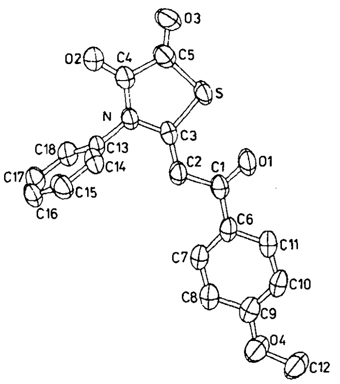

Fig. 2. The molecule with the atom-numbering scheme.

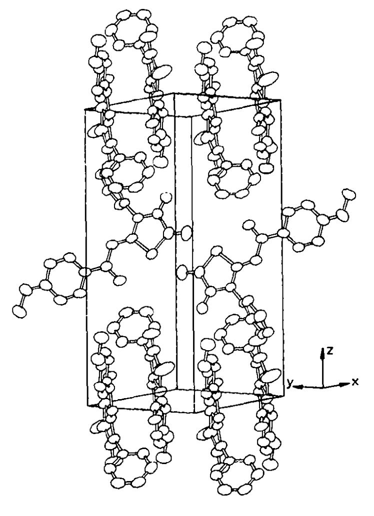

Fig. 3. Packing diagram.

Table 4. *The deviations* (Å) *of the atoms from the least-squares plane in the* (*carbonylmethylene*)*thiazolidine part of the molecule*

The equation of the plane is: $4{\cdot}874x + 8{\cdot}030y - 2{\cdot}663z = 1{\cdot}029$.

S	−0·060 (3)	C3	0·003 (4)
C5	−0·079 (4)	C2	−0·079 (4)
C4	0·063 (4)	C1	−0·111 (4)
N	0·082 (3)	O1	0·182 (3)

calculation (Table 4). The discussion of the close S···O contact and the quasi-linear C—S···O arrangement would be similar to that in our previous work quoted above. The fact that the O atom is replaced at C5 by the dicyanomethylidene group for compound *A* but not for compound *B*, can be explained by the existence of the electron-withdrawing forces due to S···O interaction.

The similarity of the structures of the Knoevenagel reaction substrate and product shows that the attractive forces due to sulfur–oxygen close contact can overcompensate the usual van der Waals repulsion between neighbouring nonbonded heteroatoms, thus controlling the conformation of compounds both in the solid state and, as it can be inferred, in solution.

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Structure of 9,10-Dihydro-9,10-ethenoanthracene (Dibenzobarrelene)

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Abstract. $C_{16}H_{12}$, $M_r = 204{\cdot}27$, monoclinic, $C2$, $a = 14{\cdot}467\,(1)$, $b = 8{\cdot}043\,(1)$, $c = 11{\cdot}734\,(1)$ Å, $\beta = 126{\cdot}16\,(1)°$, $V = 1102{\cdot}2\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}231$ g cm^{-3}, Cu $K\alpha_1$, $\lambda = 1{\cdot}54056$ Å, $\mu = 4{\cdot}94$ cm^{-1}, $F(000) = 432$, $T = 295$ K, $R = 0{\cdot}034$ for 1106 unique observed reflexions with $I > 3\sigma(I)$. The molecule has approximate C_{2v} symmetry, with the three nearly planar sections at angles of about 120°. The isolated C═C double bond [1·316 (4) Å] is shorter than the equivalent bridge bond in the

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dicarbonitrile derivative [1·343 (5) Å]. The thermal parameters are interpretable in terms of rigid-body translation and libration; corrected bond lengths and angles do not differ significantly from uncorrected values.

Introduction. As part of our studies of the photochemical rearrangement of diesters of dibenzobarrelene in the solid state (Evans, Garcia-Garibay, Omkaram, Scheffer, Trotter & Wireko, 1986; Garcia-Garibay, Scheffer, Trotter & Wireko, 1987*a*), we became interested in the energy sensitization of dibenzobarrelene itself (Garcia-Garibay, Scheffer, Trotter, & Wireko, 1987*b*). To our knowledge, the crystal structure of dibenzobarrelene has not been determined which was surprising because related structures have been reported, *e.g.* dibenzobarrelenedicarbonitrile (Oliver, Fallon & Smith, 1986), triptycene (Anzenhofer & De Boer, 1970), and 1-bromotriptycene (Palmer & Templeton, 1968). The initial objective for solving the structure of dibenzobarrelene was to assist in the interpretation of the results of the triplet energy sensitization in the crystalline phase. This involves (Garcia-Garibay *et al.*, 1987*b*) co-crystallization of dibenzobarrelene with a small amount of a sensitizer such as xanthone; the dibenzobarrelene-sensitizer crystals are then irradiated at a wavelength (337 nm) at which only the sensitizer and not the dibenzobarrelene absorbs. Energy transfer from the sensitizer triplet state to the triplet excited state of dibenzobarrelene then leads exclusively to a triplet-derived dibenzosemibullvalene photoproduct.

Experimental. Crystals grown from ethanol by slow evaporation, 0·4 × 0·3 × 0·3 mm, CAD-4F diffractometer, filtered Cu$K\alpha$ radiation, lattice parameters from 25 reflexions with $30 \leq \theta \leq 46°$. Intensities for $\theta \leq 75°$, *hkl*: −18 to 14, −10 to 0, 0 to 14, ω–2θ scan, ω-scan width $(0·55 + 0·14\tan\theta)°$ at 10° min^{-1} maximum, extended 25% on each side for background measurement, horizontal aperture $(2·0 + \tan\theta)$ mm, vertical aperture 4 mm; three standard reflexions measured every 60 min (no decay). Lp corrections, 1216 unique reflexions measured, 1106 with $I \geq 3\sigma(I)$, 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 *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), refined by full-matrix least squares minimizing $\sum w(|F_o| - k|F_c|)^2$, $w = 1/\sigma^2(F) = 4F^2/\sigma^2(F^2)$, using locally modified versions of standard programs (Busing, Martin & Levy, 1962). Scattering factors from *International Tables for X-ray Crystallography* (1974). All C atoms refined anisotropically and H atoms (from a difference map) refined with isotropic thermal parameters. Isotropic type I extinction correction applied, $g = 7·4\,(2) \times 10^3$. 193 parameters consisting of 83 positional parameters (y coordinate of C10 was fixed to define the origin), 96 anisotropic thermal parameters, 12 isotropic thermal parameters, a scale factor, and an extinction factor. Final R = 0·034, wR = 0·038 for 1106 reflexions with $I \geq 3\sigma(I)$, S = 1·86, R = 0·042 for all 1216 reflexions, Δ/σ = 0·001 (mean); 0·005 (maximum). Maximum final difference density −0·23 to 0·12 e Å^{-3}. Thermal motion has been analysed in terms of the rigid-body modes of translation, libration and screw oscillations (Schomaker & Trueblood, 1968).

Discussion. Final positional and isotropic or equivalent isotropic thermal parameters are given in Table 1.* The thermal parameters are described in terms of rigid-body motion (Table 2). The r.m.s. standard error in the temperature factors (σU_{ij}) derived from the least-squares analysis is 0·0011 Å^2 and the ΔU_{ij} from the rigid-body analysis is 0·0022 Å^2. The translation motion is approximately isotropic (Table 2) with maximum and minimum r.m.s. displacements of 0·21 and 0·19 Å. The libration motion is more anisotropic with maximum and minimum r.m.s. librations of 4·1 and 2·0°. The bond lengths were corrected for libration (Cruickshank, 1956*a*, 1961) using breadth parameter q^2 (Cruickshank, 1956*b*) of 0·08 for all atoms involved. The corrected bond lengths* are longer than the uncorrected values by only 0·002–0·005 Å (*i.e.* about 1σ), and corrected bond angles are very close to uncorrected values. The uncorrected values (Table 3) are used in this discussion.

The molecule (Fig. 1) has approximate C_{2v} symmetry, and contains two nearly planar aromatic rings [χ^2 = 28·3 and 36·6, maximum displacement from mean planes 0·010 (4) Å] and an isolated C=C double bond [1·316 (3) Å], which is shorter than the equivalent C=C bridge bond [1·343 (5) Å] in the dicarbonitrile derivative (Oliver *et al.*, 1986). The three planar sections of the molecule make angles of about 120°. The angles external to the benzo rings are distorted to about 127°, and the intra-annular benzo–barrelene angles are all significantly less (mean 112·6°) than 120°. The mean of all the 12 angles around the two sp^3 C atoms is 109·4°, which is the expected tetrahedral value, although the mean value of the angles involving only the C atoms (105·6°) is less than the tetrahedral value. Despite these systematic distortions (which are generally expected in such fused-ring systems) in the bond

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* Lists of structure factors, anisotropic thermal parameters, libration-corrected bond lengths, torsion angles, and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52211 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final positional (fractional* $\times 10^4$, H $\times 10^3$) *and isotropic or equivalent isotropic thermal parameters* ($U \times 10^3$ Å^2) *with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}$(trace of diagonalized U).

	x	y	z	U_{eq}/U_{iso}
C1	5750 (2)	2978 (4)	3880 (2)	55
C2	4889 (2)	4152 (5)	3374 (2)	61
C3	4716 (2)	5350 (4)	2433 (2)	57
C4	5396 (2)	5387 (4)	1947 (2)	50
C4a	6239 (2)	4199 (4)	2425 (2)	43
C5	6492 (2)	1732 (4)	104 (2)	53
C6	6369 (2)	36 (4)	−213 (3)	60
C7	6593 (2)	−1128 (4)	787 (3)	62
C8	6926 (2)	−638 (4)	2114 (3)	54
C8a	7055 (2)	1036 (4)	2438 (2)	45
C9	7408 (2)	1824 (4)	3821 (2)	48
C9a	6428 (2)	3003 (4)	3402 (2)	45
C10	7039 (2)	3994	1988 (2)	45
C10a	6849 (2)	2221 (4)	1438 (2)	43
C11	8435 (2)	2924 (4)	4299 (2)	56
C12	8249 (2)	4031 (4)	3359 (3)	55
H1	590 (2)	206 (4)	460 (3)	60 (7)
H2	443 (2)	416 (3)	367 (3)	59 (7)
H3	415 (2)	620 (4)	216 (3)	60 (7)
H4	531 (2)	624 (4)	125 (3)	59 (7)
H5	632 (2)	252 (4)	−70 (3)	63 (7)
H6	609 (3)	−34 (5)	−126 (4)	86 (10)
H7	649 (3)	−236 (5)	51 (3)	72 (8)
H8	710 (2)	−146 (4)	288 (3)	64 (7)
H9	756 (2)	106 (4)	452 (3)	56 (7)
H10	689 (2)	481 (4)	134 (3)	50 (6)
H11	917 (2)	271 (4)	524 (3)	54 (6)
H12	879 (3)	492 (4)	343 (3)	71 (8)

Table 2. *Dibenzobarrelene: principal axes of translation* (**T**, Å^2), *libration* (**L**, deg^2), *and screw* (**S**, rad Å) *tensors, and direction cosines with respect to a, b, c* crystal axes*

Origin is at fractions 0·6279, 0·2669, 0·1980 along *a, b, c*, respectively.

T	0·044	0·1235	−0·9321	−0·3410
	0·037	0·9564	0·2037	−0·2095
	0·036	0·2642	−0·3007	0·9163
L	17·135	−0·7519	0·6139	0·2402
	11·313	−0·5133	−0·3169	−0·7976
	3·951	−0·4136	−0·7231	0·5532
S	0·0013	0·4816	0·5045	−0·7166
	0·0011	0·8714	−0·3730	0·3184
	−0·0024	−0·1070	−0·7788	−0·6183

angles, bond lengths are generally as expected and similar to those of the dicarbonitrile derivative (Oliver *et al.*, 1986) and 1-bromotriptycene (Palmer & Templeton, 1968). This is consistent with the general observation that strain induced by ring fusion is reflected in systematic angular deformations (Allen, 1981). There are no unusual intermolecular contacts; the shortest H···H distance is 2·44 (4) Å.

The photochemical data (Garcia-Garibay *et al.*, 1987*b*) suggest that one photosensitizer (xanthone) molecule can lead to the formation of about 24 photoproduct molecules. The present crystal structure determination of dibenzobarrelene indicates that one molecule (assumed to be replaced by a sensitizer molecule in the mixed crystal) has 24 neighbouring dibenzobarrelene molecules within a centre-to-centre distance of 12 Å; 10 − 15 Å is the suggested upper limit for triplet–triplet energy transfer in rigid media (Turro, 1978). Hence the photochemical and structural data are reasonably consistent.

Table 3. *Bond lengths* (Å) *and angles* (°), *with e.s.d.'s in parentheses*

C1—C2	1·387 (4)	C7—C8	1·388 (4)
C1—C9a	1·388 (3)	C8—C8a	1·381 (3)
C2—C3	1·372 (4)	C8a—C9	1·523 (3)
C3—C4	1·399 (3)	C8a—C10a	1·401 (3)
C4—C4a	1·382 (3)	C9—C9a	1·525 (3)
C4a—C9a	1·395 (3)	C9—C11	1·524 (3)
C4a—C10	1·526 (2)	C10—C10a	1·522 (3)
C5—C6	1·397 (4)	C10—C12	1·526 (3)
C5—C10a	1·385 (3)	C11—C12	1·316 (4)
C6—C7	1·381 (4)		
C2—C1—C9a	119·1 (2)	C8a—C9—C9a	104·6 (2)
C1—C2—C3	121·0 (2)	C8a—C9—C11	106·0 (2)
C2—C3—C4	120·3 (2)	C9a—C9—C11	106·1 (2)
C3—C4—C4a	119·0 (2)	C1—C9a—C4a	120·0 (2)
C4—C4a—C9a	120·5 (2)	C1—C9a—C9	127·2 (2)
C4—C4a—C10	127·0 (2)	C4a—C9a—C9	112·8 (2)
C9a—C4a—C10	112·5 (2)	C4a—C10—C10a	105·1 (2)
C6—C5—C10a	118·8 (2)	C4a—C10—C12	105·6 (2)
C5—C6—C7	120·5 (2)	C10a—C10—C12	105·9 (2)
C6—C7—C8	120·8 (2)	C5—C10a—C8a	120·5 (2)
C7—C8—C8a	119·1 (2)	C5—C10a—C10	126·8 (2)
C8—C8a—C9	127·3 (2)	C8a—C10a—C10	112·7 (2)
C8—C8a—C10a	120·3 (2)	C9—C11—C12	114·3 (2)
C9—C8a—C10a	112·4 (2)	C10—C12—C11	114·3 (2)

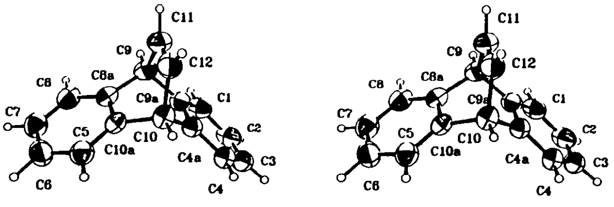

Fig. 1. Stereoscopic view of the title compound with atom numbering.

One final point is that the fortuitous crystallization of dibenzobarrelene in the chiral space group ($C2$) has prompted efforts, which have met with some success, to produce chiral products *via* a gas–solid bromination reaction (Garcia-Garibay, Scheffer, Trotter & Wireko, 1988).

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Structure of (*R*)-Tetrahydro-2-furancarboxylic Acid Monohydrate

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Abstract. $C_5H_{10}O_4$, $M_r = 134{\cdot}31$, monoclinic, $P2_1$, $a = 11{\cdot}670\,(2)$, $b = 6{\cdot}177\,(3)$, $c = 10{\cdot}704\,(2)$ Å, $\beta = 115{\cdot}11\,(2)^\circ$, $V = 698{\cdot}7\,(4)$ Å^3, $Z = 4$, $D_m = 1{\cdot}26$, $D_x = 1{\cdot}28$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 9{\cdot}69$ cm^{-1}, $F(000) = 288$, room temperature, $R = 0{\cdot}046$ for 1047 reflections with $|F_o| > 3\sigma(F)$. There are two independent molecules of the title compound in the crystal. No twofold symmetry is observed in the tetrahydrofuran rings. Hydrogen bonds between water molecules and carboxylic acid groups stabilize the crystal structure.

Introduction. In the course of development of penem antibiotics, we have found that compounds with a tetrahydrofuran ring attached to the penum nucleus show excellent activity againt a wide range of bacteria (Ishiguro, Iwata, Nakatsuka, Tanaka, Maeda, Nishihara, Noguchi & Nishino, 1988). The structural importance of the tetrahydrofuran ring has also been found in polyether antibiotics (Agtarap, Chamberlin, Pinkerton & Steinrauf, 1967).

(*R*)-Tetrahydro-2-furancarboxylic acid (Belanger & Williams, 1983) is one of the smallest tetrahydrofuran derivatives, which have a characteristic amphiphillic structure. The accurate structure of the molecule should be useful for understanding the interactions of the molecule with water molecules and biological macromolecules.

Experimental. The title compound was crystallized from tetrahydrofuran solution. D_m by flotation in chlorobenzene/bromobenzene. The crystals are deliquescent.

Diffraction intensities were measured using a colorless hexagonal-plate crystal, $0{\cdot}15 \times 0{\cdot}3 \times 0{\cdot}7$ mm, sealed in a quartz capillary tube; ω–2θ scan mode with variable scan width; maximum $2\theta = 120^\circ$; Rigaku-AFC diffractometer and Ni-filtered Cu $K\alpha$ radiation. Lattice parameters and orientation matrix refined using 20 reflections in the range $20 < \theta < 21^\circ$ by the least-squares method. 1138 unique reflections measured in the index range $-13 \leq h \leq 13$, $0 \leq k \leq 6$, $0 \leq l \leq 12$. 1047 reflections with $|F_o| > 3\sigma(F)$. Three standard reflections (004, $3\bar{1}\bar{5}$, $\bar{4}20$) were monitored every 100 reflections. Mean variation of the standard 0·3%. Intensities corrected for absorption by the method of North, Phillips & Mathews (1968) using two reflections; normalized transmission factors 0·99–0·88. No extinction correction.

The structure was solved by direct phase determination using the *RANTAN* option of *MULTAN*87 (Debaerdemaeker, Germain, Main,

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