Communication

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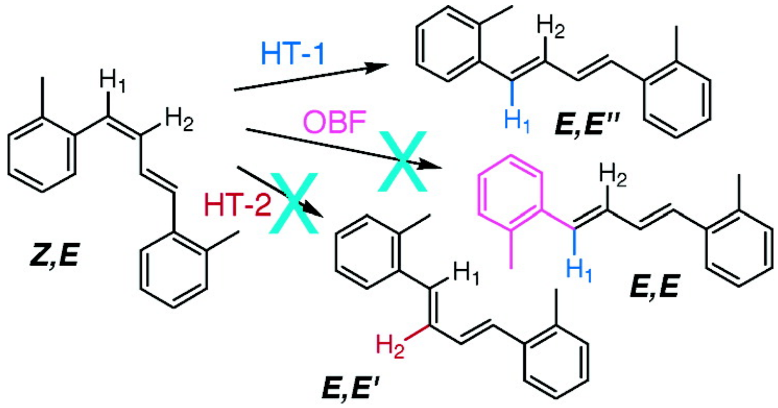

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New Aspects of Diphenylbutadiene Photochemistry. Regiospecific Hula-Twist Photoisomerization

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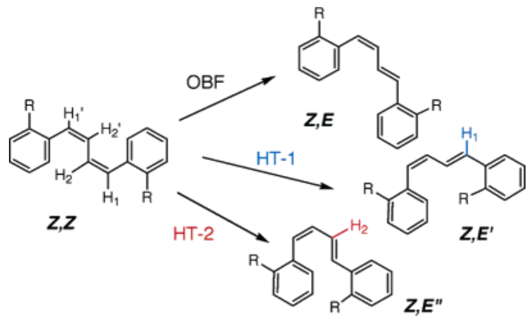
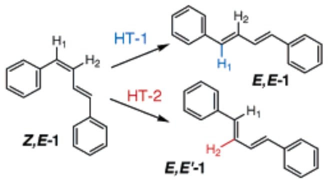
Photoisomerization of 1,4-diphenyl-1,3-butadiene (DPB, **1**) was first studied by Zechmeister.[1] In 1988, Yee et al. reported a detailed study of all three isomers under direct and triplet-sensitized irradiation with the *Z*,*Z* isomer being absent in all product mixtures.[2] Recently, photoisomerization by the volume-conserving Hula-twist (HT) mechanism[3] was shown to be involved in styrenes,[4] dienes,[5] and stilbenes[6] under confined conditions. The same mechanism, if involved in DPB, will not only lead to products different from that of the conventional torsional relaxation mechanism, or one-bond-flip (OBF) process, but also could reveal itself in two different ways (HT-1 and HT-2) as shown with the *Z*,*Z* isomer.



The *E*,*E* isomer of DPB was found to be stable under direct irradiation in EPA (ether/isopentane/ethanol = 5:5:2) glass at liquid nitrogen temperature. The *Z*,*E* and *Z*,*Z* isomers under the same conditions were found to be photolabile. The results are described below.

The progress of the reaction of ***Z*,*E*-1** is shown in Figure 1a and the difference absorption spectra (*t* spectrum minus t_0 spectrum) in Figure 1b. The semilog plot (insert) and isosbestic points showed a simple one-to-one conversion. Also, positions of the peaks of the main absorption band in the difference spectra were found to be identical to that of an authentic sample of ***E*,*E*-1**. Furthermore, we found that the relative peak heights of the spectrum of the irradiated sample minus that of the unreacted ***Z*,*E*-1** matched those of ***E*,*E*** (insert in Figure 1b). Therefore, it was concluded that the only photoproduct from ***Z*,*E*** in EPA glass was ***E*,*E***. In agreement, the absorption spectra of the irradiated sample before and after warming to 180 K and recooling to 77 K were the same. Clearly, only the stable conformer was formed in the photoreaction, which is not in agreement with HT-2. The latter should give an unstable *E*,*E* conformer (***E*,*E*′-1**). The isomerization, therefore, is regiospecific: HT-1. However, formally the OBF process could also yield the same stable *E*,*E* product. While such a volume-demanding OBF process is highly unlikely in a frozen glass medium as shown in other studies,[4−6] we decided to carry out the distinguishing experiment depicted in Figure 2.



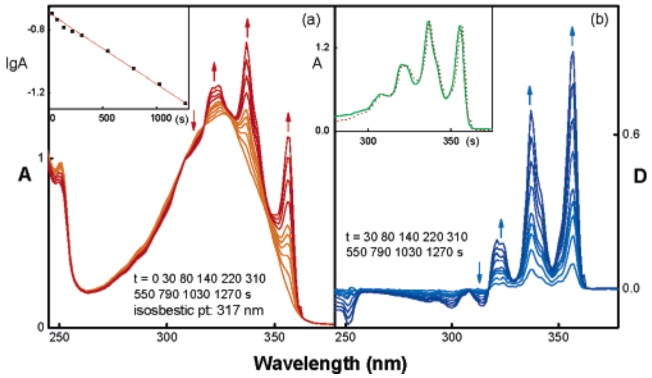


Figure 1. (a) Absorption spectra of ***Z*,*E*-1** recorded during its irradiation (>310 nm, Corning 0-54 filter) in EPA glass at liquid nitrogen temperature. Insert: log of absorbance at 337 nm versus time. (b) Difference spectra ($t - t_0$) from absorption spectra. Insert: partial absorption spectrum at t = 790 s minus that of residual amount of ***Z*,*E*-1** (dotted line) superimposed with the absorption spectrum of ***E*,*E*-1** (solid green line).

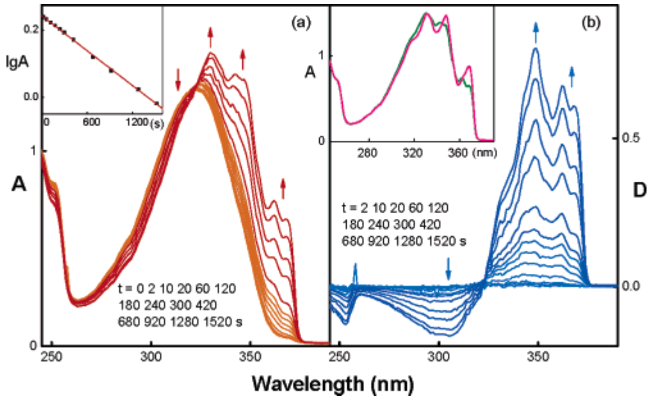


Figure 2. (a) Absorption spectra of ***Z*,*E*-2** during its irradiation (>310 nm) in EPA glass at 77 K. Insert: a semilog plot of absorbance at 350 nm versus time. (b) Difference spectra. Insert: the absorption spectrum at t = 1520 s (green) superimposed with that of the same sample (red) after warming to 180 K and recooling to 77 K.

The *Z*,*E* isomer of *o*,*o*′-dimethyl-DPB (**2**)[7] was irradiated under the same conditions. The absorption and difference spectra are shown in Figure 2a along with a semilog plot. The plot showed a single-exponential decay; however, the difference spectra showed that the photoproduct was not that of the stable conformation of the *E*,*E* isomer. The spectrum changed when the sample was

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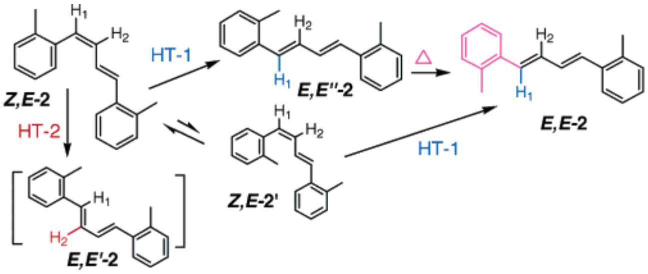
warmed to 180 K and recooled to 77 K. The new spectrum was identical to that of the stable ***E*,*E*** (see insert in Figure 2b). Thus, the primary photoproduct must be a high-energy conformer of ***E*,*E*-2** (***E*,*E*″-2**). The presence of the *o*,*o*′-substituents that removed symmetry in the phenyl ring made possible detection of the associated single-bond isomerization along with the double-bond isomerization as expected of a HT process.

Another minor difference between results of ***Z*,*E*-2** and ***Z*,*E*-1** is the slightly diffused isosbestic point for the methylated case, which appeared to be independent of the wavelength of excitation (>300 nm, Pyrex filter, or >325 nm, naphthalene solution filter). Analysis of the absorption spectrum showed the presence of the stable ***E*,*E*-2** as a minor product at all stages of irradiation (increasing slightly with time). Its formation is not consistent with HT-2 of ***Z*,*E*-2** (yielding instead ***E*,*E*′-2**) but is consistent with HT-1 of the unstable conformer ***Z*,*E*-2** present in equilibrium concentration at the setting temperature of the organic glass (∼90 K).



We have also examined the low-temperature photochemical behavior of ***Z*,*Z*-1**. The difference spectra corresponding to those of the early (Figure 3a) and later (Figure 3b) periods of irradiation are shown separately. The semilog plot (not shown) clearly showed two distinct steps of reaction giving an early product without any fine structures and a later product with fine structures in the absorption spectra. After subtracting contributions of reactants to the spectra of the irradiated sample, we readily concluded that the initial product was that of the stable *Z*,*E* isomer and the later product was that of the stable *E*,*E* isomer (see inserts), which is identical to the insert in Figure 1b. Therefore, the photoreaction must be consecutive HT-1 and HT-1′ processes (see scheme for *Z*,*Z* above). Again, HT-2 or HT-2′ would lead to new unstable conformers.

Additionally, we have examined the low-temperature photochemical behavior of isomers of *p*,*p*′- and *o*,*o*′-bistrifluoromethyl-DPB (**3** and **4**).[7] In the case of **3**, photoreactions were similar to those of the parent isomers; in the case of **4**, photoreactions were similar to those of **2**. Figures corresponding to those of Figures 1−3 are available in Supporting Information. Hence, the observed high preference for isomerization at CH-1 was unaffected by variation of electronic properties of the substituents on the phenyl rings.

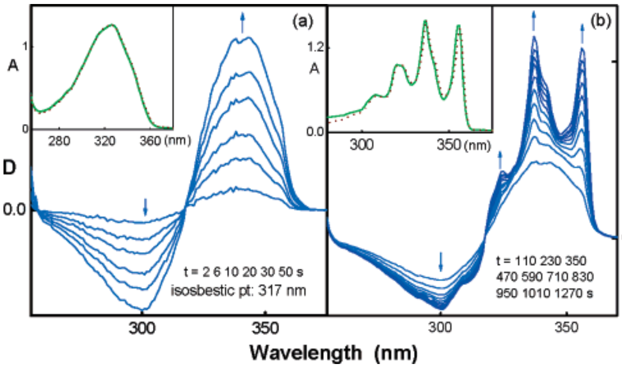


Figure 3. Difference spectra obtained from direct irradiation of ***Z*,*Z*-1** in EPA glass at 77 K. (a) Early period of irradiation (2−50 s). Insert: absorption spectrum of authentic ***Z*,*E*-1** (solid line) superimposed with that of the absorption spectrum at 50 s of irradiation minus the residual amount of ***Z*,*Z*-1** (42%) and 1.8% ***E*,*E*-1** (dotted line). (b) Later period of irradiation (110−1270 s). Insert: absorption of authentic ***E*,*E*-1** (solid line) superimposed with the absorption spectrum at *t* = 1270 s of irradiation minus 62% ***Z*,*E*-1** (dotted line).

While it is premature to suggest a primary cause for the observed regioselectivity in HT of DPB, we suspect there are two contributing factors favoring HT-1 over HT-2. The first is the possible favorable energy of the allyl-phenyl transition state structure for the HT-1 process (versus the vinyl-phenyl structure for HT-2). The second is the smaller phenyl end group in its sideways sliding movement as part of the HT-1 process (relative to the larger benzyl group for HT-2).

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Supporting Information Available: NMR data of isomers of **1**−**4** and difference absorption spectra of **3** and **4** from direct irradiation (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Isomers of **1** were prepared according to published procedures.[1,2] Similar procedures were followed for preparation of isomers of **2**−**4**. Characterization data (NMR and UV) of the latter compounds are available in Supporting Information.

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