oxygen (Mound Laboratories), the spectra revealed strong coupling to two ^{17}O nuclei (Figure 1b). The g values and ^{17}O hyperfine splitting parameters obtained by simulating the spectra (g = 2.039, 2.012, 2.003; $A_x(^{17}O)$ = 9.9, 6.1 mT)[16] agree well with those published for oleyl peroxyl radical (g = 2.035, 2.008, 2.003; $A_x(^{17}O)$ = 9.5, 5.9 mT).[17] Thiol peroxy radicals ($RSO_2^\bullet$)[18] and the superoxide anion[19] have very similar EPR parameters, but the difference between the ^{17}O hyperfine splittings of the two oxygen nuclei is significantly smaller in the former ($A_x(^{17}O)$ = 8.1, 6.4 mT) and negligible in the latter. The large (3.8 mT) difference we observe suggests that this spectrum represents an alkyl peroxyl radical, logically 13-dioxy-9,11-octadecadienoic acid.

Changes in the line shape and apparent hyperfine splittings begin to be seen as the temperature is raised through about 150 K (data not shown). In contrast, the spectra of 13-dioxy-9,11-*cis,trans*-octadecadienoic acid in a protein-free frozen matrix begin to show similar effects at about 110 K.[17] These spectral changes are thought to arise from the onset of both rotation about the C–O bond and molecular tumbling; thus, the peroxyl radical in the enzyme sample appears to be more conformationally constrained than that in the frozen matrix and probably is indeed bound to the enzyme.

After a few minutes at 4 °C, the sample recovers the visible and EPR spectra of the native ferric enzyme;[10] in particular, the spectrum of the peroxyl radical is no longer apparent. During this time, the intensities of the 585-nm absorption band and the peroxyl radical EPR spectrum decline in parallel. Treatment with more linoleic acid and oxygen regenerates both the purple color and the peroxyl radical signal. On the other hand, addition of 10 mM ethanol (known to bind in or near the active site of lipoxygenase[20]) eliminates the radical signal without affecting the intensity of the purple color. Thus, the purple state appears to be necessary but not sufficient for the existence of the radical.

The mechanistic origin and importance of the peroxyl radical are not certain. We hypothesize that it is either a trapped intermediate in the oxygenation pathway or the result of reduction of the active-site Fe^{3+} by endogenously produced 13-HPOD. The stability of the radical at 4 °C is inconsistent with its being an intermediate of the oxygenation reaction (reduction of an intermediate peroxyl radical must occur at a rate > k_{cat} > 200/s at 25 °C[21]) *unless* that reduction is driven by dissociation of the product hydroperoxide from the enzyme. In that case, the relatively high enzyme concentrations used in these experiments (in excess of 0.1 mM) may favor formation of the lipoxygenase–13-HPOD complex, which then may seek an equilibrium between Fe^{3+}–ROOH and Fe^{2+}–$ROO^\bullet$. The relatively high reduction potential of the active-site iron (≈0.6 V vs NHE) favors this possibility.[15] We are testing it by quantitation of the Fe^{3+} and peroxyl radical EPR signals as a function of enzyme and linoleic acid concentrations. If indeed this latter explanation is true, it will provide strong evidence for the existence of radical intermediates in the mechanism of fatty acid oxygenation by lipoxygenase.

Acknowledgment. We acknowledge the technical assistance of F. Wm. Barney.

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(16) The relative intensities of the features corresponding to splitting by the two oxygen nuclei were faithfully reproduced by assuming equal contribution by each nucleus. However, simulation of the relative intensities of the spectra from ^{17}O-enriched and natural-abundance peroxyl radicals required assuming approximately 25% ^{17}O enrichment, implying some contamination by unenriched oxygen either in the stock ^{17}O-enriched gas or during the experiment.

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Are Fluorocarbon Chains "Stiffer" Than Hydrocarbon Chains? Dynamics of End-to-End Cyclization in a C_8F_{16} Segment Monitored by Fluorescence

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Bending and folding of hydrocarbon chains has been probed by using fluorescence methods since the discovery by Hirayama[1] of the intramolecular excimer formation process in 1,3-diphenylpropanes. The dynamic flexibility of hydrocarbon chains depends upon the chemical type and length of the chain, the solvent or environment in which it is immersed, and the temperature.[2] Cyclizations of polymer chains have been examined by this method, especially using α,ω-dipyrenyl probes: poly(styrene),[3] poly(ethylene oxide),[4] poly(tetramethylene oxide),[5] poly(dimethylsiloxane),[6] and poly(bisphenol A–diethylene glycol carbonate).[7] Fluorocarbon polymers constitute an industrially important class of polymers whose properties are quite distinct from those of the hydrocarbon analogues.[8] We report kinetic data on a fluorocarbon and hydrocarbon pair of model compounds that show significant differences in the rates and kinetic barriers to cyclization between simple $-(CF_2)_8-$ and $-(CH_2)_8-$ chain segments.

The 18-atom-chain species bis(1-pyrenylmethyl) dodecanedicarboxylate (**1**)[2d] and analogue **2** [1,8-bis[[(1′-pyrenylmethoxy)carbonyl]ethyl]perfluorooctane] containing a C_8F_{16} core in the center of the molecule were prepared by dicyclohexylcarbodiimide coupling of 1-pyrenylmethanol with the corresponding hydrocarbon and fluorocarbon diacids. Monopyrene-containing model compounds **3** and **4** were obtained similarly from the monomethyl ester acids. Steady-state fluorescence spectra[10] of **1** and **2** in 2-methyltetrahydrofuran (MeTHF) at various temperatures in the range −10 to +50 °C (λ_{ex} = 340 nm) are shown in Figure 1. Several features are notable. First, at all temperatures, both structured pyrene-localized emission (LE) at short wavelength (370–425 nm) and broad, structureless emission

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(8) In contrast to the extended zigzag conformation of poly(ethylene), for example, poly(tetrafluoroethylene) adopts a helical conformation with a twist of 13–15° per C–C bond.[9a,b] This helical conformation for $-(CF_2)_n-$ chains also persists in monolayers[9c,d] and in the gas phase.[9e]

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(10) Fluorescence spectra were taken on a SPEX Fluorolog 222 or 212 spectrofluorimeter with photon counting detection and are corrected. Excitation spectra were measured by using a quantum counter (rhodamine B in glycerol) to correct for intensity variations on the lamp (450-W xenon arc). Samples were degassed by argon sparging.

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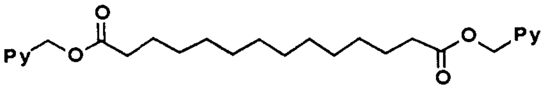

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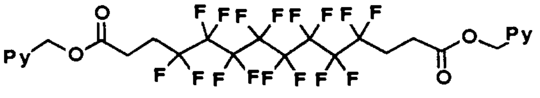

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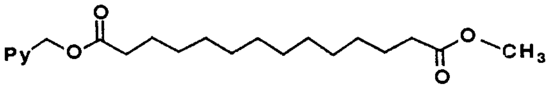

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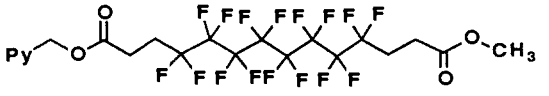

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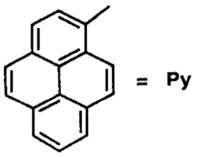

characteristic of the intramolecular pyrene excimer (425–600 nm) (EE) are observed. Absorption spectroscopy reveals no ground-state interactions in either **1** or **2**, and Beer's law is obeyed over at least the concentration range 10^{-6} to 5×10^{-4} M. The ratios of the intensities of the first and third vibronic emission bands (I_1/I_3) are equal in both **1** and **2** (e.g., 1.55 for **1**, 1.59 for **2** in CH_2Cl_2), and the total emission quantum yields are also nearly equal (e.g., $\phi_t = 0.64$ for **1**, 0.59 for **2** in CH_2Cl_2) and relatively independent of solvent (CH_2Cl_2, 2-MeTHF, CH_3CN). In addition, the emission properties of the monopyrene model compound **4** are not substantially different from those of hydrocarbon **3**. We take these facts as evidence that no unusual intramolecular effects attributable to the fluorocarbon chain influence the photophysics of the probe. Second, the relative intensity of excimer emission in fluorinated **2** is at all temperatures lower than that in hydrocarbon **1**. Quantum yields of emission and other relevant spectral features are listed in a supplementary table for compounds **1-4**.

Time correlation single photon counting methods[11] were used to determine emission lifetimes of **1-4** in CH_2Cl_2, MeTHF, and CH_3CN at room temperature. Emission decays of **1** and **2** follow the form of eqs 1 and 2[12] over at least 2.5 decades of decay, which indicates that exciplex formation is reversible for both bichromophoric systems, though the degree of reversibility is small (less than 10%). To calculate rates of cyclization from this data, we have assumed that the observed lifetimes of **3** and **4** represent inherent LE emission processes applicable to **1** and **2**. Rate constants for excimer formation derived from this treatment, associated with end-to-end cyclization (k_c), are collected in Table I.

$$I_{LE}(t) = A_1 \exp(-\lambda_1 t) + A_2 \exp(\lambda_2 t) \qquad (1)$$

$$I_{EE}(t) = A_3 \exp(-\lambda_1 t) + A_4 \exp(\lambda_2 t) \qquad (2)$$

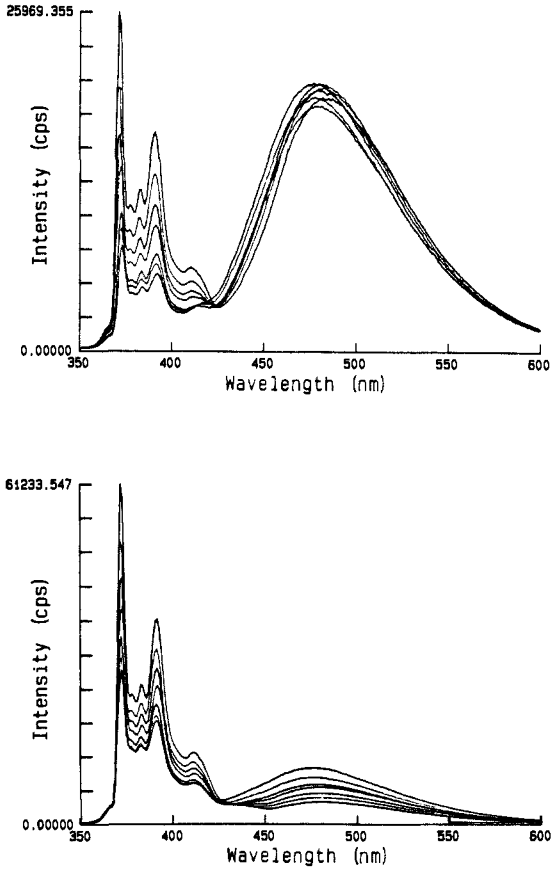

Figure 1. Steady-state fluorescence spectra at several temperatures in the range −10 to +50 °C (λ_{ex} = 340 nm) of **1** (top) and **2** (bottom) in methyltetrahydrofuran (5×10^{-6} M).

Table I. End-to-End Cyclization Rates for **1-4**[a]

solvent	compd	k_c, s^{-1}	k_c^F/k_c^H
CH_2Cl_2	1	1.7×10^8	0.13 ± 0.07
	2	2.1×10^7	
MeTHF	1	1.31×10^8	0.20 ± 0.05
	2	2.7×10^7	
CH_3CN	1	3.7×10^8	0.30 ± 0.06
	2	1.1×10^8	

[a] Rate constants obtained from single photon counting lifetimes fitted to eqs 1 and 2. Lifetimes and fitting parameters are available as supplementary material.

Since excimer reversion occurs to a small extent in these systems, steady-state values of the ratio I_{EE}/I_{LE} cannot be reliably used to estimate k_c^F/k_c^H; however, the temperature dependence of this ratio can be used to estimate the kinetic barrier (E_a) to cyclization.[13] Plots of ln (I_{EE}/I_{LE}) vs $1/T$ are linear in the region −10 to +50 °C in MeTHF, and we calculate E_a(obsd) = 4.3 kcal/mol for **1**[14] and 6.8 kcal/mol for **2**.

Our data indicate conclusively that the rate constant and the kinetic barrier for end-to-end cyclization are significantly different for the partially fluorinated molecule **2** and its hydrocarbon analogue **1**. The activation barrier difference between **1** and **2** is about 2.5 kcal/mol, which compares to the 1.0 kcal/mol difference in rotational barriers for perfluoroethane vs ethane in the gas phase.[15,16] Our data therefore suggest that, like other hy-

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(11) Our apparatus and methods are described in the following: McCullough, J. J.; MacInnis, W. K.; Eaton, D. F. *Chem. Phys. Lett.* **1986**, *125*, 155. Multichannel analyzer data was treated with a weighted nonlinear least-squares algorithm (Marquardt) and converged to χ^2 minima. Quality of fit was determined on the basis of χ^2, the Durbin–Watson parameter, and observation of residuals and autocorrelation functions. LE decay was well-analyzed by double exponentials; input for the EE decay analysis was taken as one of the decay constants obtained from the LE decay. EE decay parameters (τ's) were essentially identical with those from LE decay analysis in most cases; preexponentials (A_i) for EE were equal (±5%) and of opposite sign.

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(14) Yammamoto et al.[2d] obtained 4.9 kcal/mol in the low-temperature region −100 to −20 °C where excimer reversion is prohibited; we believe that we are still in a regime where this method has validity.

drocarbon cyclization processes,[2] fluorocarbon end-to-end cyclization requires about two or three bond rotations to effect ring closure. However, our data also reveal some unanticipated solvent effects. In CH_2Cl_2 (ϵ = 0.89), $k_c^H/k_c^F \sim 8$. In CH_3CN (ϵ = 37), k_c^H is seen to double, but k_c^F unexpectedly increases 5-fold, so that the k_c^H/k_c^F ratio is only about 3 in the much more polar solvent. We suspect that intramolecular dipole–dipole interactions between the polar CH_2–CF_2 bonds in **2**, which are absent in **1**, may play a role. Experiments on dipyrenyl systems with fluorocarbon cores of different sizes and positions along the folding chain are planned to test this possibility. We also will examine the spectroscopic properties of **1–4** in fluorocarbon solvents.

Supplementary Material Available: Tables II (Spectroscopic Properties of Compounds **1–4**) and III (Emission Decay Parameters for **1–4**) (2 pages). Ordering information is given on any current masthead page.

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Intramolecular Light-Induced Electron Transfer in a Rigid, Fixed-Distance Anthracene–*N*,*N*-Dimethylaniline System. Exciplex-like Behavior

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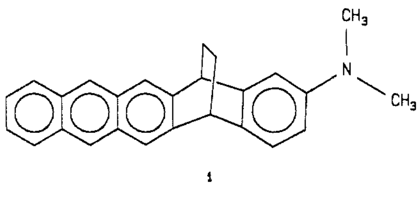
In connection with our interest in light-induced electron transfer in rigid molecules, 2-(*N*,*N*-dimethylamino)-5,14-ethanopentacene (**1**) was synthesized.[3] The anthracene electron acceptor and (*N*,*N*-dimethylamino)phenyl electron donor in **1** are held rigidly in a spatial configuration such that they are prevented from undergoing large structural changes before or after excitation.



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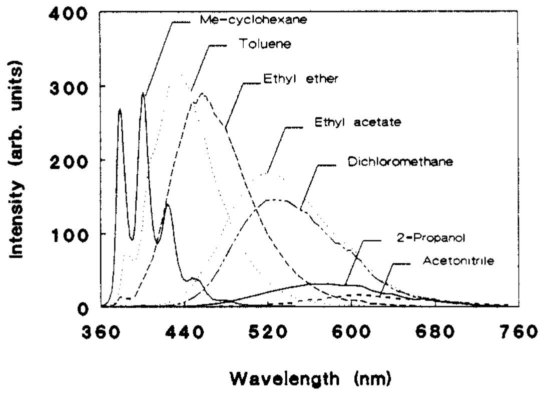

Figure 1. Fluorescence spectra of **1** in the indicated solvents. Compound **1** was excited at 358 nm.

Table I[a]

solvent	Φ_{An}	λ_{ex}, nm	Φ_{ex}	τ_{ex},[b] ns	τ_{ab}(700 nm),[b] ns
methylcyclohexane	0.25	*c*	*c*		
toluene	0.05	433	0.54	11.4	11.2
di-*n*-butyl ether	0.14	430	0.26		
trichloroethylene	0.02	440	0.43		
diethyl ether	0.01	460	0.69	20.8	22.2
n-butyl acetate	*d*	507	0.39		
ethyl acetate	*d*	522	0.38	24.0	21.6
tetrahydrofuran	*d*	520	0.39		
dichloromethane	*d*	530	0.29	15.3	14.7
2-propanol	*d*	575	0.06		
acetonitrile	*d*	605	0.03	4.2	5.7

[a] Φ_{An} is the quantum yield of uncomplexed anthryl emission, λ_{ex} is the maximum of exciplex emission, Φ_{ex} is the quantum yield of exciplex emission, τ_{ex} is the lifetime of the exciplex emission, and τ_{ab}(700 nm) is the lifetime of anthryl radical ion absorption at 700 nm. [b] Lifetimes of other systems were not measured. [c] Not detected. [d] <0.005.

The fluorescence spectroscopy of **1** was investigated in solvents of differing polarity in order to probe for electron transfer from the (*N*,*N*-dimethylamino)phenyl donor to the excited anthracene acceptor, and the results are given in Figure 1 and Table I. Although **1** displays a typical anthracene-like fluorescence spectrum in methylcyclohexane, Figure 1, the spectrum in toluene broadens and shifts to a longer wavelength. As the solvent polarity increases, the emission maximum shifts increasingly to the red in a manner parallel to that observed for anthracene–*N*,*N*-dialkylaniline exciplexes.[4,5] The results suggest that an exciplex or exciplex-like species is formed from excited **1** in solvents more polar than methylcyclohexane. From the dependence of the emission maximum on the solvent polarity factor,[4] $[(\epsilon_s - 1)/(2\epsilon_s + 1)] - 0.5[(\epsilon_{op} - 1)/(2\epsilon_{op} + 1)]$, where ϵ_{op} and ϵ_s are the optical and static dielectric constants of the solvent, a line with a slope of $-33.5 \pm 2.4 \times 10^3$ cm^{-1} is obtained. The point for toluene is excluded because $\epsilon_{op} \simeq \epsilon_s$, which lowers the exciplex energy in toluene relative to that in alkanes with similar ϵ_s. Assuming a solvent cavity diameter of 10 Å and the model as described by Weller,[4] the results suggest that the dipole moment of excited **1** is greater than 20 D, which suggests that complete charge separation may have occurred in excited **1**.

Intramolecular exciplex formation and electron transfer from acyclic systems linked by one carbon atom have been noted previously by Chandross and Thomas[6,7] as well as by Okada et al.[8] In addition, these processes have also been reported for rigid molecules possessing naphthalene donors and 1,1-dicyanoethylene acceptors.[9-12] The low quantum yield of locally excited anthracene emission from **1** in solvents more polar than diethyl ether, Table I, suggests that another state is formed rapidly from the initial locally excited anthracene singlet. The quantum yields indicate that this process should occur with a rate constant >10^{10} s^{-1}. The rise time of the exciplex-like emission from **1** in ethyl acetate or

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(1) Chemistry Division, Argonne National Laboratory.

(2) Department of Chemistry, University of Chicago.

(3) See supplementary material.

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