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The Crystal Structure of 2-Isopropylidene-1,1,7,7,9,9-hexamethyl-3,5,10,11-tetrathiadispiro[3.1.3.2]undecane-8-thione

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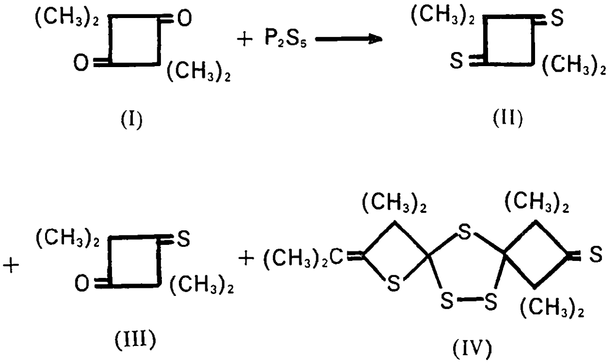
2-Isopropylidene-1,1,7,7,9,9-hexamethyl-3,5,10,11-tetrathiadispiro[3.1.3.2]undecane-8-thione ($C_{16}H_{24}S_5$) is orthorhombic, space group $P2_12_12_1$, with $a = 10{\cdot}751$ (1), $b = 25{\cdot}028$ (2), and $c = 7{\cdot}107$ (2) Å, $Z = 4$. Data were collected on a manual diffractometer with nickel-filtered Cu $K\alpha$ radiation. 2388 independent reflections were observed. The structure was solved by manual symbolic addition, tangent-formula, and difference-Fourier techniques. Absorption and extinction corrections were made. The structure was refined by full-matrix anisotropic least-squares methods to a final weighted R of 0·051. All three rings are non-planar.

Introduction

The title compound is observed as a by-product in the reaction of tetramethyl-1,3-cyclobutanedione (I) with P_2S_5. The main products are tetramethyl-1,3-cyclobutanedithione (II) and the mixed ketone–thione compound (III) (Elam & Davis, 1967).



These compounds are unusual in that they contain carbon–sulfur double bonds but show no tendency to polymerize at room temperature. As a contribution to understanding the geometry of these compounds, we have previously reported the structure of the dithione (II) (Shirrell & Williams, 1973). We are also studying the structure of the mixed ketone-thione (III). We report here the structure of (IV).

Experimental

Crystals of 2-isopropylidene-1,1,7,7,9,9-hexamethyl-3,5,10,11-tetrathiadispiro[3.1.3.2]undecane-8-thione ($C_{16}H_{24}S_5$) were prepared by the method of Elam & Davis (1967) and were recrystallized from hexane. The melting point, n.m.r. and infrared spectra confirmed their identity.

The crystal used was a rectilinear orange/pink polyhedron of approximate dimensions 0·14 × 0·19 × 0·18 mm. It was mounted in a thin-walled capillary with the 0·18 mm axis (**c**) parallel to the walls of the capillary tube.

Approximate cell dimensions, systematic absences ($h00$: h odd; $0k0$; k odd; $00l$: l odd), and orthorhombic symmetry were noted from photographic and diffractometer data taken with nickel-filtered Cu $K\alpha$ radiation. The space group is thus $P2_12_12_1$. With nickel-filtered Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5424$ Å), 13 reflection angles in the back-reflection region were accurately determined with a scintillation counter. The lattice constants were found from a least-squares fit (Williams, 1964) to these data with the extrapolation function of Nelson & Riley (1945). The values obtained for room temperature (23 °C) were $a = 10{\cdot}751$ (1), $b = 25{\cdot}028$ (2) and $c = 7{\cdot}107$ (2) Å. The volume of the unit cell is 1912·34 Å^3, and the calculated density for four molecules of $C_{16}H_{24}S_5$ (F.W. 376·46) is 1·31 g cm^{-3}. The observed density, measured by flotation in an aqueous solution of potassium iodide, was 1·29 g cm^{-3}.

The intensities of 2388 independent reflections (up to $2\theta = 160°$) were measured on a Siemens manual diffractometer with nickel-filtered Cu $K\alpha$ radiation. The diffraction unit was equipped with a single-crystal orienter, scintillation counter and a pulse-height analyzer. Intensities were measured by the θ–2θ scan technique. For 2θ values less than 120°, the scan rate was 1° min^{-1}. For 2θ values greater than 120°, the scan rate was 2° min^{-1}. The background was measured before and after each reflection. The take-off angle was 1·7° and the receiving aperture was 4 × 4 mm. A check of the intensities of several reflections, selected as standards, showed them to remain constant within statistical and instrumental fluctuations. The Lorentz and polarization corrections were made in the usual manner. For Cu $K\alpha$ X-rays, the linear absorption coefficient is 51·99 cm^{-1}. An absorption correction was made with a modification of *GONO*, a computer program originally written by W. C. Hamilton. The maximum absorption correction was 1·33 [absorption correction being defined as F(corrected)/F(observed)].

The standard deviation of each intensity measurement was estimated from

$$\sigma^2(I) = C_T + C_B + (0{\cdot}05 \times C_T)^2 + (0{\cdot}05 \times C_B)^2$$

where C_T is the total and C_B the background counts. The error in the structure factor, $\sigma(F_o)$, was calculated from $\sigma(I)$ by the finite difference method (Williams & Rundle, 1964). If $C_T < C_B$, then F_o was set to zero. In the least-squares refinement the weight of a reflection was $1/[\sigma(F_o)]^2$.

Structure determination

The structure factors were scaled by Wilson's (1942) method and were converted to normalized structure factors by *FAME* (Dewar, 1970) for use in the phase determination. Three origin-determining and one enantiomorph-determining reflections were chosen (Karle & Hauptman, 1956). A manual symbolic addition procedure was employed with the signs of the four chosen reflections (Karle & Karle, 1966). This process was facilitated by application of the computer program *DP*-3. With this procedure it was possible to determine the signs of eight of the 50 largest E values. The smallest E chosen had a value of 2·06. The signs of these eight reflections were now expanded by the tangent formula (Karle & Hauptman, 1956) to give the phases of approximately 300 reflections ($E \geq 1{\cdot}45$). A computer program, *DP*-5, was used in this process. The E map calculated with these reflections clearly showed fragments of the molecule. The top four peaks were assigned to S(3), S(5), S(10), and S(11) and were at least three times higher than any other peak on the E map. It was possible later to identify the sixth highest peak as S(19). The fifth highest peak was spurious.

With S(3), S(5), S(10), and S(11) approximately

Table 1. *Final anisotropic positional and thermal vibrational parameters* (× 10^4) *and their standard deviations*

$$T = \exp\,[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	3366 (4)	−2980 (2)	−3227 (7)	61 (3)	10 (1)	184 (8)	1 (1)	10 (5)	−2 (2)
C(2)	3397 (4)	−3446 (2)	−1840 (8)	70 (3)	10 (1)	249 (11)	0 (1)	−2 (6)	1 (2)
S(3)	3465 (1)	−3054 (1)	213 (2)	108 (1)	12 (1)	179 (2)	−2 (1)	1 (2)	8 (1)
C(4)	3235 (4)	−2544 (1)	−1625 (8)	66 (3)	9 (1)	177 (9)	0 (1)	1 (5)	−2 (2)
S(5)	4354 (1)	−2002 (1)	−1728 (2)	49 (1)	9 (1)	260 (3)	−1 (1)	6 (1)	−2 (1)
C(6)	3379 (4)	1427 (2)	1127 (7)	59 (3)	9 (1)	196 (9)	2 (1)	−16 (5)	2 (2)
C(7)	4094 (5)	−881 (2)	1533 (8)	10 (1)	235 (12)	235 (12)	−5 (1)	−5 (6)	4 (2)
C(8)	4118 (5)	−800 (2)	588 (9)	92 (5)	13 (1)	238 (13)	−6 (1)	8 (6)	−7 (2)
C(9)	3293 (5)	−1273 (2)	1045 (8)	88 (4)	11 (1)	198 (10)	−1 (1)	−12 (6)	−2 (2)
S(10)	1935 (1)	−1539 (1)	−2400 (2)	61 (1)	13 (1)	245 (3)	3 (1)	−28 (1)	−1 (1)
S(11)	1686 (1)	−2268 (1)	−1163 (2)	53 (1)	12 (1)	253 (3)	−3 (1)	26 (1)	−10 (1)
C(12)	2297 (6)	−2974 (3)	−4642 (9)	93 (5)	20 (1)	219 (12)	2 (2)	−29 (6)	−15 (3)
H(12*a*)	1745	−3312	−4462			Same as C(12)			
H(12*b*)	1755	−2637	−4468			Same as C(12)			
H(12*c*)	2651	−2978	−6008			Same as C(12)			
C(13)	4613 (5)	−2937 (2)	−4271 (8)	83 (4)	15 (1)	204 (11)	4 (1)	38 (6)	1 (2)
H(13*a*)	5322	−2908	−3292			Same as C(13)			
H(13*b*)	4573	−2584	−5045			Same as C(13)			
H(13*c*)	4720	−3279	−5095			Same as C(13)			
C(14)	3361 (11)	−4256 (3)	−3850 (15)	223 (13)	14 (1)	446 (26)	2 (3)	75 (17)	−25 (4)
H(14*a*)	2857	−4022	−4798			Same as C(14)			
H(14)*b*	4267	−4305	−4323			Same as C(14)			
H(14*c*)	2951	−4635	−3658			Same as C(14)			
C(15)	3419 (6)	−2976 (2)	−1988 (11)	116 (6)	10 (1)	348 (18)	2 (2)	31 (9)	5 (3)
C(16)	3510 (9)	−4321 (3)	−308 (14)	165 (9)	13 (1)	462 (26)	3 (2)	47 (14)	34 (4)
H(16*a*)	4322	−4546	−375			Same as C(16)			
H(16*b*)	2755	−4565	−216			Same as C(16)			
H(16)*c*	3555	−4077	894			Same as C(16)			
C(17)	5378 (6)	−914	−2425 (10)	105 (5)	15 (1)	256 (13)	−13 (2)	41 (7)	3 (3)
H(17*a*)	5548	−555	−3176			Same as C(17)			
H(17*b*)	6053	−962	−1304			Same as C(17)			
H(17*c*)	5398	−1254	−3332			Same as C(17)			
C(18)	3306 (7)	−462 (2)	−2536 (11)	142 (7)	12 (1)	339 (17)	1 (2)	−34 (11)	17 (3)
H(18*a*)	2477	−402	−1811			Same as C(18)			
H(18*b*)	3791	−106	−2626			Same as C(18)			
H(18*c*)	3098	−597	−3898			Same as C(18)			
S(19)	4820 (2)	−371 (1)	−1874 (3)	176 (3)	27 (1)	293 (5)	−36 (1)	17 (3)	−29 (1)
C(20)	3806 (8)	−1671 (3)	2448 (10)	173 (9)	18 (1)	224 (13)	10 (2)	−45 (10)	5 (3)
H(20*a*)	3883	−1492	3765			Same as C(20)			
H(20*b*)	3232	−2000	2522			Same as C(20)			
H(20*c*)	4695	−1790	2005			Same as C(20)			
C(21)	2001 (6)	−1080 (2)	1681 (11)	94 (5)	19 (1)	321 (17)	−3 (2)	59 (8)	−21 (3)
H(21)*a*	1729	−1270	2919			Same as C(21)			
H(21*b*)	1981	−669	1871			Same as C(21)			
H(21*c*)	1330	−1178	629			Same as C(21)			

located, the $R' = [\sum(F_o - |F_c|/K)^2/\sum F_o^2]^{1/2}$ was 0·394 for all data, excluding zeros. A difference map was calculated with all reflections for which $F_{\text{calc}}(hkl) \geq 0{\cdot}25 \times F_{\text{obs}}(hkl)$. From this map it was possible to place S(19) and 6 of the 16 carbon atoms. This reduced R' to 0·294 for all data. A second difference map, with the previous restrictions, revealed the positions of the remaining 10 carbon atoms. Isotropic least-squares refinement with a modification of the full-matrix program of Busing, Martin & Levy (1962) resulted in $R' =$ 0·147 for all data. The function minimized was $\sum(F_o - |F_c|/K)^2/\sigma^2(F_o)$. The scattering factors of Hanson, Herman, Lea & Skillman (1964) were used for S and C.

After several least-squares cycles with anisotropic temperature factors R' dropped to 0·065. A difference map was calculated with all data and 15 of the 24 hydrogen atoms were located. Positions for the remaining 9 hydrogen atoms [H(12*a*), H(12*b*), H(12*c*), H(13*a*), H(13*b*), H(13*c*), H(21*a*), H(21*b*) and H(21*c*)] were calculated. The anisotropic temperature factors for all hydrogen atoms were set equal to that of the methyl carbon to which they are bonded. No attempt was made to vary their coordinates or temperature factors. The scattering factors of Stewart, Davidson & Simpson (1965) were used for H. This lowered R' to 0·058. All data were corrected for secondary extinction by the method of Zachariasen (1963). The value of the extinction coefficient was $6{\cdot}3 \times 10^{-7}$. The maximum change $[(F_o - |F_{\text{corr}}|) \times 100/F_o]$ in F_o was 15%. This correction lowered R' to 0·056.

Table 2. *The observed and calculated structure factors*

The values of $|k \times F_o|$ and F_c are given.

[illegible]

Table 2 (*cont.*)

[illegible]

Another difference map with all reflections revealed that 3 out of the 9 calculated hydrogen positions were slightly incorrect: H(13*a*), H(13*b*), and H(13*c*). The observed positions from the difference map were substituted for the calculated positions. Two further cycles of anisotropic full-matrix least-squares refinement were necessary before all parameters shifted less than 0·1σ, and the final weighted R was 0·051. A difference map based on the final model showed random fluctuations from 0·38 e Å^{-3} to $-$0·20 e Å^{-3}.

The final atomic parameters are listed in Table 1 with their estimated standard deviations. A list of calculated and observed structure factors is given in Table 2.

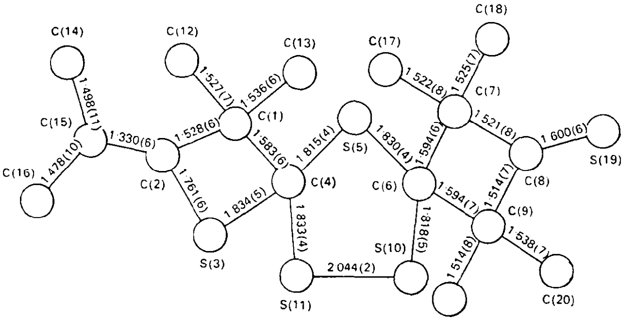


Fig. 1. The bond distances (Å) and their estimated standard deviation.

Discussion

Fig. 1 shows the molecular structure, bond distances, and atomic numbering system. Table 3 gives the bond angles.

Table 3. *The bond angles (°) and their estimated standard deviations*

C(2)C(1)C(4)	93·7 (3)
C(2)C(1)C(12)	116·7 (4)
C(4)C(1)C(12)	113·5 (4)
C(2)C(1)C(13)	110·3 (4)
C(4)C(1)C(13)	112·1 (4)
C(12)C(1)C(13)	109·7 (4)
C(1)C(2)S(3)	96·3 (3)
S(3)C(2)C(15)	128·4 (5)
C(11)C(2)C(15)	135·3 (6)
C(2)S(3)C(4)	78·0 (2)
C(1)C(4)S(3)	91·2 (2)
C(1)C(4)S(5)	115·3 (3)
S(3)C(4)S(5)	117·2 (2)
C(1)C(4)S(11)	118·0 (3)
S(3)C(4)S(11)	104·8 (2)
S(5)C(4)S(11)	109·1 (2)
C(4)S(5)C(6)	101·4 (2)
S(5)C(6)C(7)	110·8 (3)
S(5)C(6)C(9)	116·7 (3)
C(7)C(6)C(9)	89·7 (4)
S(5)C(6)S(10)	104·6 (2)
C(7)C(6)S(10)	116·9 (3)
C(9)C(6)S(10)	118·0 (3)
C(6)C(7)C(8)	86·8 (4)
C(6)C(7)C(17)	117·8 (4)
C(8)C(7)C(17)	113·9 (4)
C(6)C(7)C(18)	114·0 (4)
C(8)C(7)C(18)	112·4 (4)
C(17)C(7)C(18)	110·2 (5)
C(7)C(8)C(9)	95·6 (4)
C(9)C(18)S(19)	132·7 (5)
C(11)C(8)S(19)	131·6 (4)
C(6)C(9)C(8)	93·0 (4)
C(6)C(9)C(20)	117·2 (4)
C(8)C(9)C(20)	116·2 (5)
C(6)C(9)C(21)	114·4 (5)
C(8)C(9)C(21)	110·3 (4)
C(20)C(9)C(21)	110·0 (6)
C(6)S(10)S(11)	92·0 (1)
C(4)S(11)S(10)	98·1 (1)
C(2)C(15)C(14)	122·3 (7)
C(2)C(15)C(16)	121·4 (7)
C(14)C(15)C(16)	116·3 (6)

The average bond distance for the six CH_3–C bonds to the four-membered rings of the molecule is 1·527 Å. The CH_3–C–CH_3 angles average 110·0°, which is smaller than expected in view of the internal ring angles of approximately 90°. In every case the rotation angles of the methyl groups are such that the hydrogen atoms are approximately in the staggered conformation with respect to each other.

In the four-membered rings the average C–C distance not involving a spiro carbon is 1·521 Å. On the other hand, the average of the three C–C distances involving a spiro carbon is 1·590 Å. Since each spiro carbon is bonded to at least two sulfurs, the steric interaction with the sulfur atoms may be a factor in the bond lengthening.

The C–S bond lengths in the molecule lie between 1·761 (5) and 1·833 (5) Å. With one exception, these bond lengths are in good agreement with previously reported values. Cox & Jeffrey (1951) obtained a mean value of 1·812 Å for the C–S single bond length from a list of eleven molecules. This is also the value reported by Pauling (1960) for the sum of the covalent radii of sulfur and carbon.

The exceptional bond is between C(2) and S(3), with length 1·761 Å. However, we note that C(2) is double-bonded to C(15). It is commonly observed that a C–C single bond is shortened when one of the carbons is double-bonded to another carbon (Lide, 1962). The same effect appears to exist for C–S bonds.

The thione bond length, 1·600 (6) Å, is also very close to the value predicted by Pauling and to the observed C=S distance of 1·599 (7) Å in II (Shirrell & Williams, 1973). The disulfide bond length in the central trithiolane ring is 2·044 (2) Å. The observed CSS/SSC dihedral angle of this ring is 50·2°.

Hordvik (1966) has shown that the CSS/SSC dihedral angle influences the S–S bond length. The normal dihedral angle of 90° corresponds to a S–S bond length of 2·03 Å, while a zero dihedral angle (planar) corresponds to a S–S bond length of 2·10 Å. For our observed dihedral angle, the predicted S–S distance is 2·07 Å, showing only moderate agreement with Hordvik's correlation.

The cyclobutane, thiacyclobutane, and trithiolane rings are all nonplanar. The equations of the best least-squares planes are, for the cyclobutane ring:

$$0{\cdot}8204X-0{\cdot}5657Y+0{\cdot}0832Z=4{\cdot}8314; \qquad (1)$$

for the thiacyclobutane ring:

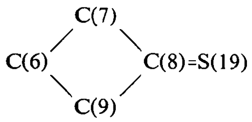
$$0{\cdot}9979X-0{\cdot}0365Y-0{\cdot}0545Z=3{\cdot}3892; \qquad (2)$$

and for the trithiolane ring:

$$-0{\cdot}0398X+0{\cdot}0684Y+0{\cdot}9969Z=1{\cdot}5993\,. \qquad (3)$$

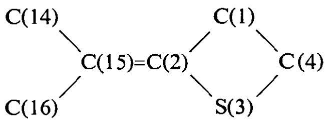
The thione sulfur was included in the calculation of the cyclobutane ring, and the isopropenyl group in the calculation of the thiacyclobutane ring. Table 4 shows the distances of the constituent atoms from the least-squares planes.

Table 4. *Distances of atoms from least-squares planes*



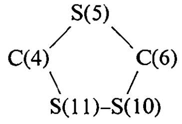
Equation (1)	
C(6)	0·103 Å
C(7)	−0·064
C(8)	−0·032
C(9)	−0·063
S(19)	0·056

Table 4 (*cont.*)



Equation (2)

C(1)	0·075 Å
C(2)	0·011
S(3)	0·041
C(4)	−0·088
C(14)	−0·023
C(15)	−0·008
C(16)	−0·007



Equation (3)

C(4)	−0·126 Å
S(5)	−0·154
C(6)	0·412
S(10)	−0·448
S(11)	0·315

The cyclobutane ring has a dihedral angle, C(7)C(8)C(9)/C(7)C(6)C(9), of 169·7 (5)°. Simple cyclobutane compounds have been found to exist in both puckered and planar conformations. Their dihedral angles range from 149 to 180°. Compound II has a planar ring (Shirrell & Williams, 1973).

The thiacyclobutane ring is also nonplanar, with an observed C(1)C(2)S(3)/S(3)C(4)C(1) dihedral angle of 170·3 (4)°. This puckered conformation is consistent with those reported in several other recent X-ray structural investigations (Andreetti, Cavalca & Sgarabotto, 1971; Nakai & Koyama, 1971, 1972). Durig & Lord (1966) have reported that a spectroscopic investigation of trimethylene sulfide (thiacyclobutane) gave a dithedral angle of 152° in the gas phase.

The trithiolane ring has four atoms approximately planar, S(11)C(4)S(5)C(6), and the fifth, S(10), is 1·08 Å out of the plane. This type of conformation is commonly found in saturated five-membered rings. Karle, Estlin & Britts (1967) have noted that the -CSSC- atoms will attempt to arrange themselves in the hydrogen peroxide configuration (Abrahams, Collin & Lipscomb, 1951), but are constrained by the ring closure. Casalone & Mugnoli (1971) found a CSS/SSC dihedral angle of 42° in the diphenylhydrazone of 1,2,4-trithiolane-3,5-dione.

The C–H bond distances lie in the range 1·032 to 1·067 Å; and all bond angles involving the hydrogen atoms are approximately tetrahedral, as obtained from the difference maps.

The thermal ellipsoids are shown in Fig. 2. All thermal motion seems to be quite normal, with the usual increase for terminal atoms and for atoms near the periphery of the molecule.

Fig. 3 shows how the molecules pack in the unit cell. The long molecular axis is parallel to **b**. Each molecule is in contact with 12 surrounding molecules, and all intermolecular contacts appear to be at normal van der Waals distances. Table 5 shows the shortest contact distances, classified by symmetry type.

Table 5. *Short intermolecular distances* (Å) *classified by symmetry type*

The specified symmetry operation is applied to the second atom of the pair. All distances are included up to the following radii: hydrogen 1·20, carbon 1·70, and sulfur 1·85 Å.

1. Translation **c**
   S(3)–H(12*c*) 2·83
2. Twofold screw axis, operation: $\frac{1}{2}-x, -y, \frac{1}{2}+z$
   H(18*b*)–H(21*b*) 2·14
3. Twofold screw axis, operation: $\frac{1}{2}-x, -y, \frac{1}{2}+z$; translation −**b**, −**c**
   H(14*c*)–H(16*b*) 2·40
4. Twofold screw axis, operation: $\frac{1}{2}+x, \frac{1}{2}-y, -z$; translation −**b**, −**c**
   H(12*a*)–H(17*c*) 2·40
5. Twofold screw axis, operation: $\frac{1}{2}+x, \frac{1}{2}-y, -z$; translation −**a**, −**b**, −**c**
   S(10)–H(13*c*) 3·01
6. Twofold screw axis, operation: $\frac{1}{2}+x, \frac{1}{2}-y, -z$; translation −**a**, −**b**
   S(3)–S(11) 3·62

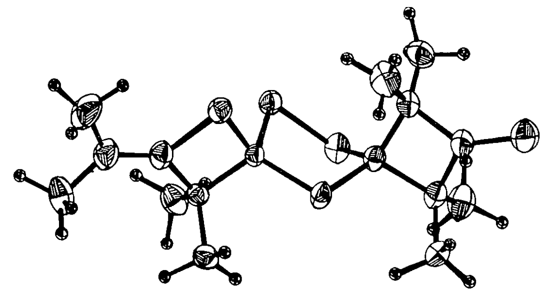


Fig. 2. The molecular structure. The thermal ellipsoids (Johnson, 1965) enclose a probability density of 0·40. For clarity the hydrogen atoms have been plotted as small spheres.

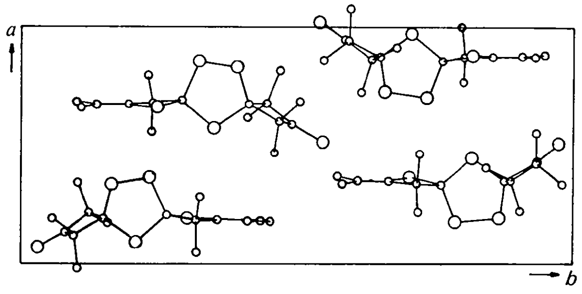


Fig. 3. The molecular packing in the crystal.

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Molekül- und Kristallstruktur des *trans,trans*-Perhydro-dibenzo[*d,i*][1,2,3,6,7,8]hexathiecins

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The crystal structure of *trans,trans*-perhydrodibenzo[*d,i*][1,2,3,6,7,8]hexathiecine has been determined by direct methods and refined by least-squares calculations. The final R index is 4·8 % for 1302 observed reflexions. The crystals are monoclinic, space group $P2_1/n$. The unit-cell dimensions are: $a=10{\cdot}77$, $b=9{\cdot}10$, $c=8{\cdot}34$ Å, $\beta=99{\cdot}6_5°$. The asymmetric unit is half a molecule. All hydrogen atoms have been located. The ten-membered ring has a conformation analogous to that of cyclodecane. The positions of the sulphur atoms bound to carbon atoms are transdiaxial with respect to the cyclohexane ring. The C–S and S–S bond lengths are indicative of single bonding.

Einleitung

Im Rahmen unserer präparativen Arbeiten wurde eine grosse Zahl neuer heterocyclischer Ringe synthetisiert, die kettenförmig gebundenen Schwefel enthalten. Da zum Teil die Strukturen der entsprechenden Kohlenstoffverbindungen oder von Derivaten derselben bereits bekannt sind, schien es uns interessant, die Strukturen dieser neuen Verbindungen zu klären, um über die Veränderungen, die durch den Einbau der Schwefelatome entstehen, Aussagen machen zu können. In der folgenden Arbeit – eine vorläufige Mitteilung erschien bereits (Lemmer, Fehér, Gieren, Hechtfischer & Hoppe, 1970) – werden die Röntgenstrukturuntersuchungen an *trans,trans*-Perhydro-dibenzo[*d, i*] [1,2,3,6,7,8]hexathiecin ($C_{12}H_{20}S_6$) (Fehér & Degen, 1967)