

## Structure of 7,16-Dithiadispiro[5.2.5.2]hexadecane

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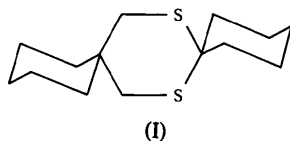
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**Abstract.**  $C_{14}H_{24}S_2$ , monoclinic,  $P2_1/n$ ,  $a = 17.912$  (5),  $b = 6.188$  (1),  $c = 12.385$  (3) Å,  $\beta = 95.14$  (4)°,  $Z = 4$ ,  $D_m = 1.24$  (1),  $D_x = 1.246$  Mg m<sup>-3</sup>. The asymmetric unit has an approximate centre of symmetry at  $\frac{1}{4}, \frac{1}{2}, \frac{1}{2}$ . The structure, which contains disordered enantiomeric molecules with site-occupancy factors of about 0.9 and 0.1 respectively, was refined to a final  $R$  of 0.048 for 1908 reflections. Both cyclohexane rings and the dithiane moiety have chair conformations.

**Introduction.** The present study is part of an investigation of the conformational behaviour of spiro compounds in the crystalline state. The title compound (I) was synthesized by Professor J. T. Wróbel and Dr K. Kabzińska (Warsaw University) in the course of research into compounds related to *Nuphar luteum* alkaloids.



Colourless, plate-shaped crystals were obtained by recrystallization from methanol. The space group was determined from the systematic absences observed on Weissenberg photographs. A crystal of dimensions about 0.3 × 0.3 × 0.3 mm was used to collect intensity data with a CAD-4 diffractometer using graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å). Reflections were measured to  $\theta = 24^\circ$  with the  $\omega$ - $2\theta$  scan mode and a  $(0.50 + 0.42 \tan \theta)^\circ$  scan range. The fluctuations in the intensities of two standard reflections were less than 4%. The intensities were corrected for Lorentz and polarization effects but not for absorption [ $\mu(\text{Mo } K\alpha) = 0.315$  mm<sup>-1</sup>]. Of the 2028 measured independent reflections, 1908 with  $|F_o| > 2\sigma(F_o)$  were used in the structure determination.

The first attempt at solving the structure by direct methods (Sheldrick, 1976) gave as a solution a

centrosymmetric image of the molecule placed at  $\frac{1}{4}, \frac{1}{2}, \frac{1}{2}$ . Least-squares refinement of this model, including disordered S atoms with site-occupancy factors of 0.5, converged to an  $R$  factor of 0.24. A detailed analysis of the three-dimensional Patterson map showed only two possible positions for the S atoms. Refinement of the ordered model of the molecule with anisotropic temperature factors and H atoms of both cyclohexane rings, as revealed by a Fourier difference map, gave a final  $R$  of 0.088. However, unreasonable C–C bond lengths in the dithiane ring (1.60 and 1.61 Å) and several residual peaks on the Fourier difference map (of about  $1 \text{ e } \text{Å}^{-3}$ ) close to C(13) and C(14) were found. Therefore, a new disordered model of the structure was considered. A Fourier difference map based on the calculated coordinates of C(13) and C(14) made it possible to estimate both the positions of the S atoms related by an approximate centre of symmetry at  $\frac{1}{4}, \frac{1}{2}, \frac{1}{2}$  to those from the main molecule, and their site-occupancy factor (about 0.1). The resulting model consisted of ordered cyclohexane rings and a disordered dithiane ring for which S(1), S(2), C(13) and C(14) were introduced with site-occupancy factor 0.9, and 0.1 for their centrosymmetric counterparts. The refinement converged at an occupancy of 0.899 (1) and  $R = 0.059$ , but bond lengths, particularly those involving C(1) and C(7), were still too long, suggesting disorder for the spiro atoms also.

In the final model we assumed two enantiomeric molecules related by a pseudocentre of symmetry at  $\frac{1}{4}, \frac{1}{2}, \frac{1}{2}$ , with initial site-occupancy factors of 0.9 and 0.1 respectively. Only non-hydrogen atoms of the minor component were introduced into the refinement as a rigid body with the program *SHELX* (Sheldrick, 1975). The final values of the discrepancy indices were  $R = 0.048$ ,  $R_w = 0.041$  and  $R_G = 0.043$  where  $R = \sum |\Delta F| / \sum |F_o|$ ,  $R_w = \sum w^{1/2} |\Delta F| / \sum w^{1/2} |F_o|$  and  $R_G = [\sum w (\Delta F)^2 / \sum w (F_o)^2]^{1/2}$ . Unit weights were used. The site-occupancy factor converged to 0.899 (1).

The H parameters of the major component were refined isotropically starting from their calculated positions. The fractional atomic coordinates obtained

Table 1. Fractional atomic coordinates ( $\times 10^5$  for S,  $\times 10^4$  for C and  $\times 10^3$  for H) and isotropic thermal parameters ( $\times 10^4$  for S and C, and  $\times 10^3$  for H)

Estimated standard deviations given in parentheses refer to the least significant digit. For non-hydrogen atoms

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$U_{eq}/U$ ( $\text{\AA}^2$ )
(a) Major component				
S(1)	17743 (4)	50946 (13)	39739 (5)	493 (4)
S(2)	24930 (4)	28751 (12)	59468 (6)	454 (4)
C(1)	3292 (1)	5868 (4)	4717 (2)	351 (7)
C(2)	3568 (1)	4049 (4)	4019 (2)	461 (7)
C(3)	3827 (2)	4854 (4)	2949 (2)	513 (7)
C(4)	4432 (2)	6554 (4)	3127 (2)	493 (7)
C(5)	4183 (2)	8416 (4)	3809 (2)	473 (7)
C(6)	3904 (2)	7639 (4)	4864 (2)	454 (7)
C(7)	1639 (1)	4133 (4)	5341 (2)	360 (7)
C(8)	1360 (1)	5958 (4)	6035 (2)	435 (7)
C(9)	1108 (2)	5139 (4)	7099 (2)	482 (7)
C(10)	511 (2)	3408 (4)	6927 (2)	474 (7)
C(11)	775 (2)	1558 (4)	6246 (2)	483 (7)
C(12)	1035 (2)	2345 (4)	5180 (2)	457 (7)
C(13)	3170 (1)	5021 (4)	5854 (2)	443 (7)
C(14)	2559 (1)	6898 (4)	4210 (2)	410 (7)
H(21)	318 (1)	292 (1)	387 (1)	49 (1)
H(22)	401 (1)	330 (1)	447 (1)	53 (1)
H(31)	337 (1)	557 (1)	250 (1)	49 (1)
H(32)	399 (1)	355 (1)	255 (1)	51 (1)
H(41)	457 (1)	714 (1)	244 (1)	50 (1)
H(42)	487 (1)	582 (1)	351 (1)	50 (1)
H(51)	378 (1)	926 (1)	337 (1)	49 (1)
H(52)	461 (1)	945 (1)	400 (1)	49 (1)
H(61)	434 (1)	700 (1)	531 (1)	49 (1)
H(62)	369 (1)	896 (1)	524 (1)	49 (1)
H(81)	94 (1)	672 (1)	561 (1)	51 (1)
H(82)	178 (1)	708 (1)	618 (1)	49 (1)
H(91)	92 (1)	644 (1)	751 (1)	52 (1)
H(92)	156 (1)	448 (1)	756 (1)	50 (1)
H(101)	8 (1)	409 (1)	655 (1)	49 (1)
H(102)	37 (1)	281 (1)	766 (1)	51 (1)
H(111)	34 (1)	50 (1)	607 (1)	50 (1)
H(112)	121 (1)	73 (1)	667 (1)	49 (1)
H(121)	129 (1)	102 (1)	477 (1)	51 (1)
H(122)	57 (1)	297 (1)	472 (1)	50 (1)
H(131)	362 (1)	444 (1)	619 (1)	54 (1)
H(132)	300 (1)	628 (1)	627 (1)	49 (1)
H(141)	244 (1)	817 (1)	464 (1)	47 (1)
H(142)	263 (1)	741 (1)	344 (1)	51 (1)
(b) Minor component refined as a rigid body (e.s.d.'s of x, y, z and $U_{eq}/U$ are 0.0002, 0.0006, 0.0003 and 0.001, respectively)				
S(1')	3195	4899	6057	49
S(2')	2475	7118	4087	50
C(1')	1673	4122	5317	50
C(2')	1398	5940	6018	50
C(3')	1140	5134	7085	50
C(4')	536	3435	6910	50
C(5')	787	1577	6226	50
C(6')	1062	2350	5169	51
C(7')	3326	5859	4693	50
C(8')	3607	4037	3999	50
C(9')	3857	4856	2933	50
C(10')	4456	6581	3106	50
C(11')	4193	8433	3789	50
C(12')	3930	7644	4851	50
C(13')	1797	4975	4173	50
C(14')	2411	3093	5844	50

in the final refinement are given in Table 1.\* The final Fourier difference map was featureless with  $0.35 \text{ e \AA}^{-3}$  as the highest peak.

**Discussion.** The thermal parameters of the atoms were analysed in terms of rigid-body motion by the method of Schomaker & Trueblood (1968), with the revised program *THMB* (Trueblood, 1977) to test the enantiomeric disorder model assumed in the structure. The centre of mass of the molecule referred to the crystal axes was in both cases the same ( $x = 0.242$ ,  $y = 0.482$ ,  $z = 0.501$ ). The values of  $\langle [\Delta^2(U_{ij})] \rangle^{1/2} = \{ \sum [\Delta^2(U_{ij})] / (N_{\text{obs}} - N_{\text{par}}) \}^{1/2}$ ,  $\Delta(U_{ij}) = U_{ij}(\text{obs}) - U_{ij}(\text{calc})$ , were  $0.0059 \text{ \AA}^2$  with  $R = \sum |\Delta U_{ij}| / \sum |U_{ij}| = 0.180$  in the model not allowing for disorder and  $0.0032 \text{ \AA}^2$  with  $R = 0.091$  in the model with enantiomeric disorder, while the  $\langle \sigma^2(U_{ij}) \rangle^{1/2}$  were  $0.0042$  and  $0.0007 \text{ \AA}^2$ , respectively. The discrepancy observed between  $\langle [\Delta^2(U_{ij})] \rangle^{1/2}$  and  $\langle \sigma^2(U_{ij}) \rangle^{1/2}$  in the latter model seems to be due to internal motion in the molecule. In both cases the eigenvalues of the **L** tensor transformed to the inertial system of the molecule and those of the **T** tensor were essentially the same. For the model with enantiomeric disorder assumed, they were  $11.63$ ,  $1.19$ ,  $0.67 \times 10^{-3} \text{ rad}^2$  and  $4.53$ ,  $3.31$ ,  $2.48 \times 10^{-2} \text{ \AA}^2$ , respectively. Corresponding eigenvectors also had similar orientations for the models. The long axes of both the **L** and **T** ellipsoids were directed roughly along the long axis of the molecule.

Bond lengths and angles of the major component are given in Fig. 1 (those for the minor component are in Table 2). The S—C bond lengths are in the range  $1.798$ – $1.831 \text{ \AA}$  ( $1.804$ – $1.837 \text{ \AA}$  after correction) and are in good agreement with those found in 1,3-dithiane substituted at position 2 [ $1.79$ – $1.83 \text{ \AA}$ : Kalfi & Romers (1966);  $1.80$ – $1.82 \text{ \AA}$ : Depmeier & Jarchow (1975*a,b*)]. The average value of the C—C bond lengths, except those involving spiro atoms, in the cyclohexane rings is  $1.519 \text{ \AA}$  (corrected value  $1.524 \text{ \AA}$ ). This is the same as found in unsubstituted cyclohexane at  $115 \text{ K}$  ( $1.52 \text{ \AA}$ ) by Kahn, Fourme, André & Renaud (1973). The C—C bond lengths involving the spiro atoms have an average value of  $1.539 \text{ \AA}$  (corrected  $1.546 \text{ \AA}$ ), close to the C—C bond distance characteristic of paraffinic hydrocarbons ( $1.541 \text{ \AA}$ , *Molecular Structures and Dimensions*, 1972). The configuration of the molecule is described by the torsion angles given in Fig. 1 and by the puckering parameters (Cremer & Pople, 1975) summarized in Table 3. The mean values of the endocyclic torsion angles in cyclohexane rings *A* and *B* are  $53.6$

\* Lists of structure factors and thermal parameters are available from the authors on request and have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36425 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

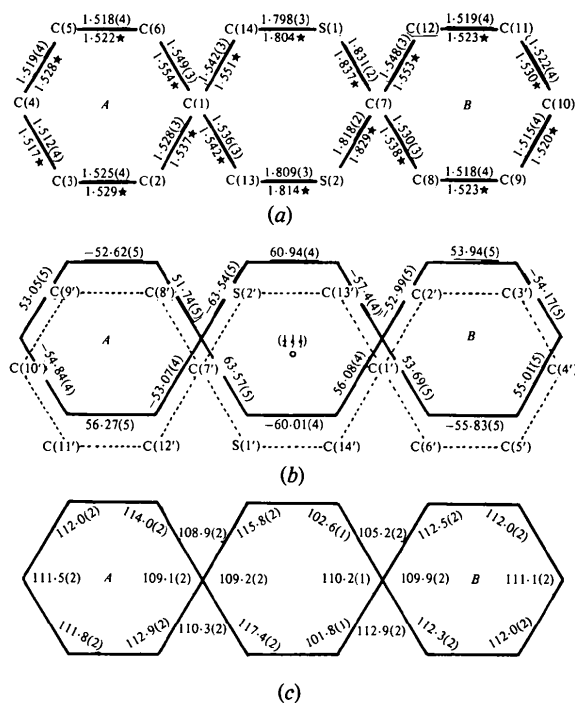


Fig. 1. (a) Atom-numbering scheme and bond lengths (Å) of the major component. E.s.d.'s are given in parentheses, the values marked with an asterisk are corrected for thermal libration. The C–H bond lengths are in the range 0.95 (1)–1.09 (1) Å with an average value of 1.01 Å. (b) Endocyclic torsion angles (°) with e.s.d.'s in parentheses. Also shown is the position and atom-numbering scheme of the minor component drawn with dashed lines. (c) Valence angles (°) with e.s.d.'s in parentheses. Missing angles are C(6)C(1)C(13) 106.9 (2), C(2)C(1)C(14) 112.4 (2), S(1)C(7)C(8) 110.9 (2) and S(2)C(7)C(12) 107.4 (2)°. The angles of CCH and HCH are in the range 113 (1)–106 (1)° with an average value of 109°.

Table 2. Bond lengths (Å) and valence angles (°) of the minor component

C(1')–C(2')	1.530 (5)	C(7')–S(2')	1.814 (5)
C(2')–C(3')	1.522 (6)	S(2')–C(13')	1.808 (5)
C(3')–C(4')	1.510 (5)	C(13')–C(1')	1.546 (5)
C(4')–C(5')	1.519 (5)	C(7')–C(8')	1.530 (5)
C(5')–C(6')	1.517 (6)	C(8')–C(9')	1.518 (6)
C(6')–C(1')	1.549 (5)	C(9')–C(10')	1.515 (5)
C(1')–C(14')	1.556 (5)	C(10')–C(11')	1.524 (5)
C(14')–S(1')	1.796 (5)	C(11')–C(12')	1.517 (6)
S(1')–C(7')	1.826 (5)	C(12')–C(7)	1.546 (5)
C(2')C(1')C(13')	110.4 (3)	C(4')C(5')C(6')	112.2 (3)
C(2')C(1')C(14')	111.6 (3)	C(3')C(4')C(5')	111.3 (3)
C(6')C(1')C(13')	106.9 (3)	C(2')C(3')C(4')	111.9 (3)
C(6')C(1')C(14')	108.9 (3)	C(1')C(2')C(3')	112.9 (3)
C(13')C(1')C(14')	109.8 (3)	C(7')C(8')C(9')	112.3 (3)
C(6')C(1')C(2')	109.1 (3)	C(8')C(9')C(10')	111.8 (3)
S(1')C(7')C(12')	105.2 (3)	C(9')C(10')C(11')	111.0 (3)
S(1')C(7')S(2')	110.4 (3)	C(11')C(12')C(7')	112.9 (3)
S(1')C(7')C(8')	110.9 (3)	C(10')C(11')C(12')	112.0 (3)
C(8')C(7')C(12')	109.6 (3)	C(1')C(14')S(1')	115.5 (3)
C(8')C(7')S(2')	113.0 (3)	C(1')C(13')S(2')	117.1 (3)
C(12')C(7')S(2')	107.3 (3)	C(7')S(2')C(13')	101.8 (2)
C(1')C(6')C(5')	113.7 (3)	C(7')S(1')C(14')	103.3 (2)

and 54.3°, respectively. For comparison, the value found from an electron diffraction study of gaseous cyclohexane by Geise, Buys & Mijlhoff (1971) is 55.9°. Both cyclohexane rings as well as the dithiane ring have chair conformations. In the case of the dithiane ring, the chair conformation can be considered as slightly distorted in the direction of a boat conformation; in the cyclohexane rings, the small distortion from pure chair is towards a twist-boat conformation.

The packing of the major component is shown in Fig. 2. The spindle-like shape of the molecule (Fig. 3) seems to be conducive to the enantiomeric disorder in the structure. This type of disorder was observed also in the crystal structure of *exo*-8,9,10-trinorborn-2-yl *p*-toluenesulphonate (Altona & Sundaralingam, 1972), where the ratio of the site occupancies of the

Table 3. Puckering parameters

	Cyclohexane A	Cyclohexane B	Dithiane
$q_2$ (Å)	0.022 (3)	0.009 (3)	0.067 (2)
$\phi_2$ (°)	80 (7)	79 (16)	171 (2)
$q_3$ (Å)	0.544 (3)	0.552 (3)	0.699 (2)
$Q$ (Å)	0.545 (3)	0.553 (3)	0.703 (2)
$\theta$ (°)	2.3 (3)	1.0 (3)	5.5 (2)

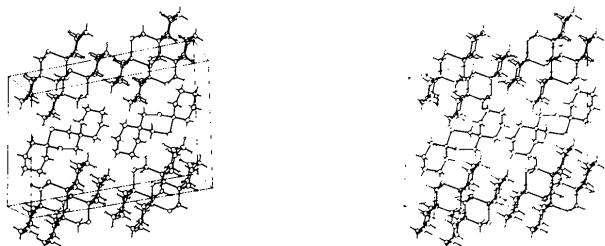


Fig. 2. Packing diagram (ORTEP; Johnson, 1965) involving only the major component. The origin is at the front lower-left corner. The *a* axis points to the right and *c* points up.

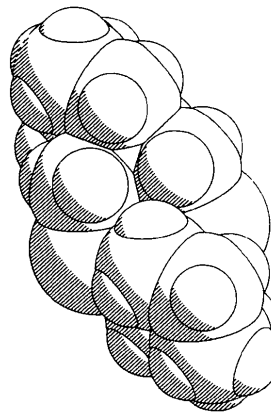


Fig. 3. A PLUTO (Motherwell, 1972) drawing of the molecular shape. Van der Waals radii of the C, S and H atoms are assumed to be 1.5, 1.9 and 1.1 Å, respectively.

enantiomers was 0.76:0.24 in an asymmetric unit of space group  $P\bar{1}$ , and in the structure of 3-(*o*-chlorophenylimino)camphor (Foulon, Baert & Fouret, 1979), where the ratio of the enantiomer site-occupancy factors was 0.72:0.28 in an asymmetric unit of space group  $P2_1/a$ . Very similar enantiomeric disorder was found for the spiro compounds showing a 'spiro-coplanar' conformation (Stadnicka & Lebioda, 1979; Stadnicka, Lebioda & Grochowski, 1979) with site-occupancy factors of 0.5.

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#### References

- ALTONA, C. & SUNDARALINGAM, M. (1972). *Acta Cryst.* **B28**, 1806–1816.
- CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- DEPMEIER, W. & JARCHOW, O. H. (1975a). *Acta Cryst.* **B31**, 939–944.
- DEPMEIER, W. & JARCHOW, O. H. (1975b). *Acta Cryst.* **B31**, 945–949.
- FOULON, M., BAERT, F. & FOURET, R. (1979). *Acta Cryst.* **B35**, 683–688.
- GEISE, H. J., BUYS, H. R. & MIJLHOFF, F. C. (1971). *J. Mol. Struct.* **9**, 447–454.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KAHN, R., FOURME, R., ANDRÉ, D. & RENAUD, M. (1973). *Acta Cryst.* **B29**, 131–138.
- KALFF, H. & ROMERS, C. (1966). *Acta Cryst.* **20**, 490–496.
- Molecular Structures and Dimensions* (1972). Vol. A1, edited by O. KENNARD. Utrecht: Oosthoek.
- MOTHERWELL, W. D. S. (1972). *PLUTO*. A program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- SHELDRICK, G. M. (1975). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.
- SHELDRICK, G. M. (1976). *SHELX 76*. Program for crystal structure determination. Univ. of Cambridge, England.
- STADNICKA, K. & LEBIODA, Ł. (1979). *Acta Cryst.* **B35**, 1517–1519.
- STADNICKA, K., LEBIODA, Ł. & GROCHOWSKI, J. (1979). *Acta Cryst.* **B35**, 2763–2765.
- TRUEBLOOD, K. N. (1977). Abstr. 4th Eur. Crystallogr. Meet., Oxford. Paper P136.

*Acta Cryst.* (1982). **B38**, 988–991

## The Structure of 7,8,8a,9,10,16c-Hexahydrophenanthro[3,4-*c*]phenanthrene

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**Abstract.**  $C_{26}H_{22}$ , orthorhombic,  $Pbca$ ,  $a = 18.338$  (2),  $b = 23.460$  (2),  $c = 8.330$  (1) Å,  $Z = 8$ ,  $D_c = 1.24$ ,  $D_m = 1.18$  Mg m<sup>-3</sup>. The structure was refined to  $R = 0.057$  for 2352 reflections. The molecule can be regarded as a composite in which two 1,2-substituted naphthalene units are linked to hydrogenated rings. The central hydrogenated rings have the half-boat half-chair conformation. The dihedral angle between two naphthalene rings is 68.1°. No intermolecular distance shorter than a van der Waals contact was observed.

**Introduction.** It has been widely accepted that highly resolved electronic spectra in *n*-alkane matrices (Shpolskii spectra) can be found only in the case of

planar organic molecules (Nurmukhametov, 1969). So far, only a few exceptions to this rule have been reported. One of the authors has observed highly resolved emission spectra of 7,8,8a,9,10,16c-hexahydrophenanthro[3,4-*c*]phenanthrene\* (hexahydrohexahelicene, HHHH) (Palewska & Ruziewicz, 1979). We believe that this was one of a very few examples of the Shpolskii effect found in a molecule consisting of planar 'active' fragments linked to non-planar 'inactive' ones. In connection with these spectroscopic studies, it was necessary to determine the molecular structure.

\* Systematic numbering. The crystallographic numbering used throughout the paper is shown in Fig. 1.