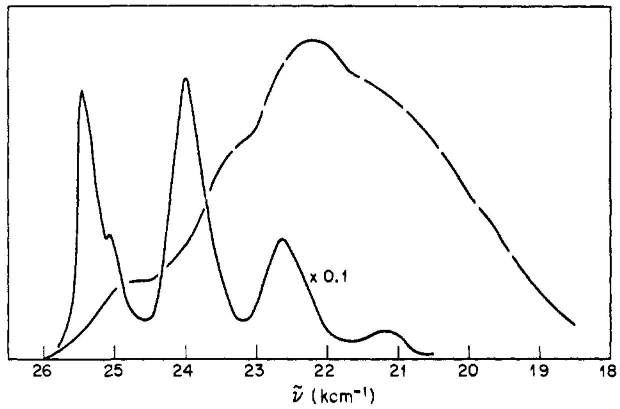

Figure 2. The fluorescence spectrum (excited at 366 nm) of the anthracene-naphthalene sandwich pair (broken line) and the fluorescence of the separated species (solid line) obtained after thawing and refreezing (at 0.1 times the gain of the previous spectrum).

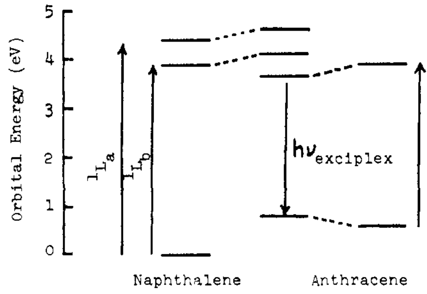

Figure 3. Schematic representation of the stabilization of the excited anthracene-naphthalene sandwich pair. The orbital energies are derived from photoelectron spectroscopic energies[6,7] and optical absorption spectra. The zero has been set at the highest bonding level of naphthalene and the mixed excimer fluorescence is indicated *schematically*.

mer.[5] The heat of formation of an excimer is usually at least one-third of this shift. In the present case the ground-state repulsion energy should be comparable to those for excimers, and we may estimate the heat of formation of the naphthalene-anthracene exciplex at 3.5-4 kcal mol⁻¹, about 60-70% that of the related homopolar excimers. This must be derived entirely from charge-transfer and polarization interactions. It may be thought of as an interaction of the first antibonding level of anthracene with the first and second antibonding levels of naphthalene as shown in Figure 3.[6,7] These orbitals have similar energies, but interaction would probably require some change in their symmetry in the exciplex, depending on the relative positions of the two components. The interaction would depend strongly on the interplanar spacing.[8] It is about the same as the heats of formation of many ground-state molecular complexes which are stabilized by polarization interactions. Anthracene is both a better donor and acceptor than naphthalene.

The lifetime of the anthracene-naphthalene exciplex is 33 nsec and the fluorescence yield is 37% of that of the methylanthracene in the open form which probably has $\Phi_F = 1.0$.[9] Thus, the natural lifetime of the exciplex is ~100 nsec, which suggests that the fluorescent state is very different from that of anthracene. A weak charge-transfer transition may be involved. We suggest that a theoretical study of this exciplex would be worthwhile. Good wave functions for the individual components are available and a perturbation treatment might be feasible.

Acknowledgments. We thank Dr. A. A. Lamola for measuring the fluorescence lifetime and both him and Dr. G. N. Taylor for useful discussions.

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Magnetic Field Effects on Oxygen Quenching of Delayed Fluorescence of Anthracene and Pyrene in Fluid Solution[1]

Sir:

The effect of a magnetic field on the rate of triplet-triplet annihilation[2,3] and on the quenching of triplets by radical cations (doublets)[4] in fluid solutions has been reported. Molecular oxygen in the triplet state is known to be an efficient quencher of the excited triplet state of organic molecules (^{3}M), probably by the reaction scheme[5-8]

$$ {}^3\mathrm{M} + {}^3\mathrm{O}_2 \longrightarrow {}^1\mathrm{M} + {}^1\mathrm{O}_2 \qquad (1)$$

The rate of this triplet-triplet interaction producing singlet products should be affected by a magnetic field,[7,8] although an investigation of the phosphorescence of several aromatic hydrocarbons adsorbed on a polystyrene matrix in the presence of oxygen showed no effect of magnetic field for fields as large as 145 kG.[8] We report here a magnetic field effect on the quenching of delayed fluorescence (DF) of anthracene and pyrene by oxygen and note an apparent solvent effect in this phenomenon.

All measurements were carried out using the phosphorimeter previously described,[9] but equipped with a circular graded spectrum filter to allow monitoring of emission at selected wavelengths and with excitation by a 200-W mercury lamp filtered by a C.S. 7-54 glass filter. The DF intensities were measured using the phase sensitive detection system previously described, the output of which was recorded on a signal averager (Fabri-Tek Model 1060). Magnetic fields up to 8 kG were applied with a Varian 9-in. electromagnet. Each

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(1) This research was supported by the Army Research Office—Durham. The electromagnet was purchased by a grant from the Research Corporation.

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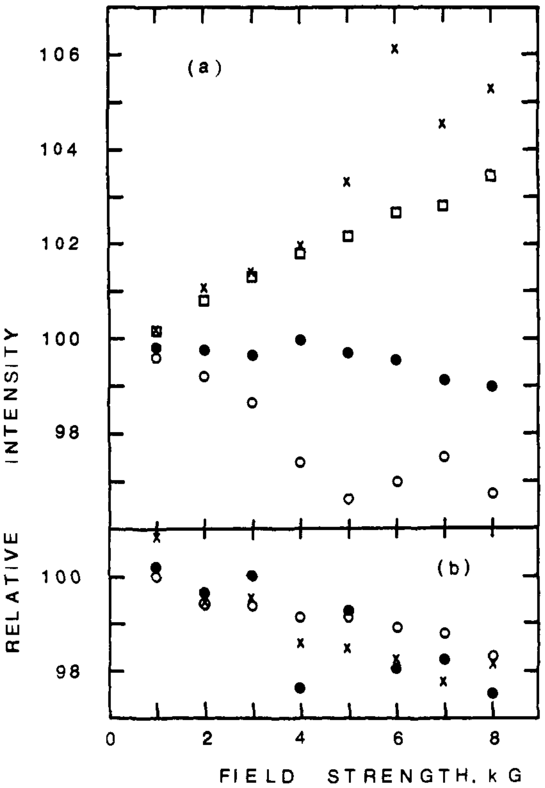

Figure 1. (a) Magnetic field effect on delayed fluorescence from 2.1 × 10^{-4} *M* anthracene and different amounts of oxygen in DMF: ○, no oxygen, delayed fluorescence lifetime, τ = 4.3 msec; ●, 7.5 × 10^{-4} atm, τ = 3.9 msec; □, 3 × 10^{-3} atm, τ = 2.7 msec; ×, 6 × 10^{-3} atm, τ = 1.9 msec. (b) 2.5 × 10^{-4} *M* anthracene and different amounts of oxygen in acetonitrile: ○, no oxygen, τ = 3.2 msec; ×, added oxygen, 1.5 × 10^{-3} atm, τ = 1.2 msec; ●, 3 × 10^{-3} atm, τ = 0.9 msec.

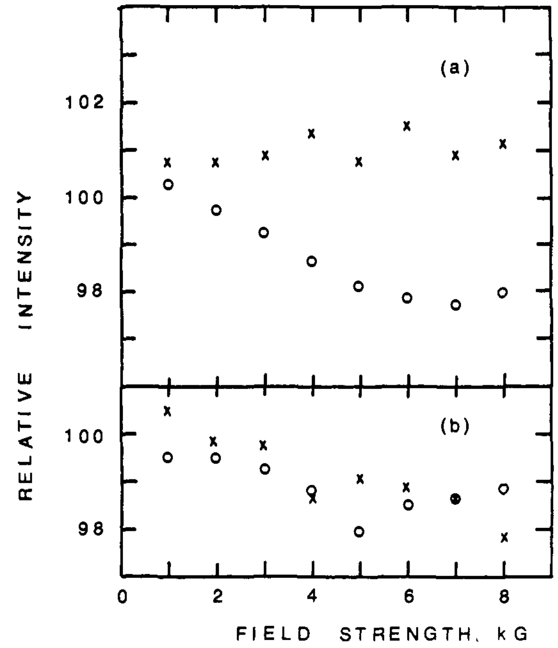

Figure 2. (a) Magnetic field effect on delayed fluorescence (emission at 390 nm) from a 2.6 × 10^{-4} *M* solution of pyrene in DMF: ○, no oxygen, τ = 1.4 msec; ×, added oxygen, 6 × 10^{-3} atm, τ = 0.7 msec. (b) 2.0 × 10^{-4} *M* pyrene in acetonitrile: ○, no oxygen, τ = 2.1 msec; ×, added oxygen, 2.2 × 10^{-5} atm, τ = 1.4 msec.

sample was prepared by at least eight freeze-pump-thaw cycles, then sufficient oxygen to partially quench the triplet state yet still yield detectable DF signals was introduced through the vacuum line, and finally the cell was sealed off with a torch. DF studies of anthracene and pyrene in *N*,*N*-dimethylformamide (DMF) and acetonitrile in the absence of oxygen showed the usual decrease in DF intensity with increasing magnetic field strength, caused by a decrease in the rate of the triplet-triplet annihilation reaction[1] (Figures 1 and 2). When oxygen was introduced into the samples, upon initial exposure to the excitation beam, no DF signal was observed. After several minutes the DF signal increased to measurable levels. This increase in DF signal with time has been observed previously in studies of DF in the solid state in the presence of oxygen[10] and is probably caused by a depletion in the concentration of oxygen by reaction with the triplet of the aromatic hydrocarbon to form the transannular peroxide. The DF signals in DMF solutions for both anthracene and pyrene show an increase in intensity with increasing magnetic field strength (Figures 1 and 2) indicating a decrease in the rate of reaction 1 at higher fields, paralleling the results observed for quenching of triplets by radical cations.[4] In acetonitrile, on the other hand, no change in DF behavior was observed upon addition of oxygen for both anthracene and pyrene, although oxygen quenching was occurring, as seen by a decrease in the lifetime (τ) of the aromatic triplet. A solvent dependency on the magnetic field effect on triplet-triplet annihilation was observed previously,[2,4] and these results lend further support to the importance of the role of the solvent in these processes.

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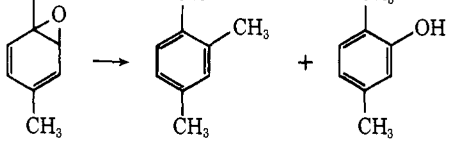
The Oxygen Walk as a Complementary Observation to the NIH Shift

Sir:

Aromatization of arene oxides may occur with or without group migration (NIH shift[1]). A well-studied example is provided in eq 1.[2] From profiles of log



(1)

k_{obsd} *vs.* pH and lack of buffer acid catalysis, the aromatization reaction can be shown to occur both by spontaneous and *specific* acid catalysis (*i.e.*, $k_{\mathrm{obsd}} = k_0 + k_{\mathrm{H}}[\mathrm{H}^+]$).[3] In addition, from values of $\Delta S^{\ddagger}$,

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