system. One measure of this effect is the equilibrium quotient for the reaction in which the monodentate complex, $Cr(OH_2)_5G^{3+}$, is converted to the bidentate complex, $Cr(OH_2)_4G^{3+}$; the statistically corrected value of this equilibrium quotient is κ_2/κ_1, which, for $Z = 0.5$, is $(0.011/0.032) = 0.34$.

References and Notes

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(12) In the present study the value of $\bar{g}$ exceeds one (1.03) at $Z = 0.955$, and in the study of ethylene glycol–chromium(III) (ref 2), values of $\bar{g}$ at $Z = 0.980$ and 0.988 exceeded one (1.02 and 1.04, respectively). It is possible that inadequate rinsing of the ion-exchange resin prior to elution is responsible for these values of $\bar{g}$ greater than one.

(13) In the study of the ethylene glycol–chromium(III) system (ref 2), separation by ion-exchange of different glycol–chromium(III) species was attempted for equilibrated solutions with $Z = 0.335$, 0.539, 0.730, 0.950, and 0.980. In each case, only two electron peaks were observed. The more easily eluted species was hexaaquachromium(III) ion, and the less easily eluted species had a value of $\bar{g} = 1.00 \pm 0.02$.

Energy Transfer from the Second Triplet State of Naphthalene and Other Aromatic Compounds[1]

Catherine C. Ladwig and R. S. H. Liu*

Contribution from the Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822.

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Abstract: Energy transfer from the second triplet state of naphthalene, 1-chloronaphthalene, and pyrene was examined with the napthalene systems studied in more detail. A modified chemical method was designed in order to increase trapping efficiency of the very short lived upper states. The method involved the use of a third compound at high concentration which trapped the T_2 of the donor and carried excitation to the eventual acceptor via excitation hopping through identical molecules. Chemistry produced by the triplet acceptor provided the handle to follow the energy transfer processes. In the case of naphthalene the energy carrier was benzene and the best acceptor was *endo*-dicyclopentadiene. The average lifetimes of the T_2 state of naphthalene and 1-chloronaphthalene were found to be 12 ± 2, 13 ± 2 ps, respectively. These values are an order of magnitude smaller than the corresponding values for substituted anthracenes (200–300 ps). From the difference in T_1–T_2 separation of the two compounds, this difference in lifetime was not unexpected.

Introduction

The presence of a second triplet state below the lowest excited singlet in aromatic compounds was first suggested by the triplet yield data. The generally high values are inconsistent with the sizable S_1–T_1 splitting in these compounds if assuming intersystem crossing involves these two states only.[2] This suspicion was subsequently confirmed by several groups through detection of low-lying second triplet levels in these molecules. Therefore, by flash-photolysis studies Kellogg[3] and McCartin and Bennett[4] placed the T_2 state of anthracene and several substituted anthracenes below the corresponding S_1. Similarly picene and pyrene were shown to have low-lying T_2 states (in the latter case T_2 is slightly above S_1).[5] By direct singlet-triplet absorption measurements a low-lying T_2 state was also detected in benzene[6] and naphthalene.[7] The T_1–T_2 separations in the latter two cases are too small for convenient triplet-triplet absorption studies. The high triplet yields in these compounds are therefore a result of rapid intersystem crossing between the nearly isoenergetic S_1, T_2 states, followed by internal conversion between the triplet states.

A small S_1–T_2 separation implies an unusually large T_1–T_2 gap. This was verified in the above mentioned spectroscopic studies. One may then logically consider the possibility that such a molecule may pause at an excited triplet level for a rather long period before undergoing internal conversion to T_1. Indeed, soon after Kellogg's assignment of the T_2 level of anthracene, Liu and Edman[8] presented evidence that such states can participate in biomolecular processes. Many of the substituted anthracene-sensitized reactions were shown to involve triplet-triplet energy transfer from the second triplet states:[9]

$$D_{T_2} + A_{S_0} \rightarrow D_{S_0} + A_{T_1}$$

Kinetic studies of these systems provided then the only available method to determine the average lifetime of such excited triplets. Subsequently spectroscopic studies of the anthracene-sensitized naphthalene phosphorescence in mixed crystals[10] and chrysene-sensitized (two-photon excitation) phosphorescence of biphenyl in toluene matrix[11] established the case of energy transfer from T_2 beyond reasonable doubt.

Nevertheless, a paper[12] did appear to suggest the above mentioned results could be instead due to the following spin-forbidden process:

$$D_{S_1} + A_{S_0} \rightarrow D_{S_0} + A_{T_1}$$

The observation of fluorescence quenching enhanced by heavy atoms was considered as supporting evidence for this process. However, the observation that singlet quenching is not accompanied by formation of the acceptor triplets as shown in an experiment of 9,10-dibromoanthracene-sensitized photodimerization of 1,3-cyclohexadiene[13] negates such a possibility. The spin-forbidden process, however, does appear to take place in other selected systems at expectedly a much slower rate.[14]

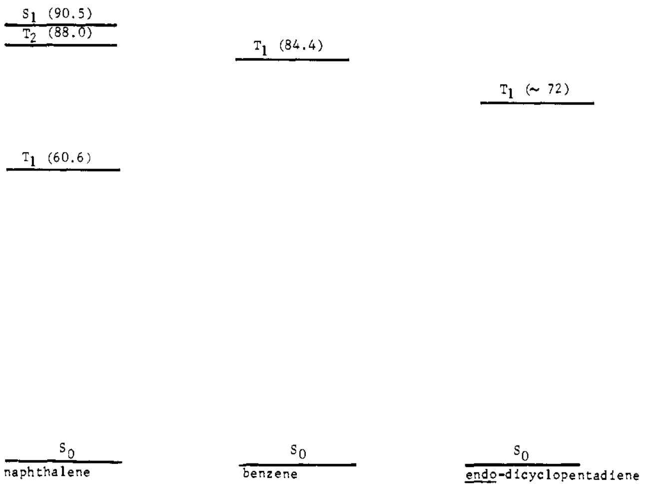

Figure 1. Energy diagram of naphthalene (donor), benzene (T_2 trap and excitation carrier) and *endo*-dicyclopentadiene (eventual acceptor) according to Hanson and Robinson (ref 7) and D. R. Arnold (ref 18).

For sometime our study of energy transfer from the second triplet states were limited to the anthracenes. There are, of course, good reasons for this. Anthracenes are known to have the largest T_1-T_2 splitting among aromatic compounds of known second triplet levels. The lifetime of the upper states are therefore expected to be longer, thus the energy more easily trapped. However, recently we reported in a preliminary study a case of energy transfer from the second triplet state of naphthalene.[15] The details of this study are now reported here along with results of a substituted naphthalene and other selected aromatic compounds.

Results and Discussion

Naphthalene as a T_2 Donor. Selection of Acceptor Systems. From an absorption study of a single crystal of 4 cm long, Hanson and Robinson[7] concluded that the second triplet state of naphthalene is slightly below that of S_1. The ordering of the lowest four states in naphthalene is shown in Figure 1. For an unambiguous study of energy transfer from the second triplet level to an acceptor, clearly, the triplet energy of the latter should be in the range of 70-85 kcal/mol—sufficiently high to avoid T_1 sensitization and sufficiently low to ensure rapid T_2 transfer. The acceptor must also exhibit a well-characterized efficient triplet state reaction which will provide the necessary handle to follow the T_2 energy-transfer process. In these regards, simple olefins with triplet excitation energy between 72-80 kcal/mol[16] should serve the purpose well. Several of their triplet state reactions (e.g., isomerization and cycloaddition) have been thoroughly examined. Of many possible systems we chose the isomerization of 2-octene,[17] cyclodimerization of norbornene,[18] and internal cycloaddition of *endo*-dicyclopentadiene[19] as possible chemical handles to follow the T_2 transfer process.

Preliminary experiments of naphthalene-sensitized isomerization of octene gave results qualitatively in agreement with what was expected from T_2 sensitization. However, results were not quantitatively reproducible.[20] We suspect other reaction pathways (for example, those initiated by free radicals) unimportant in normal sensitized reactions become competitively important in the less efficient T_2 sensitization process. Cycloaddition reactions are not expected to proceed via radical processes. Preliminary results with norbornene were encouraging showing that dimers were produced when irradiated with naphthalene as a sensitizer. But kinetically this is a more complex system in that both the T_2 trapping and the dimerization steps are dependent on norbornene concentrations not to mention other possible quenching steps. Therefore, no attempt was made to obtain extensive kinetic data. We then turned to *endo*-dicyclopentadiene. Its triplet excitation energy is expected to be approximately the same as norbornene (estimated to be around 72 kcal/mol).[18] It is known to undergo internal cycloaddition in the triplet state:[19]

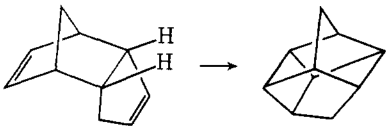

Table I. Naphthalene Sensitized Reaction of *endo*-Dicyclopentadiene and Quenching of Naphthalene Fluorescence[a]

[E], M × 10	$\phi \times 10^3$ [b]	I^0/I [c]
9.8		11.5
7.9	17.7	
1.98	4.6	3.8
1.28	2.7	
0.99	2.3	1.5
0.79	2.2	
0.69	1.44	1.8
0.59	1.22	
0.49	1.00	2.6

[a] $[N] = 2.01 \times 10^{-3}$ M; $[B] = 0$; solvent, hexane. [b] Irradiated for 29 days using 0-54 filters. [c] Excitation wavelength: 313 nm.

Table I lists the quantum yield data of naphthalene sensitized reaction of *endo*-dicyclopentadiene in hexane. Expectedly, the quantum yield of reaction increases with the increase of acceptor concentration (Table I). However, when subjected to Stern-Volmer analysis, we found the data too scattered to give unambiguous correlations (a straight line was obtained but with a negative intercept). Upon an investigation of the effect of *endo*-dicyclopentadiene (E) on the fluorescence intensity of naphthalene, the problem became evident: at high acceptor concentrations substantial singlet quenching is observed (Table I).

Quenching of fluorescence of aromatic compounds by other alkenes of course are known in the literature.[21] This complicating process does not necessarily make the kinetics of T_2 energy transfer too complex to be analyzed but rather it reduces the quantum yield values making the data less accurate. The variation of [E] through a large concentration range also decreases the accuracy in analysis by the GLC method. We therefore resorted to a modified method to minimize these complications. A third compound is added at high concentrations which serves to trap naphthalene T_2 and carry the excitation away from the adjacent naphthalene (now a quencher) by way of excitation hopping among like molecules, eventually reaching the alkene. The problems related to fluorescence quenching can now be avoided by the use of low, constant concentrations of alkenes.

This approach is analogous to studies of energy transfer in solids[10] and was qualitatively demonstrated useful in solution studies. In the latter case naphthalene was added to increase the quantum yield of anthracene sensitized isomerization of stilbene.[9c] In the present case benzene was chosen as the intermediate system which was shown not to have any significant effect on the fluorescence intensity of naphthalene (Table II, last column) and has the necessary triplet state energy to act both as an acceptor from naphthalene T_2 and donor to *endo*-dicyclopentadiene (Figure 1). Even with this approach the quantum yield of reaction remained low. To maximize the light intensity, a filtering system having only the high-energy cut-off was used (see Experimental Section). Three separate runs were performed. The data (Table II) are clearly reproducible.

Kinetics of the Naphthalene-Sensitized Reaction of *endo*-Dicyclopentadiene. The complete scheme of the naphthalene (N) sensitized reaction of *endo*-dicyclopentadiene (E) in the presence of varying amounts of benzene (B) is:

$$N_{S_0} \xrightarrow{h\nu} N_{S_1} \rightarrow N_{T_2}$$

$$N_{T_2} + B_{S_0} \xrightarrow{k_1} \overline{N_{S_0} + B_{T_1}} \tag{1}$$

$$N_{T_2} + E_{S_0} \xrightarrow{k_1'} \overline{N_{S_0} + E_{T_1}} \tag{1'}$$

$$N_{T_2} \xrightarrow{k_2} N_{T_1} \tag{2}$$

$$\overline{N_{S_0} + B_{T_1}} \xrightarrow{k_3} N_{S_0} + B_{T_1} \tag{3}$$

$$\overline{N_{S_0} + B_{T_1}} \xrightarrow{k_4} N_{T_1} + B_{S_0} \tag{4}$$

$$B_{T_1} + E_{S_0} \xrightarrow{k_5} B_{S_0} + E_{T_1} \tag{5}$$

$$B_{T_1} + N_{S_0} \xrightarrow{k_5'} B_{S_0} + N_{T_1} \tag{5'}$$

$$B_{T_1} \xrightarrow{k_6} B_{S_0} \tag{6}$$

$$E_{T_1} \xrightarrow{k_7} \text{product} \tag{7}$$

$$E_{T_1} \xrightarrow{k_8} E_{S_0} \tag{8}$$

$$N_{T_1} \xrightarrow{k_9} N_{S_0} \tag{9}$$

In this scheme it is assumed that any observed reaction of E originates from energy transfer from T_2 of naphthalene (eq 1) and that the T_1 of naphthalene being the lowest excited state of the entire system can only decay to the ground state (eq 9). Considering the energy difference between the T_1 states of N and E and that E is a rigid molecule, the assumption of inactivity of N_{T_1} should be a safe one (see the anthracene cases[9a,b] for a more detailed argument). High concentrations of benzene enhances T_2 trapping (eq 1) and increases the escape efficiency defined as the percentage of benzene triplets diffused away from the donor naphthalene molecule, now a potential quencher [i.e., $b = k_3/(k_3 + k_4)$]. At the relative concentrations of E and B, process 1′ is unimportant. Equation 6 is also probably not an important process because under the experimental conditions the concentrations of E and N are sufficiently high to ensure complete trapping of benzene triplets. If a is the intersystem crossing efficiency of naphthalene and c the product yield of E_{T_1} [i.e., $k_7/(k_7 + k_8)$], and assuming $k_5 = k_5'$ then the Stern–Volmer expression for quantum yield of the tricyclic product is:

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

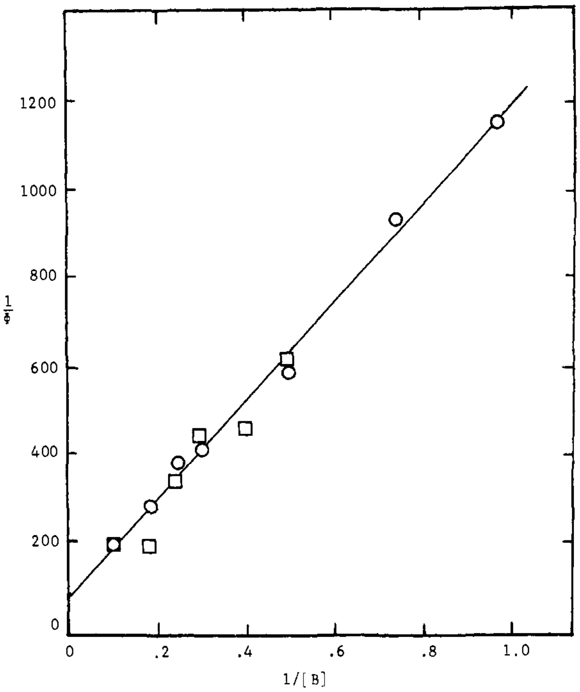

Figure 2. A Stern–Volmer plot of the naphthalene-sensitized isomerization of *endo*-dicyclopentadiene in the presence of benzene, B (○, run 1; □, run 2).

Table II. Naphthalene-Sensitized Reaction of *endo*-Dicyclopentadiene in the Presence of Benzene and Effect of Benzene on Naphthalene Fluorescence[a]

Run no.	[Benzene]	% conversion	$\phi \times 10^3$	I^0/I[b]
1[c]	10.0	10.1	5.08	
	5.68	7.34	3.57	
	4.03	5.32	2.68	
	3.36	5.08	2.56	
	2.46	3.85	1.94	
	2.00	3.52	1.77	
	1.34	2.18	1.10	0.83
	1.02	1.76	0.886	
2[d]	9.96	0.532	5.08	0.50
	5.72	0.551	5.26	
	4.04	0.292	2.79	0.61
	3.37	0.230	2.20	
	2.46	0.229	2.19	0.62
	2.03	0.173	1.65	
	1.01	0.136	1.30	
3[e]	10.0	3.96	6.25	
	5.73	3.55	5.65	
	4.03	2.81	4.44	
	3.57	2.00	3.16	
	2.45	1.65	2.61	
	2.00	1.54	2.43	
1.32	1.03	1.63		
Control	10.0	0.46[f]		
	0	0.46[g]		

[a] Hexane is the inert solvent. [b] [E] = 0; solvent, hexane; excitation wavelength: 313 nm. [c] [N] = 2.00×10^{-3} M; [E] = 1.01×10^{-1} M; irradiated for 29 days. [d] [N] = 2.00×10^{-3} M; [E] = 1.00×10^{-1} M; 34 days. [e] [N] = 2.01×10^{-3} M; [E] = 4.98×10^{-2} M; 29 days. [f] [E] = 5.0×10^{-2} M; [N] = 0; 29 days. [g] [E] = 5.0×10^{-2} M; [N] = 2.0×10^{-3} M; 29 days.

Experimentally, E and N were kept at constant concentrations. The quantum yields should, therefore, only be a function of the concentration of benzene with a linear dependence between Φ_p^{-1} and $[B]^{-1}$. When the data in Table II are plotted accordingly, this expected linear relation is verified (Figure 2). Run number 1 and 2 involves identical concentration of E. The data are therefore shown together in the same figure. The ratio of k_2/k_1, extrapolated from the slope and intercept of the line, is 13.9 ± 2.3 M. Of these two constants, k_1 is the rate constant of exothermic energy transfer from the second triplet state of naphthalene. Although it is not exactly known, one may safely assume that it should approximate the values of exothermic energy transfer when only the lowest triplet states are involved. The latter values remain reasonably constant when determined in solvents of equal viscosity and involving donor-acceptor pairs of roughly the same dimension. For example, the exothermic triplet-triplet energy transfer constants measured by kinetic flash photolysis by Herkstroeter has an average value of 6.2×10^{-9} l. M^{-1} s^{-1}.[22] Substituting this value for k_1, one obtains a value of 8.6×10^{10} s^{-1} for k_2, the internal conversion constant from naphthalene T_2. The average lifetime of naphthalene T_2 ($\tau = 1/k_2$) is, therefore $(1.2 \pm 0.3) \times 10^{-11}$ s, i.e., approximately 10 ps. The data from run number 3 yielded a slightly longer lifetime (17 ± 3 ps). But the difference is probably not statistically meaningful.

Earlier we determined the average T_2 lifetime of several substituted anthracenes also by chemical kinetic methods. The values for 9,10-dibromo-, 9-phenyl-, and 9,10-dichloroanthracene are respectively 2.0, 2.9, and 3.0×10^{-10} s. Although for these substituted anthracenes the T_2 levels are not accurately known, from indirect spectroscopic and chemical evidence[4,9b] it is believed their T_1-T_2 separations are not significantly different from that of parent anthracene (32.0 kcal/mol), therefore much larger than the corresponding value for naphthalene. The short average T_2 lifetime of naphthalene is therefore consistent with the assumption that the internal conversion process is determined by the magnitude of the Franck-Condon overlap of the two states under consideration. In agreement with this observation is our recent report of the deuterium isotope effect on the lifetime of naphthalene second triplet state.[23]

1-Chloronaphthalene as T_2 Donor. The study of T_2 energy transfer could conceivably be facilitated through the use of naphthalene with heavy atom substituents. The T_2 yield could be enhanced by the presence of the heavy atom which at the same time should have little effect on the T_2 lifetime. The use of bromo- or iodonaphthalene is, however, impossible for solution photochemical studies because these compounds darken rapidly upon irradiation presumably due to photolysis of the carbon-halogen bond. We have therefore conducted studies only with a chloro derivative—1-chloronaphthalene. Experiments parallel to those described in the previous section were performed. *endo*-Dicyclopentadiene is again the chemical handle to follow the T_2 transfer process and benzene, the energy carrier. Results of such a run are listed in Table III. Analysis of the data based on the Stern-Volmer expression shown above gave the following values of slope and intercept: 2046 ± 48 M and 168 ± 4. After again assigning a value of 6.2×10^9 M^{-1} s^{-1} for k_1, we found the $T_2 \rightsquigarrow T_1$ internal conversion rate constant for 1-chloroanthracene to be 7.5×10^{10} s^{-1} which gives an average T_2 lifetime of $(1.3 \pm 0.2) \times 10^{-11}$ s (possibly an upper limit, see below). Within experimental error this is identical with that of naphthalene which as stated earlier is not unexpected.

What is unexpected is that the quantum yield of the 1-chloroanthracene-sensitized reaction (at identical benzene concentration) is actually lower than that of the naphthalene-sensitized reaction. Just the opposite is expected when one considers that the intersystem crossing efficiency of 1-chloronaphthalene (0.94)[24] is higher than that of naphthalene (~0.70).[25] Two factors may account for this unexpected result. First, the exact T_2 energy of 1-chloronaphthalene is not known. If it is 2 or more kcal/mol lower than that of naphthalene, then it may not be 3 kcal/mol more than the triplet energy of benzene (E_T = 84.3 kcal/mol), resulting in diminished rates of energy transfer. This means trapping of chloronaphthalene T_2 by benzene would not be as efficient. The use of a slightly lower energy carrier (e.g., toluene) could conceivably improve the situation. Secondly, if spin-orbit coupling only results in enhancement of the $S_1 \rightsquigarrow T_1$ process it should have no effect on the quantum yield of a T_2-sensitized reaction.

Other Aromatic Compounds. For primarily two reasons it will be difficult to design experiments to study the low-lying T_2 state of benzene. According to Colson and Bernstein,[6] its T_1-T_2 separation (19.8 kcal/mol) is even smaller than that of naphthalene which means a further decrease of the T_2 lifetime. The ternary system designed for naphthalene allowed us to improve the time scale by an order of magnitude, i.e., to go from anthracenes with a T_2 lifetime of the order of 100 ps to naphthalene around 10 ps. Still, the reaction even at highest concentration of benzene is very inefficient requiring a prolonged irradiation period. A further decrease of donor lifetime would make the experiment very difficult. Secondly the high T_1 energy (84.3 kcal/mol) makes it rather difficult to find a chemical handle (the eventual acceptor) which can accept energy unambiguously from its T_2.

Table III. Chloronaphthalene-Sensitized Reaction of *endo*-Dicyclopentadiene in the Presence of Benzene[a]

[Benzene]	% conversion[b]	$\phi \times 10^3$	I^0/I[c]
10.0	1.02	3.26	0.86
5.69	0.550	1.76	
4.02	0.452	1.45	1.11
3.34	0.366	1.17	
2.44	0.326	1.04	0.98
2.02	0.267	0.856	
1.34	0.208	0.668	0.83
1.00	0.192	0.614	1.02

[a] [ClN] = 2.01×10^{-3} M; [E] = 1.00×10^{-1} M; solvent, hexane. [b] Irradiated for 34 day using 0-54 filters. [c] Excitation wavelength: 313 nm.

Among other aromatic compounds, pyrene is believed to have the T_2 level slightly above S_1. The temperature dependent intersystem crossing process was in fact used as an indirect evidence for its presence. The values for the three lowest excited states are: 76.6 (S_1), 77.8 (T_2), 48.3 kcal/mol (T_1).[5,26] The relatively low T_2 value precluded the use of benzene or its derivative as the T_2 trap and energy carrier. When changed to a naphthalene derivative then problems such as solubility, viscosity, and the triplet energy of the eventual acceptor will have to be considered. In a preliminary experiment with the pyrene-naphthalene-myrcene ternary system (Corning 0-52 filter), a fourfold increase of the bicyclic product[27] was observed when tubes with and without naphthalene were irradiated in parallel. However, upon prolonged irradiation pyrene absorption disappeared and the solution turned yellow. An extensive kinetic study therefore was impossible.

Direct Observation of T_2 by Spectroscopic Methods. At the time we started this program the level of sophistication of instrumentation precluded the possibility of direct observation of such short-lived T_2 states either via $T_2 \rightarrow T_1$ fluorescence or detection of such species by fast kinetic methods. An early unsuccessful attempt in fact was made at du Pont to record $T_2 \rightarrow T_1$ fluorescence of anthracene imbedded in polymethacrylate by conventional recording spectrometry.[28] The negative result did place a maximum quantum yield of fluorescence around 10^{-4}. Now with the availability of more sensitive instruments[29] and faster kinetic methods,[30] we believe their detection will soon become a reality.

Experimental Section

Materials. Naphthalene (M.C. & B.), naphthalene-d_8 (Aldrich), benzene (Mallinckrodt, analytical reagent grade), and hexanes (Mallinckrodt, analytical reagent grade) were used as supplied. The perdeuterionaphthalene sample was found, by MS analysis, to contain 91% d_8 and 9% d_7h isomers. 1-Chloronaphthalene (Eastman Kodak) and *endo*-dicyclopentadiene (M.C. & B.) were vacuum distilled before use.

Preparation of Samples. Sample tubes were 13 × 100 mm culture tubes which had been previously cleaned and matched for approximately the same transmission of 310 nm incident light on a Beckman DB. The tubes were constricted and injected with 3 ml of the desired samples. Naphthalene samples were approximately 2×10^{-3} M in donor and 1×10^{-1} M in acceptor; pyrene samples 1×10^{-3} M in donor and 1×10^{-1} M in acceptor. The concentration of the energy carrier varied from 1 to 10 M. Samples were degassed and sealed using the freeze-pump-thaw (three cycles) method.

Irradiation of Samples. Samples were irradiated in a merry-go-round apparatus[31] using a 550-W, medium-pressure Hanovia mercury lamp in a Pyrex well. Filters were chosen to prevent direct absorption by the energy carrier and acceptor while allowing absorption by the donor. Although irradiation time for these systems could be shortened by using 0-53 filters, controls showed direct absorption by the energy carrier at this wavelength. Using 0-54 filters, irradiation time was approximately 30 days. Pyrene samples were irradiated using 0-52 filters. Irradiation time was 3 to 4 days.

Fluorescence intensity of samples was analyzed using a Hitachi Perkin-Elmer MPF-2 Fluorescence Spectrometer. Emission measurements were taken on the sealed tubes themselves rather than in standard quartz cells because oxygen greatly effects emission readings. Variation in transmission of the tubes also effects results. However, since the tubes were roughly matched at the onset, this error was somewhat controlled. The emission data (Table II) ruled out the possibility of involvement of naphthalene singlet in formation of benzene triplets.

Conversion of acceptor to its product was detected and analyzed using gas chromatography. A Varian Aerograph Series 2800 with a flame ionization detector was used. Separation of *endo*-dicyclopentadiene from its cage product was effected on a 6-ft, 10% dibutyl tetrachlorophthalate column (85 °C). The cage product has a shorter retention time. The product was identified by comparison of retention time of the product obtained from acetophenone sensitized reaction.

Myrcene and its cycloaddition product were separated using a 12-ft, 5% SE 30 column at a temperature of 50 °C.[27]

Norbornene was separated from its dimer at 100 °C on a 6-ft, 5% SE 30 column. Under these conditions the norbornene elutes with the solvent. The dimer products were identified by comparison with the acetophenone-sensitized products.

Quantum yield for the naphthalene samples was determined using a naphthalene-myrcene actinometer. The naphthalene concentration in the actinometer was 2×10^{-3} M, while the myrcene concentration was 3×10^{-2} M. Solutions were irradiated from 20 h to 4 days. Since the irradiation time of the actinometer was so short when compared with the time of the ternary system, three actinometers were used throughout the ternary irradiation period, and the results were averaged. Liu and Hammond have shown that triplet sensitization of myrcene leads to the single product 5,5-dimethyl-1-vinylbicyclo[2.1.1]hexane.[27] The quantum yield they reported for the sensitized cycloaddition of myrcene is 0.023. Using the reported quantum yield and the product concentration adjusted for the time difference, the quantum yields for the naphthalene reactions were calculated.

Analysis of Data. Data were analyzed using a Wang 300 Series Calculator with a card programmer, CP-1, attachment. The prepared program 360-46 ST was used to obtain a least-squares fit of the data points. The best straight line with its slope and *y* intercept and the standard deviation were obtained from the program.

Note Added in Proof. Since the submission of this paper, two papers have appeared which deal directly with the predicted $T_2 \rightarrow T_1$ fluorescence. By the single photon counting method, the weak ($\Phi = 8{,}10^{-7}$) $T_2 \rightarrow T_1$ fluorescence spectra of two substituted anthracenes were reported (see G. D. Gillispie and E. C. Lim, *J. Chem. Phys.*, **65,** 2022 (1976)). Also, one component of the electrochemiluminescence of diphenylanthracene was attributed to $T_2 \rightarrow T_1$ fluorescence (see N. Perisamy and K. S. V. Santhanan, *Chem. Phys. Lett.*, **39,** 265 (1976)).

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