

Photoisomerization of *cis,cis*-1,4-diphenyl-1,3-butadiene in glassy media at 77 K: the bicycle-pedal mechanism†

Jack Saltiel,^{*a} Tallapragada S. R. Krishna,^a Andrzej M. Turek^b and Ronald J. Clark^a

Received (in Cambridge, UK) 17th November 2005, Accepted 15th February 2006

First published as an Advance Article on the web 28th February 2006

DOI: 10.1039/b516319f

The *cis*–*trans* photoisomerization of *cis,cis*-1,4-diphenyl-1,3-butadiene in a soft isopentane glass at 77 K gives significant two-bond photoisomerization in contrast to solution and hard glassy media where only one-bond photoisomerization takes place.

Volume restricted media, such as protein environments, or glasses at low temperatures, exert control over *cis*–*trans* photoisomerization of conjugated olefins. Two mechanisms involving concerted rotation about more than one bond in S_1 (the first excited singlet state) were postulated to explain the specificity and high photoisomerization quantum yields of the retinyl moieties of rhodopsin and bacteriorhodopsin: Warshel's bicycle-pedal mechanism (BP) involves simultaneous rotations in S_1 about the C_1 – C_2 and C_3 – C_4 bonds of a 1,3-diene moiety¹ and Liu's 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).² These mechanisms are expected to reduce the 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 recent claim that the tachysterol products obtained on irradiation of previtamin D at 92 K in EPA glass (ether : isopentane : ethyl alcohol = 5 : 5 : 2) are those predicted by the HT motion,³ has stimulated the revival of the HT mechanism.⁴ Theoretical calculations favour 1,3-bond formation in the 2^1A_g states of polyenes at conical intersections for ultra fast radiationless decay to the ground state,^{5–7} and it has been argued^{5,7,8} that such structures can lead to HT products. Involvement of cyclopropylmethylene intermediates in the direct *cis*–*trans* photoisomerization of 1,3-butadienes as a possible alternative to allylmethylene intermediates had been proposed earlier.⁹ Until now, no experimental evidence had been advanced in support of the BP mechanism.

We noted reservations concerning the HT postulate in a paper showing that the photoisomerization of *cis*-1-(2-naphthyl)-2-phenylethene in methylcyclohexane (MCH) glass at 77 K is conformer specific,¹⁰ giving the one-bond twist (OBT) product as in fluid solution.¹¹ We now present a related study on the

photoisomerization of the 1,4-diphenyl-1,3-butadienes (*cc*-DPB, *ct*-DPB, *tt*-DPB). Photoisomerization of the DPBs in solution¹² was reported by Zechmeister¹³ and later studied by Whitten¹⁴ and Yee¹⁵ and their coworkers. Recently, Liu and coworkers reported the photoisomerization of the DPBs in EPA (5 : 5 : 2) glass at 77 K.¹⁶ Starting from *cc*-DPB, sequential one-bond isomerization gives a *ct*-DPB-rich photostationary state in solution,^{12–15} and pure *tt*-DPB in EPA glass.¹⁶

DPB isomer fluorescence spectra in IP at 77 K are shown in Fig. 1. Spectra in MCH at 77 K are similar. Irradiations of dilute solutions ($\sim 4 \times 10^{-6}$ M) of the DPBs in glassy isopentane (IP) or MCH were carried out in cylindrical sample tubes immersed in liquid N_2 in the phosphorescence accessory of a Hitachi F-4500 fluorimeter using the 150-W Xe fluorimeter lamp as the excitation source. Reaction progress was followed by fluorescence spectroscopy at 77 K. In MCH glass at 77 K *cc*-DPB gives only *ct*-DPB in agreement with the earlier reports in solution and in EPA glass.^{13–15} However, our results in the softer IP glass¹⁷ at 77 K reveal a major *cc*-DPB \rightarrow *tt*-DPB *two-bond* photoisomerization process. Fluorescence spectra as a function of irradiation time of *cc*-DPB in IP at 77 K are shown in Fig. 2. The well-resolved vibronic bands of *tt*-DPB fluorescence are obvious from the start, in stark contrast to spectra from a parallel experiment in MCH that show only build-up of *ct*-DPB fluorescence. Principal component analysis (PCA) treatment^{10,18} of the spectra in Figs. 1 and 2 reveals a 3-component system. As can be seen in Fig. 3, eigenvector combination coefficients for the spectra of the irradiated glassy IP solutions (Fig. 2) fall within the normalization triangle defined by the combination coefficients of the pure isomer spectra in Fig. 1. Treatment of the analogous spectra in glassy

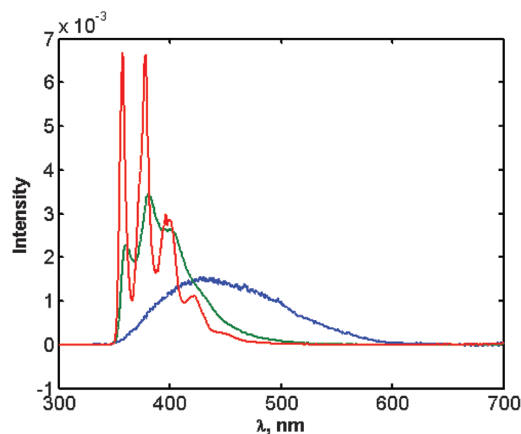


Fig. 1 Normalized corrected fluorescence spectra of *tt*-DPB (red) *ct*-DPB (green) and *cc*-DPB (blue) in IP at 77 K, $\lambda_{exc} = 320$ nm.

^aDepartment of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306-4390, USA. E-mail: saltiel@chem.fsu.edu; Fax: +1 850 644 8281; Tel: +1 850 644 5405

^bJagiellonian University, Faculty of Chemistry, 30 060 Cracow, Poland. E-mail: turek@chemia.uj.edu.pl; Fax: +48-12-634-05-15; Tel: +48-12-663-2262

† Electronic supplementary information (ESI) available: Cartesian coordinates, drawings, and total energies of optimized structures (minima on S_0); tables of X-ray data for *cc*-DPB consisting of crystallographic parameters, positional parameters, bond distances, bond angles, and torsional angles. See DOI: 10.1039/b516319f

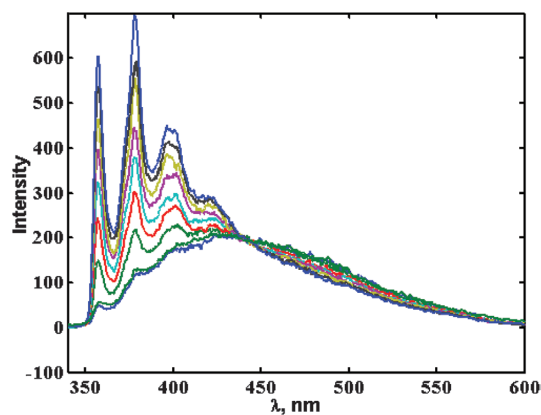


Fig. 2 Fluorescence spectra of a *cc*-DPB solution in IP recorded as a function of irradiation ($\lambda_{\text{rad}} = \lambda_{\text{exc}} = 320$ nm) time at 77 K.

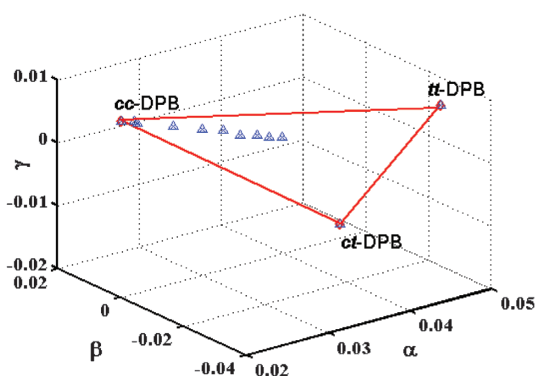


Fig. 3 Combination coefficients for the spectra in Figs. 1 and 2.

MCH shows that irradiation leads to mixture spectra whose combination coefficients lie exclusively on the *cc*-DPB–*ct*-DPB side of the normalization triangle.

Correction for the 4% *tt*-DPB fluorescence present in the spectrum at time 0, gives *ct*-DPB/*tt*-DPB = 0.7 ± 0.1 for the spectra in Fig. 2. *ct*-DPB/*tt*-DPB product ratios are almost constant but vary from experiment to experiment with slow cooling favouring the *ct*-DPB product. However, conversion of *cc*-DPB to *tt*-DPB is much faster than conversion of *ct*-DPB to *tt*-DPB under the same conditions. This direct two-bond *cc*-DPB → *tt*-DPB pathway appears to be the first example of Warshel's BP photoisomerization mechanism in an amorphous medium. Estimated fluorescence quantum yields in IP at 77 K with *trans*-stilbene in MCH at 77 K as standard¹⁹ are 1, 0.7 and 0.3 (25% uncertainty) for *tt*-, *ct*- and *cc*-DPB, respectively. The radiative rate constant, $k_{\text{F}} = 3 \times 10^8 \text{ s}^{-1}$, of *cc*-DPB can be based roughly²⁰ on its molar absorptivity at λ_{max} (compare with $8 \times 10^7 \text{ s}^{-1}$, the experimentally determined value for *cis*-stilbene²¹). It follows, that if all the radiationless decay is along the BP channel, the lower limit for that rate constant at 77 K is $1 \times 10^9 \text{ s}^{-1}$. To compete with *cc*-DPB radiative decay, the activation energy of the BP mechanism must be smaller than 2 kcal mol^{-1} .

The crystals of *cc*-DPB were disordered and not of sufficiently high quality to allow straightforward refinement of X-ray diffraction data. Numerous space groups were attempted on six data sets collected on four different crystals.²² Depending upon the random selection of reflections, the indexing analysis produced: (i)

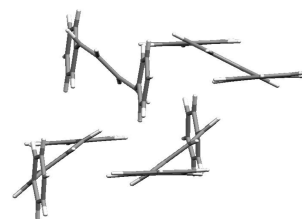


Fig. 4 X-Ray structure of *cc*-DPB; four molecules in the asymmetric unit viewed roughly end on (see ESI†).

a monoclinic cell of dimensions $a = 7.140 \text{ \AA}$, $b = 7.126 \text{ \AA}$, $c = 22.660 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 92.132^\circ$, $\gamma = 90^\circ$ with a volume of 1152.49 \AA^3 , (ii) a triclinic cell with the initial two distances a little over 10 \AA , doubling the volume of the cell in (i), or (iii) a monoclinic cell with the initial values above 14 \AA , quadrupling the cell volume in (i). Use of space groups $P2_1$ or $P2_1/c$ with the smallest cell yielded a composite structure consistent with the average of two *cc*-DPB molecules, one with phenyls in parallel planes and the other with phenyls in roughly orthogonal planes. Refinement to distinct molecules (see the four molecule asymmetric unit in Fig. 4) was achieved only by use of the Cc space group with the largest unit cell, but with a relatively high R_1 value of 9.8%† (see ESI for more details on problems we encountered†). Common to all solutions was that 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.

Calculated and X-ray structures of *cc*-DPB are in reasonable agreement. Gaussian 98²³ B3LYP calculations with the 6-31G(d,p) basis set predict that the lowest energy structure has each of the two phenyls rotated in opposite directions 31.5° to the diene plane. The structure with the phenyls in parallel planes rotated 39.6° to the diene plane is predicted to lie $1.5 \text{ kcal mol}^{-1}$ above it, Fig. 5 (ESI†). The latter structure is almost identical to the upper X-ray conformer structure shown in Fig. 4 (see, also, Fig. 6).

Least motion considerations suggest that the conformation, with phenyls in parallel planes can more readily yield *tt*-DPB via the BP mechanism. The arrows in Fig. 6 show the concerted

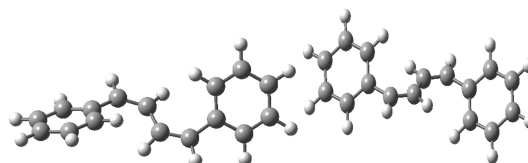


Fig. 5 Stationary point geometries on the *cc*-DPB S_0 surface; the structure on the left corresponds to the global energy minimum (see ESI†).

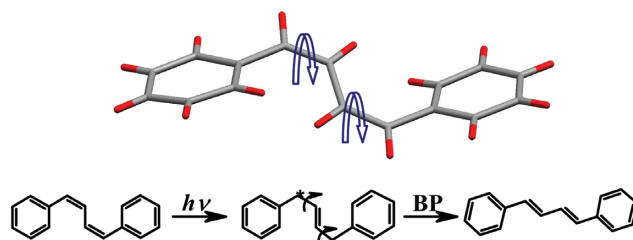


Fig. 6 The BP mechanism shown for the *cc*-DPB X-ray structure with the phenyls in parallel planes.

torsional motions about the two former double bonds in the diene moiety that convert *cc*-DPB to *tt*-DPB. Volume demand is minimized because most of the motion is confined to the diene unit, which can be viewed in the lowest singlet excited state as a 1,4-biradicaloid or zwitterionic species, with the phenyl groups held stationary. However, our observation of exclusive *cc*-DPB to *tt*-DPB photoisomerization in the solid state (crystals or powder) in a crystal to crystal reaction, albeit in kinetically distinct stages, indicates that both *cc*-DPB conformers in Fig. 4 serve as *tt*-DPB precursors.²⁴

The lower energy conformation with phenyls in perpendicular planes can, with minimal torsional motion in the diene moiety, readily form a *cis*-phenallylbenzyl intermediate on the way to *ct*-DPB. Formation of the conventional OBT intermediate requires little, if any, motion of the phenyl rings since they lie in roughly orthogonal planes at the outset and can account for one-bond photoisomerization of *cc*-DPB in MCH glass. As in the case of *c*-NPE,¹⁰ we apply Occam's razor to favour the OBT over the HT mechanism in low *T* rigid media when the two pathways predict the same product.²⁵

We can only speculate concerning the difference in behaviour of the lowest excited singlet states of *cc*-DPB in IP and MCH glassy media at 77 K. If thermodynamic equilibrium were maintained during the cooling process, and if the difference in size and shape of the cavities occupied by *cc*-DPB in the two media were not a factor, then the lower melting IP (113.3 K vs. 146.6 K for MCH) would have favoured the lower energy conformer with the phenyls in planes roughly approaching orthogonality. However, thermodynamic equilibration requires slow cooling and we observed the highest relative yields of two-bond isomerization when the sample tube was plunged into liquid N₂. It is possible that the shape of the solvent cavities in the IP host favours the conformer with phenyls in parallel planes.

This work was supported by National Science Foundation Grant No. CHE-0314784. We thank Dr Olga Dmitrenko for the DFT calculations.

Notes and references

‡ Crystallographic data for *cc*-DPB: C₁₆H₁₄, *M* = 206.27, monoclinic, space group *Cc*, *a* = 14.2760(8) Å, *b* = 14.2485(8) Å, *c* = 22.6565(13) Å, α = 90°, β = 92.136(2)°, γ = 90°, *V* = 4605.4(5) Å³, ρ_{calcd} = 1.190 Mg m⁻³ and *Z* = 16. With the use of 11375 unique reflections (*I* > $\sigma(I)$) collected at 100(2) K with Mo K α radiation (λ = 0.71073 Å) on a Bruker SMART APEX diffractometer at a detector distance of 5 cm. The number of frames taken was typically 2400 using 0.3 degree omega scans at 20 s frame collection time. The first 50 frames were repeated at the end of data collection and no significant crystal decomposition in the course of the measurements was detected. Integration was performed using the programme SAINT which is part of the Bruker suite of programmes. Absorption corrections were made using SADABS. XPREP was used to suggest the space groups and the structure was solved by direct methods and refined by SHELXTL. The refinement converged to a final *R*₁ = 0.0980, *wR*₂ = 0.2340 (*I* > 2 $\sigma(I)$) and GOF = 1.155 with the largest difference peak and hole as 0.666 and -0.339 e Å⁻³ respectively. CCDC 290241. For problems with the data analysis and crystallographic data in CIF or other electronic format see DOI: 10.1039/b516319f

1 A. Warshel, *Nature (London)*, 1976, **260**, 679.

2 (a) R. S. H. Liu and A. E. Asato, *Proc. Natl. Acad. Sci. USA*, 1985, **82**, 259; (b) R. S. H. Liu, D. Mead and A. Asato, *J. Am. Chem. Soc.*, 1985, **107**, 6609.

3 A. M. Müller, S. Lochbrunner, W. E. Schmid and W. Fuß, *Angew. Chem., Int. Ed.*, 1998, **37**, 505.

- 4 (a) R. S. H. Liu and G. S. Hammond, *Proc. Natl. Acad. Sci. USA*, 2000, **97**, 11153; (b) R. S. H. Liu, *Acc. Chem. Res.*, 2001, **34**, 555; (c) R. S. H. Liu and G. S. Hammond, *Chem.-Eur. J.*, 2001, **7**, 4537; (d) R. S. H. Liu, *Pure Appl. Chem.*, 2002, **74**, 1391; (e) R. S. H. Liu and G. S. Hammond, *Photochem. Photobiol. Sci.*, 2003, **2**, 835; (f) R. S. H. Liu and G. S. Hammond, in *Handbook of Organic Photochemistry and Photobiology*, ed. W. M. Horspool, F. Lenci, CRC Press: London, 2nd edn, 2004, pp. 26/1–26/11; (g) G. Krishnamoorthy, S. Schieffer, J. Pescatore, R. Ulsh, R. S. H. Liu and J. Liu, *Photochem. Photobiol. Sci.*, 2004, **3**, 1047.
- 5 (a) M. Olivucci, F. Bernardi, P. Celani, I. N. Ragazos and M. A. Robb, *J. Am. Chem. Soc.*, 1994, **116**, 1077; (b) P. Celani, M. Garavelli, S. Ottani, F. Bernardi, M. A. Robb and M. Olivucci, *J. Am. Chem. Soc.*, 1995, **117**, 11584; (c) M. Garavelli, P. Celani, F. Bernardi, M. A. Robb and M. Olivucci, *J. Am. Chem. Soc.*, 1997, **119**, 11487; (d) M. Garavelli, B. R. Smith, M. J. Bearpark, F. Bernardi, M. Olivucci and M. A. Robb, *J. Am. Chem. Soc.*, 2000, **122**, 5568.
- 6 For crossing to the 2¹A_g state see: (a) C. Woywood, W. C. Livingood and J. H. Frederick, *J. Chem. Phys.*, 2000, **112**, 613; (b) C. Woywood, W. C. Livingood and J. H. Frederick, *J. Chem. Phys.*, 2000, **112**, 626; (c) C. Woywood, W. C. Livingood and J. H. Frederick, *J. Chem. Phys.*, 2001, **114**, 1631; (d) C. Woywood, W. C. Livingood and J. H. Frederick, *J. Chem. Phys.*, 2001, **114**, 1645.
- 7 For a recent review of polyene photophysics see: W. Fuß, Y. Haas and S. Zilberg, *Chem. Phys.*, 2000, **259**, 273.
- 8 A. M. Müller, S. Lochbrunner, W. E. Schmid and W. Fuss, *Angew. Chem., Int. Ed.*, 1998, **37**, 505.
- 9 (a) J. Saltiel, L. Metts and M. Wrighton, *J. Am. Chem. Soc.*, 1970, **92**, 3227; (b) J. Saltiel, J. T. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton and O. C. Zafriou, *Org. Photochem.*, 1973, **3**, 1.
- 10 J. Saltiel, T. S. R. Krishna and A. M. Turek, *J. Am. Chem. Soc.*, 2005, **127**, 6938.
- 11 (a) J. Saltiel, N. Tarkalanov and D. F. Sears, Jr., *J. Am. Chem. Soc.*, 1995, **117**, 5586; (b) J. Saltiel, G. Krishnamoorthy and D. F. Sears, Jr., *Photochem. Photobiol. Sci.*, 2003, **2**, 1162.
- 12 For a review, see: J. Saltiel and Y.-P. Sun, in *Photochromism, Molecules and Systems*, ed. H. Dürr and H. Bouas-Laurent, Elsevier, Amsterdam, 1990, p. 64.
- 13 J. H. Pinckard, B. Wille and L. Zechmeister, *J. Am. Chem. Soc.*, 1948, **70**, 1938.
- 14 L. R. Eastman, Jr., B. M. Zarnegar, J. M. Butler and D. G. Whitten, *J. Am. Chem. Soc.*, 1974, **96**, 2281.
- 15 W. A. Yee, S. J. Hug and D. S. Kliger, *J. Am. Chem. Soc.*, 1988, **110**, 2164.
- 16 L. Yang, R. S. H. Liu, K. L. Boorman, N. L. Wendt and J. Liu, *J. Am. Chem. Soc.*, 2005, **127**, 2404.
- 17 For organic glass viscosities see: (a) H. Greenspan and E. Fischer, *J. Phys. Chem.*, 1965, **69**, 2466; (b) G. A. von Salis and H. Labhart, *J. Phys. Chem.*, 1968, **72**, 752.
- 18 J. Saltiel, D. F. Sears, Jr., J.-O. Choi, Y.-P. Sun and D. W. Eaker, *J. Phys. Chem.*, 1994, **98**, 35.
- 19 J. Saltiel, A. Marinari, D. W.-L. Chang, J. C. Mitchener and E. D. Megarity, *J. Am. Chem. Soc.*, 1979, **101**, 2982.
- 20 N. J. Turro, *Modern Molecular Photochemistry*, Benjamin/Cummings Publishing Co., Inc., Menlo Park, CA, 1978, p. 90.
- 21 J. Saltiel, A. S. Waller and D. F. Sears, Jr., *J. Am. Chem. Soc.*, 1993, **115**, 2453.
- 22 A Bruker SMART APEX diffractometer was used.
- 23 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, *Gaussian 98 (Revision A.7)*, Gaussian, Inc., Pittsburgh, PA, 1998.
- 24 J. Saltiel, T. S. R. Krishna and R. J. Clark, *J. Phys. Chem.*, 2006, **110**, 1694.
- 25 L. Yang, R. S. H. Liu, N. L. Wendt and J. Liu, *J. Am. Chem. Soc.*, 2005, **127**, 9378.