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THE EFFECT OF CHANGING THE ELECTRONIC CONFIGURATIONS OF THE EXCITED STATES ON THE RATE CONSTANT OF PHOTOCYCLIZATION OF ARYL ETHYLENES

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Summary

The addition of the phenyl group in the *para* position of diphenyl in the 1-(*o*-diphenyl)-1-phenylethylene (DPE) molecule was carried out in order to induce a modification of the configuration of the lowest excited states. Spectral data and theoretical calculations showed that the S_1 state of the resulting 1-(2'-*p*-terphenyl)-1-phenylethylene corresponds to an allowed transition $^1L_a \leftarrow {}^1A_1$. The lowest excited state of DPE has a mainly ^1L_a character (84%) with a weak ^1B_b contribution (5%). The moment of the corresponding transition is weak. The modification of the configuration of the lowest excited states changes both the electronic distribution and the flexibility of the molecule. The differences in the photochemical reactivity are best explained by geometric factors.

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1. Introduction

The spectroscopic properties of biphenyl and *p*-terphenyl have been extensively studied and are now quite well known. Many experimental [1 - 3] and theoretical [4] investigations have shown that the broad absorption band of biphenyl in the UV is composed of three transitions. Berlman [1] and Platt [2] have shown that the first transition $^1L_b \leftarrow {}^1A_1$ (using Platt's notation) is weak and polarized along the short axis, while the transitions $^1L_a \leftarrow {}^1A_1$ and $^1B_b \leftarrow {}^1A_1$ are strong and polarized along the long axis. Since the first transition is forbidden, the fluorescence quantum yield Φ_f of biphenyl in fluid solution is low and the fluorescence decay time τ_f is relatively long. Substitution by a phenyl group in the *para* position produces level crossing. Indeed, *p*-terphenyl has a smaller value of τ_f and a larger value of Φ_f in good agreement with the fact that the emission originates from a different spectroscopic state than in biphenyl and is assigned [4] to the allowed transition $^1L_a \leftarrow {}^1A_1$.

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Such spectroscopic considerations form the bases of rules used to explain the lasing ability of organic molecules [5] and in particular to account for the highly efficient laser action of *p*-terphenyl in contrast with biphenyl which does not lase. Although the effect of substitution on the electronic transition has been investigated from both the theoretical and the experimental viewpoints, little attention has been directed to the effects of the modification of the electronic transitions on the reactivity of the lowest excited states of the aromatic hydrocarbons. However, while the work described here was in progress, Lewis and Holman [6] reported the first example of divergent reaction pathways for two almost isoenergetic singlet states. The irradiation of 1-naphthonitrile in the presence of 1,2-dimethylcyclopentene results in the formation of [2 + 2] cycloadducts with either the nitrile group or the aromatic ring or both. They tentatively assigned the regioselectivity observed to the ^1L_a and ^1L_b spectroscopic states of 1-naphthonitrile without being able to reject the participation of a hidden state with bent nitrile geometry.

It is therefore of some interest to look for the effect of a change in configuration of a reactive singlet or triplet state related to a change in electronic distribution without a spin effect. We have looked for such an effect in the case of the cyclization of *o*-vinyldiphenyls.

Recently we proposed a mechanism for the photocyclization of 1-(*o*-diphenyl)-1-phenylethylene (DPE) in which the divergent stereochemistry from singlet and triplet states favours a multiplicity-dependent mechanism [7, 8]. We now require to determine whether a modification of the configuration of these states, introduced by a substitution in the *para* position of DPE, influences their reactivity towards cyclization.

We present here an investigation of the spectral and photochemical properties of 1-(2′-*p*-terphenyl)-1-phenylethylene (TPE) and compare them with those previously reported for DPE (an α-styryl group could strongly perturb the configuration of the aromatic, but it was necessary to have substantial triplet activity [7, 8]). The work is in two parts: firstly a spectroscopic and theoretical study to check whether the cross-over of the singlet spectroscopic states ^1L_a and ^1L_b which is observed for biphenyl and *p*-terphenyl also occurs for DPE and TPE, and secondly a photochemical study to compare the reaction quantum yields and the rates of photocyclization of both compounds under UV irradiation.

2. Experimental details

2.1. *Preparation of 1-(2′-p-terphenyl)-1-phenylethylene and of its photoproducts*

TPE was prepared from 2,5-diphenylbenzophenone [9] by the addition of methylmagnesium iodide followed by dehydration of the alcohol with phosphoric anhydride in refluxing carbon tetrachloride. After chromatography on a silica gel column an 83% yield of TPE (melting point, 108 °C) was obtained.

2,10-diphenyl-9,10-dihydrophenanthrene (I) was prepared by dissolving 166 mg of TPE in 100 cm^3 of cyclohexane. The solution was degassed and irradiated in a Rayonet reactor for 16 h at 300 nm. Thin layer chromatography and gas–liquid chromatography (GLC) showed only one product which was identified as I by mass spectroscopy and nuclear magnetic resonance. After recrystallization in methanol, 147 mg (89% yield) of I (melting point, 150 °C) was obtained.

2,10-diphenylphenanthrene (II) was prepared by dissolving 82 mg of I and 100 mg of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone in 20 ml of benzene and refluxing the solution for 1 h. After chromatography on silica gel, 72 mg of II (melting point, 142 °C) was obtained.

The preparation of DPE and its photoproducts are reported elsewhere [7].

2.2. *Absorption and fluorescence measurements*

The absorption spectra were recorded on a Beckman Acta MVI instrument, and the fluorescence and phosphorescence spectra were recorded on a Perkin–Elmer MPF 44 spectrofluorometer with accessories to correct the spectra. As the solutions are unstable after prolonged exposure to the light source of the spectrofluorometer, this effect was minimized by using very narrow slits and a high gain.

Fluorescence decay curves were determined by the single-photon counting technique [10] using a commercial instrument obtained from Applied Photophysics.

2.3. *Determination of the reaction quantum yield*

Direct and sensitized irradiations were carried out using a 2000 W Osram high pressure xenon lamp with a Jobin–Yvon irradiation monochromator to select the proper wavelength. The reaction quantum yields Φ_p were determined by measuring the initial slope $d[P]/dt$ of the curve of the concentration of the photoproduct P as a function of time and the intensity of the absorbed light. Ferrioxalate actinometry [11] as modified by Bowman and Demas [12] was used to measure the light intensity.

Since the optical absorption of P is partially overlapped by that of the parent compound A, we determined the concentration of P by measuring the optical density OD at λ_1 corrected for the absorption by A:

$$OD^{\lambda_1} = \epsilon_p^{\lambda_1}[P] + \epsilon_a^{\lambda_1}[A]$$

A similar relation was obtained for λ_2:

$$OD^{\lambda_2} = \epsilon_p^{\lambda_2}[P] + \epsilon_a^{\lambda_2}[A]$$

Therefore the concentrations of P and A are given by

$$[P] = \frac{OD^{\lambda_1}\epsilon_a^{\lambda_2} - OD^{\lambda_2}\epsilon_a^{\lambda_1}}{\epsilon_p^{\lambda_1}\epsilon_a^{\lambda_2} - \epsilon_p^{\lambda_2}\epsilon_a^{\lambda_1}}$$

$$[A] = \frac{OD^{\lambda_2}\epsilon_p^{\lambda_1} - OD^{\lambda_1}\epsilon_p^{\lambda_2}}{\epsilon_p^{\lambda_1}\epsilon_a^{\lambda_2} - \epsilon_p^{\lambda_2}\epsilon_a^{\lambda_1}} \qquad (1)$$

3. Results

3.1. *Spectroscopy of 1-(2′-p-terphenyl)-1-phenylethylene and 1-(o-diphenyl)-1-phenylethylene*

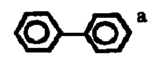
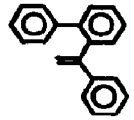
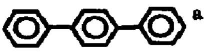
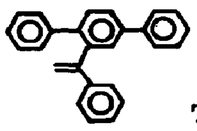
The absorption spectra of TPE and DPE in cyclohexane solutions are broad and structureless whereas the fluorescence spectra are structured. The wavelengths of the absorption maxima of TPE and DPE are slightly blue shifted compared with those of the corresponding chromophores biphenyl and *p*-terphenyl [13], whereas the emission maxima are red shifted; consequently the Stokes shift is increased (see Table 1). The fluorescence quantum yields Φ_f of TPE and DPE (0.165 and 0.09 respectively) were determined by comparing their fluorescence intensities with the corresponding chromophore for which Φ_f is known.

The fluorescence lifetimes τ_f of TPE and DPE in degassed solutions were found by the single-photon counting technique to be 0.85 ns and 4 ns respectively.

The TPE and DPE absorption spectra in stretched polyethylene film obtained using polarized light gave poor results because of the overlap of the main transitions responsible for the absorption.

TABLE 1

Spectral properties of 1-(*o*-diphenyl)-1-phenylethylene and 1-(2′-*p*-terphenyl)-1-phenylethylene

Compound	*Absorption*		*Emission*			*Stokes shift* (cm^{-1})
	λ_{max} (nm)	ϵ_{max} (10^{-4} M^{-1} cm^{-1})	λ_{max} (nm)	Φ_f	τ_f (ns)	
 [a]	247	1.5	305	0.18	16	3300
 DPE	245 225	2.8 3.3	310 322	0.09	4	3500
 [a]	276	3.3	325 328	0.93	0.95	2960
 TPE	262 248	3.1 2.9	334 348	0.165	0.85	3170

[a] From ref. 13.

3.2. *Theoretical calculations*

In order to obtain some insight into the nature of the first excited singlet states of DPE and TPE, we determined the energies, oscillator strengths and transition moments related to the first electronic transitions by calculating the Hartree–Fock interactions of 25 mono-excitations (linear combination of atomic orbitals, self-consistent field, configuration interaction). The Pariser–Parr–Pople procedure [14] for the treatment of π electrons was used. The bielectronic and bicentric integrals were evaluated by the Nishimoto–Mataga relation [15]. Idealized molecular geometries of DPE and TPE were chosen (all the C—C bonds were assumed to have a length of 1.4 Å with bond angles of 120° and the dihedral angle between the planes of the phenyl ring was assumed to be zero). The program was tested using biphenyl and *p*-terphenyl for which similar calculations have previously been reported [4] and the theoretical results given in Table 2 were found to be in good agreement with the experimental data: the values of the oscillator strength and of the transition moment show that the first electronic transition for the biphenyl is forbidden (^1L_b (or α) band, $f = 0$) while that of *p*-terphenyl is strongly allowed (^1L_a (or p) band, $f = 1.5$).

Table 2 shows that the substitution of a hydrogen atom by a phenylethylene group at the *ortho* position of one of the phenyl groups lowers the energies of S_1, S_2 and S_3. The configuration of the lowest excited state of DPE has a mainly ^1L_a character (84%) and a weak ^1B_b character (5%) but the corresponding transition is almost forbidden ($f = 0.054$). The lowest excited state of TPE has an almost pure ^1L_a character (97%) and the transition is allowed ($f = 0.34$).

Examination of the weight of the configurations appearing in the wavefunctions of the excited states of DPE and TPE shows that the first excited states correspond to a HOMO–LUMO transition. The atomic orbital coefficients for the HOMOs (labelled 1) and the LUMOs (labelled —1) are shown in Fig. 1 (see footnote to Table 2 for an explanation of the numbering of the MOs). It is clear that the energy absorbed to reach the first excited singlet state is localized on the ethylene fragment because of the large

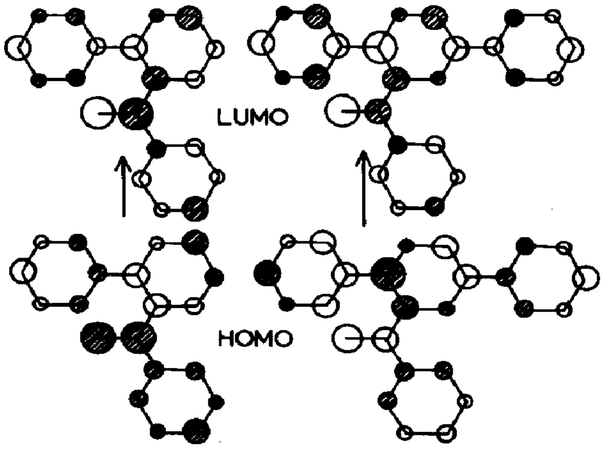


Fig. 1. Atomic orbital coefficients of DPE and TPE.

TABLE 2

Calculated properties of biphenyl, 1-(*o*-diphenyl)-1-phenylethylene, *p*-terphenyl and 1-(2′-*p*-terphenyl)-1-phenylethylene

	Biphenyl			*DPE*			*p-terphenyl*			*TPE*		
	S_1	S_2	S_3	S_1	S_2	S_3	S_1	S_2	S_3	S_1	S_2	S_3
Energy band (eV)	4.56 ^1L_b	4.62 $(1 \rightarrow -3) +$ $(3 \rightarrow -1)$	4.66 ^1L_a	3.84 ^1L_a	4.15 ^1L_b	4.60 $(1 \rightarrow -4) +$ $(4 \rightarrow -1)$	4.10 ^1L_a	4.60 $(1 \rightarrow -3) +$ $(3 \rightarrow -1)$	4.70 $(1 \rightarrow 4) +$ $(4 \rightarrow -1)$	3.74 ^1L_a	4.00 ^1L_b	4.49 ^1B_b
Oscillator strength f	0	0	0.89	0.054	0	0	1.50	0	0	0.34	0	1.57
Transition moment μ	0	0	1.47	0.18	0	0	2.04	0	0	1.0		2.0
$\mu(x)$	0	0	1.47	0.18	0	0	2.04	0	0	−0.95		1.98
$\mu(y)$	0	0	0	−0.38	0	0	0	0	0	0.38	0	0.33

^1L_b is related to the two dominant configurations corresponding to the electronic jump between the occupied molecular orbitals (MOs) 1, 2 and the virtual MOs −1, −2 according to $(1 \rightarrow -2) - (2 \rightarrow -1)$. ^1L_a is related to the electronic jump from the occupied MO 1 to the virtual MO −1. ^1B_b corresponds to the positive combination $(1 \rightarrow -2) + (2 \rightarrow -1)$. The notation $(1 \rightarrow -3) + (3 \rightarrow -1)$ for S_2 has the same meaning as ^1L_b except that MOs 3 and −3 replace MOs 2 and −2. Similar explanations hold for $(1 \rightarrow -4) + (4 \rightarrow -1)$. The numbering of the MOs is as follows: the occupied MOs are positively numbered beginning with the highest occupied MO (HOMO) labelled 1. The virtual MOs are negatively numbered beginning with the lowest unoccupied MO (LUMO) labelled −1.

values of the coefficients which are 0.31 (HOMO) and 0.55 (LUMO) for DPE and 0.23 (HOMO) and 0.44 (LUMO) for TPE.

Theoretical calculations performed for the triplet states lead to the same conclusions for the first triplet states of DPE and TPE.

3.3. Photochemical irradiation of 1-(2'-p-terphenyl)-1-phenylethylene and 1-(o-diphenyl)-1-phenylethylene

3.3.1. Direct irradiation

When a degassed cyclohexane solution of TPE is irradiated at 260 nm a new absorption band with a maximum at 292 nm is observed and the absorption band of the parent compound disappears. The plot of the optical density as a function of time (Fig. 2) reveals the existence of an isosbestic point at 278 nm, showing that only one photoproduct is formed. This product was identified by GLC as 2,10-diphenyl-9,10-dihydrophenanthrene (P_1). The concentration of P_1, calculated from eqn. (1) using the molecular extinction coefficients

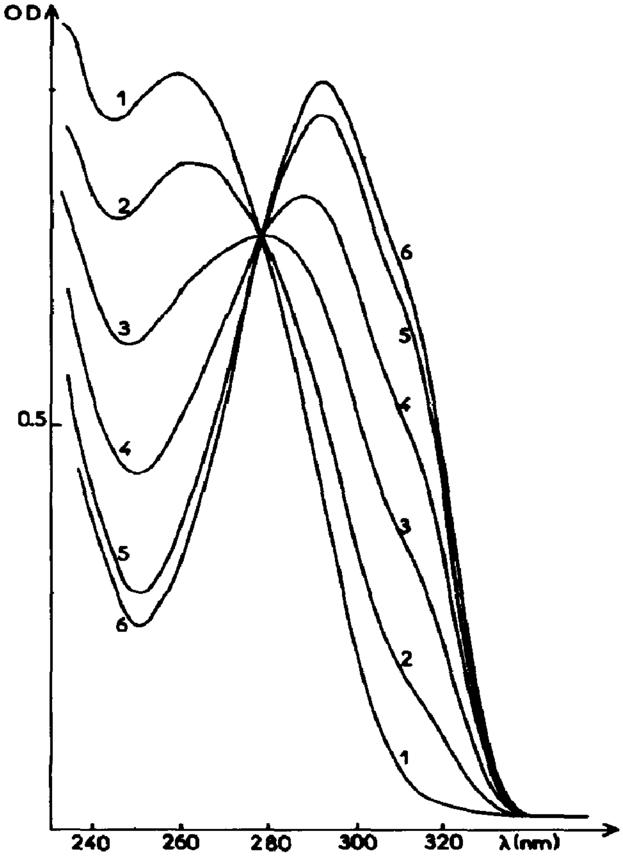


Fig. 2. Variation in the absorption spectra of TPE and its photoproduct as a function of the irradiation time: curve 1, 0 s; curve 2, 15 s; curve 3, 60 s; curve 4, 120 s; curve 5, 270 s; curve 6, 390 s.

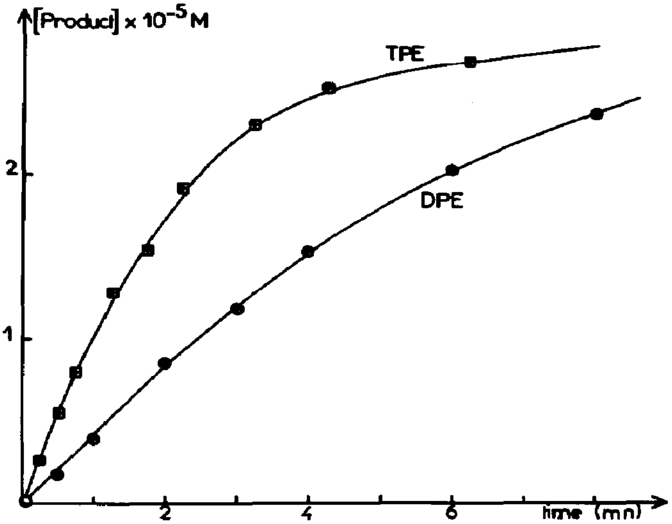


Fig. 3. Concentration of the cyclic products obtained from TPE and DPE as a function of the irradiation time.

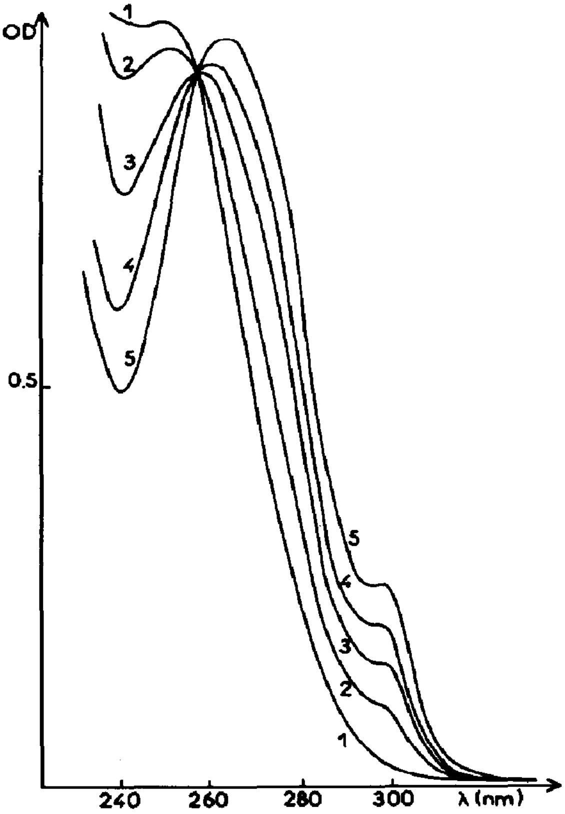


Fig. 4. Variation in the absorption spectra of DPE and its photoproduct as a function of the irradiation time: curve 1, 0 s; curve 2, 30 s; curve 3, 120 s; curve 4, 240 s; curve 5, 480 s.

$$OD_{260\,\mathrm{nm}} = 30.800[A_1] + 8.200[P_1]$$

$$OD_{310\,\mathrm{nm}} = 1.520[A_1] + 23.200[P_1]$$

is plotted as a function of time in Fig. 3. The light intensity was 2.9×10^{-7} einstein l^{-1} s^{-1}, and hence the reaction quantum yield was calculated to be 0.6 in degassed, aerated or oxygenated solutions.

A reaction quantum yield of 0.24 was found for DPE using the relations

$$OD_{240\,\mathrm{nm}} = 30.000[A_2] + 11.400[P_2]$$

$$OD_{298\,\mathrm{nm}} = 440[A_2] + 7.000[P_2]$$

This is in good agreement with a value determined previously by GLC. The absorption spectra of DPE are given in Fig. 4. The concentration of its photoproduct P_2 is plotted as a function of the irradiation time in Fig. 3.

3.3.2. Photosensitized irradiation

Photosensitized irradiation was carried out in order to determine the reaction quantum yield from the triplet state. Xanthone was chosen as the sensitizer since this compound has a strong absorption band at 340 nm ($\epsilon_{338\,\mathrm{nm}}$ = 10.200 M^{-1} cm^{-1}) [16] where TPE, DPE and their photochemical products do not absorb. A xanthone transmission window in the spectral region 290 - 320 nm allows the concentration of the photoproducts to be determined spectrophotometrically. The xanthone concentration (2×10^{-4} M) was kept low enough to ensure that the self-quenching effect of the triplet state [17] was negligible; at this concentration 99% of the incident light was absorbed at 340 nm. To avoid the formation of ketyl radicals by hydrogen abstraction, acetonitrile was used as the solvent because the xanthone triplet state is deactivated very slowly in this medium ($\tau_T \approx 8.3$ μs) [17]. The triplet state energies of DPE and TPE, as measured by phosphorescence emission at 77 K, were 63 kcal mol^{-1} and 61 kcal mol^{-1} respectively. However, as was observed in our previous study [7, 8] of DPE, the Franck–Condon triplet state probably has a higher energy in view of the different geometries of the ground and excited states. The reaction quantum yield $(\Phi_p)_{sens}$ was measured as a function of the concentration of the acceptor in order to determine the quantum yield $\Phi_p{}^T$ of reaction for the triplet state. Under the stationary state approximation, a classical linear correlation is expected between $(\Phi_p)_{sens}$ and $\Phi_p{}^T$:

$$\frac{1}{(\Phi_p)_{sens}} = \frac{1}{\Phi_p{}^T} + \frac{1}{\Phi_T k_Q (\tau_T)_{sens}}\;\frac{1}{[\mathrm{DPE}]\ \mathrm{or}\ [\mathrm{TPE}]}$$

in which $(\tau_T)_{sens}$ is the triplet lifetime of xanthone in the absence of the starting compound and k_Q is the rate constant of the energy transfer. The rate of formation of the photoproducts of TPE and DPE were measured at 310 nm and 300 nm respectively. The decrease in the optical absorption of the starting compounds, which is very low at these wavelengths, was neglected.

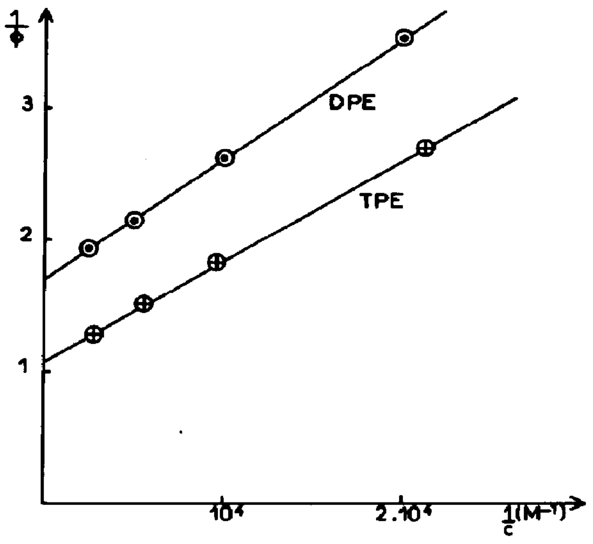


Fig. 5. Reciprocal reaction quantum yield *vs.* the reciprocal concentration of TPE and DPE.

The data obtained are shown in Fig. 5 where $1/(\Phi_p)_{sens}$ is plotted as a function of 1/[TPE] or 1/[DPE]. The following values of $\Phi_p{}^T$ and k_Q were deduced from the intercepts and the slopes of the lines obtained: for TPE, $(\Phi_p{}^T)_{TPE} = 0.89$ and $k_Q = 1.9 \times 10^9$ M^{-1} s^{-1}; for DPE, $(\Phi_p{}^T)_{DPE} = 0.59$ and $k_Q = 2.1 \times 10^9$ M^{-1} s^{-1}.

4. Interpretation

4.1. Spectroscopic and theoretical data

The lack of mirror image symmetry between the absorption and emission spectra and the Stokes shift for biphenyl and *p*-terphenyl has been ascribed to differences between the geometries of the non-planar ground state and the quasi-planar excited singlet state [13]. In solution the angle θ of twist around the interannular C—C bond has been estimated to be about 20° - 23° in the ground state [18, 19]. In the case of DPE and TPE, the increase in the Stokes shift indicates a larger difference between the geometries of the ground state and the excited state. Substitution in the *ortho* position of diphenyl is known to increase the dihedral angle θ in the ground state. Theoretical calculations show that the nature of the first excited states of DPE and TPE is not very different from those of biphenyl and *p*-terphenyl: for TPE the first transition is allowed and has a p character, while for DPE it is a nearly forbidden transition with a p and an α character. The large values of the atomic orbital coefficients of the carbons of the double bond reveal the importance of the acyclic double bond in the photochemical process.

Electronic excitation is also expected to play an important part in the rotation of the double bond in the first singlet excited state as well as in the first triplet state and therefore favours cyclization.

4.2. *Efficiency of photocyclization from the singlet state*

The following rate constants for cyclization were deduced from the values of τ_f and $\Phi_p^{S_1}$ measured in direct irradiation experiments:

$$k_p^{S_1}(\text{TPE}) = 7.05 \times 10^8\ \text{s}^{-1} \qquad k_p^{S_1}(\text{DPE}) = 5.2 \times 10^7\ \text{s}^{-1}$$

The irreversibility of the formation of the cyclic intermediate (Fig. 6) as discussed in ref. 8 was taken into account in these calculations. The results show that the rate of cyclization from the singlet state is 14 times more efficient for TPE than for DPE, whereas the quantum yield is only three times larger. The addition of a phenyl group in the *para* position of the diphenyl group of DPE could modify several properties of the reactive excited singlet state, in particular the energy, the electronic distribution and the geometry.

The energy (Table 3) and the calculated electronic distributions (Fig. 1) for both compounds are quite similar and cannot explain the larger

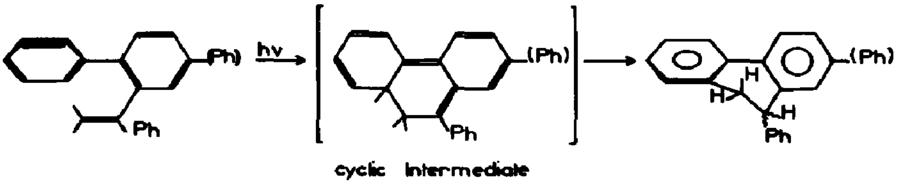
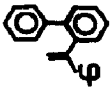
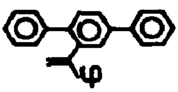
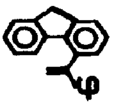


Fig. 6. Photocyclization of *o*-vinyldiphenyl.

TABLE 3

Experimental results obtained under direct and sensitized irradiations

Compound		*Direct irradiation*			*Sensitized irradiation*			
		$\Phi_p^{S_1}$	$k_p^{S_1}$ (s^{-1})	E_{S_1} (kcal mol^{-1})	Φ_p^{T}	τ_T (μs)	k_p^{T} (s^{-1})	E_T (kcal mol^{-1})
	DPE	0.24	5×10^7	92	0.59	1.75	3.3×10^5	63
	TPE	0.61	7.05×10^8	86	0.89	0.7	12.7×10^5	61
	FPE	0.33	1.3×10^8		$< 5 \times 10^{-3}$			

rate of cyclization of TPE. However, the relative geometries of TPE and DPE at the level of the hexatrienic system which is the centre of the reaction could account for the difference in the observed reactivities. Indeed, it has recently been shown theoretically [4] that the increase in the potential energy as a function of the angle of twist is much larger for the ^1L_a spectroscopic state of *p*-terphenyl than for the ^1L_b state of biphenyl (Fig. 7). If it is assumed that TPE and DPE show similar behaviour to their respective parent chromophores, the S_1 state of TPE will be more planar than that of DPE because the potential energy will increase more rapidly when the angle of twist is increased. Thus the change in the nature of the excited state from ^1L_b in DPE to ^1L_a in TPE could account for an increased rate of cyclization mainly because the molecules of the two compounds do not behave in the same way in their excited planar configuration (Fig. 6). The molecules in TPE are held more rigidly in the planar position than they are in DPE. This rigidity must favour the formation of the new bond (Fig. 6) that appears in the cyclic intermediate.

Interesting behaviour is exhibited by 1-(4-fluorenyl)-1-phenylethylene (FPE), a molecule similar to DPE but with the dihedral angle maintained close to zero by the methylene group. The value of $k_p^{S_1}$ previously reported for FPE [7] lies between those of DPE and TPE (Table 3). This does not disagree with the values found for DPE and TPE. The planar molecule held rigidly in that geometry by the methylene group indeed provides the best overlap for cyclization. Thus the rate for FPE should be faster than those for DPE and TPE, but since the cyclic intermediate state is also held planar it must have a higher energy than the corresponding states for DPE and FPE. The rate constant for FPE reflects the role played by both effects. A measure of the rigidity of the intermediate is given by the rate of the 1,5 hydrogen shift which leads to the stable product (Fig. 6). It was observed experimentally that the rate of the 1,5 hydrogen shift (which was measured from the reciprocal of the lifetime of the cyclic intermediate in degassed solutions) is rather similar for DPE and TPE (1.6×10^2 s^{-1}) but much smaller for FPE (0.5 s^{-1}).

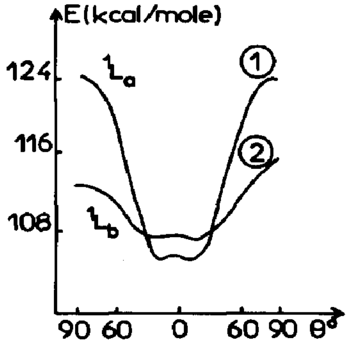


Fig. 7. Potential energy curves for the twisting of the interannular bonds of *p*-terphenyl (curve 1) and biphenyl (curve 2) (from ref. 4).

4.3. *Efficiency of photocyclization from the triplet state*

The reaction quantum yields Φ_p^T from the triplet state were calculated from the results of sensitization experiments to be 0.89 and 0.59 for TPE and DPE respectively. Laser flash photolysis revealed a transient absorption near 400 nm for TPE with lifetimes τ_T of 120 ns and 750 ns in aerated and degassed solutions respectively. This transient is assigned to the triplet state of TPE which is quenched by oxygen with a rate constant of 3×10^9 M^{-1} s^{-1}. From Φ_p^T and τ_T we deduce k_p^T(TPE) = 12.7×10^5 s^{-1}. The triplet lifetime for DPE has previously been reported to be 1.75 μs in degassed solution, giving a reaction rate constant k_p^T of 3.3×10^5 s^{-1} for DPE. (These reaction rate constants were calculated by assuming that the triplet states observed by flash spectroscopy are the cyclizing species. This point is discussed further in refs. 7 and 8.) No cyclization from the triplet state was observed for FPE. The data are summarized in Table 3 and demonstrate extremely high efficiency of cyclization of TPE.

These results can be explained by assuming cyclization from the triplet state after rotation of the double bond. This was substantiated by the absence of cyclization of triplet FPE [7] and by the stereochemistry of 2-methylated DPE isomers [20]. According to this mechanism the calculated rate constant k_p^T does not correspond to the true cyclization step; the rate of cyclization of the "twisted" triplets should be much larger than the value found because the lifetimes of these species must be much shorter than those of the Franck–Condon triplets observed by laser flash photolysis. Nevertheless the observed trend in the efficiency of triplet cyclization is TPE > DPE ≫ FPE. As already noted the non-reactivity of the TPE triplets would result from the orthogonal interaction between the atoms to be linked. The increased triplet reactivity of TPE relative to DPE could be due to a reduction of the distance between these atoms in view of the possible more planar conformation of TPE.

5. Conclusion

The addition of a phenyl group in the *para* position of diphenyl in the DPE molecule induces a modification of the configuration of the lowest excited states. Spectral and theoretical calculations show that the lowest singlet transition of DPE has an allowed and forbidden character with a weak transition moment. The S_1 state of TPE corresponds to an allowed transition in *p*-terphenyl which probably has a ^1L_a character. A study of the quantitative reactivity of TPE compared with that of DPE revealed that the shift of the configuration of the excited singlet state to the ^1L_a character increases the rate of singlet cyclization and the efficiency of the reaction, although the $S_1 \rightarrow S_0$ transition is more allowed. The efficiency of the reaction from the triplet state is also increased despite a possible larger planarity which in the case of FPE inhibits the triplet reactivity. The results have been tentatively explained by the differences in the planarity and flexibility of the three reactants. However, these geometric parameters are related to the configuration of the excited state: *para* substitution of DPE increases the ^1L_a character of the ^1S state of TPE and also increases the potential energy as a function of the angle of twist.

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