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Cyclooctatetraene Formation in the Photolyses of Dibenzobarrelene Diesters

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Abstract

A study of cyclooctatetraenes (COTs) derived from the photolyses of dibenzobarrelene derivatives indicates the formation of two types of COT with different substitution patterns; the structures of one example of each type have been determined by X-ray crystal analyses. Crystal data: $T = 294$ K, Cu $K\alpha$, $\lambda = 1.5418$ Å. (1), dimethyl 6-methyldibenzo[a,e]cyclooctatetraene-5,11-dicarboxylate, $C_{21}H_{18}O_4$, $M_r = 334.37$, orthorhombic, $Pna2_1$, $a = 18.364$ (4), $b = 10.485$ (3), $c = 9.031$ (4) Å, $V = 1739$ (2) Å^3, $Z = 4$, $D_x = 1.28$ g cm^{-3}, $F(000) = 704$, $\mu = 6.8$ cm^{-1}, $R = 0.054$ for 1303 reflexions. (2), 11-methyl 5-(2-propyl) dibenzo[a,e]cyclooctatetraene-5,11-dicarboxylate, $C_{22}H_{20}O_4$, $M_r = 348.40$, monoclinic, $P2_1/n$, $a = 9.121$ (1), $b = 20.486$ (1), $c = 10.028$ (1) Å, $\beta = 100.91$ (1)°, $V = 1839.9$ (3) Å^3, $Z = 4$, $D_x = 1.26$ g cm^{-3}, $F(000) = 736$, $\mu = 6.6$ cm^{-1}, $R = 0.043$ for 2688 reflections. COT (2) has a structure consistent with formation *via* a normal $[2\pi + 2\pi]$ intramolecular cycloaddition, while formation of (1) provides another example of abnormal behaviour, with reaction *via* fragmentation of a bis-benzylic 1,4-biradical. The difference in reaction pathways probably results from intramolecular steric effects, which are more severe in the dibenzobarrelene from which (1) is derived (three substituents), in comparison with the formation of (2) (two substituents).

Introduction

Bridgehead-substituted dibenzobarrelene diesters have been found to react *via* their S_1 states to give cyclooctatetraenes (COTs) with substitution patterns different from those obtained in previous studies on benzo- and naphthobarrelenes (Pokkuluri, Scheffer & Trotter, 1993a). It is, therefore, intriguing to ask whether all dibenzobarrelenes behave similarly, or is the 'abnormal' behaviour specific to some cases. To answer this question, two COTs have been re-examined, which were earlier characterized assuming 'normal' structures based on a $[2 + 2]$ mechanism; the two COTs (1) and (2) are obtained by photolyses of the 9-methyl-11,12-dimethoxycarbonyl and 9-isopropoxycarbonyl-12-methoxycarbonyl diesters,

respectively (Fig. 1) (Pokkuluri, Scheffer & Trotter, 1989, 1993b; Garcia-Garibay, 1988).

Experimental

The crystal and molecular structures of photo-products (1) and (2) 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 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).
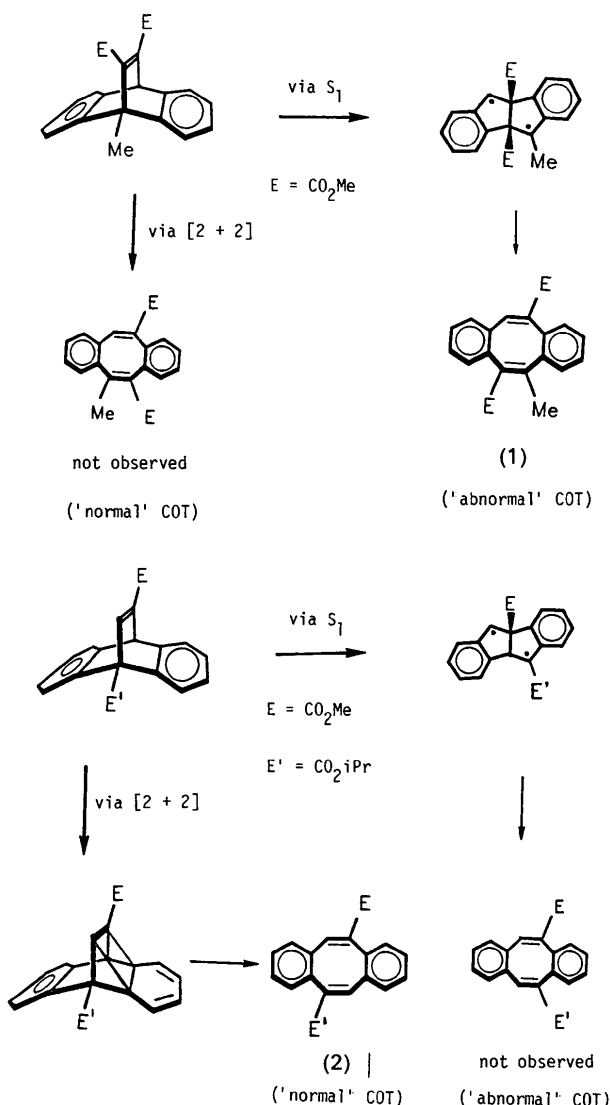

Fig. 1. Proposed reaction mechanisms for COT formation in the photolyses of dibenzobarrelene diesters.

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

	(1)*	(2)*
Crystal data		
Solvent	Ethyl acetate/ petroleum ether	Diethyl ether
Dimensions (mm)	0.3 × 0.2 × 0.4	0.3 × 0.3 × 0.4
Formula	$C_{21}H_{18}O_4$	$C_{22}H_{20}O_4$
M_r	334.37	348.40
Crystal system	Orthorhombic	Monoclinic
Space group	$Pna2_1$	$P2_1/n$
a (Å)	18.364 (4)	9.121 (1)
b (Å)	10.485 (3)	20.486 (1)
c (Å)	9.031 (4)	10.028 (1)
α (°)	90	90
β (°)	90	100.91 (1)
γ (°)	90	90
V (Å^3)	1739 (2)	1839.9 (3)
Z	4	4
D_x (g cm^{-3})	1.28	1.26
$F(000)$	704	736
μ (cm^{-1})	6.8	6.6
Data collection (Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å)		
Reflections for cell		
No. of reflections	23	20
2θ (°)	50–70	50–81
Intensity measurements		
2θ(max.) (°)	155	155
ω scan (°)	0.94 + 0.30 tan θ	1.15 + 0.30 tan θ
Scan speed (° min^{-1}) (up to 8 rescans)	16	32
h	0→23	−12→12
k	0→13	0→26
l	0→11	0→13
Total reflections measured	2132	4212
Total unique reflections	2132	3821
Reflections with $I \geq 3\sigma(I)$	1303	2688
%	61.1	70.3
Absorption, transmission factor	0.57–1.0	—
Structure refinements		
No. of parameters	246	316
Data/parameter ratio	5.3	8.5
Δ/σ(max.)	0.003	0.008
$\Delta\rho$ (e Å^{-3})	−0.19 to +0.20	−0.22 to +0.21
$R[I \geq 3\sigma(I)]$	0.054	0.043
wR	0.068	0.063
S (goodness fo fit)	1.99	1.85
R (all data)	0.100	0.094
Extinction, g	0.72 × 10^{-5}	0.66 × 10^{-5}

Notes: Both crystals are colorless prisms (Pokkuluri *et al.*, 1989, 1993b; Garcia-Garibay, 1988). For each data set, three standard reflections at intervals of 150 reflections, 0.4% decay for (1), no decay (standard variation about 0.5%) for (2), scattering factors from TEXSAN, extinction factors (TEXSAN) 0.72 (10) × 10^{-5} for (1), 0.66 (6) × 10^{-5} for (2). For (1) the empirical absorption correction range is somewhat larger than calculated from the extreme crystal dimensions (0.79–1.0); for (2) the empirical range was 0.98–1.0, and no corrections were applied. For (1) the opposite polarity was tested, but gave insignificantly different R factors.

* (1) = dimethyl 6-methyldibenzo[a,e]cyclooctatetraene-5,11-dicarboxylate. (2) = 11-methyl 5-(2-propyl) dibenzo[a,e]cyclooctatetraene-5,11-dicarboxylate.

Refinement was by full-matrix least-squares methods on F, minimizing $\sum w(|F_o| - |F_c|)^2$, with $w = 1/\sigma^2(F)$ ($p = 0.05$). H atoms were fixed in calculated positions for (1); H parameters were refined for

(2). The structure for (1) with opposite polarity gave a marginally higher value of wR. Details of the refinements are in Table 1.

Discussion

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

The COT molecules (1) and (2) have normal conformations and dimensions (Fig. 2, Table 3 and depository material, cf. Pokkuluri et al., 1993a,c). The central eight-membered rings have tub conformations (Dunitz, 1968), and the bond angles at the ring junctions show little distortion from normal values. The CO_2Me ester group adjacent to the 9-Me substitutent in (1) is rotated out of the plane of the ring double bond, C9—C11—C13—O2 torsion angle 119.5 (7)° [cos²(angle) = 0.24]; the other CO_2Me group in (1) and the $CO_2{}^iPr$ and Co_2Me groups in (2) are all not far from coplanar with the double bonds, C=C—C=O torsion angles 17.5 (7), −12.5 (3) and 173.7 (2)° [cos²(angles) = 0.91, 0.95, 0.99], respectively. Thus, three of the four ester groups are conjugated with the double bonds; one ester group is rotated away from a conjugated conformation, doubtless as a result of steric interaction with the adjacent methyl substituent.

The crystal structure analysis of COT (1) (Fig. 2), formed from photolysis of the 9-methyl-11,12-diester, has shown that this COT is probably derived via fragmentation of a bis-benzylic 1,4-biradical (Fig. 1), and is an 'abnormal' COT, i.e. different substitution pattern from COTs previously formed from benzo- and naphthobarrelenes. GC retention times and ^1H NMR spectra indicate that the same COT is formed both in solution and in the solid state. The 9-methyl-11,12-diester also undergoes normal di-π-methane rearrangement via the T_1 triplet state (cf. Pokkuluri et al., 1993a,c).

Of the two possible structures for COT (2), formed from the 9-isopropyl 12-methyl diester, X-ray analysis has shown that the actual structure (Fig. 2) is consistent with a $[2\pi + 2\pi]$ reaction mechanism, i.e. (2) is a 'normal' COT. Hence there are at least two different pathways by which COTs may be formed from dibenzobarrelene derivatives. Three bridge-head-substituted derivatives produce 'abnormal' COTs: 9,10-dimethyl-11,12-diester (Pokkuluri et al., 1993a), 9-phenyl-11,12-diester (Pokkuluri et al.,

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* Lists of anisotropic thermal parameters, hydrogen positions, bond lengths and angles, and structure factors, together with molecular and packing diagrams have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71268 (53 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

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

	x	y	z	B_{eq}
(1)				
O1	0.5342 (2)	1.1651 (3)	0.2595	5.5 (2)
O2	0.4501 (2)	1.0374 (4)	0.1635 (8)	7.1 (2)
O3	0.7983 (2)	0.9718 (4)	0.5092 (7)	5.8 (2)
O4	0.8428 (2)	1.0275 (4)	0.2890 (7)	5.6 (2)
C1	0.5050 (3)	0.7682 (6)	0.1972 (9)	4.9 (3)
C2	0.4934 (3)	0.6527 (6)	0.270 (1)	6.0 (3)
C3	0.5393 (4)	0.6160 (6)	0.380 (1)	5.8 (3)
C4	0.5976 (3)	0.6885 (5)	0.4179 (8)	5.2 (3)
C4a	0.6135 (2)	0.8033 (5)	0.3435 (7)	3.7 (2)
C5	0.7960 (3)	0.7921 (6)	0.0993 (9)	4.7 (3)
C6	0.8051 (3)	0.7568 (6)	−0.047 (1)	5.4 (3)
C7	0.7588 (3)	0.8024 (7)	−0.153 (1)	5.9 (3)
C8	0.7017 (3)	0.8839 (7)	−0.1113 (8)	5.2 (3)
C8a	0.6901 (2)	0.9154 (5)	0.0350 (7)	3.9 (2)
C9	0.6297 (2)	1.0046 (5)	0.0708 (8)	4.1 (2)
C9a	0.5661 (2)	0.8425 (4)	0.2321 (7)	3.9 (2)
C10a	0.7386 (3)	0.8705 (5)	0.1429 (7)	3.6 (2)
C10	0.6770 (3)	0.8755 (5)	0.3892 (9)	4.0 (2)
C11	0.5749 (2)	0.9714 (5)	0.1614 (7)	3.8 (2)
C12	0.7331 (2)	0.9066 (4)	0.3018 (8)	3.5 (2)
C13	0.5129 (3)	1.0597 (5)	0.1911 (8)	4.7 (3)
C14	0.4801 (3)	1.2586 (6)	0.292 (1)	6.2 (3)
C15	0.7970 (3)	0.9755 (5)	0.3632 (8)	4.2 (2)
C16	0.8565 (4)	1.0377 (8)	0.580 (1)	7.8 (4)
C17	0.6349 (3)	1.1317 (6)	−0.005 (1)	5.6 (3)
(2)				
O1	0.0106 (2)	0.31638 (7)	0.4617 (2)	5.32 (7)
O2	0.2269 (2)	0.36977 (8)	0.4795 (2)	6.22 (8)
O3	0.2693 (2)	0.04000 (6)	0.5736 (1)	4.49 (6)
O4	0.4763 (2)	0.08467 (9)	0.6917 (2)	6.90 (8)
C1	0.2936 (2)	0.05291 (9)	0.2833 (2)	4.03 (7)
C2	0.2088 (3)	0.0349 (1)	0.1600 (2)	4.92 (9)
C3	0.0962 (3)	0.0756 (1)	0.0966 (2)	4.81 (9)
C4	0.0680 (2)	0.1334 (1)	0.1570 (2)	4.12 (7)
C4a	0.1551 (2)	0.15296 (8)	0.2801 (2)	3.32 (6)
C5	0.3761 (3)	0.3199 (1)	0.2415 (2)	4.71 (8)
C6	0.5146 (3)	0.3274 (1)	0.2069 (3)	5.6 (1)
C7	0.6331 (3)	0.2899 (1)	0.2704 (3)	5.6 (1)
C8a	0.4719 (2)	0.23318 (8)	0.3958 (2)	3.59 (6)
C8	0.6128 (2)	0.2443 (1)	0.3652 (2)	4.73 (9)
C9a	0.2712 (2)	0.11245 (8)	0.3446 (2)	3.28 (6)
C9	0.3680 (2)	0.12981 (8)	0.4762 (2)	3.41 (6)
C10	0.1154 (2)	0.21358 (8)	0.3440 (2)	3.56 (6)
C10a	0.3521 (2)	0.27214 (8)	0.3349 (2)	3.53 (6)
C11	0.4564 (2)	0.18246 (8)	0.4966 (2)	3.67 (6)
C12	0.2020 (2)	0.26607 (8)	0.3711 (2)	3.49 (6)
C13	0.1500 (2)	0.32321 (9)	0.4422 (2)	4.16 (7)
C14	−0.0445 (4)	0.3662 (2)	0.5407 (4)	6.9 (1)
C15	0.3793 (2)	0.08339 (9)	0.5927 (2)	3.99 (7)
C16	0.2714 (3)	−0.0116 (1)	0.6748 (2)	4.85 (9)
C17	0.1906 (5)	0.0106 (2)	0.7820 (3)	7.1 (2)
C18	0.1968 (7)	−0.0694 (2)	0.5994 (5)	9.4 (2)

1993c) and 9-methyl-11,12-diester (present paper); one produces a 'normal' COT: $9\text{-}CO_2{}^iPr\text{-}12\text{-}CO_2Me$ (present paper). An examination of the substitution patterns of these dibenzobarrelenes indicates that those molecules with three or four substituents on the barrelene unit do not undergo $[2\pi + 2\pi]$ cyclo-addition, but give 'abnormal' COT photoproducts; the $9\text{-}CO_2{}^iPr\text{-}2\text{-}CO_2Me$ compound, with only two substituents, does undergo such an addition to give a 'normal' COT. Hence the differences in behaviour

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

	(1)	(2)
C=C	1.339, 1.343 (7)	1.331, 1.339 (2)
C—C(arom.)	1.356–1.405 (8)	1.370–1.403 (3)
C—CO$_2$Me	1.485, 1.492 (7)	1.494, 1.494 (2)
C—C(other)	1.450–1.504 (7)	1.474–1.498 (4)
C=O	1.203, 1.205 (6)	1.201, 1.198 (2)
C—OMe	1.325, 1.320 (7)	1330, 1.327 (3)
O—Me	1.426, 1.423 (7)	1.440, 1.463 (3)
Ring-junction angles		
External	118.2–119.4 (5)	118.5–119.3 (2)
Internal	120.3–123.7 (5)	121.6–122.5 (2)
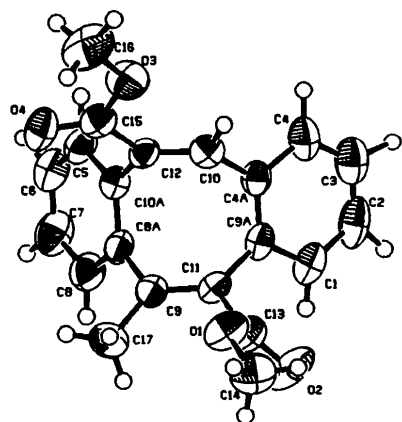
(1)
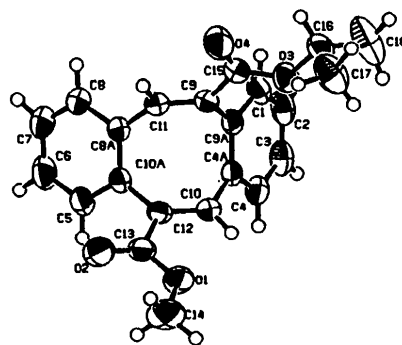
(2)

Fig. 2. Views (50% thermal ellipsoids) of (1) and (2) (stereo version in depository material; the dibenzobarrelene numbering system is retained).

probably result from differences in steric crowding in the intermediate cage compound in the intramolecular $[2\pi + 2\pi]$ cycloadditions. The 9,10-dimethyl-11,12-di(COPh) compound (with four substituents) was originally reported to produce a 'normal' COT (Kumar, Murthy, Lahiri, Chackachery, Scaiano & George, 1984), but reinvestigation has shown this to be an 'abnormal' COT (Asokan, Kumar, Das, Rath & Geroge, 1991), consistent with the results for the other derivatives.

Finally, one interesting point of observation is that not all dibenzobarrelene derivatives produce COTs under direct irradiation conditions. While unsubstituted dibenzobarrelene itself produces a COT *via* S_1 (Rabideau, Hamilton & Friedman, 1968), there does not seem to be any correlation between the number or the positions of various substituents present in dibenzobarrelenes and COT formation *via* their S_1 states. This may be a simple consequence of the relative difference between the rate of the reaction to produce COT and other deactivation modes available to the S_1 states of respective molecules.

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