



Cite this: DOI: 10.1039/c9pp00113a

## The photoisomerization of *cis,trans*-1,2-dideuterio-1,4-diphenyl-1,3-butadiene in solution. No bicycle-pedal†

Jack Saltiel, \* Christopher E. Redwood and Ratheesh Kumar V. K.‡

*cis,trans*-1,2-Dideuterio-1,4-diphenyl-1,3-butadiene (*ct*-DPB<sub>d2</sub>) was synthesized and its *cis*–*trans* photoisomerization in cyclohexane-*d*<sub>12</sub> (C<sub>6</sub>D<sub>12</sub>) at room temperature was monitored by <sup>1</sup>H NMR spectroscopy. The results reveal formation of only *trans,trans*-1,2-dideuterio-1,4-diphenyl-1,3-butadiene (*tt*-DPB<sub>d2</sub>). The failure to detect formation of *trans,cis*-1,2-dideuterio-1,4-diphenyl-1,3-butadiene (*tc*-DPB<sub>d2</sub>) eliminates the possibility that an identity bicycle pedal process contributes to inefficiency in the *cis*–*trans* photoisomerization of *cis,trans*-1,4-diphenyl-1,3-butadiene (*ct*-DPB).

Received 9th March 2019,  
Accepted 16th May 2019

DOI: 10.1039/c9pp00113a

rsc.li/pps

## Introduction

Previous studies have shown that, in contrast to *trans*-stilbene,<sup>1–7</sup> the *trans*–*cis* photoisomerization and fluorescence of *trans,trans*-1,4-diphenyl-1,3-butadiene (*tt*-DPB) are not the sole complementary processes.<sup>8–11</sup> In several solvents fluorescence and photoisomerization quantum yields of *tt*-DPB do not account for all excited state decay and it has been suggested that solvent dependent access to the 2 <sup>1</sup>A<sub>g</sub> state leads to unreactive radiationless decay.<sup>10</sup> The low photoisomerization quantum yields of the other two DPB isomers, that are essentially non-fluorescent in solution, must also be explained. It was shown recently that the photoisomerization of *cc*-DPB occurs exclusively by simultaneous two-bond rotation in the solid state,<sup>12,13</sup> and partially so in glassy media at 77 K.<sup>14,15</sup> The two bond bicycle-pedal (BP) mechanism was first proposed by Warshel to account for photoisomerization of polyenes in free volume constraining media such as the protein environments of the rhodopsins.<sup>16</sup> The interconversions of *trans,cis,trans*- and *cis,trans,trans*-1,6-diphenyl-1,3,5-hexatriene<sup>17,18</sup> and *cc*-DPB and *tt*-DPB are examples of one photon/two bond photoisomerizations in solution.<sup>10,11</sup> More intriguing is the recent demonstration that the central bond photoisomerizations of *trans,cis,trans*- and *trans,trans,trans*-1,6-

dideuterio-1,3,5-hexatriene in solution occur primarily by a concerted BP process.<sup>19</sup> The BP process would be an identity reaction in *ct*-DPB and it occurred to us that it might account for some of the inefficiency in its *cis*–*trans* photoisomerization. In this paper, we describe the synthesis and photoisomerization of *ct*-DPB<sub>d2</sub>. The results presented here establish that the BP process plays no role in the photoisomerization of *ct*-DPB in solution.

## Experimental

### Materials

Cyclohexane-*d*<sub>12</sub>, benzene-*d*<sub>6</sub>, chloroform-*d*<sub>1</sub> (Cambridge Isotope Labs) and hexanes (HPLC grade, EMD) were used as received. Silica was (Technical Grade, 230–400 mesh, 43–60 μm, Sigma-Aldrich). The photoisomerization of *tt*-DPB yielded *ct*-DPB as previously described.<sup>9,10</sup> The synthesis of *ct*-DPB<sub>d2</sub> using the Horner–Wadsworth–Emmons reaction<sup>20</sup> follows. **Diethyl benzylphosphonate:** Benzyl bromide (2.86 g, 2.0 mL, 16.7 mmol, Sigma Aldrich) and triethyl phosphite (9.69 g, 10.0 mL, 58.3 mmol, Sigma Aldrich) were taken in a 100 mL single necked round bottom flask and refluxed in an oil bath. The progress of the reaction was monitored by TLC using hexane as eluent, and the reaction was stopped after 3 h (TLC showed complete loss of benzyl bromide). Excess triethyl phosphite was distilled off under reduced pressure and the reaction mixture was cooled and extracted with ethyl acetate and 0.1 M sodium bicarbonate (3 × 25 mL). The organic layer was collected, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to yield 3.5 g (92%) of diethyl benzylphosphonate, a pale yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 1.18–1.21 (t, *J* = 7.2 Hz, 6H),

Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306-4390, USA. E-mail: saltiel@chem.fsu.edu; Fax: +850644 8281; Tel: +850 644 5405

† This paper is dedicated to the memory of Professor Ugo Mazzucato and his seminal contributions to Photochemistry.

‡ Present Address: Department of Chemistry, VTM NSS College, Trivandrum, Kerala, India

3.09–3.13 (d, 2H), 3.94–3.99 (m, 4H), 7.21–7.27 (m, 5H). **trans-1,4-Diphenyl-1-buten-3-yne**: Diethyl benzylphosphonate (1.0 g, 4.4 mmol) in THF (5.0 mL, freshly distilled over Na-benzophenone) was added dropwise to a stirred suspension of NaH (360.0 mg, 9 mmol, 60% in mineral oil, Sigma) in THF (10.0 mL) taken in an oven dried, N<sub>2</sub> flushed round bottom flask kept in dry ice. The reaction mixture was stirred for 30 minutes under N<sub>2</sub> flushed conditions at low temperature followed by the dropwise addition of a solution of 3-phenylpropanal (572.0 mg, 540 μL, 4.4 mmol, Aldrich) in THF (5.0 mL). After stirring the reaction mixture for 1 h maintaining the cold conditions, the temperature was slowly raised to room temperature and the solution was refluxed for 24 h (the reaction mixture turned deep red and TLC showed loss of the aldehyde). The reaction mixture was cooled to room temperature and a few drops of brine were added to quench excess NaH. It was then extracted with dichloromethane and brine (3 × 20 mL). The organic layer was collected, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The product was then purified by column chromatography over silica gel using hexane as eluent. White powder, yield = 200.0 mg (22%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 6.38–6.41 (d, *J* = 16.25 Hz, 1H), 7.03–7.07 (d, *J* = 16.25 Hz, 1H), 7.29–7.37 (m, 6H), 7.42–7.44 (m, 2H), 7.47–7.49 (m, 2H). <sup>1</sup>H NMR showed the presence of ~10% *cis*-enyne. The doublets due to the *cis* protons were observed at δ 5.92–5.95 (*J* = 11.95 Hz) and 6.70–6.73 (*J* = 11.95 Hz). This isomer mixture was used for the reduction reaction. ***cis,trans*-1,2-Dideuterio-1,4-diphenylbutadiene**: The enyne mixture (100.0 mg, 0.49 mmol) was dissolved in methanol (10.0 mL) in a single-necked round bottom flask and flushed with D<sub>2</sub> (D<sub>2</sub> filled balloon connected to the rubber septum on the RB flask using a needle) for 10 min. Lindlar Pd (5% Pd/C-CaCO<sub>3</sub>-PbO<sub>2</sub>, 10.0 mg, Sigma) was added to the solution and stirred under a D<sub>2</sub> atmosphere. The reaction was terminated after 90 min based on TLC analysis. The reaction mixture was passed through a short plug of silica gel to remove the catalyst and the methanol solution was concentrated. Products were isolated by column chromatography over silica gel using hexane. Two pure fractions were isolated from the column and the <sup>1</sup>H NMR analysis showed that the first fraction (yield = 5.0 mg, 5%) was the *cis,cis*-isomer (*J* = 11.55 Hz) and the second fraction (yield = 53.0 mg, 52%) was the *cis,trans*-isomer (*J* = 15.55 Hz). The third fraction was unreacted starting material. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): *cc*-DPB<sub>d<sub>2</sub></sub>: δ 6.58–6.60 (d, *J* = 11.55 Hz, 1H), 6.71–6.74 (d, *J* = 11.55 Hz, 1H), 7.26–7.29 (m, 2H), 7.36–7.43 (m, 8H). *ct*-DPB<sub>d<sub>2</sub></sub>: δ 6.71–6.74 (d, *J* = 15.55 Hz, 1H), 7.17–7.42 (m, 11 H).

## Measurements

Samples were irradiated in degassed 5 mm o.d. precision quartz NMR sample tubes (Wilmad Low Pressure/Vacuum Valve (LPV) 7" L, 500 MHz) and the progress of the reaction was followed by <sup>1</sup>H NMR with the use of a Bruker Avance III 500 MHz NMR spectrometer. The NMR tubes were placed in a small cylindrical merry-go-round attached to a stirring motor,<sup>21</sup> fitted to accept 5 mm tubes. The merry-go-round was placed as close as possible to the center arc of a Hanovia 450

W medium pressure Hg lamp housed in a double walled Pyrex probe. Cold water was circulated through the inner compartment of the probe and a 313 nm aqueous filter solution<sup>22</sup> was in the outer compartment.

## Sample preparation

Freshly purified *ct*-DPB and *ct*-DPB<sub>d<sub>2</sub></sub> decompose on standing in the dark in the refrigerator. Two <sup>1</sup>H NMR peaks that develop close to δ 10 indicate that photooxidation to aldehydes is in part to blame. Accordingly, the DPB samples used in our experiment were not completely free of minor contaminants. Solutions of *ct*-DPB (3 × 10<sup>-2</sup> M) and *ct*-DPB-*d*<sub>2</sub> (4.5 × 10<sup>-2</sup> M) were prepared in benzene-*d*<sub>6</sub> and cyclohexane-*d*<sub>12</sub>, respectively. They were degassed using 5 freeze pump thaw cycles to 1 × 10<sup>-4</sup> Torr. *tt*-DPB contamination in the 0-time <sup>1</sup>H NMR spectra was significantly less than 1% (see below). The degassed samples were irradiated in open air to ~1 and 2% conversion.

## Results

### <sup>1</sup>H NMR spectra

The <sup>1</sup>H NMR spectrum of *ct*-DPB in the degassed benzene-*d*<sub>6</sub> solution was assigned using 1D proton and 2D COSY spectra, Fig. 1 and 2 respectively. Protons H<sub>a</sub>–H<sub>d</sub> integrate very close to 1 H each. H<sub>a</sub> and H<sub>d</sub> doublets have coupling constants of 15 and 12 Hz, respectively, consistent with *trans* and *cis* coupling, Fig. 1. Single cross peaks reveal correlation between H<sub>a</sub> and H<sub>b</sub>, and between H<sub>c</sub> and H<sub>d</sub>, Fig. 2.

Coupling between H<sub>b</sub> and H<sub>c</sub> leads to a pair of off-diagonal peaks for those two protons. The only vinyl protons in the <sup>1</sup>H NMR spectrum of *ct*-DPB<sub>d<sub>2</sub></sub> in degassed C<sub>6</sub>D<sub>12</sub>, Fig. 3, are H<sub>a</sub> and H<sub>b</sub>. The H<sub>b</sub> doublet of *ct*-DPB<sub>d<sub>2</sub></sub> in C<sub>6</sub>D<sub>12</sub> overlaps the signals of the aromatic protons, being significantly up field from the corresponding signal of *ct*-DPB in C<sub>6</sub>D<sub>6</sub>, Fig. 1. The H<sub>b</sub> signals at the downfield edge of the aromatic protons are readily seen in the COSY spectrum of *ct*-DPB<sub>d<sub>2</sub></sub>, Fig. 4.

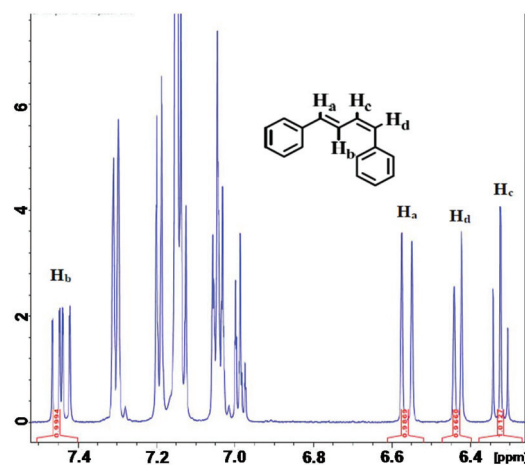


Fig. 1 The <sup>1</sup>H NMR spectrum of *ct*-DPB in C<sub>6</sub>D<sub>6</sub>. Integration values from left to right: 0.9994, 0.9869, 0.9660 and 1.0127.

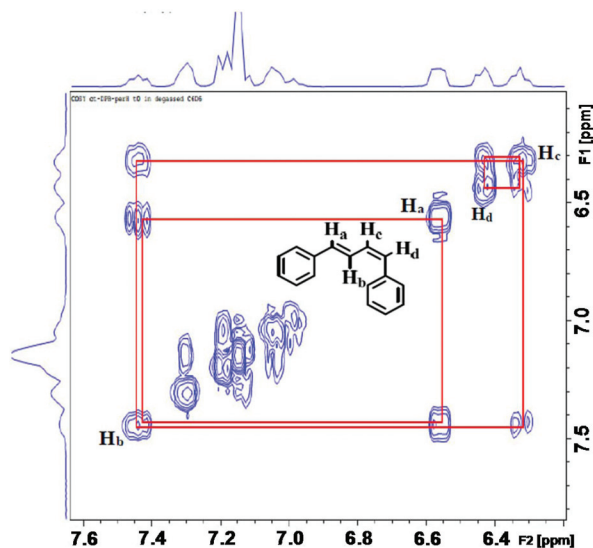


Fig. 2 The COSY spectrum of *ct*-DPB in  $C_6D_6$ .

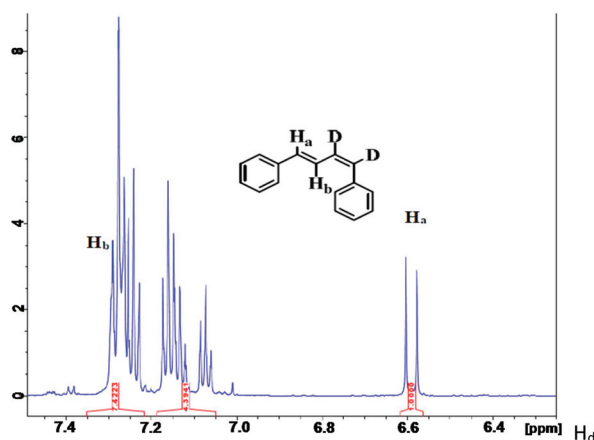


Fig. 3 The  $^1H$  NMR spectrum of *ct*-DPB $_{d_2}$  in  $C_6D_{12}$ . Integration values from left to right: 7.422, 4.394 and 1.000.

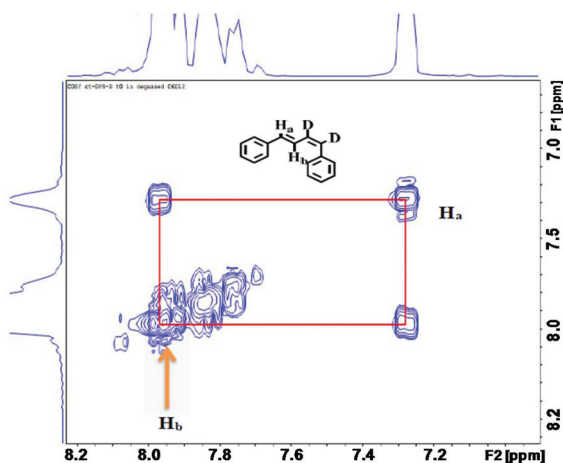


Fig. 4 The COSY spectrum of *ct*-DPB $_{d_2}$  in  $C_6D_{12}$ .

### $^1H$ NMR spectra of irradiated *ct*-DPB and *ct*-DPB $_{d_2}$

The 0-time  $^1H$  NMR spectra of the *ct*-DPB and *ct*-DPB $_{d_2}$  solutions are shown in Fig. 1 and 3, respectively. Spectra were also recorded following 313 nm irradiation in parallel, in the small merry-go-round to about 1 and 2% conversions. The *ct*-DPB spectra show the growth of two doublets of doublets, one centred at  $\delta$  6.48 $_3$  and the other at  $\delta$  6.81 $_9$ , with a coupling constant of 15 Hz, consistent with the vinyl protons of *tt*-DPB, the expected photoproduct, Fig. 5 and 6. Corresponding spectra for *ct*-DPB $_{d_2}$  are shown in Fig. 7 and 8. That the  $H_a$  and  $H_b$  protons of the *tt*-DPB $_{d_2}$  photoproduct emerge with equal intensity is evident in Fig. 7. The reader should not be deceived by Fig. 8 where the expansions of the  $H_a$  and  $H_b$  regions differ. Peaks of unknown minor contaminants that developed in the purified *ct*-DPB $_{d_2}$  samples on storage in the refrigerator are

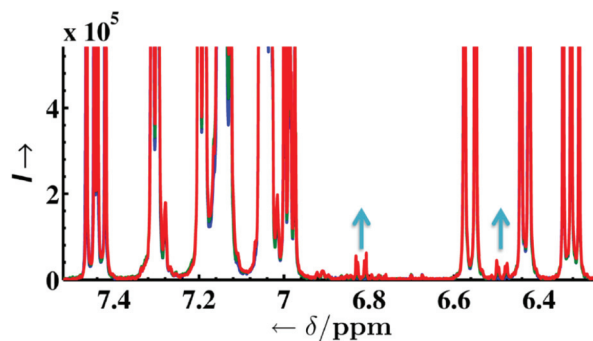


Fig. 5 Irradiation of *ct*-DPB in  $C_6D_6$ ; the arrows show *tt*-DPB formation.

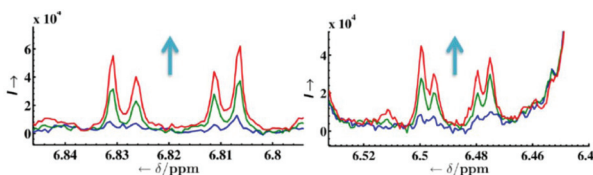


Fig. 6 Expanded regions from Fig. 5 showing the *tt*-DPB vinyl protons.

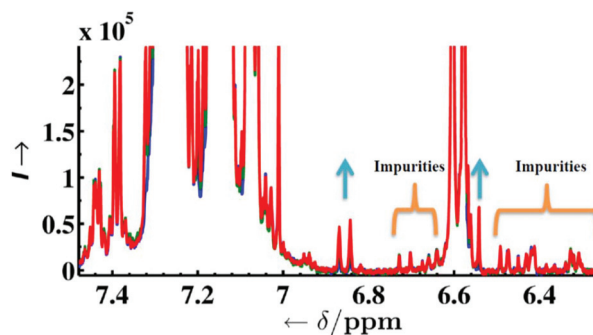


Fig. 7 Irradiation of *ct*-DPB $_{d_2}$  in  $C_6D_{12}$ ; the arrows show *tt*-DPB $_{d_2}$  formation.

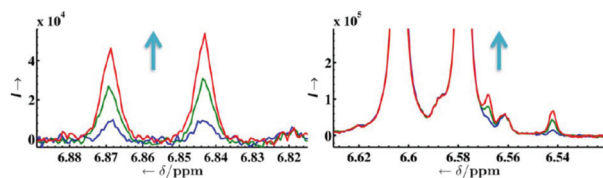


Fig. 8 Expanded regions from Fig. 7 showing the *tt*-DPB<sub>d2</sub> vinyl protons.

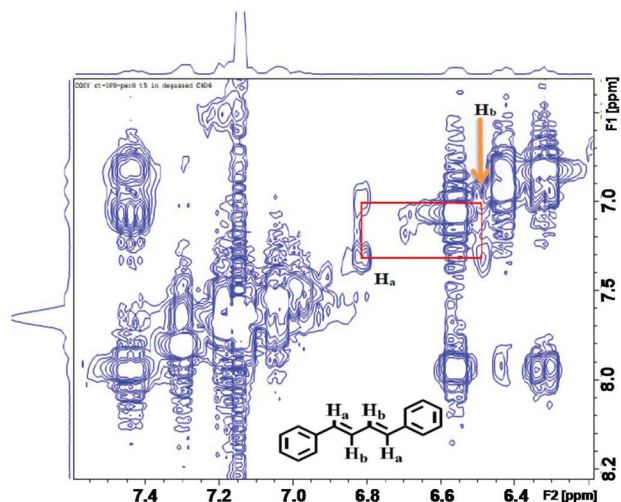


Fig. 9 COSY spectrum showing the *tt*-DPB region from the *ct*-DPB irradiation in C<sub>6</sub>D<sub>6</sub>.

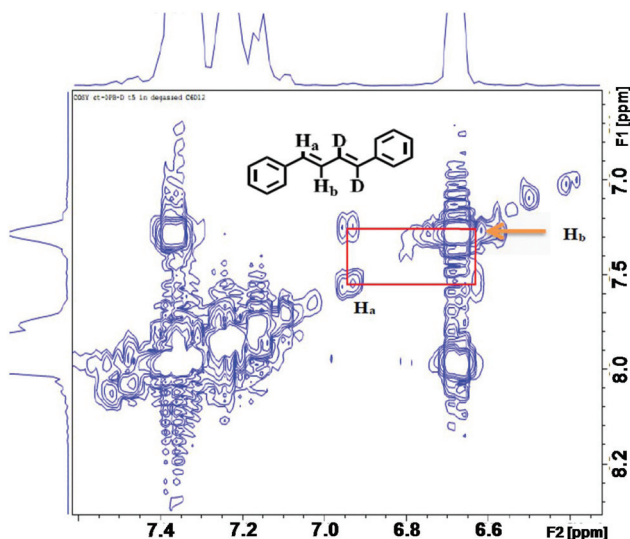


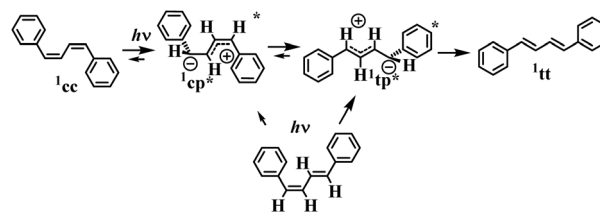
Fig. 10 COSY spectrum showing the *tt*-DPB<sub>d2</sub> region from the *ct*-DPB<sub>d2</sub> irradiation in C<sub>6</sub>D<sub>12</sub>.

marked as impurities. The amplitudes of those peaks did not change on irradiation. Cosy spectra for the *tt*-DPB photoproduct regions are shown in Fig. 9 and 10 starting from *ct*-DPB and *ct*-DPB<sub>d2</sub>, respectively.

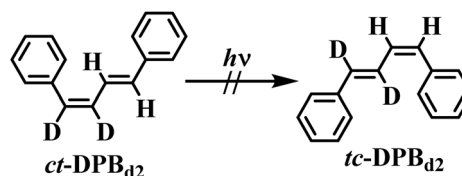
## Discussion

Zechmeister and coworkers established long ago that the DPBs undergo mainly one photon/one bond photoisomerization in hexane.<sup>23,24</sup> Minor two bond photoisomerization pathways were revealed by the more sensitive GC analysis in the *tt*-DPB → *cc*-DPB direction in hexane ( $\phi_{tt \rightarrow cc} = 0.002$ )<sup>10,11</sup> and in both the *tt*-DPB → *cc*-DPB ( $\phi_{tt \rightarrow cc} = 0.004$ )<sup>11</sup> and the *cc*-DPB → *tt*-DPB ( $\phi_{cc \rightarrow tt} = 0.03$ )<sup>11</sup> directions in ethanol. Furthermore, ether formation *via* trapping of twisted allylmethylene zwitterionic intermediates established that the *tt*-DPB → *cc*-DPB photoreaction in ethanol occurs by the sequential two-step mechanism shown in Scheme 1 and not by a concerted BP process. Involvement of zwitterionic intermediates has not been established in nonpolar, non-hydroxylic solvents. Starting from *ct*-DPB, photoisomerization quantum yields favour *tt*-DPB over *cc*-DPB formation by a factor of 17 in ethanol indicating that torsional relaxation to the *trans*-phenallylmethylene intermediate occurs much faster than torsional relaxation to the *cis*-phenallylmethylene intermediate, Scheme 1.<sup>11</sup> Decay is, therefore, primarily from <sup>1</sup>tp\*. This mechanism would account for an identity reaction if the distortion in the *trans*-allylmethylene intermediate were transferred from side to side: <sup>1</sup>tp\* ⇌ <sup>1</sup>pt\*, as occurs in 2,4-hexadiene triplets.<sup>25</sup>

The H<sub>a</sub> *trans* vinyl proton appears cleanly as a doublet at  $\delta$  6.6 in the 0-time <sup>1</sup>H NMR spectrum of *ct*-DPB<sub>d2</sub>, Fig. 3. The absence of *cis* vinyl protons that are evident at  $\delta$  6.35–6.45 in the *ct*-DPB <sup>1</sup>H NMR spectrum, Fig. 1, shows that our synthesis yielded the desired product. The product that would form from the identity *ct*- to *tc*-DPB reaction is shown in Scheme 2. It has a deuterated *trans* double bond and protons in the *cis* double bond. The *cis* vinyl protons of *tc*-DPB<sub>d2</sub> would be observed at  $\delta$  6.35–6.45 if the BP process contributed to <sup>1</sup>ct-DPB\* decay. The fact that that region is unchanged establishes the absence of the BP photoproduct under conditions that allow conversion to *tt*-DPB<sub>d2</sub>, Fig. 7, to be easily observed. It is



Scheme 1 Sequential two-bond photoisomerization of *cc*-DPB.<sup>11</sup>



Scheme 2 No *tc*-DPB<sub>d2</sub> BP photoproduct from *ct*-DPB<sub>d2</sub>.



reasonable to expect that decay of the *cis*-phenallylmethylene intermediate in Scheme 1 would give similar amounts of *cc*- and *tc*-DPB. The  $\phi_{ct \rightarrow cc}$  value is not known in cyclohexane, but if we use the quantum yield ratio in ethanol<sup>11</sup> as a guide and assume  $\phi_{ct \rightarrow tc} \approx \phi_{ct \rightarrow cc}$  then the yield of *tc*-DPD<sub>d2</sub> would be too small to detect in our experiment.

## Conclusions

We showed that the BP process does not play a significant role in the photochemistry of *ct*-DPB. Assuming that the decays of the phenallylmethylene intermediates in Scheme 1 give *cis* and *trans* double bonds with equal probability, the fraction of <sup>1</sup>*ct*-DPB\* that avoid torsional relaxation by undergoing radiationless decay directly to the *ct*-DPB ground state can be estimated from  $\phi_{ic} = 1 - 2\phi_{ct \rightarrow tt}$ , where  $\phi_{ic}$  is the quantum yield of internal conversion. Values of  $\phi_{ic}$  range from a low of ~0.65 in benzene to a high of 0.88 in saturated hydrocarbon solvents.<sup>10,11</sup> Similarly large  $\phi_{ic}$  values were estimated for <sup>1</sup>*tt*-DPB\* where decay *via* an unreactive 2<sup>1</sup>A<sub>g</sub> state was implicated.<sup>10</sup> An unreactive 2<sup>1</sup>A-like state may also be involved in the decay of <sup>1</sup>*ct*-DPB\*.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This research was supported by the National Science Foundation, most recently by Grant No. CHE-1361962, and by the Florida State University.

## Notes and references

- S. Malkin and E. Fischer, Temperature Dependence of Photoisomerization. III. Direct and Sensitized Photoisomerization of Stilbenes, *J. Phys. Chem.*, 1964, **68**, 1153–1163.
- S. Sharafy and K. A. Muszkat, Viscosity Dependence of Fluorescence Quantum Yields, *J. Am. Chem. Soc.*, 1971, **93**, 4119–4125.
- M. Sumitani, N. Nakashima, K. Yoshihara and S. Nagakura, Temperature Dependence of Fluorescence Lifetimes of *trans*-Stilbene, *Chem. Phys. Lett.*, 1977, **51**, 183–185.
- J. L. Charlton and J. Saltiel, An Analysis of *trans*-Stilbene Fluorescence Quantum Yields and Lifetimes, *J. Phys. Chem.*, 1977, **81**, 1940–1944.
- J. Saltiel and J. L. Charlton, Cis-Trans Isomerization of Olefins, in *Rearrangements in Ground and Excited States*, ed. P. de Mayo, 1980, vol. III, pp. 25–89.
- J. Saltiel and Y.-P. Sun, Cis-Trans Isomerization of C,C Double Bonds, in *Photochromism, Molecules and Systems*, ed. H. Dürr and H. Bouas-Laurent, Elsevier, Amsterdam, 1990, pp. 64–164.
- D. H. Waldeck, Photoisomerization Dynamics of Stilbenes, *Chem. Rev.*, 1991, **91**, 415–436.
- L. R. Eastman Jr., B. M. Zarnegar, J. M. Butler and D. G. Whitten, Unusual Case of Selectivity in a Photochemical Reaction. Photoisomerization of Unsymmetrical 1,3-Dienes, *J. Am. Chem. Soc.*, 1974, **96**, 2281–2282.
- W. A. Yee, S. J. Hug and D. S. Kliger, Direct and Sensitized Photoisomerization of 1,4-Diphenylbutadienes, *J. Am. Chem. Soc.*, 1988, **110**, 2164–2169.
- J. Saltiel, T. S. R. Krishna, S. Laohhasurayotin, Y. Ren, K. Phipps, W. A. Yee and P. H. Davis, Medium Effects on the Direct Cis-Trans Photoisomerization of 1,4-Diphenyl-1,3-butadiene in Solution, *J. Phys. Chem. A*, 2011, **115**, 2120–2129.
- J. Saltiel and C. E. Redwood, Photochemistry of the 1,4-Diphenyl-1,3-butadienes in Ethanol. Trapping Conical Intersections, *J. Phys. Chem. A*, 2016, **120**, 2832–2840.
- J. Saltiel, T. S. R. Krishna and R. J. Clark, Photoisomerization of *cis,cis*-1,4-Diphenyl-1,3-butadiene in the Solid State: The Bicycle-Pedal Mechanism, *J. Phys. Chem. A*, 2006, **110**, 1694–1697.
- J. Saltiel, T. S. R. Krishna, S. Laohhasurayotin, K. Fort and R. J. Clark, Photoisomerization of *cis,cis*- to *trans,trans*-1,4-Diaryl-1,3-butadienes in the Solid State: The Bicycle-Pedal Mechanism, *J. Phys. Chem. A*, 2008, **112**, 199–209.
- J. Saltiel, T. S. R. Krishna, A. M. Turek and R. J. Clark, Photoisomerization of *cis,cis*-1,4-Diphenyl-1,3-butadiene in Glassy Media at 77 K: The Bicycle-Pedal Mechanism, *J. Chem. Soc., Chem. Commun.*, 2006, 1506–1508.
- J. Saltiel, M. A. Bremer, S. Laohhasurayotin and T. S. R. Krishna, 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, *Angew. Chem., Int. Ed.*, 2008, **47**, 1237–1240.
- A. Warshel, Bicycle-Pedal Model for the First Step in the Vision Process, *Nature*, 1976, **260**, 679–683.
- J. Saltiel, D.-H. Ko and S. A. Fleming, Differential Medium Effects on the Trans to Cis Photoisomerization of *all-trans*-1,6-Diphenyl-1,3,5-hexatriene. Competing Diradicaloid vs Zwitterionic Pathways, *J. Am. Chem. Soc.*, 1994, **116**, 4099–4100.
- J. Saltiel, S. Wang, L. P. Watkins and D.-H. Ko, Direct Photoisomerization of the 1,6-Diphenyl-1,3,5-hexatrienes. Medium Effect on Triplet and Singlet Contributions, *J. Phys. Chem. A*, 2000, **104**, 11443–11450.
- J. Saltiel, C. E. Redwood, K. Laohhasurayotin and R. Samudrala, Photochemistry of the 1,6-Dideuterio-1,3,5-hexatrienes in Solution: Efficient Terminal Bond Photoisomerization in One-Bond-Twist and Bicycle Pedal Ways, *J. Phys. Chem. A*, 2018, **122**, 8477–8489.
- W. S. Wadsworth Jr., Synthetic Applications of Phosphoryl Substituted Anions, *Org. React.*, 1977, **25**, 73–253.
- J. Saltiel, A. D. Rousseau and A. Sykes, Temperature and Viscosity Effects on the Decay Characteristics of *s-trans*-1,3-Diene Triplets, *J. Am. Chem. Soc.*, 1972, **94**, 5903–5905.

- 22 G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt and C. Dalton, Photochemical Cis-Trans Isomerization, *J. Am. Chem. Soc.*, 1964, **86**, 3197–3217.
- 23 A. Sandoval and L. Zechmeister, Spectroscopic Changes Connected with the Stereoisomerization of Diphenylbutadiene, *J. Am. Chem. Soc.*, 1947, **69**, 553–557.
- 24 J. H. Pickard, B. Wille and L. Zechmeister, A Comparative Study of the Three Stereoisomeric 1,4-Diphenylbutadienes, *J. Am. Chem. Soc.*, 1948, **70**, 1938–1944.
- 25 J. Saltiel, A. D. Rousseau and A. Sykes, Temperature and Viscosity Effects on the Decay Characteristics of *s-trans*-1,3-Diene Triplets, *J. Am. Chem. Soc.*, 1972, **94**, 5903–5905.