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 $CH_2Cl_2$ ($\epsilon$ = 0,89), $k_c^H/k_c^F \sim 8$. In $CH_3CN$ ($\epsilon$ = 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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(16) Our analysis assumes that the difference in rotational barriers for higher perfluoroalkanes vs alkanes is similar to that observed for perfluoroethane vs ethane. A more reliable comparison would require experimental data on torsional barriers in perfluoro-*n*-alkanes, which at present are not available.

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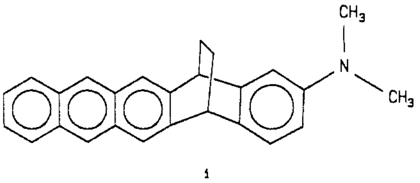
In connection with our interest in light-induced electron transfer in rigid molecules, 2-(*N*,*N*-dimethylamino)-5,14-ethanopentacene (**1**) was synthesized.[3] The anthracene electron acceptor and (*N*,*N*-dimethylamino)phenyl electron donor in **1** are held rigidly in a spatial configuration such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



1

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 $\epsilon_{op}$ and $\epsilon_s$ 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 $\epsilon_s$. 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**.

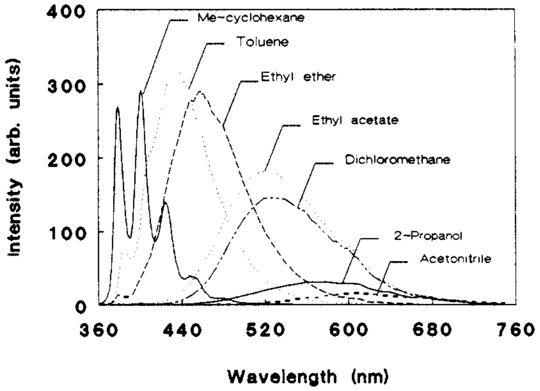


**Figure 1**. Fluorescence spectra of **1** in the indicated solvents. Compound **1** was excited at 358 nm.

**Table I**[a]

| solvent | $\Phi_{An}$ | $\lambda_{ex}$, nm | $\Phi_{ex}$ | $\tau_{ex}$,[b] ns | $\tau_{ab}$(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] $\Phi_{An}$ is the quantum yield of uncomplexed anthryl emission, $\lambda_{ex}$ is the maximum of exciplex emission, $\Phi_{ex}$ is the quantum yield of exciplex emission, $\tau_{ex}$ is the lifetime of the exciplex emission, and $\tau_{ab}$(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.

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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(2) Department of Chemistry, University of Chicago.

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ethyl ether is less than 15 ps and is at the limit of our instrumental resolution.[13] Nanosecond transient absorption measurements[14] on excited **1** show the characteristic absorption maximum at 700 nm for the anthracene radical anion.[15] The decay time of the 700-nm transient absorption feature agrees very well with the decay time of the exciplex-like luminescence in **1**, Table I. Thus, we suggest that the exciplex-like luminescence from excited **1** is radiative ion-pair recombination. A parallel mode of decay of the ion pair of **1** is also observed by monitoring the rise of the lowest excited triplet state of anthracene at 430 nm. This rise time parallels the decay time of the transient absorption at 700 nm.

These results suggest that intramolecular electron transfer in **1** occurs with a rate constant $>7 \times 10^{10}\ \mathrm{s^{-1}}$ to yield a species that exhibits properties commonly attributed to both a radical ion pair and an exciplex without the large changes in molecular geometry normally requisite for exciplex formation. The efficient formation of the ion pair in **1** is presumably due to significant electronic coupling of the chromophores across the single saturated carbon atom bridges joining the chromophores. Further investigations on this and related molecules are underway in our laboratories to ascertain the conditions under which radical ion pairs decay radiatively to the ground state.

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**Supplementary Material Available:** Scheme outlining the synthesis of **1** and listing of physical data for **1** including HRMS, (electron impact), 500-MHz $^1$H NMR data, and a graph of emission frequency of **1** vs solent polarity factor (3 pages). Ordering information is given on any current masthead page.

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# Trigonal Mercuric Complex of an Aliphatic Thiolate: A Spectroscopic and Structural Model for the Receptor Site in the Hg(II) Biosensor MerR

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As the heavy metal receptor component of an Hg(II)-responsive genetic switch, the MerR metalloregulatory protein[1,2] has been shown to possess nanomolar mercuric ion sensitivity and a $10^2$–$10^3$-fold selectivity for Hg(II) over other soft metals such as Cd(II), Zn(II), and Au(I).[3] Results from X-ray absorption,[4] chemical protection studies, and mutagenesis studies on Hg–MerR have been interpreted in terms of models with two,[5a,b] three,[4,5c] or four[5,6] cysteines coordinating to Hg(II) in the metal-receptor site. Further elucidation of the coordination number and chemistry underlying mercuric ion recognition by MerR has been hampered by the absence of spectroscopic probes and appropriate three- and four-coordinate mercuric thiolate model complexes.[7] We report evidence from spectroscopic and structural studies of a trigonal mercuric complex of an aliphatic thiolate, $[\mathrm{Et_4N}][\mathrm{Hg(SBu^t)_3}]$ (**1**), and from spectroscopic studies of Hg–MerR that Hg(II) is coordinated to *three* cysteines in the latter. Distorted four-coordinate

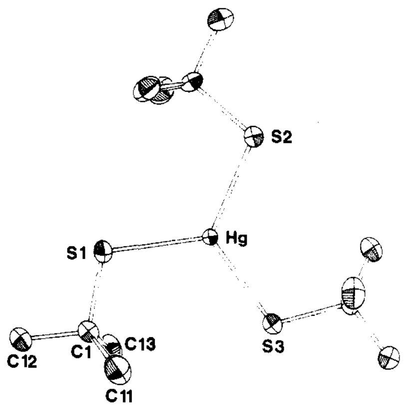

**Figure 1**. ORTEP drawing of $[\mathrm{Hg(SBu^t)_3}]^{1-}$ (**1**), showing 50% thermal probability ellipsoids. Selected bond distances (Å) and angles (deg): Hg–S1, 2.438 (1); Hg–S2, 2.451 (1); Hg–S3, 2.436 (1); S1–Hg–S2, 121.24 (4); S1–Hg–S3, 120.85 (4); S2–Hg–S3, 117.90 (4). Mean Hg displacement from the S1–S2–S3 plane: 0.0185 Å.

**Table** I. Principal Electronic Transitions in Hg(II)–Thiolate Complexes

| Hg complex | $\lambda_{\max}$, nm | $\Delta\epsilon$,[a] $\mathrm{M^{-1}\,cm^{-1}}$ | $\epsilon$, $\mathrm{M^{-1}\,cm^{-1}}$ | ref |
|---|---|---|---|---|
| *Neurospora* $\mathrm{Hg_3}$–MT[b] | 283 | 8800 | | 8 |
| $\mathrm{Hg_7}$–MT | 304 | NR[f] | | 9 |
| Hg–plastocyanin | 247 | 9800 | | 10 |
| | 280 (sh)[b] | 2130 | | |
| Hg–MerR[c] | 240 | 16620 | | this work |
| | 260 (sh) | 11150 | | |
| | 290 (sh) | 4120 | | |
| $[\mathrm{Et_4N}][\mathrm{Hg(SBu^t)_3}]$[d] | 235 | | 24000 | this work |
| | 260 (sh) | | 17700 | |
| $\mathrm{Hg(SEt)_2}$[e] | 228 (sh) | | 4700 | this work |
| | 282 (sh) | | 740 | |
| $\mathrm{Hg(SPr^i)_2}$ | 228 (sh) | | 3400 | this work |
| | 262 (sh) | | 650 | |

[a] $\Delta\epsilon = \epsilon_{\text{Hg-protein}} - \epsilon_{\text{protein}}$. [b] MT = metallothionein; sh = shoulder. [c] See Figure 2 for experimental details; mean value of five separate titrations. Largest deviation from mean <3%. [d] Data obtained from Beer's law plot in concentration range (2–5) × $10^{-3}$ M. $\epsilon_{235}$ for $[\mathrm{Et_4N}][\mathrm{SBu^t}] = 500\ \mathrm{M^{-1}\,cm^{-1}}$. [e] 5 × $10^{-3}$ M in acetonitrile. Single measurement; see ref 19 for preparation of compounds. [f] NR = not reported.

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[‡] Department of Biochemistry, Molecular Biology and Cell Biology.

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