

Fig. 1. Représentation des molécules de l'unité asymétrique de la forme I par le programme *PLUTO* (Motherwell & Clegg, 1978).

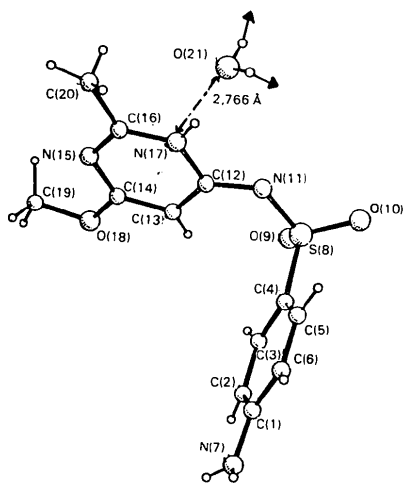


Fig. 2. Représentation de la molécule de l'unité asymétrique du solvate SII.

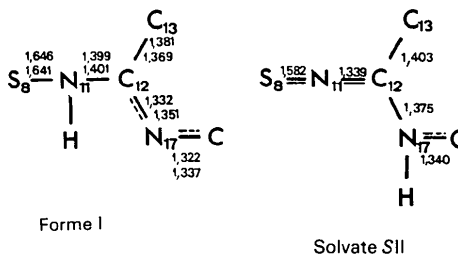


Fig. 3. Modifications structurales induites par le déplacement du proton amide. (Distances en Å.)

lui aussi un transfert du proton amide et donc n'est pas un vrai polymorphe mais plus exactement un isomère de la forme I.

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Structure of Pentathia[9]heterohelicene,* C₂₈H₁₂S₅

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Abstract. $M_r = 508.70$, monoclinic, $C2/c$, $a = 100.31(1)^\circ$, $V = 2150.0(3) \text{ \AA}^3$, $Z = 4$, $D_m = 1.55$ (floatation), $D_x = 1.57 \text{ g cm}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.70926 \text{ \AA}$, $\mu = 5.34 \text{ cm}^{-1}$, $F(000) = 1040$, $T = 297 \text{ K}$, final $R = 0.062$ for 1054 unique observed reflections. The molecule, having a C_2 axis, displays a helical geometry

* Thieno[2,3-*l*:5,4-*l'*]bis(benzo[*d*]benzo[1,2-*b*:4,3-*b'*]dithiophene).

with more than one turn. The dihedral angle between the intramolecular facing planes of maximum overlap is $22.6(3)^\circ$. *P* and *M* enantiomers are alternately stacked along *c* with a greater part of the molecular planes overlapping each other, and the same chiral molecules form a layer on the *ab* plane.

Introduction. In the course of our study on thiaheterohelicenes consisting of alternate thiophene and benzene rings, we revealed that trithia[5]heterohelicene (**I**), the youngest helicene among this series of compounds, shows a characteristic crystal structure which differs significantly from that of [5]carbohelicene (Nakagawa, Yamada, Kawazura & Miyamae, 1984). Our next interest was directed toward the larger heterohelicenes in view of the structural alteration with an increase in the number of rings. We obtained the crystals of the title heterohelicene, like (**I**), in racemic form, whereas all the carbohelicenes higher than [6] were reported to give the crystals only in enantiomeric forms (Kuroda, 1982). Thus, the present investigation will help remedy the lack of knowledge of the crystal habit of helicene racemates.

Experimental. Pale-yellow needles from benzene/dichloromethane (1/1), crystal $ca\ 0.6 \times 0.2 \times 0.2$ mm; Rigaku AFC-5 four-circle diffractometer, graphite-monochromated Mo $K\alpha$, least-squares fit of 2θ values of 23 reflections ($18 < 2\theta < 24^\circ$) to obtain cell dimensions, 3268 independent reflections measured with $2\theta \leq 60^\circ$ ($h\ 0 \rightarrow 20, k\ 0 \rightarrow 15, l\ -8 \rightarrow 7$), 1054 with $|F|/\sigma(|F|) \geq 2.0$ employed for structure determination, 2θ - ω scans, max. variation of 0.013 for three intensity monitors; Lp corrections, absorption ignored, direct methods using *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), refinement by block-diagonal least squares with anisotropic thermal factors for all the non-H atoms, isotropic for H atoms (two from difference synthesis, remaining four by calculation), function minimized $\sum w(|F_o| - |F_c|)^2$ with $w = 1.0$; final $R = 0.062$, $wR = 0.066$, $S = 3.284$, $(\Delta/\sigma)_{\max} = 0.132$, final $\Delta\rho$ excursions $\leq |0.27| e\ \text{\AA}^{-3}$; 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 isotropic thermal parameters are listed in Table 1.* A view of the molecular conformation is shown in Fig. 1 with the atom-numbering scheme and the labeling of the rings.

* 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 39948 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

$$B_{eq} = \frac{2}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}(\text{\AA}^2)$
S(1)	0	-3315 (3)	7500	4.3 (1)
S(2)	1608 (1)	1095 (2)	123 (2)	4.1 (1)
S(3)	-1845 (1)	3677 (2)	7830 (2)	5.1 (1)
C(1)	-2187 (5)	2177 (8)	7465 (7)	4.2 (3)
C(2)	-1505 (4)	1310 (7)	7737 (6)	2.9 (3)
C(3)	-673 (4)	1873 (6)	8273 (6)	2.9 (3)
C(4)	-764 (5)	3163 (6)	8414 (7)	3.3 (3)
C(5)	-103 (6)	3902 (7)	9014 (8)	3.9 (3)
C(6)	662 (5)	3296 (7)	9555 (7)	4.0 (3)
C(7)	764 (4)	2007 (7)	9427 (7)	3.3 (3)
C(8)	169 (4)	1295 (6)	8729 (6)	2.4 (3)
C(9)	493 (4)	24 (6)	8687 (6)	2.3 (3)
C(10)	1202 (4)	-246 (7)	9499 (7)	3.2 (3)
C(11)	1525 (5)	-1468 (7)	9749 (7)	3.8 (3)
C(12)	1140 (5)	-2432 (7)	9168 (7)	3.9 (3)
C(13)	521 (5)	-2183 (6)	8314 (7)	3.0 (3)
C(14)	250 (4)	-942 (6)	7997 (6)	2.3 (3)

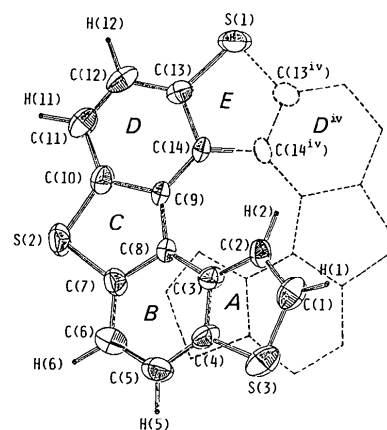


Fig. 1. View of the molecule with 50% probability ellipsoids. For clarity broken lines show the half of the molecule at $(-x, y, -z - 0.5)$.

As the molecule possesses a C_2 symmetry axis, broken lines were used to depict the half of the molecule which is represented by the symmetry operation (iv) $-x, y, -z - 0.5$. Bond lengths and angles are given in Table 2.

As is clear by inspection of Fig. 1, the major overlap in the molecule is seen in rings *A* and *B*, suggesting large steric repulsion around these portions. The following structural features are observed, presumably a result of reducing the repulsive forces by lessening the overlapping area. (1) The C-C bonds in the inner core are lengthened whereas those in the outer core are shortened: C(3)-C(8) 1.425 (9) and C(9)-C(14) 1.412 (10) against C(5)-C(6) 1.359 (11) and C(11)-C(12) 1.367 (11) Å. (2) The lengths of the radial bonds in the benzene rings gradually increase from the terminal ring to the center of the molecule: C(3)-C(4) [1.399 (10)] < C(7)-C(8) [1.409 (10)] < C(9)-C(10)

Table 2. Bond lengths (Å) and angles (°)

S(1)—C(13)	1.738 (8)	S(2)—C(7)	1.731 (7)
S(2)—C(10)	1.724 (8)	S(3)—C(1)	1.726 (9)
S(3)—C(4)	1.738 (7)	C(1)—C(2)	1.366 (10)
C(2)—C(3)	1.444 (9)	C(3)—C(4)	1.399 (10)
C(3)—C(8)	1.425 (9)	C(4)—C(5)	1.405 (11)
C(5)—C(6)	1.359 (11)	C(6)—C(7)	1.396 (11)
C(7)—C(8)	1.409 (10)	C(8)—C(9)	1.441 (9)
C(9)—C(10)	1.423 (10)	C(9)—C(14)	1.412 (10)
C(10)—C(11)	1.409 (11)	C(11)—C(12)	1.367 (11)
C(12)—C(13)	1.390 (11)	C(13)—C(14)	1.428 (9)
C(14)—C(14 ^{iv})	1.450 (10)		
C(13)—S(1)—C(13 ^{iv})	92.0 (4)	C(7)—S(2)—C(10)	91.9 (4)
C(1)—S(3)—C(4)	92.3 (3)	S(3)—C(1)—C(2)	112.6 (5)
C(1)—C(2)—C(3)	112.0 (7)	C(2)—C(3)—C(4)	112.8 (6)
C(2)—C(3)—C(8)	129.7 (6)	C(4)—C(3)—C(8)	117.3 (6)
S(3)—C(4)—C(3)	110.3 (5)	C(3)—C(4)—C(5)	124.2 (6)
C(4)—C(5)—C(6)	117.8 (7)	C(5)—C(6)—C(7)	118.7 (7)
S(2)—C(7)—C(8)	112.3 (5)	C(6)—C(7)—C(8)	123.4 (7)
C(3)—C(8)—C(7)	117.2 (6)	C(3)—C(8)—C(9)	130.9 (6)
C(7)—C(8)—C(9)	111.5 (6)	C(8)—C(9)—C(10)	111.0 (7)
C(8)—C(9)—C(14)	131.9 (6)	C(10)—C(9)—C(14)	117.1 (6)
S(2)—C(10)—C(9)	111.9 (5)	C(9)—C(10)—C(11)	123.4 (7)
C(10)—C(11)—C(12)	117.5 (7)	C(11)—C(12)—C(13)	120.2 (7)
S(1)—C(13)—C(14)	112.1 (6)	C(12)—C(13)—C(14)	123.1 (7)
C(9)—C(14)—C(13)	116.2 (7)	C(9)—C(14)—C(14 ^{iv})	132.6 (6)
C(13)—C(14)—C(14 ^{iv})	111.2 (6)		

[1.423 (10)] < C(13)—C(14) [1.428 (9) Å]. (3) The interior angles controlling the cavity size of the molecule become larger from the terminal ring to the center: C(2)—C(3)—C(8) [129.7 (6)] < C(3)—C(8)—C(9) [130.9 (6)] < C(8)—C(9)—C(14) [131.9 (6)] < C(9)—C(14)—C(14^{iv}) [132.6 (6)°]. Trends (2) and (3) are characteristic of this molecule, while trend (1) is common to (I). In spite of these features, the distance between the facing planes is very close. The three closest non-bonded contacts are C(2)⋯C(9^{iv}), C(2)⋯C(8^{iv}) and C(3)⋯C(8^{iv}) with distances of 3.02 (1), 3.08 (1) and 3.08 (1) Å, respectively, which are significantly shorter than the van der Waals distance of carbon.

The dihedral angles of the least-squares best planes between the consecutive rings and the terminal rings are as follows: *A*–*B* 9.7 (3), *B*–*C* 9.1 (3), *C*–*D* 11.4 (3), *D*–*E* 9.2 (3) and *A*–*A*^{iv} 17.1 (3)°. The most widely overlapping portions among the rings are observed between rings *A* and *B*^{iv}, which make a dihedral angle of 22.6 (3)°. The portion from rings *A* to *E* in the molecule has the same skeletal structure as (I). It seems intriguing that the dihedral angle of 35.6 (3)° between rings *A* and *E* is meaningfully comparable with that of 36.6 (1)° in the corresponding part of (I). The maximum deviations of the skeletal atoms from each of the least-squares planes of the rings are 0.027 (7) for *A*, 0.065 (5) for *B*, 0.076 (6) for *C*, 0.099 (6) for *D* and 0.061 (5) Å for ring *E*. These deviations together with the values of the dihedral angles indicate that the moieties around rings *C* and *D* bear the largest distortion in the molecule.

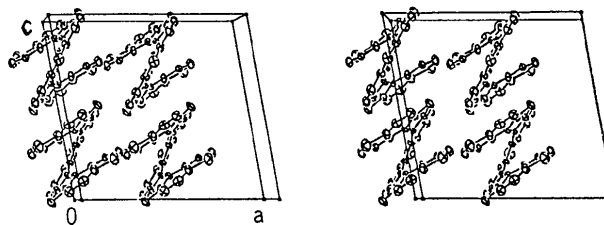
Fig. 2. Packing diagram of the molecules viewed down *b*.

Fig. 2 shows the packing diagram of the molecules in a unit cell as a projection down *b*. Alternating *P* and *M* enantiomers are piled up with an inversion center relating one to another to make a columnar stack along *c*. As a consequence of the crystal symmetry the screw axes of the molecules coincide with the *c* axis, and in addition the *C*₂ axes are parallel to the *b* axis. In consequence, the overlap between heterochiral molecules extends over large parts of the molecular planes as confirmed by viewing the molecules along *c*. The nearest approach between them is observed for rings *A* and *D*ⁱⁱⁱ [symmetry code: (iii) $-x, -y, -z$]. There are eight intermolecular non-bonded contacts within the van der Waals distances between heterochiral molecules, of which the shortest one is seen for C(3)⋯C(11ⁱⁱⁱ) at 3.26 (1) Å. Homochiral molecules are arranged on the *ab* plane so as to make a layer. The closest intermolecular non-bonded contact occurs at C(11)⋯C(11^{iv}) with a distance of 3.58 (1) Å [(vii) $-x + 0.5, -y + 0.5, -z$], and all the other contacts are over the ranges of the van der Waals distances. As a whole, this mode of packing exhibits considerable similarities to that of (I), though being quite different from those of enantiomeric carbohelicenes. The increase in the number of component rings, however, profoundly affects the differences in the molecular structure, compared with (I).

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