

4-methylenespiro[2.3]heptane derivatives (Boese, 1992) with fixed *s-cis*-orientations of the CP rings and double bonds. The opposing influence of strain forces, leading to the distal bond elongation in the CP ring, and the conjugation of the CP molecular orbital with the double bond leading to this bond shortening results in the almost undisturbed CP ring geometry in this class of compound, as well as in molecule (1). This effect is the same for molecules with either *s-cis* or *s-trans*-orientation [*e.g.* (1)] of the double bond and CP ring.

The small lengthening of the C(2)—C(5) bond is probably also caused by the strain in the bicyclic system. The lengths of the double bonds in the vinyl substituted CP ring are not sensitive to conjugation (Allen, 1981), and therefore the absence of any elongation of the C(2)=C(3) bond distance in (1) is not unusual. The other geometrical parameters of (1) are unexceptional.

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## Structure of 4,5-(Pentasulfane-1,5-diyl)-1,3-dithiole-2-thione

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**Abstract.** [1,3]Dithiolo[4,5-*f*]pentathiepine-7-thione, C<sub>3</sub>S<sub>8</sub>, *M<sub>r</sub>* = 292.5, triclinic, *P* $\bar{1}$ , *a* = 4.4204 (5), *b* = 9.136 (1), *c* = 11.762 (2) Å,  $\alpha$  = 101.61 (1),  $\beta$  = 96.20 (1),  $\gamma$  = 92.28 (1)°, *V* = 461.6 (1) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 2.105 Mg m<sup>-3</sup>,  $\lambda$ (Mo *K* $\alpha$ ) = 0.71069 Å,  $\mu$  = 1.790 mm<sup>-1</sup>, *F*(000) = 292, *T* = 290 K, *R* = 0.035, *wR* = 0.042 for 1170 observed reflections. The C<sub>3</sub>S<sub>8</sub> molecule in the crystal has a local *m* symmetry and shows a chair conformation of the seven-membered ring containing five S and two C atoms. The central part of this ring makes dihedral angles of 68.6° with the C<sub>3</sub>S<sub>5</sub> group and 71.6° with the terminal S<sub>3</sub> group.

**Introduction.** Sulfur–organic compounds containing the 2-thioxo-1,3-dithiole-4,5-dithiolate group C<sub>3</sub>S<sub>5</sub>

(dmit) are used for synthesis of organic metals and superconductors such as BEDT–TTF salts and square-planar organometallics (Kaminskii, Prokhorova, Shibaeva & Yagubskii, 1984; Cassoux, Valade, Kobayashi, Kobayashi, Clark & Underhill, 1991; Shklover, Nagapetyan & Struchkov, 1990). We have carried out the synthesis of the new 4,5-poly-sulfanediy-1,3-dithiole-2-thiones, details of which will be published elsewhere (Starodub & Baumer, 1993). X-ray structure analysis was used for characterization of each component of the mixture of reaction products. The main product of the synthesis is 4,5-(pentasulfane-1,5-diyl)-1,3-dithiole-2-thione, the structure of which is reported in this paper.

**Experimental.** The title compound forms thin yellow folium-shaped blocked crystals with dimensions of

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about  $1.0 \times 1.0 \times 0.1$  mm. Preliminary investigation (Cu  $K\alpha$  radiation, Weissenberg camera) could not detect suitable single crystals for further data collection. The triangular plate fragment of a folium consisting of at least four crystals was used for investigation on a four-circle automated Siemens P3/PC diffractometer (Mo  $K\alpha$  radiation, graphite monochromator). An attempt to determine the unit cell *via* the blind-search procedure was unsuccessful, but suitable reflections for autoindexing were observed at high diffraction angles on the rotation polaroid photograph. Unit-cell dimensions were then refined from 24 reflections in the range  $24 \leq 2\theta \leq 35^\circ$ . Data were collected using the  $2\theta/\theta$  scan technique at variable speed  $2.0$  to  $10.0^\circ \text{ min}^{-1}$  (in  $\omega$ ), scan range  $2^\circ$ . Two check reflections ( $2\bar{1}4$  and  $15\bar{3}$ ) were monitored every 98 measured intensities. Data were collected for  $3 \leq 2\theta \leq 60^\circ$ ,  $-1 \leq h \leq 5$ ,  $-12 \leq k \leq 12$ ,  $-16 \leq l \leq 16$ ; background to peak time ratio was 0.5. The number of measured intensities was 1397 (excluding 4 rejected with bad backgrounds; maximum deviation of check-reflection intensities did not exceed 2% of value), of which 1218 were independent ( $R_{\text{int}} = 1.58\%$ ) and 1170 were observed [ $I > 3\sigma(I)$ ]. During the data reduction, intensities were corrected for Lorentz, polarization and absorption effects ( $T_{\text{min}}, T_{\text{max}} = 0.6723, 0.9156$ ). During the refinement an extinction correction in the form  $F^* = F[1 + 0.002x F^2/\sin(2\theta)]^{1/4}$ , where  $x = 0.0008$  (2), was applied.

Since the formula unit was not known *a priori*, the structure was solved by direct methods without symmetry restrictions (space group  $P1$ ). Two  $C_3S_8$  molecules were found and a symmetry centre was detected. Further calculations were carried out in the  $P\bar{1}$  space group. All atoms were refined anisotropically, the quantity minimized was  $\sum w(F_o - F_c)^2$  and the weighting scheme  $w = 1/\sigma^2(F)$  was used. Final  $R = 0.035$ ,  $wR = 0.042$  (for all observed reflections),  $S = 4.34$ ,  $(\Delta/\sigma)_{\text{max}} = 0.038$ ,  $(\Delta/\sigma)_{\text{av}} = 0.004$ , data-to-parameter ratio was 11.6,  $(\Delta\rho)_{\text{max}} = 0.45$ ,  $(\Delta\rho)_{\text{min}} = -0.4 \text{ e } \text{Å}^{-3}$ . All computations were performed using the *SHELXTL-Plus* program package (Sheldrick, 1990).

**Discussion.** Positional and equivalent isotropic thermal parameters are listed in Table 1.† Interatomic distances, bond angles and torsion angles are summarized in Table 2. The atomic numbering scheme and molecular geometry of the title compound are

† Lists of structure factors, anisotropic thermal parameters, non-bonded distances and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71079 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: VS1006]

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement coefficients ( $\text{Å}^2 \times 10^3$ )

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U_{\text{eq}}$
S(1)	8644 (4)	-1583 (2)	3419 (2)	38 (1)
S(2)	5568 (4)	1242 (2)	4130 (1)	29 (1)
S(3)	4755 (4)	-257 (2)	1704 (1)	34 (1)
S(4)	1511 (4)	3706 (2)	3821 (1)	32 (1)
S(5)	3925 (4)	5417 (2)	3347 (2)	35 (1)
S(6)	1688 (4)	5551 (2)	1741 (2)	38 (1)
S(7)	3166 (4)	3764 (2)	634 (2)	39 (1)
S(8)	655 (4)	1947 (2)	896 (2)	38 (1)
C(1)	6433 (13)	-277 (6)	3097 (5)	26 (2)
C(2)	3256 (13)	2080 (6)	3179 (5)	24 (2)
C(3)	2888 (14)	1388 (6)	2057 (5)	26 (2)

Table 2. Bond lengths (Å), bond angles ( $^\circ$ ) and selected torsion angles ( $^\circ$ )

S(1)—C(1)	1.648 (6)	S(4)—C(2)	1.771 (6)
S(2)—C(1)	1.736 (6)	S(5)—S(6)	2.063 (3)
S(2)—C(2)	1.744 (6)	S(6)—S(7)	2.050 (2)
S(3)—C(1)	1.728 (6)	S(7)—S(8)	2.053 (3)
S(3)—C(3)	1.742 (6)	S(8)—C(3)	1.769 (6)
S(4)—S(5)	2.059 (3)	C(2)—C(3)	1.333 (8)
C(1)—S(2)—C(2)	97.1 (3)	S(1)—C(1)—S(3)	124.1 (3)
C(1)—S(3)—C(3)	97.4 (3)	S(2)—C(1)—S(3)	112.7 (3)
S(5)—S(4)—C(2)	103.6 (2)	S(2)—C(2)—S(4)	116.4 (3)
S(4)—S(5)—C(6)	103.8 (1)	S(2)—C(2)—C(3)	116.4 (5)
S(5)—S(6)—S(7)	103.0 (1)	S(4)—C(2)—C(3)	127.2 (5)
S(6)—S(7)—S(8)	104.3 (1)	S(3)—C(3)—S(8)	116.7 (3)
S(7)—S(8)—C(3)	103.3 (2)	S(3)—C(3)—C(2)	116.4 (5)
S(1)—C(1)—S(2)	123.2 (4)	S(8)—C(3)—C(2)	126.9 (5)
C(2)—S(4)—S(5)—S(6)	87.4	S(7)—S(8)—C(3)—C(2)	73.4
S(4)—S(5)—S(6)—S(7)	-76.8	S(8)—C(3)—C(2)—S(4)	2.4
S(5)—S(6)—S(7)—S(8)	78.2	C(3)—C(2)—S(4)—S(5)	-76.7
S(6)—S(7)—S(8)—C(3)	-88.8		

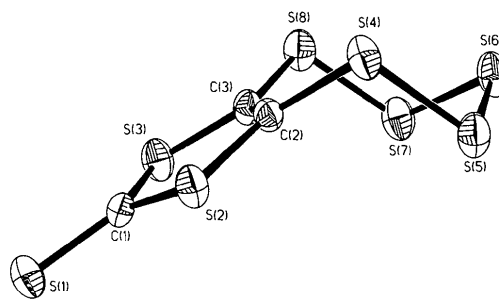


Fig. 1. The molecular conformation of the title compound showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 40% probability level.

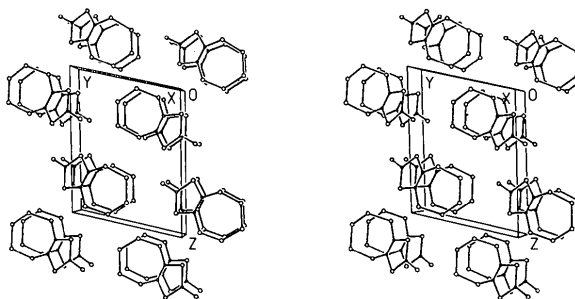


Fig. 2. Stereoview of the packing of molecules of the title compound in the unit cell.

shown in Fig. 1. The packing of molecules in the unit cell is shown in Fig. 2. The  $C_3S_8$  molecule includes a seven-membered non-planar ring having a chair conformation. There are three planar fragments in the molecule: (i) dmit fragment  $C_3S_5$ ; (ii) atoms S(4), S(5), S(7) and S(8), and (iii) atoms S(5), S(6) and S(7). Corresponding dihedral angles are  $68.6^\circ$  between (i) and (ii),  $71.6^\circ$  between (ii) and (iii), and  $3.1^\circ$  between (i) and (iii). According to molecular-mechanics calculations, the observed conformation of the  $C_3S_8$  molecule is the most stable of all possible conformations for seven-membered cycles containing two C and five S atoms. The observed bond distances and angles are usual for sulfur-containing cyclic compounds and do not depend on their conformations (Steudel, Pickardt & Steudel, 1978; Steudel & Schuster, 1978).

The crystal structure of the title compound may be considered as composed of columns of  $C_3S_8$  molecules along the crystallographic [100] direction. The closest intermolecular S...S distances are shorter than the sum of the van der Waals radii for S atoms

(3.68 Å); S(2)...S(1) ( $1-x, -y, -z$ ) 3.567 (2), S(2)...S(2) ( $1-x, -y, -z+1$ ) 3.406 (2), S(4)...S(2) ( $x-1, y, z$ ) 3.488 (2), S(5)...S(1) ( $x, y+1, z$ ) 3.359 (2), S(6)...S(1) ( $x-1, y+1, z$ ) 3.367 (2), S(7)...S(6) ( $-x, 1-y, -z$ ) 3.510 (3), S(7)...S(7) ( $1-x, 1-y, -z$ ) 3.398 (3), S(8)...S(3) ( $x-1, y, z$ ) 3.556 (2) Å.

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### Structure of the Laser Host Material $LiYF_4$

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**Abstract.** Lithium yttrium tetrafluoride,  $LiYF_4$ ,  $M_r = 171.8$ , tetragonal,  $I4_1/a$ ,  $a = 5.164$  (1),  $c = 10.741$  (2) Å,  $V = 286.5$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 3.99$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.7107$  Å,  $\mu = 204$  cm<sup>-1</sup>,  $F(000) = 312$ ,  $T = 295$  K,  $R = 0.015$  for 156 unique observed [ $F > 4\sigma(F)$ ] reflections. The scheelite ( $CaWO_4$ ) structure is confirmed. Lithium is located at a  $\bar{4}$  site with four equidistant fluoride ions. Yttrium is in an eightfold coordination typical for rare-earth ions.

**Experimental.** Light-green crystals of the title compound were obtained from an equimolar mixture of

$LiF$  and  $YF_3$ . Since interest in this material is based on solid-state laser applications this mixture also contained 2% wt of  $PrF_3$ . The dried powders were heated in a platinum crucible in an inert atmosphere furnace (Ar) to 1123 K (melting point 1083 K) and allowed to cool slowly over 6 h. The solidified mass was broken up and a suitable crystal obtained.

Selected crystal  $ca$   $0.04 \times 0.04 \times 0.07$  mm. Siemens  $R3m/V$  diffractometer,  $\theta$ - $2\theta$  scan. Total scan range,  $1.2^\circ$  plus  $K\alpha$  separation. Scan speed, 2.0 to  $15^\circ$  min<sup>-1</sup> in  $\theta$ . Background stationary crystal and counter beginning and end of scan, each 25% of total scan time. Graphite-monochromated  $Mo K\alpha$