

## EFFECT OF TEMPERATURE ON THE FLUORESCENCE OF METHYL- AND PHENYL-SUBSTITUTED BIPHENYL MOLECULES

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### Summary

The effect of temperature on the absorption, fluorescence excitation and emission spectra, the fluorescence quantum yields and the decay times of methyl- and phenyl-substituted biphenyls have been studied in solution. The fluorescence quantum yields  $\phi_F$  and decay times  $\tau_F$  increased with decreasing temperature and the ratio  $\phi_F/\tau_F$  remained essentially constant. Non-radiative decay was found to consist of temperature-independent and temperature-dependent parts. The results are interpreted in terms of a model in which, following excitation, configurational changes, rapid internal conversion and solvent reorganization result in the population of a low-lying excited state from which the probability of both radiative and non-radiative decay is decreased.

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### 1. Introduction

The fluorescence properties of planar chromophores in which there is an approximate mirror symmetry between the absorption and the fluorescence emission spectra have received much attention [1, 2]. For these molecules the measured radiative probability  $\tau_0 = q/\tau$ , where  $q$  and  $\tau$  are the fluorescence efficiency and the measured decay time, compares closely with theoretical values derived from the absorption and emission spectra [3, 4]. A more complex situation arises when there is a change in configuration between the ground and the excited states and the measured radiative probability of flexible molecules such as the polyenes [5 - 7] and biphenyls [8, 9] exceeds the theoretical radiative probability by orders of magnitude. It is apparent that changes in molecular geometry have a profound influence on the photophysical parameters and the relative effects of fluorescence, intersystem crossing and internal conversion processes can be affected.

The luminescence spectra of these flexible aromatic molecules can exhibit unusual features and Beriman [10] has formulated a number of

principles which give indications of the expected correlations between the absorption and the fluorescence properties for different configurations of the ground and excited states. For the linear polyenes ( $R-(CH=CH)_n-R$ ) (where R represents an alkyl or phenyl group) with  $n > 3$  there is clear theoretical [11] and experimental [12, 13] evidence indicating the involvement of a spectroscopically forbidden low-lying excited state and fluorescence from the well-known scintillator all-*trans*-1,6-diphenyl-1,3,5-hexatriene has been shown to occur from both the  $S_2$  and the  $S_1$  excited states [14, 15].

The fluorescence spectra of biphenyls and polyphenyls [16, 17] in rigid solution and the fluorescence quantum yields of biphenyl [18] in viscous solution are dependent on the wavelength of the exciting light. The spectra have been interpreted in terms of a model [16] in which molecules with varying degrees of non-planarity act as absorbers giving rise to structureless excitation spectra but rapid relaxation to nearly planar configurations of the excited state in fluid solution leads to a retention of some vibrational structure in the emission spectra. Furthermore, there is considerable evidence that the broad structureless absorption band of biphenyl is composed of more than a single transition and a reordering of the excited states with substitution can lead to dramatic changes in the fluorescence characteristics of the biphenyl analogues [8]. The quantitative effect that these factors have on the photophysical processes such as fluorescence, intersystem crossing and internal conversion of substituted biphenyls requires elucidation. A detailed examination of temperature and solvent effects is essential in understanding environmental influences on the change in shape which follows excitation and of the consequent effects on the radiative and non-radiative aspects of hidden or weak transitions. This has been attempted in this investigation by examination of the fluorescence quantum yields and decay times of several methyl- and phenyl-substituted biphenyl molecules in fluid media.

## 2. Experimental details

*p*-terphenyl (PTP) (Nuclear Enterprises scintillation grade), 3-methylbiphenyl (3MB), 4-methylbiphenyl (4MB), 4,4'-dimethylbiphenyl (44'DMB) and 3,3'-dimethylbiphenyl (33'DMB) (Aldrich Chemicals; purity, more than 99%) were used without further purification. *m*-terphenyl (MTP) (Phase Separations), *o*-terphenyl (OTP) (Kodak), 2-methylbiphenyl (2MB) and 2,2'-dimethylbiphenyl (22'DMB) (ICN Pharmaceuticals) were purified by gas chromatography using a Varian Aerograph preparative instrument equipped with a column containing silicone oil (Phase Separations OV1) on Chromasorb W acid-washed support. 3-methylpentane (Aldrich), acetonitrile (BDH special for spectroscopy) and ethanol (BP spectrograde) were treated as described previously [5].

The solutions were contained in Spectrosil cuvettes 1 cm  $\times$  1 cm in cross section or in cylindrical Spectrosil cuvettes 1 cm in diameter for both steady state and pulse excitation experiments. A side-arm attached to the

cells enabled the solutions to be degassed by repeated freeze-thaw cycles on a conventional high vacuum system and sealed before use. The absorption spectra were determined using either a Pye-Unicam SP1800 or a Perkin-Elmer 402 spectrophotometer. The fluorescence excitation and emission spectra were measured on optically dilute solutions (optical density, less than 0.1) using a fully corrected spectrofluorometer [19]. The quantum yields were determined relative to a value of 0.83 for 9,10-diphenylanthracene in cyclohexane at 25 °C [20] by methods identical with those described elsewhere [21]. The fluorescence decay measurements were obtained using time-correlated single-photon counting [5]. Temperature control for all measurements at room temperature and above was achieved with an electrically heated aluminium block and regulated by a Pye-Ether digital temperature controller connected to a platinum resistance thermometer located in a hole in the block. The absorption and fluorescence spectra below room temperature were obtained using an Oxford Instruments CF103 cryostat whilst a cryostat similar in design to that described by Fischer [22] was used for the fluorescence lifetime experiments. The temperatures were measured using previously calibrated thermocouples located close to the sample.

### 3. Results and discussion

The absorption spectra of 2MB, 3MB, 4MB, 33'DMB, 44'DMB and PTP in 3-methylpentane solvent are shown in Figs. 1 and 2. With the exceptions of 22'DMB and OTP, the absorption spectra were broad and remained structureless even at the lowest temperatures employed. Substitution of phenyl or

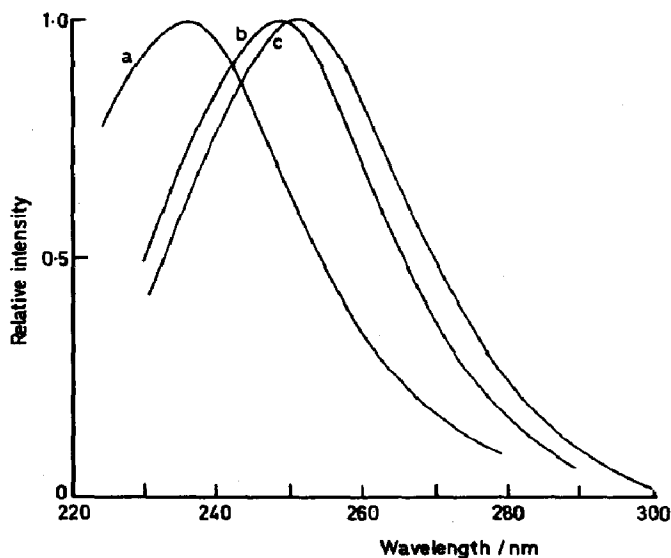


Fig. 1. Absorption spectra of 2MB (curve a), 3MB (curve b) and 4MB (curve c) in 3-methylpentane at 298 K.

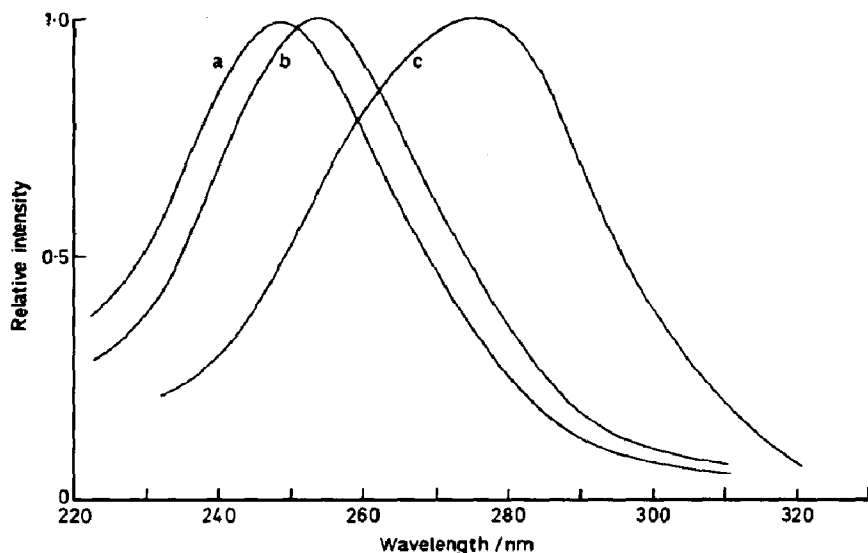


Fig. 2. Absorption spectra of 33'DMB (curve a), 44'DMB (curve b) and PTP (curve c) in 3-methylpentane at 298 K.

methyl groups into the 4 and 4' positions of biphenyl resulted in significant bathochromic shifts compared with biphenyl but the red shifts in the absorption spectra of 3MB, 33'DMB and MTP were small. Substitution of phenyl or methyl into the 2 and 2' positions of biphenyl resulted in a hypsochromic shift of the main absorption band. The absorption spectrum of OTP showed a shoulder at around 250 nm approximately 20 nm to the red of the absorption maximum while that for 22'DMB shows two peaks of low relative intensity on the low energy side of the main transition [1].

In acetonitrile and ethanol the absorption spectra of all the compounds examined showed bathochromic shifts compared with the spectra obtained in the non-polar solvent but the spectral shapes remained unchanged. Fluorescence excitation spectra obtained using optically dilute solutions (optical density, less than 0.1) were found to be essentially identical with the corresponding absorption spectra.

The fluorescence emission spectra of the biphenyl derivatives in 3-methylpentane solvent showed evidence of structure and mirror image relationships to the corresponding absorption or excitation spectra were not apparent. Substituents in the *para* position gave rise to more structured emission spectra (Fig. 3) than the *meta* derivatives (Fig. 4) whilst the *ortho* derivatives showed the least structure and the highest Stokes loss (Fig. 5). For the methyl derivatives more structure was apparent in the fluorescence emission spectra of disubstituted derivatives (Fig. 6) than in those for the monosubstituted biphenyls (Fig. 7). Decreasing the temperature resulted in a progressive increase in the structure of the fluorescence emission spectra. The more polar solvents acetonitrile and ethanol had little effect on the

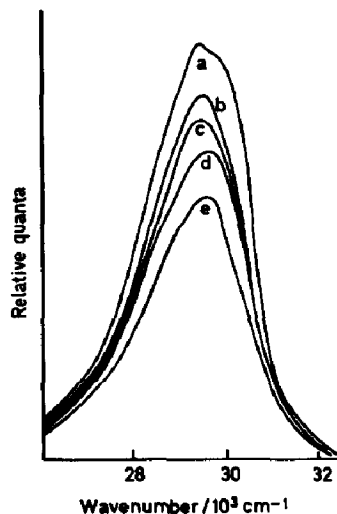
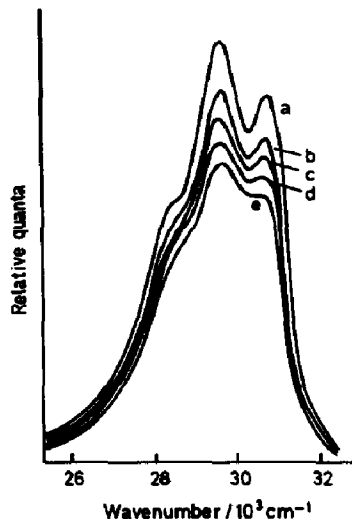


Fig. 3. Effect of temperature on the fluorescence emission spectra of PTP in 3-methylpentane: curve a, 210 K; curve b, 270 K; curve c, 300 K; curve d, 330 K; curve e, 360 K.

Fig. 4. Effect of temperature on the fluorescence emission spectra of MTP in 3-methylpentane: curve a, 210 K; curve b, 270 K; curve c, 300 K; curve d, 330 K; curve e, 360 K.

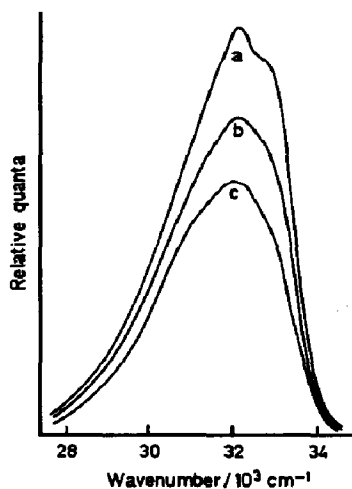


Fig. 5. Effect of temperature on the fluorescence emission spectra of OTP in 3-methylpentane: curve a, 180 K; curve b, 300 K; curve c, 360 K.

positions of the band maxima and the overall shapes of the fluorescence emission spectra were unchanged.

The fluorescence quantum yields and decay times with the exception of 22'DMB were found to be independent of excitation wavelength over the temperature range studied. No evidence was found for photochemical reaction within the time of measurement and the results for 4MB presented in Table 1, which were typical of those obtained, showed that the solvent had little effect on the fluorescence quantum yields and decay times. At room

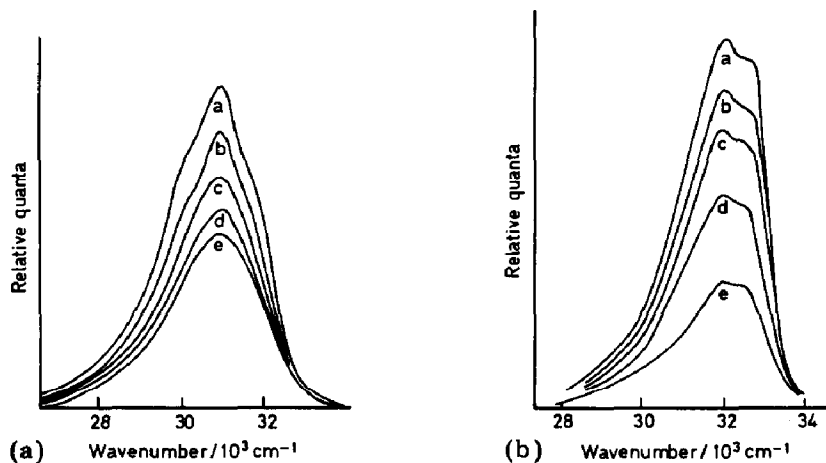


Fig. 6. Fluorescence spectra of (a) 44'DMB (curve a, 180 K; curve b, 240 K; curve c, 300 K; curve d, 330 K; curve e, 360 K) and (b) 33'DMB (curve a, 210 K; curve b, 270 K; curve c, 300 K; curve d, 330 K; curve e, 360 K) in 3-methylpentane.

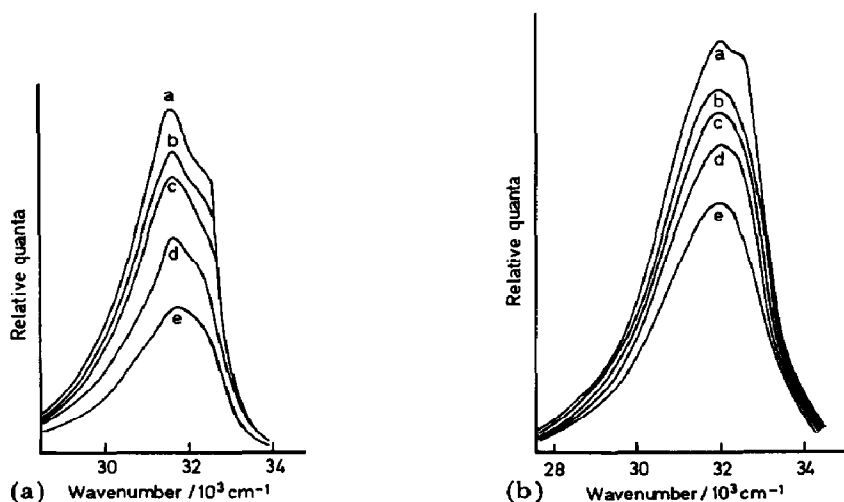


Fig. 7. Fluorescence spectra of (a) 4MB (curve a, 180 K; curve b, 240 K; curve c, 270 K; curve d, 300 K; curve e, 330 K) and (b) 3MB (curve a, 210 K; curve b, 270 K; curve c, 300 K; curve d, 330 K; curve e, 360 K) in 3-methylpentane.

temperature the quantum yields and decay times for 3MB, 4MB, 33'DMB, 44'DMB and MTP were close to those reported for biphenyl [2] ( $\phi_F = 0.15$ ;  $\tau_F = 11.0$  ns). Substitution in the 2 and 2' positions by methyl and phenyl groups resulted in a dramatic reduction in the fluorescence quantum yields but the fluorescence lifetimes were not nearly so affected. Below about 200 K the fluorescence response functions for 2MB and 22'DMB did not correspond to single-exponential behaviour. The quantum yields and decay times for the biphenyl derivatives examined decreased with increasing temperature in all solvents. Table 2 shows the effects of temperature on the quantum yields and decay times in 3-methylpentane. The quantum yields for PTP

TABLE 1

Effect of solvent on the fluorescence quantum yields and decay times of 4-methylbiphenyl

Temperature (K)	Data for the following solvents					
	3-methylpentane		Acetonitrile		Ethanol	
	$\tau_F$ (ns)	$\phi_F$	$\tau_F$ (ns)	$\phi_F$	$\tau_F$ (ns)	$\phi_F$
210	20.3	0.25			22.3	0.28
240	20.1	0.22	19.8	0.21	20.8	0.28
270	19.1	0.19	18.7	0.20	18.9	0.23
300	17.6	0.18	16.0	0.19	16.6	0.20
330	14.7	0.15	13.8	0.18	14.9	0.17
360	12.7	0.12	10.7	0.17	12.7	0.14

approached unity at low temperatures and from the short fluorescence lifetime and relatively highly structured emission spectra it was clear that the photophysical properties of PTP were different from those of the other biphenyls examined. The increase in the fluorescence quantum yields for 4MB, 3MB, 44'DMB, 33'DMB and MTP with decreasing temperature was mirrored by a similar increase in the fluorescence decay times leading to  $\phi_F/\tau_F$  ratios for each compound which effectively were constant. With the exception of 22'DMB the values obtained at room temperature for fluorescence quantum yields and lifetimes compared favourably with values reported in the literature [2, 8]. For 22'DMB the value for the quantum yield at room temperature in 3-methylpentane was half the value in cyclohexane reported by Berlman [8] ( $\phi_F = 0.006$ ). However, the intensity of the 450 W xenon excitation source decreases rapidly below 250 nm and this, combined with the intrinsically small fluorescence yield, results in some uncertainty in the intensity of the corrected emission spectrum. Furthermore, 22'DMB was the only compound which showed a significant solvent effect on the fluorescence decay times and a dependence of the emission spectra on excitation wavelength could not be ruled out.

The fact that the fluorescence emission spectra of the substituted biphenyls are structured while the absorption spectra are not is indicative of chromophores that are non-planar in their ground states and more planar in their excited states [10]. It has been estimated that in solution the preferred interplanar angle of biphenyl is approximately  $23^\circ$  [23] and the large Stokes loss is in accord with a change in topology between the ground and the excited states. Naqvi *et al.* [16] have shown from studies of the fluorescence spectra of biphenyl and PTP that the lowest singlet and triplet excited states are nearly planar. The absorption, excitation and emission spectra of the substituted biphenyls are consistent with a model in which transitions occur from a variety of non-planar configurations of the ground state to excited states  $^1A^{*'}$  which in solution undergo rapid vibrational and solvent relaxation to more planar thermally equilibrated configurations  $^1A^{*''}$ :

TABLE 2

Effect of temperature on the fluorescence quantum yields  $\phi_F$  and decay times  $\tau_F$  of methyl- and phenyl-substituted biphenyls in 3-methylpentane

Temperature (K)	3MB		2MB		44'DMB		33'DMB		MTP		PTP		22'DMB		OTP	
	$\tau_F$ (ns)	$\phi_F$	$\tau_F$ (ns)	$\phi_F$	$\tau_F$ (ns)	$\phi_F$	$\tau_F$ (ns)	$\phi_F$	$\tau_F$ (ns)	$\phi_F$	$\tau_F$ (ns)	$\phi_F$	$\tau_F$ (ns)	$\phi_F$	$\tau_F$ (ns)	$\phi_F$
210	21.2	0.26	—	0.008	19.2	0.26	18.4	0.23	31.1	0.28	—	0.85	22.2 <sup>a</sup>	—	26.0	—
240	19.2	0.22	18.6	0.003	18.4	0.25	17.4	0.23	30.1	0.27	1.6	0.83	18.7 <sup>b</sup>	0.008 <sup>b</sup>	29.2 <sup>b</sup>	—
270	14.5	0.21	—	0.006	17.4	0.23	—	0.20	27.9	0.26	—	0.82	—	—	—	—
300	13.0	0.20	14.3	0.005	16.2	0.22	13.7	0.18	25.6	0.24	1.5	0.77	10.2	0.003	21.1	0.04
330	9.1	0.15	—	0.004	14.8	0.17	10.2	0.13	22.2	0.22	1.3	0.76	12.7 <sup>b</sup>	0.003 <sup>b</sup>	—	0.02
360	6.1	0.10	9.1	0.003	13.7	0.14	6.8	0.08	20.5	0.20	1.3	0.74	6.9	0.001	19.1	0.01

<sup>a</sup>The solvent was ethanol.

<sup>b</sup>The solvent was acetonitrile.





For biphenyl derivatives substituted in the *para* and *meta* positions the shifts in the absorption spectra with changes in solvent and temperature and the high molar absorptivity coefficients are consistent with the absorption arising from the highly allowed  ${}^1A \rightarrow {}^1B_u$  transition which may mask weaker transitions to other low-lying excited states [8]. The similarity of the absorption and fluorescence excitation spectra and the lack of dependence of the fluorescence on excitation wavelength show that in solution internal conversion from higher excited states and vibrational deactivation are very efficient.

The high fluorescence quantum yields and short decay times for PTP in both polar and non-polar solvents over a range of temperatures show that radiative decay is highly efficient. The emission spectra of PTP are structured with no evidence on changing solvent or temperature for the presence of more than one emitting state. The ratio of the measured lifetime to the quantum yield ( $\tau_0 = \tau_F/\phi_F$ ) is close to the value derived for the natural radiative lifetime and confirms that for PTP emission is a highly allowed process arising from thermally equilibrated levels of a nearly planar excited state ( ${}^1A^{*''}$ ):



Non-radiative processes such as internal conversion or intersystem crossing from  ${}^1A^{*''}$  are of minor importance:



From examination of the absorption and fluorescence of biphenyl and several bridged and non-bridged analogues, Beriman concluded that the broad structureless absorption band of biphenyl at around 250 nm was composed of bands from one weak transition and two stronger transitions analogous respectively to the  ${}^1A \rightarrow {}^1L_u$ ,  ${}^1A \rightarrow {}^1L_a$  and  ${}^1A \rightarrow {}^1B_u$  transitions of benzene. The values of the ratios  $\tau_F/\phi_F$  obtained from the measured fluorescence decay times and quantum yields of the methyl-substituted biphenyls MTP and OTP exceed the theoretical radiative lifetimes obtained from the integrated absorption and emission spectra. The very large Stokes losses [1] are in accord with the changes in topology between the ground and the  ${}^1A^{*''}$  states but the shapes of the absorption and emission spectra for the methyl-substituted biphenyls and MTP provide no evidence for Franck-Condon forbidden transitions. Although emission from the  ${}^1A^{*''}$  state with considerably reduced oscillator strength cannot be ruled out, it is more likely that the large configurational changes which follow excitation result in intramolecular cross-over from  ${}^1A^{*''}$  to another state ( ${}^1A^{*'''}$ ) from which the probability of radiative decay is decreased. The process



could be facilitated by the geometric angle of twist which results in a reordering of the excited state energy levels and allows a nominally forbidden state to become energetically the lowest excited state. The fluorescence quantum yields and decay times decreased with increasing temperature and, although radiative decay from the  $^1A^{*''}$  state occurs, it is apparent that non-radiative processes such as internal conversion and intersystem crossing are of major importance:



The fluorescence emission spectra in the polar solvents acetonitrile and ethanol are virtually identical in shape with those found in methylcyclohexane and emission from an exciplex is unlikely. The main effect of a decrease in temperature on the emission spectra is an increase in structure and there is no evidence to suggest the presence of more than one emitting state. When two excited states are in close proximity, intensity borrowing from an allowed transition can result in an enhanced radiative probability of a nominally forbidden transition which is lower in energy [6, 14, 24]. For most of the compounds examined the ratios  $\tau_F/\phi_F$  remained constant and insensitive to changes in solvent and temperature, indicating that interaction between the excited states of the biphenyls is not important. A consequence of the large Stokes loss observed for the biphenyl derivatives may be that the energy gap, between the excited state responsible for emission and those states populated in absorption, is relatively large so that thermal repopulation of  $S_2$  from  $S_1$  is not significant. The experimental data show that, with the exception of PTP, emission from the phenyl- and methyl-substituted biphenyls arises exclusively from the  $^1A^{*''}$  state.

Under photostationary state conditions, consideration of processes (1), (2) and (5) - (7) leads to an expression for the fluorescence quantum yield  $\phi_F$  given by

$$\phi_F = \frac{k_6}{k_6 + k_7}$$

With the exceptions of 2MB and 22'DMB the fluorescence decays of the substituted biphenyls were exponential over all conditions of temperature and solvents. Internal conversion between states of similar energy and multiplicity can be extremely rapid ( $10^{-12}$  s) [25] and, with the assumption that vibrational relaxation and solvent reorganization of the initially formed state  $^1A^{*'}$  are fast, the fluorescence response function following a  $\delta$  pulse of light will be governed by the reciprocal sum of radiative and non-radiative decay from the  $^1A^{*''}$  state such that

$$[^1A^{*''}]_t = [^1A^{*''}]_0 \exp\{-(k_6 + k_7)t\}$$

where the measured fluorescence lifetime  $\tau_F$  is given by

$$\tau_F = (k_6 + k_7)^{-1}$$

Table 3 shows the experimental radiative rate constants  $k_f$  in 3-methylpentane derived from the ratios  $\phi_F/\tau_F$ . For the phenyl and methyl biphenyls substituted in the *para* and *meta* positions, these ratios were effectively independent of solvent and temperature.

TABLE 3

Radiative rate constants for *para*- and *meta*-substituted biphenyls in 3-methylpentane

Compound	Radiative rate constant $k_f (= \phi_F/\tau_F)$ ( $\times 10^7 \text{ s}^{-1}$ )
4MB	1.1
3MB	1.4
44'DMB	1.3
33'DMB	1.1
PTP	53.0
MTP	0.9

Fluorescence emission from biphenyl is believed to arise via a weak transition from an almost planar state analogous to the  $^1L_b$  state of benzene [8]. The magnitude and behaviour of the radiative rate constants for 4MB, 3MB, 44'DMB, 33'DMB and MTP show that a similar situation exists for these derivatives.

The fluorescence emission spectra for 2MB, 22'DMB and OTP showed the least structure and the values of the ratios  $\phi_F/\tau_F$  found for these *ortho*-substituted derivatives were indicative of highly forbidden transitions (Table 4). The most likely explanation for these effects is that the presence of an *ortho* substituent leads to non-planar equilibrium configurations of the lowest excited state and unfavourable Franck-Condon factors reduce the probability of radiative transitions. The radiative rates for 2MB and 22'DMB increased with decreasing temperature and this may be indicative of an intensity borrowing effect.

The fluorescence quantum yields for 4MB, 3MB, 44'DMB, 33'DMB and MTP approached limiting values at low temperature which were less than unity. In addition, the fluorescence decay times for these compounds approached maximum values asymptotically as the temperature was decreased. This shows that the non-radiative rate constants  $k_7$  are composed of both temperature-independent and temperature-dependent processes and have the form

$$k_7 = k_7^0 + A_7 \exp\left(-\frac{E_7}{RT}\right)$$

TABLE 4

Effect of temperature on the  $\phi_F/\tau_F$  ratios for *ortho*-substituted biphenyls

Temperature (K)	$\phi_F/\tau_F$ ( $\times 10^5$ s $^{-1}$ ) for the following compounds		
	2MB <sup>a</sup>	22'DMB <sup>b</sup>	OTP <sup>a</sup>
240	5.9	4.2	
300	5.3	3.8	31.0
330	—	2.4	
360	4.8	1.8	26.0

<sup>a</sup>The solvent was ethanol.

<sup>b</sup>The solvent was acetonitrile.

It follows that

$$\ln\left(\frac{1}{\tau_F} - \frac{1}{\tau_F^0}\right) = \ln A_7 - \frac{E_7}{RT}$$

where  $\tau_F^0 = (k_6 + k_7)^{-1}$  is the low temperature lifetime which becomes effectively constant below 210 K. Plots of  $\ln(1/\tau_F - 1/\tau_F^0)$  against reciprocal temperature for 4MB, 3MB, 44'DMB, 33'DMB and MTP over the temperature range investigated are presented in Fig. 8 and the Arrhenius parameters are presented in Table 5 for the temperature-dependent non-radiative rate constants. Estimates of these parameters obtained from the quantum yield data are also included in Table 5 using the relationship

$$\ln\left(\frac{1}{\phi_F} - \frac{1}{\phi_F^0}\right) = \ln\left(\frac{A_7}{k_6}\right) - \frac{E_7}{RT}$$

where  $\phi_F^0 = k_6/(k_6 + k_7^0)$  is the limiting fluorescence quantum yield achieved at low temperature. With the exception of 4MB, the agreement between the two sets of data was within the experimental errors.

Intersystem crossing and internal conversion can be temperature dependent when upper vibrational levels of the state responsible for fluorescence possess mechanisms for radiationless transitions which are different from those of the lowest vibrational level. Experimentally, the observed rate constant for radiationless decay from the substituted biphenyl derivatives becomes temperature independent below about 210 K. A common mechanism for this type of behaviour is thermally activated intersystem crossing and the temperature dependence of the intersystem rate constant for certain anthracene derivatives has been explained in terms of a temperature-dependent  $S_1 \rightarrow T_2$  intersystem crossing [26]. The temperature dependence of the triplet state quantum yields for the substituted biphenyls cannot be explained by thermally activated intersystem crossing. The triplet quantum yields [27] for 4MB, 3MB, 44'DMB, 33'DMB and MTP increase with decreasing temperature in a manner similar to those of the fluorescence

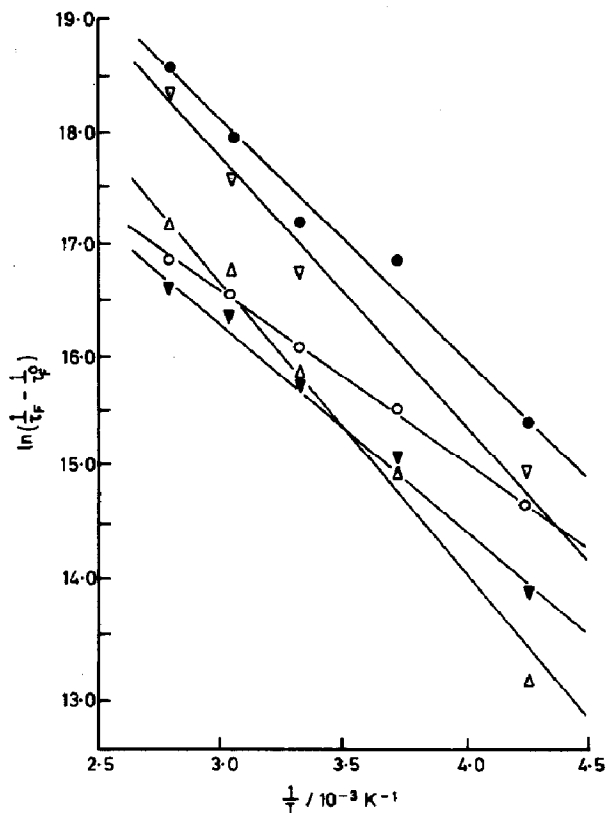


Fig. 8. Plots of  $\ln(1/\tau_F - 1/\tau_F^0)$  vs. reciprocal temperature for 4MB ( $\Delta$ ), 3MB ( $\bullet$ ), 44'DMB ( $\circ$ ), 33'DMB ( $\nabla$ ) and MTP ( $\blacktriangledown$ ).

TABLE 5

Arrhenius parameters for the temperature-dependent non-radiative rate constants

Compound	$E$ (kJ mol <sup>-1</sup> )	$A$ ( $\times 10^{10}$ s <sup>-1</sup> )
44'DMB	$12.7 \pm 1.1$ ( $15.0 \pm 2.1$ )	$0.2 \pm 0.1$ ( $0.7 \pm 0.4$ )
33'DMB	$19.0 \pm 0.7$ ( $21.4 \pm 2.0$ )	$6.0 \pm 3.0$ ( $8.0 \pm 3.0$ )
4MB	$20.6 \pm 1.5$ ( $14.0 \pm 2.0$ )	$3.0 \pm 2.0$ ( $0.05 \pm 0.3$ )
3MB	$17.5 \pm 1.3$ ( $18.0 \pm 5.0$ )	$4.0 \pm 2.0$ ( $7.0 \pm 4.0$ )
MTP	$15.0 \pm 1.7$ ( $13.0 \pm 2.0$ )	$0.3 \pm 0.2$ ( $0.2 \pm 0.1$ )

The values in parentheses were obtained from the quantum yield data.

quantum yields and lifetimes and approach maximum values asymptotically at low temperature.

However, the limiting triplet quantum yields  $\phi_T$  were consistently lower than the limiting  $1 - \phi_F^0$  values obtained at low temperature and it is apparent that whilst intersystem crossing is a process of major importance in the substituted biphenyl molecules a further temperature-independent non-radiative process is also operative.

The behaviour of the fluorescence quantum yields and the decay times of the substituted biphenyls is consistent with a model based on empirical rules deduced by Berlman [8]. Absorption results from the highly allowed  $^1A \rightarrow ^1B_b$  transition from non-planar equilibrium configurations of the ground state. For monomethyl and dimethyl substitution in the *para* and *meta* positions and for phenyl substitution in the *meta* position vibrational relaxation and solvent reorganization lead to a reordering of excited state energy levels. The enhanced importance of non-radiative processes such as intersystem crossing and internal conversion and the increase in the molecular fluorescence lifetimes compared with those of PTP support the conclusion that fluorescence arises from near-planar configurations of a low-lying excited singlet state of  $L_b$  symmetry.  $S_1 \rightarrow S_0$  internal conversion is generally not important for aromatic hydrocarbons when the energy gap between the ground and the first excited singlet state is large and, although the magnitude of the pre-exponential factors for the temperature-dependent non-radiative processes is consistent with an intersystem crossing process, the behaviour of the triplet quantum yields does not support this interpretation. For the substituted biphenyl compounds, the proximity of more than one excited state close in energy to the lowest excited state cannot be ignored and this may result in both temperature-independent and thermally activated internal conversion processes.

The low fluorescence quantum yields and long molecular fluorescence lifetimes of the *ortho*-substituted derivatives show that steric factors greatly influence the probabilities for both radiative and non-radiative decay. It is apparent that molecular geometry has a profound influence on the photo-physical properties of these molecules.

## Acknowledgment

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