

Structures and Photochemistry of 1,5-Disubstituted Dibenzobarrelenes

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Abstract

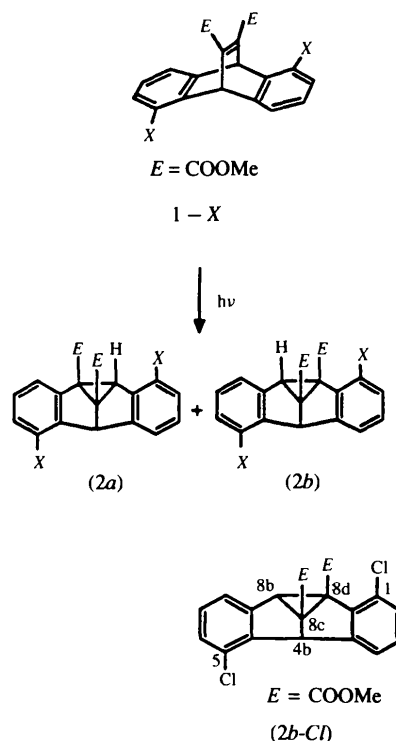
The effect of 1,5-disubstitution on the photochemistry of 9,10-ethenoanthracene-11,12-diester has been studied and correlated with the crystal structures determined for several derivatives; photoproduct structures have been established from a crystal structure analysis of one of the products and from NMR correlations. The crystals studied are: (1)-Cl, dimethyl 1,5-dichloro-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate, $C_{20}H_{14}Cl_2O_4$, $P2_1/n$; (1)-CN, 1,5-dicyano derivative, $C_{22}H_{14}N_2O_4$, $P2_1/n$; (1)-CN.0.5*p*-xylene, $C_{22}H_{14}N_2O_4 \cdot 0.5C_8H_{10}$, $P2_1/c$; (1)-CN.*xx*ylylene, $C_{22}H_{14}N_2O_4 \cdot xC_8H_{10}$, $P2_1/n$; (1)-OMe, 1,5-dimethoxy derivative, $C_{22}H_{20}O_6$, $P\bar{1}$; (2*b*)-Cl, $C_{20}H_{14}Cl_2O_4$, dimethyl 1,5-dichloro-4*b*,8*b*,8*c*,8*d*-tetrahydrodibenzo[*a,f*]cyclopropano[*c,d*]pentalene-8*c*,8*d*-dicarboxylate, $Pna2_1$. The dibenzobarrelene molecules all have geometries and dimensions similar to those of related materials. In particular, the orientations of the two ester groups in each molecule differ, one being in general almost fully conjugated with the C(11)=C(12) double bond and the other almost non-conjugated. Relationships are sought between the ratios of the two regioisomeric photoproducts and molecular and crystal structures; both electronic and steric effects are considered, but no one effect seems to dominate.

1. Introduction

Studies of the photochemistry of dibenzobarrelene diesters (Pokkuluri, Scheffer & Trotter, 1993*a,b*) have been extended to examine the influence of 1,5-disubstitution. Photolysis of these (1)-*X* materials in solution and in the solid state gives two regioisomeric photoproducts (2*a* and 2*b*). The crystal structures of several derivatives have been determined, (1)-*X*, *X* = Cl, CN (unsolvated and two xylene solvates) and OMe. The molecular structure of one of the photoproducts, (2*b*)-Cl, was determined by crystal structure analysis and the structures of all the other photoproducts could then be deduced from NMR data.

2. Experimental

The dibenzobarrelene diesters were synthesized by Diels–Alder reaction from dimethyl acetylenedicarboxy-



Scheme 1

late and the appropriate 1,5-disubstituted anthracenes [prepared from 1,5-dichloroanthraquinone and the appropriate substitutions and reduction (Yang, 1993)]. X-ray data, measured on a Rigaku AFC-6*S* diffractometer, are summarized in Table 1. The structures were solved by direct methods and refined by full-matrix least-squares procedures, with $w = 1/\sigma^2(F)$.

H-atom parameters were refined for (1)-Cl and fixed at calculated values for the other structures. For (1)-CN unsolvated crystals were obtained from acetone and two types of solvated crystals from xylenes. Both solvates have an asymmetric unit containing two molecules of (1)-CN and approximately one xylene molecule. In one form the solvent seems to be *p*-xylene molecules lying on symmetry centres (two half-molecules per asymmetric unit). The thermal motion for the xylene is high, with perhaps some disorder, and the geometry is far from ideal; nevertheless, the solvent is relatively well defined. In the second form the solvent

appears as a region of electron-density peaks in a general position and approximately in one plane; the peaks appear to correspond to five full-weight and one half-weight C atoms, but the distribution could not be readily interpreted in terms of disordered xylene molecules. In addition, one carbomethoxy group exhibits disorder [0.72/0.28 occupancies for the C(15) methyl group]. In (1)-OMe there are two molecules per asymmetric unit; a

high thermal parameter for one O atom, O(2), suggests possible disorder, but no satisfactory disordered model could be refined.

Scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV); computer programs as supplied in *TEXSAN* (Molecular Structure Corporation, 1989). Details of the refinements are given in Table 1.

Table 1. *Experimental details*

	(1)-Cl	(1)-CN	(1)-CN.0.5 <i>p</i> -xylene	(1)-CN.0.35xylene	(1)-OMe	(2 <i>b</i>)-Cl
Crystal data						
Chemical formula	C ₂₀ H ₁₄ Cl ₂ O ₄	C ₂₂ H ₁₄ N ₂ O ₄	C ₂₂ H ₁₄ N ₂ O ₄ · 0.5C ₈ H ₁₀	C ₂₂ H ₁₄ N ₂ O ₄ · 0.35C ₈ H ₁₀	C ₂₂ H ₂₀ O ₆	C ₂₀ H ₁₄ Cl ₂ O ₄
Chemical formula weight	389.23	370.36	423.45	407.52	380.40	389.23
Melting point (K)	479–481	545–546	–	–	512–513	459–461
Cell setting	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>Pna</i> 2 ₁
<i>a</i> (Å)	7.672 (1)	7.864 (2)	15.328 (3)	15.174 (2)	14.900 (2)	14.867 (1)
<i>b</i> (Å)	8.217 (2)	27.588 (2)	14.483 (2)	14.408 (2)	15.128 (9)	8.109 (1)
<i>c</i> (Å)	29.042 (2)	8.760 (2)	20.421 (1)	20.531 (2)	8.809 (3)	14.944 (1)
α (°)	90.0	90.0	90.0	90.0	105.03 (3)	90.0
β (°)	92.41 (1)	101.88 (2)	105.65 (1)	109.21 (1)	90.22 (2)	90.0
γ (°)	90.0	90.0	90.0	90.0	82.79 (3)	90.0
<i>V</i> (Å ³)	1829.2 (4)	1859.8 (6)	4365 (1)	4239 (2)	1902 (2)	1801.6 (4)
<i>Z</i>	4	4	8	8	4	4
<i>D_x</i> (Mg m ⁻³)	1.413	1.322	1.288	1.277	1.328	1.435
<i>F</i> (000)	800	768	1768	1698	800	800
Radiation type	Cu <i>K</i> α	Cu <i>K</i> α	Cu <i>K</i> α	Cu <i>K</i> α	Cu <i>K</i> α	Cu <i>K</i> α
Wavelength (Å)	1.54178	1.54178	1.54178	1.54178	1.54178	1.54178
No. of reflections for cell parameters	25	25	25	25	25	25
θ range (°)	34.3–43.1	38.4–47.3	22.6–42.0	42.6–50.1	12.0–42.8	43.6–57.3
μ (mm ⁻¹)	3.44	0.72	0.68	0.70	0.76	3.49
Temperature (K)	294	294	294	294	294	294
Crystal form	Prism	Needle	Prism	Plate	Plate	Prism
Crystal size (mm)	0.45 × 0.20 × 0.10	0.35 × 0.10 × 0.10	0.20 × 0.12 × 0.08	0.40 × 0.40 × 0.10	0.25 × 0.25 × 0.10	0.40 × 0.30 × 0.30
Crystal colour	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless
Data collection						
Diffractometer	Rigaku AFC-6S	Rigaku AFC-6S	Rigaku AFC-6S	Rigaku AFC-6S	Rigaku AFC-6S	Rigaku AFC-6S
Data collection method	ω -2 θ	ω -2 θ	ω -2 θ	ω -2 θ	ω -2 θ	ω -2 θ
ω scan width (°)						
<i>a</i> + <i>b</i> tan θ						
<i>a</i>	0.99	1.26	1.10	1.10	1.15	1.21
<i>b</i>	0.20	0.30	0.25	0.20	0.20	0.20
Scan speed* (° min ⁻¹)	32.0	16.0	16.0	16.0	16.0	32.0
Absorption correction	<i>DIFABS</i> (Walker & Stuart, 1983)	ψ scans	ψ scans	ψ scans	ψ scans	ψ scans
<i>T</i> _{min}	0.82	0.82	0.95	0.92	0.88	0.82
<i>T</i> _{max}	1.0	1.0	1.0	1.0	1.0	1.0
No. of measured reflections	4023	4135	9379	9755	8066	1964
No. of independent reflections	3945	3852	8653	9400	7745	1964
No. of observed reflections	2689	2348	2888	4451	4156	1882
%	66.8	61.0	33.4	47.4	53.7	95.8
Criterion for observed reflections†	<i>I</i> > 3 σ (<i>I</i>)	<i>I</i> > 3 σ (<i>I</i>)	<i>I</i> > 3 σ (<i>I</i>)	<i>I</i> > 3 σ (<i>I</i>)	<i>I</i> > 3 σ (<i>I</i>)	<i>I</i> > 3 σ (<i>I</i>)
<i>R</i> _{int}	0.019	0.018	0.026	0.034	0.022	–
θ _{max} (°)	77.5	77.5	77.5	77.5	77.5	77.5
Range of <i>h</i> , <i>k</i> , <i>l</i>	0 → <i>h</i> → 9 0 → <i>k</i> → 10 –34 → <i>l</i> → 34	0 → <i>h</i> → 9 0 → <i>k</i> → 34 –11 → <i>l</i> → 10	0 → <i>h</i> → 19 0 → <i>k</i> → 17 –25 → <i>l</i> → 24	0 → <i>h</i> → 19 0 → <i>k</i> → 18 –25 → <i>l</i> → 24	0 → <i>h</i> → 18 –19 → <i>k</i> → 19 –11 → <i>l</i> → 11	0 → <i>h</i> → 19 0 → <i>k</i> → 10 –19 → <i>l</i> → 0
Intensity decay (%)	8.2	2.5	Negligible	1.7	0.7	Negligible

Table 1 (cont.)

	(1)-Cl	(1)-CN	(1)-CN.0.5 <i>p</i> -xylene	(1)-CN.0.35xylene	(1)-OMe	(2 <i>b</i>)-Cl
Refinement						
Refinement on	<i>F</i>	<i>F</i>	<i>F</i>	<i>F</i>	<i>F</i>	<i>F</i>
<i>R</i>	0.040	0.035	0.055	0.067	0.076	0.027‡
<i>wR</i>	0.050	0.038	0.043	0.085	0.077	0.037
<i>S</i>	2.55	2.08	1.91	4.50	4.88	2.79
No. of reflections used in refinement	2689	2348	2888	4451	4156	1882
No. of parameters used	292	254	578	570	506	235
Data/parameters	9.2	9.2	5.0	7.8	8.2	8.0
H-atom treatment	Refined	Fixed	Fixed	Fixed	Fixed	Fixed
Weighting scheme	$w = 1/\sigma^2(F)$	$w = 1/\sigma^2(F)$	$w = 1/\sigma^2(F)$	$w = 1/\sigma^2(F)$	$w = 1/\sigma^2(F)$	$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max}$	0.02	0.001	0.09	0.03	0.0001	0.04
$\Delta\rho_{\max}$ (e Å ⁻³)	0.19	0.12	0.27	0.45	0.36	0.18
$\Delta\rho_{\min}$ (e Å ⁻³)	-0.26	-0.11	-0.24	-0.28	-0.31	-0.24
Extinction method	TEXSAN	TEXSAN	TEXSAN	TEXSAN	TEXSAN	TEXSAN
Extinction coefficient	3.4×10^{-6}	2.2×10^{-6}	0.037×10^{-6}	0.63×10^{-6}	0.11×10^{-6}	7.8×10^{-6}
<i>p</i> factor§	0.01	0.01	0.01	0.01	0.00	0.01
Source of atomic scattering factors						

International Tables for X-ray Crystallography (1974, Vol. IV)

* Up to eight rescans for reflections with $I < 40\sigma(I)$. † Essentially $> 1\sigma(I)$, since a prescan cut-off of $1\sigma(I)$ results in very few reflections between 1 and $3\sigma(I)$. ‡ Refinement of the other polarity resulted in significantly higher *R* and *wR* values (ratios 1.19 and 1.22). § $\sigma^2(I) = S + 4(B_1 + B_2) + (pI)^2$, where *S* = scan, *B*₁, *B*₂ = background counts.

3. Discussion

Final positional parameters are given in Table 2, selected molecular parameters in Table 3 and other data have been deposited.*

All the dibenzobarrelene molecules have geometries and dimensions (Fig. 1 and Table 3) similar to those of related materials (Pokkuluri *et al.*, 1993*a,b*). The external angles at the ring junctions are increased to *ca* 127° (Table 3) as a result of ring junction strain. The angles adjacent to and remote from the *X* substituents do not differ in value, except perhaps for the Cl derivative, where the C—C—C junction angle adjacent to Cl is enlarged to 128.2(2)° compared with 126.0(2)° for the remote angle; the C(junction)—C(1)—Cl angle is also marginally larger [120.5(2)°] than the C(2)—C(1)—Cl angle [119.2(2)°]. The two CO₂Me groups in each dibenzobarrelene diester molecule exhibit different amounts of conjugation with the C(11)=C(12) double bond; this is presumably due to intermolecular interactions, since the 1,5-disubstituted dibenzobarrelene ring skeleton has *C*₂ symmetry. The C=C—C=O torsion angles (φ , Table 3) indicate that one group is almost fully conjugated and the other non-conjugated; the $\cos^2 \varphi$ values (a measure of the amount of conjugation) suggest 73–100% conjugation for one group and 3–19% for the other in (1)-Cl, (1)-CN (non-solvated) and (1)-OMe. For the two solvated crystals, the differences are less extreme: 46–54 and 33–48%. The differences in the individual values of the corresponding C—CO₂Me bond distances

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*
$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
(1)-Cl				
Cl(1)	0.77215 (8)	0.2667 (1)	0.43411 (3)	5.97 (4)
Cl(2)	0.0277 (1)	0.8871 (1)	0.42092 (3)	6.97 (4)
O(1)	0.3473 (3)	0.4258 (2)	0.26058 (6)	5.8 (1)
O(2)	0.4613 (3)	0.2049 (2)	0.29357 (7)	5.9 (1)
O(3)	0.0279 (2)	0.2946 (3)	0.29564 (7)	6.2 (1)
O(4)	-0.1127 (2)	0.4980 (3)	0.32900 (7)	5.7 (1)
C(1)	0.5585 (3)	0.3023 (3)	0.44924 (9)	4.3 (1)
C(2)	0.5016 (4)	0.2409 (4)	0.4906 (1)	5.4 (1)
C(3)	0.3337 (5)	0.2685 (4)	0.5031 (1)	5.7 (2)
C(4)	0.2195 (4)	0.3605 (4)	0.47534 (9)	4.6 (1)
C(4a)	0.2775 (3)	0.4216 (3)	0.43440 (8)	3.6 (1)
C(5)	0.2339 (3)	0.8409 (3)	0.40211 (8)	4.3 (1)
C(6)	0.3494 (4)	0.9667 (3)	0.3944 (1)	5.0 (1)
C(7)	0.5124 (4)	0.9331 (4)	0.3794 (1)	5.2 (1)
C(8)	0.5664 (3)	0.7730 (3)	0.37213 (9)	4.3 (1)
C(8a)	0.4494 (3)	0.6492 (3)	0.37998 (7)	3.4 (1)
C(9)	0.4844 (3)	0.4682 (3)	0.37420 (8)	3.5 (1)
C(9a)	0.4467 (3)	0.3918 (3)	0.42056 (7)	3.4 (1)
C(10)	0.1735 (3)	0.5268 (3)	0.39995 (8)	3.5 (1)
C(10a)	0.2821 (3)	0.6806 (3)	0.39454 (7)	3.5 (1)
C(11)	0.3394 (3)	0.4092 (3)	0.34016 (7)	3.28 (9)
C(12)	0.1791 (3)	0.4402 (3)	0.35369 (7)	3.37 (9)
C(13)	0.3885 (3)	0.3318 (3)	0.29604 (8)	3.7 (1)
C(14)	0.3771 (9)	0.3592 (8)	0.2151 (1)	8.1 (3)
C(15)	0.0144 (3)	0.4151 (3)	0.32554 (8)	4.0 (1)
C(16)	-0.1157 (5)	0.2799 (9)	0.2611 (2)	8.9 (3)
(1)-CN				
O(1)	0.4415 (2)	0.21845 (5)	-0.0712 (2)	5.65 (7)
O(2)	0.6129 (2)	0.17026 (5)	0.1000 (2)	5.27 (7)
O(3)	0.1276 (2)	0.25284 (5)	0.0444 (2)	6.53 (8)
O(4)	0.0027 (2)	0.22436 (6)	-0.1867 (2)	7.8 (1)
N(1)	0.6401 (3)	0.05264 (9)	0.4335 (2)	7.3 (1)
N(2)	-0.4110 (3)	0.09459 (9)	-0.1885 (2)	7.5 (1)
C(1)	0.3304 (2)	0.08637 (7)	0.3855 (2)	4.02 (8)
C(2)	0.2386 (3)	0.08957 (8)	0.5069 (2)	4.9 (1)
C(3)	0.0719 (3)	0.10673 (8)	0.4771 (2)	5.0 (1)
C(4)	-0.0091 (2)	0.12168 (7)	0.3285 (2)	4.24 (8)
C(4a)	0.0823 (2)	0.11936 (6)	0.2097 (2)	3.46 (7)
C(5)	-0.0956 (2)	0.06434 (7)	-0.1545 (2)	4.12 (8)

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete geometry and NMR data, and molecular and packing diagrams have been deposited with the IUCr (Reference: FG0003). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2 (cont.)

	x	y	z	B_{eq}
C(6)	-0.0561 (3)	0.02267 (8)	-0.2312 (2)	5.1 (1)
C(7)	0.1124 (3)	0.00620 (7)	-0.2057 (2)	5.2 (1)
C(8)	0.2439 (3)	0.02996 (7)	-0.1026 (2)	4.47 (9)
C(8a)	0.2048 (2)	0.07106 (7)	-0.0270 (2)	3.71 (8)
C(9)	0.3299 (2)	0.10134 (6)	0.0917 (2)	3.61 (7)
C(9a)	0.2522 (2)	0.10174 (6)	0.2372 (2)	3.49 (7)
C(10)	0.0166 (2)	0.13397 (6)	0.0397 (2)	3.59 (7)
C(10a)	0.0353 (2)	0.08866 (6)	-0.0540 (2)	3.65 (8)
C(11)	0.3123 (2)	0.15339 (6)	0.0314 (2)	3.59 (7)
C(12)	0.1498 (2)	0.17023 (6)	0.0027 (2)	3.59 (7)
C(13)	0.4722 (3)	0.18078 (7)	0.0241 (2)	4.06 (8)
C(14)	0.5885 (4)	0.2503 (1)	-0.0715 (3)	7.7 (1)
C(15)	0.0870 (3)	0.21852 (7)	-0.0598 (2)	4.26 (9)
C(16)	0.0743 (5)	0.30180 (9)	-0.0035 (4)	9.5 (2)
C(17)	0.5051 (3)	0.06731 (8)	0.4134 (2)	4.8 (1)
C(18)	-0.2735 (3)	0.08136 (9)	-0.1759 (2)	5.1 (1)
(1)-CN.0.5p-xylene				
O(1)	0.3714 (3)	0.0609 (3)	0.5656 (2)	5.4 (2)
O(2)	0.2992 (3)	0.1654 (3)	0.6128 (2)	5.8 (2)
O(3)	0.5312 (3)	0.1613 (3)	0.5738 (2)	5.5 (2)
O(4)	0.6265 (3)	0.0469 (3)	0.6204 (2)	6.6 (2)
N(1)	0.2704 (4)	0.2566 (4)	0.8202 (3)	7.6 (3)
N(2)	0.7895 (3)	-0.0467 (4)	0.8241 (3)	6.6 (3)
C(1)	0.4343 (4)	0.2636 (4)	0.8120 (3)	3.6 (3)
C(2)	0.4895 (4)	0.3386 (4)	0.8398 (3)	4.1 (3)
C(3)	0.5781 (4)	0.3386 (4)	0.8396 (3)	4.3 (3)
C(4)	0.6157 (4)	0.2651 (4)	0.8135 (3)	3.8 (3)
C(4a)	0.5617 (4)	0.1919 (3)	0.7850 (2)	2.9 (2)
C(5)	0.6208 (4)	-0.0464 (4)	0.8201 (2)	3.2 (3)
C(6)	0.5850 (4)	-0.1186 (4)	0.8500 (3)	4.1 (3)
C(7)	0.4946 (4)	-0.1188 (4)	0.8475 (3)	4.2 (3)
C(8)	0.4378 (4)	-0.0484 (4)	0.8158 (3)	3.8 (3)
C(8a)	0.4723 (4)	0.0222 (3)	0.7863 (2)	3.1 (2)
C(9)	0.4216 (3)	0.1054 (4)	0.7483 (3)	3.2 (2)
C(9a)	0.4701 (4)	0.1907 (4)	0.7837 (3)	3.1 (3)
C(10)	0.5896 (3)	0.1075 (4)	0.7516 (3)	3.2 (2)
C(10a)	0.5637 (4)	0.0243 (3)	0.7879 (2)	3.0 (2)
C(11)	0.4386 (4)	0.1049 (3)	0.6778 (3)	3.5 (3)
C(12)	0.5265 (4)	0.1050 (3)	0.6799 (3)	3.3 (2)
C(13)	0.3612 (4)	0.1139 (4)	0.6158 (3)	4.1 (3)
C(14)	0.3112 (4)	0.0823 (5)	0.4990 (3)	7.9 (4)
C(15)	0.5669 (4)	0.1002 (4)	0.6219 (3)	4.1 (3)
C(16)	0.5662 (5)	0.1586 (5)	0.5145 (3)	9.2 (5)
C(17)	0.3418 (5)	0.2601 (4)	0.8145 (3)	4.8 (3)
C(18)	0.7159 (4)	-0.0465 (4)	0.8217 (3)	4.2 (3)
O(1')	0.1060 (3)	0.3160 (3)	0.4319 (2)	5.4 (2)
O(2')	0.1733 (3)	0.4383 (3)	0.4013 (2)	6.7 (2)
O(3')	-0.0553 (2)	0.4200 (3)	0.4260 (2)	5.1 (2)
O(4')	-0.1612 (3)	0.3246 (3)	0.3654 (2)	6.9 (3)
N(1')	0.2291 (3)	0.5357 (4)	0.2000 (3)	6.9 (3)
N(2')	-0.2974 (3)	0.2306 (4)	0.1641 (3)	6.9 (3)
C(1')	0.0586 (4)	0.5364 (4)	0.1913 (3)	3.7 (3)
C(2')	0.0035 (4)	0.6076 (4)	0.1571 (3)	4.3 (3)
C(3')	-0.0881 (4)	0.6068 (4)	0.1504 (3)	4.3 (3)
C(4')	-0.1275 (4)	0.5352 (4)	0.1774 (3)	3.8 (3)
C(4a')	-0.0734 (4)	0.4649 (4)	0.2109 (3)	3.1 (3)
C(5')	-0.1258 (4)	0.2246 (4)	0.1776 (3)	3.4 (3)
C(6')	-0.0848 (4)	0.1522 (4)	0.1520 (3)	4.0 (3)
C(7')	0.0068 (4)	0.1521 (4)	0.1609 (3)	4.4 (3)
C(8')	0.0598 (3)	0.2251 (4)	0.1927 (3)	3.8 (3)
C(8a')	0.0203 (4)	0.2970 (4)	0.2186 (2)	3.1 (2)
C(9')	0.0676 (3)	0.3805 (4)	0.2577 (3)	3.3 (2)
C(9a')	0.0202 (4)	0.4651 (4)	0.2190 (2)	3.2 (3)
C(10')	-0.1045 (3)	0.3803 (4)	0.2428 (3)	3.2 (2)
C(10a')	-0.0724 (4)	0.2971 (4)	0.2103 (3)	3.1 (3)
C(11')	0.0413 (4)	0.3793 (3)	0.3247 (3)	3.5 (3)
C(12')	-0.0475 (4)	0.3800 (3)	0.3168 (3)	3.5 (3)
C(13')	0.1144 (4)	0.3827 (4)	0.3894 (3)	4.2 (3)
C(14')	0.1716 (5)	0.3170 (5)	0.4981 (3)	8.5 (4)
C(15')	-0.0947 (5)	0.3713 (4)	0.3708 (3)	4.3 (3)
C(16')	-0.0961 (5)	0.4106 (5)	0.4819 (3)	9.2 (5)
C(17')	0.1545 (4)	0.5371 (4)	0.1968 (3)	4.6 (3)
C(18')	-0.2223 (4)	0.2269 (4)	0.1698 (3)	4.2 (3)

Table 2 (cont.)

	x	y	z	B_{eq}
C(19)	0.571 (1)	0.0463 (9)	0.9913 (5)	8.2 (6)
C(20)	0.486 (1)	0.0765 (8)	0.9645 (4)	10.5 (6)
C(21)	0.4086 (8)	0.042 (1)	0.9676 (6)	13 (1)
C(22)	0.6565 (7)	0.0909 (8)	0.9852 (5)	14.0 (7)
C(23)	0.046 (2)	0.558 (2)	-0.006 (1)	19 (2)
C(24)	-0.010 (2)	0.620 (1)	-0.0420 (9)	22 (2)
C(25)	-0.075 (1)	0.522 (2)	-0.0309 (6)	10.6 (9)
C(26)	0.148 (1)	0.617 (1)	0.0047 (7)	25 (2)
(1)-CN.xylene				
O(1)	0.7589 (3)	0.4067 (4)	0.9334 (2)	6.3 (2)
O(2)	0.6486 (4)	0.3021 (4)	0.8854 (3)	7.4 (3)
O(3)	0.9782 (3)	0.4114 (3)	0.8745 (2)	6.0 (2)
O(4)	0.9278 (3)	0.3010 (3)	0.9307 (2)	6.4 (2)
O(5)	0.1436 (3)	0.4181 (3)	0.5644 (2)	5.3 (2)
O(6)	0.0681 (3)	0.3005 (3)	0.5962 (2)	6.9 (2)
O(7)	0.3117 (3)	0.3188 (3)	0.5796 (2)	5.0 (2)
O(8)	0.4123 (3)	0.4224 (4)	0.6443 (2)	6.7 (2)
N(1)	0.9805 (4)	0.4996 (4)	0.6750 (3)	6.6 (3)
N(2)	0.4608 (4)	0.1963 (4)	0.6912 (3)	6.9 (3)
N(3)	0.0222 (4)	0.2094 (4)	0.8012 (3)	6.7 (3)
N(4)	0.5582 (4)	0.5124 (4)	0.8456 (3)	7.3 (3)
C(1)	0.6330 (4)	0.5144 (4)	0.6871 (3)	4.1 (3)
C(2)	0.6666 (4)	0.5867 (4)	0.6567 (3)	4.6 (3)
C(3)	0.7549 (4)	0.5842 (4)	0.6535 (3)	4.4 (3)
C(4)	0.8131 (4)	0.5093 (4)	0.6818 (3)	3.5 (2)
C(4a)	0.7809 (3)	0.4387 (4)	0.7126 (3)	3.1 (2)
C(5)	0.8062 (4)	0.1985 (4)	0.6781 (3)	3.9 (3)
C(6)	0.7449 (4)	0.1274 (4)	0.6483 (3)	4.4 (3)
C(7)	0.6572 (4)	0.1278 (4)	0.6516 (3)	4.5 (3)
C(8)	0.6269 (4)	0.2001 (4)	0.6837 (3)	3.8 (2)
C(8a)	0.6868 (4)	0.2723 (4)	0.7136 (3)	3.2 (2)
C(9)	0.6677 (3)	0.3563 (4)	0.7507 (3)	3.6 (2)
C(9a)	0.6904 (4)	0.4412 (4)	0.7149 (3)	3.3 (2)
C(10)	0.8347 (3)	0.3534 (4)	0.7469 (3)	3.2 (2)
C(10a)	0.7769 (4)	0.2702 (4)	0.7105 (3)	3.3 (2)
C(11)	0.7420 (4)	0.3554 (4)	0.8219 (3)	3.8 (2)
C(12)	0.8282 (4)	0.3536 (4)	0.8200 (3)	3.5 (2)
C(13)	0.7140 (5)	0.3531 (6)	0.8836 (4)	5.8 (4)
C(14)	0.9152 (4)	0.3504 (4)	0.8821 (3)	4.3 (3)
C(15a)	0.727 (1)	0.4037 (8)	0.9923 (5)	8.0 (7)
C(15b)	0.625 (2)	0.336 (2)	0.950 (1)	7 (2)
C(16)	1.0678 (5)	0.4125 (7)	0.9312 (4)	10.0 (5)
C(17)	0.9086 (4)	0.5052 (4)	0.6782 (3)	4.1 (3)
C(18)	0.5324 (4)	0.1983 (4)	0.6882 (3)	4.6 (3)
C(21)	0.1930 (4)	0.2027 (4)	0.8094 (3)	3.4 (2)
C(22)	0.2500 (4)	0.1286 (4)	0.8436 (3)	3.9 (3)
C(23)	0.3437 (4)	0.1284 (4)	0.8515 (3)	4.1 (3)
C(24)	0.3835 (3)	0.2008 (4)	0.8269 (3)	3.4 (2)
C(24a)	0.3286 (3)	0.2733 (4)	0.7933 (3)	3.0 (2)
C(25)	0.3841 (4)	0.5147 (4)	0.8282 (3)	3.5 (2)
C(26)	0.3443 (4)	0.5888 (4)	0.8524 (3)	4.3 (3)
C(27)	0.2487 (4)	0.5893 (4)	0.8399 (3)	4.5 (3)
C(28)	0.1923 (4)	0.5164 (4)	0.8057 (3)	3.8 (2)
C(28a)	0.2322 (3)	0.4429 (4)	0.7829 (3)	2.9 (2)
C(29)	0.1828 (3)	0.3588 (4)	0.7435 (2)	3.2 (2)
C(29a)	0.2322 (3)	0.2743 (4)	0.7828 (3)	3.0 (2)
C(30)	0.3590 (3)	0.3580 (4)	0.7621 (2)	3.1 (2)
C(30a)	0.3282 (3)	0.4419 (4)	0.7939 (3)	2.9 (2)
C(31)	0.2076 (4)	0.3602 (4)	0.6771 (3)	3.4 (2)
C(32)	0.3001 (4)	0.3605 (4)	0.6872 (3)	3.3 (2)
C(33)	0.1311 (4)	0.3555 (4)	0.6084 (3)	4.2 (2)
C(34)	0.3479 (4)	0.3709 (4)	0.6349 (3)	4.2 (3)
C(35)	0.0803 (6)	0.4097 (6)	0.4938 (4)	8.8 (4)
C(36)	0.3568 (5)	0.3295 (6)	0.5271 (4)	8.2 (5)
C(37)	0.0952 (4)	0.2054 (4)	0.8034 (3)	4.2 (3)
C(38)	0.4826 (4)	0.5146 (4)	0.8380 (3)	4.4 (3)
(1)-Ome				
O(1)	0.7868 (3)	0.3428 (3)	0.6212 (5)	7.4 (3)
O(2)	0.7178 (4)	0.3195 (6)	0.8151 (6)	16.7 (6)
O(3)	0.8190 (3)	0.1420 (3)	0.5299 (6)	8.2 (3)
O(4)	0.7556 (3)	0.0394 (4)	0.3608 (7)	9.4 (3)
O(5)	0.4163 (2)	0.3861 (3)	0.7806 (5)	5.1 (2)

Table 2 (cont.)

	x	y	z	B_{eq}
O(6)	0.5825 (3)	0.1274 (3)	0.0341 (5)	5.8 (2)
O(21)	-0.1323 (2)	0.3351 (3)	1.1120 (5)	6.3 (2)
O(22)	-0.0536 (3)	0.3334 (4)	1.3201 (5)	10.5 (3)
O(23)	-0.0959 (3)	0.1419 (3)	1.0532 (5)	6.6 (2)
O(24)	-0.0213 (3)	0.0534 (3)	0.8410 (6)	7.4 (3)
O(25)	0.1295 (2)	0.1540 (3)	0.5357 (4)	5.3 (2)
O(26)	0.2306 (2)	0.3950 (3)	1.2917 (4)	4.7 (2)
C(1)	0.4223 (3)	0.2985 (4)	0.6923 (7)	4.3 (3)
C(2)	0.3620 (4)	0.2354 (5)	0.6954 (8)	5.7 (3)
C(3)	0.3741 (4)	0.1467 (5)	0.5974 (9)	6.1 (4)
C(4)	0.4448 (4)	0.1179 (4)	0.4913 (7)	4.8 (3)
C(4a)	0.5063 (3)	0.1783 (4)	0.4854 (6)	3.8 (3)
C(5)	0.5707 (3)	0.2172 (4)	0.1192 (7)	4.3 (3)
C(6)	0.5548 (3)	0.2924 (5)	0.0556 (7)	5.0 (3)
C(7)	0.5442 (3)	0.3807 (5)	0.1530 (8)	5.0 (3)
C(8)	0.5491 (3)	0.3978 (4)	0.3141 (7)	4.3 (3)
C(8a)	0.5637 (3)	0.3229 (4)	0.3769 (6)	3.8 (3)
C(9)	0.5679 (3)	0.3260 (4)	0.5523 (6)	3.7 (2)
C(9a)	0.4961 (3)	0.2678 (4)	0.5808 (6)	4.1 (3)
C(10)	0.5883 (3)	0.1602 (4)	0.3718 (6)	3.8 (2)
C(10a)	0.5745 (3)	0.2329 (4)	0.2806 (6)	3.7 (2)
C(11)	0.6593 (3)	0.2682 (4)	0.5661 (6)	4.0 (3)
C(12)	0.6703 (3)	0.1827 (4)	0.4721 (6)	4.1 (3)
C(13)	0.7235 (4)	0.3125 (5)	0.6840 (7)	6.1 (4)
C(14)	0.8578 (4)	0.3813 (5)	0.724 (1)	8.7 (5)
C(15)	0.7507 (4)	0.1157 (4)	0.4535 (8)	5.1 (3)
C(16)	0.9052 (4)	0.0841 (6)	0.496 (1)	9.0 (5)
C(17)	0.3457 (4)	0.4149 (5)	0.8980 (8)	6.9 (4)
C(18)	0.5817 (6)	0.1094 (5)	-0.1323 (8)	9.1 (5)
C(21)	0.0913 (3)	0.4190 (4)	0.8394 (7)	4.4 (3)
C(22)	0.0970 (4)	0.4082 (5)	0.6795 (8)	5.0 (3)
C(23)	0.1098 (4)	0.3235 (5)	0.5759 (7)	5.2 (3)
C(24)	0.1176 (3)	0.2428 (4)	0.6279 (6)	4.2 (3)
C(24a)	0.1116 (3)	0.2523 (4)	0.7893 (6)	3.7 (2)
C(25)	0.2741 (3)	0.1296 (4)	0.9875 (7)	4.4 (3)
C(26)	0.3379 (3)	0.1595 (4)	1.0971 (7)	5.0 (3)
C(27)	0.3262 (3)	0.2465 (5)	1.1988 (7)	4.7 (3)
C(28)	0.2487 (3)	0.3084 (4)	1.1974 (6)	3.8 (3)
C(28a)	0.1827 (3)	0.2791 (4)	1.0884 (4)	3.6 (2)
C(29)	0.0946 (3)	0.3354 (4)	1.0629 (6)	3.6 (2)
C(29a)	0.0983 (3)	0.3399 (4)	0.8918 (6)	3.8 (2)
C(30)	0.1182 (3)	0.1743 (4)	0.8712 (6)	3.7 (2)
C(30a)	0.1960 (3)	0.1918 (4)	0.9855 (6)	3.6 (2)
C(31)	0.0203 (3)	0.2762 (4)	1.0714 (6)	3.6 (2)
C(32)	0.0327 (3)	0.1931 (4)	0.9723 (6)	3.6 (2)
C(33)	-0.0582 (3)	0.3177 (4)	1.1850 (7)	4.8 (3)
C(34)	-0.2156 (4)	0.3639 (5)	1.2075 (8)	7.7 (4)
C(35)	-0.0294 (3)	0.1203 (4)	0.9465 (7)	4.3 (3)
C(36)	-0.1651 (5)	0.0805 (6)	1.027 (1)	9.4 (5)
C(37)	0.1393 (5)	0.1412 (5)	0.3701 (7)	8.0 (5)
C(38)	0.2939 (4)	0.4267 (5)	1.4074 (7)	6.7 (4)
(2b)-Cl				
Cl(1)	0.57318 (5)	0.73934 (9)	0.3358	4.81 (3)
Cl(2)	0.55317 (6)	0.0657 (1)	-0.00078 (8)	4.96 (3)
O(1)	0.6056 (2)	0.3921 (3)	0.4789 (1)	4.7 (1)
O(2)	0.7309 (1)	0.4818 (3)	0.4116 (2)	4.9 (1)
O(3)	0.7707 (1)	-0.0026 (3)	0.2749 (2)	4.58 (9)
O(4)	0.7333 (1)	0.0824 (3)	0.4122 (1)	4.9 (1)
C(1)	0.6014 (2)	0.6281 (3)	0.2410 (2)	3.5 (1)
C(2)	0.6102 (2)	0.7104 (4)	0.1601 (2)	4.6 (1)
C(3)	0.6293 (2)	0.6249 (4)	0.0827 (2)	4.6 (1)
C(4)	0.6405 (2)	0.4555 (3)	0.0844 (2)	3.6 (1)
C(4a)	0.6343 (1)	0.3745 (3)	0.1654 (2)	2.68 (8)
C(5)	0.4945 (2)	0.0850 (3)	0.0991 (2)	3.6 (1)
C(6)	0.4045 (2)	0.0403 (4)	0.1052 (3)	5.0 (1)
C(7)	0.3614 (2)	0.0528 (4)	0.1866 (3)	5.2 (2)
C(8)	0.4043 (2)	0.1091 (4)	0.2633 (2)	4.2 (1)
C(8a)	0.4950 (1)	0.1510 (3)	0.2563 (2)	3.05 (9)
C(9)	0.5591 (1)	0.1947 (3)	0.3287 (2)	2.92 (8)
C(9a)	0.6158 (1)	0.4602 (3)	0.2453 (2)	2.70 (8)
C(10)	0.6370 (1)	0.1917 (3)	0.1850 (2)	2.58 (8)
C(10a)	0.5402 (1)	0.1357 (3)	0.1751 (2)	2.93 (9)
C(11)	0.6194 (1)	0.3478 (3)	0.3237 (2)	2.76 (8)

Table 2 (cont.)

	x	y	z	B_{eq}
C(12)	0.6521 (1)	0.1822 (3)	0.2869 (2)	2.61 (8)
C(13)	0.6591 (2)	0.4134 (3)	0.4092 (2)	3.4 (1)
C(14)	0.6368 (4)	0.4549 (7)	0.5634 (3)	7.5 (2)
C(15)	0.7226 (1)	0.0847 (3)	0.3325 (2)	3.15 (9)
C(16)	0.8386 (3)	-0.1089 (7)	0.3135 (3)	7.8 (2)

* The crystallographic atom numbering is based on that for the dibenzobarrelene ring system, which is also used for (2b)-Cl (rather than the dibenzosemibullvalene chemical numbering). For structures with two molecules per asymmetric unit, the second molecule is numbered C(*n'*) or C(*n* + 20). The 1,5-substituents are bonded to either C(1)/C(5) or C(4)/C(8).

are generally not significant, but the mean values for all the molecules are 1.479 and 1.494 Å for the conjugated and non-conjugated bonds, respectively, in accordance with predicted values (Allen, 1981).

The molecular structures of the photoproducts were determined by X-ray analysis of (2b)-Cl (Fig. 1), which indicates an 8c,8d-dicarboxylate (dibenzosemibullvalene numbering system, Scheme 1). The structures of the other photoproducts could then be determined from ¹H NMR data for the 4b, 8b and 8d protons (Table 4). These resonances are singlets, with the H(4b) (in 2a-X and 2b-X) proton signals shifted downfield (higher δ) compared with (2a)-H (identical with 2b-H), as a result of the proximity of H(4b) to an electronegative X substituent; the H(4b) δ 's in (2b)-X are marginally larger than those in (2a)-X. The 8d protons (present in 2a-X only) also show significant shifts, since they are also in close proximity to the X substituents, while the 8b protons (present in 2b-X only and not adjacent to the X substituents) show only small shifts. Thus, in a mixture of photoproducts, two inner signals belong to (2a)-X and two outer signals to (2b)-X (Table 4 and deposited material). NOE (nuclear Overhauser effect) experiments give additional corroboration of the structural assignments. Irradiation on H(4b) (in 2a-X and 2b-X) or H(8b) (in 2b-X only) results in aromatic proton enhancement, since H(4b) and H(8b) are close to protons on adjacent aromatic rings. H(8d) (in 2a-X only) is close only to the X substituent, so no aromatic signal enhancement is observed.

The geometry and dimensions of (2b)-Cl (Fig. 1 and Table 3) are close to those in related compounds (Pokkuluri *et al.*, 1993a,b). The ring junction angles are further increased, to 129.5 (2)°, as a result of the additional strain introduced by the formation of the three-membered ring.

3.1. Photochemistry

All the 1,5-disubstituted dibenzobarrelenes undergo the di- π -methane reaction in solution and in the solid state. The accepted mechanism for the di- π -methane photochemical reaction in ethenoanthracenes involves initial vinyl-benzo carbon-carbon bond formation

(Zimmerman, 1991); in an asymmetrical reactant such as (1)-X, two pathways are possible (path *a* and path *b*), leading to two isomeric products, (2*a*) and (2*b*) (bridging on the left in Scheme II leads to the enantiomers of 2*a* and 2*b*). The ratios of the products (2*a*) and (2*b*) vary from 80:20 to 15:85 (Table 5). The exact ratios vary

with solvent (for 1-Cl, for example, the amount of 2*a*-Cl is *ca* 10% higher in non-polar solvents, *i.e.* more like the solid-state ratio) and solution/solid-state reactions show some differences in the ratios of the products. The preferred reaction pathway (path *a* or path *b*) is influenced by several factors.

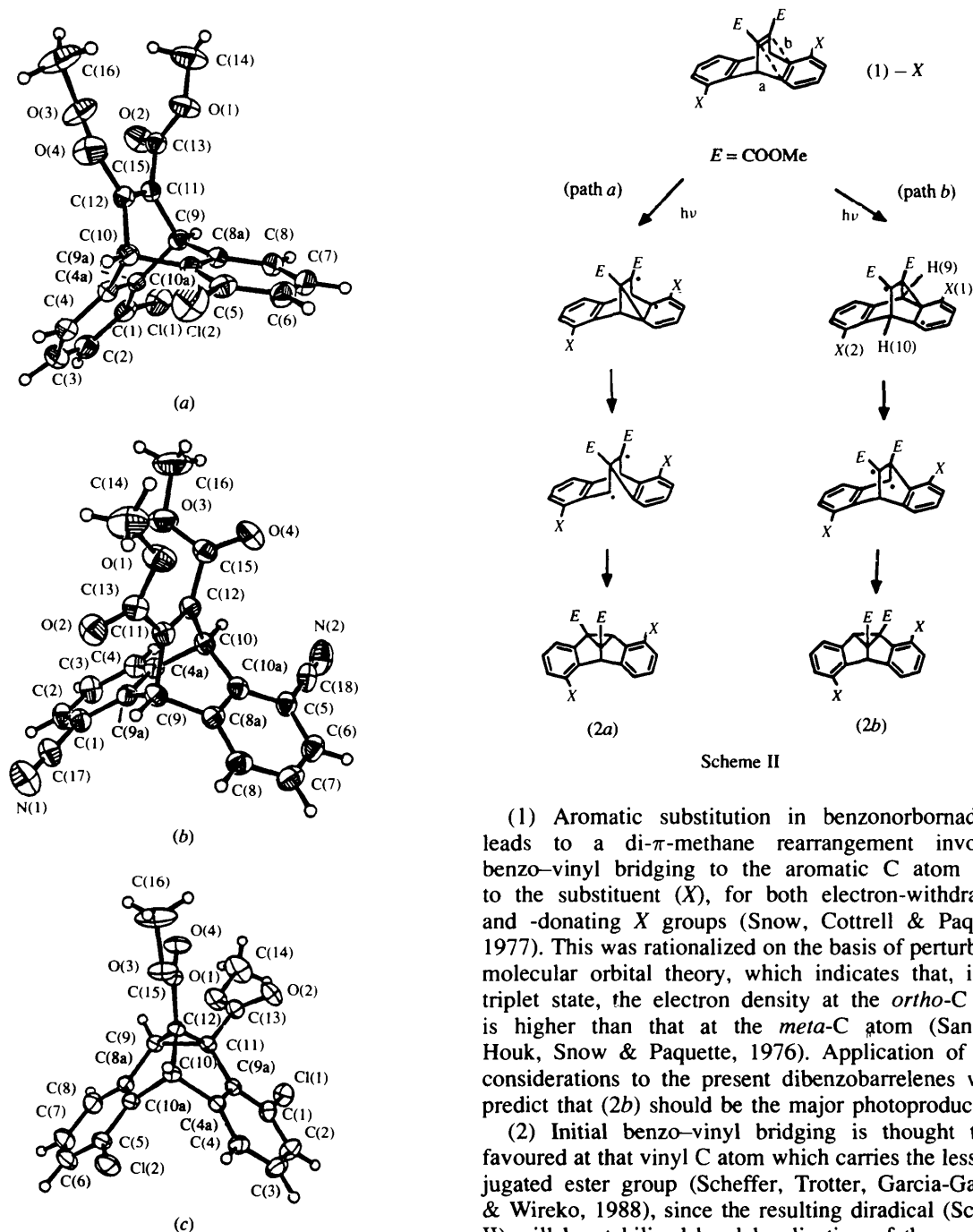


Fig. 1. Views of the molecules of (a) (1)-Cl, (b) (1)-CN (other derivatives are similar; views are in the supplementary material) and (c) (2*b*)-Cl; 33% thermal probability ellipsoids.

(1) Aromatic substitution in benzonorbornadienes leads to a di- π -methane rearrangement involving benzo-vinyl bridging to the aromatic C atom *ortho* to the substituent (X), for both electron-withdrawing and -donating X groups (Snow, Cottrell & Paquette, 1977). This was rationalized on the basis of perturbation molecular orbital theory, which indicates that, in the triplet state, the electron density at the *ortho*-C atom is higher than that at the *meta*-C atom (Santiago, Houk, Snow & Paquette, 1976). Application of these considerations to the present dibenzobarrelenes would predict that (2*b*) should be the major photoproduct.

(2) Initial benzo-vinyl bridging is thought to be favoured at that vinyl C atom which carries the less conjugated ester group (Scheffer, Trotter, Garcia-Garibay & Wireko, 1988), since the resulting diradical (Scheme II) will be stabilized by delocalization of the unpaired electron on the vinyl C atom over the more conjugated group. However, since bridging on the two sides of the

Table 3. Selected bond lengths (Å) and angles (°); mean values where appropriate (with individual *e.s.d.*'s)

	(1)-Cl	Unsolvated	(1)-CN -0.5xylenc	-xxylene	(1)-OMe	(2b)-Cl
C(11)=C(12)	1.331 (3)	1.334 (3)	1.332 (7)	1.336 (8)	1.329 (7)	[1.520 (3)]
C—Cl	1.739 (3)					1.734 (3)
C—CN		1.448 (3)	1.443 (7)	1.46 (1)		
C≡N		1.120 (3)	1.126 (6)	1.11 (1)		
C(ar)—OMe					1.357 (7)	
C(ar)O—Me					1.422 (7)	
C=O	1.192 (3)	1.193 (2)	1.197 (6)	1.21 (1)	1.173 (7)	1.204 (3)
OC—OMe	1.320 (3)	1.316 (2)	1.327 (6)	1.32 (1)	1.295 (7)	1.323 (3)
OCO—Me	1.459 (4)	1.452 (2)	1.452 (6)	1.46 (1)	1.454 (7)	1.444 (4)
C—C (ring junction, external)	126.0 (2) 128.2 (2)	127.0 (2)	127.2 (5)	127.2 (5)	126.4 (5)	129.5 (2)
Conjugated CO ₂ Me						
C=C—C=O	-148.5 (3)	152.9 (2)	-132.9 (7)	-135.6 (7)	-177.9 (7)	
(φ)*			-137.4 (7)	133.6 (6)	168.2 (6)	
cos ² φ	0.73	0.79	0.46, 0.54	0.51, 0.48	1.00, 0.96	
C—CO ₂ Me	1.490 (3)	1.480 (3)	1.490 (7)	1.46 (1)	1.449 (8)	
			1.479 (7)	1.49 (1)	1.497 (8)	
Non-conjugated CO ₂ Me						
C=C—C=O	-116.0 (3)	109.2 (3)	-130.9 (7)	46 (1)	-99.3 (9)	
(φ)*			-125.3 (7)	129.4 (7)	111.3 (8)	
cos ² φ	0.19	0.11	0.43, 0.33	0.48, 0.40	0.03, 0.13	
C—CO ₂ Me	1.493 (3)	1.486 (3)	1.479 (7)	1.504 (7)	1.495 (8)	
			1.485 (7)	1.504 (7)	1.504 (7)	

* Signs of the torsion angles are for the parameters in Table 2 and have no absolute significance, since the materials are all racemic.

Table 4. ¹H NMR chemical shifts, δ (ppm)

X	H	Cl	CN	OMe	
(2b)-X	4b	5.03	5.32	5.45	5.23
(2a)-X	4b	5.03	5.28	5.40	5.18
(2a)-X	8d	4.49	4.66	4.81	4.61
(2b)-X	8b	4.49	4.51	4.70	4.40

Table 5. Ratios of photoproducts (%)

	Solution		Solid state	
	% (2a)	% (2b)	% (2a)	% (2b)
(1)-Cl	70	30	80	20
(1)-CN	20	80	30	70
(1)-OMe	15	85	55	45

1,5-disubstituted dibenzobarrelenes produces different photoproducts, (2a) and (2b) [e.g. C(12)···C(4a) and C(12)···C(10a) in Fig. 1], the CO₂Me dihedral angles cannot predict a preference for one type of product.

(3) The stability of the proposed diradicals can also be increased by delocalization of the unpaired electron on the benzo C atom onto the C atom to which X is bonded and hence onto the X substituent. This is possible only for the diradical in path (b) and because such species have been shown to have electron-rich radical centres (Zimmerman, 1991), will lead to increased stability only for electron-withdrawing substituents. Hence, product (2b) is favoured for (1)-CN, less so for (1)-Cl and disfavoured for the electron-donating OMe derivative.

(4) In the 1,5-disubstituted dibenzobarrelenes moderately severe non-bonded repulsions occur between the

X substituents and neighbouring bridgehead H atoms, with X···H distances *ca* 0.2 Å shorter than the sums of the van der Waals radii (Table 6). Previous studies have indicated that relief of such steric repulsions *via* specific reaction pathways leads to sterically favoured photoproducts (Chen, Pokkuluri, Scheffer & Trotter, 1990; Jones, Scheffer, Trotter & Yap, 1993). Molecular models suggest that benzo-vinyl bridging [as shown in Scheme II; C(12)···H(4a) and C(11)···H(9a) in Fig. 1] leads to even shorter X(2)···H(10) distances for both paths (a) and (b), and to longer X(1)···H(9) distances, especially for path (a). More quantitative estimates of the changes in X···H distances were obtained by MMX calculations (PC Model, 1988; Table 6). The MMX results reproduce the measured distances in the (1)-X molecules well (to within a few hundredths of an Å), but are probably only roughly correct for the diradicals, since experimental data for carbon radicals are not available. The detailed results reinforce the qualitative indications, with increases in X···H(9) (path a) to greater than van der Waals distances for X = Cl, OMe, and to just below the van der Waals distance for X = CN (Table 6), thus relieving the steric strain; the X···H distances in path (b) all remain shorter than van der Waals, with X···H(9) in (2b) about 0.1 Å shorter than in (2a).

The predictions of these four types of effect are therefore somewhat conflicting (Table 7). For (1)-Cl the favoured reaction pathway (path a, which produces the observed major photoproduct) seems to be controlled by the intramolecular steric repulsions involving the Cl substituent. The small distortions in the exocyclic bond angles noted above for (1)-Cl are additional evidence for this steric strain. For (1)-CN the electronic effect of

Table 6. *Intramolecular X...H non-bonded distances (Å)*

X	Reactant mol. mean		Diradical a		Diradical b		van der Waals
	X...H(9)/H(10)	X...H(9)	X...H(10)	X...H(9)	X...H(10)		
Cl	2.78	2.99*	2.70	2.88	2.73	2.95	
C(N)	2.66	2.84*	2.55	2.74	2.59	2.90	
-O(Me)	2.56	2.75*	2.44	2.65	2.48	2.72	

* Greater than van der Waals for Cl and OMe.

Table 7. *Predicted and observed major photoproducts*

	Perturbation by X substituent	Favoured photoproduct			Observed major photoproduct	
		CO ₂ Me conjugation	X conjugation	Intramolecular steric effects	Solution	Solid state
(1)-Cl	b	a/b	b	a*	a (70%)	a (80%)
(1)-CN	b*	a/b	b*	a	b (80%)	b (70%)
(1)-OMe	b	a/b	a	a	b (85%)	a (55%)

* Apparent dominant effects.

the strongly electron-withdrawing CN substituent seems to be dominant, producing the electronically favoured (*b*)-type photoproduct. (1)-OMe appears to represent a balance between steric interactions and two (conflicting) electronic effects. Intermolecular steric effects (Garcia-Garibay, Scheffer, Trotter & Wireko, 1990*a,b*) do not seem to be important, since the product ratios for (1)-Cl and (1)-CN are rather similar in solution and in the solid state, and the amounts of products are almost equal for (1)-OMe in the solid state. The final conclusion is that no one effect seems to dominate.

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