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Structure of Trithia[5]heterohelicene,* $C_{16}H_8S_3$

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Abstract. $M_r = 296\cdot42$, monoclinic, $P2/c$, $a = 10\cdot845\,(1)$, $b = 8\cdot420\,(1)$, $c = 7\cdot265\,(1)$ Å, $\beta = 109\cdot08\,(1)°$, $V = 626\cdot9\,(1)$ Å^3, $Z = 2$, $D_m = 1\cdot56$ (flotation), $D_x = 1\cdot58$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0\cdot7107$ Å, $\mu = 0\cdot552$ mm^{-1}, $F(000) = 304$, $T = 297$ K, final $R = 0\cdot050$ for 1362 unique reflections. The molecule presents a typical helicenic geometry with a C_2 axis. The dihedral angle between the terminal thiophene rings is 36·6 (1)°. *M* and *P* enantiomers of the molecules are stacked alternately along **c** with nearly parallel overlap of the central thiophene moieties.

Introduction. Although the crystallographic features of carbohelicenes (all-benzene helicene) have been extensively studied (Kuroda, 1982), the influence of heteroatoms on the molecular structures of helicenes is largely unknown as yet. Whether bulkier heteroatoms than carbon may enhance or suppress the twist of the helicene molecule is of absorbing interest. We studied a series of thiaheterohelicenes composed of alternate thiophene and benzene rings, and found marked differences in their spectroscopic properties from those of carbohelicenes (Yamada, Tanaka, Nakagawa, Ogashiwa & Kawazura, 1982). Thus, the present X-ray analysis of the title compound was undertaken to disclose the characteristic heterohelicene structure crystallographically.

Experimental. Pale yellow needles from acetonitrile, crystal *ca* 0·3 × 0·3 × 0·3 mm, Rigaku AFC-5 four-circle diffractometer, graphite-monochromated Mo $K\alpha$, least-squares fit of 50 reflections ($28 < 2\theta < 32°$) to obtain cell dimensions, 2088 reflections measured with $2\theta \leq 60°$ ($\pm h$, $k \geq 0$, $l \geq 0$), 1362 with $|F|/\sigma(|F|) \geq 3\cdot0$, of which one ($\bar{1}02$) with large extinction ignored, 1361 used for structure determination, θ–2θ scan technique, max. variation of 0·014 for three intensity monitors; Lp corrections, no absorption correction; heavy-atom and Fourier methods, block-diagonal least-squares refinement, anisotropic thermal factors for all non-H atoms, isotropic for H atoms (by difference synthesis), function minimized $\sum w(|F_o| - |F_c|)^2$ with $w = 1\cdot0$; final $R = 0\cdot050$ and $R_w = 0\cdot050$, $S = 0\cdot628$, $(\Delta/\sigma)_{\max} = 0\cdot286$, final $\Delta\rho$ excursions $\leq |0\cdot35|$ e Å^{-3}; complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974), calculations carried out on a FACOM M-160F computer with *UNICS* III (Sakurai & Kobayashi, 1978).

Discussion. Final atomic coordinates and thermal parameters are listed in Table 1.† The atom-numbering scheme, together with the indication of the rings are shown in Fig. 1. The molecule possesses a C_2 symmetry axis through S(1) and the center of the C(1)—C(1$^{\rm i}$) bond. The planarity of each aromatic ring in the molecule is examined by the deviations of the component atoms in the skeleton from each of the least-squares planes. Ring *C* has an almost flat configuration [maximum deviation 0·012 (3) Å], while rings *A* and *B* exhibit somewhat twisted-boat forms [0·045 (2) and 0·057 (2) Å, respectively]. Dihedral angles between each of the mean planes are as follows; *A—B* 7·9 (2), *A—C* 18·5 (1), *B—C* 10·6 (1), *B—B*$^{\rm i}$ 15·6 (3), and *C—C*$^{\rm i}$ 36·6 (1)°. These values are considerably smaller than those of [5]carbohelicene (Kuroda, 1982), suggesting a less torsional structure for this molecule. This difference may also account for the experimental fact that [5]carbohelicene can be resolved into optical antipodes by diastereomeric complex formation (Goedicke & Stegemeyer, 1970) or by high-performance liquid chromatography (Mikes, Boshart & Gil-av, 1976) at ambient temperature, whereas no enantiomer of trithia[5]heterohelicene can be obtained in similar conditions owing to rapid racemization. The heterohelicene, however, still has the structural features of the helicene family as is obvious from inspection of Fig. 2, in which two fundamental forces

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* IUPAC name: thieno[3,2-*e*:4,5-*e*′]bis(benzo[*b*]thiophene).

† Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares-planes' data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39251 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters*

$$B_{\rm eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a^*_i a^*_j \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$(Å^2)
S(1)	0	−7149 (1)	2500	3·20 (3)
S(2)	−3963 (1)	−1666 (1)	672 (1)	5·21 (3)
C(1)	−704 (2)	−4153 (3)	2295 (3)	2·28 (6)
C(2)	−1635 (2)	−2903 (3)	1766 (3)	2·71 (7)
C(3)	−1523 (3)	−1301 (4)	1164 (4)	3·45 (8)
C(4)	−2679 (4)	−529 (4)	543 (5)	4·82 (11)
C(5)	−2943 (3)	−3283 (4)	1538 (4)	3·43 (8)
C(6)	−3358 (3)	−4817 (4)	1777 (4)	3·79 (9)
C(7)	−2490 (3)	−6037 (4)	2106 (4)	3·46 (8)
C(8)	−1180 (3)	−5707 (3)	2300 (4)	2·68 (7)

Table 2. *Bond distances* (Å) *and angles* (°)

S(1)—C(8)	1·736 (3)	S(2)—C(5)	1·738 (3)
S(2)—C(4)	1·717 (4)	C(1)—C(1^{i})	1·456 (3)
C(1)—C(2)	1·423 (4)	C(2)—C(3)	1·435 (4)
C(3)—C(4)	1·352 (5)	C(2)—C(5)	1·409 (4)
C(1)—C(8)	1·407 (4)	C(5)—C(6)	1·398 (5)
C(6)—C(7)	1·360 (5)	C(7)—C(8)	1·408 (4)
C(8)—S(1)—C(8^{i})	91·2 (1)	C(4)—S(2)—C(5)	91·4 (2)
S(1)—C(8)—C(1)	112·9 (2)	S(2)—C(5)—C(2)	111·2 (2)
S(2)—C(4)—C(3)	113·2 (3)	C(8)—C(1)—C(1^{i})	111·2 (2)
C(3)—C(2)—C(5)	111·1 (3)	C(2)—C(3)—C(4)	113·1 (3)
C(2)—C(1)—C(8)	117·4 (2)	C(1)—C(2)—C(5)	117·5 (3)
C(2)—C(5)—C(6)	123·2 (3)	C(5)—C(6)—C(7)	119·2 (3)
C(6)—C(7)—C(8)	119·1 (3)	C(1)—C(8)—C(7)	122·9 (3)
S(2)—C(5)—C(6)	125·2 (2)	C(2)—C(1)—C(1^{i})	131·3 (2)
C(1)—C(2)—C(3)	130·9 (3)	S(1)—C(8)—C(7)	124·2 (2)

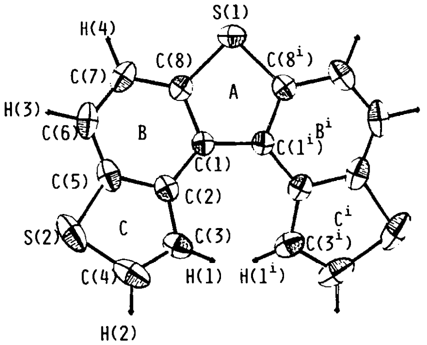

Fig. 1. Schematic drawing of the molecule with 50% probability ellipsoids.

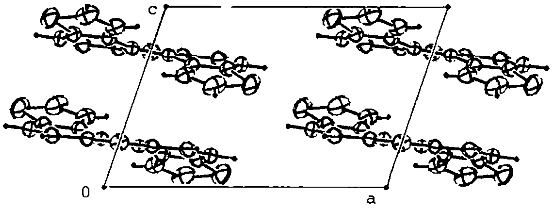

Fig. 2. Packing diagram of the molecules viewed down **b**.

are expected to be equipoised: one concerns the retention of planar configuration, extending the π conjugation, and the other is the steric repulsion between the terminal rings to build up the helical geometry. The closest non-bonded contacts in the inner core of the molecule which occur are H(1)–H(1^{i}), H(1)–C(3^{i}) and C(3)–C(3^{i}) with distances of 2·12 (4), 2·64 (3) and 3·239 (4) Å, respectively, which are significantly shorter than the sum of the van der Waals radii of 1·8 and 1·2 Å for C and H atoms. H(1) and H(2) show large displacements from the mean plane of ring *C*, 0·03 (3) and 0·07 (4) Å, respectively, indicating the highly steric hindrances around these moieties.

Bond distances and angles are given in Table 2. The length of the central S(1)—C(8) bond is slightly shorter than the value of 1·740 Å observed in dibenzothiophene (Schaffrin & Trotter, 1970), but the terminal S(2)—C(4) bond distance is in agreement with that of 1·718 Å reported in the thiophene molecule (Harshbarger & Bauer, 1970). As for the benzene ring, the C—C bond distance in the inner core, C(1)—C(2), is the longest, that in the outer core, C(6)—C(7), is the shortest, the radial ones, C(2)—C(5) and C(1)—C(8), being of medium length. This trend appears to be characteristic of helicenes, in which the steric repulsion between the contiguous rings is kept as small as possible.

Fig. 2 shows a projection of the structure along **b**. The C_2 axis of the molecule is parallel to the crystal *b* axis. The crystal symmetry produces alternate *P* and *M* layers parallel to the crystal *ab* plane. Both of the enantiomers along **c** are stacked in the opposite direction so as to overlap the central thiophene moieties with an intermolecular dihedral angle of 0·1 (1)°. The mean interplanar distance between them is calculated as approximately 3·5 Å, which seems close enough to anticipate some kind of intermolecular interactions. Among the adjacent columns, the majority of short atom–atom contacts are observed between the heterochiral molecules, while the shortest H–H distance occurs between the homochiral molecules, H(3)–H(3^{ii}) [symmetry operation: (ii) $x+1, y, z$], with a distance of 2·40 (5) Å. This packing mode, being as a whole quite different from those of carbohelicenes, is thought to characterize the crystallographic properties of thiaheterohelicenes.

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The Structures of 9-Hydroxy-10-methyl-*cis*-2-decalone,* $C_{11}H_{18}O_2$ (I), and 11-Oxatricyclo[4.4.3.0^{1,6}]tridecane-3,12-dione, $C_{12}H_{16}O_3$ (II)

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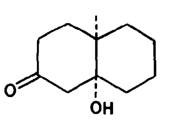
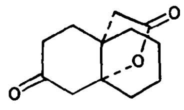
Abstract. (I): $M_r = 182{\cdot}3$, monoclinic, $P2_1/a$, $a = 13{\cdot}643\,(4)$, $b = 5{\cdot}989\,(1)$, $c = 12{\cdot}265\,(3)$ Å, $\beta = 93{\cdot}62\,(2)°$, $U = 1000{\cdot}2$ Å^3, $Z = 4$, D_m (flotation) = 1·20, $D_x = 1{\cdot}210$ g cm^{-3}, $\mu(\mathrm{Cu}\ K\alpha) = 6{\cdot}52$ cm^{-1}, $F(000) = 400$, room temperature, final $R = 0{\cdot}037$ over 1181 reflections. (II): $M_r = 208{\cdot}3$, monoclinic, $P2_1$, $a = 7{\cdot}565\,(2)$, $b = 10{\cdot}585\,(3)$, $c = 7{\cdot}422\,(2)$ Å, $\beta = 117{\cdot}62\,(2)°$, $U = 527$ Å^3, $Z = 2$, D_m (flotation) = 1·30, $D_x = 1{\cdot}312$ g cm^{-3}, $\mu(\mathrm{Cu}\ K\alpha) = 7{\cdot}70$ cm^{-1}, $F(000) = 224$, room temperature, final $R = 0{\cdot}033$ over 750 reflections. Both molecules adopt chair–chair conformations in which the oxygen ring substituent is axial in the ring containing the carbonyl group. The presence of a γ-lactone which incorporates the atoms of the ring junction significantly flattens the entire decalone system of (II). All intermolecular separations for (I) and (II) are normal van der Waals contacts except for an O···O hydrogen bond of 2·837 (2) Å in (I).


(I)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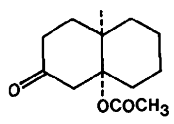
(III)

Introduction. In connection with a study of the relative β-elimination reactivities of 11-oxatricyclo[4.4.3.0^{1,6}]-tridecane-3,12-dione (II) and 9-acetoxy-10-methyl-*cis*-2-decalone (III) (Mayer, Spencer & Onan, 1984), we wished to determine if the greatly enhanced reactivity of (II) is associated with an elongated C(sp^3)—O bond length, as previously found to be the case in the hydrolysis of a series of acetals (Jones & Kirby, 1979). Direct comparison of the C(sp^3)—O bond lengths of these two compounds proved impossible because suitable crystals of (III) could not be obtained. Because 9-hydroxy-10-methyl-*cis*-2-decalone (I), 9-hydroxy-10-methyl-*trans*-2-decalone, and 9-acetoxy-10-methyl-*trans*-2-decalone all crystallize well, it was decided to use the observed C(sp^3)—O bond lengths for these three compounds to estimate the C(sp^3)—O bond length for (III). Here we report the structures of the *cis*-fused lactone (II) and β-ketol (I).

Experimental. Lath-like crystals of (I) were grown from isopentane, chunky crystals of (II) were grown from ether, crystal dimensions *ca* 0·12 × 0·20 × 0·40 mm (I) and 0·20 × 0·20 × 0·32 mm (II); Syntex $P2_1$ automated diffractometer, Cu $K\alpha$ radiation, cell dimensions for each by least-squares refinement of 2θ values of 15 reflections with $60 \leq 2\theta \leq 80°$, $\theta/2\theta$ scans, variable-speed scan, $4 \leq 2\theta \leq 115°$, 1591 (I) and 832 (II) independent reflections collected, 1181 with $I > 2\sigma(I)$ considered observed for (I), 750 for (II); two check reflections measured every 48 reflections showed a maximum variation in intensity of 6% for (I), 4% for (II); Lorentz–polarization and empirical absorption corrections applied, scattering factors for C and O from Cromer & Waber (1965), for H from Stewart, Davidson & Simpson (1965); structures solved by direct methods [*MULTAN*80 (Germain, Main & Woolfson, 1971)], full-matrix least-squares refinement minimizing $\sum w||F_o| - |F_c||^2$ with weights $w^{1/2} = 1$ for $|F_o| \leq 7{\cdot}0$ and $w^{1/2} = 7{\cdot}0/|F_o|$ for $|F_o| > 7{\cdot}0$ (program based on *FMLS* by P. K. Gantzel, R. A. Sparks and K. N. Trueblood, modified by A. T. McPhail); all H atoms located in difference syntheses,

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* 8a-Hydroxy-4a-methyl-*cis*-decahydro-2-naphthalenone.
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