nm after 5, 10, 20, and 30 min of irradiation were 0.24, 0.35, 0.43, and 0.46, respectively, and it was not increased appreciably upon further irradiation, while the intensity of the latter absorption continued to increase. When irradiated with 366-nm light, the former absorption had largely been bleached after 1 min. The absorption at 340 nm remained unchanged for more than 1 h at 77 K in the dark but had disappeared when the frozen solution was thawed in an ethanol bath at −100 °C and immediately refrozen in liquid $N_2$. Irradiation of **1a** in EPA or pentane/isopentane (1:1) also led to development of an absorption with $\lambda_{max}$ 260 and 340 nm (relative intensity, ca. 2:1) that showed similar thermal and photochemical behaviors.

**(b) 1b.** When a solution of 8 mg of **1b** (45 μmol) in 6 mL of ethanol was irradiated with 254-nm light at 77 K, development of an absorption with $\lambda_{max}$ 267 ± 2 and 346 ± 2 nm (relative intensity, ca. 2:1) was observed. Absorbances at 346 nm after 5 and 9 min of irradiation were 0.35 and 0.47, respectively. By subsequent irradiation with 366-nm light for 2 min, the generated absorption was largely bleached but a broad band in the 270–310-nm region (absorbance <0.10) remained unbleached. The absorption at 346 nm remained unchanged for more than 1 h at 77 K in the dark but had disappeared when the frozen solution was thawed in an ethanol bath at −100 °C and immediately refrozen in liquid $N_2$.

**(c) 1c.** When a solution of 10 mg of **1c** (53 μmol) in 6 mL of ethanol was irradiated with 254-nm light at 77 K, development of an absorption with $\lambda_{max}$ 280 ± 2, 348 ± 2, and 425 ± 3 nm (relative intensity, ca. 7:2:1) was observed. Absorbances after 4, 8, 12, and 16 min of irradiation were 0.24, 0.38, 0.47, and 0.50, respectively. By subsequent irradiation with 366-nm light, the generated absorption was bleached and the original absorption spectrum of **1c** was cleanly restored. The newly developed absorption remained unchanged for more than 1 h at 77 K in the dark but had disappeared when the frozen solution was thawed in an ethanol bath at −100 °C and immediately refrozen in liquid $N_2$. Irradiation of **1c** in pentane/isopentane (1:1) with 254-nm light led to development of an absorption with $\lambda_{max}$ 278 ± 2, 347 ± 2, and 425 ± 3 nm (relative intensity, ca. 6:2:1) that showed similar thermal and photochemical behaviors.

**Trapping of Intermediate Exhibiting Absorption at 340 nm with Ethanol.** To a chilled solution of 20 mg of **1a** (0.15 mmol) in 6 mL of ethanol was added 6 mL of 2% (v/v) ethanolic solution of sulfuric acid. In two quartz tubes (12-mm i.d.) were placed 5-mL portions of the above solution and degassed by freeze–pump–thaw cycles. The solution in the first tube was frozen in liquid $N_2$ in the Dewar used for the measurement of the electronic absorption spectra, irradiated with 254-nm light for 5 min through one of the windows and for additional 5 min from the opposite direction through the other window, and then warmed up to room temperature. This freeze–irradiation (2 × 5 min)–thaw cycle was repeated 10 times. The solution in the second tube was irradiated with 254-nm light in the same manner, but each time before the frozen solution was thawed, the generated absorption was bleached by irradiating the solution with 366-nm light through the two windows for 1 min at a time. Each photolyzed mixture was neutralized with aqueous $NaHCO_3$, concentrated in vacuo, and extracted with pentane. The extract was washed with water, dried with $MgSO_4$, concentrated, and analyzed by GLC (columns C and F, 135 °C) and GLC–MS. The ethanol adduct **3b** was detected in both the photolysates, but the amount of **3b** produced in the second tube was only ca. one-tenth of that formed in the first tube. A residual 2 mL of the acidic ethanolic solution of **1a** was worked up after standing 16 h in the dark at room temperature. The GLC analysis showed that **1a** largely remained unconsumed and that **3b** was not formed in a detectable amount in the dark. When the above experiment was repeated, good reproducibility was observed.

**Trapping of 14 Generated in Photolysis of 1a with 254-nm Light at 77 K.** A solution of 10 mg of **1a** (76 μmol) in 15 mL of pentane/isopentane (1:1) was distributed among three quartz tubes (12-mm i.d.). The solution in each tube was bubbled with $N_2$ for 15 min at 0 °C, frozen in liquid $N_2$, and irradiated with 254-nm light for 4.5 h, whereupon absorbance at 300 nm went up to over 2. A dilute solution of bromine in dichloromethane was added, and the frozen mixture was warmed up to room temperature while agitating it well. The mixtures in the three tubes were combined, washed with aqueous $Na_2S_2O_3$ and water, and dried with $MgSO_4$. The analysis of the mixture by GLC (column F, 150 °C) and HPLC [μ-Porasil eluted with ether/hexane (1:99)] showed peaks at the retention times coinciding with those of *p*-xylylene dibromide. The product mixture was subjected to chromatography on silica gel eluted with ether/hexane (1:99), and the eluent containing the product was analyzed by GLC–MS. The fragmentation pattern of the product was superimposable to that of authentic *p*-xylylene dibromide.[33]

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# Direct and Sensitized Photoisomerization of 1,4-Diphenylbutadienes

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**Abstract:** Photoisomerization of the three stereoisomers of 1,4-diphenylbutadiene (DPB) in room-temperature cyclohexane solution was studied by direct excitation and by triplet sensitization. The photostationary mixtures in both singlet and triplet experiments contain only trans,trans and cis,trans isomers; no cis,cis isomer or any photoproducts were observed. The two cis isomers exhibit no measurable fluorescence or triplet formation. Results are interpreted in terms of allylmethylene-like intermediates. Efficient internal conversion of singlet DPBs is inferred from low isomerization quantum yields by direct excitation. Triplet-sensitized isomerizations show a marked DPB concentration dependence of photostationary compositions and quantum yields. Analysis of these data reveals a quantum chain process involving excited triplet DPB as the chain-carrying species. Transient absorption measurements show that sensitized excitation of any DPB isomer leads directly to a fast equilibrium between triplet all-trans and trans-twisted forms.

Linear aliphatic polyenes[2] and α,ω-diphenylpolyenes[3,4] have been extensively investigated in recent years as models for important biological chromophores that undergo cis–trans photoisomerization. This has led to a great deal of theoretical interest in the electronic structure of polyene excited states[5] and in their dynamical behavior.[6]

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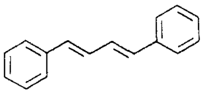
The role of twisted excited-state geometries is crucial to understanding the photoisomerization process. Photophysical studies of diphenylpolyene singlets and triplets are often interpreted in terms of the well-known stilbene system.[7] Direct excitation or triplet sensitization of either *cis*- or *trans*-stilbene leads to a low-energy common intermediate having perpendicular geometry, which in turn decays to isomerization products. In the excited-singlet case, a small barrier separates the planar *trans*-stilbene from the perpendicular intermediate.[8] The triplet reaction involves an equilibrium between the trans-planar and perpendicular forms.[9] In analogy to stilbene, diphenylpolyenes are presumed to isomerize via perpendicular intermediates on both singlet and triplet potential surfaces, even though these surfaces may be somewhat more complicated.

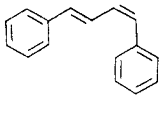
The relationship between nonplanar conformations and isomerization of 1,4-diphenylbutadiene (DPB) has been the subject of numerous studies. These studies include fluorescence,[10] dependence on viscosity,[11] and triplet-state photophysical behavior.[12,13] We reported earlier on the photophysical properties of a rigid analogue of *all-trans*-DPB, 1,5-diphenylhexahydronaphthalene (HHN), which is constrained to prevent diene isomerization.[14] By comparing its excited-singlet and excited-triplet absorption spectra to those of DPB, we concluded that these excited states of *all-trans*-DPB are nearly planar and not highly twisted. In contrast, Wilbrandt and co-workers[15] obtained the resonance Raman spectrum of the *all-trans*-DPB triplet, which suggests that the relaxed triplet geometry may be twisted. Further insight would be acquired if the excited-singlet and excited-triplet potential surfaces of DPB were known and if isomerization quantum yields were available.

Since the pioneering work of Zechmeister,[16] photochemical studies of isomerization of DPB's have received little attention in comparison to photophysical and spectroscopic studies. The analogous aliphatic system 2,4-hexadiene was studied first by Hammond's group[17] and later in detail by Saltiel and co-workers.[18,19] We briefly describe here the previous photochemical work on isomerization of DPBs. (1) Zechmeister and co-workers used broad-band UV excitation to study *n*-hexane solutions of the three DPB isomers.[20] The photoequilibrium composition was found to be mostly *cis,trans*-DPB, and isomerization products were observed to result from discrete one-bond rotations. (2) Whitten and co-workers[21] measured direct photoisomerization quantum yields for *trans,trans*-DPB and *cis,trans*-DPB in benzene solution, which suggested that internal conversion may compete with isomerization. They reported isomerization of triplet *all-trans*-DPB using biacetyl as a sensitizer in benzene. (3) Gorner[13] studied relative rates of direct trans → cis photoisomerization of the all-trans forms of DPB, diphenylhexatriene (DPH), and diphenyloctatetraene (DPO) under varying conditions of solvent and temperature. These were measured as initial rates of disappearance and followed the order DPB > DPH > DPO. Of particular interest is the fact that no measurable photoisomerization of $10^{-2}$ M *all-trans*-DPB was found when it was sensitized with benzophenone in benzene solvent. An activation barrier to isomerization in the triplet state was proposed to account for this behavior.

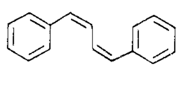
The present paper describes our investigation of photoisomerization of the three DPB isomers shown below in room temperature cyclohexane solution. To our knowledge, no previous quantum-yield studies involving the complete set of DPB isomers have been conducted. Complementary information about the cis isomers is important to establish the nature of the entire $S_1$ and $T_1$ potential surfaces. A specific goal of this study is to understand the photochemical and photophysical behavior of nonplanar excited-state DPB geometries in terms of current photoisomerization models and also to resolve the issue of why, as previously reported, triplet tt does not seem to undergo photosensitized isomerization. Quantum yields were measured by using direct excitation at 325 nm and by triplet sensitization with 9-fluorenone. Other triplet energy donors were also used, and transient absorption studies were carried out. Our results show that isomerization of DPBs is similar but not identical with that found in other systems.



tt



ct



cc

## Experimental Section

**Materials.** All room-temperature photolyses were conducted in spectrophotometric grade solvents. *all-trans*-DPB (Aldrich) was purified by multiple recrystallizations from ethanol. The ct isomer was prepared photochemically by irradiation of optically dense cyclohexane solutions of tt in Pyrex flasks with the full arc of a 450-W xenon lamp; separation was achieved by chromatography on neutral alumina. The cc isomer was synthesized by modification of Zechmeister's procedure[20] with catalytic hydrogenation of diphenyldiacetylene (Aldrich) at atmospheric pressure, followed by chromatography on neutral alumina and then crystallization from methanol. Purity of cis isomers was confirmed by HPLC analysis. 9-Fluorenone (J. T. Baker) was recrystallized from cyclohexane. Other triplet energy donors used (9,10-dichloroanthracene, anthracene, and crystal violet) were of special purity for photosensitization (J. T. Baker). Azulene (Aldrich, 99%) was used as received for triplet quenching studies.

**Direct Irradiation Experiments.** Stirred samples of DPBs in rectangular quartz cuvettes were deoxygenated by bubbling with argon and then placed in the beam of a 2-mW 325-nm He–Cd laser (Liconix Model 4110), which was expanded to fill the sample cuvette. Actinometer solutions of potassium ferrioxalate[22] were simultaneously irradiated with a beam splitter placed in front of the sample. Absorption spectra of the photolyzed solution were taken at convenient time intervals with an IBM Instruments Model 9420 spectrophotometer and digitized with a Z80-based microcomputer. The spectra were analyzed by using Beer's law to obtain solution compositions. These could be determined typically to within 1 or 2 mol % of each isomer present and to better precision than by HPLC analysis.

Photolysis of cc for short times was conducted by using excitation at 300 nm. The fourth harmonic (266 nm) of a Nd:YAG laser (Quanta Ray Model DCR-1) was passed through a Raman shifter to give pulses at 300 nm with energies of about 1 mJ. Samples received up to several hundred laser pulses.

**Photosensitization Experiments.** Triplet states of DPBs were studied with sensitizers excited at 416 nm by using the Raman-shifted third

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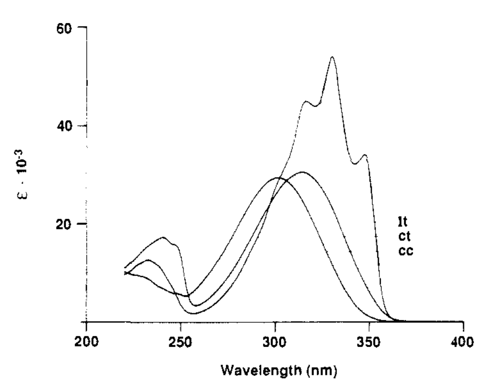

**Figure 1.** Absorption spectra of the three isomers of 1,4-diphenylbutadiene in room-temperature cyclohexane solution.

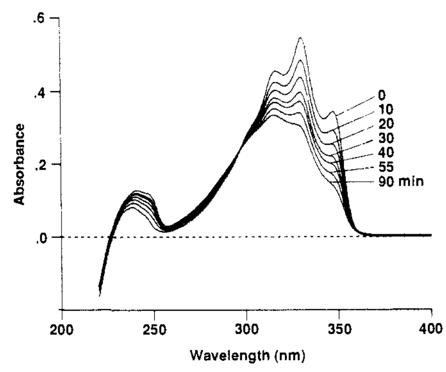

**Figure 2.** Absorption spectra showing tt photoisomerization to ct by using 325-nm excitation. Spectra were taken at the indicated times. Note the isosbestic point at 297 nm. Negative absorption at the far left arises from the argonated condition of the sample; it is due to the absorption by oxygen in the reference cell.

harmonic of the Nd:YAG laser, or at 390 nm with the xenon source in a conventional fluorescence spectrophotometer (Spex Fluorolog). For lower DPB concentrations, a special dual-cuvette sample holder was employed so that photolysis could be conducted with use of a 10-mm path length cell and spectra could be obtained with use of a 1-mm or 2-mm path length cell; higher concentrations required dilution before absorption measurements. Samples were degassed with argon, and ferrioxalate actinometry was used. Control samples were checked to assure that no isomerization proceeded in the absence of sensitizer when samples were irradiated at these wavelengths. Transient absorption measurements were made with a nanosecond laser photolysis apparatus that employed multichannel detection. Details of this method to obtain excited-state spectra are described elsewhere.[23]

**HPLC Analyses.** DPB isomers were separated on a reverse-phase C-18 column (Alltech Associates, Lichrosorb RP18, 25 cm, 5 μm) with use of 70/30 acetonitrile/water. Flow rates were about 1 mL/min, and typical retention times were about 1 h.

## Results

**Isomerization by Direct Irradiation.** Absorption spectra of the three DPB isomers in cyclohexane solution are shown in Figure 1. They are virtually identical with those obtained by Zechmeister in *n*-hexane[20] and are presented here to assist description of our experimental results. The diffuseness of the longer wavelength absorption bands of the cis isomers and their lower molar absorptivities compared to the all-trans isomer have been interpreted by Baraldi et al.[24] in terms of hindered nonplanar conformations.

Figures 2 and 3 show spectral changes resulting from 325-nm photolysis of tt and cc, respectively. Similar to Zechmeister's result, we find the photostationary mixture at this wavelength to contain predominately ct and no measurable amounts of cc or other photoproducts[25] (see Table I). The isosbestic point at 297 nm in Figure 2 demonstrates that tt and ct form a closed system. Data shown in Figure 4 indicate that at very short irradiation times cc forms ct, which then reacts to form tt. The latter result was confirmed by HPLC experiments with 300-nm excitation. Quantum yields for photoisomerization of tt to ct and the reverse reaction were determined from our data by use of Zimmerman's method,[26] and they are given in Table I along with the disappearance quantum yield of cc.

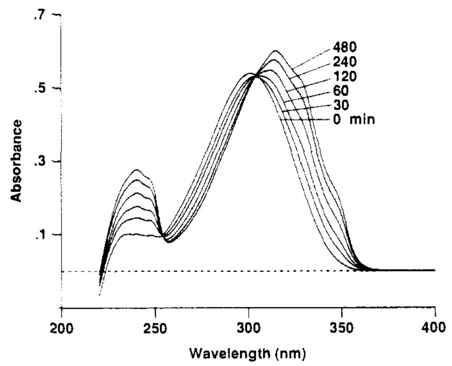

**Figure 3.** Absorption spectra showing cc photoisomerization by using 325-nm excitation. Spectra were taken at the indicated times. After initial formation of ct, rapid interconversion of ct and tt takes place so that apparent isosbestic points are seen at 253 and 304 nm. See Figure 4.

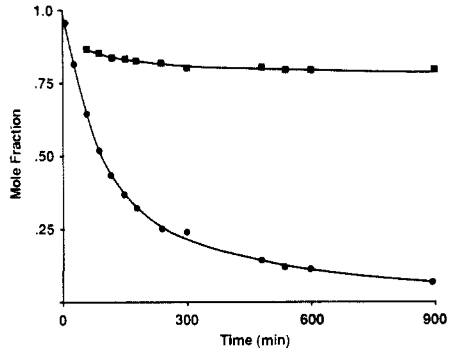

**Figure 4.** Composition of the reaction mixture as a function of time for the 325-nm photolysis of cc. The lower curve is the cc mole fraction. The upper curve describes the reaction products as the ratio ct/(ct + tt).

**Table I.** DPB Photoisomerization Efficiencies with Use of Direct Excitation at 325 nm and Photophysical Properties of DPB Excited-Singlet States

| | tt | ct | cc |
|---|---|---|---|
| mole fraction at photoequilibrium | 0.19 | 0.81 | 0.00 |
| photoisomerization quantum yield | 0.11[a] | 0.04[b] | 0.20[c] |
| τ(singlet) | 0.6 ns[d] | | |
| fluorescence quantum yield | 0.42[d] | $<10^{-3}$ | $<10^{-3}$ |
| intersystem-crossing quantum yield | 0.02[e] | <0.01 | <0.01 |
| estimated quantum yield of twisting | 0.22 | 0.16 | 0.20 |
| estimated internal-conversion yield | 0.34 | 0.84 | 0.80 |

[a] tt → ct. [b] ct → tt. [c] cc → ct. [d] Reference 14. [e] Reference 12a.

Further experiments were conducted to examine the photophysical properties of the $S_1$ states of ct and cc. First, fluorescence from room-temperature solutions of each compound was sought, and none was found even though an emission yield as low as $10^{-3}$ could have been detected easily. Second, with direct excitation at 266 nm, no $S_1 \rightarrow S_n$ or $T_1 \rightarrow T_n$ absorptions due to these isomers were observed in the region 350–750 nm.[27] Our sensitivity would have allowed detection of weak triplet absorption as that observed for tt by direct excitation if extinction coefficients are about the

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(27) At very high excitation doses, long-lived transient absorption was observed near 550 nm. This is apparently due to formation of DPB cations. Unpubished results of S. Hug and D. S. Kliger.

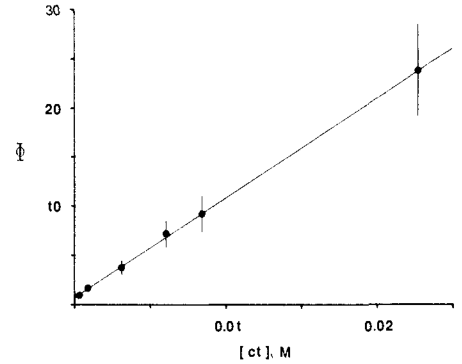

**Figure 5.** Initial quantum yields of ct → tt photoisomerization by sensitization with 9-fluorenone as a function of [ct]. Quantum yield values correspond to low conversions (10–20%) and are corrected for the back reaction. The straight line is a linear least-squares fit to eq 14.

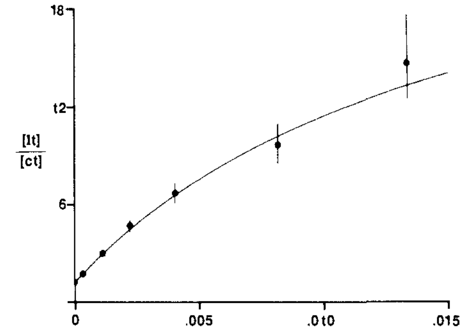

**Figure 6.** Photostationary tt/ct ratios obtained by sensitization with 9-fluorenone as a function of starting [ct]. The abscissa is labeled as total [DPB] because the triplet isomerization of ct gives only tt. The curve is a least-squares fit to eq 15; see text for details.

same. Thus it appears that excited singlets of ct and cc decay virtually entirely by isomerization and internal conversion processes.

**Isomerization by Triplet Sensitization.** Our quantum-yield studies of DPB triplet isomerization employed 9-fluorenone as sensitizer ($E_T$ = 53 kcal/mol[28]) at (3–4) × $10^{-3}$ M. The photostationary mixtures of DPBs obtained by this method are similar to those found in direct photolysis experiments: only ct and tt are present, and no other photoproducts are produced. Good Stern–Volmer behavior is seen in DPB quenching of the 9-fluorenone triplet state, and quenching constants for all three isomers are 5 × $10^9$ (±10%) $M^{-1}$ $s^{-1}$. By use of other triplet donors, the triplet-state energy of ct was determined to be about 40 kcal/mol, only slightly lower than that of tt ($E_T$ = 42).[29]

The most striking behavior in DPB triplet isomerization is a significant dependence on DPB concentration. To illustrate this effect, results for ct solutions are presented in Figures 5 and 6, showing initial isomerization quantum yields and photostationary tt/ct ratios, respectively. It can be seen from the data that quantum yields for ct → tt isomerization rise well above unity and that photostationary mixtures become dramatically richer in tt with increasing ct concentration. Such behavior is characteristic of a quantum chain mechanism[19,30,31] in which the chain-carrying species is a DPB triplet state. Quenching of the excited triplet by ground-state DPB leads to isomerization and propagation of the excitation energy.

Since no triplet–triplet absorption was observed upon direct excitation of either ct or cc, we measured the triplet spectra of each of the three isomers sensitized with 9-fluorenone. These three spectra were collected 1 μs after excitation of the sensitizer, and they are shown scaled in Figure 7 for comparison. They appear to be virtually identical. This suggests that the same triplet state is obtained upon energy transfer to any of the DPB isomers. If this is a common triplet state and also the chain-propagating species, the chain mechanism requires that the triplet lifetime be independent of concentration because each quenching event that occurs does not affect the number of chain carriers. To test this idea, we measured the lifetime of absorption of triplet-sensitized ct and of sensitized tt using concentrations over a 100-fold range. Decay of these triplets followed first-order kinetics with the same lifetime at all concentrations, 1.5 (±0.3) μs for tt and 1.6 (±0.2) μs for ct, in agreement with the earlier reported value of 1.6 (±10%) μs obtained by direct excitation of tt.[12a]

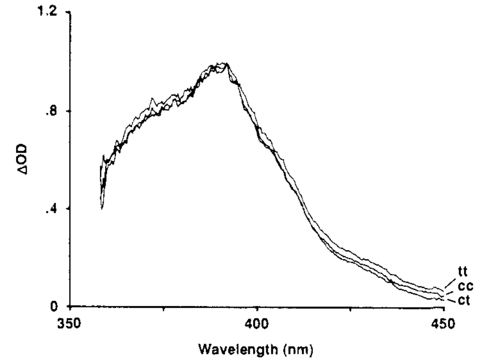

**Figure 7.** Triplet–triplet absorption spectra obtained by energy transfer to tt, cc, or ct, following initial excitation of 9-fluorenone. Spectra were collected 1 μs after the 7-ns laser pulse and are shown scaled to the same maximum absorption.

The mechanism shown below accounts for our triplet-sensitized isomerization results for ct and tt. Here, F represents 9-fluorenone.

$$\mathrm{F} \xrightarrow{h\nu} {}^1\mathrm{F}^* \qquad (1)$$

$${}^1\mathrm{F}^* \xrightarrow{k_{\mathrm{isc}}} {}^3\mathrm{F}^* \qquad (2)$$

$${}^3\mathrm{F}^* + \mathrm{tt} \xrightarrow{k_{\mathrm{ETtt}}[\mathrm{tt}]} \mathrm{F} + {}^3\mathrm{tt}^* \qquad (3)$$

$${}^3\mathrm{F}^* + \mathrm{ct} \xrightarrow{k_{\mathrm{ETct}}[\mathrm{ct}]} \mathrm{F} + {}^3\mathrm{ct}^* \qquad (4)$$

$${}^3\mathrm{ct}^* \xrightarrow{\mathrm{fast}} {}^3\mathrm{te}^* \qquad (5)$$

$${}^3\mathrm{tt}^* \xrightarrow{\mathrm{fast}} {}^3\mathrm{te}^* \qquad (6)$$

$${}^3\mathrm{te}^* \xrightarrow{k_{\mathrm{tt}}} \mathrm{tt} \qquad (7)$$

$${}^3\mathrm{te}^* \xrightarrow{k_{\mathrm{ct}}} \mathrm{ct} \qquad (8)$$

$${}^3\mathrm{te}^* + \mathrm{ct} \xrightarrow{k_{\mathrm{qct}}[\mathrm{ct}]} \alpha\mathrm{tt} + (1-\alpha)\mathrm{ct} + {}^3\mathrm{te}^* \qquad (9)$$

$${}^3\mathrm{te}^* + \mathrm{tt} \xrightarrow{k_{\mathrm{qtt}}[\mathrm{tt}]} \alpha\mathrm{tt} + (1-\alpha)\mathrm{ct} + {}^3\mathrm{te}^* \qquad (10)$$

Sensitization of either DPB isomer leads to direct formation of an equilibrated triplet, ${}^3$te*, whose structure is not specified for the moment. Unimolecular decay occurs in steps 7 and 8. Upon quenching by either isomer,[32] the probabilities for decay to tt or ct are given by $\alpha$ and $(1 - \alpha)$,[33] respectively, in steps 9 and 10.

On the basis of the mechanism presented above, the expression for initial quantum yield of sensitized isomerization of ct to tt is

$$\Phi_{\mathrm{isom}} = k_{\mathrm{tt}}/(k_{\mathrm{ct}} + k_{\mathrm{tt}}) + \alpha[k_{\mathrm{qct}}/(k_{\mathrm{ct}} + k_{\mathrm{tt}})][\mathrm{ct}] \qquad (11)$$

Least-squares fit of the data of this equation is shown in Figure 5. The intercept obtained is 0.69 (±15%) and the slope is 1020 (±10%) $M^{-1}$.

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[28] Triplet energies are from ref 22 and Barltrop, J. A.; Coyle, J. D. *Excited States in Organic Chemistry*; Wiley: London, 1975; p 130.

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[30] Butt, Y. C. C.; Singh, A. K.; Baretz, B. H.; Liu, R. S. H. *J. Phys. Chem.* **1981**, *85*, 2091–2097.

[31] Karatsu, T.; Arai, T.; Sakuragi, H.; Tokumaru, K. *Chem. Phys. Lett.* **1985**, *115*, 9–15.

[32] Self-quenching to give adduct biradicals is another possibility (see ref 19). However, we observed no stable dimers or an effect on the triplet lifetime.

[33] The parameter $\alpha$ should not be confused with the unimolecular partition coefficient often used to describe decay of stilbene excited states.

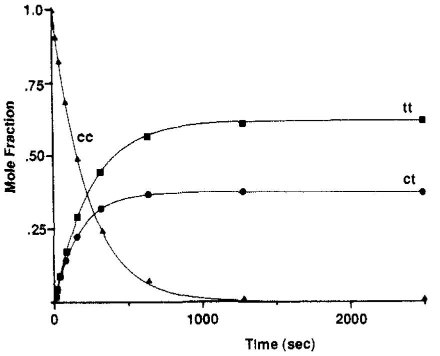


**Figure 8.** Composition of the reaction mixture as a function of time for the 9-fluorenone-sensitized isomerization of cc; [DPB] = $2.6 \times 10^{-4}$ M.

For analysis of photostationary tt/ct ratios shown in Figure 6, the resulting expression is

$$\frac{[\mathrm{tt}]}{[\mathrm{ct}]} = \frac{k_{\mathrm{ETct}}}{k_{\mathrm{ETtt}}}\left[\frac{\alpha(k_{\mathrm{qct}}[\mathrm{ct}] + k_{\mathrm{qtt}}[\mathrm{tt}]) + k_{\mathrm{tt}}}{(1-\alpha)(k_{\mathrm{qct}}[\mathrm{ct}] + k_{\mathrm{qtt}}[\mathrm{tt}]) + k_{\mathrm{ct}}}\right] \quad (12)$$

We assume $k_{\mathrm{ETct}} = k_{\mathrm{ETtt}}$ because the measured rates of quenching of the 9-fluorenone triplet state by ct and tt are the same within experimental error. When the data in Figure 6 are extrapolated to zero concentration, the intercept value yields the unquenched partitioning ratio of the intermediate $^3$te*, $k_{\mathrm{tt}}/k_{\mathrm{ct}} = 1.22$ (±5%), corresponding to 55% tt and 45% ct. By use of this ratio and the DPB triplet lifetime of 1.6 μs, $k_{\mathrm{ct}}$ and $k_{\mathrm{tt}}$ are calculated to be $2.8 \times 10^5$ s$^{-1}$ and $3.4 \times 10^5$ s$^{-1}$, respectively.

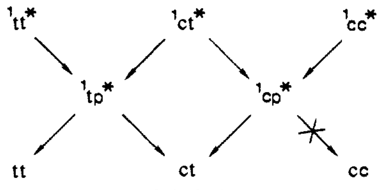
We note that $\alpha$ and the two remaining constants in eq 12 cannot be uniquely determined from our data. The curve shown in Figure 6 is obtained by selecting $k_{\mathrm{qct}} = k_{\mathrm{qtt}} = 6.0 \times 10^8$ M$^{-1}$ s$^{-1}$ where $\alpha$ is calculated to be 0.97. In general, we find that good fits are obtained for quenching constants in the range (6.0–6.5) × 10$^8$ M$^{-1}$ s$^{-1}$ and for $\alpha$ = 0.96–0.98. Analysis of the data is extremely sensitive to $\alpha$, and values below 0.96 are entirely unsatisfactory.

Sensitized isomerization of cc as a function of time is illustrated in Figure 8 with data for [cc] = $2.6 \times 10^{-4}$ M. At this concentration, the photostationary tt/ct ratio is 1.7. It can be seen that the isomerization products are produced at early times in roughly equal amounts. This behavior agrees with the partitioning ratio of 1.22 obtained from extrapolation of photostationary tt/ct ratios to zero concentration. Within experimental error, our measured disappearance quantum yield for sensitized isomerization of cc is unity. No quantitative experiments were performed to study cc concentration dependence.

Finally, quenching of the DPB triplet state by azulene ($E_{\mathrm{T}}$ = 31) was investigated to further test the triplet isomerization mechanism. By use of 390-nm excitation of 9-fluorenone, [ct] = $2.15 \times 10^{-4}$ M, and [azulene] = $1.96 \times 10^{-3}$ M, the photostationary mixture obtained is 96–97% tt. In contrast, photosensitized isomerization of ct at the same concentration without azulene present produces a photostationary mixture of about 60% tt.

## Discussion

**Singlet Isomerization.** We will discuss results for isomerization of DPBs by direct excitation using the conventional scheme presented below.



Here, the intermediates are labeled as tp and cp to mean a perpendicular geometry at one end of the diene and either cis or trans at the other end. These twisted intermediates are the DPB analogues to the allylmethylene intermediates involved in photoisomerization of aliphatic 1,3-dienes.[17] The doubly twisted $^1$pp* is excluded because this structure, as well as the case of rapidly interconverting single-twisted intermediates, would allow one-photon two-bond isomerizations, which were not observed. We interpret results obtained by direct excitation in terms of a singlet mechanism because intersystem crossing in all DPBs appears relatively inefficient.

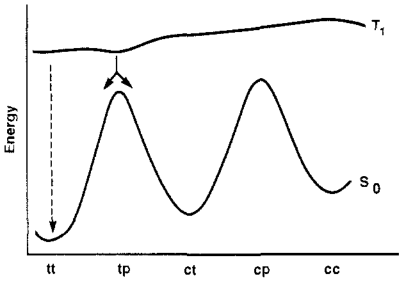


**Figure 9.** Qualitative one-dimensional potential energy surfaces involved in sensitized photoisomerization of DPBs. Solid arrows denote unimolecular decay of DPB triplets. The dashed arrow represents bimolecular decay by self-quenching (quantum chain mechanism) or by azulene quenching.

The absence of cc in the photoequilibrium mixture suggests that the process $^1$cp* → cc is highly inefficient. Though we have no direct experimental evidence to explain this result, it is reasonable if the $^1$cp* geometry is severely distorted.[24] This would be a simple extension to DPBs of the case of sterically hindered 1,2-diarylethylenes where photochemical formation of cis isomers is not observed.[34]

Because quantum yields by direct excitation are relatively low in all three isomers, significant internal-conversion rate processes are implied. In the case of tt, fluorescence and intersystem crossing quantum yields total to about 0.44 in room-temperature cyclohexane solution. Thus 56% of the singlet deactivation must be accounted for. Our measured isomerization quantum yield is 0.11, which means that 45% of tt excited singlets could end up as ground states by direct internal conversion, $^1$tt* → tt, but some of these must return via $^1$tp* intermediates as shown in the scheme. If equal partitioning from the $^1$tp* intermediates is assumed, then 0.22 is the quantum yield of formation of twisted intermediates, and we can estimate the internal conversion quantum yield to be about 0.34 for tt. From this reasoning, we agree with the conclusion of Gorner,[13] who determined that DPB fluorescence and intersystem-crossing quantum yields do not sum to unity in low-temperature rigid media, that there is substantial internal conversion in *all-trans*-DPB.

Since the two cis isomers lack observable fluorescence and triplet formation at room temperature when directly excited, internal-conversion quantum yields for ct and cc can be roughly estimated from isomerization quantum yields in the same manner as for tt. Convenient assumptions are that twisting is equally probable about either double bond in the excited state and that $^1$tp* decays symmetrically whereas $^1$cp* gives only ct. These estimated quantum yields for internal conversion and for twisting are listed in Table I, showing their relation to other competing first-order decay processes.

Considered as a whole, the excited-singlet behavior of tt and ct is much like that of *trans*- and *cis*-stilbene.[7] Apart from efficient internal conversion in DPBs, the following comparisons are of interest. (1) The two isomers in both systems share a common twisted intermediate. The role of cc is effectively another source of ct. (2) The trans isomers in both systems fluoresce while the cis isomers do not. (3) In both systems the trans isomers have planar ground-state geometries and near-planar excited-state geometries. (4) A small potential barrier to isomerization exists for the trans isomers.[8a,11b,c]

**Triplet Isomerization.** Figure 9 shows qualitative ground-state and excited-triplet-state potential surfaces, which are consistent

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[34] Becker, H. D.; Sandros, K.; Hansen, L. *J. Org. Chem.* **1981**, *46*, 821–823. For other examples of unsymmetrical excited state decay, see also Wismonski-Knittel, T.; Fischer, E. *J. Chem. Soc., Perkin Trans. 2* **1979**, 449–457.

with all of our sensitized-photoisomerization results. The solid arrows represent unimolecular decay of DPB triplets to the ground-state surface. The dashed arrow represents bimolecular decay through quenching by DPB ground states (quantum chain mechansim) and by other species, if present, having similar or lower triplet energies. These two decay paths are competitive processes. For low [DPB] and no additional quencher present, unimolecular decay is prevalent; at higher [DPB], decay by self quenching is more important.

A deep potential well on the $T_1$ surface at the cp geometry is excluded because photostationary mixtures contain no cc. Such a well would produce both cc and ct. A deep well between tp and cp geometries also must be excluded from results of sensitized photoisomerization of cc at low concentration. Here, unimolecular decay is dominant and gives initial formation of tt and ct in a ratio equal to that of the final photostationary-state composition of a very dilute solution (see Figures 5, 6, and 8). A minimum between the tp and cp geometries would lead to the appearance of only ct from cc at early times. Unimolecular decay must occur from $^3$tp*, which represents an energy minimum of the $T_1$ surface.

Another minimum on the triplet surface must be located at $^3$tt*. This is based on the isomerization behavior in the presence of azulene where the photostationary mixture is about all tt. From sensitization experiments with various triplet energy donors, we concluded that the $T_1$–$S_0$ gap is 42 kcal/mol for tt and about 40 kcal/mol for ct. Exothermic energy transfer from these triplet states to azulene should occur at roughly the same diffusion-controlled rates. At an azulene concentration that makes quenching the dominant decay process, the photostationary mixture indicates the relative amounts of $^3$tt* and $^3$ct*.

These minima on the $T_1$ surface lie such that $^3$tt* and $^3$tp* are in fast equilibrium like the case of stilbene. This system of equilibrated triplets is the kinetic intermediate represented as $^3$te* in the mechanism presented earlier. In the quantum chain process, only the $^3$tt* structure is capable of energy transfer to DPB ground states. High [DPB] are thus expected to produce photostationary mixtures rich in tt. Furthermore, the quantity $\alpha$ must have a value near unity. In terms of physical meaning, $\alpha$ is the photostationary composition that would result if DPB triplets decay only through bimolecular quenching and not by unimolecular events.

The relative amounts of the two geometric forms can be estimated as follows. At [DPB] = $1 \times 10^{-3}$ M where rates of unimolecular and bimolecular decay are nearly equal, the photostationary mixture is about 75% tt. Because unimolecular decay gives 55% tt and bimolecular decay gives 97% tt, these planar and twisted triplets must be present in about equal amounts at room temperature.

An equilibrium between $^3$tt* and $^3$tp* forms of DPB has been proposed also by Chattopadhyay et al.[35] in their study of *all-trans*-DPB triplets in benzene. It was found that these triplets were quenched at slower rates than aromatic triplets having similar spectroscopic triplet energies when acceptors of lower energy were used. To explain the slower quenching of DPB compared to quenching of anthracene, an equilibrium between the planar trans form and the twisted form was proposed. Quenching of the twisted form in DPB is energetically unfavorable whereas no comparable situation holds in the rigid aromatics. The DPB self-quenching rate was determined to be $1.2 \times 10^8$ M$^{-1}$ s$^{-1}$ and their estimate of the equilibrium constant is $K = 0.6$ in benzene. Therefore, this kinetic quenching behavior is the same phenomenon that explains the concentration dependence of DPB triplet isomerization in our study.

A common triplet-state equilibrium for all three DPB isomers also explains the results shown in Figure 7. This triplet spectrum is identical with that observed when using direct excitation of tt.[12a] Because the ground-state absorption spectra are so different for the three isomers, it is not expected for them all to have the same triplet–triplet spectrum. Therefore, subsequent to sensitized excitation by 9-fluorenone (highly exothermic energy transfer), everything on the potential surface rolls downhill to the equilibrated pair, $^3$tt*–$^3$tp*. It is noteworthy that the adiabatic isomerization of cc triplets seen here is similar to the case of 2-styrylanthracene recently reported by Hamaguchi et al.[36] However, they observed decay to only the trans isomer while DPB gives quenched decay to tt and unquenched decay to ct and tt.

An interesting question that remains is which DPB structure is responsible for the triplet absorption. It has been pointed out[13,15] that the peak wavelength of this transition in diphenylpolyenes varies with the length of the polyene chain so excitation is probably localized in the butadiene part of DPB. While Gorner[13] has assigned this transition to $^3$tt*, the resonance Raman spectrum of the DPB triplet obtained by Wilbrandt and co-workers as mentioned earlier appears to be incompatible with $C_{2h}$ symmetry.[15] This suggests that the electronic absorption could occur from a highly twisted state. However, the $T_1 \rightarrow T_n$ spectra of tt and that of the rigid analogue HHN are very similar,[14] so that we strongly suspect the spectra in Figure 7 are due to a triplet state of tt, $^3$tt*, whose relaxed conformation is not completely planar but has slight polyene or phenyl twists. Lack of absorption by $^3$tp* in our study may be due to low extinction coefficients and/or low concentration, or to its absorption in another wavelength region.

The observation mentioned in the introduction that $10^{-2}$ M tt does not undergo photoisomerization[13] with use of benzophenone as sensitizer in benzene solvent can now be understood. Our results in cyclohexane show a strong concentration dependence of the triplet isomerization, which drives the photostationary composition in the direction of tt. We find that photostationary mixtures for a given DPB concentration are richer in tt for benzene solvent than for cyclohexane solvent. For example, at about $2.7 \times 10^{-4}$ M, the mixture is 62% tt in cyclohexane and 77% tt in benzene with use of 9-fluorenone as sensitizer. If the quantum chain mechanism described in this study also applies to DPBs in benzene, then isomerization of triplet tt will not be seen there. Our results demonstrate that triplet tt does undergo efficient isomerization and that this process is masked by the concentration effect.

## Conclusions

Our experimental results for isomerization by direct excitation are in accord with a singlet mechanism of one-bond rotations for all three DPB isomers. Formation of cc is unfavorable because of hindered interactions in the excited state. These interactions contribute significantly to the differences in isomerization behavior between DPB and aliphatic 1,3-dienes. Direct $S_1$–$S_0$ internal conversion is an efficient decay process, which competes with twisting. On the triplet surface, interconversion of allylmethylene intermediates is not found, but rather a fast equilibrium between all-trans and trans-perpendicular forms is established. Sensitized excitation of any DPB isomer leads directly to these equilibrated species. A kinetic quantum chain mechanism for triplets explains the DPB concentration effect on photostationary compositions and on quantum yields. The photochemical behavior of DPB in excited-singlet and excited-triplet states were found in many ways to be like that of stilbene and other 1,2-diarylethylenes.

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**Registry No.** *trans,trans*-DPB, 538-81-8; *cis,trans*-DPB, 5808-05-9; *cis,cis*-DPB, 5807-76-1; azulene, 275-51-4; PhC≡CC≡CPh, 886-66-8; 9-fluorenone, 486-25-9; 9,10-dichloroanthracene, 605-48-1; anthracene, 120-12-7; crystal violet, 548-62-9.

**Supplementary Material Available:** Derivation of eq 11 and 12 (2 pages). Ordering information is given on any current masthead page.

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(35) Chattopadhyay, S. K.; Kumar, C. V.; Das, P. K. *J. Photochem.* **1984**, *26*, 39–47.

(36) Hamaguchi, H.; Tasumi, M.; Karatsu, T.; Arai, T.; Tokumaru, K. *J. Am. Chem. Soc.* **1986**, *108*, 1698–1699.