

SINGLET MECHANISM FOR *trans* → *cis* PHOTOISOMERIZATION OF α,ω -DIPHENYLPOLYENES IN SOLUTION: LASER FLASH STUDY OF THE TRIPLET STATES OF DIPHENYLBUTADIENE, DIPHENYLHEXATRIENE AND DIPHENYLOCTATETRAENE

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Summary

The lowest triplet states of all-*trans* isomers of 1,4-diphenyl-1,3-butadiene (DPB), 1,6-diphenyl-1,3,5-hexatriene (DPH) and 1,8-diphenyl-1,3,5,7-octatetraene (DPO) were studied by laser flash photolysis. In benzene solutions at room temperature the DPB triplet was formed only by sensitized excitation whereas the DPH and DPO triplets were also formed by direct excitation. The maxima of the triplet-triplet absorption spectra (380 - 440 nm), the triplet lifetimes (10 - 100 μ s) and the rate constants for triplet quenching by oxygen ($(3 - 6) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and azulene were determined. The effects of temperature and viscosity on the quantum yields of fluorescence and of triplet formation, as well as on the initial rates of *trans* → *cis* photoisomerization, were studied in several solvents. On the basis of these results, a singlet mechanism is suggested for the *trans* → *cis* photoisomerization of the three all-*trans* α,ω -diphenylpolyene derivatives.

1. Introduction

Phenylpolyenes have received considerable attention because of their photochemical significance as simple model compounds for the visual chromophore [1]. The excited singlet states of linear all-*trans* phenylpolyene derivatives have been the object of absorption and emission spectroscopy studies [2 - 12] and theoretical calculations [11 - 14]. However, little is known about the kinetic and spectroscopic properties of the triplet states of the phenylpolyenes. Heinrich *et al.* [15] have studied the triplet lifetimes of α,ω -diphenylpolyenes with different triplet energies in ether-isopentane-ethanol (EPA) matrices at -196 °C. Triplet-triplet (T-T) absorption spectra and triplet energies of 1,6-diphenyl-1,3,5-hexatriene (DPH) and 1,8-diphenyl-1,3,5,7-octatetraene (DPO) in solution have been determined by Bensasson *et al.* [16]. Although photochemical processes such as *trans* → *cis* photoisomerization and decomposition have been reported

for DPO, DPH and 1,4-diphenyl-1,3-butadiene (DPB) [17 - 19], the primary photophysical processes competing with fluorescence are still unknown.

In the present work the formation and decay of the lowest triplet states of DPB, DPH and DPO were studied. T-T absorption spectra and triplet yields in fluid and viscous media and the effect of triplet quenchers were measured. A scheme based on spectroscopic and kinetic triplet observations, *trans* → *cis* photoisomerization studies and the known emission properties is proposed to describe the role of excited singlet and triplet states involved in the deactivation of excited all-*trans* α, ω -diphenylpolyenes.

2. Experimental details

The laser flash photolysis arrangement and the methods used were essentially the same as those described in recent work [20 - 23]. Laser pulses (pulse width, 5 - 20 ns) at 265, 353 and 308 nm were produced from the fourth and third harmonics of a neodymium laser (J.K. Lasers) [20 - 23] and an excimer laser (Lambda Physik) [23] respectively. A dye laser constructed in the laboratory (dye, Coumarin 2 (Lambda Physik) in methanol; bandwidth, 10 nm) pumped by the excimer laser (308 nm) was used for excitation at 450 nm. The conventional flash photolysis apparatus (cell length, 7 cm) has been described elsewhere [24]. The irradiation and emission measurements were carried out as described earlier [20 - 23]. The values for ϕ_f were measured from corrected fluorescence spectra using the same optical density at λ_{exc} (0.1 or less) and 9,10-diphenylanthracene (EGA) as a standard ($\phi_f = 1.0$ in ethanol at -196°C [25]) (see ref. 21). Unless indicated otherwise, the samples were purged with argon.

All-*trans* DPB (Merck) was purified by recrystallization, all-*trans* DPH (Aldrich) and all-*trans* DPO (EGA or Fluka) were used as received and *trans*-stilbene was the same as used in previous work [21, 22]. Benzophenone (EGA), biacetyl (EGA) and ferrocene (FE) (Merck) were purified by zone refining, fractional distillation and recrystallization respectively. Acetone (Merck) and azulene (Az) (Aldrich) were used as received. The solvents (Merck) were of the highest purity commercially available; for fluorescence measurements they were further purified by fractional distillation (methylcyclohexane (MCH), methylcyclopentane (MCP), 2-methyl-tetrahydrofuran (MTHF) and ethanol).

3. Results

3.1. Triplet absorption spectrum

The transient absorption spectra of all-*trans* isomers of DPB, DPH and DPO in benzene solutions at room temperature are shown in Fig. 1. Identical transient absorption spectra were recorded for DPH using the following methods: (i) photolysis by excitation with a flash lamp; (ii) direct excitation

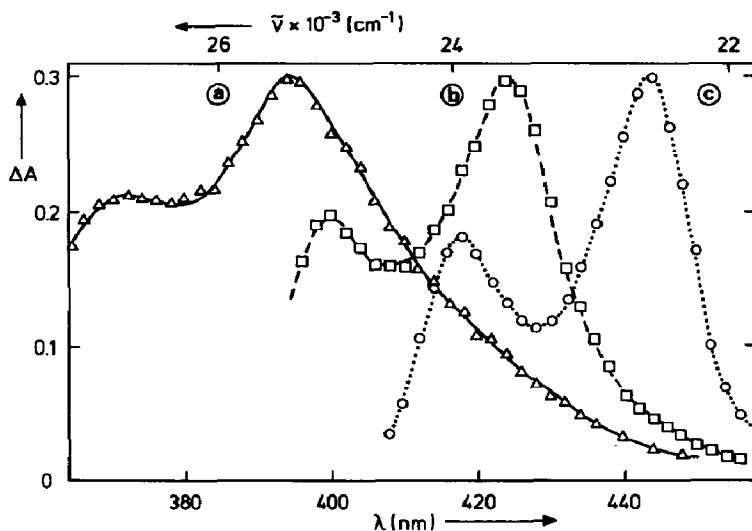


Fig. 1. T-T absorption spectra of diphenylpolyenes in deoxygenated benzene solutions at room temperature under biacetyl-sensitized excitation ($\lambda_{\text{exc}} = 450 \text{ nm}$): (a) DPB (Δ); (b) DPH (\square); (c) DPO (\circ).

with laser pulses at 265, 308 and 353 nm; (iii) excitation with laser pulses at 308, 353 and 450 nm in the presence of a triplet donor (sensitized excitation). Similar results were found for DPO. Since the transient absorption spectra obtained under triplet-sensitized and direct excitation conditions are identical, the transients are assigned to triplet states. While no transient absorbing between 360 and 500 nm was found for DPB in benzene and acetonitrile solutions under conditions (i) and (ii), the sensitized excitation (condition (iii)) of DPB using acetone ($\lambda_{\text{exc}} = 308 \text{ nm}$), benzophenone ($\lambda_{\text{exc}} = 353 \text{ nm}$) and biacetyl ($\lambda_{\text{exc}} = 450 \text{ nm}$) yielded triplets (Table 1).

Triplet absorption maxima λ_{max} at about 390, 425 and 443 nm were observed for benzene solutions of DPB, DPH and DPO respectively. Very similar λ_{max} values were found for DPH and DPO in acetonitrile and MTHF solutions at room temperature. On going to low temperatures the triplet absorption spectra of DPH and DPO in MTHF and glycerol triacetate (GT) were similar in shape and the maxima were slightly red shifted (10 nm or less). Triplets were observed at low temperatures and in viscous solutions for the direct excitation of DPB (Table 1).

In addition to absorption from triplets, short-lived transients were observed in cyclohexane, benzene and GT solutions at wavelengths above 600 nm (e.g. λ_{max} values of 670 nm and 700 nm and half-lives $\tau_{1/2}$ of 5 ns or less and about 10 ns for DPB and DPH respectively in deoxygenated cyclohexane solutions ($\lambda_{\text{exc}} = 353 \text{ nm}$) at 25 °C). Because of the short lifetime even in rigid media (e.g. $\tau_{1/2} \leq 10 \text{ ns}$ for DPB in GT at -75 °C), the transient absorption is tentatively assigned to an $S_1 \rightarrow S_n$ transition. Picosecond time-resolved $S_1 \rightarrow S_n$ absorption spectra ($\lambda_{\text{max}} = 585 \text{ nm}$) have been reported for *trans*-stilbene [26]. No short-lived transient (at $\lambda >$

TABLE 1

Triplet-triplet maxima and triplet lifetimes in the absence of oxygen

Compound	Sensitizer	Solvent	λ_{exc} (nm)	λ_{max}^a (nm)	$\tau_0^{a,b}$ (μs)
DPB	None	Benzene	— ^c	— ^d	— ^d
	None	MTHF	265	(≈ 395)	
	None	GT	353	≈ 390 (396)	4 (1500)
	Acetone	Benzene	308	370, ≈ 394	{3}
	Benzophenone	Benzene	353	392	10
	Benzophenone	Acetonitrile	353	384	{3}
	Biacetyl	Benzene	450	372, 394	{2}
DPH	None	Benzene	— ^c	400, 425	100
	None	Benzene	308	400, 425	{2}
	None	Benzene	353	425	{12}
	None	Acetonitrile	— ^c	390, 413	70
	None	Acetonitrile	265	412	{2}
	None	MTHF	353	396, 420 (428)	{12} (400)
	None	GT	353	418 (422)	40 (300)
	Benzophenone	Benzene	353	400, 425	{15}
	Biacetyl	Benzene	450	400, 424	{5}
DPO	None	Benzene	— ^c	419, 444	100
	None	Benzene	353	418, 443	{8}
	None	Acetonitrile	— ^c	408, 432	70
	None	Acetonitrile	353	432	{3}
	None	MTHF	353	435 (440)	
	None	GT	353	440 (444)	60 (100)
	Benzophenone	Benzene	353	418, 444	{3}
Biacetyl	Benzene	450	418, 443	{5}	

^a Obtained at 25 °C except for the values in parentheses which were obtained at -150 °C for MTHF and -75 °C for GT.

^b The values in braces indicate the occurrence of self-quenching due to [DPP] values of 5×10^{-5} - 2×10^{-3} M.

^c Excitation by conventional flash photolysis using [DPP] $\leq 2 \times 10^{-5}$ M.

^d No triplet absorption observed.

600 nm) was found for DPO possibly because of the stronger fluorescence intensity in the red. S-S absorption spectra of DPB, DPH and DPO have recently been reported [27]. A third longer-lived transient ($\tau_{1/2} > 1 \mu s$ at 25 °C; $\lambda_{exc} = 353$ nm) was observed for DPH and DPO in acetonitrile and ethanol solutions (e.g. λ_{max} values of about 600 nm and 640 nm for DPH and DPO respectively) but not in cyclohexane and benzene solutions. Although this transient has not yet been identified, a triplet nature is excluded since it was not quenched by oxygen.

3.2. Triplet lifetime

On excitation with the flash lamp or at moderately small laser intensities (incident laser energy below 10 mJ) the decay of the triplets was first order, whereas at higher laser intensities a second-order decay component was also observed. Although the first-order rate constant for triplet

decay k_{obs} was independent of the wavelength of observation (380 - 460 nm), different triplet lifetimes ($\tau_0 = k_{\text{obs}}^{-1}$) depending on the excitation conditions were found. For example, triplet lifetimes in the vicinity of 100 μs were observed for DPH and DPO at low concentrations (less than about 2×10^{-5} M) on excitation by conventional flash photolysis in the absence of any additive. τ_0 was reduced to varying degrees in all cases where the triplet was formed by direct and sensitized laser excitation (Table 1). The data in Table 1 indicate that τ_0 and λ_{max} do not depend on λ_{exc} but that τ_0 depends on the concentration [DPP] of the diphenylpolyenes. The shorter triplet lifetimes on excitation with a laser pulse at higher [DPP] (above 5×10^{-5} M) are explained by a pseudo-first-order self-quenching process: $k_{\text{obs}} = \tau_0^{-1} + k_s[\text{DPP}]$ where k_s is the rate constant for self-quenching. k_s values in the range $(1 - 3) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ were estimated for DPH and DPO in benzene solutions. In rigid media (e.g. GT at -75°C) where quenching effects and twisting processes about C=C double bonds are significantly reduced, τ_0 ranges between 100 μs for DPO and 1.5 ms for DPB (Table 1).

Owing to efficient quenching by oxygen, the triplet lifetimes τ_a and τ_{ox} in air-saturated solutions and oxygen-saturated solutions respectively were in the 10 - 100 ns range (Table 2). Plots of k_{obs} versus $[\text{O}_2]$ were linear. The slopes k_{ox} of these plots, representing the rate constant for quenching of the triplet by oxygen, increased slightly in the sequence DPB, DPH, DPO (Table 2). The lifetime of the DPB triplet formed by benzophenone-

TABLE 2

Triplet lifetimes in the presence of oxygen and rate constants for triplet quenching by oxygen and azulene^a

Compound	Sensitizer	Solvent	τ_a (ns)	τ_{ox} (ns)	k_{ox}^b ($\times 10^{-9} \text{ M}^{-1} \text{ s}^{-1}$)	k_{Az}^c ($\times 10^{-9} \text{ M}^{-1} \text{ s}^{-1}$)
DPB	Benzophenone	Benzene	150	35	3.7	2.3 (1.5)
	Benzophenone Biacetyl ^d	Acetonitrile Benzene	130 155	35 ≤ 45	4.0 3.5	
DPH	None	Benzene	100	23	5.7	< 0.01
	None	Acetonitrile	105	22	5.8	
	Benzophenone	Benzene	100	24	5.5	
DPO	None	Benzene	95	22	6.2	< 0.01
	None	Acetonitrile	85	20	6.4	
	Benzophenone	Benzene	95	21	6.0	
	Biacetyl ^d	Benzene	100	22	5.8	

^a At 25 $^\circ\text{C}$. Unless otherwise indicated the samples were excited at 353 nm and observed at λ_{max} (Table 1).

^b Slopes obtained from linear plots of k_{obs} versus $[\text{O}_2]$ using $[\text{O}_2]$ values of 1.6×10^{-3} M and 1.7×10^{-3} M for air-saturated solutions of benzene and acetonitrile respectively.

^c The value in parentheses was obtained with FE as quencher.

^d $\lambda_{\text{exc}} = 450 \text{ nm}$.

sensitized excitation in benzene solutions at 25 °C was also reduced on addition of Az or FE. Quenching rate constants k_{Az} and k_{FE} rather below the diffusion-controlled limit were determined from the linear dependence of k_{obs} on the quencher concentration (Table 2). However, Az failed to quench the DPH and DPO triplets, consistent with endothermic energy transfer to Az (see Section 4.1).

3.3. Triplet yield

Relative triplet yields at low and high temperatures were estimated from the maximum transient absorbances at λ_{max} after the laser pulse and fluorescence decay by assuming temperature-independent extinction coefficients ϵ_{TT} . The quantum yields for intersystem crossing ϕ_{isc} at 25 °C were obtained by using the ϕ_{isc} values previously determined for DPH and DPO in

TABLE 3

Quantum yields of fluorescence and of intersystem crossing in fluid and rigid media

Compound	Solvent	t (°C)	ϕ_f^a	ϕ_{isc}^b
DPB ^c	Cyclohexane	25	0.44 ^d	
	Ethanol	25	0.03	
	Ethanol	-196	0.4	
	MTHF	-196	0.3	
	GT	25	0.1	≤ 0.01
	GT	-75	0.9	≤ 0.02
DPH	3-methylpentane	22	0.62 ^e	
	3-methylpentane	-196	1.0 ^e	
	Benzene	27	0.71 ^e	0.019 ^f
	Ethanol	26	0.24 ^e	0.020 ^f
	Ethanol	-196	0.8	
	MTHF	25		0.02
	MTHF	-196	0.9	≤ 0.01
	GT	25	0.5	0.02
	GT	-75	0.8	≤ 0.02
DPO	Cyclohexane	25	0.09 ^d	
	Benzene	25	0.10 ^d	0.005 ^f
	Ethanol	25	0.05 ^d	0.006 ^f
	Ethanol	-196	0.1	
	MTHF	25		0.005
	MTHF	-196	0.1	≤ 0.005
	GT	25	< 0.1	0.008
	GT	-75	≤ 0.1	≤ 0.005

^aIn deoxygenated solutions; $\lambda_{exc} = 366$ nm unless otherwise indicated.

^bObtained from relative maximum transient absorbances (see text); in deoxygenated solutions; $\lambda_{exc} = 353$ nm.

^c $\lambda_{exc} = 313$ nm.

^dTaken from refs. 8 and 11.

^eTaken from ref. 4.

^fTaken from ref. 14.

benzene and ethanol solutions [16] as reference values and assuming that ϵ_{TT} for DPB and DPH are identical. In fluid and rigid media ϕ_{isc} was found to be 0.02 or less throughout (Table 3).

3.4. Quantum yield of fluorescence

The quantum yields of fluorescence ϕ_f of the all-*trans* isomers are listed in Table 3 together with selected literature values [4, 8, 11]. ϕ_f and the fluorescence spectra were found to be independent of λ_{exc} (300 - 400 nm) even at -196°C in agreement with previous observations for DPH [4]. In the presence of oxygen, ϕ_f decreased and concomitantly ϕ_{isc} increased. In air-saturated benzene solutions of DPO for example, ϕ_f was reduced relative to deoxygenated solutions by about 30% whereas ϕ_{isc} was enhanced by more than 300%. Fluorescence quenching by oxygen into the lowest triplet state may account for this effect. An evaluation of the oxygen effect will not be given here since a knowledge of the rate constants for fluorescence, inter-system crossing and internal conversion is required. Addition of FE or Az also reduced ϕ_f . Slopes of about 100 M^{-1} or less were obtained from Stern-Volmer plots of the fluorescence intensities of DPB and DPH in benzene solutions at 25°C .

3.5. *Trans* \rightarrow *cis* photoisomerization

In order to study the involvement of triplet states in *trans* \rightarrow *cis* photoisomerization steady state irradiation measurements were carried out. The absorption spectra of the all-*trans* isomers of DPB, DPH and DPO in acetonitrile solutions before and after irradiation are shown in Fig. 2. The amount of spectral change decreased in the sequence DPB, DPH, DPO. For DPB the percentage (% all-*trans*)_s of starting material in the photostationary state (and for DPH an upper limit for (% all-*trans*)_s) was estimated from the

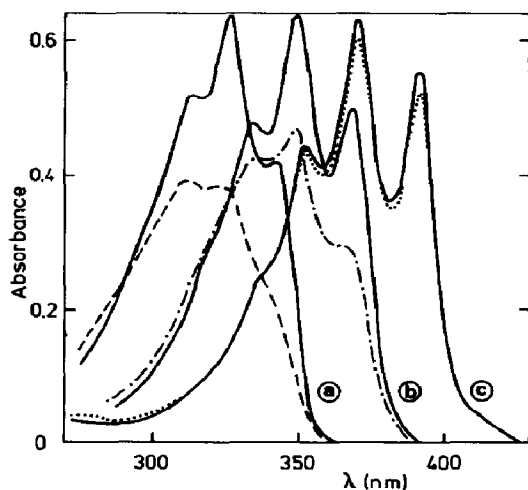


Fig. 2. Absorption spectra of all-*trans* isomers of (a) DPB ($\lambda_{irr} = 313\text{ nm}$), (b) DPH and (c) DPO ($\lambda_{irr} = 366\text{ nm}$) in deoxygenated acetonitrile solutions at 25°C before irradiation (—) and in the photostationary state (---, - · - ·, ·····).

UV spectra and from data given by Zechmeister [17]. The photochemical rearrangement and/or decomposition of the all-*trans* α, ω -diphenylpolyenes show a significant solvent dependence. For example, irreversible processes involving acid catalysis have been reported [17, 19]. Almost total destruction of DPB and DPH could be achieved in acetic acid, whereas in methanol solutions a quasi-photostationary state was formed which slowly decomposed on further irradiation [19]. Therefore only the relative initial rate of disappearance k_r of the starting material was determined. The addition of FE or Az to benzene solutions of DPB and DPH reduced k_r only slightly, corresponding to Stern-Volmer constants of about 100 M^{-1} or less. The effects of solvent properties, oxygen and temperature on k_r are summarized in Table 4. The addition of oxygen had only a small effect on k_r which decreased on lowering the temperature and/or increasing the solvent viscosity. The effect of temperature on k_r is shown in a 1:1 mixture of MCH and MCP. The viscosity effect is illustrated by a plot of k_r versus T^{-1} for GT solutions of DPB, DPH and *trans*-stilbene as a reference (Fig. 3). As in the case of stilbene [21, 28], the decrease in the yield of *trans* \rightarrow *cis* photoisomerization is explained by the hindrance of twisting about a C=C double bond as a result of solvent viscosity changes (more than 10 orders of magnitude in GT between 25 and -75°C [29]).

Attempts to carry out sensitized *trans* \rightarrow *cis* photoisomerization in benzene solutions under various conditions, e.g. anthraquinone ($8 \times 10^{-3} \text{ M}$) or benzanthrene ($5 \times 10^{-3} \text{ M}$) for DPH ($1 \times 10^{-2} \text{ M}$, $\lambda_{\text{irr}} = 405 \text{ nm}$) and

TABLE 4

Relative initial rates of *trans* \rightarrow *cis* photoisomerization and the percentage of all-*trans* isomers in the photostationary state^a

Compound	Solvent	t ($^\circ\text{C}$)	(% all- <i>trans</i>) _s	k_r
DPB ^b	Cyclohexane	25	35	1.0
	MCH-MCP	-50	≈ 80	0.2
	MCH-MCP	-100	>99	<0.05
	Benzene	25	38	0.9 (0.9) ^c
	Acetonitrile	25	40	0.9 (0.9)
	GT	25	38	0.9
DPH	Cyclohexane	25	<85	0.1
	MCH-MCP	-50		0.05
	MCH-MCP	-100		<0.01
	Benzene	25	<90	0.2 (0.25)
	Acetonitrile	25	<60	1.0 (1.25)
	GT	25	<85	0.6
DPO	Benzene	25		≈ 0.02
	Acetonitrile	25		≈ 0.02

^aIn deoxygenated solutions with $\lambda_{\text{irr}} = 366 \text{ nm}$ unless otherwise indicated.

^b $\lambda_{\text{irr}} = 313 \text{ nm}$.

^cThe values in parentheses refer to air-saturated solutions.

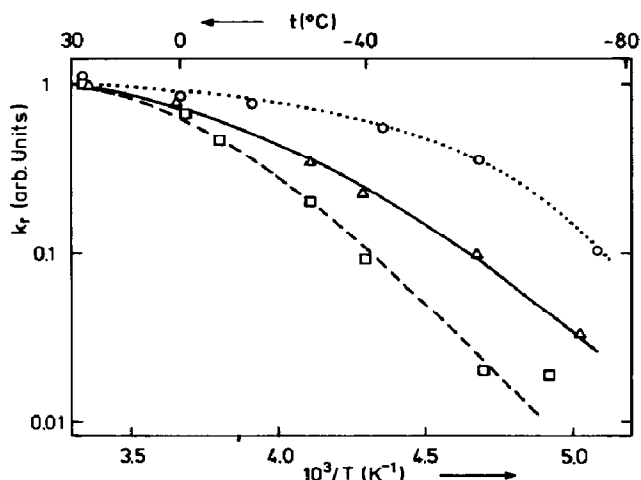


Fig. 3. Relative initial rates of disappearance of all-*trans* DPB ($\lambda_{\text{irr}} = 313$ nm) (Δ), all-*trans* DPH ($\lambda_{\text{irr}} = 366$ nm) (\square) and *trans*-stilbene ($\lambda_{\text{irr}} = 313$ nm) (\circ) plotted vs. T^{-1} in deoxygenated GT solutions.

benzophenone (5×10^{-3} M) for DPB (1×10^{-2} M, $\lambda_{\text{irr}} = 366$ nm), were unsuccessful. In the latter case k_r values of less than 0.05 were estimated in comparison with those for *trans*-stilbene ($\phi_{t \rightarrow c}^{\text{sens}} \approx 0.5$ [28]).

4. Discussion

4.1. Deactivation of the lowest all-*trans* triplet

The formation of triplet states of all-*trans* α, ω -diphenylpolyenes in fluid and rigid media have been reported previously [15, 16]. The triplet absorption spectra shown in Fig. 1 and the absorption maxima listed in Table 1 agree well with these findings, e.g. λ_{max} values of 423 nm and 440 nm for DPH and DPO respectively in benzene solutions [16] and of 398 nm and 429 nm for DPB and DPH respectively in EPA at -196 °C [15]. Vibrational progressions of $(1.4 - 1.5) \times 10^3$ cm^{-1} were obtained from the appearance of a second weaker T-T absorption maximum in benzene solutions. The T-T absorption maxima of diphenylpolyenes are red shifted when the number n of C=C double bonds is increased, e.g. from less than 360 nm for stilbene at room temperature ($n = 1$) [22] to about 440 nm for DPO ($n = 4$). On going from fluid to glassy solutions the T-T absorption spectra of each diphenylpolyene remained similar in shape with the maxima slightly red shifted (Table 1). Temperature- and/or viscosity-induced red shifts (5 - 20 nm) have also been reported for rigid model compounds of *cis*- and *trans*-stilbene (e.g. 1,2-diphenylcyclobutene and 2-phenylindene) [22].

The observed triplets are assigned to the all-*trans* configuration $^3t^*$. Upon excitation of the all-*trans* diphenylpolyenes, twisting about the C=C double bonds occurs in fluid solutions [17 - 19] at rates depending on n , the solvent, the viscosity and the temperature (Table 4). These twisting

processes are slowed down on increasing the viscosity, *e.g.* in GT by decreasing the temperature (Fig. 3). Thus the triplet in frozen media is assigned to $^3t^*$. Since the T-T absorption spectra in fluid and viscous solutions are very similar in shape (Table 1), it follows that the observed triplet also has the all-*trans* configuration in fluid solutions. On the basis of theoretical calculations and experimental results for stilbene, the simplest diphenylpolyene (see refs. 22 and 28), it seems unlikely that the absorption spectra of a twisted configuration would be identical with those of the all-*trans* configuration. The formation of $^3t^*$ for DPB at higher viscosities only is consistent with similar observations for stilbene [21, 28].

Assignment of the observed triplets to $^3t^*$ is further supported by kinetic arguments. The triplet lifetimes are of the order of 10 - 100 μs in fluid solutions (Table 1), equal to those of rigid aromatic molecules of similar triplet energy when self-quenching at the relatively high concentrations used is taken into account. Triplet energies E_T of 177 kJ mol⁻¹, 143 kJ mol⁻¹ and 120 kJ mol⁻¹ have been reported for the all-*trans* isomers of DPB, DPH and DPO respectively [15, 16]. However, deactivation at a perpendicular triplet configuration $^3p_t^*$ where the energy gap is much lower is probably not in accordance with the observed triplet lifetime. A rate constant for intersystem crossing at the perpendicular configuration ($^3p_t^* \rightarrow ^1p$) of $1.8 \times 10^7 \text{ s}^{-1}$ has been determined for stilbene [22]. The quenching rate constants of the three phenylpolyenes by oxygen, Az and FE are consistent with the assignment of the observed triplets to $^3t^*$. The rate constants for quenching of the DPB triplet by Az and FE (Table 2) are below the diffusion-controlled limit [30]. This result and the slightly lower k_{FE} value are in agreement with the triplet energies of 177 kJ mol⁻¹, 165 kJ mol⁻¹ and 163 kJ mol⁻¹ for DPB [15], FE and Az [31] respectively. Inefficient quenching of the DPH and DPO triplets by Az is expected because of their lower triplet energies.

In GT at -75°C , τ_0 increases from 100 μs for DPO to 1.5 ms for DPB and further to 10 ms for *trans*-stilbene [21, 28]. The reduction in E_T on increasing the number of C=C double bonds accounts for this effect since a decrease of the intersystem crossing rate constant is expected [15]. On going from rigid to fluid GT solutions τ_0 increases only slightly for DPO but significantly for DPB (Table 1). If self-quenching is neglected in GT solutions at 25°C (or if k_s is the same for the three diphenylpolyenes), this effect can be explained by intersystem crossing to the ground state at the all-*trans* configuration for DPO and at an angle of twist larger than 0° but smaller than 90° for DPB. Upon increasing n , the energy of $^3t^*$ may decrease more than that of $^3p_t^*$, thereby increasing the activation barrier between $^3t^*$ and $^3p_t^*$.

4.2. Deactivation pathways of the excited all-*trans* singlet

The fluorescence characteristics of the phenylpolyene derivatives have been intensively studied by several groups [2 - 12]. Temperature-dependent solvent-induced radiationless transitions competing with fluorescence have

been reported for DPH [4]. According to Cehelnik *et al.* [4] solvent rearrangement and conformational changes lead, after excitation of DPH into the Franck-Condon state $^1t^{*'}$, to a second excited singlet which decays to another excited singlet $^1t^*$ from which fluorescence and an activated radiationless transition finally occur [4]. However, this mechanism has been questioned by Birks *et al.* [8]. Nevertheless, radiationless deactivation necessarily competes with fluorescence at room temperature since ϕ_f is well below unity (Table 3). The question arises as to the nature of the radiationless transitions.

In a simple approach intersystem crossing or internal conversion at the all-*trans* configuration or twisting about a C=C double bond in an excited singlet state may account for the radiationless deactivation. The small values for ϕ_{isc} (Table 3), the occurrence of efficient *trans* \rightarrow *cis* photoisomerization for DPB and DPH (Table 4) and the presence of a thermally activated process in competition with fluorescence (*e.g.* for DPH [4]) suggest that the initial twisting step occurs in an excited singlet state.

Trans \rightarrow *cis* photoisomerization via the lowest triplet as an alternative pathway can be excluded by the following.

(1) Photosensitized excitation of DPB and DPH did not lead to measurable *trans* \rightarrow *cis* photoisomerization (see Section 3.5). This is also evidence against a possible pathway via a higher triplet ($E_T \lesssim 250 \text{ kJ mol}^{-1}$).

(2) Quenching measurements of the initial rates of *trans* \rightarrow *cis* photoisomerization and of the fluorescence by Az and FE yielded Stern-Volmer constants of less than 100 M^{-1} for DPB and DPH. These results can be explained by a quenching step of an excited all-*trans* singlet state (*e.g.* $^1t^* + Q \rightarrow ^1t + Q^*$). However, Stern-Volmer constants of 10^4 M^{-1} or more should be expected from a pathway via the lowest triplet state in DPB from the τ_0 and k_Q values (Tables 1 and 2).

(3) A triplet lifetime of up to $100 \mu\text{s}$ seems inconsistent with a twisting process about a C=C double bond (see above).

The involvement of an upper excited triplet is unlikely since ϕ_{isc} is low at room temperature as well as in frozen solutions. If twisting were to occur in an upper excited triplet state, an increase of the observed triplet yield on increasing the viscosity would be expected (at least for non-activated intersystem crossing). It has been recently shown [21] for *trans*-4-bromostilbene that the yield of the lowest *trans* triplet increases significantly if twisting about the C=C bond in an upper excited triplet is hindered. However, this effect was not observed for the diphenylpolyenes examined here (Table 3).

Besides twisting about a C=C double bond in an excited singlet state (with the yield $\phi_{ic}^{t \rightarrow c}$ proportional to k_r), a second internal conversion step at the all-*trans* configuration ϕ_{ic}^t is suggested from the temperature dependences of ϕ_f and ϕ_{isc} as follows. Since twisting in an upper excited triplet is unlikely, deactivation of $^1t^*$ can be described by the relationship

$$\phi_f + \phi_{isc} + \phi_{ic}^t + \phi_{ic}^{t \rightarrow c} = 1$$

In all cases examined ϕ_{isc} is lower than 0.05 and, except for DPB in GT and DPH where $\phi_t = 1$ at -196°C [4], ϕ_t approaches values well below 0.5 in rigid media. Since k_r decreases at lower temperatures and photoisomerization into *cis* isomers is strongly inhibited in viscous media ($\phi_{ic}^{t \rightarrow c} = 0$), ϕ_{ic}^t is larger than 0.5 for DPB and DPO. Therefore an internal conversion step ($^1t^* \rightarrow ^1t$) has to exist which contributes to the deactivation of the excited singlet states of all-*trans* DPB and DPO.

4.3. *Trans* \rightarrow *cis* photoisomerization

A scheme for the photoisomerization of α,ω -diphenylpolyenes based on the above considerations is presented in Fig. 4. The main features are summarized below. Twisting about C=C double bonds occurs predominantly in excited singlet states. By analogy with stilbene it is proposed that twisting leads to perpendicular configurations (e.g. $^1p_t^*$ and $^1p_c^*$ for DPB) which are deactivated by internal conversion and further twisting in ground states. At room temperature the all-*trans* isomer and the various *cis* isomers are separated in the ground state by sufficiently high activation barriers [17]. Although triplet states are formed in low yields, it is suggested that they do not contribute to the *trans* \rightarrow *cis* photoisomerization.

The proposed mechanism for simple diphenylpolyene derivatives shows some similarities with the well-established mechanism for the direct *trans* \rightarrow *cis* photoisomerization of stilbene (singlet mechanism [28]) but differs from stilbene in that the lowest all-*trans* triplet is formed by direct

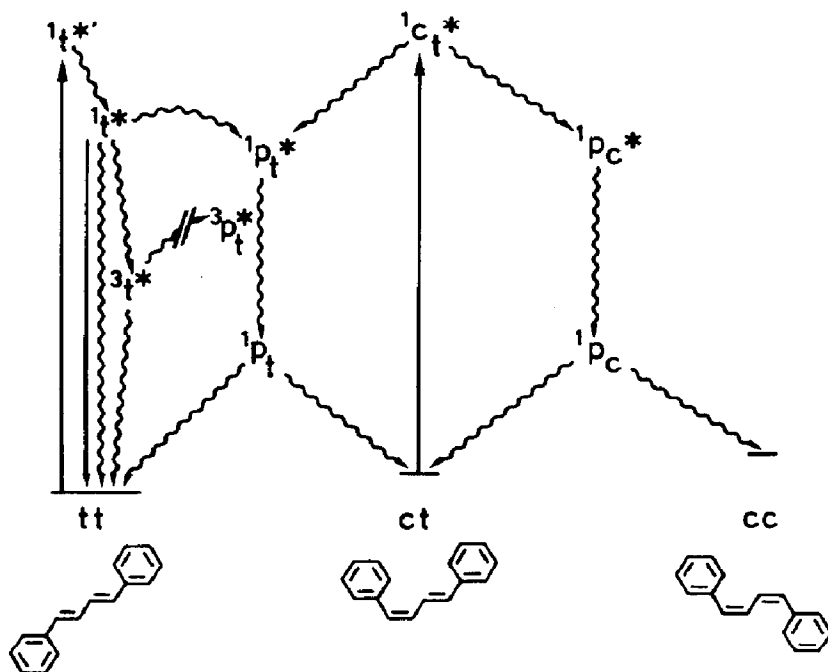


Fig. 4. Scheme illustrating the proposed primary photophysical processes of all-*trans* DPB after excitation.

excitation at room temperature and by the inefficiency of sensitized *trans* → *cis* photoisomerization. Apparently the perpendicular triplet configurations of the diphenylpolyenes examined are separated from the all-*trans* triplet by activation barriers. Calculation of the potential energy curves of the lowest triplet state may give a more detailed picture.

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