

Photorearrangements of bridgehead-disubstituted dibenzobarrelene esters and lactones ☆

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Abstract

This study deals with the photorearrangements of a few bridgehead-disubstituted dibenzobarrelenes, i.e. dimethyl-9-hydroxymethyl-10-methyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (**1**) and the dibenzobarrelene lactone derivatives (**10a,b**). Irradiation of **1** in benzene gives a 77% yield of a dibenzocyclooctatetraene (**8**) with C_2 symmetry with respect to its substituents. In contrast, the photolysis of **10a** yields the dibenzosemibullvalene (**15a**) in nearly quantitative yield. Similarly, the dibenzobarrelene lactone (**10b**) undergoes facile photoisomerization to the corresponding dibenzosemibullvalene (**15b**) in 92% yield. The structures of the photoproducts **8** and **15a** have been unambiguously established through X-ray crystallographic analysis.

Keywords: Photorearrangement; Dibenzobarrelene esters; Lactones

1. Introduction

It is well established that dibenzobarrelenes undergo facile photoisomerization to the corresponding cyclooctatetraenes and dibenzosemibullvalenes, depending on the nature of the substituents and the reaction conditions (for some pertinent reviews related to dibenzobarrelene photochemistry, see Ref. [1]). There have been several reports on the effect of bridgehead substituents on the reaction pathways of dibenzobarrelenes. The bridgehead as well as vinylic substituents play a significant role in controlling both the product selectivity and the regioselectivity of these rearrangements.

The effective control of the regioselectivity of these photochemical processes by the judicious variation of the substituents in the starting dibenzobarrelenes has been examined by different groups of workers. It has been suggested that both steric and electronic effects exerted by the substituents affect the regioselectivity of these photoreactions. In the present investigation,

we have examined the phototransformations of a few dibenzobarrelene esters, bearing different substituents at the bridgehead positions, with a view to studying the nature of the products formed in these reactions and to obtaining an understanding of the effect of the substituents on the outcome of the phototransformations. The substrates chosen for the present study are dibenzobarrelenes containing unsymmetrical bridgehead substituents and a carbomethoxy group at the vinylic position. These include dimethyl-9-hydroxymethyl-10-methyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (**1**), its lactonized derivative (**10a**) and another bridgehead-unsymmetrically-substituted dibenzobarrelene containing both ester and lactone functionalities, i.e. **10b**.

2. Experimental details

All melting points (m.p.) are uncorrected and were determined using a Büchi-530 melting point apparatus. The IR spectra were recorded on a Perkin-Elmer model 882 IR spectrophotometer and the electronic spectra were recorded on a Shimadzu UV-2100 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded using a Varian EM-360, Brüker WH-

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270 or JOEL EX-90 NMR spectrometer, with tetramethylsilane as internal standard. The mass spectra were recorded on a Finnegan MAT model 8430 or JOEL JMS AX505HA mass spectrometer. The steady state photolysis experiments were performed using either a Srinivasan–Griffin–Rayonet photochemical reactor (RPR, 3000 Å light source) or a Hanovia 450 W medium-pressure mercury vapor lamp. Solvents used for the photolysis experiments were purified before use. The petroleum ether used was the fraction with a boiling point (b.p.) of 60–80 °C.

2.1. Starting materials

Dimethylacetylenedicarboxylate (DMAD) [2] (b.p. 95–98 °C at 19 mm), 9-hydroxymethyl-10-methylantracene [3] (m.p. 223–224 °C) and 9-hydroxymethyl-10-methoxyanthracene [4] (m.p. 149–150 °C) were prepared by known procedures.

2.2. Preparation of 1, 10a and 10b

Compound 1

The benzobarrelene 1 was prepared by refluxing a mixture of 9-hydroxymethyl-10-methylantracene (444 mg, 2 mmol) and DMAD (284 mg, 2 mmol) in dry toluene (5 ml) for 6 h. The solvent was removed under reduced pressure and the residue was recrystallized from acetone to give 1 (502 mg, 69%) (m.p. 189–190 °C). IR ν_{\max} (KBr): 3530 (OH), 1728 (C=O), 1706 (C=O) cm^{-1} ; UV λ_{\max} (CH₃OH): 214 nm ($\epsilon=34\,400\text{ M}^{-1}\text{ cm}^{-1}$), 258 (12 500); ¹H NMR (CDCl₃): δ 2.18 (3 H, s, CH₃), 3.70 (3 H, s, OCH₃), 3.77 (3 H, s, OCH₃), 3.86 (1 H, s, D₂O-exchangeable, OH), 5.13 (2 H, d, CH₂), 7.05–7.50 (8 H, m, aromatic); ¹³C NMR (CDCl₃): δ 12.97, 50.12, 52.48, 55.28, 60.23, 120.83, 121.84, 122.23, 124.89, 125.06, 125.72, 143.26, 145.56, 147.14, 166.23 (C=O), 166.71 (C=O); mass spectrum m/z (relative intensity): 364 (M⁺, 32), 332 (81), 304 (100), 274 (71), 229 (79), 78 (16), 59 (28); molecular weight calculated for C₂₂H₂₀O₅, 364.1311; found, 364.1410 (high-resolution mass spectrometry).

Compound 10a

A mixture of 9-hydroxymethyl-10-methylantracene (444 mg, 2 mmol) and DMAD (284 mg, 2 mmol) was heated at 180 °C for 12 h. The reaction mixture was chromatographed over silica gel. Elution of the column with a mixture (1 : 5) of ethyl acetate and petroleum ether gave 10a (495 mg, 68%) (m.p. 175–176 °C). IR ν_{\max} (KBr): 1761 (C=O), 1745 (C=O) cm^{-1} ; UV λ_{\max} (CH₃OH): 213 nm ($\epsilon=46\,600$), 231 (9350); ¹H NMR (CDCl₃): δ 2.2 (3 H, s, CH₃), 3.7 (3 H, s, OCH₃), 5.4 (2 H, s, CH₂), 6.7–7.5 (8 H, m, aromatic); ¹³C NMR (CDCl₃): δ 12.72, 52.49, 52.90, 56.28, 65.46, 120.24, 121.82, 125.28, 125.70, 141.39, 144.39, 145.39, 150.80,

164.55 (C=O), 166.00 (C=O); mass spectrum m/z (relative intensity): 332 (M⁺, 7), 300 (11), 276 (10), 245 (96), 229 (21), 217 (16), 202 (11), 78 (100), 51 (18); molecular weight calculated for C₂₁H₁₆O₄, 332.1049; found, 332.1046 (high-resolution mass spectrometry).

Compound 10b

A mixture of 9-hydroxymethyl-10-methoxyanthracene (222 mg, 1 mmol) and DMAD (142 mg, 1 mmol) was heated at 180 °C for 12 h. The reaction mixture was chromatographed over silica gel. Elution of the column with a mixture (1 : 5) of ethyl acetate and petroleum ether gave 10b (365 mg, 80%) (m.p. 161–162 °C). IR ν_{\max} (KBr): 1768 (C=O), 1730 (C=O) cm^{-1} ; UV λ_{\max} (CH₃OH): 214 nm ($\epsilon=55\,500$), 240 (9300); ¹H NMR (CDCl₃): δ 3.90 (3 H, s, OCH₃), 4.00 (3 H, s, OCH₃), 5.50 (2 H, s, CH₂), 7.00–7.90 (8 H, m, aromatic); ¹³C NMR (CDCl₃): δ 53.11, 55.50, 57.11, 65.38, 90.65, 120.27, 122.30, 125.70, 126.03, 126.36, 140.32, 142.02, 143.00, 164.04 (C=O), 164.13 (C=O); mass spectrum m/z (relative intensity): 348 (M⁺, 100), 257 (48), 245 (80), 221 (32), 202 (19); molecular weight calculated for C₂₁H₁₆O₅, 348.0998; found, 348.0974 (high-resolution mass spectrometry).

2.3. Photolysis of 1

A benzene solution of 1 (364 mg, 1 mmol in 250 ml) was irradiated for $\frac{1}{4}$ h (Hanovia 450 W medium-pressure mercury lamp). After removal of the solvent under reduced pressure, the residual material was chromatographed over silica gel. Elution with a mixture (1 : 5) of ethyl acetate and petroleum ether gave 255 mg (77%) of 8 as colorless crystals (m.p. 220–221 °C). IR ν_{\max} (KBr): 1764 (C=O), 1719 (C=O) cm^{-1} ; UV λ_{\max} (CH₃OH): 211 nm ($\epsilon=25\,200$), 240 (15 300), 280 (3900); ¹H NMR (CDCl₃): δ 2.21 (3 H, s, CH₃), 3.70 (3 H, s, OCH₃), 5.03–5.29 (2 H, dd, CH₂), 7.12–7.30 (8 H, m, aromatic); ¹³C NMR (CDCl₃): δ 24.53, 52.10, 71.07, 120.27, 125.79, 126.48, 127.43, 127.58, 127.81, 128.95, 129.07, 129.46, 129.73, 130.92, 131.91, 137.31, 142.50, 145.39, 161.89, 168.60 (C=O), 172.15 (C=O); mass spectrum m/z (relative intensity): 332 (M⁺, 11), 288 (91), 229 (100), 59 (9); molecular weight calculated for C₂₁H₁₆O₄, 332.1049; found, 332.1039 (high-resolution mass spectrometry).

2.4. Photolysis of 10a

A solution of 10a (332 mg, 1 mmol) in benzene (250 ml) was irradiated for 1 h (Hanovia 450 W medium-pressure mercury lamp). The solvent was removed under reduced pressure and the residual solid on recrystallization from benzene gave 15a (320 mg, 96%) (m.p. 179–180 °C). IR ν_{\max} (KBr): 1760 (C=O), 1731 (C=O) cm^{-1} ; UV λ_{\max} (CH₃OH): 219 nm ($\epsilon=19\,000$), 257

(3450); ^1H NMR (CDCl_3): δ 2.00 (3 H, s, CH_3), 3.77 (3 H, s, OCH_3), 4.81–5.14 (2 H, dd, CH_2), 7.19–7.52 (8 H, m, aromatic); ^{13}C NMR (CDCl_3): δ 16.39, 52.40, 55.71, 60.66, 61.56, 64.81, 73.01, 120.03, 120.69, 122.66, 125.10, 127.55, 127.85, 128.36, 128.92, 130.39, 131.81, 148.50, 150.29, 165.95 ($\text{C}=\text{O}$), 170.13 ($\text{C}=\text{O}$); mass spectrum m/z (relative intensity): 332 (M^+ , 100), 304 (55), 276 (65), 261 (12), 245 (31), 229 (37), 217 (73), 202 (36), 78 (16); molecular weight calculated for $\text{C}_{21}\text{H}_{16}\text{O}_4$, 332.1049; found, 332.1048 (high-resolution mass spectrometry).

2.5. Photolysis of 10b

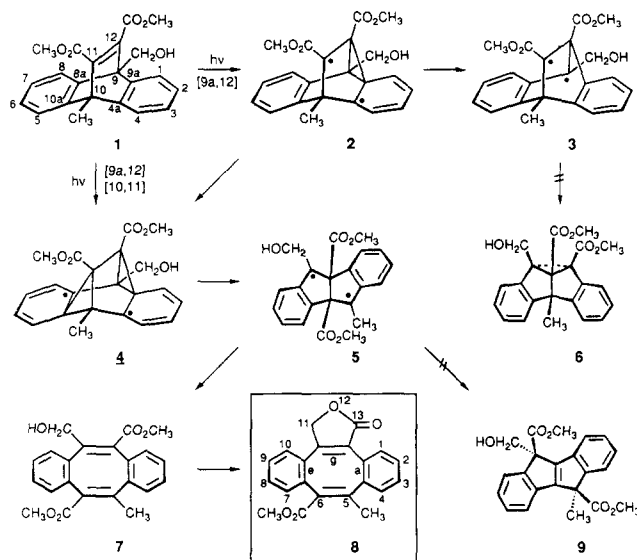
A solution of **10b** (250 mg, 0.72 mmol) in benzene (250 ml) was irradiated for 1 h (RPR, 3000 Å light source) and the solvent was removed under vacuum. The residual solid was recrystallized from a mixture (3 : 1) of benzene and petroleum ether to give **15b** (230 mg, 92%) (m.p. 158–159 °C). IR ν_{max} (KBr): 1776 ($\text{C}=\text{O}$), 1723 ($\text{C}=\text{O}$) cm^{-1} ; UV λ_{max} (CH_3OH): 213 nm ($\epsilon = 25\,500$), 234 (14\,700); ^1H NMR (CDCl_3): δ 3.45 (3 H, s, OCH_3), 3.80 (3 H, s, OCH_3), 4.75–5.45 (2 H, dd, CH_2), 7.15–8.30 (8 H, m, aromatic); ^{13}C NMR (CDCl_3): δ 52.66, 54.74, 55.34, 59.91, 64.47, 72.20, 98.60, 120.74, 121.31, 122.74, 125.74, 128.17, 128.26, 128.59, 128.82, 129.66, 145.05, 145.29, 164.89 ($\text{C}=\text{O}$), 168.80 ($\text{C}=\text{O}$); mass spectrum m/z (relative intensity): 348 (M^+ , 68), 316 (53), 261 (74), 260 (100), 202 (44); molecular weight calculated for $\text{C}_{21}\text{H}_{16}\text{O}_5$, 348.0998; found, 348.1012 (high-resolution mass spectrometry).

2.6. X-Ray structure determination of 8 and 15a

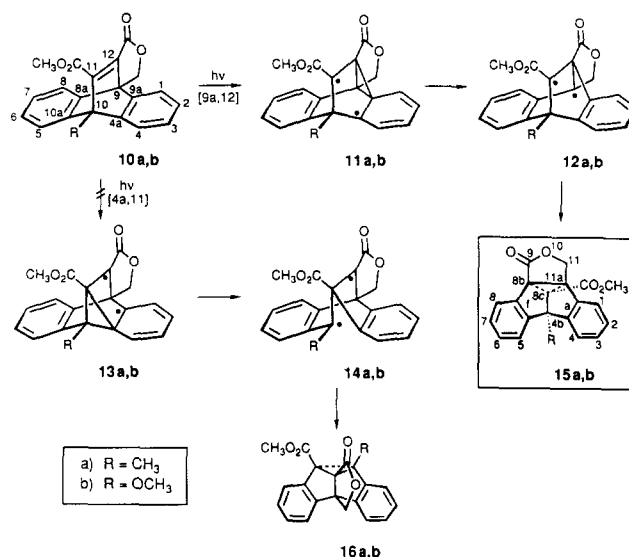
Crystals of **8** and **15a** were mounted on glass fibers in random orientation. Data collection was done using a Siemens R3 automated, single-crystal X-ray diffractometer with graphite monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073$ Å). A summary of the crystal data and intensity collection parameters is presented in Table 1. Data reduction, structure solution and refinement were achieved by the SHELXTL-PLUS (VMS) structure solution software package [5].

2.7. Supplementary material available

A complete list of the atomic coordinates, anisotropic displacement coefficients, hydrogen atom coordinates, isotropic displacement coefficients, bond distances and bond angles for **8** and **15a** is available at the Cambridge Crystallographic Data Centre (CCDC).



Scheme 1.



Scheme 2.

3. Results

3.1. Preparative photochemistry and product identification

Irradiation of a benzene solution of **1** gave a good yield (77%) of the dibenzocyclooctatetraene lactone (**8**) (Scheme 1). The structure of **8** was derived on the basis of analytical data and spectral evidence. The IR spectrum of **8** did not show any absorption due to the OH group, whereas it showed two peaks at 1764 and 1719 cm^{-1} due to the $\text{C}=\text{O}$ groups. The ^1H NMR spectrum of **8** showed singlets at δ 2.21 and 3.70, assigned to the methyl and methoxy protons respectively. The CH_2 protons appeared as a double doublet at δ 5.03–5.29, whereas the aromatic protons appeared as a multiplet centered around δ 7.21. Confirmation of

the structure of **8** was derived through X-ray crystallographic analysis.

Similarly, irradiation of benzene solutions of **10a** and **10b** gave the corresponding dibenzosemibullvalene lactones (**15a** and **15b**) in 96% and 92% yield respectively (Scheme 2). The structures of both **15a** and **15b** were established on the basis of analytical results and spectral evidence. The structure of one of the products, **15a**, was confirmed through X-ray crystallographic analysis.

3.2. X-Ray crystallographic analysis of **8** and **15a**

A single-crystal X-ray structure determination of **8** showed discrete molecular units at general positions. Crystals of **8** suitable for X-ray diffraction studies were

obtained by recrystallization from acetonitrile. The structure was solved and refined in the monoclinic space group $P2_1/c$ with unit cell dimensions of $a=9.351$ Å, $b=18.953$ Å, $c=9.353$ Å and $\beta=93.23^\circ$. The projection view of **8** is shown in Fig. 1. Table 2 lists the atomic coordinates for **8**, whereas selected bond distances and bond angles are shown in Table 3. The tub shape of the cyclooctatetraene ring, having two benzene rings fused at C(1), C(6) and C(9), C(14) carbons, is shown in Fig. 2. Both the carbomethoxy functionality and the lactone ring are on the same outer face of the cyclooctatetraene ring.

Colorless rectangular crystals of **15a** were obtained by slow crystallization from benzene. Final cell parameters for **15a** are $a=15.622$ Å, $b=12.472$ Å, $c=16.616$

Table 1

Summary of crystal data and intensity collection parameters for **8** ($C_{21}H_{16}O_4$) and **15a** ($C_{21}H_{16}O_4$)

Crystal data/parameter	8	15a
Empirical formula	$C_{21}H_{16}O_4$	$C_{21}H_{16}O_4$
Color; habit	Colorless; rectangular	Colorless; rectangular
Crystal size (mm)	$0.5 \times 0.4 \times 0.3$	$0.5 \times 0.4 \times 0.4$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
Unit cell dimensions	$a=9.351(3)$ Å $b=18.953(6)$ Å $c=9.353(3)$ Å $\beta=93.23(2)^\circ$ $1654.9(9)$ Å ³	$a=15.622(5)$ Å $b=12.472(3)$ Å $c=16.616(4)$ Å $\beta=101.39(2)^\circ$ $3173.8(14)$ Å ³
Volume		
Z	4	8
Formula weight	332.4	332.4
Density (calculated)	1.334 mg m^{-3}	1.391 mg m^{-3}
Absorption coefficient	0.086 mm^{-1}	0.096 mm^{-1}
$F(000)$	696	1392
Diffractometer	Siemens R3 m/V	Siemens R3 m/V
Radiation	Mo $K\alpha$ ($\lambda=0.71073$ Å)	Same as in 8
Temperature (K)	298	173
Monochromator	Highly oriented graphite crystal	Same as in 8
2θ range	3.5° – 55.0°	3.5° – 60°
Scan type	2θ – θ	2θ – θ
Scan speed	Variable; 3.97° – $14.65^\circ \text{ min}^{-1}$ in ω	Variable; 3.97° – $29.30^\circ \text{ min}^{-1}$ in ω
Scan range (ω)	1.20° plus $K\alpha$ -separation	1.20° plus $K\alpha$ -separation
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time	
Standard reflection	3 measured for every 50 reflections	Same as in 8
Reflections collected	4109	4436
Independent reflections	3829 ($R_{\text{int}}=1.60\%$)	4103 ($R_{\text{int}}=1.83\%$)
Observed reflections	2551 ($F>4.0\sigma(F)$)	2964 ($F>4.0\sigma(F)$)
Absorption correction	N/A	N/A
Hydrogen atoms	Refined positions and isotropic U	Refined positions and isotropic U
Weighting scheme	$w^{-1}=\sigma^2(F)+0.0013F^2$	$w^{-1}=\sigma^2(F)+0.0017F^2$
Number of parameters refined	290	290
Final R indices (observed data)	$R=4.9\%$; $wR=6.22\%$	$R=4.47\%$; $wR=6.16\%$
Goodness-of-fit	1.23	1.13
Largest difference peak	$0.22 \text{ e } \text{\AA}^{-3}$	$0.36 \text{ e } \text{\AA}^{-3}$
Largest difference hole	$-0.22 \text{ e } \text{\AA}^{-3}$	$-0.24 \text{ e } \text{\AA}^{-3}$

N/A, not applicable.

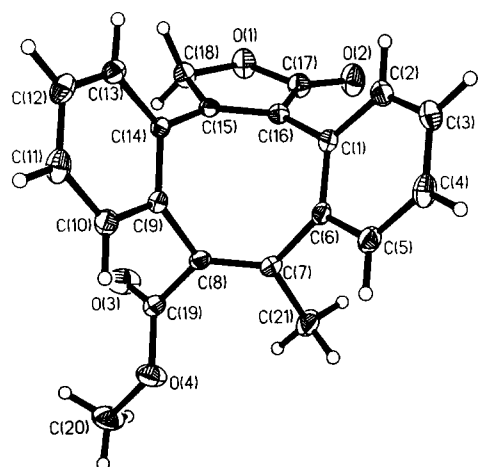
Fig. 1. Projection view of **8** with 50% probability ellipsoids.

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for **8**

Atom	x	y	z	$U(\text{eq})^a$
O(1)	3808(2)	9510(1)	1049(2)	50(1)
O(2)	5676(2)	9931(1)	2388(2)	60(1)
O(3)	-727(2)	10268(1)	3222(2)	74(1)
O(4)	-1136(2)	11205(1)	4546(2)	55(1)
C(1)	4102(2)	11383(1)	2243(2)	31(1)
C(2)	5351(2)	11694(1)	1799(3)	40(1)
C(3)	5720(3)	12371(1)	2207(3)	47(1)
C(4)	4863(3)	12745(1)	3097(3)	49(1)
C(5)	3651(3)	12435(1)	3592(3)	41(1)
C(6)	3243(2)	11757(1)	3161(2)	32(1)
C(7)	1974(2)	11420(1)	3793(2)	33(1)
C(8)	787(2)	11257(1)	3001(2)	31(1)
C(9)	555(2)	11394(1)	1434(2)	30(1)
C(10)	-521(2)	11860(1)	949(2)	39(1)
C(11)	-808(3)	11976(1)	-495(3)	47(1)
C(12)	-52(3)	11614(1)	-1485(3)	44(1)
C(13)	995(2)	11137(1)	-1036(2)	36(1)
C(14)	1314(2)	11029(1)	420(2)	28(1)
C(15)	2470(2)	10538(1)	876(2)	29(1)
C(16)	3659(2)	10684(1)	1674(2)	31(1)
C(17)	4526(2)	10038(1)	1790(2)	41(1)
C(18)	2480(3)	9783(1)	429(3)	41(1)
C(19)	-420(2)	10853(1)	3598(2)	38(1)
C(20)	-2336(4)	10834(2)	5145(4)	72(1)
C(21)	2170(3)	11274(2)	5372(3)	52(1)

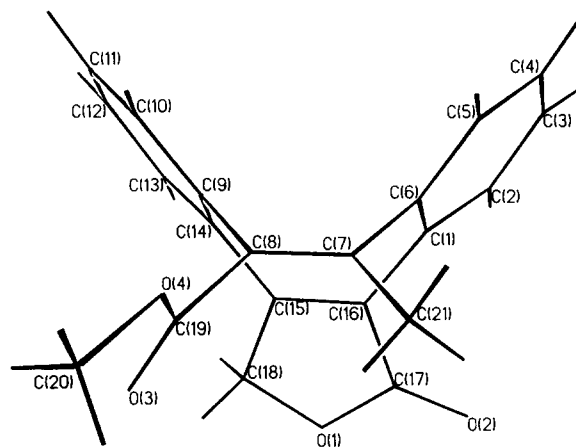
^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

\AA , $\beta = 101.39^\circ$ and space group $= C_2/c$. The projection view of **15a** is shown in Fig. 3. The atomic coordinates and selected bond distances and bond angles of **15a** are presented in Tables 4 and 5 respectively. The angle between the two planes of the five-membered rings of the pentalene skeleton was found to be 103.5° . The cyclopropane ring of the semibullvalene is nearly equilateral with C(1)–C(2), C(1)–C(16) and C(2)–C(16) bond distances being 1.487 \AA , 1.526 \AA and 1.580 \AA respectively.

Table 3

Selected bond lengths (\AA) and bond angles ($^\circ$) for **8**

O(1)–C(17)	1.371(3)	O(1)–C(18)	1.437(3)
O(2)–C(17)	1.201(3)	O(3)–C(19)	1.194(3)
O(4)–C(19)	1.321(3)	O(4)–C(20)	1.461(5)
C(1)–C(16)	1.478(3)	C(1)–C(6)	1.400(3)
C(7)–C(8)	1.335(3)	C(6)–C(7)	1.498(3)
C(8)–C(9)	1.493(3)	C(7)–C(21)	1.504(3)
C(13)–C(14)	1.393(3)	C(9)–C(14)	1.400(3)
C(14)–C(15)	1.471(3)	C(15)–C(16)	1.333(3)
C(15)–C(18)	1.490(3)	C(16)–C(17)	1.469(3)
C(17)–O(1)–C(18)	109.3(2)	C(19)–O(4)–C(20)	116.3(2)
C(2)–C(1)–C(6)	119.3(2)	C(2)–C(1)–C(16)	119.6(2)
C(6)–C(1)–C(16)	121.0(2)	C(1)–C(2)–C(3)	120.8(2)
C(1)–C(6)–C(7)	121.4(2)	C(5)–C(6)–C(7)	119.3(2)
C(6)–C(7)–C(8)	122.2(2)	C(6)–C(7)–C(21)	114.2(2)
C(8)–C(7)–C(21)	123.6(2)	C(7)–C(8)–C(9)	125.1(2)
C(7)–C(8)–C(19)	122.2(2)	C(9)–C(8)–C(19)	112.6(2)
C(8)–C(9)–C(10)	119.5(2)	C(8)–C(9)–C(14)	121.9(2)
C(9)–C(14)–C(15)	120.6(2)	C(9)–C(14)–C(13)	120.1(2)
C(14)–C(15)–C(16)	127.3(2)	C(13)–C(14)–C(15)	119.3(2)
C(16)–C(15)–C(18)	109.8(2)	C(14)–C(15)–C(18)	122.8(2)
C(1)–C(16)–C(17)	125.4(2)	C(1)–C(16)–C(19)	126.6(2)
O(1)–C(17)–O(2)	120.8(2)	C(15)–C(16)–C(17)	107.9(2)
O(2)–C(17)–C(16)	130.6(2)	O(1)–C(17)–C(16)	108.6(2)
O(3)–C(19)–O(4)	123.0(2)	O(1)–C(18)–C(15)	104.5(2)
O(4)–C(19)–C(8)	114.5(2)	O(3)–C(19)–C(8)	122.6(2)

Fig. 2. View of **8**, indicating spatial disposition of substituent groups.

4. Discussion

Based on the known photochemistry of bridgehead-disubstituted dibenzobarrelenes, the photolysis of **1**, in principle, can lead to the formation of the dibenzos-semibullvalene (**6**), dibenzocyclooctatetraene (**7**) and dibenzopentalene (**9**). However, the photolysis of **1** in benzene was found to give exclusively the dibenzocyclooctatetraene (**8**). The formation of **8** from **1** could be rationalized in terms of the pathway shown in Scheme 1. A di- π -methane rearrangement route involving the [9a,12] interaction in **1** could result in the 1,3-diradical

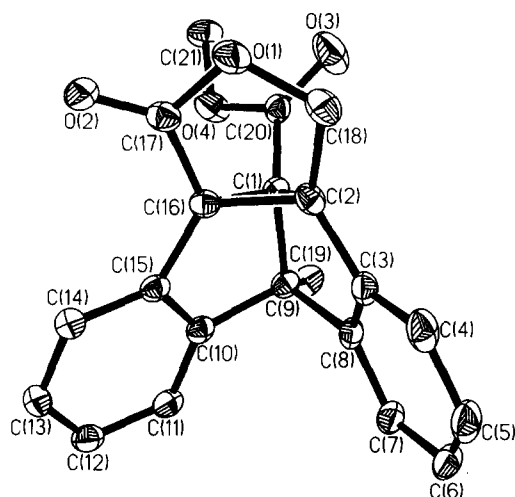
Fig. 3. Projection view of **15a** with 50% probability ellipsoids.

Table 4

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for **15a**

Atom	x	y	z	$U(\text{eq})^a$
O(1)	7474(1)	1844(1)	5830(1)	30(1)
O(2)	6187(1)	1170(1)	5969(1)	28(1)
O(3)	8888(1)	-178(1)	6123(1)	47(1)
O(4)	7823(1)	-1104(1)	6516(1)	31(1)
C(1)	8246(1)	471(1)	7224(1)	18(1)
C(2)	8335(1)	1655(1)	7174(1)	20(1)
C(3)	8823(1)	2041(1)	7973(1)	20(1)
C(4)	9129(1)	3065(1)	8209(1)	28(1)
C(5)	9556(1)	3223(2)	9015(1)	32(1)
C(6)	9669(1)	2380(2)	9577(1)	30(1)
C(7)	9352(1)	1360(2)	9346(1)	25(1)
C(8)	8937(1)	1192(1)	8535(1)	19(1)
C(9)	8453(1)	183(1)	8159(1)	19(1)
C(10)	7560(1)	276(1)	8397(1)	19(1)
C(11)	7303(1)	-75(1)	9107(1)	22(1)
C(12)	6458(1)	147(2)	9209(1)	25(1)
C(13)	5887(1)	728(2)	8624(1)	25(1)
C(14)	6150(1)	1109(1)	7921(1)	23(1)
C(15)	6985(1)	873(1)	7812(1)	18(1)
C(16)	7405(1)	1125(1)	7113(1)	18(1)
C(17)	6939(1)	1356(1)	6268(1)	22(1)
C(18)	8298(1)	2170(2)	6348(1)	26(1)
C(19)	8926(1)	-871(1)	8384(1)	26(1)
C(20)	8379(1)	-294(1)	6567(1)	20(1)
C(21)	7825(2)	-1854(2)	5854(1)	28(1)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

intermediate (**2**), which could ultimately lead to the dibenzosemibullvalene (**6**), as shown in Scheme 1. The fact that **6** or products derived from it are not observed in the photolysis of **1** suggests that alternative pathways may be involved. A second possible route to the further transformation of **2** is through the 1,4-diradical intermediate (**4**), which could subsequently give rise to yet

Table 5

Selected bond lengths (\AA) and bond angles ($^\circ$) for **15a**

O(1)–C(17)	1.357(2)	O(1)–C(18)	1.457(2)
O(2)–C(17)	1.204(2)	O(3)–C(20)	1.195(3)
O(4)–C(20)	1.323(2)	O(4)–C(21)	1.446(2)
C(1)–C(2)	1.487(2)	C(1)–C(9)	1.565(2)
C(1)–C(16)	1.526(2)	C(1)–C(20)	1.495(2)
C(2)–C(3)	1.476(2)	C(2)–C(16)	1.580(3)
C(2)–C(18)	1.506(3)	C(8)–C(9)	1.536(2)
C(3)–C(8)	1.400(2)	C(9)–C(19)	1.519(2)
C(9)–C(10)	1.527(3)	C(10)–C(15)	1.400(2)
C(15)–C(16)	1.476(3)	C(16)–C(17)	1.477(2)
C(17)–O(1)–C(18)	120.0(1)	C(20)–O(4)–C(21)	116.2(2)
C(2)–C(1)–C(9)	106.3(1)	C(2)–C(1)–C(16)	63.2(1)
C(9)–C(1)–C(16)	104.2(1)	C(2)–C(1)–C(20)	124.4(1)
C(9)–C(1)–C(20)	123.2(1)	C(16)–C(1)–C(20)	119.5(1)
C(1)–C(2)–C(3)	108.1(1)	C(1)–C(2)–C(16)	59.6(1)
C(3)–C(2)–C(16)	119.9(2)	C(1)–C(2)–C(18)	119.2(1)
C(3)–C(2)–C(18)	126.9(2)	C(16)–C(2)–C(18)	104.6(1)
C(2)–C(3)–C(4)	129.8(2)	C(2)–C(3)–C(8)	109.2(1)
C(4)–C(3)–C(8)	121.0(2)	C(7)–C(8)–C(9)	128.0(2)
C(3)–C(8)–C(9)	111.2(1)	C(1)–C(9)–C(10)	102.7(1)
C(1)–C(9)–C(8)	101.8(1)	C(1)–C(9)–C(19)	116.0(1)
C(8)–C(9)–C(10)	103.5(1)	C(10)–C(9)–C(19)	115.3(1)
C(8)–C(9)–C(19)	115.6(1)	C(9)–C(10)–C(15)	110.8(1)
C(9)–C(10)–C(11)	128.9(1)	C(10)–C(15)–C(14)	121.0(2)
C(10)–C(15)–C(16)	109.5(2)	C(10)–C(9)–C(16)	129.4(1)
C(1)–C(16)–C(2)	57.2(1)	C(1)–C(16)–C(15)	107.3(1)
C(2)–C(16)–C(15)	125.8(1)	C(1)–C(16)–C(17)	118.0(1)
C(2)–C(16)–C(17)	104.7(1)	C(15)–C(16)–C(17)	125.2(2)
O(1)–C(17)–O(2)	121.3(2)	O(1)–C(17)–C(16)	110.9(1)
O(2)–C(17)–C(16)	127.8(2)	O(1)–C(18)–C(2)	106.8(2)
O(3)–C(20)–O(4)	124.2(2)	O(3)–C(20)–C(1)	125.3(2)

another diradical intermediate (**5**). An alternative pathway for the formation of **4** from **1** is through a tri- π -methane rearrangement, involving both [9a,12] and [10a,11] interactions [6]. The diradical intermediate (**5**) can further undergo a Grob-type fragmentation to the dibenzocyclooctatetraene (**7**), and the thermal lactonization of **7** will ultimately give the dibenzocyclooctatetraene derivative (**8**).

The formation of the hexacyclic lactones (**15a,b**) from **10a,b** can be understood in terms of the pathway shown in Scheme 2. The di- π -methane rearrangement of **10a,b**, involving [9a,12] interaction, could result in the diradical intermediates **11a,b**, which could lead to **12a,b** and ultimately **15a,b**. It is interesting to note that the alternative pathway, involving a [4a,11] bridging, leading to the diradical intermediates **13a,b** and ultimately the rearrangement products **16a,b**, is not followed in the case of **10a,b**. The regioselectivity observed in the transformations of **10a,b** could be attributed to a decrease in the steric interference of the methylene protons of the lactone moiety in **10a,b** with the ortho hydrogens at positions 1 and 8 of the barrelene skeleton, through a [9a,12] bridging, followed by rapid successive rearrangements. Mention may be made in this connection

that the regioselectivity observed in the photorearrangements of certain dibenzobarrelenes bearing lactone functionalities has been explained in terms of such a release of steric strain [7].

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