Crystal and Molecular Structure of Dimorpholinotetrasulphane

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The tetrasulphane $S_4(NC_4H_8O)_2$ crystallizes in the tetragonal space group $I4_1/a$ (no. 88) with $a = b = 12.812(1)$, $c = 16.733(2)$ Å, and $Z = 8$. The structure has been determined by *X*-ray diffraction from Mo-K_α diffractometer data and refined by full-matrix least squares to *R* 0.045 for 948 observed reflections. The molecules lie across crystallographic two-fold axes. The N–S–S–S–S–N chains occur in the *trans-trans* form, with N–S 1.668(3), S–S (terminal) 2.061(2), S–S (central) 2.078(3) Å, N–S–S 109.1(2), S–S–S 105.8(1)°, NSS–SSS 90.3, and SSS–SSS 79.9°. The morpholine groups occur in the chair form, with N–S equatorial. The S–S bonds alternate only slightly in length along the chain, like the Se–Se bonds in the isomorphous tetraselane analogue.

CRYSTAL structures of three acyclic tetrasulphanes X–S–S–S–S–X are known, or four if caesium hexasulphide [1] ($X = S^-$) is included. The three are the hexathionates *trans*-$[Co(en)_2Cl_2]_2[S_6O_6]\cdot H_2O$ [2] (en = ethylenediamine), $K_2[Ba(S_6O_6)_2]$ [3] ($X = SO_3^-$), and dibenzylideneaminotetrasulphane [4] ($X = N{=}CHC_6H_5$). Abrahams and Grison [1a] in their structure analysis of caesium hexasulphide noted an alternation of S–S bond lengths along the chain, such an effect is also manifest in the three other structures. In dibenzylideneaminotetrasulphane, where the terminal sulphur atoms are *N*-bonded, the effect is large: S–S 2.020(4), 2.083(4), and 2.033(4) Å.[4]

We recently determined the crystal structures of dimorpholino- and dipiperidino-tetraselane [5] (X–Se–Se–Se–Se–X; $X = NC_4H_8O$ or NC_5H_{10}) and there found smaller, although still significant, alternations of bond lengths: Se–Se 2.336(2), 2.356(2), 2.336(2), and 2.327(2), 2.347(2), 2.327(2) Å. In order to compare more directly a tetraselane and a tetrasulphane (with the same terminal group), and noting that crystals of dimorpholinotetrasulphane were described [6] as octahedra and were probably therefore isomorphous with crystals of the tetraselanes, we prepared dimorpholinotetrasulphane and carried out a structure analysis.

EXPERIMENTAL

The compound $S_4(NC_4H_8O)_2$ was first prepared by Goebell [6] from the dichlorosulphane and morpholine. We obtained it from sulphur (8 g), PbO (12 g), and morpholine (25 cm^3), by heating the mixture for 30 min, filtering, and evaporating the filtrate to dryness in a stream of air. The residue was treated with cold CH_2Cl_2 and filtered off. On evaporation, the filtrate left a crystalline mass from which bipyramids of the tetrasulphane were picked out.

X-Ray data were collected on a Siemens AED diffractometer, as described earlier,[5] using niobium-filtered Mo-K_α radiation ($\lambda = 0.710\,7$ Å) and were treated as before.[5] Three reference reflections, measured at intervals of 50 reflections, indicated no deterioration of the crystal. Unit-cell dimensions [Mo-$K_{\alpha(1)}$ peaks, $\lambda = 0.709\,26$ Å] were based on 14 reflections with $2\theta = 40$—$46°$. Calculations were made by use of the '*X*-Ray '72' programs,[7] with atomic scattering factors taken from ref. 8 (from ref. 9 for H) and with anomalous dispersion [10] for S included. Refinement was by full-matrix least squares, the sum minimized being $\Sigma w\Delta^2(F)$ with $w = 1/\sigma^2(F)$. Reflections with $I > 3\sigma(I)$ were regarded as observed and were used in the refinement.

Crystal Data.—$C_8H_{16}N_2O_2S_4$, $M = 300.5$, Tetragonal, space group $I4_1/a$ (no. 88), $a = b = 12.812(1)$, $c = 16.733(2)$ Å, $U = 2\,746\,9$ Å^3, $Z = 8$, $D_c = 1.45$ g cm^{-3}, $F(000) = 1\,264$, μ(Mo-K_α) = 6.6 cm^{-1}, 948 observed unique reflections within $2\theta = 56°$. Absorption corrections ranged from 1.125 to 1.141.

The refinement began from the positional parameters of the corresponding atoms in dimorpholinotetraselane.[5] With anisotropic thermal parameters, *R* became 0.058. At this point the hydrogen atoms were located from a $\Delta(F)$ map and their parameters (positional and isotropic thermal) were refined in the last cycles together with the parameters of the other atoms. The final *R* was 0.045, $R' = 0.060$, and $\sigma_1 = [\Sigma w\Delta^2(F)/(n - m)]^{\frac{1}{2}} = 0.95$. The largest shift-to-error ratio in the last cycle was 0.004, and the largest peaks and holes in the $\Delta(F)$ map based on the final parameters were 0.4 and −0.3 e Å^{-3}. Final co-ordinates for non-hydrogen atoms are in Table 1. Observed and calculated structure factors, thermal parameters, and hydrogen co-ordinates are in Supplementary Publication No. SUP 22698 (14 pp.).*

TABLE 1

Fractional atomic co-ordinates (× 10^4) for $S_4(NC_4H_8O)_2$ with estimated standard deviations in parentheses. Origin at a centre of symmetry

Atom	*x*	*y*	*z*
S(1)	928.0(8)	1 201.1(7)	543.2(6)
S(2)	−42.2(7)	1 690.2(8)	−365.0(7)
N	2 125(2)	1 016(2)	178(2)
C(1)	2 274(4)	132(4)	−361(3)
C(2)	3 420(4)	−55(5)	−476(4)
O	3 916(3)	842(4)	−789(3)
C(4)	3 789(4)	1 695(6)	−256(5)
C(5)	2 664(3)	1 952(4)	−102(4)

RESULTS AND DISCUSSION

Molecular and Crystal Structure.—The molecules lie across crystallographic two-fold axes (see Figure). Dimensional data based on the atomic co-ordinates of Table 1 are in Table 2. The conformations of the N–S–S–S–S–N chains, the morpholino-groups, and the molecules as a whole are as for the tetraselane molecules in the isomorphous crystals of dimorpholino- and dipiperidino-tetraselane.[5]

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† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

The intermolecular S • • • S contacts generated by the four-fold inversion centres, *cf.* ref. 5, are S(1) • • • S(1) 3.737, S(1)—S(2) 4.208 and 4.796, S(2) • • • S(2) 5.601 Å, and those generated by the symmetry centres are S(1) • • • S(1) 4.293, S(1) · · · S(2) 3.886, and S(2) · · · S(2) 4.501 Å. All but the longest one lie well within the attractive range of the S • • • S van der Waals potential curve;[11] for $r = 5.601$ Å, the function gives $V = -0.086$ kcal * mol^{-1}.

TABLE 2

Distances (Å) and angles (°) in $S_4(NC_4H_8O)_2$ with estimated standard deviations in parentheses [a]

(*a*) Bond lengths		(*b*) Bond angles	
S(1)–S(2)	2.061(2)	N–S(1)–S(2)	109.1(1)
S(2)–S(2′) [b]	2.078(2)	S(1)–S(2)–S(2′)	105.8(1)
S(1)–N	1.668(2)	S(1)–N–C(1)	117.2(3)
N–C(1)	1.459(6)	S(1)–N–C(5)	115.8(3)
C(1)–C(2)	1.501(8)	C(1)–N–C(5)	112.1(4)
C(2)–O	1.414(8)	N–C(1)–C(2)	109.4(5)
O–C(4)	1.420(9)	C(1)–C(2)–O	110.9(5)
C(4)–C(5)	1.500(7)	C(2)–O–C(4)	110.0(5)
C(5)–N	1.462(6)	O–C(4)–C(5)	112.7(5)
		C(4)–C(5)–N	109.2(5)

(*c*) Dihedral angles [c]

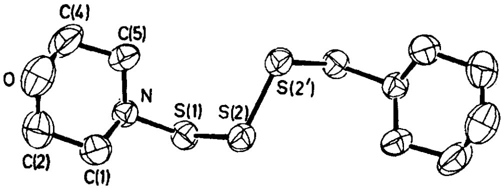
S(1)–S(2)	90.3	S(2)–S(2′)	73.3

(*d*) Least-squares plane [d]

Distances from plane: S(2) −0.741, S(1) 1.001, N 0.624, C(1) −0.012, C(2) 0.012, O −0.651, C(4) −0.013, C(5) 0.012 Å; angles with plane C(1)–N–C(5) 50.0, C(2)–O–C(4) 53.1, N–S(1)–S(2) 87.7°; angle of normal to plane with two-fold axis 13.0°

[a] For distances and angles involving hydrogen, the average values (with average deviations) are: C–H 0.962(55) Å, H–C–H 109.6(3.9), C–C–H 109.0(2.9), N–C–H 108.4(1.7), O–C–H 109.9(7.0)°. [b] S(2)–S(2′) across molecular two-fold axis. [c] At the indicated bond. Zero for planar *cis*. [d] Of the carbon atoms of the morpholino-group. The equation of the plane in direct space is $1.4396x - 2.4936y + 16.3053z = -0.2816$.

Diaminotetra-sulphane and -selane Chains.—Comparing alternations of S–S or Se–Se bond lengths along the chain, for acyclic tetra-sulphanes or -selanes containing *N*-bonded terminal S or Se, it is seen that for dimorpholinotetrasulphane the alternation is of the same magnitude as for dimorpholino- and dipiperidinotetraselane, the central S–S bond being 0.017(4) Å longer than the terminal bonds, against 0.020(3) Å for the Se–Se bonds in the tetraselanes.[5] The more pronounced alternation in $S_4(N{=}CHC_6H_5)_2$,[4] S–S 2.020(4), 2.083(4), and 2.033(4) Å, may then be taken as being an effect of the nature of the terminal group, it being imino instead of amino. The compound $S_4(N{=}CHC_6H_5)_2$ is a *cis-cis* rotamer in the crystals, whereas $S_4(NC_4H_8O)_2$ is a *trans-trans* rotamer. It seems unlikely that rotameric form should influence bond lengths, other factors such as dihedral angles (their numerical values) being equal. The dihedral angles are 89.4, 73.5, and 85.7° in $S_4(N{=}CHC_6H_5)_2$ [4,12] and 90.3, 73.3, and 90.3° in $S_4(NC_4H_8O)_2$. The only tetrasulphane derivative that has been studied in both rotameric forms is the hexathionate ion; the *trans-trans* form occurs in *trans*-$[Co(en)_2Cl_2]_2[S_6O_6]\cdot H_2O$ [2] and the *cis-cis* form in $K_2[Ba(S_6O_6)_2]$.[3] The lengths of the S–S bonds of the tetrasulphane chain in the two forms differ slightly, being 2.018(3), 2.069(3), and 2.018(3) Å in the *trans-trans* rotamer and 2.042(2), 2.056(2), and 2.039(2) Å in the *cis-cis* rotamer, as do the dihedral angles, 85.7, 71.4, and 85.7° in the former and 109.4, 89.0, and 106.3° in the latter. Different ionic lattice forces also operate on the sulphur chains through the sulphonate groups. The reasons for alternations of bond lengths along sulphur chains, and factors affecting S–S bond lengths, have been discussed by many authors,[1,13] more recently by Marøy [14] and Steudel.[15] The evidence available so far concerning the lengths of Se–Se bonds indicates a picture as varied for selenium as for sulphur. For example, the triselenide ion in K_2Se_3 [16] has Se–Se 2.383(2) Å, and in the diselenotetrathionate ion in two dimorphs of *trans*-$[Co(en)_2Cl_2]_2[Se_2S_2O_6]\cdot H_2O$,[17] Se–Se 2.293(1) and 2.305(2) Å.



Dimorpholinotetrasulphane as seen along the two-fold axis (thermal ellipsoids drawn to enclose 50% probabilities)

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† Throughout this paper: 1 cal = 4.184 J.