

Ultrafast dynamics of sterically hindered tetraphenylmethylbutadiene in liquids

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Abstract

Ultrafast transient dynamics of photoexcited tetraphenylmethylbutadiene (TPMB) were measured as a function of probe wavelength and solvent viscosity. In contrast to diphenylbutadiene, which undergoes simple isomerization dynamics, and tetraphenylbutadiene, which exhibits a viscosity-independent transient absorption, TPMB undergoes complex spectral dynamics with distinctly different time constants and viscosity dependence. Results at different probe wavelengths provide evidence for at least two molecular photoisomerization channels and also suggest that the distribution of ground state conformations may be viscosity dependent. The rich dynamics of TPMB demonstrate the dramatic changes induced by the steric effect of the methyl group and the sensitivity of the potential energy surfaces to molecular geometry and solvent environment.

1. Introduction

The photophysics of trans,trans-1,4-diphenyl-1,3-butadiene (DPB) has been the focus of great interest [1–3] given the role of this molecule as a photoisomerization model in liquids with obvious implications to the visual process [4–6]. The study of the viscosity dependence of its excited state isomerization dynamics [7,8] has been also used to test various

liquid phase reaction rate theories [9,10]. Of particular interest is the nature of the potential energy surface near the barrier region, and the number and type of molecular coordinates along which this molecule undergoes non-radiative decay.

The study of structurally related phenylbutadienes with possible variations in their excited state potential energy surfaces may lead to different excited state dynamics and thus provide new insights into photoisomerization reactions [11]. Two phenylbutadienes were chosen for the present study: trans-1,1,4,4-tetraphenyl-1,3-butadiene (TPB) and trans-1,1,4,4-tetraphenyl-2-methyl-1,3-butadiene (TPMB), the structures of which are shown in Fig. 1a. Both molecules bear obvious structural resemblance to DPB, providing an expectation of excited state double-bond torsional relaxation leading to photoisomer-

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ization. The isomerization rate constant should depend on the activation-energy barrier characteristic to each of these molecular systems. Steric crowding in TPMB causes the ground state equilibrium configuration to be quite non-planar. Thus, in the excited state, two types of processes are expected: photoisomerization around the carbon backbone as well as phenyl group rotational relaxation, the latter leading to a more planar structure in the excited state equilibrium configuration. Evidence of phenyl group relaxation in the excited state has been derived from steady-state fluorescence measurements of TPB and TPMB in solution and rigid glass [12,13].

The absorption and fluorescence spectra of DPB, TPB and TPMB in both hydrocarbon solutions at room temperature and rigid glasses at 77 K are shown in Fig. 1b. It is important to notice that the absorption band maximum of TPMB lies 2280 and 1050 cm^{-1} to higher energies than those of TPB and DPB, respectively. This large spectral blue-shift is due primarily to the steric effect of the methyl group in TPMB. The diffuseness of the absorption band of TPMB [6] which persists at 77 K is due to low-

frequency torsional vibrational modes and is characteristic of floppy molecules. This spectral diffuseness also may be the result of ground state conformers with slightly different geometries; relief of steric strain imposed by the methyl group may cause the phenyl groups to assume different torsional angles and may even cause the butadiene backbone to deviate from planarity.

Another manifestation of steric effects in phenyl-substituted butadienes is evident in the decrease of the integrated intensity of the first electronic absorption band. This intensity is reduced by 17% between DPB and TPB, and by 63% from DPB to TPMB. As is obvious from Fig. 1b, the relative intensities of the first two absorption bands are changed in TPB compared with DPB and are in fact reversed in TPMB. The first excited singlet state of DPB is delocalized over both the butadiene backbone and the phenyl groups, while the second excited state is localized predominantly on just the phenyl moieties [14]. Thus the energy and the intensity of the first absorption band, unlike the second absorption band, is expected to be sensitive to geometric changes affecting the

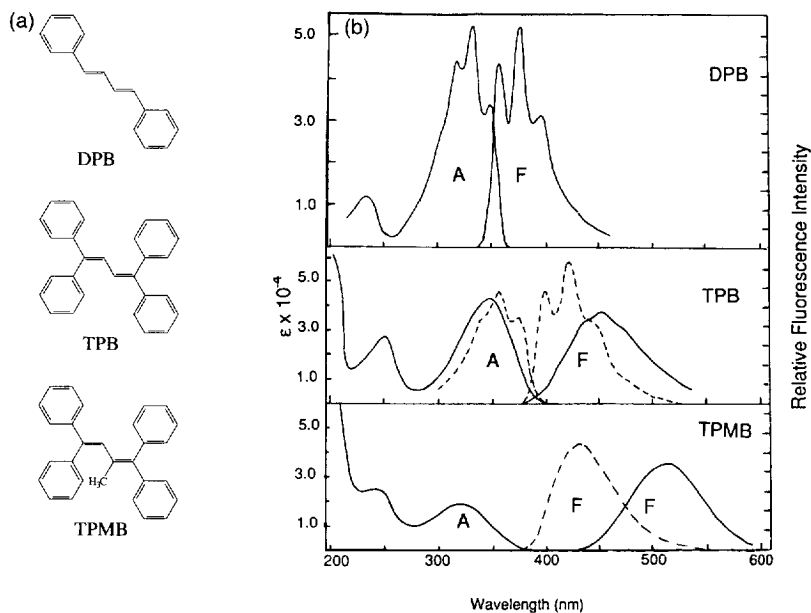


Fig. 1. (a) The chemical structures of: trans,trans-1,4-diphenyl-1,3-butadiene (DPB), trans-1,1,4,4-tetraphenyl-1,3-butadiene (TPB) and trans-1,1,4,4-tetraphenyl-2-methyl-1,3-butadiene (TPMB). (b) Ground state absorption (A) and emission (F) spectra of DPB, TPB and TPMB in hexane at room temperature (solid lines) and at 77 K (dashed lines). Molar extinction coefficients (units of $1\text{ mol}^{-1}\text{ cm}^{-1}$) are plotted for absorption spectra; fluorescence intensities shown do not reflect real or relative intensities. Fluorescence quantum yields at room temperature are: 0.35 for DPB, ≈ 0.9 for TPB, ≈ 0.003 for TPMB and near unity for all three compounds at 77 K.

extent of conjugation. In contrast, the intensity of the second absorption band is roughly proportional to the number of phenyl groups in the molecule.

The fluorescence spectrum of TPMB also reveals a great deal of sensitivity to geometrical structure and solvent viscosity. The fluorescence spectrum of TPMB is weak and red-shifted compared to TPB, but undergoes a large blue-shift and a large intensity enhancement when the medium is made rigid at 77 K. The 11900 cm^{-1} observed Stokes shift ($\Delta\nu$) between the absorption and fluorescence maxima at room temperature is considerably reduced to 6700 cm^{-1} when the solvent is made rigid at 77 K. For comparison, the corresponding shifts for TPB are 6700 cm^{-1} in fluid medium and 4070 cm^{-1} in rigid glass. The weak fluorescence quantum yield of 0.003 for TPMB at room temperature is appreciably enhanced to near unity at 77 K. Moreover, the fluorescence spectrum of TPMB does not show the 1300 cm^{-1} butadiene backbone vibrational progression evident in the spectra of DPB and TPB. These results have been interpreted [12,13] in terms of viscosity-dependent intramolecular twisting relaxation processes that occur in fluid media but not in the rigid glass at 77 K. In the rigid glass, the fluorescence originates from an excited state configuration locked near the Franck–Condon region by the rigid environment, and not from the equilibrium excited state configuration.

The purpose of this Letter is to present the femtosecond and picosecond transient absorption and stimulated emission spectroscopy of TPMB in hydrocarbon solvents with different viscosities. The excited state dynamics of TPMB are compared with those of DPB and TPB, and the role of molecular geometry and the solvent environment on such dynamics is explored. The dynamics of TPMB exhibit an unusual richness which is attributed to the interplay of steric interactions induced by the presence of the methyl group and local friction induced by the surrounding solvent environment.

2. Experimental

2.1. Materials

DPB and TPB were purchased from Aldrich and were recrystallized twice from ethanol. TPMB was

synthesized⁴ using 1-methyl-2,2-diphenylcyclopropanecarboxylic acid according to a previously published synthesis [15]. TPMB was then crystallized from ethanol and its purity was confirmed using UV absorption, fluorescence, NMR, mass spectrometry and gas chromatography. Solvents used in this work were spectral grade and used as received.

2.2. Spectral measurements

Ground state absorption measurements and fluorescence emission measurements were performed according to procedures previously described [12,13].

2.3. Absorption dynamics measurements

The laser system used for the picosecond transient absorption experiments has been described previously [16]. 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 1 mJ pulses of 1 ps duration at 10 Hz. This light is doubled in a 1 mm thick KD*P crystal and attenuated to produce 10 μ J excite 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. Bandpass filters are used to select a 10 nm fwhm portion of the continuum for use as the probe light. Transient absorption data were collected using a typical pump–probe Michelson interferometer; details have been described in previous publications [11].

Femtosecond transient absorption studies were conducted with a copper vapor laser amplified, colliding pulse mode-locked (CPM) ring laser [17–19] which produced 3 μ J, 90 fs pulses at 620 nm. For these experiments, samples were excited with 500 nJ of the laser second harmonic at 310 nm and probed with either a small portion of the 620 nm fundamental or continuum, providing an instrument resolution

⁴ TPMB used in these experiments was synthesized by M.A. El-Bayoumi and M.A. Nashed from starting materials provided by H.M. Walborsky.

of 120 fs. Further details are described elsewhere [20].

3. Results

Transient absorption dynamics of TPB were measured using the picosecond laser system (excitation pulse wavelength: 295 nm) and the CPM femtosecond system (excitation pulse wavelength: 310 nm) as a function of probe pulse wavelength. The transient absorption, which is observed to be wavelength independent [11], exhibits a pulse width-limited rise and a single exponential decay with time constant of 460 ± 10 ps in hexane and 780 ± 30 ps in hexadecane, in accord with previous work [1,11,20,21].

The transient absorption dynamics of TPB in hexane using a 295 nm pump wavelength and a variety of probe wavelengths are shown in Fig. 2. The data at all wavelengths are fit very well by simple exponential dynamics, with rise and decay times summarized in Table 1. At 500 nm, the stimulated emission shows two rise components of ≈ 3.5 and 25 ps and a decay time of 1.7 ns. The signal at

Table 1
TPB transient absorption fitting parameters

Probe wavelength (nm)	Absorption/emission	Rise time (ps)	Decay time (ns)
500	emission emission	3.5 25	1.7
560	absorption emission	pulsewidth limited 25	0.025 1.5–3.5
620	absorption	pulsewidth limited	1.9
900	absorption	pulsewidth limited	2.0

560 nm is an initial transient absorption which decays in 25 ps, leaving a weak stimulated emission at later times. From the steady-state fluorescence spectrum (Fig. 1b), stimulated emission at 560 nm is expected, although with a smaller intensity than that observed at 500 nm. Thus, while the initially prepared excited state species strongly absorbs 560 nm light, after 25 ps, excited state dynamics produce a species with nearly identical 560 nm absorption and

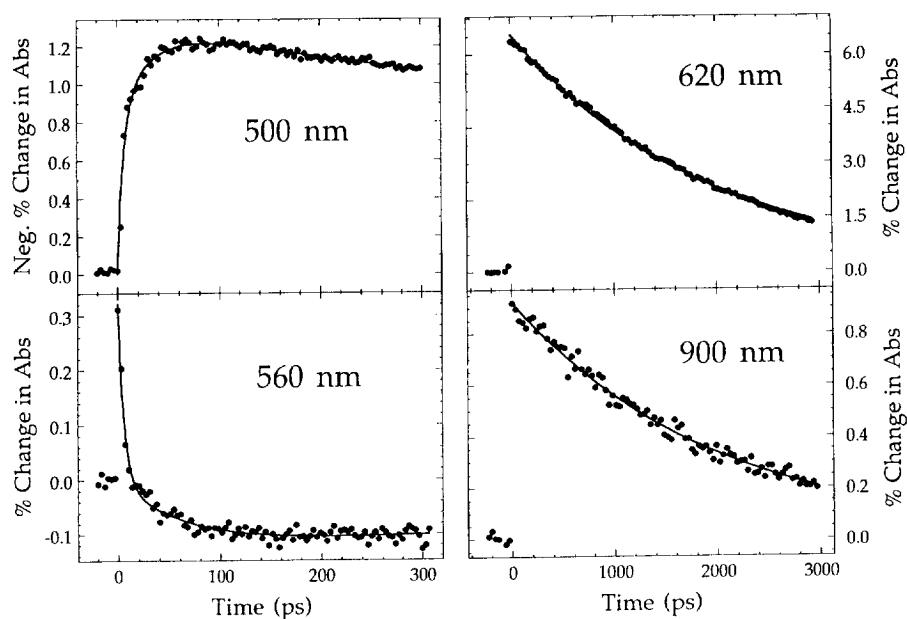


Fig. 2. Transient absorption of TPB in hexane pumped with a 295 nm, 1 ps pulse and probed at 500, 560, 620 and 900 nm. Time scales for 500 and 560 nm scans are a factor of 10 shorter than for 620 and 900 nm. Solid circles are the data, lines are fits to simple combinations of single exponentials convoluted with a Gaussian representing the instrument response with fitting parameters reported in Table 1.

emission cross sections, leading to the expected (weak) net emission signal. The amplitude of this net emission component is sufficiently small that the emission decay time constant can be only approximately determined (1.5–3.5 ns) at this wavelength. At 620 and 900 nm, transient absorptions are observed with single exponential decay time constants of 1.9 ± 0.2 and 2.0 ± 0.2 ns, respectively.

Transient absorption measurements were recorded for TPMB in hexane and tetradecane solvents using the CPM laser system with a 310 nm pump pulse and probe pulses at 620 and 680 nm. For each solution, the results were identical at both probe wavelengths. The transient absorption dynamics, however, were found to depend strongly on the solvent viscosity when a series of alkane solvents was used to vary the viscosity [20]. The data are fit to double exponential decays, convoluted with a Gaussian representing the instrument function. Neither decay time constant shows a significant viscosity dependence, however, as the viscosity of the solvent increases, the amplitude of the slower decay component increases relative to the faster decay component. A plot of the fast:slow decay component amplitude ratio as a function of viscosity is shown in Fig. 3.

Using the picosecond laser system with a pump wavelength of 295 nm, the transient absorption dynamics of TPMB were also measured in hexane and

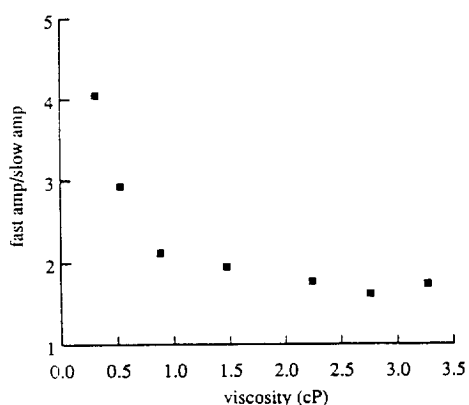


Fig. 3. Ratio of the amplitudes of the fast (≈ 0.6 ps) decay to slow (≈ 11 ps) decay components for the 620 nm transient absorption of TPMB in alkane solvents as a function of viscosity. TPMB solutions were pumped at 310 nm using ≈ 100 fs pulses from the femtosecond CPM laser system.

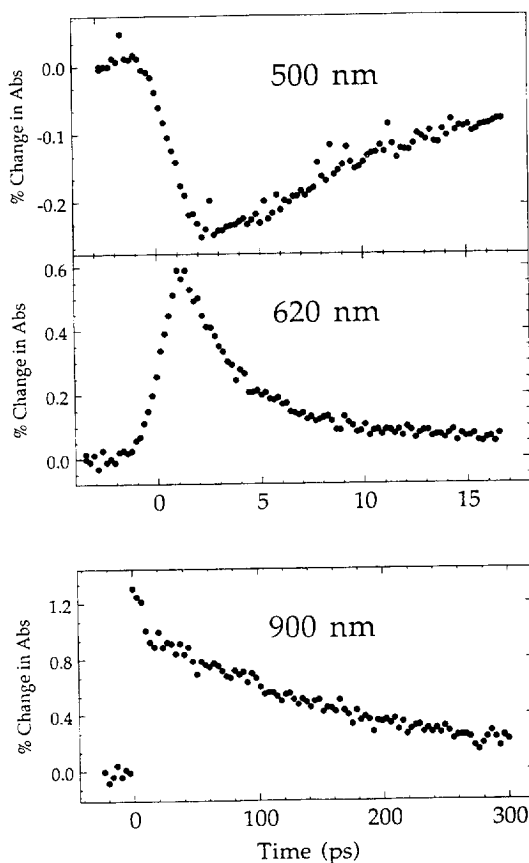


Fig. 4. Transient absorption of TPMB in hexane, pumped with a 295 nm, 1 ps pulse and probed at 500, 620 and 900 nm. Time scales for 500 and 620 nm scans are a factor of 20 shorter than 900 nm; lifetimes obtained from fits to simple combinations of single exponentials convoluted with a Gaussian representing the instrument response are reported in Table 2.

hexadecane at a variety of probe wavelengths: 500, 620 and 900 nm. The results in hexane are presented in Fig. 4. The hexane solution data are qualitatively the same as the hexadecane data; quantitatively, however, spectral dynamics occur significantly more rapidly in hexane than hexadecane at both 500 and 900 nm. The fitting parameters for all the probe wavelengths are summarized in Table 2. At a probe wavelength of 500 nm (the fluorescence maximum of TPMB) the observed stimulated emission has an instrument limited rise and a decay time constant of 23 ps in hexane and 51 ps in hexadecane. At a probe wavelength of 620 nm, the results are similar to those obtained using the CPM laser system. At a

Table 2
TPMB transient absorption fitting parameters

Solvent	Probe wavelength	Rise (ps)	Decay (ps)	Decay (ps)
hexane	500 nm (emission)	pulsewidth limited		23
hexadecane	500 nm (emission)	pulsewidth limited		51
hexane	620 nm (absorption)	pulsewidth limited	0.6	11
hexadecane	620 nm (absorption)	pulsewidth limited	0.6	12
hexane	900 nm (absorption)	pulsewidth limited		172
hexadecane	900 nm (absorption)	pulsewidth limited		271

probe wavelength of 900 nm, a transient absorption is observed with a pulse width limited rise followed by a single exponential decay with a time constant of 172 ps in hexane and 271 ps in hexadecane.

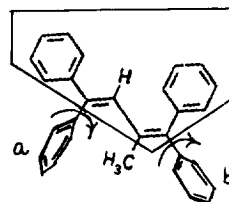
4. Discussion

Previous investigations [1,11,21,22] have shown that phenyl torsional motions do not play an important role in the excited state dynamics of DPB. The 460 ps transient absorption decay of DPB in hexane can be simply accounted for [1] by a 1B_u excited state which decay radiatively to the ground state plus a single non-radiative channel induced by twisting around a polyene double bond. These results are in contrast to earlier suggestions [23] of a mechanism involving a solvent-assisted level inversion of 1A_g and 1B_u excited states induced by phenyl twisting motions. It is now well established that the excited state isomerization dynamics of DPB are effectively one-dimensional [1] with a single exponential decay at different viscosities [1,11,21], fitting well to simple barrier-crossing isomerization theories [9].

The excited state dynamics of TPB show that the addition of another two terminal phenyl groups of DPB causes a dramatic change: the viscosity-dependent picosecond transient absorption decay of DPB is replaced by a viscosity-independent nanosecond transient absorption decay in TPB. Steady-state fluorescence measurements [12] have shown that the

emission maximum shifts 1650 cm^{-1} to higher frequencies when the solution forms a rigid glass at 77 K; this shift was interpreted in terms of geometric relaxation that occurs prior to fluorescence only when the medium is fluid. This relaxation process can be attributed to phenyl group intramolecular twisting leading to a more planar configuration in the equilibrium excited state. Compared to DPB, the lack of planarity in TPB decreases the extent of phenyl–polyene interaction and thus lowers the bond-order reversal that occurs as a result of $\pi-\pi^*$ excitation [14], leading to an activation energy for carbon bond torsion which is high enough to shut off the photoisomerization channel. With no other channels available for fast non-radiative decay, the stimulated emission in TPB at 500 nm has a decay time of 1.7 ns, which is essentially the radiative lifetime. The rise time of 3.5 ps associated with the stimulated emission signal at 500 nm most likely corresponds to phenyl group intramolecular twisting relaxation.

To interpret the rich excited dynamics of TPMB, one must recall that steric crowding makes this molecule quite floppy and non-planar. The energy and intensity of the first absorption band is clear evidence of this, as discussed in Section 1. The absorption spectrum of TPMB approximates that of *cis*–*trans* diphenylbutadiene [24], which is consistent with a configuration where phenyl groups a and b are forced to assume a nearly perpendicular configuration to avoid steric repulsion with the methyl group, as pictured in Fig. 5. Thus, for TPMB, one expects at



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Fig. 5. Perspective structure of TPMB. The two phenyl rings labeled a and b are rotated out of butadiene plane due to the steric effect of the methyl group in the molecule; the absorbing chromophore approximates that of *cis*,*trans* DPB. The steric strain of the methyl group may also be relieved by twisting around the butadiene backbone (not shown).

least two viscosity-dependent relaxation processes: a relatively fast phenyl group twisting relaxation about an essentially single C– ϕ bond, and photoisomerization relaxation processes about ground state C=C double bonds in the butadiene backbone. Indeed, the data indicate two separate viscosity-dependent relaxation processes on two distinct time scales which are probed separately at 500 (stimulated emission) and at 900 nm (transient absorption). Both these processes appear to correspond to photoisomerization dynamics with time constants smaller than corresponding dynamics in DPB, consistent with TPMB activation energies which are smaller than those in DPB and much smaller than those in TPB. The presence of the two independent relaxations with time constants of 23 and 172 ps in hexane also points to the possibility of two distinct classes of ground-state conformers. One class of conformers may be similar to the structure shown in Fig. 5; in the other class, the relief of steric strain, may be caused by a small twist about the butadiene essential single bond. Due to the floppy nature of the molecule, each class of conformers is expected to have a continuous distribution of structures. This presents a special difficulty in assigning a given decay process to motion about a specific coordinate as the excited state molecule relaxes toward planarity. Nonetheless, it is important to point out that the steric effect of the methyl group and the floppy nature of the TPMB molecule has led to a situation where several different picosecond time scale relaxation processes are observed. The wide variety of dynamical processes available to excited-state TPMB is also reflected in the transient absorption observed at 620 nm. In this case, it is the ratio of the amplitude of the two dynamic components that depends on viscosity (Fig. 3) [20]. This amplitude variation may be a reflection of excitation of different proportions of floppy ground state conformers as solvent viscosity is changed. Thus, in addition to excited state isomerization dynamics, the effective potential energy surface of TPMB and hence the distribution of available ground state geometries may also change with viscosity [25].

If the interpretation that the 500 and 900 nm decay processes are due to molecular isomerizations is correct, then the magnitude of the effect of viscosity on these relaxation times should be roughly predicted by Kramers' theory. A crude calculation [20],

using the barrier frequencies and hydrodynamic values of stilbene [26] and assuming that the Stokes–Einstein–Debye relation holds, gives a ratio of approximately 2 for the isomerization rate in hexane compared to hexadecane. For the process occurring in excited TPMB measured at 500 nm, the ratio of the rates is ≈ 2.2 , while for those observed at 900 nm the corresponding ratio is ≈ 1.6 . The calculation is very sensitive to the value of the barrier frequency, so within the error inherent in using molecular parameters derived for stilbene as an approximation to those for TPMB, the viscosity effect appears satisfactorily described by Kramers' theory.

In summary, this study clearly demonstrates that even small changes in molecular geometry can lead to large differences in electronic structure which result in vastly different excited state dynamics and photochemistry. Three molecules with very similar structures, DPB, TPB, and TPMB, show dramatically different excited state behaviors and viscosity-dependent dynamics, revealing how subtle changes in structure and geometry as well as the local friction of the condensed environment are valuable in understanding the photophysics of floppy molecules in solution.

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