hydroxyl groups of adjacent molecules related by a twofold axis; the $O(3)\cdots O(3)$ $(1 - x, y, 1 - z)$ spacing is 2·853 (3) Å. Although the hydroxyl H-atom site was not located, it can be presumed that the oxygen acts both as a donor and an acceptor in this inter-action which results in a four-atom dimer ring con-taining two oxygens and their protons. The dimers are linked by hydrogen bonds between the C(25) hydroxyl substituent and O(3) into double layers parallel to the ab crystal plane; the $O(25)\cdots O(3)$ $(-\frac{1}{2} + x, -\frac{1}{2} + y, z)$ spacing is 2·896 (5) Å. These layers are held together in the crystal by van der Waals interactions. All other intermolecular contacts are normal.

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Crystal Structure and Photochemistry of a Methyl Phenyl Diester Derivative of Dibenzobarrelene*

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Abstract. Methyl phenyl dibenzobarrelene-2,3-dicarboxylate, $C_{25}H_{18}O_4$, $M_r = 382·42$, monoclinic, $P2_1/c$, $a = 11·557$ (1), $b = 9·170$ (1), $c = 18·714$ (1) Å, $\beta = 93·20$ (1)°, $V = 1980$ (1) Å^3, $Z = 4$, $D_x = 1·282$ g cm^{-3}, Cu $K\alpha_1$, $\lambda = 1·54056$ Å, $\mu = 6·64$ cm^{-1}, $F(000) = 800$, $T = 295$ K, $R = 0·046$ for 2535 reflections with $I \geq 3\sigma(I)$. The two ester car-bonyl groups show different degrees of conjugation to the central double bond, with the relevant bond lengths indicating some extent of electron deloca-lization over the α,β-unsaturated carbonyl system. The length of the bridging double bond [C11=C12, 1·336 (3) Å] is virtually the same as in the methyl isopropyl diester [1·334 (4) Å] and in agreement with that of the dicarbonitrile [1·343 (5) Å] derivatives of dibenzobarrelene. The aromatic ring of the phenoxy-carbonyl group is rotated 60° out of its carbonyl plane; the O—C(Ph) bond in the phenyl ester [1·407 (3) Å] is significantly shorter than the corre-sponding O—C(Me) [1·443 (3) Å]. Two regioisomeric photoproducts are obtained upon photolysis, with identical product ratios in the solid state and in solution. Analysis of the photochemical pathways from crystal-structure and molecular-conformational points of view leads to the same predicted major product, which is consistent with the experimental results.

Introduction. Crystal and photochemical studies (Scheffer, Trotter, Garcia-Garibay & Wireko, 1988; Garcia-Garibay, Scheffer, Trotter & Wireko, 1990*a,b*) of dibenzobarrelene derivatives have given detailed structural information on the pathways of the di-π-methane rearrangement in the solid state. In the case of dibenzobarrelenes substituted at C11 and

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* Methyl phenyl 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate.

C12 by two non-equivalent ester groups, two regio-isomeric dibenzosemibullvalene products are possible, in both solid-state and solution photolyses (Fig. 1), with higher regioselectivities generally observed in the solid state than in solution. Predicted reaction pathways from electronic and steric considerations are sometimes contrary to one another. In the case of the methyl isopropyl diester derivative (Garcia-Garibay et al., 1990a), the pathway leading to the formation of the major product was different from the predicted pathway based on an odd-electron stabilization mechanism (Zimmerman, 1980; Hixson, Mariano & Zimmerman, 1973; Zimmerman, Keck & Pflederer, 1976). The observed major product was, however, consistent with steric packing factors estimated from (a) qualitative visual inspection of the local packing differences around the ester groups, (b) calculation of the van der Waals inter-molecular steric energy as a result of the movement of the ester groups and (c) superposition of the structures of major and minor products on the structure of the starting material in order to determine the best molecular fit.

In the present study, the substituents on the ester groups are electronically very different (Me versus Ph). Consequent changes in photochemical regioselectivity are examined and rationalized from electronic and steric arguments.

Experimental. The compound (Me/Ph) was crystallized from methylcyclohexane:chloroform solvent mixture, cut fragment of approximate dimensions $0.3 \times 0.2 \times 0.2$ mm; CAD-4F diffractometer, filtered Cu $K\alpha$ radiation; lattice parameters from 25 reflections with $35 \le \theta \le 49°$. Intensities for $\theta \le 75°$, hkl: 0 to 14, 0 to 11, -23 to 23; $\omega-2\theta$ scan, ω-scan width

(1)

hν ↓

(2)   (2')
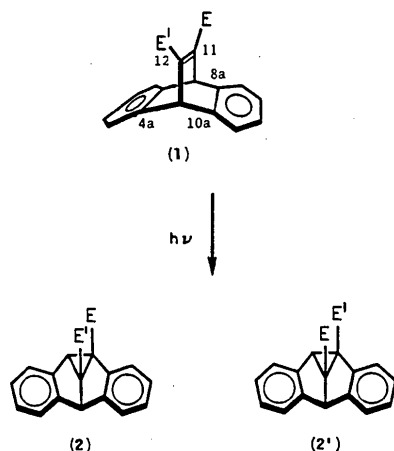
Fig. 1. Di-π-methane rearrangement in the dibenzobarrelenes. For the present Me/Ph derivative (1), $E = CO_2Me$, $E' = CO_2Ph$ and the ratio of the amounts of photoproducts (2):(2') (both racemic) is 70:30 in both solid-state and solution photolysis.

$(0.55 + 0.14\tan\theta)°$ at $1-10°$ min^{-1}, extended 25% on each side for background measurement, horizontal aperture $(2.0 + \tan\theta)$mm, vertical aperture 4 mm; three standard reflections measured every 60 min (no decay). Lp but no absorption corrections; 4069 unique reflections measured, 2535 (62.3%) with $I \ge 3\sigma(I)$, where $\sigma^2(I) = S + 4(B_1 + B_2) + (0.04S)^2$, $S =$ scan, B_1 and B_2 background counts. Structure solved by direct methods using MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), refined by full-matrix least-squares methods on F, minimizing $\Sigma w(|F_o| - k|F_c|)^2$, $w = 1/\sigma^2(F)$ giving uniform values of $\Sigma w\Delta F^2$, using locally modified versions of standard programs (Busing, Martin & Levy, 1962, 1964). Scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV, pp. 99–102). All C and O atoms refined anisotropically, H atoms placed in calculated positions. Isotropic type I extinction correction applied, $g = 1.2$ (2) $\times 10^4$ (Becker & Coppens, 1974). 263 parameters consisting of 87 positional parameters, 174 anisotropic thermal parameters, a scale factor and an extinction factor. Final $R = 0.046$, $wR = 0.063$, for 2535 reflections with $I \ge 3\sigma(I)$, $S = 2.44$; $R = 0.081$ for all 4069 reflections; $\Delta/\sigma = 0.002$(mean), 0.007(maximum). Maximum final difference density -0.34 to 0.48 e Å^{-3}.

Discussion. Final positional parameters are in Table 1* and bond lengths and angles involving non-H atoms are in Table 2. Fig. 2 shows the stereo diagram of the molecule with atomic numbering. The aromatic rings, including the phenoxycarbonyl group, show no significant deviation from planarity, χ^2 values being 3.9, 4.5 and 9.0, with no C atom displaced more than 0.007 (3) Å from its corresponding least-squares mean plane. The dibenzobarrelene ring skeleton in Me/Ph is similar to that of the methyl isopropyl ester (Garcia-Garibay et al., 1990a) and to that of dibenzobarrelene itself (Trotter & Wireko, 1990), with evidence of systematic angular deformation (Allen, 1981a) at the benzene–cyclohexadiene ring junctions. Aromatic bond lengths and angles are within expected values: C—$C_{aromatic} = 1.367–1.406$ Å, mean 1.384 Å; C—C—$C_{aromatic} = 118.2–121.3°$, mean 120.0°. The aromatic ring of the phenoxycarbonyl group is rotated 60° out of its carboxyl plane.

The O—C(Ph) bond in the phenyl ester [O3—C16, 1.407 (3) Å] is significantly shorter than the corresponding O—C(Me) [O1—C14, 1.443 (3) Å], partly a

* Lists of anisotropic thermal parameters, H-atom positions, torsion angles, structure factors and packing diagrams have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53406 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final positional (fractional* $\times 10^4$*) and equivalent isotropic thermal parameters (*$U \times 10^3$ Å^2*) for Me/Ph with e.s.d.'s 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}
C1	4736 (3)	5459 (3)	8367 (2)	72
C2	5329 (3)	6483 (4)	8810 (2)	85
C3	4926 (3)	6865 (3)	9457 (2)	81
C4	3933 (2)	6240 (3)	9696 (2)	62
C4a	3337 (2)	5237 (2)	9267 (1)	49
C5	335 (2)	5696 (3)	8855 (2)	66
C6	−291 (3)	6069 (4)	8227 (3)	88
C7	87 (3)	5710 (4)	7579 (2)	89
C8	1122 (3)	4933 (3)	7520 (2)	71
C8a	1753 (2)	4561 (3)	8138 (1)	52
C9	2927 (2)	3784 (3)	8198 (1)	53
C9a	3735 (2)	4847 (3)	8601 (1)	52
C10	2201 (2)	4498 (2)	9419 (1)	49
C10a	1363 (2)	4936 (2)	8804 (1)	50
C11	2767 (2)	2491 (2)	8695 (1)	48
C12	2403 (2)	2862 (2)	9335 (1)	45
C13	3009 (2)	1011 (3)	8431 (1)	57
C14	2385 (3)	−1432 (3)	8344 (2)	84
C15	2131 (2)	1879 (3)	9925 (1)	52
C16	2588 (2)	−398 (3)	10465 (1)	53
C17	1576 (3)	−1172 (3)	10370 (2)	65
C18	1401 (3)	−2348 (3)	10816 (2)	82
C19	2226 (4)	−2726 (3)	11333 (2)	90
C20	3235 (4)	−1934 (4)	11423 (2)	85
C21	3424 (3)	−749 (3)	10985 (2)	67
O1	2212 (2)	56 (2)	8566 (1)	63
O2	3852 (3)	728 (3)	8121 (2)	138
O3	2843 (1)	732 (2)	9989 (1)	53
O4	1375 (2)	2101 (2)	10322 (1)	99

Table 2. *Bond lengths (Å) and angles (°) for Me/Ph with e.s.d.'s in parentheses*

C1—C2	1·406 (5)	C10—C12	1·528 (3)
C1—C9a	1·379 (4)	C11—C12	1·336 (3)
C2—C3	1·367 (5)	C11—C13	1·476 (3)
C3—C4	1·380 (4)	C12—C15	1·472 (3)
C4—C4a	1·378 (3)	C13—O1	1·306 (3)
C4a—C9a	1·399 (3)	C13—O2	1·190 (3)
C4a—C10	1·518 (3)	C14—O1	1·443 (3)
C5—C6	1·387 (5)	C15—O3	1·337 (3)
C5—C10a	1·385 (4)	C15—O4	1·196 (3)
C6—C7	1·353 (5)	C16—C17	1·371 (4)
C7—C8	1·402 (5)	C16—C21	1·371 (4)
C8—C8a	1·376 (4)	C16—O3	1·407 (3)
C8a—C9	1·532 (4)	C17—C18	1·386 (4)
C8a—C10a	1·392 (4)	C18—C19	1·364 (5)
C9—C9a	1·521 (4)	C19—C20	1·376 (5)
C9—C11	1·524 (3)	C20—C21	1·386 (4)
C10—C10a	1·516 (4)		
C2—C1—C9a	118·3 (3)	C5—C10a—C10	126·5 (2)
C1—C2—C3	120·9 (3)	C8a—C10a—C10	112·9 (2)
C2—C3—C4	120·8 (3)	C9—C11—C12	113·8 (2)
C3—C4—C4a	119·1 (3)	C9—C11—C13	118·6 (2)
C4—C4a—C9a	120·7 (2)	C12—C11—C13	127·5 (2)
C4—C4a—C10	126·7 (2)	C10—C12—C11	113·5 (2)
C9a—C4a—C10	112·5 (2)	C10—C12—C15	119·0 (2)
C6—C5—C10a	118·4 (3)	C11—C12—C15	127·4 (2)
C5—C6—C7	121·3 (3)	C11—C13—O1	113·8 (2)
C6—C7—C8	121·0 (3)	C11—C13—O2	122·6 (3)
C7—C8—C8a	118·2 (3)	O1—C13—O2	123·6 (3)
C8—C8a—C9	127·1 (2)	C12—C15—O3	113·2 (2)
C8—C8a—C10a	120·6 (3)	C12—C15—O4	123·8 (2)
C9—C8a—C10a	112·2 (2)	O3—C15—O4	123·0 (2)
C8a—C9—C9a	104·8 (2)	C17—C16—C21	122·2 (2)
C8a—C9—C11	105·6 (2)	C17—C16—O3	120·4 (2)
C9a—C9—C11	106·8 (2)	C21—C16—O3	117·2 (2)
C1—C9a—C4a	120·2 (3)	C16—C17—C18	118·4 (3)
C1—C9a—C9	127·2 (2)	C17—C18—C19	120·4 (3)
C4a—C9a—C9	112·5 (2)	C18—C19—C20	120·5 (3)
C4a—C10—C10a	105·2 (2)	C19—C20—C21	120·1 (3)
C4a—C10—C12	106·3 (2)	C16—C21—C20	118·4 (3)
C10a—C10—C12	106·1 (2)	C13—O1—C14	117·9 (2)
C5—C10a—C8a	120·5 (3)	C15—O3—C16	119·2 (2)

result of the different hybridizations at the C atoms, but possibly indicating some Ph—CO conjugation, in spite of the fact that the phenyl group is rotated out of the carbonyl plane by 60° ($\cos^2 60° = 0.25$) (Schweizer & Dunitz, 1982). In this, as in other unsymmetrically substituted diester derivatives (Scheffer *et al.*, 1988; Garcia-Garibay *et al.*, 1990*a*), the ester groups are chemically and geometrically different in the degree of conjugation of the carbonyl groups to the vinyl double bond (C11=C12). The dihedral angles C12—C11—C13—O2 (φ_1) and C11—C12—C15—O4 (φ_2) are −134·9 (4) and −145·0 (3)°, respectively, *i.e.* both C=C—C=O systems have *anti* conformations. The two ester groups are thus partially conjugated to the central double bond, with the phenoxycarbonyl group ($\cos^2\varphi_2 = 0.67$) being slightly more conjugated than the methoxycarbonyl group ($\cos^2\varphi_1 = 0.50$). The sp^2—sp^2 single-bond lengths [C11—C13, 1·476 (3) Å and C12—C15, 1·472 (3) Å] suggest some extent of electron delocalization over the α,β-unsaturated systems; the expected bond length for complete delocalization for such a system is 1·470 (2) Å, with 1·497 (2) Å indicating no significant electron delocalization (Allen, 1980, 1981*b*).

There are no exceptionally short intermolecular contacts, although there is a relatively short H···H contact of length 2·23 Å between H19 and a symmetry-related H14*b*.

All the dibenzobarrelenes studied so far undergo the di-π-methane reaction upon irradiation in solution and in the solid state (Garcia-Garibay, 1988; Scheffer *et al.*, 1988). In the unsymmetrical 11,12-diester derivatives, two regioisomeric products (major and minor) are usually identified. In general, for compounds where the ester substituents are both alkyl groups, more pronounced regioselectivity is observed in the solid state than in solution. In the present instance, the substituents are electronically very different (Me *versus* Ph) and the product ratios (major *versus* minor) are insensitive to the reaction
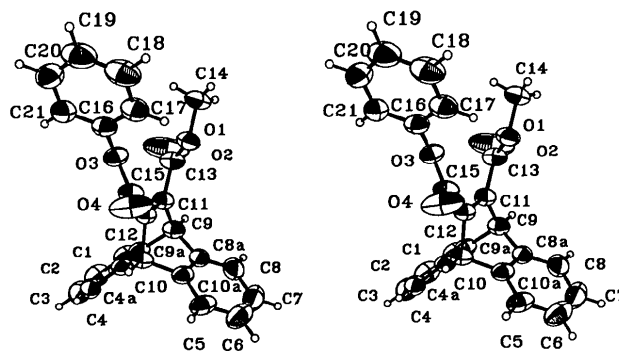

Fig. 2. Stereo diagram of Me/Ph with atomic numbering; 50% ellipsoids for C and O atoms, arbitrary circles for H atoms.

medium (70:30 in both media). Thus, even in solution there is a significant preference for one photoproduct, just as in the solid state, although not necessarily due to the same effects.

The photoreaction is considered to proceed by one (or more) of four possible pathways, the first steps of which involve bond formation between vinyl and benzo C atoms, C11—C8a or C9a, C12—C4a or C10a (Garcia-Garibay et al., 1990b). The pathway leading to the formation of the major product in the solid state can be examined from electronic and steric points of view (Garcia-Garibay et al., 1990a). The $\cos^2 \varphi$ values (0·50 for CO_2Me, 0·67 for CO_2Ph), which are an approximate measure of the relative odd-electron stabilization in the intermediate biradicals due to electron delocalization, predict preferred initial bond formation at C11, leading to photoproduct (2) (Fig. 1) [and its enantiomer, since crystals of (1) are racemic]; this is in accord with the preponderance (70%) of (2) over (2′) observed in this photolysis. It is not clear, however, that the difference of 0·17 in the relative extents of odd-electron stabilization in the solid state is large enough to account for the observed difference in the amounts of photoproducts. [The molecular structures of (2) and (2′) have not been determined by X-ray analysis, but are well established by spectroscopic methods and comparison with the photoproducts for differently substituted analogs of (1); the reaction pathways postulated are similar to those for the other derivatives (Garcia-Garibay et al., 1990a, b).]

Consideration of intramolecular steric effects suggests that C11···C8a and C12···C4a bondings are the favorable pathways (for the numbering system and conformational chirality shown in Fig. 2), since these involve movement of the ester groups away from each other; the other two possible pathways would involve intramolecular steric repulsions between O1 and O3. The C11···C8a and C12···C4a pathways result in the S,S,S,S isomers of (2) and (2′), respectively (Fig. 1), for the conformational chirality of (1) shown in Fig. 2, with R,R,R,R isomers being produced from the centrosymmetrically related molecule of (1) in the $P2_1/c$ crystal.

A qualitative study of the crystal packing* indicates that the phenyl ester group is more tightly surrounded by neighboring atoms than the methyl group, particularly if one considers not just the overall space but the space in the direction the phenyl ester group would have to move in order to engage in vinyl–benzo bridging. On each side of the carbonyl oxygen of the phenyl ester, and in the direction of vinyl–benzo bridging, is an H atom which may hinder easy bond formation. Initial bond

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* Packing diagram in deposited material.

formation preferentially involving the vinyl C atom bearing the less sterically hindered methyl ester group (i.e. C11) is therefore expected. This is also consistent with the experimental result.

The 6–12 Lennard–Jones non-bonded potential-energy profiles (Hagler, Huller & Lifson, 1974), which represent the simulated interactions as a result of the required movements of the vinyl C atoms and their respective ester groups in the initial bond formation, are shown in Fig. 3, as functions of the angle of rotation around a defined vector (C10···C11 etc.). (see Garcia-Garibay et al., 1990a for details). The angle 0° corresponds to the molecular structure as determined from the crystal structure analysis and positive and negative degrees correspond to clockwise and anticlockwise rotations, respectively. It appears from the profiles that the movement of the vinyl C atom bearing the methyl ester group (ME) corresponds to a lower-energy process and therefore is expected to be preferred in the initial vinyl–benzo bridging. This analysis is also consistent with the experimental results.

Thus, the correlation of structural and photochemical data has shown that in Me/Ph the formation of the observed major product can be rationalized from either electronic or steric packing considerations. There is, however, some uncertainty as to the contributions of the electronic effects since the difference in the odd-electron stabilization abilities of both ester groups is rather small. In any event, the observed major product is also consistent with steric arguments.
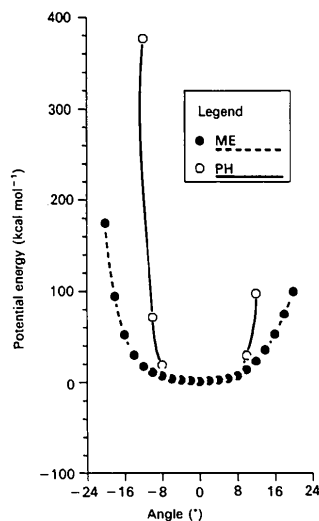
Fig. 3. Potential-energy profiles for Me/Ph. 1 kcal mol^{-1} = 4·1868 kJ mol^{-1}.

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Structure of Solanid-4-en-6-one

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Abstract. $C_{27}H_{41}NO$, $M_r = 395.6$, orthorhombic, $P2_12_12_1$, $a = 31.312$ (4), $b = 12.400$ (2), $c = 5.928$ (2) Å, $V = 2301.7$ (8) Å^3, $Z = 4$, $D_{calc} = 1.14$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.54184 Å, $\mu = 0.44$ mm^{-1}, $F(000) = 872$, $R = 0.074$ for 2422 unique observed reflections. The *A*, *B* and *C* rings show the usual conformation of 4-en-6-one structures. Conformational analysis of rings *D*, *E* and *F* confirms that the absolute configuration of the chiral centre at C(22) corresponds to the 22α(H) isomer.

Introduction. In our previous reports (Miljković, Sakač, Gaši, Stanković & Ribár, 1990; Stanković, Miljković, Gaši & Sakač, 1990) some new chemical transformations of solanidine were described. Oxidation of solanidine with monoperphthalic acid afforded 3β-hydroxy-5α,6α-epoxysolanidan *N*-oxide (1). By thermolysis of (1), solanida-2,4,6-triene (2) and solanid-4-en-6-one (3) were obtained as the

minor products. In this paper, the detailed X-ray determination of compound (3), as final proof of its proposed structure, is described.