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Singlet-State Cis–Trans Photoisomerization of 1-Phenylpropene

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The behavior of the lowest electronically excited states of *trans*- and *cis*-stilbene (t-**1** and c-**1**) have been investigated in great detail.[1,2] Because of the small barriers for twisting about the double bond (ca. 3.5 kcal/mol for t-**1** and <1 kcal/mol for c-**1** in hydrocarbon solvents), only weak fluorescence ($\Phi_F = 0.04$ and 10^{-4} for t-**1** and c-**1**, respectively) and no intersystem crossing or internal conversion are observed at room temperature.[1] Much less is known about the behavior of the singlet states of styrene and its β-methyl derivatives, *trans*- and *cis*-1-phenylpropene (t-**2** and c-**2**). In comparison to the stilbenes, styrene possesses a significantly longer singlet lifetime (14.6 ns) and larger quantum yields for fluorescence (0.24)[3,4] and intersystem crossing (0.40).[5] Spectroscopic investigations of jet-cooled styrene indicate that the lowest excited singlet state, like the ground state, is planar and has a barrier for twisting about the double bond at least as large as t-**1**.[6,7] Several attempts to calculate this barrier have led to values ranging from 4 to 25 kcal/mol and disagreement as to whether the lowest twisted singlet is a 1,2-diradical or dipole.[8-10] Rockley and Salisbury[11] attributed the moderately efficient photoisomerization observed for t-**2** and c-**2** at room temperature in the vapor phase ($\Phi_i = 0.22$ and 0.33, respectively) to a triplet mechanism and proposed that the barrier for twisting about the double bond on the singlet surface is >10 kcal/mol for both isomers. We report the preliminary results of our investigation of the effects of temperature and solvent polarity upon the singlet lifetimes and isomerization quantum yields for t-**2** and c-**2**. Among the findings of this investigation are (a) the occurrence of both singlet and triplet isomerization pathways, (b) a significantly larger barrier for singlet state isomerization of t-**2** vs c-**2**, (c) the occurrence of internal conversion as well as singlet-state isomerization and intersystem crossing, and (d) a relatively modest dependence of the singlet-state barriers upon solvent polarity.

Singlet lifetimes, fluorescence quantum yields, and isomerization quantum yields for t-**2** and c-**2** obtained upon irradiation in the long-wavelength absorption band at room temperature in deoxygenated hexane or acetonitrile solution are summarized in Table I.[12,13] The singlet lifetimes of both t-**2** and c-**2** are sufficiently long to permit their measurement by conventional time-correlated single photon counting. Singlet lifetimes and isomerization quantum yields were measured at and below room temperature using a nitrogen-cooled optical dewar and at elevated temperatures using a heated stainless steel cell with a single sapphire window capable of withstanding high pressures. Isomerization quantum yields were measured at low conversion (<5%) and did not require correction for back reaction. No corrections were made for the effects of changing pressure or viscosity with temperature as these were judged to be insignificant over the temperature range of these experiments. Since the lowest temperatures investigated (220 K in hexane and 235 K in acetonitrile) were well above the melting points of the solvents, a large increase in viscosity is not expected at low temperature. At the highest temperature employed (575 K), the vapor pressure of hexane is 18 bar. Only minor changes in the fluorescence quantum yield for t-**1** were observed by Brey *et al.*[14] over this range of pressure and viscosity. t-**2** and c-**2** are expected to have lower volumes of activation than t-**1** and should be less sensitive to changes in pressure and viscosity.

Table I. Photophysical Data of t-**2** and c-**2** in Hexane and Acetonitrile

	t-**2**		c-**2**	
	n-hexane	acetonitrile	n-hexane	acetonitrile
Φ_F[a]	0.30		0.03	
τ[b] (ns)	11.8	10.9	2.6	2.2
Φ_i[c]	0.12	0.17	0.14	0.14
E_a[d] (kcal/mol)	8.8	8.0	4.6	4.8
log *A*	12.1	12.5	11.5	11.9

[a] Data from ref 12. [b] Lifetimes were measured on dilute (ca. 10^{-4} M) nitrogen-purged solutions. [c] Quantum yields for monochromatic 281-nm irradiation of nitrogen-purged 0.01 M solutions. Light intensities determined using isomerization of 0.01 M t-**1** in hexane solution as the actinometer. [d] ±0.2 kcal/mol.

Arrhenius plots of the rate constant for isomerization of t-**2** and c-**2** obtained assuming a singlet state mechanism ($k_i = \Phi_i\tau_s^{-1}$) are curved (Figure 1).[15] At low temperature, the isomerization rate of t-**2** shows no temperature dependence, indicating that isomerization proceeds via intersystem crossing. Caldwell *et al.*[16] have shown the triplet states of t-**2** and c-**2** to undergo barrierless twisting to a perpendicular triplet which decays with equal probability to the ground states of t-**2** and c-**2**. From this, the intersystem crossing quantum yield can be estimated to be 0.28 (twice the isomerization quantum yield) and the intersystem crossing rate constant to be $4.8 \times 10^7 s^{-1}$. These values are similar to those reported by Bonneau[5] for styrene and 1-phenylbutene. Above ambient temperature, the rate constant for isomerization of t-**2** increases with increasing temperature, indicative of an additional isomerization mechanism involving the singlet state. Following the conventional model for singlet state photoisomerization,[1] torsion about the double bond yields a twisted intermediate, $^1p^*$, which partitions to the ground-state isomers with nearly equal probability: $\alpha \approx 1 - \alpha' \approx 0.5$ (Figure 2). It is possible to partition the overall isomerization quantum yield of t-**2** into contributions from the singlet and triplet isomerization pathways using eqs 1 and 2, in which k_{tp} and k_{is} are the rate

$$\Phi_i = \alpha k_{tp}\tau_s + {}^1/_2 k_{is}\tau_s \tag{1}$$

$$k_{tp} = 2\Phi_i\tau_s^{-1} - {}^1/_2 k_{is} \tag{2}$$

constants for twisting from S_1 and intersystem crossing, respec-

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[1] (a) Saltiel, J.; Sun, Y.-P. In *Photochromism, Molecules and Systems*; Dürr, H., Bouais-Laurent, H., Eds.; Elsevier: Amsterdam, 1990; p 64. (b) Saltiel, J.; Waller, A. S.; Sears, D. F., Jr. *Photochem. Photobiol.* **1992**, *65*, 29.

[2] Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415.

[3] Condirston, D. A.; Laposa, J. D. *Chem. Phys. Lett.* **1979**, *63*, 313.

[4] Lyons, A. L., Jr.; Turro, N. J. *J. Am. Chem. Soc.* **1978**, *100*, 3177.

[5] Bonneau, R. *J. Am. Chem. Soc.* **1982**, *104*, 2921.

[6] Syage, J. A.; Al Adel, F.; Zewail, A. H. *Chem. Phys. Lett.* **1983**, *130*, 15.

[7] Grassian, V. H.; Bernstein, E. R.; Secor, H. V.; Seeman, J. I. *J. Phys. Chem.* **1989**, *93*, 3470.

[8] Orlandi, G.; Palmieri, P.; Poggi, G. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 71.

[9] Said, M.; Malrieu, J.-P. *Chem. Phys. Lett.* **1983**, *102*, 312.

[10] Hemley, R. J.; Dinur, U.; Vaida, V.; Karplus, M. *J. Am. Chem. Soc.* **1985**, *107*, 836.

[11] Rockley, M. G.; Salisbury, K. *J. Chem. Soc., Perkins Trans. 2* **1973**, *69*, 1582.

[12] Lewis, F. D.; Reddy, G. D.; Schneider, S.; Gahr, M. *J. Am. Chem. Soc.* **1991**, *113*, 3498.

[13] The singlet lifetimes and fluorescence quantum yields are the same as previously reported by us;[12] however, the quantum yields are larger and reflect a more accurate experimental procedure.

[14] Brey, L. A.; Schuster, G. B.; Drickamer, H. G. *J. Am. Chem. Soc.* **1979**, *101*, 129.

[15] Similar behavior has been reported for the photoisomerization of *trans*-1-styrylnaphthalene. Bartocci, G.; Masetti, F.; Mazzucato, U. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 1093.

[16] Caldwell, R. A.; Sovocool, G. W.; Peresie, R. J. *J. Am. Chem. Soc.* **1973**, *95*, 1496.

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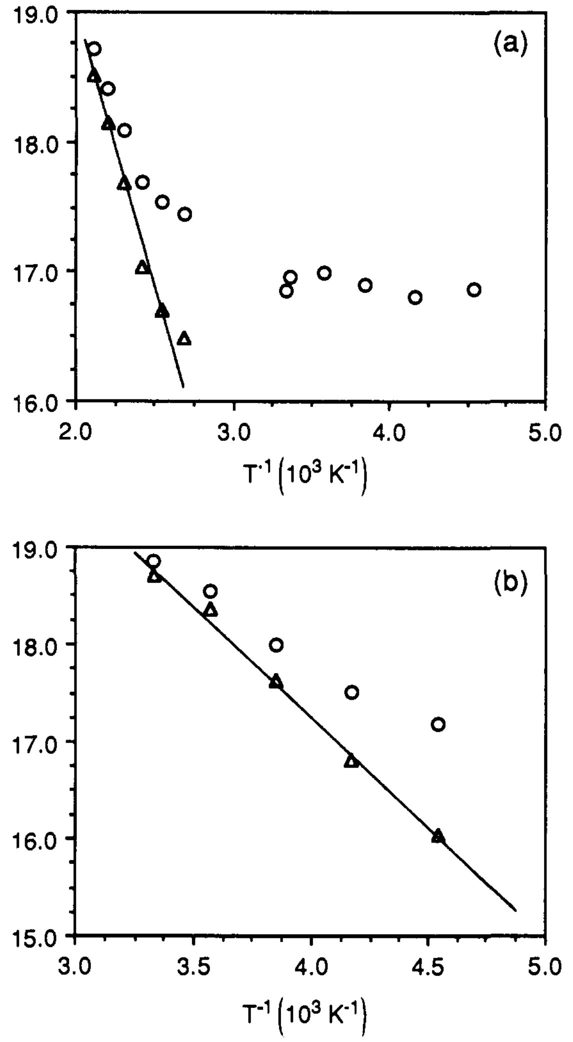

Figure 1. Plots of the overall isomerization rates, k_i (O) and singlet isomerization rates, k_{tp} and k_{cp} (Δ), of (a) t-**2** and (b) c-**2** in hexane solution.

tively. The calculated values of k_{tp} for $\alpha = 0.5$ are ploted in Figure 1a and result in a linear Arrhenius plot from which an activation energy of 8.8 kcal/mol for t-**2** in hexane can be determined. In contrast to the behavior of t-**2**, the lifetime of c-**2** increases while its isomerization quantum yield decreases with decreasing temperature (220–300 K), as is the case for t-**1**.[1] The assumption that isomerization occurs exclusively via the singlet state results in a curved Arrhenius plot (Figure 1b). Modification of this assumption to include competition of temperature-independent intersystem crossing with the same rate constant as that for t-**2** (eq 2) provides values of the rate constant for twisting of c-**2**, k_{cp}, resulting in a linear Arrhenius plot from which an activation energy of 4.6 kcal/mol can be determined. The preexponential factors (Table I) may not reflect those associated with the excited-state twisting of the double bond since the actual partitioning of the twisted singlet intermediate (α and α') remains to be determined but are sufficiently large to support the conclusion that the temperature-dependent isomerization of t-**2** and c-**2** occurs via a singlet-state mechanism.

On the basis of our data for the singlet-state photoisomerization of t-**2** and c-**2** and the published results of Caldwell and coworkers[16,17] for the triplet-state isomerization, the potential energy diagram shown in Figure 2 can be constructed. The most obvious difference between this diagram and its stilbene counterpart is the much larger barrier for singlet-state isomerization of t-**2** or

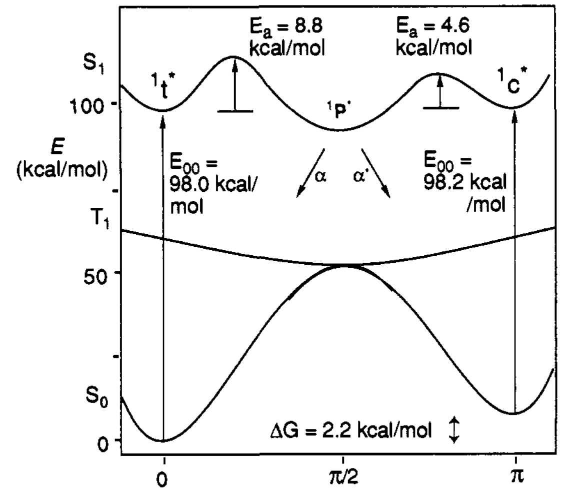

Figure 2. Potential energy diagram for twisting around the double bond of 1-phenylpropene in S_0 and S_1. Singlet-state energies are estimated from the fluorescence spectra; the value of ΔG is obtained from room-temperature iodine atom-catalyzed isomerization equilibrium. The barrier to torsion in the ground state (53.5 kcal/mol) and the triplet surface are from ref 17.

c-**2** vs t-**1** and c-**1**. At room temperature, intersystem crossing provides the exclusive pathway for isomerization of t-**2** but only a minor (ca. 25%) pathway for the isomerization of c-**2**. This configuration dependence of the photoisomerization mechanism is, to our knowledge, without precedent. A second difference is the occurrence of significant internal conversion for the singlet 1-phenylpropenes, but not the stilbenes. Since the sum of the quantum yields for fluorescence and intersystem crossing (Table I) is less than unity for t-**2**, internal conversion from planar S_1 to S_0 must contribute to nonradiative decay of the singlet state. The low isomerization quantum yield for c-**2** indicates either that internal conversion competes with isomerization or that the twisted singlet state decays preferentially to c-**2** vs t-**2**. Additional research is needed to establish the shape of the singlet-state potential energy surface and to determine whether the decay of the twisted singlet(s) yields c-**2** and t-**2** with equal probability ($\alpha = \alpha'$).[18]

In view of continuing debate concerning the polarization of the perpendicular singlet states of styrene and other aryl olefins,[8-10,19] the temperature dependence of the singlet lifetimes and isomerization quantum yields for t-**2** and c-**2** was also investigated in a polar solvent, acetonitrile. The resulting activation parameters for singlet-state isomerization are reported in Table I. The value of E_a for t-**2** decreases modestly with increasing solvent polarity whereas the slight increase in the value for c-**2** is within the limits of experimental error. Although the measured activation energies certainly contain a contribution from viscous flow (ca. 10% for t-**1** in nonpolar solvents),[20] its effect is not expected to be significant. Thus, the effect of solvent polarity on E_a is smaller for the styrenes than for t-**1**,[21] contrary to the prediction that styrene, being nonsymmetrically substituted, should be more likely to form a polar perpendicular singlet-state than stilbene.[6] We are currently seeking additional information about the transition state for singlet-state photoisomerization of t-**2** by investigating the effects of electron-donating and -accepting substituents upon the barrier height.

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[17] Tuqiang Ni; Caldwell, R. A.; Melton, L. A. *J. Am. Chem. Soc.* **1989**, *111*, 457.

[18] Said and Malrieu[8] propose that the twisted minimum on the styrene potential energy surface has a dihedral angle of 75°.

[19] Sun, Y.-P.; Fox, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 747.

[20] Sun, Y.-P.; Saltiel, J.; Park, N. S.; Hoburg, E. A.; Waldeck, D. H. *J. Phys. Chem.* **1991**, *95*, 10336.

[21] Sivakumar, N.; Hoburg, E. A.; Waldeck, D. H. *J. Phys. Chem.* **1989**, *90*, 2305.