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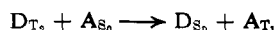
Triplet-Triplet Energy Transfer from the Second Triplet State of Anthracene. Spectroscopic Methods¹

R. S. H. Liu and R. E. Kellogg

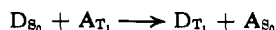
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Abstract: Selective excitation of anthracene in mixed crystals (host, dibenzofuran or biphenyl) containing guest molecules of anthracene and naphthalene-*d*₈ at -195° produces naphthalene phosphorescence. This result is interpreted as energy transfer from T₂ of anthracene to the host triplet, followed by exciton diffusion to naphthalene traps. Escape efficiency of triplet excitation from anthracene to naphthalene-*d*₈ traps in dibenzofuran is $(1.1 \pm 0.3) \times 10^{-4}$.

The second triplet states, T₂, of anthracene² and several substituted anthracenes³ have been shown to lie energetically below the lowest excited singlet states, S₁. In these cases, intersystem crossing from S₁ populates the T₂ state first.^{2,3} The lifetimes of these higher triplet states are apparently sufficiently long, as demonstrated in several chemical studies,⁴ that they can act as donors in triplet-triplet energy-transfer processes in solution with reasonable efficiency. For 9,10-dibromoanthracene, the T₂ lifetime was shown from Stern-Volmer plots to be $(2.2 \pm 0.5) \times 10^{-10}$ sec.^{4a}



While some transfer pairs in solution diffuse apart without "reverse" quenching,⁵ the slow radiative rate of the triplet acceptor makes spectroscopic detection difficult because of "reverse" quenching by later collisions, *i.e.*



We report here a study of energy transfer from anthracene T₂ in mixed crystals where the excitation transfers to the host crystal, migrates to a remote trap, and ultimately emits.

Results and Discussion

The donor-acceptor pair chosen for this study is anthracene and naphthalene-*d*₈ with either biphenyl (BP) or dibenzofuran (DBF) as host. The important energy levels for these compounds are shown schematically in Figure 1.^{6,7}

(1) The Role of Second Triplet States in Solution Photochemistry. V.

(2) R. E. Kellogg, *J. Chem. Phys.*, **44**, 411 (1966).

(3) R. G. Bennett and P. J. McCartin, *ibid.*, **44**, 1969 (1966).

(4) (a) R. S. H. Liu and J. R. Edman, *J. Am. Chem. Soc.*, in press; and also previous papers of this series; (b) R. S. H. Liu and J. R. Edman, *ibid.*, **90**, 213 (1968); (c) R. S. H. Liu and D. M. Gale, *ibid.*, **90**, 1897 (1968); (d) N. C. Yang, N. Nussim, M. J. Jorgenson, and S. Murov, *Tetrahedron Letters*, 3657 (1964); (e) O. L. Chapman, T. H. Koch, F. Klein, P. J. Nelson, and E. L. Brown, *J. Am. Chem. Soc.*, **90**, 1957 (1968); (f) P. de Mayo, J. P. Pete, and M. Tchir, *ibid.*, **89**, 5712 (1967). The last three report chemical reactions involving higher triplet states.

(5) Such a "reverse" transfer has been identified in one case: R. S. H. Liu, *ibid.*, **90**, 1899 (1968).

The mixed crystals were prepared between quartz plates separated by lead spacers. The spectrophotometer used to record emission spectra has been described.³ A collimated beam from a PEK 100-W high-pressure mercury lamp was used as the excitation source. The 3660-Å line was isolated with a *f*/3.5 Bausch & Lomb monochromator, combined with a Corning 7-54 filter. A Corning 3-74 filter was placed at the entrance slit. Samples of purified biphenyl and dibenzofuran were generously provided by Dr. G. J. Sloan.

Excitation with 3660-Å light of 0.1-mm mixed crystals containing 0.1% (by weight) anthracene and 1% naphthalene-*d*₈ at 77°K showed weak naphthalene phosphorescence (in addition to anthracene fluorescence (Figure 2)). The intensity in dibenzofuran (DBF) was five times that in biphenyl (BP).

In view of the relative energy levels of these compounds, the logical pathway to produce naphthalene phosphorescence is (1) S₀ → S₁ excitation of anthracene followed by intersystem crossing to T₂; (2) energy transfer to the host T₁ and exciton migration away; (3) trapping by naphthalene-*d*₈ T₁ and subsequent phosphorescence.

Control samples containing only naphthalene-*d*₈ showed the phosphorescence down by a factor of 20 in DBF and by a factor of 10 in BP, showing that direct absorption by the naphthalene is not responsible. In DBF, the control phosphorescence appeared to be due to residual anthracene impurity in DBF or naphthalene or both. Doping with 9,10-diphenylanthracene⁸ ($\Phi_f = 1.00 \pm 0.05$)⁹ in lieu of anthracene shows a weaker phosphorescence than the control due to competition for excitation with the anthracene impurity and less efficient intersystem crossing indicating that the donor state is in

(6) Naphthalene T₂ is not included in the diagram because the state is too high in energy (30,800 cm⁻¹)⁷ to be involved in this study.

(7) D. M. Hanson and G. W. Robinson, *J. Chem. Phys.*, **43**, 4175 (1965).

(8) We acknowledge Dr. R. G. Beunnett for first suggesting this experiment to us.

(9) E. C. Lim, J. D. Laposa, and J. M. H. Yu, *J. Mol. Spectry.*, **19**, 412 (1966); see also, I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965, p 130.

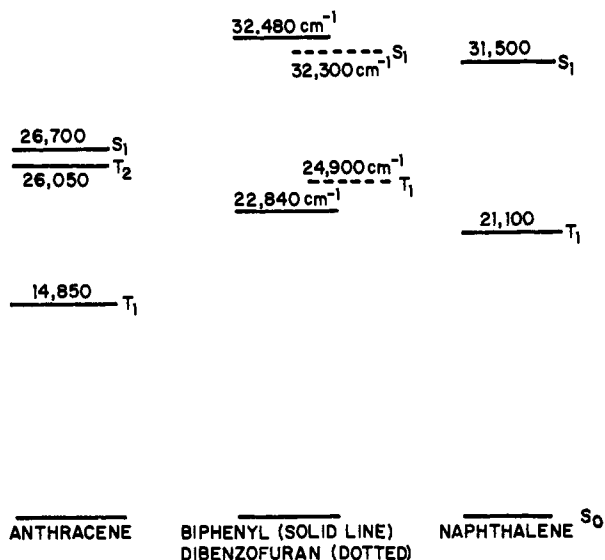
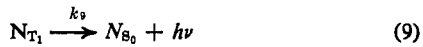
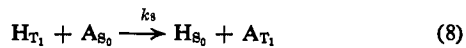
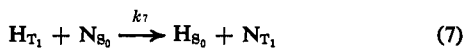
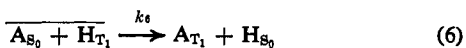
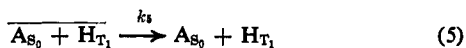
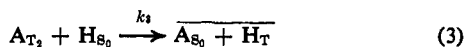


Figure 1. Energy diagram for anthracene,² biphenyl,¹⁰ dibenzofuran (W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964)), and naphthalene-*d*₈,¹⁰ showing the important low-lying states.

the triplet manifold. In the unlikely event that the anthracene S₁ state is the donor, 9,10-diphenylanthracene would have increased the sensitized phosphorescence.

The suggested path of energy migration predicts a dependence of phosphorescence yield upon the concentration of naphthalene. In fact, following the scheme below, a Stern-Volmer expression (11) is obtained relating these quantities.



$$\frac{1}{\Phi_p} = \frac{1}{abc} \left(1 + \frac{k_8[A]}{k_7[N]} \right) \quad (11)$$

where a (intersystem crossing efficiency) = $k_1/(k_1 + k_2)$, b (escape efficiency) = $\{k_3[H]/(k_3[H] + k_4)\} \cdot \{k_5/(k_5 + k_6)\}$, and c (phosphorescence efficiency) = $k_9/(k_9 + k_{10})$.

The scheme has been verified experimentally (Table I) with the results shown graphically in Figure 3. It is evident that in the low naphthalene concentration region ($[N] < 0.1$ mole/kg with $[A]$ being constant) $1/(\Phi_p)$ is

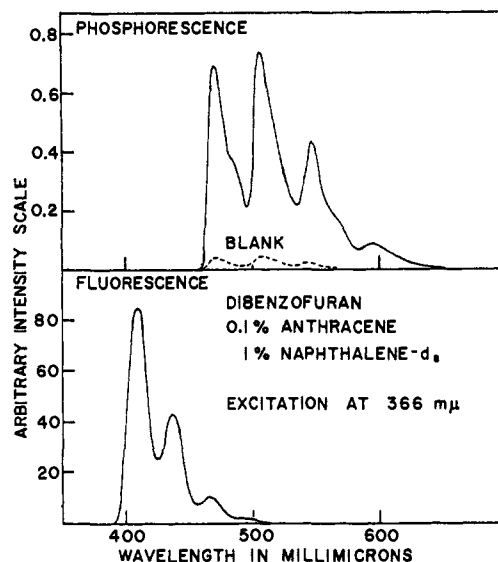


Figure 2. Phosphorescence and fluorescence at 77°K of a 0.1-mm dibenzofuran crystal doped with 0.1% anthracene and 1% naphthalene-*d*₈ using 366- μ excitation. The dotted line is the phosphorescence of a similar DBF crystal doped only with naphthalene-*d*₈. While the absolute intensity units are arbitrary, the relative units have meaning.

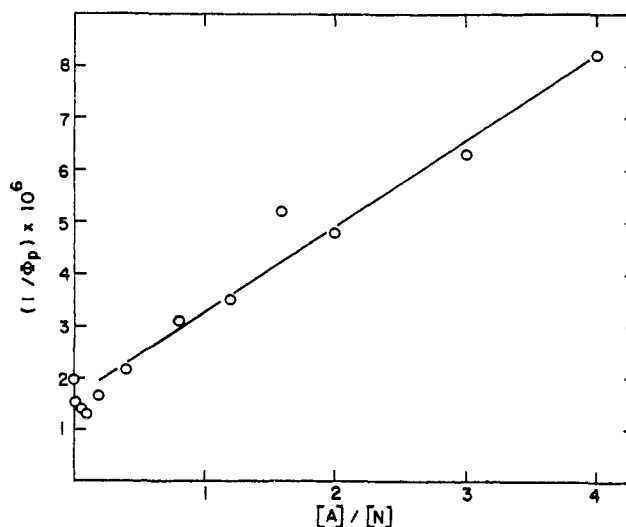


Figure 3. Stern-Volmer plot of the sensitized naphthalene-*d*₈ phosphorescence in mixed crystals.

indeed linearly related to $[A]/[N]$. From the values for intercept and slope obtained from a "least-squares" fit of the points in this range, the ratio of the two diffusion rate constants was found to be $k_8/k_7 = 1.00 \pm 0.34$. Within experimental error the ratio is unity (indicating $k_7 = k_8$) as might be expected. In the range of high naphthalene concentrations (>0.1 mole/kg, ~ 1.6 wt %), exchange interaction between closely lying naphthalenes is expected to become important,¹⁰ leading to triplet naphthalene to naphthalene migration and subsequent quenching by triplet-triplet annihilation or trapping by anthracenes. Thus, a decrease of phosphorescence intensity in this range is predicted. Experimentally, this is verified by the upward curvature for points near the intercept (Figure 3).¹¹

(10) N. Hirota, *J. Chem. Phys.*, **43**, 3354 (1965).

(11) Because of higher emission intensity, the points near the inter-

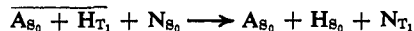
Table I. Variation of Intensity of Naphthalene-*d*₈ Phosphorescence Sensitized by Anthracene in DBF Mixed Crystals^a

Sample ^b	[A], mole/kg	[N], mole/kg	[A]/[N]	$\Phi_p \times 10^5$ ^c
1	0.01	1.00	0.010	5.1
2	0.01	0.400	0.025	6.5
3	0.01	0.200	0.050	7.5
4	0.01	0.100	0.100	7.7
5	0.01	0.0500	0.200	6.1
6	0.01	0.0250	0.400	4.7
7	0.01	0.0125	0.800	3.2
8	0.01	0.00833	1.20	2.9
9	0.01	0.00625	1.60	2.0
10	0.01	0.00500	2.00	2.1
11	0.01	0.00333	3.00	1.6
12	0.01	0.00250	4.00	1.2
4A	0.001	0.0100	0.100	10
10A	0.001	0.00050	2.00	2

^a At -195° , 3660-Å light. ^b Samples 1–12, light path length = 0.1 mm; samples 4A and 10A, 1 mm. ^c Anthracene fluorescence as internal standard; $\Phi_f = 0.28$ was used for calculations.

The escape efficiency, a composite quantity accounting for competitions against internal conversion of anthracene T_2 to T_1 and reverse molecular pair quenching, can be calculated from the intercept. Assuming the intersystem crossing efficiency in anthracene is 0.75,¹² and the phosphorescence efficiency in naphthalene-*d*₈ is 0.78,¹³ then the escape efficiency is estimated as $b = (1.1 \pm 0.3) \times 10^{-4}$. Unfortunately without additional information, it is not possible to separate the importance of internal conversion (T_2 to T_1) from molecular pair quenching.

cept are more accurate. Therefore, the slight dip of the line just before its upturn could be outside experimental error. If so, it could be a reflection of a decreasing amount of "reverse" quenching through exchange interaction of the host with naphthalene, e.g.



Such an effect is expected to be critically dependent upon distance of separation of the molecules concerned.

(12) T. Medinger and F. Wilkinson, *Trans. Faraday Soc.*, **61**, 620 (1965).

(13) R. E. Kellogg and R. G. Bennett, *J. Chem. Phys.*, **41**, 3042 (1964).

Samples 4A and 10A, which represent tenfold dilution of samples 4 and 10, showed comparable intensity of naphthalene phosphorescence (Table I). Therefore, the observed sensitized emission cannot be due to direct one-way transfer between a statistically few close-lying donor-acceptor (anthracene-naphthalene) pairs.¹⁴

Hirota¹⁰ and Hutchinson¹⁵ studied triplet energy transfer between phenanthrene (donor) and naphthalene (acceptor) in biphenyl crystals in considerable detail. They first identified two types of triplet energy transfer: one, being temperature dependent and the other, temperature independent. A third type of transfer mechanism due to exchange interaction was later also observed at high donor-acceptor concentrations.¹⁰ Convincing evidence was presented that the temperature-dependent process involves first an activated energy-transfer process from the donor triplet to the host and then diffusion through exciton band to the acceptor.¹⁵ The temperature-independent process was not clearly understood. Two possible mechanisms were considered: one through higher donor triplet states (vibrational or electronic) and the second by the presently unknown $S_1 \rightarrow T_1$ transfer. The former was considered unlikely because of the common notion that "the vibrational relaxation is supposed to be much faster than the guest-host triplet transfer rate."¹⁰

Our results in mixed crystals as well as in solution⁴ show that $T_2 \rightarrow T_1$ internal conversion in anthracene is sufficiently slow to allow bimolecular transfer from the higher triplet state. This suggests that the temperature-independent energy-transfer process observed by Hirota and Hutchinson might also be due to energy transfer from a higher triplet of phenanthrene although the lowest currently known excited triplet is above S_1 .¹⁶⁻¹⁸

(14) This process is not expected to be important because the long triplet lifetime of naphthalene-*d*₈ makes reverse transfer to T_1 of the neighboring anthracene more likely.

(15) N. Hirota and C. Hutchinson, Jr., *J. Chem. Phys.*, **42**, 2869 (1965).

(16) Triplet-triplet absorption studies^{17,18} failed to find a lower T_2 . However, T_2 lower than S_1 requires a T_2-T_1 absorption $< 7000 \text{ cm}^{-1}$, which is not detectable by this method.

(17) B. R. Henry and M. Kasha, *J. Chem. Phys.*, **47**, 3319 (1967).

(18) R. E. Kellogg, unpublished results.