tions. First, it possesses superior nucleophilic properties; second, it is easily prepared and the THF solutions of this reagent are stable indefinitely; and third, the products of the displacement reaction are simple alkanes and readily analyzed by simple techniques. Even more exciting is the discovery, after 25 years, of a nucleophilic reducing agent for alkyl halides far superior to lithium aluminum hydride. We have synthesized a wide range of trialkylborohydrides and all prove to be exceptionally active nucleophiles. Moreover, these derivatives possess extremely attractive properties for other reductions, such as the reduction of cyclic ketones with enzyme-like stereoselectivity.[9–11] We are currently exploring the utility of these new reagents in organic syntheses.[12]

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(9) H. C. Brown and S. Krishnamurthy, *J. Amer. Chem. Soc.*, **94**, 7159 (1972).

(10) E. J. Corey, S. M. Albonico, V. Koelliker, T. K. Schaaf, and R. K. Varma, *ibid.*, **93**, 1491 (1971).

(11) E. J. Corey and R. K. Varma, *ibid.*, **93**, 7319 (1971).

(12) Research in progress with Dr. S. Krishnamurthy and S. C. Kim.

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Absorption and Exciplex Emission Spectra of the Naphthalene–Anthracene Sandwich Pair

Sir:

The formation of fluorescent exciplexes by singlet excited aromatic hydrocarbons and other species which are usually easily classified as electron donors or acceptors is a well-known phenomenon. Such exciplexes are stabilized by charge-transfer interactions in contrast to the homopolar excimers which derive a considerable portion of their stabilization from exciton interaction. We have been able to prepare the anthracene–naphthalene sandwich pair in a rigid matrix, and we report the first study of a sandwich pair of two completely different aromatic hydrocarbons. This species exhibits exciplex fluorescence even though exciton interaction should be negligible and charge-transfer should not be particularly favorable. The absorption spectrum of the pair shows weak interaction in the ground-state geometry.

The discovery of the reversible intramolecular photoaddition of naphthalene to anthracene in 1-(9-anthryl)-3-(1-naphthyl)propane[1] suggested the possibility of generating the naphthalene–anthracene sandwich pair *via* the photodissociation of the adduct in a rigid matrix at low temperature. This has proved to be a useful technique for the study of hydrocarbon sandwich pairs. The adduct was prepared as a 2 × 10^{-5} *M* solution in methylcyclohexane, which was concentrated approximately threefold in order that the absorption spectrum could be measured easily in a 3-mm tube. It was broken by irradiation with 254-nm Hg light at 77°K in the usual manner.

The absorption spectra of the naphthalene–anthracent sandwich pair and the separated moieties formed after thawing and refreezing are given in Figure 1.

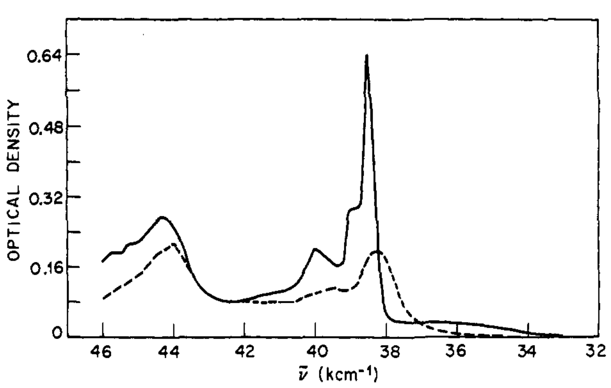

Figure 1. The absorption spectrum of the naphthalene–anthracene sandwich pair formed by photodissociation of the photoadduct (broken line) and the separated moieties obtained after thawing and refreezing (solid line).

The characteristic anthracene absorption system in the 320–380-nm region, which is not shown, was virtually the same in both configurations, and, because of the difficulties in measuring relatively weak absorption with high accuracy in our technique, no meaning is attributed to the slight differences.

Anthracene has an intense (ϵ 1.6 × 10^5, $f = 2.3$) long-axis polarized transition at 38.3 kcm^{-1}; naphthalene has a strong (ϵ 1.3 × 10^5, $f = 1.7$) long-axis polarized transition at 44.2 kcm^{-1}.[2] There does not appear to be any strong interaction between these two transitions in the sandwich pair, presumably a consequence of the substantial energy gap. This may be contrasted with the single transition observed[3] for the anthracene–9,10-dichloroanthracene pair in the same region where the individual transitions are separated by 1 kcm^{-1}. In the present case each absorption has been shifted to lower energy as might be expected to result from having a neighboring molecule of substantial polarizability in the proper orientation for interaction.[4] There is also considerable hypochromism, a more sensitive measure of interaction than a shift in energy. The corresponding effects on the much weaker first transition of anthracene would be much smaller.

The most interesting feature of the naphthalene–anthracene sandwich pair is its fluorescence spectrum. This is shown in Figure 2 along with the normal fluorescence of the methylanthracene moiety obtained after thawing and refreezing. The sandwich pair fluorescence is clearly not simply derived from the absorption spectrum, and it can be identified as an exciplex fluorescence. There appears to be a small amount of structure, whose frequency is about 1.4 kcm^{-1}, superimposed on a typical exciplex band. This is the characteristic vibrational frequency in the anthracene spectrum, but we cannot be sure that the structure is real.

The fluorescence maximum of the sandwich pair lies at 22.2 kcm^{-1}, 3.2 kcm^{-1} to the red of the 9-methylanthracene 0–0 band. This is much less than the normal 5.5-kcm^{-1} shift for the 9-methylanthracene excimer.[3] The excimer derived from 1,3-bis(1-naphthyl)propane is shifted 7 kcm^{-1} to the red of the mono-

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(1) E. A. Chandross and A. H. Schiebel, *J. Amer. Chem. Soc.*, **95**, 611 (1973).

(2) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, Chapter 13.

(3) E. A. Chandross and J. Ferguson, *J. Chem. Phys.*, **45**, 3554 (1966).

(4) J. N. Murell, "The Theory of the Electronic Spectra of Organic Molecules," Wiley, New York, N. Y., 1963, Chapter 7.

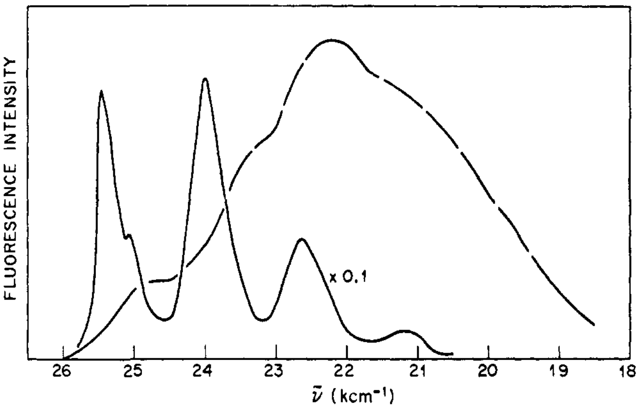

Figure 2. The fluorescence spectrum (excited at 366 nm) of the anthracene–naphthalene sandwich pair (broken line) and the fluorescence of the separated species (solid line) obtained after thawing and refreezing (at 0.1 times the gain of the previous spectrum).

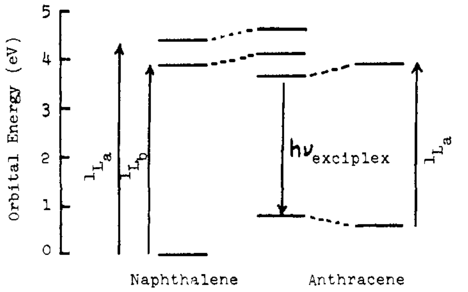

Figure 3. Schematic representation of the stabilization of the excited anthracene–naphthalene sandwich pair. The orbital energies are derived from photoelectron spectroscopic energies[6,7] and optical absorption spectra. The zero has been set at the highest bonding level of naphthalene and the mixed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

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(5) E. A. Chandross and C. J. Dempster, *J. Amer. Chem. Soc.*, **92**, 704 (1970).

(6) R. S. Becker and E. Chen, *J. Chem. Phys.*, **45**, 2403 (1966).

(7) R. S. Becker and W. E. Wentworth, *J. Amer. Chem. Soc.*, **85**, 2210 (1963).

(8) For a discussion of the theory of the excimer state, see J. N. Murrell and J. Tanaka, *Mol. Phys.*, 7, 363 (1964).

(9) E. C. Lim, J. D. Laposa, and J. M. H. Yu, *J. Mol. Spectrosc.*, **19**, 412 (1966).

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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.

(2) L. R. Faulkner and A. J. Bard, *J. Amer. Chem. Soc.*, **91**, 6495 (1969).

(3) D. Wyrsch and H. Labhart, *Chem. Phys. Lett.*, **8**, 217 (1971).

(4) L. R. Faulkner and A. J. Bard, *J. Amer. Chem. Soc.*, **91**, 6497 (1969).

(5) D. R. Kearns, *Chem. Rev.*, 71, 395 (1971).

(6) L. K. Patterson, G. Porter, and M. R. Topp, *Chem. Phys. Lett.*, 7, 612 (1970).

(7) D. R. Kearns and A. J. Stone, *J. Chem. Phys.*, **55**, 3383 (1971).

(8) E. Geacintov and C. E. Swenberg, *ibid.*, 57, 378 (1972).

(9) L. R. Faulkner and A. J. Bard, *Chem. Instrum.*, **2**, 337 (1970).