Torsional Barriers for Planar versus Twisted Singlet Styrenes

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The magnitude of the C=C torsional barrier for the lowest singlet state (S$_1$) of styrene (**1**) has been the subject of speculation for over three decades but has not been directly measured.[1,2] Both gas-phase spectroscopy[3] and theory[2,4] agree that styrene S$_1$ is benzene-localized and has a large barrier for torsion about the double bond. Nearly a decade ago we reported an S$_1$ barrier of 8.8 kcal/mol for *trans*-1-phenylpropene (**2**), substantially smaller than several calculated values for styrene.[5-7] Our experimental values were determined from the temperature-dependent isomerization rate constant, which was calculated from the measured isomerization quantum yields and singlet decay times obtained over a wide range of temperatures. This method cannot be employed for styrenes that do not possess geometric isomers. However, if C=C torsion is the only activated singlet-state decay process, the barrier can be obtained simply from nonlinear fitting of the singlet decay time using eq 1

$$\tau(T) = 1/[\sum k + A \exp(E_a/RT)] \tag{1}$$

where $\sum k$ is the sum of all nonactivated processes (fluorescence and intersystem crossing), and A and E_a are the preexponential and activation energy for the activated process.[8] We report the application of this methodology to styrenes **1**−**6** (Chart 1). The C=C torsional barrier depends on the phenyl−vinyl dihedral angle, ϕ, decreasing from ca. 7 kcal/mol for planar styrenes to 4−5 kcal/mol for partially twisted styrenes. Highly twisted styrenes decay via exceptionally rapid intersystem crossing.

Chart 1
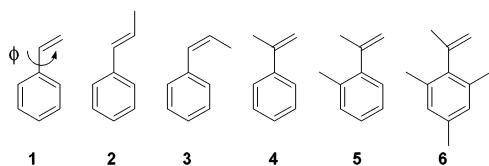
Styrenes **2** and **3** undergo trans,cis isomerization upon irradiation in dilute solution, whereas styrenes **1** and **4**−**6** show no apparent photochemical reaction. Temperature-dependent lifetime data for **1**, **4**, and **5** are shown in Figure 1 along with fits to eq 1. The resulting activation parameters for these and the other styrenes in Chart 1 are reported in Table 1 along with the fluorescence quantum yields at room temperature, the fluorescence decay times at room temperature and 80 K, and the calculated rate constants for singlet-state torsion, k_t, and intersystem crossing, k_{isc}, at room temperature. The values of E_a obtained from fitting the published lifetime data for **2** and **3** are in good agreement with the values previously determined from Arrhenius plots of the isomerization rate constants.[5,6] The barrier obtained for styrene is very similar to that previously reported for **2** and larger than the barrier reported for **3**. The barrier for the α-methylstyrene **4** is slightly lower than that for **3**. Styrenes **1**−**4** have values of log $A \approx$ 12, consistent with a unimolecular isomerization processes. Fitting of the temperature-
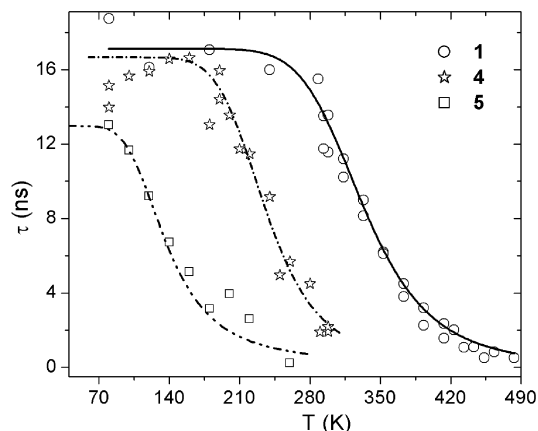

Figure 1. Temperature-dependent lifetimes for styrenes **1**, **4**, and **5** in methylcyclohexane and nonlinear fits to eq 1.

Table 1. Excited Singlet-State Properties of the Styrenes

styrene[a]	1	2	3	4	5	6
log A^b	12.2	12.2	12.6	11.6	10.3	9.6
E_a, kcal/mol^b	6.6	7.2	5.4	4.2	1.6	1.4
$10^{-7} k_t$, s^{-1} ^{b}	1.8	0.89	4.1	35		
$10^{-7} k_{isc}$, s^{-1} ^{c}	4.0	4.6	4.6	5.2	150	86
Φ_f^d	0.24	0.19	0.03	0.008		
τ_s, ns, RT^e	13.5	11.3	2.6	1.5		
τ_s, ns, 80 K^e	18.6			15.8	12.4	18.1
ϕ, deg^f	0	0	35	37	80	85

^{a} See Chart 1 for styrene structures. Data for **1** and **4**−**6** are in methylcyclohexane, and those for **2** and **3** are in hexane. ^{b} Activation parameters and k_t obtained from nonlinear fitting of the lifetime data using eq 1. ^{c} Calculated from the total unactivated decay rate minus the fluorescence rate. ^{d} Fluorescence quantum yield at room temperature (**5** and **6** are not fluorescent at room temperature). ^{e} Fluorescence decay times at room temperature and 80 K. ^{f} Estimated phenyl−vinyl dihedral angles, ±10°.

dependent lifetimes of styrenes **5** and **6** provides much smaller values of $E_a \approx$ 1.5 kcal/mol and log $A \approx$ 10. Because the solvent viscosity increases rapidly in the region where the lifetimes of these styrenes increase (Figure 1), the intrinsic barrier may be smaller than the observed barrier.[9] Thus, both E_a and log A are exceptionally small for an activated isomerization process.

The ground-state geometry and the electronic spectra of the styrenes depend on the location of methyl substituents.[10] The ground-state phenyl−vinyl dihedral angles ϕ reported in Table 1 are based on a composite of calculated and literature values.[11] They are inversely correlated with the C=C torsional barriers, planar styrenes having the largest barriers. The absorption spectra of the planar styrenes **1** and **2** have weak, structured long-wavelength absorption bands with maxima at ∼296 nm and strong structureless bands at ∼246 nm.[11] In comparison, the long-wavelength bands of the moderately nonplanar styrenes **3** and **4** are weaker and structureless, and the short-wavelength band is blue-shifted. The highly nonplanar styrene **6** has a well-resolved long-wavelength
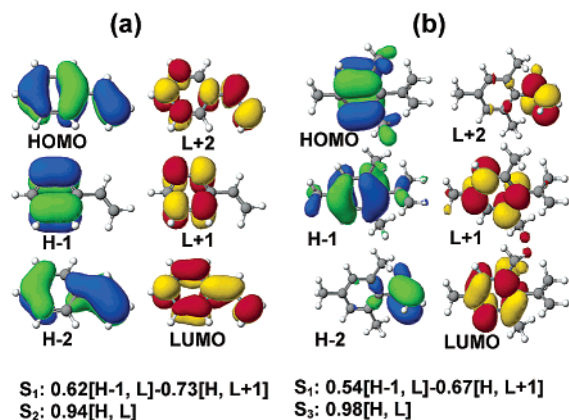
Figure 2. ZINDO frontier orbitals and the character of the S$_1$ and S$_2$ or S$_3$ singlet states for styrenes **1** (a) and **6** (b).
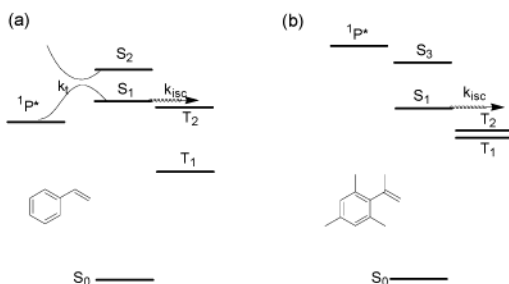

Figure 3. Approximate state energy diagrams for styrenes **1** (a) and **6** (b). Singlet energies are from ZINDO calculations; triplet energies are from the literature.[12,13]

band and a strongly blue-shifted, short-wavelength band. The ZINDO derived frontier orbitals for **1** and **6** are shown in Figure 2. Most of the frontier orbitals of **1** are delocalized, as are those of **3** (not shown), whereas the frontier orbitals of **6** are localized on benzene or ethylene.

The activation parameters for styrenes **1** and **4** are consistent with those of the model proposed previously for **2** and **3** (Figure 3a).[6] In the case of **1** and **2**, the C=C torsional barriers leading to the perpendicular singlet state ^{1}P* are relatively large. These planar styrenes decay predominantly via fluorescence and intersystem crossing at room temperature. Styrenes **3** and **4** have smaller barriers (and smaller fluorescence rate constants) and decay via both C=C torsion and intersystem crossing at room temperature. The S$_0$ and S$_1$ singlet states of **1** and **2** are planar,[14] whereas S$_0$ is nonplanar for **3** and **4** but S$_1$ is planar for **3**[15] and, presumably, for **4**. Increased nonbonded repulsion in the planar S$_1$ state of **3** or **4** can account for their decreased torsional barriers.

The values of log A and E_a for **5** and **6** are distinctly smaller than those for **1**−**4**, suggesting a change in the mechanism for activated excited singlet-state decay. The breaking of conjugation resulting from the large ground-state phenyl−vinyl dihedral angles is clearly evident in the frontier orbitals of **6** (Figure 2b). The ethylene-localized twisted ^{1}P* state of **6** should lie well above the benzene-localized singlet states, rendering singlet torsion unlikely. However, the geometry of **6** provides the orthogonal relationship of the benzene and vinyl p-orbitals needed for effective spin−orbit coupling between the benzene-localized S$_1$ state and the ethylene-localized T$_1$ state.[13,16] Thus, the rate constant calculated from the activation parameters for **5** and **6** is assigned to k_{isc} (Table 1). The values of k_{isc} for **5** and **6** are substantially faster than those for the

planar styrenes **1**−**4**, but slower than that of acetophenone ($k_{isc} = 4 \times 10^{10}$ s^{-1}). This difference can be attributed to the location of the orthogonal p-orbitals of **5** on adjacent atoms, rather than on the same atom, as in acetophenone. Out-of-plane vibrations can serve as promoting modes for $^1\pi,\pi*$ to $^3\pi,\pi*$ intersystem crossing.[17] The activated nature of the singlet decay of **5** and **6** (Figure 1) may reflect the solvent viscosity dependence of these vibronic interactions.

In summary, kinetic modeling of the temperature-dependent lifetime data provides a barrier of 6.6 kcal/mol for excited singlet-state C=C torsion in styrene, thus putting to rest decades of speculation about the magnitude of this barrier. The torsional barrier decreases slightly for styrenes with moderately large phenyl−vinyl dihedral angles. Styrenes with large phenyl−vinyl dihedral angles undergo exceptionally rapid intersystem crossing as their dominant decay pathway at room temperature. The unexpected dependence of decay pathway on ground-state geometry is attributed to a change in the character of the singlet states from delocalized for planar styrenes to localized for twisted styrenes. This model can also account for the ring-size dependence of the singlet lifetimes of 1-phenylcycloalkenes[18] and benzocycloalkenes.[19]

Supporting Information Available: Ground-state dihedral angles and absorption and fluorescence emission spectra of **1**−**6** (Figure S1) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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