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# The Photophysics and Photochemistry of $\alpha,\omega$-Diphenylpolyene Singlet States

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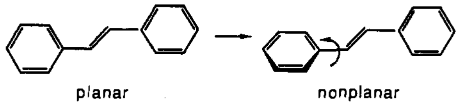
## I. Introduction

The electronic structure and spectroscopy of linear polyenes were reviewed by Hudson and Kohler in 1974 and again in 1982.[1,2] Although some parallels exist between the photophysical character of linear polyenes and their diphenyl analogues, there has been no review of the solution photophysics of the family of diphenylpolyene chromophores. In two reviews of the cis–trans isomerization of olefins Saltiel and co-workers presented thorough treatments of what was known about stilbene photochemistry at the time.[3,4] Stilbene has long served as a prototype by which the isomerization of other olefins can be understood. However, there are important differences between the photophysics and photochemistry of stilbene and those of the longer diphenylpolyenes. It is the goal of this paper to highlight those similarities and differences in a comprehensive review of what is known about diphenylpolyene photophysics and their photochemical properties in solution. Given that fluorescence and isomerization via the singlet state are the principal paths of deexcitation for diphenylpolyenes, this review focuses on the singlet-state chemistry of this family of chromophores. This paper review the efforts of the photochemists, chemical physicists, and theoreticians who are attempting to sort out the complex solution behavior of diphenylpolyenes. It is anticipated that this paper will serve as a resource for those working to understand diphenylpolyene photophysics and photochemistry as well as for those who wish to use diphenylpolyenes and their derivative chromophores as probes of microheterogeneous media.

*trans*-Diphenylpolyenes (see Figure 1) are highly symmetric molecules that transform under the $C_{2h}$ point group. Their ground states are characterized by $A_g$ symmetry while their excited singlet $\pi,\pi^*$ states can have either $A_g^-$ or $B_u^+$ symmetry. Allowed ${}^1B_u{}^*$–${}^1A_g$ transitions occur through absorption or emission of a single photon. Population of ${}^1A_g{}^*$ states by direct irradiation (a formally forbidden process) is limited by a very weak oscillator strength but can be achieved by two-photon excitation. Upon formation of an ${}^1A_g$ excited state, forbidden ${}^1A_g{}^* \rightarrow {}^1A_g$ emission can occur via Herzberg–Teller vibronic coupling of the ${}^1A_g{}^*$ and ${}^1B_u{}^*$ states; the transition becomes partially allowed through a reduction in symmetry and concurrent relaxation of the symmetry requirements. Consequently, most discussions of the photophysics of compounds in this family center on the relationship between $S_0$ and the first two excited singlet states, $S_1$ and $S_2$. The singlet-state photochemistry of $\alpha,\omega$-diphenylpolyenes is governed by several factors: the order of symmetry assignments of the two lowest excited singlet state levels, the electronic $S_2$–$S_1$ energy gap, the $S_2$–$S_1$ interstate mixing, and the isomerization dynamics. A schematic representation of the effects of these properties on the photophysics of diphenylpolyenes is shown in Figure 2. Due to the large $S_2$–$S_1$ energy gap in the longer polyenes, the relative contributions of the level order and excited-state mixing are important to the photophysics of only the first three diphenylpolyene molecules in the series. The solution photochemistry of *trans*-stilbene (tS), diphenylbutadiene (DPB), and diphenylhexatriene (DPH) will be reviewed in detail. What is known about the effects of solvents and substituents on the photoreactivity of these molecules will also be discussed. The photophysics of diphenyloctatetraene (DPO) and higher order polymers will be discussed more generally.

## II. Ground-State Structure

Diphenylpolyenes are nominally planar molecules with substantial $\pi$-electron resonance stabilization. However, the ability for distortion from planarity and single-bond rotamerism is currently under experimental and theoretical investigation. Thermally activated rotation about the phenyl–$\alpha$-carbon single bond reduces the extent to which $\pi$ bonding is delocalized within a diphenylpolyene chromophore. A detailed analysis of



the vibrational modes of *trans*-stilbene fluorescence in a supersonic jet performed by Syage et al. indicates that there is a significant change in the phenyl–$\alpha$-carbon force constant upon excitation.[5] More recently, Zwier

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Mary Tedd Allen was born in Clinton, NY, in 1962. She attended Mount Holyoke College where she received a B.A. in chemistry, cum laude, in 1984. Her graduate work studying the fluorescence behavior of diphenylpolyene chromophores in solutions and organized assemblies was carried out at the University of Rochester under the direction of Professor David G. Whitten. After receiving a Ph.D. chemistry in 1988, Mary Tedd accepted a postdoctoral research position in the Department of Dermatology at the Harvard Medical School where she is currently studying the mechanism of drug phototoxicity with Dr. Irene Kochevar. In addition to her interests in photochemical and photobiological research, Mary Tedd is an avid horsewoman and enjoys backpacking.

David G. Whitten was born in Washington, DC, in 1938 and earned his Ph.D. at the Johns Hopkins University in 1963. After 2 years of military service carrying out research on loan to NASA at the Jet Propulsion Lab in Pasadena, he spent a year of postdoctoral study with George Hammond at Caltech. He joined the faculty of the University of North Carolina at Chapel Hill in 1966 and rose through the ranks to M. A. Smith Professor in 1980. He moved to the University of Rochester in 1983 and is currently C. E. K. Mees Professor and Department Chair. At Chapel Hill and Rochester he and his co-workers have carried out studies of thermal and photochemical reactions in solution, at interfaces, and in microheterogeneous media. He has served on educational advisory boards of the *Journal of the American Chemical Society* and *The Journal of Physical Chemistry* and as an organizer of several scientific conferences, including the Xth IUPAC Photochemistry Symposium. He was President of the Interamerican Photochemical Society from 1983 to 1986. Outside of the laboratory he attempts to keep up with his wife and son in road races and other running activities.

and co-workers determined from studies of *p*-methyl-[6] and $\alpha$-deuteriostilbene[7] derivatives that both the ground and first excited singlet states of *trans*-stilbene prefer a planar geometry. MNDO calculations by Rulliere et al. suggest that in the equilibrium geometry of ground-state diphenylbutadiene the phenyl rings are twisted 75° out of the polyene plane.[8]

A 180° rotation about a single bond that separates two double bonds produces s-cis rotamers in polyenes. One such conformer exists for diphenylbutadiene, while there are two possible s-cis rotamers of diphenylhexatriene: a single s-cis structure and one in which both single bonds have the cis conformation. Preliminary results obtained by Saltiel and co-workers, using the technique of principal component analysis,[9] indicate that at room temperature approximately 25% of the fluorescence area of *trans,trans*-diphenylbutadiene spectra arises from the s-cis conformation.[10] No analysis of the extent of rotamerism in diphenylhexatriene is known at this time. Clearly, the details concerning the ground-state geometry of diphenylpolyenes have not been established unequivocally. This may be due in

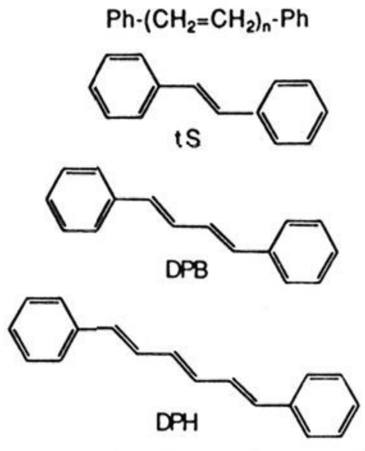


**Figure 1.** *trans*-Diphenylpolyene ($n$ = 1–3) structures.

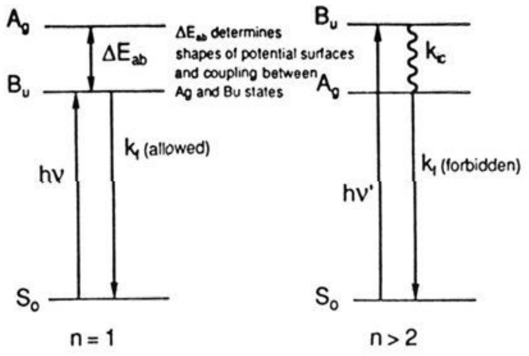


**Figure 2.** Effects of level order and energy gap on photophysics of diphenylpolyenes.

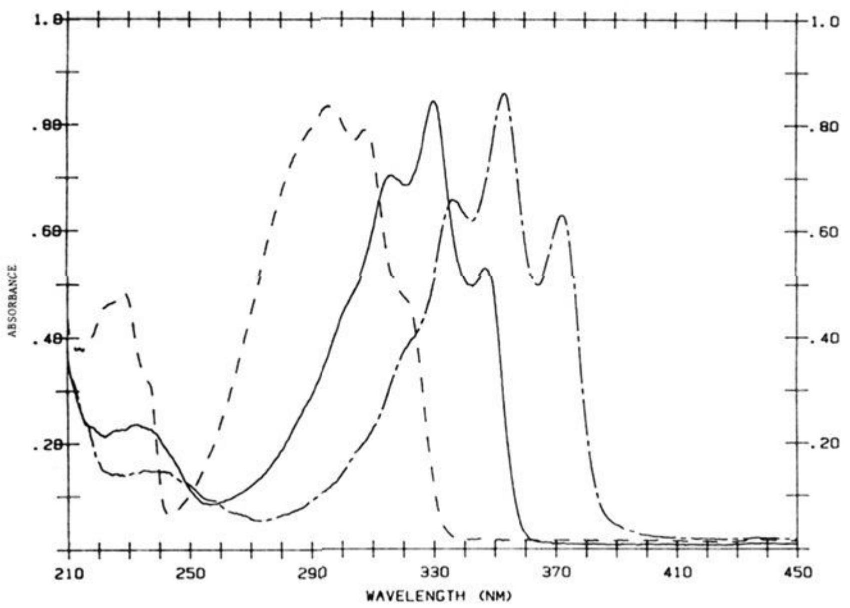
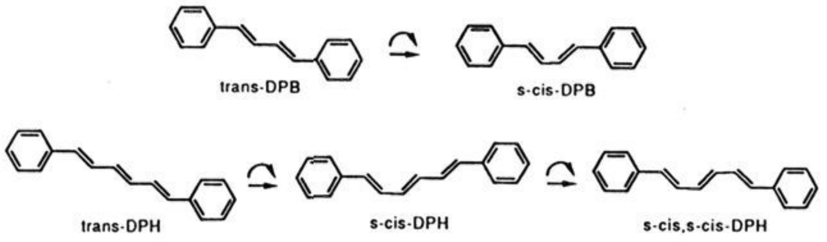


**Figure 3.** Diphenylpolyene absorption spectra: (---) tS, (—) DPB, and (---) DPH.



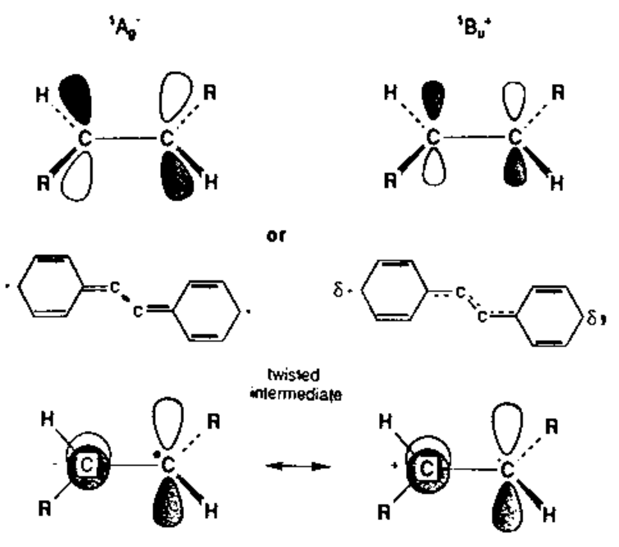


**Figure 4.** Orbital representations of $^1A_g^-$ and $^1B_u^+$ and twisted polyene states.

part to the shallowness of the potential wells attributed to different conformations.[11]

However, the equilibrium governing the formation of geometrical (double bond) isomers of diphenylpolyenes is better understood. The ground-state potential energy surface of a polyene has a maximum at a C=C rotation angle of 90°. The barrier to thermal isomerization requires 48 kcal/mol for *trans*-stilbene and ~43 kcal/mol for *cis*-stilbene; steric repulsion in the cis isomer leads to a nonplanar ground state and a 4.6 kcal/mol loss of resonance stabilization relative to that of the trans isomer.[12] As the length of the polyene chain increases, there is an increase in the resonance delocalization of the $\pi$ electrons. This reduces the energy of the $\pi,\pi^*$ transition. Upon increasing the number of double bonds in a diphenylpolyene, the corresponding absorption spectrum becomes progressively red shifted relative to that of *trans*-stilbene (see Figure 3). Similar vibrational structure is exhibited in the absorption envelopes of the first three molecules in the diphenylpolyene series of chromophores.

## *III. Excited Electronic States*

To facilitate a discussion of diphenylpolyene photophysics, a brief description of the nature of the $A_g$ and $B_u$ electronic states is necessary. $A_g$ is the classification assigned to a highly symmetric state. From a valence bond standpoint, $A_g^-$ is a "covalent" state in which the electrons are correlated (tend to avoid one another). A $B_u^+$ state has more "ionic" character due to a lower electron correlation; the electrons are less likely to avoid one another, resulting in an increased local electron density and a higher degree of charge separation. Excitation energy in an $A_g^-$ state is localized in the polyene moiety of diphenylpolyenes and is associated with a greater degree of bond order reversal than that of a $B_u^+$ state in which the excitation energy is more evenly distributed throughout the molecule. Although planar $B_u^+$ states have partial charge associated with them and $A_g^-$ states do not, considerable separation of charge may develop in an $A_g^-$ state upon twisting to a perpendicular geometry (see Figure 4).[13] Salem has proposed that the development of charge as a function of twist angle in olefins containing carbons of different electronegativities causes a rapid increase in dipole moment as the perpendicular geometry is approached.[14] This "sudden polarization effect" has been refuted on theoretical grounds by Malrieu et al., who maintained that the singlet-state isomerizations of polyenes and the triplet-state photoisomerization of stilbene involve nonionic intermediates.[15,16] Additional theoretical and experimental work is needed to establish whether the perpendicular excited singlet states of diphenylpolyenes are best described as nonionic or zwitterionic states.

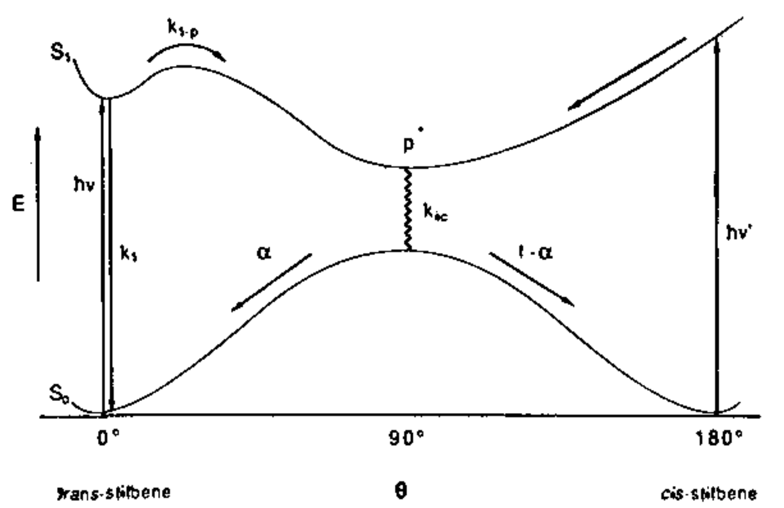


**Figure 5.** Potential energy surfaces of stilbene ground and excited states as a function of the angle of C=C rotation.

### A. *trans*-Stilbene (tS)

1,2-Diphenylethylene, known as stilbene, is both the simplest member of the diphenylpolyene series ($n = 1$) and the most extensively studied. The comprehensive review of olefin isomerization by Saltiel and Charlton remains an important resource for anyone interested in stilbene photochemistry and substituent effects in condensed media.[4] However, much work has been published recently regarding experimental and theoretical treatments of stilbene isomerization in the vapor phase. Although the factors governing photoisomerization under collision-free conditions are somewhat different than those in solution, these studies provide detailed information about the nature of the excited-state surface. It is not within the scope of this paper to review that work and the interested reader is referred to the publications of Hochstrasser and others.[17-20]

The excited singlet state behavior of tS is governed by two processes. Fluorescence from $S_1$ ($B_u$ symmetry) competes effectively with the activated twisting of stilbene into a perpendicular geometry (see Figure 5). This $^1p^*$ state decays within ~5 ps to an energy maximum on the ground-state potential energy surface.[21] From there, an exothermic 90° rotation produces either the cis or the trans isomer. The "phantom" $^1p^*$ state has been observed by Doany et al. in a picosecond spectroscopic study of 1,1′-biindanylidene, a "stiff" stilbene derivative.[22] A small barrier to forming the twisted $^1p^*$ state has been attributed to a crossing of the $^1B_u^*$ surface and the second excited-state surface ($A_g$ symmetry) as the molecule rotates out of its planar conformation.[23] However, it has not been established whether this barrier is indeed attributable to a nonadiabatic surface crossing or to a barrier in the lowest excited $^1A_g^*$ state.[24] On the basis of Arrhenius data extrapolated to zero viscosity, Saltiel and D'Agostino determined that the inherent thermal barrier to excited-state rotation requires 2.7–3.0 kcal/mol in nonpolar solvents.[25] Subsequent molecular beam measurements of the barrier height under collision-free conditions have yielded values from 900 to 1200 cm$^{-1}$ (2.6–3.5 kcal/mol).[26,27] Calculations by Landanyi and Evans indicate that 1200 $cm^{-1}$ provides an upper limit to the barrier height for tS in room-temperature hydrocarbon solutions.[28]

## B. Diphenylbutadiene (DPB)

The $^1A_g$* state is stabilized relative to the $^1B_u$* state with increasing polyene chain length. For diphenylpolyenes in which $n \geq 3$ (DPH and longer), the $^1A_g$* state is lower in energy than the $^1B_u$* state; there is a reversal in the $S_1$ and $S_2$ symmetry assignments. In DPB, the $^1A_g$*–$^1B_u$* energy gap in solution is small and the actual order of the two lowest excited states has not been resolved adequately. Fleming and co-workers have observed that the photophysical properties of DPB are more like those of tS than DPH and that the radiative rate of DPB is relatively insensitive to the solvent, indicating that the emitting state is not significantly different in character from the absorbing state, $^1B_u$*.[29,30] However, studies in the gas phase have shown that the $^1A_g$* state is lowest by 1050–1150 $cm^{-1}$.[31,32] Bennett and Birge determined by two-photon spectroscopy that in an EPA solvent glass the system origin of the $^1A_g$* state lies 130 $cm^{-1}$ below the $^1B_u$* state.[33] Their PPP–SCF–MO–Cl calculations indicate that the $^1B_u$*–$^1A_g$ excitation is ~54% localized in the polyene chain with an oscillator strength of 1.07. The $^1A_g$*–$^1A_g$ two-photon transition was determined to be 55% localized in the phenyl moieties.

The small energy gap between the two lowest singlet states gives rise to efficient coupling between the states. A normal mode analysis of DPB indicates that the $^1A_g^* \rightarrow {}^1A_g$ forbidden emission derives oscillator strength from a low-frequency $b_u$ inplane bending mode.[34] The $^1A_g$*–$^1B_u$* coupling has been studied by monitoring the fluorescence efficiency of DPB in a supersonic jet at various levels of excess vibrational energy, $E_v$. Amirav et al. found the rate of isomerization showed no mode selectivity for $E_v$ = 0–6660 $cm^{-1}$.[35] By analogy to the fluorescence behavior of a "stiff" DPB molecule, 1,5-diphenyl-2,3,4,6,7,8-hexahydronaphthalene (HHN), Yee et al. determined that the excited state of DPB is nearly planar.[36] This is supported by the calculations of Rulliere et al. which indicate that the angle between the phenyl and polyene moieties in DPB is reduced from 75° in the ground state to only 30° in the excited state.[8]

Although the $S_2$–$S_1$ energy gap in DPB is small, the barrier to excited-state rotation in DPB appears to be slightly larger than it is in tS. The $E_{act}$ has been estimated from isoviscosity studies in a series of linear alkanes to be 4.7 kcal/mol in DPB.[30] This is somewhat greater than the value of 3.1 kcal/mol determined for an isolated DPB molecule from the supersonic jet experiments of Shepanski et al.[31] This difference between the internal barrier calculated from measurements in solutions of several different viscosities and that obtained from the vapor phase may be attributable to differential state ordering; while the $^1B_u$ state appears to be lower in energy in solution, the $^1A_g$ state was reported to be lower in energy in the isolated molecule experiment. However, an internal barrier to excited-state rotation of 3–4 kcal/mol for a molecule whose $S_1$ and $S_2$ states are very nearly isoenergetic indicates that some phenomenon other than, or in addition to, the avoided crossing between two surfaces plays a role in determining the barrier height in diphenylpolyenes containing two or more C=C bonds. In fact, the agreement between the heights of the internal barriers in tS and DPB may be fortuitous since the origin of the barrier in DPB cannot be attributable to an avoided crossing of the same magnitude as in tS. To complicate matters, calculations of the barrier height for DPB are based on Arrhenius plots of fluorescence yield data in a manner analogous to that used for *trans*-stilbene. Unlike tS, though, a significant fraction of the excited *trans*-DPB molecules may undergo nonrotational radiationless decay. Coupled with the fact that the temperature dependence of the isomerization quantum yield has not been determined, the barrier estimates for DPB may, therefore, be inaccurate.

## C. Diphenylhexatriene (DPH)

Diphenylhexatriene is the first chromophore in the diphenylpolyene series in which it has been clearly established that the $S_1$ surface is characterized by $A_g$ symmetry. Early fluorescence studies by Cehelnik et al. indicated unusual solvent effects on DPH emission.[37,38] Birks was the first to suggest that the seemingly anomalous fluorescence behavior of DPH, such as the lack of a mirror image relationship between the absorption and emission spectra and its relatively long lifetime, could be attributed to a low-lying $A_g$ state coupled to $^1B_u$*.[39-41] Theoretical and experimental investigations have since culminated in a description of DPH photophysics that is generally accepted. Absorption in DPH involves an allowed $S_2$–$S_0$ transition. This is followed by rapid internal conversion to $S_1$, from which either fluorescence or rotation can occur. $S_1 \rightarrow S_0$ emission is relatively slow due to the small transition moment ($f < 1$) of this symmetry-forbidden transition. This results in a fluorescence lifetime (~13 ns in HC solvents) that is significantly longer than that calculated from the integrated absorption intensity (1.56 ns).[41,42]

Current studies of DPH have focused on measuring the energy separation between $S_1$ and $S_2$, $\Delta E_{a,b}$, and determining the effect of the gap size on such phenomena as excited-state coupling and isomerization dynamics. Measurements of the fluorescence excitation and emission of DPH in a supersonic free jet have placed the doubly excited $^1A_g$* state 25 742 $cm^{-1}$ above the ground state.[43-44] The second excited singlet state, $S_2$, was determined to be 3400 $cm^{-1}$ above $S_1$. Itoh ahd Kohler estimate that the $^1A_g$* state lies ~1000 $cm^{-1}$, below the $^1B_u$* state for DPH in hexane.[45] In a rigid EPA matrix, $\Delta E_{a,b}$ was determined by two-photon spectroscopy to be 990 $cm^{-1}$.[46] Simple PPP–SCF–Cl calculations (including both single and double electronic excitations) have proven inadequate for modeling the spectroscopic properties of diphenylpolyenes in which $n \geq 2$; estimations of both the order of energy levels and the magnitude of $\Delta E_{a,b}$ were far from the observed properties of DPB, DPH, and longer polyenes.[47] However, extension of the configuration interaction term to include triple and quadruple excitations markedly improves the agreement between theoretical predictions and experimentally observable transitions in polyenes. Using this method, Taven and Schulten calculated that $^1A_g$* lies 800 $cm^{-1}$ below the $^1B_u$* for DPH in hexane.[48] According to Birge et al., the lowest excited $^1A_g$* state in DPH has 70% polyene-like character.[49] The relative positions and energies of the first two excited singlet

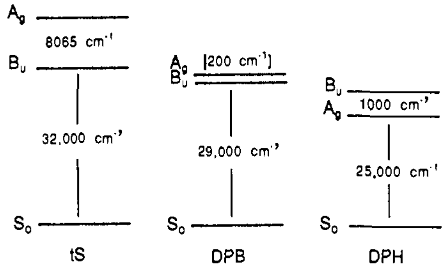


**Figure 6.** Potential energies of $^1A_g{}^{**}$ and $^1B_u{}^*$ states in tS, DPB, and DPH.

states in tS, DPB, and DPH are shown for hydrocarbon solutions in Figure 6.

## D. Diphenyloctatetraene (DPO) and Higher Polyenes

Hudson and Kohler reported the first observation of a low-lying weak transition in DPO in 1972.[50] They reported an oscillator strength of 0.06 for that transition. The corresponding value for the allowed $^1B_u{}^*$–$^1A_g{}^*$ transition is ~1.5. The assignment of $A_g$ symmetry to the lowest excited state of DPO was supported by PPP calculations.[51] It was shown that the intensity of the low-lying weak transition in polyenes becomes progressively weaker as the length of the polyene chain increases.[52] Fang et al. confirmed the assignment of $S_1$ to an $^1A_g{}^*$ state by two-photon excitation experiments and estimated $\Delta E_{a,b}$ to be ~2000 cm$^{-1}$ for DPO in EPA at 77 K.[53] The $^1B_u{}^*$–$^1A_g{}^*$ energy gap for DPO in octane was reported as 1520 cm$^{-1}$.[54] Although the intensities are smaller for DPO than for DPH, this relatively large energy gap does not preclude either emission from $^1B_u{}^*$ directly or thermal equilibration between $S_1$ and $S_2$.[45,55–57]

The nature of the coupling between the first two excited singlet states in diphenylpolyenes has been explored by many research groups. Ikeyama and Azumi propose that the anomalous fluorescence behavior of DPO is only partially accounted for by Herzberg–Teller vibronic coupling of $S_1$ and $S_2$ and that the molecule may be distorted somewhat from the symmetry of the $C_{2h}$ point group.[58] A more accurate treatment of the coupling, involving direct diagonalization of the appropriate Hamiltonian matrix, has since been proposed.[59] Studies of the effects of solvents and substituents on the fluorescence and isomerization behavior of diphenylpolyenes complement such calculations and, as discussed in the following sections, have revealed much about the nature of barriers, curve crossing, and isomerization dynamics.

## *IV. Fluorescence*

The emission spectra of the first three *trans*-diphenylpolyenes in hydrocarbon solvents are overlaid in Figure 7. As observed in the absorption spectra, the vibrational structure among tS, DPB, and DPH is similar. The most pronounced difference occurs in the fluorescence spectrum of DPH, which contains a low-intensity band at 380 nm, on the blue edge (high-energy side) of the emission. This transition has been attributed to delayed emission from $S_2$ due to thermal repopulation of the $^1B_u{}^*$ state.[45,60] Table I lists the lifetimes obtained from the integrated absorption intensities of these chromophores as well as the natural radiative lifetime calculated from the observed lifetime and quantum yield for each in a hydrocarbon solution. As discussed above, fluorescence originates from the lowest excited singlet state in diphenylpolyenes. For tS and DPB in hydrocarbon solvents, allowed emission occurs from a low-lying $^1B_u{}^*$ state. The rates of fluorescence ($k_f$), determined from fluorescence quantum yield and lifetime measurements ($k_f = \Phi_f/\tau_f$), 5.9 × 10$^8$ s$^{-1}$ for tS and 7.4 × 10$^8$ s$^{-1}$ for DPB, are reasonable for allowed transitions. In longer diphenylpolyenes the lowest excited singlet state is characterized by $A_g$ symmetry and the corresponding fluorescence transition is forbidden.[62] The corresponding fluorescence rate for DPH, 5.0 × 10$^7$ s$^{-1}$, indicates that emission in DPH is an order of magnitude slower than the emission of *trans*-stilbene. This is a reflection of the weakly allowed nature of the transition governing fluorescence in DPH. Due to a larger $S_1$–$S_2$ energy gap, emission in DPO is more forbidden and the rate of fluorescence is even slower; $k_f$ = 1.5 × 10$^7$ s$^{-1}$.

The differences between the photophysics of the first four diphenylpolyene chromophores are also reflected in their fluorescence lifetimes. Table I shows three different lifetimes for each molecule: $\tau_{rad}$, the radiative lifetime that is calculated from the absorption spectrum, $\tau_f$, the observed fluorescence lifetime, and $\tau_0$, the natural or intrinsic lifetime calculated as the inverse of the fluorescence rate, $1/k_f$. The radiative lifetimes derived from the absorption spectra do not vary much among the chromophores, reflecting only the similarity between the excitation transitions and *not* the differences in the

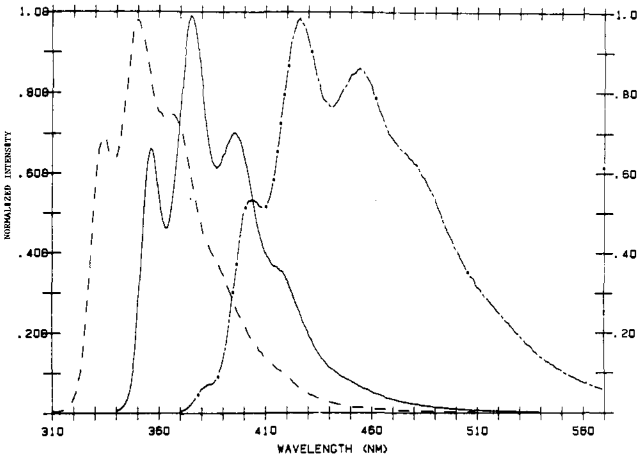


**Figure 7.** Diphenylpolyene fluorescence spectra: (---) tS, (—) DPB, and (---) DPH.

**TABLE I. Radiative Rates, Quantum Yields, and Lifetimes[a] of Diphenylpolyene ($n$ = 1–4) Fluorescence in Hydrocarbon Solvents[b]**

| chromophore | $\tau_{rad}$[c] | $\tau_f$[d] | $\Phi_f$ | $k_f$[e] | $\tau_0$[f] |
|---|---|---|---|---|---|
| tS | 1.7 | ~0.085 | 0.05 | 5.9 × 10$^8$ | 1.7 |
| DPB | 1.5 | 0570 | 0.42 | 7.4 × 10$^8$ | 1.4 |
| DPH | 1.5 | 13.3 | 0.67 | 5.0 × 10$^7$ | 19.9 |
| DPO | 2.3 | 6.7 | 0.10 | 1.5 × 10$^7$ | 67 |

[a] All lifetimes are reported in nanoseconds. [b] Solvents are CH (DPB and DPO), MCH (DPH), and MCH/IH (tS). [c] $\tau_{rad}$ is the pure radiative lifetime calculated from the integrated absorption intensity according to a modified Strickler–Berg relationship.[42] [d] Taken from ref 4 and 61 (tS), 30 (DPB), and 41 (DPH and DPO). [e] The radiative rate, $k_f = \Phi_f/\tau_f$. [f] The intrinsic fluorescence lifetime, $\tau_0 = 1/k_f$.

emission. The observed lifetimes increase from about 85 ps in tS to 570 ps in DPB to 13.3 ns in DPH. This parallels the increase in fluorescence quantum yields observed from tS to DPH ($\Phi_f$ = 0.05, 0.42, and 0.67). In contrast, there is a decrease in both the quantum yield (0.10) and lifetime (6.7 ns) of DPO. This may be attributable to effective competition from other deactivation pathways such as internal conversion and intersystem crossing due to the slow rate of the forbidden emission. This is emphasized by the long intrinsic fluorescence lifetime, $\tau_0$ = 67 ns, obtained as the inverse of the measured rate. Although emission is forbidden in both DPH and DPO, coupling between $S_1$ and $S_2$ causes the fluorescence in DPH to remain on a time scale that is competitive with nonradiative processes. In DPO and longer polyenes, the relationship between fluorescence and nonradiative decay is markedly different from that in the shorter members of the diphenylpolyene series. The use of different solvent properties to investigate that relationship in diphenylpolyenes is discussed below.

## V. Medium Effects

The nature of the $^1A_g^-$ and $^1B_u^+$ excited states has important consequences for diphenylpolyene photophysics and photochemistry. Solvent properties such as polarity and polarizability can change the relative positions of the $^1A_g{}^*$ and $^1B_u{}^*$ states. This not only alters fluorescence properties but can also change the shape of the $S_1$ potential surface, influencing the isomerization dynamics. Other solvent properties such as solvent viscosity do not affect the energies of the $^1A_g{}^*$ and $^1B_u{}^*$ states but can still change the shape of the potential surface on which isomerization occurs. Both solvent pressure and temperature influence diphenylpolyene photochemistry in more than one way. Prior to a discussion of the complex effects of solvents on diphenylpolyene photochemistry, the influences of each of these solvent parameters on the $^1A_g^-$ and $^1B_u^+$ states are outlined:

1. *Polarity.* Due to its "covalent" nature, an $A_g^-$ state is relatively insensitive to the solvent polarity while an "ionic" $B_u^+$ state is stabilized somewhat by polar solvents. In diphenylpolyenes the relative stabilization of the $^1B_u{}^*$ state by polar solvents results in slightly red shifted absorption spectra. In contrast, if the twisted form of $^1A_g{}^*$ involves charge separation, it should be strongly stabilized by polar solvents.

2. *Polarizability.* The solvent polarizability, $\alpha_s$, is a function of the refractive index, $n$, of the medium; $\alpha_s = (n^2 - 1)/(n^2 + 2)$. Although a polarizable solvent does not stabilize formal charges, it can compensate for the buildup of electron density. Therefore, a $^1B_u^+$ state in which electron density is partially localized is stabilized by increasing $\alpha_s$ while a highly correlated $^1A_g^-$ state is insensitive to changes in $\alpha_s$. This parallels the effect of solvent polarity except that a zwitterionic perpendicular $^1A_g{}^*$ state is not stabilized by increasing the solvent polarizability to the extent that it is stabilized by a polar solvent.

3. *Viscosity.* Solvent viscosity does not affect the $^1A_g^-$ and $^1B_u^+$ states themselves but can have a pronounced effect on diphenylpolyene photochemistry depending upon the mechanism(s) of nonradiative decay; C–C bond rotation is inhibited in some polyenes by the friction imposed by viscous solvents. Increasing the solvent viscosity can, therefore, lead to changes in the fluorescence and isomerization behavior of diphenylpolyenes.

4. *Pressure.* Moderately high pressures can be imposed on a solution to induce viscosity changes in the solvent without changing either the solvent or its temperature.[63] However, increasing the solvent pressure increases its density (refractive index), which leads to an increase in the solvent polarizability. Thus, both the solvent viscosity and polarizability change as the solvent pressure changes.

5. *Temperature.* In addition to its kinetic role in diphenylpolyene photochemistry, solvent temperature has an indirect effect upon the relative energies of the $A_g$ and $B_u$ excited states. Increasing the temperature of a solvent causes a small decrease in its polarizability (lower solvent density); the $^1B_u{}^*$ state is destabilized slightly while the energy of the $^1A_g{}^*$ state remains unchanged. Changes in solvent viscosity with temperature must also be accounted for in diphenylpolyene photochemistry.

As noted, increases in the solvent viscosity can lead to changes in diphenylpolyene photochemistry due to the large-amplitude motion associated with isomerization. In *trans*-stilbene, there is a viscosity-added component to the barrier to excited-state rotation. The observed barrier is the sum of its inherent component and one that is induced by viscosity: $E_{obs} = E_t + E_v$. The barrier height increases from 3.5 kcal/mol in cyclohexane/isohexane to 9.7 kcal/mol in glycerol.[25] This allows the rate of twisting in the excited state to be enhanced, at the expense of fluorescence efficiency, by either increasing the temperature or decreasing the viscosity. At 25 °C, the fluorescence quantum yield, $\Phi_f$, is 0.05 in cyclohexane.[25] Upon incorporation into a rigid glass, $\Phi_f$ increases to near unity with a concomitant decrease in the trans → cis isomerization efficiency. The corresponding fluorescence lifetime ranges from 60 ps in an isotropic hydrocarbon solvent to 1.7 ns in a rigid environment. In DPB the barrier to excited-state rotation is also greater in solution than in the isolated molecule.[30,31] Velsko and Fleming measured activation energies in the range 5.3–6.2 kcal/mol for DPB in a series of alkane solvents and determined that the internal barrier accounts for 4.7 kcal/mol.[30] Allen et al. measured activation energies of 5.3 and 4.5 kcal/mol for DPB/CH and DPH/MCH, respectively.[60] However, no attempt was made in that study to determine the contribution of inherent versus viscosity-added components to those values.

Solvent polarity also plays a role in polyene photochemistry. The absorption spectrum of tS is red shifted by 175 $cm^{-1}$ (0.5 kcal/mol) upon changing from a hydrocarbon solvent to glycerol. This can be attributed to stabilization of the $^1B_u{}^*$ excited state by the more polar glycerol solvent.[25] Increasing the solvent polarity also causes a decrease in the height of the internal barrier to rotation in tS. In nonviscous alcohol solvents the barrier to isomerization is reduced to <1 kcal/mol ($\Phi_f$ = 0.005 in ethanol[64]).[65] It has been proposed that this is due to the larger stabilization of the perpendicular $^1A_g{}^*$ state relative to that of $^1B_u{}^*$.[66] The height of the barrier to photoisomerization is thus a function of *both* the solvent polarity and the viscosity. Furthermore, Hicks et al. have shown that the strong interactions between polar solvents and the highly polar twisted intermediate in *trans*-stilbene produce time-dependent polarity effects on the isomerization dynamics.[66] That is, solvent rearrangement as a function of rotation and changes in charge density may occur on the same time scale as barrier crossing, causing the potential energy surface to change continually during the isomerization process.

The longer diphenylpolyenes are similarly influenced by solvent polarity. The excited-state barrier height for DPB decreases with increasing solvent polarity. The activation energy has been determined to be 4.0 kcal/mol in ethanol.[29] For DPH, the absorption spectrum is slightly sensitive to the solvent polarity while its fluorescence spectrum does not shift with solvent, in agreement with the assignment of $A_g$ symmetry to $S_1$. In 1975 Cehelnik et al. observed that in the polar solvents ethanol and acetonitrile there is evidence for temperature-dependent solvent-induced radiationless transitions in DPH which compete with fluorescence.[38] It could not be determined from the data whether this path of nonradiative decay represents internal conversion, intersystem crossing, or isomerization. To date, no measurements of the barrier height have been reported for DPH in polar solvents.

Interest in DPH photochemistry has centered on the role of solvents in determining the rate of radiative decay. The ${}^1A_g{}^* \rightarrow {}^1A_g$ transition in DPH derives oscillator strength through intensity borrowing from the ${}^1B_u{}^*$ state. The rate of fluorescence, therefore, is dependent upon the $S_2$–$S_1$ energy gap. Using perturbation theory, Hug and Becker developed a coupling model to explain the solvent dependence of $\tau_0$, the intrinsic fluorescence lifetime, in diphenylpolyenes.[67] They determined that as the strength of solvent-induced state mixing increases, $\tau_0$ decreases. Looking again at the intrinsic lifetimes shown Table I, this would imply that the greatest ${}^1A_g{}^*$–${}^1B_u{}^*$ coupling occurs for DPB. Although the analysis of Hug and Becker was not meant to apply to stilbene or other polyenes in which the ${}^1A_g{}^*$ state is higher in energy than ${}^1B_u{}^*$, this is corroborated by the estimates of $\Delta E_{ab}$ shown in Figure 6; the 200-cm$^{-1}$ $S_1$–$S_2$ energy gap determined for DPB is smaller than that of the other diphenylpolyenes. Since solvent polarity and polarizability influence the relative stability of the ${}^1B_u{}^*$ state, $\Delta E_{a,b}$ is a function of both. An extensive investigation of the effect of solvent polarizability on the radiative rate was carried out by Andrews and Hudson.[68] As the solvent polarizability was varied from 0.16 to 0.3, the radiative rate increased exponentially from $1.3 \times 10^7$ to $7.3 \times 10^7$ s$^{-1}$; as $\alpha_s$ increases, ${}^1B_u{}^*$ is stabilized relative to ${}^1A_g{}^*$ and $\Delta E_{a,b}$ decreases, causing enhanced coupling and faster fluorescence rates. Fluorescence quantum yield and lifetime measurements of DPH in nonpolar hydrocarbon solvents by Allen et al. also demonstrated that an increase in the solvent polarizability (from 0.31 to 0.35) increases the rate of fluorescence (from $4.6 \times 10^7$ to $6.7 \times 10^7$ s$^{-1}$).[60] However, in agreement with a change in state ordering, the same change in $\alpha_s$ produced a slight decrease in $k_f$ for DPB (from $7 \times 10^8$ s to $6.5 \times 10^8$ s$^{-1}$).' Andrews and Hudson also observed that the primary effect of decreasing the solvent temperature is to further stabilize the ${}^1B_u{}^*$ state and decrease $\Delta E_{a,b}$.[68] This effect is caused by the additional increase in the solvent density, and $\alpha_s$, at lower temperatures.

In 1979, Brey et al. showed that it is possible to use increases in the hydrostatic pressure to induce increases in solvent viscosity without changing the temperature.[69] Using this method they determined that for tS at ambient temperature $\Phi_{isc} = 0.02$ in $n$-hexane while $\Phi_{isc} = 0.21$ in glycerol. Saltiel and D'Agostino had previously estimated the quantum efficiency for intersystem crossing to be 1% in MCH and 5% in glycerol.[25] Although Brey and co-workers noted that the degree to which the cis isomer undergoes photocyclization does not change with solvent pressure, their calculations of intersystem crossing efficiencies did not take into account the increase in solvent polarizability that accompanies increases in solvent pressure. Nevertheless, their data reveal that while the room-temperature photochemical processes of tS in nonviscous media arise almost exclusively from within the singlet manifold, a significant fraction of molecules cross into the triplet state in viscous solvents. Brey et al. also found that in DPH the excited singlet nonradiative decay, $k_{nr}$, appears to be affected by increasing the pressure very differently than it is by increasing the viscosity through lowering the temperature.[70] Both tS and DPH show decreased nonradiative rates upon lowering the temperature. However, for the same increase in viscosity imposed by 10 kbar, the stilbene $k_{nr}$ decreased by a factor of 4 while there was a factor of 10 *increase* observed for DPH. The authors propose that the increase in viscosity produced by high pressures may open a new radiationless pathway in DPH. Similar to the effect of high viscosity on stilbene, this may be caused by an enhancement of $\Phi_{isc}$ under these conditions. Interestingly, while the absorption spectrum of DPO is shifted much more by $\alpha_s$ than is the spectrum of DPH, Brey et al. found that $k_{nr}$ for DPO does not change with changing solvent pressure.[70]

Finally, studies of the fluorescence of both DPH and DPO may be complicated by $S_2 \rightarrow S_0$ transitions. Short-lived emission directly from $S_2$ has been observed as a contribution to the blue edge of the DPH and DPO fluorescence spectra.[57,71] Jones and Cundall used moderately high hydrostatic pressures to induce increases in the solvent refractive index (thus increasing $\alpha_s$) of hexane and toluene solutions of DPH and DPO.[72] Upon increasing the solvent polarizability, they observed a greater increase in the ${}^1B_u{}^*$ emission component in the spectrum of DPH than was observed for DPO. Itoh and Kohler recently showed by varying the temperature and the solvent than as $\alpha_s$ is increased, the weak fluorescence emission from ${}^1B_u{}^*$ shifts to lower energies while the position of the ${}^1A_g{}^*$ emission remains constant for both DPH and DPO in hydrocarbon solutions.[45] It has been proposed by Alford and Palmer that delayed fluorescence due to thermal repopulation of $S_2$ from $S_1$ proceeds at a rate comparable to that of the radiative and nonradiative decay from $S_1$ (see Figure 8).[73] This was based on studies of the fluorescence quantum yields and lifetimes of DPH in a range of solvents. In the event of competing processes, the observed rate of fluorescence would take the form $k_{obs} = (1 + K)^{-1}(k_f + Kk_f')$ or $k_{obs} = k_f + Kk_f'$ (for $K \ll 1$), where $K$ could be determined from the free energy relationship: $\Delta G = -RT \ln K$. For nonpolar solvents in

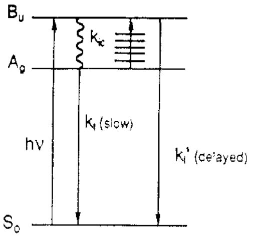


**Figure 8.** Thermal repopulation and delayed fluorescence in DPH.

which the $S_2$–$S_1$ energy gap is ~1000 cm$^{-1}$, the rate constant governing thermodynamic equilibration between $S_2$ and $S_1$ is quite small; $K = 0.008$ at 25 °C (298 K). It is possible, however, that in solvents of high polarity $\Delta E_{ab}$ might become small enough to render thermal repopulation of $S_2$ significant. In that case, dual emission could interfere not only with the fluorescence from $S_1$ but also with estimates of the energy gap between the two lowest excited state surfaces, $S_2$ and $S_1$.

## *VI. Isomerization*

### A. Experimental

It was almost 20 years after the landmark work of Zechmeister before other researchers began to tackle the complex isomerization of diphenylpolyenes. In their early studies, Zechmeister and co-workers found *cis,-trans*-DPB to be the predominant photoproduct formed upon irradiation of *all-trans*-DPB.[74] Only discrete one-bond/photon rotations were observed, implicating an allyl methylene intermediate in the isomerization process. Eastman et al. determined from measurements of the isomerization efficiency in DPB (25% trans,trans to cis,trans) that radiationless decay may compete with isomerization.[75] The quantum yield for internal conversion from the planar state, $\Phi_{ic}$, can be estimated from the sum of the quantum yields for radiative decay, $\Phi_f$, intersystem crossing, $\Phi_{isc}$, and excited-state rotation, $\Phi_{tt\rightarrow tp}$: $\Phi_{ic} + \Phi_f + \Phi_{isc} + \Phi_{tt\rightarrow tp} = 1.0$. Assuming equal partitioning from the trans,perpendicular* to the trans,trans and trans,cis isomers of DPB, Yee et al. estimated an internal conversion efficiency of 34%.[76] A value of only 6% is obtained for $\Phi_{ic}$ using Eastman's value of 0.25 for $\Phi_{tt\rightarrow ct}$ (or 0.50 for $\Phi_{tt\rightarrow tp}$). This discrepancy may be attributable to a difference in solvents used in these two studies, benzene vs *n*-hexane. Clearly, however, fluorescence and excited-state rotation are not as tightly coupled in DPB as in *trans*-stilbene.

In 1954 Lunde and Zechmeister isolated five different stereoisomers of diphenylhexatriene.[77] These isomers were produced by iodine atom catalysis and zone refinement on a magnesia–lime–Celite column. They recorded absorption spectra of the three mono-cis isomers and reported that only the trans,cis,trans isomer is not hindered by steric repulsion between an aliphatic hydrogen and an ortho hydrogen on one of the phenyl rings. Momicchioli et al. developed expressions for the potential functions of the $A_g$ and $^1B_u$* states to describe the absorption spectra of *α,ω*-diphenylpolyene isomers in 1972.[78] This was the first attempt to correlate the isomerization in these compounds with their spectroscopically observable properties. Mason and Cehelnik investigated the photolysis of DPH in a variety of solvents and observed that 100% transmittance at 366 nm could be achieved in glacial acetic acid with ~6 min of irradiation time while a cyclohexane solution required ~21 h of irradiation time.[79] They were also able to corroborate the assignments of the absorption spectra for the three mono-cis isomers reported by Lunde and Zechmeister. Studies by Baretz et al. have shown that the distribution of isomers formed upon direct irradiation of DPH is not dependent on solvent polarity.[80]

A topic of recent interest is the effect of state ordering on the photoisomerization process. The higher degree of correlative stability in a doubly excited $^1A_g$ state leads to a greater bond order reversal compared to that in a $^1B_u$ excited state. This might be expected to produce lower barriers to excited-state rotation for a low-lying $^1A_g$ state than for a $^1B_u$ state. Allen et al. have investigated the relationship between the barrier height and the rate of isomerization in DPB and DPH molecules.[60] Despite the changing $S_1$ and $S_2$ level order, relatively large barriers were measured for DPB (5.3 kcal/mol) and DPH (4.5 kcal/mol) in low-viscosity hydrocarbon solvents. Furthermore, their studies showed that upon 4,4′-dialkyl substitution the barrier to nonradiative decay in hydrocarbon solvents is reduced to 1.6 kcal/mol in DPB and to 0.2 kcal/mol in DPH. In contrast, similar substitution of *trans*-stilbene produced a slight increase (to 4.0 kcal/mol) in the barrier to excited-state rotation.[60] This difference may implicate a concerted, viscosity-independent isomerization mechanism in dialkyl-substituted diphenylpolyenes of $n \geq 2$. Measurements of the relative rates of isomerization revealed that the low barriers in the alkylated derivatives of DPB and DPH are accompanied by quantum efficiencies of isomerization that are 80% and 390% larger, respectively, than those of their parent compounds.[81] Isomerization quantum yields of alkylated stilbenes, on the other hand, are slightly less than that of *trans*-stilbene, reflecting the small increase in the fluorescence yield produced by the addition of alkyl chains.[82] Thus, while examination of the unsubstituted molecules suggests similar isomerization pathways among the diphenylpolyenes, important differences have been observed upon the addition of substituents.

Although the direct photoisomerization of *trans*-stilbene was confirmed to be a singlet-state process by about 1973,[83] the triplet-state involvement in the photoisomerization of higher diphenylpolyenes has been investigated only recently. It was determined by laser flash photolysis that triplet-state DPB could be formed only by sensitized excitation while the DPH and DPO triplets could be formed by direct excitation.[84] However, Goerner concluded that quantum yield and rate evidence suggest a singlet-state mechanism for photoisomerization in all three compounds. Chattopadhyay et al. showed that the rate of intersystem crossing decreases as the length of the polyene chain increases.[85] The efficiency of intersystem crossing has been estimated at <3% for both DPH and DPO.[86] The quenching of diphenylpolyene singlet and triplet states by stable free radicals has also been studied. For the series from tS to DPO, 6–60% of singlet quenching events result in the generation of triplet states and a parabolic dependence of triplet quenching rate constants on triplet energy was observed.[87] Quenching of the DPB triplet has been studied with a range of quenchers and indicates a rapid equilibration between and transoid and twisted forms of the DPB triplet state.[88]

## B. Theoretical

Generally, the rates observed for intramolecular isomerization in the absence of a barrier can be described by the Stokes–Einstein equation, which describes the inverse relationship between viscosity and diffusion; increasing the solvent friction reduces the rates of isomerization that are controlled by collisions with surrounding solvent molecules. However, it it necessary to consider theories such as Kramers' one-dimensional stochastic model of chemical reaction dynamics to describe activated barrier crossing. Kramers' model is based on the Langevin equation for the motion of a point on a potential surface, which takes into account the particle mass, the coordinate, the potential energy surface of the particle, and the friction coefficient.[89] This model assumes a constant friction coefficient that is proportional to the solvent shear viscosity and expresses the net effect of the interaction between the solvent and the solute. Although Kramers' model has received wide recognition as one of the first theories developed to explain barrier crossing, the rate of isomerization of tS and DPB in alkane solvents falls off more slowly with viscosity than is predicted by the theory.[30,90] Grote and Hynes have proposed a non-Markovian or frequency-dependent friction model to describe barrier crossing in solution.[91] Their model includes a generalized Langevin equation in which the solvent reorganization is considered to be on the same time scale as crossing over the barrier. Such an approach has been suggested for isomerizations that are governed by high-frequency motions.[92,93]

The dependence of the rate of isomerization in the presence of a barrier on the solvent friction falls into two regimes: a high-friction (diffusion controlled or Smoluchowski) domain in which increasing the solvent friction results in decreased reaction rates and a low-friction (energy controlled) domain in which collisions with solvent molecules provide the energy necessary to overcome the barrier. Courtney and Fleming studied the photoisomerization of stilbene in liquid alkanes and in the gas phase.[94] They reported that while no low-friction or energy-controlled regime could be found in solution experiments, even at the lowest viscosities studied, an increase in the reaction rate was observed with increasing friction in thermal vapor experiments. However, the observed dynamics were not adequately described by a model of intramolecular vibrational energy transfer. It has been proposed that entropy considerations are necessary for agreement between theory and experiment in this regime.[94,95] The Kramers' "turnover" region, or the intermediate-friction regime, was observed by Lee et al. for the isomerization of tS in an ethane solution.[96]

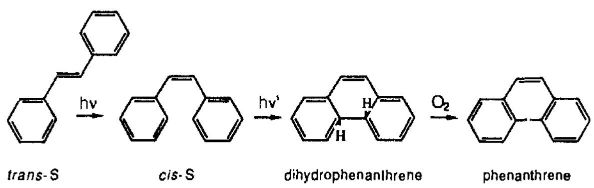
Although it is generally accepted that Kramers' theory qualitatively predicts the influence of friction on the rate of photoisomerization of *trans*-stilbene in nonpolar solvents,[21] no one theory has been shown to adequately model solution-phase isomerizations. Rothenberger et al. found the effect of friction on the isomerization of stilbene in *n*-alkanes to fit best to the frequency-dependent model of Grote and Hynes while the isomerization of "stiff" stilbene, 1,1′-biindanylidene, was best described by Kramers' model.[90] Although the theory of Grote and Hynes has been more successfully applied to polyene isomerization than that of Kramers, it often generates values of the well and barrier frequencies that are unphysically low. This may be caused by the sensitivity of the solvent–solute friction to the relative size and mass of the solvent and solute molecules, as proposed by Sundstrom and Gillbro.[97] This interpretation is supported by the measurements of solute rotational reorientation times by Kim and Fleming which showed that the solvent–solute coupling decreases as the size of the solvent increases.[98] Recent attempts have been made to extend the theory of Kramers, making it more universally applicable.[99,100] In addition, studies of the picosecond conformational dynamics of 1,1′-binaphthyl in alcohol solvents show agreement with Kramers' theory for both the intermediate- and high-friction regimes.[101] Millar and Eisenthal propose that deviations from Kramers' theory may be due to factors other than non-Markovian friction.[101]

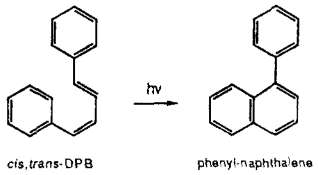
The photoisomerization of tS in alcohol solvents falls within the diffusion limit of solvent friction; the barrier is low ($E_{act} < 1$ kcal/mol) and the reaction rate is a linear function of the inverse of the solvent viscosity. Sundstrom and Gillbro have proposed that Kramers' theory is not applicable for stilbene isomerization in *n*-alcohol solutions and that either a diffusion-type theory in which $E_{act} = 0$ or a theory for relaxation in the absence of a barrier (see ref 102) is necessary to explain barrier crossing of excited tS in polar solvents.[65] Smedarchina later showed that the observed rate data fall into the strong-interaction (or diffusion) limit.[103] Although most treatments of rate data involve modification of the theory to best fit the observed data, failure of Kramers' or any other theory may reflect more the inability of solvent viscosity to represent the microfriction in alcohols than the inadequacy of the theory. For a discussion of polarity and hydrogen-bonding effects on photoisomerization, see the works of Hicks et al.[104]

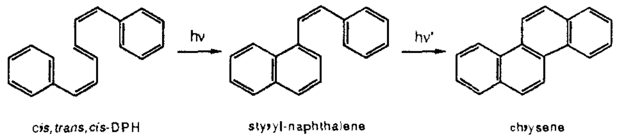
For diphenylbutadiene, the photoisomerization in polar solvents is *limited* by the solvent viscosity. Keery and Fleming have determined that the viscosity dependence of DPB isomerization falls within the Smoluchowski limit in polar solvents.[29] Bagchi et al. have shown that, if the *effective* friction produced by a frequency-dependent model is considered, the theory of Grote and Hynes accurately explains the rate data obtained by Fleming and co-workers.[105] Excellent agreement was obtained between the rates of photoisomerization in jet-cooled DPB molecules and RRKM theory.[106] Comparison between the reaction rates of DPB in the gas phase and in solution indicates that, although intermolecular vibrational redistribution (from collisions) enhances the rate of barrier crossing, both inter- and intramolecular vibrational redistribution contribute to the observed rate in solution.[107] As in the case of tS, recent attention has focused on the validity of using the solvent viscosity as representative of the friction in fitting the photoisomerization solution rate data for DPB to existing theories.[108]

## VII. Cyclization

According to the Woodward–Hoffmann rules governing the symmetry requirements for cyclization reactions, a molecule containing $4n + 2$ $\pi$ electrons (tS and DPH with 14 and 18 $\pi$ electrons, respectively) will undergo a conrotatory photochemical ring closure. Such a reaction should result in anti-dihydro cyclization products for tS and DPH. In the case of DPB, which has 16 or $4n$ $\pi$ electrons, photochemical cyclization should produce a dihydro product with the syn stereochemistry, due to disrotatory rotation of the p orbitals. Oxidation of any of the products should yield an aromatic polycyclic molecule. However, cyclization of diphenylpolyenes is observed in both the presence and absence of oxygen.[109] Blackburn and Timmons presented a short review of the photocyclization of tS, DPB, and DPH in 1969.[10] At that time, the products of intramolecular cyclization had been identified as phenanthrene for tS, 1-phenylnaphthalene for DPB, and chrysene for DPH. As shown in the diagram, formation of chrysene from *cis,trans,cis*-DPH is not a concerted process; the intermediate styrylnaphthalene must be formed first. Since this early work, investigations have focused on the effects of substituents on the photocyclization of diphenylpolyenes.[111-113] For an in-depth treatment of the photocyclization of stilbenes and related molecules, see the review of Mallory and Mallory.[114]







## VIII. Substituent Effects

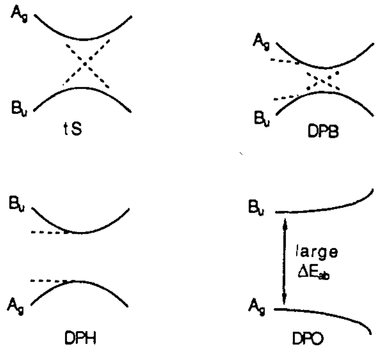
In attempts to better understand the nature of polyene excited-state surfaces, the effects of substituents on diphenylpolyene photochemistry have been studied. Increases in the barrier height have been proposed upon substitution of *trans*-stilbene at the para positions with methoxy and hydroxy groups. Zeglinski and Waldeck measured activation energies of 4.6 and 4.9 kcal/mol for the internal barrier to rotation in *n*-alcohol solutions for the 4,4′-dihydroxy and 4,4′-dimethoxy derivatives of stilbene, respectively.[115] The value increases to 5.6 kcal/mol for the dimethoxy derivative in *n*-alkane solvents.[116] The larger barrier heights were accompanied by a weaker viscosity dependence even though larger amplitude motions are involved in the isomerization of these stilbene derivatives. Complete deuteration of stilbene results in a fluorescence lifetime that is 50% longer than that of *trans*-stilbene in both alkane and alcohol solvents, while similar nonexponential decays are observed for the two molecules in the gas phase.[117] Substitution of tS by nitro groups enhances the rate of intersystem crossing and leads to isomerization via a triplet pathway. Subsequent addition of an electron-accepting group, such as an amine, results in donor–acceptor substituted stilbenes which undergo very little photoisomerization. Highly solvent dependent mixed singlet–triplet mechanisms are observed in the photoisomerization of donor–acceptor stilbenes.[118]

Again, studies of the effects of added substituents on diphenylhexatriene photochemistry have focused on determining how various groups will influence the $^1A_g^*$–$^1B_u^*$ coupling. The rate of fluorescence increases in the series fluoro-, chloro-, methyl-, isopropyl-, and methoxyphenyl derivatives of DPH.[73] This is due, presumably, to the decrease in lifetime (caused by a decrease in the energy gap, $\Delta E_{a,b}$) observed in this series as the quantum yields vary randomly. This result is accompanied by a red shift in the absorption spectra for these compounds.[71] Cundall et al. observed marked solvent shifts and a loss of vibrational fine structure in the adsorption spectra of several nitro-, acetamido-, cyano-, and pyridylphenyl DPH derivatives.[119] The degree to which the absorption spectrum is red shifted increases with increasing substitution. Also, the addition of cyano substituents to DPB causes a change in the distribution of photoisomers produced.[80]

Interest in surfactant derivatives of diphenylpolyenes as fluorescent probes of membranes has prompted studies of their photophysical properties. As mentioned above, Allen et al. measured the height of the barrier to nonradiative decay in fatty acid derivatives of DPB and DPH.[60] Their studies indicate that alkyl substitution at the para positions, which lowers the activation energy calculated from Arrhenius data and increases the rate of photoisomerization, may alter the mechanism by which isomerization proceeds. It was also observed that the extent of $^1B_u^*$ emission increased in the alkylated derivative of DPH. Using sodium iodide as the quencher, Cranney et al. found that the fluorescence was quenched to different degrees for 1-(4-(trimethylaminophenyl)-6-phenyl)-1,3,5-hexatriene (TMA-DPH), 1-palmitoyl-2-DPH-propanoylphosphatidylcholine (DPH-PC), and DPH in phosphatidylcholine vesicles and interpreted this to indicate different depths of the DPH chromophore in the bilayer for the probes.[120] The use of DPH derivatives as probes of synthetic membranes is supported by studies of the orientation of DPH in stretched polyethylene films which indicate that DPH provides the best alignment of the diphenylpolyenes without complications due to the increased flexibility of longer chains.[121] However, studies by Allen et al. indicate that a range of solubilization sites exist for DPH in phosphatidylcholine vesicles which is dependent upon both the probe:lipid ratio and the phase of the bilayer.[122]

## IX. Conclusions

The solution photochemistry of $\alpha,\omega$-diphenylpolyenes is governed by the shape of the lowest excited state potential surface. Thus, fluorescence and isomerization of tS, DPB, and DPH should be highly dependent upon the order of the first two excited singlet states and the degree to which they interact. The size and nature of the barrier to excited-state rotation have, therefore, been the focus of much of the investigation of diphenylpolyenes. As we have shown, an important anomaly exists in that the three molecules exhibit what appears to be closely related photochemical behavior despite evidence of what should be quite different excited-state ordering and disparate interactions. In *trans*-stilbene the barrier appears to originate from an avoided crossing between the $^1A_g$ and $^1B_u$ excited states. The internal barrier in DPB may also be attributed, in part, to an avoided crossing. However, due to the small energy gap between the two states, an avoided crossing cannot account for the size of the barrier in DPB and must be accompanied by another form of interaction such as repulsion between the $S_1$ and $S_2$ surfaces (see diagram). The barrier in DPH must also be attributed to a potential interaction between $^1A_g{}^*$ and $^1B_u{}^*$ since no crossing of the states would be anticipated for a molecule in which the $^1B_u{}^*$ state is higher in energy than the $^1A_g{}^*$ state. While DPO should also lack an avoided crossing, the energy gap is large enough (~2000 cm$^{-1}$) that unfavorable interactions might be limited and little or no barrier would be anticipated. This rationalization permits the occurrence of similar barriers for the first three molecules and yet is consistent with the clear indications of differing $^1A_g{}^*$ and $^1B_u{}^*$ state levels and mixing.



The level order and coupling in polyenes, which determine the shape of the barrier, are influenced by the solvent, temperature, and conformation of the molecules. In addition, the resulting potential energy surface associated with photoisomerization is strongly coupled to the solvent dynamics, necessitating a better understanding of the interactions of these systems on a microscopic, ultrashort time scale. Molecular beam studies and theoretical calculations have, therefore, yielded much information regarding the solution photochemistry of these compounds. The addition of substituents can also have profound studies on the radiative and nonradiative decay processes of diphenylpolyenes and have been important in the determination of their photophysical properties. Continued efforts in these areas should provide additional insight for problems concerning the nature of barriers and barrier crossing as well as a better understanding of the relationship between photophysical properties and the corresponding photochemistry of polyene chromophores.

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