Trienes

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Photoisomerization of All-*cis*-1,6-diphenyl-1,3,5-hexatriene in the Solid State and in Solution: A Simultaneous Three-Bond Twist Process[**]

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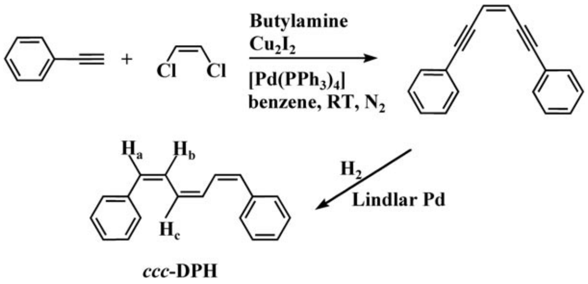
The photophysical[1] and photochemical[2] behaviors of all-*trans*-1,6-diphenyl-1,3,5-hexatriene (*ttt*-DPH) have attracted a great deal of attention because, as the first member of the family of vinylogous α,ω-diphenylpolyenes with a $2A_g$ lowest excited state, *ttt*-DPH serves as a polyene model. Medium-imposed constraints enhance the torsional barriers of olefins in the lowest excited singlet state[3] and inhibit *cis–trans* photoisomerization.[4] Two mechanisms involving concerted rotation about two bonds in the S_1 state, which were initially postulated to explain retinyl photoisomerization within the protein environments 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 the S_1 state about two polyene double bonds,[5] and the hula–twist mechanism (HT) involves simultaneous rotation about a double bond and an adjacent essential single bond (equivalent to a 180° translocation of one CH unit).[6] Our recent work on the *cis*,*cis*-1,4-diphenyl- and *cis*,*cis*-1,4-di(*o*-tolyl)-1,3-butadienes (*cc*-DPB and *cc*-DTB) revealed the BP process as the only photoisomerization pathway in the solid state at room temperature[7] and as a significant pathway competing with the usual one-bond-twist pathway in the soft isopentane glass at 77 K.[8] Recognizing that the BP process accounts for the interconversion of *ctt*-DPH and *tct*-DPH isomers in solution[2] and for the one-way *ctc*-DPH→*ttt*-DPH photoisomerization of symmetrical *p*,*p*′-disubstituted *cis*,*trans*,*cis*-1,6-diphenyl-1,3,5-hexatriene derivatives in the solid state,[9] we reasoned that the analogous extended BP process in the hitherto unknown all-*cis* DPH might give *tct*-DPH in the solid state. Observations reported herein show that instead, irradiation of *ccc*-DPH in the solid state gives *ttt*-DPH directly in a crystal-to-crystal reaction. To our knowledge this is the first observation of simultaneous three-bond *cis–trans* photoisomerization.

cis-1,6-Diphenylhex-3-en-1,5-diyne was prepared from phenylethyne and *cis*-1,2-dichloroethene as previously described[10] and hydrogenated over the Lindlar palladium catalyst to afford *ccc*-DPH as an oil (Scheme 1). Purification by chromatography on alumina, followed by crystallization from hexane yielded white crystals of *ccc*-DPH (m.p. 71 °C). The compound was characterized mainly by ^{1}H NMR spectroscopy[11] and X-ray crystallography.[12] The synthesis, purification, and handling of *ccc*-DPH were carried out under red light to avoid photoisomerization. The other DPH isomers are present in the photostationary state and were previously described.[13]



Scheme 1. Synthesis of *ccc*-DPH.

Powder X-ray diffraction patterns were measured before and after irradiation (λ = 400 nm) of samples of *ccc*-DPH (≈5 mg) that had been ground to a powder with a mortar and pestle. The X-ray diffraction data were collected with 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 calibration 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. A Bruker Smart Apex diffractometer was used for X-ray crystallography.[12] For the crystallographic data in CIF electronic format and the data analysis see the Supporting Information.

The X-ray structure of *ccc*-DPH (Figure 1) shows that the planes of the phenyl groups form an angle of roughly 72°; the two planes are twisted in opposite directions, each forming an angle of 36° with the hexatriene moiety, which is almost planar (the largest deviations from planarity in the triene are dihedral angles of 11.4° between the central and terminal

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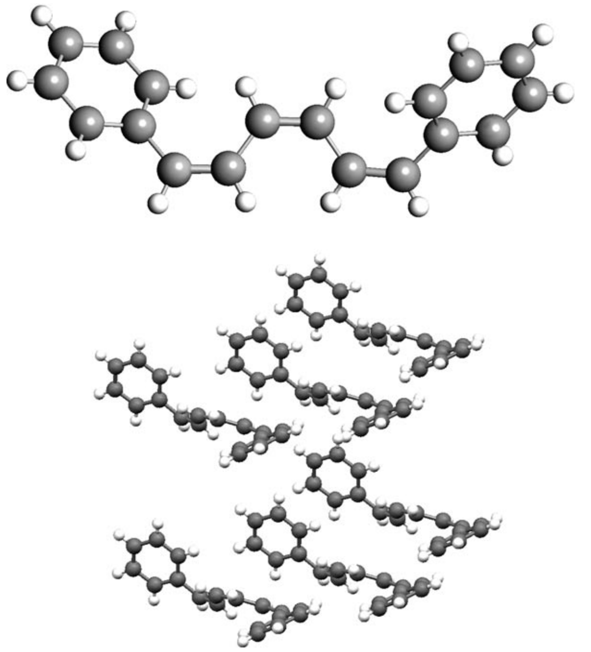


Figure 1. X-ray crystal structure (top) and crystal packing (bottom) of *ccc*-DPH molecules.

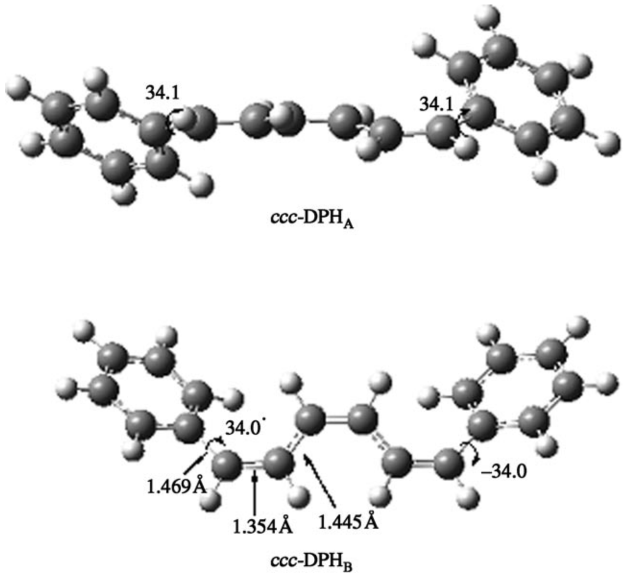


Figure 2. Stationary point geometries on the DPH S_0 surface; *ccc*-DPH$_A$ is lower in energy by 0.23 kcal mol^{-1}.

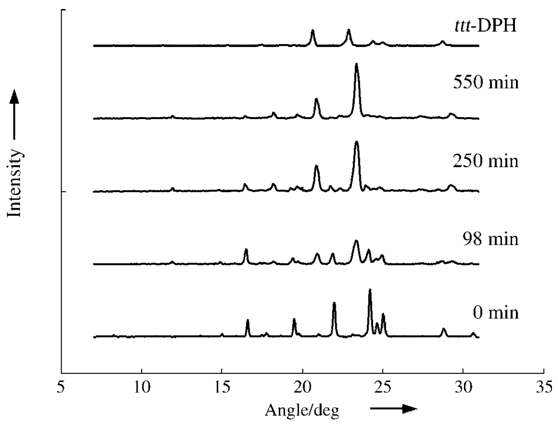


Figure 3. Powder X-ray diffraction patterns measured in the course of irradiation of *ccc*-DPH ($\lambda = 400$ nm); the upper pattern is for *ttt*-DPH.

double bonds). *ccc*-DPH possesses an axis of chirality and exists in enantiomerically pure form in the crystal, as was first observed for 1,1′-binaphthyl.[14]

Gaussian 98[15] B3LYP calculations with the 6-31G(d,p) basis set predict that in the gas phase *ccc*-DPH exists as two conformers, *ccc*-DPH$_A$ and *ccc*-DPH$_B$ (Figure 2). Conformer *ccc*-DPH$_B$ closely resembles the X-ray structure since the two phenyl groups are each rotated in opposite directions 34° to the triene plane; *ccc*-DPH$_B$ is predicted to lie 0.23 kcal mol^{-1} higher in energy than conformer *ccc*-DPH$_A$. The phenyl groups of *ccc*-DPH$_A$ lie in parallel planes rotated 34.1° relative to the triene plane, and in contrast to *ccc*-DPH$_B$ this conformer has no chirality axis (see the Supporting Information for calculation details). *ccc*-DPH$_A$ and *ccc*-DPH$_B$ are predicted to lie 8.5 and 8.7 kcal mol^{-1}, respectively, above the global energy minimum of *ttt*-DPH on the ground-state energy surface of DPH (both 9.1 kcal mol^{-1} higher in relative free energy);[16] this prediction is consistent with the absence of the *ccc*-DPH isomer in thermally equilibrated DPH mixtures.[13,17]

Irradiation of *ccc*-DPH in crystal or powder form at 400 nm (150 W Xe lamp of a Hitachi F4500 spectrophotometer) converts it directly to the all-*trans* isomer (*ttt*-DPH), the only isomer detected in ^{1}H NMR spectra measured in the course of the irradiation (up to 68 % conversion, see the Supporting Information). HPLC analysis of a sample irradiated to 6.4 % conversion is consistent with this conclusion (see the Supporting Information). Powder X-ray diffraction measurements show it to be a crystal-to-crystal reaction (Figure 3). Reaction progress was also followed by fluorescence spectroscopy. The broad emission band of the *ccc*-DPH powder is replaced by the red-shifted structured emission band of *ttt*-DPH (Figure 4). Changes observed on irradiation of the *ccc*-DPH crystal are similar. The evolution of product fluorescence is analogous to that for the spectra of *tt*-DPB and *tt*-DTB photoproducts arising from the irradiation of solid *cc*-DPB and *cc*-DTB, respectively.[7] The 0–0 vibronic band at 449 nm for *ttt*-DPH decreases in relative intensity as the reaction progresses and is replaced by the 0–1 band at 469 nm as the most intense band in the spectrum (Figure 4). The 0–1 band, blue-shifted by about 11 nm, is also the most intense band in the fluorescence spectrum of pure *ttt*-DPH crystals. Differences in the fluorescence spectra and powder X-ray spectra of pure *ttt*-DPH crystals and the *ttt*-DPH photoproduct show that the spectra are sensitive to intermolecular interactions that depend on the crystal packing arrangement. Fluorescence excitation spectra were also measured in the course of irradiation of solid *ccc*-DPH. The structureless *ccc*-DPH fluorescence excitation spectrum, $\lambda_{max} = 400$ nm, is replaced by the broader, vibronically structured *ttt*-DPH fluorescence excitation spectrum with the 0–0 band at 418 nm.

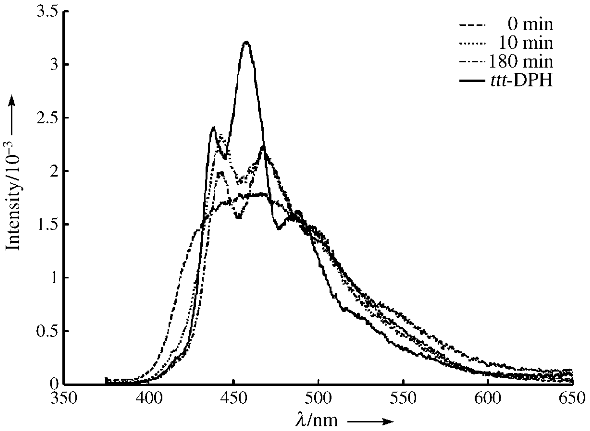


Figure 4. Fluorescence spectra obtained in the course of irradiation of *ccc*-DPH powder (λ = 400 nm) compared with the fluorescence spectrum of solid *ttt*-DPH.

The stereospecific three-bond photoisomerization of *ccc*-DPH in the solid state is all the more remarkable when one considers that on excitation in solution *ccc*-DPH gives all five DPH isomers. Preliminary photoisomerization quantum yields obtained for low conversions on irradiation of *ccc*-DPH at 365 nm in degassed methylcyclohexane (MCH) and acetonitrile (AN) solutions at 20 °C are given in Table 1. The photoisomerization of *ttt*-DPH in AN was used as actinometer.[2] As in the case of *ttt*-DPH, the photoisomerization quantum yields are very sensitive to the polarity of the solvent.[2] Isomerization of the terminal bond is favored over central one-bond photoisomerization (OBT) in both solvents. However, as observed for *ttt*-DPH,[2] OBT at the terminal bond is dramatically enhanced in the more polar solvent, such that formation of *cct*-DPH is the major photoreaction in AN (Figure 5).

Table 1: Quantum yields for *ccc*-DPH photoisomerization in solution.[a]

Solvent	φ_{cct}	φ_{ctc}	φ_{ctt}	φ_{tct}	φ_{ttt}
MCH	0.012	0.006	0.002	0.003	0.02
AN	0.06	0.009	0.02	0.01	0.03

[a] Solutions were *ccc*-DPH = 1.46×10^{-3} M and 1.02×10^{-3} M in MCH and AN, respectively; analysis was by HPLC as previously described.[2]

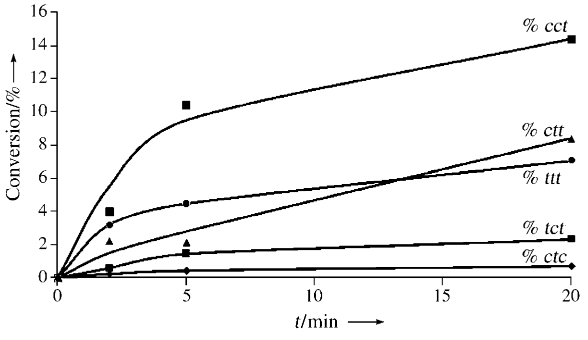


Figure 5. Time evolution of DPH isomers on irradiation (λ = 365 nm)of 6.5×10^{-4} M *ccc*-DPH in degassed AN at 20 °C (HPLC).

Simultaneous two-bond photoisomerizations leading to *ctt*- and *tct*-DPH are minor reactions in MCH, but are significant processes, possibly following BP pathways, in AN. In both solvents simultaneous three-bond photoisomerization is a primary process. In MCH, formation of *ttt*-DPH is the major photoreaction, leading to the possibility that it may be the precursor of significant fractions of the observed *ctt*- and *tct*-DPH photoproducts by sequential absorption of a second photon. Successive UV/Vis spectra recorded in MCH indicate the evolution of photoisomer formation (Figure 6).

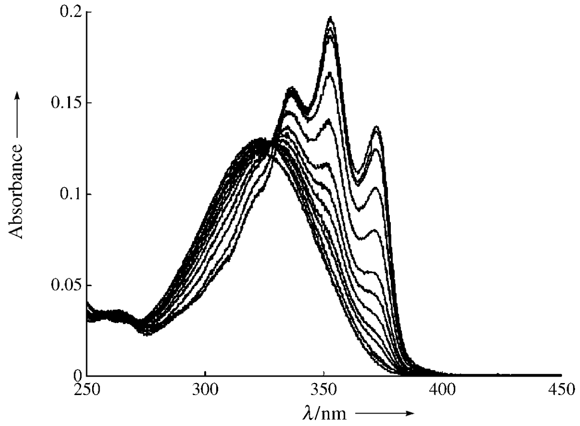
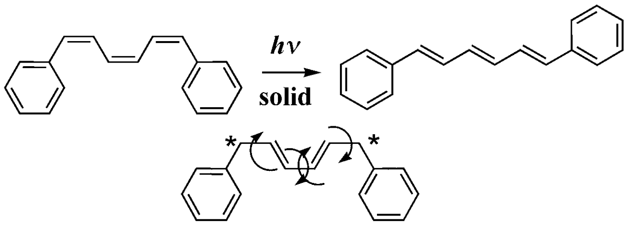


Figure 6. Successive UV/Vis spectra recorded in the course of irradiation (λ = 365 nm) of 1.1×10^{-5} M *ccc*-DPH in degassed MCH at 20 °C.

Simultaneous three-bond photoisomerization is consistent with the expected reversal of single-/double-bond character in the triene moiety on $S_0\rightarrow S_1$ excitation. The initial structureless fluorescence spectrum of *ccc*-DPH in the solid state (Figure 4) shows that, as in the cases of *cc*-DPB and *cc*-DTB,[7] the light-induced *ccc*-DPH→*ttt*-DPH reaction is not adiabatic. A two-stage process is envisioned with a first stage involving torsional motions in S_1 that bring the molecule to a conical intersection at an intermediate geometry between ^{1}*ccc*-DPH* and ^{1}*ttt*-DPH* and a second S_0 stage in which the formation of ground-state *ttt*-DPH is completed. The overall reaction is consistent with two simultaneous BP processes occurring in disrotatory fashion about the central bond (Scheme 2).



Scheme 2. The disrotatory double BP process in the S_1 stage of the *ccc*-DPH→*ttt*-DPH photoreaction.

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[11] ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.32$–7.38 (m, 3H, Ph), 7.22–7.28 (m, 2H, Ph), 6.74–6.86 (m, 2H$_b$), 6.61–6.67 (m, 2H$_c$), 6.55, 6.58 (d, 2H$_a$). UV (hexane)λ (nm)(ε in M^{-1}cm^{-1}) 229 (1.05×10^4), 262 (1.04×10^4), 321 (3.94×10^4).

[12] Crystallographic data for *ccc*-DPH: $C_{18}H_{16}$, $M = 232.31$, monoclinic, space group C2, $a = 11.5889$ Å, $b = 5.3763(7)$ Å, $c = 10.4492(13)$ Å, $\alpha = 90°$, $\beta = 92.319°$, $\gamma = 90°$, $V = 650.51(14)$ Å^3, $\rho_{\text{calcd}} = 1.186$ Mg m^{-3} and $Z = 2$. A Bruker SMART APEX diffractometer at a detector distance of 5 cm with the sample at 173 (2) K and Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) was used to take 2400 frames with 20 s collection time. The result was 4123 reflections with 794 ($I > \sigma(I)$, [R(int) = 0.0272]) being independent and a data to parameter ratio of about 10:1. See the Supporting Information for structural details.

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