Photochemistry and Photobiology, 2007, 83: 1436–1440

Mechanism of Photoisomerization of 1-Naphthyl-2-Phenylethylenes in Organic Glasses

Lan-Ying Yang and Robert S. H. Liu*

Department of Chemistry, University of Hawaii, Honolulu, HI

Received 24 February 2007; accepted 1 June 2007; DOI: 10.1111/j.1751-1097.2007.00183.x

ABSTRACT

Photoisomerization reactions of *cis* isomers of 1-β-naphthyl-2-phenylethylene, an *o*-methylated homolog and 1-α-naphthyl-2-phenylethylene in organic glasses at liquid nitrogen temperature were studied. Reactions were followed by changes in UV-absorption spectra of the irradiated samples. Formation of an unstable *trans*-photoproduct was detected only with the *o*-methylated homolog. The results are consistent with high regioselective Hula-twist photoisomerization at the benzylic sites of the three compounds examined. Calculated data on relative energies of the conformers of both the *cis* and the *trans* isomers are in agreement with the suspected conformational population of the starting materials and the photoproducts.

INTRODUCTION

Recently, there has been a renewed interest in search of the exact mechanism of photoisomerization in confined media (whether a chromophore embedded within a protein binding cavity or a simple organic molecule trapped within a rigid host, such as an organic glass or in a crystal). (See *e.g.*, 1,2) The question was first raised when the photoisomerization of rhodopsin chromophore was found to be an extremely fast process (subpico seconds) (3,4) seemingly incompatible with the volume demanding, albeit commonly accepted, torsional relaxation (also known as one-bond-flip [OBF]) process taking place within a rigid binding cavity. Two volume-conserving processes have since been introduced: the bicycle-pedal (BP) process in which the middle two CH fragments of a diene unit rotate simultaneously (5) and the Hula-twist (HT) process in which one CH unit transposes across the polyene skeleton (6) (Fig. 1). The stereochemical consequences for the two processes are different, BP leading to simultaneous isomerization of two adjacent double bonds (configurational changes only), while HT to simultaneous isomerization of a pair of adjacent double and single bonds (conformational as well as configurational changes).

Definitive examples of simultaneous isomerization of two double bonds are rare. The first example was reported by Matsumoto and coworkers on crystals of the muconate (*cis,cis*) salt (7). More recently there were similar reports on crystals of *cis,cis*-1,4-diphenyl-1,3-butadienes (2,8). All these examples showed direct formation of the more stable *trans,trans* isomer from the *cis,cis* isomer without detectable intermediacy of the *cis,trans* isomer. The first example of a pair of a double-bond and a single-bond isomerization was reported by Fuss and coworkers on pre-vitamin D (9). Since then many other examples of photochemical transformation involving such stereochemical consequences have appeared in the literature (10–13). At the same time there was a report questioning the need to invoke the two bond isomerization HT process in discussing results of the only example, 1-β-naphthyl-2-phenylethylene, **1**, used in that paper (14).

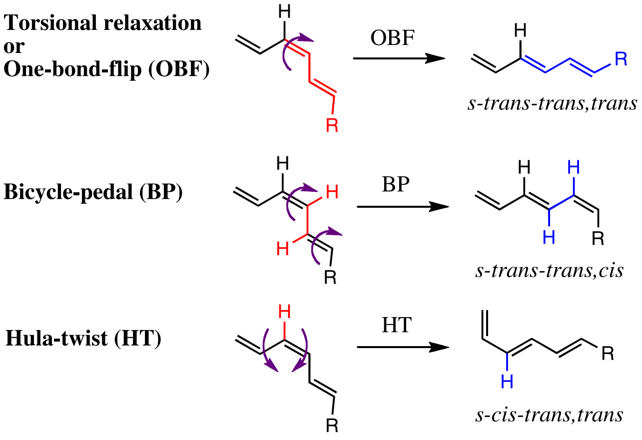

Figure 1. Mechanisms of photoisomerization of a model *cis*-triene fragment: upper, torsional relaxation or one-bond-flip (OBF); middle, bicycle-pedal (BP); lower, Hula-twist (HT). The characteristic stereochemical consequences for the three processes are the following: one double-bond isomerization for OBF, two double-bond isomerization for BP and adjacent single- and double-bond isomerization for HT. Changes of color red to blue indicates change of sidedness of that portion of the molecule as a result of the photochemical transformation.†

Recently, in a report on low temperature photoisomerization of stilbene derivatives (15), the need to choose and design systems carefully for such mechanistic studies was emphasized. It was pointed out that the only chosen system in the said report (14) is incapable of yielding information suitable for establishing or eliminating any of the above-mentioned reaction mechanisms. In this paper, we report results of our investigation on low temperature photochemical reactions of isomers of **1** and related systems (**2** and **3**).

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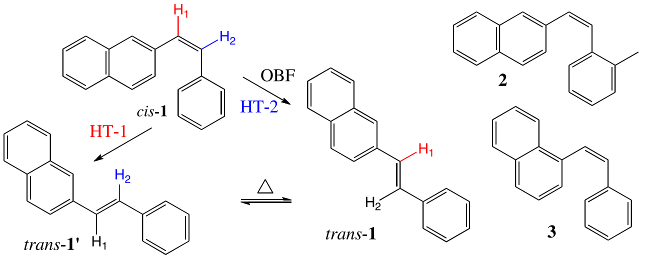
*Corresponding author email: rshl@hawaii.edu (Robert S. H. Liu)

†Figures and schemes are in color in the online version of the superscript manuscript, but appear in shaded gray in the printed version.



2

3

EXPERIMENTAL

Synthesis

Compounds **1**–**3** were prepared following standard Wittig coupling reactions (16) of the corresponding Wittig salt and arylaldehyde (obtained from Aldrich). In general, the *trans* isomer was obtained in slight excess. Conditions for chromatographic separation of the isomers were essentially those described (15). The H NMR spectra, obtained on a Nicolet 300 MHz spectrometer, were most indicative of the structure with expected larger vicinal coupling constants for the *trans* isomers (~16 Hz) and smaller coupling constants for the *cis* isomers (~12 Hz). UV spectra were recorded on a Varian 50 spectrometer.

Compound **1**. H NMR (acetone-d_6): *trans*, 7.28 (t, 1H), 7.40 (t, 2H), 7.40 (d, 1H), 7.43 (d, 1H) (J = 16.2 Hz from a sample in toluene-d_8), 7.48 (m, 2H), 7.65 (d, 2H), 7.86–7.91 (m, 4H), 7.99 ppm (s, 1H); UV (ether:isopentane:ethanol = 5:5:2 [EPA]) λ_{max} = 223.8, 272.3, 281.8 and 316.9 nm. *cis*, 6.73 (d, 1H, J = 12.2 Hz), 6.80 (d, 1H, J = 12.1 Hz), 7.20–7.26 (m, 3H), 7.27 (d, 1H), 7.46 (m, 2H), 7.66 (d, 1H), 7.70–7.79 (m, 3H), 7.77 (s, 1H), 7.81–7.86 ppm (m, 1H). UV (EPA) λ_{max} = 225.2, 268.9 and 301.0 nm.

Compound **2**. H NMR (acetone-d_6): *trans*, 2.47 (s, 3H), 7.21 (m, 4H), 7.30 (d, 1H, J = 16.4 Hz), 7.48 (m, 2H), 7.62 (d, 1H, J = 16.3 Hz), 7.25 (d, 1H), 7.90 (m, 3H), 8.01 ppm (s, 1H); UV (EPA) λ_{max} = 223.9, 274.9 and 316.0 nm. *cis*, 2.28 (s, 3H), 6.78 (d, 1H, J = 12.1 Hz), 6.85 (d, 1H, J = 12.2 Hz), 7.04 (t, 1H), 7.11 (d, 1H), 7.18 (d, 1H), 7.17 (d, 1H), 7.22 (d, 1H), 7.44 (m, 2H), 7.62 (d, 1H), 7.68 (s, 1H), 7.70 (m, 1H), 7.78 ppm (m, 1H); UV (EPA) λ_{max} = 226.3 and 301.0 nm.

Compound **3**. H NMR (acetone-d_6): *trans*, 7.28 (d, 1H, J = 16.2 Hz), 7.31 (t, 1H), 7.41 (t, 2H), 7.50–7.61 (m, 3H), 7.74 (d, 2H), 7.87 (d, 2H), 7.93 (d, 1H), 8.08 (d, 1H, J = 16.2 Hz), 8.39 ppm (d, 1H), UV (EPA) λ_{max} = 227.3 and 321.6 nm; *cis*, 6.90 (d, 1H, J = 12.0 Hz), 7.08 (s, 5H), 7.09 (d, 1H, J = 12.0 Hz), 7.33 (d, 1H), 7.38 (t, 1H), 7.47–7.56 (m, 2H), 7.85 (d, 1H), 7.91–7.97 (m, 1H), 8.06–8.09 ppm (m, 1H); UV (EPA) λ_{max} = 225.5, 267.9 and 310 (sh) nm.

Irradiation Procedure

The Oxford low temperature cell holder (Optistat DN), used in conjunction with a Varian 50 spectrometer, was the same as that described before (13,15). A 100 W Xenon Xe–Hg arc lamp was used as the irradiation light source. Corning O-54 filter was inserted for obtaining light of > 310 nm for the more red-shifted compound **3**. Samples were not deoxygenated because oxygen was found not to have a noticeable effect on reactions of these frozen samples. Sample cooling was slow (~30 min to reach equilibrium) by way of heat conduction through the metal framework of the sample holder.

RESULTS AND DISCUSSION

In addition to compound **1**, we have now prepared the *o*-methylated homolog **2** and the related α-naphthyl analog **3** and examined their photochemical reactions in EPA glass at liquid nitrogen temperature. The results are shown below.

Low temperature photochemical reactions of **1** were first reported some time ago (17,18). Photoisomerization in organic glasses was described. However, formation of the unstable product conformer(s) was interpreted in terms of the OBF concept, the only recognized photoisomerization process available at that time. We have now repeated the low temperature irradiation of **1** in an EPA glass with progress of reactions followed by changes of UV absorption spectra. The *trans* isomer of **1** (and that of the other two analogs) was found to be photostable in low temperature glasses. Figure 2 summarizes results obtained during irradiation of *cis*-**1** in EPA glass at 77 K. The immediate increase in absorption with a simultaneous red-shift and the appearance of fine structures (Fig. 2a) is characteristic of formation of the *trans* isomer. Upon warming of the product mixture followed by recooling to 77 K, the absorption spectrum remained virtually the same (Fig. 2b) (only minor changes of relative heights of some of the fine vibrational structures). The obvious conclusion of formation of stable conformer(s) of the *trans* isomer (based on UV absorption spectra) is similar to that reported earlier (based on fluorescence studies) (14). However, formation of such a stable product(s) is consistent with any one of the three reaction pathways: OBF around the double bond, HT of the benzylic C–H unit or HT of the C–H unit near the naphthyl group if a conformer mixture similar to that of the *trans* isomer is obtained.

The slight difference in the relative heights of the finer structures between 330 and 350 nm is likely due to perturbed population of the two conformers of the *trans* isomer from HT photoisomerization of the two conformers of the *cis* isomer.

To clarify the situation, we investigated the low temperature photochemical reaction of homolog **2**, in which the additional

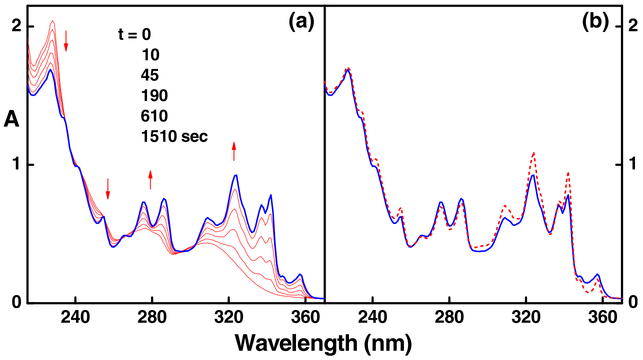


Figure 2. Low temperature photochemistry of **1**. (a) Irradiation (100 W Xe–Hg lamp, no filter) of *cis*-**1** in EPA glass (ether/isopentane/ethanol = 5:5:2) in a quartz cell at 77 K showing progressive changes of UV–Vis absorption spectra; the final spectrum being in blue. (b) The same final product absorption before (blue solid line) and after warming to 200 K and recooling to 77 K (red dashed line).

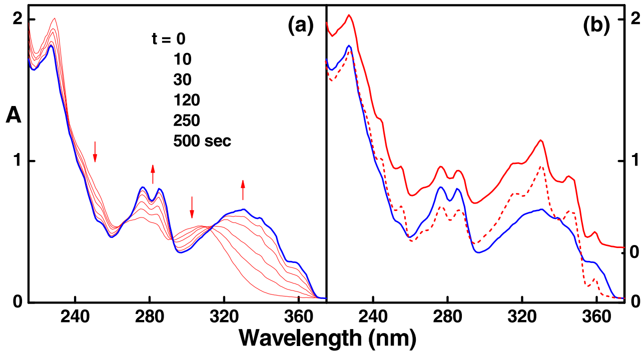
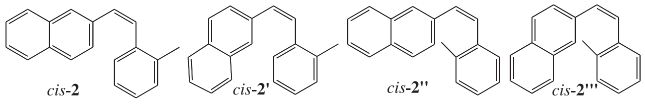


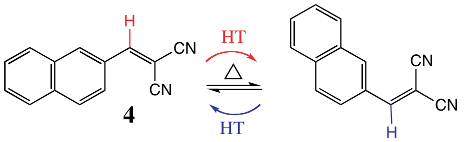
Figure 3. Low temperature photochemistry of **2**. (a) Irradiation (100 W Xe–Hg lamp, no filter) of *cis*-**2** in EPA glass at 77 K showing progressive changes of UV–Vis absorption spectra; the final spectrum being in blue. (b) Final product absorption before (blue solid line) and after warming to 200 K and recooling to 77 K (red dashed line). The absorption spectrum of *trans*-**2** (solid red line) is shown on top.

methyl group allows detection of conformational changes nearby the phenyl group, following the thought process outlined in earlier papers (13,15). Irradiation of *cis*-**2** in EPA glass also led to an immediate increase in intensity of the absorption spectrum, however, producing a new structureless broadband (Fig. 3a). Warming the product mixture followed by recooling to 77 K resulted in a further increase in absorption and the display of some vibrational structures (Fig. 3b). In fact, the final spectrum was the same as that of the authentic sample of *trans*-**2**. This sequence of spectral changes is reminiscent of octatetraene in *n*-octane crystal reported by Ackerman *et al.* (19), trienes in pre-vitamin D (9) and that of *o*,*o*′-dimethyl-*cis*,*trans*-1,4-diphenyl-1,3-butadiene (DPB) in EPA glass (13). Hence, similarly we interpret the result to mean photochemical formation of an unstable conformer of *trans*-**2** followed by thermal equilibration upon thawing of the glass to the stable conformer.

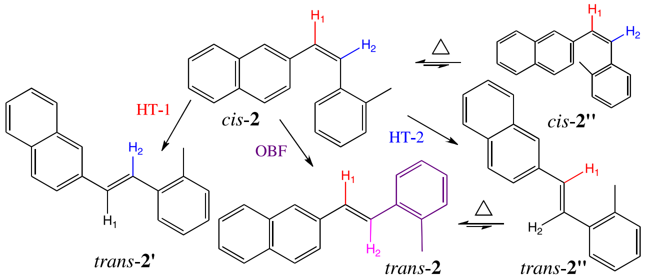
This result can be readily rationalized by consideration of conformational population controlled by relative stability of conformers. There are four possible conformers for *cis*-**2**.



Earlier we showed in a low temperature photochemical study of 1,1-dicyano-2-β-naphthylethylene (**4**) that two conformers close in energy are likely to be present (11).



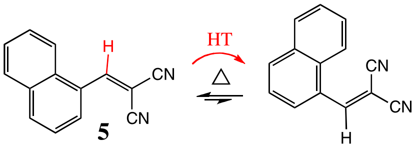
For *cis*-**2**, conformers around the naphthyl single bond (*e.g., cis*-**2** *vs cis*-**2**′) have identical steric environment as in **4**. Hence they should both be present as an equilibrated mixture, again making it difficult to detect (by the UV absorption method) an increase of the high energy conformer formed from HT photoisomerization. On the other hand, conformers around the tolyl single bond (*e.g. cis*-**2** *vs cis*-**2**″ or *cis*-**2**′ *vs cis*-**2**‴) differ in their steric environments, making *cis*-**2** (or *cis*-**2**′) more stable (hence dominant in an equilibrated mixture) than *cis*-**2**″ (by 1.13 kcal mol^{-1} as revealed from results from *ab initio* calculations)* (20). This unequal conformer population should lead to HT products enriched in the high energy conformer (more twisted, hence blue-shifted), which upon thawing of the organic glass, reverses to one enriched in the stable conformer (more planar, red-shifted). (Conformer *trans*-**2** was found to be more stable than *trans*-**2**″ by 1.69 kcal mol^{-1})* (20).



It should be equally clear that formation of the unstable photoproduct does not agree with OBF photoisomerization from the stable conformer of *cis*-**2**. Such a process can only lead to the stable conformer of *trans*-**2**.

The combined results of *cis*-**1** and *cis*-**2** revealed a high regioselectivity for HT photoisomerization favoring the benzylic site. Similar selectivity was, in fact, detected in low temperature photoisomerization of isomers of DPB (13) and a cinnamate ester (21).

We have also examined low temperature photochemistry of an α-substituted naphthalene analog. Earlier we showed that for 1,1-dicyano-2-α-naphthylethylene (**5**), because of the expected naphthyl-alkene conformational preference, photoirradiation readily led to enrichment of the unstable product conformer. It might be of interest to see whether such a conformational preference will be revealed in low temperature photochemical studies of an α-naphthylphenylethylene analog, such as **3**.



Result of such a study of *cis*-**3** is shown in Fig. 4. Low temperature irradiation led to an immediate increase in intensity and the red-shift of the UV absorption spectrum (Fig. 4a) reflecting formation of the *trans* isomer. However, the absorption spectrum of the product did not change upon warming and recooling, in fact, being identical to that of stable *trans*-**3** (Fig. 4b). In contrast to the same spectral changes in Fig. 2b, there were no discernible changes of relative heights of minor peaks. The apparent conversion to a simple product conformer is consistent with the above-noted conformational preference in such α-naphthyl analogs. These

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*We might mention that at ∼90 K, the approximate setting temperature of the EPA glass, an energy difference of 1.0 kcal mol^{-1} should result in less than 1% of the high energy conformer based on Boltzmann distribution.

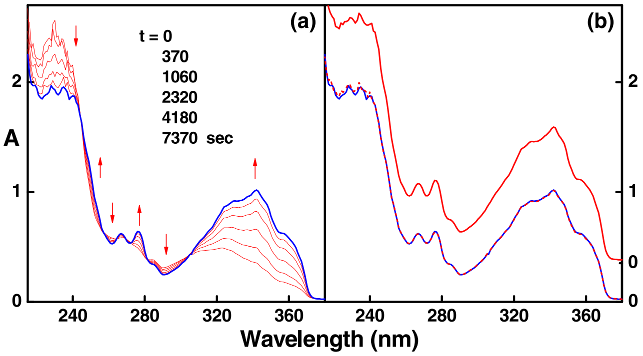
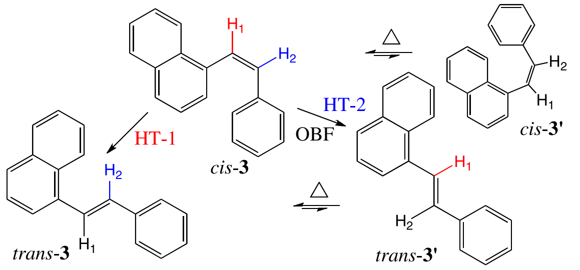


Figure 4. Low temperature photochemistry of **3**. (a) Irradiation (> 310 nm, Corning O-54 filter) of *cis*-**3** in EPA glass at 77 K showing progressive changes of UV–Vis absorption spectra; final spectrum being in blue. (b) Final product absorption (blue solid line) overlapping with that after warming to 200 K and recooling to 77 K (red dashed line). The absorption spectrum of *trans*-**3** (red solid line) is shown on top.

results also are not consistent with HT nearby the naphthyl site (HT-1), suggesting, same as the β-analogs (**1** and **2**), a highly regioselective HT isomerization at the benzylic site (HT-2).



In summary, based on the results reported above, we conclude that naphthylphenylethylenes undergo regioselective HT photoisomerization at the benzylic site when irradiated in low temperature glasses. This conclusion is in agreement with other reported examples of HT photoisomerization, in particular the regioselective HT isomerization of diphenylbutadienes (13) and cinnamates (21) and computational results (22,23). It questions the conclusion of "No HT" of *cis*-**1** (14) and whether it is appropriate to apply the Occam razor principle in determining reaction mechanisms of concern (8).

At the same time, we should point out that the current result does not address the suggestion (23) that HT photoisomerization might be taking place in all photoisomerization reactions including reactions at room temperature in fluid solutions.

We might also point out the following refined view concerning photochemical reactivity of confined chromophores (2,24). Examples of small molecules trapped in close-interacting rigid hosts, such as an organic glass, can be quite different from an anchored chromophore embedded within a protein binding cavity. Thus, in the case of rhodopsin, instead of close interaction of the surrounding protein host with the 11-*cis*-retinyl chromophore, there is, in fact, substantial empty space on one side of the polyene chain (25), that allows the chromophore to undergo OBF photoisomerization process as revealed in a recent crystal structure of bathorhodopsin, the primary photoproduct (26).

Acknowledgement—The work was supported by a grant from the National Science Foundation (CHE-0132250). We thank Professor J. Head for his assistance in obtaining the calculated values of energy differences between conformers.

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