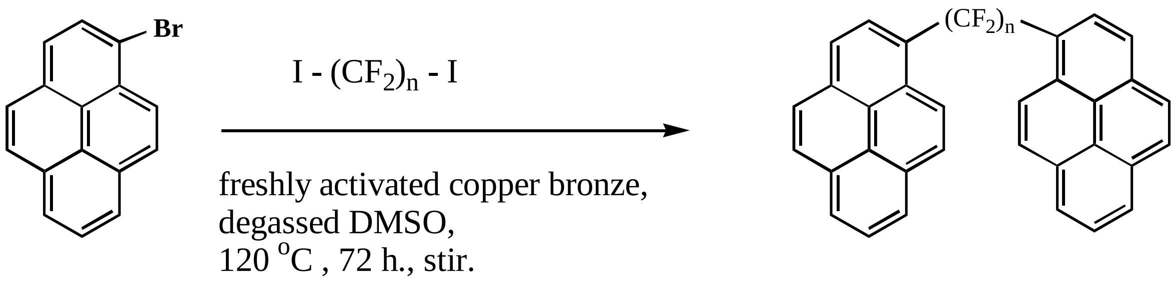
Pyridine:	9	45	27	9	9	trace
DMF:	66	0	11	9	14	trace
	(**43**)	(**44**)	(**45**)	(**46**)	(**47**)	(**48**)

halogenated carbon and by cuprous ion on halogen. If the reactivity of the aryl halide is low, trifluoromethyl copper can decompose completely to give cuprous fluoride and difluorocarbene. The latter can then react with another molecule of trifluoromethyl copper to give pentafluoroethyl copper, which then gives pentafluoroethyl compounds on reaction with aryl halides.

Ojima *et al.* in 1982 perfluoroalkylated substituted benzenes[77] (**49**) using the copper catalysed mechanism, in moderate to good yields. Employing the solvent DMSO almost always gave higher yields than DMF, collidine, pyridine, HMPA or triethylamine. Interestingly, perfluoroalkyl bromide gave similar yields in substitution on difunctionalised benzene. All previously reported perfluoroalkylations were specific with iodoperfluoroalkyls in these copper catalysed reactions.

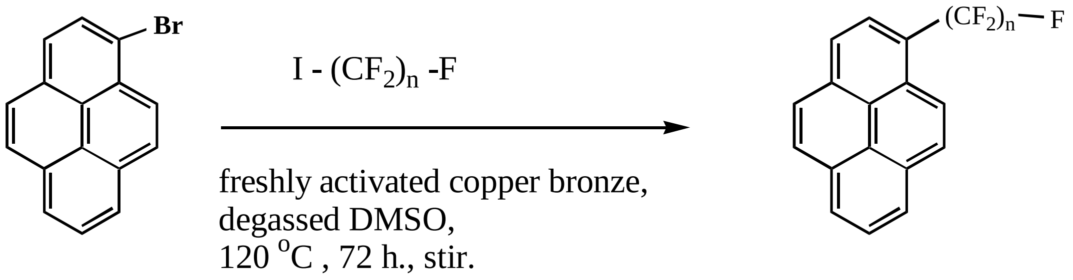
I.6 PRESENT WORK

A coupling reaction of 1-bromopyrene and the corresponding di-iodoperfluoro alkanes in presence of copper, (Scheme IV) was used to prepare the fluorocarbons (**XII**). Although in previous reports,[73,74] the aryliodides were preferred in the coupling reactions, our reactions worked equally well with the 1-bromopyrene, which was more easily available. The reactions proceeded to moderate yields in DMSO at 120 °C over 72hrs.



Scheme IV.

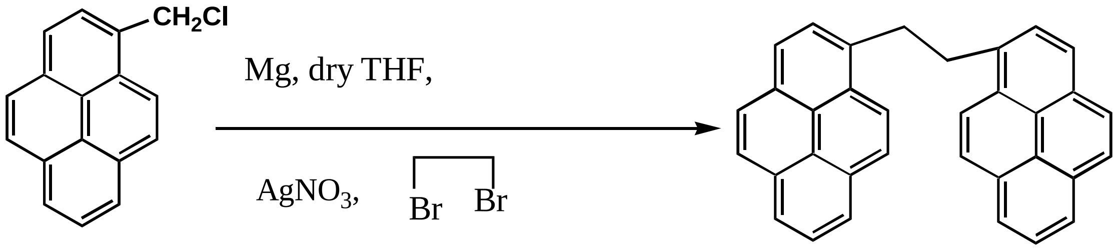
A similar strategy of coupling mono-iodoperfluoroalkanes with iodo- or bromopyrene was employed for the syntheses of the fluorocarbons (**XIII**), (Scheme V).



Scheme V.

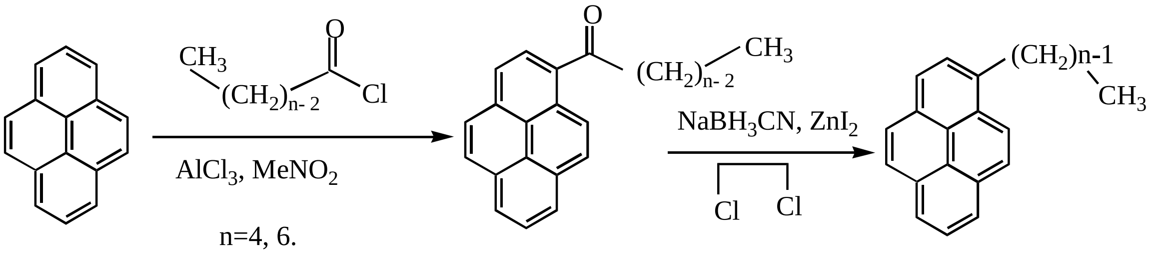
The copper bronze obtained from Aldrich was activated using the standard procedure.[78] It turned out that using freshly activated copper was crucial for the yields and purification in these reactions.

The Grignard coupling[79] reaction (Scheme VI) of 1-chloromethyl pyrene (**50**) in the presence of $AgNO_3$ generated the dimerized product (**51**).



SchemeVI.

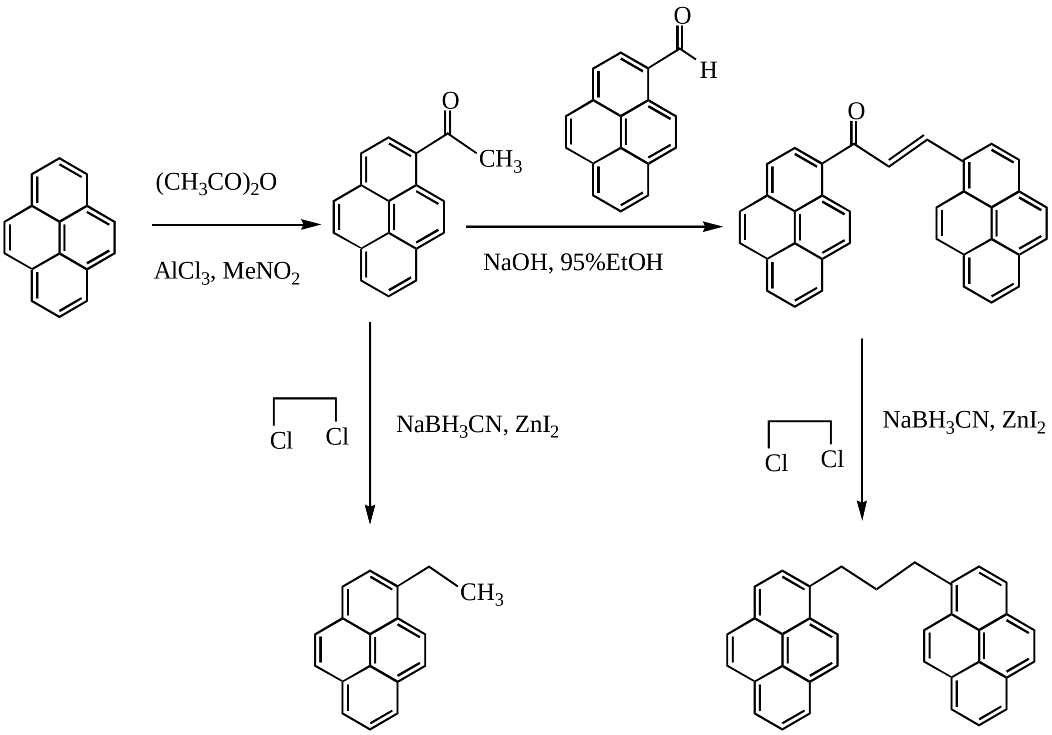
Although the hydrocarbons have been reported[47] previously, it was convenient to modify the procedures slightly. The Friedel-Crafts acylation of pyrene (Scheme VII) in the presence of $AlCl_3$, with the acyl chlorides gave the corresponding ketones, which could be reduced to the alkanes in high overall yields.



Scheme VII.

A similar Friedel-Crafts reaction with acetic anhydride reacted almost quantitatively to yield 1-pyrenyl methyl ketone (**52**) which was then used for two separate reactions (Scheme VIII). A simple reduction gave the monomer (**53**) with the two carbon chain; the Aldol condensation product (**54**) with pyrene-1-carboxaldehyde on reduction gave the dimer with the three carbon chain (**55**).

The $NaBH_3CN/ZnI_2$ system was used for reducing[80] the Friedel-Crafts acylated ketones. The reaction procedure involved was much simpler than the previously employed Huang-Minlon modification of the Wolff-Kishner modification.



Scheme VIII.

III. EXPERIMENTAL

The ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian Gemini 200 MHz Fourier transform spectrometer (chemical shifts are relative to tetramethylsilane) and the ^{19}F spectra were recorded on a Varian 300 MHz Fourier transform spectrometer, scan frequency 282 MHz, (chemical shifts are relative to fluorotrichloromethane) at the University of North Texas, Department of Chemistry NMR facility. The HREI mass spectra were obtained from Nebraska Center for Mass Spectrometry, University of Nebraska, Lincoln. The solvents pyridine and DMSO were dried by standard procedures[81] - pyridine by distillation from KOH and DMSO at reduced pressure over CaH_2.

Copper bronze obtained from Aldrich Chemicals Co. was activated freshly by the standard procedure ----- 1.00g copper bronze was treated with a 10% solution of iodine in dry acetone till the iodine colour of the solution faded off; the copper was then filtered and washed three times with a 1:1 solution of concentrated HCl and dry acetone, followed twice by acetone and dried overnight in a vacuum dessicator over calcium chloride.

The mono- and di-iodoperfluoroalkane starting materials were obtained from Lancaster Synthesis Inc. All yields were unoptimised. 1-Iodopyrene was synthesized by a Friedel Craft's reaction of pyrene with cyanogen iodide in the presence of $AlCl_3$ following a reported procedure.[59]

1-(chloromethyl)pyrene (50):

1-(1-pyrenyl)methanol (4g, 17.2mmol) was stirred with thionyl chloride (3.2mL, 20mmol) in the presence of pyridine (1.4mL, 17.2mmol) in chloroform (300mL) for 6 hrs at room temperature followed by hydrolysis on ice to yield a deep reddish brown solution, which was then extracted with chloroform to give 1-(chloromethyl) pyrene (**50**). ^{1}H NMR ($CDCl_3$, δ ppm): 7.9-8.2 (m, 7H), 8.27-8.32 (br d, J = 10Hz, 2H), 5.24 (s,2H). ^{13}C NMR ($CDCl_3$, δ ppm): 44.75, 122.75, 124.73, 125.01, 125.65, 126.18, 127.29, 127.66, 128.02, 128.38.

1-[2-(1-pyrenyl)ethyl]pyrene (51, P2HP):

1-(chloromethyl) pyrene (**50**, 0.5g, 2mmol) was dissolved in dry THF (30mL) in a flame dried addition funnel and dibromoethane (1mL) was added to this solution. 5mL of this solution was then added on to magnesium fillings (0.25g, 10mmol) and $AgNO_3$ (0.032g, 0.2mmol) dissolved in dry THF (5mL) in a 100mL flame dried three necked flask fitted with a condenser under argon and the reaction initiated by warming. The successful initiation was indicated by evolution of gas from the reaction mixture and formation of a white precipitate. After the initiation, the heat source was set to a constant temperature of

60 ^{o}C and stirring started while the reagents were slowly added into the reaction vessel over 2 hrs. After completion of addition, the reaction mixture was allowed to stir overnight, during which the colour turned yellowish. The reaction mixture was filtered through a fritted funnel and the THF vacuum evaporated. **51** thus obtained was purified by column chromatography in silica gel (100% hexanes eluent).

^{1}H NMR ($CDCl_3$, δ ppm): 7.9-8.2 (m,7H), 8.27-8.32 (br d, J = 10Hz, 2H), 3.0 (s, 4H).

2-(1-pyrenyl)ethane-2-one (**52**)**:**

Pyrene (0.5g, 2.47mmol) was dissolved in degassed nitromethane (50mL) and acetic anhydride (**16**, 0.23mL, 2.47mmol) was added. The reaction mixture was cooled in an ice bath, $AlCl_3$ (0.66g, 4.9mmol) was added, and a dark solution formed. The reaction mixture was stirred at 70 ^{o}C (bath temperature) for 2 h, quenched with ice and 1mL conc. HCl. The reaction mixture had turned red. It was then extracted in chloroform and the pure 2-(1-pyrenyl)ethane-2-one (**52**) was obtained after a silica gel column chromatograph (100% hexanes eluent).

^{1}H NMR ($CDCl_3$, δ ppm): 7.8-8.2 (m,7H), 8.99-9.03 (br d, J = 9.9Hz, 2H), 2.8 (s, 3H).

1-(1-pyrenyl)ethane (**53, P2HH**)**:**

(1-pyrenyl)ethane-2-one (**52**, 0.217g, 0.9mmol), sodium cyanoborohydride (0.417g, 6.6mmol) and zinc iodide (0.427g, 2.2 mmol) were dissolved in 1,2-dichloroethane (50 mL) and stirred at room temperature for half hour to give **53**, purified by column chromatography in silica gel (100% hexanes eluent).

^{1}H NMR (CDCl$_3$, δ ppm): 7.97-8.36 (m,7H), 7.93-7.97 (br d, J = 8Hz, 2H), 3.41-3.56 (q, 2H), 1.57-1.65 (t,3H).

^{13}C NMR (CDCl$_3$, δ ppm): 16.5, 26.7, 124, 125.2, 125.6, 125.9, 126.2, 126.5, 126.6, 127.8, 128.2, 128.5, 130.2, 131.8, 132.0, 139.2.

1-[1-(prop-2-ene-1-one)pyrenyl]pyrene (**54**)**:**

(1-pyrenyl)ethane-2-one (**52**, 0.217 g, 0.9 mmol), and pyrene-1-carboxaldehyde (0.200 g, 0.9 mmol) were refluxed in 95% ethanol/water overnight, to give 1-[1-(prop-2-ene-1-one)pyrenyl]pyrene (**54**).

^{1}H NMR (CDCl$_3$, δ ppm): 8-8.35 (m,5H), 8.79-8.80 (br d, J=8.4 Hz, 2H), 9.94-9.96(br d, J=10 Hz, 2H), 7.88-7.89(br d J=20 Hz, 2H).

^{13}C NMR (CDCl$_3$, δ ppm): 123.8, 125.0, 126.1, 126.5, 127.0, 128.0, 129.0, 130.2, 131.5, 132.2, 137.0, 194, 142.5, 150.0.

1-[1,3-di-(1-pyrenyl)propyl]pyrene (**55, P3HP**)**:**

1-[1-(prop-2-ene-1-one)pyrenyl]pyrene (**54**, 0.150 g, 0.3 mmol) sodium cyanoborohydride (0.417 g, 6.6 mmol) and zinc iodide (0.427 g, 2.2 mmol) were dissolved in 1,2-dichloroethane (50 mL) and stirred at room temperature for a half hour to give **55**. **55** was purified by column chromatography in silica gel (100% hexanes eluent).

^{1}H NMR ($CDCl_3$, δ ppm): 8-8.25 (m,7H), 7.9-7.95 (br d, J=10 Hz, 2H), 3.45-3.55 (t, J=10 Hz, 4H), 2.39-2.56 (m,2H).

^{13}C NMR ($CDCl_3$, δ ppm): 33.7, 33.9, 123.8, 125.0, 126.1, 126.5, 127.0, 128.0, 129.0, 130.2, 131.5, 132.2, 137.0.

1-[1-(butane-1-one)]pyrene (**56**)

Pyrene (0.5g, 2.47mmol), butyryl chloride (0.26mL, 2.47mmol) and $AlCl_3$ (0.130g, 0.82mmol) were reacted in nitromethane (50mL) following the procedure for (**52**). The product 1-[1-(butane-1-one)]pyrene (**56**) was purified from a silica gel column (100% hexanes eluent).

^{1}H NMR ($CDCl_3$, δ ppm): 7.97-8.35 (m,5H), 8.54-8.60 (br d, J=10.5 Hz, 2H), 3.1-3.33 (t, 2H), 1.8-2.0 (m,2H), 1.0-1.2 (t, J=7 Hz,3H).

1-(1-pyrenyl)butane (**57, P4HH**)**:**

1-[1-(butane-1-one)]pyrene (**56**, 0.217g, 889mmol), sodium cyanoborohydride (0.417g, 6.6 mmol) and zinc iodide (0.427g, 2.2 mmol) was dissolved in 1,2-dichloroethane (50 mL) and stirred at room temperature for 1/2 h. to give **57** purified by column chromatography in silica gel (100% hexanes eluent)..

^{1}H NMR ($CDCl_3$, δ ppm): 7.9-8.3 (m, 7H), 7.82-7.88 (br d, J=12 Hz, 2H), 3.13-3.27 (t, J=7.35 Hz, 2H), 1.05-1.1(t, J=11 Hz, 3H).

1-[1-(hexane-1-one)]pyrene (**58**)**:**

Pyrene (0.5g, 2.47mmol), hexanoyl chloride (0.35mL, 2.47mmol) and $AlCl_3$ (0.130g, 0.82mmol) were reacted in degassed nitromethane (50mL) following the procedure for **52**. 1-[1-(Pentane-1-one)]pyrene (**58**) was obtained after a column chromatographic purification in silica gel (100% hexanes eluent).

^{1}H NMR ($CDCl_3$, δ ppm): 8.1-8.35 (m, 7H), 8.85-8.89 (br d, J=8 Hz, 2H), 3.19-3.25 (t, J=6 Hz, 2H), 1.8-1.95 (m, 2H), 1.39-1.42 (m, 4H), 0.89-0.95 (t, J=7 Hz, 3H).

1-(1-pyrenyl)hexane (**59, P6HP**)**:**

1-[1-(pentane-1-one)]pyrene (**58**, 0.217g, 889mmol), sodium cyanoborohydride (0.417g, 6.6 mmol) and 0.427g(2.2 mmol) of zinc iodide were reacted in 1,2-dichloroethane (50 mL) following the procedure for **52**, to give **59**, purified by column chromatography (100% hexanes eluent).

^{1}H NMR ($CDCl_3$, δ ppm): 7.98-8.25 (m, 5H), 7.86-7.91 (br d, J = 6 Hz, 2H), 8.31-8.35 (br d, J=8 Hz, 2H), 3.3-3.4 (t, 2H), 1.8-2.0 (m, 2H), 1.3-1.6 (m, 6H), 0.94-1.03 (t, 3H).

^{13}C NMR ($CDCl_3$, δ ppm): 14, 22.8, 29.2, 32, 33.5, 33.9, 122.9, 124.5, 124.6, 124.7, 126.0, 126.5, 126.6, 126.8, 128.4, 130.0, 131.1, 131.9, 137.2.

1-(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)pyrene (**60, P6FF**)**:**

A mixture of 1-bromopyrene (500 mg, 1.5 mmol), copper bronze (315 mg, 5 mmol) and 1-iodoperfluorohexane (668 mg, 1.5 mmol) in pyridine (4 mL) was heated for 24 hours at 85 °C under a positive pressure of nitrogen. It was then filtered through a short pad of celite and the resulting dark solution was chromatographed with chloroform. The fastest moving fraction was collected and it was rechromatographed using a precoated TLC plate (silica gel HLO 20×20 cm, 500 microns) eluting with 10 % ethyl acetate in hexanes upon which pure **60** was obtained (240 mg, 31 % with respect to 1-iodoperfluorohexane) as a yellow solid.

^{1}H NMR (CDCl$_3$, δ ppm): 7.85-8.20 (m, 7H), 8.40-8.50 (br d, J = 8.14 Hz, 2H).

^{13}C NMR (CDCl$_3$, δ ppm): 96.22, 124.88, 125.34, 125.69, 125.79, 125.83, 126.33, 126.96, 127.32, 127.86, 129.25, 130.87, 131.07, 131.26, 136.69.

^{19}F NMR (CFCl$_3$, δ ppm): -81.34, -103.38, -120.51, -121.99, -123.28, -126.71.

Mass (M/z): (HREI): $M^{+\cdot}$ = 520.0496 Calcd. For $C_{22}H_9F_{13}$ (520.0496).

1-(1,1,2,2,3,3,4,4,4-nonafluorobutyl)pyrene (61, P4FF):

Synthesis and purification of **61** was carried out as described earlier for **60** using 1-bromopyrene (500 mg, 1.5 mmol), 1-iodononafluorobutane (420 mg, 1.5 mmol) and copper bronze (315 mg, 5 mmol) in DMSO (4 mL). The yield was 48.8 % (95 mg) with respect to 1-iodononafluorobutane.

^{1}H NMR (CDCl$_3$, δ ppm): 7.9-8.1 (m, 7H), 8.3-8.55 (br d, J = 10.4 Hz, 2H).

^{19}F NMR (CFCl$_3$, δ ppm): -93.7, -111.5, -118.5, -131.8.

Mass(M/z): (HREI): $M^{+\cdot}$ = 420.0567, Calcd. For $C_{20}H_9F_9$ (420.0560)

1-[1,1,2,2,3,3,4,4,5,5,6,6,-dodecafluoro-6-(1-pyrenyl) hexyl]pyrene (62, P6FP):

Synthesis and purification of **62** was carried out as described earlier for **60** using 1-bromopyrene (500 mg, 1.5 mmol), 1,6-diiodoperfluorohexane (415.4 mg, 0.75 mmol) and copper bronze (315 mg, 5 mmol) in DMSO (4 mL). The yield was 37.9 % (200 mg) with respect to 1,6-diiodoperfluorohexane.

^{1}H NMR ($CDCl_3$, δ ppm): 7.95-8.30 (m, 14 H), 8.45-8.50 (br d, J = 10.4 Hz, 4H)

^{19}F NMR ($CFCl_3$, δ ppm): -103.02, -120.12, -121.28.

Mass (M/z): (HREI): Found $M^{+\cdot}$ = 702.1207 Calcd. for $C_{38}H_{18}F_{12}$ (702.1217).

1-[1,1,2,2,3,3,4,4-octafluoro-4-(1-pyrenyl)butyl]pyrene (63, P4FP):

Synthesis and purification of **63** was carried out as described earlier for **60** using 1-bromopyrene (500 mg, 1.5 mmol), 1,4-diiodoctafluorobutane (340.4 mg, 0.75 mmol) and copper bronze (315 mg, 5 mmol) in DMSO (4 mL). The yield was 33.4 % (150 mg) with respect to 1,4-diiodoctafluorobutane.

^{1}H NMR ($CDCl_3$, δ ppm): 7.9-8.3 (m, 14H), 8.3-8.4 (d, J = 8.4 Hz, 4H).

^{19}F NMR ($CFCl_3$, δ ppm): -100.717, -113.577.

Mass (M/z): (HREI): Found $M^{+\cdot}$ = 602.3, Calcd. For $C_{36}H_{18}F_8$ (602.1781)

III. DISCUSSION

III.1 Synthesis and characterization of the fluorocarbons

Although in previous reports,[73,74] the aryliodides were preferred in the perfluoroalkyl coupling reactions, my reactions worked equally well with the more easily available 1-bromopyrene. The work was initiated with 1-iodopyrene,[82] which was prepared by a Friedel-Crafts reaction of pyrene and cyanogen iodide in the presence of $AlCl_3$ as the Lewis acid catalyst. Later on, cyanogen iodide was no longer commercially available and I tried 1-bromopyrene instead. After getting reasonable results for P6FP (**62**), the rest of the scheme was executed with 1-bromopyrene.

1-bromopyrene and the 1,6-diiodoperfluorohaxane were reacted in a 2:1 molar ratio with five times excess copper in DMSO at 120 ^{o}C over 72 h. to give P6FP (**62**). The reaction proceeded to a moderate yield of 37.9% with respect to 1,6-diiodoperfluorohaxane, unoptimised. The product P6FP (**62**) was fully characterised using ^{19}F- and ^{1}H-NMR and Mass spectrometry. The three fluorine peaks at –103.02, -120.12, -121.28 ppm. correspond to the α-, β- and γ-CF_2 respectively. The molecule is symmetrical about the γ-CF_2. The ^{1}H NMR shows that the aromatic protons are shifted downfield from pyrene and a large (0.4ppm) downfield shift in the position of H2/H3 doublet, with respect to the other aromatic protons. The shift in the position of these protons is due to the inductive effect of the perfluoroalkyl group as well as its steric crowding which adds to the deshielding of the aromatic protons. The large coupling constant of 10.4Hz for this doublet, indicates ortho coupling; this also indicates that the substitution had occured at the desired 1-pyrenyl position. The HREI mass ion peak of 702.1207 was observed corresponding to the molecular ion. Other identified fragments included the peak with mass 251, which corresponds to the formation of pyreneCF_2 by benzylic fragmentation.

P4FP (**63**) was similarly prepared by reacting 1-bromopyrene with 1,4-diiodooctafluoro butane in 2:1 molar ratio with 5 mole equivalents of copper, in DMSO. Carrying out the reaction at 120 ^{o}C over 72 h. give a 33.4% yield of **63** with respect to 1,4- diiodooctafluoro butane**,** unoptimised. The molecule is symmetrical about the β-CF_2 group, which is evident from the observation of two fluorine peaks at -100.717 and –113.577 ppm, corresponding to the α- and β- CF_2, respectively. In the ^{1}H NMR the aromatic protons are shifted downfield from pyrene. A (0.4ppm) downfield shift in the position of H2/H3 doublet, with respect to the other aromatic protons, at 8.3-8.4ppm is due to the inductive and steric effects of the perfluoroalkyl group. A large coupling constant of 8.4 Hz. for this doublet indicates ortho-coupling and that the substitution had occured at the desired 1-pyrenyl position. The LREI mass ion peak of 602.3 was observed corresponding to the molecular ion. Other identified fragments included the peak with mass 251, which corresponds to the formation of pyreneCF_2 by benzylic fragmentation.

The mono-coupling reactions proceeded similarly but with a higher in the case of P4FF (**61**). Thus, on reacting 1-bromopyrene with 1-iodoperfluorohexane in a 1:1 molar ratio, in DMSO at 120 °C over 72 h. gave 31% P6FF (**60**). The fluorine NMR had six peaks, which were assaigned as: the α-CF_2 at –81.34, β-CF_2 at –103.87, γ-CF_2 at –120.51, δ-CF_2 at –121.99 and ω– CF_2 at -123.28 ppm, while the -CF_3 was the farthest upfield at –126.71 ppm. In the ^{1}H NMR, the aromatic protons are shifted downfield from pyrene. A (0.4 ppm) downfield shift in the position of H2/H3 doublet, with respect to the other aromatic protons, at 7.85 –8.20 ppm is due to the inductive and steric effects of the perfluoroalkyl group. The H2/H3 coupling was strong, 8.14Hz, indicating ortho-coupling. The HREI mass ion peak of 520.0496 was observed corresponding to the molecular ion. Other identified fragments included the peak with mass 251, which corresponds to the formation of pyreneCF_2 by benzylic fragmentation.

(**61**) was similarly obtained in a 48.8% yield on reacting 1-bromopyrene with 1-iodononafluorobutane in a 1:1 molar ratio, in DMSO at 120 °C over 72 h.. The α- CF_2 peak appeared at –93.7 ppm in the ^{19}F NMR and the –CF_3 peak appeared at –131.8 ppm while the β- and γ- CF_2 appeared at –111.5 and –118.5 ppm respectively. The H2/H3 coupling was of 10.4Hz and was shifted downfield with respect to the aromatic protons by 0.4 ppm. The HREI mass ion peak of 420.0567 was observed corresponding to the molecular ion. Other identified fragments included the peak with mass 251, which corresponds to the formation of pyreneCF_2 by benzylic fragmentation.

The melting points of all the fluorinated pyrenes were greater than 200 °C and the materials were stable and not sensitive to moisture or light.

From previous reports[77] on perfluoroalkylation of aromatic systems using the copper catalyzed method, it may be assumed that this reaction follows the radical pathway (Scheme IX). The theoretical yield for the mono-perfluoroalkylation (**XIII**) should not exceed 50% and di-substitution (**XII**) would lessen the yield. Under these considerations, the yields obtained were reasonable. Ojima *et al.'*s work also suggest that the direct reaction, at least involves an 'active species' other than a perfluoroalkylcopper species, which is probably generated prior to the formation of the perfluoroalkyl copper species.

$$2\ R_fX\ +\ 2Cu\ \text{(metal)} \longrightarrow 2\ R^{\cdot}_{f}\ +\ 2CuX \qquad \text{(a)}$$

$$R^{\cdot}_{f}\ +\ ArH \longrightarrow R_fArH^{\cdot} \qquad \text{(b)}$$

$$R_fArH^{\cdot} \longrightarrow R_fAr\ +\ H^{\cdot} \qquad \text{(c)}$$

$$H^{\cdot}\ +\ R^{\cdot}_{f} \longrightarrow R_fH \qquad \text{(d)}$$

$$2\ R_fX\ +\ 2Cu\ \text{(metal)} + ArH \longrightarrow R_fAr\ +\ R_fH\ +2CuX$$

$$2H^{\cdot} \longrightarrow H_2 \qquad \text{(e)}$$

Scheme IX. Possible Mechanistic Pathway for the Copper-coupling reactions.

To avoid forming the complex mixture of products on carrying out the reactions at the elevated temperatues, other solvents were tried. Pyridine is known[73,77] to give acceptable yields in these reactions at lower temperatures. I therefore tried the reaction of 1-bromopyrene with 1-iodoperfluorohexane to make **60.** The coupling was facile in pyridine, at lower temperatures of 85-95 ^{o}C, and the yield was comparable to that in DMSO. Using a 1:1 mixture of pyridine and HMPA did not alter the yields to a very large extent.

The reaction of 1,2-diiodotetrafluoroethane with 1-bromopyrene**,** to give 1-[1,1,2,2-tetrafluoro-2-(1-pyrenyl)ethyl]pyrene (**64, P2FP**) however was unsuccessful with the copper catalyzed method. The starting iodo-compond in this case is a lower boiling liquid (bp 120 ^{o}C), which could have adverse effect on the reaction yield. The reaction is presently being investigated by Dr.Debasis Chakraborty in the group.

The proton decoupled ^{13}C NMR showed very low intensity multiplets between 120-124ppm for the fluorinated carbons which could not be assigned to provide any useful information about the fluorocarbon chain. The pyrenyl carbons could however be assigned in the P6FF case. Characterization of these molecules therefore had to be based primarily on the ^{19}F-NMR, ^{1}H-NMR and the mass spectra. The observation of single fluorine peaks in the ^{19}F NMR for the $–CF_2$ units indicate that at 21 ^{o}C the geminal fluorines are equivalent and there is free rotation about the carbon-carbon bonds. Low temperature (-30 ^{o}C) ^{19}F NMR studies however failed to show any fluorine couplings. Lower temperature studies could not be carried out due to the current unavailability of a suitable solvent.

III.2 Synthesis and characterization of the hydrocarbons

The Grignard reaction of 1-bromopyrene with formaldehyde would have been a convenient route to generate the hydrocarbons sequentially. However, the dimerized product was isolated in this reaction. The excessive stability of the benzylic type carbocation involved is responsible for the facile dimerization of these intermediates. P2HP (**51**) was therefore generated by the Grignard self-coupling reaction of **50** at 60 ^{o}C, overnight, in the presence of $AgNO_3$ catalyst[79] which is known to catalyze these reactions. The reaction involved two steps: 1-(1-pyrenyl)methanol was converted to its chloride **50** by $SOCl_2$ in the presence of pyridine. The ^{1}H NMR showed the H2/H3 doublet shifted downfield by 0.1 ppm, with respect to the other aromatic protons with a very strong coupling constant of 10 Hz, characteristic of ortho-coupling. This is due to the inductive and steric effect of the chlorine atom. The methyl protons get downfield shifted by 2 ppm to 5.24ppm with respect to that in the starting alcohol. In the ^{13}C NMR spectrum, the methyl carbon peak is at 44.75 ppm, while the pyrene carbons are between 122.75 and 128.38 ppm. In the second step, **50** was self coupled under Grignard conditions. The ^{1}H NMR peak for the methyl protons now were at 3.0 ppm.

The Friedel-Crafts acylation of pyrene followed by reduction was a general procedure which gave three of the hydrocarbon monomers in satisfactory yields. With acetic anhydride the reaction was almost quantitative. Pyrene and acetic anhydride in 1:1 molar ratio were stirred at 70 ^{o}C, for 2 h. in nitromethane, with $AlCl_3$ (1.1 equivalent) as the catalyst to give **52** in 97% yield. Nitrobenzene was also tried as the solvent, but due to purificational problems, nitromethane was later used as the solvent in all the reactions. The ^{1}H NMR of showed the doublet shifted downfield with respect to the aromatic protons corresponding to the H2/H3 coupling at 8.99-9.03 ppm with a coupling constannt of 9.9Hz. The carbonyl group exerts an induction effect which is responsible for this deshielding. The reduction was also a very high yielding reaction in this case. 7 mole ratios of sodium cyanoborohydride and 3 mole ratios of ZnI_2 were added to **50** and stirred at room temperature to give the product **53** in 90% yield in 2 hours. The sodium cayanoborohydride is however best when added slowly in small fractions. The product **53** had the H2/H3 doublet shifted upfield (7.93-7.97 ppm), with a coupling constant characterristic of ortho-coupling, 8 Hz. This is explained by considering the +I effect of the aliphatic hydrocarbon chain as opposed to the electron withdrawing –I effect of the carbonyl and the CF_2 units. The triplet corresponding to the CH_3 protons were at 1.6 ppm while the CH_2 protons were a quartet at 3.45 ppm. The CH_3 carbon was at 16.5 ppm while the CH_2 carbon was at 26.7 ppm.

The pyrene acylation reactions with the acid chlorides were not so high yielding. In the case of **56**, pyrene and butyryl chloride were stirred in a molar ratio of 1:1 to give the desired product in 75% yield. The H2/H3 doublet shifted 0.2 ppm downfield with respect to the aromatic protons to 8.6 ppm with a coupling constant of 10.5 Hz. The methyl protons were a triplet with coupling constant of 7 Hz. at 1.0 ppm and the methylene protons were a multiplet at 1.8 ppm. The α-CH_2 was a triplet at 3.1 ppm. On reduction 7 equivalents of sodium cyanoborohydride and 3 equivalents of ZnI_2 the product **57** was obtained in 73% yield. **57** had the H2/H3 doublet shifted upfield (7.82-7.88 ppm), with a coupling constant characterristic of ortho-coupling, 12 Hz. This is explained by considering the +I effect of the aliphatic hydrocarbon chain as opposed to the electron withdrawing –I effect of the carbonyl and the CF_2 units. The triplet corresponding to the CH_3 protons were at 1.05 ppm while the α-CH_2 was a triplet at 3.1 ppm. Methylene protons were a multiplet at 1.8 ppm.

Pyrene and hexanoyl chloride were stirred in a mole ratio of 1:1 to give **58** in 75% yield. The H2/H3 doublet shifted 0.5 ppm downfield with respect to the aromatic protons to 8.86 ppm with a coupling constant of 8 Hz. The methyl protons were a triplet with coupling constant of 7 Hz. at 0.9 ppm and the β- methylene protons were a multiplet at 1.4 ppm and γ- methylene protons were a multiplet at 1.9 ppm. The α-CH_2 was a triplet at 3.2 ppm. On reduction with 7 equivalents of sodium cyanoborohydride and 3 equivalents of ZnI_2 the product **59** was obtained in 78% yield. **59** had the H2/H3 doublet shifted upfield (7.86-7.91 ppm), with a coupling constant characteristic of ortho-coupling, 6 Hz. This is explained by considering the +I effect of the aliphatic hydrocarbon chain as opposed to the electron withdrawing –I effect of the carbonyl and the CF_2 units. The triplet corresponding to the CH_3 protons were at 0.9 ppm while the α-CH_2 was a triplet at 3.3 ppm, the β- methylene protons were a multiplet at 1.9 ppm and γ- methylene protons were a multiplet at 1.5 ppm.

The Friedel-Crafts reaction was sensitive to the amount of the Lewis acid catalyst used. According to the literature, 1.1 equivalents of $AlCl_3$ gives best yields of the acylation reactions. I tried the reaction with varying amounts of the catalyst and found 0.3 equivalents to be the optimum amount. Excess $AlCl_3$ resulted in a black granular precipitate with no product formation. Further, the reactions had to be carried out under a constant flow of Argon, so that the evolved HCl could be purged. Cooling down the reaction mixture while the Lewis acid was added also gave a better control on the reaction. I used the $NaBH_3CN/ZnI_2$ system for reducing the Friedel-Crafts acylated products. This system could be equally efficient to reduce the ketones as well as the enone group. The reaction procedure involved was much simpler than the previously employed Huang-Minlon modification of the Wolff-Kishner reduction.

The aldol condensation in the case of (**54**) was a straight forward high yield reaction. **54** was made by a straightforward aldol coupling of **52** and pyrene-1-carboxaldehyde in a 1:1 molar ratio in 95% ethanol, under reflux conditons. The olefinic protons were observed at 5.39 ppm. The H2/H3 doublet was downfield shifted to 8.79-8.80 ppm and the H9/H10 protons to 9.94-9.96 ppm with respect to the aromatic protons due to the inductive and steric effects of the carbonyl group. The carbonyl carbon was observed at 194.2 ppm. While the olefinic carbons were observed at 142.5 and 150 ppm. Reduction with 7 equivalents of sodium cyanoborohydride and 3 equivalents of ZnI_2 afforded the final product **55.** **55** showed the H2/H3 protons as a broad doublet upfield shifted from the aromatic protons at 7.9-7.95 ppm due to the +I effect of the alkyl group. The aliphatic carbons were observed at 33.7 and 33.9 ppm.

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