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Halogenation effects on the conformational properties of alkanes

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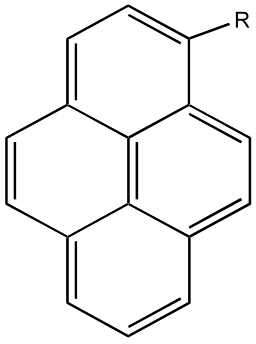
Abstract—The rotational barriers of the C–C bonds of halocarbons are believed to be rather different than those of hydrocarbons. We wish to systematically study the effect of halogen substituents on the conformational flexibility of hydrocarbons. As our initial approach to this problem, we have synthesized the following molecules: Pyrene–$(CF_2)_n$–Pyrene ($n=3$, 4, and 6) and Pyrene–$(CF_2)_n$–F ($n=4$ and 6). We describe here the concentration and temperature dependence of the emissive behavior of these materials.

Introduction. Fluorocarbons are important as high-temperature-resistant lubricants and insulators.[1] The exotic properties of these materials are thought to be due in part to the different rotational barriers of their C–C bonds compared to those of hydrocarbons.[2] Indeed the experimental barrier for rotation of CF_3–CF_3 has been reported to be 3.9 kcal/mol, while the corresponding barrier in ethane is 2.9 kcal/mol.[2] While investigations of perfluoro-*n*-butane have appeared,[2c] conformational investigations of other small-molecule perfluorocarbons or of substituted perfluorocarbon chains are scarce. We wish to understand the effect of halogenation of alkanes on conformational flexibility with an initial emphasis on perfluorinated alkanes. For this initial study, we have synthesized a series of fluorophores of the general formula: Pyrene–$(CF_2)_n$–Pyrene (**1**, $n=3$, 4, and 6). We have recently reported the detailed syntheses of these molecules.[3] Fluorocarbon monomers (**2**) were studied as control compounds.

Pyr-$(CF_2)_n$-Pyr (**1**), Pyr-$(CF_2)_n$-F (**2**)

The 1-pyrenyl system was selected as the fluorophore due to its rather long fluorescence lifetime. 1-Pyrenyl hydrocarbon excimers have previously been studied to obtain conformational information about the flexibility of hydrocarbon chains.[4] The effect of a fluorocarbon chain on pyrene-excimer formation was also previously studied[5] with a mixed hydrocarbon–fluorocarbon chain in between pyrene units; the pyrene units were attached via ester linkages. The temperature-dependent kinetics, obtained from single photon counting lifetime measurements, exhibited by the species with the mixed hydrocarbon–fluorocarbon chain were compared with an analog that had only a hydrocarbon chain; the comparison demonstrated that the rate constant is significantly slower and the kinetic barrier higher for end-to-end excimer formation for the partially fluorinated molecules than for the hydrocarbon analog. Our study features a series of homologous perfluoro-*n*-alkanes whose members do not contain the ester and hydrocarbon portions that were present in the earlier study.[6]

1-Pyr :



Synthetic methods. We used the protocols[3] described in our previous communication to prepare the necessary materials. Pyr-$(CF_2)_6$-Pyr (P6FP), Pyr-$(CF_2)_6$-F (P6FF), Pyr-$(CF_2)_4$-Pyr (P4FP), and Pyr-$(CF_2)_4$-F (P4FF) were prepared by copper-catalyzed reaction of α,ω-diiodoperfluoroalkanes with 1-bromo- or 1-iodohalopyrenes in either pyridine or DMSO; Pyr-$(CF_2)_3$-Pyr (P3FP) was prepared by decarboxylative arylation of hexafluoroglutaric acid with XeF_2 in the presence of pyrene.

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Conformational studies. Absorbance measurements: Ground-state interactions in the di-pyrenyl systems were probed in the 10^{-4} to 10^{-6} M concentration range in acetonitrile with absorbance spectroscopy; concentrations were chosen that mirrored those planned for the emission measurements. Absorbance measurements in this range indicated that Beer's law was followed for each of the di-pyrenyl cases, demonstrating that ground state pyrene complex formation is not important under the conditions chosen in this study.

Concentration dependence study: We next used steady-state emission spectroscopy to infer conformational information about our fluorocarbon systems. At 1×10^{-3} M, pyrene itself exhibits structured pyrene-localized emission (LE) with a maximum at about 374 nm (range: 360–425 nm) as well as a broad, structureless emission maximum at about 480 nm (range: 420–550 nm) in acetonitrile; the low-energy band has been assigned to intermolecular pyrene excimer emission (EE) and the EE/LE peak ratio is about 1. On decreasing concentration, the EE peak diminishes in intensity and the LE peak increases. 1-Methylpyrene exhibits similar photophysical behavior to pyrene in methylcyclohexane.[4a] At a concentration of 1.0×10^{-5} M, the peak height of emission due to EE is not distinguishable from the baseline and only LE is apparent (below 400 nm); upon increasing the concentration of 1-methylpyrene the EE band starts to become apparent at 480 nm. At 1.4×10^{-3} M, the EE/LE peak ratio is about 2.

The fluorinated monomers exhibit quite different behavior. At 2.2×10^{-3} M, no distinct emission at lower energy than LE is apparent for P6FF. Upon increasing concentration, however, a broad featureless band appears that is centered around 460 nm (Fig. 1).

We assign this band to EE. At 1.3×10^{-2} M the ratio of EE peak height to LE peak height is about 0.3. The behavior of P4FF is similar—emission from the excimer is only apparent at concentrations much higher than in the cases of either pyrene or 1-methylpyrene. We thus conclude that excimer formation is disfavored in the fluorinated systems compared to either pyrene or 1-methylpyrene. Since 1-methylpyrene does not exhibit similar inhibition of excimer emission, we ascribe the inhibition of excimer formation in the fluorinated species to be an electronic effect; thus the electronic effect of the fluorinated substituent both inhibits excimer formation and causes a blue-shift in the excimer emission upon comparison with unsubstituted pyrene.

The dimeric species, P3FP, P4FP, and P6FP, all exhibited appreciable amounts of both LE and EE emission at all concentrations studied. In all three cases, the ratio of peak heights varied much less than observed for the monomer species, P4FF and P6FF. P6FP, for example, exhibited a EE/LE peak height ratio of about 0.6 at 3.0×10^{-5} M and about 0.7 at 1.0×10^{-4} M (Fig. 1). Analogous to previous studies, this relatively small change in the peak ratio is due to predominantly intramolecular excimer formation; the increased ratio at higher concentration is due to some formation of excimer by intermolecular means.

It is clear that excimer emission in the spectrum of P3FP is intense and that excimer formation is especially

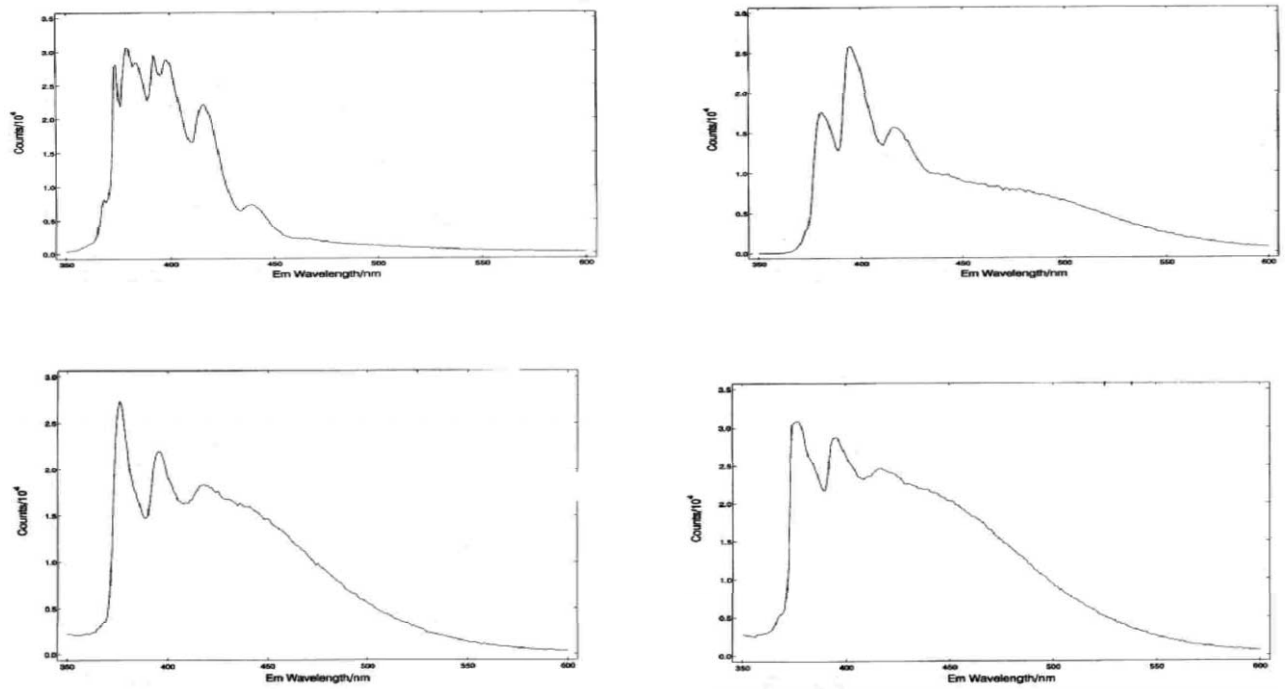

Figure 1. Steady-state fluorescence spectra of P6FF (2.2×10^{-3} M, top left and 1.3×10^{-2} M, top right) and P6FP (3.0×10^{-5} M, bottom left and 1.0×10^{-4} M, bottom right) in acetonitrile.

facile (Fig. 2); this is the only fluorinated case in which the monomer emission is almost absent. This parallels observations in the hydrocarbon series as the corresponding hydrocarbon exhibits similar behavior. Thus P3FP obeys the so-called Hirayama rule, which indicates that excimer formation is especially facile for short, 3-carbon chains. P4FP also clearly shows intramolecular excimer formation (Fig. 2).

The amount of excimer formed for P4FP and P6FP is apparently substantially less than in the corresponding hydrocarbons. The corresponding hydrocarbons have EE/LE peak height ratios of >2 at 1×10^{-5} M,[4] while P6FP and P4FP have corresponding peak height ratios of about 0.6 and 0.1 at this concentration at room temperature. This of course supports the notion that the fluorocarbon chains are stiffer than the hydrocarbon chains; however, since the excimer formation is apparently inherently disfavored in the fluorocarbon series this conclusion cannot be made based solely on this concentration dependence data. Accordingly, we next attempted a temperature dependence study to determine the barrier to intramolecular excimer formation directly.

Temperature dependence study: Due to excimer reversion, steady-state values of the EE/LE peak ratios at a single temperature cannot reliably be used to estimate the relative end-to-end excimer formation rates;[5,7] therefore, we conducted a temperature-dependence study to determine the kinetic barrier to intramolecular excimer formation, analogous to that of previous studies of pyrene excimers. We studied P6FP, P4FP, and P3FP in the region 10–50°C in acetonitrile (Fig. 2).

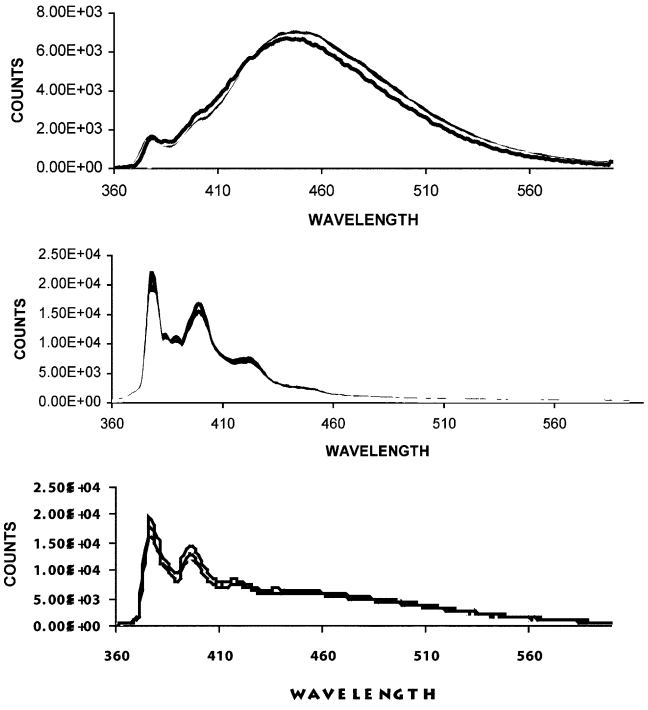

Figure 2. Steady-state fluorescence spectra of P3FP (top), P4FP (middle) and P6FP (bottom) at several temperatures in the range 10–50°C ($\lambda_{ex}=459$ nm in acetonitrile at 1×10^{-5} M).

Unlike the previous studies,[5,7] plots of $\ln(\text{Intensity}_{EE}/\text{Intensity}_{LE})$ versus $1/T$ were not linear in this temperature region (Fig. 3 is an example). This suggests more complicated kinetics for our systems, likely due to *significant* excimer reversion competing with EE. Apparently, the regime where excimer reversion is prohibited does not extend to the temperature range we were able to use in this study, unlike the behavior of pyrene dimers with hydrocarbon spacers or that with the mixed fluorocarbon/hydrocarbon spacer.[8] This is supported by our observation that excimer formation is unfavorable for the fluorinated pyrene compared with the hydrocarbon analogs (vide supra). The same electronic factors that disfavor excimer formation would also modulate the excimer lifetimes and shift the regimes where excimer reversion is prohibited. To understand the complete behavior of our systems, we are currently working on obtaining variable-temperature transient-fluorescence data.

Conclusion. To date, we have reached the following conclusions in our study: (1) excimer formation for the fluorinated pyrene monomers is highly dependent on concentration and less efficient than for pyrene; (2) excimer formation for the fluorinated pyrene dimers is efficient compared to the corresponding fluorinated monomers and it is much less dependent on concentration; (3) excimer formation for the fluorinated pyrene dimers P6FP and P4FP is less efficient than for corresponding hydrocarbon analogs based on relative peak intensities of EE versus LE; however, pyrene dimer P3FP exhibits excimer emission almost exclusively, much like its hydrocarbon analog, indicating that the three-carbon linker still leads to especially facile excimer formation even when perfluorinated; and (4) apparently the regime where excimer reversion is prohibited does not extend to the temperature range accessible to us for this study for the fluorinated dimers; thus, direct attachment of the fluorinated chain to the pyrene moiety significantly modulates the photophysics of the probe, requiring further measurements to obtain the rates and activation barriers for intramolecular excimer formation in our series.

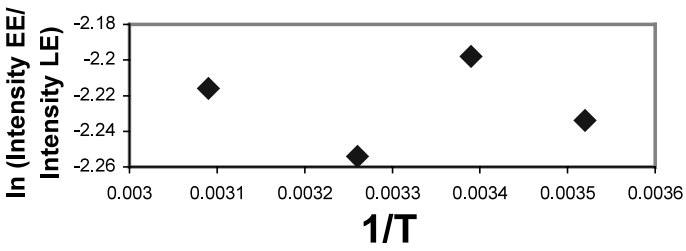

Figure 3. Plot of $\ln(\text{Intensity}_{EE}/\text{Intensity}_{LE})$ versus $1/T$ for P6FP.

Acknowledgements

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6. (a) Esters are well known to have intrinsic conformational preferences (*s-cis* vs. *s-trans*) with energy differences between conformers as high as 4 kcal/mol and corresponding rotational barriers as high as 10 kcal/mol.[6b] The electronic properties of the polar ester group could also influence the behavior of the mixed hydrocarbon–fluorocarbon species studied in 5; (b) Dale, J. *Stereochemistry and Conformational Analysis*; Verlag Chemie: New York, 1978; pp. 83–85.
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8. In the study by Eaton and Smart,[5] the pyrene moieties were sufficiently separated from the fluorocarbon-chain segment that the photophysics of the pyrene probe itself was apparently not altered. Unlike our systems, no intramolecular interactions between the fluorocarbon chain and the pyrene probe appear to be present in their materials.