Crystal Structures and Rotameric Forms of Some Diarylsulphonyl-mono-, -di-, and -tri-selanes and Their Sulphur Analogues†

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The crystal structures of the compounds $S_2(SO_2Ph)_2$ (**1**), $Se_2(SO_2Ph)_2\cdot\frac{1}{2}C_6H_6$ (**2**), $S_2(SO_2C_6H_4Me\text{-}p)_2$ (**3**), $Se_2(SO_2C_6H_4Me\text{-}p)_2$ (**4**), $S(SO_2C_6H_4Me\text{-}p)_2$ (**5**), $Se(SO_2C_6H_4Me\text{-}p)_2$ (**6**), $S_3(SO_2C_6H_4Me\text{-}p)_2$ (**7**), and $Se_3(SO_2C_6H_4Me\text{-}p)_2$ (**8**) have been determined by *X*-ray methods and refined to *R* 0.033—0.045 for 1 384—3 058 observed reflections. Crystals of (**3**) and (**4**) are isomorphous, as are those of (**5**) and (**6**), and (**7**) and (**8**). In (**5**)—(**8**) the molecules lie across crystallographic two-fold axes. In the disulphonyl-sulphane or -selane chains, the lengths of the terminal bonds are S–S 2.101(1)—2.141(1) and S–Se 2.242(1)—2.286(1) Å, and the lengths of the central bonds, between bivalent atoms, are S–S 1.987(1)—2.037(1) and Se–Se 2.246(1)—2.304(1) Å. The rotameric forms, and reasons for variations in the lengths of bonds of the same type, are discussed. With three exceptions, the YXSC torsion angles (X,Y = S or Se) of 12 independent sulphonyl groups lie in the range 70—89, average 80°. In the S–SO_2R groups of the disulphonylsulphanes the S–S bond lengths correlate with the triple angle averages around the bonds.

Disulphonylsulphanes are polythionic compounds, formally derived from the polythionic acids through substitution of organic groups for the hydroxy-groups of the acids. Blomstrand[1] in 1870 reported the first representative, di-*p*-tolylsulphonyltrisulphane. Diphenyl- and di-*p*-tolyl-sulphonyl-selanes up to and including the triselanes were reported by Foss[2] in 1952. The crystal structures of $S(SO_2Ph)_2$,[3] $Se(SO_2Ph)_2$,[4] and $S_2(SO_2Me)_2$[5] have been determined.[6]

The disulphonyl-sulphane and -selane series offer an opportunity to compare the molecular dimensions and conformations of these types of compounds. Since the crystals of each of the three di-*p*-tolylsulphonyl-mono-, -di-, and -tri-sulphane and -selane pairs are isomorphous, these were selected for study. The di-sulphane and -selane were found to have rather unsymmetrical shapes in the crystals, and so diphenylsulphonyl-di-sulphane and -selane were included. The structures are reported here.

Experimental

The compounds were prepared and recrystallized as described.[2,7]

Crystallographic data are given in Table 1. *X*-Ray measurements were made on a CAD4 diffractometer using graphite-monochromated Mo-K_α radiation, $\lambda = 0.710\,69$ Å. The unit cells and space groups were reported earlier.[2,8,9] More accurate cell dimensions were determined from the diffractometer angles for 20—25 automatically centred reflections. The ω-scan mode was used for intensities, with a scan width of $1.00 + 0.35 \tan \theta$, plus 25% on each side for background. For compounds (**7**) and (**8**), where the space group is enantiomorphous, intensity data for an octant of the reciprocal lattice were collected and used. This octant comprises reflections of the type hhl, hkl, and $\bar{k}hl$, where $l \geqslant 0$ and $k > h \geqslant 0$, and includes a complete set of Friedel pairs of acentric reflections, plus equivalent pairs of $0kl$ and $k0l$ reflections and of $hk0$ and $kh0$ reflections.

The intensities were corrected for Lorentz and polarization effects, decay, and absorption. The decay corrections, based on the intensities of three reference reflections recorded every 2 h of exposure time, were insignificant except for compound (**6**) where the largest correction factor was 1.11. The Enraf–Nonius SDP programs were used for calculations. Atomic scattering factors, including anomalous dispersion terms, were from ref. 10. Refinement was by full-matrix least squares, the sum minimized being $\Sigma w\Delta^2(F)$ with $w^{-1} = \sigma^2(F) = \sigma^2(I)/4LpI$, and $\sigma^2(I) = \sigma^2(I)_{\text{count}} + (0.02I)^2$. Reflections with $I > 2\sigma(I)$ were regarded as observed and were used in the calculations. Anisotropic thermal parameters were used for all atoms except hydrogen. For compounds (**2**) and (**3**) an empirical extinction correction, $F_{\text{corr}} = F_c(1 + gI_c)^{-1}$, was applied to F_c in the last cycles, and g was refined along with the other variables.

The structures of compounds (**1**)—(**3**) and (**6**) were solved by direct (MULTAN) and Fourier difference methods, that of (**8**) by reference to the reported structure of $Te(S_2O_2C_6H_4\text{-}Me\text{-}p)_2$,[11] isomorphous with (**7**) and (**8**) [z for C(7) in ref. 11 should read 0.145 and not 0.105]. Starting co-ordinates for compounds (**4**), (**5**), and (**7**) were those of isomorphous (**3**), (**6**), and (**8**) respectively. Hydrogen atoms bonded to aromatic carbons were placed geometrically, at C–H 0.95 Å, and the *p*-Me hydrogen atoms were located from difference maps. For compounds (**5**) and (**6**), positions and isotropic thermal parameters for hydrogen were then refined along with the other variables, while for the other structures the hydrogen atoms were kept fixed, with a common fixed isotropic thermal parameter. The structure of compound (**2**), entered as $Se_2(SO_2Ph)_2$, did not refine satisfactorily, and a difference map revealed peaks around the symmetry centre at $\frac{1}{2}$, $\frac{1}{2}$, 0 indicating a benzene molecule which was then included, with hydrogen atoms placed and kept fixed as above. The crystals of (**2**) had been obtained from a mixture containing benzene, as described,[2] and the presence of benzene of crystallization went unnoticed at the time of the first synthesis.

The shifts in the last refinement cycles were less than one hundredth of the estimated standard deviations. Atomic co-ordinates for non-hydrogen atoms are listed in Tables 2 and 3.

Refinements of the inverted structures of compounds (**7**) and (**8**) in the enantiomorphous space group $P4_32_12$ gave for (**8**) a marked increase in agreement indexes R, R', and S: 0.051, 0.052, and 1.773. For (**7**) the indexes also increased but not significantly.

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† *Supplementary data available* (No. SUP 56078, 121 pp.): thermal parameters, complete bond lengths and angles, torsion angles, H-atom co-ordinates, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix.

Table 1. Crystallographic data

(*a*) Di-sulphanes and -selanes[a]

Compound	$S_2(SO_2Ph)_2$ (**1**)	$Se_2(SO_2Ph)_2\cdot\frac{1}{2}C_6H_6$ (**2**)	$S_2(SO_2C_6H_4Me\text{-}p)_2$ (**3**)	$Se_2(SO_2C_6H_4Me\text{-}p)_2$ (**4**)
Formula	$C_{12}H_{10}O_4S_4$	$C_{15}H_{13}O_4S_2Se_2$	$C_{14}H_{14}O_4S_4$	$C_{14}H_{14}O_4S_2Se_2$
M	346.47	479.32	374.52	468.31
a/Å	12.339(1)	5.531(1)	9.947(1)	10.123(2)
b/Å	6.107(1)	14.221(2)	15.050(2)	15.387(2)
c/Å	20.804(2)	23.164(2)	11.215(3)	11.242(3)
β/°	109.43(1)	108.41(1)	94.94(2)	94.18(2)
U/Å^3	1 478.4(7)	1 728.8(8)	1 672.6(9)	1 746.5(1.0)
D_c/g cm^{-3}	1.557	1.841	1.487	1.781
F(000)	712	940	776	920
μ(Mo-K_α)/cm^{-1}	6.30	48.48	5.63	47.96
Crystal size/mm^3	0.0140	0.0104	0.0176	0.0032
Transmission factors	0.90—0.87	0.58—0.44	0.94—0.85	0.64—0.49
$\theta_{max.}$/°	28	28	28	28
ω-Scan rate/°min^{-1}	6.7—1.0	5.0—0.8	2.5—0.4	2.5—0.4
No. of reflections[b]	3 550	4 166	4 015	4 204
Reflections $I > 2\sigma$	2 071	2 789	3 058	2 141
No. of variables	181	209	200	199
Extinction coefficient, $g \times 10^7$		0.740	1.558	
R	0.045	0.033	0.034	0.043
R'	0.047	0.032	0.040	0.039
S	1.624	1.205	1.859	1.392
Max. residual electron density/e Å^{-3}	0.35	0.43	0.28	0.54

(*b*) Mono-and tri-sulphanes and -selanes[c]

Compound	$S(SO_2C_6H_4Me\text{-}p)_2$ (**5**)	$Se(SO_2C_6H_4Me\text{-}p)_2$ (**6**)	$S_3(SO_2C_6H_4Me\text{-}p)_2$ (**7**)	$Se_3(SO_2C_6H_4Me\text{-}p)_2$ (**8**)
Formula	$C_{14}H_{14}O_4S_3$	$C_{14}H_{14}O_4S_2Se$	$C_{14}H_{14}O_4S_5$	$C_{14}H_{14}O_4S_2Se_3$
M	342.46	389.35	406.59	547.27
System	Monoclinic	Monoclinic	Tetragonal	Tetragonal
Space group	$C2/c$ (no. 15)	$C2/c$ (no. 15)	$P4_12_12$ (no. 92)	$P4_12_12$ (no. 92)
a/Å	18.837(2)	19.014(2)	7.700(1)	7.787(1)
b/Å	5.844(1)	5.752(1)		
c/Å	16.480(2)	16.786(2)	29.305(5)	29.673(8)
β/°	119.90(1)	118.59(1)		
U/Å^3	1 572.7(8)	1 612.0(8)	1 737.4(6)	1 799.3(9)
D_c/g cm^{-3}	1.446	1.604	1.554	2.020
F(000)	712	784	840	1 056
μ(Mo-K_α)/cm^{-1}	4.70	27.64	6.59	68.34
Crystal size/mm^3	0.0187	0.0020	0.0054	0.0067
Transmission factors	0.94—0.90	0.86—0.74	0.93—0.92	0.49—0.41
$\theta_{max.}$/°	30	28	30	30
ω-Scan rate/°min^{-1}	2.5—0.4	2.5—0.4	5.0—0.8	5.0—0.8
No. of reflections[b]	2 289	1 939	2 898	2 993
Reflections $I > 2\sigma$	1 882	1 384	1 571	1 822
No. of variables	124	124	105	105
R	0.035	0.034	0.044	0.041
R'	0.046	0.032	0.043	0.039
S	2.343	1.405	1.222	1.346
Max. residual electron density/e Å^{-3}	0.31	0.41	0.40	0.86

[a] Data common to each compound: system, monoclinic; space group, $P2_1/c$ (no. 14); $Z = 4$. [b] Unique reflections for compounds (**1**)—(**6**); for (**7**) and (**8**), see text. [c] Data common to each compound: $Z = 4$.

Results and Discussion

Views of the molecules, for (**3**)—(**8**) one from each isomorphous pair, are shown in Figures 1 and 2.

Rotameric Forms.—The forms of the sulphane and selane chains including the sulphonyl sulphur and carbon atoms are listed in Table 4 together with the torsion angles along the chains. One of the two lone pairs of bivalent sulphur or smallest and largest torsion angles reported are 67.1° in Rb_2Se_5[15] and 112.1° in $Se_2[CH(Bu^t)_2]_2$.[16] For the disulphonyl-di- and -tri-sulphanes and -selanes the values lie in the normal range.

The range appears to be wider, but the torsion angles involving the sulphonyl S–C bonds (Table 4, first and last angle for a chain) indicate that the oxygen atoms of sulphonyl sulphur exert a stereochemical effect comparable to that of the active

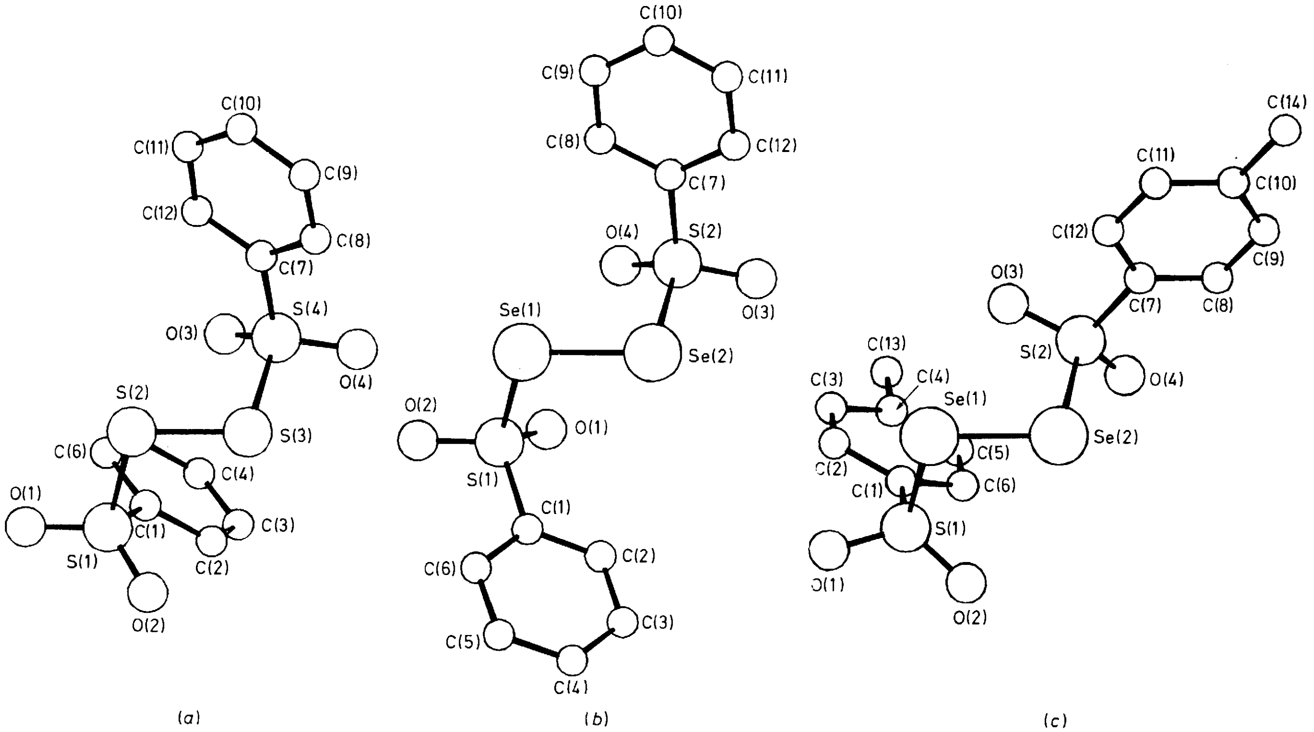

Figure 1. The disulphonyldi-sulphane and -selane molecules (*a*) $S_2(SO_2Ph)_2$, (*b*) $Se_2(SO_2Ph)_2$, and (*c*) $Se_2(SO_2C_6H_4Me\text{-}p)_2$

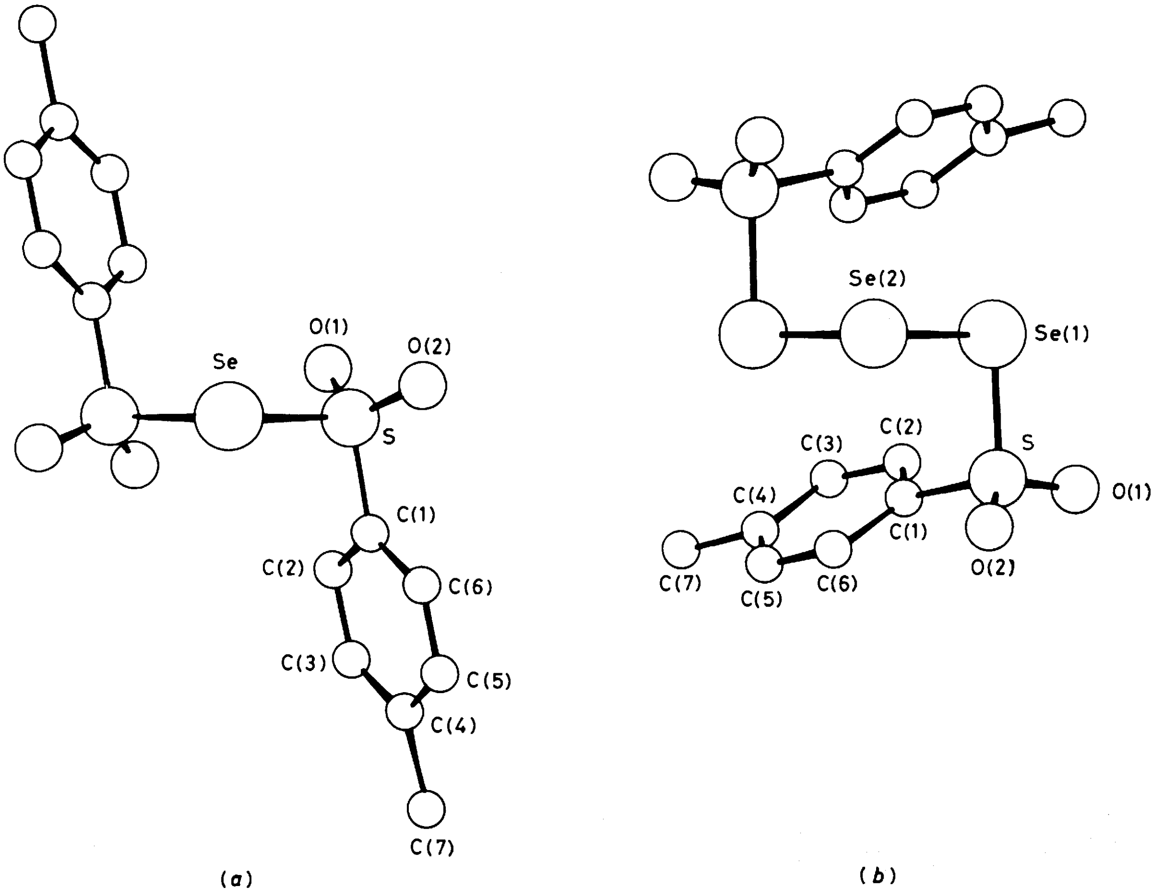

Figure 2. The disulphonyl-mono- and -tri-selane molecules (*a*) $Se(SO_2C_6H_4Me\text{-}p)_2$ and (*b*) $Se_3(SO_2C_6H_4Me\text{-}p)_2$ as seen along the two-fold axes

Table 2. Fractional atomic co-ordinates for compounds **(1)**—**(4)** with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z	x	y	z
(*a*) $S_2(SO_2Ph)_2$				(*b*) $S_2(SO_2C_6H_4Me\text{-}p)_2$		
S(1)	0.163 95(7)	0.427 69(16)	0.493 37(4)	0.228 85(5)	0.042 93(3)	0.085 51(5)
S(2)	0.326 50(8)	0.436 42(20)	0.479 51(5)	0.118 19(6)	0.110 45(4)	-0.054 52(5)
S(3)	0.350 97(8)	0.118 27(20)	0.464 28(4)	-0.024 14(6)	0.173 69(4)	0.026 19(6)
S(4)	0.321 84(7)	0.101 01(16)	0.358 61(4)	0.063 35(6)	0.301 78(4)	0.063 22(5)
O(1)	0.144 8(2)	0.653 0(4)	0.502 56(13)	0.293 10(17)	-0.023 52(10)	0.018 86(16)
O(2)	0.171 2(2)	0.274 7(5)	0.546 34(11)	0.142 76(16)	0.108 21(11)	0.174 85(14)
O(3)	0.228 4(2)	0.238 5(5)	0.322 43(11)	0.185 11(15)	0.306 28(10)	0.005 85(15)
O(4)	0.316 2(2)	-0.130 7(5)	0.347 17(15)	0.065 54(21)	0.312 70(13)	0.189 46(14)
C(1)	0.065 7(2)	0.331 9(5)	0.416 70(14)	0.351 05(19)	0.116 66(13)	0.148 45(17)
C(2)	0.022 8(3)	0.122 2(6)	0.413 02(16)	0.467 47(22)	0.129 63(15)	0.092 42(19)
C(3)	-0.057 7(3)	0.054 8(7)	0.352 88(20)	0.563 86(22)	0.186 26(16)	0.143 64(21)
C(4)	-0.093 5(3)	0.194 5(7)	0.298 18(19)	0.546 38(22)	0.230 29(15)	0.250 00(21)
C(5)	-0.048 9(3)	0.401 5(7)	0.302 11(18)	0.428 37(24)	0.216 10(16)	0.303 51(20)
C(6)	0.031 8(3)	0.471 7(6)	0.361 98(17)	0.330 35(22)	0.159 88(15)	0.253 93(19)
C(7)	0.448 9(2)	0.204 3(6)	0.349 32(14)	-0.059 02(21)	0.372 56(13)	-0.006 59(18)
C(8)	0.546 3(3)	0.073 7(6)	0.367 92(15)	-0.146 64(25)	0.416 38(16)	0.060 70(20)
C(9)	0.644 0(3)	0.153 8(7)	0.360 43(18)	-0.244 62(25)	0.469 57(16)	0.003 97(24)
C(10)	0.646 4(3)	0.358 6(8)	0.334 85(17)	-0.257 72(23)	0.479 64(14)	-0.118 93(22)
C(11)	0.549 2(3)	0.488 7(6)	0.316 33(17)	-0.166 63(25)	0.436 21(16)	-0.183 98(21)
C(12)	0.449 5(3)	0.412 3(6)	0.324 10(15)	-0.067 65(23)	0.382 69(16)	-0.129 97(19)
C(13)				0.653 95(29)	0.291 45(22)	0.303 94(30)
C(14)				-0.364 82(28)	0.537 39(19)	-0.181 71(31)
(*c*) $Se_2(SO_2Ph)_2\cdot\frac{1}{2}C_6H_6$				(*d*) $Se_2(SO_2C_6H_4Me\text{-}p)_2$		
Se(1)	-0.714 08(7)	0.188 44(3)	0.101 06(2)	0.126 19(7)	0.107 84(4)	-0.066 61(5)
Se(2)	0.404 95(7)	0.078 26(3)	0.062 66(2)	-0.039 20(6)	0.172 44(4)	0.022 71(7)
S(1)	0.584 77(19)	0.246 40(7)	0.177 70(4)	0.234 81(15)	0.041 36(10)	0.089 59(14)
S(2)	0.106 82(17)	0.165 61(8)	-0.006 81(4)	0.054 60(17)	0.305 33(10)	0.063 10(14)
O(1)	0.316 0(5)	0.265 2(2)	0.157 35(12)	0.302 1(4)	-0.025 8(3)	0.029 1(4)
O(2)	0.762 3(6)	0.321 4(2)	0.200 91(13)	0.146 6(4)	0.019 9(3)	0.178 4(4)
O(3)	-0.118 9(5)	0.108 1(2)	-0.018 00(12)	0.174 6(4)	0.310 4(3)	0.003 2(4)
O(4)	0.106 5(5)	0.260 1(2)	0.014 12(12)	0.056 9(5)	0.315 7(3)	0.188 9(4)
C(1)	0.645 7(7)	0.155 6(3)	0.232 12(15)	0.352 2(5)	0.115 8(3)	0.152 2(5)
C(2)	0.454 2(8)	0.092 7(3)	0.230 87(17)	0.469 1(6)	0.126 4(4)	0.098 1(5)
C(3)	0.506 6(8)	0.019 9(3)	0.271 75(19)	0.561 1(6)	0.183 5(4)	0.148 6(6)
C(4)	0.745 8(9)	0.010 0(3)	0.312 86(19)	0.539 9(6)	0.229 2(4)	0.249 9(6)
C(5)	0.932 3(9)	0.074 4(4)	0.315 25(19)	0.422 1(7)	0.216 8(4)	0.302 2(5)
C(6)	0.884 0(8)	0.147 5(3)	0.273 85(19)	0.327 7(6)	0.160 2(4)	0.253 4(5)
C(7)	0.206 4(7)	0.166 4(3)	-0.072 17(16)	-0.064 9(6)	0.375 2(3)	-0.003 6(5)
C(8)	0.369 4(8)	0.236 3(3)	-0.078 10(18)	-0.149 8(7)	0.418 4(4)	0.064 4(5)
C(9)	0.454 6(8)	0.234 4(4)	-0.128 09(19)	-0.247 8(6)	0.471 0(4)	0.009 2(6)
C(10)	0.374 8(9)	0.164 4(4)	-0.170 46(18)	-0.259 4(6)	0.481 3(4)	-0.111 7(6)
C(11)	0.213 3(9)	0.095 8(3)	-0.164 14(19)	-0.171 6(7)	0.438 1(4)	-0.177 7(6)
C(12)	0.125 7(8)	0.096 0(3)	-0.114 69(17)	-0.074 8(6)	0.385 1(4)	-0.125 6(5)
C(13)	0.692 9(9)	0.438 6(3)	0.027 04(22)	0.644 2(8)	0.291 6(5)	0.304 8(8)
C(14)	0.523 4(9)	0.464 1(4)	0.056 11(19)	-0.366 7(7)	0.538 9(5)	-0.171 9(8)
C(15)	0.332 6(9)	0.525 9(4)	0.029 51(21)			

and only one of the enantiomers occurs in each unit cell; in the other crystals each unit cell contains both enantiomers.

Dimensions of the Sulphonyl Groups.—Data are summarized in Table 5.* Of the 12 independent groups, six are derived from sulphanes and six from selanes. The ranges of distances and angles are small, and the sulphonyl groups are thus fairly rigid. The averages of the O–S–O angle and the two O–S–C angles for a group range from 112.90(4) to 113.39(5) in the sulphanes and from 112.41(10) to 113.18(15)° in the selanes.

Bond Lengths in the Disulphonyl-sulphane and -selane Chains.—The lengths and the bond angles are listed in Table 6. The lengths vary considerably for bonds of the same type. The terminal bonds, from bivalent sulphur or selenium to sulphonyl sulphur, are S–S 2.101(1)—2.141(1) and S–Se 2.242(1)—2.286(1) Å, and the central bonds, between bivalent atoms, are S–S 1.987(1)—2.037(1) and Se–Se 2.246(1)—2.304(1) Å. In an attempt to rationalize the variations, we focus on the sulphanes.

The disulphonyldisulphanes are the oxidative dimerization products of the thiosulphonate ions. In the latter ions, the S–S bonds are partially double bonds.[18–20] They are relatively short, but the lengths vary: S–S 1.979(6) Å in $MeSO_2SNa\cdot H_2O$[19] and 1.940(2) Å in a $PhSO_2S^-$ salt.[21] Upon oxidation, or bonding through sulphur to other centres, the S–S bonds of the thiosulphonate groups become longer; the double-bond character is reduced or lost. The lengths vary; for example, in $S_2(SO_2C_6H_4Me\text{-}p)_2$ the terminal S–S bonds are 2.101(1) and 2.141(1) Å.

For insular and polymerized oxy-anions TO_4^{n-} (T = central atom, *e.g.* S), among them the sulphate ion, Gibbs and co-

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* Throughout this paper means are weighted means, $x_m = \Sigma(x_i/\sigma_i^2)/\text{-}\Sigma(1/\sigma_i^2)$, with estimated standard deviations (e.s.d.s) given in parentheses as $\sigma_m = \{\Sigma[(x_i - x_m)/\sigma_i]^2/(N - 1)\Sigma(1/\sigma_i^2)\}^{\frac{1}{2}}$ or as $\sigma_m' = 1/[\Sigma(1/\sigma_i^2)]^{\frac{1}{2}}$ whichever is largest, *cf.* ref. 17.

Table 3. Fractional atomic co-ordinates for compounds (**5**)—(**8**) with e.s.d.s in parentheses

Atom	x	y	z	x	y	z
(*a*) $S(SO_2C_6H_4Me\text{-}p)_2$				(*b*) $S_3(SO_2C_6H_4Me\text{-}p)_2$		
S(1)	0.461 29(2)	0.188 64(8)	0.133 69(2)	0.069 15(13)	0.554 02(14)	0.029 20(3)
S(2)	$\frac{1}{2}$	0.407 35(11)	$\frac{1}{4}$	0.147 24(13)	0.407 25(14)	−0.027 68(3)
S(3)				0.165 28(14)	0.165 28[a]	0
O(1)	0.424 32(7)	−0.011 2(2)	0.146 50(8)	0.035 0(4)	0.720 7(4)	0.009 97(9)
O(2)	0.414 55(7)	0.344 2(3)	0.058 60(8)	−0.064 2(3)	0.464 4(4)	0.053 12(9)
C(1)	0.550 59(8)	0.114 9(3)	0.131 73(9)	0.256 5(4)	0.562 3(5)	0.063 22(11)
C(2)	0.589 76(10)	−0.090 3(3)	0.170 28(12)	0.400 1(5)	0.650 3(5)	0.047 47(11)
C(3)	0.659 30(11)	−0.143 4(4)	0.166 10(13)	0.546 6(5)	0.659 3(5)	0.073 39(12)
C(4)	0.689 63(9)	0.000 2(4)	0.124 91(11)	0.553 9(5)	0.580 0(5)	0.116 17(12)
C(5)	0.649 84(10)	0.203 0(4)	0.087 75(11)	0.408 4(5)	0.490 0(5)	0.130 90(11)
C(6)	0.580 73(9)	0.262 6(3)	0.091 06(11)	0.260 3(5)	0.478 5(5)	0.105 15(11)
C(7)	0.764 65(12)	−0.065 2(5)	0.119 22(15)	0.713 4(6)	0.594 0(6)	0.145 17(14)
(*c*) $Se(SO_2C_6H_4Me\text{-}p)_2$				(*d*) $Se_3(SO_2C_6H_4Me\text{-}p)_2$		
Se(1)[b]	$\frac{1}{2}$	0.423 27(8)	$\frac{1}{4}$	0.141 67(9)	0.418 80(8)	−0.032 68(2)
Se(2)				0.150 51(8)	0.150 51[a]	0
S	0.464 42(4)	0.177 91(16)	0.132 13(4)	0.064 53(20)	0.568 93(21)	0.028 52(5)
O(1)	0.431 43(11)	−0.029 5(4)	0.147 84(13)	0.041 4(6)	0.740 5(6)	0.011 61(14)
O(2)	0.416 83(11)	0.325 7(5)	0.057 03(12)	−0.071 7(5)	0.484 4(7)	0.051 18(13)
C(1)	0.553 78(14)	0.112 4(5)	0.130 43(16)	0.249 4(7)	0.564 8(7)	0.062 65(13)
C(2)	0.595 77(17)	−0.085 1(6)	0.171 56(18)	0.393 4(7)	0.649 2(8)	0.048 22(16)
C(3)	0.664 84(19)	−0.133 4(6)	0.167 45(22)	0.538 2(7)	0.649 2(8)	0.074 61(19)
C(4)	0.692 38(17)	0.009 0(7)	0.123 19(18)	0.538 2(8)	0.566 9(8)	0.116 02(18)
C(5)	0.649 85(17)	0.206 3(7)	0.083 32(18)	0.392 0(8)	0.481 6(8)	0.128 93(16)
C(6)	0.581 22(17)	0.258 5(6)	0.086 97(18)	0.249 0(8)	0.477 9(8)	0.103 57(16)
C(7)	0.767 15(20)	−0.051 0(9)	0.117 14(25)	0.695 6(9)	0.572 8(10)	0.146 05(20)

[a] $y = x$ by symmetry. [b] Se for $Se(SO_2C_6H_4Me\text{-}p)_2$.

Table 4. Rotameric forms of the disulphonyl-mono, -di-, and -tri-sulphane and -selane chains[a]

Compound	Chain and torsion angles/°	Rotamer
	C–S–X–S–C	
$S(SO_2C_6H_4Me\text{-}p)_2$[b]	−83.6, −83.6	*trans*
$Se(SO_2C_6H_4Me\text{-}p)_2$[b]	−86.1, −86.1	*trans*
	C–S–X–X–S–C	
$S_2(SO_2Ph)_2$	−62.9, 105.5, 77.7	*cis-trans*
$Se_2(SO_2Ph)_2 \cdot \frac{1}{2}C_6H_6$	70.5, 89.2, 82.9	*trans-trans*
$S_2(SO_2C_6H_4Me\text{-}p)_2$	−86.2, 93.5, 124.2	*cis-trans*
$Se_2(SO_2C_6H_4Me\text{-}p)_2$	−88.8, 92.8, 125.6	*cis-trans*
	C–S–X–X–X–S–C	
$S_3(SO_2C_6H_4Me\text{-}p)_2$[b]	2.0, −85.6, −85.6, 72.0	*cis-trans-cis*
$Se_3(SO_2C_6H_4Me\text{-}p)_2$[b]	70.8, −83.2, −83.2, 70.8	*cis-trans-cis*

[a] In this and subsequent Tables, X = S or Se. [b] Molecular two-fold axis.

workers[22] showed that, as predicted in calculations of bond-overlap populations, the observed T–O bond lengths correlate with the average of the three O–T–O angles common to each bond, with shorter bonds tending to be involved in wider angles. We now examine the bond angles in the present groups.

Thiosulphonate groups. For the S–S bond of tetrahedral CSO_2S, the triple angle average, $\langle\alpha\rangle$, is the average of the S–S–C angle and the two S–S–O angles. Data, for compounds where the S–S bond length has been determined with an e.s.d. better than 0.01 Å, are listed in Table 7 and plotted in Figure 3. In the square-planar tellurium(II) complexes $TeL_2(S_2O_2R)_2$ included, bonding to the ligands is of the three-centre four electron type, and the thiosulphonate S–S bonds are relatively short.[23] The least-squares line ($r = -0.985$) in Figure 3 for the 17 pairs of

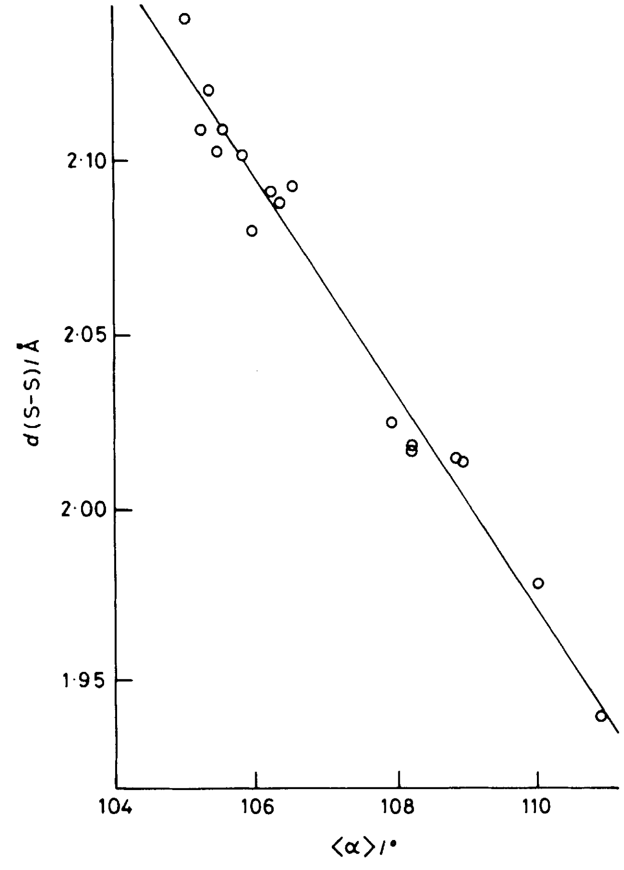

Figure 3. Plot of d(S–S) against triple angle average $\langle\alpha\rangle$ for thiosulphonate groups

values obeys equation (1). It fits the observed S–S bond lengths with a root-mean-square deviation ($\Delta_{r.m.s.}$) of 0.009 Å.

$$d(\text{S–S}) = 5.383 - 0.031\,03\langle\alpha\rangle \qquad (1)$$

The disulphonylsulphanes are represented by the six upper points in Figure 3. The uppermost point, at S–S 2.141(1) Å and above the line, derives from a group in $S_2(SO_2C_6H_4Me\text{-}p)_2$ which displays anomalous torsion angles: the SSSC angle is 124.2°, see Table 4, and the SSSO angles are 7.6 and −122.0°. Repulsions occur, and the S–S bond is long.

A dependence of S–O bond length on angles should also be expected, but to a smaller degree. The ranges of values for the disulphonylsulphanes, S–O 1.420(2)—1.433(2) Å and $\langle\alpha\rangle$ 105.0—105.8°, may be compared with the values for the $PhSO_2S^-$ salt,[21] S–O 1.447(4) and 1.464(3) Å and $\langle\alpha\rangle$ 110.9°.

We conclude that in thiosulphonate groups there is an interplay between bond lengths and angles.

Table 5. Summary of distances (Å) and angles (°) in the sulphonyl groups of the disulphonyl-sulphanes and -selanes. Upper values, sulphanes; lower, selanes

	Range	Mean
S–O	1.420(2)—1.433(2)	1.426(1)
	1.418(4)—1.446(3)	1.431(2)
S–C	1.749(1)—1.759(3)	1.751(1)
	1.747(5)—1.767(4)	1.757(2)
O–S–O	119.92(19)—120.82(6)	120.55(12)
	119.96(18)—120.71(13)	120.36(15)
O–S–C	108.74(7)—110.82(7)	109.44(22)
	108.05(24)—110.40(24)	109.06(17)
O···O	2.465(3)—2.486(1)	2.480(4)
	2.476(6)—2.488(4)	2.484(2)
O···C	2.591(2)—2.618(2)	2.599(3)
	2.579(6)—2.618(6)	2.605(4)

Overall means: S–O 1.427(1) and S–C 1.752(1) Å; O–S–O 120.51(9) and O–S–C 109.38(15)°; O···O 2.481(2) and O···C 2.600(2) Å.

Selenosulphonate groups. For these, structural data are more scarce. Apart from the less accurately determined structure of $Se(SO_2Ph)_2$,[4] the only examples are the four disulphonylselanes of the present paper, with in all six independent groups. Ionic selenosulphonates have not been prepared; aqueous sodium toluene-*p*-sulphinate did not add selenium.[2] For the six groups, d(Se–S) = 2.242(1)—2.286(1) Å. The correlation with

Table 7. Sulphur–sulphur bond lengths (Å) and triple angle averages $\langle\alpha\rangle$ (°) in thiosulphonate groups

Compound	S–S	$\langle\alpha\rangle$	Ref.
$S(SO_2C_6H_4Me\text{-}p)_2$	2.109(1)	105.2(1)	*a*
$S_2(SO_2Ph)_2$	2.120(1)	105.3(1)	*a*
	2.109(1)	105.5(1)	
$S_2(SO_2C_6H_4Me\text{-}p)_2$	2.101(1)	105.8(1)	*a*
	2.141(1)	105.0(1)	
$S_3(SO_2C_6H_4Me\text{-}p)_2$	2.102(1)	105.4(1)	*a*
$RSSO_2R$[b]	2.091(6)	106.2(1)	*c*
$Te(S_2O_2Me)_2$	2.093(1)	106.5(1)	*d*
	2.088(1)	106.3(1)	
$Te(S_2O_2Ph)_2$	2.080(1)	105.9(2)	*e*
$Te(etu)_2(S_2O_2Me)_2$ (triclinic)[f]	2.014(9)	108.9(5)	*g*
(monoclinic)	2.015(7)	108.8(3)	*g*
$Te(etu)_2(S_2O_2Ph)_2$[f]	2.016(5)	108.2(3)	*h*
$Te(trtu)_2(S_2O_2Ph)_2$[i]	2.018(4)	108.2(2)	*j*
$Te(tmtu)_2(S_2O_2Ph)_2$[k]	2.025(6)	107.9(3)	*l*
$MeSO_2SNa{\cdot}H_2O$	1.979(6)	110.0(4)	19
$[Te(trtu)_4][S_2O_2Ph]_2{\cdot}2MeOH$[i]	1.940(2)	110.9(1)	21

[a] This work. [b] R = *p*-BrC_6H_4. [c] J. H. Noordik and A. Vos, *Recl. Trav. Chim. Pays-Bas*, 1976, **86**, 156. [d] O. Foss and E. H. Vihovde, *Acta Chem. Scand.*, 1954, **8**, 1032. The data quoted are from a refinement of the structure. [e] P. Øyum and O. Foss, *Acta Chem. Scand.*, 1956, **10**, 279; K. Åse, *ibid.*, 1971, **25**, 838. [f] etu = Ethylenethiourea. [g] O. Foss, N. Lyssandtræ, K. Maartmann-Moe, and M. Tysseland, *Acta Chem. Scand.*, 1973, **27**, 218. [h] K. Åse, K. Maartmann-Moe, and J. O. Solheim, *Acta Chem. Scand.*, 1971, **25**, 2467. [i] trtu = Trimethylenethiourea. [j] K. Åse, *Acta Chem. Scand.*, 1969, **23**, 3206. [k] tmtu = Tetramethylthiourea. [l] K. Åse and I. Roti, *Acta Chem. Scand., Ser. A*, 1974, **28**, 104.

Table 6. Bond lengths (Å) and angles (°) in the C–S–X_n–S–C chains

(*a*) Di-sulphanes and -selanes

	$S_2(SO_2Ph)_2$	$S_2(SO_2C_6H_4Me\text{-}p)_2$		$Se_2(SO_2Ph)_2{\cdot}\frac{1}{2}C_6H_6$	$Se_2(SO_2C_6H_4Me\text{-}p)_2$
C(1)–S(1)	1.752(3)	1.749(1)	C(1)–S(1)	1.761(4)	1.760(5)
S(1)–S(2)	2.120(1)	2.101(1)	S(1)–Se(1)	2.268(1)	2.249(1)
S(2)–S(3)	2.008(1)	1.987(1)	Se(1)–Se(2)	2.282(1)	2.246(1)
S(3)–S(4)	2.109(1)	2.141(1)	Se(2)–S(2)	2.275(1)	2.286(1)
S(4)–C(7)	1.759(3)	1.751(2)	S(2)–C(7)	1.767(4)	1.747(5)
C(1)–S(1)–S(2)	106.50(8)	107.22(5)	C(1)–S(1)–Se(1)	104.9(1)	107.1(2)
S(1)–S(2)–S(3)	101.30(5)	103.84(3)	S(1)–Se(1)–Se(2)	99.89(3)	100.96(5)
S(2)–S(3)–S(4)	103.33(5)	103.05(3)	Se(1)–Se(2)–S(2)	100.80(3)	99.92(5)
S(3)–S(4)–C(7)	104.33(9)	101.87(5)	Se(2)–S(2)–C(7)	104.9(1)	101.6(2)

(*b*) Mono- and tri-sulphanes and -selanes[a]

	$S(SO_2C_6H_4Me\text{-}p)_2$	$Se_3(SO_2C_6H_4Me\text{-}p)_2$		$Se(SO_2C_6H_4Me\text{-}p)_2$	$Se_3(SO_2C_6H_4Me\text{-}p)_2$
C(1)–S(1)	1.752(1)	1.754(3)	C(1)–S	1.754(2)	1.761(5)
S(1)–S(2)	2.109(1)	2.102(1)	S–Se(1)[b]	2.255(1)	2.242(1)
S(2)–S(3)		2.037(1)	Se(1)–Se(2)		2.304(1)
C(1)–S(1)–S(2)	105.41(4)	103.6(1)	C(1)–S–Se(1)[b]	105.23(9)	103.7(2)
S(1)–S(2)–S(1′)	105.37(2)		S–Se–S′	102.50(4)	
S(1)–S(2)–S(3)		101.28(5)	S–Se(1)–Se(2)		98.05(5)
S(2)–S(3)–S(2′)		106.46(9)	Se(1)–Se(2)–Se(1′)		103.37(4)

[a] Primed atoms related to unprimed ones by a molecular two-fold axis. [b] Se for $Se(SO_2C_6H_4Me\text{-}p)_2$.

Table 8. Lengths (Å) of terminal bonds in isomorphous pairs of disulphonyl-sulphanes and -selanes

Compounds	S–S	Se–S	Δ
$X(SO_2C_6H_4Me\text{-}p)_2$	2.109(1)	2.255(1)	0.146(1)
$X_2(SO_2C_6H_4Me\text{-}p)_2$	2.101(1)	2.249(1)	0.148(1)
	2.141(1)	2.286(1)	0.145(1)
$X_3(SO_2C_6H_4Me\text{-}p)_2$	2.102(1)	2.242(1)	0.140(1)
Mean	2.113(9)	2.258(10)	0.145(2)

Table 9. Bond lengths (Å) in isomorphous pairs of di-, tri-, and tetra-sulphanes and -selanes

Compounds	S–S	Se–Se	Δ	Ref.
$X_2(C_6F_5)_2$	2.059(4)	2.319(4)	0.260(6)	*a*
$X_2(SO_2C_6H_4Me\text{-}p)_2$	1.987(1)	2.246(1)	0.259(1)	*b*
$X_3(CN)_2$	2.067(1)	2.334(1)	0.267(1)	*c*
$X_3(SO_2C_6H_4Me\text{-}p)_2$	2.037(1)	2.304(1)	0.267(1)	*b*
$X_4(NC_4H_8O)_2$[d]	2.061(2)	2.336(2)	0.275(3)	30
	2.078(3)	2.356(2)	0.278(4)	

[a] C. M. Woodard, D. S. Brown, J. D. Lee, and A. G. Massey, *J. Organomet. Chem.*, 1976, **121**, 333. [b] This work. [c] $S_3(CN)_2$: F. Feher and K-H. Linke, *Z. Anorg. Allg. Chem.*, 1964, **327**, 151; J. W. Bats, *Acta Crystallogr., Sect. B*, 1977, **33**, 2264; $Se_3(CN)_2$: O. Aksnes and O. Foss, *Acta Chem. Scand.*, 1954, **8**, 1787; S. Hauge, *ibid., Ser. A*, 1979, **33**, 313. [d] NC_4H_8O = morpholino.

triple angle average is weak at best, but the range is small. If the values are averaged in pairs, a trend is seen: 2.246, 2.262, and 2.281 Å and 105.9, 105.8, and 105.5°.

Comparisons of Bond Lengths in Disulphonyl-sulphanes and -selanes.—The bonds discussed, in thiosulphonate and selenosulphonate groups, are the terminal bonds in the thionate chains. These bonds are long. The central bonds, between bivalent atoms, are as in other sulphanes and selanes.

Since factors like bond angles and torsion angles influence the bonds, meaningful comparisons can be made only when the influencing factors are as like as possible. In ref. 24 comparisons were made between pairs of di-selanes and -sulphanes with the same terminal groups, so as to eliminate factors like the electronegativity of the terminal groups. However, for compounds in the crystalline state, packing effects and lattice forces may greatly influence torsion angles and bond angles and thereby bond lengths. In each of the disulphonyldi-sulphanes and -selanes the two halves display different angles and bond lengths. Therefore, for crystalline compounds, we preferentially restrict our comparisons to isomorphous pairs.

The terminal bonds. Data for the three isomorphous di-*p*-tolylsulphonyl-sulphane and -selane pairs are listed in Table 8. The difference, Δ, between the $Se{-}SO_2C_6H_4Me\text{-}p$ and $S{-}SO_2C_6H_4Me\text{-}p$ bond lengths is 0.140(1)—0.148(1) Å with a mean of 0.145(2) Å. For $Se_2(SO_2Ph)_2$ and $S_2(SO_2Ph)_2$, which are not isomorphous, the mean Δ is 0.157(4) Å.

The central bonds. Table 9 gives a list of S–S and Se–Se bonds in isomorphous pairs of sulphanes and selanes. As before, data only with e.s.d.s less than 0.01 Å are included. The lengths vary, by 0.091 Å for S–S and 0.110 Å for Se–Se. The difference, Δ, is more consistent: 0.259(1) Å for the two X_2R_2 pairs, 0.267(1) Å for the two X_3R_2 pairs, and 0.276(2) Å for the one X_4R_2 pair. The increase of Δ from X_2R_2 over X_3R_2 to X_4R_2 might indicate a significant trend. However, for a pair in the gas phase, X_2Me_2 with S–S 2.022(3)[25] or 2.029(3) Å[26] and Se–Se 2.326(4) Å,[27] Δ is 0.301(5) Å, and for an isomorphous pair of salts, K_2X_3 with S–S 2.083(1) and Se–Se 2.383(2) Å,[28] Δ is 0.300(2) Å.

The central bonds in the $X_2(SO_2C_6H_4Me\text{-}p)_2$ pair, S–S 1.987(1) and Se–Se 2.246(1) Å, are among the shortest reported for sulphanes or selanes. The shortness is due, partly at least, to the length of the adjacent, terminal bond, S–S 2.141(1) and Se–S 2.286(1) Å in one of the $XSO_2C_6H_4Me\text{-}p$ groups; in chains of sulphur or selenium atoms the bond lengths alternate.[20,29,30]

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