Excited State Spectra and Dynamics of Phenyl-Substituted Butadienes

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A combination of steady-state and dynamic spectral measurements are used to provide new insights into the nature of the excited-state processes of *all-trans*-1,4-diphenyl-1,3-butadiene and several analogs: 1,4-diphenyl-1,3-cyclopentadiene, 1,1,4,4-tetraphenylbutadiene, 1,2,3,4-tetraphenyl-1,3-cyclopentadiene, and *E,E*-diindanylidenylethane. Ground-state absorption, fluorescence, and nanosecond transient absorption measurements identify geometry changes upon excitation and provide information regarding the nature of the first excited singlet state. Femtosecond and picosecond transient absorption data indicate that phenyl torsional motion is not important to the excited-state dynamics and reveal alternative excited-state reaction pathways. The results demonstrate how molecular systems that are structually similar can exhibit different electronic properties and excited-state dynamics.

Introduction

Phenyl-substituted polyenes have often been used as model compounds in an attempt to understand mechanisms of polyene photoisomerization. Of this class of polyene, the substituted butadienes, especially *all-trans*-1,4-diphenyl-1,3-butadiene (DPB), have received considerable attention.[1-3] Because of its high molar absorptivity and relatively large fluorescence quantum yield, DPB has been studied by many researchers as a prototype for isomerization processes in the chromophore of visual pigments[4-6] and has also served as a test for liquid-phase chemical reaction rate theories such as Kramers's theory.[7,8] However, despite this interest, there still remains ambiguity in the ordering of the first two electronic excited states of DPB in condensed phase because of the possibility of state mixing and interactions with the solvent environment.[9] Given that the photoisomerization of these compounds is intimately connected to the electronic structure of the excited states, it is surprising that there have been few attempts to correlate photoisomerization dynamics with steady-state spectroscopic information. Adequate knowledge of the first excited state is imperative before these compounds can serve as useful models for understanding isomerization processes.

DPB belongs to a class of molecules, *all-trans* α-ω-diphenylpolyenes, whose excited states are characterized in terms of the A_g or B_u representations of the C_{2h} symmetry group. These A and B representations can also adequately describe the excited states of α-ω-diphenylpolyenes even when the actual symmetry of the polyene deviates somewhat from C_{2h}. The electronic ground states of all the diphenylpolyenes are described by the totally symmetric A_g representation, whereas the symmetry of the first electronic excited state (S_1) is dependent on the polyene chain length. The S_1 states of diphenylhexatriene (DPH) and the longer chain polyenes have A_g symmetry, while the S_1 state of stilbene (diphenylethylene) has B_u symmetry. For DPB, the first two excited states of A_g and B_u symmetry are nearly degenerate, with

the ordering dependent on the environment. In the gas phase, the $2A_g$ state has been determined to lie below the $1B_u$.[10] However, interactions with the solvent can stabilize the $1B_u$ state so the state ordering can differ in different condensed-phase media.[11,12]

Most solution-phase spectroscopic studies have identified the S_1 state of DPB as a B_u state, and an excellent review of this work was recently published by Saltiel and Sun.[4] The small Stokes shift and the good mirror image of the absorption and fluorescence bands indicate that the absorbing and emitting states are the same. Theoretical calculations and excited-state absorption measurements by Goldbeck et al.[9] have identified the S_1 state as B_u. In addition, the spectral properties of DPB are more similar to stilbene than to DPH and the longer polyenes, further supporting the B_u assignment of the S_1 state. However, two-photon fluorescence excitation studies of DPB in cyclohexane solutions[13,14] and one-photon absorption and fluorescence measurements of DPB in EPA glass[15] concluded that the $2A_g$ state lies slightly below the $1B_u$ in condensed phase. It should be noted that Saltiel and Sun[4] recently suggested that these studies are more consistent with a lowest B_u excited-state assignment for DPB. Thus, consensus on the electronic nature of the S_1 state of DPB in condensed phase still has not been achieved.

One significant attempt to correlate the ambiguous DPB S_1 spectral assignment and the excited-state dynamical processes of DPB in condensed phase has been the work of Rulliere et al.[16] In this study the authors used picosecond flash photolysis to examine the dynamics of the $S_n \leftarrow S_1$ excited-state absorption. To explain their observed dynamics, Rulliere et al. invoked a model of solvent-assisted level inversion modulated by large-amplitude phenyl torsional motion. While this model adequately explained the data obtained in their experiments, it predicts a dependence of the transient absorption spectrum on solvent polarizability that is not observed.[17] Furthermore, isomerization studies of DPB derivatives with locked phenyl groups[1] show a one-dimensional excited-state motion similar to DPB and do not support the hypothesis that phenyl motions are important to the excited-state dynamics in DPB. Clearly, the role of phenyl torsional motions in the excited-state ordering and dynamics for DPB in solution is not completely understood.

In this paper, we have investigated the excited-state dynamics and photophysics of DPB and four structurally related phenyl-substituted butadienes: 1,4-diphenyl-1,3-cyclopentadiene (DPCP), *E,E*-diindanylidenylethane (stiff-5-DPB), 1,1,4,4-tetraphenyl-

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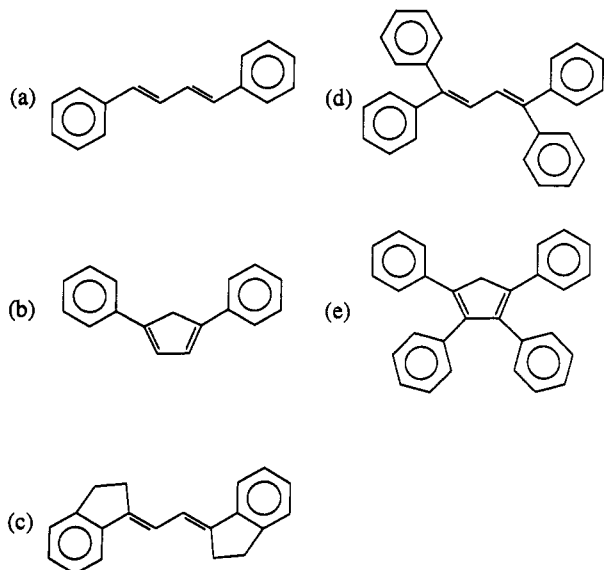
Figure 1. Structures of (a) *all-trans*-1,4-diphenyl-1,3-butadiene (DPB), (b) 1,4-diphenyl-1,3-cyclopentadiene (DPCP), (c) *E,E*-diindanylidenylethane (stiff-5-DPB), (d) 1,1,4,4-tetraphenylbutadiene (TPB), and (e) 1,2,3,4-tetraphenyl-1,3-cyclopentadiene (TPCP).

butadiene (TPB), and 1,2,3,4-tetraphenyl-1,3-cyclopentadiene (TPCP). Structures of these compounds are shown in Figure 1. With these studies we examine the effects of phenyl substitution and symmetry changes on the electronic structure and dynamic behavior of DPB, and the role of phenyl twisting in modulating these effects. Stiff-5-DPB provides a DPB analog with locked phenyl rings, and DPCP and TPCP produce a DPB locked in the *s-cis* configuration with phenyl rings free to rotate, while TPCP and TPB allow us to examine the effects of additional phenyl substitution which most likely lead to nonplanar phenyl orientations. The radically different dynamics found in these structurally similar molecules in this study show that one must exercise caution when using these molecules as models for polyene isomerization or as tests of condensed-phase reaction rate theories and emphasize the importance of correlating electronic structure and dynamical information in these systems.

Experimental Section

Materials and Methods. DPB, TPB, and TPCP were purchased from Aldrich and recrystallized twice from ethanol. Stiff-5-DPB[1] was provided by Professor Amos B. Smith III (University of Pennsylvania) and used without further purification. DPCP was prepared according to a known procedure[18] by condensation of methyl β-benzoylpropionate with acetophenone in the presence of sodium ethoxide. The crude product was recrystallized twice from ethanol, yielding yellow crystals (flakes) with a melting point of 152–154 °C (lit. mp 158 °C).[18] ^{1}H NMR (CDCl$_3$): δ 3.45 (2H, s), 6.80 (2H, s), 7.25 (10H, m). The mass spectrum showed a molecular weight of 218 g/mol. Solvents were spectrograde and used without further purification.

All measurements in this study were carried out at room temperature. Samples were contained in a standard 1-cm quartz cuvette with absorbances of ~0.3 at λ$_{max}$ for the steady-state and ~1.0 at the excitation wavelength for transient absorption measurements. Samples for the former were bubbled with argon for approximately 5 min prior to use. To avoid interference from possible photoproducts, samples were stirred during data collection. For dynamic measurements, a gas-tight flow system employing a peristaltic pump (Cole-Parmer) circulated samples at a rate sufficient to ensure that a fresh sample volume was being probed by every laser shot. The solution reservoir was purged with dry nitrogen prior to pumping the sample through the system. Samples had absorbances of ~2 at 310 nm through the optical pathlength (~1 mm) of the quartz flow cell.

Spectral Measurements. Ground-state absorption measurements were made using an IBM 9420 UV–visible spectrophotometer. Fluorescence emission measurements were obtained using a Spex Industries Fluorolog 2 Series spectrofluorimeter using right angle detection with excitation and emission slits of 0.5 mm. The fluorescence quantum yields, Φ$_u$, were determined using the following relationship:

$$\Phi_u = (\Phi_s)\frac{a_u(1 - 10^{-A_s(\lambda_x)})}{a_s(1 - 10^{-A_u(\lambda_x)})}$$

where Φ$_s$ is the quantum yield of a standard (in this case DPB in hexane was used as the standard),[19] *a* is the integrated area of the fluorescence spectrum, and $A(\lambda_x)$ is the absorption at a fixed wavelength.

The excited-state absorption was measured using an apparatus which has been previously described.[20,21] Briefly, samples were excited with the third harmonic of a Quanta Ray DCR-2 Nd: YAG laser (355 nm) with energies of ~5 mJ/pulse and monitored with a short-arc xenon flashlamp (pulse width approximately 7 µs), monitored with a Princeton Applied Research EG&G PARC model 1461/1420 intensified optical multichannel analyzer (OMA). The OMA intensifier was gated on for 5-ns periods, a duration that is close to the full width at half maximum of the laser pulse. The short lifetimes of all the molecules studied relative to the sampling pulse width lead to steady-state conditions in these excited-state absorption measurements.

Absorption Dynamics Measurements. The laser system used for the picosecond transient absorption experiments has been described previously.[22] Briefly, a mode-locked argon ion laser synchronously pumps a dye laser to produce 1–2 ps pulses at 590 nm. These pulses are then amplified in a three-stage dye cell amplifier pumped longitudinally by a 10-Hz, Q-switched Nd: YAG laser. The final output consists of pulses ~1 ps in duration with ~1 mJ/pulse at 10 Hz. This light is frequency doubled in a 1 mm thick KDP crystal to produce 0.1-mJ excitation pulses at 295 nm. The residual fundamental light is focused into a 5-cm cell containing water or acetone to generate a white-light picosecond continuum. Band-pass filters are used to select a 10-nm FWHM portion of the continuum for use as the probe light.

The 295-nm pump pulses were sent through a variable double-pass optical delay line with 10-µm (67-fs) resolution before arriving at the sample. The probe light was split into signal and reference beams, collected on large area photodiodes (EG&G DT-110), and processed by a 386 computer-controlled gated integrator. Probe light levels outside the linear response regime of the detection system were rejected from data collection. Data were normalized on every laser shot with a typical spread in the normalized ratios for 100 shots of 0.2% (±1 standard deviation).

Transient absorption data were collected in the following manner: for each delay, absorption measurements from 20 normalized laser pulses were averaged for a single data point, the delay between the pump and probe pulses changed, another 20 laser pulses were averaged at the new stage position, and the process repeated until an entire scan was complete. In the results presented below, 10–50 of these scans were averaged together (200–1000 total shots averaged) with the stage moving in opposite directions on alternating scans to remove long-term drift artifacts.

The pump and probe beams passed through the sample collinearly. Since large pump intensities lead to multiphoton excitation of solvent molecules, resulting in large interfering transient absorption signals, the pump intensity was attenuated with neutral density filters until no signal was seen from the neat solvent. The typical pump energies used in the experiments were 3–10 µJ. Average signal sizes obtained in this manner were absorbance changes of 2–6%.

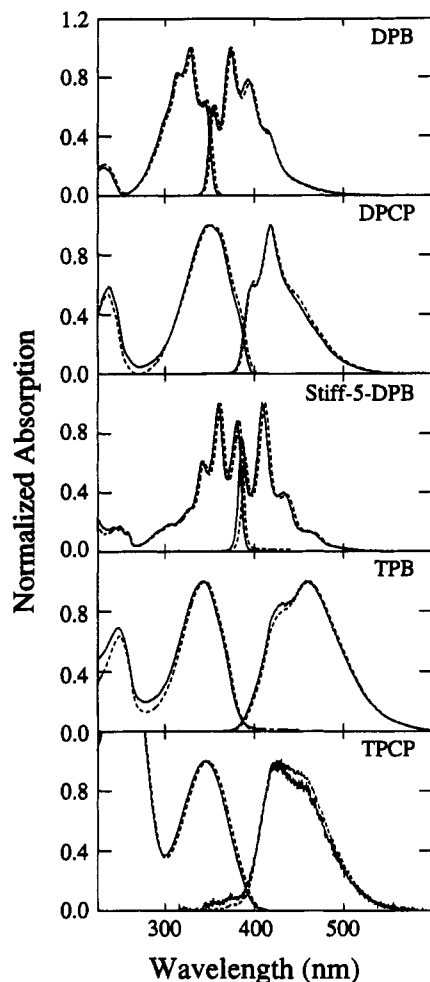To insure that the absorption rises were instrument-limited,

Figure 2. Ground-state absorption and emission spectra of DPB, DPCP, stiff-5-DPB, TPB, and TPCP in hexane (solid line) and dodecane (dashed line). All of the spectra are normalized in the region of 300–500 nm to facilitate comparison between spectra. The maximum extinction coefficients $((M\ cm)^{-1} \times 10^4)$ for the absorption bands in this region as determined in hexane solutions are as follows: DPB $\sim$5.5, DPCP $\sim$2.8, stiff-5-DPB $\sim$4.2, TPB $\sim$4.0, and TPCP $\sim$1.8.

we performed additional scans with femtosecond pulses limited to probe wavelengths near 620 nm. These femtosecond transient absorption studies were conducted in a similar manner with a copper vapor laser amplified[23] colliding pulse mode-locked ring laser[24,25] which produces 3-μJ, 90-fs pulses at 620 nm. For these experiments, samples were excited with $\sim$500 nJ of the laser second harmonic at 310 nm and probed with a small portion of the 620-nm fundamental, providing an instrument resolution of $\sim$120 fs. Further details are described elsewhere.[26]

Results

In order to better understand the excited-state processes of these phenyl-substituted butadienes, both spectral and dynamical measurements were obtained. The results for each compound are described below.

Spectral Measurements. The electronic nature of the ground and first excited singlet states of the molecules shown in Figure 1 were investigated using ground-state absorption, emission, and excited-state absorption measurements.

Ground-State Absorption and Fluorescence Emission Measurements. The ground-state absorption and fluorescence spectra for DPB and all of the DPB analogs measured in hexane and dodecane solutions are shown in Figure 2. Only the absorption spectra of DPB and stiff-5-DPB show vibronic structure, while the emission spectra of all the compounds studied show at least some vibrational structure. The polarizability, α,[27] of dodecane

($\alpha = 0.253$) is 0.025 larger than the polarizability of hexane ($\alpha = 0.228$). This increase in solvent polarizability results in similar red shifts of the absorption and emission bands of all of the molecules studied. Significant red shifting of the absorption and emission bands should only be observed if the absorbing and emitting states contain B-type character. The magnitude of these polarizability shifts are reported in Table 1. The Stokes shifts measured in hexane for DPB and stiff-5-DPB measured at the 0–0′ band are also reported in Table 1. The lack of structure in the TPB, TPCP, and DPCP spectra prevents the identification of the 0–0′ band for these molecules. Thus, the Stokes shift was measured as the separation between the midpoints (point of half-maximum intensity) of the red edge of the absorption and the blue edge of the emission bands. These values are reported in Table 1 as well.

It is interesting to note how the absorption spectra shift with modification to the DPB and DPCP parent compounds. A red shift of the $S_1 \leftarrow S_0$ transition is predicted with alkyl or phenyl substitution on either the polyene or phenyl portions of the molecule.[28,29] This results from electronic changes caused by the substitution and sometimes by small geometrical factors. This red shift is observed for stiff-5-DPB and to a smaller extent in TPB. However, TPCP does not show a red shift from the diphenylbutadiene parent compound by addition of two phenyl groups. In fact, the transition in TPCP is slightly blue-shifted compared with DPCP. This smaller than expected red shift in TPB and the blue shift in TPCP are explained by considering the ground-state geometry of the tetraphenyl-substituted compounds. One would expect steric hindrance between the phenyl groups to force them out of the plane of the polyene chain, thereby lowering the extent of π conjugation.

The ground-state absorption and emission spectral characteristics of stiff-5-DPB are very similar to those of DPB. Mirror image symmetry and vibrational structure are observed for the absorption and emission bands of both molecules, indicating good Franck–Condon overlap. The small Stokes shift reported in Table 1 suggests that the absorbing and emitting states are the same for stiff-5-DPB and that the geometry does not change significantly on the S_1 surface prior to fluorescence, similar to that of DPB. Also, the ground-state absorption and emission spectra exhibit similar shifts with increasing solvent polarizability, further support that the absorbing and emitting states are the same. Thus it appears that the S_1 state of stiff-5-DPB is similar to the S_1 state of DPB in both excited-state geometry and electronic character.

TPB, TPCP, and DPCP show shifts with solvent polarizability similar to those of DPB; however, the other absorption and emission characteristics are quite different. The ground-state absorption spectra for TPB, DPCP, and TPCP are structureless while the emission spectra are somewhat more structured. In addition, these molecules exhibit larger Stokes shifts. This is indicative of a molecule that is more planar in the excited state than the ground state, resulting in different Franck–Condon overlaps for these two transitions.[30] Thus, these molecules become more rigid, and the phenyls become more planar on the excited-state surface, resulting in a more structured fluorescence spectrum and a larger Stokes shift.

Examination of the TPB and TPCP absorption and emission spectra also reveals that the emission bands of these molecules are much broader than the absorption bands. This observation may be the result of Franck–Condon overlaps between the S_0 and the S_1 states that are different from those of DPB and DPCP for the polyene vibrational modes coupled to the electronic transition. This is most likely due to a flatter minimum on the S_1 surface than on the S_0 surface along these coordinates. Another interesting feature of the emission bands for these two molecules is that the solvents enhance the band features differently. Dodecane enhances the red shoulder in the TPCP emission band while pentane enhances the blue shoulder in the TPB emission

TABLE 1

compound	spectal shifts (A) with solvent polarizability[a,d] (cm^{-1})		fluorescence Stokes shift,[b] (cm^{-1}) in hexane	fluorescence quantum yield in hexane (±0.02)	excited state τ (ps)[f]	
	absorption[b]	emission[b]			hexane	hexadecane
DPB	230	160	650	0.35[e]	465 ± 10	780 ± 30
DPCP	180	160	1200[c]	0.98	1900 ± 100	1900 ± 100
stiff-5-DPB	160	200	270	0.32	455 ± 10	700 ± 30
TPB	170	230	2920[c]	0.78	1900 ± 100	1900 ± 100
TPCP	220	250	2320[c]	0.04	90 ± 6	280 ± 8

[a] Change in polarizability between hexane and dodecane, $\Delta\alpha = 0.025$; $A = (\nu' - \nu)\Delta\alpha$. [b] Values rounded to the nearest 10. [c] Measured between the midpoints of the red edge of the absorption and blue edges of the emission bands. [d] Shifts determined from weighted band average $\Sigma_{band}\lambda I\lambda/\Sigma_{band}I\lambda$. [e] Reference 19. [f] Uncertainties estimated from the quality of the fit.
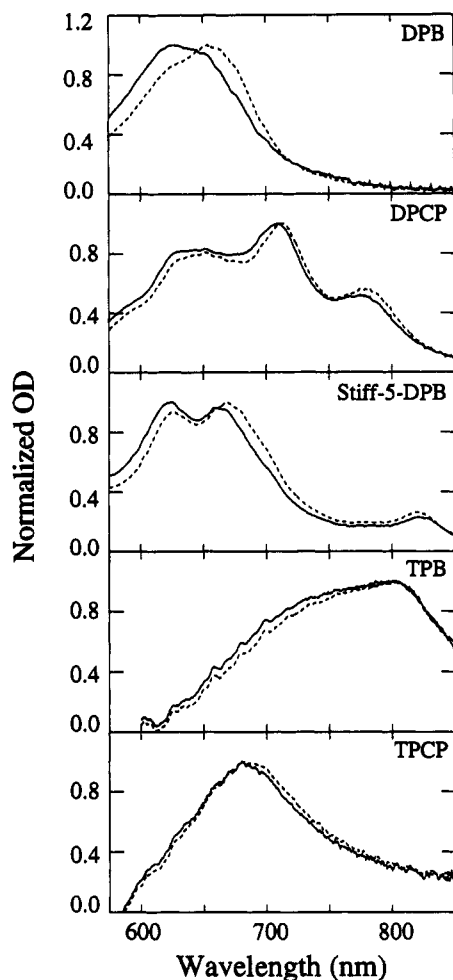

Figure 3. Excited-state absorption spectra in pentane (solid line) and dodecane (dashed line) solutions of DPB, DPCP, stiff-5-DPB, TPB, and TPCP. All spectra are normalized at the absorption maximum for comparison between spectra.

spectrum. This may be due to a solvent-sensitive Franck–Condon overlap between the S_0 and S_1 states for these two molecules, suggesting different degrees of solvent-induced geometry changes from different solvent–molecule interactions.

Excited-State Absorption Measurements. Excited-state absorption spectra were obtained in pentane and dodecane using 355-nm excitation. The results are shown in Figure 3. The DPB spectra appear as broad structureless bands whose shape is strongly dependent on solvent polarizability. In contrast, the DPCP spectra appear as structured bands with maxima near 780, 720, and 650 nm and a shoulder at 600 nm. The DPCP spectra show no significant shape changes with the solvents used in this study, although the spectra do exhibit a red shift with increasing solvent polarizability.

The excited-state absorption spectra for stiff-5-DPB are somewhat structured with maxima at approximately 620 and 680 nm, and an additional small peak observed around 825 nm.

The shape of the excited-state absorption band in the 650-nm region is dependent on the solvent. In pentane, the 620-nm peak is slightly higher in amplitude than the 680-nm peak; in dodecane, the opposite is observed. The band also appears to red-shift as the polarizability is increased from pentane to dodecane. Similar spectral behavior is observed for DPB under these conditions. The excited-state absorption spectral similarities and the absorption and emission measurements indicate that the electronic excited states giving rise to the broad 650-nm bands in stiff-5-DPB and DPB are very similar. That is, the S_1 state of stiff-5-DPB is of B_u character, and the S_1 surfaces are similar for these two molecules. However, the band observed at 825 nm for stiff-5-DPB behaves very differently from the stronger 650-nm band. This band shows little change when the polarizability is increased (although the relative amplitude of the peak does increase slightly for the dodecane solvent). The different spectral change with solvent polarizability of the 825-nm band suggests that this transition orginates from a different excited-state surface than the main 650-nm band. This transition may originate from the closely lying $2A_g$ state. The $2A_g$ state may be closer in energy to the $1B_u$ in stiff-5-DPB as a result of perturbations from the five-membered rings. The predominant configurations in the $2A_g$ state contain orbital promotions from molecular orbitals with density on carbon atoms bonded to the alkyl substituents (five-membered rings).[15] Simple perturbed molecular orbital (PMO) considerations indicate that this will lower the $2A_g$ state relative to the $1B_u$, making thermal population of the $2A_g$ state more probable.

The $S_n \leftarrow S_1$ absorption for TPB and TPCP (Figure 3) appear as broad structureless bands centered near 790 and 690 nm, respectively, with only a slight dependence on solvent polarizability. No shape changes such as those observed in DPB occur. However, it does appear that the TPB band is somewhat broader in pentane, while the TPCP band is broader in dodecane. Both bands shift only slightly with changes in solvent polarizability, and in this respect are more similar to the $S_n \leftarrow S_1$ bands observed for DPH and DPO,[31] whose S_1 states have been determined to be $2A_g$, than for DPB.

Absorption Dynamics Measurements. Excited-state absorption dynamic measurements were also obtained for these molecules.

DPB. The femtosecond transient absorption dynamics of DPB in hexane solution at 620 nm after 310-nm excitation are shown in Figure 4. The data are well fit to an instrument-limited rise ($\leq$120 fs) followed by a 465 ± 10 ps exponential decay. This result is in excellent agreement with previous transient absorption[2] and fluorescence[1,19] measurements. Additional femtosecond measurements taken at 660 and 690 nm showed identical dynamics, indicating uniform evolution of the entire S_1 absorption band. Thus there is no evidence for state-dependent dynamics, including thermal population of one state at the expense of another as has been previously suggested,[16] or for vibrational relaxation. Experiments on DPB in different solvents (results not shown) show a strong S_1 lifetime dependence on viscosity, in good agreement with the extensive investigations by others.[1,2,19,32]

DPCP. The picosecond transient absorption dynamics of DPCP in hexane solution pumped with 295-nm light were probed at several wavelengths throughout the S_1 absorption band. These

Transient Absorption of DPB in Hexane
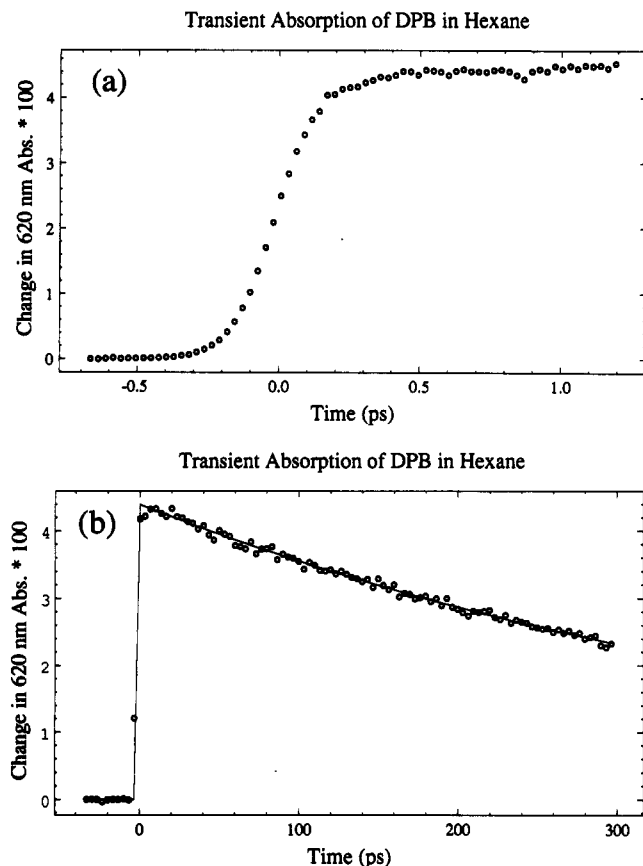

Transient Absorption of DPB in Hexane

Figure 4. Transient absorption of DPB in hexane pumped with 310-nm light and probed at 620 nm on the time scale of (a) 0–1 ps and (b) 1–300 ps. Circles are the data points, and the solid lines are simple exponential fits to the data with the lifetime reported in Table 1.
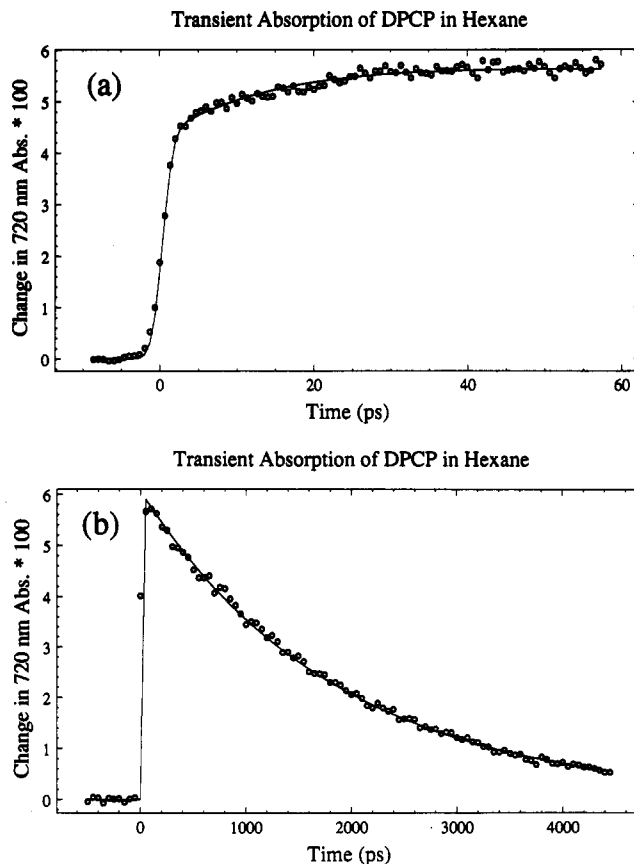
Transient Absorption of DPCP in Hexane

Transient Absorption of DPCP in Hexane

Figure 5. Transient absorption of DPCP in hexane pumped with 295-nm light and probed at 690 nm on the time scale from (a) 1–60 ps and (b) 1 ps to 4.4 ns. Circles are the data points, and solid lines are simple exponential fits to the data with the lifetime reported in Table 1.

wavelengths correspond to three of the features observed in the DPCP S_1 absorption: the sharp peak at 720 nm, the broad shoulder centered near 650 nm, and the red edge of the second shoulder in the absorption near 600 nm. The picosecond data were fit with combinations of simple exponentials convoluted with a 1-ps Gaussian representing the instrument response function. The data show an instrument-limited rise (≤ 1 ps) followed by a slower rise of roughly 15 ps which has a much smaller amplitude (the amplitude ratio is 1:5 for the slower rise: initial rise, making accurate determination of the slower rise time difficult). The absorption at all three wavelengths then undergoes single exponential decay with a lifetime of 1.9 ± 0.1 ns. Typical scans at 720 nm are shown in Figure 5. Femtosecond transient absorption measurements at 620 nm after 310-nm excitation showed identical results: an instrument-limited absorption rise of ≤ 120 fs followed by a slower 15-ps rise of smaller amplitude and a decay of ~ 2 ns.

To measure the effects of solvent polarizability and viscosity on the picosecond transient absorption dynamics of DPCP, experiments were performed on decane and hexadecane solutions. The results for all three probe wavelengths in both solvents were identical to those measured in hexane solutions within the error of the fit. These results are in agreement with the static transient absorption data (Figure 3) which showed no significant spectral changes between solvents of different polarizability. The lack of viscosity dependence in the dynamics also indicates that there is no significant large amplitude motion associated with the dynamics of the S_1 state of DPCP.

Other DPB Analogs. To better understand the excited-state processes of DPB, we also investigated the excited-state dynamics of the other DPB analogs pictured in Figure 1.

a. Stiff-5-DPB. The picosecond transient absorption decay at 620 nm after 295-nm excitation of stiff-5-DPB in hexane is

shown in Figure 6. A pulse-width-limited rise (≤ 1 ps) followed by a single exponential decay were observed here as well as at 680 nm. Different dynamics were observed in dodecane solution, with a small-amplitude (1:6) 15-ps rise following the initial absorption rise, similar to that observed in DPCP. This 15-ps rise was followed by a viscosity-dependent decay. The decay values (455 ps (hexane) and 780 ps (hexadecane)) are in good agreement with those previously reported (406 ps (hexane) and 765 ps (hexadecane)).[1]

b. TPB. The 620-nm picosecond transient absorption dynamics of 295-nm-excited TPB in hexane are shown in Figure 7. The data reflect a pulse-width-limited rise followed by a 1.9-ns exponential decay, in agreement with previous fluorescence measurements.[33] A more extensive wavelength study is reported elsewhere.[32] TBP shows no change in excited-state lifetime as a function of viscosity; the absorption dynamics were identical in hexane and dodecane solutions.

c. TPCP. Figure 8 presents the picosecond transient absorption dynamics of TPCP in hexane pumped at 295 nm and probed at 690 nm, the peak of the S_1 absorption. The results show a pulse-width-limited rise (≤ 1 ps) followed by a single exponential decay with a 90-ps lifetime. Transient absorption data taken at 550 and 740 nm, on the wings of the S_1 absorption band, showed identical dynamics to those at 690 nm. Femtosecond transient absorption experiments in which TPCP was excited with 310-nm light and probed at 620 nm also displayed identical dynamics, but with an initial rise of ≤ 120 fs. To test the effects of solvent viscosity on the dynamics of TPCP, picosecond measurements were also made in hexadecane solution. The results showed an instrument-limited absorption rise of ≤ 1 ps followed by a single exponential decay of 280 ps. This 10-fold solvent viscosity increase from hexane (0.326 cP) to hexadecane (3.34 cP) produces a 3-fold change in the excited-state lifetime. Similar viscosity-dependent
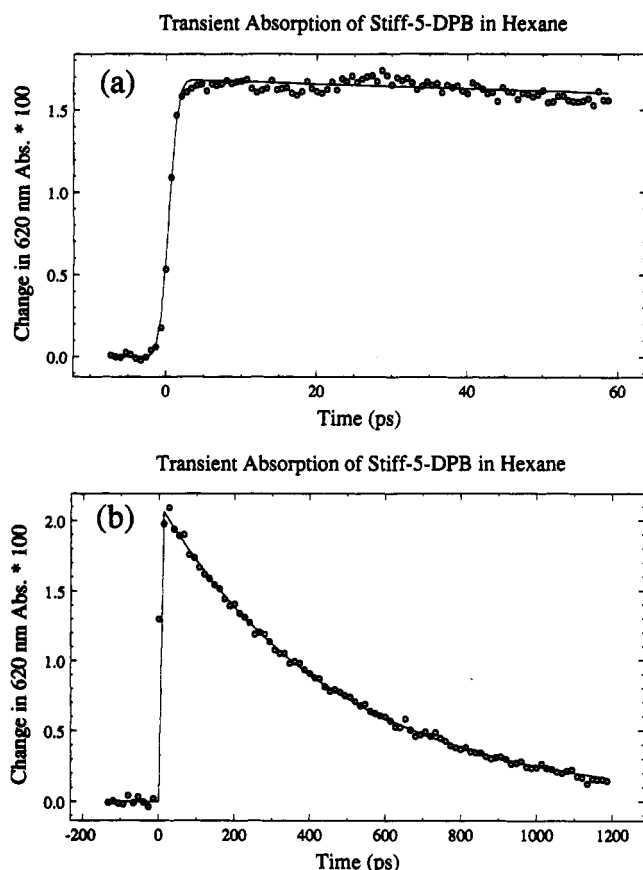
Transient Absorption of Stiff-5-DPB in Hexane

Transient Absorption of Stiff-5-DPB in Hexane

Figure 6. Transition absorption of stiff-5-DPB in hexane pumped with 295-nm light and probed at 620 nm on the time scale from (a) 1–60 ps and (b) 1 ps to 1.2 ns. Circles are the data points, and solid lines are simple exponential fits to the data with the lifetime reported in Table 1.

Transient Absorption of TPB in Hexane

Transient Absorption of TPB in hexane

Figure 7. Transient absorption of TPB in hexane pumped with 295-nm light and probed at 620 nm on the time scale from (a) 1–4 ps and (b) 1 ps to 3 ns. Circles are the data points, and solid lines are simple exponential fits to the data with the lifetime reported in Table 1.

lifetime behavior has been observed for DPB and other flexible polyenes and has been assigned to large-amplitude isomerizational motion. This assignment is not tenable for TPCP, given its locked carbon backbone. One possibility is that the dynamics of TPCP may be due to a photocyclization reaction,[34] similar to that observed in cis-stilbene, to form dihydrophenanthrene.[35]

Discussion

With this combination of spectral and dynamical measurements, we can begin to elucidate details of the excited-state processes of these compounds. We first discuss the most studied of these molecules, DPB, and then consider related systems.

DPB. The transient absorption dynamics of DPB observed in this study can be accounted for by a single B_u excited state decaying through two principal channels: radiative decay to S_0 and a nonradiative channel involving twisting around a polyene double bond.[36] Our results do not support the suggestion of Rulliere et al.[16] that solvent-assisted level inversion of A_g and B_u excited states by phenyl twisting motions is necessary to explain the excited-state dynamics of DPB. In particular, we find no evidence for the transient absorption rises at 625 nm and 690 nm of 80 and 100 ps, respectively, reported by Rulliere and co-workers. Our results show pulse-width-limited rises of less than 120 fs at several wavelengths in the absorption band, consistent with the picosecond rise observed by Gehrke et al.[37] at 620 nm. In addition, we cannot account for the apparent discrepancy between the excited-state lifetime of 465 ± 10 ps measured in this and other studies,[1,19,32,38] and the lifetime of 700 ± 100 ps reported by Rulliere et al. The identical dynamics that we observe at 625 nm and 690 nm also suggest the evolution of a single electronic state. Furthermore, studies on phenyl twisting in triphenylmethane dyes indicate that large-amplitude phenyl torsion takes place on the
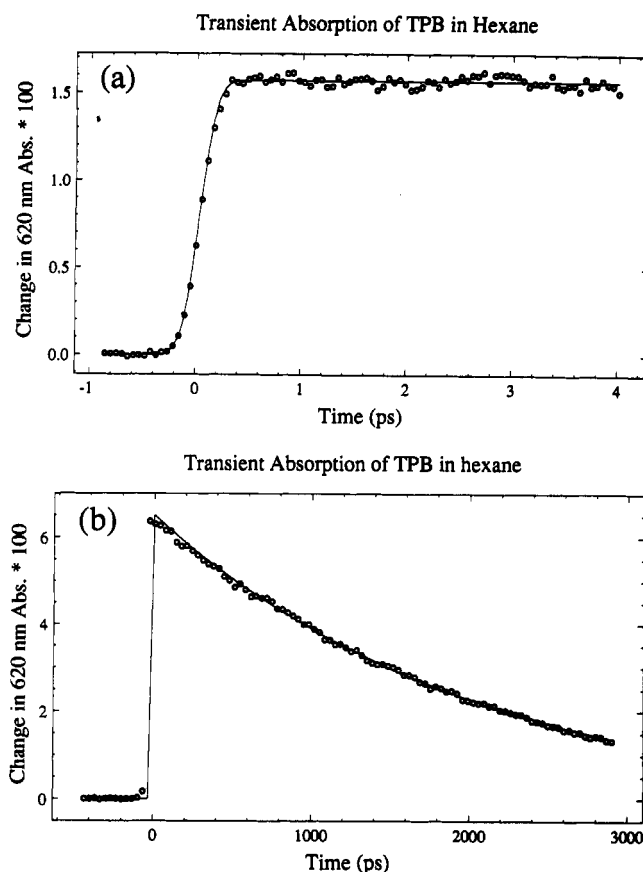
time scale of a few picoseconds at these viscosities;[39] this motion would have been easily observed in DPB with our 120-fs-time resolution.

DPCP. *Excited-State Dynamics.* The identical dynamics at all three probe wavelengths (corresponding to the features observed at 600, 650, and 720 nm in the excited-state absorption spectrum, Figure 3) suggest that the entire transient absorption band reflects the evolution of a single excited state as observed in DPB. There is no evidence for thermal population of one state at the expense of another, nor any wavelength-dependent shifts suggesting any significant state-dependent dynamics. Thus, the peaks and shoulders in the DPCP transient absorption spectrum (Figure 3), like that of DPB, are better assigned to a C=C stretching progression from a single electronic manifold, not to absorption from different A_g and B_u excited states.

The lack of dynamics on early time scales eliminates the possibility that large-amplitude motions, such as phenyl twisting, play an important role in the excited-state electronic structure of DPCP. As discussed above, large-amplitude phenyl twisting motion usually occurs on the time scale of 1–3 ps in low-viscosity solutions. The small 15-ps rise observed in the DPCP absorption dynamics is an order of magnitude too long to reflect large-amplitude phenyl torsion. This conclusion is also supported by the hexadecane results (Table 1) which show no dynamical changes for an order of magnitude viscosity increase, whereas the dynamics of the nearly barrierless phenyl twist should scale more or less linearly with viscosity. Hence we can conclude that large-amplitude phenyl or isomerizational motion is not important to the excited-state dynamics of DPCP and, more generally, that a phenyl-twisting-level inversion mechanism is not relevant to the excited-state dynamics of either DPB or DPCP.

The small 15-ps rise in the DPCP absorption (Figure 5) is probably best assigned to vibrational relaxation in the S_1 state,

Transient Absorption of TPCP in Hexane

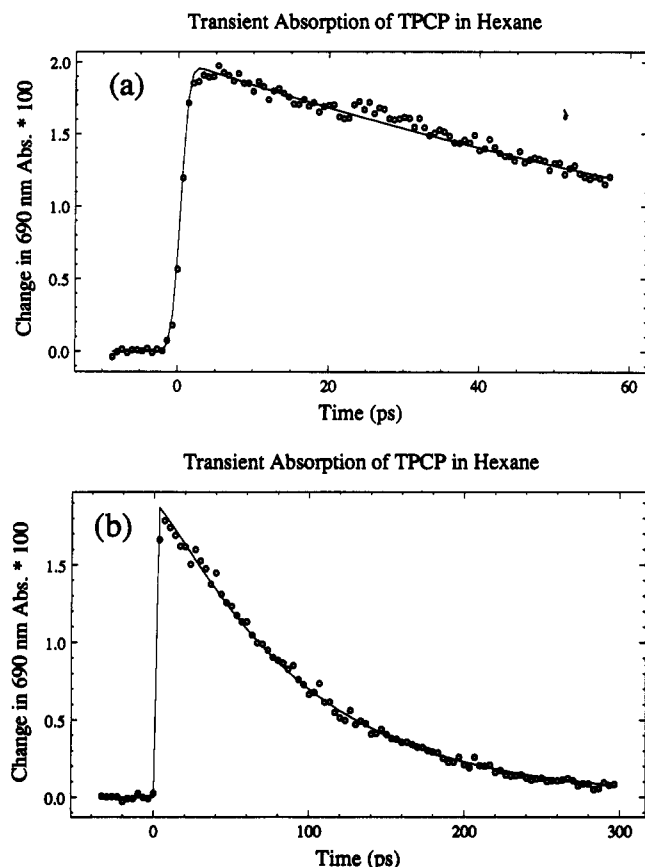Transient Absorption of TPCP in Hexane

Figure 8. Transient absorption of TPCP in hexane pumped with 295-nm light and probed at 690 nm on the time scale from (a) 1–60 ps and (b) 1–300 ps. Circles are the data points, and solid lines are simple exponential fits to the data with the lifetime reported in Table 1.

in agreement with the cooling rate of other conjugated hydrocarbons in molecular solvents.[40] Vibrational cooling is usually accompanied by a blue shift in the electronic absorption because the equilibrium displacement of a vibrational coordinate is usually larger in more highly excited electronic states. Thus, the electronic vertical transition energy between a vibrationally excited state in the lower electronic well is usually smaller than that of a vibrationally cool state near the equilibrium displacement.[40] This would be evidenced by faster rise times to redder wavelengths and slower rise times to the blue. This signature is most likely masked in the DPCP transient absorption spectrum due to the extremely small relative amplitude of the signal. The small amplitude of the cooling signature is expected for DPCP by comparison to studies on similar molecules, including stilbene and DPB, which show no evidence for vibrational cooling in transient absorption. This implies that all these systems have very little displacement between their S_1 and S_n electronic states, resulting in little change in the S_1 electronic absorption spectrum with vibrational excitation. The change in Franck–Condon overlap upon vibrational cooling in DPCP is consistent with the increased structure in the fluorescence band as described above.

Quantum Yield and Lifetime. The viscosity-independent quantum yield of 0.98 ± 0.1 and excited-state lifetime of 1.9 ± 0.1 ns, presented in Table 1, indicate that there are no significant nonradiative channels accessible to DPCP. Since DPCP has only phenyl torsional motion available due to its locked carbon backbone, this supports the conclusion of Lee et al.[1] that in the one-dimensional isomerization of DPB, only motion about the butadiene backbone, not phenyl torsional motion, is important. One may note that stilbene, which has fewer degrees of freedom than DPB, has been suggested to undergo multidimensional isomerization.[41]

Given the similar conjugated electronic structure of DPCP

and DPB, the S_1 radiative lifetime should be similar for the two molecules. Thus the radiative lifetime of DPCP is expected to be ~2.0 ns.[4] It is interesting to note that the natural fluorescence lifetime obtained from fluorescence quantum yield and lifetime data for DPCP is 2 ns while the natural lifetime calculated from the integrated absorption intensity is ~4.2 ns. This most likely indicates that DPCP molecules in the excited state are more planar on the average than those in the ground state.[42,43] This is consistent with a fluorescence spectrum that is more resolved than the absorption spectrum and a relatively large fluorescence Stokes shift.

Characterization of Lowest Excited Singlet State. Examination of Figure 2 shows that the ground-state absorption and the emission bands of DPCP show a red shift with increasing solvent polarizability similar to that for DPB. This type of shift is expected for allowed $1B_u \leftarrow 1A_g$ (absorption) and $^1B_u \rightarrow {}^1A_g$ (emission) transitions, because the more ionic B_u states are stabilized by solvent polarizability whereas the A_g states are relatively unaffected. If the absorbing and emitting states are the same, the fluorescence emission and ground-state absorption should shift by similar amounts, as is observed. Thus it appears that the electronic nature of the S_1 state of DPCP is very similar to that of DPB. However, the effects of solvent and temperature on the excited-state absorption spectrum of DPCP are different from that of DPB. Wallace-Williams et al.[17] reported large changes in the excited-state absorption spectra of DPB in hydrocarbon solvents with changing solvent polarizability and temperature, while the spectral shapes of DPCP under the same conditions remained fairly constant. The differences in the excited-state processes of DPCP and DPB raise the question of the effect of rotamers and substitutions on these diphenylpolyene models.[17,44,45]

Other Substituted Diphenylpolyenes. The results of the stiff-5-DPB, TPB, and TPCP studies further shed light on how the excited-state processes of DPB are affected not only by symmetry changes and alkyl substitution but also by additional phenyl substitution.

Stiff-5-DPB. Steady-state and dynamic spectroscopic measurements show that stiff-5-DPB is very similar to DPB in electronic structure, geometry, and isomerizational motion. The small fluorescence Stokes shift, the mirror image symmetry, and the similar polarizability shifts in absorption and emission all point to B_u character of the S_1 state, as is the case for DPB. This similarity suggests that phenyl torsional motion, which is unavailable in stiff-5-DPB, is not important to the excited-state dynamics of DPB, in agreement with previous studies on this molecule[1] and the conclusions of the above experiments on DPCP. The similarity of the viscosity-dependent dynamics argues that stiff-5-DPB, like DPB, makes a good model for one-dimensional isomerization reactions.[1] Results on the other DPB analogs, however, show that simple structural considerations are not enough to predict whether or not a given species is useful as a model compound for isomerization reactions.

TPB and TPCP. Additional phenyl substitution onto DPB or DPCP changes the spectroscopic and dynamic properties of these compounds. The S_1 state surface appears to become flatter, causing a broader emission than absorption band, and the large fluorescence Stokes shift indicates a much larger geometry change in the excited state than found in the DPB and DPCP parent compounds.

The effects of viscosity on the lifetime of the polyenes also change considerably with the additional phenyl substitution. TPB, a DPB analog with two additional terminal phenyl groups, shows no change in excited-state lifetime as a function of viscosity. The S_1 state lifetime of TPB is equal to its radiative lifetime of ~2.0 ns,[33] which is essentially the radiative lifetime of DPB. Somehow, the presence of the two extra phenyl groups must shut off the large-amplitude isomerization without opening other

channels for nonradiative decay. This is surprising in light of studies on stiff-6-DPB and stiff-7-DPB[1] where the radiative lifetime decreased significantly as steric constraints were increased. This may be explained by considering the effects of π-conjugation for these phenyl-substituted polyenes. The single excitation from the highest occupied molecular orbital to the lowest unoccupied molecular orbital in DPB represents a bond-order reversal that is mainly (90%) localized in the polyene chain. Both MO's are 57% localized in the polyene moiety.[15] Thus it appears that deviation from planarity of the phenyl ring with respect to the polyene π-system will decrease conjugation and bond-order reversal. One expects that the larger the bond-order reversal, the smaller the activation energy for photoisomerism about the double bond of the butadiene moiety. In the case of stiff-5-DPB and DPB, the phenyl groups are nearly planar and photoisomerization competes with nonradiative channels (internal conversion) and with fluorescence, giving rise to viscosity-dependent dynamics (465 ps in hexane). In the case of TPB, steric effects of the additional phenyl rings prevent planarity, resulting in a barrier large enough to block photoisomerization during the lifetime of the excited state of TPB, leading to a viscosity-independent long-lived transient absorption (1.9 ns).

The DPCP analog with additional phenyl substitution, TPCP, shows a simple viscosity-dependent S_1 lifetime like that of DPB, but here the trans → cis nonradiative channel is not available because of the constrained butadiene moiety. DPCP and TPCP show a trend in excited-state dynamics with phenylation that is reversed from DPB and TPB: creation of TPB from DPB reduces phenyl–polyene interactions, which turns off the isomerization channel; creation of TPCP from DPCP apparently results in a nonradiative channel where none existed before. The completely new nonradiative channel implied by the short–lived viscosity-dependent lifetime of TPCP may possibly be a photocyclization reaction.

These results show that for DPB, DPCP, TPB, and TPCP, there is no *a priori* way to determine which compounds would show viscosity-dependent S_1 dynamics from their structures alone, indicating that care should be exercised when choosing such systems as model compounds for one-dimensional isomerization reactions.

Conclusions

The steady-state spectroscopic measurements of several DPB structural analogs suggest that modification of the polyene chain with both alkyl and phenyl groups can greatly change the characteristics of the first excited singlet electronic state. The connection between electronic structure and dynamical measurements is integral to the understanding of the photophysics of these systems. An earlier model of solvent-assisted level inversion in DPB that attempted to correlate DPB electronic structure with dynamical information is not supported by the spectral dynamics observed here. In addition, we do not find an important role for phenyl torsional motion in the excited-state dynamics of DPB, stiff-5-DPB, and DPCP, though the phenyl–polyene interactions are important in determining the shape of the excited-state surface and the activation energy for photoisomerization. Such an effect is evidenced in TPB where the energy of activation is increased to the point where the isomerization channel is shut off, leading to viscosity-independent dynamics. The viscosity-dependent dynamics of TPCP are due to a new channel, possibly a photocyclization reaction similar to that in *cis*-stilbene. Our results show that isomerization pathways cannot be simply predicted from structural considerations alone and that seemingly minor structural alterations of diphenylpolyenes can significantly change the nature of the excited state and resulting dynamics.

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