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# Conformational isomerizations of symmetrically substituted styrenes. No-reaction photoreactions by Hula-twist

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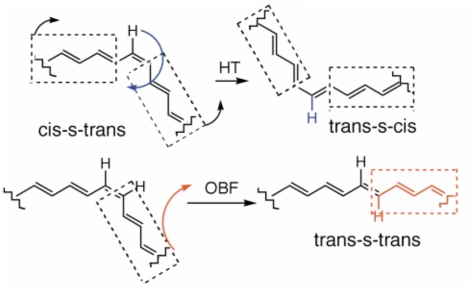
**Symmetrically substituted styrenes photochemically gave unstable conformers in low temperature organic glass in a manner consistent with the recently postulated Hula-twist mechanism of photoisomerization.**

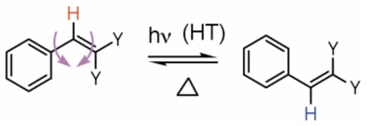
The Hula-twist (HT) mechanism of photoisomerization is a two-bond isomerization process that leads to simultaneous conformational and configurational changes in a conjugated system. It was argued that such a mechanism of isomerization invoking flipping of a single H, demands much less reaction volume than the conventional torsional relaxation process (or the one-bond-flip, OBF, process); therefore, it should be favored in confined media[1] (see Scheme 1 for the two processes). Test systems were postulated designed to distinguish between the HT and the OBF mechanisms.[1,2]



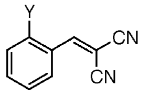
**Scheme 1** The Hula-twist (HT) mechanism of isomerization leads to conformational and configurational isomerization. The one-bond-flip (OBF) mechanism leads to configurational isomerization only. Color change emphasizes a change of sidedness.

New experimental results on substituted stilbenes are now available[3]—further substantiating the simultaneous conformational and configurational isomerization reported for previtamin D.[4] These new examples demonstrate that indeed in solution a one-bond isomerized product (hence OBF) was produced while in an organic glass, a two bond (double and single bonds) isomerized product was produced instead.

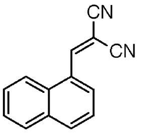
Photoisomerization of styrene by HT is a no-reaction reaction—the product being indistinguishable from the starting material:



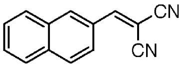
They can be made visible by introducing a substituent on the phenyl ring to remove the symmetry. An *o*-substitutent will have the added benefit of producing two conformers with different absorption properties. Therefore, in this paper, we report the photochemical transformation of *o*-substituted styrenes (**1**), and two naphthyl analogs (**2** and **3**)[5] (the cyano groups are there to extend the UV absorption nearer to the visible region).



**1a**: Y = Me
**1b**: Y = F
**1c**: Y = Cl
**1d**: Y = OMe



**2**



**3**

None of these or other similarly substituted styrenes were reported to give any unimolecular photoproducts. Indeed, we found that irradiation of an EPA (ether–pentane–ethanol in 5 : 5 : 2 proportion) solution of any of the above compounds at room temperature resulted in no detectable changes in the UV absorption spectra (see *e.g.* insert b in Fig. 1). On the other hand, irradiation (Corning O-52 filter, > 340 nm light) of a dilute solution of any one of the above compounds at −196 °C in EPA glass resulted in changes of its absorption spectra. The changes ranged from a decrease of its absorption near the long-wavelength absorption band in the cases of **1a,b** and **c** to an increase of absorption in the case of **2**. Compound **1d** showed negligible changes in the long wavelength 378 nm band (probably a charge transfer band) but an increase in intensity of the 290 band. In Fig. 1 are shown in detail spectral changes during irradiation of **1b** in EPA glass (insert a) and the difference spectra. The one-to-one correspondence between the starting material and the photoproduct is clearly revealed by the sharp isosbestic point at 305 nm.

The photochemical reactions are reversible. For example, in the case of **1b** the blue-shift caused by irradiation with light > 310 nm (Corning O-54 filter) can be partially reversed upon irradiation with 310 nm light (interference filter, 10 nm width). Separately we found that in all cases upon warming to room temperature, the photoproduct produced at liquid nitrogen temperature reverted completely to the starting material (see, *e.g.*, top of Fig. 2). Thus, the photoproduct is consistent with a high energy conformer.

Spectral data for the two naphthyl derivatives **2** and **3** are shown in Fig. 2. Compound **3** showed negligible changes upon

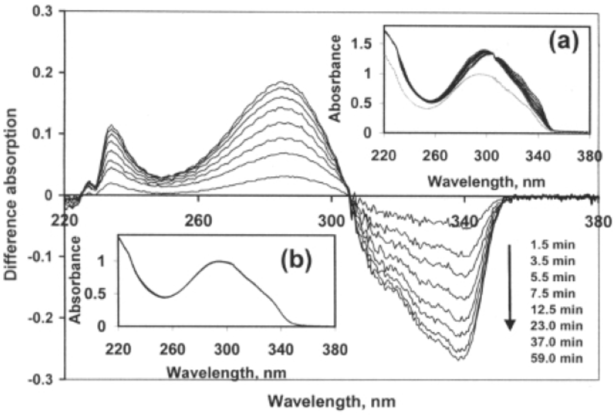


**Fig. 1** Difference spectra calculated from the stacked spectra obtained during irradiation of **1b** in EPA glass at −196 °C (insert a, time intervals for irradiation shown in the figure). The room temperature spectra, before and after 300 min of irradiation, are shown in insert b. Light of > 310 nm (Corning-54 filter) was used for irradiation.

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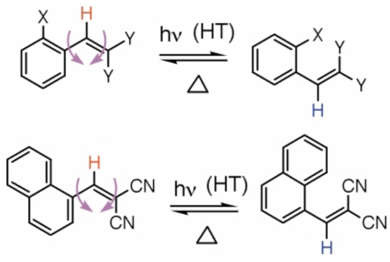
irradiation at −196 °C, in agreement with involvement of uncongested conformers. Compound **2** yielded a more red-shifted photoproduct that reverted to the starting material upon warming to room temperature. Thus, photochemically the congested conformer was produced.

These conformational interconversions are not known for the styryl derivatives; however, the results are reminiscent of the cases of butadiene[6] and 1,3,5,7-octatetraene,[7] where photochemical conformational interconversions were reported under matrix isolation conditions. The latter cases have since been included in a general scheme of HT photoisomerization.[8,9] Not surprisingly, the present results are not accountable by the conventional torsional relaxation mechanism but they are understandable when the HT mechanism is invoked:



Reported conformational changes in arylethylenes were limited to those with large aryl rings of which a longer excited lifetime is expected.[10] We suspect the absence of such reports on styrenes, or others with small aryl rings, is due to the fact that such a no-reaction reaction is observable only with properly substituted styrenes imbedded in rigid media at low temperatures.

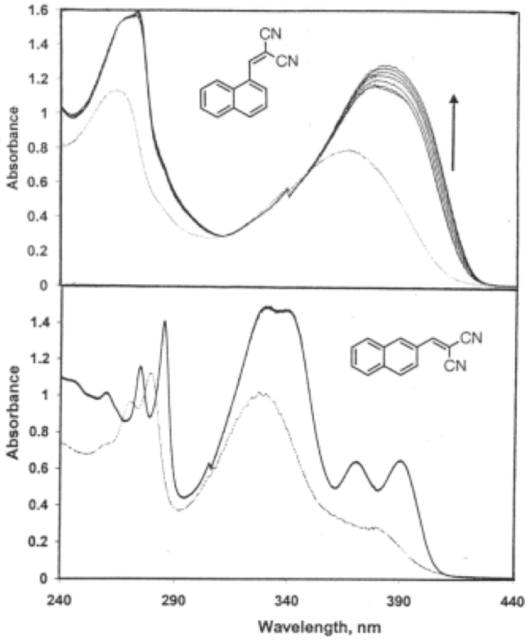


**Fig. 2** Absorption spectra of **2** and **3** in EPA glass at −196 °C while irradiating with > 340 nm light (Corning O-52 filter), time intervals: 8, 29, 61, 91 151 and 205 min. Grey lines are superimposed spectra of the sample at room temperature before irradiation and the 205 m irradiated sample after warming to room temperature.

Lewis and Zuo[11] recently reported quantum yields of isomerization and fluorescence of a series of simple styrene derivatives. Interestingly they observed varied activation energies for isomerization in the excited singlet state (ranging from as high as 7.2 kcal $mol^{-1}$ for planar styrenes to as low as 1.4 kcal $mol^{-1}$ for highly twisted styrenes). The isomerization data were interpreted exclusively in terms of the OBF (or torsional relaxation) process. Nevertheless, it should be clear that their experimental conditions would not allow ready detection of Hula-twist products. For the current set of styryl derivatives, the *ortho*-substituents, needed for revealing the conformational changes, should qualify them as non-planar styrenes as defined by Lewis and Zuo, *i.e.*, a low barrier of "isomerization" is expected. The low temperature results reported in this paper are in agreement with this expectation.

We might point out that the observed metastable products from the styrene derivatives are not consistent with formation of radical anions through electron transfer from solvent to the dicyanoethylene unit. Radical anions are expected to have substantially red-shifted absorption bands from those of the neutral molecules.[12] The reported cases are mostly blue-shifted. Also, the negative result of **3** *versus* **2** is not readily accountable by electron transfer processes.

It will be of interest to determine the quantum efficiency of this chemical channel for deactivation of arylethylenes as well as quantum yields of conformational isomerization and fluorescence and as a function of changing media of confinement. Of particular interest will be detection of a complementary relationship between fluorescence quantum efficiencies and conformational isomerization quantum yields as is known to exist for *trans*-stilbene in the configurational isomerization reaction.[13]

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