Photoisomerization

Photoisomerization by Hula Twist: 2,2′-Dimethylstilbene and a Ring-Fused Analogue[**]

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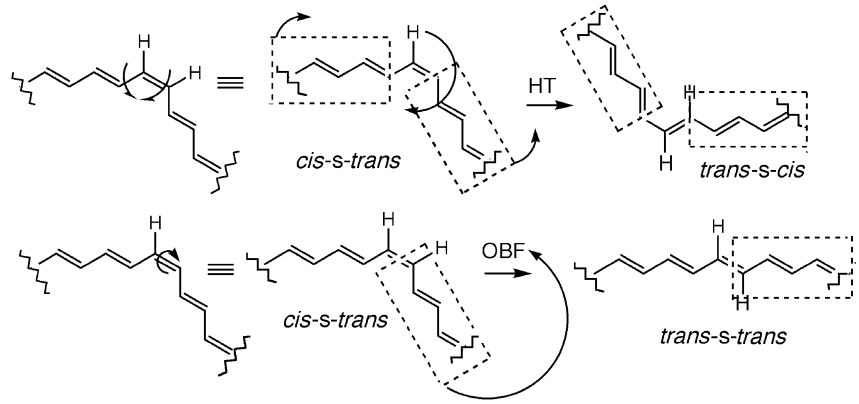
Recently, the case for medium-dependent photoisomerization from the S_1 state was made;[1] it was argued that the one-bond-flip (OBF) process (or torsional relaxation)[2] dominates in solutions, but this volume-demanding process is unlikely in confined media. Instead, a volume-conserving reaction mechanism that involves the simultaneous rotation around two adjacent single and double bonds was suggested. The net result was a CH group rotating out of the plane of a polyene (which is not volume demanding; Scheme 1) and the process was termed the "Hula twist".[3,4] The concept was first introduced to account for the rapid isomerization of the confined visual chromophore in rhodopsin.[3] Interest was recently rekindled after the successful demonstration of a Hula twist in a simple organic system: pre-vitamin D in an organic glass.[5]



Scheme 1. Top: *cis* to *trans* isomerization by Hula twist (HT) with simultaneous conformational reorganization and one CH unit rotating out of the plane. Bottom: *cis* to *trans* isomerization by one-bond-flip (OBF) with half of the molecule rotating around a double bond.

The specific role of the Hula twist process in a general mechanistic scheme that accounts for all the photoisomerization reactions made it possible to design specific examples to test the validity of the concept and allowed for the possibility to further broaden its scope.[2] Now we report experimental results on the first set of test systems: 2,2′-dimethylstilbene (**1**) and a related ring-fused analogue **2**[6] (which minimizes the number of possible conformers). The location of the alkyl substituent was chosen to facilitate the investigation of conformational changes occurring during photoisomerization. The results are relevant to current thoughts on the photoisomerization of organic systems,[1,2] although it does not necessarily relate to the protonated Schiff bases of the visual chromophore.[3]

We previously predicted the photochemical reactions of 2,2′-substituted stilbenes **1** and the ring-fused stilbene **2** to be those shown in Scheme 2.[2a,b] In a fluid solution, OBF photoisomerization should lead to a stable conformer of the isomerized photoproduct, while in a frozen solid solution, HT photoisomerization should give an unstable conformer of the isomerized product. The latter should be readily converted into the stable conformer by warming.

We have now investigated the irradiation of isomers of **1** and **2** in 2-methylpentane both in a fluid solution (at 0 °C) and in the glassy state (−193 °C). The low-temperature irradiation apparatus used in this study was essentially that described in the literature.[7] The progress of the photoreactions was followed by UV/Vis spectroscopy (Figures 1–4).

These sets of data show that all these compounds indeed exhibit different photochemical behavior in solvent media of different rigidity. The difference absorption curves obtained during irradiation of *trans*-**1** and *cis*-**1** (Figure 1 d and 2 d), or (*E*)-**2** and (*Z*)-**2** in fluid solutions at 0 °C Figure 3 d and 4 d) were essentially mirror images of each other, which reflects that the same equilibrium mixture is reached from both directions. On the other hand, the absorption spectra obtained during low-temperature irradiation of (*E*)-**2** and (*Z*)-**2** (Figure 3 a and 4 a; less exactly for **1** because of the low conversion of the *trans* isomer making the difference spectra (Figure 1 c) rather noisy) showed no mirror image relationship. At high conversion, the absorption spectrum (calculated after subtracting the residual amount of (*E*)-**2**) of the low-temperature product from (*E*)-**2** was found to be different from that of (*Z*)-**2** cooled to 80 K. At lower conversions, the difference spectra substantially deviate from that of the stable isomer. Warming the low-temperature product to 0 °C resulted in its facile conversion into the stable product (*Z*)-**2**. Such a conversion under the mild conditions of thawing and warming to 0 °C can only suggest formation of unstable conformers (namely, the hindered s-*cis* form) at low temperature. In other words, the observed photochemical events of these compounds (more clearly shown for (*E*)-**2** and (*Z*)-**2**) paralleled the reactions outlined in Scheme 2.

Not surprisingly, the efficiency of the isomerization of stilbene **1** favors reaction of the *cis* isomer over the *trans*

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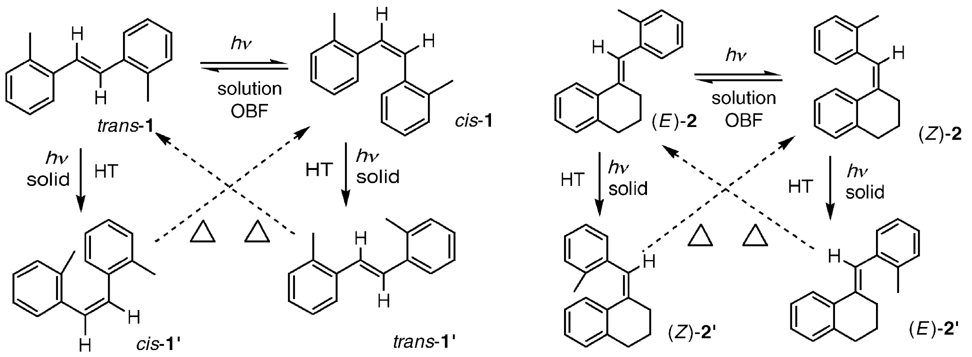


Scheme 2. Predicted photoisomerization pathways. Left: 2,2′-substituted stilbenes **1**; right: ring-fused stilbene analogues **2**. Horizontal: photoisomerization in solution by OBF; vertical: isomerization in frozen solution by HT; diagonal: warming and thawing of the solid solution containing the HT product.

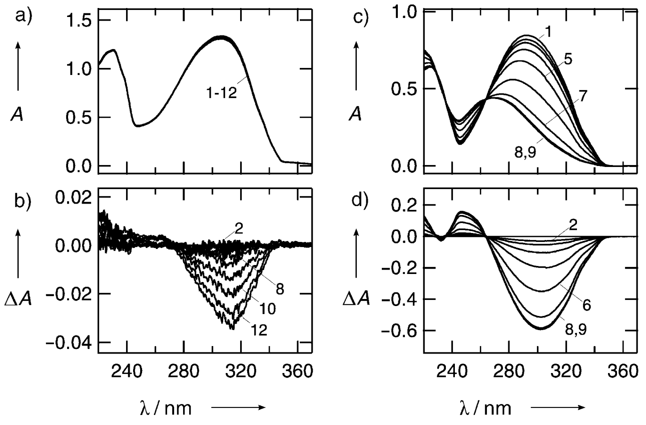


Figure 1. Progress of the photoreaction ($\lambda > 280$ nm) of *trans*-**1** at 80 K in 2-methylpentane glass (a and c) and in 2-methylpentane solvent at 273 K (b and d). Changes in the absorption spectra versus time (0, 5, 10, 20, 40, 80, 160, 320, 640, 1280, 2560, and 5120 s for a; the same intervals to 640 s for b) and difference absorption bands (A_t—A_0) for the 80 K (c) and 273 K (d) data are shown.

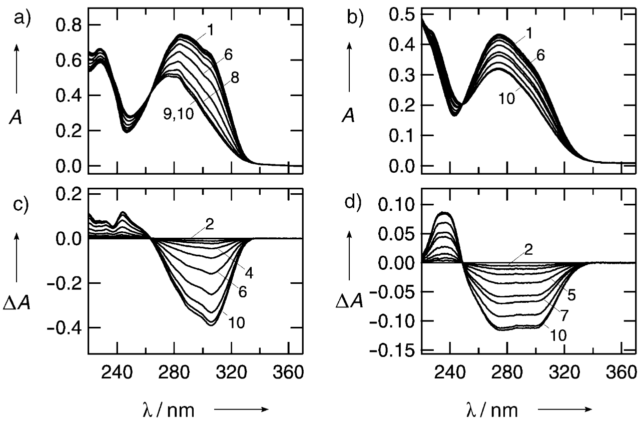


Figure 3. Progress of the photoreaction ($\lambda > 280$ nm) of (*E*)-**2** at 80 K in 2-methylpentane glass (a and c) and in 2-methylpentane solvent at 273 K (b and d). Changes in the absorption curves versus time (0, 5, 10, 20, 40, 80, 160, 320, 640, and 1280 s for a and b) and difference absorption bands (A_t—A_0) for the 80 K (c) and 273 K (d) data are shown.

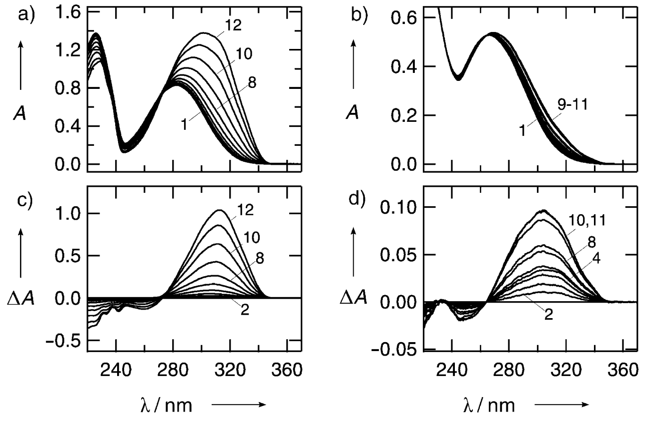


Figure 2. Progress of the photoreaction ($\lambda > 280$ nm) of *cis*-**1** at 80 K in 2-methylpentane glass (a and c) and in 2-methylpentane solvent at 273 K (b and d). Changes in the absorption curves versus time (0, 5, 10, 20, 40, 80, 160, 320, 640, 1280, 2560, and 5120 s for a; same intervals to 2560 s for b) and difference absorption bands (A_t—A_0) for the 80 K (c) and 273 K (d) data are shown.

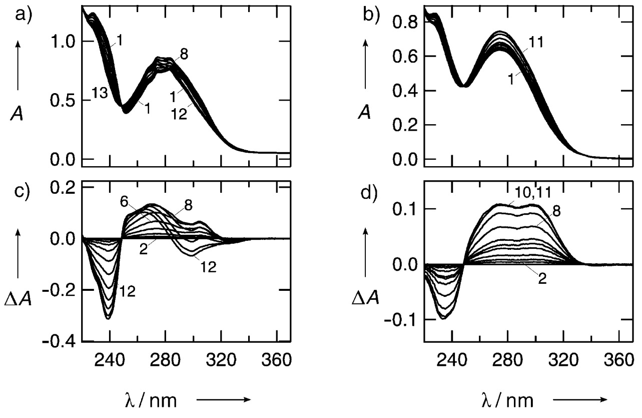


Figure 4. Progress of the photoreaction ($\lambda > 280$ nm) of (*Z*)-**2** at 80 K in 2-methylpentane glass (a and c) and in 2-methylpentane solvent at 273 K (b and d). Changes in the absorption curves versus time (0, 5, 10, 20, 40, 80, 160, 320, 640, 1280, 2560, and 5120 s for a; same intervals to 2560 s for b) and difference absorption bands (A_t—A_0) for the 80 K (c) and 273 K (d) data are shown.

isomer at low temperature in organic glass. However, the *trans* isomer was not entirely photochemically inert, as claimed for many other *trans*-1,2-diarylethylenes.[8] (At 80 K, the *trans* isomer is estimated to be about 100 times less reactive than the *cis* isomer.) There are, however, distinct differences in the low-temperature photochemical behavior of the conformationally more restricted **2** relative to that of **1**. The presence of the extra ring made (*E*)-**2** sterically *cis*-stilbene-like. Therefore, the (*E*)-**2** to (*Z*)-**2** photoisomerization also proceeded efficiently. The quantum yield of the reaction was found to be 0.18 ± 0.02.[10] On the basis of the relative irradiation periods, we believe that this value is a good reflection of the ease of isomerization of *cis*-diarylethylenes in low-temperature glass.

Changes in the absorbances of isomers of **1** and **2** versus time are shown in Figure 5. It is clear that compounds *trans*-**1**, *cis*-**1**, and (*E*)-**2** all exhibit single exponential decay, which indicates the reactions occur from a single species and that the reactant is conformationally homogeneous at liquid-nitrogen temperature. However, the decay of (*Z*)-**2** is clearly not a single exponential. In fact, the curve in Figure 5 d suggests the involvement of two species. Calculated results indeed support that notion: the two s-*E* and s-*Z* conformers of (*Z*)-**2** differ by $1.03\ \text{kcal mol}^{-1}$ while for (*E*)-**2**, there was no other stable conformer within $1.5\ \text{kcal mol}^{-1}$ of the s-*E* conformer.[9]

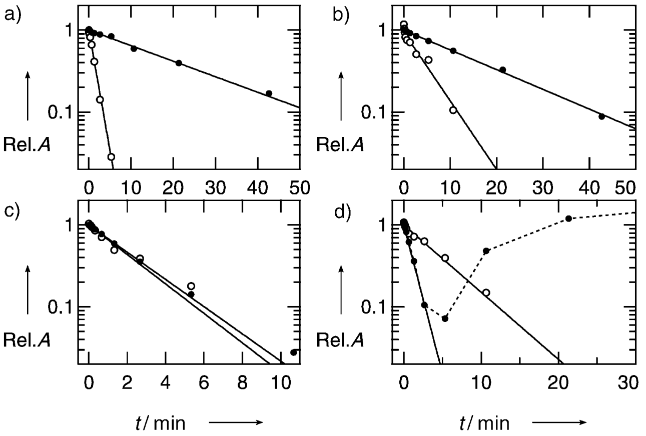
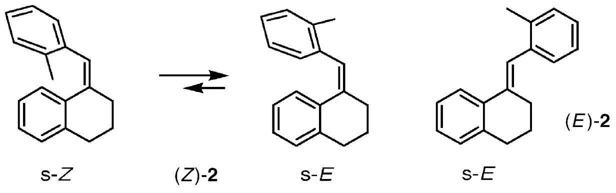


Figure 5. Changes in the absorbance maxima during irradiation of *trans*-**1** (a), *cis*-**1** (b), (*E*)-**2** (c), and (*Z*)-**2** (d) at 80 K in 2-methylpentane glass and 273 K in 2-methylpentane solution. The closed and open circles represent absorbance changes at 80 and 273 K, respectively.



In conclusion, the results presented above demonstrate conclusively that photoisomerization in fluid solution involves only configurational changes, that is, by OBF. However, conformational as well as configurational changes, that is, by HT, occur in a solid solution.[1] These results reinforce the suggestion that all photoisomerizations of polyenes in rigid media (pre-vitamin D in organic glass,[5] 1,3-butadiene in argon matrix,[11] 1,3,5,7-octatetraene in an *n*-octane matrix,[12] and selected cases of diarylethylenes in organic glasses[13]) proceeded by way of HT.[1] However, at the same time, we recognize that the current results do not necessarily rule out the possibility that the isomerization at room temperature could also proceed by way of HT.[14] The fluid medium and the higher temperature would complicate detection of the unstable conformer. We consider this possibility unlikely; however, we intend to carry out similar irradiation experiments on samples in constrained and unconstrained media, but at an identical reaction temperature.

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[6] (*E*)-**2**: ^{1}H NMR (300 MHz, CDCl$_3$): $\delta=1.82$ (dd, 2H), 2.30 (s, 3H), 2.58 (t, 2H), 2.87 (t, 2H), 7.01 (brs, 1H), 7.1–7.3 (m, 7H), 7.73 ppm (m, 1H); UV/Vis (hexane): $\lambda_{\max}$ 273 nm, $\varepsilon=9500\ \text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$. (*Z*)-**2**: ^{1}H NMR (300 MHz, CDCl$_3$) : $\delta=2.02$ (q, 2H); 2.23 (s, 3H), 2.58 (q, 2H), 2.90 (dd, 2H), 6.43 (m, 1H), 6.76 (dd, 1H), 6.88 (d, 1H), 6.9–7.3 ppm (m, 6H); UV/Vis (hexane): $\lambda_{\max}$ 275 nm, $\varepsilon=10700\ \text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$. As expected, the *Z* isomer has a shorter retention time than the *E* isomer on silica gel.

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