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Crystal Structure Correlations in the Photochemistry of Dimethyl 9,10-Dimethyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate

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Abstract

The photochemistry of the title 9,10-dimethyldibenzobarrelene-11,12-diester (1) in solution and in the solid state exhibits unique differences as a function of reaction medium. In acetone the normal di- π -methane reaction leads to a semibullvalene derivative, dimethyl 4b,8b-dimethyl-4b,8b,8c,8d-tetrahydrodibenzo[*a,f*]cyclopropa[*cd*]pentalene-8c,8d-dicarboxylate (2), while in acetonitrile an additional cyclooctatetraene (COT) photoproduct, dimethyl 5,11-dimethyldibenzo[*a,e*]cyclooctene-6,12-dicarboxylate (3), is obtained. In the solid state a new pentalene, dimethyl 5,10-dimethyl-5,10-dihydroindeno[2,1-*a*]indene-5,10-dicarboxylate (4), is formed as the major product. Crystal data for (1), (3) and (4): $T = 294$ K, $\text{Cu K}\alpha$, $\lambda = 1.5418$ Å, $\text{C}_{22}\text{H}_{20}\text{O}_4$, $M_r = 348.40$; (1), triclinic, $P\bar{1}$, $a = 8.695$ (1), $b = 13.633$ (1), $c = 8.273$ (1) Å, $\alpha = 98.51$ (1), $\beta = 113.34$ (1), $\gamma = 80.97$ (1)°, $V = 885.2$ (1) Å³, $Z = 2$, $D_x = 1.307$ g cm⁻³, $\mu = 6.9$ cm⁻¹, $F(000) = 368$, $R = 0.057$ for 3046 reflections; (3), monoclinic, $P2_1/n$, $a = 9.124$ (2), $b = 14.392$ (2), $c = 14.328$ (1) Å, $\beta = 94.30$ (1)°, $V = 1876.1$ (5) Å³, $Z = 4$, $D_x = 1.233$ g cm⁻³, $\mu = 6.5$ cm⁻¹, $F(000) = 736$, $R = 0.048$ for 2289 reflections; (4), monoclinic, $I2/a$, $a = 19.020$ (6), $b = 11.963$ (1), $c = 17.083$ (4) Å, $\beta = 105.15$ (1)°, $V = 3752$ (2) Å³, $Z = 8$ (two independent half-molecules per asymmetric unit), $D_x = 1.233$ g cm⁻³, $\mu = 6.5$ cm⁻¹, $F(000) = 1472$, $R = 0.072$ for 1574 reflections. The structure of the solid-state photoproduct (4) provides an important clue in deriving a mechanism for its formation, involving a biradical intermediate with a pentalene-like skeleton.

This mechanism also accounts for the formation of COT (3), whose structure is not that expected on the basis of previous mechanistic studies.

Introduction

Correlation of photochemical and crystal structural data for dibenzobarrelene-11,12-diester [with molecular skeletons similar to that of (1) in Fig. 1] has given detailed descriptions of the possible reaction pathways in the solid-state photolyses (Garcia-Garibay, Scheffer, Trotter & Wireko, 1990*a,b*). The reactions proceed *via* the di- π -methane rearrangement (Zimmerman, 1980) to give dibenzosemibullvalene photoproducts [such as (2) in Fig. 1]. For unsymmetrically substituted dibenzobarrelenes, two regioisomeric semibullvalene photoproducts are obtained, and rationalization of the regio- and enantioselectivity has been derived from the photochemical-structural correlations; the most important factor has proved to be crystal packing (Garcia-Garibay *et al.*, 1990*a,b*).

The di- π -methane rearrangement of the barrelenes is believed to proceed *via* the triplet excited state (T_1) (the semibullvalene products are formed exclusively in the presence of a triplet sensitizer, such as acetone solvent) (Zimmerman, 1980). Direct irradiation also produces cyclooctatetraene (COT) derivatives, *via* a mechanism involving the singlet state (S_1) (Fig. 1). These COTs have been well characterized for barrelene, benzobarrelene and naphthobarrelene derivatives, and support for the proposed intramolecular [2 + 2] cycloaddition mechanism (Fig. 1)

has been obtained from deuterium-labelling studies (Zimmerman & Grunewald, 1966; Zimmerman, Binkley, Givens & Sherwin, 1967; Zimmerman, Givens & Pagni, 1968; Zimmerman & Bender, 1970). For dibenzobarrelenes, COT photoproducts have been reported in direct irradiations; these COTs were assumed to form *via* the same mechanisms as in the benzobarrelenes (Fig. 1), but their structures have not been established definitively (Rabideau, Hamilton & Friedman, 1968; Paddick, Richards & Wright, 1976; Pratapan, Ashok, Cyr, Das & George, 1987).

The present paper extends the studies of the dibenzobarrelenes to the 9,10-dimethyl bridgehead substituted derivative (1) (Figs. 1 and 2). Photolysis in acetone solvent (Fig. 2) produces a semibullvalene photoproduct (2), and photolysis in acetonitrile or benzene results in an additional product which proves to be a COT derivative (3). Solid-state photolysis gives as the major product a novel and unexpected diester (4), whose structure provides a clue to the

mechanism of the photoreactions. The structures of (1), (3) and (4) have been established by X-ray crystal analysis [suitable crystals of (2) could not be obtained].

Experimental

Infrared spectra

A Perkin-Elmer 1710 Fourier transform infrared spectrometer was used for obtaining spectra in KBr pellets. A pellet typically contained 2–3 mg of sample and 100–150 mg of KBr and was made using a Perkin-Elmer evacuated die 186-0002 and a Carver laboratory press model B.

Nuclear magnetic resonance spectra

All ¹H NMR and ¹³C NMR spectra were recorded on a Varian XL-300 spectrometer at 300 and 75.4 MHz respectively using deuteriochloroform as solvent. Signal positions are reported in units of δ , parts per million downfield from tetramethylsilane, which was the internal standard used. Multiplicity, number of protons and assignment are given in parentheses following δ . For ¹³C NMR spectra, the signals were assigned based in part on the attached proton test.

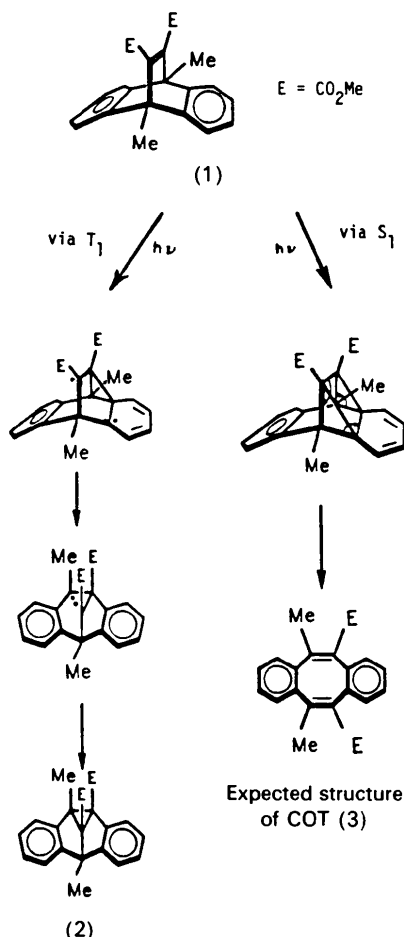
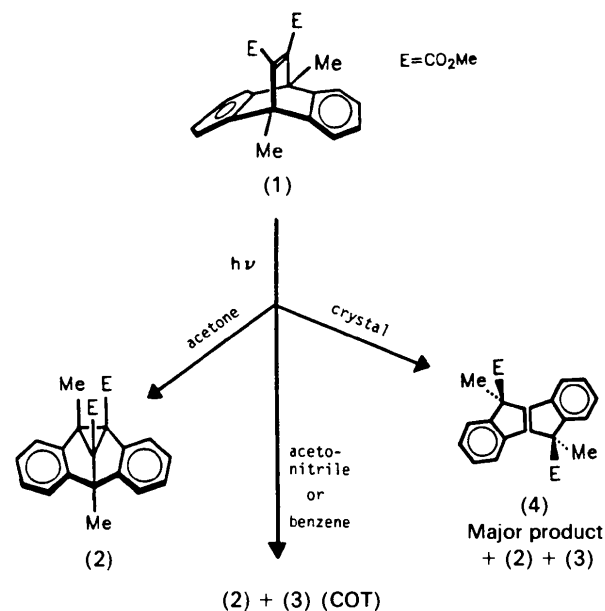


Fig. 1. Triplet (T_1) and singlet (S_1) reaction pathways in the photolysis of dibenzobarrelenes.



Photoproduct percentages as a function of medium

Medium	(2)	(3)	(4)	Unknown (%)
Acetone	89	0	0	±2
Acetonitrile	27	51	0	±3
Benzene	40	32	0	±5
Crystal	12	7	80	±2
Powder	27	12	50	±2

Fig. 2. Photolysis of compound (1).

Mass spectra

Both low-resolution and high-resolution mass spectra were recorded on a Kratos MS 50 mass spectrometer. A Kratos MS 80 mass spectrometer coupled with a Karlo-Erba gas chromatograph was used for GC-MS study.

Photolysis procedures

All analytical and preparative photolyses were performed using a Hanovia 450 W medium pressure mercury lamp placed in a water-cooled Pyrex immersion well (thickness = 4 mm, transmits $\lambda > 290$ nm). For analytical photolyses in presence of a sensitizer, a PRA/MODEL UV-12 pulsed nitrogen laser ($\lambda = 337$ nm, pulse rate = $20\text{--}30\text{ s}^{-1}$) or a Hanovia lamp with a uranium glass filter (thickness = 2 mm, transmits $\lambda > 340$ nm) were used. All photolyses were done at room temperature.

For preparative photolysis, in general, the compound under investigation was dissolved in the solvent and purged with nitrogen for a least $\frac{1}{2}$ h prior to the photolysis and purging was continued during the photolysis. For analytical photolysis, the samples were degassed by several freeze-thaw-pump cycles and sealed under nitrogen atmosphere prior to the photolysis.

Synthesis and photolysis

Dimethyl 9,10-dimethyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (1). In a round-bottomed flask fitted with a reflux condenser and a drying tube, 0.75 g (3.6 mmol) of 9,10-dimethylanthracene and 0.82 g (5.8 mmol) of dimethyl acetylenedicarboxylate were heated together at 470 K for 45 min. The brown mass obtained was subjected to silica gel flash chromatography and elution with 8% (v/v) ethyl acetate in petroleum ether gave the Diels-Alder adduct as a solid which was recrystallized from chloroform-diethyl ether (0.77 g, 61%). M.p.: 463-464 K. IR: 1726 (ester carbonyl stretch), 1622 (C=C stretch) cm^{-1} . ^1H NMR: δ , 2.27 (s, 6H, bridgehead methyl hydrogens), 3.71 (s, 6H, ester methyl hydrogens), 7.03-7.09 (m, 4H, aromatic) and 7.31-7.37 (m, 4H, aromatic). ^{13}C NMR: δ , 13.60 (bridgehead CH_3), 49.73 (bridgehead C), 51.99 (ester CH_3), 120.80, 124.93 (aromatic C-H), 147.40, 150.16 (quaternary aromatic and vinylic C), 166.00 (carbonyl C). MS: *m/e* (relative intensity): 348 (M^+ , 8.8), 316 (5.9), 288 (78.0), 273 (5.4), 257 (8.9), 242 (5.1), 229 (100), 215 (38.2), 202 (13.4), 189 (9.3), 121 (5.1), 113 (4.7), 101 (6.3), 59 (9.1), 44 (6.7). Exact mass calculated ($\text{C}_{22}\text{H}_{20}\text{O}_4$): 348.1362; measured: 348.1366. Elemental analysis: ($\text{C}_{22}\text{H}_{20}\text{O}_4$) calculated: C 75.84, H 5.79%. Found: C 75.89, H 5.82%. UV (acetonitrile): 278 ($\epsilon = 1851$), 271 ($\epsilon = 1984$) nm.

Photolysis of (1) in acetone. Compound (1) (0.25 g, 0.72 mmol) was photolyzed for 40 min in 300 ml of spectral grade acetone. GC analysis of the reaction mixture indicated mainly the presence of two new peaks at R_t 7.47 and 7.87 min and traces of some other products. Solvent evaporation *in vacuo* gave an oil which was dissolved in diethyl ether and the solvent was allowed to evaporate slowly. The yellow solid obtained from this treatment was washed with diethyl ether until all the color was removed. The resulting white solid (75 mg, 30%) was characterized as compound (2) and found to decompose on the GC column to show two peaks. Repeated attempts to obtain single crystals of this material for X-ray analysis were not successful.

Dimethyl 4b,8b-dimethyl-4b,8b,8c,8d-tetrahydrodi-benzo[a,f]cyclopropa[cd]pentalene-8c,8d-dicarboxylate (2). M.p.: 435-438 K. IR: 1723 (ester carbonyl stretch) cm^{-1} . ^1H NMR: δ , 1.90 and 1.98 (two s, 3H each, methyl hydrogens), 3.76 and 3.88 (two s, 3H each, ester methyl hydrogens), 7.04-7.59 (m, 8H, aromatic). ^{13}C NMR: δ , 13.87 and 15.47 (CH_3), 51.68 and 52.36 (ester CH_3), 52.8, 56.3, 56.6, 61.44 (quaternary sp^3 C), 119.13, 119.26, 124.36, 125.69, 126.94, 127.19, 127.51, 127.63 (aromatic C-H), 133.60, 138.33, 152.54, 152.67 (quaternary aromatic C), 167.67, 168.80 (carbonyl C). MS: *m/e* (relative intensity): 348 (M^+ , 7.5), 316 (4.1), 289 (14.5), 288 (43.7), 273 (7.6), 257 (5.0), 242 (4.7), 229 (100), 215 (39.4), 202 (9.7), 189 (4.4), 106 (5.0), 94 (3.4), 59 (2.7). Exact mass calculated ($\text{C}_{22}\text{H}_{20}\text{O}_4$): 348.1362; measured: 348.1364. Elemental analysis: ($\text{C}_{22}\text{H}_{20}\text{O}_4$) calculated: C 75.84, H 5.79%. Found: C 75.61, H 5.89%.

Photolysis of (1) in acetonitrile. Compound (1) (0.22 g, 0.63 mmol) was photolyzed for $5\frac{1}{2}$ h in 300 ml of reagent grade acetonitrile. GC analysis of the mixture indicated new peaks at R_t 's 4.59 (47%), 6.82 (10%), 7.52 (20%), 7.93 (6%), and a few other smaller peaks. Evaporation of the solvent *in vacuo* left an oily foam which upon scratching with 5 ml of diethyl ether gave a brown solid which did not show any peaks on GC. The solid was filtered off and the filtrate was found to contain all the photoproducts as shown by GC. Removal of solvent gave an oil which was flash chromatographed over silica gel by using 8% (v/v) ethyl acetate in petroleum ether. Although this did not result in complete separation, a few fractions contained the photoproduct with R_t 4.59 min in about 95% GC purity. Removal of solvent from these fractions gave an oil which crystallized. Recrystallization from diethyl ether gave nice prisms (55 mg, 25%) which were subsequently characterized as compound (3). Attempts to isolate the photoproduct with R_t 6.82 min were not successful. The peaks at 7.52 and 7.93 min correspond to (2) isolated from the photolysis in acetone.

Table 1. Crystal data, data-collection and refinement parameters for compounds (1), (3) and (4)

	(1)	(3)	(4)
Crystal data			
Compound type	Dibenzobarrelene	COT	Dibenzopentalene
Solvent	Chloroform/ diethyl ether	Diethyl ether	Petroleum ether/ diethyl ether
Dimensions (mm)	0.4 × 0.2 × 0.4	0.25 × 0.1 × 0.3	0.3 × 0.2 × 0.2
Formula	C ₂₂ H ₂₀ O ₄	C ₂₂ H ₂₀ O ₄	C ₂₂ H ₂₀ O ₄
M _r	348.40	348.40	348.40
Crystal system	Triclinic*	Monoclinic	Monoclinic
Space group	P1	P2 ₁ /n	I2/a
a (Å)	8.695 (1)	9.124 (2)	19.020 (6)
b (Å)	13.633 (1)	14.392 (2)	11.963 (1)
c (Å)	8.273 (1)	14.328 (1)	17.083 (4)
α (°)	98.51 (1)	90	90
β (°)	113.34 (1)	94.30 (1)	105.15 (1)
γ (°)	80.97 (1)	90	90
V (Å ³)	885.2 (1)	1876.1 (5)	3752 (2)
Z	2	4	8
D _c (g cm ⁻³)	1.307	1.233	1.233
F(000)	368	736	1472
μ (cm ⁻¹)	6.9	6.5	6.5
Data collection (Cu Kα radiation, λ = 1.5418 Å)			
Reflections for cell			
Number	25	10	20
2θ (°)	110–119	86–94	50–81
Intensity measurements			
2θ(max.) (°)	155	155	155
ω scan (°)	1.15 + 0.30tanθ	0.94 + 0.30tanθ	1.05 + 0.30tanθ
Scan speed (min ⁻¹)	32	8	16
(up to 8 rescans)			
h	-11 → 11	-12 → 12	-24 → 24
k	-17 → 17	0 → 18	0 → 15
l	0 → 10	0 → 18	0 → 21
Total reflections measured	3835	4045	4282
Total unique reflections	3576	3729	3878
R(int)	0.021	0.015	0.014
Reflections with I ≥ 3σ(I)	3046	2289	1577
%	85.2	61.4	40.7
Transmission factor	0.79–1.0	0.87–1.0	0.95–1.0
Structure refinements			
Number of parameters	324	276	235
Data/parameters ratio	9.4	8.3	6.7
Δ/σ(max.)	0.01	0.01	0.01
Δρ (e Å ⁻³)	-0.31 to +0.32	-0.22 to +0.28	-0.30 to +0.32
R [I ≥ 3σ(I)]	0.057	0.048	0.074
wR	0.092	0.065	0.062
S (goodness of fit)	3.0	1.9	4.3
R (all data)	0.068	0.101	0.184
Extinction, g	0.81 × 10 ⁻⁴	0.98 × 10 ⁻⁵	

* Reduced cell with $c < a < b$, and α, β non-acute (*Crystal Data*, 3rd ed., Vol. 4, p. 4). The type I cell with $a < b < c$ (*International Tables for X-ray Crystallography*, Vol. A, p. 737) is obtained by the transformation (001/100/010).

Dimethyl 5,11-dimethyldibenzo[a,e]cyclooctene-6,12-dicarboxylate (3). M.p.: 405–407 K. IR: 1713 (ester carbonyl stretch), 1642 (C=C stretch) cm⁻¹. ¹H NMR: δ, 2.40 (s, 6H, methyl hydrogens), 3.71 (s, 6H, ester methyl hydrogens), 7.01–7.16 (m, 8H, aromatic). ¹³C NMR: δ, 22.63 (CH₃), 51.93 (ester CH₃), 125.73, 126.85, 127.35, 127.92 (aromatic C—H), 129.87, 135.64, 142.99, 149.73 (quaternary aromatic and vinylic C), 168.20 (carbonyl C). MS: *m/e* (relative intensity): 348 (*M*⁺, 9.5), 317 (6.2), 288 (100), 257 (8.8), 245 (4.2), 229 (96.6), 215 (55.2), 202 (12.6), 189 (5.9), 113 (23.5), 100 (20.0), 94 (4.0), 88 (9.4), 75 (5.5), 59 (3.7), 44 (5.9), 32 (3.8). Exact mass calculated (C₂₂H₂₀O₄): 348.1362; measured: 348.1361. Elemental analysis: (C₂₂H₂₀O₄) calculated: C 75.84, H 5.79%. Found: C 75.84, H 5.73%.

Photolysis of (1) in the solid state. Compound (1) (0.3 g, 0.9 mmol) was photolyzed in the form of polycrystalline samples between Pyrex plates (2.5 × 7.5 cm) for 24 h (5% conversion by GC). The reaction mixture was dissolved in chloroform–diethyl ether and the unreacted starting material was crystallized out. Then the starting material was photolyzed again in the crystalline form as described above. This process was repeated several times until enough photolysis mixture was obtained to chromatograph. An oil (0.2 g) containing approximately 50% unreacted (1) and the photoproducts was subjected to silica gel flash chromatography by using 8% (v/v) ethyl acetate in petroleum ether. This resulted in the separation of photoproducts from the unreacted (1). The resulting mixture (oil, 0.1 g), rich in the solid-state product (*R*_f 5.26 min), was subjected to conventional gravity silica gel column chromatography, and elution with 4% (v/v) ethyl acetate in petroleum ether gave products with *R*_f's 4.50 (3) and 5.26 min (4) as a mixture (21:78 by GC) in the form of a colorless solid. Repeated fractional crystallization from petroleum ether–diethyl ether yielded nice needles (20 mg, 7%) of the product with *R*_f 5.26 min which was later characterized as compound (4).

Dimethyl 5,10-dimethyl-5,10-dihydroinden[2,1-a]-indene-5,10-dicarboxylate (4). M.p.: 431–433 K. IR: 1733 (ester carbonyl stretch) cm⁻¹. ¹H NMR: δ, 1.79 (s, 6H, methyl hydrogens), 3.68 (s, 6H, ester methyl hydrogens), 7.24–7.66 (m, 8H, aromatic). ¹³C NMR: δ, 22.26 (CH₃), 29.77 (quaternary *sp*³ C), 52.76 (ester CH₃), 120.31, 123.89, 125.85, 128.01 (aromatic C—H). Other carbon signals were not observed as the concentration of the solution was very low. MS: *m/e* (relative intensity): 348 (*M*⁺, 49.6), 289 (12.9), 273 (4.0), 257 (18.6), 245 (18.0), 230 (100), 215 (96.4), 202 (10.2), 189 (7.4), 169 (12.7), 113 (11.4), 101 (11.7), 94 (3.4), 88 (5.2), 69 (17.5), 44 (14.3), 32 (4.0). Exact mass calculated (C₂₂H₂₀O₄): 348.1362; measured: 348.1370.

X-ray analyses

The crystal and molecular structures of reactant (1) and photoproducts (3) and (4) were determined by single-crystal X-ray diffraction analysis. The general procedures and parameters of data collection are summarized in Table 1. Intensities were measured at 294 K with a Rigaku AFC6 diffractometer and Cu Kα radiation (λ = 1.5418 Å). Lp and absorption corrections (ψ scan) were applied. The structures were solved by direct methods using *TEXSAN* (Molecular Structure Corporation, 1990); for (4), solution was achieved in space group *Ia* (after failed attempts in *I2/a*), but the derived structure contained two independent molecules lying on twofold axes in *I2/a*.

Refinement was by full-matrix least-squares methods on F , minimizing $\sum w(|F_o| - |F_c|)^2$, with $w = 1/\sigma^2(F)$ ($p = 0.05$). Residual electron-density peaks of 0.5–0.8 e Å⁻³ and relatively large oxygen thermal parameters suggested minor disorder in one ester group in each of the structures; this was modeled by introducing split oxygen sites for (1) (0.9/0.1) and (3) (0.85/0.15), with the lower occupancy sites refined isotropically. For (1), H atoms were refined (except for the lower occupancy methyl group); for (3), aromatic H atoms were refined, methyl H atoms were fixed; for (4), all H were fixed in calculated positions. Details of the refinements are in Table 1.

Discussion

Final positional parameters are in Table 2,* and selected bond lengths and angles are in Table 3. Fig. 3 shows views of the three molecules, (1), (3) and (4).

The structure and dimensions of the molecule of the dibenzobarrelele derivative, (1), are very similar to those of the parent hydrocarbon (Trotter & Wireko, 1990) and of other derivatives (Garcia-Garibay *et al.*, 1990*a,b*). The bond angles external to the aromatic rings, mean 125.9° (Table 3), and the intra-annular benzene-barrelele angles, mean 114.0°, are distorted to about the same extent as in the other derivatives. The C11—C12 distance [1.335 (2) Å] corresponds to a double bond. The two ester groups are rotated out of the plane of the double bond to different extents; the C12—C11—C13—O2 (φ_1) and C11—C12—C15—O4 (φ_2) dihedral angles are +88.5 (3) and -151.4 (3)° [+157.9 (7)° for the lower occupancy site], respectively (for the enantiomer in Fig. 3; the crystals are racemic). Thus the ester group at C11 is not conjugated to the C11—C12 bond ($\cos^2\varphi_1 = 0$) while the group at C12 is considerably conjugated [$\cos^2\varphi_2 = 0.77$ (0.86)]; this difference is not reflected in the C11—C13 [1.489 (2) Å] and C12—C15 [1.488 (1) Å] bond lengths, which are equal and between the expected conjugated (1.470 Å) and non-conjugated (1.497 Å) lengths (Allen, 1981).

In the COT molecule, (3), the central eight-membered ring has the tub conformation (Dunitz, 1968), with dihedral angles 0–3.6 (4)° at the double bonds and 63.4–70.0 (3)° at the single bonds (and hence little or no conjugation between the aromatic rings and the double bonds of the eight-membered ring). The bond angles at the ring junctions show

Table 2. Positional and equivalent isotropic thermal parameters, with estimated standard deviations in parentheses

$$B_{eq} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq} (Å ²)
(1)				
O1	0.3043 (2)	0.3878 (1)	0.3091 (2)	4.65 (6)
O2	0.3247 (2)	0.3144 (1)	0.0567 (2)	5.07 (7)
O3	0.5739 (2)	0.4745 (1)	0.2842 (3)	5.00 (8)
O4	0.8339 (3)	0.4304 (2)	0.3031 (5)	8.1 (1)
O3'	0.586 (2)	0.449 (1)	0.212 (2)	3.5 (3)
O4'	0.836 (2)	0.456 (1)	0.405 (2)	2.9 (2)
C1	0.5920 (3)	0.1787 (2)	0.7230 (3)	4.28 (8)
C2	0.6923 (4)	0.1966 (2)	0.9018 (3)	5.3 (1)
C3	0.8436 (4)	0.2341 (2)	0.9512 (3)	5.1 (1)
C4a	0.8027 (2)	0.2341 (1)	0.6474 (2)	3.20 (6)
C4	0.9010 (3)	0.2529 (2)	0.8259 (2)	4.20 (7)
C5	0.9606 (3)	0.0910 (2)	0.3360 (3)	3.95 (7)
C6	0.9306 (3)	-0.0000 (2)	0.2362 (3)	4.71 (8)
C7	0.7770 (3)	-0.0354 (2)	0.1849 (3)	4.87 (9)
C8	0.6489 (3)	0.0201 (2)	0.2316 (3)	4.04 (7)
C8a	0.6791 (2)	0.1111 (1)	0.3314 (2)	3.24 (6)
C9a	0.6484 (2)	0.1973 (1)	0.5970 (2)	3.24 (6)
C9	0.5544 (2)	0.1810 (1)	0.3960 (2)	3.13 (6)
C10a	0.8348 (2)	0.1469 (1)	0.3830 (2)	3.09 (6)
C10	0.8487 (2)	0.2493 (1)	0.4920 (2)	3.11 (6)
C11	0.5478 (2)	0.2820 (1)	0.3306 (2)	2.97 (6)
C12	0.6960 (2)	0.3170 (1)	0.3775 (2)	2.94 (6)
C13	0.3822 (2)	0.3300 (1)	0.2147 (2)	3.31 (6)
C14	0.1514 (3)	0.4477 (3)	0.2106 (5)	6.3 (1)
C15	0.7139 (2)	0.4124 (1)	0.3226 (2)	3.52 (6)
C16	0.5733 (5)	0.5688 (2)	0.2283 (5)	6.1 (1)
C17	0.3836 (3)	0.1435 (2)	0.3388 (3)	4.36 (8)
C18	1.0207 (2)	0.2862 (2)	0.5506 (3)	4.23 (8)
(3)				
O1	0.4596 (3)	0.3172 (2)	0.8591 (2)	6.0 (1)
O2	0.3366 (4)	0.2099 (2)	0.9283 (2)	8.5 (2)
O3	0.8945 (3)	0.0571 (2)	0.7936 (2)	5.8 (1)
O4	0.9908 (3)	0.1179 (3)	0.6740 (3)	10.5 (2)
O3'	0.907 (2)	0.033 (1)	0.749 (1)	4.2 (3)
O4'	0.977 (2)	0.175 (1)	0.755 (1)	6.3 (3)
C1	0.2778 (3)	0.2523 (2)	0.6546 (2)	4.3 (1)
C2	0.2563 (4)	0.2992 (2)	0.5705 (2)	5.1 (1)
C3	0.3752 (4)	0.3201 (2)	0.5200 (2)	5.1 (1)
C4a	0.5380 (3)	0.2460 (2)	0.6379 (2)	3.3 (1)
C4	0.5147 (4)	0.2950 (2)	0.5537 (2)	4.2 (1)
C5	0.6734 (3)	-0.0085 (2)	0.5910 (2)	3.9 (1)
C6	0.5924 (3)	-0.0866 (2)	0.5666 (2)	4.4 (1)
C7	0.4689 (3)	-0.1062 (2)	0.6137 (2)	4.4 (1)
C8a	0.5121 (3)	0.0306 (2)	0.7095 (2)	3.2 (1)
C8	0.4295 (3)	-0.0492 (2)	0.6844 (2)	4.0 (1)
C9a	0.4182 (3)	0.2248 (2)	0.6892 (2)	3.3 (1)
C9	0.4737 (3)	0.0866 (2)	0.7912 (2)	3.5 (1)
C10a	0.6351 (3)	0.0513 (2)	0.6615 (2)	3.3 (1)
C10	0.6908 (3)	0.2212 (2)	0.6730 (2)	3.6 (1)
C11	0.4346 (3)	0.1763 (2)	0.7816 (2)	3.5 (1)
C12	0.7315 (3)	0.1328 (2)	0.6854 (2)	3.5 (1)
C13	0.4036 (3)	0.2337 (2)	0.8641 (2)	4.2 (1)
C14	0.4459 (6)	0.3794 (4)	0.9374 (3)	6.9 (2)
C15	0.8848 (3)	0.1068 (2)	0.7176 (2)	4.7 (1)
C16	1.0375 (5)	0.0196 (5)	0.8231 (5)	8.2 (3)
C17	0.4884 (5)	0.0357 (3)	0.8835 (2)	5.3 (2)
C18	0.7927 (4)	0.3029 (3)	0.6904 (3)	6.1 (2)
(4)				
O1	0.3601 (3)	0.4838 (4)	0.1120 (3)	9.3 (3)
O2	0.3493 (4)	0.5804 (5)	0.2122 (3)	13.4 (4)
C1	0.1639 (3)	0.6685 (5)	0.1308 (3)	5.6 (3)
C2	0.0903 (4)	0.6650 (6)	0.1269 (4)	6.7 (4)
C3	0.0385 (4)	0.6646 (6)	0.0536 (4)	7.6 (4)
C4	0.0583 (4)	0.6677 (6)	-0.0189 (4)	6.6 (4)
C4a	0.1313 (3)	0.6691 (5)	-0.0160 (3)	4.9 (3)
C9	0.3336 (3)	0.6744 (5)	0.0867 (3)	4.8 (3)
C9a	0.1827 (3)	0.6702 (4)	0.0579 (3)	4.6 (3)
C11	0.2539 (3)	0.6713 (4)	0.0400 (3)	4.5 (2)
C13	0.3506 (3)	0.5759 (7)	0.1434 (4)	5.9 (3)
C14	0.3741 (4)	0.3837 (6)	0.1607 (4)	9.2 (5)
C17	0.3522 (4)	0.7834 (5)	0.1355 (4)	7.3 (4)
O1'	0.6754 (3)	0.7205 (4)	0.0555 (3)	8.2 (3)
O2'	0.6338 (5)	0.8016 (5)	0.1429 (4)	17.4 (5)
C1'	0.8458 (4)	0.9147 (5)	0.1778 (4)	6.0 (3)
C2'	0.9214 (4)	0.9145 (6)	0.2109 (4)	7.0 (4)
C3'	0.9689 (3)	0.9157 (6)	0.1622 (4)	7.0 (4)
C4'	0.9436 (4)	0.9160 (5)	0.0781 (4)	6.2 (3)

* Lists of anisotropic thermal parameters, hydrogen positions, bond lengths and angles, and structure factors, together with packing diagrams have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55370 (61 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0614]

Table 2 (*cont.*)

	x	y	z	B _{eq}
C4a'	0.8695 (4)	0.9151 (5)	0.0451 (4)	5.1 (3)
C9'	0.6729 (3)	0.9152 (5)	0.0474 (4)	5.4 (3)
C9a'	0.8212 (3)	0.9151 (5)	0.0935 (4)	4.9 (3)
C11'	0.7476 (3)	0.9161 (4)	0.0380 (3)	4.8 (3)
C13'	0.6585 (4)	0.8073 (6)	0.0885 (4)	6.4 (4)
C14'	0.6644 (4)	0.6122 (5)	0.0871 (4)	8.3 (4)
C17'	0.6557 (4)	1.0170 (5)	0.0942 (4)	7.1 (4)

For (1) and (3), occupancies for O3/O4 are 0.9 and 0.85, for O3'/O4' 0.1 and 0.15. For (4), primed atoms are the second independent half-molecule (full occupancies).

Table 3. Selected bond lengths (Å) and angles (°) (mean values where appropriate)

	(1)	(3)	(4)
C=C	1.335 (2)	1.340 (3)	1.33 (1)
C—C(arom.)	1.372–1.397 (3)	1.371–1.400 (3)	1.374–1.400 (8)
C—CO ₂ Me	1.488, 1.489 (2)	1.484, 1.486 (3)	1.506, 1.529 (8)
C—C(others)	1.517–1.545 (2)	1.485–1.508 (3)	1.463–1.575 (8)
C=O	1.191 (3)	1.196 (4)	1.166 (7)
C—OMe	1.324 (3)	1.308 (4)	1.261 (7)
O—Me	1.439 (3)	1.444 (4)	1.442 (7)
Ring-junction angles			
External	125.7–126.1 (2)	118.4–119.6 (2)	129.9 (mean, 5/6-rings) 136.7 (mean, 5/5-ring)
Internal	113.6–114.3 (1)	121.1–122.8 (2)	108 (mean, 5-ring) 120 (mean, 6-ring)

little distortion from normal values; the external angles average 119.0°, and the intra-annular benzene–cyclooctene angles, mean 122.0°, are similar to the other angles in the eight-membered ring, mean 122.4°. The C9—C11 [1.339 (3) Å] and C10—C12 [1.341 (3) Å] bond lengths (Fig. 3 and Table 3) correspond to double bonds, and the other bond lengths in the eight-membered ring to aromatic [1.391, 1.394 (3) Å] or single bonds [1.485–1.498 (3) Å]. The ester groups are again rotated out of the planes of the double bonds, the group at C11 by 41.2 (4)° and that at C12 by 65.2 (5)° [or 15.1 (8)° for the minor occupancy site].

Crystals of the pentalene derivative, (4), contain two independent molecules, each lying on a twofold axis and hence having exact C₂ symmetry. The ring system is nearly planar in each molecule, the central bond in the ring system being a C=C double bond [1.328, 1.324 (9) Å]. Bond angles are in the range of expected values for fused five- and six-membered rings; the external angle at the junction of the two five-membered rings is 137.5° (mean).

Photochemistry of (1)

The photochemistry of compound (1), in solution and in the solid state, exhibits unique differences as a function of medium. In acetone, a solvent and a triplet energy sensitizer, mainly one product is obtained, which has been characterized as the semi-

bullvalene derivative, (2) (Fig. 2). In acetonitrile (direct irradiation), (2) and an additional product (3), a cyclooctatetraene (COT) derivative, are formed. Some additional minor products are also formed in both solvent media (as indicated by GC), but were not isolated. In the crystalline state, however, a new product (4) is formed as a major product, along with minor amounts of the solution products (2) and (3). The product ratios in various media

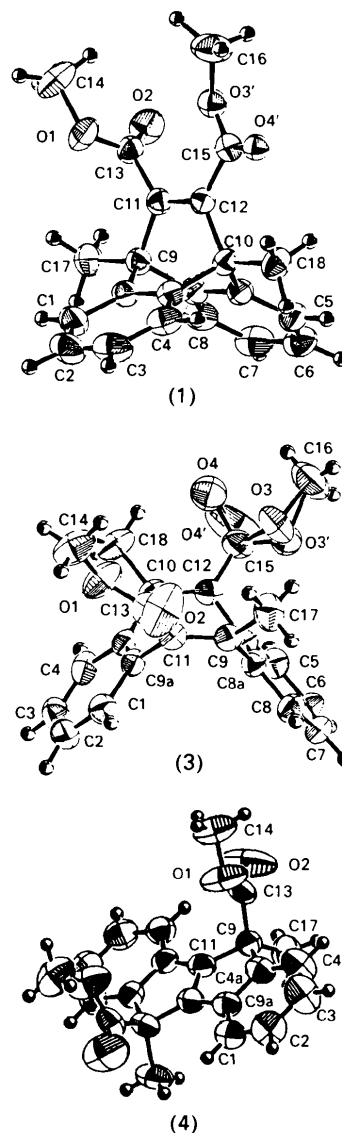


Fig. 3. Views (50% thermal ellipsoids) of (1), (3) and (4) [for (4), the enantiomer of Figs. 2 and 4; crystals are racemates]. The dibenzobarrelene numbering system of (1) is retained in (3) and (4). In (1), only one of the two C12-ester orientations is shown, and the four unlabelled atoms in the lower middle of the drawing are (from left to right) C9a, C4a, C8a, C10a. In (3), the unlabelled atom bonded to C8a is C10a. In (4), atoms O1, O2, C9, 11, 13, 14, 17 shown are related to those listed in Table 2 by the C₂ molecular symmetry axis.

along with their absolute error limits are included in Fig. 2; sums of all unidentified peaks observed on GC are given in the 'unknown' column. The product ratios in solution are found to be sensitive to both the solute concentration and percent conversion to products. Control experiments indicate that photo-product interconversion is not occurring under the photolysis conditions used, hence we may conclude that compounds (2), (3) and (4) are primary photo-products of (1). The structure of the solid-state product (4) provided an important clue to the interpretation of the photochemistry of these bridgehead-substituted dibenzobarrelene diester derivatives.

Solution photolysis

The formation of compound (2) can easily be envisaged in terms of the di- π -methane rearrangement of (1) *via* its triplet excited state. This is consistent with the fact that (2) is formed exclusively in the presence of a sensitizer. Since (1) is symmetrically substituted, the di- π -methane reaction is expected to produce only one semibullvalene derivative (2) as a racemate (Fig. 2).

Application of Zimmerman's mechanism of COT formation from benzo- and naphthobarrelenes to compound (1) would produce a COT with *mirror* symmetry (Fig. 1). The COT is formed only when irradiated in the absence of a triplet sensitizer, indicating that it is singlet-derived.

Solid-state photolysis

The solid-state photolysis of (1) produces a new compound (4) as the major product (Fig. 2). Mass spectrometry indicated that (4) is isomeric with the starting material, IR spectroscopy that its ester carbonyl groups are saturated, and the ^1H NMR spectrum that the compound is symmetric, as only one methyl (6H) and one ester methyl (6H) signal are observed. Based on literature precedent, compounds similar to (1) are expected to undergo only the di- π -methane rearrangement and a rearrangement to a COT derivative under the photolysis conditions used, and it was not possible to characterize the solid-state product based only on its spectral data. Since compound (4) was crystalline, single-crystal X-ray diffraction analysis was used as the definitive step in its characterization; (4) was found to have an interesting pentalene-like structure with the stereochemistry shown in Figs. 2 and 3. The structure of (4) presented an interesting puzzle as to how it may be formed from compound (1). Inspection of the structure of (4) provided a mechanism which is reasonably convincing in rationalizing its formation (Fig. 4). A biradical (5) which contains a pentalene-like skeleton can be formed from (1) by two 1,2-aryl shifts to the two different carbon atoms of the

central double bond (Fig. 4). It is apparent that biradical (5) is quite stable, as it is bis(benzylic) and the radical centers in it are tertiary in nature. Then, sequential 1,2-ester migration (involving the carbonyl group of the ester) to the radical sites would give (4) with the observed stereochemistry. The 1,2-ester migration involves the formation of an intermediate cyclopropyloxy radical, and hence migration cannot be to a different face of the dibenzopentalene. Aldehydes, ketones and thioester groups are known to undergo 1,2-migration to adjacent radical sites (Wollowitz & Halpern, 1984; Lindsay, Luszyk & Ingold, 1984); however, the present example seems to be a first example of such an ester migration (Pokkuluri, Scheffer & Trotter, 1990).

The possible involvement of biradical (5) in the photorearrangement to (4) suggested the intriguing possibility that a COT may arise by the Grob-type fragmentation of (5) (Fig. 4). The striking feature of such a possibility is that the COT thus formed would have C_2 symmetry and *not* the C_1 symmetry expected from the $2\pi + 2\pi$ mechanism of Zimmerman (Fig. 1). This means that the actual structure of (3) may be either of the two COT structures which are difficult to distinguish from the spectral data. Again, a solution to this problem was sought in the determination of the crystal structure of (3). Single-crystal X-ray analysis proved unambiguously that the COT formed from (1) is of C_2 symmetry (Figs. 3 and 4) and is not the one shown in Fig. 1. Since the X-ray analysis was performed on the COT isolated from the solution photolysis, it leaves open the possibility that the COT formed in the solid state may be a different one. Comparison of the GC retention times (DB-1 and DB-17 columns), including co-injection of an authentic sample of COT isolated from solution along with the solid-state photolysis mixture, indicates that both COTs are the same. Additional corroboration came from the ^1H NMR spectrum of the solid-state mixture, in which the methyl groups of the COT appear at the same frequency as those of the COT isolated from solution.

The reluctance of compound (1) to undergo $2\pi + 2\pi$ photocycloaddition to produce a cage compound may reasonably be attributed to steric factors resulting from the presence of two bridgehead methyl substituents; the stability of biradical (5) may be the driving force for the alternative rearrangement pathway observed.

Origin of biradical (5)

Since compounds (3) and (4) are not formed in the photolysis of (1) in the presence of a triplet energy sensitizer, it is reasonable to assume that the proposed biradical (5) is singlet-derived. A likely pathway by which (5) could be formed is included in

Fig. 4. Double bridging on opposite sides of the central double bond in the case of barrelene has been considered as one of the possible routes of the di- π -methane rearrangement (Fig. 4) (Zimmerman & Grunewald, 1966; Zimmerman *et al.*, 1967); on the basis of Hückel calculations, it was concluded that such double bridging would have a slightly higher energy barrier if it were to be a concerted rather than a stepwise process. Similar arguments may be extended to the present case, which means that biradical (5) probably arises from a stepwise process (Fig. 4). The two biradical structures prior to the formation of (5) are not necessarily intermediates, but are points on the energy surface leading to biradical (5), which may be regarded as an intermediate that leads to the products.

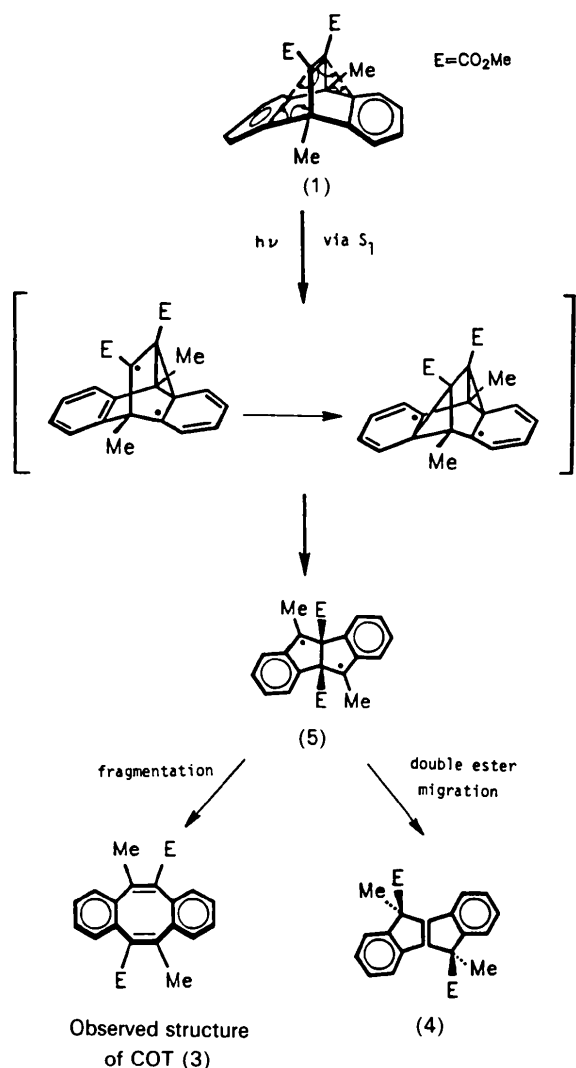


Fig. 4. Proposed reaction mechanism, involving intermediate biradical (5), in the formation of photoproducts (3) and (4).

Unique reactivity of (1) in the solid state

If a common biradical is involved in the formation of both compounds (3) and (4), the question then arises as to why (4) is formed only in the crystalline state, and not even a trace (as indicated by GC and 1H NMR spectroscopy) is formed in solution phase. Experience in such a situation suggests that this difference may be due to some unique features of (1) in the solid state, and its rationalization was approached from different points of view as discussed below.

Recently, Zimmerman & Zuraw (1989) have used the differences in volumes (ΔV) between starting material, the intermediate biradical species and the final products in attempting to rationalize the formation of solid-state products different from those formed in solution. They found that the volume change, in going from starting material to intermediate biradical species, as well as biradical to product, was less for products formed in the solid state, as would be expected based on topochemical restrictions. With these ideas in mind, the molecular volumes of starting material (1), the two photoproducts [(3) and (4)] and the biradical (5) [generated by *MM2* calculations (Allinger & Flanagan, 1983)], were calculated using the program *MOLENC* (Ariel, 1985). The van der Waals radii used for C, O and H were 1.75, 1.40 and 1.17 Å, respectively (Mirsky, 1978), and all C—H bond distances were taken as 1.11 Å. It was anticipated that if the volume change in going from (1) to (4) is smaller than that in going from (1) to (3), then the formation of (4) may be favoured in the solid state owing to topochemical restrictions. The calculated molecular volumes are 313.3, 312.2, 314.4, 318.6 Å³ for (1), (5), (4), (3), respectively. Thus the volume changes for (1)→(4) (+1.1 Å³) and (5)→(4) (+2.2 Å³) are smaller than those for (1)→(3) (+5.3 Å³) and (5)→(3) (+6.4 Å³), favouring the formation of (4). However, the differences are very small, and probably not significant enough to cause such a dramatic difference in reactivity.

In another attempt using the best molecular fit (*BMFIT*) program (Nyburg, 1978), the molecular structures of the starting material (1) and the two photoproducts (3) and (4) (one at a time) were superimposed in order to determine which of the photoproducts has better congruence with the structure of the starting material, based on sums of the squares of the distances between respective atoms, $\sum \Delta^2$, a smaller value for which indicates a better overlap (*i.e.* a better fit in shape) of the two structures. A limitation of this approach is that the product structures used are derived from the X-ray crystal structures of the pure products, which may not be the conformations in which they were formed

in the lattice of the starting material during the photoreaction. The *BMFIT* analysis has proved to be successful in explaining the solid-state regioselectivities of the di- π -methane reactions of several dibenzobarrelene diesters (Garcia-Garibay *et al.*, 1990*a,b*), but in the present case it does not seem to be consistent with the observed results. In fact, the structures of the COT (3) and (1) have a slightly better fit compared to the solid-state product (4) and (1), as indicated by the values of $\Sigma\Delta^2$ of 64.8 and 67.1 Å², respectively. Once again the differences are small and the significance of such an interpretation is questionable.

Kinetic factors

If biradical (5) exhibits different reactivity in solution and the solid state, it may reflect the fact that its conversion to COT in solution is much more rapid than in the solid state. In other words, the biradical may be longer lived in the solid state and be capable of exploring alternative reaction pathways, such as double ester migration leading to (4). The difference in the rate of fragmentation of (5) in the solid state may be attributed to topochemical factors, because (speculatively) it appears that the structure of (4) resembles closely that of (5) (in the sense that planarity of the molecular frame is retained), whereas the structure of (3) does not. It is reasonable to assume that fragmentation of the 1,4-biradical (5) may be difficult in the solid state because of poor orbital overlap which requires much molecular motion to overcome. However, a careful examination of packing* and intermolecular contact distances of the lattice of the starting material (1) failed to reveal any specific details that may help rationalize the unusual photobehaviour.

Single crystal versus powder reactivity

As indicated in Fig. 2, it was observed that, in general, the photoproduct selectivity in the solid state is lowered when powdered material is irradiated. In several runs, the percent of product (4) formed in single crystals varied from 70 to 90% depending on the size and quality of the crystals used; in contrast, (4) is formed in 45–55% in photolyses using powdered material. This can be taken as added support for the suggestion that (4) is formed in the solid state owing to some unique features related to the bulk structure of the starting material. Also, percent conversion for a given length of irradiation was typically lower ($\leq 5\%$) in single-crystal irradiations compared to that in powdered samples (5–10%), and melting was not observed in any of the solid-state irradiations. Similar behaviour

observed in the analogous case of 9-methyldibenzobarrelene diester was attributed to a lower reaction selectivity at the surface of the crystal compared to that in the bulk, and since surface area increases when the crystal is powdered, the selectivity is lost to some extent (Pokkuluri, Scheffer & Trotter, 1989).

Structure of photoproduct (2)

Compound (2), thought to be triplet-derived, was characterized based on its spectral data, and is assigned the semibullvalene structure shown in Fig. 2. The assignment of the structure is based largely on its ¹H NMR spectrum, in which two non-equivalent methyl signals and two non-equivalent ester methyl signals are observed. The argument that compound (2) may have a structure resulting from the direct coupling of the radical centers in biradical (5) can be dismissed because such a structure would be symmetric to ¹H NMR spectroscopy [*i.e.* would give rise to only one (6H) methyl signal and one (6H) ester methyl signal]. The ¹³C NMR spectrum of compound (2) also supports the assigned structure. It should be mentioned here that the possibility of a structure for (2) that results from radical closure after one ester migration cannot be ruled out completely; however, such a structure is not very likely owing to its ring strain. Also, compound (2) is not likely to come from biradical (5), because (5) is singlet-derived and (2) is not. Several attempts to obtain good-quality single crystals of (2) for X-ray analysis were not successful.

Thus, it is reasonable to conclude that the triplet excited state of (1) is behaving as expected by undergoing the di- π -methane rearrangement, whereas the singlet excited state is behaving unexpectedly by rearranging to an abnormal COT (3), and to an unusual ester migration product (4) in the solid state.

The dibenzobarrelene derivative (6) [(1) in Fig. 4, but with *E* = COPh], an analogue of compound (1), was reported earlier to produce a COT which was assigned a structure based on the $2\pi + 2\pi$ mechanism (Kumar, Murty, Lahiri, Chackachery, Scaiano & George, 1984). Following our suggestion, these authors reinvestigated the structure of the COT formed by X-ray diffraction methods and found it to be of *C*₂ symmetry analogous to (3) and not the earlier assumed structure (Asokan, Kumar, Das, Rath & George, 1991). Compound (6) was also found to rearrange to a dibenzopentalene derivative analogous to (4) (Fig. 4). These results provide additional support for the involvement of 1,4-biradicals such as (5), and for the generality of the unexpected photorearrangements of compound (1).

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* The packing diagrams were deposited. See deposition footnote.

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Structures of *meso*- and (\pm)-1,2-Dinitro-1,2-diphenylethane and 2,3-Dinitro-2,3-diphenylbutane

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Abstract

The crystal and molecular structures of *meso*-1,2-dinitro-1,2-diphenylethane, C₁₄H₁₂N₂O₄, (1), (\pm)-1,2-dinitro-1,2-diphenylethane, C₁₄H₁₂N₂O₄, (2), *meso*-2,3-dinitro-2,3-diphenylbutane, C₁₆H₁₆N₂O₄, (3), and (\pm)-2,3-dinitro-2,3-diphenylbutane, C₁₆H₁₆N₂O₄, (4), have been determined by single-crystal X-ray diffraction methods. Compound (1): monoclinic, *P*2₁/*n*, *M*_r = 272.3, *a* = 5.597 (3), *b* = 8.185 (4), *c* = 14.389 (6) Å, β = 90.51 (2)°, *V* = 659.2 (6) Å³, *Z* = 2, *D*_x = 1.372 Mg m⁻³, Mo *K*α (λ = 0.71069 Å), μ = 0.096 mm⁻¹, *F*(000) = 284, *T* = 297 K, *R* = 0.051 for 604 reflections. Compound (2): monoclinic, *C*2/*c*, *M*_r = 272.3, *a* = 18.260 (5), *b* = 9.888 (3), *c* = 17.660 (4) Å, β = 119.40 (2)°, *V* = 2778.2 (13) Å³, *Z* = 8, *D*_x = 1.302 Mg m⁻³, Mo *K*α (λ = 0.71069 Å), μ = 0.091 mm⁻¹, *F*(000) = 1136, *T* = 297 K, *R* =

0.053 for 1000 reflections. Compound (3): monoclinic, *P*2₁/*n*, *M*_r = 300.3, *a* = 7.763 (2), *b* = 18.406 (3), *c* = 10.240 (2) Å, β = 90.10 (2)°, *V* = 1463.2 (5) Å³, *Z* = 4, *D*_x = 1.363 Mg m⁻³, Mo *K*α (λ = 0.71068 Å), μ = 0.099 mm⁻¹, *F*(000) = 632, *T* = 297 K, *R* = 0.033 for 1749 reflections. Compound (4): monoclinic, *C*2/*c*, *M*_r = 300.3, *a* = 17.928 (5), *b* = 8.713 (2), *c* = 12.366 (4) Å, β = 129.14 (2)°, *V* = 1498.2 (7) Å³, *Z* = 4, *D*_x = 1.331 Mg m⁻³, Mo *K*α (λ = 0.71069 Å), μ = 0.097 mm⁻¹, *F*(000) = 632, *T* = 297 K, *R* = 0.041 for 898 reflections. Compound (1) adopts a structure in which the two nitro groups are *trans* to each other. In compounds (2), (3) and (4) the two nitro groups are *gauche*. Contrary to normal expectation, (3) (the *meso* compound) has a lower melting point than (4) (the racemate). Semiempirical MO studies on the geometries and *gauche:trans* population distributions of these compounds in the gas phase are also reported.

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