Table 6. *Values of* $\Delta_n(x_0)$ [*cf. definition* (3)]

$\frac{1}{2}x_0$ is the ratio (amount of splitting)/full width at half maximum.

		$\frac{1}{2}x_0$: 0.15	0.3	0.6	0.9
Lorentz	$n = 1$	1.0055	1.0210	1.0710	1.1270
	2	1.0028	1.0109	1.0395	1.0747
	4	1.0014	1.0059	1.0245	1.0509
	8	1.00076	1.0034	1.0173	1.0402
	16	1.00041	1.0022	1.0138	1.0354
	32	1.00024	1.0015	1.0121	1.0335
Gauss	∞	1.00007	1.0009	1.0105	1.0309

It can be shown that under these conditions always

$$\int_{-\infty}^{\infty} g_n^2(x;a,b)\,\mathrm{d}x \Big/ \int_{-\infty}^{\infty} f_n^2(x;x_0)\,\mathrm{d}x \leq 1$$

but a general statement on the behaviour of

$$\Delta_n(x_0) = \int_{-\infty}^{\infty} g_n(x;a,b)\,\mathrm{d}x \Big/ \int_{-\infty}^{\infty} f_n(x;x_0)\,\mathrm{d}x, \qquad (3)$$

which is our quantity of interest, is not possible. $\Delta_n(x_0)$ may be considered as the calculated population parameter and should be 1. Obviously it is 1 for $x_0 = 0$.

The numerical evaluation of the least-squares fit shows that $\Delta_n(x_0)$ increases with increasing x_0, at least for the functions of type (2). For functions $\rho(x)$ with very steep flanks such as $\rho(x) = \exp(-|x|^z)$ with $z > 2$ the increase of Δ with increasing x_0 is preceded by a narrow x_0 range with $\Delta < 1$.

Table 6 lists values of Δ_n as function of n and x_0. In three dimensions, $(\Delta - 1)$ should be about three

times as large. Then the magnitude of order of Δ is comparable with the observed effect.

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

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Abstract

A study of the photochemistry of the title 9-phenyl-dibenzobarrelene-11,12-diester (1) reveals the formation of a semibullvalene derivative, dimethyl 8b-phenyl-4b,8b,8c,8d-tetrahydrodibenzo[a,f]cyclopropa[cd]pentalene-8c,8d-dicarboxylate (2), in acetone solution, with an additional cyclooctatetraene (COT) photoproduct, dimethyl 5-phenyldibenzo[a,e]cyclooctene-6,12-dicarboxylate (3), in acetonitrile, benzene and in solid-state photolysis. Crystal data: $T =$ 294 K, Cu $K\alpha$, $\lambda = 1.5418$ Å, $C_{26}H_{20}O_4$, $M_r = $ 396.44. (1), triclinic, $P\bar{1}$, $a = 10.713$ (1), $b = $ 11.991 (1), $c = 8.177$ (1) Å, $\alpha = 95.71$ (1), $\beta = $ 105.14 (1), $\gamma = 79.61$ (1)°, $V = 995.9$ (2) Å^3, $Z = 2$, $D_x = 1.322$ g cm^{-3}, $F(000) = 416$, $\mu = 6.8$ cm^{-1}, $R = $ 0.060 for 3069 reflections. (2), monoclinic, $P2_1/n$, $a = $ 10.206 (3), $b = 16.485$ (1), $c = 11.758$ (4) Å, $\beta = $ 95.48 (2)°, $V = 1969.2$ (8) Å^3, $Z = 4$, $D_x = $ 1.337 g cm^{-3}, $F(000) = 832$, $\mu = 6.9$ cm^{-1}, $R = 0.039$ for 2882 reflections. (3), triclinic, $P\bar{1}$, $a = 11.074$ (2), $b = 25.298$ (6), $c = 7.668$ (2) Å, $\alpha = 94.22$ (2), $\beta = $

94.53 (2), $\gamma = 101.77$ (2)°, $V = 2087.5$ (8) Å^3, $Z = 4$ (two molecules per asymmetric unit), $D_x = 1.261$ g cm^{-3}, $F(000) = 832$, $\mu = 6.5$ cm^{-1}, $R = 0.039$ for 4668 reflections. Compound (2) has a structure consistent with formation via normal di-π-methane reaction involving the triplet excited state, while formation of (3) provides another example of unexpected behaviour of the singlet excited state.

Introduction

Previous crystal structure studies of a 9,10-dimethyl-dibenzobarrelene diester (Pokkuluri, Scheffer & Trotter, 1993) have shown the production of the normal di-π-methane semibullvalene photoproduct via the triplet excited state (T_1) in acetone solvent, an additional cyclooctatetraene (COT) photoproduct in acetronitrile or benzene, and a different and unusual pentalene-type major product in solid-state photolysis, the COT and pentalene arising via the singlet excited state (S_1). Determination of the structures of the photoproducts suggested a mechanism for the reaction, which predicts (correctly) that the COT has a different substitution pattern from that expected on the basis of previously proposed mechanisms.

Acetone-sensitized photolysis of a 9-phenyl derivative (1) (Fig. 1) has been reported to produce only one of two possible di-π-methane regioisomers, (2) (Iwamura, Tukada & Iwamura, 1980); no COT formation was reported. In the present study, compound (1) has been photolysed in acetone, acetonitrile, benzene, and in the solid state. Triplet-sensitized photolysis gives mainly one photoproduct, (2), as previously described (Iwamura et al., 1980), whereas direct irradiation in solution (and in the solid state) gives an additional product (3) (Fig. 1) whose spectroscopic properties are consistent with a COT structure. The crystal structures of (1), (2) and (3) have been determined for correlation with the photochemical results.
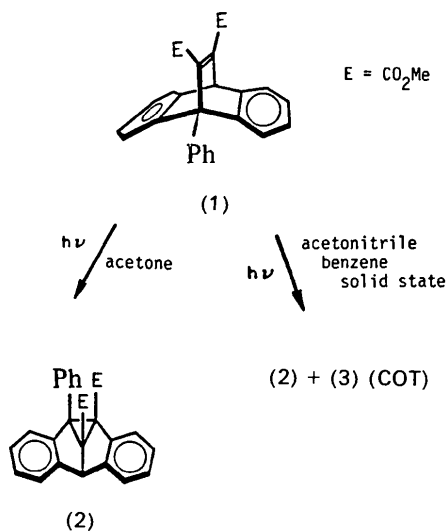
Experimental

Synthesis and photolysis

Spectroscopic characterization of materials and photolyses were carried out by standard procedures (Pokkuluri et al., 1993).

Synthesis of dimethyl 9-phenyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (1). In a round-bottomed flask fitted with a reflux condenser and a drying tube, 9-phenylanthracene (1.39 g, 5.47 mmol) and dimethyl acetylenedicarboxylate (1.02 g, 7.18 mmol) were heated together at 470 K for 1 h. Gas chromatography (GC) analysis of the reaction mixture showed 9% of unreacted 9-phenylanthracene and two products at retention times (RT) 6.03 min (66%) and 7.70 min (25%). The reaction mixture was flash chromatographed over silica gel. Unreacted 9-phenylanthracene was eluted with 8% (v/v) ethyl acetate in petroleum ether. Although this did not afford a good separation of the two products, upon standing overnight the fractions gave nice crystals of the product with RT 6.03 min (0.25 g) which was subsequently characterized as compound (1). The fractions containing both products were concentrated under reduced pressure and the oil obtained was dissolved in diethyl ether and allowed to crystallize. This yielded nice colorless crystals (0.68 g). Careful examination of these crystals revealed two morphologies, and the GC analysis of them separately showed that they belong to the two products and are each about 99% pure. The stout prisms are of (1) and the thin rectangular plates are of compound (4). These crystals were hand separated and recrystallization from diethyl ether–ethyl acetate gave 0.33 g of (1) (total yield 27%) and 0.15 g of (4) (7%).

Dimethyl 9-phenyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (1). M.p.: 449–451 K. IR: 1742, 1721 (ester carbonyl stretches), 1632 (C=C stretch) cm^{-1}. ^{1}H NMR: δ, 3.67 and 3.78 (two s, 3H each, ester methyl hydrogens), 5.70 (s, 1H, bridgehead methine), 6.93–7.78 (m, 13H, aromatic). ^{13}C NMR: δ, 51.34 (bridgehead C—H), 52.20, 52.52 (ester CH$_3$), 123.77, 124.78, 124.93, 125.44, 127.65, 128.39, 130.38 (aromatic C—H), 134.82, 144.55,

Fig. 1. Photolysis of compound (1).

(1)

E = CO$_2$Me

Ph

$h\nu$ acetone

$h\nu$ acetonitrile benzene solid state

(2) + (3) (COT)

(2)

Product percentages as a function of medium

	(2)	(3)	(%)
Acetone	97	3	± 2
Acetonitrile	27	73	± 3
Benzene	47	53	± 2
Crystal	48	52	± 3

145.24, 146.02, 154.27 (quaternary aromatic and vinylic C), 164.07, 168.17 (carbonyl C). MS: m/e (relative intensity): 397 ($M + 1$, 7.4), 396 (M^+, 26.8), 364 (11.5), 336 (79.0), 305 (31.8), 293 (25.0), 278 (100), 265 (6.9), 252 (28.0), 200 (6.9), 152 (7.3), 138 (32.5), 126 (21.1), 113 (22.1), 100 (10.3), 91 (9.6), 77 (16.5), 59 (98.9), 44 (46.1). Exact mass calculated (C$_{26}$H$_{20}$O$_4$): 396.1362; measured: 396.1363. Elemental analysis: (C$_{26}$H$_{20}$O$_4$) calculated: C, 78.77; H, 5.09%. Found: C, 78.58; H, 5.04%.

Dimethyl 9-phenyl-1,4-dihydro-1,4-ethenoanthracene-11,12-dicarboxylate (4). M.p.: 491–494 K. IR: 1732, 1722 (ester carbonyl stretches), 1642 (C=C stretch) cm^{-1}. ^{1}H NMR: δ 3.74 and 3.80 (two s, 3H each, ester methyl hydrogens), 5.07 (dd, $J = 6$ and 3 Hz, 1H, bridgehead methine), 5.39 (dd, $J = 6$ and 3 Hz, 1H, bridgehead methine), 6.78–6.85 (m, 1H, vinylic), 6.98–7.05 (m, 1H, vinylic), 7.28–7.78 (m, 10H, aromatic). ^{13}C NMR: δ, 47.55, 49.55 (bridgehead C—H), 52.15, 52.36 (ester CH$_3$), 121.22, 125.82, 125.86, 125.91, 126.41, 127.53, 127.61, 128.21, 128.33, 130.33, 130.77, 137.95, 138.78 (aromatic and vinylic C—H), 130.78, 131.36, 134.33, 137.85, 138.71, 140.62, 145.97, 147.91 (quaternary aromatic and vinylic C), 165.81, 166.45 (carbonyl C). MS: m/e (relative intensity): 397 ($M + 1$, 21.4), 396 (M^+, 74.0), 364 (16.3), 336 (80.7), 322 (5.9), 309 (23.3), 305 (49.6), 293 (11.3), 276 (100), 265 (17.0), 252 (98.8), 239 (19.4), 226 (13.3), 215 (10.2), 200 (14.4), 182 (7.0), 138 (32.2), 126 (26.4), 125 (26.2), 119 (11.0), 113 (16.4), 59 (12.0). Exact mass calculated (C$_{26}$H$_{20}$O$_4$): 396.1362; measured: 396.1363.

Photolysis of (1) *in acetonitrile.* Compound (1) (0.45 g, 1.14 mmol) was photolyzed in 300 ml of spectral grade acetonitrile until all the starting material was reacted (13 h). GC analysis showed new peaks at RT's 3.68, 3.75, 4.20 and 7.26 min. Solvent removal gave an oil which was subjected to silica gel flash chromatography by using 8% (v/v) ethyl acetate in petroleum ether. The fractions containing the product with RT 3.7 min were collected, and solvent removal under reduced pressure gave a white solid which upon recrystallization from chloroform–diethyl ether gave colorless needles (40 mg, 9%) which were later charcterized as compound (3). The fractions showing GC peaks at RT's 4.20 and 7.26 were combined and upon removal of solvent gave a colorless solid which was recrystallized from chloroform–diethyl ether to give nice prisms (21 mg, 5%); these were subsequently characterized as compound (2). This compound was found to decompose on GC to show two peaks at RT 4.20 and 7.26 min.

Dimethyl 5-phenyldibenzo[a,e]cyclooctene-6,12-dicarboxylate (3). M.p.: 466–469 K. IR: 1719 (ester carbonyl stretch), 1636 (C=C stretch) cm^{-1}. ^{1}H NMR: δ, 3.43 and 3.80 (two s, 3H each, ester methyl hydrogens), 6.88–7.59 (m, 13H, aromatic),

Table 1. Crystal data, data-collection and refinement parameters for compounds (1), (2) and (3)

	Compound (1)	Compound (2)	Compound (3)
Crystal data			
Compound type	Dibenzobarrelene	Semibullvalene	COT
Solvent	Diethyl ether/ethyl acetate	Chloroform/diethyl ether	Chloroform/diethyl ether
Dimensions (mm)	0.03 × 0.1 × 0.4	0.3 × 0.1 × 0.4	0.3 × 0.1 × 0.4
Formula	C$_{26}$H$_{20}$O$_4$	C$_{26}$H$_{20}$O$_4$	C$_{26}$H$_{20}$O$_4$
M_r	396.44	396.44	396.44
Crystal system	Triclinic*	Monoclinic	Triclinic*
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a (Å)	10.713 (1)	10.206 (3)	11.074 (2)
b (Å)	11.991 (1)	16.485 (1)	25.298 (6)
c (Å)	8.177 (1)	11.758 (4)	7.668 (2)
α (°)	95.71 (1)	90	94.22 (2)
β (°)	105.14 (1)	95.48 (2)	94.53 (2)
γ (°)	79.61 (1)	90	101.77 (2)
V (Å^3)	995.9 (2)	1969.2 (8)	2087.5 (8)
Z	2	4	4
D_x (g cm^{-3})	1.322	1.337	1.261
$F(000)$	416	832	832
μ (cm^{-1})	6.8	6.9	6.5
Data collection (Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å)			
Reflections for cell			
No.	25	21	23
2θ (°)	87–97	50–87	84–94
Intensity measurements			
$2\theta(\text{max.})$ (°)	155	155	155
ω scan (°)	0.89 + 0.30tanθ	0.94 + 0.30tanθ	1.05 + 0.30tanθ
Scan speed (° min^{-1}) (up to 8 rescans)	32	8	16
h	−14 to 14	0 to 13	0 to 14
k	−15 to 15	0 to 21	−32 to 32
l	0 to 10	−15 to 15	−10 to 10
Total reflections measured	4357	4426	7776
Total unique reflections	4066	4195	7301
R(int)	0.066	0.043	0.034
Reflections with $I \geq 3\sigma(I)$	3069	2882	4668
%	75.5	68.7	63.9
Absorption, transmission factor	0.89–1.00	0.84–1.00	0.92–1.00
Structure refinements			
No. of parameters	352	352	654
Data/parameter ratio	8.7	8.2	7.1
$\Delta/\sigma(\text{max.})$	0.01	0.01	0.08
$\Delta\rho$ (e Å^{-3})	−0.30 to +0.25	0.18 to +0.21	0.17 to +0.17
R [$I \geq 3\sigma(I)$]	0.060	0.039	0.039
wR	0.095	0.056	0.053
S (goodness of fit)	2.8	1.7	1.6
R (all data)	0.081	0.074	0.087
Extinction, g	4.4 × 10^{-5}	0.53 × 10^{-5}	0.55 × 10^{-5}

* Reduced cells with $c < a < b$, and at least two angles non-acute (*Crystal Data*, 3rd ed., Vol. 4, p. 4). The cells with $a < b < c$ (*International Tables for Crystallography*, Vol. A, p. 737) are obtained by the transformation matrices: for (1), (001/$\bar{1}$00/0$\bar{1}$0) (type I cell); for (3), (001·100/010) (type II cell).

8.19 (s, 1H, vinylic). ^{13}C NMR: δ, 51.93, 52.37 (ester CH$_3$), 126.96, 127.15, 127.45, 127.52, 127.92, 128.01, 128.10, 128.56, 128.63, 129.09, 129.56, 141.87, 141.92, 142.03 (aromatic and vinylic C—H), 132.83, 134.61, 135.52, 136.14, 136.59, 139.68, 141.30, 146.89 (quaternary aromatic and vinylic C), 166.93, 168.85 (carbonyl C). MS: m/e (relative intensity): 397 ($M + 1$, 14.4), 396 (M^+, 50.7), 365 (5.3), 336 (43.6), 305 (47.1), 293 (19.4), 278 (100), 276 (57.0), 265 (5.1), 250 (5.1), 236 (7.6), 215 (7.3), 201 (7.3), 152 (2.9), 138 (23.7), 125 (9.9), 112 (3.6), 83 (7.2), 59 (5.5), 44 (3.4). Exact mass calculated (C$_{26}$H$_{20}$O$_4$): 396.1362; measured: 396.1352. Elemental analysis: (C$_{26}$H$_{20}$O$_4$) calculated: C, 78.77; H, 5.09%. Found: C, 78.63; H, 5.02%.

Table 2. *Positional and equivalent isotropic thermal parameters* ($Å^2$), *with estimated standard deviations in parentheses*

$$U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	U_{eq}
Compound (1)				
O1	0.1263 (2)	0.0189 (2)	0.8578 (3)	5.0 (1)
O2	0.1627 (2)	0.0159 (2)	0.6005 (3)	4.8 (1)
O3	0.5514 (2)	0.1036 (2)	0.7838 (3)	4.8 (1)
O4	0.4368 (2)	−0.0302 (2)	0.8041 (3)	5.3 (1)
C1	0.1086 (3)	0.4623 (2)	0.7151 (3)	3.6 (1)
C2	0.1655 (3)	0.5464 (3)	0.6702 (4)	4.5 (1)
C3	0.2994 (3)	0.5420 (3)	0.7148 (4)	4.6 (1)
C4	0.3798 (3)	0.4539 (3)	0.8078 (3)	4.0 (1)
C4a	0.3237 (2)	0.3706 (2)	0.8531 (3)	3.3 (1)
C5	0.4078 (3)	0.2805 (3)	1.2764 (4)	4.3 (1)
C6	0.3433 (4)	0.2820 (3)	1.4039 (4)	5.0 (1)
C7	0.2113 (4)	0.2791 (3)	1.3620 (4)	4.8 (1)
C8	0.1395 (3)	0.2778 (3)	1.1931 (3)	3.9 (1)
C8a	0.2024 (2)	0.2795 (2)	1.0654 (3)	3.3 (1)
C9	0.1421 (2)	0.2738 (2)	0.8704 (3)	3.0 (1)
C9a	0.1883 (2)	0.3733 (2)	0.8071 (3)	3.1 (1)
C10a	0.3377 (2)	0.2787 (2)	1.1088 (3)	3.4 (1)
C10	0.3959 (2)	0.2702 (2)	0.9562 (3)	3.4 (1)
C11	0.2237 (2)	0.1650 (2)	0.8119 (3)	3.2 (1)
C12	0.3530 (2)	0.1644 (2)	0.8524 (3)	3.4 (1)
C13	0.1687 (3)	0.0589 (2)	0.7404 (3)	3.5 (1)
C14	0.0669 (7)	−0.0831 (4)	0.8089 (8)	7.5 (3)
C15	0.4488 (3)	0.0675 (2)	0.8115 (3)	3.6 (1)
C16	0.6516 (4)	0.0173 (4)	0.7384 (7)	6.0 (2)
C17	−0.0066 (2)	0.2854 (2)	0.8127 (3)	3.2 (1)
C18	−0.0710 (3)	0.2256 (2)	0.6691 (3)	3.7 (1)
C19	−0.2069 (3)	0.2432 (3)	0.6142 (4)	4.3 (1)
C20	−0.2808 (3)	0.3234 (3)	0.6979 (4)	4.9 (1)
C21	−0.2191 (3)	0.3858 (3)	0.8352 (4)	5.0 (1)
C22	−0.0836 (3)	0.3674 (3)	0.8916 (4)	4.0 (1)
Compound (2)				
O1	0.4978 (1)	0.28867 (8)	0.3784 (1)	3.43 (5)
O2	0.3043 (1)	0.34086 (8)	0.3096 (1)	4.11 (6)
O3	0.5299 (1)	0.1114 (1)	0.4425 (1)	4.21 (6)
O4	0.6876 (1)	0.1392 (1)	0.3312 (1)	5.55 (8)
C1	0.3927 (2)	0.1590 (1)	−0.0643 (2)	3.83 (9)
C2	0.3526 (2)	0.0977 (2)	−0.1407 (2)	4.5 (1)
C3	0.3220 (2)	0.0211 (1)	−0.1032 (2)	4.1 (1)
C4a	0.3716 (2)	0.0643 (1)	0.0892 (1)	2.74 (6)
C4	0.3293 (2)	0.0039 (1)	0.0127 (2)	3.46 (8)
C5	0.1314 (2)	0.0381 (1)	0.2472 (2)	3.27 (8)
C6	0.0099 (2)	0.0740 (1)	0.2582 (2)	3.63 (8)
C7	−0.0017 (2)	0.1572 (1)	0.2621 (2)	3.40 (8)
C8a	0.2289 (2)	0.1717 (1)	0.2472 (1)	2.52 (6)
C8	0.1073 (2)	0.2075 (1)	0.2562 (2)	3.03 (7)
C9a	0.4029 (2)	0.1414 (1)	0.0519 (1)	2.80 (7)
C9	0.4548 (2)	0.1942 (1)	0.1491 (1)	2.63 (6)
C10	0.3783 (2)	0.0642 (1)	0.2185 (2)	2.70 (6)
C10a	0.2402 (2)	0.0874 (1)	0.2428 (1)	2.61 (6)
C11	0.3622 (2)	0.2095 (1)	0.2492 (1)	2.52 (6)
C12	0.4614 (2)	0.1410 (1)	0.2536 (1)	2.60 (6)
C13	0.3832 (2)	0.2867 (1)	0.3141 (1)	2.72 (6)
C14	0.5271 (3)	0.3623 (2)	0.4424 (2)	4.7 (1)
C15	0.5745 (2)	0.1324 (1)	0.3433 (2)	2.92 (7)
C16	0.6277 (3)	0.1044 (2)	0.5391 (2)	6.1 (1)
C17	0.5521 (2)	0.2579 (1)	0.1216 (1)	2.78 (7)
C18	0.6797 (2)	0.2355 (1)	0.1041 (2)	3.35 (8)
C19	0.7673 (2)	0.2918 (1)	0.0680 (2)	3.83 (9)
C20	0.7288 (2)	0.3708 (1)	0.0484 (2)	3.85 (8)
C21	0.6027 (2)	0.3937 (1)	0.0650 (2)	4.1 (1)
C22	0.5142 (2)	0.3378 (1)	0.1011 (2)	3.61 (8)
Compound (3)				
O1	0.6337 (1)	0.12216 (6)	0.1587 (2)	4.27 (6)
O2	0.7117 (2)	0.1457 (1)	0.4360 (3)	6.60 (9)
O3	0.1304 (2)	0.08046 (6)	−0.0750 (2)	4.73 (7)
O4	0.1397 (1)	−0.00642 (6)	−0.0545 (2)	4.59 (6)
C1	0.5051 (2)	0.0963 (1)	0.6649 (3)	4.3 (1)
C2	0.4717 (2)	0.0587 (1)	0.7833 (3)	4.7 (1)
C3	0.3867 (2)	0.0116 (1)	0.7302 (3)	4.7 (1)
C4	0.3322 (2)	0.0027 (1)	0.5599 (3)	4.2 (1)
C4a	0.3599 (2)	0.04105 (8)	0.4403 (3)	3.29 (7)
C5	0.0755 (2)	0.1114 (1)	0.3096 (3)	3.70 (8)
C6	0.0479 (2)	0.1564 (1)	0.3978 (3)	4.0 (1)
C7	0.1403 (2)	0.2008 (1)	0.4506 (3)	4.08 (9)
C8	0.2603 (2)	0.20110 (9)	0.4138 (3)	3.80 (8)
C8a	0.2902 (2)	0.15570 (8)	0.3278 (3)	3.11 (7)
C9	0.4211 (2)	0.15850 (8)	0.2880 (3)	3.23 (7)
C9a	0.4494 (2)	0.08857 (8)	0.4930 (3)	3.32 (8)

Table 2 (*cont.*)

	x	y	z	U_{eq}
C10	0.2940 (2)	0.02942 (8)	0.2632 (3)	3.49 (8)
C10a	0.1969 (2)	0.11006 (8)	0.2764 (3)	3.12 (7)
C11	0.4918 (2)	0.12803 (8)	0.3650 (3)	3.42 (8)
C12	0.2223 (2)	0.05966 (8)	0.1875 (3)	3.15 (7)
C13	0.6247 (2)	0.13396 (9)	0.3286 (3)	3.85 (8)
C14	0.7561 (2)	0.1304 (1)	0.1008 (4)	6.4 (1)
C15	0.1598 (2)	0.03997 (9)	0.0092 (3)	3.48 (8)
C16	0.0715 (3)	0.0669 (1)	−0.2513 (4)	6.6 (1)
C17	0.4690 (2)	0.19847 (8)	0.1636 (3)	3.50 (8)
C18	0.4227 (2)	0.1899 (1)	−0.0106 (3)	4.7 (1)
C19	0.4708 (3)	0.2254 (1)	−0.1292 (4)	6.1 (1)
C20	0.5629 (3)	0.2699 (1)	−0.0749 (5)	6.6 (2)
C21	0.6060 (3)	0.2794 (1)	0.0996 (5)	6.5 (1)
C22	0.5610 (2)	0.2439 (1)	0.2188 (4)	4.9 (1)
O1′	0.2992 (2)	0.47959 (7)	−0.2740 (3)	6.01 (9)
O2′	0.3427 (2)	0.50518 (8)	0.0119 (3)	7.4 (1)
O3′	−0.0300 (2)	0.30617 (7)	−0.5506 (2)	4.87 (7)
O4′	−0.1907 (2)	0.34637 (9)	−0.5290 (2)	6.34 (9)
C1′	0.1519 (3)	0.4402 (1)	0.2211 (4)	5.4 (1)
C2′	0.0669 (4)	0.4500 (1)	0.3350 (4)	6.5 (1)
C3′	−0.0551 (4)	0.4451 (1)	0.2741 (4)	6.3 (1)
C4′	−0.0943 (4)	0.4287 (1)	0.1008 (4)	5.1 (1)
C4a′	−0.0110 (2)	0.41626 (9)	−0.0161 (3)	4.05 (9)
C5′	−0.0525 (2)	0.2564 (1)	−0.1867 (3)	4.3 (1)
C6′	0.0009 (3)	0.2170 (1)	−0.1166 (3)	4.7 (1)
C7′	0.1238 (3)	0.2284 (1)	−0.0564 (3)	4.6 (1)
C8′	0.1949 (2)	0.2790 (1)	−0.0691 (3)	4.1 (1)
C8a′	0.1429 (2)	0.31978 (8)	−0.1391 (3)	3.36 (8)
C9′	0.2247 (2)	0.37273 (8)	−0.1605 (3)	3.61 (8)
C9a′	0.1145 (2)	0.42373 (9)	0.0440 (3)	4.15 (9)
C10′	−0.0587 (2)	0.3956 (1)	−0.1977 (3)	4.03 (9)
C10a′	0.0173 (2)	0.30869 (8)	−0.1962 (3)	3.46 (8)
C11′	0.2095 (2)	0.41928 (9)	−0.0806 (3)	4.02 (9)
C12′	−0.0451 (2)	0.34884 (9)	−0.2782 (3)	3.67 (8)
C13′	0.2917 (2)	0.4721 (1)	−0.1052 (4)	4.8 (1)
C14′	0.3878 (4)	0.5265 (1)	−0.3116 (6)	9.1 (2)
C15′	−0.0993 (2)	0.3343 (1)	−0.4625 (3)	4.2 (1)
C16′	−0.0659 (3)	0.2913 (1)	−0.7350 (4)	6.3 (1)
C17′	0.3270 (2)	0.36986 (8)	−0.2741 (3)	3.94 (9)
C18′	0.3006 (3)	0.3474 (1)	−0.4449 (4)	5.1 (1)
C19′	0.3960 (3)	0.3446 (1)	−0.5513 (5)	6.3 (1)
C20′	0.5172 (3)	0.3633 (1)	−0.4820 (6)	6.7 (2)
C21′	0.5439 (3)	0.3858 (1)	−0.3147 (6)	6.2 (1)
C22′	0.4505 (2)	0.3895 (1)	−0.2084 (4)	5.3 (1)

Dimethyl 8b-*phenyl*-4b,8b,8c,8d-*tetrahydrodibenzo*-[a,f]*cyclopropa*[cd]*pentalene*-8c,8d-*dicarboxylate* (2). M.p.: 474–476 K. IR: 1745 and 1715 (ester carbonyl stretches) cm^{-1}. ^{1}H NMR: δ, 3.52 and 3.71 (two *s*, 3H each, methyl hydrogens), 5.08 (*s*, 1H, cyclopropylcarbinyl methine), 6.61–7.84 (*m*, 13H, aromatic). ^{13}C NMR: δ, 51.91, 51.94 (ester CH$_3$), 58.47 (sp^3 C—H), 63.35, 68.16 (quaternary sp^3 C), 120.73, 121.32, 126.37, 126.52, 126.97, 127.06, 127.51, 127.75, 127.93, 130.96 (aromatic C—H), 133.66, 135.41, 139.69, 148.41, 150.14 (quaternary aromatic C), 168.08, 168.40 (carbonyl C). MS: *m/e* (relative intensity): 397 ($M + 1$, 1.0), 396 (M^+, 3.0), 365 (2.3), 336 (72.7), 305 (12.5), 293 (25.4), 278 (100), 265 (8.3), 252 (4.1), 230 (5.7), 200 (3.8), 189 (2.3), 168 (2.6), 152 (7.1), 138 (25.5), 125 (7.2), 113 (3.0). Exact mass calculated (C$_{26}$H$_{20}$O$_4$): 396.1362; measured: 396.1360.

X-ray analyses

The crystal and molecular structures of reactant (1) and photoproducts (2) and (3) 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 AFC-6 diffractometer and

Table 3. *Selected bond lengths* (Å) *and angles* (°)

	Compound (1)	Compound (2)	Compound (3)
C=C	1.336 (3)	—	1.337 (3)
C—C(aromatic)	1.371-1.399 (4)	1.373-1.395 (3)	1.350-1.404 (4)
C—CO₂Me	1.500, 1.480 (4)	1.489, 1.494 (2)	1.494, 1.483 (3)
C—C(other)	1.511-1.556 (3)	1.502-1.599 (2)	1.468-1.493 (3)
C=O	1.197 (3)	1.191 (2)	1.201 (3)
C—OMe	1.328 (3)	1.335 (2)	1.332 (3)
O—Me	1.451 (4)	1.444 (2)	1.439 (3)
Ring junction angles			
External	125.5-127.7 (2)	128.2-129.8 (1)	117.9-120.1 (2)
Internal	112.6 114.4 (2)	109.2-111.5 (1)	120.9-123.2 (2)

Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). Lp and absorption corrections (ψ scan) were applied. The structures were solved by direct methods using *TEXSAN* (Molecular Structure Corporation, 1990); for (3), there are two molecules per asymmetric unit.

Refinement was by full-matrix least-squares methods on F, minimizing $\Sigma w(|F_o| - |F_c|)^2$, with $w = 1/\sigma^2(F)$ ($p = 0.05$). H-atom parameters were refined except for the methyl H atoms of (3). Details of the refinement are in Table 1.

Discussion

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

The structure and dimensions of the molecule of the dibenzobarrelene derivative, (1), are very similar to those of the parent hydrocarbon (Trotter & Wireko, 1990) and of other derivatives (Pokkuluri *et al.*, 1993). The bond angles external to the aromatic rings, mean 126.4° (Table 3), and the intra-annular benzene-barrelene angles, mean 113.4°, are distorted to about the same extent as in the other derivatives. The C11—C12 distance [1.336 (3) 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 −72.9 (4) and −31.8 (4)°, respectively. Thus the ester group at C11 is only slightly conjugated to the C11=C12 bond (cos²φ_1 = 0.09), while the group at C12 is considerably conjugated (cos²φ_2 = 0.72); the difference is doubtless due to the steric effect of the phenyl substituent. The difference is reflected also in the C—CO₂Me bond lengths: the C11—C13 distance [1.500 (4) Å] is equal to the expected non-conjugated length (1.497 Å) while C12—C15 [1.480 (4) Å] is between the non-conjugated and fully conjugated (1.470 Å) distances (Allen, 1981).

* Lists of anisotropic thermal parameters, hydrogen positions, bond lengths and angles, and structure factors, and packing diagrams have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55931 (124 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0631]

The ring system in the dibenzosemibullvalene photoproduct (2) (Fig. 2) shows the usual additional strain as a result of the formation of the three-membered ring (Garcia-Garibay, Scheffer, Trotter & Wireko, 1990). The angles at the five/six-membered ring junctions are farther from 120°: mean 129.0 (external), 110.1° (internal) (Table 3); angles in the three-membered ring are in the range 57.8–63.9 (1)°.
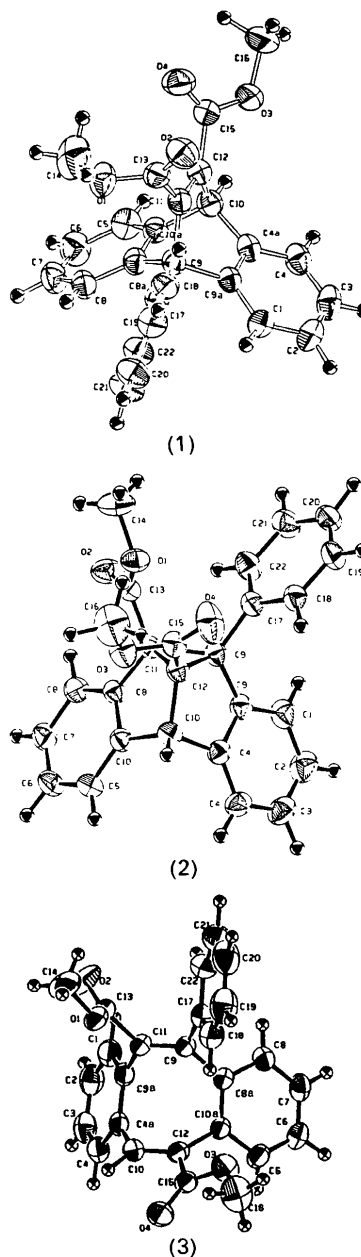

(1)

(2)

(3)

Fig. 2. Views (50% thermal ellipsoids) of (1), (2) and (3) [for (2), the enantiomer of Figs. 1 and 3, crystals are racemates]; stereo versions, and for (3) the second molecule in the asymmetric unit are shown in the supplementary material. The dibenzobarrelene numbering system of (1) is retained for (2) and (3).

The two crystallographically independent molecules of COT (3) have similar conformations and geometries (Fig. 2, Table 3, and supplementary material). The central eight-membered ring has the tub conformation (Dunitz, 1968), like in related compounds (Pokkuluri *et al.*, 1993). The bond angles at the ring junctions show little distortion from normal values; the external angles average 118.9°, and the intra-annular benzene–cyclooctene angles, mean 122.0°, are similar to the other angles in the eight-membered ring, which average 122.0° at C9, 125.6° at C10 and 124.5° at C11 and C12 (Ph, H and CO₂Me substitutents, respectively). The C9—C11 and C10—12 bond lengths [1.334–1.340 (3) Å] correspond to double bonds, and the other bond lengths in the eight-membered ring to aromatic [1.390–1.404 (3) Å] or single bonds [1.468–1.493 (3) Å]. The ester groups are again rotated out of the planes of the double bonds: the group at C11 by 60° (51° in the primed molecules), $\cos^2\varphi = 0.25$ (0.40), mean C11—C13 = 1.494 (3) Å; that at C12 by 22° (32°), $\cos^2\varphi = 0.86$ (0.72), mean C12—C15 = 1.483 (3) Å.
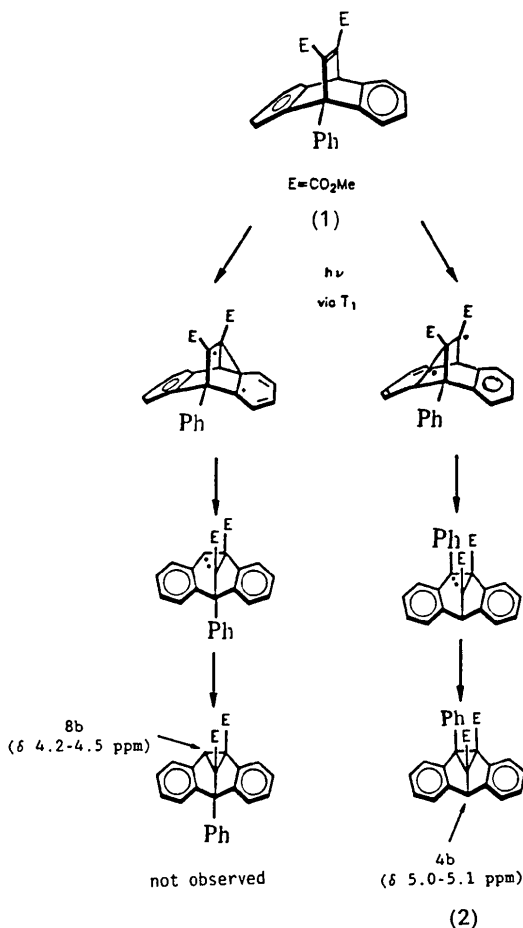
The phenyl group is rotated 66° out of the plane of the C9—C11 double bond.

Discussion of the photolysis results

In acetone (a triplet energy sensitizer), the photoproduct obtained has been characterized as a di-π-methane regioisomer (2) (Figs. 1 and 2). In the case of compound (1), which is not symmetrically substituted, the di-π-methane rearrangement can proceed, in principle, *via* two different pathways. The first step of vinyl–benzo bridging can occur at a vinyl site adjacent to the bridgehead phenyl group or away from it. Characterization of such regioisomers from bridgehead-substituted dibenzobarrelene diesters has been based largely on ¹H NMR data, in which the chemical shifts of the methine protons are dependent on their locations (Richards, Tillman & Wright, 1975; Paddick, Richards & Wright, 1976; Iwamura *et al.*, 1980). It was observed that the methine hydrogens on the 4b and 8b carbons of dibenzosemibullvalene derivatives resonate at δ 5.0–5.1 and 4.2–4.5 p.p.m., respectively (Iwamura *et al.*, 1980). Compound (2) shows a one-proton signal at 5.08 p.p.m., which is consistent with the product formed (Fig. 3). In light of possible unusual photorearrangements (Pokkuluri *et al.*, 1993), it was thought desirable to prove the structure of (2) by X-ray analysis, which showed the structure (Fig. 2) to be that consistent with di-π-methane rearrangement as in Fig. 3. This also provides a general support of the expected methine hydrogen resonance in NMR spectra of similar compounds.

The formation of only one of the two possible regioisomers (Fig. 3) has been interpreted in terms of the effect of the bridgehead substituent on the strength of the new bond formed close to it (in the
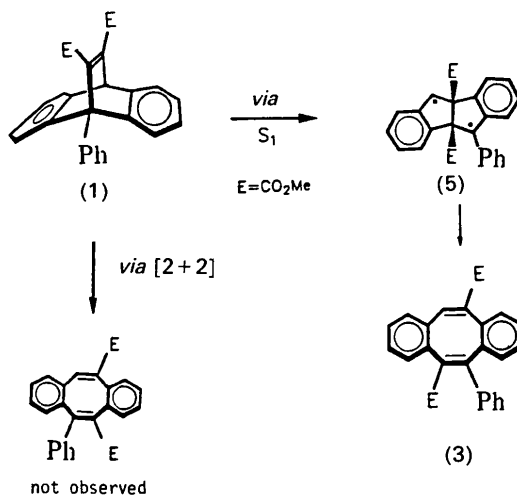

Fig. 3. Proposed reaction mechanism in the di-π-methane photolysis of (1), with ¹H NMR data.

Fig. 4. Proposed reaction mechanism for COT formation in the photolysis of (1).

cyclopropyldicarbinyl biradical), in the same way as a substituent affects the equilibrium between nor-caradiene and cycloheptatriene. In the latter case, it was known that electron-accepting groups (such as Ph, CN, *etc.*) strengthen the opposite bond in the cyclopropyl ring and hence favor the equilibrium towards norcaradiene, whereas electron-donating groups weaken the same bond and hence favor cyclo-heptatriene (Hoffman & Stohrer, 1971; Wehner & Günther, 1975). Iwamura *et al.* (1980) have rational-ized the exclusive formation of (2) from (1) by arguing that vinyl–benzo bridging is favored close to the bridgehead phenyl group. In addition, the 1,3-biradical formed is more stable than that formed *via* the alternative pathway because of the stabilization offered by the phenyl substituent in the former case. Traces of COT (3) formed in acetone (Fig. 1) may be attributed to partial direct excitation of the starting material.

Structure of COT (3)

On direct irradiation, a product (3), spectroscopi-cally consistent with a COT structure, is formed *via* the singlet excited state of (1) (since it is not formed in the presence of a triplet energy sensitizer). The actual structure of the COT may be either that derived by a $(2\pi + 2\pi)$ mechanism or that from the fragmentation of biradical (5) (Fig. 4), which is difficult to distinguish based on spectral data (Pokkuluri *et al.*, 1993). Hence, a single-crystal X-ray structure determination was carried out which proved the structure of (3) to be that derived from the fragmentation of biradical (5) (Fig. 4). Based on GC retention times, the COTs formed in solution and in the solid-state photolysis of (1) are the same.

This study provides another example of the unex-pected behavior of the singlet excited state of a bridgehead-substituted dibenzobarrelene in produc-ing an abnormal COT, while reacting as expected *via* the triplet excited state. It can also be taken as additional support for the assignment of the di-π-methane rearranged structure for the semibull-valene formed in the triplet sensitized photolysis of the 9,10-dimethyl compound (Pokkuluri *et al.*, 1993). The reasons for not obtaining any ester migration product from (1), similar to that observed in the solid-state photolysis of the 9,10-dimethyl com-pound, are not clear.

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Stabilizing Role of Included Solvent in Ternary Complexation: Synthesis, Structures and Thermal Analyses of Three 18-Crown-6/Sulfonamide/Acetonitrile Inclusion Compounds

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Abstract

The synthesis, thermal analyses and X-ray crystal structures of three ternary inclusion compounds, each containing 1,4,7,10,13,16-hexaoxacycloocta-decane (18-crown-6), ethanenitrile (acetonitrile) and a sulfonamide, in different molar ratios, are reported. The compounds are: (I) 1,4,7,10,13,16-hexa-oxacyclooctadecane–4-amino-*N*-(5-methoxy-2-pyrim-idinyl)benzenesulfonamide–ethanenitrile (1/2/4),