

Double Stereochemical Labeling in Stilbene Photochemistry: Tracing Phenyl Rotation Reveals Stereochemically Distinct Reaction Pathways for Formation of the *E* Photoproducts

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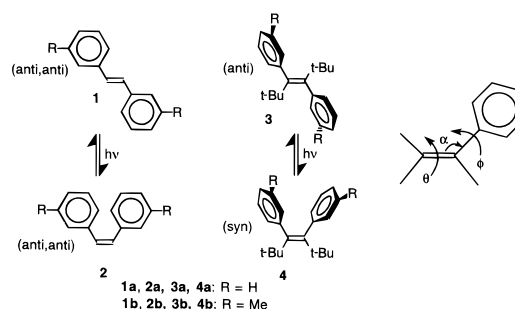
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The mechanistic details of the *Z/E* photoisomerization of stilbenes **1a** and **2a** are thought to be generally understood.^{1–3} They differ little from the original proposal put forth by Saltiel in 1967.^{4,5} Currently, there is a lively interest in this system as finer details of the excited state reaction coordinate are slowly unveiled through spectroscopic investigations employing modern techniques.^{6–11} Although stereochemistry was utilized in the 1,2-dinaphthylethene systems,^{12,13} it has not been used to study stilbene photochemistry beyond the level of Stoermer's original discovery of *E/Z* photoisomerization.^{14,15} The rapid interconversion of stereoisomers prevented traditional stereochemical labeling experiments.

The first double stereochemical labeling experiments, rotation about θ and ϕ in stilbene photochemistry, are reported below (Scheme 1). Cautious extensions of these results to other stilbenes are very instructive.

Studies in our laboratories have focused on the sterically congested stilbenes **3** and **4** (2,2,4,4-tetramethyl-3,4-diphenylhex-3-enes).^{16–22} Their geometries are distinctly different from planar **1** and slightly twisted **2**.³ Both **3** and **4** are planar about the $C_e=C_e$ bond; however, steric repulsion rotates the phenyl groups 90° out of the molecular plane so their planes are perpendicular to the plane of the central $C_e=C_e$ bond.^{20,23} Due

Scheme 1



to steric congestion, rotation about the C_e –Ph bond in **3** and **4** is sufficiently slow to study the stereochemistry of the phenyl rotation during the *Z/E* photoisomerization.

A mixture of *E* isomers **3b_{syn}** and **3b_{anti}** (~1:1) was prepared from 3-methylbenzonitrile.²⁴ Distinction of the isomers and their separation were difficult. Ultimately, **3b_{anti}** was caused to crystallize selectively from a methanol solution containing **3b_{anti}** and **3b_{syn}** through slow solvent evaporation over a period of 6 months at room temperature. ¹H NMR analysis of 15 crystals of **3b_{anti}** showed each contained 8–12% of **3b_{syn}**. X-ray diffraction analysis of one half of a single crystal determined the structure to be **3b_{anti}**. NMR analysis of the remaining half of the same crystal made the correlation with the observed methyl chemical shift. Attempts to crystallize **3b_{syn}** always resulted in cocrystallization (~1:1) with **3b_{anti}**.²⁵

Excitation of **3b** at 229 nm produced an ~1:1:1:1 mixture of **3b_{syn}**, **3b_{anti}**, **4b_{syn}**, and **4b_{anti}** from which an ~1:1 mixture of **4b_{syn}** and **4b_{anti}** was obtained by column chromatography as described for the parent compound.¹⁶ Slow crystallization of the **4b_{syn}** and **4b_{anti}** mixture from methanol gave crystals of two distinct forms, long triangular prisms and diamond-shaped plates, which could be individually selected under a microscope. X-ray diffraction analysis of the triangular prism-shaped crystals determined them to be **4b_{anti}**. These had the methyl resonance at $\delta = 2.07$.²⁶

Both **3b_{syn}** and **3b_{anti}** were stable indefinitely at room temperature. Although **4b_{syn}** and **4b_{anti}** were stable in the solid, slow *syn/anti* interconversion occurred in solution. The half lives for **4b_{syn}** \rightarrow **4b_{anti}** and **3b_{anti}** \rightarrow **3b_{syn}** were 3.7×10^3 and 1.0×10^5 s, respectively, at 58 °C. The *Z/E* isomerization, **4b** \rightarrow **3b**, is unimportant under the conditions of this study.^{16a}

Photolyses were performed with 0.005 M solutions of **3b_{anti}**, **4b_{syn}**, or **4b_{anti}** in hexane purged of oxygen and continually stirred. Normally, irradiation used 229 nm light. The distribution of stereoisomers was monitored by ¹H NMR in benzene-*d*₆ to distinguish **3b_{anti}** from **3b_{syn}**.^{16b} The results for photolysis of **3b_{anti}** are shown in Figure 1. Similar results were obtained for **4b_{anti}** and **4b_{syn}**. Also, similar results were obtained for **3b_{anti}** when the 229 nm light was replaced with 254 nm light.

By combining the (**3b_{anti}** + **3b_{syn}**)/(**4b_{anti}** + **4b_{syn}**) ratio at the photostationary state with the UV spectra in the usual manner, "excited state partitioning ratios" are found to be the same for irradiation at 229 and 254 nm, 1.8 and 1.6, respectively.

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(26) For spectral data of compounds **4b_{syn}** and **4b_{anti}**, see: Supporting Information.

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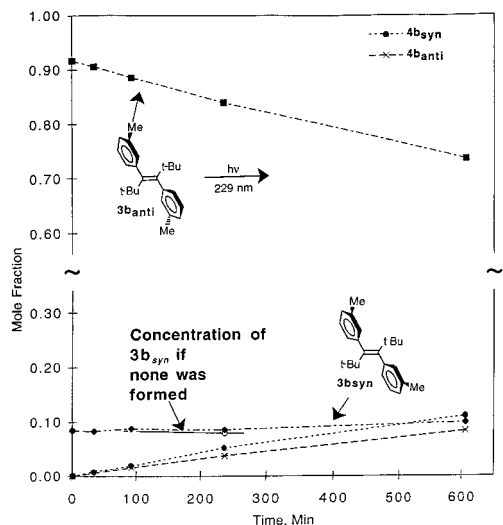


Figure 1. Change in mole fraction of stereoisomers as a hexane solution containing 92% **3b_{anti}** and 8% **3b_{syn}** was irradiated at 229 nm. Since error limits are approximately the size of the data points, the error bars are not shown.

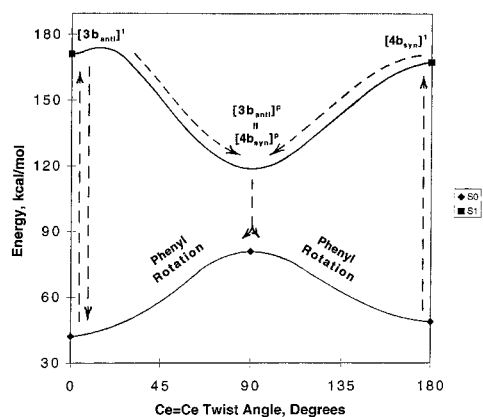


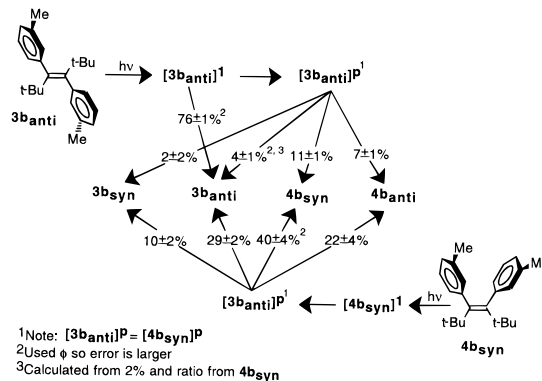
Figure 2. Reaction coordinate depicting the *E/Z* isomerization of **3b** and **4b**.

Assuming that **3b_{syn}** disappears similarly to **3b_{anti}**, the concentration for **3b_{syn}**, if none was formed during the photolysis, can be calculated to be the solid line in Figure 1. Subtraction of this value gives the **3b_{syn}** formed. Both **4b_{syn}** and **4b_{anti}** were corrected for the amounts formed from **3b_{syn}**. The quantum yields of isomerization of **3a** and **4a** with 254 nm excitation are $\phi_{E \rightarrow Z} = 0.18$ and $\phi_{Z \rightarrow E} = 0.38$, respectively. Assuming **3b_{anti}** has a similar quantum yield at 229, the sum of **3b_{anti}** and **3b_{syn}** formed from the excited state can be calculated from the sum of **4b_{syn}** and **4b_{anti}**. Subtraction of **3b_{syn}** leaves the amount of **3b_{anti}** formed. The **4b_{syn}** photolysis is treated likewise. Making these corrections leads to the distribution of decay processes shown in Scheme 2.

The energy profiles for the ground and *S*₁ excited states as **3b** twists about θ were explored by using MOPAC.²⁷ Those results along with earlier reports on the thermal chemistry are included in Figure 2.¹⁶ For the radical anion and cation of **3b**, MOPAC shows a small maximum around $\theta = 90^\circ$.²⁸ This feature is absent on the *S*₁ surface.

Simple schemes were inconsistent with these observations and discarded. The processes described in Scheme 2 and the reaction coordinate in Figure 2 are entirely consistent with the observations. The features of the diagram in Figure 2, based

Scheme 2



on the stereochemical observations reported herein, are analogous to those derived from spectroscopic studies on other systems.

In Scheme 2, 76% of $[3b_{anti}]^1$ undergoes stereospecific internal conversion to its ground state. This justifies addition of an energy barrier for $[3b_{anti}]^1$ to surmount as it twists toward $[3b_{anti}]^P$. Such a barrier, which was not evident in the single-state MOPAC calculation, is expected if upper excited states are mixed into the calculation. The remaining 24% of $[3b_{anti}]^1$ twists about θ , but not ϕ , to stereospecifically (*vide infra*) form $[3b_{anti}]^P$. In the **4b_{syn}** photolysis, all of $[4b_{syn}]^1$ twists about θ , but not ϕ , to stereospecifically form $[3b_{anti}]^P$. No direct internal conversion of $[4b_{syn}]^1$ is necessary (*vide infra*).

No isomerization about ϕ occurs along the *S*₁ surface. If it did, the common intermediate, $[3b_{anti}]^P$, requires the **4b_{syn}**/**4b_{anti}** and **3b_{anti}**/**3b_{syn}** to be identical. This is not observed.

Isomerization about ϕ occurs after $[3b_{anti}]^P$ drops to the ground state surface. The hot ground state rotates around θ and ϕ to partition between **3b_{syn}**, **3b_{anti}**, **4b_{syn}**, and **4b_{anti}**. This proposal requires the ratio of **3b_{syn}**/**3b_{anti}**/**4b_{syn}**/**4b_{anti}** from **3b_{anti}** and **4b_{syn}** to be the same, which it is. This also explains why the observed **3b_{anti}**/**3b_{syn}** ratio from **4b_{syn}** is greater than the **4b_{syn}**/**4b_{anti}** ratio from **3b_{anti}**. It is due to the larger barrier in the ground state to rotation about ϕ for **3b** than **4b** noted above.

Photoisomerization accounts for all the absorbed light quanta in the photolysis of **4b_{syn}**. A direct internal conversion path for $[4b_{syn}]^1 \rightarrow 4b_{syn}$ is not necessary. Scheme 2 accounts for the fate of all $[4b_{syn}]^1$. Specifically, the **4b_{syn}**/**4b_{anti}** ratio observed independently from the photolysis of **3b_{anti}** matches that ratio from the photolysis of **4b_{syn}**.

A detailed description of the *S*₁ energy surface in the photolysis of **2** is shown to involve motion about θ , ϕ , and α .^{11,29} The phenyl pivots back and forth about ϕ up to 30° but does not rotate 180° to the new configuration. The stereochemical studies of **3b** and **4b** support similar events in that system. Further, however, they identify isomerization about ϕ occurring once the ground state energy surface is attained.

Saltiel's observation of emission from the excited state of **1** upon excitation of **2** provides direct evidence for the existence of a common intermediate (**1**)^P along the stilbene *S*₁ surface.¹⁰ The stereochemical studies herein provide a second piece of evidence supporting such an intermediate and a new photochemical isomerization reaction: *syn/anti* isomerization.

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