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Sudden Polarization in the Twisted, Phantom State of Tetraphenylethylene Detected by Time-Resolved Microwave Conductivity

Wouter Schuddeboom,[†] Stephan A. Jonker,[†] John M. Warman,[*,†] Matthijs P. de Haas,[†] Martien J. W. Vermeulen,[†] Wolter F. Jager,[‡] Ben de Lange,[‡] Ben L. Feringa,[‡] and Richard W. Fessenden[§]

Contribution from IRI, Delft University of Technology, Mekelweg 15, 2629 JB Delft,
The Netherlands, Chemical Laboratories, University of Groningen, Nijenborgh 16,
9747 AG Groningen, The Netherlands, and Radiation Laboratory,
University of Notre Dame, Notre Dame, Indiana 46556

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Abstract: Photoexcitation of the symmetrical molecules tetraphenylethylene and tetra-*p*-methoxyphenylethylene dissolved in saturated hydrocarbon solvents results in a transient increase in the dielectric loss of the solutions as monitored using the nanosecond time-resolved microwave conductivity (TRMC) technique. This provides direct evidence for the dipolar, or "zwitterionic", nature of the ^{1}p* phantom state formed from S_1 by rotation around the central carbon–carbon bond. Dipole relaxation occurs mainly by charge inversion between the two energetically equivalent zwitterionic configurations, $Z_\pm$, on a timescale of several picoseconds. A minimum dipole moment of ca. 7.5 D for the individual $Z_\pm$ states is found. The fluorescence of TPE in alkane solvents has two decay components, one with a decay time less than 200 ps and a second with a decay time of 1.9 ns. The former ($\lambda_{max} \approx 490$ nm) is assigned to emission from the partially relaxed S_1 state prior to twisting. The latter ($\lambda_{max} \approx 540$ nm) is assigned to emission from a small, ca. 1%, concentration of the relaxed S_1 state in equilibrium with the ^{1}p* state in saturated hydrocarbon solvents.

Introduction

Photoinduced cis–trans isomerization of ethylenic double bonds is a process of fundamental importance in both biological and technological chemistry. The mechanism of vision is without doubt the most vivid example of this, with rotation around a carbon–carbon bond following photon absorption setting off a chain of events, which lead to data storage of enormous complexity. The twisting process is also the basis underlying the operation of many of the proposed candidates for molecular opto-electric and opto-mechanical switching and storage devices.

Much fundamental theoretical and experimental attention has focused on the details of the intermediate steps in the isomerization mechanism including the breaking of the π-bond, rotation within the biradical state, and the re-formation of the π-bond either in the original or 180° rotated configuration of the ground-state molecule. An intuitively somewhat surprising prediction of theoretical studies has been that the most stable excited state of even simple, symmetrical ethylene derivatives most probably involves, in addition to partial rotation, complete charge separation across the carbon–carbon bond.[1-10] Direct experimental evidence for this "sudden polarization" effect, first proposed by Bonacic-Koutecky et al.,[1] has proven difficult to find. Recently, however, strong evidence was provided for the formation of a "zwitterionic" excited state of tetraphenylethylene.[11,12]

In the work reported here, we have used the time-resolved microwave conductivity (TRMC) technique[13] to look directly for the change in dipole moment of tetraphenylethylene that should accompany photoexcitation, if charge separation does, in fact, take place. Positive results have been found.

Experimental Section

The solvents *n*-hexane (Merck), cyclohexane (Merck), and benzene (Fluka) were UV spectroscopic grade and were used without further purification. The *trans*-decalin (Fluka, purum) was passed over a column of freshly activated silica gel prior to use. The tetraphenylethylene, TPE, was obtained from Aldrich as a white crystalline solid. The purity was checked by elemental analysis and by ^{1}H and ^{13}C NMR. The compound proved to be analytically pure and was therefore used without further purification: mp 216.3–217.9 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.06–7.18 (m, 2 OH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 126.42 (d), 127.65 (d), 132.33 (d), 140.97 (s), 143.73 (s). Anal. Calcd for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 93.97; H, 6.16. The tetra(*p*-methoxy)phenylethylene, MeOTPE, was prepared from 4,4′-dimethoxybenzophenone according to the procedure used for the preparation of bixanthylidines.[14] Crystallization from *p*-xylene yielded analytically pure MeOTPE as a slightly yellow crystalline solid (81.4% yield): mp 183.8–185.1 °C; ^{1}H NMR, δ 3.76 (s, 12 H), 6.76 (dd, $J = 8.9$, 2.1 Hz, 8 H), 6.96 (dd, $J = 8.9$, 2.1 Hz, 8 H); ^{13}C NMR δ 55.06 (q), 113.01 (d), 132.53 (d), 136.87 (s), 138.36 (s), 157.75 (s). HRMS: calcd for $C_{30}H_{28}O_4$, 452.199; found, 452.198. Anal. Calcd: C, 79.62; H, 6.24. Found: C, 79.85; H, 6.38.

Dilute (ca. 10^{-4} M) solutions of TPE and MeOTPE contained within a microwave cavity cell were flash-photolyzed using a single 7-ns fwhm pulse of 308-nm light from a Lumonics HyperEX 400 excimer laser. Any transient change occurring in the microwave conductivity, $\Delta\sigma(\omega)$, of the solution was monitored as a change in the microwave power reflected by

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[†] Delft University of Technology.

[‡] University of Groningen.

[§] University of Notre Dame.

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Table I. Fluorescence Characteristics of Tetraphenylethylene

solvent (ϵ, η)[a]	emission maximum[b] (nm)	lifetime (ps)	quantum[d] yield × 10^4
n-hexane (1.89, 0.31)	485	<200	2.3
	530	1800	13.3
cyclohexane (2.02, 1.00)	495	<200	6.1
	545	1900	10.9
trans-decalin (2.17, 2.18)	500	15[c]	10.0
	545	1900	10.6
benzene (2.28, 0.65)	485	<200	4.5

[a] Relative dielectric constant and viscosity in centipoise at room temperature. [b] Fast and slow decay components separated by kinetic fits to fluorescence transients; both bands had an average fwhm width of 0.65 eV. [c] Reference 17. [d] Based on a total (spectrofluorimeter) quantum yield for cyclohexane of 17.0 × 10^{-4} and relative areas of time-resolved spectral components.

the cell. The time-resolved microwave conductivity (TRMC) technique and the method of data reduction have been described fully elsewhere.[13] The change in microwave conductivity is related to the change in the relative dielectric loss of the solution, $\Delta\epsilon''$, by $\Delta\epsilon'' = \Delta\sigma(\omega)/\omega\epsilon_0$, with ω the radian microwave frequency and ϵ_0 the permittivity of vacuum. Changes of as little as 2×10^{-7} in ϵ'' can be detected with a response time of 5 ns.

If photoexcitation of a solute molecule in a nonpolar solvent results in a dipole moment change from zero in the ground state to μ_* in the excited state, then the change in the high-frequency conductivity of the medium will be given by

$$\Delta\sigma(\omega) = (\epsilon' + 2)^2\mu_*^2F(\omega\theta)N_*/27k_BT\theta \qquad (1)$$

In (1), N_* is the concentration of excited states present, ϵ' is the relative dielectric constant of the solution, k_BT is the characteristic thermal energy, and Θ is the dipole relaxation time. For a single relaxation time, $F(\omega\Theta)$ in (1) is given by the Debye expression:

$$F(\omega\Theta) = (\omega\Theta)^2/[1 + (\omega\Theta)^2] \qquad (2)$$

For the microwave frequencies used of ca. 10 GHz, the reciprocal radian frequency, $1/\omega$, is approximately 15 ps.

The TRMC signal from a benzene solution of *N*,*N*-dimethylaminonitrostilbene, DMANS, was used for internal actinometry taking for the lifetime and dipole moment of the S_1 state of DMANS 3.1 ns and 24.5 D, respectively. The integrated beam intensity incident on the solution was ca. 7 mJ/cm^2 and corresponded to ca. 0.3 photon per solute molecule in the irradiated region. All solutions were purged with CO_2 to remove oxygen and to scavenge any mobile electrons, which might be formed by low-yield, multiphoton ionization events.

Time-resolved fluorescence measurements were carried out using a nitrogen laser (Laser Photonics, LN 1000) with an excitation wavelength of 337 nm, a pulse width of 0.8 ns (fwhm), and an energy per pulse of approximately 1.4 mJ. The beam cross section at the position of the cell containing the solution was 3 mm × 7 mm. The light emitted from a 1-cm quartz cuvette containing the OD $\approx$ 0.2 solutions was monitored at 90° to the laser beam and was detected using a ITL TF1850 photodiode with a response time of 100 ps after passing through a monochromator (Jobin Ivon). The wavelength range covered was 390 to 650 nm. The transient output voltage of the photodiode was amplified by a factor of 27, using Picosecond Pulse Labs 5800 series amplifiers (risetime < 150 ps) prior to monitoring with a Tektronix 7912 (0.5 GHz) transient digitizer. A single-shot pulse mode was used with a maximum number of 64 traces being averaged. The data presented in Figure 2 are uncorrected for the photodiode spectral sensitivity. The wavelength maxima and quantum yields reported in the text and in Table I have, however, been corrected for this.

The quantum yield of fluorescence from a solution of TPE in cyclohexane was determined to be 17.0 × 10^{-4} over the spectral range 390 to 790 nm using a SPEX Fluorolog-2 spectrofluorimeter and 9,10-diphenylanthracene in cyclohexane (with $\phi_{DPA} = 0.90$) as reference. The quantum yields of the individual components in the pulse experiments were based on the absolute total yield found for cyclohexane and the height x half-width product of the individual time-resolved spectra.

Results and Discussion

Time-Resolved Microwave Conductivity. Our initial attempt to look for the sudden polarization effect on photolysis of TPE derivatives using the TRMC technique was carried out on solutions of TPE and MeOTPE in benzene. The results are shown in Figure 1, traces A and B. The occurrence of a transient increase in dielectric loss on flash photolysis of the TPE solution is barely visible even to the "trained eye". That a small transient change does occur can be seen, however, if the TPE data are compared with those for MeOTPE, for which no TRMC signal at all was discernible. Because the TPE signal was so close to the noise level, it was considered that this did not provide convincing evidence for the formation of a dipolar excited state.

The work of Greene[15] and Schilling and Hilinski,[11] using picosecond optical absorption spectroscopy, and Morais et al.[12] using picosecond optical calorimetry, has provided strong evidence for a zwitterionic nature of the relaxed upper singlet state of TPE in the form of a very pronounced sensitivity of its lifetime to the polarity of the solvent. Of particular relevance was the finding that in all solvents, except saturated hydrocarbons, the lifetimes were only a few hundred picoseconds or less.

Based on the $E_T(30)$ parameter for benzene and the correlation found with this parameter by the previous authors, the expected lifetime in benzene can be estimated to be approximately 200 ps. Such a short lifetime, compared with the 7-ns laser pulse width, would result in a considerably diminished TRMC signal even for a transient with a dipole moment of several debye. For alkane solvents, however, much longer lifetimes of a few nanoseconds have been found. In view of this, it was decided to repeat the TRMC experiments using cyclohexane as solvent.

As can be seen by trace C in Figure 1, the cyclohexane solution of TPE did, in fact, give a TRMC signal much larger than that found in benzene and well outside of the noise limits of detection. Similar TRMC transients were observed for solutions of TPE in *n*-hexane and *trans*-decalin. Also, while MeOTPE displayed no detectable dielectric loss at all in benzene, a readily measurable signal was observed in cyclohexane as shown by trace D in Figure 1.

We exclude the possibility that the TRMC transients observed are due to multiphoton ionization of the solute on the basis of the relatively low laser pulse intensity. This corresponded to only ca. 0.3 photon per solute molecule in the irradiated region. Also, if highly mobile electrons did happen to be formed in low-yield, multiphoton processes, they would be scavenged within a few tens of picoseconds by the ca. 10^{-2} M CO_2 present in the solution.

Therefore, we attribute the TRMC transients in the saturated hydrocarbon solutions to the zwitterionic nature of the fully relaxed excited singlet states of TPE and MeOTPE in agreement with the conclusion of previous workers.[11,12,15] The present results thus provide direct, "electrical" confirmation that charge separation can and does occur on photoexcitation of ethylene derivatives even when they have symmetrical ground-state configurations.

The TRMC signal follows closely the laser pulse shape convoluted with the instrumental time response of approximately 5 ns. This is in agreement with expectations if the lifetime of the species responsible is only a few nanoseconds as found for the $^1p^*$ state based on the work of the previous authors.[11,12,15] Because of the short lifetime, however, quantitative analysis of the TRMC data, which can yield a value for the excited-state dipole moment, can only be made if an absolute value of the lifetime is available. The published estimates of the lifetime of the $^1p^*$ state of TPE in saturated hydrocarbons show a considerable spread: 1.4 ns,[11] 1.5–1.7 ns,[12] 3.0 ± 0.5 ns.[15] Therefore, it was decided to attempt to gain independent information on the lifetime of the $^1p^*$ state by single-shot, time-resolved fluorescence measurements.

Time-Resolved Fluorescence. In the inset to Figure 2A is shown a kinetic trace of the emission from a TPE–cyclohexane solution taken at 500 nm. This displays a fast component which follows the pulse shape and a slow component which decays over the first

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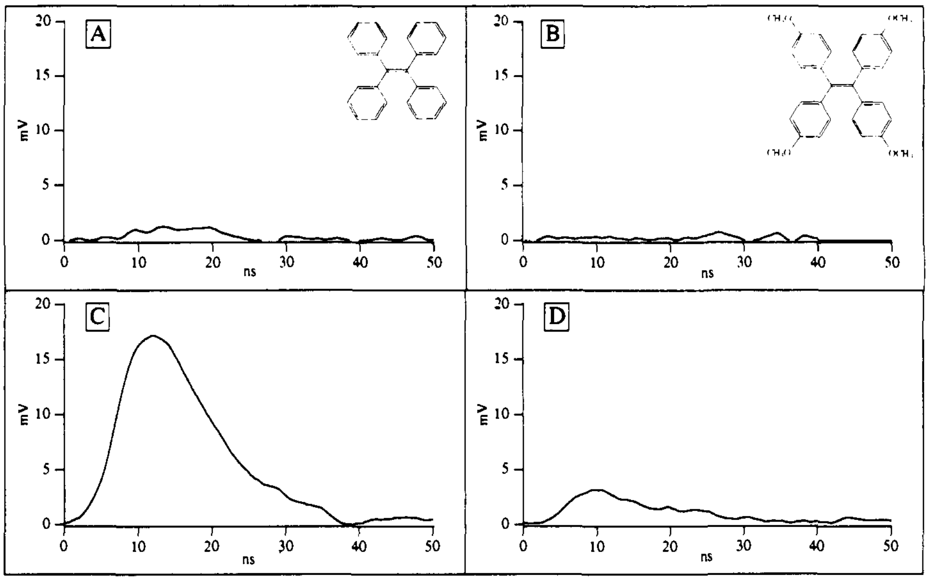

Figure 1. Transient changes in the dielectric loss on UV flash photolysis of solutions of: tetraphenylethylene in benzene, trace A; tetra-*p*-methoxyphenylethylene in benzene, trace B; tetraphenylethylene in cyclohexane, trace C; tetra-*p*-methoxyphenylethylene in cyclohexane, trace D; monitored by time-resolved microwave conductivity.

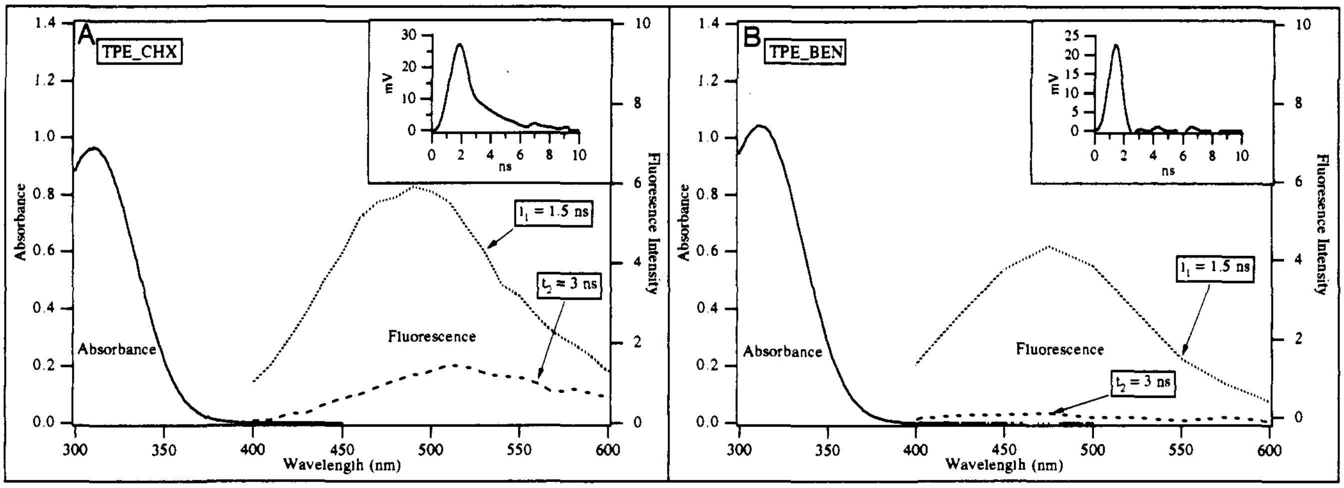

Figure 2. (A) Fluorescence spectra on 337-nm flash photolysis of a solution of tetraphenylethylene in cyclohexane taken at the maximum (in time) of the transient and 1.5 ns later. Inset: the time-resolved fluorescence emission transient monitored at 500 nm. (B) Fluorescence spectra on 337-nm flash photolysis of a solution of tetraphenylethylene in benzene taken at the maximum (in time) of the transient and 1.5 ns later. Inset: the time-resolved fluorescence emission transient monitored at 480 nm. The spectra shown are experimental data and have not been corrected for the response function of the photodiode detector.

few nanoseconds following the flash. The two components have slightly different spectral characteristics as is shown by the spectra in Figure 2A, taken at the peak (in time) of the transient and at a time 1.5 ns later. A shift to longer wavelengths is clearly seen. The bathochromic shift and after-pulse tail are found for all alkane solvents, but are absent for benzene as shown by Figure 2B. Solutions in benzene display only a single emission band with a maximum at approximately 490 ns which follows the shape of the laser pulse.

On kinetic analysis of the data for TPE in the alkane solvents, the two spectral components can be resolved into one with a lifetime of less than 200 ps and a maximum at ca. 490 nm and the other with a lifetime of 1.9 ns and a maximum in the region of 540 nm. (The band maxima and quantum efficiencies quoted in the text have been corrected for the spectral response characteristics of the photodiode; the spectral data plotted in Figure 2 are raw photodiode outputs.) The band maxima correspond to energies of 2.5 and 2.3 eV. These are to be compared with the first absorption maximum of TPE at 4.0 eV, illustrating the already well-known, large Stokes shift.[16] The intensity of the 490-nm component is found to increase with increasing viscosity of the solvent. This is accompanied by a slight shift in λ_{max} from 485 to 500 ns in going from *n*-hexane to *trans*-decalin. The 540-nm component is close to viscosity independent both in its magnitude and lifetime.

The fluorescence band of TPE at ca. 490 nm is well known from previous work and is attributed to emission from the planar S_1 state. The large Stokes shift is thought to be due to rotation of the phenyl rings from their propeller configuration in the ground state to a close to planar arrangement in the fully relaxed S_1 state. The emission spectrum and decay time are both viscosity dependent.[17-19] It has been suggested, however, that these two effects are most probably due to independent conformational rearrangements.[17] The blue shift in the spectrum with increasing

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viscosity has been attributed to increased hindrance to the rotational relaxation of the phenyl groups in the planar configuration. The increase in lifetime and quantum yield with viscosity is attributed to frictional hindrance to the out-of-plane twisting motion around the central C–C bond which leads to formation of the more stable $^1p^*$ state which subsequently decays nonradiatively.

The lifetime of the S_1 state of TPE has been determined to be 6 ps and 15 ps for 3-methylpentane and decalin solvents, respectively,[17] at room temperature. The time resolution of the present measurements was insufficient to be able to determine absolute lifetimes of the "fast", 490-nm component. Its intensity did, however, increase by a factor of close to 3 on going from *n*-hexane to cyclohexane and by a further factor of approximately 2 from cyclohexane to decalin in reasonable agreement with the viscosity effect expected based on the picosecond study. The cyclohexane solution of MeOTPE displayed approximately twice the emission intensity in the 490-nm region than TPE itself, presumably due to the increased lifetime in S_1 resulting from the greater hindrance to twisting caused by the peripheral methoxy groups. The slight red shift with increasing viscosity observed for the rapidly decaying component could be due to the increased time available for further phenyl group relaxation prior to twisting.

As mentioned above, the intensity and the decay kinetics of the 540-nm emission were found to be almost independent of the alkane used. The lifetimes of 1.8 to 1.9 ns lie within the range of previous estimates for the lifetime of the $^1p^*$ state in saturated hydrocarbon solvents given above and very close to the most recently reported value of 1.7 ns found for methylcyclohexane.[20] The fact that no delayed emission is observed for benzene is in agreement with the order of magnitude shorter lifetime expected for the $^1p^*$ state in this solvent.

The energy levels with respect to S_0 of $^1p^*$ and the diradicaloid, twisted ground state of TPE have been estimated to be 2.90 eV[12] and 1.54 eV,[21] respectively. Radiative emission from $^1p^*$ would therefore be expected to be situated in the region of 900 nm rather than 500 nm, as found. An explanation for this apparent anomaly in which the twisted $^1p^*$ state of TPE is in equilibrium with the relaxed, planar S_1 state has been proposed recently.[20] The equilibrium lies well to the side of $^1p^*$, so that while the emission is characteristic of S_1 it decays with the nonradiative lifetime of the former. This will be discussed further below, after considering the fluorescence quantum yields.

Fluorescence Quantum Yields. The integrated (390–790 nm) steady-state fluorescence quantum yield of TPE in cyclohexane at room temperature was found to be 17.0×10^{-4}. This is close to the value expected for TPE in a saturated hydrocarbon medium with a viscosity of 1 cP based on previous work.[18] The separate quantum yields of the fast and slowly decaying components were determined based on the relative values of the products of the intensities and half-widths of the individual spectral components derived from a kinetic analysis of the flash photolysis data. The individual quantum yields are listed in Table I together with the wavelength of maximum emission and the full width at half-maximum in electron volts.

The quantum yield of the long-lived component is seen to be almost independent of the alkane solvent used and equal to $12 \pm 2 \times 10^{-4}$. The quantum yield of the short-lived, 490-nm emission, on the other hand, increases substantially with increasing viscosity as mentioned above from 2.3×10^{-4} for *n*-hexane (η = 0.31 cP) to 10.0×10^{-4} for *trans*-decalin (η = 2.2 cP) with benzene (η = 0.61 cP) lying between *n*-hexane and cyclohexane (η = 1.02 cP) as would be expected.

Taking the lifetime of 15 ps for S_1 in *trans*-decalin[17] to be controlled almost exclusively by radiationless internal conversion to $^1p^*$, then the radiative lifetime of S_1 can be estimated from the fluorescence quantum yield of 10×10^{-4} to be ca. 15 ns. This is close to the values of several nanoseconds found for the lifetime of S_1 in rigid media,[19] where a quantum efficiency of fluorescence approaching unity is found.

Table II. Dipolar Characteristics of the $^1p^*$ State of Tetraphenylethylene

solvent	lifetime (ns)	rotation time,[a] Θ_R (ps)	$\mu_*^2F(\omega\Theta)/\Theta$ (D^2/ps)	dipole moment[b] (D) $\Theta = \Theta_R$	$\Theta = 1/\omega$	Θ_1 = 10 ps
n-hexane	1.8	35	1.94	9.0	7.8	8.6
cyclohexane	1.9	115	1.55	13.5	7.0	7.6
trans-decalin	1.9	241	2.00	22.0	8.1	8.7
benzene	≤0.2	83	≥1.16	≥10	≥6	≥7

[a] Based on Stokes equation for a sphere of density 1.2 g/cm^3. [b] The last column is for $1/\Theta = 1/\Theta_R + 1/\Theta_1$.

If the same radiative lifetime applies to those planar S_1 states in equilibrium with $^1p^*$ during its decay, then the fraction of S_1 in the equilibrium can be estimated to be 0.0095. This corresponds to a free-energy difference of 0.12 eV between the $^1p^*$ and fully relaxed S_1 state, close to the value of 0.11 eV recently obtained by Ma and Zimmt.[20] This difference would be expected to be considerably larger in more polar solvents, or pseudo-polar solvents such as benzene. This, together with the much reduced lifetime of $^1p^*$, would explain the lack of observation of delayed S_1 fluorescence in anything but completely nonpolar solvents.

The Excited-State Dipole Moment. The lifetime of the planar S_1 state with respect to twisting of ca. 10 ps is sufficiently short to ensure that it could not be responsible for the TRMC transient observed. Furthermore, the S_1 lifetime is approximately three orders of magnitude shorter than the mean time for the S_1 to S_0 transition. Therefore, the quantum yield for formation of the $^1p^*$ state, which is the remaining potential source of the dielectric loss, can be taken to be effectively unity. Taking the $^1p^*$-state lifetime to be equal to the lifetime determined from the fluorescence decay, we can determine the parameter $\mu_*^2F(\omega\Theta)/\Theta$ from the absolute magnitude of the microwave conductivity transients; see eq 1. Inclusion in the data analysis of the very small fraction of a nondipolar S_1 component in equilibrium with $^1p^*$ would result in a correction of less than 1%. In order to derive the excited-state dipole moment, a knowledge of the dipole relaxation time, Θ, is required.

For the dipolar excited states of donor–acceptor compounds, dipole relaxation is controlled usually by molecular rotation. The timescale of relaxation is then expected to be close to linearly dependent on the solvent viscosity. The simplest theoretical expression which allows a quantitative estimate of the rotational relaxation time, Θ_R, is that due to Stokes for a spherical rotor in a medium of viscosity η:

$$\Theta_R \approx V\eta/k_BT \tag{3}$$

Taking a molecular density of 1.2 g/cm^3 together with a molecular weight of 332 for TPE and the known solvent viscosities, the values of Θ_R shown in Table II are calculated. The dipole moments obtained, assuming $\Theta = \Theta_R$, are listed in the adjacent column.

Dipole moments of 9.0, 13.5, and 22.0 D are calculated on this basis for the $^1p^*$-state dipole moment in *n*-hexane, cyclohexane, and *trans*-decalin, respectively. These values are very large, with the value in decalin corresponding to complete charge separation over a distance of 4.5 Å, i.e., approximately three times the length of a C–C bond. Corrections to Θ_R for the nonspherical (more closely oblate elipsoidal) shape of TPE would result, if anything,

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in longer relaxation times[25] and correspondingly larger values of the dipole moments calculated. In addition to the unexpectedly large magnitude of $\mu_\bullet$, the marked solvent dependence based on $\Theta = \Theta_R$ is most unusual and highly unlikely.

Similar "anomalous" results have been found for the dipolar excited state of bianthryl[22,23] which also represents a symmetry-breaking situation. By monitoring both the real (dielectric loss) and imaginary (dielectric constant) components of the photoinduced microwave conductivity,[23] it was possible to show in the bianthryl case that the dipole relaxation time was, in fact, much shorter than the calculated time for molecular rotation and close to 10 ps. In addition, Θ was found to be close to independent of temperature and viscosity. These results were explained by taking into account that dipole relaxation can occur in such a basically symmetrical system by rapid charge inversion between the two energetically equivalent zwitterionic states. Since this flip–flop-type process probably involves only small conformational changes, it is expected to be much less sensitive to the viscosity of the medium than molecular rotation.

In view of the bianthryl results, it seems probable that dipole relaxation is being controlled mainly by charge inversion also for TPE. Unfortunately, because of the much shorter lifetime of the excited state of TPE, an accurate, direct estimate of Θ_I using the method of ref 23 could not be made.

By monitoring the TRMC transient off-resonance, using the present equipment, we can probe changes in ϵ' in addition to ϵ''. We observe definite evidence for a large, transient change in dielectric constant in addition to the change in dielectric loss. This indicates that the dipole relaxation time is close to or shorter than the 15-ps reciprocal radian frequency of the microwaves. We are at present in the process of attempting to quantify this type of measurement and hope to be able to present better defined estimates of Θ_I for TPE in the near future. The large change in ϵ' observed corresponds to a hyperpolarizability of the excited state as a consequence of its zwitterionic nature. This hyperpolarizability of the S_1 states of ethylene derivatives was predicted some time ago by Wulfman and Kumei.[26]

It is possible to obtain the minimum value of the dipole moment, corresponding to a given value of $\mu_\bullet{}^2F(\omega\Theta)/\Theta$, by taking $\Theta = 1/\omega$. These values are listed in Table II. While there is some spread in the values, the differences are seen to be much smaller than when $\Theta = \Theta_R$ is used. The data indicate that the dipole moment of the individual zwitterionic states must be at least ca. 7.5 D. This is somewhat larger than the value of 6 D estimated on the basis of the solvent dependence of the $^1p^*$-state energy.[12] If the dipole relaxation time is either shorter or longer than $1/\omega$, larger dipole moments than obtained for $\Theta = 1/\omega$ will be derived.

If both rotation and inversion are operative, then the overall dipole relaxation time is given by[23,27]

$$1/\Theta = 1/\Theta_R + 1/\Theta_I \tag{4}$$

In Table II we list the values of the dipole moment calculated taking a charge inversion time of 10 ps, similar to that found for bianthryl, together with the rotation times listed. The dipole moments found are slightly larger than the minimum values. If Θ_I were to be as short as 3 ps, then the dipole moments determined from the present data would be closer to 14 D. It is perhaps worth mentioning that $\Theta_I = 1/2k_I$ where k_I is the rate constant for the forward and backward charge exchange processes.[27]

The eventual value of the dipole moment determined is relatively insensitive to the lifetime used in fitting the kinetic traces. For transients with lifetimes less than the pulse width, the eventual dipole moment derived is inversely proportional to the square root of the lifetime. If we take the extreme limits reported in the literature for the lifetime of the $^1p^*$ state of TPE from 1.4 to 3 ns, mentioned previously, then minimum $\mu_\bullet$ values of 9 and 6 D, respectively, would be calculated from the TRMC transients rather than the value of 7.5 D based on our own lifetime determination of 1.9 ns. In conclusion, therefore, we can state conservatively that the dipole moment of the relaxed excited state of TPE must be 7.5 ± 1.5 D or larger.

Summary

The twisted excited state formed by out-of-plane rotation subsequent to photoexcitation of tetraphenylethylene has a lifetime of 1.9 ns in saturated hydrocarbon solvents and a dipole moment of at least 7.5 D. Dipole relaxation is controlled mainly by charge inversion between the two degenerate zwitterionic states on a picosecond timescale. The twisted $^1p^*$ state is in equilibrium with the planar, relaxed S_1 state leading to delayed S_1 emission at 540 nm.

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