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Symmetry-Enforced Conformational Control of Photochemical Reactivity in 2-Vinyl-1,3-terphenyl

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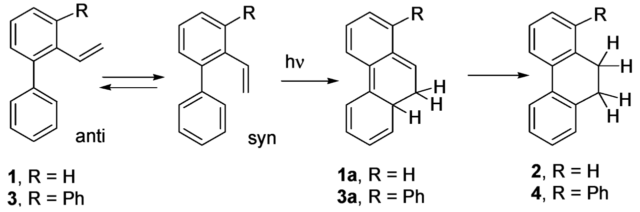
The photochemical conversion of 2-vinylbiphenyl (**1**) to 9,10-dihydrophenanthrene (**2**) was reported by Horgan et al. three decades ago.[1] They proposed a two-step mechanism: photocyclization to yield the unstable 8a,9-dihydrophenanthrene intermediate **1a**, which then undergoes a thermal [1,*n*]-sigmatropic hydrogen shift [$n = 5$, 9, or 13] to yield the observed product (Scheme 1).[2] Attempts to detect 8a,9-dihydrophenanthrene intermediates from **1** and other vinylbiphenyls under steady-state irradiation conditions have been unsuccessful;[1,3] however, a short-lived transient observed by laser flash photolysis was assigned to the 10-phenyl derivative of **1a**.[4] In the ground state, **1** is expected to exist as an equilibrium mixture of syn and anti rotamers. Assuming that the NEER (nonequilibration of excited rotamers) principle applies, only the syn rotamer should undergo cyclization.[5] Unfortunately, the low population of *syn*-**1** (ca. 1%) renders investigation of its photocyclization and thermal hydrogen shift problematic. This led us to investigate the photochemical behavior of 2-vinyl-1,3-terphenyl (**3**),[6] in which molecular symmetry enforces a syn relationship between the vinyl and ortho phenyl groups. We report here that the 8a,9-dihydrophenanthrene **3a** can be observed upon irradiation of **3** in a rigid methylcyclohexane (MC) glass at 77 K and that the photocyclization of **3**, the photochemical ring opening of **3a** to yield **3**, and the thermal hydrogen shift of **3a** to yield **4** all have remarkably low activation energies.

Scheme 1. Photochemistry of 2-Vinylbiphenyl



Minimized geometries and potential energy surfaces for rotation about the phenyl−vinyl bonds of **1** and **3** were obtained using the Jaguar package.[7] The phenyl−phenyl dihedral angles are ca. 60° for both molecules. The phenyl−vinyl dihedral angles are ca. 40° for **1** and ca. 55° for **3**. The anti rotamer of **1** is more stable than the syn rotamer by 2.6 kcal/mol, corresponding to an equilibrium population of ca. 1% of the syn rotamer. The absorption and fluorescence spectra of **1** in MC solution resemble those of biphenyl and styrene,[8] displaying an allowed transition at 235 nm and a weak shoulder at 290 nm. The fluorescence quantum yield and singlet decay time for **1** are $\Phi_f = 0.36$ and $\tau_s = 15.5$ ns. The absorption spectrum of **3** (Figure 1) is similar to that of **1**. However, **3** is essentially nonfluorescent both at room temperature and at 77 K. Irradiation of **1** at room-temperature results in bleaching of the absorption bands and fluorescence of **1** as well as the appearance of new bands assigned to **2** (Scheme 1). Irradiation of **3** results in similar changes in the absorption spectrum and the growth of a weakly structured fluorescence band with a maximum at 330 nm assigned to **4** (Figure 1). The quantum yields for the formation of **2** and **4** are <0.01 and 0.64, respectively

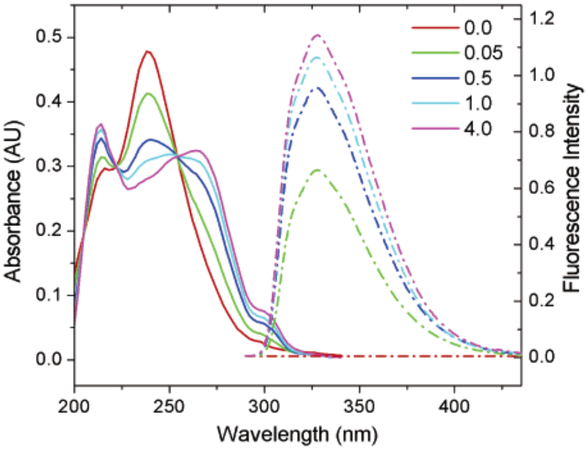


Figure 1. Photoreaction of 2-vinyl-1,3-terphenyl (**3**) monitored by UV (solid lines) and fluorescence (dashed lines) changes. $\lambda_{ex} = 260$ nm, irradiation time in minutes.

Irradiation of **1** in a MC glass at 77 K results in no change in either its absorption or fluorescence spectrum. In contrast, irradiation of **3** at 77 K results in the appearance of new absorption bands at 325 and 500 nm (Figure 2). The long-wavelength absorbing species is stable in the dark at 77 K. However, 500-nm irradiation at 77 K results in its complete reversion to **3**. Upon warming the glass to near its melting temperature (120 K), the 500-nm absorption band rapidly disappears, accompanied by the appearance of the fluorescence assigned to **4**. At 100 K the half-life of the 500-nm absorption band is ca. 2 min, and its decay results in essentially quantitative conversion to **4**. At higher temperatures ($>$110 K), the fluorescence of **4** appears without detectable formation of the 500-nm absorption band. The long-wavelength absorption band observed upon low-temperature irradiation of **3** is assigned to the intermediate **3a**, in accord with the mechanism proposed by Horgan et al.[1] (Scheme 1). Support for this assignment is provided by a TD-B3LYP/3-21G* calculation[9] of the absorption spectrum of **3a**. The calculated and observed maxima and intensities are in excellent agreement (Figure 2). In addition, the weak vibronic structure observed in the 500-nm band is consistent with a polyene structure.

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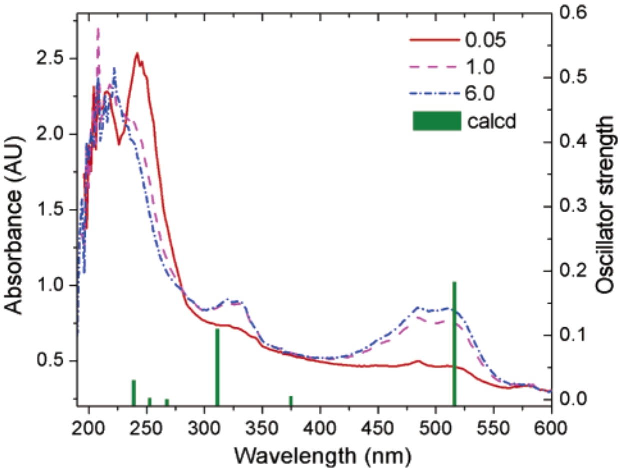
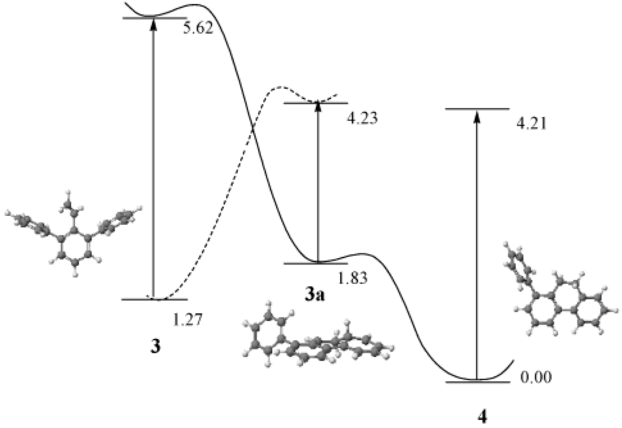


Figure 2. UV spectra of irradiated 2 × 10^{-5} M 2-vinyl-1,3-terphenyl (**3**) in methylcyclohexane at 77 K (time in minutes) and the calculated UV spectrum of intermediate **3a**.

The photochemical behavior of **1** can be readily explained with reference to Scheme 1. The long-lived fluorescence is assigned to the major (99%) rotamer, *anti*-**1**, which has a florescence quantum yield and decay time similar to those of 1-phenylpropene.[10] The photocyclization of **1** to yield **2** is attributed to the minor (1%) rotamer, *syn*-**1**. The absence of spectral changes upon irradiation of **1** at 77 K is attributed to the very low population of *syn*-**1** at low temperature. The photochemical behavior of **3** can be explained with reference to Scheme 2. The ground-state energies in Scheme 2 have been estimated using MM/PM3 calculations, and the excited-singlet-state energies, using ZINDO calculations for **3** and **4** and a TD-DFT calculation for **3a**.[9,11] The absence of fluorescence from **3** both at room temperature and 77 K, the high quantum yield for formation of **4** at room temperature, and the formation of **3a** in a rigid MC glass at 77 K are all indicative of a low barrier for photocyclization. In this respect, the photocyclization behavior of singlet **3** is similar to that of *cis*-stilbene, for which a barrier of ≤1 kcal/mol has been estimated for formation of 4a,4b-dihydrophenanthrene.[12] The singlet energy of **3** lies well above that of **3a**, making adiabatic conversion of ^{1}**3*** to ^{1}**3a*** energetically feasible. However, the observation that irradiation of **3a** yields **3** even in a 77 K glass indicates that electrocyclic ring closure of singlet **3** and ring opening of singlet **3a** occur via a pericyclic funnel with small or nonexistent barriers.[13] Entry to this funnel from singlet **3** results in formation of **4** with a quantum yield of 0.64, providing an upper bound of 0.36 for the quantum yield of return to the ground state of **3** via the pericyclic funnel.

Scheme 2. Potential Energy Surfaces for the Photoreaction of 2-Vinyl-1,3-terphenyl (**3**) (Energies in eV)



The thermal sigmatropic hydrogen shift of **3a** also has a low inherent barrier. In fact, **3a** can be detected by means of steady-state irradiation only at low temperatures and high solvent viscosities. A barrier of ≤2 kcal/mol for the hydrogen-shift reaction appears to be consistent both with our data and with the laser flash photolysis data of Lapouyade et al.[4] for the α-phenyl analogue of **1**. This barrier is substantially lower than the value of 41 kcal/mol reported for the sigmatropic hydrogen shift of 1,3-cyclohexadiene.[14] It also lower than the lowest barrier reported to date for a sigmatropic hydrogen shift, the conversion of isoindene to indene (ca. 14 kcal/mol).[15] The low barrier for the rearrangement of **3a** to **4** is, no doubt, a consequence of the highly exergonic nature of this process.

In summary, molecular symmetry confines **3** to a single ground-state conformation in which the vinyl and an *o*-phenyl group have a syn relationship favorable for photocyclization. Cyclization yields the intermediate **3a**, the first 8a,9-dihydrophenanthrene to be directly observed under steady-state irradiation conditions. Irradiation of **3a** at 500 nm results in reversion to **3**, whereas warming of the glass or irradiation of **3** in fluid solution results in formation of **4**. Both the photochemical and thermal rearrangements are remarkable for their low activation energies. Further details of this and related reactions are under investigation.

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