

N—C—N angles ($\approx 125^\circ$) produce a compressed six-membered ring in which all bonds (N—N ≈ 1.32 and C—N ≈ 1.34 Å) have partial ($\approx 50\%$) double-bond character consistent with the resonance structure. The exocyclic bonds, C(3)—O(3') = $1.328(2)$ Å in (V) and C(2)—N(3) = $1.385(1)$ Å in (VI), are also remarkably short. As in the case of (IV) we interpret this finding as a result of the strong electron-acceptor property of the 1,2,4,5-tetrazine system. The methoxy and also, surprisingly, the 1-aziridinyl substituents serve as weak π -electron donors. The interaction of the lone pair of electrons at the exocyclic heteroatoms with the electron-deficient π system of the molecule gives the exocyclic C(3)—O(3') and C(2)—N(3) bonds some double-bond character. Bond distances and angles of the aziridinyl substituents correspond to known data for the aziridine ring (e.g. Boese, Rademacher & Treschanke, 1985; Rudchenko, D'yachenko, Zolotoi, Atovmyan, Chervin & Kostyanovsky, 1982).

The molecular packing of (V) viewed along **b** is shown in Fig. 3. The 1,2,4,5-tetrazine moieties are positioned in a herringbone arrangement. (VI) shows layers in the (201) plane in which each 1,2,4,5-tetrazine unit is surrounded by four neighbouring molecules. The packing arrangement of the layers, separated from each other by 3.18 Å and with the shortest intermolecular contact C(2)⋯C(2)($-x, y, 1-z$) = 3.244 Å, is illustrated in Fig. 4.

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Structure of 4,5-Di(benzoylthio)-4,5-didehydro-1,3-dithiolane-2-thione

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Abstract. $C_{17}H_{10}O_2S_5$, $M_r = 406.6$, monoclinic, $P2_1/a$, $a = 17.369(4)$, $b = 10.687(3)$, $c = 9.695(3)$ Å, $\beta = 93.83(3)^\circ$, $V = 1796(1)$ Å³, $Z = 4$, $D_x = 1.50$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 6.3$ cm⁻¹, $F(000) = 832$, $T = 288$ K, $R = 0.070$ for 2815 observed reflections. The structure consists of discrete molecules linked by van der Waals forces. One C_6H_5CO moiety is nearly coplanar with the five-membered ring; the second C_6H_5CO moiety is rotated around the S—C(ring) bond, the C(O)—S—C(ring)—S(ring) torsion angle being $87.9(4)^\circ$. Packing forces may cause the 2-thione S atom to lie $0.178(5)$ Å from

the plane of the five-membered ring. The C—S bond lengths are generally larger than those observed in metal complexes with 4,5-dimercapto-1,3-dithio-2-thione as ligand.

Introduction. 4,5-Dimercapto-1,3-dithiole-2-thione has been used frequently as a ligand in metal complexes. A study of the variation of the bond lengths of this ligand according to the oxidation state of the metal has been carried out by Valade, Legros, Bousseau, Cassoux, Garbaskas & Interrante (1985) and Kato, Mori, Kobayashi, Sasaki & Kobayashi (1984). We now

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report the structure of a compound where the metal has been replaced by an organic moiety.

Experimental. Prismatic crystal (0.1 × 0.1 × 0.15 mm). Philips PW 1100 diffractometer, cell parameters from 25 reflections ($4 \leq \theta \leq 9^\circ$) and refined by least squares. Graphite-monochromatized Mo K α radiation, ω -scan technique, scan width 0.8° , scan speed $0.03^\circ \text{ s}^{-1}$. Three reflections every 2 h as orientation and intensity control, significant intensity decay not observed. 3164 measured reflections with $2 \leq \theta \leq 30^\circ$, hkl range -24 to 24 , 0 to 14 , 0 to 13 . R_{int} (on F) = 0.039 . 2815 reflections with $I \geq 2.5\sigma(I)$. Lp corrections applied, absorption ignored.

Structure solved by direct methods with *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix least-squares refinement using *SHELX76* (Sheldrick, 1976), function minimized $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F_o) + 0.0053|F_o|^2]^{-1}$, f , f' and f'' taken from *International Tables for X-ray Crystallography* (1974). H atoms located from $\Delta\rho$ maps and refined with an overall isotropic temperature factor; the remaining atoms were refined anisotropically. This gave $R = 0.079$ ($wR = 0.090$), but atom O(7) showed high anisotropic thermal coefficients [$U_{11} = 0.153$ (5), $U_{22} = 0.178$ (6), $U_{33} = 0.068$ (3), $U_{23} = 0.062$ (4), $U_{13} = -0.049$ (3) and $U_{12} = -0.114$ (5)] and hence disorder was assumed for this atom. A Fourier map showed three peaks which could be assigned as the disordered positions of O(7). Occupancies of 1/3 were assigned to each site and coordinates and thermal parameters refined. Final $R = 0.070$ ($wR = 0.079$) for all observed reflections. Max. shift/e.s.d. = 0.24 in U_{iso} for H atoms, max. and min. $\Delta\rho = 0.3$ and $-0.3 \text{ e } \text{\AA}^{-3}$, respectively. IBM 3083 computer.

Discussion. Atomic coordinates are given in Table 1* and bond lengths in Table 2. The structure consists of discrete molecules linked by van der Waals forces. The shortest intermolecular distances between non-H atoms are S(11)⋯S(11^b) 3.623 (3) Å and S(11)⋯S(14^b) 3.673 (3) Å [symmetry codes: (i) $2-x, \bar{y}, 1-z$; (ii) $2-x, \bar{y}, \bar{z}$]. Packing forces may be the cause of the rotation of the C₆H₅CO moiety around the C(13)–S(14) bond [torsion angles C(9)–C(13)–S(14)–C(15) and S(12)–C(13)–S(14)–C(15) -97.9 (4) and 87.9 (4) $^\circ$], the large C(9)–C(13)–S(14) and small S(12)–C(13)–S(14) bond angles [125.5 (4) and 117.8 (3) $^\circ$], and the deviations of S(8), S(14) and S(11) [0.026 (5),

-0.059 (4) and -0.178 (5) Å, respectively] from the planar five-membered ring [largest deviation from the mean ring plane 0.008 (5) Å for S(12)].

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (\AA^2)

| | $B_{\text{eq}} = \frac{1}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$ | | | |
|--------|---|-----------|-----------|-----------------|
| | x | y | z | B_{eq} |
| C(1) | 11596 (3) | 5532 (5) | −1068 (6) | 4.87 (24) |
| C(2) | 11938 (3) | 6481 (5) | −1786 (7) | 5.29 (26) |
| C(3) | 11653 (4) | 6780 (5) | −3101 (7) | 5.43 (27) |
| C(4) | 11023 (4) | 6149 (5) | −3729 (6) | 5.14 (25) |
| C(5) | 10679 (3) | 5205 (5) | −3011 (5) | 4.40 (22) |
| C(6) | 10965 (3) | 4886 (4) | −1685 (5) | 3.93 (19) |
| C(7) | 10626 (3) | 3893 (5) | −868 (5) | 4.53 (22) |
| O(7)' | 10629 (25) | 4055 (54) | 401 (18) | 3.92 (101)† |
| O(7) | 10863 (41) | 3641 (54) | 401 (18) | 4.09 (271)† |
| O(7)'' | 10991 (29) | 3291 (42) | 95 (38) | 6.47 (153)† |
| S(8) | 9922 (1) | 2939 (2) | −1747 (1) | 6.12 (8) |
| C(9) | 9595 (2) | 1942 (4) | −474 (4) | 3.53 (17) |
| S(10) | 9923 (1) | 1959 (1) | 1276 (1) | 3.70 (4) |
| C(11) | 9339 (2) | 764 (4) | 1815 (5) | 3.66 (18) |
| S(11) | 9396 (1) | 279 (1) | 3434 (1) | 4.81 (6) |
| S(12) | 8731 (1) | 145 (1) | 493 (1) | 4.47 (6) |
| C(13) | 9045 (3) | 1086 (4) | −839 (5) | 3.97 (19) |
| S(14) | 8684 (1) | 757 (1) | −2537 (1) | 4.62 (6) |
| C(15) | 7809 (2) | 1696 (4) | −2624 (4) | 3.70 (18) |
| C(15) | 7663 (2) | 2376 (4) | −1691 (4) | 6.12 (20) |
| C(16) | 7330 (2) | 1540 (4) | −3945 (4) | 3.43 (17) |
| C(17) | 7482 (3) | 630 (5) | −4912 (5) | 4.03 (19) |
| C(18) | 7027 (3) | 539 (5) | −6149 (5) | 4.79 (24) |
| C(19) | 6412 (3) | 1381 (6) | −6390 (6) | 5.60 (27) |
| C(20) | 6264 (3) | 2283 (6) | −5449 (6) | 5.47 (26) |
| C(21) | 6721 (3) | 2375 (5) | −4211 (6) | 4.33 (21) |

† Disordered O(7); site occupation 1/3.

Table 2. Bond lengths (Å)

| | | | |
|-------------|------------|-------------|-----------|
| C(2)–C(1) | 1.386 (8) | C(11)–S(10) | 1.732 (5) |
| C(6)–C(1) | 1.396 (7) | S(11)–C(11) | 1.650 (5) |
| C(3)–C(2) | 1.374 (9) | S(12)–C(11) | 1.737 (5) |
| C(4)–C(3) | 1.390 (9) | C(13)–S(12) | 1.752 (5) |
| C(5)–C(4) | 1.383 (7) | S(14)–C(13) | 1.758 (5) |
| C(6)–C(5) | 1.389 (7) | C(15)–S(14) | 1.819 (4) |
| C(7)–C(6) | 1.472 (6) | O(15)–C(15) | 1.200 (5) |
| O(7)'–C(7) | 1.241 (20) | C(16)–C(15) | 1.489 (6) |
| O(7)–C(7) | 1.299 (30) | C(17)–C(16) | 1.388 (6) |
| O(7)''–C(7) | 1.268 (52) | C(21)–C(16) | 1.395 (6) |
| S(8)–C(7) | 1.767 (5) | C(18)–C(17) | 1.395 (7) |
| C(9)–S(8) | 1.753 (5) | C(19)–C(18) | 1.404 (8) |
| S(10)–C(9) | 1.753 (4) | C(20)–C(19) | 1.364 (9) |
| C(13)–C(9) | 1.353 (6) | C(21)–C(20) | 1.397 (7) |

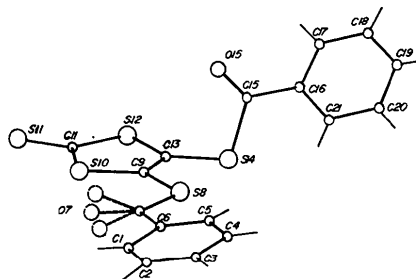


Fig. 1. View of the molecule with the atom-numbering scheme.

* Lists of structure factors, anisotropic thermal parameters, bond lengths involving H atoms, all bond angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43862 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The difference in length of the S(14)—C(15) and S(8)—C(7) bonds [1.819 (4) and 1.767 (4) Å, respectively] may be related to the different orientations of these bonds relative to the five-membered ring (see Fig. 1). If a comparison of the C(9)—C(13) bond length with those observed in the literature in 4,5-dimercapto-1,3-dithiole-2-thiones, ethenetetrathiols and tetrathiooxalates is carried out, it is observed that the length alters from 1.33 (1) Å in an ethenetetrathiol (Broadhurst, Johnson, Lewis & Raithby, 1982) to 1.46 (2) Å in a tetrathiooxalate (Lund, Hoyer, & Hazell, 1982). The length in the title compound [1.353 (6) Å] is similar to those observed by Lindquist, Sjölin, Sieler, Steimecke & Hoyer (1982) in bis-(tetrabutylammonium) bis(isotrithionedithiolato)-nickel(II), Lindquist, Andersen, Sieler, Steimecke & Hoyer (1982) in tetrabutylammonium bis(isotrithionedithiolato)nickel(III), and Solans, Font-Altaba, Vicente & Ribas (1987) in μ -tetrathio-oxalatebis[4,5-mercapto-1,3-dithiole-2-thione]copper(II)tetraphenylarsenine [average value 1.355 (7) Å]. However, the C(9)—S(8) and C(13)—S(14) bond lengths [average 1.755 (2) Å] are slightly greater than the average value of 1.712 (11) Å observed in the preceding compounds. This fact can be explained by the metal coordination and the loss of planarity of S(8) and S(14) atoms from the five-membered ring. The average C(9)—S(10) and C(13)—S(12) bond length [1.752 (1) Å] is slightly greater than the 1.734 (6) Å observed in the metal complexes with the ligand [see preceding references, Valade *et al.* (1985) and Bousseau, Valade, Legros, Cassoux, Garbaskas & Interrante (1986)], whereas the

average C(11)—S(10) and C(11)—S(12) bond length [1.734 (2) Å] is similar to that observed in the metal complexes with this ligand [1.733 (8) Å].

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Diméthyl-1,6 Oxa-7 Bicyclo[4.1.0]heptanedicarbonitrile-3-*trans*,4-*cis*

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Abstract. C₁₀H₁₂N₂O, $M_r = 176.22$, orthorhombic, *Pnma*, $a = 8.470$ (2), $b = 13.274$ (4), $c = 9.010$ (3) Å, $V = 1013$ Å³, $Z = 4$, $D_x = 1.156$ Mg m⁻³, $\lambda(\text{Cu K}\alpha)$

$= 1.5418$ Å, $\mu = 0.625$ mm⁻¹, $F(000) = 376$, room temperature, $R = 0.057$ for 707 reflections. This compound crystallizes as a solid solution in perfect disorder.

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