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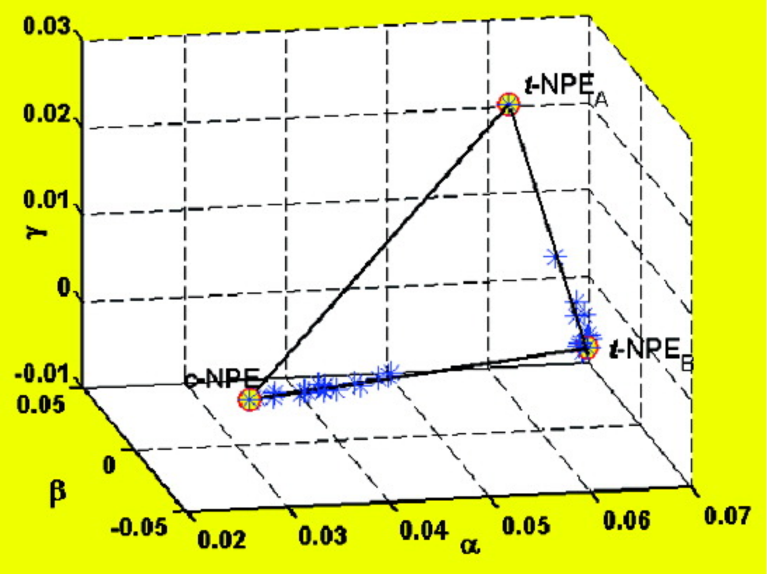

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Photoisomerization of *cis*-1-(2-Naphthyl)-2-phenylethene in Methylcyclohexane at 77 K: No Hula-Twist

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Cis−trans photoisomerization of olefins in solution is thought to occur in the singlet excited state via torsional relaxation about the pertinent bond. First proposed for stilbene photoisomerization,[1] such reactions may be subject to small energy barriers and are inhibited when the molecules are confined in rigid media. How volume restricted media, such as protein environments or amorphous glasses at low temperatures, exert control over cis−trans photoisomerization of diarylethenes and conjugated polyenes is a subject of intense current interest. Attention has been focused on the hula-twist mechanism (**HT**) advanced by Liu and co-workers to explain the high photoisomerization quantum yields of the retinyl moieties in rhodopsin and bacteriorhodopsin, within the space limitations of the surrounding opsin. The **HT** mechanism involves simultaneous rotation about a double bond and an adjacent essential single bond (equivalent to a 180° translocation of one CH unit)[2] and is postulated to reduce the volume requirements associated with 90° torsional relaxation (the one bond twist, **OBT**) by confining most of the motion to the vicinity of the isomerizing double bonds while delaying a sliding motion of bulky substituents attached to these bonds. Evidence supporting the **HT** mechanism, late in coming, appears to be growing at a rapid pace. A recent claim that the photoconversion of previtamin D to tachysterol at 92 K in a rigid glass (5/5/1 ether/isopentane/ethyl alcohol) is consistent with the **HT** mechanism may provide the first experimental demonstration of this process in an amorphous medium.[3] It breathed new life into this concept and has motivated its revival.[4] Experimental evidence appears to be strong for protein-bound chromophores, and the **HT** has captured the imagination of the photochemical community. Theoretical calculations favor 1,3-bond formation in the 2A$_g$ states of polyenes at the conical intersection (CI) geometry for ultrafast radiationless decay to the ground state,[5−7] and it has been argued, on both theoretical[5,7,8] and experimental grounds,[3] that such structures play a role in **HT** cis−trans photoisomerization.[2]

Formation of nonequilibrium distributions of trans conformers upon irradiation of *cis*-1,2-diarylethylenes in glassy solutions at 77 K[4b,f] was cited as evidence for the **HT** mechanism. Work by Alfimov[9] and Fischer[10] and their co-workers with *cis*-1,2-di-(1-naphthyl)ethene was singled out as particularly pertinent, and the **HT** process was recently extended to account for similar observations in 2,2′-dimethylstilbene.[11] These interpretations are not secure because they are based on assumed cis conformer distributions and on assumed propensities of these conformers to photoisomerize under the conditions of the experiment. They also require that initial photoproducts form in relaxed geometries such that spectral changes on warming can be assigned to conformer redistribution and not to conformer geometry optimization. We provide a more definitive test of the **HT** mechanism from a study of the cis−trans photoisomerization of *cis*-1-(2-naphthyl)-2-phenylethene (***c*-NPE$_\mathrm{A}$** and ***c*-NPE$_\mathrm{B}$**) for which structures have been assigned to the spectra of the trans conformers (***t*-NPE$_\mathrm{A}$** and ***t*-NPE$_\mathrm{B}$**) in solution[12] and in glassy media,[13] and cis−trans photoisomerization in solution occurs mainly in ***c*-NPE$_\mathrm{B}$** by a combination of adiabatic and diabatic **OBT** pathways.[14] The primary photoreaction of ***c*-NPE$_\mathrm{A}$** is photocyclization.[15]

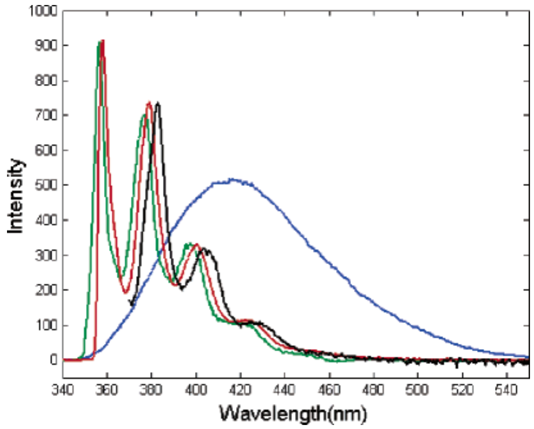
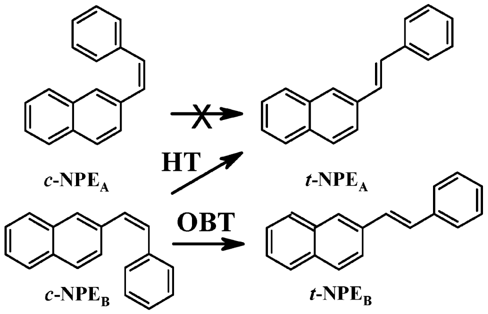


Figure 1. Normalized corrected fluorescence spectra of ***t*-NPE** excited at 285 (green, ***t*-NPE$_\mathrm{B}$**), 350 (red), and 360 nm (black, ***t*-NPE$_\mathrm{A}$**) and of ***c*-NPE** (blue) in **MCH** at 77 K.



Irradiations of dilute solutions of the **NPE** isomers in glassy methylcyclohexane (**MCH**) (1.2 × 10^{-4} and 3.6 × 10^{-4} M ***t*-NPE** and ***c*-NPE**, respectively) were carried out at 77 K in cylindrical sample tubes immersed in liquid nitrogen in the phosphorescence accessory of a Hitachi F-4500 emission spectrophotometer, and the progress of the reactions was followed by fluorescence spectroscopy. The fluorescence spectrum of ***t*-NPE** shifts subtly to the red on excitation with longer wavelengths, λ_{exc} (1 nm for 285−350 nm), and much more (7 nm) with λ_{exc} at the red edge of the absorption spectrum. No analogous shifts are observed in ***c*-NPE** fluorescence with changes in λ_{exc}. The low T eliminates the adiabatic channel for cis−trans photoisomerization.[14a] The ***c*-NPE** fluorescence spectrum and those of the two ***t*-NPE** conformers (Figure 1) are similar to those reported by Fischer in a glassy hydrocarbon

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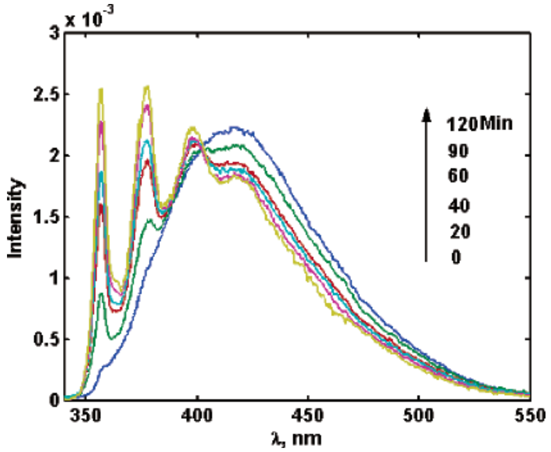

Figure 2. Fluorescence spectra of ***c*-NPE** in **MCH** recorded as a function of irradiation ($\lambda_{rad} = \lambda_{exc} = 300$ nm) time at 77 K.

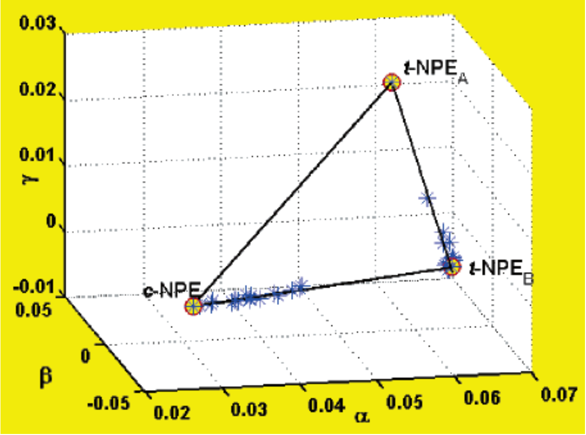

Figure 3. Combination coefficients of the partial spectral matrix (370−550 nm) of ***c*-NPE** spectra as a function of irradiation ($\lambda_{rad} = 300$, 320 nm; $\lambda_{exc} = 300$, 320, 335 nm) time and ***t*-NPE** spectra as a function of λ_{exc}.

mixture.[13] We tentatively assign the ***t*-NPE** spectrum for $\lambda_{exc} = 360$ nm to pure ***t*-NPE$_A$** fluorescence (its very weak intensity prevented correction for scattered light). Only the reliably known portion of the spectrum is shown in Figure 1. ***t*-NPE** fluorescence undergoes no change on continuous irradiation at $\lambda_{rad} = 320$ nm in the fluorimeter (150-W Xe lamp, 2.5 nm excitation slit), whereas irradiation of ***c*-NPE** under the same or similar conditions leads to development of the sharp ***t*-NPE** fluorescence features on the structureless ***c*-NPE** spectrum (Figure 2; $\lambda_{rad} = 300$ nm: analysis, $\lambda_{exc} = 300$, 320, or 335 nm).

Principal component analysis with self-modeling (PCA-SM) of the spectra in Figure 2 together with spectra for the reaction with $\lambda_{rad} = 320$ nm reveals a two-component system with a ***t*-NPE$_B$** product spectrum nearly identical to the spectrum obtained from ***t*-NPE** in **MCH** at 285 nm. That the ***c*-NPE** product is ***t*-NPE$_B$** is established by including, in PCA, ***t*-NPE** spectra for different λ_{exc} (all spectra confined to the 370−550 nm range). This analysis reveals that, on irradiation of ***c*-NPE**, points corresponding to the combination coefficients of mixture spectra move exclusively on the ***c*-NPE**−***t*-NPE$_B$** edge of the normalization triangle (Figure 3). The more stable extended B conformers of both isomers should be favored at low *T*. Also, ***c*-NPE$_A$** shows little, if any, tendency to undergo cis−trans photoisomerization even in solution.[14,15] Hence, in the rigid glass, as in solution, ***c*-NPE** photoisomerizes exclusively by conformer specific **OBT**: ***c*-NPE$_B$** → ***t*-NPE$_B$**.

Claims of **HT** cis−trans photoisomerization processes in low *T* amorphous glassy media should be viewed with caution. To occur at all at low *T*, they must be subject to very small intrinsic energy barriers. Even the simplest HOMO−LUMO considerations, whose spectacular success in predicting photoreactions of small conjugated molecules is undeniable,[18] predict single double bond reversal on excitation and favor **OBT** over **HT** on electronic grounds. It is contended that the **OBT** mechanism is volume demanding because it requires 90° rotation about one bond. However, for a barrierless process, such as the photoisomerization of *cis*-stilbene[1d] or ***c*-NPE**,[14] even a small twist along the central bond sets the excited molecule on a downhill energy trajectory.

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