

Triplet and ground state potential energy surfaces of 1,4-diphenyl-1,3-butadiene: theory and experiment†‡

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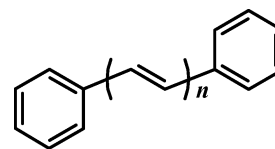
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Relative energies of the ground state isomers of 1,4-diphenyl-1,3-butadiene (DPB) are determined from the temperature dependence of equilibrium isomer compositions obtained with the use of diphenyl diselenide as catalyst. Temperature and concentration effects on photostationary states and isomerization quantum yields with biacetyl or fluorenone as triplet sensitizers with or without the presence of O₂, lead to significant modification of the proposed DPB triplet potential energy surface. Quantum yields for *ct*-DPB formation from *tt*-DPB increase with [*tt*-DPB] revealing a quantum chain process in the *tt* → *ct* direction, as had been observed for the *ct* → *tt* direction, and suggesting an energy minimum at the ³*ct** geometry. They confirm the presence of planar and twisted isomeric triplets in equilibrium (*K*), with energy transfer from planar or quasi-planar geometries (quantum chain events from *tt* and *ct* triplets) and unimolecular decay (*k_d*) from twisted geometries. Starting from *cc*-DPB, $\phi_{cc \rightarrow tt}$ increases with increasing [*cc*-DPB] whereas $\phi_{cc \rightarrow ct}$ is relatively insensitive to concentration changes. The concentration and temperature dependencies of the decay rate constants of DPB triplets in cyclohexane are consistent with the mechanism deduced from the photoisomerization quantum yields. The experimental ΔH between ³*tt*-DPB* and ³*tp*-DPB*, 2.7 kcal mol⁻¹, is compared with the calculated energy difference [DFT with B3LYP/6-31+G(d,p) basis set]. Use of the calculated $\Delta S = 4.04$ eu between the two triplets gives *k_d* = (2.4–6.4) × 10⁷ s⁻¹, close to 1.70 × 10⁷ s⁻¹, the value for twisted stilbene triplet decay. Experimental and calculated relative energies of DPB isomers on the ground and triplet state surfaces agree and theory is relied upon to deduce structural characteristics of the equilibrated conformers in the DPB triplet state.

1 Introduction

Because the quantum yield of intersystem crossing of *tt*-DPB in solution, $\phi_{is} = 0.02$,¹ is low, studies of the photoisomerization behaviour of DPB triplets have relied on triplet excitation transfer to the DPB isomers.^{2,3} Triplet excitation energies (*trans* double bonds) and lifetimes for the first three members of the diphenylpolyene series, Scheme 1, *n* = 1–3, are summarized in Table 1. Triplet energies, *E_T*, based on triplet excitation transfer, phosphorescence and S₀ → T₁ measurements, show that *E_T* for *tt*-DPB, 42 kcal mol⁻¹,^{1b,4-7} is almost equal to the average of the triplet energies of its diphenylpolyene relatives, *trans*-stilbene, *t*-St, 49 kcal mol⁻¹,⁴⁻⁶ and *ttt*-DPH, 34 kcal mol⁻¹.^{1a,4} Medium and *T* effects on the triplet lifetimes similarly reveal intermediate behaviour for DPB. In glassy media at 77 K torsional excursions



Scheme 1

Table 1 Diphenylpolyene triplet behaviour; the first three members of the series^a

<i>n</i>	<i>E_T</i> /kcal mol ⁻¹	$\tau_{77\text{K}}$ /ms	$\tau_{300\text{K}}$ /μs	$\sim t/c$ decay
1, <i>t</i> -St	49	22	0.060	0.5/0.5
2, <i>tt</i> -DPB	42	2.5	1.60	0.5/0.5 ^b
3, <i>ttt</i> -DPH	34	0.4	60	0.94.0.05/0.01 ^c

^a See text for references. ^b *tt*/*ct*. ^c *ttt*/*tct*/*ctt*.

to twisted geometries are inhibited and decay is primarily from nearly planar triplets in which transoid geometries about S₀ double bonds are maintained.^{7,8} As expected, decay rate constants in diethyl ether–isopentane–ethanol (5 : 5 : 2, EPA) increase with decreasing T₁–S₀ energy gap, Table 1.⁷ The opposite lifetime trend is observed in fluid hydrocarbon solution at ambient *T*. Under those conditions the triplets exist as freely equilibrating

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‡ Electronic supplementary information (ESI) available: Cartesian coordinates, drawings, and total energies of optimized structures and transition states in S₀ and T₁. See DOI: 10.1039/b801075g

conformer mixtures whose compositions are governed by the respective triplet potential energy surfaces. T_1 - S_0 energy gaps vanish at almost perpendicular geometries and twisted triplets are characterized by large decay rate constants and nearly equal partitioning fractions to *trans* and *cis* isomers. St and DPH represent two extreme cases because extension of conjugation lowers the triplet energies of planar conformers more than those of twisted conformers. Both St and DPH have rather flat triplet potential energy surfaces with respect to torsional motion about formerly olefinic double bonds in S_0 . However, the perpendicular geometry, ${}^3p^*$, corresponds to an energy minimum in stilbene,^{9,10} whereas perpendicular geometries, ${}^3ptt^*$ and ${}^3tp^*$, can be regarded as energy maxima in DPH.¹¹ Decay from ${}^3p^*$ triplets in St and from roughly planar ${}^3ttt^*$, ${}^3tct^*$ and ${}^3ctt^*$ triplets in DPH accounts for the 1000-fold difference in triplet lifetimes (~ 60 ns for stilbene,¹⁰ ~ 60 μ s for DPH¹¹). Roughly equal partitioning between ground state isomers in St is consistent with decay from a perpendicular triplet,^{9,10} whereas the DPH decay fractions reflect an equilibrium distribution of ${}^3ttt^*$, ${}^3tct^*$ and ${}^3ctt^*$ triplets that strongly favours ${}^3ttt^*$.¹¹

The initial report by Whitten and co-workers that biacetyl ($E_T = 55$ kcal mol⁻¹)¹² is an effective photosensitizer for *tt*- to *ct*-DPB isomerization,³ was followed by a detailed study of the fluorenone-sensitized ($E_T = 53$ kcal mol⁻¹)¹² photoisomerization of the DPBs by Yee and co-workers.² They observed that quantum yields in the *ct* \rightarrow *tt* direction, $\phi_{ct \rightarrow tt}$, and photostationary state *trans,trans* to *cis,trans* isomer ratios, $([tt]/[ct])_s$, increase considerably with increasing DPB concentration. The same triplet transient absorption spectrum was observed at low [DPB] starting from all three DPB isomers. It was concluded that the triplet potential energy surface of DPB is rather flat with a shallow minimum close to the *trans,trans* (${}^3tt^*$) geometry and, another energetically slightly higher minimum, at the *trans,perpendicular* (${}^3pt^*$) geometry. Similar conclusions concerning the geometry and energetics of DPB triplets had been reached by Das *et al.* on the basis of triplet quenching studies.^{1b} According to that model, at low DPB concentrations unimolecular decay from ${}^3pt^*$ gives *tt*- and *ct*-DPB with partitioning fractions of 0.55 and 0.45, respectively, and at higher *ct*-DPB concentrations a quantum chain process involving triplet excitation transfer from ${}^3tt^*$ to *ct*-DPB accounts for enhanced $\phi_{ct \rightarrow tt}$ and $([tt]/[ct])_s$ values.² The presence of a potential energy minimum at the *cis,trans* geometry, ${}^3ct^*$, or significant decay from such a geometry was ruled out. Decay from a *cis,twisted*, ${}^3cp^*$, geometry was ruled out because *cc*-DPB was not detected as a photoproduct from the other isomers or as a component in photostationary mixtures. Instead, irradiation of fluorenone in the presence of 2.6×10^{-4} M *cc*-DPB in cyclohexane was reported to yield a photostationary state containing 37% *ct*-DPB and 63% *tt*-DPB.²

Our study of the triplet sensitized photoisomerization of *tt*- and *cc*-DPB complements the Yee study and leads to a more complete understanding of the energetics of the triplet energy surface of DPB. Contrary to Yee's conclusion,² ${}^3ct^*$ and ${}^3cp^*$ DPB triplets are energetically accessible and play important roles in the photoisomerization. Furthermore the *T* dependencies of DPB equilibrium isomer mixtures and triplet lifetimes allow a more precise evaluation of the energetics of S_0 and T_1 DPB potential energy surfaces and a meaningful comparison with theoretical predictions.

2 Experimental

2.1 Materials

Unless stated otherwise, reagents and solvents were obtained from commercial sources and used as received. Cyclohexane (Fisher, HPLC Grade) was distilled over P_2O_5 before use. Fluorenone (Aldrich, 98%) was purified by Dr Donald Sears, Jr., by column chromatography on alumina with benzene as eluent followed by recrystallization twice from 95% ethanol to $\geq 99.97\%$ purity *via* GC. Biacetyl (Aldrich, 97%) was distilled twice at atmospheric pressure using an 8 in. vacuum jacketed and silvered column. The fraction boiling at 87.5–88.0 °C was collected and stored under nitrogen in a refrigerator. *tt*-DPB (Aldrich, reagent) was recrystallized from ethanol. *cc*-DPB was synthesized using a modification of a previously described procedure.¹³ 1,4-Diphenylacetylene (Aldrich) was dissolved in methanol and reduced to *cc*-DPB (65% by GC) with H_2 over Lindlar's Pd. Addition of water followed by extraction with methylene chloride, drying over anhydrous sodium sulfate and solvent evaporation yielded the organic mixture as a yellow oil. The pure (99.7%, GC) *cc*-DPB was obtained by recrystallization twice from methanol. Methanol (Fisher, HPLC grade) was used as received for preparing the oscillator and amplifier solutions for the laser. DCM laser dye (Exciton) was used as received. Benzene (Fisher, spectranalyzed) was passed through an alumina column and *tert*-butylbenzene (Aldrich) was distilled prior to use, bp 167–169 °C, then passed through an alumina column.

2.2 Transient absorption studies

2.2.1 Instrumentation. Excitation laser pulses were generated by a Spectra-Physics Nd:YAG laser (Spectra-Physics DCR-3G) producing 8 ns pulses at 10 Hz. The laser fundamental (1064 nm) was frequency-doubled to 532 nm to pump a dye laser (Spectra-Physics PDL2) containing DCM dye producing tunable emission with $\lambda_{max} = 640$ nm. Dye emission was mixed with the residual 1064 nm fundamental of the Nd:YAG laser in a wavelength mixing module (Spectra-Physics WEX-1) to give 404 nm excitation. Transient absorption was monitored perpendicular to the excitation pulse using a 75 Watt Xe lamp (Oriel model 6251) powered by an Online Instruments, Inc. stabilized power supply. A monochromator (Jarrell Ash 82-410 0.25 m Ebert) was employed to select 400 nm, the monitoring wavelength. Solutions were placed in 1 cm² quartz cuvettes as described below. Photomultiplier (Hamamatsu R 928) output was detected with a digital oscilloscope (Lecroy 9410 dual-channel, 150 MHz bandwidth, 100 Msamples/s) where it was summed and averaged and then transferred to a computer. Pulse energy was monitored with an energy power meter (RJP-735, Laser Precision Corp.). Temperature was controlled with a PolyScience model 9101 Digital Temperature Controlled circulating water bath (50 : 50 water : ethylene glycol bath) and monitored with an Ertco-Eutechnics model 4400 Digital Thermometer. Waveforms were typically collected at 2 μ s intervals for 2000 pts. with a 10% pretrigger to record I_0 , averaged for 1000 pulses, with 50 Ω DC coupling and the bandwidth limit set at 20 MHz to eliminate high frequency noise. Power at the cell, measured using an Ophir 2A 2 W power meter averaged over 10 s, was 6 mW (0.6 mJ pulse⁻¹).

Measurement of fluorescence decay with the arc lamp off preceded measurement of transient absorption decay for each run.

2.2.2 Sample preparation. Three mL aliquots of 0.010 M fluorenone solutions containing the desired *tt*-DPB concentration in cyclohexane were delivered into degassing tubes (13 × 100 mm Pyrex test tubes) equipped with 10/30 standard-taper joints and grease traps and attached to quartz cell side arms (homemade from square quartz tubing) at a right angle *via* graded seals. They were then degassed under high vacuum (Edwards High Vacuum International, model 100 MK2 diffusion pump coupled with a floor vacuum pump) for 5 freeze–pump–thaw cycles to about 10^{−6} Torr. The pressure was measured using a 280 Digital Ionization Gauge Controller (Granville-Philips, model 270006). Each tube was flame sealed at a constriction. Sample preparation and degassing were performed under red light conditions and the samples were stored in the dark until needed.

2.3 Irradiation procedure

Solutions, 3.0 mL, were pipetted into Pyrex ampoules, 13 mm o.d., fitted with 10/30 standard-taper joints and grease traps. Degassing was as described above for the transient studies. Air-saturated solutions were stoppered lightly with Teflon covered stoppers. Sample preparation and degassing were performed under red light. Degassed samples were stored in the freezer until used. Irradiation at 20 °C were carried out in a Moses merry-go-round apparatus as previously described.¹⁴ Irradiations at different temperatures were carried out by placing the sample tubes in a small cylindrical merry-go-round attached to a stirring motor and immersed in a Pyrex dewar containing a transparent liquid thermostatted to the desired temperature. The excitation wavelength was selected by passing the light from an Osram HBO 200 W super-high-pressure lamp through a Bausch and Lomb high intensity monochromator as described previously.¹¹ The biacetyl sensitized photoisomerization of *trans*-stilbene in benzene was employed for actinometry ($\phi_{t \rightarrow c} = 0.49$ at 366 nm was determined for the actinometer using the benzophenone sensitized isomerization of *trans*-stilbene as standard).¹⁴ In some experiments fluorenone was employed as the sensitizer both for DPB and for stilbene actinometry ($\phi_{t \rightarrow c} = 0.47$).¹⁵ All conversions were corrected for back reaction.¹⁴

2.4 Thermal equilibration

Sample preparation, degassing and irradiation procedures were as described in section 2.3 except that the solutions contained 5.0 × 10^{−3} M of *tt*-DPB and of diphenyl diselenide (Ph₂Se₂) in benzene (Bz) and excitation to produce PhSe radicals was at 425 nm. The sum of UV-Vis absorption spectra measured for benzene solutions containing 5.0 × 10^{−3} M *tt*-DPB and 5.0 × 10^{−3} M Ph₂Se₂ alone was identical to that of the solution containing their mixture. To ensure that equilibration was complete at each, but the highest, temperature, duplicate tubes were irradiated for one and two h periods. The irradiated solutions were passed through a small silver nitrate coated alumina column and eluted with ~20 mL of benzene to remove the Ph₂Se₂. This was essential as Ph₂Se₂ interferes with the GC analysis. Each sample was prepared for GC analysis by placing it in a water bath maintained at ~50 °C and blowing a slow stream of N₂ across the top of it until the

volume was reduced to about 1 mL. GC analyses were carried out in triplicate. The solvent for the experiment at 98.3 °C was *tert*-butylbenzene (*t*-BuBz). The degassed samples were heated with refluxing water in an Abderhalden drying apparatus for 168 h in the dark.

2.5 Analytical procedures

Analysis of stilbene isomerization was by GC as described previously.¹⁶ Analysis of DPB isomerization was either by GC or by HPLC. A Varian 3300 gas chromatograph equipped with an electronic integrator was used with a DB-5 capillary column (17 m) Analyses were carried out at 12 psi He and an initial temperature of 170 °C held for 10 min followed by 1 °C min^{−1} ramp to 190 °C. Detector and injector temperatures were set at 250 °C. Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 5 UV-Vis spectrophotometer.

2.6 Computational details

Quantum mechanical calculations were carried out using the Gaussian98 program¹⁷ system utilizing gradient geometry optimization.¹⁸ All geometries were fully optimized using the B3LYP functional¹⁹ 6-31+G(d,p) basis set. The location of the triplet *EtZ* (*trans-s-trans-cis*) stationary point was also investigated using 6-311+G(3df,2p), the larger basis set. Vibrational frequency calculations at the same level of the geometry optimization were performed to characterize the stationary points as either minima or transition state structures (first-order saddle points). The cyclohexane solvent effect was investigated with B3LYP/6-31+G(d,p) + COSMO (solvent = cyclohexane) without ZPVE correction (structures fully optimized using the Gaussian03 program).

3 Results and discussion

3.1 The ground state

Equilibration of the DPB and DPH isomers was first reported by Zechmeister and co-workers who irradiated dilute hexane solutions in the presence of iodine.^{12,20} As we described earlier for DPH,^{11b} at the higher concentrations required for GC and HPLC analysis of isomeric compositions, this procedure leads to irreproducible isomerization results and interference by side reactions, especially at the higher *T*s. These problems were avoided by use of diphenyl diselenide as the free radical source. First used to equilibrate the stilbenes and other olefins by Alfimov and co-workers,²¹ this catalyst promotes isomerization by reversible addition of thermally or photochemically generated phenylselenium radicals to CC double bonds.^{11,22} The isomerization of the DPBs was cleanly and efficiently catalyzed under our conditions yielding the equilibrium constants K_{ct} and K_{cc} shown in Table 2 as defined by eqn (1) and (2), respectively.



Plots of the data according to

$$\ln K = -(\Delta H/RT) + (\Delta S/R) \quad (3)$$

Table 2 Temperature dependence of DPB isomer equilibrium ratios in the ground state

$T/^\circ\text{C}$	$10^2 K_{ct}$	$10^4 K_{cc}$
10.0	1.45	
20.2	1.56	1.11
30.0	1.99	1.47
40.0	2.42	
50.0	2.86	2.79
59.3	3.23	3.37
69.8	3.85	4.65
98.3 ^c	5.65	9.1

^a All duplicate samples 5×10^{-3} M DPB and 5×10^{-3} M Ph₂Se₂ in Bz were irradiated 1 and 2 h, respectively, unless otherwise indicated. ^b K_{ct} and K_{cc} values are averages of at 4–8 GC analyses; standard deviations were generally $\leq 5\%$ of the mean (2–7% range). ^c Thermal equilibration in *t*-BuBz; the K s are based on 2 GC analyses and values in parentheses are average deviations from the mean affecting the last significant figures shown.

are shown in Fig. 1 and give $\Delta H = 3.3 \pm 0.1$ and 5.9 ± 0.1 kcal mol⁻¹ and $\Delta S = 3.1 \pm 0.2$ and 1.8 ± 0.3 cal mol⁻¹ K for $[ct]/[tt]$ and $[cc]/[tt]$ equilibrium ratios, respectively. Uncertainties in enthalpy and entropy values reflect the reproducibility of multiple GC analyses. Actual uncertainties may be larger, especially for K_{cc} because the GC analysis for *cc*-DPB was close to the detection limit. As described in the theoretical section the enthalpy differences are close to calculated values. Slightly positive entropy differences are consistent with the relative nonplanarity in the *cis* isomers because they are expected to explore larger ranges of torsional space.^{11,23}

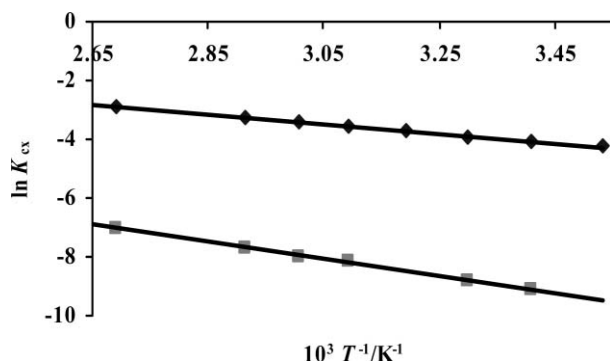
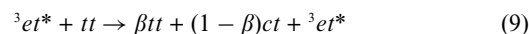
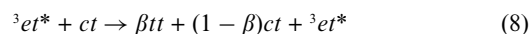
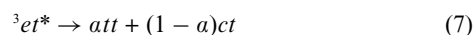


Fig. 1 Thermal equilibrium constants defined in eqn (1) and (2) plotted according to eqn (3).

3.2 The triplet state

3.2.1 Photoisomerization quantum yields. As pointed out in the introduction, Yee *et al.* using fluorenone, F, as the triplet sensitizer observed strong dependencies of $\phi_{ct \rightarrow tt}$ and $([tt]/[ct])_s$ values on [DPB].² With formation of triplet sensitizer omitted, their proposed photoisomerization mechanism is given by eqn (4)–(9).



$$\phi_{ct \rightarrow tt} = a + \beta k_{ct} \tau [ct] \quad (10)$$

Excitation transfer from fluorenone triplets to the DPB isomers, being almost 10 kcal mol⁻¹ exothermic, was as expected, found to be indiscriminate and close to the diffusion controlled limit ($k_{ct}^{ct} = k_{ct}^{tt} = 5 \times 10^9$ M⁻¹ s⁻¹ for *ct*- and *tt*-DPB, respectively).² Fast formation of the equilibrated triplet ${}^3et^*$ (assumed $\equiv {}^3tt^* \rightleftharpoons {}^3pt^*$) from either DPB isomer is consistent with the transient absorption measurements. Analysis of the data on the basis of this mechanism led to the conclusion that DPB triplets decay mainly from ${}^3pt^*$, partitioning almost equally ($a = 0.69$ and 0.55 from the dependence of $\phi_{ct \rightarrow tt}$ and $([tt]/[ct])_s$ values on [DPB], respectively) between *tt*- and *ct*-DPB.² Treatment of the [DPB] dependence, based on eqn (10), where k_{ct} is the rate constant for the quantum chain process in eqn (8) and τ is the lifetime of the DPB triplet state, gave $a = 0.69$ and $\beta k_{ct} \tau = 1020$ M⁻¹.² Similarly, treatment of the dependence of $([tt]/[ct])_s$ values on [DPB] gave $a = 0.55$ and $\beta = 0.96$ – 0.98 ; the small deviation of β from unity suggesting that eqn (9) can be regarded as an identity reaction.

$$\phi_{tt \rightarrow ct} = (k_{ct}^{ct}/k_{ct}^{tt})\phi_{ct \rightarrow tt}([ct]/[tt])_s \quad (11)$$

The mechanism in eqn (4)–(9), although in the main satisfactory, is questionable in two respects. First, the assumption of identical partitioning fractions β from the interaction of *ct*- and *tt*-DPB ground state molecules with the equilibrated DPB triplet state is unjustified, and second, it is silent on the presence of a significant quantum chain process in the *tt*- to *ct*-DPB direction, which can be inferred from the relationship of the quantum yields and the photostationary states, eqn (11). Setting the ratio of energy transfer rate constants to unity, substitution of experimental quantities in eqn (9) predicts that $\phi_{tt \rightarrow ct}$ values should increase from 0.50 to 1.33 in the 0–0.023 M [*tt*-DPB] range. This prediction was confirmed experimentally in this work, Table 3. Back reaction corrections were applied to isomerization conversions using the known photostationary states.² The modest increase in $\phi_{tt \rightarrow ct}$ agrees well with the calculated values from the results of Yee *et al.*² and suggests that ${}^3ct^*$ transfers excitation to *tt*-DPB and must be included as an accessible conformation of the equilibrated DPB triplet. Conversions to *cc*-DPB were too low for accurate quantum yield determination. However, we established the presence of *cc*-DPB in photoequilibrium mixtures (see below). Because *cc*-DPB most likely forms on ${}^3cp^*$ decay, the latter must also contribute, albeit to a very small extent, to the equilibrated DPB triplet.

Table 3 Concentration dependence of $\phi_{tt \rightarrow ct}$ for the biacetyl-sensitized photoisomerization of *tt*-DPB in degassed CH₂, 430 nm, 20 °C^a

[<i>tt</i> -DPB]/M	$\phi_{tt \rightarrow ct}$	[<i>tt</i> -DPB]/M	$\phi_{tt \rightarrow ct}$	[<i>tt</i> -DPB]/M	$\phi_{tt \rightarrow ct}$
0.00048	0.35	0.0036	0.58	0.0096	0.89
0.00096	0.42	0.0060	0.66	0.012	1.01

^a Average values from 3–5 independent irradiations; estimated error $\pm 5\%$; 0.20 M biacetyl was used for both DPB and St actinometer solutions.

Table 4 Concentration dependence of $\phi_{cc \rightarrow tt}$ and $\phi_{cc \rightarrow ct}$ for the biacetyl-sensitized photoisomerization of *cc*-DPB in degassed CH, 460 nm, 20 °C^a

<i>cc</i> -DPB/mM	$\phi_{cc \rightarrow ct}$	$\phi_{cc \rightarrow tt}$	$\phi_{cc \rightarrow tt}/\phi_{cc \rightarrow ct}$
0.5	0.51	0.54	1.06
1.03	0.50	0.66	1.48
2.15	0.39	0.66	1.67
3.59	0.42	0.84	1.99
4.00	0.34	0.83	2.44
6.0	0.33	0.98	3.0
10.0	0.29	1.2	4.2

^a Average values from two or more independent experiments; estimated error $\pm 15\%$ for $\phi_{cc \rightarrow tt}$ and $\pm 20\%$ for $\phi_{cc \rightarrow ct}$.

Quantum yields for the photoisomerization of *cc*-DPB were measured in cyclohexane using both biacetyl and fluorenone as triplet sensitizers. The results consistently reproduced an increasing trend in the *tt*-DPB direction with increasing [*cc*-DPB]. However, quantum yields in the *ct*-DPB direction, although less sensitive to [*cc*-DPB], showed no reproducible trend with change in concentration. Average $\phi_{cc \rightarrow ct}$ values of 0.41 ± 0.06 (GC analysis) and 0.40 ± 0.07 (HPLC analysis) were obtained for the biacetyl- and fluorenone-sensitized isomerizations, respectively, for [*cc*-DPB] in the 10^{-3} – 10^{-2} M range. The results in Table 4 are typical. The changes in the $\phi_{cc \rightarrow tt}$ values are very close to those for $\phi_{tt \rightarrow ct}$ in Table 3, indicating that a modest quantum chain process operates in the *cc*- to *tt*-DPB direction. In contrast to the $\phi_{cc \rightarrow tt}$ values, the $\phi_{cc \rightarrow ct}$ values in Table 4 decrease with increasing [*cc*-DPB], suggesting that they are subject to a small quenching interaction. However, in view of the small changes involved and the fact that this trend was not reproduced in independent experiments, we are reluctant to consider this result as outside experimental error. Treatment of the quantum yields in this section will follow the presentation of the transient observations.

$$k_{\text{obsd}} = [K_{\text{tp}}/(1 + K_{\text{tp}})]k_{\text{d}} \quad (12)$$

3.2.2 Transient observations. Transient spectroscopic decay measurements have yielded lifetimes for the equilibrated² DPB triplet state of 2.6 ± 0.2 and 1.6 ± 0.2 μs in Bz^{1b} and CH,² respectively. The lifetime was reported to be independent of [DPB] in CH over a 100-fold concentration range² which, however, was lower than the range employed in the photoisomerization studies.²⁴ Consideration of the relative magnitude of triplet energy transfer rate constants from DPB to lower triplet energy acceptors and of quenching rate constants by the spin exchange quenchers molecular oxygen and di(*tert*-butyl)nitroxide led to the conclusion that the equilibrated DPB triplet in benzene could be represented as ${}^3tt^* \rightleftharpoons {}^3pt^*$ with $K_{\text{tp}} = 0.6$.^{1b} Because the photoisomerization results are consistent with decay predominantly from ${}^3pt^*$, the observed DPB triplet decay rate constant, k_{obsd} is given by eqn (12), where k_{d} is the decay rate constant of the 1-phenylallyl-benzyl twisted triplet. Substitution of the k_{obsd} and K_{tp} values in eqn 12 gave $k_{\text{d}} = 1.0 \times 10^6 \text{ s}^{-1}$ in benzene at 25 °C.^{1b}

The same analysis had been applied successfully to the analogous decay model for stilbene triplets.^{9,10} Comparison of the results for the two systems is instructive. For stilbene triplets in benzene at ambient *T* (20–22 °C) use of $K_{\text{tp}} = 5$ and the observed lifetime of 70 ns¹⁰ gives $k_{\text{d}} = 1.7 \times 10^7 \text{ s}^{-1}$, more than an order of magnitude larger than the corresponding value for DPB.^{9c} The fact that

Table 5 *T* dependence of DPB triplet decay rate constants in CH^a

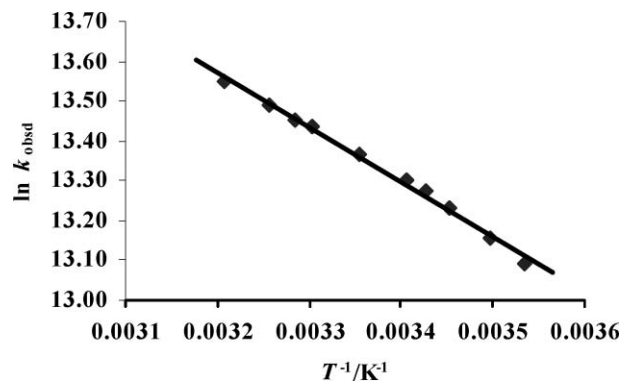
<i>T</i> /°C	$10^5 k_{\text{obsd}}/\text{s}^{-1}$	<i>T</i> /°C	$10^5 k_{\text{obsd}}/\text{s}^{-1}$	<i>T</i> /°C	$10^5 k_{\text{obsd}}/\text{s}^{-1}$
9.7 ₂	4.85	18.6 ₃	5.81	29.5 ₀	6.85
12.7 ₆	5.16	20.3 ₈	5.99	31.3 ₂	6.96
16.4 ₈	5.58	24.8 ₈	6.37	33.9 ₉	7.23

^a Fluorenone (0.010 M) and *tt*-DPB (5.0×10^{-4} M) in degassed; excitation pulse and monitoring wavelengths were 404 and 400 nm, respectively.

the stilbene triplet lifetime is *T* independent within experimental uncertainty,¹⁰ is consistent with K_{tp} large and k_{d} *T*-independent in eqn (12).

In order to properly apply eqn (12) to DPB triplet decay, we measured the *T* dependence of DPB's triplet decay rate constants in degassed CH, Table 5. In contrast to stilbene triplets, a pronounced *T* dependence is observed suggesting that ${}^3pt^*$ lies significantly higher in energy than ${}^3tt^*$, such that K_{tp} is significantly smaller than the previous estimate. For $K_{\text{tp}} \ll 1$, eqn (12) reduces to $k_{\text{obsd}} = K_{\text{tp}}k_{\text{d}}$. Assuming that k_{d} , the decay rate constant of ${}^3pt^*$, is *T* independent as in stilbene and neglecting the entropy difference between ${}^3tt^*$ and ${}^3pt^*$, the slope of the plot of $\ln k_{\text{obsd}}$ vs. T^{-1} (K) should equal the enthalpy difference between these two triplet conformers and the intercept of that plot should equal $k_{\text{d}} + {}^3\Delta S_{\text{tp}}/R$. Plotted in this way in Fig. 2, the data give ${}^3\Delta H_{\text{tp}} = 2.74 \pm 0.02 \text{ kcal mol}^{-1}$ and $k_{\text{d}} = 6.4 \times 10^7 \text{ s}^{-1}$ (assuming ${}^3\Delta S_{\text{tp}} = 0$, with ${}^3\Delta S_{\text{tp}} = 2 \text{ eu}$, $k_{\text{d}} = 2.4 \times 10^7 \text{ s}^{-1}$). Solving for K_{tp} in eqn (12) gives

$$K_{\text{tp}} = k_{\text{obsd}}/(k_{\text{d}} - k_{\text{obsd}}) \quad (13)$$

**Fig. 2** Dependence of DPB triplet decay rate constants on *T*.

Substitution of the derived k_{d} value and the k_{obsd} values in Table 5 into eqn (13) gives K_{tp} values that range between 7.6×10^{-3} and 1.20×10^{-2} . Fully two orders of magnitude smaller than the previous estimate for Bz,^{1b} our K_{tp} values for CH justify the $K_{\text{tp}} \ll 1$ assumption that was used in their derivation. The derived k_{d} value is sensibly very close to the corresponding value for stilbene.

Our previous study on DPH triplets revealed a significant self-quenching interaction in competition with quantum chain excitation transfer events.^{11a} The absence of a concentration effect on the lifetime of DPB triplets in CH² appeared to be in contradiction to the report of a substantial self-quenching rate constant, $k_{\text{sq}} = 1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, in Bz.^{1b} The discrepancy was due, at least in part, to the different concentration ranges employed in the two studies.²⁴ We measured the dependence of DPB triplet decay rate constants on [*tt*-DPB] because self-quenching might have to be taken into

Table 6 Concentration dependence of DPB triplet decay rate constants in CH, 22 °C^a

[<i>tt</i> -DPB]/M	$k_{\text{obsd}}/\text{s}^{-1}$	[<i>tt</i> -DPB]/M	$k_{\text{obsd}}/\text{s}^{-1}$
0.502	6.25	2.01	6.43
1.00	6.32	4.02	6.64

^a Fluorenone (10^{-2} M) was used as sensitizer as in Table 5.

account in the interpretation of the photoisomerization quantum yields in the preceding section and because it was necessary to eliminate the possibility that the rate constants in Table 5 are not strictly unimolecular because they include a concentration term. Table 6 shows our results which are plotted according to eqn (14) in Fig. 3.

$$k_{\text{obsd}} = k_{\text{d}} + k_{\text{sq}}[\textit{tt}\text{-DPB}] \quad (14)$$

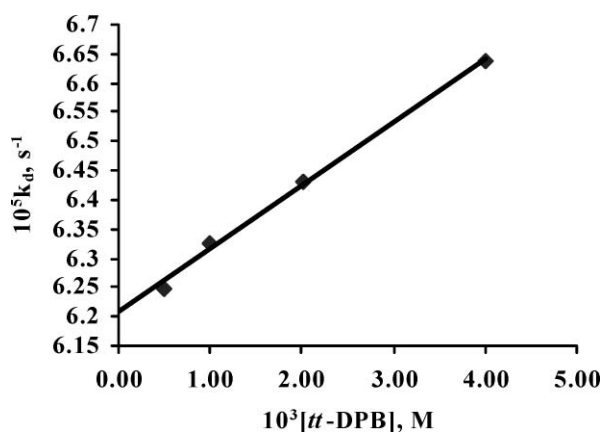
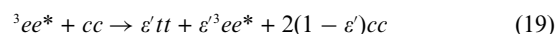
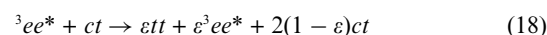
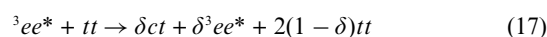
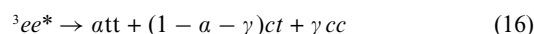
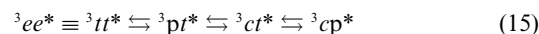


Fig. 3 Dependence of DPB triplet decay rate on [*tt*-DPB].

The slope of the plot in Fig. 3 gives $k_{\text{sq}} = (1.08 \pm 0.04) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and the intercept gives $k_{\text{d}} = 6.21 \times 10^5 \text{ s}^{-1}$ at 22 °C in CH. The k_{d} value corresponds to a triplet lifetime, τ , of 1.61 μs in excellent agreement with the value reported by Yee *et al.*² The self-quenching rate constant in CH is considerably smaller than the value reported for Bz,^{1b} being similar in magnitude to the analogous rate constant for the quenching of DPH triplets by *ttt*-DPH, $k_{\text{sq}} = 6.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, in methylcyclohexane.^{11a} The assumption that the decay rate constants in Table 5 are unimolecular was justified because the contribution of the self-quenching term is smaller than 1% of k_{d} at [*tt*-DPB] = $5.0 \times 10^{-4} \text{ M}$ at 22 °C.

3.2.3. Revised mechanism and treatment of photoisomerization quantum yields. The observation of a quantum chain process in the *tt*- to *ct*-DPB direction, the presence of *cc*-DPB in photostationary mixtures (see section 3.2.4) and the self-quenching of DPB triplets require refinement of the photoisomerization mechanism in eqn (6)–(9). Assuming that triplet energy transfer occurs from planar, or for the *cis* isomers quasi-planar, DPB triplet geometries, requires that ${}^3\textit{ct}^*$ contribute to the equilibrated triplet. Furthermore, because ${}^3\textit{cp}^*$ is the probable precursor of *cc*-DPB, that geometry must also be accessible. Because the DPB triplet equilibration involves both CC bonds of the diene moiety, we rename it ${}^3\textit{ee}^*$, eqn (15), and include *cc*-DPB as a minor decay product, eqn (16). The treatment of the concentration dependence

of the isomerization quantum yields can now be based on the bimolecular interactions in eqn (17)–(19). As far as unimolecular decay is concerned, eqn (16) is almost equivalent to eqn (7) because the fraction of DPB triplets, γ , that decay to *cc*-DPB is very small. Eqn (17)–(19) combine excitation transfer and self-quenching interactions between appropriate conformers of the DPB triplet and each ground state DPB isomer. For example, in eqn (17) δ is the fraction of productive interactions between ${}^3\textit{ee}^*$ and *tt*-DPB that lead to excitation transfer with formation of *ct*-DPB and $(1 - \delta)$ is the fraction of self-quenching interactions. This approach has been used in interpreting quantum chain and self-quenching interactions between equilibrated DPH triplets and ground state DPH isomers.^{11a}



The [*tt*-DPB] dependence of $\phi_{\textit{tt} \rightarrow \textit{ct}}$ is given by eqn (20), where $K_{\text{sq}}^{\textit{tt}} = (1 - \delta)k_{\text{tt}}\tau = k_{\text{sq}}^{\textit{tt}}\tau$ is the self-quenching constant, 17.4 M^{-1} derived from the plot in Fig. 3, k_{tt} is the combined rate constant for eqn (17) and ϕ_{is} , the intersystem crossing yield of the triplet sensitizer, can be set equal to unity for biacetyl²⁵ and fluorenone²⁶ in CH. The decay fraction γ was neglected in eqn (20) and (21) because *cc*-DPB is not observed at low *tt*- to *ct*-DPB conversions. The quantum yields in Table 3 adhere well to the rearranged eqn (21), Fig. 4, giving $(1 - a) = 0.34$ and $\delta k_{\text{tt}}\tau = 72_8 \text{ M}^{-1}$ from the intercept and slope, respectively. It follows that the excitation transfer rate constant from ${}^3\textit{ee}^*$ to *tt*-DPB is $\delta k_{\text{tt}} = 4.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $\delta = 0.81$.

$$(\phi_{\textit{tt} \rightarrow \textit{ct}}/\phi_{\text{is}}) = \{(1 - a) + \delta k_{\text{tt}}\tau[\textit{tt}]\} / \{1 + K_{\text{sq}}^{\textit{tt}}[\textit{tt}]\} \quad (20)$$

$$(\phi_{\textit{tt} \rightarrow \textit{ct}}/\phi_{\text{is}})\{1 + K_{\text{sq}}^{\textit{tt}}[\textit{tt}]\} = (1 - a) + \delta k_{\text{tt}}\tau[\textit{tt}] \quad (21)$$

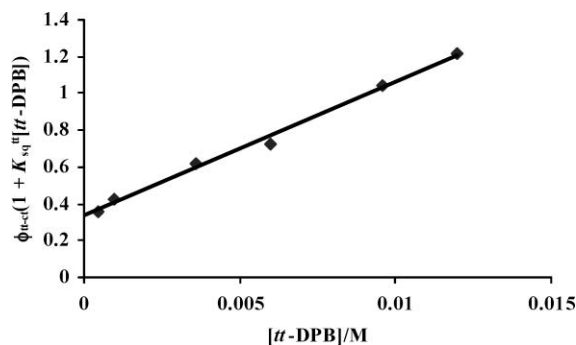


Fig. 4 Dependence of $\phi_{\textit{tt} \rightarrow \textit{ct}}$ for the biacetyl-sensitized isomerization on [*tt*-DPB].

The analogous concentration dependence of $\phi_{\textit{ct} \rightarrow \textit{tt}}$ is given by

$$(\phi_{\textit{ct} \rightarrow \textit{tt}}/\phi_{\text{is}}) = (a + \varepsilon k_{\text{ct}}\tau[\textit{ct}]) / (1 + K_{\text{sq}}^{\textit{ct}}[\textit{ct}]) \quad (22)$$

where $K_{sq}^{ct} = (1 - \varepsilon)k_{ct}\tau = k_{sq}^{ct}\tau$, the self-quenching constant for *ct*-DPB, was not measured. Eqn (22) reduces to eqn (11), the equation employed by Yee *et al.*,² if self-quenching were negligible in this case. Indeed, that self-quenching does not contribute was demonstrated by applying the rearranged eqn (22) with $K_{sq}^{ct} = 15 \text{ M}^{-1}$ and plotting the $\phi_{ct \rightarrow tt}$ values in ref. 2 as in Fig. 4. Although the least squares linear fit is good ($r^2 = 0.997$), the intercept gives $a = -0.20$, an impossible negative value. With a smaller $K_{sq}^{ct} = 5 \text{ M}^{-1}$ value, linearity is improved ($r^2 = 0.9997$), a is reduced from 0.69 to 0.40 and the slope ($\varepsilon k_{ct}\tau$) increases from 1020 to 1150 M^{-1} . It follows that K_{sq}^{ct} is probably smaller than 5 M^{-1} , ε in eqn (18) must be very close to unity, and the treatment of the $\phi_{ct \rightarrow tt}$ values in ref. 2, based on eqn (11) was justified.

There is no quantum chain process in the *ct*-DPB direction starting from *cc*-DPB, because $\phi_{cc \rightarrow ct}$ values either decrease, Table 4, or remain constant at 0.42 ± 0.08 with increasing [*cc*-DPB]. Inclusion of eqn (19) in the mechanism leads to the prediction that quantum yields should vary with concentration as shown in eqn (23)–(25).

$$(\phi_{cc \rightarrow ct}/\phi_{is}) = (1 - a)/(1 + K_{sq}^{cc}[ct]) \quad (23)$$

$$(\phi_{cc \rightarrow tt}/\phi_{is}) = (a + \varepsilon'k_{cc}\tau[cc])/[1 + K_{sq}^{cc}[cc]] \quad (24)$$

$$(\phi_{cc \rightarrow tt}/\phi_{cc \rightarrow ct}) = (a + \varepsilon'k_{cc}\tau[cc])/(1 - a) \quad (25)$$

Although self-quenching would account for the decrease in $\phi_{cc \rightarrow ct}$ at the higher [*cc*-DPB], it seems unlikely that the effect would be larger for *cc*-DPB than for *ct*-DPB for which it is negligible. The $\phi_{cc \rightarrow tt}$ values in Table 4 are plotted against [*cc*-DPB] in Fig. 5. Setting $K_{sq}^{cc} = 0$ in eqn (24), the intercept and slope of the linear least squares fit ($r^2 = 0.971$) in Fig. 5 give values of $a = 0.55$ and $\varepsilon'k_{cc}\tau = 67 \text{ M}^{-1}$, respectively (exclusion of the lowest concentration point from the fit gives $a = 0.58$ and $\varepsilon'k_{cc}\tau = 63 \text{ M}^{-1}$). Although the derived a value has a large uncertainty, it is pleasingly consistent with $(1 - a) = 0.41$, the average experimental value of $\phi_{cc \rightarrow ct}$. Application of eqn (25) to the data in Table 4 involves acceptance of an unrealistically large self-quenching constant for *cc*-DPB and gives much less reliable values of $a = 0.50$ and $\varepsilon'k_{cc}\tau = 160 \text{ M}^{-1}$.

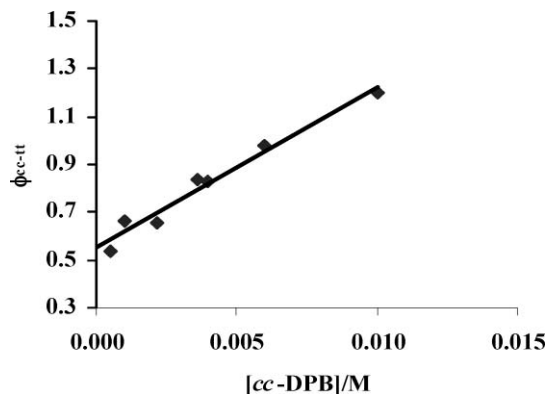


Fig. 5 Dependence of $\phi_{cc \rightarrow tt}$ for the biacetyl-sensitized isomerization on [*cc*-DPB].

3.2.4. The effect of oxygen on photostationary states and quantum yields. Molecular oxygen is known to be a very efficient quencher of DPB triplets ($k_q = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in Bz).^{1b} Since

$[\text{O}_2] = 2.1 \times 10^{-3} \text{ M}$ in air-saturated cyclohexane²⁷ the DPB triplet lifetime is expected to decrease from $1.6 \mu\text{s}$ to $\sim 100 \text{ ns}$ in the presence of air ($\sim 20 \text{ ns}$ in O_2 -saturated CH). It follows that, in the presence of air, $\sim 94\%$ of DPB triplets decay by bimolecular quenching interactions with O_2 . As for DPH,^{11b} quenching by O_2 is expected to deactivate the equilibrated triplet conformers, providing a snap shot of their distribution. As an added bonus of using O_2 quenching as a structural probe of olefin triplet structure, the process applies to both twisted and quasi-planar geometries but with predictably different rate constants and consequences. Quenching at quasi-planar geometries occurs by energy transfer yielding $^1\text{O}_2^*$ at a diffusion-controlled rate that is limited by a spin-statistical factor of $1/9$ ($k_q = 3.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for $^3t^*$ in stilbene in Bz).^{9c} On the other hand, quenching at twisted geometries involves spin exchange, yields no $^1\text{O}_2^*$ and is three times faster being subject to a spin-statistical factor of $1/3$ ($k_q = 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for $^3p^*$ in stilbene in Bz).^{9c,27} The experimental quenching rate constant and $^1\text{O}_2^*$ quantum yield for DPB triplets in Bz, $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and 0.7 ± 0.1 , respectively,^{1c} are consistent with quenching mainly at planar geometries.

Table 7 gives photostationary isomer ratios as a function of T for the fluorenone-sensitized photoisomerization of DPB in air-saturated CH. Two irradiation time intervals were employed to ensure that PSS had been attained. At the lower three T s, the fraction of *cc*-DPB was too small for accurate GC determination. Logarithmic plots of the ratios, analogous to those in Fig. 1 are shown in Fig. 6. The interpretation of the van't Hoff plots in Fig. 6 can be based on Scheme 2. We have inferred from the T dependence of the DPB triplet lifetime that $^3pt^*$ lies $2.74 \text{ kcal mol}^{-1}$ higher in energy than $^3tt^*$ and that, consequently, its contribution to the conformer distribution is roughly 1% in the T range under consideration. Because quenching of $^3pt^*$ by O_2 should contribute negligibly to the presence *ct*-DPB in PSS,

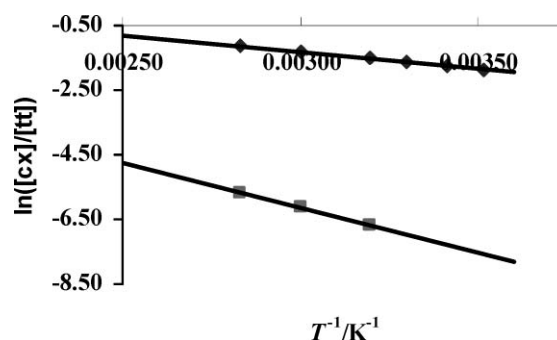
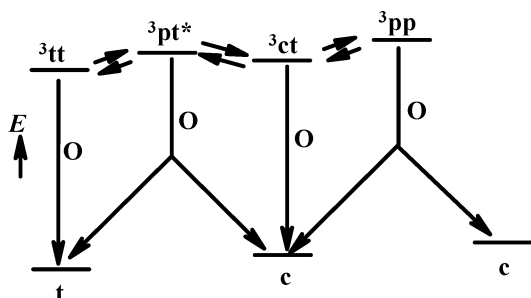


Fig. 6 Dependence of fluorenone-sensitized DPB PSS-isomer ratios in air-saturated CH on T ; ($[ct]/[tt]$), ratios (\blacklozenge) and ($[cc]/[tt]$), ratios (\blacksquare).

Table 7 Temperature dependence of DPB photostationary state ratios for the fluorenone-sensitized isomerization in air-saturated CH, 405 nm^a

$T/^\circ\text{C}^b$	$[ct]/[tt]$	$T/^\circ\text{C}$	$ct/[tt]$	$10^2 [cc]/[tt]$
11.3 (0.1)	0.153	39.7 (0.2)	0.217	0.00121
20.0 (0.1)	0.173	59.7 (0.2)	0.266	0.00216
29.7 (0.1)	0.196	80.1 (0.5)	0.315	0.00335

^a Duplicate samples $1.0 \times 10^{-3} \text{ M}$ DPB and $2.0 \times 10^{-2} \text{ M}$ fluorenone; each sample GC analyzed thrice, reproducibility to better than 1% and 3% for $[ct]/[tt]$ and $[cc]/[tt]$, respectively. ^b Values in parentheses are uncertainties in the last significant figure.



Scheme 2 Quenching of the DPB triplets by O₂.

the significant contributions of *ct*-DPB, evident in the $([ct]/[tt])_s$ ratios in Table 7 must be due to O₂ quenching of ${}^3ct^*$. It follows that the $([ct]/[tt])_s$ ratios are a good measure of the $[{}^3ct^*]/[{}^3tt^*]$ ratios. Similar reasoning leads to the conclusion that the $([cc]/[tt])_s$ ratios in Table 7 are a good measure of $[{}^3cp^*]/[{}^3tt^*]$ ratios (the alternative possibility is that they reflect $[{}^3cc^*]/[{}^3tt^*]$ ratios cannot be ruled out). The slopes and intercepts of the lines in Fig. 6 give ΔH^* values of 2.1 ± 0.1 and 5.5 ± 1 kcal mol⁻¹ and ΔS^* values of 3.6 and -0.4 eu for the ${}^3tt^* \rightleftharpoons {}^3ct^*$ and ${}^3tt^* \rightleftharpoons {}^3cp^*$ equilibria, respectively.

The transient observations of Yee *et al.* had established that conformer triplet equilibration is complete within the DPB triplet lifetime. However, the assumption in the preceding paragraph that equilibration was also achieved in the presence of air within the much shorter DPB triplet lifetime is open to question. As a test of this assumption we measured fluorenone-sensitized photoisomerization quantum yields in CH starting from *cc*-DPB. Quantum yields for *tt*- and *ct*-DPB formation, $\phi_{cc \rightarrow tt}$ and $\phi_{cc \rightarrow ct}$, respectively, are shown as function of $[cc\text{-DPB}]$ in Table 8. Variation of the *cc*-DPB concentration was necessary because O₂ competitively quenches the fluorenone triplet state. Assuming complete ${}^3\text{DPB}^*$ conformer equilibration, the mechanism in Scheme 2 predicts that the photoisomerization quantum yields should be given by eqn (26)–(28), where K^* is the equilibrium constant for ${}^3tt^* \rightleftharpoons {}^3ct^*$ equilibration and $k_{q^{\text{ox}}}$ and k_{st}^{cc} are the rate constants for fluorenone triplet quenching by O₂ and *cc*-DPB, respectively.

$$(\phi_{is}/\phi_{cc \rightarrow ct}) = \{(1 + K^*)/K^*\} (1 + k_{q^{\text{ox}}}[\text{O}_2]/k_{st}^{cc}[cc]) \quad (26)$$

$$(\phi_{is}/\phi_{cc \rightarrow tt}) = (1 + K^*)(1 + k_{q^{\text{ox}}}[\text{O}_2]/k_{st}^{cc}[cc]) \quad (27)$$

Table 8 Fluorenone-sensitized photoisomerization of *cc*-DPB in air-saturated CH, 405 nm, 20 °C^a

$10^3[cc\text{-DPB}]^b/\text{M}$	$\phi_{cc \rightarrow ct}^c$	$\phi_{cc \rightarrow tt}^c$	$\phi_{cc \rightarrow ct}/\phi_{cc \rightarrow tt}$
0.67 (0.70)	0.070 (1)	0.42 (2)	0.17
0.84 (0.88)	0.074 (1)	0.47 (1)	0.16
1.18 (1.23)	0.093 (7)	0.52 (2)	0.18
1.61 (1.69)		0.60 (2)	
1.68 (1.76)	0.101 (5)	0.59 (2)	0.17
2.54 (2.64)		0.69 (2)	
3.27 (3.38)	0.130 (3)	0.70 (2)	0.19
4.93 (5.07)	0.131 (4)	0.76 (2)	0.17
5.15 (5.28)	0.143 (5)	0.77 (3)	0.19
		Ave:	0.17 ₅

^a Actinometry with fluorenone (0.0223 M) *trans*-stilbene (0.100M) in degassed Bz. ^b Initial concentration in parentheses; averaged initial and final values were used. ^c Values in parentheses are uncertainties in the last significant figure.

$$(\phi_{cc \rightarrow ct}/\phi_{cc \rightarrow tt}) = K^* \quad (28)$$

As shown in Fig. 7, the quantum yields in Table 8 adhere well to eqn (26) and (27). Because $\phi_{is} = 1$ for fluorenone in CH,²⁶ the intercepts of the plots in Fig. 7 give $(1 + K^*)/K^* = 6.10 \pm 0.20$ and $(1 + K^*) = 1.14 \pm 0.04$ for the upper and lower lines, respectively. The inverses of these fractions are the predicted quantum yields at infinite $[cc\text{-DPB}]$, $\phi_{cc \rightarrow ct} = 0.16 \pm 0.01_4$ and $\phi_{cc \rightarrow tt} = 0.88 \pm 0.03$. Their sum, 1.04 ± 0.04 , is within experimental error of unity as expected, and their ratio, 0.18 is within experimental error of the $[ct]/[tt]$ photostationary ratio in Table 7. More important is the fact that the quantum yield ratio is independent of *cc*-DPB concentration as predicted in eqn (28). We have thus established complete ${}^3\text{DPB}^*$ conformer equilibration even in the presence of air.

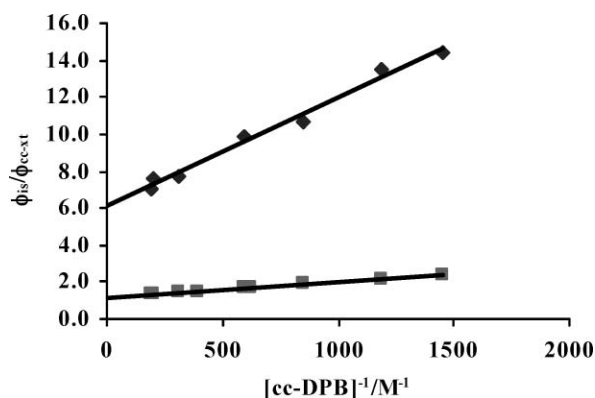


Fig. 7 Concentration dependence of $\phi_{cc \rightarrow ct}$ and $\phi_{cc \rightarrow tt}$ for the fluorenone-sensitized isomerization of *cc*-DPB in air-saturated CH at 20 °C.

The intercept/slope ratios of the plots in Fig. 7 should be identical and equal to $k_{st}^{cc}/k_{q^{\text{ox}}}[\text{O}_2]$. The values obtained, 1040 and 1290 M⁻¹, from the *ct*- and *tt*-DPB lines, respectively, are within experimental error of each other. Use of the average intercept/slope value, 1165 M⁻¹ and the oxygen concentration in CH, $[\text{O}_2] = 2.1 \times 10^{-3}$ M,²⁷ gives $(k_{st}^{cc}/k_{q^{\text{ox}}}) = 2.4$. Using $k_{q^{\text{ox}}} = 3 \times 10^9$ M⁻¹ s⁻¹ (5.0×10^9 M⁻¹ s⁻¹ is the value reported for Bz^{1b}) gives $k_{st}^{cc} = 7.2 \times 10^9$ M⁻¹ s⁻¹ which is close to 5.0×10^9 M⁻¹ s⁻¹, the value measured by Yee *et al.*²

3.3 Computational predictions

3.3.1 Introduction. A strong motivation for our research has been to provide accurate experimental benchmarks against which theoretical predictions could be tested. Our work on the 2,4-hexadiene triplets presented such an opportunity.²⁸ After a critical evaluation of different theoretical approaches for the calculation of triplet 1,3-diene and 1,3,5-hexatriene potential energy surfaces,²⁹ use of the less-CPU costly density functional theory (DFT) approach was favoured. We applied this approach to the 2,4-hexadiene system in the ground and triplet states.²⁸ Predicted relative energies and structures of conformers and isomers and transition states for their interconversion agreed very well with experimental expectations. The experimental findings in this paper afford a similar opportunity in the DPB system. In this section we present results from DFT calculations and compare them to our experimental findings.

Table 9 Relative energies of triplet (T_1) and singlet (S_0) stationary points for DPB based on UB3LYP/6-31+G(d,p) calculations^a

	E_{rel}	$(E + ZPE)_{\text{rel}}$	H_{rel}	ΔH_{expt}
Triplet state, T_1				
$^3\text{pc}^*$	45.4	43.2	43.4	47.1
$^3\text{ti}^{*b}$	43.5 (44.3)	41.7	41.4	44.1
$^3\text{tp}^*$	41.4 (42.2)	39.0	39.2	44.7
$^3\text{tt}^*$	38.9 (38.8)	37.0	37.2	42.0
Ground state, S_0				
^1cc	6.0 (3.6)	6.3	6.1	5.9 ± 0.1
$^1\text{cp-TS}$	45.3	42.9	42.7	47.2
^1ct	3.3 (4.2)	3.4	3.3	3.3 ± 0.1
$^1\text{tp-TS}$	41.3	38.4	38.3	43.9
^1tt	0 (0)	0	0	0

^a Values for CH are given in parenthesis; all energies are in kcal mol⁻¹ relative to the ^1tt global minimum in S_0 (see Table S1 in ESI[†] for absolute values). ^b TS characterized by a small imaginary frequency (see text).

3.3.2 The ground state. Calculated energies for stationary points of DPB in *s-trans* conformations and for transition states for their interconversion in S_0 and T_1 are given in Table 9 relative to the planar *tt*-DPB (^1tt) global energy minimum in S_0 . Calculated gas phase structures for S_0 are shown in Fig. 8. The calculated differences for the ground state isomers, 3.25 and 5.96 kcal mol⁻¹ for ^1ct and ^1cc , respectively, are in remarkably good agreement with the experimental ΔH values of 3.3 ± 0.1 and 5.9 ± 0.1 kcal mol⁻¹ in benzene (last column in Table 9). Inclusion of CH as solvent increases the calculated relative energy of ^1ct by 0.9 kcal mol⁻¹. X-Ray diffraction analysis of the *cc*-DPB crystal has revealed the presence of equal populations of two conformers, one with the phenyl groups in almost perpendicular planes (actually, 80° to each other for phenyl-vinyl dihedral angles of 40°) and the other with the phenyls in parallel planes (again with 40° phenyl-vinyl dihedral angles).²⁸ The former is shown in Fig. 8 because the gas phase calculation predicts it to be lower in energy by 1.5 kcal mol⁻¹.³⁰ In contrast to ^1ct , the calculated CH solvent effect predicts significant relative stabilization of the two ^1cc conformers.

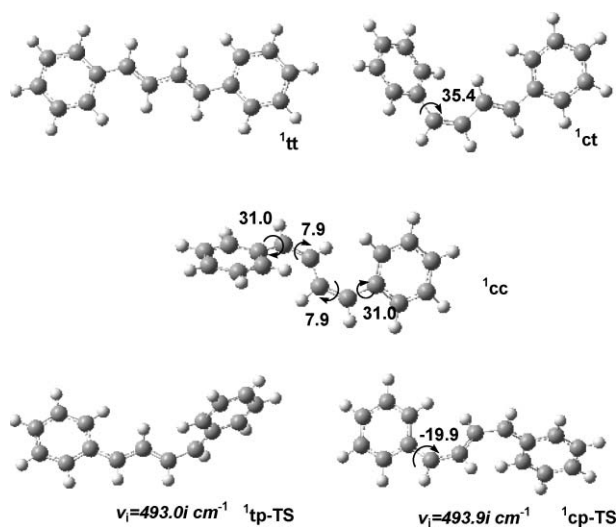


Fig. 8 Ground state stationary points and transition states for DPB optimized at the UB3LYP/6-31+G(d,p) level of theory.

The E_{rel} of the conformer with the phenyls in parallel planes decreases from 7.5 kcal mol⁻¹ in the gas phase to 5.6 kcal mol⁻¹ in CH, whereas the corresponding decrease for the conformers with phenyls in different planes (67° calculated for CH) is from 6.0 to 3.6 kcal mol⁻¹. The CH solvent corrections maintain the order of relative energies of the two *cc*-DPB conformers. However, the predicted stability reversal of the *ct*- and *cc*-DPB isomers in CH is obviously inconsistent with our experimental observations.

No experimental value is available for the transition state energy for thermal ^1tt to ^1ct isomerization. The empirical estimate of that activation enthalpy of 43.9 kcal mol⁻¹, based on conjugative stabilization energies for benzyl and 1-phenylallyl radicals,^{11b} (the predicted value would be 0.9 kcal mol⁻¹ higher if a slightly lower conjugative stabilization energy for the 1-phenylallyl radical were employed)³¹ is 2.6 kcal mol⁻¹ larger than the calculated E_{rel} value. Addition of 3.3 kcal mol⁻¹ for the *cis* double bond of the 1-phenylallyl moiety to the 43.9 kcal mol⁻¹ value gives 47.2 kcal mol⁻¹ as the estimated enthalpy for $^1\text{cp-TS}$, the TS for ^1ct and ^1cc equilibration. Calculated structures for the ground state isomers and the transition states for their interconversion are shown in Fig. 8.

3.3.3 The triplet state. Calculated E_{rel} values in Table 9 can be compared to the experimental ΔH values in the last column of that Table. The latter were obtained by adding the ΔH values determined in this work to the spectroscopic energy value of 42.0 kcal mol⁻¹ for $^3\text{tt}^*$.^{4,5} As in the case of the biradicaloid TSs in the ground state, calculated E_{rel} triplet energies are 2–3 kcal mol⁻¹ lower than their experimental counterparts. Using $^3\text{tt}^*$ as reference, $^3\text{tp}^*$ is calculated to lie 2.5 kcal mol⁻¹ (3.4 kcal mol⁻¹ in CH) higher in energy, in reasonable agreement with the experimental 2.7 kcal mol⁻¹ enthalpy difference. We sought but were unable to locate an energy minimum at a planar $^3\text{tc}^*$ geometry. The calculated energy in Table 9 corresponds to a TS structure characterized by a small imaginary frequency ($\nu_i = 74.5i$ cm⁻¹ at the B3LYP/6-311+G(d,p) level, 74.4i cm⁻¹ with solvent correction, and $\nu_i = 64.9i$ cm⁻¹ at the B3LYP/6-311 + G(3df,2p) level). Animation of this imaginary frequency reveals distortion of planarity by a twisting motion in the *cis* part of the molecule. Use of the bigger basis set leads to a slightly smaller imaginary frequency. In retrospect our failure to locate a planar $^3\text{tc}^*$ structure is not surprising in view of the steric interactions that cause the *cis* moiety to assume a non-planar geometry in S_0 (see ^1tc). In any case, this exercise suggests that distortion towards a planar ^3tc geometry is energetically feasible.

Details on S_0 and T_1 structures, Fig. 8–10, are given in the ESI.[†] In contrast to the biradicaloid TSs in S_0 , we could locate no energy minima for $^3\text{tp}^*$ with *trans*-1-phenylallyl/benzyl dihedral angles close to 90°. Instead, two mirror image conformers were located, one of which is labelled $^3\text{tp}^*$ in Fig. 9, whose *trans*-1-phenylallyl/benzyl dihedral angles, + and -79°, deviate by 11° from the orthogonal. In the case of $^3\text{pc}^*$ we located two, almost isoenergetic, enantiomeric pairs one of which has the expected 90° dihedral angle between *cis*-1-phenylallyl and benzyl moieties and the other deviates from this geometry by about 15°. The structures of the four “ $^3\text{cp}^*$ ” conformers and their relative energies are shown in Fig. 10. In view of their energetic proximity, the choice of the $^3\text{cp}^*$ structure in Fig. 9 is arbitrary. It appears that the triplet potential energy surface is very flat at regions close to

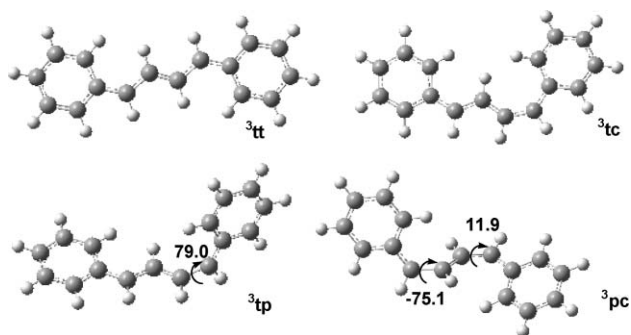


Fig. 9 Triplet state stationary points for DPB optimized at the UB3LYP/6-31+G(d,p) level of theory (${}^3tc^*$ may be a TS, see text).

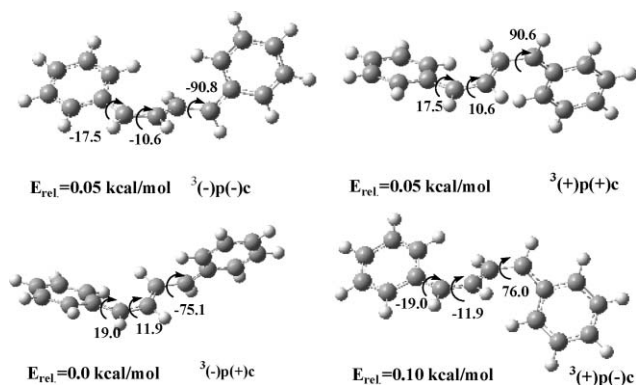


Fig. 10 UB3LYP/6-31+G(d,p) optimized ${}^3cp^*$ conformers.

the geometries of the ground state TSs. The ready accessibility of structures with dihedral angles that deviate from the orthogonal may have significant implications. Calculations have shown that intersystem crossing rate constants from alkene triplet state geometries that depart from the ideal orthogonal biradicaloid structure by rotation away from 90° and/or by distortion from sp^2 towards sp^3 pyramidalization are significantly enhanced.³² It follows that if the calculated structures of the twisted triplets are correct, they should be subject to enhanced spin–orbit coupling interactions.

Conclusions

Fig. 11 summarizes the findings in Table 9 in an idealized 3D diagram of S_0 and T_1 DPB potential energy curves. The angles Φ and Θ in Fig. 11 are rotation coordinates about the two double bonds of the diene unit. However, although they may be viewed as the main reaction coordinates, it should be understood that other coordinates, such as bond lengths and other dihedral angles differ in the two states, assuming optimum values as the reaction progresses. Enthalpy differences between ground state DPB isomers in benzene agree exactly with calculated gas phase energy differences. The agreement is not as good when CH is included as solvent in the calculations. The predicted reversal of relative ct - and cc -DPB energies in S_0 is not borne out experimentally and brings into question the theoretical evaluation of the solvent effect. Calculated gas phase TS energies for isomer equilibrations in S_0 are 2.6 and 1.9 kcal mol⁻¹ lower for 1tp -TS and 1pc -TS, respectively, than biradicaloid energies obtained using the empirical procedure of Doering and co-workers.^{11b,31}

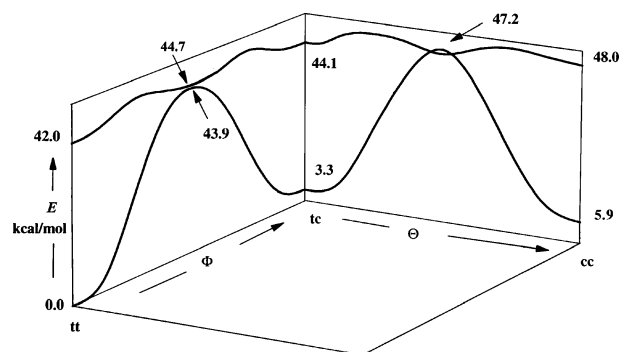


Fig. 11 Potential energy diagrams for twisting about the C_1C_2 and C_3C_4 bonds of DPB in S_0 and T_1 ; values given are experimental energies. The T_1 potential energy curves at ${}^3pt^*$ and ${}^3cp^*$ are idealized, as theory indicates energy minima at significant deviation from orthogonal geometries (see text and Fig. 10).



Our findings require significant revision of the previously proposed DPB T_1 potential energy surface. Results from triplet sensitization experiments of DPB photoisomerization in the presence of air show that ${}^3tt^*$ (85%) and ${}^3ct^*$ (15%) are the major contributors to the conformer equilibrium distribution of DPB triplets at ambient T . The equilibration between these conformers is sufficiently fast to be complete within the 100 ns lifetime of DPB triplets in the presence of air. The T dependence of this equilibrium shows that ${}^3ct^*$ is 2.1 kcal mol⁻¹ higher in energy than ${}^3tt^*$.

The presence of ${}^3ct^*$ is consistent with the observation of a quantum chain isomerization process in the tt - to ct -DPB direction. The mechanism applied thus far employs the equilibrated ${}^3ee^*$ triplet as the chain carrier in quantum chain events, eqn (17)–(19). Knowledge of the triplet conformer distribution allows interpretation of the quantum chain processes in terms of the elementary steps in eqn (29)–(31). Because only 15% of the triplets exist as the ${}^3ct^*$ conformer, division of the derived $\delta k_{tt} = 4.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ value by 0.15 converts it to the energy transfer rate constant in eqn (29) $k_{ct}^{tt-ct} = 3.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. Division of the analogous values by 0.85 gives $k_{ct}^{tt-ct} = 7.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{ct}^{tt-cc} = 4.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for eqn (30) and (31), respectively. These energy transfer rate constants deviate from the diffusion controlled limit by at least a factor of 10,²⁷ being similar in magnitude to those obtained for the excitation transfer rate constants among the triplet states of the DPH isomers.^{11a} Although nonvertical excitation processes are probably involved as suggested for DPH,^{11a} the relative magnitude of the rate constant for eqn (29)–(31) suggests that E_T values for the DPB isomers increase in the order ct -, tt - and cc -DPB. This is consistent with Fig. 11 and the conclusion, based on triplet energy transfer rate constants from a series of triplet donors to ct -DPB, that the triplet energy of the latter is 40 kcal mol⁻¹.²

The T dependence of the triplet lifetime in degassed CH is consistent with activated decay mainly from ${}^3pt^*$ twisted triplets, 2.7 kcal mol⁻¹ above the global energy minimum at ${}^3tt^*$, that contribute less than 1% to the triplet conformer equilibrium

mixture at ambient T . Theory predicts that the structure of this triplet deviates from the orthogonal relationship of the benzyl and *trans*-1-phenylallyl moieties by 11° in either the *tt* or the *ct* direction.

Finally, the observation of *cc*-DPB in photostationary states obtained by fluorenone-sensitization in the presence of air at high T s reveals a minor decay pathway from ${}^3\text{pc}^*$ which lies $5.5 \pm 1 \text{ kcal mol}^{-1}$ above ${}^3\text{tt}^*$. Although, in this case, structures with orthogonal benzyl and *cis*-1-phenylallyl moieties are consistent with theory, other structures having the same energy are accessible by 15° torsional motion away from the orthogonal relationship. Twisted structures corresponding to energy minima at 1-phenylallyl/benzyl dihedral angles that deviate from the orthogonal may play significant roles in $T_1 \rightarrow S_0$ relaxation.

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