

## EXTINCTION COEFFICIENTS FOR TRIPLET-TRIPLET ABSORPTION IN ETHANOL SOLUTIONS OF ANTHRACENE, NAPHTHALENE, 2,5-DIPHENYLOXAZOLE, 7-DIETHYLAMINO-4-METHYL COUMARIN AND 4-METHYL-7-AMINO-CARBOSTYRIL

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### SUMMARY

Triplet-triplet absorption spectra and extinction coefficients for anthracene, naphthalene, 2,5-diphenyloxazole, 7-diethylamino-4-methyl coumarin and 4-methyl-7-amino-carbostyryl in ethanol are reported.

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### INTRODUCTION

The absorption spectra and decay kinetics of triplet state molecules in solution may be conveniently investigated using flash photolytic and kinetic spectroscopy techniques<sup>1-6</sup>. Considerable conflict, however, still exists concerning the magnitudes of extinction coefficients for triplet-triplet absorptions due to the difficulties involved in accurate determination of triplet state concentrations following flash excitation. In the present work the ground state depletion technique<sup>3,5,7</sup> was used for determination of the extinction coefficients for anthracene triplet-triplet absorption in ethanol. The high intersystem crossing ratio,  $\Phi_T$ , and intense triplet-triplet absorption of anthracene are convenient characteristics for use of this compound in triplet-triplet energy transfer studies. In the present work energy transfer techniques were used for determination of extinction coefficients for triplet-triplet absorption in ethanol solutions of naphthalene, 2,5-diphenyloxazole (PPO), 7-diethylamino-4-methyl coumarin (C1) and 4-methyl-7-amino-carbostyryl (CS). The triplet-triplet absorption characteristics of highly fluorescent compounds such as PPO, C1 and CS are of particular interest to workers in the dye laser field<sup>8-10</sup>.

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## EXPERIMENTAL

*Chemicals*

Naphthalene and ethanol were purified as described previously<sup>11</sup>. The PPO was scintillation grade (purified by chromatography) as supplied by Koch-Light Ltd. The anthracene (B.D.H.), C1 (Eastman-Kodak) and CS (I.C.I.) were purified by recrystallization.

*Apparatus and procedure*

The flash photolysis systems used were identical to those described previously<sup>11,12</sup>. In several of the experiments reported below electrical input energies of 2 J (*i.e.* 0.01  $\mu\text{F}$  at 20 kV) were applied to the photolyzing flashtube which was identical in design to that reported previously<sup>11</sup>. The photon pulse obtained for a 2 J electrical input energy had a half width of 0.7  $\mu\text{s}$  decreasing to 10% of its peak intensity after 2  $\mu\text{s}$ . The photon output per flash as measured on a photodiode was reproducible to within  $\pm 2\%$ . In all experiments, unless otherwise stated, a band pass of 4 nm was used in the transient analyzing system and a Pyrex glass filter jacket (wall thickness  $\sim 2$  mm) was placed around the reaction cell in order to minimize photodecomposition of solutes and/or solvent by exciting wavelengths  $< 300$  nm.

The symbols  $\varrho_\lambda$  and  $\gamma_\lambda$  which refer to changes in optical density due to absorption (*i.e.* decrease in transmission on photolysis) and depletion (*i.e.* increase in transmission on photolysis) signals respectively are discussed in detail elsewhere<sup>11</sup>.

## RESULTS AND DISCUSSIONS

*Anthracene*

When anthracene-ethanol solutions ( $10^{-6}$ – $10^{-5}$  M) were flash photolyzed using a 50 J flash in the presence of a Pyrex filter the anthracene triplet-triplet absorption in the wavelength region 380–440 nm and the ground state depletion in the wavelength region 330–380 nm were observed to decay predominantly *via* second order kinetics. A mixed order kinetics analysis yielded values of  $k_1^{\text{Anth}} = 3 \pm 2 \times 10^2 \text{ s}^{-1}$  and  $k_2^{\text{Anth}} = 7 \pm 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for the first and second order rate constants for anthracene decay respectively. The latter value for  $k_2^{\text{Anth}}$  was calculated assuming the extinction coefficient  $\epsilon_{420}^{\text{T}}$ , for anthracene triplet absorption at 420 nm to be 75,000  $\text{M}^{-1} \text{ cm}^{-1}$  as reported below.

The anthracene triplet-triplet absorption spectrum in the region 390–440 nm, shown in Fig. 1, was obtained by measuring the optical density, *i.e.*  $\varrho_\lambda(t = 200) = \epsilon^{\text{T}} \cdot C_{\text{T}} \cdot l$ , at 200  $\mu\text{s}$  after flash photolyzing a  $4.2 \times 10^{-6}$  M anthracene solution using a 50 J flash. The ground state depletion spectrum in the region 324–380 nm, presented as  $\gamma_\lambda$  values at 200  $\mu\text{s}$  after the flash is shown in Fig. 2 where the ground

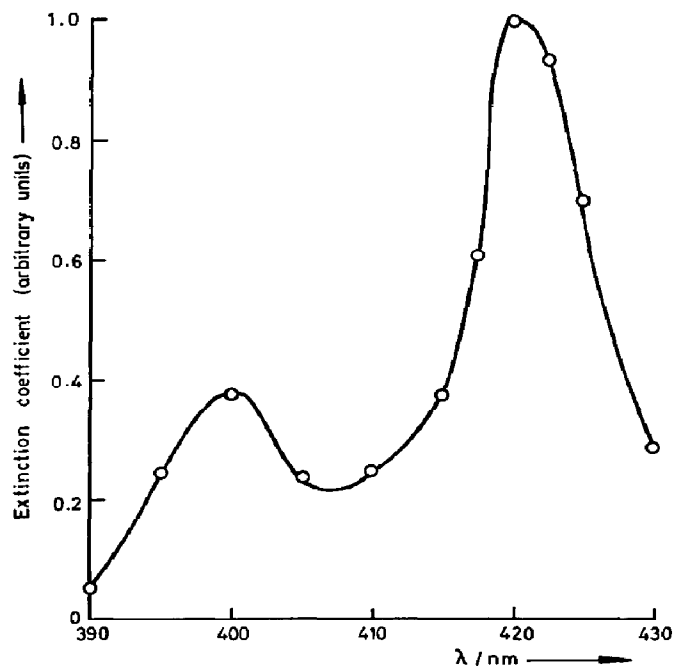


Fig. 1. Wavelength profile of anthracene triplet-triplet absorption in the region 390–430 nm (normalized to unity at peak for convenience).

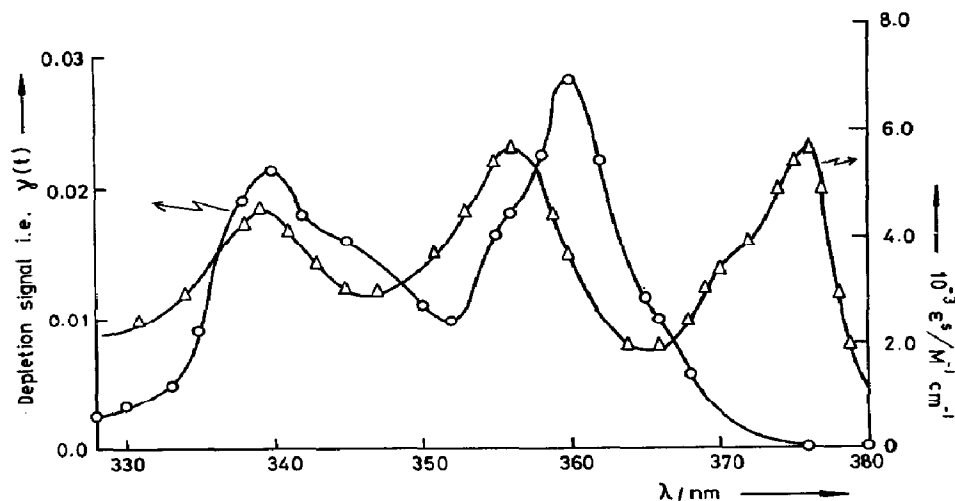


Fig. 2. Normal ground state absorption spectrum of anthracene in ethanol ( $\Delta$ ) and the depletion spectrum ( $\circ$ ), *i.e.*  $\gamma(t)$ , measured at 200  $\mu$ s after flash photolyzing a  $4.2 \times 10^{-6}$  M anthracene solution. Both spectra were recorded using a bandpass of 4 nm.

state absorption spectrum of anthracene (*i.e.*  $\epsilon_\lambda^S$ ) on the same bandpass is also shown for comparison. As can be seen from Fig. 2 considerable variation was observed between the normal ground state absorption and depletion spectra due to overlap of the triplet-triplet and ground state absorption spectra. The strong ground state absorption band ( $\epsilon > 5000 M^{-1} \text{ cm}^{-1}$ ) centred at 376 nm would be expected to yield a large transient depletion signal provided no triplet-triplet absorption (or other absorption) occurred in this region. The absence of this band in the observed depletion spectrum (Fig. 2) indicated that  $\epsilon_\lambda^S = \epsilon_\lambda^T (\pm 100) M^{-1} \text{ cm}^{-1}$  within this wavelength region (*i.e.* 370–380 nm). The absence of a depletion signal at 324 nm where  $\epsilon^S = 2750 M^{-1} \text{ cm}^{-1}$  again indicates that  $\epsilon^T (\lambda = 324 \text{ nm}) = \epsilon^S (\lambda = 324 \text{ nm}) \pm 100 M^{-1} \text{ cm}^{-1}$ . The fixed points on the triplet-triplet absorption spectrum, deduced from the above considerations, are indicated as squares on Fig. 3.

Since at any wavelength  $\lambda_1$ , within the region 380–440 nm,  $\epsilon_{\lambda_1}^S = 0$  we may write:

$$\frac{\rho_{\lambda_2}}{\gamma_{\lambda_2}} = \frac{\epsilon_{\lambda_2}^T}{(\epsilon_{\lambda_2}^S - \epsilon_{\lambda_2}^T)} \quad (1)$$

where  $\lambda_2$  refers to a wavelength where a large depletion signal is observed. In regions where  $\epsilon^S = \epsilon^T$  and  $\gamma = 0$  eqn. (1) is indeterminate. In order to obtain an accurate estimate of  $\epsilon_{\lambda_2}^T$  from eqn. (1) we require a knowledge of  $\epsilon_{\lambda_2}^T$ , *i.e.* the experimentally measured ground state depletion spectrum must be separated into its triplet-triplet absorption and ground state depletion components. The wavelength profile,  $\gamma_\lambda(t)$  versus  $\lambda$ , given in Fig. 2 was used to construct a series of equations of general type (2) where  $G = C_{TT}$ .

$$\{\epsilon_\lambda^S - \epsilon_\lambda^T\}G = \gamma_\lambda \quad (2)$$

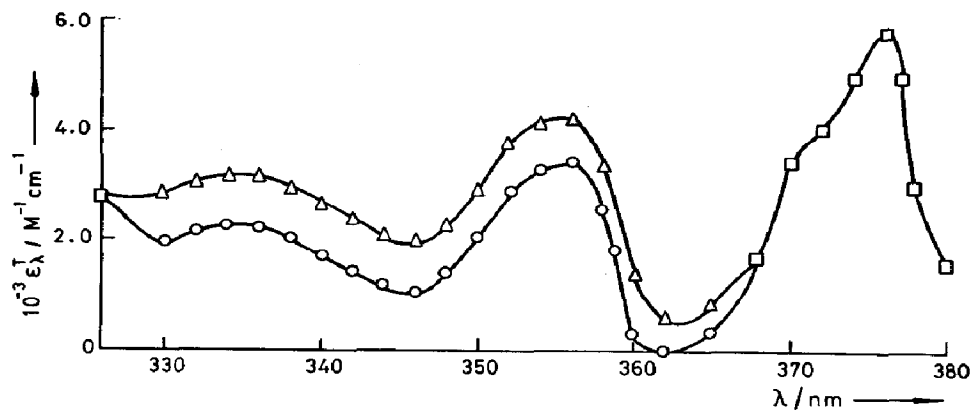


Fig. 3. Possible anthracene triplet-triplet absorption profiles in the wavelength region 320–380 nm. The profiles shown as circles and triangles were calculated assuming  $\epsilon^T$  at 365 nm to be 300 and 700  $M^{-1} \text{ cm}^{-1}$  respectively.

The eqns. (2) cannot, however, be solved directly for  $\epsilon_{\lambda}^T$ . At 365 nm  $\epsilon^S$  is relatively small (*i.e.*  $\sim 1800 M^{-1} \text{ cm}^{-1}$ ) but a large depletion signal was observed experimentally indicating that  $\epsilon_{365}^T$  is also small. As a first approximation it was therefore assumed that  $\epsilon_{365}^T = 0$  and using the equations of the type (2) the wavelength profile  $\epsilon^T$  in the region 324–370 nm was calculated. This profile, however, was unrealistic since  $\epsilon^T$  obtained in the region 360–363 nm was negative. A series of wavelength profiles of  $\epsilon^T$  in the region 324–370 nm were calculated assuming values of  $\epsilon_{365}^T$  between 0 and  $1000 M^{-1} \text{ cm}^{-1}$ . Two of these are shown in Fig. 3. On the information available all of these profiles were consistent with the experimental results obtained using a 4 nm bandpass in the analyzing system.

In order to ascertain which of the series of profiles, calculated above, was the correct profile  $\gamma_{\lambda}$  versus  $\lambda$  was measured (see Fig. 4) using a bandpass of 20 nm in the analyzing system. The series of profiles for 4 nm bandpass obtained above were integrated to 20 nm in order to estimate the expected depletion profiles for the experiment employing a 20 nm bandpass. By comparing the measured depletion profile obtained using a 20 nm bandpass, indicated as circles in Fig. 4, with the calculated profiles for a 20 nm bandpass (*i.e.* the solid and broken curves in Fig. 4) it was possible to decide which of the profiles shown in Fig. 3 was the correct triplet-triplet profile. It can be seen from Fig. 4 that this procedure was quite sensitive to the value of  $\epsilon_{365}^T$  used to obtain the 4 nm profile. The best fit to the experimental results indicated that  $\epsilon_{365}^T = 300 \pm 100 M^{-1} \text{ cm}^{-1}$  and the profile given by the circles in Fig. 3 was therefore the correct triplet-triplet profile in the

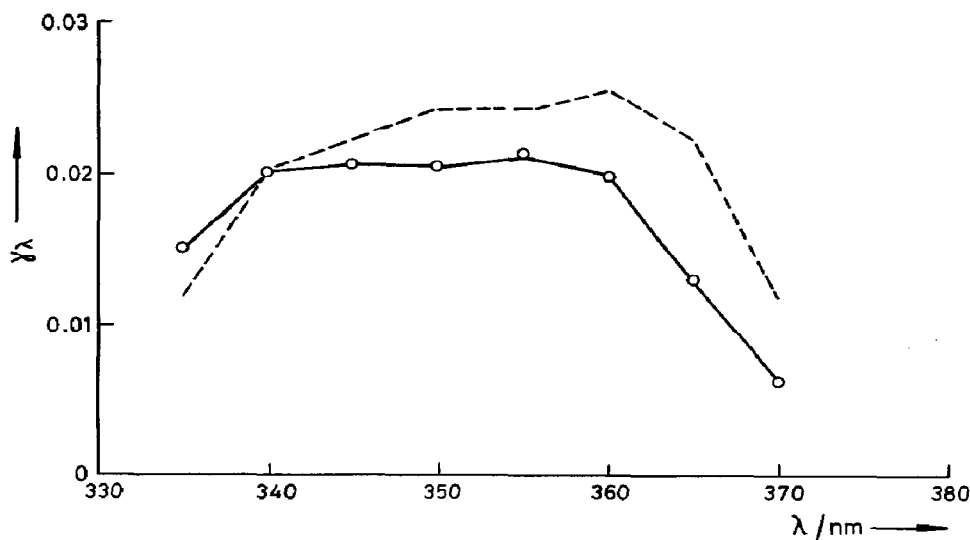


Fig. 4. Ground state depletion spectrum (O), *i.e.*  $\gamma_{\lambda}$ , observed at 200  $\mu\text{s}$  after flash photolyzing a  $4.2 \times 10^{-6} M$  anthracene in ethanol solution using a bandpass of 20 nm. The solid and broken lines were calculated assuming that  $\epsilon_{335}^T$  to be 300 and  $700 M^{-1} \text{ cm}^{-1}$  respectively.

region 325–380 nm. Using the triplet–triplet absorption spectrum obtained above in the region 324 nm to 380 nm the ground state depletion spectrum was corrected for triplet–triplet overlap and using eqn. (1) the values of  $\epsilon^T$  in the wavelength range 380–440 nm were calculated. The extinction coefficients and the relative intensities of the peaks in the anthracene triplet–triplet absorption spectrum are presented in Table 1.

The anthracene triplet–triplet absorption spectrum (Figs. 1 and 3) in the region 325–440 nm obtained by the above technique showed absorption maxima at 420 nm and 400 nm in agreement with those reported by previous workers<sup>1,7,13</sup>. The separation of 1400  $\text{cm}^{-1}$  observed between the peaks at 376 nm and 356 nm was of similar magnitude to the separation observed between the triplet–triplet peaks at 420 nm and 400 nm and between the peaks in the ground state absorption spectrum at 356 nm and 376 nm. The latter separations are characteristic of the vibrational modes in the molecule<sup>13</sup>. The work of Pariser<sup>14</sup> indicates that the peak at 420 nm can be assigned to transitions between the states  ${}^3B^+_{2u}$  and  ${}^3B^-_{1g}$  with calculated energies of 1.66 eV and 4.94 eV above the singlet ground state respectively. The peak at 376 nm can probably be assigned to transitions between the lowest triplet state  ${}^3B^+_{2u}$  (1.66 eV) and the symmetry state  ${}^3A^-_{1g}$ , with a calculated electronic energy of 4.977 eV, the energy separation between the levels being 3.317 eV.

In a series of experiments anthracene–ethanol solutions ( $10^{-4}$ – $10^{-5}$  M) were photolyzed using the second harmonic of a ruby laser ( $\lambda = 347$  nm) as excitation source. The photon output per pulse from the laser system was determined using potassium ferrioxalate chemical actinometry as described previously<sup>11,12</sup>. The second order plots for anthracene triplet decay were extrapolated to yield the concentration of anthracene triplet present immediately after the exciting laser pulse and the total concentration of anthracene excited to the singlet state was calculated from the laser output and the percentage absorption of the sample at 347 nm. The results obtained yielded a mean value of 0.7 with a probable deviation of 0.02 for the intersystem crossing ratio of anthracene in ethanol. The latter value is in agreement with the value of  $0.73 \pm 0.03$  recommended by Demas and Crosby<sup>15</sup>.

TABLE 1

ANTHRACENE TRIPLET–TRIPLET ABSORPTION MAXIMA

Wavelength, $\lambda$ /nm	Extinction coefficient $\epsilon^T_{\lambda}$ (Anth)/ $M^{-1} \text{ cm}^{-1}$
420	$75,000 \pm 5000$
400	$28,000 \pm 2000$
376	$5,750 \pm 400$
356	$3,350 \pm 250$
335	$2,250 \pm 150$

### Naphthalene

The wavelength profile of the naphthalene triplet-triplet absorption shown in Fig. 5 was obtained from the optical densities,  $\rho_\lambda$ , observed at 100  $\mu\text{s}$  after flash photolyzing a  $10^{-3}$  M naphthalene solution using a 50 J flash. A mixed order kinetics analysis yielded values of  $k_1^{\text{Naph}} = 5.5 \pm 2 \times 10^2 \text{ s}^{-1}$  and  $k_2^{\text{Naph}} = 1.8 \pm 0.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  for the first and second order rate constants for naphthalene decay. The latter value for  $k_2^{\text{Naph}}$  was calculated assuming  $\epsilon_{415}^{\text{T}} = 40,000 \text{ M}^{-1} \text{ cm}^{-1}$  as reported below.

The extinction coefficients for naphthalene triplet absorption were determined by investigation of the triplet energy transfer from naphthalene to anthracene. In these experiments the concentrations of donor and acceptor triplets were kept as low as possible in order to minimize second order decay processes. The transient absorptions at 415, 420 and 430 nm were investigated following flash photolysis of  $10^{-3}$  M naphthalene/ $10^{-6}$  M anthracene/ethanol solutions using a 2 J flash. Since the triplet absorption spectra of anthracene and naphthalene overlap considerably in the region 415–430 nm the component optical densities due to the anthracene triplet and the naphthalene triplet at times  $< 500 \mu\text{s}$  after the flash

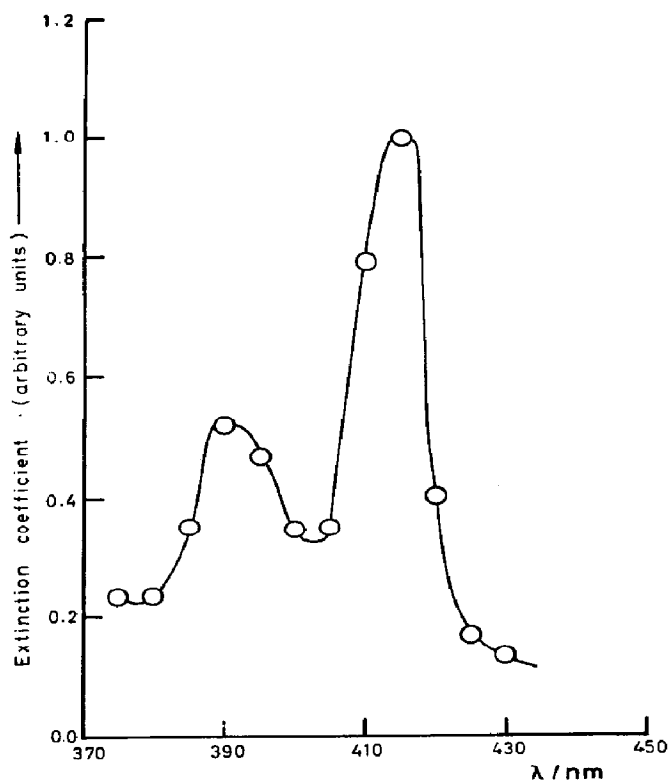


Fig. 5. Wavelength profile of naphthalene triplet-triplet absorption (normalized to unity at peak).

were computed using expressions (3) and (4) where  $B = \varepsilon_{420}^T(\text{Anth})/\varepsilon_{415}^T(\text{Anth})$  and  $E = \varepsilon_{420}^T(\text{Naph})/\varepsilon_{415}^T(\text{Naph})$  were obtained from Figs. 1 and 5 respectively.

$$\varrho_{415}(\text{Naph}) = \frac{B \cdot \varrho_{415} - \varrho_{420}}{B - E} \quad (3)$$

$$\varrho_{415}(\text{Anth}) = \varrho_{415} - \varrho_{415}(\text{Naph}) \quad (4)$$

Since the 2 J exciting flash used in the energy transfer experiment described above was of extremely short duration (half width  $< 1 \mu\text{s}$ ) it may be assumed that all the triplet state anthracene molecules formed at times  $> 10 \mu\text{s}$  after the photolyzing flash are formed *via* triplet energy transfer from naphthalene. It was in fact shown by flash photolyzing a  $10^{-6} M$  anthracene in ethanol solution using the 2 J flash that the concentration of anthracene triplets formed as a result of direct excitation of anthracene by the exciting flash was negligibly small. The rate constant  $k_T$  for the triplet energy transfer from naphthalene to anthracene was determined to be  $1.26 \pm 0.1 \times 10^{10} M^{-1} \text{s}^{-1}$ . It can easily be shown from the rate constants  $k_1^{\text{Naph}}$ ,  $k_2^{\text{Naph}}$ ,  $k_1^{\text{Anth}}$  and  $k_2^{\text{Anth}}$ , reported above, that under the conditions used in the energy transfer experiment the first and second order decay processes involving these rate constants are negligibly slow in comparison to the triplet energy transfer process during the period 10–150  $\mu\text{s}$  after the exciting flash. It may therefore be assumed that during short time intervals (*i.e.* 50  $\mu\text{s}$ ) within the period 10–150  $\mu\text{s}$  after the exciting flash the number of naphthalene triplet state molecules deactivated will be equal to the number of anthracene triplet state molecules formed during that interval. The results obtained yielded a value of  $\varepsilon_{415}^T(\text{Naph}) = 40,000 \pm 2000 M^{-1} \text{cm}^{-1}$  assuming  $\varepsilon_{420}^T(\text{Anth}) = 75,000 M^{-1} \text{cm}^{-1}$  as reported above.

The value of  $k^{\text{AD}}$  the rate constant for the triplet-triplet annihilation process involving one anthracene triplet molecule and one naphthalene triplet molecule was estimated from results obtained on flash photolyzing an ethanol solution containing  $10^{-3} M$  naphthalene and  $8 \times 10^{-6} M$  anthracene using a 50 J flash. Under these conditions the initial concentrations of anthracene and naphthalene triplets were high (*i.e.*  $> 10^{-6} M$ ) and second order decay processes predominated. Analysis of the results obtained using the values of  $k_1^{\text{Anth}}$ ,  $k_2^{\text{Anth}}$ ,  $k_1^{\text{Naph}}$ ,  $k_2^{\text{Naph}}$  and  $k_T$  reported above indicated that  $k^{\text{AD}}$  lay in the region  $10^9 - 2 \times 10^{10} M^{-1} \text{s}^{-1}$ .

### 2,5-Diphenyloxazole (PPO)

The wavelength profile of the transient absorption observed at 200  $\mu\text{s}$  and 600  $\mu\text{s}$  after flash photolyzing a  $5 \times 10^{-4} M$  PPO – ethanol solution using a 50 J flash is shown in Fig. 6. The complete absorption band observed in the region 350–600 nm exhibited the same decay characteristics and was therefore attributed to the lowest triplet state of PPO. A mixed order kinetics analysis yielded values of  $k_1^{\text{PPO}} = 4 \pm 2 \times 10^2 \text{s}^{-1}$  and  $k_2^{\text{PPO}} = 1.05 \pm 0.15 \times 10^{10} M^{-1} \text{s}^{-1}$  for the first and second order rate constants for PPO decay.



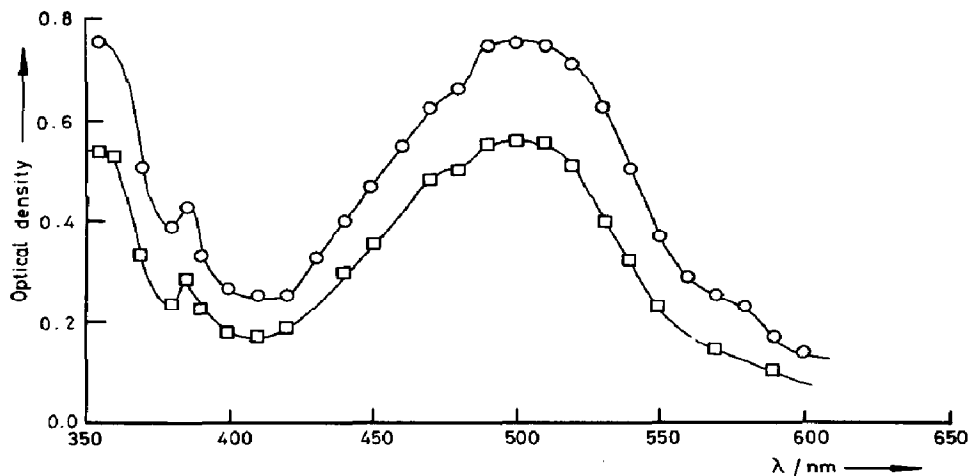


Fig. 6. Wavelength profiles of PPO triplet-triplet absorption observed at 200 and 600  $\mu$ s after flash photolyzing a  $5 \times 10^{-4}$  M PPO-ethanol solution using a 50 J flash.

The extinction coefficients for absorption by the triplet state of PPO were determined by investigating the triplet energy transfer from naphthalene to PPO<sup>16</sup> on flash photolyzing a  $10^{-3}$  M naphthalene/ $10^{-6}$  M PPO/ethanol solution using a 2 J flash. The transient absorption signals observed after photolysis at 360, 415, 480 and 500 nm were analyzed to yield the individual optical densities due to naphthalene triplet and PPO triplet absorptions. This analysis was relatively simple since the triplet absorptions of naphthalene and PPO overlap only for wavelengths  $<450$  nm. When a  $10^{-6}$  M PPO solution was flash photolyzed in the absence of donor using the 2 J flash the initial optical density at 500 nm was  $\sim 0.001$  indicating that the concentration of PPO triplet formed in the energy transfer experiment by direct excitation of the PPO during the photolyzing flash is negligibly small. The slope of the first order plot for decay of the naphthalene triplet in the presence of  $10^{-6}$  M PPO yielded a value for the rate constant of the triplet energy transfer from naphthalene to PPO of  $9.2 \pm 1.0 \times 10^9$   $M^{-1} s^{-1}$ .

The extinction coefficients for PPO triplet-triplet absorption were calculated as for naphthalene above by assuming that the rate of decay of donor triplet was equal to the rate of formation of acceptor triplet during the period 0–150  $\mu$ s after the photolyzing flash. The results obtained yielded  $\epsilon_{480}^T(\text{PPO}) = 25,500 \pm 1300$   $M^{-1} \text{cm}^{-1}$ ,  $\epsilon_{500}^T(\text{PPO}) = 28,400 \pm 1500$   $M^{-1} \text{cm}^{-1}$  and  $\epsilon_{480}^T(\text{PPO}) = 25,200 \pm 1200$   $M^{-1} \text{cm}^{-1}$ , assuming that  $\epsilon_{415}^T(\text{Naph}) = 40,000$   $M^{-1} \text{cm}^{-1}$ . The extinction coefficients for PPO triplet-triplet absorption at various wavelengths within the region 360–600 nm are given in Table 2.

#### 7-Diethylamino-4-methylcoumarin (C1)

The transient absorption observed in the wavelength region 380–660 nm at 200  $\mu$ s and 500  $\mu$ s after flash photolyzing a  $5 \times 10^{-5}$  M C1 – ethanol solution

TABLE 2  
TRIPLET-TRIPLET ABSORPTION OF 2,5-DIPHENYL OXAZOLE

Wavelength, $\lambda/\text{nm}$	$\epsilon^{\text{T}}_{\lambda}$ (PPO)/ $M^{-1} \text{ cm}^{-1}$ ( $\pm 10\%$ )
360	26,600
380	14,600
400	10,100
420	9,450
440	15,200
460	20,800
480	25,300
500	28,400
520	27,200
540	18,900
560	11,000
580	8,500
600	5,350

using a 50 J flash is shown in Fig. 7. The complete absorption band in the region 350–660 nm exhibited the same decay characteristics and was therefore attributed to the lowest triplet state of C1. A mixed order kinetics analysis yielded values of  $k_1^{\text{C1}} = 3 \pm 1 \times 10^2 \text{ s}^{-1}$  and  $k_2^{\text{C1}} = 1.0 \pm 0.15 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  for the first and second order rate constants for C1 decay.

In the region 350–420 nm, corresponding to a region of intense absorption by the ground state of C1 (see Fig. 7), transient increases in transmission due to depletion of ground state absorption after the exciting flash were not observed but transient absorption signals were observed. Since no transient changes in optical density were observed at 400 and 410 nm it may be assumed that  $\epsilon^{\text{T}}_{400} = \epsilon^{\text{S}}_{400} = 7000 \pm 1000 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\epsilon^{\text{T}}_{410} = \epsilon^{\text{S}}_{410} = 2000 \pm 1000 \text{ M}^{-1} \text{ cm}^{-1}$ .

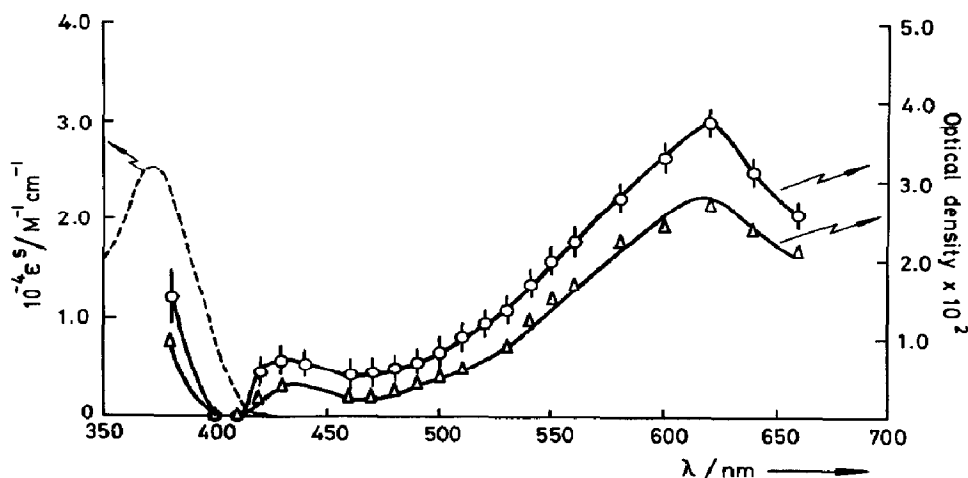


Fig. 7. The transient absorption observed at 200 and 500  $\mu\text{s}$  after flash exciting a  $5 \times 10^{-5} \text{ M}$  solution of 7-diethylamino-4-methyl coumarin using a 50 J flash. The broken line is the ground state absorption spectrum of 7-diethylamino-4-methyl coumarin.

The extinction coefficients for triplet-triplet absorption of C1 were determined by investigating energy transfer from the triplet state of C1 to the lower lying triplet state of anthracene. The transient absorption signals observed at 420 nm and 600 nm after flash exciting a  $5 \times 10^{-5} M$  C1/ $10^{-6} M$  anthracene/ethanol solution using a 20 J flash were analyzed to yield the individual optical densities due to the anthracene triplet and C1 triplet at 420 nm. This analysis was relatively simple since the triplet-triplet absorptions due to anthracene and C1 overlap only for wavelengths  $<450$  nm. The slope of the first order plot for decay of the C1 triplet in the presence of  $10^{-6} M$  anthracene yielded a value for the rate constant of the triplet energy transfer process from C1 to anthracene of  $6.9 \pm 1.0 \times 10^9 M^{-1} s^{-1}$ .

The extinction coefficients, given in Table 3, were calculated as for PPO above by assuming that the rate of decay of donor triplet is equal to the rate of formation of acceptor triplet during the period 50–175  $\mu s$  after the photolyzing flash. The period 0.50  $\mu s$  was not used since a considerable anthracene triplet state concentration was formed as a result of direct excitation of anthracene by the exciting flash. As can be seen from Table 3 the value  $\epsilon^{T_{600}}$  (C1) was found to be  $19,000 \pm 2000 M^{-1} cm^{-1}$  assuming  $\epsilon^{T_{420}}$  (Anth) =  $75,000 M^{-1} cm^{-1}$ .

In a series of experiments, using the ruby laser excitation technique described earlier, attempts were made to measure the intersystem crossing ratio for C1. The results obtained indicate that the intersystem crossing ratio for C1 is  $<4.0 \times 10^{-3}$ .

#### 4-Methyl-7-amino-carbostyryl (CS)

The transient absorption observed in the region 350–600 nm at 100  $\mu s$  and 300  $\mu s$  after flash photolyzing a  $5 \times 10^{-5} M$  CS-ethanol solution using a 50 J

TABLE 3  
TRIPLET-TRIPLET ABSORPTION OF 7-DIETHYLAMINO-4-METHYL COUMARIN

Wavelength, $\lambda/nm$	$\epsilon^{T_{\lambda}}$ (C1)/ $M^{-1} cm^{-1}$ ( $\pm 10\%$ )
400	7,400
420	3,700
440	3,900
460	3,050
480	3,600
500	4,750
520	6,850
540	9,800
560	13,200
580	16,400
600	19,000
620	21,600
640	17,800
650	16,500

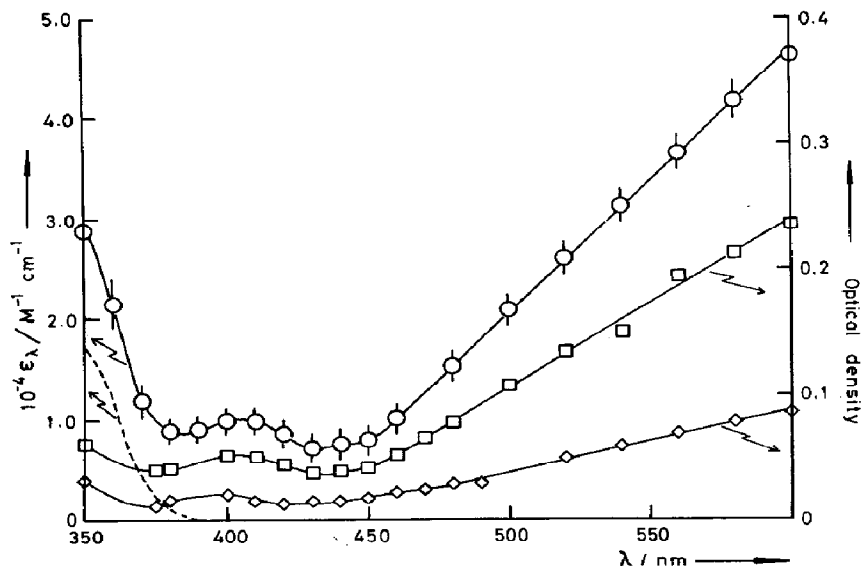


Fig. 8. The transient absorption observed at 100  $\mu\text{s}$  ( $\square$ ) and 300  $\mu\text{s}$  ( $\diamond$ ) after flash excitation of a  $5 \times 10^{-5} M$  solution of 4-methyl-7-amino-carbostyryl using a 50 J flash. The extinction coefficients for ground state absorption (broken line) and triplet-triplet absorption ( $\circ$ ) of 4-methyl-7-amino carbostyryl are also shown.

flash in shown in Fig. 8. The complete absorption band observed in the region 350–600 nm exhibited the same decay characteristics and was therefore attributed to the lowest triplet state of CS.

The extinction coefficients for the triplet-triplet absorption of CS were determined by investigating the energy transfer from the triplet state of CS to the lower lying triplet state of anthracene. The transient absorption signals observed at 420 nm and 600 nm after flash exciting a  $5 \times 10^{-5} M$  CS/ $10^{-6} M$  anthracene/ethanol solution using a 2 J flash were recorded and the traces obtained were analyzed to yield the optical densities due to anthracene triplet and CS triplet absorptions at 420 nm. This analysis was relatively simple since the triplet-triplet absorptions due to anthracene and CS overlap only for wavelengths  $< 450$  nm. The slope of the first order plot for decay of the CS triplet in the presence of  $10^{-6} M$  anthracene yielded a value for the rate constant of the energy transfer process from CS to anthracene of  $1.4 \pm 0.5 \times 10^{10} M^{-1} s^{-1}$ .

The extinction coefficients for three consecutive experiments were calculated as previously by assuming that the rate of decay of donor triplet is equal to the rate of formation of acceptor triplet during the period 50–150  $\mu\text{s}$  after the flash. As can be seen from Table 4 the value  $\epsilon_{600}^T$  (CS) was found to be  $46,200 \pm 4500 M^{-1} \text{ cm}^{-1}$ . The extinction coefficients for the triplet-triplet absorption of CS in the wavelength region 350–650 nm are given in Table 4 and in Fig. 8.

TABLE 4  
TRIPLET-TRIPLET ABSORPTION OF 4-METHYL-7-AMINO-CARBOSTYRIL

Wavelength, $\lambda$ /nm	$\epsilon^T_{\lambda}$ (CS)/ $M^{-1} \text{ cm}^{-1}$ ( $\pm 10\%$ )
350	28,800
360	21,400
370	11,840
380	8,840
390	9,000
400	9,800
410	9,800
420	8,600
430	7,050
440	7,650
450	8,000
460	10,200
480	15,300
500	20,800
520	26,000
540	31,200
560	36,400
580	41,500
600	46,200

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