ACTA CHEMICA SCANDINAVICA 27 (1973) 756–762

The Crystal Structure of Bis(4-morpholinethiocarbonyl) Trisulphide

STEINAR HUSEBYE

Chemical Institute, University of Bergen, N-5000 Bergen, Norway

The structure of bis(4-morpholinethiocarbonyl) trisulphide has been determined by three-dimensional X-ray methods. The yellow crystals are orthorhombic with $a = 22.284(6)$ Å, $b = 8.840(3)$ Å, $c = 15.937(4)$ Å, and $Z = 8$. The space group is *Pbca*, and the density is: calc. 1.51, found 1.50 g/cm³.

Using multiple-film Weissenberg techniques and Cu$K\alpha$ radiation, 724 reflections above background were estimated visually. The structure was solved by means of the symbolic addition procedure, and refined by full-matrix least squares methods to a conventional R-value of 9.2 %.

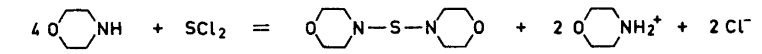
The bond lengths and angles involving the trisulphide group are: S0–S1 = 2.011(9) Å, S0–S3 = 2.016(8) Å, ∠S1S0S3 = 108.8(4)°, ∠S0S1C1 = 104.6(8)°, and ∠S0S3C6 = 103.7(6)°. For the dihedral angles C1S1S0/S1S0S3 and C6S3S0/S3S0S1, the values 92.4 and 101.5°, respectively, were found.

During the investigation of structures of compounds of divalent selenium and tellurium with dithio and related ligands, a strong tendency to planar four-coordination around the central atoms were found.[1–4] Of the ligands used, dithiocarbamates seemed to form the stronger Te–S and Se–S bonds. Examples of such dithiocarbamate complexes are the isomorphous tellurium and selenium bis(4-morpholinecarbodithioates).[3,4] (These compounds were earlier [3,4] termed morpholyldithiocarbamates.) Their structures are trapezoid-planar with two short and two long M–S bonds, each short bond roughly *trans* to a long one, with the bonding probably being of the three-center four electron type.

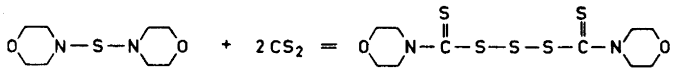
The present structure investigation of the analogous sulphur compound was undertaken to see if the tendency to planar four-coordination found for divalent tellurium and selenium could be observed for divalent sulphur also.

EXPERIMENTAL

Bis(4-morpholinethiocarbonyl) trisulphide was synthesized following the procedure of Blake.[5] In the first step, 4-morpholine monosulphide was made by the reaction between morpholine and sulphur dichloride in petrol ether:



In the next step, the sulphide was dissolved in excess carbon disulphide and the mixture refluxed for 30 h:



Upon cooling, small yellow prisms of the trisulphide crystallized out, m.p. 146 – 147°C. Recrystallization from benzene gave crystals with m.p. 152°C, while the m.p. reported by Blake [5] is 152 – 153°C. The bis(4-morpholinethiocarbonyl) trisulphide is very stable and does not break down into mixtures of mono- and polysulphides like its non-cyclic aliphatic analogs.[3]

Unit cell data were computed from 57 high-order reflections, read from NaCl-calibrated Weissenberg films, using a least squares program. The orthorhombic crystals are elongated along *c*, with $a = 22.284(6)$ Å, $b = 8.840(3)$ Å, $c = 15.937(4)$ Å, and $Z = 8$. The density is: calc. 1.51, found 1.50 g/cm³. From systematic extinctions, the space group is D_{2h}^{15}-*Pbca*.

Integrated Weissenberg equi-inclination photographs were taken of the *h*0*l*, *h*1*l*, *h*2*l*, *hk*0, and *hk*1 layers, using the multiple-film technique and Cu$K\alpha$ radiation. Reflection intensities were estimated visually, and 724 out of 1385 independent reflections with $\sin\theta \leq 0.985$ were observed and measured. During exposure, the reflections had a tendency to split in two with increasing exposure time, thus the crystals had to be changed several times. Only small crystals were obtained during preparation and recrystallization, the average size of the crystals used for obtaining intensities was: cross-section 0.03×0.09 mm², length 0.15 mm. The small size is probably the reason why so many reflections were not observed. The intensities were corrected for secondary extinction effects, but not for absorption ($\mu = 43$ cm^{-1}).

STRUCTURE ANALYSIS

After the usual corrections had been made, the intensities were put on the same relative scale by comparison of reflections common to two layers. Overall scale and temperature factors were then computed from a Wilson plot [6] and used in calculation of normalized structure factors for all reflections, using a program written by Shiono.[7]

Phase determination for the 144 reflections with $|E| > 1.50$ was then carried out by the symbolic addition procedure, using a program written by Long.[8] Origin of the unit cell was specified by arbitrarily assigning positive phases to three reflections with high E-values; and three other reflections with high E-values were given variable signs.

Of the resulting eight sign sets, the one with the highest consistency index was chosen as basis for computing an E map.

The five sulphur atoms and most light atoms showed up in this map and the rest of the atoms were found from successive Fourier syntheses. Full-matrix least squares methods were then employed to refine the structure. The program used minimizes the expression $r = \sum W[|F_o| - |KF_c|]^2 / \sum W|F_o|^2$, where K is a variable scale factor and W, the relative weight assigned to a reflection, is equal to $1/\sigma^2(F)$. $\sigma^2(F)$ is evaluated as $(Ka_1)^2 + (a_2F_o)^2/4W_o$, where W_o is a weight factor related to the reliability with which the intensity of a given reflection is measured, and a_1 and a_2 are constants, here put equal to 2.0 and 1.0, respectively.

With anisotropic temperature factors for the sulphur atoms, the reliability index $R = \sum||F_o| - |F_c||/\sum|F_o|$ converged to the final value of 0.092. A three-dimensional difference synthesis after the refinement showed no spurious peaks.

The final observed and calculated structure factors can be obtained from the author upon request. Atomic scattering factors for sulphur, nitrogen, and carbon were taken from *International Tables*,[9] those for sulphur were corrected for anomalous dispersion according to Cromer.[10] Atomic parameters are listed in Tables 1 and 2, while interatomic distances and angles based on the coordinates from Table 1 are listed in Tables 3 and 4.

Table 1. Final atomic coordinates in fractions of cell edges, with standard deviations.

	x	y	z
S0	0.0112(2)	0.1420(9)	0.3370(4)
S1	0.0509(2)	0.3000(8)	0.2651(3)
S2	0.1587(2)	0.1501(8)	0.3426(4)
S3	0.0035(2)	0.2226(9)	0.4548(3)
S4	−0.0804(2)	0.4289(9)	0.3611(3)
O1	0.2269(6)	0.4511(21)	0.0783(9)
O2	−0.1617(6)	0.3736(19)	0.6660(9)
N1	0.1602(6)	0.3305(24)	0.2097(10)
N2	−0.0868(6)	0.3762(25)	0.5239(9)
C1	0.1296(7)	0.2556(28)	0.2700(11)
C2	0.1363(9)	0.4490(36)	0.1507(14)
C3	0.1609(10)	0.4315(37)	0.0692(15)
C4	0.2506(11)	0.3247(36)	0.1305(14)
C5	0.2295(9)	0.3372(33)	0.2136(13)
C6	−0.0604(7)	0.3474(29)	0.4491(10)
C7	−0.0665(8)	0.3102(31)	0.6057(12)
C8	−0.1210(9)	0.2507(34)	0.6529(14)
C9	−0.1857(8)	0.4294(27)	0.5874(12)
C10	−0.1350(7)	0.4876(29)	0.5338(11)

Table 2. Components of atomic vibration tensors, $U \times 10^3$, in Å^2 with standard deviations, referred to crystallographic axes. For Te and S, the expression is $\exp\{-2\pi^2 [h^2a^{-2}U_{11} + k^2b^{-2}U_{22} + l^2c^{-2}U_{33} + 2\ hka^{-1}b^{-1}U_{12} + 2\ klb^{-1}c^{-1}U_{13} + 2\ hla^{-1}c^{-1}U_{13}]\}$. For the other atoms, the expression is $\exp[-8\pi^2U(\sin^2\theta/\lambda^2)]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
S0	72.1(3.0)	67.6(6.2)	96.6(4.2)	−12.7(4.1)	−18.3(6.9)	17.5(3.2)
S1	52.5(2.2)	75.5(5.0)	64.4(2.9)	4.2(3.7)	3.4(6.0)	2.3(2.4)
S2	73.5(2.9)	64.8(4.7)	77.6(3.6)	9.3(4.0)	30.6(6.6)	−0.6(2.9)
S3	66.5(2.7)	80.2(7.1)	69.3(3.1)	8.7(4.2)	9.7(6.5)	7.4(2.7)
S4	73.2(3.0)	95.3(7.1)	49.5(2.5)	11.9(4.3)	8.7(5.6)	2.3(2.7)

	U		U		U		U
O1	83.6(4.8)	C1	54.7(5.1)	C5	83.9(7.1)	C9	58.0(5.5)
O2	74.9(4.4)	C2	87.0(7.6)	C6	47.9(5.0)	C10	54.7(5.3)
N1	69.1(5.0)	C3	98.8(8.5)	C7	69.2(6.2)		
N2	59.5(4.5)	C4	110.1(8.0)	C8	85.3(7.4)		

Table 3. Bond lengths and angles in the trisulphide molecule, with standard deviations.

Distance		Angle	
S0–S1	2.011(9) Å	∠ S1–S0–S3	108.8(4)°
S0–S3	2.016(8)	∠ S0–S1–C1	104.6(8)
S1–C1	1.800(16)	∠ S0–S3–C6	103.7(6)
S2–C1	1.621(21)	∠ S1–C1–S2	123.1(11)
S3–C6	1.803(21)	∠ S1–C1–N1	110.8(14)
S4–C6	1.638(19)	∠ S2–C1–N1	126.0(13)
C1–N1	1.35(3)	∠ S3–C6–S4	121.8(10)
C6–N2	1.35(2)	∠ S3–C6–N2	114.5(14)
N1–C2	1.51(3)	∠ S4–C6–N2	123.5(16)
C2–C3	1.42(3)	∠ C1–N1–C2	127.3(16)
C3–O1	1.49(3)	∠ C1–N1–C5	119.7(16)
O1–C4	1.49(3)	∠ C2–N1–C5	110.6(17)
C4–C5	1.41(3)	∠ N1–C2–C3	111.1(22)
C5–N1	1.55(3)	∠ C2–C3–O1	106.2(19)
N2–C7	1.50(3)	∠ C3–O1–C4	108.6(19)
C7–C8	1.52(3)	∠ O1–C4–C5	110.3(22)
C8–O2	1.43(3)	∠ C4–C5–N1	107.0(17)
O2–C9	1.45(2)	∠ C6–N2–C7	124.1(17)
C9–C10	1.51(3)	∠ C6–N2–C10	122.8(16)
C10–N2	1.47(3)	∠ C7–N2–C10	112.9(15)
		∠ N2–C7–C8	108.9(15)
		∠ C7–C8–O2	108.4(22)
		∠ C8–O2–C9	111.5(16)
		∠ O2–C9–C10	109.3(14)
		∠ C9–C10–N2	112.4(19)

Table 4. Some intramolecular distances and angles.

Distance		Angle	
S0–S2	3.288(5) Å	∠ S1–S0–S2	64.0(2)°
S0–S4	3.278(9)	∠ S1–S0–S4	78.6(3)
S1–S2	3.009(8)	∠ S2–S0–S3	93.0(2)
S3–S4	3.008(9)	∠ S2–S0–S4	127.0(3)
S2–S4	5.877(8)	∠ S3–S0–S4	64.2(3)
S1–S3	3.275(7)	∠ S0–S2–C1	66.0(6)
S2–S3	3.946(7)	∠ S0–S4–C6	65.8(8)
S1–S4	3.492(7)		

THE STRUCTURE OF THE BIS(4-MORPHOLINETHIOCARBONYL) TRISULPHIDE

In Fig. 1, the molecule is seen in projection along *b*, with bond lengths and angles indicated. The molecules are monomeric and non-planar, thus there is no tendency to planar four-coordination around the central sulphur atom, as was found for the central tellurium and selenium atoms in analogous molecules. The two dithiocarbamate groups S1S2C1N1C2C5 and S3S4C6N2C7C10 are nearly planar, no atom deviating more than 0.12 and 0.15 Å, respectively, from the least squares planes through those groups. If one includes S0 in both

Table 5. Intermolecular distances. The left column represents distances from an atom in the original molecule to an atom in a molecule whose transformation from the original one is listed in the next column.

S4 – C4	$-\frac{1}{2}+x,\ y,\ \frac{1}{2}-z$	3.88 Å
O2 – C5	$-\frac{1}{2}+x,\ \frac{1}{2}-y,\ 1-z$	3.61
S0 – S1	$-x,-\frac{1}{2}+y,\ \frac{1}{2}-z$	3.70
S0 – C2	$-x,-\frac{1}{2}+y,\ \frac{1}{2}-z$	3.71
S1 – C7	$x,\ \frac{1}{2}-y,-\frac{1}{2}+z$	3.78
S4 – C8	$x,\ \frac{1}{2}-y,-\frac{1}{2}+z$	3.79
C1 – C4	$\frac{1}{2}-x,\ \frac{1}{2}+y,\ z$	3.44
S4 – C1	$-x,\ \frac{1}{2}+y,\ \frac{1}{2}-z$	3.73
S2 – C3	$x,\ \frac{1}{2}-y,\ \frac{1}{2}+z$	3.68
O1 – C9	$\frac{1}{2}+x,\ y,\ \frac{1}{2}-z$	3.29
O1 – C10	$\frac{1}{2}+x,\ y,\ \frac{1}{2}-z$	3.57
C4 – C9	$\frac{1}{2}+x,\ y,\ \frac{1}{2}-z$	3.86
C4 – C10	$\frac{1}{2}+x,\ y,\ \frac{1}{2}-z$	3.93
S2 – C8	$-x,\ -y,\ 1-z$	3.64
S2 – C9	$\frac{1}{2}+x,\ \frac{1}{2}-y,\ 1-z$	3.71
S2 – C10	$-x,\ 1-y,\ 1-z$	3.80
S3 – C10	$-x,\ 1-y,\ 1-z$	3.90
O2 – N1	$-x,\ 1-y,\ 1-z$	3.28
O2 – C1	$-x,\ 1-y,\ 1-z$	3.51
O2 – C2	$-x,\ 1-y,\ 1-z$	3.36
O2 – C5	$-x,\ 1-y,\ 1-z$	3.54
C1 – C9	$-x,\ 1-y,\ 1-z$	3.81
C1 – C10	$-x,\ 1-y,\ 1-z$	3.86
C5 – C9	$-x,\ 1-y,\ 1-z$	3.91

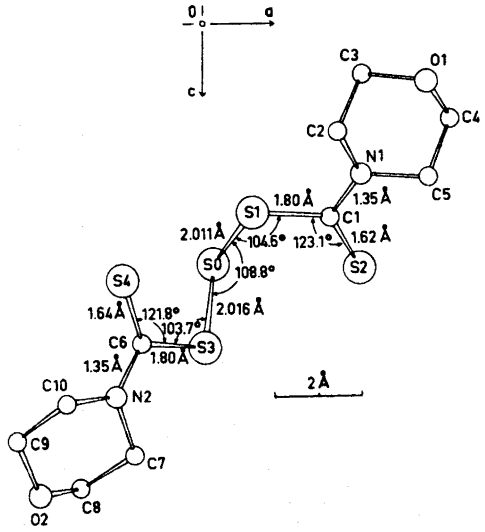


Fig. 1. The structure of the bis(4-morpholinethiocarbonyl) trisulphide molecule seen along the *b*-axis.

groups above, they are still roughly planar, the maximum deviation of any atom from the plane to which it belongs, now being 0.26 Å. The interplanar angle S0S1S2C1N1C2C5/S0S3S4C6N2C7C10 is 52.0°. This angle represents the twisting of the two halves of the molecule relative to a planar configuration.

The central part of the molecule, represented by the C6S3S0S1C1 chain, has the *trans* configuration often found in pentathionates,[11] thus C6 is 1.7 Å above the S1S0S3 plane while C1 is 1.7 Å below. The dihedral angles C1S1S0/S1S0S3 and C6S3S0/S3S0S1 are 92.4 and 101.5°, respectively. The S – S bond lengths in the trisulphide group are S1 – S0 = 2.011(9) Å, and S3 – S0 = 2.016(8) Å. These values are not significantly different from the corresponding values, 2.03 Å and 2.04 Å, estimated on the basis of Hordvik's single bond length-dihedral angle relationship for sulphur-sulphur bonds.[12] Although the S0 – S2 and S0 – S4 distances are only 3.28 Å and 3.29 Å, they cannot be regarded as bonds. They are both significantly longer than the S – S "bites" in the dithiocarbamate groups, which are both 3.01 Å, and they are about equal to the S1 – S3 distance of 3.28 Å. The central sulphur atom has a valency angle of 108.8(4)°. This value is higher than those usually found for sulphur,[13] but is not significantly different from the average value of 107°54′ found in orthorhombic sulfur.[14] Other compounds in which sulphur has large valency angles are 3,3′-trithiobis(2,4-pentanedione) with 106.7°,[15] 1,2,3,6,7,8-hexathiecan with 109.5°,[16] cyclodecasulphur with 107.8°,[17] and potassium pentathionate with 107.4°.[18]

The other two sulphur valency angles, ∠S0 – S1 – C1 and S0 – S3 – C6, are 104.6 and 103.7°, which is quite normal.

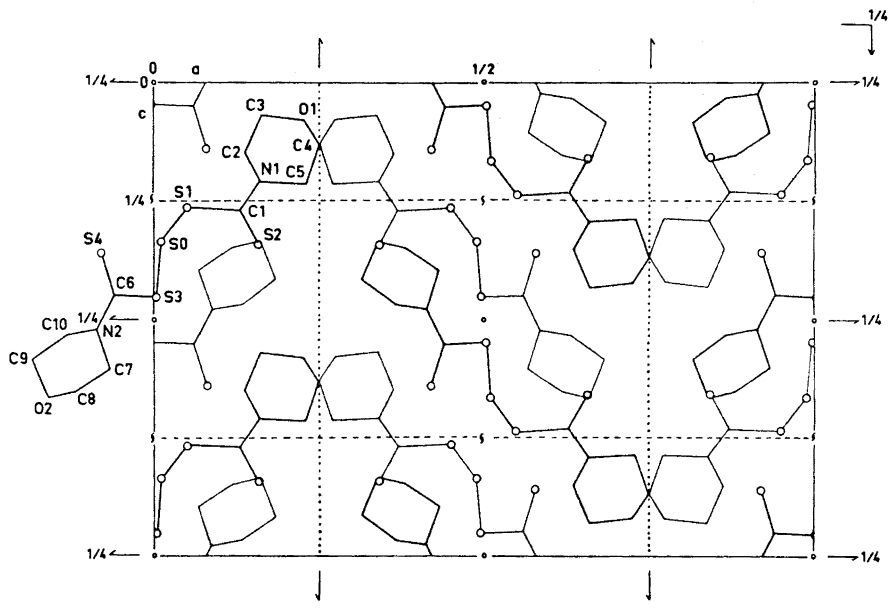


Fig. 2. The molecular arrangement seen along the *b*-axis.

In each dithiocarbamate group there is a short and a long C–S bond. The lengths correspond within the error limit to double and single bonds, respectively, and agree well with the values found for corresponding bonds in tetramethylthiuram disulfide where the short and long bonds are 1.634 and 1.829 Å, respectively.[19] Similar values are also found in tetraethylthiuram disulphide.[20] In complexes where both sulphur atoms in a dithiocarbamate ligand are bonded to the central atom, the two C–S bonds are more equal, a short M–S bond corresponding to a long C–S bond and *vice versa*.[3,4]

The two C–N bonds are both 1.35 Å, which is normal for such a bond. Bond lengths and angles in the morpholine rings are similar to those found in the (4-morpholine)-carbodithioates of divalent selenium and tellurium.[3,4]

No unusually short intermolecular contacts were found.

REFERENCES

1. Husebye, S. *Acta Chem. Scand.* **20** (1966) 24.
2. Husebye, S. *Acta Chem. Scand.* **21** (1967) 47.
3. Husebye, S. *Acta Chem. Scand.* **23** (1969) 1389.
4. Husebye, S. and Helland-Madsen, G. *Acta Chem. Scand.* **23** (1969) 1398.
5. Blake, E. S. *J. Am. Chem. Soc.* **65** (1943) 1267.
6. Wilson, A. J. C. *Nature* **150** (1942) 151.
7. Shiono, R. *Normalized Structure Factors Program*, The Crystallography Laboratory, University of Pittsburgh, Pittsburgh 1966.
8. Long, R. E. *Ph. D. Dissertation*, University of California at Los Angeles 1965.
9. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III, p. 204.
10. Cromer, D. T. *Acta Cryst.* **18** (1965) 17.
11. Foss. O. *Advan. Inorg. Chem. Radiochem.* **2** (1960) 237.
12. Hordvik, A. *Acta Chem. Scand.* **20** (1966) 1885.
13. Abrahams, *Quart. Rev.* **10** (1956) 407.
14. Caron, A. and Donohue, J. *Acta Cryst.* **14** (1961) 548.
15. Power, L. F. and Jones, R. D. G. *Inorg. Nucl. Chem. Lett.* **7** (1971) 33.
16. Lemmer, F., Feher, F., Gieren, A., Hechtfischer, S. and Hoppe, W. *Angew. Chem.* **82** (1970) 319.
17. Kutoglu, A. and Hellner, E. *Angew. Chem.* **78** (1966) 1020.
18. Marøy, K. *Acta Chem. Scand.* **25** (1971) 2580.
19. Marøy, K. *Acta Chem. Scand.* **19** (1965) 1509. *Private communication.*
20. Karle, I. L., Estlin, J. A. and Britts, K. *Acta Cryst.* **22** (1967) 273.

Received September 11, 1972.