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Photoisomerization of *cis,cis*-1,4-Diphenyl-1,3-butadiene in the Solid State: The Bicycle-Pedal Mechanism

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The cis−trans photoisomerization of crystalline or powdered *cis,cis*-1,4-diphenyl-1,3-butadiene (***cc***-DPB) was studied at room temperature. The progress of the reaction was monitored by fluorescence spectroscopy, powder X-ray diffraction, ^{1}H NMR and HPLC. High conversions (up to 90%) to the trans,trans isomer were observed in a crystal to crystal reaction. Formation of the cis,trans isomer, the sole product obtained in solution and in very viscous glassy media at 77 K is entirely suppressed in the solid state. The observed two-bond photoisomerization is explained by Warshel's bicycle-pedal photoisomerization mechanism (**BP**). The results are consistent with X-ray diffraction measurements, which have revealed that ***cc***-DPB molecules exist in crystals in edge to face alternating arrays of two conformer structures whose phenyl rings deviate significantly from the plane of the central diene moiety (∼40°).[1] One of the conformers has the two phenyls in parallel planes and the other in roughly perpendicular planes. Least motion considerations suggest that the former should undergo the two-bond photoisomerization more easily, in agreement with observations that indicate that the reaction proceeds in discrete stages. Recently reported *cis,cis*- to *trans,trans*-muconate photoisomerizations in the solid state are proposed to also proceed via the **BP** mechanism. The reactions are consistent with the X-ray crystal structures of the *cis,cis*-muconate isomers.

Introduction

Irradiation of *cis,cis*-1,4-diphenyl-1,3-butadienes (***cc*-DPB**) in the soft isopentane glass at 77 K gives the trans,trans isomer (***tt*-DPB**) as a primary photoproduct in addition to the cis,trans isomer (***ct*-DPB**),[1] the one bond isomerization product that forms exclusively in solution[1−4] and in glassy media of relatively high viscosity at 77 K.[1,5] Significant two bond photoisomerization in ***cc***-DPB is consistent with Warshel's bicycle pedal photoisomerization mechanism (**BP**), which involves simultaneous rotation about two S_0 double bonds in a 1,3-diene moiety in S_1.[6] The **BP** mechanism had been proposed to explain the specificity and high photoisomerization quantum yields of the retinyl moieties of rhodopsin and bacteriorhodopsin despite volume restrictions imposed by the protein environments.[6] Liu's Hula-twist mechanism (**HT**), which involves simultaneous rotation about a double bond and an adjacent essential single bond (equivalent to a 180° translocation of one CH unit) was similarly motivated.[7] **BP** and **HT** mechanisms are expected to reduce volume requirements associated with torsional relaxation by confining most of the motion to the vicinity of the isomerizing double bonds while minimizing the motion of bulky substituents. The **HT** mechanism has been claimed to account for photoisomerization of several olefins in amorphous glassy media at low temperatures.[8,9] Theoretical calculations suggest that 1,3-bond formation in the 2 ^1A_g states of polyenes at a conical intersection for ultrafast radiationless decay to the ground state[10−12] may open a pathway to **HT** products.[10−13] We reported recently that the photoisomerization of *cis*-1-(2-naphthyl)-2-phenylethene in methylcyclohexane glass at 77 K is conformer specific,[14] giving the one bond twist (**OBT**) product as in solution.[15] Direct ***cc*-DPB** to ***tt*-DPB** conversion is the only example, thus far, of the **BP** mechanism under similar conditions.[1]

X-ray crystal diffraction measurements reveal arrays of two ***cc*-DPB** conformer structures whose phenyl rings deviate significantly from the plane of the central diene moiety.[1] The average phenyl/diene dihedral angle is 40° in alternating layers of molecules with the two phenyls in parallel planes and molecules with the two phenyls in roughly perpendicular planes. Neighboring molecules are arranged edge to face.[1] The X-ray structures are in reasonable agreement with Gaussian 98[16] calculations utilizing gradient geometry optimization[17] with the B3LYP exchange-correlation functional[18] and the 6-31G(d,p) basis set that predict that the structure with the two phenyls rotated in opposite directions (31.5°) to the diene plane corresponds to the global energy minimum and the structure with the phenyls in parallel planes (rotated 39.6° with respect to the diene plane) lies 1.5 kcal/mol above it.[1] Relying on least motion considerations, we suggested that the ***cc*-DPB** conformation with phenyls in parallel planes should easily form ***tt*-DPB** via the **BP** mechanism, whereas the structure with the phenyls in perpendicular planes might more readily form a *trans*-phenallylbenzyl intermediate on the way to ***ct*-DPB**.[1] The latter, lower energy, structure may account for one bond isomerization in solution. Because edge to face phenyl/phenyl interactions in the crystal tend to anchor the phenyl rings in place, excitation of at least the conformer with phenyls in parallel planes in ***cc*-DPB** crystals could lead to two-bond isomerization by the **BP** mechanism. The experiments in this paper substantiate this expectation.

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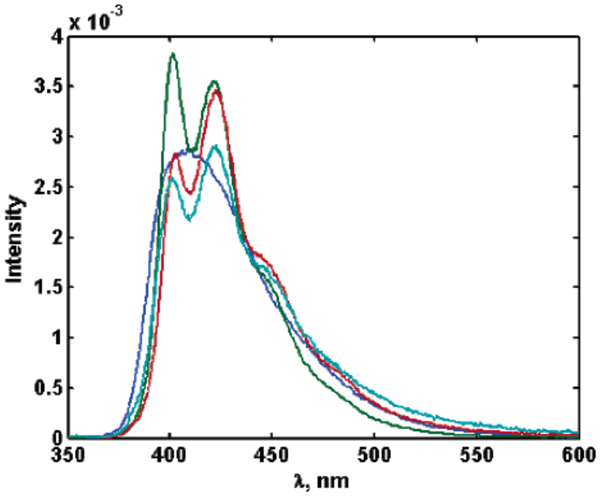

Figure 1. Normalized fluorescence spectra ($\lambda_{exc} = 370$ nm) of solid *cc*-DPB (blue) and spectra obtained after 2 h (green), 10 h (red) and 20 h (cyan) 366 nm irradiation intervals.

Experimental Section

_cc_-DPB crystals were obtained from methanol as previously described.[3] Solid samples, ~20 mg, placed between 2 glass slides (Fischer brand microscope glass plates) and secured with rubber bands were irradiated at ambient temperature at 366 nm (200 or 450 W Hanovia Hg medium-pressure lamps equipped with Corning glass filters 0-52 and 7-54). The progress of the reaction was monitored by fluorescence spectroscopy (Hitachi F-4500 fluorometer: 2400 nm/min, excitation and emission slits 1.0/2.5 nm, and PMT 700 V), by ^{1}H NMR (300 MHz Varian model Gemini 2000 or 270 MHz IBM/Bruker spectrometers; $CDCl_3$) and by HPLC (Beckman Coulter gold system with 125 and 166 solvent and detector modules, respectively; a Beckman Ultra sphere 0.5 μ silica 4.6 × 250 mm column was employed with *n*-hexane mobile phase, 0.5 mL/min flow rate and detector λ set at 315 nm; correction factors were based on the DPB isomer spectra in *n*-hexane given in ref 2). A smaller sample of *cc*-DPB (~4 mg) sandwiched between slides as above, was placed in the solid sample holder and irradiated directly in the fluorometer (150 W Xe lamp, $\lambda_{exc} = 370$ nm, 2.5 nm slits). Care was taken not to change the position of the glass slides. Fluorescence spectra ($\lambda_{exc} = 350$ and 370 nm) were recorded periodically at 15 and later 30 min irradiation intervals. Powder X-ray diffraction patterns were measured before and after 366 nm irradiation of mortar and pestle powdered **_cc_-DPB** samples (~5 mg). The X-ray diffraction data were collected with the use of a Rigaku X-ray diffractometer Ultima III (scan angle 7−31°, 176 KW, 0.01° resolution, 1.5418 Å, slits 0.5 nm, 600 s for data collection and calibrated to silicon). Fluorescence spectra and ^{1}H NMR spectra of the powdered samples were recorded following the powder X-ray diffraction measurements for different irradiation intervals.

Results and Discussion

Fluorescence spectra measured in the course of a 366 nm irradiation with 200 W Hanovia lamp are shown in Figure 1. The structureless spectrum of **_cc_-DPB** ($\lambda_{max} = 408$ nm, 360−600 nm range) is independent of excitation wavelength (300−370 nm) and is remarkably similar to the spectrum obtained at 77 K in isopentane glass.[1] On irradiation the spectrum gains in intensity as it develops into a structured emission with λ_{max} at 402 nm and vibronic bands at 422 and 450 (shoulder) nm. Prolonged irradiation leads to attenuation in overall intensity, broadening at long λ and a shift of the λ_{max} from 402 to 422 nm. The structured fluorescence is consistent with **_tt_-DPB** formation.[19] The near identity of the starting emission spectrum to that of pure **_cc_-DPB** shows that, at least initially, the photoisomerization is not adiabatic. The time evolution of the spectral changes was determined more quantitatively for a crystalline sample irradiated at 370 nm directly in the fluorometer. Under those conditions the reaction is confined by the excitation slit of the fluorometer to a small horizontal reaction zone. Spectra were measured every 15 min for the first 90 min, because the changes are more rapid initially, and then every 30 min for the 90−480 min irradiation period. The full set of spectra is given as Supporting Information (SI). Principal component analysis[20] of the partial spectral matrix consisting of the first four spectra (0−45 min irradiation) reveals a two-component system that evolves into a three-component system if the first seven spectra (0−2 h irradiation) are included in the partial matrix. Treatment of the entire spectral matrix (0−4 h irradiation) reveals a robust four-component system. The experimental spectra are faithfully reproduced as linear combinations of the four principal eigenvectors ($\mathbf{V}_\alpha$, $\mathbf{V}_\beta$, $\mathbf{V}_\gamma$ and $\mathbf{V}_\delta$)

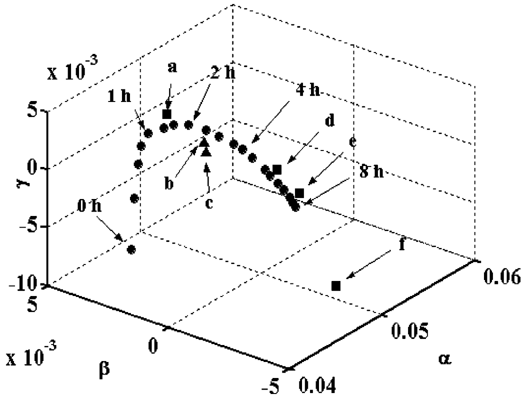

Figure 2. 3-D (α, β, γ) combination coefficient plot for the four-component matrix consisting of the spectral set obtained by irradiation of the crystal in the fluorometer (150 W Xe lamp; circles, points corresponding to 0, 1, 2, 4 and 8 h irradiation times are indicated) and typical spectra of crystalline (triangles) and powdered (squares) samples irradiated with Hanovia Hg lamps. Conversions to **_tt_**-DPB determined by ^{1}H NMR spectroscopy are: **a** 15%, **b** 13%, **c** 27%, **d** 20%, **e**: 18% and **f**: 64%.

$$\mathbf{S}_i = \alpha_i \mathbf{V}_\alpha + \beta_i \mathbf{V}_\beta + \gamma_i \mathbf{V}_\gamma + \delta_i \mathbf{V}_\delta \qquad (1)$$

A plot of the combination coefficients (α_i, β_i, γ_i) of the three major eigenvectors is shown in Figure 2. The (α_i, β_i, δ_i) plot is similar (SI). Irradiation of powdered samples leads to similar changes in the fluorescence spectra. Inclusion of typical fluorescence spectra from samples for which ^{1}H NMR conversions are available, as in Figure 1, in the spectral matrix corresponding to Figure 2 revealed a reasonable, albeit not quantitative, correlation between the shape of the fluorescence spectrum and the % conversion to **_tt_-DPB**. It appears that a fast reaction phase involving photoisomerization of ~15% of the molecules in the crystal (close to the 1 h point in Figure 2) is followed by much slower conversion of the rest of the material.

Formation of **_tt_-DPB** as the sole isomerization product was established by ^{1}H NMR, HPLC and X-ray powder diffraction analyses of irradiated samples. The ^{1}H NMR spectrum of a solid *cc*-DPB sample irradiated at 366 nm for 20 h and then dissolved in $CDCl_3$ is shown in Figure 3. The combination coefficients of the fluorescence spectrum of this sample, immediately

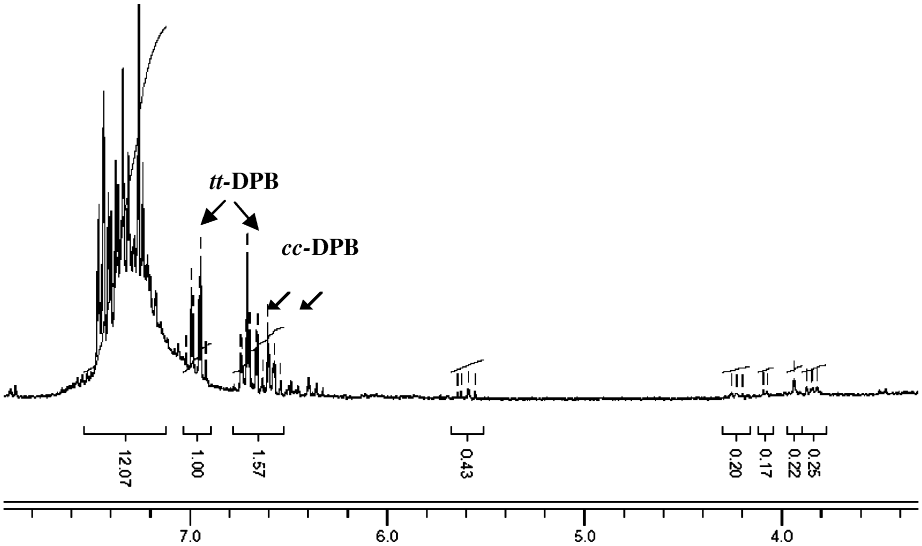

Figure 3. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) following 20 h irradiation of solid ***cc*-DPB**; signals of three of the vinyl Hs of ***ct*-DPB** in the δ 6.32−6.72 region, if present, are too small to quantify.

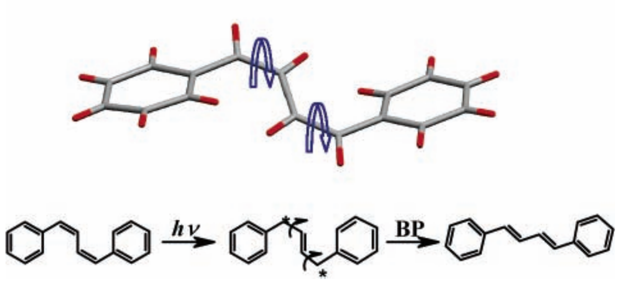

Figure 4. The **BP** mechanism shown for the ***cc*-DPB** X-ray structure[1] with phenyls in parallel planes.

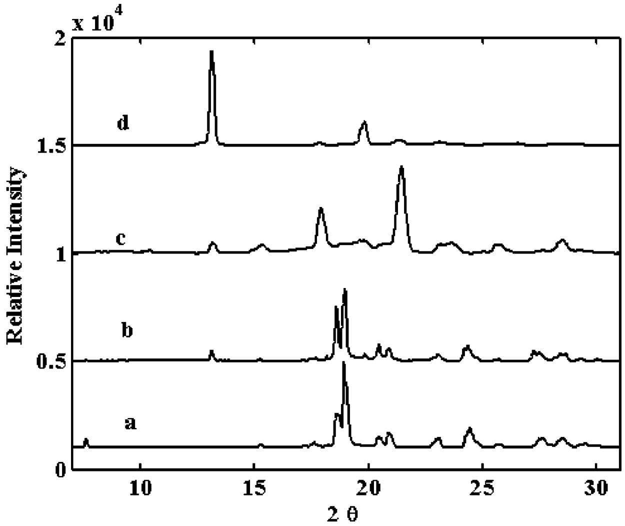

Figure 5. Powder X-ray diffraction profiles of ***cc*-DPB** (a), ***tt*-DPB** (d) and two irradiated ***cc*-DPB** samples; conversions to ***tt*-DPB** by ^{1}H NMR: (b) 16% and (c) 90%.

following irradiation (Figure 1, cyan curve), corresponds to point **f** in Figure 2 (see also Figure 2S in SI). Comparison with NMR spectra of the pure isomers shows that the multiplet centered at δ 6.97 corresponds to the two benzylic vinyl Hs of ***tt*-DPB**, the signals of the other two vinyl Hs overlap those of ***cc*-DPB**, as labeled in Figure 3. Signals in the δ 6.32−6.72 region corresponding to three of the four vinyl Hs of ***ct*-DPB** are too small to quantify. HPLC analysis of an irradiated solid sample of ***cc*-DPB** that showed 49% conversion to ***tt*-DPB** indicated 0.5% conversion to ***ct*-DPB**, but ***ct*-DPB** was not detected by HPLC at lower ***tt*-DPB** conversions (e.g., 29%).

Small signals at lower δ values correspond to vinyl hydrogens of minor photodimer products whose structures are under investigation. The spectrum in Figure 3 shows 64% conversion to ***tt*-DPB**. Initially, ***cc*-DPB** to ***tt*-DPB** conversions are very rapid (15% ***tt*-DPB** and 3% photodimer after 2 h of irradiation) and then appear to reach a plateau for 4−10 h irradiation intervals (18% ***tt*-DPB** and 4.5% photodimer after 10 h), and product formation resumes at a lower rate at longer irradiation times (64% ***tt*-DPB** and 14% dimer for 20 h irradiation). The reaction appears to proceed in stages that could be due to the difference in reactivity of the two conformers and could be further controlled by changes in crystal microenvironment.[21] A highly conformer-specific crystal to crystal photoreaction in a two-layer crystal was reported recently.[22] The attenuation of the reaction rate may also be due to quenching by the ***tt*-DPB** product.

Powder X-ray diffraction measurements establishing that the reaction is a crystal to crystal reaction are shown in Figure 5. The powder X-ray diffraction profile of ***cc*-DPB** (curve a) is very close to that calculated from the X-ray crystallographic diffraction data.[1] Most of the new peaks that emerge on irradiation are present in the diffraction pattern of ***tt*-DPB** crystals, but their relative intensities differ markedly, indicating that the photoproduct forms in a different crystalline modification controlled by the arrangement of ***cc*-DPB** molecules in the crystal lattice.

Substituted derivatives of ***tt*-DPB** photodimerize in the solid state. No photoisomerization has been observed, but high conversions to specific [2 + 2] photodimers have been obtained.[19,23−25] In every case the substituent accounts for product specificity by controlling the relative orientation of ***tt*-DPB** pairs. Cis−trans photoisomerization is a rare event in the solid state.[26] The conversion of bis(*n*-butylammonium) (*Z*,*Z*)-muconate directly to the (*E*,*E*)-muconate isomer in a crystal to crystal reaction[27] is a precedent for two bond photoisomerization in the solid state. However, the reaction has been claimed to proceed with simultaneous rotation of the carbonyl group in supposed double **HT** fashion[28] and it has been cited as an example of photoisomerization under constrained conditions that can be explained by the **HT** mechanism.[29] Our own examination of the crystallographic files, provided in .cif format with ref 27, shows each of the oxygen atoms in the carboxylate groups of (*Z*,*Z*)-muconate hydrogen bonded to two ammonium ions. Thus anchored by eight strong hydrogen bonds, rotation of the carboxylate moieties is not likely. It is more reasonable to conclude that the two-bond photoisomerizations observed in muconate systems are also examples of the **BP** mechanism.

Solid state two-bond photoisomerization reactions were recently reported for a series of dialkyl (*Z*,*E*,*Z*)-1,6-bis(4-carboxylatephenyl)-1,3,5-hexatrienes (alkyl: methyl, ethyl, propyl, butyl).[30] X-ray powder diffraction measurements showed that here also direct formation of the corresponding *E*,*E*,*E* isomers are photochemical crystal to crystal reactions.[30] This opens the interesting possibility that the **BP** mechanism is not limited to adjacent double bonds but can involve simultaneous rotation of the terminal double bonds of the triene unit.

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Supporting Information Available: Complete ref 16, Figures of the complete spectral set of fluorescence spectra corresponding to the circles in Figure 2, and a Figure showing the 3-D (α, β, δ) combination coefficient plot corresponding to Figure 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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