

induce some deviations from the TBP geometry in the sense that there will be a bending of the equatorial bonds toward the oxygen atom.^{13,14} This, however, is equivalent to appearance of more s character in the axial and an s decrease in the equatorial orbitals. Interestingly, a $^1J(\text{PC}_{\text{eq}})$ of as much as 128 Hz has been found¹⁵ for $(\text{CH}_3)_3\text{PF}_2$, where such a distortion is ruled out by symmetry. In this case, however, a special inductive effect of the fluorine atoms on $^1J(\text{PC}_{\text{eq}})$ is also to be considered. Thus only the investigation of the hitherto unreported $(\text{CH}_3)_3\text{P}$ is likely to provide pertinent unequivocal evidence. Pentamethylantimony¹⁶ and the recently reported pentamethylarsenic¹⁷ are unfortunately undergoing too rapid reorganization processes even at very low temperatures to yield straight-forward information.

(13) A. L. Beauchamp, M. J. Bennett, and F. A. Cotton, *J. Amer. Chem. Soc.*, **91**, 297 (1969). In the crystal structure of $(\text{C}_6\text{H}_5)_3\text{SbOH}$ an average bond angle of 86.7° was found for $\text{C}_{\text{eq}}-\text{Sb}-\text{O}$!

(14) K. Shen, W. E. McEwen, S. I. La Plata, W. C. Hamilton, and A. P. Wolf, *J. Amer. Chem. Soc.*, **90**, 1718 (1968). In the crystal structure of $(\text{C}_6\text{H}_5)_3\text{SbOCH}_3$ an average bond angle of 87.3° was found for $\text{C}_{\text{eq}}-\text{Sb}-\text{O}$.

(15) H. Dreiskamp, C. Schumann, and R. Schmutzler, *Chem. Commun.*, 671 (1970). $^1J(\text{HC})$ is 129.3 Hz for $(\text{CH}_3)_3\text{PF}_2$, $^2J(\text{PC}_{\text{eq}}\text{H})$ is 17.5 Hz.

(16) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, **3**, 1298 (1964).

(17) K.-H. Mitschke and H. Schmidbaur, *Chem. Ber.* **106**, 3645 (1973).

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The Second Triplet State of Naphthalene in a Sensitized Reaction in Solution¹

Sir:

In a series of papers we reported examples of triplet-triplet energy transfer from the second triplet states of anthracene² and substituted anthracenes.³⁻⁵ It was shown that the average lifetime of 9,10-dibromoanthracene T_2 is $(2.2 \pm 0.5) \times 10^{-10}$ sec,³ much longer than that commonly assumed for a higher excited state in condensed media.⁶ We now wish to report a case of energy transfer from naphthalene T_2 and the determination of its lifetime.⁷

One of the common and successful approaches to study the second triplet states of anthracenes is chemical sensitization where the excited state properties can be derived from examination of yields of products of acceptors.³⁻⁵ However, direct application of this method to naphthalene T_2 as donor may present diffi-

(1) The Role of Second Triplet States in Solution Photochemistry. VIII. For No. VII, see ref. 5.

(2) R. S. H. Liu and R. E. Kellogg, *J. Amer. Chem. Soc.*, **91**, 250 (1969).

(3) R. S. H. Liu and J. R. Edman, *J. Amer. Chem. Soc.*, **91**, 213 (1969).

(4) K. S. Y. Lau, R. O. Campbell, and R. S. H. Liu, *Mol. Photochem.*, **4**, 315 (1972).

(5) R. O. Campbell and R. S. H. Liu, *J. Amer. Chem. Soc.*, **95**, 6560 (1973).

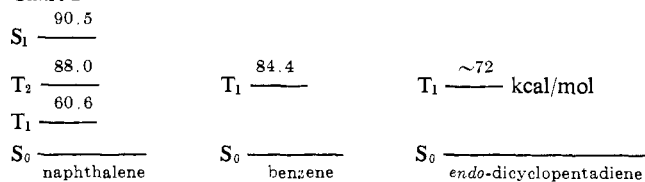
(6) See, e.g., F. Wilkinson, *Advan. Photochem.*, **3**, 241 (1964).

(7) A possible case of reaction from the T_2 of a substituted naphthalene is in the literature, see p 4371 in H. E. Zimmerman and C. O. Bender, *J. Amer. Chem. Soc.*, **92**, 4366 (1970).

culties at least in two ways. One is that many of the olefin acceptors when used at high concentrations are known to quench the S_1 state of naphthalene.⁸ Secondly, because of closer spacing between the T_1 and T_2 states (see Chart I),⁹ its lifetime may become too short for the bimolecular energy transfer process to be competitive with its unimolecular decay, particularly at acceptor concentrations where singlet quenching is negligible. Some modifications will have to be introduced.

The procedure we used with some success is one parallel to that used in studies of energy transfer in solid²; i.e., a host compound (solvent) with appropriate triplet energy is introduced which serves both as a T_2 trapping agent and a carrier of excitation energy to the eventual acceptor *via* excitation-hopping among like molecules. This approach has been successfully tested in the anthracenes.⁴ The system described below involves the following compounds: donor, naphthalene (N); T_2 trap and energy carrier, benzene (B); inert cosolvent, hexane; acceptor, *endo*-dicyclopentadiene (E) which is known to undergo internal cycloaddition in the triplet state.¹⁰ The key energy levels of the compounds involved are shown in Chart I. Clearly, the

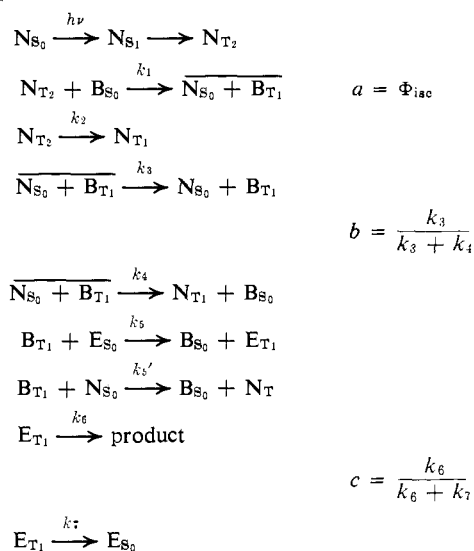
Chart I



level of benzene T_1 makes it ideal both to trap N_{T_2} and to excite E.¹¹

With this four component mixture, the scheme of naphthalene sensitized reaction of *endo*-dicyclopentadiene becomes that shown in Scheme I.

Scheme I



(8) (a) L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, **16**, 125 (1968); (b) D. A. Labianca, G. N. Taylor, and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 3679 (1972).

(9) The energy of N_{T_2} was based on absorption study on a single crystal of naphthalene: D. M. Hanson and G. W. Robinson, *J. Chem. Phys.*, **43**, 4175 (1965).

(10) G. O. Schenck and R. Steinmetz, *Chem. Ber.*, **96**, 520 (1963).

(11) We assumed the E_{T_1} energy is close to that of norbornene which is estimated to be close to 72 kcal/mol: D. R. Arnold, *Advan. Photochem.*, **6**, 330 (1968).

N_{T_1} is assumed to decay to N_{S_0} without affecting product formation. The step of energy transfer from N_{T_2} to E has been omitted. Under the experimental condition that $[B] \gg [E]$, this step is of negligible importance. Also, k_5 should be equal to k_5' with both approaching k_{diff} .¹² With these assumptions, the Stern-Volmer expression for the product formation becomes

$$\frac{1}{\phi_p} = \frac{1}{abc} \left(\frac{[E]}{[E] + [N]} \right) \left(1 + \frac{k_2}{k_1} \frac{1}{[B]} \right)$$

Preparation of samples and irradiation procedure are similar to those reported.³ To avoid singlet quenching complications, $[E]$ was kept constant for all samples (Table I). Also, $[N]$ was kept constant so that the

Table I. Naphthalene Sensitized Cyclization of *endo*-Dicyclopentadiene^a

[Benzene], <i>M</i>	% conversion to product ^b	[Benzene], <i>M</i>	% conversion to product ^b
10.0	3.96	2.00	1.54
5.73	3.55	1.32	1.03
4.03	2.79	0	0.46
3.57	2.08	10.0 ^c	0.46
2.45	1.65		

^a Concentration of naphthalene, $2.0 \times 10^{-3} M$; concentration of *endo*-dicyclopentadiene, $5.0 \times 10^{-2} M$. ^b Irradiated for 29 days in "M.-G.-R." quantum yield apparatus (F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, **1**, 245 (1969) a 550-W Hanovia Hg lamp with Corning 0-54 filters. ^c In the absence of naphthalene.

same amount of light quanta was absorbed by all samples even though only the Corning 0-54 filters were used. The omission of the long wavelength cut-off filter permits higher light intensity, necessary for this low quantum yield reaction. After irradiating samples for the same period of time relative product yield becomes relative quantum yield. Results of such a run are summarized in Table I with a corresponding Stern-Volmer plot shown in Figure 1.¹³

It is clear that benzene enhances the efficiency in T_2 sensitization and within the concentration range, there is a linear relation between $1/\phi$ (rel) and $1/[B]$ as predicted by the above Stern-Volmer equation. From the ratio of the slope and intercept, k_2/k_1 can be calculated and is equal to $9.7 M$. If one assumes that exothermic triplet-triplet energy transfer proceeds at diffusion rate, i.e., $k_1 = 6.2 \times 10^9 \text{ sec}^{-1} M^{-1}$,¹⁴ then k_2 , the rate constant of radiationless deactivation of naphthalene T_2 , is $6.0 \times 10^{10} \text{ sec}^{-1}$. Its average lifetime ($\tau = 1/k_2 = (1.7 \pm 0.5) \times 10^{-11} \text{ sec}$) is therefore about an order of magnitude shorter than that of anthracene T_2 , consistent with the relative spacing between the two lowest triplet states in the two compounds.

With recent interest in "intermolecular intersystem

(12) For a recent discussion on this point, see N. J. Turro, N. E. Schore, H. Steinmetzer, and A. Yekta, *J. Amer. Chem. Soc.*, **96**, 1936 (1974).

(13) The last two samples in Table I are controls to show that the observed effects are not due to direct sensitization by naphthalene nor due to imperfect filtering systems resulting in direct excitation of benzene molecules.

(14) An experimental value from flash photolysis studies: W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4769 (1966).

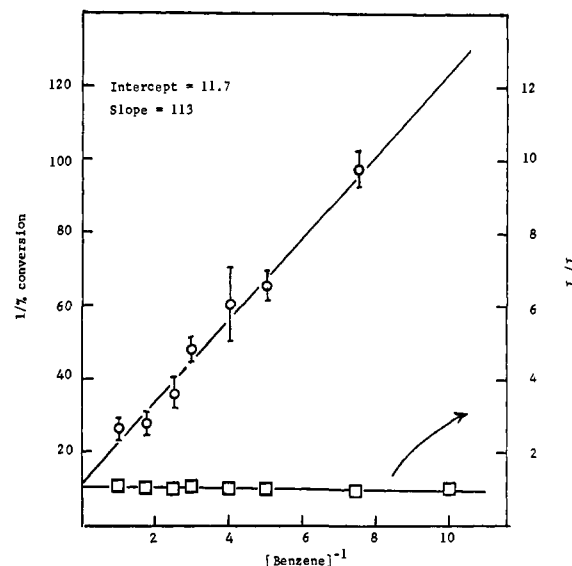


Figure 1. Stern-Volmer plots of (a) the naphthalene sensitized reaction of *endo*-dicyclopentadiene (○) and (b) the fluorescence of naphthalene in the presence of benzene (□).

crossing,"¹⁵ we carried out additional quenching experiments to show that our results are not due to energy transfer processes originating from the singlet state of naphthalene. Therefore, we showed that in the same concentration range as in the chemical study benzene has only a negligible effect on the intensity of naphthalene fluorescence (Figure 1). In fact, if anything, it shows a weak enhancement.

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(15) (a) G. Vaubel, *Chem. Phys. Lett.*, **9**, 51 (1971); (b) H. Zimmerman, D. Stehlike, and K. H. Hausser, *ibid.*, **11**, 496 (1971); (v) G. Vaubel and H. Baessler, *ibid.*, **11**, 613 (1971); (d) V. L. Ermolaev and E. B. Svshnikova, *Opt. Spectrosc. (USSR)*, **29**, 324 (1970).

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An Electron Spin Resonance Study of the Steric Rigidity in the Allyl and 1,1-Disubstituted Allyl Radicals

Sir:

Despite a large expenditure of effort and the application of various experimental techniques, the stabilization energy of the allyl radical continues to be a subject of controversy.¹ Estimates range from 9 to 24 kcal/mol although a value of about 10 kcal/mol is now

(1) K. W. Egger, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **86**, 5420 (1964); D. M. Golden, A. S. Rogers, and S. W. Benson, *ibid.*, **88**, 3196 (1966); D. Golden, N. Gac, and S. W. Benson, *ibid.*, **91**, 2136 (1969); D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969); S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965); Z. B. Alfassi, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **5**, 155 (1973); J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966); F. P. Lossing, *Can. J. Chem.*, **49**, 357 (1971); D. K. S. Sharma and J. L. Franklin, *J. Amer. Chem. Soc.*, **95**, 6562 (1973); A. S. Rogers and M. C. R. Wu, *ibid.*, **95**, 6913 (1973); J. A. Berson and E. J. Walsh, Jr., *ibid.*, **90**, 4730 (1968); R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 959 (1964); A. B. Trenwith, *J. Chem. Soc., Faraday Trans. 1*, 1737 (1973); M. Szwarc and A. H. Sehon, *J. Chem. Phys.*, **18**, 237 (1950); W. v. E. Doering and G. H. Beasley, *Tetrahedron*, **29**, 2231 (1973); P. S. Engel, A. I. Dalton, and L. Shen, *J. Org. Chem.*, **39**, 384 (1974); R. J. Field and P. I. Abell, *J. Amer. Chem. Soc.*, **91**, 7226 (1969).