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Temperature dependence of aryl butatriene fluorescence: barrier to twisting on S_1 for 1,1,4,4-tetraphenylbutatriene

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Abstract

The temperature dependence of aryl butatriene fluorescence is assigned to a competition between radiative decay and butatriene chain rotation against a barrier followed by radiationless decay from S_1. Fluorescence quantum yields were measured as a function of temperature for 1,1,4,4-tetraphenylbutatriene (TPBT) in a series of *n*-alkane solvents. Application of the medium-enhanced barrier model and transition state theory allow the observed barrier to be expressed in terms of an intrinsic and solvent-induced contribution ($\Delta H^{\ddagger}_{obsd} = \Delta H^{\ddagger}_{t} + \Delta H^{\ddagger}_{v}$). It is found that there is little or no intrinsic barrier to rotation ($\Delta H^{\ddagger}_{t}$ = 0.075 ± 0.155 kcal/mol) on S_1 for TPBT. The solvent-induced component is related to E_{η}, the activation energy for viscous flow, by $\Delta H^{\ddagger}_{v} = aE_{\eta}$ with $a = 0.86 \pm 0.06$ for TPBT. This is in contrast to twisting on S_1 for *trans*-stilbene for which a significant intrinsic barrier has been reported. AM1 molecular orbital calculations for gas phase TPBT show a twist angle of ~0°on S_0 with a barrier to rotation of 20.1 kcal/mol. Consistent with the experimental results, the calculations show that TPBT undergoes a barrierless relaxation on S_1 from its Franck–Condon structure to a minimum with a twist angle of 85.6°. © 1998 Elsevier Science B.V.

Keywords: Butatriene; Fluorescence; Radiationless; Isomerization; Barrier

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1. Introduction

During the course of our studies of the spectroscopic and photophysical properties of aryl-substituted butatrienes, we have observed that the intensity of fluorescence exhibits a strong temperature dependence [1]. For example, in 3-methylpentane (3MP), the fluorescence quantum yield, ϕ_f, for 1,1,4,4-tetraphenylbutatriene (TPBT, Fig. 1) increases from 2.0×10^{-4} at 300K to 0.90 at 77K [2]. A similar temperature affect on ϕ_f for *trans*-stilbene has been shown to be coupled with photoinduced *cis/trans* isomerization [3]. In the case of *trans*-stilbene, a competition is believed to exist between radiative decay from S_1 and rotation against a potential barrier to a twisted "phantom" state from which fast nonradiative decay to the ground state occurs with nearly equal partitioning to the *cis*- and *trans*-isomers [3].

In a series of papers, Saltiel et al. [4] have developed and successfully applied a medium-enhanced barrier model to study twisting about the central double bond on the S_1 surface for *trans*-stilbene and several of its derivatives. Their model equates the rate of radiationless decay from S_1 to the rate of crossing the potential barrier, represented in transition state theory by $k_{obsd} = (\kappa kT/h)\exp(\Delta S^{\ddagger}_{obsd}/R)\exp(-\Delta H^{\ddagger}_{obsd}/RT)$.

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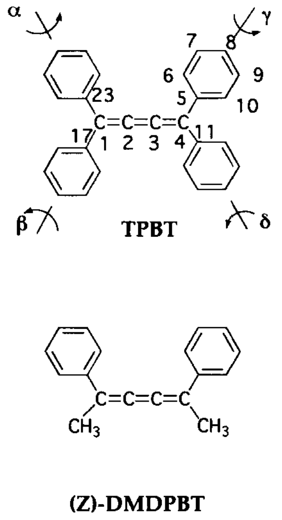

Fig. 1. Molecular structures of TPBT and (*Z*)-DMDPBT.

In this model $\Delta S^{\ddagger}_{obsd} = \Delta S^{\ddagger}_{t} + \Delta S^{\ddagger}_{v}$ and $\Delta H^{\ddagger}_{obsd} = \Delta H^{\ddagger}_{t} + \Delta H^{\ddagger}_{v}$, where $\Delta S^{\ddagger}_{v}$ and $\Delta H^{\ddagger}_{v}$ are entropy of activation and enthalpy of activation terms, respectively, for the medium imposed (via viscosity) portion of the barrier, and $\Delta S^{\ddagger}_{t}$ and $\Delta H^{\ddagger}_{t}$ are activation parameters associated with the portion of the twisting barrier that is intrinsic to the molecule (a detailed description of the model is provided in the original papers). A plot of $\ln(k_{obsd}/T)$ versus $1/T$ in a given solvent yields a straight line with slope equal to $\Delta H^{\ddagger}_{obsd}$. Experimental results in a series of *n*-alkane solvents show that there is a linear relationship between the medium-imposed portion of the barrier, $\Delta H^{\ddagger}_{v}$, and the activation energy for viscous flow for a particular solvent, E_{η}, given as $\Delta H^{\ddagger}_{v} = aE_{\eta}$, where a is a constant. Thus, by plotting $\Delta H^{\ddagger}_{obsd}$ versus E_{η} for the *n*-alkane series, a straight line is obtained with slope equal to a and intercept equal to $\Delta H^{\ddagger}_{t}$. Analysis of the data for *trans*-stilbene in *n*-alkane solvents indicates that the molecule has an intrinsic barrier equal to 2.788 ± 0.003 kcal/mol [4]. The value of a, which represents the fraction of the activation energy for viscous flow that is added to $\Delta H^{\ddagger}_{t}$ by the medium, was found to be 0.41. Supersonic jet studies of gas phase *trans*-stilbene suggest an intrinsic barrier to twisting of 3.4 ± 0.3 kcal/mol [5]. The source of the intrinsic barrier for *trans*-stilbene is still an open question. Theoretical calculations have suggested that it is due to an avoided crossing of $^1A^*$ and $^1B^*$ states along the reaction coordinate for twisting [6]. However, this view has not been universally accepted [7].

In this study, evidence is provided that is consistent with the view that the temperature dependence of aryl butatriene fluorescence is due to a competition between radiative decay and butatriene chain (>C:C:C:C<) rotation against a barrier followed by radiationless decay from S_1. Transition state theory has been used to determine the rates of barrier crossing for TPBT in a series of *n*-alkane solvents. In addition, the medium-enhanced barrier model has been employed to measure $\Delta H^{\ddagger}_{obsd}$ along with its medium-imposed and intrinsic contributions. Semi-empirical molecular orbital calculations have been performed to compute equilibrium geometries and barriers to rotation for TPBT on the S_0 and S_1 potential energy surfaces.

2. Experimental

TPBT was synthesized according to the method described by Zweig and Hoffmann [8]. (*Z*)-dimethyldiphenylbutatriene [(*Z*)-DMDPBT, Fig. 1] was prepared following the procedure of Westmijze et al. [9] using the method of Schmidt and Potschka [10] to synthesize the 1-methylthio-2-phenylacetylene starting material. Purification of the butatrienes was achieved by multiple recrystallization. Pentane (99 + %), hexane (99 + %), heptane (99%), octane (99 + %), decane (99 + %), dodecane (99 + %), tetradecane (99 + %), hexadecane (99 + %) and 3MP (99 + %) were obtained from Aldrich and used without further purification.

Electronic absorption spectra were measured with a Schimadzu UV2100U spectrometer. Fluorescence spectra were obtained with a Perkin Elmer LS 50 luminescence spectrometer equipped with a thermostatted cell holder. Temperature control was maintained by circulating a water/ethylene glycol solution through the cell holder with a VWR refrigerated/heated circulating bath. Sample temperatures were measured with an Omega model DP460 digital thermometer. Solutions for fluorescence measurements were prepared with an absorbance of approximately 0.1 at the wavelength of excitation. Quartz fluorescence cells were equipped with a rubber septum fitted with inlet and outlet syringe needles for degassing of the solutions. Dry nitrogen gas was bubbled slowly through the inlet needle for at least 5 min to remove dissolved oxygen from the solutions. The needles were removed and the cell was placed in the cell holder. Once constant temperature had been attained, a fluorescence spectrum was recorded from 415 to 650 nm with excitation at 400 nm. The temperature of the bath was then increased and the process repeated. Background spectra of the solvents were also collected and subtracted from the spectra of the TPBT solutions. The entire process was completed within 3 h for each *n*-alkane solution. Fluorescence quantum yields were determined relative to TPBT in 3MP at 300K ($\phi_f = 2.0 \times 10^{-4}$) with index of refraction corrections [11]. Areas under the fluorescence spectra were computed with Perkin Elmer FLDM software (v. 2.50).

Photoisomerization studies were carried out by irradiating solutions of (*Z*)-DMDPBT (10–15 mg/ml) in acetone-d_6 with the output of a 150 Watt Xe arc lamp passed through 10 cm of a 1 M $CuSO_4$ filter solution. Samples were analyzed using a Perkin Elmer 60 MHz H^1-NMR spectrometer.

Molecular orbital calculations employing the AM1 Hamiltonian [12] were carried out using the MOPAC program [13].

3. Results and discussion

Although it is reasonable to assume that the dramatic temperature dependence of fluorescence intensity that we have observed for aryl substituted butatrienes can be attributed to a thermally activated competition between fluorescence and twisting about the cumulene π bond, experimental evidence supporting this assumption has not been reported. Therefore, a series of photochemical experiments was carried out to examine this hypothesis. Solutions of (*Z*)-DMDPBT in acetone-d_6 were subjected to broad band irradiation with a Xe arc lamp filtered by a $CuSO_4$ solution at 30°C. The light transmitted by the filter limits photoexcitation to the lowest energy absorption band (λ_{max} = 387 nm; $\epsilon_{max} = 4.2 \times 10^4$ M^{-1} cm^{-1}). After various intervals of irradiation, NMR spectra were recorded in the region of the methyl group signals for the *Z* and *E* isomers of DMDPBT [14]. As shown in Fig. 2, prior to irradiation, a single methyl group peak at δ2.40, corresponding to the *Z* isomer, is observed. After 10 min of irradiation, a new peak at δ2.35, corresponding to the *E* isomer was clearly evident. A 1:1 photostationary state ratio of (*Z*) and (*E*)-DMDPBT isomers was achieved after approximately 2 h of irradiation.

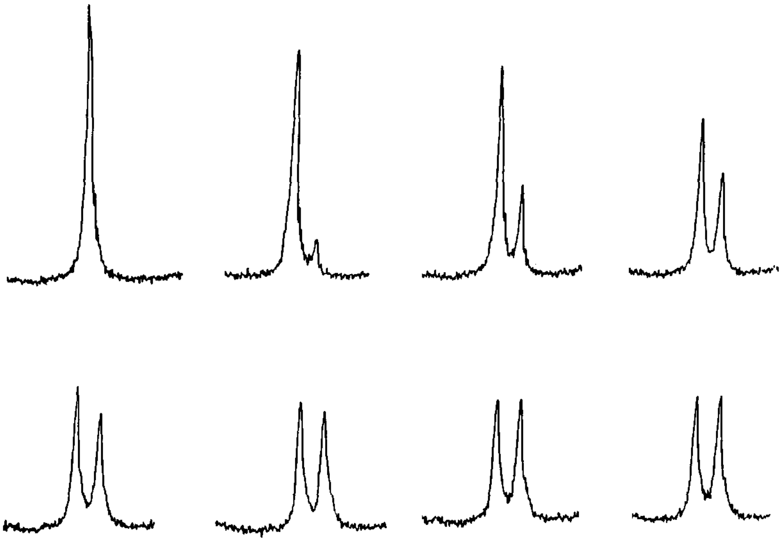

Fig. 2. NMR spectra in the methyl group region of the *Z* and *E* isomers of DMDPBT as a function of irradiation time for a solution of *Z*-DMDPBT. Top (l to r) 0, 10, 20, 30 min: bottom (l to r) 50, 90, 120, 180 min.

However, no indication of conversion to (*E*)-DPDMBT was observed by NMR for a solution that had been irradiated for 2 h at 77K and then warmed to room temperature. Further, no isomerization was observed for a solution of (*Z*)-DMDPBT that had been prepared and held in the dark for 2 h at 30°C prior to recording its NMR spectrum. Thus, at 30°C, ϕ_f is quite small (~10^{-4}) and $Z \rightarrow E$ photoisomerization is facile, whereas at 77K, ϕ_f increases to ~1, and photoisomerization is essentially quenched. The inverse relationship between fluorescence yield and photoisomerization yield is consistent with a thermally activated competition between the two processes. We assume that this is the case for other aryl butatrienes, and that methods that have been used previously to study twisting about a central π bond can be applied to TPBT.

Following Saltiel et al. [4], the rate constant for excited state twisting in solution has been calculated utilizing fluorescence quantum yield data

$$k_{\mathrm{obsd}} = k_f(\phi_f^0 - \phi_f)/\phi_f^0\phi_f \qquad (2)$$

where ϕ_f^0 is the limiting fluorescence quantum yield at low temperature in a glass and k_f is the rate constant for radiative decay. The value of k_f can be determined from fluorescence lifetime measurements, τ_f, and ϕ_f values using the relationship $k_f = \phi_f\,\tau_f^{-1}$, or it can be calculated from the Strickler–Berg equation [15]. Based on ϕ_f and τ_f measurements made at 77K in 3MP, we have taken $\phi_f^0 = 1$ and $k_f = 5.0 \times 10^8\ \mathrm{s}^{-1}$. The latter value is in good agreement with $k_f = 4.5 \times 10^8\ \mathrm{s}^{-1}$ calculated from the Strickler–Berg equation. Index of refraction effects on k_f were neglected.

In measuring relative fluorescence quantum yields as a function of temperature, it was necessary to determine the behavior of the TPBT absorption spectrum with temperature to determine if variations in fluorescence intensity were linked in any way to changes in absorption intensity at the excitation wavelength. It was found that the absorption intensity of TPBT in a particular alkane solvent remains essentially constant over the range of temperatures studied, whereas the fluorescence intensity over the same temperature range changes significantly.

Rate constants for twisting have been calculated from Eq. (2) for TPBT in a series of *n*-alkane solvents and are listed in Table 1. Transition state plots showing the temperature dependence of the rate constants

Table 1
Rate constants for twisting about the butatriene bond for TPBT in S_1

n-Alkane	*T*(K)	$10^{-12} K_{\mathrm{obsd}}$ (s^{-1})
C_5	285	2.56
	292	2.78
	298	2.99
	305	3.17
	314	3.41
	321	3.68
C_6	284	2.26
	291	2.44
	294	2.56
	298	2.69
	308	2.92
C_7	280	1.59
	288	1.74
	295	1.89
	303	2.10
	311	2.33
	319	2.52
	325	2.74
C_8	282	1.38
	286	1.41
	291	1.60
	298	1.75
	304	1.90
	313	2.13
	321	2.34
	330	2.78
C_{10}	284	1.19
	291	1.41
	298	1.60
	306	1.86
	311	2.00
	319	2.26
	326	2.45
	330	2.60
C_{12}	286	0.86
	296	1.08
	302	1.24
	308	1.37
	313	1.48
	320	1.64
	326	1.78
	327	1.83
	330	1.87
C_{14}	288	0.72
	292	0.83
	309	1.14
	314	1.25
	321	1.41
	328	1.57
C_{16}	294	0.70
	301	0.81
	307	0.93
	313	1.02
	319	1.16
	324	1.26
	332	1.42

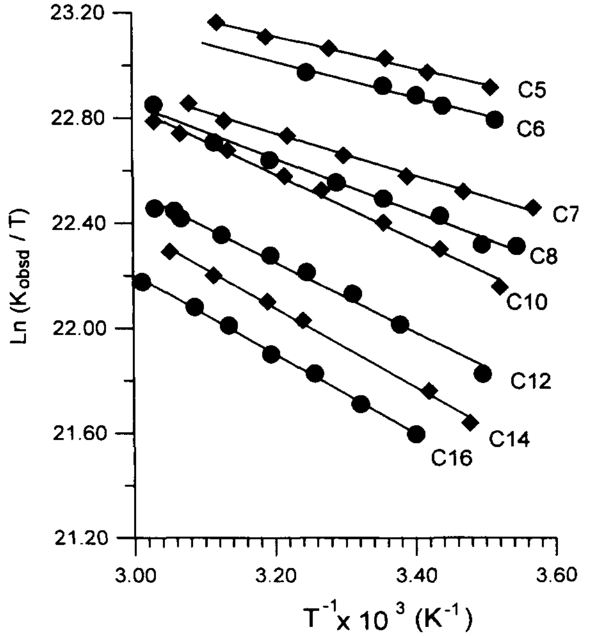

Fig. 3. Plots of $\ln(k_{obsd}/T)$ versus $1/T$ for TPBT in n-alkane solvents.

for twisting have been prepared according to Eq. (1) by plotting $\ln(k_{obsd}/T)$ versus $1/T$ (Fig. 3). The values of $\Delta H^{\ddagger}_{obsd}$ which are obtained from the slopes of these linear plots are presented in Table 2 along with the value of E_η for each of the solvents [16]. It is observed that the value of $\Delta H^{\ddagger}_{obsd}$ increases as the length of the alkane chain increases. A medium-enhanced barrier plot of $\Delta H^{\ddagger}_{obsd}$ versus E_η is shown in Fig. 4. The slope and intercept of this reasonably linear plot yield $a = 0.86 \pm 0.06$ and $\Delta H^{\ddagger}_{I} = 0.075 \pm 0.155$ kcal/mol. Thus, the twisting of TPBT in S_1 is found to occur with little or no intrinsic barrier. The barriers determined from the transition state plots are dominated by the solvent-imposed barrier term, $\Delta H^{\ddagger}_{V} = a\,E_\eta$. It is worth noting that the value obtained for a is consistent with the theoretical model which predicts that $a \rightarrow 1$ as $\Delta H^{\ddagger}_{I} \rightarrow 0$ [17].

3.1. Molecular orbital calculations

We have also carried out a theoretical modeling of TPBT on the S_0 and S_1 potential energy surfaces using semi-empirical molecular orbital theory. Structures and energies were computed using the AM1 Hamiltonian. The ground state AM1 optimized structure has been reported by us previously [2]. In that study it was found that the butatriene system is essentially planar; i.e. twist angle ~0°, with the phenyl groups rotated out of the plane of the butatriene system (α, β, γ, δ) by 33°. In this study we have extended the characterization of S_0 by locating the transition structure (TS) between the degenerate *cis* and *trans* forms of TPBT. The TS is calculated to have a twist angle of 86.7° and a barrier height of 20.1 kcal/mole. Confirmation of a true TS was obtained with a vibrational FORCE calculation which yielded one negative vibration with displacement vectors that correspond to motion along the reaction coordinate for twisting. The magnitude of this calculated barrier seems reasonable when compared to the experimentally determined values of 13 ± 3 kcal/mol for (*Z*)-DMDPBT [1] and 26.9 ± 0.5 kcal/mol for (*Z*)-di-t-butyl-diphenylbutatriene [18]. Optimization of TPBT on S_1 was performed by starting with the AM1 ground state structure to simulate the Franck–Condon transition. Energy minimization yields a geometry with a

Table 2
Activation enthalpy for twisting about the butatriene bond in S_1 for TPBT

n-alkane	E_η(kcal/mol)	$\Delta H^{\ddagger}_{obsd}$ (kcal/mol)	$\Delta H^{\ddagger}_{calc}$ (kcal/mol)[a]
C_5	1.36	1.21 ± 0.05	1.25
C_6	1.61	1.34 ± 0.13	1.46
C_7	1.85	1.60 ± 0.06	1.67
C_8	2.08	2.02 ± 0.09	1.87
C_{10}	2.61	2.49 ± 0.08	2.32
C_{12}	2.99	2.66 ± 0.10	2.65
C_{14}	3.35	2.99 ± 0.08	2.96
C_{16}	3.60	3.01 ± 0.06	3.18

[a] $\Delta H^{\ddagger}_{calc} = 0.075 + 0.86\,E_\eta$.

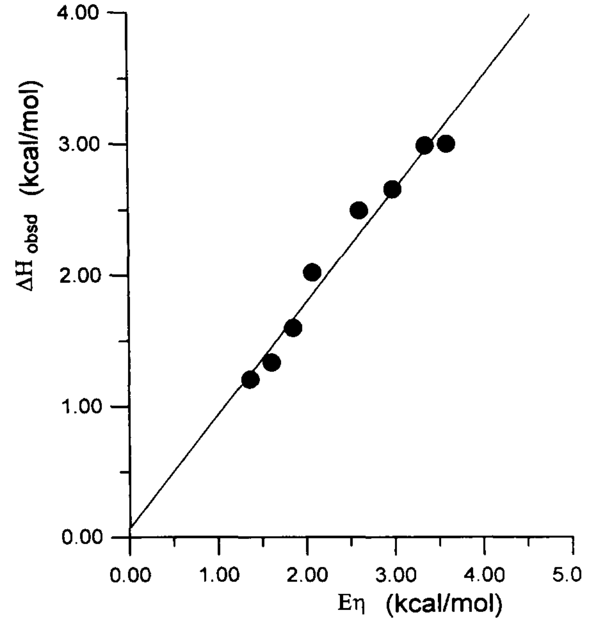

Fig. 4. Plot of $\Delta H^{\ddagger}_{obsd}$ versus $E_{\eta}$for TPBT in *n*-alkane solvents.

Table 3
S_1 and S_0 (transition state) calculated geometry of TPBT

	S_1	S_0 (TS)
	Bond lengths (Å)	
C_1–C_2	1.307	1.386
C_2–C_3	1.289	1.213
C_4–C_5	1.473	1.448
C_5–C_6	1.404	1.406
C_5–C_{10}	1.400	1.406
C_6–C_7	1.394	1.392
C_7–C_8	1.390	1.394
C_8–C_9	1.393	1.394
C_9–C_{10}	1.392	1.393
	Bond angles (°)	
C_1–C_2–C_3	177.9	178.5
C_2–C_3–C_4	174.3	178.4
C_3–C_4–C_5	121.4	118.7
C_4–C_5–C_6	120.1	120.2
C_4–C_5–C_{10}	121.7	121.0
C_5–C_6–C_7	120.9	120.5
C_6–C_7–C_8	120.1	120.2
C_7–C_8–C_9	119.6	119.8
C_8–C_9–C_{10}	120.3	120.3
C_9–C_{10}–C_5	120.9	120.4
	Torsion angles (°)	
$\alpha, \beta, \gamma, \delta$	32.3	28.2
C_5–C_{11}–C_{17}–C_{23}	85.6	86.7

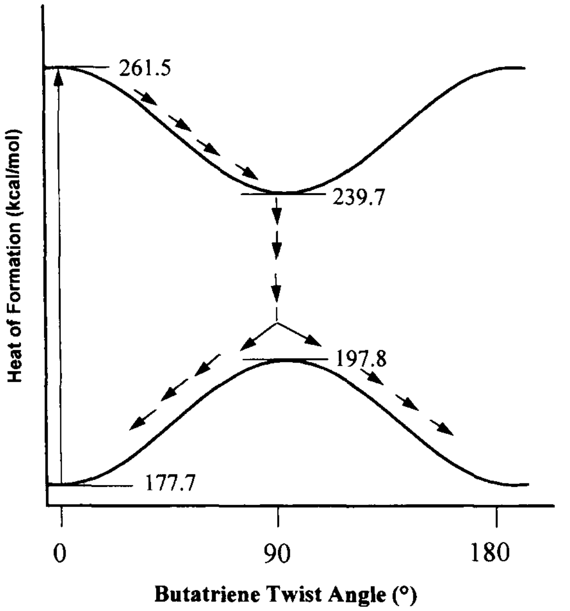

Fig. 5. Surface diagram for twisting about the butatriene chain for TPBT on S_0 and S_1. Stationary points and Franck–Condon (vertical) energy calculated using the AM1 Hamiltonian.

heat of formation of 239.7 kcal/mol and a twist angle about the butatriene chain of 85.6°. Thus, relaxation on the S_1 surface leads directly to a structure that lines up with the TS along the reaction coordinate for twisting on S_0. Geometric parameters for AM1 optimized S_1 and S_0 (TS) structures are presented in Table 3 (calculated and experimental values for ground state TPBT can be found in ref. [2]). The theoretical results agree with the experimental findings by showing that TPBT does not encounter an intrinsic barrier to twisting following excitation to the S_1 surface. Efficient internal conversion as depicted in Fig. 5 for gas phase TPBT explains the low ϕ_f that is observed for TPBT in low viscosity solvents where the medium-imposed barrier will be quite small.

Acknowledgements

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