

PHOTODIMERIZATION — RELEVANT TRIPLET STATE PARAMETERS OF METHYL CINNAMATE, DIETHYL 1,4-PHENYLENEDIACRYLATE AND METHYL 1-NAPHTHYLACRYLATE

WILLIAM G. HERKSTROETER and SAMIR FARID

Research Laboratories, Eastman Kodak Company, Rochester, NY 14650 (U.S.A.)

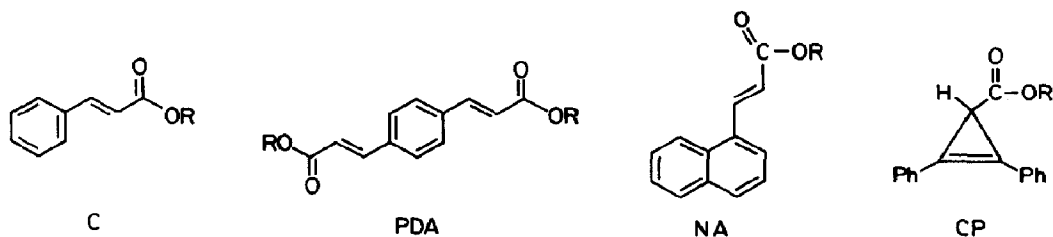
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Summary

A number of photo-cross-linkable polymers are based on triplet state dimerizations of aryl acrylate esters, such as cinnamate (C), phenylene-1,4-diacrylate (PDA) and 1-naphthylacrylate (NA). A detailed study of the triplet state properties and photodimerization kinetics of these chromophores was conducted. The energy transfer method was applied to determine the triplet energies and the extent of configurational changes between the ground and the triplet states of these compounds. The so-determined 0-0 triplet energies of C, PDA and NA are $54.8 \text{ kcal mol}^{-1}$, $49.3 \text{ kcal mol}^{-1}$ and $48.5 \text{ kcal mol}^{-1}$ respectively. The triplet state configurational change is largest for C ($1.6 \text{ kcal mol}^{-1}$), decreases with extended conjugation over two ethylenic bonds in PDA ($0.9 \text{ kcal mol}^{-1}$) and is immeasurably small for NA, where the conjugation involves a larger aryl group. Triplet lifetimes (10.3 ns, 6.9 μs and 10 μs for C, DPA and NA respectively), dimerization rate constants and dimerization efficiencies were determined from steady state kinetics of the photodimerization.

1. Introduction

Many photo-cross-linkable polymers used in photoresist and lithographic applications are based on 2 + 2 cyclodimerization of olefinic moieties which either are attached as side chains or constitute part of the polymer backbones [1, 2]. These reactions are usually induced by triplet sensitization. Cinnamate (C), *p*-phenylenediacrylate (PDA), 1-naphthylacrylate (NA) and diphenylcyclopropenecarboxylate (CP) are among the most common monomers used as components of such cross-linkable polymers.



We embarked on a detailed study of the mechanism of these cross-linking reactions, which involves, in turn, energy transfer from triplet sensitizers to the reactive moieties, energy migration among the latter until a reactive site is reached and, finally, dimerization (cross-linking). To achieve this goal for these molecules requires the determination of several of their triplet state parameters, including the energy content relative to the ground state, the activation energy for conformational changes from the ground state, the lifetime and, for the dimerization reaction, the bimolecular rate constant together with the reaction efficiency.

We recently reported data concerning the cyclopropene derivative CP ($R \equiv \text{Me}$) [3]. We now contrast the data for methyl cinnamate (C, $R \equiv \text{Me}$) with those of the structurally related analogs diethyl 1,4-phenylenediacrylate (PDA, $R \equiv \text{Et}$) and methyl 1-naphthylacrylate (NA, $R \equiv \text{Me}$). The kinetics of energy transfer from a series of triplet sensitizers (energy donors) to these compounds were determined by using flash photolysis. From these data the triplet energies and the reorganizational energies associated with the excitation of these olefinic compounds were obtained. We used steady state chemical kinetics to determine triplet lifetimes as well as reaction constants and efficiencies of dimerization. The data show surprisingly large differences among the triplet state properties of C, PDA and NA.

2. Results

To measure rate constants for energy transfer, we monitored the disappearance of sensitizer triplets, excited with a single pulse of light, in the absence and the presence of the individual acceptor molecules. All measurements were made with degassed benzene solutions at room temperature. The sensitizers were mostly ketocoumarins and aromatic hydrocarbons selected so that their triplet energies spanned a broad range (see Fig. 1 for ketocoumarin structures and Table 1 for sensitizer triplet energies).

The individual rate constants for energy transfer were equal to the slopes of the linear plots of the rate constants for disappearance of the flash-generated sensitizer triplets *versus* acceptor concentrations. Figure 2 shows an example for 1,2-benzanthracene with PDA as the acceptor.

To ensure that the data analysis consists merely of measuring linear slopes as in Fig. 2, it is advantageous to keep to negligible proportions the reverse energy-transfer process from the excited acceptor $^3A^*$ to the sensitizer S as in reaction (1):

STRUCTURE	DESIGNATION	STRUCTURE	DESIGNATION
	K-1		K-8
	K-2		K-9
	K-3		K-10
	K-4		K-11
	K-5		K-12
	K-6		
	K-7		

Fig. 1. Ketocoumarin sensitizers.



As the triplet lifetimes of the acceptors under consideration are relatively short (see below), this goal could be achieved simply by keeping the sensitizer concentrations at about 1×10^{-6} M.

All our energy-transfer measurements were made with the trans isomers of C, PDA and NA as starting materials. To avoid interference from the other isomers the solutions for rate-constant determinations were pulsed

TABLE 1

Rate constants for energy transfer to methyl C, diethyl PDA and methyl NA

Sensitizer	E_T^a (kcal mol ⁻¹)	Monitoring wavelength ^b (nm)	$k_q(C)$ (M ⁻¹ s ⁻¹)	$k_q(PDA)$ (M ⁻¹ s ⁻¹)	$k_q(NA)$ (M ⁻¹ s ⁻¹)
Triphenylene	66.5 ^c	630	4.7×10^9		
Phenanthrene	61.9 ^c	490	4.1×10^9	4.9×10^9	
2,6-Dimethylquinoline	60.5 ^d	435	4.0×10^9		
K-1	58.9 ^e	550	3.7×10^9	4.3×10^9	
K-2	57.9 ^e	630	2.8×10^9	3.1×10^9	
K-3	56.2 ^e	485	1.6×10^9		
K-4	56.0 ^e	620	1.5×10^9	3.7×10^9	
K-5	55.4 ^f	630	8.6×10^8	2.5×10^9	
Coronene	54.5 ^c	634	3.1×10^8		
Fluoranthene	53.0 ^c	670		4.8×10^9	
4,5-Benzpyrene	53.0 ^c	630	7.3×10^7		
1,2,5,6-Dibenzanthracene	52.2 ^c	542	1.3×10^7	3.9×10^9	5.1×10^9
K-6	51.6 ^f	620	6.8×10^6	2.9×10^9	
K-7	51.6 ^f	620	6.5×10^6	2.9×10^9	
K-8	51.5 ^f	725	7.7×10^6	3.3×10^9	4.4×10^9
K-9	51.3 ^f	730	4.1×10^6	2.9×10^9	
1,2,3,4-Dibenzanthracene	50.8 ^c	615	2.4×10^6	3.2×10^9	
K-10	50.7 ^f	730	2.5×10^6	2.5×10^9	
Tetrabenzonaphthalene	49.4 ^c	585	3.4×10^5	1.6×10^9	3.1×10^9
K-11	48.6 ^f	725	1.1×10^5	7.3×10^8	
K-12	48.5 ^e	725		6.0×10^8	3.1×10^9
1,2,4,5-Dibenzpyrene	47.7 ^g	570	4.0×10^4		
1,2-Benzanthracene	47.2 ^c	640		1.9×10^8	1.0×10^9
1,12-Benzperylene	46.2 ^c	640		1.9×10^7	
Acridine	45.3 ^h	445		4.3×10^6	2.7×10^7
9,10-Dimethyl-1,2- benzanthracene	44.3 ⁱ	640		6.9×10^5	
Phenazine	44.3 ^j	435		1.3×10^6	3.4×10^6
9-Chloroacridine	43.9 ^k	435		4.0×10^5	1.4×10^6
Anthracene	42.6 ^l	424		5.2×10^4	

^aBased on the 0-0 band in low temperature phosphorescence measurements.^bWavelength where triplet-triplet absorption in the sensitizer was monitored. This wavelength is not necessarily the maximum in the triplet-triplet absorption spectrum.^cFrom ref. 4.^hFrom ref. 7.^dFrom ref. 5.ⁱFrom ref. 8.^eFrom ref. 2.^jFrom ref. 9.^fFrom ref. 3.^kThis work.^gFrom ref. 6.^lFrom ref. 10.

with light only once. Because the sensitizer absorbed most of the light, energy transfer occurred from the sensitizer triplets to nearly pure trans isomers.

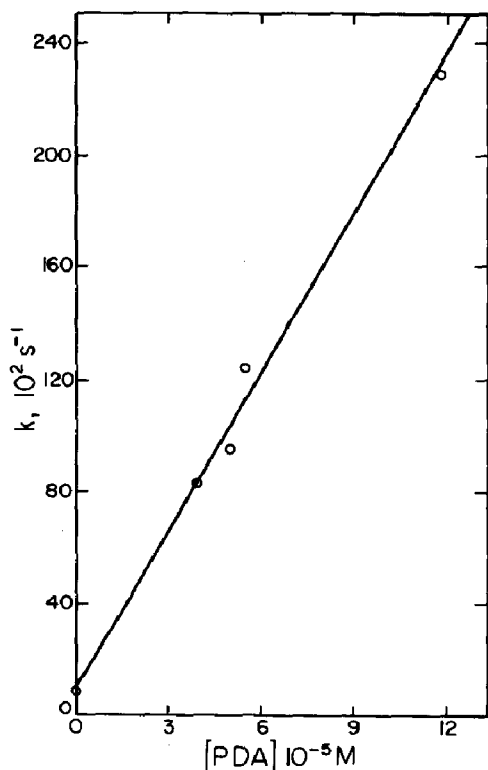
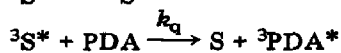
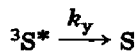


Fig. 2. Plot of the measured rates of disappearance of $^3S^*$ ($S \equiv 1,2$ -benzanthracene) as a function of the diethyl PDA concentration. The slope gives the rate constant for energy transfer from $^3S^*$ to PDA:



$$k = k_y + k_q[\text{PDA}]$$

$$\text{Slope} = k_q = 1.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$$

Table 1 lists all the rate constants for energy transfer to C, PDA and NA. Figures 3 - 5 show that for each acceptor the logarithms of these rate constants are smooth functions of the sensitizer triplet energies. Exothermic energy transfer has limiting rate constants of about $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in each case. Energy transfer efficiency drops as the process becomes less exothermic, and rate constants become much smaller with increasingly endothermic energy transfer. Plots of this type are well established in the literature, and our maximum limiting values for energy transfer in benzene agree well with published values [3, 11 - 24].

The Sandros equation is the traditional equation relating the rate constant for energy transfer to the triplet-energy difference between the sensitizer and the acceptor [11]:

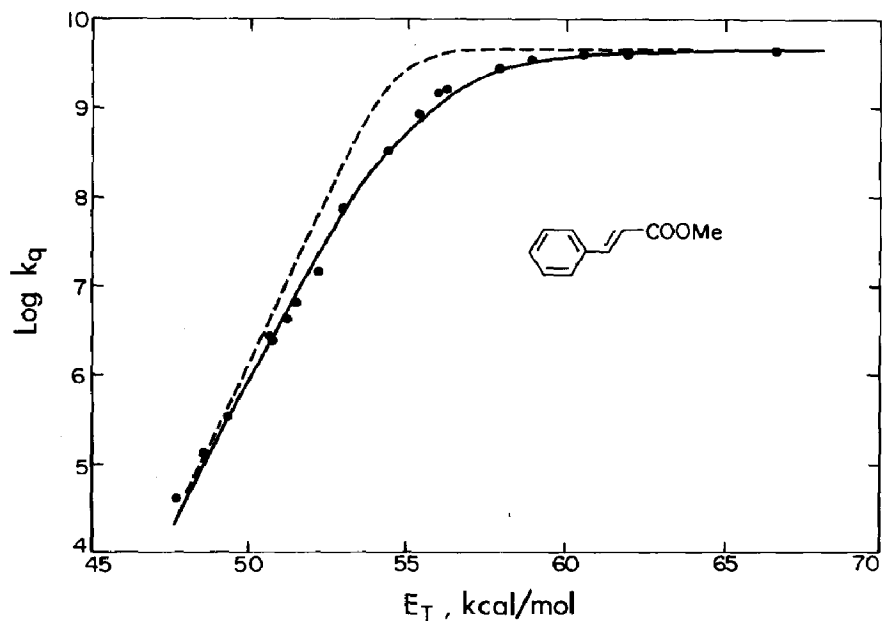


Fig. 3. Plot of the logarithm of the rate constants for energy transfer from a series of triplet sensitizers to methyl C: —, theoretical curve predicted by eqn. (II) for $\Delta G^\ddagger(0) = 1.6 \text{ kcal mol}^{-1}$; ---, theoretical curve for $\Delta G^\ddagger(0) = 0$. Linear extrapolations (not shown) from the exothermic and endothermic limits of the theoretical curves intersect at the assigned triplet energy value of $54.8 \text{ kcal mol}^{-1}$.

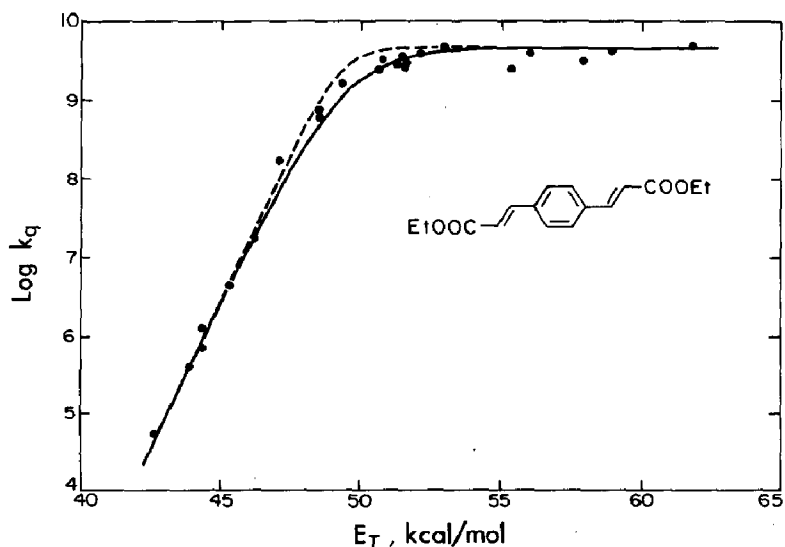


Fig. 4. Plot of the logarithm of the rate constants for energy transfer from a series of triplet sensitizers to diethyl PDA: —, theoretical curve predicted by eqn. (II) for $\Delta G^\ddagger(0) = 0.9 \text{ kcal mol}^{-1}$; ---, theoretical curve for $\Delta G^\ddagger(0) = 0$. Linear extrapolations (not shown) from the exothermic and endothermic limits of the theoretical curves intersect at the assigned triplet energy value of $49.3 \text{ kcal mol}^{-1}$.

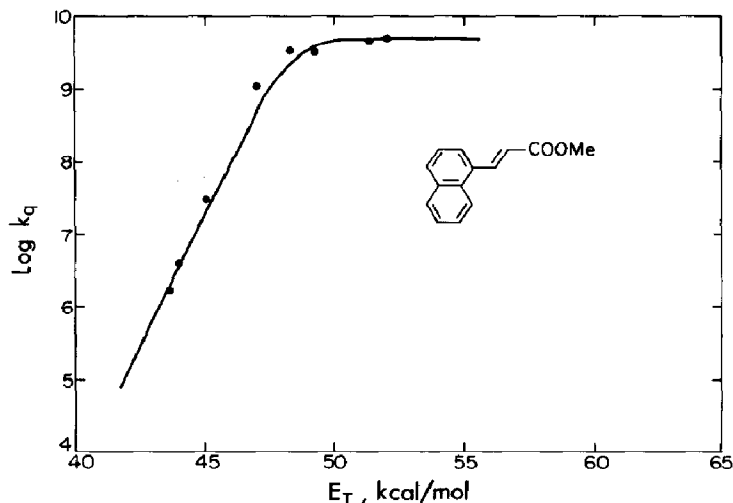


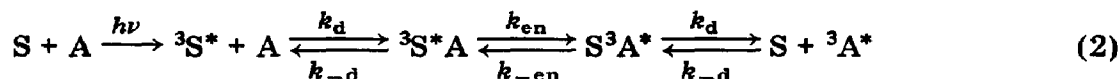
Fig. 5. Plot of the logarithm of the rate constants for energy transfer from a series of triplet sensitizers to methyl NA. The theoretical curve predicted by eqn. (II) for $\Delta G^\ddagger(0) = 0$ best fits the data points. Linear extrapolations (not shown) from the exothermic and endothermic limits of the theoretical curves intersect at the assigned triplet energy value of $48.5 \text{ kcal mol}^{-1}$.

$$k_q = \frac{k_d}{1 + \exp(\Delta G/RT)} \quad (\text{I})$$

Here k_q and k_d are the rate constants for actual energy transfer and for diffusion-limited energy transfer respectively, and the free-energy change ΔG for the energy transfer can be taken to be equal to the triplet-energy difference between the energy donor and the energy acceptor.

Sandros' treatment of energy transfer applies strictly only when the geometry of the acceptor molecule does not change upon excitation to its triplet state. When, relative to the ground state, energy transfer leads to molecular distortion (a process termed non-vertical energy transfer [25, 26]), the energy-transfer data can be satisfied by an equation derived by Balzani and coworkers [27, 28].

They extended the treatment of electron transfer in fluid solution to energy-transfer quenching. The energy-transfer scheme is



where S and A represent the energy donor (sensitizer) and the acceptor respectively, and the corresponding equation is

$$k_q = \frac{k_d}{1 + k_{-d}/k_{en} + \exp(\Delta G/RT)} \quad (\text{II})$$

where k_q is the overall rate constant for energy transfer. ΔG has the same meaning as in the Sandros equation.

Two different theoretical bases were used to calculate k_{en} . The first is based upon the Eyring theory of absolute reaction rates and leads to k_{en} being defined [27] as

$$k_{en} = k_{en}^0 \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) \quad (\text{III})$$

The standard free energy ΔG^\ddagger of activation is given by

$$\Delta G^\ddagger = \Delta G + \frac{\Delta G^\ddagger(0)}{\ln 2} \ln \left\{ 1 + \exp\left(-\frac{\Delta G \ln 2}{\Delta G^\ddagger(0)}\right) \right\} \quad (\text{IV})$$

Distortions in the triplet state relative to the ground state are accommodated by the empirical parameters k_{en}^0 and $\Delta G^\ddagger(0)$. The former is defined as a pre-exponential factor and the latter as a measure of the barrier to reorganization of the nuclear positions that occur to make energy transfer possible.

The second theoretical basis [28] extends the Ulstrup-Jortner quantum-mechanical description of electron-transfer reactions to triplet-triplet energy transfer. This leads to k_{en} being defined as the product of electronic and nuclear terms. The electronic term is equal to the square of the electron-exchange interaction between $^3S^*$ and A in the encounter complex, and the nuclear term represents the Franck-Condon factor for energy transfer.

Balzani's method has successfully matched experimental rate constants for triplet energy transfer with the corresponding calculated values using both definitions of k_{en} . For such molecules as the stilbene isomers, ferrocene and ruthenocene [27], experimental plots of energy-transfer data were matched with calculated curves by trial-and-error selection of ΔG to find the proper position along the ordinate as well as with the empirical parameters k_{en}^0 and ΔG^\ddagger to determine the appropriate curve shape. Application of the second definition of k_{en} requires knowledge of the spectral properties of both S and A, including the frequency of the dominant modes, the bandwidth and the displacement parameters. Where these properties were known, as with stilbene and azobenzene, the calculated and experimental energy-transfer curves coincided quite well [22, 28].

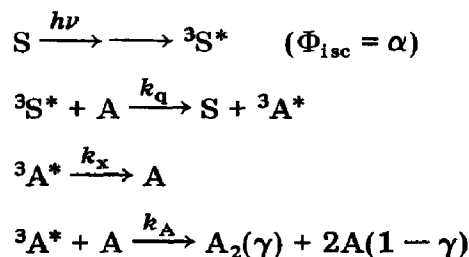
Because of the lack of spectral data for C, PDA and NA necessary to apply Balzani's second method to these molecules, we used only his first method to calculate theoretical curves to satisfy best the experimental data points of Figs. 3 - 5. Using eqns. (II) - (IV), the parameters to be satisfied were k_d , k_{-d} , k_{en}^0 , $\Delta G^\ddagger(0)$ and ΔG . The term k_d is the rate constant for the diffusion-controlled reaction, whereas k_{-d} is a dissociation rate constant; the significance of both rate constants in energy transfer is evident from reaction (2). The former is given by the Debye equation [29] and the latter by the Eigen equation [27, 28, 30].

Our maximum experimental rate-constant values for all three substrates are near $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and agree with the k_q for many other exothermic energy-transfer reactions in benzene. Accordingly, the same k_{en}^0 value of $1 \times 10^{10} \text{ M}^{-1}$ used previously for stilbene [27] and CP [3] is also taken here.

The interpretation of non-vertical energy transfer continues to be controversial. Saltiel [31] has recently pointed out that his experimental data require that the distribution of the free energy of activation between entropy and enthalpy should favor the former rather than the latter as assigned by Balzani [27]. Saltiel also proposed different values for k_{-d} and k_{en}^0 , at least for *trans*-stilbene [31]. Whether we use Balzani's or Saltiel's values for these parameters actually makes little difference in our calculation of curve shapes which match experimental data points.

The experimental points for the methyl derivative of C best fit the curve calculated according to eqn. (II) for $\Delta G^\ddagger(0) = 1.6 \text{ kcal mol}^{-1}$ and for $\Delta G = 0$ at $54.8 \text{ kcal mol}^{-1}$ (Fig. 3), the last of which is the value to be assigned to the triplet energy of the cinnamate ester. From Fig. 4, the corresponding values for the diethyl ester of PDA are $0.9 \text{ kcal mol}^{-1}$ for $\Delta G^\ddagger(0)$ and $49.3 \text{ kcal mol}^{-1}$ for the triplet energy. The plot for NA in Fig. 5, although based on fewer data points, indicates a $\Delta G^\ddagger(0)$ close to zero and a triplet energy of $48.5 \text{ kcal mol}^{-1}$.

Triplet lifetimes and dimerization rate constants were obtained from steady state kinetics. According to the reaction scheme



the reciprocal of the dimerization quantum yield ($1/\Phi_{A_2}$) is linearly related to the reciprocal of the olefin concentration, as stated in the equation

$$\frac{1}{\Phi_{A_2}} = \frac{1}{\alpha\gamma} + \frac{1}{\alpha\gamma} \frac{k_x}{k_A[A]} \quad (\text{V})$$

In the foregoing, α is the independently determined sensitizer intersystem crossing efficiency and γ is the dimerization reaction efficiency. Thus, the γ are obtained from the intercepts of the linear plots according to eqn. (V), whereas the slope-to-intercept ratios yield the k_x/k_A .

For dimerizations carried out at constant concentrations of A but at several different concentrations of added quencher Q, the quenching efficiency $(\Phi_0/\Phi)_{\text{CORR}}$, corrected for direct interception of ${}^3S^*$ by Q, depends linearly on [Q], as given by eqn. (VI).

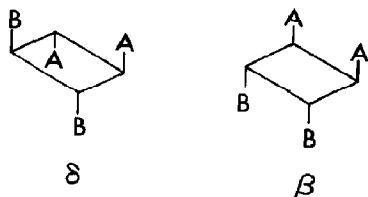




$$(\Phi_0/\Phi)_{\text{corr}} = \frac{\Phi_0/\Phi}{1 + [\text{Q}]/[\text{A}]} = 1 + \frac{k_q}{k_x + k_A[\text{A}]} [\text{Q}] \quad (\text{VI})$$

Through proper selection of sensitizers and quenchers, the energy-transfer steps can be made exothermic, and the rate constants for these reactions are expected to have the limiting value of $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. With this value assigned to the rate constants for reactions (3) and (4) and with the k_x/k_A ratios determined from eqn. (V), the slopes of the linear plots according to eqn. (VI) yielded individual k_x and k_A values. Table 2 lists experimental data for C, PDA and NA as well as, for comparison, CP.

The cycloaddition dimers from C, PDA and NA were isolated and characterized by nuclear magnetic resonance (NMR) spectroscopy. Triplet-sensitized irradiations of PDA and of NA in toluene yield about 90% of the corresponding δ -truxinate derivative, the head-to-head all-trans cyclobutane dimer (δ). One of the minor dimers (5% yield) in the case of NA was identified as the β -truxinate analog (β). The corresponding reaction of methyl C, however, is less stereoselective; δ -truxinate is formed in 63% and β -truxinate in 25% yield.



The stereochemistry of the dimers was determined from the AA'BB' NMR spectra of the cyclobutane protons, *cf.* Table 3, where A represents carboxylate groups and B aryl groups.

The assignment of the signals to H_A , the cyclobutane protons on the carboxylate-substituted carbon atoms, and H_B , the cyclobutane protons on the aryl-substituted carbon atoms, was made on the basis of slight broadening of the latter due to weak long-range coupling with the aromatic protons. In the δ isomers all vicinal couplings are similar ($9.5 \pm 0.2 \text{ Hz}$)

TABLE 2

Triplet state lifetimes and photodimerization parameters

A	k_x (s^{-1})	τ_T	k_A ($\text{M}^{-1} \text{ s}^{-1}$)	γ
Methyl C	9.7×10^7	10.3 ns	8.8×10^6	0.5
Diethyl PDA	1.4×10^5	6.9 μs	2.4×10^6	0.35
Methyl NA	1.0×10^5	10 μs	8.9×10^5	0.18
Methyl CP	2.8×10^3	360 μs	3.8×10^7	0.8

TABLE 3

¹H NMR data for the cyclobutane dimers of C, PDA and NA

Dimer	δ (ppm)		J (Hz)			
	H_A	H_B	J_{AB}	$J_{AB'}$	$J_{AA'}$	$J_{BB'}$
C (δ)	3.29	3.74	9.5	≈ 0	9.4	9.4
PDA (δ)	3.47	3.77	9.5	≈ 0	9.7	9.7
NA (δ)	3.74	4.74	9.5	-0.1	9.7	9.7
C (β)	3.85	4.40	7.1	-1.1	10.2	10.2
NA (β)	4.07	5.39	7.1	-0.9	9.5	9.5

and the 1,3-couplings are almost zero. These values indicate that these cyclobutanes are puckered with the substituents in quasi-equatorial positions. The β isomers, however, show distinct differences between the trans (7.1 Hz) and cis (9.5 or 10.2 Hz) vicinal couplings and have a relatively large negative 1,3-coupling (-1.0 ± 0.01 Hz) that is consistent with their trans configuration.

3. Discussion

To date, the energy-transfer method when properly applied has always resolved controversies surrounding triplet-energy determination, and the reliability of this experimental method is recognized [32]. For methyl C, diethyl PDA and methyl NA, no definitive triplet energies had been determined before our work. For the first, calculated triplet energies ranged between 64.2 and 80.0 kcal mol⁻¹ [33, 34], whereas the bounds on experimental values were 56.1 and 64.2 kcal mol⁻¹ [35 - 37]. For diethyl PDA there is but one report of an unusual high energy phosphorescence [38], whereas for methyl NA we found no reports whatsoever.

As pointed out by Balzani *et al.* [27], molecular triplet energy determinations can be based on vertical absorption, vertical emission of phosphorescence, or differences in energy between the lowest vibrational levels (0-0 levels) of the ground and triplet states. For molecules that do not change their configurations in the triplet state, these three values will be identical. However, these triplet energy differences are meaningful when molecules take on different equilibrium configurations in the different electronic states. It is the 0-0 triplet energy that is obtained from eqn. (II) by the method we used.

In our three substrates, the most likely geometrical change to occur upon excitation from the ground state to the triplet state is twisting about isomerizable double bonds. There is ample precedent for such behavior, the "phantom" triplet state of stilbene with its perpendicular geometry being a well-known example [31]. The $\Delta G^\ddagger(0)$ which we have determined indicate that propensities to twist decrease in the order C, PDA and NA, and we must ask the reasons why.

For C (*trans* isomer), the $\Delta G^\ddagger(0)$ of 1.6 kcal mol⁻¹ that we determined is almost identical with the $\Delta G^\ddagger(0)$ which best fits the energy-transfer data for *trans*-stilbene [27], whereas the smaller $\Delta G^\ddagger(0)$ of 0.9 kcal mol⁻¹ for PDA indicates that the barrier to configurational change upon excitation to the triplet state of this molecule is only about half as large as for C or stilbene. PDA and C differ in structure by the presence in the former of a second acrylate substituent. Because both acrylate substituents are *para* to each other across a benzene ring, PDA has two double bonds in conjugation through the intermediacy of an aromatic ring. There have been previous investigations of the influence of polyene conjugation of triplet states. These studies show for linear polyenes with aromatic end groups that an increase in the number of double bonds leads to lower triplet energies, longer triplet lifetimes and less twisting or configurational change in the excited state. This trend is evident, for example, when stilbene is compared with 1,4-diphenyl-1,3-butadiene, although there is disagreement as to how much the triplet state of the latter is twisted [39, 40]. We are aware of no previous investigations of the effects of conjugation where the relative placement of double bonds and aromatic ring is as in PDA. Our experimental results show that, in PDA relative to C, we also have a lower triplet energy, a much longer triplet lifetime and less geometrical change after excitation to the triplet state.

For NA in comparison with C, there is an increase in the size of the aromatic substituent. Our results are consistent with previous determinations, which show that a change from phenyl to larger aryl substituents in substituted ethylenes shifts triplet state equilibria between planar and twisted forms in favor of the former and triplet lifetimes increase [41]. According to the model proposed by Arai *et al.*, this equilibrium shift is due to "avoided crossing" between the lowest-lying ethylenic and arenic states, giving rise to dual minima at *transoid* and twisted geometries [42].

4. Experimental details

4.1. Apparatus

Triplet-triplet absorption and energy transfer were measured using a flash photoelectric apparatus. Two xenon flashlamps (Kemlite Z8H20) were positioned on opposite sides of a sample cell holder inside a cylindrical housing whose inner walls were coated with highly reflective paint (Eastman white reflectance coating). The flash discharge energy was 156 J, corresponding to a 2 μ F capacitor charged to 12.5 kV. Glass color filters (Corning 9863) were placed between the flashlamps and the sample cell holder. The monitoring source was a quartz-halide 100 W lamp (Osram 64625) powered by a regulated d.c. power supply (Sorensen QSB12-8). The lamp was mounted in an appropriate housing on an optical bench in series with a collimating lens, the flash chamber, a focusing lens and a monochromator 0.25 m long (Jarrell-Ash). The monitoring beam, after passing through the

sample cell, was focused on the entrance slit of the monochromator. Light intensity was measured as a function of time by using a photomultiplier tube (RCA 4463) mounted on the exit slit of the monochromator. The photomultiplier output was fed into a cathode follower amplifier and then into a wide-band digital storage oscilloscope (Nicolet model 1090). The output voltage of the photomultiplier, read directly in digital form on the oscilloscope screen as a function of time, was linear with regard to the light intensity transmitted by the sample so that an observed change in voltage after flash excitation could be readily converted mathematically to a change in absorbance in the sample. Transient lifetimes were measured by the recovery rate of the monitoring beam after the excitation flash. The kinetic analysis was performed using the method of Linschitz and Sarkanen [43, 44].

The procedures for phosphorescence measurements have been described elsewhere [2].

The steady state kinetic studies were carried out in toluene solutions degassed with three freeze-pump-thaw cycles; either K-4 or K-8 was the sensitizer. Samples were irradiated on a "merry-go-round" apparatus [45] using a PEK 200W super-high pressure mercury arc lamp. Samples containing K-8 were irradiated at 436 nm using the combination of a water-cooled Corning 5-58 glass filter and a Kodak 2A Wrattan filter to eliminate light of shorter wavelengths. With K-4 as the sensitizer, the light was filtered by Corning 5-58 and 3-75 glass filters. Dimers were analyzed by gas chromatography using a 1.5% Dexil on Chromosorb W80/100 column (1/8 in \times 6 ft).

4.2. Methyl C

Using K-4 sensitizer, a slope-to-intercept ratio of 11 was obtained from the linear plot of $1/\Phi_{A_2}$ versus $1/[A]$, where $[A]$ was varied between 0.3 and 3.0 M. A plot of $(\Phi_0/\Phi)_{\text{corr}}$ versus $[Q]$ for $[A] = 0.8$ M and using methyl 1-pyrenebutyrate as quencher gave a slope of 37 M^{-1} . Since the viscosity of this solution was 1.4 times higher than that of toluene, k_q is assumed to be lower than $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ by this factor.

4.3. Diethyl PDA

A plot of $1/\Phi_{A_2}$ versus $1/[A]$ (K-8 sensitizer), where $[A]$ ranged between 0.04 and 0.2 M, was linear; the slope-to-intercept ratio was 0.06 M. A plot of $(\Phi_0/\Phi)_{\text{corr}}$ versus $[Q]$ (K-4 sensitizer), where $[A]$ was kept constant at 0.2 M and with azulene as quencher (up to 0.0015 M), gave a slope of 7940 M^{-1} . In a similar experiment using ferrocene as a quencher (up to 0.001 M), a slope of 7890 M^{-1} was obtained.

4.4. Methyl NA

Using K-4 as sensitizer, a plot of $1/\Phi_{A_2}$ versus $1/[A]$, where $[A]$ ranged between 0.1 and 0.4, gave a slope-to-intercept ratio of 0.117 M. A plot of $(\Phi_0/\Phi)_{\text{corr}}$ versus $[Q]$ at $[A] = 0.2$ M and with azulene as quencher (up to 5×10^{-4} M) gave a slope of $17\,800 \text{ M}^{-1}$.

4.5. Chemicals

The benzene and toluene solvents for the experiments were Mallinckrodt Nanograde and Kodak Spectrograde respectively, and were used as received. Methyl C (Chemicals Procurement Laboratories, Inc.) was used as received, whereas PDA was synthesized by condensing terephthalaldehyde and malonic acid in the presence of piperidine [46]. Reaction of PDA with thionyl chloride gave PDA chloride, which was refluxed in ethanol to yield the diethyl ester [47].

Sources and purification procedures for most sensitizers are given elsewhere [2, 3, 16]. Coronene and 4,5-benzopyrene were purchased from Pfaltz and Bauer and were recrystallized from benzene and ethanol respectively. 1,2,4,5-Dibenzopyrene and 2,6-dimethylquinoline (Chemicals Procurement Laboratories, Inc.) were used as received, as was 9-chloroacridine (Molecular Probes). Acridine and phenazine (Kodak Laboratory Chemicals) were recrystallized from ethanol.

Of the quenchers, azulene and ferrocene are described elsewhere [17]. Methyl 1-pyrenebutyrate was prepared by esterification of 1-pyrenebutyric acid (Kodak Laboratory Chemicals) and was purified by recrystallization from hexane.

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