

EFFECT OF TEMPERATURE ON THE TRIPLET STATES OF METHYL- AND PHENYL-SUBSTITUTED BIPHENYL MOLECULES

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Summary

The temperature dependence of the quantum yields $\Phi_{c \rightarrow t}$ and $\Phi_{t \rightarrow c}$ of the cis \rightarrow trans and trans \rightarrow cis isomerization respectively of 1,3-pentadiene sensitized by phenyl- and methyl-substituted biphenyls has been studied in fluid media. The triplet-state quantum yields for the substituted biphenyls increased with decreasing temperature but approached maximum values at the lowest temperatures. The sums of the fluorescence and triplet quantum yields Φ_F and Φ_T for 4-methylbiphenyl, 3-methylbiphenyl, 4,4'-dimethylbiphenyl and 3,3'-dimethylbiphenyl were less than unity at all temperatures and the nature of the temperature-dependent non-radiative process(es) is discussed. An attempt has been made to compare triplet-state quantum yields determined by the olefin isomerization technique with those obtained using sensitized biacetyl phosphorescence.

1. Introduction

The effect of significant changes in molecular configuration on the various primary processes following excitation is an important aspect of photophysics and photochemistry which requires detailed study [1]. Changes in molecular geometry can have a profound influence on the structure and intensity of absorption and emission spectra resulting in changes in the relative efficiencies of fluorescence, intersystem crossing and internal conversion [2]. A further complexity arises when there are other excited states in close proximity to the lowest excited singlet state. The nature of the solvent and the substitution can effect a re-ordering of the excited-state energy levels leading in some cases to quite dramatic changes in fluorescence spectra and photophysical parameters [3, 4].

Biphenyl and its analogues are examples of π -bonded molecules whose photochemical excitation in fluid media results in differences in nuclear topology between the non-planar ground states and nearly planar excited states [4 - 6]. This is manifested both by their absorption and luminescence properties [4, 6, 7] and by the differences in radiative probability [8] (derived from measurement of fluorescence quantum yields and decay times)

compared with the theoretical values calculated from expressions due to Strickler and Berg [9] or Birks and Dyson [10]. Theoretical and experimental studies have demonstrated that the fluorescence characteristics of biphenyl molecules are determined by hidden transitions and it has been shown that the magnitude of the energy shift imparted to the various excited states depends upon the nature and position of substitution [4].

A detailed examination of temperature effects is necessary to understand the influence of change of shape and re-ordering of energy levels on radiative and non-radiative processes. The effects of temperature on the fluorescence quantum yields and decay times for methyl- and phenyl-substituted biphenyls have established the presence of non-radiative processes that are both temperature dependent and temperature independent [11] but detailed information on triplet-state quantum yields is required to clarify the relative importance of intersystem crossing and internal conversion.

The triplet state of biphenyl and several rigid analogues have received considerable attention [11, 12] but there have been relatively few solution measurements on the triplet-state quantum yields of flexible substituted biphenyls and the effects of temperature have been examined only rarely. The photosensitized *cis-trans* isomerization of olefins has proved to be an accurate monitor of triplet-state yields for many aromatic compounds in both vapour and liquid phases [13, 14]. The use of simple olefins such as 2-butene is restricted to triplet sensitizers with energies in excess of about 300 kJ mol⁻¹ [15], but the photosensitized *cis-trans* isomerization of 1,3-pentadiene (piperylene) provides an elegant means of examining sensitizers such as biphenyls whose triplet-state energies are close to 250 kJ mol⁻¹ [14]. For these reasons, a detailed investigation of the effects of temperature and solvent upon the *cis-trans* isomerization of 1,3-pentadiene photosensitized by flexible substituted biphenyl molecules has been attempted.

2. Experimental details

2.1. Materials

3-Methylbiphenyl (3MB), 4-methylbiphenyl (4MB), 4,4'-dimethylbiphenyl (44'DMB), 3,3'-dimethylbiphenyl (33'DMB) (all Aldrich; purity, 98%), *o*-terphenyl (OTP) (Kodak) and *m*-terphenyl (MTP) (Phase Separations) were purified by column chromatography and recrystallized from ethanol (BDH, spectroscopic grade). 2-Methylbiphenyl (2MB) and 2,2'-dimethylbiphenyl (22'DMB) (both K and K, ICN Pharmaceuticals) were purified by column chromatography followed by fractional distillation under vacuum. The purity of the sensitizers was checked by comparing their absorption spectra and extinction coefficients with those in the literature.

n-Pentane (Aldrich, spectroscopic grade), *n*-hexane (Merck, fluorescence spectroscopy grade) and ethanol (BDH, spectroscopic grade) were used as solvents and were treated as described in ref. 16.

cis- and *trans*-1,3-Pentadiene (Aldrich, spectrograde: better than 99% pure) were subject to fractional distillation under vacuum. Gas chromatographic analysis showed that each isomer was effectively free from the other.

2.2. Methods

For triplet-yield measurements the sample photolyses were carried out in "Spectrosil" cuvettes 1 cm in diameter. Samples were degassed by repeated freeze-pump-thaw cycles on a conventional high-vacuum system equipped with greaseless taps. A U-shaped low-pressure mercury vapour discharge lamp (Hanovia) mounted in an aluminium block was used as the light source. The lamp housing was continually flushed with nitrogen to minimize the build-up of ozone from the lamp. The cell housing on one side of the light source was used for photolysis at room temperature and above. The temperature was controlled by a small heater linked to a mercury cut-off thermometer which was located in the aluminium block. The other side of the cell housing was connected to a cryostat [17] which was used to carry out experiments at low temperature. Light from the lamp was passed through filters (OX 7 glass) before it entered the reaction cell. The intensity of the lamp was monitored using photocells (Rank QVA 395) operated in conjunction with a voltmeter (Phillips G 6020). Actinometry was performed on a regular basis in each of the cells used for photolysis. The actinometer was a solution of potassium ferrioxalate; the ferrous ions produced were complexed with 1,10-phenanthroline and the absorption of the red complex was monitored at 510 nm [18].

Following irradiation, the photolysed solution was distilled under vacuum leaving behind the less volatile biphenyl compounds. The *cis*- and *trans*-1,3-pentadienes were analysed using gas chromatography (Perkin-Elmer F11) with a 2 m column packed with β,β -oxydipropionitrile (35 wt.% on Chromosorb P).

Absorption measurements were made using a Perkin-Elmer 402 spectrophotometer. Fluorescence was monitored using a fully corrected spectrofluorometer [3, 19] and fluorescence lifetimes were determined as described in previous studies [16].

3. Results and discussion

Photolysis of the substituted biphenyl-1,3-pentadiene mixtures, with the exceptions of OTP and 22'DMB, gave rise to the *cis*-*trans* isomerization of 1,3-pentadiene at all the temperatures investigated and no other products were detected. The isomerization quantum yields were found to be independent of solvent and irradiation time when proper allowance was made for back reaction [20]. The dependence of the quantum yield $\Phi_{c \rightarrow t}$ for the *cis* \rightarrow *trans* isomerization and the quantum yield $\Phi_{t \rightarrow c}$ for the *trans* \rightarrow *cis* isomerization on the concentration of the respective 1,3-pentadiene isomer at 293 K are shown for 4MB, 3MB, 2MB, 44'DMB, 33'DMB and MTP in Figs.

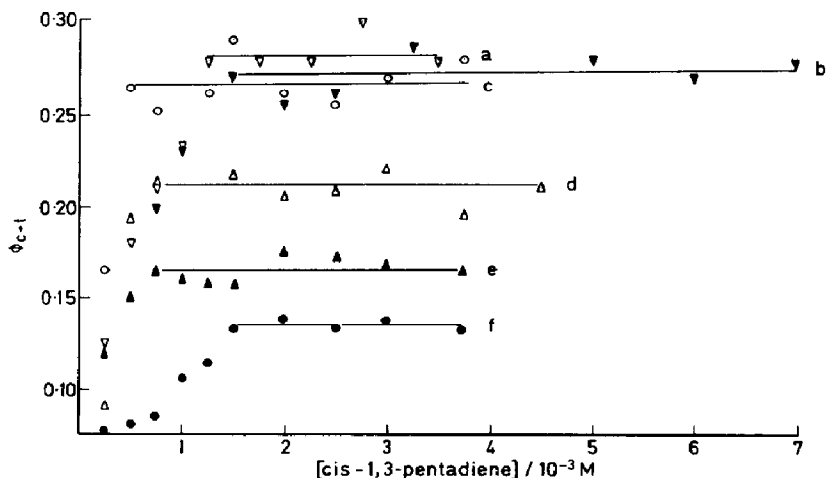


Fig. 1. Dependence of $\Phi_{c \rightarrow t}$ on the concentration of *cis*-1,3-pentadiene at 293 K: ∇ , MTP (curve a); \blacktriangledown , 4MB (curve b); \circ , 44'DMB (curve c); \triangle , 3MB (curve d); \blacktriangle , 33'DMB (curve e); \bullet , 2MB (curve f). The lines represent the mean values for Φ_{isom} over a concentration range indicated by their length.

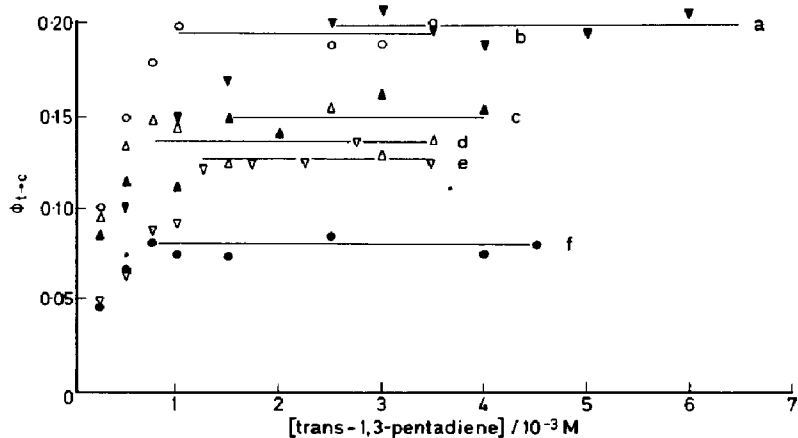


Fig. 2. Dependence of $\Phi_{t \rightarrow c}$ on the concentration of *trans*-1,3-pentadiene at 293 K: \blacktriangledown , 4MB (curve a); \circ , 44'DMB (curve b); \blacktriangle , 33'DMB (curve c); \triangle , 3MB (curve d); ∇ , MTP (curve e); \bullet , 2MB (curve f). The lines represent the mean values for Φ_{isom} over a concentration range indicated by their length.

1 and 2. The quantities $\Phi_{c \rightarrow t}$ and $\Phi_{t \rightarrow c}$ approached maximum values at diolefin concentrations of about 1×10^{-3} M. For a given biphenyl compound the maximum value for $\Phi_{c \rightarrow t}$ was found to be greater than that for $\Phi_{t \rightarrow c}$ and this was most notable for MTP. OTP was found to sensitize the isomerization of 1,3-pentadiene from *cis* to *trans* but not from *trans* to *cis* and no isomerization of 1,3-pentadiene could be detected in the presence of 22'-DMB as a sensitizer. The limiting maximum isomerization yields $\Phi_{c \rightarrow t}(\text{max})$ and $\Phi_{t \rightarrow c}(\text{max})$ derived from Figs. 1 and 2 by averaging the isomerization yields for individual experiments over the concentration range indicated are given in Table 1 which shows that the ratios of the limiting values achieved

TABLE 1

Isomerization yields, branching ratios, photostationary states and triplet quantum yields Φ_T for the biphenyl-sensitized isomerization of 1,3-pentadiene at 293 K

Compound	$\Phi_{c \rightarrow t}(\text{max})$	$\Phi_{t \rightarrow c}(\text{max})$	$\frac{\Phi_{c \rightarrow t}(\text{max})}{\Phi_{t \rightarrow c}(\text{max})}$	Photostationary state (%)		Φ_T
				Trans	Cis	
44'DMB	0.27(0.02)	0.20(0.02)	1.35 ± 0.26	57	43	0.47 ± 0.04
33'DMB	0.17(0.01)	0.15(0.01)	1.13 ± 0.16	53	47	0.32 ± 0.02
4MB	0.27(0.01)	0.20(0.01)	1.35 ± 0.12	57	43	0.47 ± 0.02
3MB	0.21(0.01)	0.14(0.01)	1.50 ± 0.20	60	40	0.35 ± 0.02
2MB	0.13(0.01)	0.08(0.01)	1.63 ± 0.37	62	38	0.21 ± 0.02
MTP	0.28(0.01)	0.13(0.01)	2.15 ± 0.27	69	31	0.41 ± 0.02

The numerals in parentheses are the standard deviations

$$\sigma = \left(\sum_{n} \frac{d_i^2}{n-1} \right)^{1/2}$$

where d_i is the residual from the mean of the i th value.

for $\Phi_{c \rightarrow t}$ and $\Phi_{t \rightarrow c}$ depend on the nature of the sensitizer. The branching ratios for 4MB, 3MB, 44'DMB and 33'DMB were similar to the value 1.25 found for high-energy sensitizers [21]. The branching ratios for 2MB and MTP were considerably higher than this value but in view of the experimental error, the ability of 2MB to act as a high-energy sensitizer cannot be ruled out.

The temperature dependence of the isomerization yields was investigated for 4MB, 3MB, 2MB and MTP over a range of olefin concentrations (Fig. 3). The values obtained for the limiting maximum isomerization yields and standard deviations (derived from Fig. 3) are given in Table 2. $\Phi_{c \rightarrow t}$ and $\Phi_{t \rightarrow c}$ were measured for 33'DMB and 44'DMB and $\Phi_{c \rightarrow t}$ for 2MB and MTP in the temperature range 193 - 273 K using a sufficiently high concentration of *cis*- or *trans*-1,3-pentadiene ($(3 - 4) \times 10^{-3}$ M) respectively to achieve the limiting values. For 4MB, 3MB, 2MB and MTP at 193, 205, 233 and 273 K, $\Phi_{t \rightarrow c}$ was measured using a *trans*-1,3-pentadiene concentration of 3×10^{-3} M. For these measurements the errors in the $\Phi_{t \rightarrow c}$ values presented in Table 2 were estimated to be $\pm 8\%$. The dependence of $\Phi_{c \rightarrow t}$ and $\Phi_{t \rightarrow c}$ for biphenyl and $\Phi_{c \rightarrow t}$ for OTP on the concentration of the respective 1,3-pentadiene isomers was investigated at 293 K and the mean and standard deviation of the maximum isomerization yields which were derived at a concentration sufficiently high to achieve limiting values are also included in Table 2.

The increase in the limiting isomerization yields with decreasing temperature over the temperature range 293 - 193 K was small for 4MB, 3MB, 2MB, 44'DMB, 33'DMB and MTP and it is apparent from Table 2 that below about 233 K the isomerization yields were effectively constant. For 2MB,

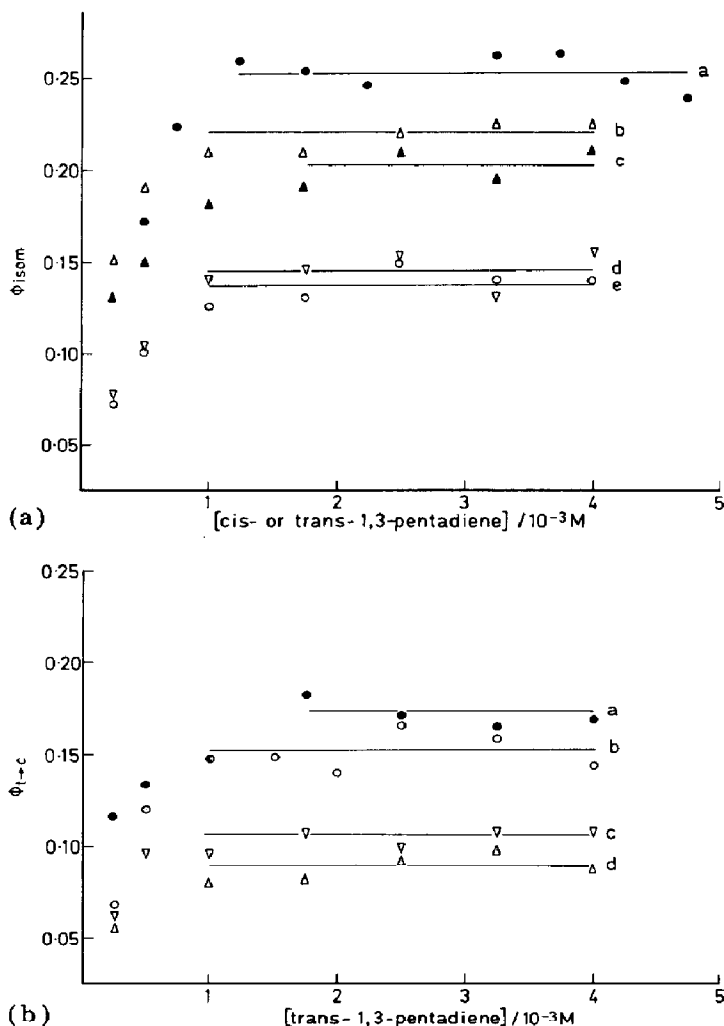


Fig. 3. Temperature dependence of the isomerization quantum yields: (a) ●, 4MB (curve a), $\Phi_{c \rightarrow t}$ at 308 K; Δ , 4MB (curve b), $\Phi_{t \rightarrow c}$ at 213 K; \blacktriangle , 4MB (curve c), $\Phi_{t \rightarrow c}$ at 253 K; ∇ , MTP (curve d), $\Phi_{c \rightarrow t}$ at 213 K; \circ , MTP (curve e), $\Phi_{t \rightarrow c}$ at 253 K. (b) ●, 3MB (curve a), $\Phi_{t \rightarrow c}$ at 213 K; \circ , 3MB (curve b), $\Phi_{t \rightarrow c}$ at 253 K; ∇ , 2MB (curve c), $\Phi_{t \rightarrow c}$ at 213 K; Δ , 2MB (curve d), $\Phi_{t \rightarrow c}$ at 253 K. The lines represent the mean values for Φ_{isom} over a concentration range indicated by their length.

44'DMB, 33'DMB and MTP the branching ratios were found to be independent of temperature and the triplet quantum yields

$$\Phi_T = \Phi_{c \rightarrow t} + \Phi_{t \rightarrow c}$$

which increased slightly as the temperature decreased, approached maximum values that were less than unity at the lowest temperatures employed. The triplet quantum yields for 4MB and 3MB at temperatures other than 293 K were calculated from the respective $\Phi_{c \rightarrow t}(\text{max})$ or $\Phi_{t \rightarrow c}(\text{max})$ values assuming that the branching factors determined at 293 K were independent of temperature.

TABLE 2

Effect of temperature on the limiting quantum yields $\Phi_{c \rightarrow t}(\max)$ and $\Phi_{t \rightarrow c}(\max)$ for isomerization and triplet quantum yields Φ_T for the substituted biphenyls

Temperature (K)	$\Phi_{c \rightarrow t}(\max)$	$\Phi_{t \rightarrow c}(\max)$	Φ_T
<i>44'DMB</i>			
193	0.31 ± 0.02	0.23 ± 0.02	0.54 ± 0.04
213	0.32 ± 0.02	0.23 ± 0.02	0.55 ± 0.04
233	0.30 ± 0.02	0.23 ± 0.02	0.53 ± 0.04
253	0.30 ± 0.02	0.22 ± 0.02	0.52 ± 0.04
273	0.28 ± 0.02	0.21 ± 0.02	0.49 ± 0.04
<i>33'DMB</i>			
193	0.19 ± 0.02	0.17 ± 0.02	0.36 ± 0.04
213	0.19 ± 0.02	0.17 ± 0.02	0.36 ± 0.04
233	0.19 ± 0.02	0.16 ± 0.02	0.35 ± 0.04
253	0.18 ± 0.02	0.16 ± 0.02	0.34 ± 0.04
273	0.18 ± 0.02	0.16 ± 0.02	0.34 ± 0.04
<i>2MB</i>			
193	0.15 ± 0.01	0.11 ± 0.01	0.26 ± 0.02
213	0.16 ± 0.01	0.11 (0.01)	0.27 ± 0.02
233	0.14 ± 0.01	0.11 ± 0.01	0.25 ± 0.02
253		0.09 (0.01)	0.24 ± 0.02 ^a
273	0.14 ± 0.01	0.10 ± 0.01	0.24 ± 0.02
<i>3MB</i>			
193		0.17 ± 0.02	0.43 ± 0.04 ^a
213		0.17 (0.01)	0.43 ± 0.02 ^a
233		0.16 ± 0.02	0.40 ± 0.04 ^a
253		0.15 (0.01)	0.38 ± 0.02 ^a
273		0.15 ± 0.01	0.38 ± 0.02 ^a
<i>4MB</i>			
193		0.23 ± 0.02	0.54 ± 0.04 ^a
213		0.22 (0.01)	0.52 ± 0.02 ^a
233		0.21 ± 0.02	0.49 ± 0.04 ^a
253		0.20 (0.01)	0.47 ± 0.02 ^a
273		0.19 ± 0.02	0.45 ± 0.04 ^a
308	0.25 (0.02)		0.44 ± 0.04 ^a
<i>MTP</i>			
193	0.31 ± 0.02	0.15 ± 0.01	0.46 ± 0.03
213	0.31 ± 0.02	0.15 (0.02)	0.46 ± 0.04
233	0.30 ± 0.02	0.14 ± 0.01	0.44 ± 0.03
253		0.14 (0.01)	0.45 ± 0.02 ^a
273	0.29 ± 0.02	0.14 ± 0.01	0.43 ± 0.03
<i>OTP</i>			
293	0.13 ± 0.01		
<i>Biphenyl</i>			
293	0.22 (0.02)	0.17 (0.01)	0.39 ± 0.03

The numerals in parentheses are the standard deviations of several measurements.

^aCalculated assuming that the photostationary state composition is independent of temperature.

TABLE 3

Effect of the sensitizer concentration on the isomerization yields of 4MB^a and 33'DMB^b

Sensitizer concentration ($\times 10^{-3}$ mol dm ⁻³)	Photolysis time (min)	$\Phi_{t \rightarrow c}$	$\Phi_{c \rightarrow t}$
<i>4MB</i>			
2.5	122	0.17	
3.7	109	0.19	
5.0	74	0.17	
7.5	67	0.18	
10.0	87	0.17	
15.0	81	0.17	
17.5	83	0.19	
22.5	77	0.21	
27.5	90	0.19	
32.5	87	0.17	
27.5	81	0.17	
50.0	70	0.18	
62.5	73	0.19	
75.0	74	0.17	
<i>33'DMB</i>			
6.3	60		0.16
12.5	62		0.16
37.5	61		0.16
62.5	60		0.17

^a[*trans*-1,3-Pentadiene] = 6.0×10^{-3} mol dm⁻³.^b[*cis*-1,3-Pentadiene] = 3.8×10^{-3} mol dm⁻³.

The effect of the sensitizer concentration on the *cis*-*trans* isomerization of 1,3-pentadiene was investigated for 4MB and 33'DMB. Table 3 shows that a 30-fold variation in the concentration of 4MB and a tenfold variation in the concentration of 33'DMB had no effect on $\Phi_{t \rightarrow c}$ and $\Phi_{c \rightarrow t}$ respectively. In contrast, for the bridged biphenyl fluorene the isomerization and triplet quantum yields were dependent on the concentration of the sensitizer (Table 4) and did not show significant increases with decreasing temperature over the range 193 - 293 K (Table 5).

1,3-Pentadienes can quench singlet states and the anomalously low values reported for triplet quantum yields in the naphthalene-sensitized isomerization of 1,3-pentadiene have been shown to be due to the quenching of the singlet state at high olefin concentrations [22]. Table 6 shows that the quenching of fluorescence from 4MB by 1,3-pentadiene was very small even at the highest olefin concentrations used in this investigation.

There is considerable evidence to suggest that in biphenyl-type molecules three electronic transitions with different oscillator strengths may be present in the spectral region of the first absorption band [4, 7]. The ordering of these close-lying electronic levels and the oscillator strengths of the

TABLE 4

Effect of sensitizer concentration on the isomerization yields for 1,3-pentadiene sensitized by fluorene

Fluorene concentration ($\times 10^{-4}$ mol dm $^{-3}$)	$\Phi_{c \rightarrow t}(\text{max})$	$\Phi_{t \rightarrow c}(\text{max})$	Φ_T	$\frac{\Phi_{c \rightarrow t}(\text{max})}{\Phi_{t \rightarrow c}(\text{max})}$
1.3	0.15 ± 0.01		0.27 ± 0.02^a	
2.5	0.15 ± 0.01		0.27 ± 0.02^a	
12.5	0.16 ± 0.01	0.13 ± 0.01	0.29 ± 0.02	1.23
62.5	0.18 ± 0.01		0.33 ± 0.02^a	
125.0	0.17 ± 0.01	0.14 ± 0.01	0.31 ± 0.02	1.21
230.0	0.22 ± 0.02	0.18 ± 0.01	0.40 ± 0.03	1.22
480.0	0.24 ± 0.02		0.44 ± 0.04^a	

Temperature, 293 K.

^aCalculated assuming that the photostationary state composition is independent of fluorene concentration.

TABLE 5

Effect of temperature on the isomerization yields for 1,3-pentadiene sensitized by fluorene

Temperature (K)	$\Phi_{c \rightarrow t}(\text{max})$	$\Phi_{t \rightarrow c}(\text{max})$	Φ_T	$\frac{\Phi_{c \rightarrow t}(\text{max})^a}{\Phi_{t \rightarrow c}(\text{max})}$
193	0.15 ± 0.01	0.11 ± 0.01	0.26 ± 0.02	1.36
213	0.15 ± 0.01	0.13 ± 0.01	0.28 ± 0.02	1.15
233	0.14 ± 0.01	0.13 ± 0.01	0.27 ± 0.02	1.08
253	0.14 ± 0.01	0.12 ± 0.01	0.26 ± 0.02	1.17
273	0.14 ± 0.01	0.12 ± 0.01	0.26 ± 0.02	1.17
293	0.14 ± 0.01	0.11 ± 0.01	0.25 ± 0.02	1.27

[Fluorene] = 3×10^{-4} mol dm $^{-3}$.

^aMean, 1.21 ± 0.15 .

TABLE 6

Quenching of fluorescence of 4MB by *trans*-1,3-pentadiene

Concentration of <i>trans</i> -1,3-pentadiene ($\times 10^{-3}$ mol dm $^{-3}$)	Relative fluorescence intensity
0.0	48.0
2.0	47.0
4.0	44.0
6.0	42.5
8.0	39.5

[4MB] = 2×10^{-2} mol dm $^{-3}$; excitation wavelength, 250 nm.

transitions will depend on the nature and geometry of the molecule and this will affect its radiative and non-radiative properties.

The initial absorption is given by reaction (1):



where B represents the ground-state molecule and ${}^1B^{*'}$ represents initially formed excited-state molecules surrounded by solvent molecules in the ground-state configuration. At ambient temperatures in non-viscous media, solvent rearrangement and configurational changes will be rapid resulting in an equilibrated excited state ${}^1B^{*''}$:



Fluorescence, internal conversion or intersystem crossing from the thermally equilibrated ${}^1B^{*''}$ excited state may occur:



A complete characterization of the absorption and fluorescence spectra requires a consideration of more than one transition and, with the exception of *p*-terphenyl, internal conversion to a low-lying excited state ${}^1B^{*'''}$ must be possible for the phenyl- and methyl-substituted biphenyls:



The radiative decay



occurs but evidence will be given that intersystem crossing and internal conversion are important.



Phosphorescence is an unimportant process in fluid solution and the most likely fate of molecules in the equilibrated triplet state ${}^3B^*$ is the non-radiative decay



The sensitized *cis-trans* photoisomerization of the 1,3-pentadienes has been studied in detail [21, 23]. Sensitizers with triplet energies above about 250 kJ mol⁻¹ can undergo triplet excitation transfer to *cis*- and *trans*-1,3-pentadiene at close to diffusion controlled rates yielding a single photo-stationary [trans]/[cis] value of 1.25 ± 0.05. For these high energy sensitizers a consistent mechanism is given by





where *c*-P and *t*-P represent ground-state *cis*- and *trans*-1,3-pentadiene respectively and *s*-*t*³P* represents the 1,3-diene triplet produced by excitation transfer to the *s*-*trans* conformers. For low-energy sensitizers the probable involvement of two diene triplets leads to complications and reactions (10) and (11) cannot be regarded as an accurate interpretation of the sensitized *cis*-*trans* isomerization.

The long wavelength absorption spectra of the simple biphenyls is dominated by a strong allowed transition similar to the ¹B_b ← ¹A transition in benzene. Only in the case of *p*-terphenyl [6] is there rapid radiative decay from the thermally equilibrated levels of this initially formed state ¹B^{**}. Fluorescence studies [11] have shown that radiative decay from 4MB, 3MB, 2MB, 44'DMB, 33'DMB, 22'DMB, MTP and OTP are long lived and occur from states not directly populated during absorption. It is evident that cross-over from ¹B^{**} to ¹B^{***} must be very rapid and that radiative and non-radiative decay from ¹B^{**} are not important in solution for the molecules under investigation. Ignoring reactions (3) and (4), a conventional steady-state treatment of reactions (1), (2) and (5) - (11) yields the following expressions for the *cis*-*trans* isomerization of 1,3-pentadienes by high-energy triplet sensitizers.

$$\Phi_{c \rightarrow t} = \frac{k_{11b}}{k_{11a} + k_{11b}} \frac{k_{10a}[c\text{-P}]}{k_{10a}[c\text{-P}] + k_9} \frac{k_7}{k_6 + k_7 + k_8}$$

$$\Phi_{t \rightarrow c} = \frac{k_{11a}}{k_{11a} + k_{11b}} \frac{k_{10b}[t\text{-P}]}{k_{10b}[t\text{-P}] + k_9} \frac{k_7}{k_6 + k_7 + k_8}$$

At high concentrations where $\Phi_{c \rightarrow t}$ and $\Phi_{t \rightarrow c}$ reach limiting values, the mechanism for high-energy triplet sensitizers predicts that the total isomerization quantum yield

$$\Phi_{\text{T}} = \Phi_{c \rightarrow t}(\text{max}) + \Phi_{t \rightarrow c}(\text{max})$$

becomes equal to the intersystem crossing yield Φ_{isc} , *i.e.*

$$\Phi_{\text{T}} = \frac{k_7}{k_6 + k_7 + k_8}$$

The 0-0 band in the phosphorescence spectrum of fluorene in ethyl ether-isopentane-ethanol (volume ratio, 5:5:2) glass occurs around 23 800 cm⁻¹ [24] and the value of the branching ratio $\Phi_{c \rightarrow t}/\Phi_{t \rightarrow c} = 1.21 \pm 0.15$ is indicative of a high energy triplet sensitizer. The total isomerization quantum yield 0.26 ± 0.02 is in reasonable agreement with the value 0.31 obtained using other methods [25, 26]. Fluorescence quantum yields Φ_{T} and lifetimes τ_{F} for dilute solutions of fluorene in *n*-hexane are presented in Table 7.

TABLE 7

Fluorescence quantum yields Φ_F and lifetimes τ_F of fluorene in *n*-hexane solution

Temperature	Φ_F	τ_F	$\Phi_F + \Phi_T$
193	0.73	7.6	0.99
213	0.69	7.6	0.97
233	0.69	7.6	0.96
253	0.68	7.6	0.94
273	0.68	7.6	0.94
293	0.68	7.5	0.93
313	0.67	7.7	
333	0.66	7.7	

Excitation wavelength, 265 nm.

The very small increase in the fluorescence quantum yields with increasing temperature from 333 to 193 K is within the estimated experimental uncertainty of $\pm 6\%$, and the fluorescence lifetimes which were reproducible to ± 0.1 ns exhibited no trend on varying the temperature. It is apparent that radiative decay and intersystem crossing are the principal fates of the excited singlet state of fluorene at all temperatures investigated.

The branching ratios $\Phi_{c \rightarrow t} / \Phi_{t \rightarrow c}$ (Table 1) for 4MB, 3MB, 44'MB and 33'DMB are close to those found for efficient high-energy triplet-state sensitizers and this is consistent with the fact that the triplet-state energies of these molecules exceed 250 kJ mol^{-1} , and indicates, in principle, that the *cis-trans* isomerization of 1,3-pentadiene can be used as an effective monitor for the triplet-state quantum yields. The fluorescence quantum yields and lifetimes for 4MB, 3MB, 44'DMB and 33'DMB obtained by interpolation from published data [11] over the temperature range 193–293 K are presented in Table 8. The values for Φ_T / τ_F also presented in Table 8 show that the intersystem rate constants k_7 for 4MB, 44'DMB and 33'DMB are effectively independent of temperature and have magnitudes similar to the intersystem crossing rate constants found for other aromatic hydrocarbons [1]. The values of Φ_T / τ_F for 3MB increase slightly at higher temperatures and this suggests that intersystem crossing for this compound may involve a temperature-dependent process. The branching rates $\Phi_{c \rightarrow t} / \Phi_{t \rightarrow c}$ of 1.63 and 2.23 found for 2MB and MTP respectively imply photostationary states similar to those reported for the sensitization of 1,3-pentadiene by naphthalene [3]. For low-energy sensitizers a significant fraction of the 1,3-diene-sensitizer-triplet encounters can lead to the formation of *s-cis*-diene triplet states, resulting in an increased decay to the *trans* isomer. Thus for 2MB and MTP the high-energy triplet-sensitizer mechanism may not be appropriate and the sum of $\Phi_{t \rightarrow c}$ and $\Phi_{c \rightarrow t}$ cannot be regarded as a measure of the intersystem crossing quantum yield. The failure of OTP to photosensitize the isomerization of *trans*-1,3-pentadiene, despite the fact that the highest energy band in the phosphorescence spectrum [27] appears

TABLE 8

Fluorescence quantum yields Φ_F , lifetimes τ_F , intersystem crossing rate constants k_7 and total non-radiative rate constants ($k_7 + k_8$) for 4MB, 3MB, 44'DMB and 33'DMB

Temperature (K)	Φ_F	τ_F (ns)	k_7^a ($\times 10^7 \text{ s}^{-1}$)	$k_7 + k_8^b$ ($\times 10^7 \text{ s}^{-1}$)
4MB				
193	0.27 ± 0.02	20.4	2.6 ± 0.2	3.5 ± 0.2
213	0.25 ± 0.02	20.3	2.7 ± 0.1	3.6 ± 0.2
233	0.23 ± 0.02	20.2	2.6 ± 0.2	3.8 ± 0.2
253	0.21 ± 0.02	19.7	2.6 ± 0.1	4.0 ± 0.2
273	0.19 ± 0.02	19.1	2.6 ± 0.2	4.2 ± 0.2
293	0.18 ± 0.02	17.9	2.6 ± 0.1	4.5 ± 0.2
3MB				
193	0.28 ± 0.02	22.3	1.9 ± 0.2	3.2 ± 0.2
213	0.25 ± 0.02	21.0	2.0 ± 0.1	3.6 ± 0.2
233	0.23 ± 0.02	19.7	2.0 ± 0.2	3.9 ± 0.2
253	0.22 ± 0.02	17.2	2.2 ± 0.1	4.5 ± 0.2
273	0.21 ± 0.02	14.3	2.7 ± 0.2	5.5 ± 0.2
293	0.20 ± 0.02	13.4	2.6 ± 0.2	6.0 ± 0.2
44'DMB				
193	0.27 ± 0.02	19.7	2.7 ± 0.2	3.7 ± 0.2
213	0.26 ± 0.02	19.3	2.8 ± 0.2	3.8 ± 0.2
233	0.25 ± 0.02	18.6	2.8 ± 0.2	4.0 ± 0.2
253	0.24 ± 0.02	18.0	2.9 ± 0.2	4.2 ± 0.2
273	0.23 ± 0.02	17.3	2.8 ± 0.2	4.5 ± 0.2
293	0.22 ± 0.02	16.5	2.8 ± 0.2	4.7 ± 0.2
33'DMB				
193	0.23 ± 0.02	19.0	1.9 ± 0.2	4.0 ± 0.2
213	0.23 ± 0.02	18.3	2.0 ± 0.2	4.2 ± 0.2
233	0.23 ± 0.02	17.6	2.0 ± 0.2	4.4 ± 0.2
253	0.22 ± 0.02	16.6	2.0 ± 0.2	4.7 ± 0.2
273	0.20 ± 0.02	15.4	2.2 ± 0.2	5.2 ± 0.2
293	0.18 ± 0.02	14.1	2.3 ± 0.2	5.8 ± 0.2

$$^a k_7 = \Phi_T / \tau_F.$$

$$^b k_7 + k_8 = (1 - \Phi_F) / \tau_F.$$

at an energy of 257 kJ mol^{-1} , shows that energetics is not the controlling factor in the energy transfer process.

For all the methyl- and phenyl-substituted biphenyls examined, the sum of Φ_F and Φ_T was significantly less than unity even at the lowest temperatures investigated. The triplet quantum yields Φ_T for 4MB, 3MB, 44'DMB and 33'DMB over the range 293 - 193 K were consistently less than $1 - \Phi_F$ and although intersystem crossing is a process of great importance in these substituted biphenyls, other non-radiative processes are operative. Table 8 shows that the total non-radiative rate constants ($k_7 + k_8$) decreased with decreasing temperature and approached constant values which were greater than the intersystem rate constants k_7 at the lowest temperatures

investigated. The radiative rate constants $k_6 = \Phi_F/\tau_F$ and the intersystem rate constants $k_7 = \Phi_T/\tau_F$ for 4MB, 44'DMB and 33'DMB were constant with temperature and it is apparent that for these compounds the internal conversion rate constants k_8 are composed of both temperature-independent and temperature-dependent processes. The temperature dependence of the fluorescence lifetimes τ_F for 4MB, 44'DMB and 33'DMB have been shown to obey the relationship [11]

$$\ln\left(\frac{1}{\tau_F} - \frac{1}{\tau_F^0}\right) = \ln A - \frac{E}{RT}$$

where τ_F^0 is the low-temperature fluorescence lifetime which becomes effectively constant below 210 K, and this is consistent with the internal conversion rate constants k_8 taking the form

$$k_8 = k_8^0 + A_8 \exp\left(-\frac{E_8}{RT}\right)$$

The triplet quantum yield found for biphenyl at 293 K was similar to the triplet quantum yields for 4MB, 3MB, 44'DMB, 33'DMB and MTP at this temperature. Several measurements of the triplet quantum yield for biphenyl in fluid solution have been made. Although there is little information on the effect of temperature it would appear that the biphenyl intersystem crossing yields obtained using the olefin isomerization method [28] ($\Phi_T = 0.25$) give consistently lower values than those obtained using the sensitized phosphorescence of biacetyl ($\Phi_T = 0.81$ [25]; $\Phi_T = 0.73$ [29]). Previous work has suggested that the biphenyl-sensitized isomerization of 1,3-pentadiene results in a trans-rich photostationary state [23] but the value for the branching ratio of 1.3 ± 0.2 found in the present investigation and the fact that the 0-0 band in phosphorescence occurs at $22\,800\text{ cm}^{-1}$ [24] are indicative of a high-energy triplet sensitizer. For 4MB, fluorescence quenching by 1,3-pentadiene (about $4 \times 10^{-3}\text{ dm}^3\text{ mol}^{-1}$) in the plateau region is small (approximately 8%) and diene quenching of the excited-singlet state is unlikely to account for the large discrepancies between the triplet yields measured by the biacetyl phosphorescence and the olefin isomerization methods. Even at low temperatures fluorescence quenching by 1,3-pentadiene of the singlet-excited state of 4MB is significantly less than the residual non-radiative processes ($1 - \Phi_F - \Phi_T = 0.19$) and a temperature-independent non-radiative path (k_8^0) seems essential.

The magnitude of the activation energies E_a derived from the temperature dependence of the fluorescence lifetimes [11] for 4MB ($E_a = 12.7 \pm 1.1\text{ kJ mol}^{-1}$), 44'DMB ($E_a = 20.6 \pm 1.5\text{ kJ mol}^{-1}$) and 33'DMB ($E_a = 19.0 \pm 0.7\text{ kJ mol}^{-1}$) show that the temperature-dependent non-radiative process emanates from low vibrational levels of the thermally equilibrated $^1B^{*''}$ state and the pre-exponential factors A (4MB, $A = (3 \pm 2) \times 10^{10}\text{ s}^{-1}$; 44'DMB, $A = (2 \pm 1) \times 10^9\text{ s}^{-1}$; 33'DMB, $A = (6 \pm 3) \times 10^{10}\text{ s}^{-1}$) are indicative of internal

conversion processes. The internal conversion $S_1 \rightarrow S_0$ is usually negligibly small relative to fluorescence and intersystem crossing for non-photoreactive and relatively rigid aromatic molecules for which the energy gap for $S_1 \rightarrow S_0$ is large [23]. For these molecules the presence of higher triplet states of energies slightly above the level of the first-excited singlet state can result in a decrease in the probability of fluorescence with increasing temperature and a simultaneous increase in the probability for intersystem crossing. However, a temperature-dependent intersystem crossing would be expected to lead to an enhancement of triplet quantum yields and not to the experimentally observed decrease; an explanation which is more likely is that the ability of the substituted biphenyl molecules to twist about the carbon-carbon central bond leads to a relaxation of the (normally unfavourable) Franck-Condon overlap which results in an enhanced probability for the internal conversion $S_1 \rightarrow S_0$. Departures from the relationship $\Phi_F + \Phi_T = 1$ (Ermolaev's rule [30]) can be anticipated if a photoreaction occurs or if the molecule possesses a low-lying singlet state. For the substituted biphenyl molecules a temperature-dependent internal conversion to a higher excited singlet state may occur and the possibility cannot be discounted that subsequent intersystem crossing and vibrational deactivation result in the population of a normally inaccessible triplet state which lies below the energy threshold for 1,3-pentadiene isomerization but above that for biacetyl phosphorescence. For these reasons, intersystem rate constants determined for the substituted biphenyl molecules using the olefin isomerization method should be regarded as lower limits for the process.

It is apparent that phenyl and methyl substitution can modify the excited-state behaviour of a flexible aromatic molecule such as biphenyl. Berleman [4] has shown that the dramatic increase in radiative decay for *p*-terphenyl relative to biphenyl is due to cross-over to the 1B_b and 1L_b energy levels. Methyl substitution in the para positions and both phenyl and methyl substitution in the meta positions of biphenyl result in only a small increase in the intersystem crossing yields and it can be concluded that the ordering of energy levels in 4-MB, 3-MB, 33'DMB, 44'DMB and MTP are similar to those of biphenyl. Methyl and phenyl substitution in the 2 position of biphenyl leads to trans-rich stationary states of the photosensitized diene which are indicative of relatively low triplet energies and it is apparent that the steric hindrance induced in the biphenyl ring by substituents in the ortho position has a major effect on the photophysical behaviour of the molecule.

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