Photoisomerization

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Photoisomerization of *cis*,*cis*- and *cis*,*trans*-1,4-Di-*o*-tolyl-1,3-butadiene in Glassy Media at 77 K: One-Bond-Twist and Bicycle-Pedal Mechanisms**

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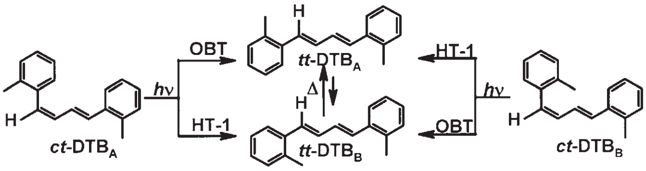
Viscous media enhance torsional barriers of olefins in the lowest excited singlet state[1] and inhibit one-bond-twist (OBT) *cis–trans* photoisomerization.[2] Two mechanisms involving concerted rotation about two bonds in S_1, initially postulated to explain retinyl photoisomerization within the protein environment in rhodopsin and bacteriorhodopsin, have been applied generally to account for photoisomerization in volume-confining media. The bicycle-pedal mechanism (BP) involves simultaneous rotation in S_1 about two polyene double bonds,[3] and the hula-twist mechanism (HT) involves simultaneous rotation about a double bond and an adjacent single bond (equivalent to a 180° translocation of one CH unit).[4] These mechanisms are assumed to reduce free-volume requirements by confining motion to the vicinity of the isomerizing double bonds while minimizing the motion of bulky substituents. The claim that the photoisomerization of previtamin D to tachysterol at 92 K in an EPA glass (ether/isopentane/ethylalcohol = 5:5:2) gives HT products[5] stimulated the revival of the HT mechanism.[6] Observations of *trans* photoproduct conformer mixtures that differ from their equilibrium compositions on irradiation of *cis* isomers in organic glasses at low tempertaure were assumed to support the formation of HT products.[6,7] The alternative interpretation, advanced earlier by the Alfimov[8] and Fischer[9] groups, that such results reflect different equilibrium conformer compositions for the two isomers, was ignored.

A case in point is the photoisomerization of 1,4-diphenyl-1,3-butadiene (DPB) in organic glasses at 77 K[7,10] and in the solid state.[11] Irradiation of the *cis*,*cis* isomer *cc*-DPB in glassy media of relatively high viscosity, EPA[7] or methylcyclohexane[10] at 77 K,[12] gives only the *cis*,*trans* isomer *ct*-DPB. Spectroscopic observations show that in the rigid glasses the *ct*-DPB product forms as the s-*trans* conformer, consistent with OBT in fluid solution.[13] Nevertheless, *ct*-DPB formation was attributed to the HT process (HT-1) about the benzylic CH group of the diene moiety, despite the fact that HT-1 and OBT products from the *cis* DPB isomers are indistinguishable.[7]

The photoisomerization of *cis*,*trans*-1,4-di-*o*-tolyl-1,3-butadiene (*ct*-DTB) in EPA at 77 K was studied in an attempt to avoid that ambiguity. It was reasoned that starting from the more stable conformer *ct*-DTB_A, HT-1 and OBT mechanisms would give unstable (*tt*-DTB_B) and stable (*tt*-DTB_A) conformers, respectively. Claims to the contrary notwithstanding,[7] that study also failed to distinguish between OBT and HT-1 mechanisms, because a mixture of *ct*-DTB_A and *ct*-DTB_B conformers was present at the outset. As shown in Scheme 1, both mechanisms account for the formation of a non-equilibrium mixture of *tt*-DTB_A and *tt*-DTB_B conformers.[10]



Scheme 1. Illustration of OBT and HT-1 mechanisms for *ct*-DTB.

Our observation of a major direct *cis*,*cis*- to *trans*,*trans*-1,4-diphenyl-1,3-butadiene (*cc*-DPB→*tt*-DPB) reaction channel on irradiation of *cc*-DPB in isopentane (IP) glass at 77 K provided the first experimental evidence for BP photoisomerization under such conditions.[10] The BP process also accounts for the two-bond photoisomerizations of *cc*-DPB,[11] muconate salts,[14a] and *cis*,*trans*,*cis*-1,6-diphenyl-1,3,5-hexatriene (*ctc*-DPH) derivatives in the solid state.[14b] The interconversion of *ctt*-DPH and *tct*-DPH isomers are examples of BP photoisomerization in solution.[15] We describe herein results that show unequivocally that *cc*-DTB→*tt*-DTB photoisomerization in IP glass at 77 K proceeds by sequential two-step OBT processes via the *ct*-DTB isomer in competition with the direct two-bond BP process.

The preparation of the DTB isomers has been described.[7,16] Irradiations of approximately 4 and 9×10^{-5} M *ct*- and *cc*-DTB solutions, respectively, in EPA and IP glasses at 77 K were carried out in the dewar flask of the phosphorescence accessory of a Hitachi F-4500 fluorimeter using a 450-W Hanovia Hg lamp (Pyrex filter).[7,17] Reaction progress was monitored in situ by fluorescence spectroscopy. Results in EPA confirm the report on *ct*-DTB[7] and extend it to *cc*-DTB. Starting from either *ct*- or *cc*-DTB, similar mixtures of *tt*-DTB_A and *tt*-DTB_B conformers form. Principal component

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analysis (PCA) treatment[10,18] of a matrix of spectra obtained on irradiation of both *cis* DTB isomers reveals a four-component system, which consists of the three pure isomer spectra (insensitivity to changes in the excitation wavelength λ_{exc} shows that *tt*-DTB exists as the *tt*-DTB$_A$ conformer and that the A and B conformers of *ct*-DTB and *cc*-DTB have very similar spectra) and a fourth spectrum, obtained by self-modeling,[18] corresponding to the higher-energy *tt*-DTB$_B$ conformer (Figure 1). The pure spectra define a tetrahedron in eigenvector combination coefficient space. The *cc*-DTB→*ct*-DTB→*tt*-DTB sequence is revealed by the time evolution of the combination coefficient points of the spectra starting from *cc*-DTB (Figure 2). Beginning at the *cc*-DTB corner of the tetrahedron, the spectra move on the *cc*-DTB/*ct*-DTB edge and eventually proceed to a mixture containing the two conformers, *tt*-DTB$_A$ and *tt*-DTB$_B$. The broad features of the final fluorescence spectra narrow significantly on warming and recooling. Points for spectra obtained after thermal equilibration using a range of λ_{exc} (◇ in Figure 2) move to the *ct*-DTB/*tt*-DTB$_A$ edge of the tetrahedron, consistent with *tt*-DTB$_B$→*tt*-DTB$_A$ relaxation and the presence of residual *ct*-DTB. Points for spectra starting from *ct*-DTB, omitted for the sake of clarity, lie on the *ct*-DTB/*tt*-DTB$_A$/*tt*-DTB$_B$ plane of the same tetrahedron.

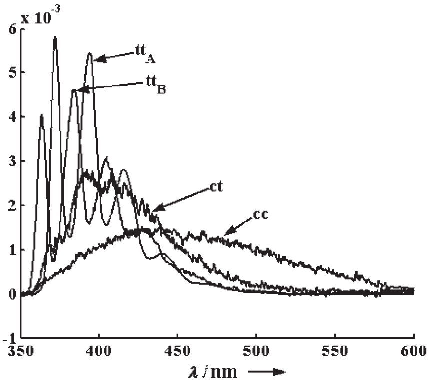


Figure 1. Normalized fluorescence spectra of *tt*-DTB$_B$ (tt$_B$), *tt*-DTB$_A$ (tt$_A$), *ct*-DTB (ct), and *cc*-DTB (cc) in EPA at 77 K.

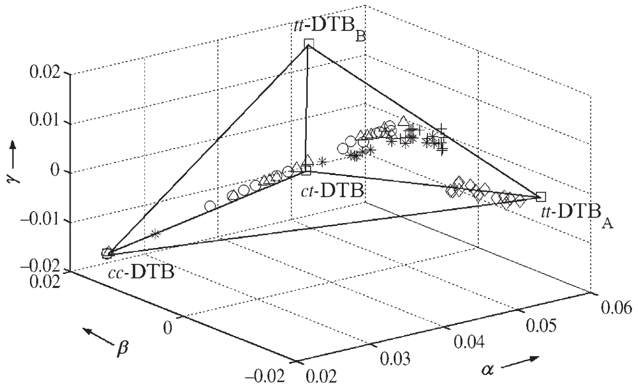


Figure 2. Combination coefficients (α, β, γ) for the spectral matrix (λ_{exc} = 300 ○, 315 △, 345 ⋆, before +, and after thawing ◇, 330–350 nm, pure components □) obtained on irradiation of *cc*-DTB in EPA at 77 K. (λ_{rad} > 300 nm).

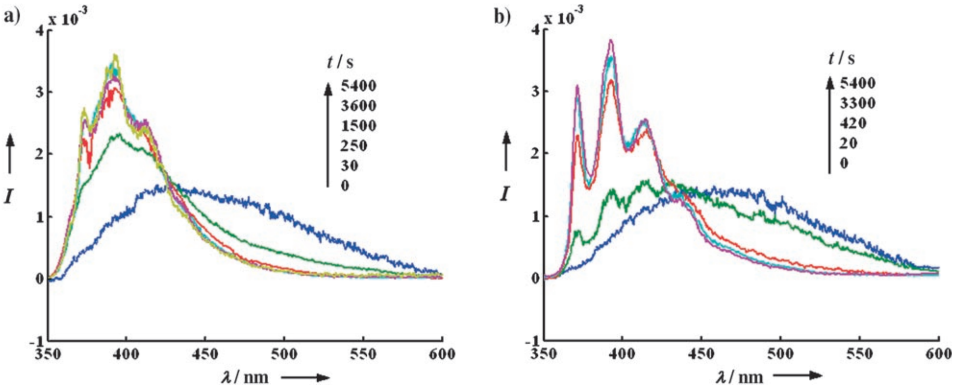


Figure 3. Evolution of fluorescence spectra (normalized) during the first 90 min of irradiation under similar conditions (300 nm, 77 K in the fluorimeter) in EPA (a) and in IP (b).

Results in IP are strikingly different. Comparison of the initial spectral evolution of *cc*-DTB photoisomerization in the two media allows visual confirmation of *tt*-DTB formation by a sequential two-step pathway in EPA and by a direct pathway in IP (Figure 3). The structured *tt*-DTB fluorescence is clearly evident after 20 s of 300-nm irradiation in IP whereas the early spectra in EPA resemble the fluorescence spectrum of *ct*-DTB (see also Figures 1 and 4). These results mirror the behavior of *cc*-DPB in the two media.[7,10]

Analogous PCA treatment of the combined matrix of spectra starting from both *cc*- and *ct*-DTB in IP reveals a three-component system that is accounted for exactly by the three pure isomer spectra (Figure 4). Beginning from *cc*-DTB, spectral points in the combination coefficient plot (Figure 5) deviate from the *cc*-DTB/*ct*-DTB edge of the triangle from

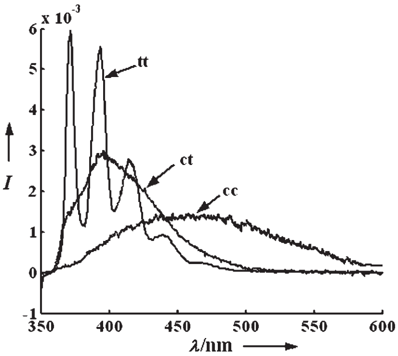


Figure 4. Fluorescence spectra of pure *tt*-, *ct*-, and *cc*-DTB isomers in IP at 77 K.

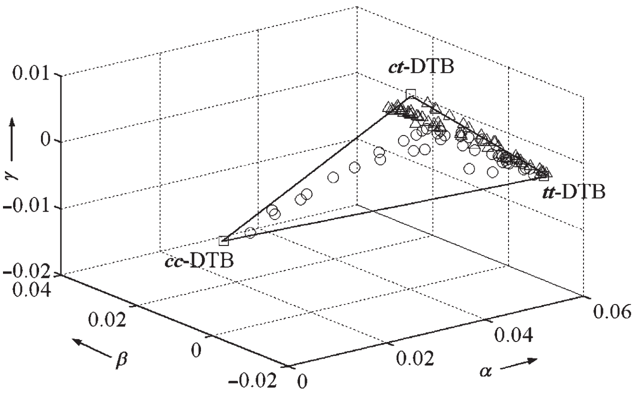
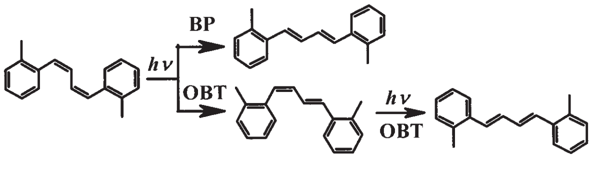


Figure 5. Combination coefficients for the spectral matrix obtained on irradiation of *cc*-DTB (○) and *ct*-DTB (△) in IP at 77 K ($\lambda_{\mathrm{rad}} > 300$ nm). Points on the *ct*-DTB/*tt*-DTB side are for $\lambda_{\mathrm{exc}} = 345$ nm. Spectra for $\lambda_{\mathrm{exc}} = 300$ and 315 nm define the lower line, revealing some *cc*-DTB contaminations in *ct*-DTB.

the start, consistent with direct *cc*-DTB$_A$→*tt*-DTB$_A$ two-bond isomerization in competition with the one-bond *cc*-DTB$_A$→*ct*-DTB$_A$ process.

In contrast to the situation in EPA, there is no significant spectral change on thawing and recooling the solution after irradiation of either *cc*- or *ct*-DTB. Starting from either *cis* isomer, final photoproduct spectra coincide with the highly structured *tt*-DTB$_A$ spectrum. The medium change from EPA to IP has a dramatic effect on the equilibrium conformer distributions of *cc*- and *ct*-DTB, shifting each to a single dominant conformer. This serendipitous medium effect allows us to establish that in IP the photoisomerizations of *cc*- and *ct*-DTB involve no unstable conformer products. *Cis–trans* photoisomerizations that convert stable reactant conformers to stable product conformers are accounted for by BP and OBT pathways (Scheme 2). HT pathways are eliminated in IP, because they require formation of unstable conformers. The inhibition of the BP process aside, we see no reason to expect a mechanism change in EPA.[10]



Scheme 2. The competing photoisomerization pathways of *cc*-DTB in IP at 77 K.

The X-ray crystal structure of *cc*-DTB reveals a single conformer, *cc*-DTB$_A$, with the *o*-tolyl groups in parallel planes oriented at 56° to the plane of the diene moiety.[16] Calculated conformer structures (B3LYP with the 6-31G(d,p) basis set) for *ct*-DTB similarly show large *o*-tolyl–diene dihedral angles (42.1 and 19.7° for *ct*-DTB$_A$ and 62.0 and 20.8° for *ct*-DTB$_B$ on the *cis* and *trans* sides of the molecule, respectively, Figure 6).[16] *ct*-DTB$_B$ is predicted to be 1.95 kcal mol^{-1} higher in energy in the gas phase.[16]

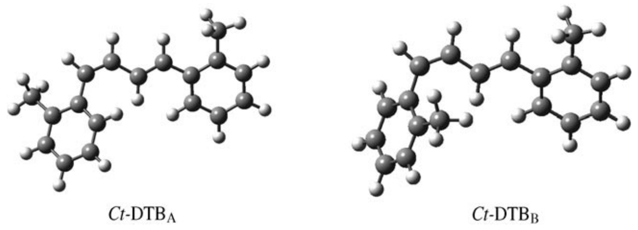


Figure 6. Stationary-point geometries on the *ct*-DTB S° surface; *ct*-DTB$_A$ on the left corresponds to the global energy minimum.[16]

To the extent that this energy difference is maintained in IP, the predominance of the *ct*-DTB$_A$ conformer at 77 K in that medium is not surprising. The presence of both conformers in EPA might appear remarkable if it were not for a highly significant precedent. Strong CD spectral evidence shows that the previtamin D and tachysterol conformer distributions change significantly on changing the medium from a hydrocarbon glass to EPA at 92 K.[19] The claim of HT products from previtamin D in EPA[5] is questionable, because it did not consider that medium effect.

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