

# JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

© Copyright, 1982, by the American Chemical Society

VOLUME 104, NUMBER 17

AUGUST 25, 1982

## Photoprocesses in Diphenylpolyenes. Oxygen and Heavy-Atom Enhancement of Triplet Yields<sup>1</sup>

S. K. Chattopadhyay,<sup>††</sup> P. K. Das,<sup>†</sup> and G. L. Hug\*<sup>†</sup>

Contribution from the Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556, and Chemistry Department, Tulane University, New Orleans, Louisiana 70118. Received December 4, 1981

**Abstract:** Results, obtained by nanosecond laser flash photolysis (337.1 nm) and fluorescence measurements, are presented concerning triplet-triplet spectra and excited-state dynamics of three all-trans  $\alpha,\omega$ -diphenyl-substituted polyenes,  $\text{Ph}(\text{CH}=\text{CH})_n\text{Ph}$  ( $n = 2-4$ ), in various solvents and in the presence of oxygen and heavy-atom-containing molecules. The spectra of triplets, generated by both direct excitation and energy transfer, display the characteristics of an intense Franck-Condon allowed transition with vibrational spacings in the range 1200–1600  $\text{cm}^{-1}$  and show solvent-effect and chain-length dependence very similar to those observed for the strongly allowed band system in ground-state absorption. The quantum yields of occupation of lowest triplet are small (0.5–3%) in deaerated solvents such as cyclohexane, methanol, and benzene, but become significantly enhanced in heavy-atom-containing solvents (e.g., ethyl bromide and bromobenzene) and in the presence of oxygen and heavy-atom species. The intersystem crossing rate constants for  $T_1 \leftarrow S_1$  and  $S_0 \leftarrow T_1$  are in the ranges  $7 \times 10^5$ – $9 \times 10^7$  and  $2 \times 10^4$ – $7 \times 10^5$   $\text{s}^{-1}$ , respectively, and exhibit a decreasing trend as the polyene chain length is increased. Based on kinetic data concerning singlet quenching and triplet yield enhancement by  $\text{O}_2$  and ethyl iodide in methanol and cyclohexane, the fraction of the singlet quenching events that result in triplet generation is found to range from 0.1 to 0.8. The correlation (or lack of it) between intersystem crossing rate constants and those for bimolecular quenching of singlet and triplet is discussed in the context of the energy gap law observed in similar studies for aromatic hydrocarbons.

### Introduction

Much of the current interest in polyene photophysics is related in one way or other to two principal aspects. First, the nature of the lowest lying singlet state in some polyenes of relatively long chain length has been shown to be of primarily dipole-forbidden  $^1A_g^*$  character.<sup>2,3</sup> Second, distorted geometric configurations (nonplanar)<sup>4,5</sup> in both singlet and triplet excited states are believed to play important roles in polyene photoisomerization (cis-trans). As far as diphenylpolyenes are concerned, experimental evidence in support of the low-lying  $^1A_g^*$  state in these systems has been obtained by high-resolution one-photon spectroscopy,<sup>6</sup> photophysical considerations,<sup>6</sup> and two-photon-excitation spectral studies<sup>7</sup> involving the long-chain members. On the other hand, implication of nonplanar excited-state configurations has been based primarily on the results of many, extensive photochemical and photophysical studies involving stilbenes.<sup>4,8</sup>

In this paper, we present the results of a study concerning some broad-based photophysical aspects of three all-trans  $\alpha,\omega$ -diphenyl-substituted polyenes, namely, 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). The photophysical properties under consideration include spectral and kinetic behaviors of both the lowest singlet and triplet excited states, with special emphasis on the latter, as revealed by low-resolution absorption-emission spectral measurements and 337.1-nm laser flash photolysis com-

bined with nanosecond kinetic spectrometry. In contrast to many fluorescence spectral studies<sup>9-11</sup> of diphenylpolyenes, there have been only a very few flash photolytic studies<sup>12,13</sup> related to trip-

(1) The work described herein is supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2300 from the Notre Dame Radiation Laboratory.

(2) For a review, see Hudson, B.; Kohler, B. *Annu. Rev. Phys. Chem.* **1974**, *25*, 437–460.

(3) Tavan, P.; Schulten, K. *J. Chem. Phys.* **1979**, *70*, 5407–5413, and references therein.

(4) For a review, see Saltiel, J.; D'Agostino, E. D.; Megarity, E. D.; Helts, L.; Neuberger, K. R.; Wrighton, M.; Zafiriou, O. C. *Org. Photochem.* **1973**, *3*, 1.

(5) Tavan, P.; Schulten, K. *Chem. Phys. Lett.* **1978**, *56*, 200–204, and references therein.

(6) Hudson, B. S.; Kohler, B. E. *Chem. Phys. Lett.* **1972**, *14*, 299–304. Hudson, B. S.; Kohler, B. E. *J. Chem. Phys.* **1973**, *59*, 4984–5002.

(7) (a) Fang, H. L.-B.; Thrash, R. J.; Leroi, G. E. *Chem. Phys. Lett.* **1978**, *57*, 59–63. (b) Fang, H. L.-B.; Thrash, R. J.; Leroi, G. E. *J. Chem. Phys.* **1977**, *67*, 3389–3391. (c) Bennett, J. A.; Birge, R. R. *Ibid.* **1980**, *73*, 4234–4246. (d) Swofford, R. L.; McClain, W. M. *Ibid.* **1973**, *59*, 5740–5741.

(8) Görner, H.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1981**, *85*, 1835–1841, and references to earlier work therein.

(9) (a) Birks, J. B.; Birch, D. J. S. *Chem. Phys. Lett.* **1975**, *31*, 608–610. (b) Birks, J. B.; Tripathi, G. N. R.; Lumb, M. D. *Chem. Phys. Lett.* **1978**, *33*, 185–194.

(10) (a) Cehelnik, E. D.; Cundall, R. B.; Lockwood, J. R.; Palmer, T. F. *Chem. Phys. Lett.* **1974**, *27*, 586–588. (b) Cehelnik, E. D.; Cundall, R. B.; Lockwood, J. R.; Palmer, T. F. *J. Phys. Chem.* **1975**, *79*, 1369–1376.

(11) Klochkov, V. P.; Bogdanov, V. L. *Opt. Spectrosc.* **1980**, *48*, 421–424. (12) Bensasson, R.; Land, E. J.; Lafferty, J.; Sinclair, R. S.; Truscott, T. G. *Chem. Phys. Lett.* **1976**, *41*, 333–335.

(13) Heinrich, G.; Holzer, G.; Blume, H.; Schulte-Frohlinde, D. *Z. Naturforsch. B* **1970**, *25*, 496–499.

<sup>†</sup>University of Notre Dame.

<sup>††</sup>Tulane University.

Table I. Absorption-Emission Spectral Data of Diphenylpolyenes in Various Solvents at 295 K

polyene	solvent	absorption spectral maxima <sup>a</sup> (nm) and extinction coeff <sup>b</sup> ( $10^4 \text{ M}^{-1} \text{ cm}^{-1}$ )	fluorescence spectral maxima <sup>c</sup> (nm)	fluorescence quantum yield <sup>d</sup>	obsd fluorescence lifetime (ns) <sup>e</sup>	natural radiative lifetime (ns)
DPB	cyclohexane	329 (5.49)	376	0.42	0.60 ± 0.15	1.4
	methanol	327 (6.00)	374	0.021		
DPH	cyclohexane	353 (8.24)	427	0.65 (1.4)	12.9 (1.5)	19.8
	methanol	350 (8.28)	427	0.27 (1.2)	5.2 (1.2)	19.3
	benzene	358 (7.50)	429	0.56 (1.3)	7.2 (1.3)	12.9
	bromobenzene	361 (6.91)	431	0.42	2.8	6.7
DPO	ethyl bromide	355 (8.38)	428	0.37	5.3	14.3
	cyclohexane	374 (10.25)	517	0.085 (1.3)	6.7 (1.2)	78.8
	methanol	371 (10.87)	518	0.091 (1.4)	6.8 (1.3)	74.7
	benzene	380 (9.36)	487 <sup>f</sup>	0.088	7.1	80.7
	bromobenzene	384 (8.89)	490 <sup>f</sup>	0.073	6.5	89.0
	ethyl bromide	376 (10.41)	519	0.063	6.5	103.2

<sup>a</sup> ±1 nm. <sup>b</sup> Given in the parentheses; ±5%. <sup>c</sup> ±2 nm. <sup>d</sup> ±15%; the ratio of quantum yield in degassed solution to that in air-saturated solution is given in the parentheses. <sup>e</sup> ±5% except for DPB; the ratio of lifetime in degassed solution to that in air-saturated solution is given in the parentheses. <sup>f</sup> The peaks at 521 nm (benzene) and 523 nm (bromobenzene) are nearly as intense as the ones at 487 and 490 nm, respectively.

let-state photophysics of these systems. This is quite surprising, particularly in view of the fact that phosphorescence is not observed<sup>13</sup> in these polyene systems.

Our interest in the laser flash photolytic investigation of triplet-state phenomena and intersystem crossing quantum efficiencies of diphenylpolyenes has also been inspired by our initial observation that the singlet-mediated triplet yields in these systems are usually very low in solvents containing no heavy atoms, but are enormously enhanced in the presence of small concentrations of oxygen and molecules containing heavy atoms. We have explored in detail the photodynamical aspects of the quenching processes where both polyene singlet and triplet states participate, and discussed the results in the context of analogous phenomena observed for aromatic hydrocarbons.

### Experimental Section

The diphenylpolyenes (all from Aldrich) were purified by crystallization from ethanol. Cyclohexane (MCB), methanol (Aldrich), and benzene (Aldrich)—all of spectral grade—were used without further purification. Bromobenzene (Fisher), ethyl bromide (Aldrich), and ethyl iodide (Fisher, distilled once and stored over mercury) were passed through columns of alumina and anhydrous sodium thiosulfate before use. Solutions containing varying concentrations of oxygen were obtained by bubbling custom-made mixtures of nitrogen and oxygen (Linde). Except where the effect of the presence of oxygen or air was studied, the solutions for laser flash photolysis and fluorescence measurements were deaerated by bubbling argon.

All absorption spectra were recorded in a Cary 219 spectrophotometer with 1-nm bandpass. Fluorescence spectra and quantum yields were measured in an SLM photon counting spectrofluorometer (SPC 823 + SMC 220). It consists of a xenon arc lamp (OSRAM XBO 450 W/2), a dual excitation monochromator (MC 640, with concave holographic gratings), and a pair of detection assemblies, each consisting of a single, analyzing monochromator (MC 320, with a holographic grating) and an EMI 9635 QA photomultiplier tube (PMT). The excitation and detection were at a right angle to one another. Fluorescence was measured in square (1 cm × 1 cm) cells of Suprasil quartz using a bandpass of 1–2 nm for the exciting light and 1–4 nm for the emitted light.

For fluorescence quantum yield ( $\phi_f$ ) measurements, DPH in cyclohexane ( $\phi_f = 0.65$ ) was used as the reference.<sup>10a</sup> The integrated areas under the fluorescence spectra, obtained from solutions optically matched at the exciting wavelength, and corrected for the relative response of the detection system (as a function of wavelength), were multiplied<sup>14</sup> by the square of the refractive index of the solvent used and compared with the area obtained for the reference under identical conditions of bandpass and excitation wavelength (320 nm for DPB and 360–370 nm for DPH and DPO). The determination of fluorescence lifetimes was based on measuring<sup>15</sup> the time-correlated experimental profile of fluorescence events and comparing it iteratively, for the best fit, with curves obtained

by convolution<sup>16</sup> from the lamp profile. A photon counting setup from Photochemical Research Associates furnished with a thyratron-operated spark lamp with hydrogen between tungsten electrodes and a small monochromator (20–30-nm bandpass) for excitation was used for this purpose.

The laser flash photolysis apparatus is described elsewhere.<sup>17</sup> Nitrogen laser pulses (337.1 nm, 8 ns, 2–3 mJ) from a Moletron UV-400 system are used for excitation. The kinetic spectrophotometer for monitoring transients from their spectral absorption at 300–750 nm consists of a pulsed xenon lamp (Osram XBO 450W), a B & L high-intensity monochromator (UV-visible, bandpass 2–4 nm), and an RCA 4840 PMT. The signal from the PMT is terminated via 93 ohm into a Tektronix 7912 digitizer. Both the excitation and detection system including a number of electromechanical shutters are interfaced with a multiuser PDP 11/55 computer system for controlling experiments, processing data, and storing information. All laser flash photolysis experiments were carried out in 3 mm × 7 mm rectangular cells (Suprasil quartz) in which the laser pulses intersected the monitoring light beam at about 20° along the 3-mm path length from the side of the PMT-monochromator assembly.

### Results

The results of the present study can be divided into three parts, namely, (i) absorption-emission spectral data in various solvents, (ii) triplet-state photophysical properties in various solvents, and (iii) fluorescence quenching and triplet yield enhancement by oxygen and molecules containing heavy atoms.

(i) **Spectra and Photophysical Data from Absorption and Emission.** Although a substantial amount of spectral and photophysical data for diphenylpolyenes are available in the literature,<sup>6–13</sup> it became pertinent in the present work to carry out quantitative measurements concerning low-resolution absorption-emission spectra and fluorescence lifetimes in various solvents of our interest under experimental conditions comparable to those used for laser flash photolysis. As will be seen later, the resulting data are necessary to obtain quantitative information from the results of laser flash photolysis and quenching studies. Table I summarizes the results. While the general agreement between the data in Table I with those reported in the literature (where available) is reasonably good, minor discrepancies have been observed in a few cases. For example, the fluorescence quantum yield ( $\phi_f$ ) of DPH in benzene has been found to be lower than that in cyclohexane (Table I), although previous workers<sup>10</sup> have obtained opposite results.

Some observations, not all necessarily new as far as the previous studies are concerned, can be made based on the data presented in Table I. The locations (wavelength maxima) and intensities

(14) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley: New York, 1970.

(15) Ware, W. R. In "Creation and Detection of the Excited State"; Lammola, A. A., Ed.; Marcel Dekker: New York, 1971; Vol 1A.

(16) Lewis, C.; Ware, W. R.; Doemeny, L. J.; Nemzek, T. L. *Rev. Sci. Instrum.* **1973**, *44*, 107–114.

(17) Das, P. K.; Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965–6970. Das, P. K.; Bhattacharyya, S. N. *J. Phys. Chem.* **1981**, *85*, 1391–1395.

Table II. Triplet-State Photophysical Data of Diphenylpolyenes in Various Solvents at 295 K

polyene	solvent	spectral data			intersystem crossing quantum yield <sup>d</sup>	intersystem crossing rate constant (10 <sup>7</sup> s <sup>-1</sup> )
		triplet-triplet $\lambda_{\max}$ (nm) <sup>a</sup>	$\epsilon_{\max}^{\text{triplet}}$ (10 <sup>4</sup> M <sup>-1</sup> cm <sup>-1</sup> ) <sup>b</sup>	triplet lifetime ( $\mu$ s) <sup>c</sup>		
DPB	cyclohexane	390	6.0	1.6	0.020	3.3
	cyclohexane + 0.31 M EtI			1.1	0.15	
	methanol	385	5.8		≤0.002	
	methanol, satd with KI			2.4	0.040	
	benzene	395	4.5	2.6	0.006	
	bromobenzene	416	4.5	1.5	0.083	
	ethyl bromide	392	5.5	2.5	0.047	
DPH	cyclohexane	416	11.4	20	0.029 (7)	0.22
	methanol	410	12.1	30	0.015 (10)	0.29
	methanol + 0.31 M EtI			8	0.14	
	methanol satd with KI			15	0.30	
	benzene	426	10.4	10	0.029	0.40
	bromobenzene	430	10.5	13	0.26	9.3
	ethyl bromide	420	11.4	12	0.16	3.0
DPO	cyclohexane	437	21.0	40	0.005 (24)	0.075
	methanol	430	19.1	34	0.005 (29)	0.074
	methanol + 0.31 M EtI			14	0.031	
	methanol, satd with KI			14	0.046	
	benzene	445	18.8	21	0.009	0.13
	bromobenzene	450	17.9	14	0.076	1.2
	ethyl bromide	440	23.0	11	0.062	0.95

<sup>a</sup> ± 2 nm. <sup>b</sup> ± 15%. <sup>c</sup> ± 10%. <sup>d</sup> ± 20%; the numbers in parentheses are the ratios of  $\phi_T$  in air-saturated solutions to those in degassed ones.

(extinction coefficients) of the lowest energy absorption spectral band system, assigned as due to the strongly allowed  ${}^1B_u^* \leftarrow {}^1A_g$  transitions of the polyenes, are fairly strongly dependent on solvents; the directions of these solvent effects are parallel for all of the three polyenes. Interestingly, the fluorescence spectral maxima ( $\nu_{F,\max}$ ) also show a slight dependence on solvents, and their locations are shifted in the same direction as the corresponding absorption spectral maxima ( $\nu_{A,\max}$ ); for example, for both DPO and DPH,  $\nu_{F,\max}$  and  $\nu_{A,\max}$  decrease in the order: cyclohexane ~ methanol > ethyl bromide > benzene > bromobenzene. There is also a slight, but nonnegligible, dependence of the relative intensity of the fluorescence vibronic bands on solvents. For example, in the corrected fluorescence spectra of DPO in methanol, cyclohexane, and ethyl bromide the peak at ~520 nm is of higher intensity than that at ~485 nm; the situation is reversed in benzene and bromobenzene. The natural radiative lifetime,  $\tau_{\text{rad}}$ , calculated from the observed lifetime ( $\tau_S$ ) and fluorescence quantum yield ( $\phi_F$ ) using the relationship

$$\tau_{\text{rad}} = \tau_S / \phi_F \quad (1)$$

becomes progressively longer as the polyene chain length is increased from DPB to DPO. The nature of the lowest lying singlet excited state in all three diphenylpolyenes has been shown<sup>6,7</sup> to be primarily of dipole-forbidden  ${}^1A_g^*$  character. The gradual increase in  $\tau_{\text{rad}}$  on going from DPB to DPO suggests a corresponding decrease in the participation of the strongly allowed  ${}^1B_u^* \leftarrow {}^1A_g$  transition in determining the radiative character through vibronic coupling or other mechanisms.<sup>9,18-20</sup> Finally,  $\tau_{\text{rad}}$  of DPH shows a greater sensitivity toward solvent effects than that of DPO. This is understandable in terms of a greater interaction between the two low-lying states,  ${}^1A_g^*$  and  ${}^1B_u^*$ , in DPH, presumably because of closer proximity between them.

(ii) **Triplet-State Photophysics and Intersystem Crossing Quantum Efficiencies.** All of the three polyenes under study absorb relatively strongly at 337.1 nm ( $\epsilon = 35\text{--}60 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  in methanol/cyclohexane) and are very appropriate for a flash photolytic study using a nitrogen laser for excitation. In well-

degassed solutions in solvents containing no heavy atom, e.g., cyclohexane, benzene, or methanol, direct laser excitation of the three polyenes leads to the formation of the corresponding triplets in small but measurable yields. Relatively high extinction coefficients of triplet-triplet absorption compensate for the low triplet yields. In heavy-atom containing solvents such as bromobenzene or ethyl bromide and in the presence of oxygen or a heavy-atom containing species such as ethyl iodide (EtI) or I<sup>-</sup> (see next section), the triplet yields are enhanced to a large extent. Figure 1 shows some representative experimental traces for decay of triplet-triplet absorption of DPH and DPO in air and Ar-saturated solutions in cyclohexane. It is noted that a few points in the decay profiles immediately following the laser pulse are distorted because of contribution from fluorescence (dominant in the case of DPH) and singlet-singlet absorption (dominant in the case of DPO).<sup>21</sup>

Data concerning triplet-state properties and intersystem crossing quantum yields are given in Table II. In solvents containing no heavy atom, the triplet-triplet absorption spectra were obtained wavelength by wavelength in the presence of 0.1–1 mM oxygen or 0.05–0.2 M EtI, whereby the triplet yield was enhanced. The triplet-triplet extinction coefficients were determined by comparing the change (positive) in absorbance ( $\Delta OD_{TT}^{\max}$ ) at the triplet-triplet absorption spectral maximum with the change (negative) in absorbance ( $\Delta OD_{SS}^{\lambda}$ ) in the spectral region where the ground-state polyene strongly absorbs. The T-T extinction coefficient,  $\epsilon_{TT}$ , is given by the equation:

$$\epsilon_{TT}^{\max} = \epsilon_{SS}^{\lambda} [1 - \epsilon_{TT}^{\lambda} / \epsilon_{SS}^{\lambda}] \Delta OD_{TT}^{\max} / -\Delta OD_{SS}^{\lambda} \quad (2a)$$

$$\epsilon_{TT}^{\max} = \epsilon_{SS}^{\lambda} \Delta OD_{TT}^{\max} / -\Delta OD_{SS}^{\lambda} \quad (\text{if } \epsilon_{TT}^{\lambda} \ll \epsilon_{SS}^{\lambda}) \quad (2b)$$

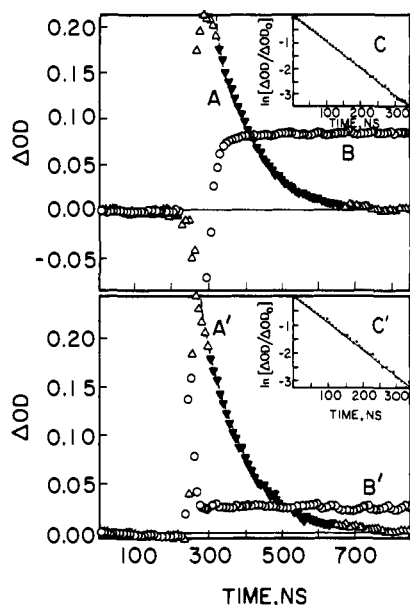
where  $\epsilon_{SS}^{\lambda}$  and  $\epsilon_{TT}^{\lambda}$  are the extinction coefficients of ground-state and triplet-triplet absorption, respectively, at the wavelength ( $\lambda$ ) where the singlet depletion has been measured. The method becomes straightforward if a spectral region corresponding to  $S_n \leftarrow S_0$  absorption is found where  $\epsilon_{TT}^{\lambda}$  is negligible compared to  $\epsilon_{SS}^{\lambda}$ . As the following arguments will show, this condition (i.e.,

(18) Hug, G.; Becker, R. S. *J. Chem. Phys.* **1976**, *65*, 55–63.

(19) Andrews, J. R.; Hudson, B. S. *J. Chem. Phys.* **1978**, *68*, 4587–4594.

(20) Birks, J. B. *Chem. Phys. Lett.* **1978**, *54*, 430–434.

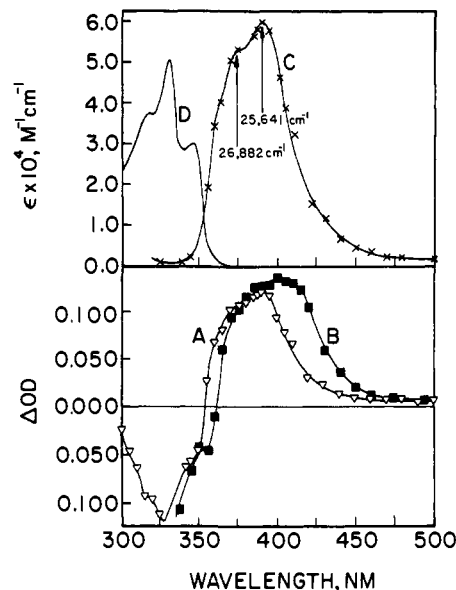
(21) Chattopadhyay, S. K.; Das, P. K. *Chem. Phys. Lett.* **1982**, *87*, 145–150.



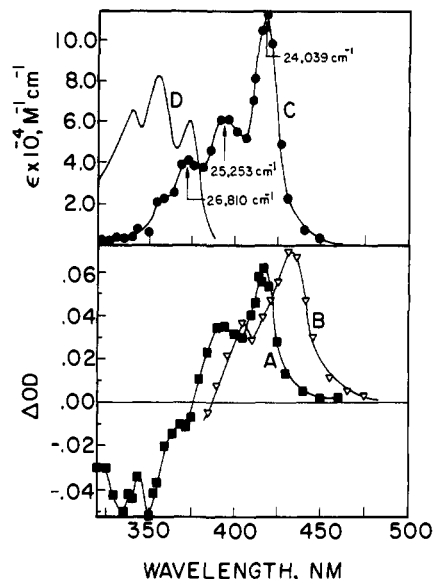
**Figure 1.** Experimental traces for decay of triplet produced by direct excitation in cyclohexane solution of DPH (A, air-saturated; B, degassed) monitored at 415 nm and of DPO (A', air-saturated; B', degassed) monitored at 435 nm. The insets C (for DPH) and C' (for DPO) show the first-order fit for the portions of decay profiles (in air-saturated solutions), indicated by inverted shaded triangles in the main figures.

$\epsilon_{SS}^{\lambda} \gg \epsilon_{TT}^{\lambda}$ ) appears to have been fulfilled at the short wavelength sides of the main absorption band systems of the three polyenes (310–330 nm for DPB, 320–340 nm for DPH, and 340–360 nm for DPO). Measurements of singlet depletion ( $\Delta OD_{SS}^{\lambda}$ ) at several wavelengths, corresponding to peaks and troughs of ground-state absorption in these spectral regions, gave essentially constant values for  $\epsilon_{SS}^{\lambda}/(-\Delta OD_{SS}^{\lambda})$ . This suggests that  $\epsilon_{TT}^{\lambda}/\epsilon_{SS}^{\lambda}$  at these wavelengths is either  $\sim 0$  or a constant. The second possibility seems highly unlikely because it requires that the triplet-triplet absorption spectra follows the  $S_0 \rightarrow S_n$  spectra in a parallel manner through their maxima and minima in these spectral regions. As a matter of fact, for DPH and DPO, T-T extinction coefficient data, measured by energy transfer from pulse radiolytically generated biphenyl triplet in benzene, are available<sup>12</sup> in the literature. The agreement between our data and the reported values are well within the experimental errors, suggesting that the assumption  $\epsilon_{TT}^{\lambda}/\epsilon_{SS}^{\lambda} \sim 0$  (in the proper spectral region) is valid at least for DPO and DPH in benzene.

Mention should be made of two sources of complications that we encountered in measuring  $\epsilon_{TT}^{max}$  values based on singlet depletion. First, for DPH and DPO in methanol, processes that could be best described as biphotonic photoionization of the polyenes leading to the formation of radical cations were observed. Contribution of these processes to singlet depletion was minimized by attenuating the laser intensity to 15–20% of the original value (by neutral density filters) and corrected for by subtracting  $\Delta OD_{SS}^{\lambda}$  at the end of triplet decay from the end-of-pulse  $\Delta OD_{SS}^{\lambda}$  value. Second, in the case of DPB, a small, permanent contribution to  $\Delta OD_{SS}^{\lambda}$  was found to persist even after the completion of decay of triplet, particularly in the long-wavelength region of the ground-state absorption band (340–360 nm). There was, however, no photoionization. It appears that this contribution to  $\Delta OD_{SS}^{\lambda}$  arises from trans  $\rightarrow$  cis photoisomerization, and cis isomer(s) having smaller extinction coefficients than the all-trans form. Although we have not explored this aspect in detail, comparisons of the magnitudes of this negative, permanent  $\Delta OD_{SS}^{\lambda}$  values (at the end of triplet decay) in degassed and air-saturated solutions and in solutions containing EtI (with enhanced triplet yield) suggest that the trans  $\rightarrow$  cis isomerization occurs mostly in the singlet manifold. In view of uncertainty regarding correcting for this contribution, we have measured the end-of-pulse singlet depletion under conditions where the triplet yield was high, rendering the correction negligible and unnecessary.



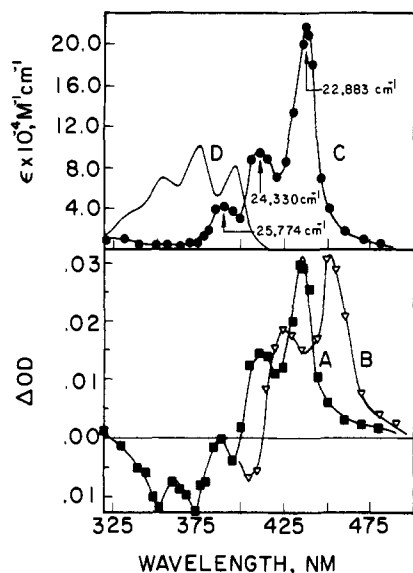
**Figure 2.** Triplet-triplet spectra of DPB in terms of observed absorbance changes in cyclohexane (A) and bromobenzene (B). C and D are the triplet-triplet spectrum (corrected for ground-state depletion) and the ground-state absorption spectrum, respectively, of DPB in cyclohexane.



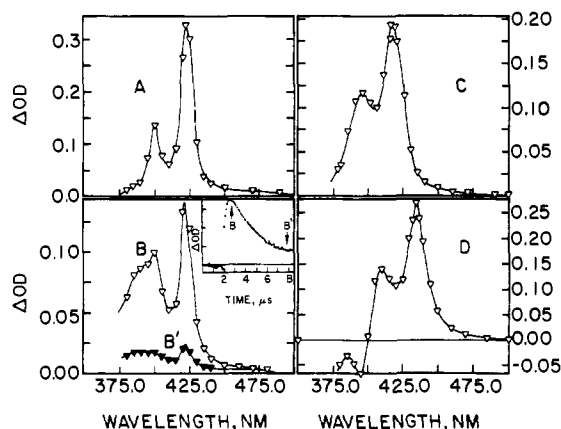
**Figure 3.** Triplet-triplet spectra of DPH in terms of observed changes in cyclohexane (A) and bromobenzene (B). The triplet-triplet spectrum (C, after correction for ground-state depletion) and ground-state absorption spectrum (D) of DPH in cyclohexane are shown in terms of extinction coefficients in the upper half.

Figures 2–4 show the triplet-triplet absorption spectra of the three polyenes. In all three cases, unlike the absorption and fluorescence spectra of the diphenylpolyenes, the T-T spectra display the characteristics of a Franck-Condon allowed transition (the 0–0 vibronic transition is the most intense). The vibronic structures are particularly apparent in the cases of DPH and DPO. The vibrational spacings are in the range 1200–1600  $\text{cm}^{-1}$  (in cyclohexane). For comparison, the spacings among the observed vibronic peaks of absorption and fluorescence spectra of DPO and DPH in cyclohexane are in the ranges 1350–1490 and 1200–1500  $\text{cm}^{-1}$ , respectively. It is also noted that the directions of the changes in the locations and extinction coefficients of T-T absorption spectra of the polyenes, on varying chain length and on changing solvent, are very similar to those observed for the ground-state absorption spectra.

Figure 5 shows the T-T spectra of the three diphenylpolyenes as obtained by energy transfer from anthracene in cyclohexane.

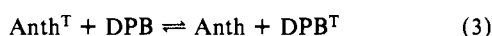


**Figure 4.** Triplet-triplet spectra of DPO in terms of observed absorbance changes in cyclohexane (A) and bromobenzene (B). In the upper half, the triplet-triplet spectrum (C, after correction for ground-state absorption) and ground-state absorption spectrum (D) of DPO in cyclohexane are presented in terms of extinction coefficients.



**Figure 5.** Triplet-triplet spectra of anthracene (A) and anthracene-sensitized DPB (B, B'), DPH (C), and DPO (D) in cyclohexane (shown in terms of observed absorbance changes). The inset in the lower left quadrant shows the profile for formation and decay of DPB (+anthracene) triplet monitored at 390 nm; B and B' are the spectra corresponding to the times marked by the two arrows in the inset. The spectra C and D correspond to  $\sim 0.5 \mu\text{s}$  after the maximum in the formation-decay profiles.

In these experiments, 60–80% of the laser photons absorbed was used in the excitation of anthracene and resultant triplet generation. Since  $\phi_T$  is small for the polyenes, practically all of the polyene triplets observed were produced through energy transfer from anthracene. It is noted that the triplet-triplet spectra observed through sensitization are virtually identical with those observed by direct excitation in degassed solution or in the presence of  $\text{O}_2$  or EtI. Interestingly, in the case of DPB (Figure 5B, B') the donor triplet (anthracene) persists until the end of decay of DPB triplet, suggesting that energy transfer occurs in a reversible manner.<sup>22</sup>



This is what is expected because the triplets of anthracene ( $E_T = 42 \text{ kcal/mol}$ )<sup>23</sup> and DPB ( $E_T = 42.3 \text{ kcal/mol}$ )<sup>13</sup> are nearly isoenergetic.

The quantum yields of lowest triplet occupation ( $\phi_T$ ), assumed to be the same as the quantum yields of intersystem crossing, were determined using benzophenone in benzene as an actinometer.  $\phi_T$  is given by the equation:

$$\phi_T = (\Delta\text{OD}_{\text{TT,P}} / \Delta\text{OD}_{\text{TT,R}}) (\epsilon_{\text{TT,R}} / \epsilon_{\text{TT,P}}) \quad (4)$$

where  $\Delta\text{OD}$ 's are the changes in absorbance due to polyene and reference (benzophenone) triplets at the respective wavelength maxima, measured in optically matched solutions, and  $\epsilon$ 's are the corresponding extinction coefficients. For benzophenone in benzene,  $\phi_T$  is assumed to be unity and the value of  $\epsilon_{\text{TT}}$  is taken as  $7630 \text{ M}^{-1} \text{ cm}^{-1}$  at  $532 \text{ nm}$ .<sup>24</sup> One important consideration in choosing benzophenone as reference was that the products,  $\phi_T \times \epsilon_{\text{TT}}$ , were comparable for both reference and samples giving  $\Delta\text{OD}_{\text{TT}}$ 's of similar magnitudes in optically matched solutions.

$\phi_T$  data are given in column 6 of Table II. As noted in the beginning of this section,  $\phi_T$ 's are small (0.5–3%) in solvents such as methanol, cyclohexane, and benzene. As far as polyene chain length dependence is concerned,  $\phi_T$  follows the order: DPH > DPB > DPO. In solvents containing heavy atoms, e.g., ethyl bromide, bromobenzene, or methanol saturated with KI,  $\phi_T$  becomes pronounced (4–30%). It would be worthwhile to see the effects in a few iodine-containing solvents (e.g., ethyl iodide and iodobenzene); however, these solvents are not suitable for nitrogen laser flash photolysis because of strong absorption at  $337.1 \text{ nm}$ . Bromobenzene also absorbs to a small extent at  $337.1 \text{ nm}$ ; for experiments in this solvent, the polyene concentrations were kept high enough to minimize the fraction of laser light absorbed by the solvent. Also, blank laser flash photolysis experiments were carried out in pure bromobenzene and no significant transient phenomena were observed from the solvent itself in the spectral region of interest.

In analogy to the gradual transition of the nature of the lowest lying excited state ( $^1A_g^*$  vs.  $^1B_u^*$ ) in the singlet manifold as the polyene chain length is increased, one obvious question is if a similar change occurs in the lowest triplet state. Triplet-triplet absorption spectroscopy has been found to be useful in determining the nature of the lowest lying triplet ( $n,\pi^*$  vs.  $\pi,\pi^*$ ) of carbonyl compounds.<sup>25</sup> The results of our study show that there is no abrupt change in the T–T absorption spectral features, namely, shape, location, intensity, and vibronic progression on going from DPO to DPB. This is taken to mean that even if there is a change in the lowest triplet nature on going from DPO to DPB, this is too subtle to be detected by the present low-resolution T–T spectral data.

(iii) **Singlet Quenching and Triplet Yield Enhancement by Oxygen and Heavy Atoms.** The data concerning the effect of heavy-atom-containing solvents on  $\phi_T$ , given in Table II and discussed in the preceding section, clearly demonstrate the external heavy-atom effect on the intersystem crossing efficiencies in the polyenes. Also, as Figure 1 illustrates, oxygen enhances the intersystem crossing rates in a pronounced manner. In order to obtain insight into the interactions of polyene singlet and triplet with oxygen and heavy-atom-containing molecules, we have carried out a detailed kinetic study based on fluorescence quenching (both yield and lifetime), triplet yield enhancement, and triplet decay in cyclohexane and methanol. Ethyl iodide, added up to the concentration of  $0.8 \text{ M}$ , has been chosen as a representative external heavy-atom perturber for this purpose.

The following equations (Stern–Volmer or analogous) based on a kinetic model that assumes bimolecular quenching of polyene singlet and triplet by oxygen and ethyl iodide have been used.

$$\phi_{F,0} / \phi_F = \tau_{S,0} / \tau_S = 1 + k_q^S \tau_{S,0} [Q] \quad (5)$$

$$[\phi_T / \phi_{T,0} - 1]^{-1} = [\delta / \phi_{T,0} - 1]^{-1} \{1 + 1 / k_q^S \tau_{S,0} [Q]\} \quad (6)$$

$$\tau_T^{-1} = \tau_{T,0}^{-1} + k_q^T [Q] \quad (7)$$

(22) Sandros, K. *Acta Chem. Scand.* **1964**, *18*, 2355–2374.

(23) Murov, S. L. "Handbook of Photochemistry"; Marcel-Dekker: New York, 1973.

(24) Bensasson, R.; Land, E. J. *Trans. Faraday Soc.* **1971**, *67*, 1904–1915.

(25) Lutz, H.; Breheret, E.; Lindquist, L. *J. Phys. Chem.* **1973**, *77*, 1758–1762.

Table III. Kinetic Data Concerning Singlet Quenching and Triplet Yield Enhancement of Diphenylpolyenes by Oxygen and Ethyl Iodide

polyene	quencher	solvent	$k_q^S \tau_{S,0} (M^{-1})$		$k_q^S (M^{-1} s^{-1})^c$	$\delta/\phi_{T,0}^d$	$\delta^d$	$k_q^T (M^{-1} s^{-1})^e$
			from $\phi_F$ quenching <sup>a</sup>	from $\phi_T$ enhancement <sup>b</sup>				
DPB	oxygen	cyclohexane	36.0		$6.0 \times 10^{10}$			$5.3 \times 10^9$
	ethyl iodide	cyclohexane	3.8	4.0	$8.3 \times 10^9$	13	0.2	$8.1 \times 10^5$
DPH	oxygen	cyclohexane	256	189	$2.0 \times 10^{10}$	25	0.7	$4.4 \times 10^9$
		methanol	122	169	$2.3 \times 10^{10}$	36	0.5	$4.5 \times 10^9$
	ethyl iodide	cyclohexane	2.2	3.6	$1.7 \times 10^8$	21	0.6	$7.0 \times 10^4$
		methanol	1.0	1.5	$1.9 \times 10^8$	26	0.4	$5.2 \times 10^4$
DPO	oxygen	cyclohexane	125	96	$1.9 \times 10^{10}$	159	0.8	$4.8 \times 10^9$
		methanol	180	161	$2.6 \times 10^{10}$	119	0.6	$5.1 \times 10^9$
	ethyl iodide	cyclohexane	0.4	1.1	$6.0 \times 10^7$	26	0.1	$1.1 \times 10^5$
		methanol	0.5	0.9	$7.4 \times 10^7$	24	0.1	$1.3 \times 10^5$

<sup>a</sup>  $\pm 10\%$ . <sup>b</sup> Estimated error,  $\pm 30\%$ . <sup>c</sup> Calculated from  $k_q^S \tau_{S,0}$  data from  $\phi_F$  quenching (column 4). <sup>d</sup>  $\delta$  is the fraction of quenching events that result in triplet formation. <sup>e</sup>  $\pm 10\%$ .

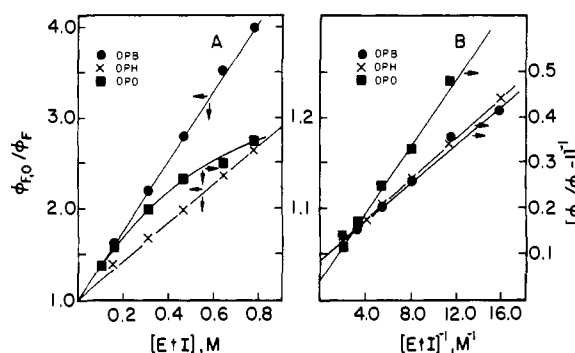


Figure 6. Typical plots based on eq 5 (A) and 6 (B), for DPB (●), DPH (×), and DPO (■) in cyclohexane with ethyl iodide as quencher.

In these equations, the "0" subscript refers to the absence of the quenchers, Q.  $\delta$  in eq 6 represents the fraction of the singlet quenching events that lead to the formation of triplet.

In nearly all the cases, both fluorescence lifetimes and quantum yields have been followed as functions of quencher concentrations. The fluorescence spectra determined in the presence of the highest concentrations of the quenchers show no difference with the ones determined in pure solvents, suggesting the absence of emission from exciplex or ground-state charge-transfer complexes. More importantly, the Stern-Volmer plots (eq 5) of a particular system based on lifetimes have similar characteristics in terms of linearity and slope ( $k_q^S \tau_{S,0}$ ) as the ones based on fluorescence yield. This strongly establishes the dynamic nature of the quenching processes involving the lowest excited singlet states.

Figure 6A shows some typical Stern-Volmer plots based on fluorescence yield measurements. Among all of the systems studied, only for DPO in methanol and cyclohexane, with EtI as the quencher, were the Stern-Volmer plots found to deviate from linearity at relatively high quencher concentrations (see Figure 6A). Possible causes of the deviation will be discussed in detail in the next section. Nevertheless,  $k_q^S \tau_{S,0}$  were determined for these systems from the slopes of the initial parts of the plots (that is, at relatively low [Q]).

Figures 6B and 7A show some plots based on eq 6, with ethyl iodide (in cyclohexane) and oxygen (in methanol) as quenchers, respectively. It should be noted that to measure triplet yield enhancements in the presence of oxygen, we have obtained the end-of-pulse  $\Delta OD_{TT}$  values by extrapolation from  $\Delta OD_{TT}$  values at longer times based on first-order triplet decay. This was necessary because the end-of-pulse  $\Delta OD_{TT}$ 's as read from the experimentally observed triplet decay profiles, were distorted because of contribution of fluorescence and singlet-singlet absorption. This distortion was particularly severe in the profiles in the presence of relatively high concentration of oxygen because of the shortening of the triplet lifetime by oxygen. As evident from eq 6, while the intercept-to-slope ratio from a plot in Figure 6B or 7A gives  $k_q^S \tau_{S,0}$ , the intercept alone gives an estimate of  $\delta/\phi_{T,0}$  and hence,  $\delta$  (using  $\phi_{T,0}$  values from Table II).

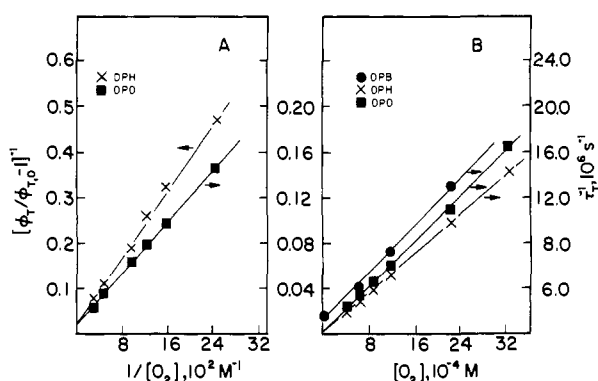


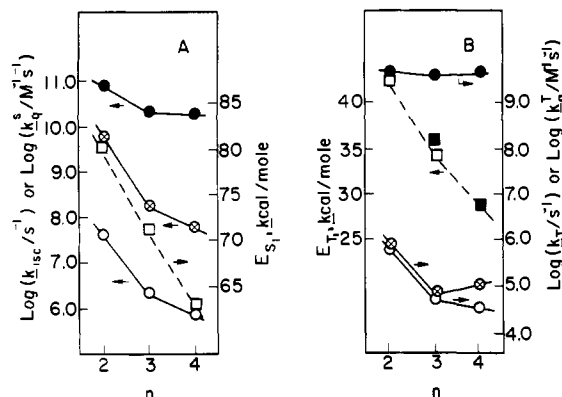
Figure 7. (A) Plots according to eq 6 for oxygen enhancement of triplet yield for DPH (×) and DPO (■) in methanol. (B) Typical plots based on eq 7 for oxygen quenching of DPB (●), DPH (×), and DPO (■) triplets in cyclohexane.

Figure 7B shows some typical plots, based on eq 7, concerning the effect of oxygen on polyene triplet lifetimes (in cyclohexane). The effect of EtI on triplet lifetimes was very small. Estimates of  $k_q^T$  with EtI as quencher were made from the triplet lifetimes observed at the highest [EtI] values.  $k_q^T$  values are in the range  $5 \times 10^4 - 8 \times 10^5 M^{-1} s^{-1}$ . On the other hand,  $k_q^T$  values for oxygen are higher by three to four orders of magnitude.

Kinetic data concerning  $k_q^S$ ,  $k_q^T$ , and  $\delta$  are summarized in Table III. It should be noted that the  $k_q^S \tau_{S,0}$  values obtained from the plots based on eq 6 are subject to large errors primarily because of uncertainty in the determination of small intercepts. For accurate determination of intercepts one can usually take more points at very high concentrations of the quenchers. However, this was not tried because at large  $\Delta OD_{TT}$ , namely at high [Q], this laser system and its associated data collection system have some small nonlinearities that could exacerbate the problem with small intercepts. In addition, in the case of EtI as quencher, complication arises from the absorption and screening of the laser light by the quencher itself (at high concentration). In view of all these, the fact that in most cases,  $k_q^S \tau_{S,0}$  values from triplet yield enhancement were found to be within 50% of  $k_q^S \tau_{S,0}$  values from fluorescence quenching is considered to be satisfactory.

## Discussion

(i) **Radiative Rate Constants of Singlet State.** The radiative decay of diphenylpolyenes exhibits one of the many anomalies<sup>9</sup> in the photophysics of these and related polyene compounds. It has been shown that if the photophysics of these compounds is interpreted in the usual model of competing first-order processes, the radiative lifetime is solvent and temperature dependent. The data reported here vary only in minor details from the data<sup>10</sup> that form the basis of the theories of temperature and solvent effects on the radiative lifetime.<sup>9,10,18-20</sup> Although we do not discuss the nature of the solvent effects in this work, it is important to note that for a given solvent neither oxygen nor ethyl iodide changes



**Figure 8.** (A) Polyene chain-length dependence of intersystem crossing rate (O), of rate constants for singlet quenching by oxygen (●) and EtI (⊙), and of lowest singlet energy (□) as obtained from the maxima of the highest energy vibronic peak in fluorescence spectra. (B) Polyene chain-length dependence of triplet decay rate constant (O), of rate constants for triplet quenching by oxygen (●) and EtI (⊙) and of lowest triplet energy (□, ■). The data in both A and B correspond to DPB ( $n = 2$ ), DPH ( $n = 3$ ), and DPO ( $n = 4$ ) in cyclohexane, except for the lowest triplet energy data which are taken from ref 13 (□, based on  $T_1 \leftarrow S_0$  absorption spectra in chloroform) and 12 (■, based on energy transfer kinetics in hexane).

the natural lifetime ( $\tau_{rad}$ ) calculated by eq 1. Thus in the quenching studies one does not have to be concerned about changing natural radiative lifetimes if the usual model of competing first-order decays holds.

(ii) **Triplet State and Its Nonradiative Decay.** A topic that has generated much work in the photophysics and photochemistry of the diphenylpolyenes has been the existence of the "phantom" or perpendicular triplets and singlets.<sup>4,5</sup> In order to understand the photophysics of the diphenylpolyenes, one must try to see the role of these states. The triplet-triplet absorption spectra give some indication of their role in the photophysics of diphenylpolyenes. The spectra are all relatively sharp and exhibit a well-resolved Franck-Condon progression. It is not unlike the structure observed for *trans*-stilbene at low temperature that has been assigned as a *trans* triplet.<sup>26</sup> The structure in the diphenylpolyene spectra makes it unlikely that there is an equilibrium between several triplet isomers, such as *trans* and perpendicular triplets as may be the case in stilbene,<sup>8</sup> unless the spectra of the two isomers are almost identical. The triplet-triplet spectra obtained from photosensitization (see Figure 5) were as structured as the spectra obtained by direct excitation. Thus it appears that the same triplet isomer is populated by direct excitation and by photosensitization. From the data presented here, it is difficult to determine the structure of this isomer.

In addition to the anomalies in the photophysics of diphenylpolyenes already in the literature,<sup>9</sup> they also appear to be anomalous in that their triplet-state lifetimes increase with increasing chain length. Stilbene with a relatively short-lived triplet ( $\tau_T \sim 50$  ns in various solvents)<sup>8</sup> falls well into this pattern. As the chain length increases, the energy difference, based on  $T_1 \leftarrow S_0$  absorption spectra<sup>13</sup> and energy-transfer data,<sup>12</sup> between the triplet state and the all-*trans* ground state decreases. Thus decreasing  $k_T$  correlates with decreasing  $E_T$  (See Figure 8B). However, other evidence<sup>13</sup> in low-temperature glasses, where the *trans* configuration is assumed to be frozen in place, showed that the diphenylpolyene triplet lifetimes decrease with increasing chain length. The low-temperature behavior follows the trends of the energy gap law found in aromatic hydrocarbons.<sup>27</sup> In aromatic hydrocarbons, when the energy between two states increases, the nonradiative rate constant for decay of the upper state usually decreases. In fact, an energy-gap law has been derived from a model using the Condon approximation for the electronic matrix

elements and using displaced harmonic potentials for the nuclear motion.<sup>28</sup>

It seems likely that the torsional motions in diphenylpolyenes are responsible in some manner for the apparent failure of the observed  $k_T$ 's at room temperature to obey the energy-gap law. This viewpoint is supported by the results<sup>13</sup> in the glass matrix (77 K) where the torsional motions are largely restricted to small harmonic motions and where the energy gap law does hold. There are several ways that the torsional motions can be instrumental in the nonradiative  $S_0 \leftarrow T_1$  process in such a way that the energy gap law will not be obeyed. First the harmonic and Condon approximations<sup>29</sup> do not hold for the torsional motions, and second, the torsional motions provide degrees of freedom in which the potential surfaces of  $T_1$  and  $S_0$  approach closely or even cross.<sup>30</sup> The details of these crossings are not yet known,<sup>29</sup> but the details of the crossing can have a large effect on the transition probability,  $P$ , as calculated by the Landau-Zener formula<sup>31</sup>

$$P = \exp\{-2\pi V^2 / \hbar v |F_2 - F_1|\} \quad (8)$$

where  $V$  is the matrix element of the interaction at the crossing point between the two zero-order states,  $v$  is the speed of the system at the point of crossing, and  $|F_2 - F_1|$  is the difference in the slopes of the two surfaces at the point of crossing. In addition to these aspects of the radiationless process, the torsional modes bring in the question of the role of an out-of-plane triplet. Even if the triplet states seen in the triplet-triplet absorption spectra are all-*trans* triplets, the out-of-plane triplets can still play roles either as states in a horizontal transition<sup>20</sup> or as providers of intensity for the Franck-Condon overlap.

(iii) **Oxygen and External Heavy-Atom Quenching of Singlet and Triplet States.** The quenching of diphenylpolyene triplet states by oxygen again provides a contrast with the quenching of aromatic hydrocarbons. Oxygen quenching of triplet states of aromatic hydrocarbons is usually thought of as energy transfer to  $O_2$  ( $^1\Delta$ ).<sup>32</sup> In ref 33, it was found that oxygen quenching of aromatic triplet states could be accounted for by an energy-transfer theory,<sup>34</sup> using Franck-Condon factors, that leads again to an energy-gap law that is analogous to the energy-gap law of radiationless transitions. It was found that the larger the energy gap the smaller was the rate constant for oxygen quenching. The behavior of the triplet states of the diphenylpolyenes appears to violate this rule. The rate constants,  $k_q^T$ , for quenching of triplets by oxygen, including the value of  $(8-9) \times 10^9 M^{-1} s^{-1}$  for stilbene in toluene,<sup>35</sup> decrease as the polyene chains increase in length except for a slight increase on going from DPH to DPO (see Figure 8B). The work<sup>36</sup> with oxygen quenching of  $\beta$ -carotene has already suggested that the triplet states of polyenes might not always follow an energy-transfer mechanism of oxygen quenching. The oxygen quenching of  $\beta$ -carotene made plausible the suggestion that oxygen quenching of this system involved a spin-exchange mechanism without the formation of  $O_2$  ( $^1\Delta$ ). Thus the failure of oxygen quenching of diphenylpolyene triplets to follow the energy gap

(28) Englman, R.; Jortner, J. *Mol. Phys.* **1970**, *18*, 145-164.

(29) Simple Hückel calculations show a dramatic change in the molecular orbitals as the conjugation is broken by rotating one of the central double bonds according to  $\beta \cos \theta$ , where  $\beta$  is the Hückel resonance integral and  $\theta$  is the angle of rotation. CNDO/M calculations, using QCPE Program No. 315 modified at Notre Dame, show that the lowest, perpendicular DPB triplet is 1.1 eV below the lowest, perpendicular singlet (ground state). This supports the idea that some triplet state crosses the lowest singlet state at some angle between the *trans* and the perpendicular configuration. Hug, G. L., unpublished results.

(30) For example, see: Orlandi, G.; Siebrand, W. *Chem. Phys. Lett.* **1975**, *30*, 352-354.

(31) Landau, L. D.; Lifshitz, E. M. "Quantum Mechanics"; Pergamon: London, 1958; pp 304-313. Zener, C. *Proc. R. Soc. London, Ser. A* **1932**, *137*, 696-702.

(32) Stevens, B.; Algar, B. E. *Ann. N.Y. Acad. Sci.* **1970**, *171*, 50-60.

(33) Patterson, L. K.; Porter, G.; Topp, M. R. *Chem. Phys. Lett.* **1970**, *7*, 612-614.

(34) Kawaoka, K.; Khan, A. U.; Kearns, D. R. *J. Chem. Phys.* **1967**, *46*, 1842-1853.

(35) Bonneau, R. *J. Photochem.* **1981**, *17*, 24.

(36) Saltiel, J.; Thomas, B. *Chem. Phys. Lett.* **1976**, *37*, 147-148.

(26) Görner, H.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1979**, *83*, 3107-3118.

(27) Siebrand, W. *J. Chem. Phys.* **1966**, *44*, 4055-4057.

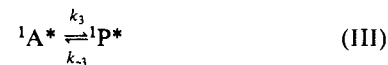
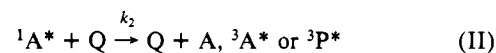
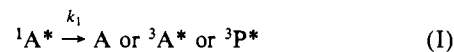
law may be an indication that the spin-exchange mechanism is competing with the energy-transfer mechanism.

The external heavy-atom quenching of the diphenylpolyene singlet states seems to be much less at variance with the corresponding behavior of aromatic hydrocarbons. In aromatic hydrocarbons, heavy atoms in solvents and solutes have been observed to quench the singlet states, affecting the radiative lifetimes and to a lesser extent intersystem crossing rates.<sup>37,38</sup> There has been much disagreement in the literature about the exact mechanism of the heavy-atom effect.<sup>38</sup> However, one theory<sup>39</sup> based on the spin-orbit coupling<sup>40</sup> mechanism, leads to a rationalization of an empirical correlation<sup>39</sup> between rate constants for intersystem crossing,  $k_{isc}$ , and rate constants for quenching by external heavy atoms,  $k_q^S$ . The empirical relationship showed that both rate constants increase together, and a log-log relationship holds between them. From Tables II and III and Figure 8A, the general trend of increasing rate constants of intersystem crossing with decreasing polyene chain length is seen to match the trend of increasing external heavy atom quenching. The current results show an external heavy-atom effect for diphenylpolyenes, which is in conflict with a recent study<sup>41</sup> that found no external heavy-atom effects in certain photoprocesses of diphenylpolyenes.

An attempt to make a similar correlation with triplet-state quenching by external heavy atoms was not so successful. In order to do this, the rate constant for intersystem crossing from the triplet state to the ground state was taken to be roughly measured by the reciprocal of the observed triplet lifetime. These numbers should not be taken to be precise because the lifetimes are so long that trace amounts of oxygen or impurities can affect the measured lifetime. Still, taken to indicate a trend, the results show that the trend of increasing  $k_q^T$  with increasing  $k_{isc}$  for  $S_0 \leftarrow T_1$  is obeyed on going from DPB to DPH, but is violated by the triplet state of DPO (Figure 8B). One possible reason for this deviation in the trend is that the mechanism of spin-orbit coupling, on which the correlation was based, is not the only mechanism involved. A recent theory<sup>38</sup> argues the importance of the polarizability of the molecules in the overall external heavy-atom effect. Since DPO is the most polarizable of the diphenylpolyenes considered, it may be that the polarizability mechanism becomes more important in it than in the shorter diphenylpolyenes.

The external heavy-atom quenching of DPO singlets showed an unusual nonlinear behavior that was not observed in any of the other quenching experiments in this work. The Stern-Volmer plot for the quenching of the DPO singlet by EtI (Figure 6A) is curved in a downward (sublinear) fashion. There have been many explanations given for supralinear behavior,<sup>42</sup> but very little attention has been paid to sublinear Stern-Volmer plots.<sup>43</sup> If the activity coefficient of the quencher varies considerably with the concentration, then a sublinear Stern-Volmer plot is likely. However, we rule out this possibility on the ground that DPB and DPH singlets do not show the sublinear behavior in the quenching by EtI (Figure 6A). The following model gives a rationalization for sublinear behavior in DPO singlets, with the assumption of

the involvement of perpendicular singlets. The existence of a stable phantom singlet in diphenylpolyenes has already been suggested by both theoretical<sup>20</sup> and experimental work.<sup>9</sup>



Using steady-state approximations for [ ${}^1A^*$ ] and [ ${}^1P^*$ ], where  $A^*$  is the excited trans DPO and  $P^*$  is the excited perpendicular DPO, one can derive

$$\phi_{F,0}/\phi_F = J^{-1}[k_1 + k_3 + k_2[Q] - k_{-3}k_3/(k_5 + k_{-3} + k_4[Q])] \quad (9)$$

where

$$J = k_1 + k_3 - k_{-3}k_3/(k_5 + k_{-3}) \quad (10)$$

In the approximation that  $k_4[Q]/(k_5 + k_{-3})$  is a small number, eq 9 reduces to

$$\phi_{F,0}/\phi_F = 1 + [Q]J^{-1}[k_2 + k_4k_{-3}k_3/(k_5 + k_{-3})^2] - [Q]^2J^{-1}k_4^2k_{-3}k_3/(k_5 + k_{-3})^3 + \dots \quad (11)$$

The model will lead to nonexponential decay in general. However, when the rates  $k_3$  and  $k_{-3}$  are very fast compared to  $k_1$ , then only one exponential will be observed. The fluorescence decay of DPO quenched by EtI was exponential. The behavior is consistent with a fast equilibrium between singlet trans and singlet perpendicular DPO. When  $k_3$  becomes small compared to  $k_2$  and  $k_1$  (as may be the case with DPB and DPH), eq 11 reduces to the usual Stern-Volmer result of eq 5.

An interesting observation concerning the efficiency ( $\delta$ ) of singlet quenching processes in generating triplets can be made on the basis of  $\phi_{T,0}$  and  $\delta/\phi_{T,0}$  data; see tables II and III, respectively. Combining the two sets of data, we obtain  $\delta$  values ranging from 0.1 to 0.8 (Table III, column 8). The case where  $\delta$  is the highest ( $\sim 0.8$ ) is the quenching of DPO by oxygen in cyclohexane. In view of large errors associated with the determination of  $\phi_{T,0}$  and particularly  $\delta/\phi_{T,0}$ , this value, 0.8, should not be considered different from unity. However, the preponderance of  $\delta$  values much smaller than unity indicates strongly that the quenching of polyene singlets by  $O_2$  or EtI shows up in terms of not only enhanced intersystem crossing but also enhanced internal conversion. There is no reason to exclude a direct enhancement of the internal conversion process in this case, but the efficiency of the quenchers for intersystem crossing processes suggests that the enhanced internal conversion may be due to a two-step process, involving an intersystem crossing in one (or both) step(s) of the process. Again the perpendicular triplets would be likely candidates for intermediate states in this process because of the ease with which they undergo intersystem crossing to the ground state.

**Acknowledgment.** The authors are grateful to Professor S. P. McGlynn, Dr. L. K. Patterson, and Dr. G. N. R. Tripathi for valuable comments and discussions.

**Registry No.** DPB, 886-65-7; DPH, 1720-32-7; DPO, 3029-40-1; A, 120-12-7.

(37) Kasha, M. *J. Chem. Phys.* **1952**, *20*, 71-74.

(38) Streck, W.; Wierzchaczewski, M. *Chem. Phys.* **1981**, *58*, 185-193, and references therein.

(39) Patterson, L. K.; Rzed, S. *J. Chem. Phys. Lett.* **1975**, *31*, 254-256.

(40) McGlynn, S. P.; Sunseri, R.; Christodouleas, N. *J. Chem. Phys.* **1962**, *37*, 1818-1824.

(41) Song, P.-S.; Chae, Q.; Fujita, M.; Baba, H. *J. Am. Chem. Soc.* **1976**, *98*, 819-824.

(42) Baird, J. K.; Escott, S. P. *J. Chem. Phys.* **1981**, *74*, 6993-6995, and references therein.

(43) Fang, T.-S.; Brown, R. E.; Kwan, C. L.; Singer, L. A. *J. Phys. Chem.* **1978**, *82*, 2489-2496. Brown, R. E.; Fang, T.-S.; Kwan, C. L.; Singer, L. A. *Chem. Phys. Lett.* **1977**, *51*, 526-529.