THE STEREOCHEMISTRY OF SUB-GROUP VIB OF THE PERIODIC TABLE

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THE properties of the elements in sub-group VIB of the Periodic Table, oxygen, sulphur, selenium, tellurium, and polonium, undergo striking transitions as the group is ascended. The chemical behaviour of the group passes from that of the typical non-metals oxygen and sulphur, to the typical metal polonium. A systematic change is also found in the structure of the elements, from diatomic molecules, through ring and chain molecules, to a simple lattice composed of polonium atoms. A corresponding transition in electrical properties accompanies the structural evolution, for oxygen and sulphur are insulators, selenium and tellurium are semiconductors, and polonium shows metallic conduction. The interrelation between structure and conductivity has already been discussed.[1]

Within this sub-group, chemical bonds to one, two, three, four, and six other atoms are known, and this complexity in bond formation has attracted sustained interest over many years. In the last decade, a great increase in both theoretical and, particularly, experimental knowledge regarding the nature of the various kinds of chemical bond formed by the atoms of sub-group VIB has become available. The present Review is an attempt to bring together the most important information concerning the geometrical and electronic configuration of these atoms in their different bonded states.

The Stereochemistry of Oxygen

(a) *Two-bonded Oxygen.*—The mechanism of bond formation by bivalent oxygen is well exemplified by the case of the water molecule. The H–O–H angle would be 90° if pure p orbitals alone were used by the oxygen atom. Experimentally, this angle is found to be 104·5° (Table 1), which could be the result of an admixture of some s with the oxygen p orbitals. A full account of the electronic nature of the water molecule has been given by Coulson.[2] In general, the amount of s-character in the bonds formed by bivalent oxygen will be determined by the nature of the other atoms present. The s-admixture could vary from small percentages, giving bond angles close to 90°, to that required for sp^2 hybridisation.

An examination of Table 1 reveals that the values for the oxygen valency angle measured in a variety of molecules fall, within the limits of error, into two fairly distinct groups. With the exception of ozone, the angle is

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[1] von Hippel, *J. Chem. Phys.*, 1948, **16**, 372.

[2] Coulson, " Valence ", Oxford Univ. Press, Oxford, 1952.

TABLE 1. *Oxygen valency angle*

Molecule	Angle	Method *	Ref.
Ethylene oxide	61·6° ± 0·1°	M.W.	3
Trimethylene oxide	94·5° ± 3°	E.D.	4
Mercury diethylene oxide . . .	96° ± 6°	*X*-Ray	5
Fluorine monoxide	101·5° ± 1·5°	Spec.	6
	103·8° ± 1·5°	E.D.	7
Hydrogen deutero-oxide . . .	104·0° ± 0·5°	Spec.	8
Water	104·5° ± 0·1°	,,	9
	105·1° ± 0·1°	,,	10
Dimethyl peroxide	105° ± 3°	E.D.	4
Furan	106·2°	M.W.	11
	108·1°	E.D.	12
Divinyl ether	107° ± 3°	,,	13
	112° ± 2°	,,	4
Diethyl ether	108° ± 3°	,,	4
Mercuric oxide	109·8°	*X*-Ray and N.D.	14
Chlorine monoxide	110·8° ± 1°	E.D.	15
Dimethyl ether	110°	D.M.	16
1 : 4-Dioxan	108° ± 5°	E.D.	17
	112° ± 5°	,,	4
Benzofurazan	112° ± 12°	*X*-Ray	18
Potassium ethyl sulphate . . .	114° ± 4°	,,	19
Ozone	116·8° ± 0·5°	M.W.	20
p-Dimethoxybenzene	121° ± 2°	*X*-Ray	21
Di-*p*-bromophenyl ether . . .	123° ± 1°	,,	22†
Di-*p*-iodophenyl ether	123° ± 2°	,,	23
	123° ± 1°	,,	24
Diphenyl ether	124° ± 5°	D.M.	25

* Abbreviations used in this and in all subsequent tables are : D.M., dipole moment ; E.D., electron diffraction ; M.W., microwave ; N.D., neutron diffraction ; Spec., spectroscopy ; *X*-Ray, *X*-ray diffraction.

† A number of references to earlier determinations are given in this paper.

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[3] Cunningham, Boyd, Myers, Gwinn, and Le Van, *J. Chem. Phys.*, 1951, **19**, 676.

[4] Quoted by Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46.

[5] Grdenić, *ibid.*, 1952, **5**, 367.

[6] Bernstein and Powling, *J. Chem. Phys.*, 1950, **18**, 685.

[7] Ibers and Schomaker, *J. Phys. Chem.*, 1953, **57**, 699.

[8] Strandberg, *J. Chem. Phys.*, 1949, **17**, 901.

[9] Darling and Dennison, *Phys. Rev.*, 1940, **57**, 128.

[10] Herzberg, "Infrared and Raman Spectra", 1945, p. 489, D. van Nostrand Co. Inc., N.Y.

[11] Bak, Hansen, and Rastrup-Andersen, *Discuss. Faraday Soc.*, 1955, **19**, 30.

[12] Almenningen, Bastiansen, and Hansen, *Acta Chem. Scand.*, 1955, **9**, 1306.

[13] Barricelli and Bastiansen, *ibid.*, 1949, **3**, 201.

[14] Roth, *Acta Cryst.*, 1956, **9**, 277.

[15] Dunitz and Hedberg, *J. Amer. Chem. Soc.*, 1950, **72**, 3108.

[16] Gibbs, *J. Chem. Phys.*, 1954, **22**, 1460.

[17] Hassel and Viervoll, *Acta Chem. Scand.*, 1947, **1**, 149.

[18] Luzzati, *Acta Cryst.*, 1951, **4**, 193.

[19] Jarvis, *ibid.*, 1953, **6**, 327.

[20] Trambarulo, Ghosh, Burrus, and Gordy, *J. Chem. Phys.*, 1953, **21**, 851 ; Hughes, *ibid.*, 1956, **24**, 131.

[21] Goodwin, Przybylska, and Robertson, *Acta Cryst.*, 1950, **3**, 279.

[22] Toussaint, *Mem. Soc. roy. Sci., Liège*, 1952, **12**, 1.

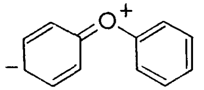
[23] Plieth, *Z. Naturforsch.*, 1947, **2a**, 409.

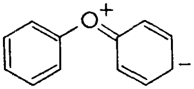
[24] Toussaint, *Bull. Soc. Sci. Liège*, 1946, **15**, 86.

[25] Coop and Sutton, *J.*, 1938, 1869.

about 109·5° or less, unless one or both of the attached groups are aromatic, in which case the angle is very close to 120°. It hence appears that in these non-aromatic molecules, use is made of the oxygen 2*s* orbitals to approach sp^3 (tetrahedral) hybridisation. Where an aromatic group is involved, the hybridisation appears to be sp^2 (trigonal). Both in ozone and in the aromatic ethers, various ionic canonical forms are likely to contribute to the final electronic structure, *e.g.*, (I) and (II).

(I)

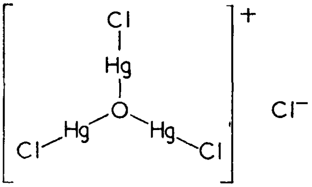




(II)

In ethylene oxide, which appears to be an example of strain in the classical sense, p^2 bonding has been assumed [3] for the oxygen atom, with " bent " bonds lying along the arc, tangents to the carbon and oxygen orbitals.

(b) *Higher Valencies of Oxygen.*—The literature gives but few reports of critical measurements of molecular dimensions for compounds containing oxygen exhibiting a valency higher than two. Recently, the crystal structure of trischloromercurioxonium chloride has been solved [26, 27] and shown to consist of the ions (III). The two studies are essentially in complete agreement and show that the planar trischloromercurioxonium ion possesses trigonal symmetry, the O–Hg–Cl group being nearly linear (O–Hg–Cl=175°).



(III)

The unsubstituted hydroxonium ion OH_3^+ has been studied [28] by infrared spectroscopy, and reported to possess C_3 symmetry, with angles close to tetrahedral. This ion is hence very similar to NH_3 with which it is isoelectronic. These determinations of the symmetry of two OR_3^+ ions are thus in disagreement, possibly because of the difference in size between hydrogen and mercury.

There are no unambiguous examples of oxygen forming four simultaneous covalent bonds. The cases of basic beryllium acetate and the zinc blende-type oxides have been discussed by Wells.[29]

(c) *The Oxygen–Oxygen Dihedral Angle.*—A fundamental stereochemical property of oxygen that has received considerable attention is the dihedral angle formed by the planes containing the oxygen–oxygen bond, and, severally, each of the other oxygen valency bonds. A discussion of this

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[26] Šćavničar and Grdenić, *Acta Cryst.*, 1955, **8,** 275.

[27] Weiss, Nagorsen, and Weiss, *Z. anorg. Chem.*, 1953, **274,** 151.

[28] Ferriso and Hornig, *J. Chem. Phys.*, 1955, **23,** 1464.

[29] Wells, " Structural Inorganic Chemistry ", Oxford U.P., 1945.

angle (ϕ in Fig. 1) was given for the case of H_2O_2 by Penney and Sutherland,[30] who assumed that only oxygen p orbitals were used in bonding.

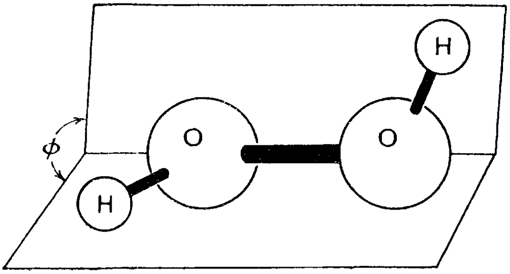

FIG. 1
Structure of the hydrogen peroxide molecule.

They showed that the predominant steric factor governing the dihedral angle is not the interaction between hydrogen atoms, nor that between OH bonds, but is the repulsive interaction between the unpaired electrons on each oxygen atom. This repulsion is greatest when the orbitals containing the lone pairs are parallel. They calculated the molecule to have a minimum potential energy for ϕ about 100°. Lassettre and Dean [31] took additional interactions into account, and did not make the assumption that p orbitals alone would be used. They found that the combined effect of all the interaction energies resulted in an equilibrium dihedral angle that lay in the range 94—113°.

A crystallographic study [32] of the hydrogen peroxide–urea addition complex led to the assignment of $106° \pm 2°$ for the dihedral angle, and a later *X*-ray study [33] of solid hydrogen peroxide at $-20°$ gave $\phi = 94° \pm 1{\cdot}5°$. Giguère [34] quotes the value $80° \pm 20°$ for hydrogen peroxide, based upon a spectroscopic study.

Disulphur decafluorodioxide has now been shown [35] by an electron-diffraction study to possess a peroxide structure, with a S–O–S bond angle of $105° \pm 3°$ and a dihedral angle ϕ of $107° \pm 5°$.

A microwave study [36] of hydrogen peroxide gave the height of the potential barrier as 0·3 kcal./mole, a sinusoidal approximation being used for the hindering potential, while a subsequent paper [37] showed that the then available microwave data were equally applicable to a model in which there is a high *cis*- and a low *trans*-barrier to internal rotation, such as 8 and 0·6 kcal./mole, respectively. Luft [38] places the energy barrier, V_0,

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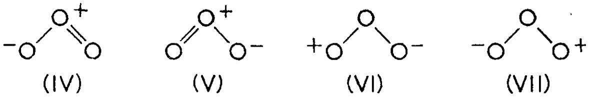
[30] Penney and Sutherland, *Trans. Faraday Soc.*, 1934, **30,** 898.
[31] Lassettre and Dean, *J. Chem. Phys.*, 1949, **17,** 317.
[32] Lu, Hughes, and Giguère, *J. Amer. Chem. Soc.*, 1941, **63,** 1507.
[33] Abrahams, Collin, and Lipscomb, *Acta Cryst.*, 1951, **4,** 15.
[34] Giguère, *Bull. Soc. chim. France*, 1954, **21,** 720.
[35] Harvey and Bauer, *J. Amer. Chem. Soc.*, 1954, **76,** 859.
[36] Massey and Bianco, *J. Chem. Phys.*, 1954, **22,** 442.
[37] Massey and Hart, *ibid.*, 1955, **23,** 942.
[38] Luft, *ibid.*, 1953, **21,** 179.

at $6 < V_0 < 18$ kcal./mole, and has recently reviewed [39] the spectroscopic and thermodynamic data for hydrogen peroxide.

(d) *The Oxygen–Oxygen Bond.*—The oxygen–oxygen bond has now been extensively studied in a variety of different circumstances. The nature of this bond in the oxygen molecule has been discussed by Coulson,[2] in terms of molecular orbital theory. The length of the oxygen–oxygen bond in the ground state for O_2 is given in Table 2, and very closely corresponds to a pure double bond. In ozone, it has been suggested [20] that the bond of length 1·278 Å possesses 50% double-bond character, the canonical structures (IV) and (V) being considered most important with small contributions from (VI) and (VII). Although the preparation of several alkali ozonides has been reported,[40] no structural information was given. Giguère and Harvey [41] have claimed that the ozonide ion does not exist.



The oxygen–oxygen bond length in the HO_2 radical, determined [42] with the aid of Badger's rule, has been taken as indicating a bond similar to that observed in the superoxide ion. Magnetic-susceptibility measurements [43] have shown that the superoxide ion O_2^- contains a three-electron bond. This bond, of length 1·28 Å, may be regarded as derived from the oxygen molecule by filling one of the two vacant antibonding $p\pi$ orbitals. Thus, as in the case of ozone, the oxygen–oxygen bond length of 1·28 Å corresponds to 50% double-bond character.

Bond type (*e*) in Table 2 may be taken as a standard single bond. The identity of bond types (*d*) and (*e*) has been demonstrated [44] on the basis of the magnetic susceptibilities, -18×10^{-6} for O_2^{2-} in Na_2O_2 and $-17{\cdot}7 \times 10^{-6}$ for H_2O_2. This view is strengthened by the identity in bond lengths, and also by a consideration of the electronic structures, for each type may be considered as derived from the oxygen molecule by filling both vacant antibonding $p\pi$ orbitals, thus producing a single bond. The length of a single oxygen–oxygen bond may hence be regarded as 1·49 Å.

The bond in O_2^+, of length 1·12 Å in the $^2\Pi_g$ state, can be considered to possess approximately 150% double-bond character with only one electron in an antibonding orbital. A smooth bond order–bond length curve may now be constructed as in Fig. 2, passing through each point discussed above, within the overall error in that point.

(e) *The Carbon–Oxygen Bond.*—Bond-length and related information is now available for bonds between oxygen and many other atoms. However, apart from the oxygen–oxygen bond, the only bonds for which enough data

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[39] Luft, *Monatsh.*, 1955, **86,** 528.
[40] Whaley and Kleinberg, *J. Amer. Chem. Soc.*, 1951, **73,** 79.
[41] Giguère and Harvey, *ibid.*, 1954, **76,** 5891.
[42] Giguère, *J. Chem. Phys.*, 1954, **22,** 2085.
[43] Klemm and Sodomann, *Z. anorg. Chem.*, 1935, **225,** 273.
[44] Neĭding and Kazarnovskii, *Doklady Akad. Nauk S.S.S.R.*, 1950, **74,** 735.

TABLE 2. *Oxygen–oxygen bond types and lengths*

Case	Bond	Example	Bond length (Å)	Ref.
(*a*)	O—O	O_2	1·2074 ± 0·0001	45
(*b*)	—O—O	O_3	1·278 ± 0·003	20
		HO_2	1·30	42
(*c*)	[O—O]$^-$	β-NaO_2	1·33 ± 0·06	46
			1·31 ± 0·03	47
		α-KO_2	1·28 ± 0·07	48
			1·28 ± 0·02	49
(*d*)	[O—O]$^{2-}$	BaO_2	1·47	50
			1·49 ± 0·04	51
		$CaO_2,8H_2O$	1·48	52
		$SrO_2,8H_2O$	1·49	52
		$BaO_2,8H_2O$	1·48	52
		Li_2O_2	1·3 ± 0·1	53
(*e*)	—O—O—	H_2O_2	1·47 ± 0·02	54
			1·49 ± 0·02	33
			1·49 ± 0·01	34
		$SF_5{\cdot}O_2{\cdot}SF_5$	1·47 ± 0·03	35
(*f*)	[O—O]$^+$	O_2^+	1·1227 ± 0·0001	55

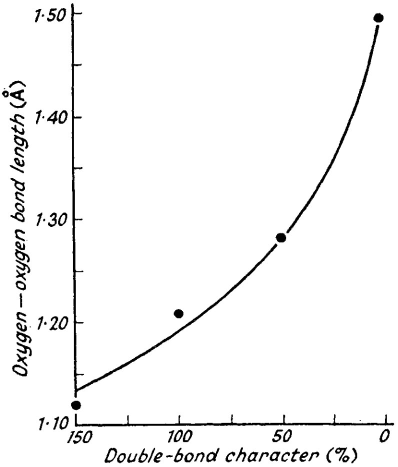

FIG. 2

Variation of the oxygen–oxygen bond length with bond character.

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[45] Babcock and Herzberg, *Astrophys. J.*, 1948, **108,** 167.

[46] Templeton and Dauben, *J. Amer. Chem. Soc.*, 1950, **72,** 2251.

[47] Zhdanov and Zvonkova, *Doklady Akad. Nauk S.S.S.R.*, 1952, **82,** 743.

[48] Kasatochkin and Kotov, *Zhur. Tekhn. Fiz.*, 1937, **7,** 1468.

[49] Abrahams and Kalnajs, *Acta Cryst.*, 1955, **8,** 503.

[50] Butuzov, *Doklady Akad. Nauk S.S.S.R.*, 1947, **58,** 1411.

[51] Abrahams and Kalnajs, *Acta Cryst.*, 1954, **7,** 838.

[52] Harr, Thesis, Syracuse University, N.Y., 1952.

[53] Fehér, von Wilucki, and Dost, *Chem. Ber.*, 1953, **86,** 1429.

[54] Giguère and Schomaker, *J. Amer. Chem. Soc.*, 1943, **65,** 2025.

[55] Herzberg, " Spectra of Diatomic Molecules ", 2nd edtn., Macmillan & Co., London, 1950.

are known to establish bond length–bond order relations are probably the sulphur–oxygen and carbon–oxygen bonds. Of these the former bond is discussed on p. 427 and only the latter bond will be treated here.

The ability of bonds to oxygen to partake of double-bond character in varying degree is well illustrated by the carbon–oxygen bond. Cox and Jeffrey [56] have summarised the data for 22 different molecules containing single carbon–oxygen bonds, and find the mean carbon–oxygen distance to be 1·437 Å. The corresponding double-bond distance, based on determinations for eleven different molecules, results in a mean C═O value of 1·185 Å. Cox and Jeffrey suggest taking 1·44 Å as the standard single carbon–oxygen bond length, but feel that 1·19 Å for the standard double-bond length is less reliable, in view of the postulate [57] that the double-bond length may vary with the polarity of the bond. Vaughan and Donohue [58] have proposed C–O = 1·42 Å and C═O = 1·20 Å.

TABLE 3. *Recent carbon–oxygen bond-length determinations*

Molecule	Bond length (Å)	Method	Ref.
Carbon monoxide . .	1·131 ± 0·005	M.W.	59
Carbonyl chloride . .	1·166 ± 0·002	,,	60
	1·15 ± 0·02	*X*-Ray	61
Anthraquinone . . .	1·15 ± 0·02	,,	62
Carbonyl selenide . .	1·1588 ± 0·0001	M.W.	63
Carbonyl sulphide . .	1·1637 ± 0·0005	,,	64
*iso*Cyanic acid . . .	1·17 ± 0·01	,,	65
	1·184 ± 0·02	*X*-Ray	66
Methyl *iso*cyanate . .	1·18 ± 0·03	E.D.	67
Acetone	1·22 ± 0·03	,,	68
	1·23 ± 0·03	,,	69
	1·24 ± 0·03	,,	70
p-Dimethoxybenzene .	1·36 ± 0·02	*X*-Ray	21
Furan	1·372	M.W.	11
	1·377	E.D.	12
Diketen	1·24 ± 0·06	*X*-Ray	71
	1·39 ± 0·06	,,	71
Ethyl ether	1·43 ± 0·02	E.D.	4
1 : 4-Dioxan	1·44 ± 0·03	,,	4
Methyl ether	1·46 ± 0·03	,,	4
Methanol	1·42 ± 0·03	*X*-Ray	72
	1·43 ± 0·008	M.W.	73
	1·44 ± 0·01	E.D.	4
	1·48 ± 0·04	,,	74
Ethanol	1·48 ± 0·04	,,	74

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[56] Cox and Jeffrey, *Proc. Roy. Soc.*, 1951, **207**, *A*, 110.
[57] Walsh, *Trans. Faraday Soc.*, 1947, **43**, 60.
[58] Vaughan and Donohue, *Acta Cryst.*, 1952, **5**, 530.
[59] Gilliam, Johnson, and Gordy, *Phys. Rev.*, 1950, **78**, 140.
[60] Robinson, *J. Chem. Phys.*, 1953, **21**, 1741.
[61] Zaslow, Atoji, and Lipscomb, *Acta Cryst.*, 1952, **5**, 833.
[62] Sen, *Indian J. Phys.*, 1948, **22**, 347.
[63] Strandberg, Wentink, and Hill, *Phys. Rev.*, 1949, **75**, 827.
[64] Strandberg, Wentink, and Kyhl, *ibid.*, p. 270.
[65] Jones, Shoolery, Shulman, and Yost, *J. Chem. Phys.*, 1950, **18**, 990.
[66] von Dohlen and Carpenter, *Acta Cryst.*, 1955, **8**, 646.

Recent carbon–oxygen bond-length determinations are in good agreement with the value 1·43 Å for a single bond, and with the smaller value of about 1·17 Å for the double bond (see Table 3). The orders of bonds of intermediate length are at present insufficiently established to allow the construction of a relationship other than linear between bond order and length.

The Stereochemistry of Sulphur

(a) *Two-bonded Sulphur.*—Sulphur, in common with all the elements of sub-group VIB, has the valency electron configuration $(ns)^2(np_x)(np_y)(np_z)^2$, where $n = 3$ for sulphur. Unlike oxygen, however, the 3*d* orbitals are available for sulphur bond formation, in an expansion of the outer octet to a decet, or even a duodecet of electrons.

The experimental values for the sulphur valency angle, in which two other atoms only are linked to the atom under consideration, are listed in Table 4. The general similarity in bond angle for sulphur in this table and oxygen in Table 1 indicates that the bond mechanism for sulphur and oxygen cannot be very different. Thus, for the S–S–S bond angle, the measured values vary only from 103° to 108°, with a mean value of 106° (di-iododiethyl trisulphide is an exception). The angular range used is suggestive of a considerable *s*-admixture in the sulphur bonds, with an approach to sp^3 hybridisation.

The bond angle in S_8 has been discussed[75] on the basis of nuclear quadruple resonance measurements. If it is assumed that the observed angle of 107·8° is also the angle between the axes of the two orbitals originating at the sulphur atoms, about 20% of *s* character is estimated in the bond. An alternative view is that if the bond angle is not identical with the inter-orbital angle, then nearly pure *p* orbitals could be used, and the increased size of the bond angle over 90° could be attributed to a pivoting of the *p* orbitals. One interesting difference between the behaviour of sulphur and oxygen is that, apart from SO_2, the 2-bonded sulphur valency angle appears never to exceed 109·5°, even when aromatic groups are linked to the sulphur atom.

The small valency angle of H_2S (92·1°) appears at first sight to be a good example of the use of pure *p* orbitals. Burrus and Gordy[76] have suggested that this angle, as well as the nuclear couplings, can be accounted for by postulating roughly equal (*ca.* 15% of each) *s* and *d* contributions to the bonding orbitals. The admixture of both *s* and *d* orbitals tends to have

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[67] Eyster, Gillette, and Brockway, *J. Amer. Chem. Soc.*, 1940, **62**, 3236.
[68] Allen, Bowen, Sutton, and Bastiansen, *Trans. Faraday Soc.*, 1952, **48**, 991.
[69] Bauer, quoted in *Ann. Rev. Phys. Chem.*, 1953, **4**, 245.
[70] Kimura and Kurita, *J. Chem. Soc. Japan*, 1951, **72**, 396.
[71] Katz and Lipscomb, *Acta Cryst.*, 1952, **5**, 313.
[72] Tauer and Lipscomb, *ibid.*, p. 606.
[73] Ivash and Dennison, *J. Chem. Phys.*, 1953, **21**, 1804.
[74] Kimura, *J. Chem. Soc. Japan*, 1950, **71**, 18.
[75] Dehmelt, *Phys. Rev.*, 1953, **91**, 313.
[76] Burrus and Gordy, *ibid.*, 1953, **92**, 274.

TABLE 4. *Sulphur valency angle*

Compound	Angle	Value	Method	Ref.
(A) Sulphur linked only to two other sulphur atoms				
$(CF_3)_2S_3$		103·8° ± 3°	E.D.	77
$BaS_4O_6,2H_2O$		103° ± 2°	*X*-Ray	78
$BaSeS_4O_6,2H_2O$		103° ± 2°	,,	79
$CH_3{\cdot}SO_2{\cdot}S{\cdot}S{\cdot}SO_2{\cdot}CH_3$		104° ± 3°	,,	80
$CH_3{\cdot}S_3{\cdot}CH_3$		104° ± 5°	E.D.	81
$BaS_5O_6,2H_2O$ (orthorhombic)		104° ± 2°	*X*-Ray	82
BaS_4,H_2O		104·5° ± 1°	,,	83
$C_6H_5{\cdot}SO_2{\cdot}S{\cdot}SO_2{\cdot}C_6H_5$		106·5° ± 1°	,,	84
$BaS_5O_6,2H_2O$ (triclinic)		107° ± 3°	,,	85
S_8		107·8° ± 0·5°	,,	86
Cs_2S_6		108·8° ± 2°	,,	87
$I{\cdot}C_2H_4{\cdot}S_3{\cdot}C_2H_4{\cdot}I$		113° ± 2°	,,	88
(B) Sulphur linked only to two other atoms				
C_2H_4S	C–S–C	65·8° ± 0·1°	M.W.	3
H_2S	H–S–H	92·1° ± 0·2°	,,	76
HDS	H–S–D	93·3° ± 0·2°	,,	89
$(I{\cdot}C_2H_4)_2S_3$	S–S–C	98° ± 10°	*X*-Ray	90
$CH_3{\cdot}SH$	C–S–H	99·4° ± 0·5°	M.W.	91
As_4S_6	As–S–As	100° ± 2°	E.D.	92
SCl_2	Cl–S–Cl	100·3°	Raman	93
As_4S_4	As–S–As	102° ± 3°	*X*-Ray	94
S_4N_4	N–S–N	102° ± 3°	,,	95
P_4S_3	P–S–P	102° ± 3°	,,	96
$(p\text{-}CH_3{\cdot}C_6H_4{\cdot}SO_2{\cdot}S)_2Te$	S–S–Te	103° ± 3°	,,	97
$BaSeS_4O_6,2H_2O$	S–S–Se	103° ± 3°	,,	79
$(CH_3)_2S_3$	S–S–C	104° ± 5°	,,	81
$(C_6H_5{\cdot}SO_2{\cdot}S)_2Te$	S–S–Te	104° ± 2°	,,	98
$(NH_4)_2(S_2O_3)_2Te$	S–S–Te	104°	,,	99
$Se(SCN)_2$	Se–S–C	104° ± 5°	,,	100
P_4S_7	P–S–P	104° ± 1°	,,	101
S_2Cl_2	S–S–Cl	104·5° ± 2·5°	E.D.	4
$(CH_3{\cdot}SO_2{\cdot}S)_2Te$	S–S–Te	105° ± 3°	*X*-Ray	102
$(CF_3)_2S_2$	S–S–C	105·4° ± 3°	E.D.	77
$(CF_3)_2S$	S–S–C	105·6° ± 3°	,,	77
$(p\text{-}Br{\cdot}C_6H_4)_2S_2$	S–S–C	107° ± 1°	*X*-Ray	103
$(CH_3)_2S_2$	S–S–C	107° ± 3°	E.D.	104
$(p\text{-}CH_3{\cdot}C_6H_4)_2S$	C–S–C	109° ± 2°	*X*-Ray	105
P_4S_{10}	P–S–P	109° ± 1°	,,	101
$(p\text{-}Br{\cdot}C_6H_4)_2S$	C–S–C	109·5° ± 1°	,,	103
$C_2H_5{\cdot}SH$	C–S–H	113° ± 2°	E.D.	106
SO_2	O–S–O	119·5° ± 0·5°	M.W.	107
		119·0° ± 0·5°	,,	108

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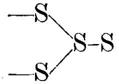
[77] Bowen, *Trans. Faraday Soc.*, 1954, **50**, 452.
[78] Foss, Furberg, and Zachariasen, *Acta Chem. Scand.*, 1954, **8**, 459.
[79] Foss and Tjomsland, *ibid.*, p. 1701.
[80] Sörum, *ibid.*, 1953, **7**, 1.
[81] Donohue and Schomaker, *J. Chem. Phys.*, 1948, **16**, 92.
[82] Foss and Zachariasen, *Acta Chem. Scand.*, 1954, **8**, 473.
[83] Abrahams, *Acta Cryst.*, 1954, **7**, 423.

a cancelling effect on the bond angle, but adds up to produce the observed asymmetry in the molecular electric field.

(b) *Poly-sulphur Chains.*—An outstanding characteristic which distinguishes the behaviour of sulphur from that of oxygen is the ability to form long chains. Thus, the stable state of elementary sulphur consists of S_8 rings, and compounds such as $S_{100}Cl_2$ are known.[109] There has been no confirmed report of a branched poly-sulphur chain, although rings, helices, and other non-branched forms are well established. A review of the *X*-ray, electron-diffraction, and spectroscopic data has been given,[110] which shows that  formation is very unlikely. The only cases in which sulphur forms a single (one only) bond to sulphur appear to be in ions such as $[O_3S{-}S]^{2-}$, and as terminal members of poly-sulphide chains. In orthorhombic sulphur [86] the puckered, eight-membered ring has the symmetry $\bar{8}2m$, within the limits of experimental error. In the $S_6{}^{2-}$ ion [87] the chain is helical, while the $[S_5O_6]^{2-}$ ion [82] possesses a plane of symmetry passing through the middle atom of the sulphur chain. The sulphur chain in this ion is hence equivalent to an S_8 ring with three linked sulphur atoms missing.

The sulphur–sulphur bond (Table 5) varies in length from 1·89 to 2·39 Å. The length chosen for a single bond by Pauling [111] was 2·08 Å, and indeed,

[84] Mathieson and Robertson, *J.*, 1949, 724.

[85] Foss and Tjomsland, *Acta Chem. Scand.*, 1955, **9**, 1016.

[86] Abrahams, *Acta Cryst.*, 1955, **8**, 661.

[87] Abrahams and Grison, *ibid.*, 1953, **6**, 206.

[88] Dawson and Robertson, *J.*, 1948, 1256.

[89] Bird and Townes, *Phys. Rev.*, 1954, **94**, 1203.

[90] Donohue, *J. Amer. Chem. Soc.*, 1950, **72**, 2701.

[91] Solimene and Dailey, *Phys. Rev.*, 1953, **91**, 464.

[92] Lu and Donohue, *J. Amer. Chem. Soc.*, 1944, **66**, 818.

[93] Stammreich, Forneris, and Sone, *J. Chem. Phys.*, 1955, **23**, 972.

[94] Ito, Morimoto, and Sadanaga, *Acta Cryst.*, 1952, **5**, 775.

[95] Clark, *J.*, 1952, 1615.

[96] van Houten, Vos, and Wiegers, *Rec. Trav. chim.*, 1955, **74**, 1167.

[97] Foss and Öyum, *Acta Chem. Scand.*, 1955, **9**, 1014.

[98] Öyum and Foss, *ibid.*, p. 1012.

[99] Foss and Larssen, *ibid.*, 1954, **8**, 1042.

[100] Ohlberg and Vaughan, *J. Amer. Chem. Soc.*, 1954, **76**, 2649.

[101] Vos and Wiebenga, *Acta Cryst.*, 1955, **8**, 217.

[102] Foss and Vihovde, *Acta Chem. Scand.*, 1954, **8**, 1032.

[103] Toussaint, *Bull. Soc. chim. Belg.*, 1945, **54**, 319.

[104] Stevenson and Beach, *J. Amer. Chem. Soc.*, 1938, **60**, 2872.

[105] Blackmore and Abrahams, *Acta Cryst.*, 1955, **8**, 329.

[106] Rouault and Gallagher, *Phys. Rev.*, 1949, **75**, 1319.

[107] Sirvetz, *J. Chem. Phys.*, 1951, **19**, 938.

[108] Crable and Smith, *ibid.*, p. 502.

[109] Fehér and Baudler, *Z. anorg. Chem.*, 1952, **267**, 293.

[110] Foss, *Acta Chem. Scand.*, 1950, **4**, 404 ; Woodrow, Carmack, and Miller, *J. Chem. Phys.*, 1951, **19**, 951 ; Minoura, *J. Chem. Soc. Japan*, 1952, **73**, 244.

[111] Pauling, " Nature of the Chemical Bond ", 2nd edtn., Cornell Univ. Press, Ithaca, N.Y., 1940.

this value is identical with the average of the 43 bond lengths given in Table 5. If 2·08 Å is accepted as a single-bond length, the measured value in orthorhombic sulphur (S_8) is short, and this bond must hence possess some double-bond character. This suggestion had previously been made [112] to account for the small heat of reaction of opening the S_8 ring. Koch [113] suggested that in addition to the conventional canonical forms which can contribute to the structure of the S_8 molecule, an alternating no-bond, double-bond structure might be important.

The only sulphur–sulphur bonds which have been measured as significantly longer than 2·08 Å, the value proposed as a standard single-bond length, occur in decafluorine disulphide and sodium dithionite. Dunitz [114] has discussed the $[S_2O_4]^{2-}$ ion sulphur–sulphur bond length in terms of Pauling's relationship,[115] $-\Delta R(n) = 0{\cdot}353 \log_{10} n$, for which n is 0·36. In the case of $F_5S{\cdot}SF_5$, n is 0·69. Both bonds are hence substantially less than single bonds. Huggins [116] has recently calculated the length of the sulphur–sulphur single bond to be 2·053 ± 0·02 Å, on the basis of a new relation between bond energies and radii.

The sulphur–sulphur bond length in S_2 in the ${}^3\Sigma_g{}^-$ (ground) state has been spectroscopically determined to be 1·887 Å. As in the case of O_2 in the ground state, this bond corresponds fairly closely to a double bond. Intermediate points between 2·08 Å and 1·89 Å for the lengths of single and double sulphur–sulphur bonds respectively are available. The short bonds, of length 2·02 Å in the tetra- and hexa-sulphide ions, have been postulated [83] to correspond to about 50—33% of double-bond character, thus defining the shape of the sulphur–sulphur bond order–bond length curve.

It may be noticed in Table 5 (B) that a variation in bond length along poly-sulphur chains has been measured only if four or more linked sulphur atoms are present. In this Table, the observed variations are close to the estimated errors in the individual bond lengths, and hence may not be significant. For the six examples reported, the sulphur–sulphur bonds are alternately short and long, for a chain containing an odd number of such bonds. If an even number of sulphur–sulphur bonds are present in the chain, the two central bonds appear to be of equal length, and the equivalent of a plane of symmetry is introduced into the chain. In both cases, chemically equivalent bonds are of identical length, within the limits of error. The outermost bonds are the short bonds, unless oxygen atoms are linked to the terminal sulphur atoms, when it is the outer sulphur–oxygen bonds that are short.

(c) *Dihedral Angle.*—The dihedral angle in sulphur, as in oxygen, is determined primarily by the $p\pi$ electron repulsion, with the greatest repulsion between the unshared pairs of electrons on adjacent sulphur atoms.

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[112] Powell and Eyring, *J. Amer. Chem. Soc.*, 1943, **65**, 648.

[113] Koch, *J.*, 1949, 408.

[114] Dunitz, *Acta Cryst.*, 1956, **9**, 579.

[115] Pauling, *J. Amer. Chem. Soc.*, 1947, **69**, 542.

[116] Huggins, *ibid.*, 1953, **75**, 4126.

TABLE 5. *Sulphur–sulphur bond lengths*

Compound	Bond length (Å)	Method	Ref.
(A) Without bond length variations			
S_2	1·887	Spec.	117
$Na_2S_2O_3,5H_2O$	1·97 ± 0·06	*X*-Ray	118
S_8	2·037 ± 0·005	,,	86
$(CH_3)_2S_3$	2·04 ± 0·02	E.D.	81
$C_{10}N_4O_6H_{18}S_2,2H_2O$ *	2·04 ± 0·005	*X*-Ray	119
H_2S_2	2·05 ± 0·02	E.D.	104
$(I{\cdot}C_2H_4)_2S_3$	2·05 ± 0·04	*X*-Ray	88
$(CF_3)_2S_2$	2·053 ± 0·019	E.D.	77
$(CF_3)_2S_3$	2·065 ± 0·016	,,	77
$(C_6H_5{\cdot}SO_2)_2S$	2·07 ± 0·02	*X*-Ray	84
Cl_2S_2	2·07 ± 0·10	E.D.	4
$(C_6H_5{\cdot}SO_2{\cdot}S)_2Te$	2·08 ± 0·03	*X*-Ray	98
$NaK_5Cl_2(S_2O_6)_2$	2·08 ± 0·04	,,	120
$NaK_6Cl_5(S_2O_6)$	2·08 ± 0·04	,,	120
$(CH_3{\cdot}C_6H_4{\cdot}SO_2{\cdot}S)_2Te$	2·11 ± 0·04	,,	97
$(NH_4)_2TeS_4O_6$	2·11 ± 0·03	,,	99
$BaSeS_4O_6,2H_2O$	2·13 ± 0·04	,,	79
$(CH_3{\cdot}SO_2{\cdot}S)_2Te$	2·14 ± 0·03	,,	102
$K_2S_2O_6$	2·14 ± 0·02	,,	121
$Na_2S_2O_6,2H_2O$	2·16 ± 0·02	,,	122
S_2F_{10}	2·21 ± 0·03	E.D.	123
$Na_2S_2O_4$	2·389 ± 0·010	*X*-Ray	114
(B) With variations in the bond length			
BaS_4,H_2O	2·02/2·07/2·02 ± 0·025	*X*-Ray	83
Cs_2S_6	1·99/2·10/2·03/2·12/2·03 ± 0·03	,,	87
$BaS_4O_6,2H_2O$	2·10/2·02/2·13 ± 0·03	,,	78
$BaS_5O_6,2H_2O$ (triclinic)	2·12/2·04/2·04/2·10 ± 0·04	,,	85
$BaS_5O_6,2H_2O$ (orthorhombic)	2·14/2·04/2·04/2·14 ± 0·03	,,	82
$(CH_3{\cdot}SO_2)_2S_2$	2·10/2·06/2·10 ± 0·03	,,	80

* *NN′*-Diglycyl-L-cystine dihydrate.

Pauling[124] has deduced a relationship between the dihedral angle and the valency angle in sulphur rings, for various numbers of sulphur atoms in the ring. For orthorhombic sulphur, Pauling's relationship predicts a dihedral

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[117] Ikenoue, *J. Phys. Soc. Japan*, 1953, **8**, 646.
[118] Taylor and Beevers, *Acta Cryst.*, 1952, **5**, 341.
[119] Yakel and Hughes, *ibid.*, 1954, **7**, 291.
[120] Stanley, *ibid.*, 1953, **6**, 187.
[121] *Idem*, *ibid.*, in the press.
[122] Martínez, García-Blanco, and Rivoir, *ibid.*, 1956, **9** 95.
[123] Harvey and Bauer, *J. Amer. Chem. Soc.*, 1953, **75**, 2840.
[124] Pauling, *Proc. Nat. Acad. Sci.*, 1949, **35**, 495.

angle of 99·0°, based on the observed bond angle of 107·8° This prediction may be compared with the observed value of 99·3° (see Table 6).

The sulphur dihedral angle has now been experimentally measured in a number of cases, and these results are tabulated in Table 6. It is found that the angles range from 74° to 110°, and hence are distributed on both sides of 90°.

The establishment of the sulphur dihedral angle at about 90° leads to the result that pentasulphide chains, or groups such as X–S–S–S–Y, may possess two isomeric forms. Foss [125] has pointed out that if the isomer is of the *cis*-form, *i.e.*, with the two terminal S–S or S–X, S–Y bonds rotated through about 90° on the *same* side of the plane of the three central atoms, the group may be considered as derived from the S_8 ring. If the isomer is of the *trans*-form, *i.e.*, with the terminal atoms on *opposite* sides of the central plane, a helix will be formed, which can be right- or left-handed.

Of the compounds in Table 6, it is noteworthy that those crystallising in the *cis*-form (S_8 and $S_5O_6^{2-}$) have dihedral angles greater than 90°, while those in the *trans*-form (S_6^{2-} and di-iododiethyl trisulphide) have dihedral angles less than 90°.

TABLE 6. *Sulphur dihedral angle*

Compound	Dihedral angle	Method	Ref.
Cs_2S_6	74·0°	*X*-Ray	87
BaS_4,H_2O	75·6°	,,	83
$(I{\cdot}C_2H_4)_2S_3$	82°	,,	90
H_2S_2	*ca.* 90°	Spec.	126
$(CH_3{\cdot}SO_2)_2S_2$	*ca.* 90°	*X*-Ray	80
$BaS_4O_6,2H_2O$	90°	,,	78
Cl_2S_2	92°	E.D.	4
$(CH_3)_2S_3$	93°	,,	81
S_8	99·3°	*X*-Ray	86
$C_{10}N_4O_6H_{18}S_2,2H_2O$ * . . .	101°	,,	119
$BaS_5O_6,2H_2O$ (triclinic) . .	106·5°	,,	85
$BaS_5O_6,2H_2O$ (orthorhombic)	110°	,,	82

* *NN'*-Diglycyl-L-cystine dihydrate.

(d) *Heterocyclic Sulphur.*—The valency angle of two-bonded sulphur does not necessarily remain unchanged when constraints are placed on it, such as when the sulphur atom forms part of a ring molecule. One of the earliest heterocycles to be investigated was thiophen, in which the C–S–C angle is not about 105°, as might be expected on the basis of Table 4 (B), but 91° [see Table 7 (A)]. The authors [127] suggested that some of the sulphur 3*d* orbitals might be used in valency-bond structures of the forms (VIII)—(X), etc.; Longuet-Higgins [128] extended this argument, employing

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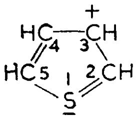
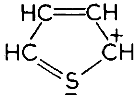
[125] Foss, *Acta Chem. Scand.*, 1953, **7**, 1221.
[126] Wilson and Badger, *J. Chem. Phys.*, 1949, **17**, 1232.
[127] Schomaker and Pauling, *J. Amer. Chem. Soc.*, 1939, **61**, 1769.
[128] Longuet-Higgins, *Trans. Faraday Soc.*, 1949, **45**, 173.

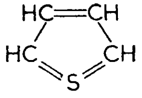
the molecular-orbital method, and computed the mobile bond orders in thiophen to be C–S = 0·59, $C_{(2)}$–$C_{(3)}$ = 0·73, and $C_{(3)}$–$C_{(4)}$ = 0·61. The



(VIII)



(IX)



(X)

bond order–length curve of Fig. 3 being used, the predicted carbon–sulphur bond length is then 1·73 Å, in excellent agreement with the experimental value of 1·74 Å. Direct calculation of the C–S bond order in thiophen as 0·58 has also been reported.[129] An accurate determination of the molecular structure by modern methods has not yet been made, although the crystal structure of the high-temperature disordered form has been studied.[130]

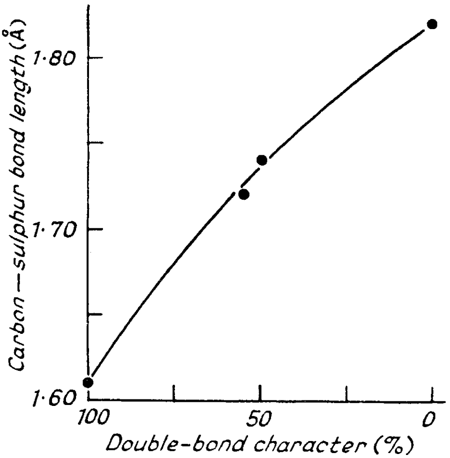


FIG. 3

Variation of the carbon–sulphur bond length with bond character.

There have not been any systematic attempts to explain the variations in the sulphur valency angle, Table 7 (A), from 91° to 101° in the system =CR—S—CR=, and from 65·8° to 106·5° in the system —CR_2–S–CR_2—. In contrast to those in Table 7 (A) the values given for the sulphur valency angle in Table 7 (B), as well as the nitrogen–sulphur bond length, show no variation.

The interesting case of the ethylene sulphide molecule, with a sulphur bond angle of 65·8°, has been compared [3] with *cyclo*propane, for which Coulson and Moffitt [131] suggested that the bonds are bent, and lie along the arc, tangents to the bonding orbitals.

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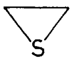
[129] de Heer, *J. Amer. Chem. Soc.*, 1954, **76,** 4802.

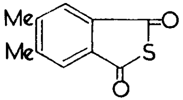
[130] Abrahams and Lipscomb, *Acta Cryst.*, 1952, **5,** 93.

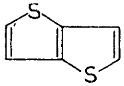
[131] Coulson and Moffitt, *Phil. Mag.*, 1949, **40,** 1.

TABLE 7 (A). *Sulphur valency angle and carbon–sulphur bond length in heterocyclic molecules*

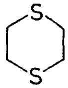

(XI)

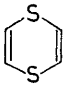

(XII)

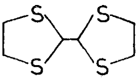

(XIII)

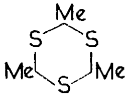

(XIV)

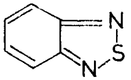

(XV)

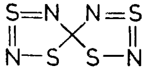

(XVI)


(XVII)


(XVIII)


(XIX)


(XX)


(XXI)

Molecule	Valency angle	C–S Bond length (Å)	Method	Ref.
(XI)	65·8°	1·819 ± 0·001	M.W.	3
(XII)	91°	1·74 ± 0·03	E.D.	127
(XIII).	91°	1·84 ± 0·03	*X*-Ray	133
(XIV)	91·2°	1·72 ± 0·013	,,	134
		1·74 ± 0·013	,,	134
(XV)	98·3°	1·752 ± 0·017	,,	135
(XVI)	99·0°	1·810 ± 0·010	,,	136
(XVII)	101°	1·78 ± 0·05	,,	137
(XVIII)	104°	1·85 ± 0·07	,,	138
(XIX).	106·5°	1·81 ± 0·03	E.D.	17

TABLE 7 (B). *Sulphur valency angle and nitrogen–sulphur bond length in heterocyclic molecules*

Molecule	Valency angle	N–S Bond length (Å)	Method	Ref.
(XX)	102°	1·60 ± 0·05	*X*-Ray	18
(XXI).	102°	1·60 ± 0·05	,,	95

A spectroscopic and thermodynamic study [132] of tri-, tetra-, and pentamethylene sulphide indicates that these molecules are all coplanar, in contrast to 1 : 4-dithian which assumes a chair configuration [136] and *p*-dithiin with a boat configuration.[137]

(e) *The Carbon–Sulphur Bond.*—Enough reliable experimental and theoretical work is now available to derive a bond order–bond length curve for the carbon–sulphur bond.

Cox and Jeffrey [56] obtained a mean value of 1·812 Å for the single carbon–sulphur bond length from a list of eleven molecules containing a

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[132] Scott, Finke, Hubbard, McCullough, Katz, Gross, Messerly, Pennington, and Waddington, *J. Amer. Chem. Soc.*, 1953, **75**, 2795.

[133] Eeles, *Acta Cryst.*, 1956, **9**, 365.

[134] Cox, Gillot, and Jeffrey, *ibid.*, 1949, **2**, 356.

[135] Jeffrey, *ibid.*, 1951, **4**, 58.

[136] Marsh, *ibid.*, 1955, **8**, 91.

[137] Howell, Curtis, and Lipscomb, *ibid.*, 1954, **7**, 498.

[138] Brahde, *Acta Chem. Scand.*, 1954, **8**, 1145.

formal single bond. This value is also the sum of the Pauling[111] covalent radii of sulphur and carbon. Huggins[116] has proposed a new system of interatomic distances, and has calculated the C–S single bond to be of length 1·83 ± 0·02 Å. The mean of the first six entries in Table 8, all of which should be close to formal single carbon–sulphur bonds involving only two bonds to the sulphur atom, is 1·83 Å. The weighted mean of all these bond lengths is 1·82 Å, and this value may hence be taken as the length of a pure single carbon–sulphur bond.

The determination of the length of a pure double carbon–sulphur bond offers greater difficulty. The sum of the Pauling radii is 1·61 Å, and among the recent data in Table 8 there is no molecule with an unambiguous double carbon–sulphur bond; *e.g.*, in $O{=}C{=}S$, the molcule is assumed[139] to have the resonance forms $O{=}C{=}S$, $\overset{-}{O}{-}C{\equiv}\overset{+}{S}$, $\overset{+}{O}{\equiv}C{-}\overset{-}{S}$ with a respective importance of 58, 14, and 28%. Molecular-orbital calculations[140] on thiophthen show that the experimental[134] carbon–sulphur bond lengths of 1·72 and 1·74 Å correspond to bond orders of 1·54 and 1·49, respectively. By assuming[56] a single-bond length of 1·81 Å, and a linear bond order–length relation, the length of a double bond was demonstrated to be about 1·65 Å. The entries in Table 8, however, suggest that the Pauling value of 1·61 Å might be closer to the length of a pure double carbon–sulphur bond. It is clearly very desirable to measure this length in a well-defined double bond.

If we take 1·61 Å for the double, 1·82 Å for the single, and the data based on thiophthen for the intermediate carbon–sulphur bond lengths as in Fig. 3, the results in Table 8 yield some interesting information. Thus, di-*p*-tolyl and di-*p*-bromophenyl sulphide each possess about 40% of double-bond character in the C–S bond. The environment for the sulphur atom in these molecules is similar to that in thiophen or thiophthen, namely, $=CH{-}S{-}CH=$, for which *pd* hybridisation was assumed (p. 419). Related evidence supporting the view that the bonds in these molecules have considerable double-bond character is provided by the tendency to planarity in the molecules. Thus, in di-*p*-tolyl sulphide, the angle between the normals to the two benzene rings is only 56°, resulting in a 3·19 Å contact between nearest carbon atoms in the different benzene rings. If this angle were 90°, the closest contact of this kind would be 3·99 Å, demonstrating that the C–S bond here cannot be single, with cylindrical symmetry. Similarly, in the case of di-*p*-bromophenyl sulphide, the two benzene rings are each rotated about 36° out of the Br–S–Br plane, resulting in a dihedral angle between the two aromatic rings of about 60°.

A similar effect is found in the sulphoxides, for dimethyl sulphoxide has a pure single bond, on the basis of Fig. 3, while diphenyl sulphoxide, in which the sulphur atom has a thiophen-like environment, again has about 35—40% of double-bond character. In the case of the sulphones, no such effect appears, for the C–S bond lengths in dimethyl and di-*p*-bromophenyl sulphone are equal, within the error of observation, to a single bond.

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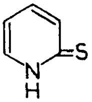
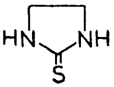
[139] Townes and Dailey, *J. Chem. Phys.*, 1949, **17**, 782.
[140] Evans and de Heer, *Acta Cryst.*, 1949, **2**, 363.

TABLE 8. *The carbon–sulphur bond length* [see also Table 7 (A)]


(XXII)


(XXIII)

Molecule	C–S Bond length (Å)	Method	Ref.
$CH_3{\cdot}SH$	1·808	M.W.	91
$(CH_3{\cdot}S)_4C$	1·81 ± 0·02	*X*-Ray	142
$(CF_3)_2S$	1·828 ± 0·015	E.D.	77
$(CF_3)_2S_2$	1·829 ± 0·017	,,	77
$(CF_3)_2S_3$	1·848 ± 0·015	,,	77
$(I{\cdot}C_2H_4)_2S_3$	1·86 ± 0·05	,,	90
CS	1·5349 ± 0·0002	M.W.	143
TeCS	1·557 ± 0·010	,,	144
HNCS	1·557 ± 0·010	,,	145
	1·561 ± 0·002	,,	146
OCS	1·5586 ± 0·0005	,,	64
CS_2	1·56 ± 0·02	E.D.	17
$[Hg(SCN)_4][Cu(en)_2]$ *	1·57 ± 0·10	*X*-Ray	147
NH_4SCN	1·59	,,	148
$(NH_2{\cdot}CS{\cdot})_2$	1·663	,,	149
(XXII)	1·68 ± 0·02	,,	150
(XXIII)	1·708 ± 0·008	,,	151
$(CH_3{\cdot}SO_2)_2C{:}C{:}N{\cdot}CH_3$	1·726 ± 0·007	,,	152
	1·770 ± 0·009	,,	152
β-$CH_3{\cdot}C_4H_4{\cdot}SO_2$ †	1·744 ± 0·017	,,	135
$(p\text{-}CH_3{\cdot}C_6H_4)_2S$	1·75 ± 0·03	,,	105
$(p\text{-}Br{\cdot}C_6H_4)_2S$	1·75 ± 0·03	,,	103
$(C_6H_5)_2SO$	1·760 ± 0·015	,,	153
$(C_6H_5{\cdot}SO_2)_2S$	1·76 ± 0·02	,,	84
$(C_6H_5{\cdot}SO_2)_2Se$	1·77 ± 0·05	,,	154
$(CH_3{\cdot}SO_2)_2S_2$	1·77 ± 0·05	,,	80
$CH_3{\cdot}CO{\cdot}SH$	1·78 ± 0·02	E.D.	155
$(CH_3)_2SO_2$	1·80 ± 0·02	,,	156
$(CH_3{\cdot}SO_2{\cdot}S)_2Te$	1·80 ± 0·06	*X*-Ray	102
$(p\text{-}Br{\cdot}C_6H_4)_2S_2$	1·80 ± 0·04	,,	103
$(CH_3)_2SO$	1·82	E.D.	157
$NaSO_2{\cdot}CH_2{\cdot}OH$	1·838 ± 0·011	*X*-Ray	158
$(p\text{-}Br{\cdot}C_6H_4)_2SO_2$	1·84 ± 0·04	,,	103
NN′-Diglycyl-L-cystine dihydrate	1·87 ± 0·017	,,	119

* en = Ethylenediamine. † β-Isoprene sulphone.

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[141] Tarbell and Harnish, *Chem. Rev.*, 1951, **49,** 1.

[142] Perdock and Terpstra, *Rec. Trav. chim.*, 1943, **62,** 687.

[143] Mockler and Bird, *Phys. Rev.*, 1955, **98,** 1837.

[144] Hardy and Silvey, *ibid.*, 1954, **95,** 385.

[145] Beard and Dailey, *J. Chem. Phys.*, 1950, **18,** 1437.

[146] Dousmanis, Sanders, Townes, and Zeiger, *ibid.*, 1953, **21,** 1416.

[147] Scouloudi, *Acta Cryst.*, 1953, **6,** 651.

[148] Zvonkova and Zhdanov, *Zhur. Fiz. Khim.*, 1949, **23,** 1495.

[149] Long, Markey, and Wheatley, *Acta Cryst.*, 1954, **7,** 140.

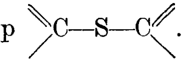
[150] Penfold, *ibid.*, 1953, **6,** 707.

[151] Wheatley, *ibid.*, p. 369.

[152] *Idem*, *ibid.*, 1954, **7,** 68.

The case of dimethanesulphonyl disulphide $(CH_3{\cdot}SO_2)_2S_2$ is interesting, for the C–S bond is again shorter than single (about 30% of double-bond character), although the sulphur atom is in a different environment from the examples just cited. However, in this molecule, the sulphur–sulphur bond lengths vary as shown in Table 5 (B), and the short carbon–sulphur bond confirms the view that in such molecules the outermost bonds are the short ones.

An excellent review of the literature dealing with the cleavage of the carbon–sulphur bond in bivalent sulphur compounds has been given by Tarbell and Harnish.[141]

(f) *Expansion of the Sulphur Valency-electron Octet.*—In the two preceding sections, *pd* hybridisation involving the sulphur 3*d* orbitals was postulated in the group  $>C-S-C<$. Considerable additional evidence supporting the premise of an expansion in the sulphur valency-electron octet to a decet or duodecet has now been presented,[159] based largely upon ultraviolet absorption spectra measurements.

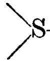
(g) *Three-bonded Sulphur.*—The stereochemistry of sulphur in the sulphoxide grouping,  $>S-O$, once a matter for much debate, is now relatively well established. The three sulphur bonds form a shallow pyramid, and the molecular dimensions of the measured sulphoxides are given in Table 9. The nature of the orbitals used by sulphur in the

TABLE 9. *Dimensions in the sulphoxide group*

Molecule	X–$\hat{S}$–O	X–$\hat{S}$–X	r_{S-O} (Å)	Method	Ref.
F_2SO . .	106·8° ± 0·1°	92·8° ± 0·1°	1·412 ± 0·001	M.W.	160
Cl_2SO . .	106° ± 1°	114° ± 2° *	1·45 ± 0·02	E.D.	161
Br_2SO . .	108° ± 2°	96° ± 2°	1·45 (assumed)	,,	162
$(CH_3)_2SO$.	107° ± 5°	100° ± 5°	1·47 ± 0·03	,,	157
	106° ± 6°	—	1·47 ± 0·03	,,	4
$(C_6H_5)_2SO$.	106·2° ± 0·7°	97·3° ± 1·0°	1·473 ± 0·015	*X*-Ray	153

* Angles smaller than 106° were not used in the models tried.

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[153] Abrahams and Grenville-Wells, M.I.T. Laboratory for Insulation Research Tech. Rep. No. 105, 1956.

[154] Furberg and Öyum, *Acta Chem. Scand.*, 1954, **8,** 42.

[155] Gordy, *J. Chem. Phys.*, 1946, **14,** 560.

[156] Lister and Sutton, *Trans. Faraday Soc.*, 1939, **35,** 495.

[157] Bastiansen and Viervoll, *Acta Chem. Scand.*, 1948, **2,** 702.

[158] Truter, *J.*, 1955, 3064.

[159] Eastman and Wagner, *J. Amer. Chem. Soc.*, 1949, **71,** 4089 ; Price and Morita, *ibid.*, 1953, **75,** 4747 ; Bordwell and Andersen, *ibid.*, p. 6019 ; Rothstein, *J.*, 1953, 3991 ; Cilento and Walter, *J. Amer. Chem. Soc.*, 1954, **76,** 4469 ; Jaffé, *J. Chem. Phys.*, 1954, **22,** 1430 ; Mangini and Passerini, *Gazzetta*, 1954, **84,** 606.

[160] Ferguson, *J. Amer. Chem. Soc.*, 1954, **76,** 850.

[161] Palmer, *ibid.*, 1938, **60,** 2360.

[162] Stevenson and Cooley, *ibid.*, 1940, **62,** 2477.

sulphoxide group has not yet been determined. In diphenyl sulphoxide [153] the angle between the benzene rings and the C–S–C plane is 81·9°, in agreement with the suggestion made for diphenyl sulphone [113, 159, 163] that the sulphur $3d$ and the carbon $2p$ orbitals overlap, resulting in the planes of the aromatic rings becoming normal to the C–S–C plane.

A striking feature of Table 9 is the constancy of the X–S–O angle, whereas the X–S–X angle varies from about 93° to 114°. In the case of the corresponding sulphides, this variation in X–S–X angle has been in part correlated with the change in admixture of *s*, *p*, and possible *d* orbitals. The presence of the non-orthogonal pyramidal bond arrangement appears to be evidence for some hybridisation, rather than for pure *p* orbitals' being used by sulphur in the sulphoxide group.

In the case of SO_3, the arrangement of the 3-bonded sulphur atom is quite different. In the gas state, this molecule has zero dipole moment, suggesting a planar molecule with a trigonal arrangement of oxygen atoms. This model has been confirmed by electron-diffraction methods [161] which show the O–S–O bond angle to be 120° $\pm$ 2°. In the solid state, both the ice- [164] and the asbestos-like form [165] of sulphur trioxide have the molecules linked together through S–O–S groups, the resulting four sulphur bonds being arranged approximately tetrahedrally.

Siebert,[166] using Raman spectra, has shown that the group symmetry for the $(CH_3)_3S^+$ ion is C_{3v}, *i.e.*, is pyramidal in shape, with the sulphur atom at the apex.

(h) *Four-bonded Sulphur.*—An excellent review of the preparative chemistry of 4-covalent sulphur has been given by Suter.[167] In the 4-bonded state, sulphur is very stable and may be observed in many different groupings. One of the commonest is the sulphate group, and Wells [29] has summarised the earlier investigations demonstrating the tetrahedral configuration of the four sulphur–oxygen bonds. A recent confirmation of this model has been made [19] for potassium ethyl sulphate, in which the mean O–S–O angle is 109°. A similar arrangement is found [118] in $Na_2S_2O_3,5H_2O$, with bond angles in the range 104—115°. Recent work on the $[S_2O_6]^{2-}$ ion,[120] the $[S_3O_{10}]^{2-}$ ion,[168] and the $[SO_4]^{2-}$ ion [169] has confirmed the earlier assignment of a tetrahedral bond distribution for 4-bonded sulphur.

A related bond arrangement is found in the sulphones. The molecular structure of several sulphones has now been elucidated, and the results are summarised in Table 10.

With the exception of β-isoprene sulphone, the carbon (or halogen)–sulphur–oxygen angle has very nearly the same constant value of about 107° in the sulphoxides and in the sulphones. The F–S–F bond angle is

[163] Koch and Moffitt, *Trans. Faraday Soc.*, 1951, **47**, 7.

[164] Westrik and MacGillavry, *Rec Trav. chim.*, 1941, **60**, 794.

[165] *Idem, Acta Cryst.*, 1954, **7**, 764.

[166] Siebert, *Z. anorg. Chem.*, 1952, **271**, 65.

[167] Suter, " The organic chemistry of sulfur ", J. Wiley Sons Inc., N.Y., 1944.

[168] Eriks and MacGillavry, *Acta Cryst.*, 1953, **7**, 430.

[169] Larson and Helmholz, *J. Chem. Phys.*, 1954, **22**, 2049.

identical at 92·8° in thionyl and in sulphonyl fluoride, and a strong similarity also exists between other corresponding pairs of angles in the sulphones and sulphoxides (Tables 9 and 10). It may be noticed that the O–S–O angle in the sulphone group is invariably the largest sulphur bond angle in a given molecule, and also is always greater than the tetrahedral value of 109·5°, in contrast with the O–S–O angle in the $[S_2O_4]^{2-}$ ion [114] of 108·2° and in the $[HO{\cdot}CH_2{\cdot}SO_2]^{--}$ ion [158] of 108·5°. The range in the C–S–C angle, from 98° to 115°, conflicts with the prediction [170] made on the basis of ring-closure experiments, that the limits for this angle were 75° and 90° (cf. Table 7).

TABLE 10. *Dimensions in the sulphone group*

Molecule	$X\widehat{S}O$	$X\widehat{S}X$	$O\widehat{S}O$	r_{S-O} (Å)	Method	Ref.
F_2SO_2	107·1° ± 0·5°	92·8° ± 0·5°	129·6° ± 0·5°	1·37 ± 0·01	M.W.	173
Cl_2SO_2	106·5° ± 2°	111·2° ± 2°	119·8° ± 5°	1·43 ± 0·02	E.D.	161
$(CH_3)_2SO_2$ . . .	105° ± 3°	115° ± 15°	125° ± 15°	1·43 ± 0·02	,,	4
β-$CH_3{\cdot}C_4H_5{\cdot}SO_2$ * .	99·6° ± 1·5°	98·3° ± 1·5°	112·9° ± 1·5°	1·436 ± 0·017	*X*-Ray	135
(*p*-$Br{\cdot}C_6H_4)_2SO_2$.	108·7° ± 5°	100° ± 0·5°	131° ± 3°	1·54 ± 0·05	,,	103
(*p*-$I{\cdot}C_6H_4)_2SO_2$ . .	111° ± 4°	106° ± 2°	111° ± 4°	—	,,	174
$CH_3{\cdot}N{:}C{:}C(SO_2{\cdot}CH_3)_2$ †	107·7° ± 1°	106·8° ± 0·4°	118·4° ± 0·4°	1·433 ± 0·006	,,	152

* β-Isoprene sulphone.
† *N*-Methyl-2 : 2-dimethylsulphonylvinylideneamine.

The sulphone and sulphoxide groups are indeed so similar that it has recently been shown [171] that diphenyl sulphoxide can dissolve in diphenyl sulphone to form a continuous series of solid solutions, which retain the diphenyl sulphone crystal structure, in proportions up to 90% of diphenyl sulphoxide. At this concentration the bonds to nine in every ten pairs of sulphone oxygen atoms are replaced by one sulphur–oxygen bond and a lone pair of electrons, which latter hence appears to have very nearly the same orientation as the missing sulphur–oxygen bond.

The dipole moment of the molecule $(C_6H_5)_2\dot{S}I_2$ has been measured [172] as 4·4 D. The analogous molecules $(p\text{-}CH_3{\cdot}C_6H_4)_2SeX_2$, where X is Br or Cl, and $(CH_3)_2TeCl_2$ have been shown to possess an unusual bond distribution, and it would be valuable to know if a similar bond distribution can also be exhibited by sulphur attached to four univalent groups.

(i) *Six-bonded Sulphur.*—Very few compounds containing 6-bonded sulphur have been examined, and their molecular shape determined. In the case of SF_6, a very stable molecule, the shape is reported [175] on the basis of electron-diffraction experiments to be that of a regular octahedron,

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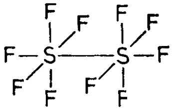
[170] Lüttringhaus and Buchholz, *Ber.*, 1939, **72**, 2057.
[171] Abrahams and Silverton, *Acta Cryst.*, 1956, **9**, 283.
[172] Jensen, *Z. anorg. Chem.*, 1943, **250**, 245.
[173] Fristrom, *J. Chem. Phys.*, 1952, **20**, 1.
[174] Keil and Plieth, *Z. Krist.*, 1955, **106**, 388.
[175] Brockway, *Rev. Mod. Physics*, 1936, **8**, 231.

with S–F = 1·58 ± 0·03 Å. Duffey [176] points out that there are no unshared electrons in the sulphur valency shell in SF_6, and predicts that the octahedral structure is more stable than the corresponding trigonal prism, even if the amount of *s*-character were allowed to change.

Another example of 6-bonded sulphur is disulphur decafluoride, and Harvey and Bauer [123] have determined this structure to be (XXIV), with a



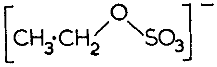
(XXIV)

regular octahedral bond distribution, and S–F = 1·56 ± 0·02 Å. The remaining example is disulphur decafluorodioxide.[35] Here again all bond angles are right angles except S–O–O, which is 105° (cf. Table 1), with S–F = 1·56 ± 0·02 Å.

(j) *The Sulphur–Oxygen Bond.*—The nature of the sulphur–oxygen bond in various molecules has been the subject of much discussion, largely centring around the question of whether the bond is a covalent double bond, or a co-ordinate link, or whether both bond types contribute. A review of much of the work in this field up to 1945 is given by Phillips, Hunter, and Sutton,[177] who regard the bond as primarily double in nature. Wells [178] has criticised this paper, and concluded that, at the time of writing, there was no satisfactory explanation for this short bond. Jeffrey and Stadler [179] have tabulated the values of reliable S–O distances in several oxides, oxy-acids, and acid salts of sulphur, and show that this bond length appears to be very constant at about 1·44 Å.

Moffitt [180] has used a molecular-orbital method to analyse the electronic structure of this bond. He finds that the sulphur–oxygen bond is largely double in character, and that the 3*d* orbitals of the sulphur atom are of importance in the formation of this bond. Moffitt's bond-order assignments, combined with the observed bond lengths in Tables 9, 10, and 11, lead to a mean value of 1·425 Å for the double sulphur–oxygen bond length.

A sulphur–oxygen bond that may be regarded as close to single has been measured [19] in potassium ethyl sulphate, the anion of which has the structure (XXV). If this bond, of length 1·60 Å, is selected as a standard single bond,



(XXV)

and the value 1·43 Å as a standard double-bond length, the resulting linear relationship closely fits Moffitt's predicted bond orders for sulphur dioxide, the sulphones, and the sulphoxides.

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[176] Duffey, *J. Chem. Phys.*, 1950, **18**, 128 and 510.

[177] Phillips, Hunter, and Sutton, *J.*, 1945, 146.

[178] Wells, *J.*, 1949, 55.

[179] Jeffrey and Stadler, *J.*, 1951, 1467.

[180] Moffitt, *Proc. Roy. Soc.*, 1950, **200**, *A*, 409.

A discussion of the nature of the sulphur–oxygen bond has recently been given by Simon and Kriegsmann,[181] who compute the length of the single bond to be 1·69 Å, based on Raman spectra observations.

TABLE 11. *Sulphur–oxygen bond lengths* (see also Tables 9 and 10)

Compound	Length (Å)	Method	Ref.
SO_3 (ice-form)	1·40 ± 0·05	*X*-Ray	164
	1·60 ± 0·05	,,	164
$(C_6H_5{\cdot}SO_2)_2Se$	1·41 ± 0·05	,,	154
$BaS_4O_6,2H_2O$	1·41 ± 0·04	,,	78
SO_3 (asbestos form)	1·41 ± 0·04	,,	165
	1·63 ± 0·04	,,	165
$(NH_4)_2TeS_4O_6$	1·43 ± 0·04	,,	99
$(CH_3{\cdot}SO_2{\cdot}S)_2Te$	1·43 ± 0·06	,,	102
$BaS_5O_6,2H_2O$	1·43 ± 0·04	,,	82
SO_2	1·4321 ± 0·0005	M.W.	108
	1·432 ± 0·005	,,	107
	1·43 ± 0·015	*X*-Ray	182
$K_2S_2O_6$	1·43 ± 0·05	,,	121
β-$CH_3{\cdot}C_4H_4{\cdot}SO_2$	1·436 ± 0·017	,,	135
$(NH_4)_2SO_3{\cdot}N_2O_2$	1·44 ± 0·01	,,	179
$K_2SO_3{\cdot}NH_2$	1·44 ± 0·03	,,	179
$K_2NH(SO_3)_2$	1·447 ± 0·005	,,	183
$Na_2S_2O_6,2H_2O$	1·46 ± 0·05	,,	122
$C_2H_5{\cdot}SO_4K$	1·46 ± 0·03	,,	19
	1·60 ± 0·03	,,	19
$HSO_3{\cdot}NH_2$	1·48 ± 0·03	,,	184
$(CH_3{\cdot}SO_2)_2S_2$	1·48 ± 0·05	,,	80
$NaK_6Cl_5(S_2O_6)$	1·48 ± 0·04	,,	120
$NaK_5Cl_2(S_2O_6)_2$	1·48 ± 0·05	,,	120
$Na_2S_2O_3,5H_2O$	1·48 ± 0·06	,,	118
$NaSO_2{\cdot}CH_2{\cdot}OH$	1·50 ± 0·01	,,	158
Li_2SO_4,H_2O	1·50 ± 0·02	,,	169
$Na_2S_2O_4$	1·505 ± 0·017	,,	114

The Stereochemistry of Selenium

(a) *Two-bonded Selenium.*—The general resemblance in bond formation between 2-bonded oxygen and sulphur is paralleled by an even greater similarity by that between sulphur and selenium. Both elements show marked allotropy, with formation of eight-membered rings and long chains. Hexagonal selenium, however, has an important characteristic not yet found in a sulphur allotrope, being a semiconductor, whereas sulphur behaves as an insulator.

The angle between the bonds linking a selenium atom with two other atoms varies over a rather small range. The Se–Se–Se bond angle has a mean value of 103·9° (Table 12) as compared with the corresponding average sulphur angle of 106·2°. The angle in H_2Se of 91° can probably be accounted for by a mechanism similar to that applied to the 92·1° angle in H_2S, where

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[181] Simon and Kriegsmann, *Z. phys. Chem.*, 1955, **204,** 369.
[182] Post, Schwartz, and Fankuchen, *Acta Cryst.*, 1952, **5,** 372.
[183] Jeffrey and Jones, *ibid.*, 1956, **9,** 283.
[184] Kanda and King, *J. Amer. Chem. Soc.*, 1951, **73,** 2315.

an admixture of *s* and *d* orbitals with the sulphur *p* orbitals has been proposed.[76] The bond angles measured in the remaining compounds have an average value of about 104° [excluding SeO_2 and $(CH_3)_2Se$, where the experimental errors are probably rather large], and in no case does this angle exceed the tetrahedral bond angle of 109·5°.

(*b*) *The Selenium–Selenium Bond.*—Although polyselenium chains of infinite length are known, such as the helices in the hexagonal selenium allotrope, there has been no evidence to suggest the formation of branched chains. The mean selenium–selenium bond length of 2·34 Å in the elementary allotropes (Table 13) may be regarded as corresponding to a pure single bond, for there is no indication of double-bond character in the Se_8 ring molecules (cf. p. 417). The Se_2 molecule, with bond length 2·19 Å, can tentatively be taken as containing a standard double bond. A linear bond length–bond order relation, based upon these two points, may then be assumed for the selenium-selenium bond.

TABLE 12. *Selenium valency angle*

Compound	Angle	Method	Ref.
H_2Se	91°	Spec.	185
SeO_2	90° ± 0·5°	*X*-Ray	186
	98° ± 2°	,,	186
$(CH_3)_2Se$	98° ± 10°	E.D.	187
$BaSeS_4O_6,2H_2O$ . . .	101° ± 3°	*X*-Ray	79
$Se(SeCN)_2$	101° ± 2°	,,	188
$Se(SCN)_2$	101° ± 3°	,,	100
$(p\text{-}Cl{\cdot}C_6H_4)_2Se_2$ . . .	101·1° ± 0·6°	,,	189
Hexagonal Se	103·6° ± 2°	,,	190
$(CF_3)_2Se$	104·4° ± 5°	E.D.	77
$(C_6H_4{\cdot}SO_2)_2Se$	105·1° ± 2°	*X*-Ray	154
α-Se_8	105·3° ± 2·3°	,,	191
β-Se_8	105·7° ± 0·8°	,,	192
$(p\text{-}CH_3{\cdot}C_6H_4)_2Se$ . . .	106° ± 2°	,,	193
$(C_6H_5)_2Se_2$	106° ± 2°	,,	194

(c) *The Selenium Dihedral Angle.*—There have not been many determinations of the dihedral angle between the bonds Se–X and Se–Y in the grouping X–Se–Se–Y. The data presented in Table 14 suggest that this angle is close to, but can lie on either side of, 90°, which is the angle to be expected if it is determined primarily by *pπ* electron repulsion, as appears to be the case for oxygen (p. 409) and sulphur (p. 417).

[185] Palik, *J. Chem. Phys.*, 1955, **23**, 980.
[186] McCullough, *J. Amer. Chem. Soc.*, 1937, **59**, 789.
[187] Goldish, Hedberg, Marsh, and Schomaker, *ibid.*, 1955, **77**, 2948.
[188] Aksnes and Foss, *Acta Chem. Scand.*, 1954, **8**, 1787.
[189] McCullough, Kruse, and Christofferson, U.S. Office of Ordnance Research Contract DA–04–495–ord–305, 1955.
[190] Grison, *J. Chem. Phys.*, 1951, **19**, 1109.
[191] Burbank, *Acta Cryst.*, 1951, **4**, 140.
[192] Marsh, Pauling, and McCullough, *ibid.*, 1953, **6**, 71.
[193] Blackmore and Abrahams, *ibid.*, 1955, **8**, 323.
[194] Marsh, *ibid.*, 1952, **5**, 458.

TABLE 13. *Selenium–selenium bond length*

Compound	Bond length (Å)	Method	Ref.
Se_2	2·19 ± 0·03	E.D.	195
$(C_6H_5)_2Se_2$	2·29 ± 0·01	*X*-Ray	194
$Se(SeCN)_2$	2·33 ± 0·03	,,	189
$(p\text{-}Cl{\cdot}C_6H_4)_2Se_2$ . . .	2·333 ± 0·008	,,	188
$(CF_3)_2Se_2$	2·335 ± 0·032	E.D.	77
α-Se_8	2·34 ± 0·02	*X*-Ray	191
β-Se_8	2·34 ± 0·014	,,	192
Hexagonal Se	2·36 ± 0·04	,,	190

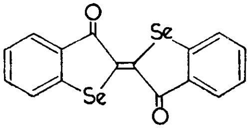
TABLE 14. *Selenium dihedral angle*

Compound	Dihedral angle	Method	Ref.
$(p\text{-}Cl{\cdot}C_6H_4)_2Se_2$	74°	*X*-Ray	188
$(C_6H_5)_2Se_2$	82°	,,	194
$(C_2H_5)_2Se_2$	83°	D.M.	196
$Se(SeCN)_2$	94°	*X*-Ray	189
Hexagonal Se	101°	,,	190
α-Se_8	102°	,,	191
β-Se_8	102°	,,	192

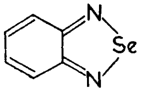
The dihedral angle for the mixed –Se–S– grouping in $BaSeS_4O_6,2H_2O$ has been determined [79] as 109°, and in $Se(SCN)_2$ it is 79°.[100]

(d) *Heterocyclic Selenium.*—A review of the organic chemistry of selenium has been given by Campbell, Walker, and Coppinger.[197] Measurements of

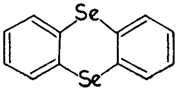
TABLE 15. *Selenium valency angle and* Se–C *bond length in selenium heterocycles*



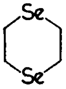
(XXVI)



(XXVII)



(XXVIII)



(XXIX)

Molecule	Se valency angle	Se-C Bond length (Å)	Method	Ref.
(XXVI)	80° ± 7°	1·86 ± 0·10	*X*-Ray	198
(XXVII) . . .	95° ± 4°	1·83 ± 0·04 (Se–N length)	,,	18
(XXVIII) . . .	96°	1·96	,,	199
(XXIX)	98·6° ± 2·0°	2·01 ± 0·03	,,	200

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[195] Maxwell and Mosley, *Phys. Rev.*, 1940, **57,** 21.

[196] Rogers and Campbell, *J. Amer. Chem. Soc.*, 1952, **74,** 4742.

[197] Campbell, Walker, and Coppinger, *Chem. Rev.*, 1952, **50,** 279.

[198] von Eller, *Compt. rend.*, 1954, **239,** 1043.

[199] Wood and Williams, *Nature*, 1942, **150,** 321.

[200] Marsh and McCullough, *J. Amer. Chem. Soc.*, 1951, **73,** 1106.

molecular constants have been reported for very few heterocyclic selenium compounds, and these data are summarised in Table 15.

The Raman and infrared-absorption spectra of liquid selenophen, C_4H_4Se, have been studied by Gerding, Milazzo, and Rossmark,[201] and shown to resemble that of thiophen. An examination of this spectrum appears to indicate that the selenophen molecule is not coplanar but bent, with a single plane of symmetry present passing through the selenium atom and the single carbon–carbon bond, in contrast to planar thiophen. The tentative interpretation given of the vibrational frequencies suggests that confirmation of the selenophen symmetry must await a more complete study. An *X*-ray study of selenanthren [199] suggests that this molecule also is not coplanar, but is bent about the Se–Se axis as the line of fold, through an angle of 127°.

(e) *Three-bonded Selenium.*—In those 3-bonded selenium compounds for which molecular constants are available, the data imply that the three selenium bonds form a pyramid, somewhat similar to the configuration of sulphur in the sulphoxides (Table 9). The possibility of a pyramidal bond arrangement of this nature had previously been discounted [202] since, although organic sulphoxides had been optically resolved, separation into enantiomorphs had not been achieved with compounds of the form R_1R_2SeO.

A pyramidal configuration was described [186] for solid SeO_2 in which the O–Se–O bond angles were reported to be 90°, 98°, 98° in each group. In F_2SeO, Rolfe and Woodward [203] report a Raman spectrum that closely resembles that of Cl_2SeO, F_2SO, and Cl_2SO. On the basis of the number of Raman fundamentals observed, they predict a pyramidal molecule (cf. p. 424). The structure of H_2SeO_3 is reported [204] also to consist of pyramidal SeO_3 groups, with a mean O–Se–O bond angle of $100° \pm 10°$, joined together by four hydrogen bonds per SeO_3 group.

Bryden and McCullough [205] have established the crystal structure of benzeneseleninic acid, and this too is found to have a pyramidal structure, with an O–Se–O bond angle of $103{\cdot}5° \pm 0{\cdot}7°$ and the C–Se–O bond angles equal to $98{\cdot}7° \pm 0{\cdot}9°$.

The crystal structure of diphenyl selenoxide is isomorphous with that of diphenyl sulphoxide [153] which is known to have a pyramidal configuration (Table 9); hence it may be predicted that in this molecule the selenium atom again has a pyramidal bond distribution.

(f) *Four-bonded Selenium.*—The stereochemistry of sulphur and selenium attached to four other atoms or groups depends upon the valency of these groups. The case of 4-bonded sulphur with bivalent groups attached has already been discussed (p. 425), and this bond distribution is entirely different from that of selenium with four univalent groups attached. The best determinations of molecules of this latter type are those of di-*p*-tolylselenium

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[201] Gerding, Milazzo, and Rossmark, *Rec. Trav. chim.*, 1953, **72**, 957.

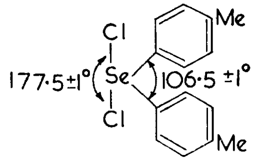
[202] Gaythwaite, Kenyon, and Phillips, *J.*, 1928, 2280.

[203] Rolfe and Woodward, *Trans. Faraday Soc.*, 1955, **51**, 778.

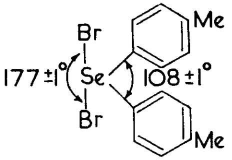
[204] Wells and Bailey, *J.*, 1949, 1282.

[205] Bryden and McCullough, *Acta Cryst.*, 1954, **7**, 833.

dichloride and dibromide,[206] which have the molecular configurations (XXX) and (XXXI). In the dichloride, the dihedral angle between the



(XXX)



(XXXI)

C–Se–C plane and the Cl–Se–Cl plane is 85° ± 2°, in the dibromide the corresponding angle is 87° ± 2°. Along the selenium–halogen bonds, the selenium radius is 1·40 Å, which is identical with the octahedral covalent radius assigned [111] to this atom. However, the selenium–carbon bonds of 1·93 and 1·95 Å in the two molecules (Table 17) are close to the normal single-bond radius for selenium of 1·17 Å. McCullough and Marsh [206] have suggested that while the selenium–carbon bond is of the $4s4p^2$ type (although the C–Se–C bond angle is intermediate between 120°, corresponding to this suggestion, and 90°, which is indicative of a higher *p*-admixture or a combination of *d* with the *s*,*p* hybrid), the selenium–halogen bond probably involves 5*s* orbitals. Pauling [206] has suggested that 4*d* and 5*s* orbitals may enter equally into hybridisation with the 4*p* electrons in forming this axial bond, while Palmer [207] has proposed the use of sp^3d^2 hybridisation.

There is a striking resemblance between the structure of the two molecules just described, if the halogen atoms are disregarded, and that of di-*p*-tolyl selenide.[193] Thus, the C–Se–C valency angles are nearly identical (cf. Table 12), the selenium–carbon bond distances are identical at 1·93 Å, and the dihedral angle between the plane of the benzene rings and of the C–Se–C plane is 35—40° for both structures.

There are no other unequivocal determinations of the structure of 4-bonded selenium compounds of this type. Lister and Sutton [208] suggested that $SeCl_4$ has a tetrahedral bond distribution, but recognised that the available electron-diffraction data were not decisively in favour of this model. However, in the solid state, $SeCl_4$, $SeBr_4$, and $TeBr_4$ are isomorphous.[209] It is likely that $TeBr_4$ has a structure similar to that of $TeCl_4$, which is known to have an unsymmetrical structure on account of its large dipole moment.[172] Hence the prediction of a regular tetrahedral bond distribution in $SeCl_4$ may be in error. In the liquid state, $SeCl_4$ has been claimed to have the structure $[SeCl_3]^+Cl^-$ on the basis of the Raman spectrum.[210]

An electron-diffraction investigation [211] of SeF_4 has indicated C_{2v} symmetry, with 4 angles [212] of 104° ± 5° and two of 120° ± 10°. The Raman

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[206] McCullough and Marsh, *Acta Cryst.*, 1950, **3**, 41.

[207] Palmer, *Endeavour*, 1953, **12**, 124.

[208] Lister and Sutton, *Trans. Faraday Soc.*, 1941, **37**, 393.

[209] Brink, private communication.

[210] Gerding and Houtgraaf, *Rec. Trav. chim.*, 1954, **73**, 737.

[211] Bowen, *Nature*, 1953, **172**, 171. [212] Lachmann, *ibid.*, p. 499.

spectrum of SeF_4 is also reported[213] to agree with C_{2v} symmetry, and it is concluded that this spectrum is most consistent with a trigonal bipyramidal arrangement, the lone pair of electrons occupying an equatorial position.

In the case of selenic acid,[214] the structure is reported to consist of tetrahedral SeO_4 groups (mean O–Se–O bond angle, 110° ± 5°) linked together by a system of O–H–O bonds, with four such bonds per SeO_4 unit. In this structure, with bivalent atoms attached to selenium, the $[SeO_4]^{2-}$ ion appears to have a bond distribution identical with that of the $[SO_4]^{2-}$ ion.

(g) *Six-bonded Selenium.*—The only 6-bonded selenium molecule for which the molecular parameters have been determined[215] is SeF_6 which, like SF_6, has an octahedral bond configuration.

(h) *The Selenium–Oxygen Bond.*—There are insufficient data for a bond length–order relation to be constructed. Table 16 summarises the available measurements on this bond.

TABLE 16. *Selenium–oxygen bond lengths*

Compound	Bond length (Å)	Method	Ref.
H_2SeO_4	1·61 ± 0·05	*X*-Ray	214
$C_6H_5{\cdot}SeO_2H$ . . .	1·707 ± 0·015	,,	205
	1·765 ± 0·015	,,	205
H_2SeO_3	1·74 ± 0·02	,,	204
SeO_2	1·76 ± 0·08	,,	186
	1·61 ± 0·03	E.D.	216

The difference in the two observed Se–O bond lengths in benzeneseleninic acid is significant (4 times the estimated standard deviation in these bonds) and is caused by one of the oxygen atoms forming a hydrogen bond.

(i) *The Selenium–Carbon Bond.*—A considerable variation in the length of the selenium–carbon bond has been reported (Table 17). As in the case

TABLE 17. *Selenium–carbon bond lengths* (see also Table 15)

Molecule	Bond length (Å)	Method	Ref.
OCSe	1·7090 ± 0·0001	M.W.	63
$Se(SeCN)_2$	1·83 ± 0·10	*X*-Ray	189
$C_6H_5{\cdot}SeO_2H$	1·903 ± 0·021	,,	205
$(p\text{-}CH_3{\cdot}C_6H_4)_2Se$ . . .	1·93 ± 0·03	,,	193
$(C_6H_5)_2Se_2$	1·93 ± 0·05	,,	194
$(p\text{-}Cl{\cdot}C_6H_4)_2Se_2$ . . .	1·93 ± 0·06	,,	188
$(p\text{-}CH_3{\cdot}C_6H_4)_2SeCl_2$ . .	1·93 ± 0·03	,,	206
$(CF_3)_2Se_2$	1·934 ± 0·018	E.D.	77
$(p\text{-}CH_3{\cdot}C_6H_4)_2SeBr_2$ . .	1·95 ± 0·03	*X*-Ray	206
$(CF_3)_2Se$	1·958 ± 0·022	E.D.	77
$(CH_3)_2Se$	1·977 ± 0·012	,,	187

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[213] Rolfe, Woodward, and Long, *Trans. Faraday Soc.*, 1953, **49,** 1388.

[214] Bailey and Wells, *J.*, 1951, 968.

[215] Maxwell, *J. Opt. Soc. Amer.*, 1940, **30,** 374.

[216] Palmer and Elliott, *J. Amer. Chem. Soc.*, 1938, **60,** 1852.

of the selenium–oxygen bond, it appears that a corresponding variation in bond character is also present, but the difficulty of assigning the correct multiplicity to these bonds does not permit an unambiguous bond order–length curve to be proposed, although linear interpolation between the value 1·97 Å for a single-bond and 1·71 Å for a double-bond length allows a reasonable interpretation for the data in Table 17.

The Stereochemistry of Tellurium

(a) *Two-bonded Tellurium.*—In the elementary state, tellurium does not exhibit the structural complexity observed in sulphur and in selenium. A single stable form is known, consisting of infinite helices of tellurium atoms. in a hexagonal crystal structure. Relatively few measurements of the tellurium bond angle, involving two bonds only to the tellurium atom, have been reported, and the available results are presented in Table 18. With the exception of TeO_2*, the tellurium valency angle involving two bonds is rather constant, with an average value of 100°. A close similarity to selenium is indicated by the formation of continuous series of solid solutions of selenium in tellurium.[190]

TABLE 18. *Tellurium bond angle*

Compound	Bond angle	Method	Ref.
$(p\text{-}Cl{\cdot}C_6H_4)_2Te_2$	94° ± 1°	*X*-Ray	188
$TeBr_2$	98° ± 3°	E.D.	217
$(CH_3{\cdot}SO_2{\cdot}S)_2Te$	100° ± 3°	*X*-Ray	102
$(p\text{-}CH_3{\cdot}C_6H_4)_2Te$	101° ± 2·7°	,,	218
$(NH_4)_2TeS_4O_6$	103° ± 3°	,,	99
Hexagonal Te	103·7° ± 2°	,,	190
TeO_2	132° ± 5°	,,	219

(b) *The Tellurium–Tellurium Bond.*—The meagre published (see Table 19) data concerning the length of this bond hardly justify any conclusions.

TABLE 19. *Tellurium–tellurium bond length*

Compound	Bond length (Å)	Method	Ref.
$FeTe_2$	2·90 ± 0·03	*X*-Ray	220
$AuAgTe_4$ *	2·87 ± 0·10	,,	221
Hexagonal Te	2·82 ± 0·02	,,	190
$(p\text{-}Cl{\cdot}C_6H_4)_2Te_2$ . . .	2·702 ± 0·005	,,	188
Te_2	2·59 ± 0·02	E.D.	195

* Sylvanite.

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[217] Rogers and Spurr, *J. Amer. Chem. Soc.*, 1947, **69**, 2102.
[218] Blackmore and Abrahams, *Acta Cryst.*, 1955, **8**, 317.
[219] Stehlík and Balak, *Coll. Czech. Chem. Comm.*, 1949, **14**, 595.
[220] Grønvold, Haraldsen, and Vihovde, *Acta Chem. Scand.*, 1954, **8**, 1927.
[221] Tunell and Pauling, *Acta Cryst.*, 1952, **5**, 375.
* Te has a distorted octahedral bond arrangement.

(c) *Dihedral Tellurium Angle.*—The values of those dihedral angles involving tellurium which have been measured are summarised in Table 20. This angle, like the corresponding angles for oxygen, sulphur, and selenium, is close to 90°.

TABLE 20. *Dihedral tellurium angle*

Compound	Atoms defining angle	Value	Ref.
$(C_6H_5{\cdot}SO_2{\cdot}S)_2Te$ . . .	SSTe/STeS	79°	98
$(CH_3{\cdot}SO_2{\cdot}S)_2Te$ . . .	SSTe/STeS	81°	102
$(CH_3{\cdot}C_6H_4{\cdot}SO_2{\cdot}S)_2Te$ . .	SSTe/STeS	86°	97
$(NH_4)_2TeS_4O_6$	SSTe/STeS	86°, 95°	99
$(p\text{-}Cl{\cdot}C_6H_4)_2Te_2$ . . .	CTeTe/TeTeC	99°	188
Hexagonal Te	TeTeTe/TeTeTe	101°	190

(d) *Higher Valencies of Tellurium.*—The stereochemistry of three-bonded tellurium does not yet appear to have been investigated. Jensen [172] has measured the dipole moment of di-*p*-tolyl telluroxide as 3·93 D and suggests that this indicates a semipolar Te–O bond.

An electron-diffraction study [222] on $TeCl_4$ was reported to be compatible with a distorted trigonal bipyramid, with the Cl–Te–Cl angle equal to 93° ± 3°. Lachman [223] has pointed out that, if five of the six angles in this molecule are 93° ± 3°, then the sixth angle will be 171° ± 9°. A similar bond distribution has been described for TeI_4 in a preliminary *X*-ray study.[224]

A study of the Raman spectrum [210] of solid $TeCl_4$ is reported to suggest strongly the presence of $[TeCl_3]^+$ ions (cf. $SeCl_4$, p. 432) as also does a corresponding study [225] on $TeCl_4,AlCl_3$.

The crystal structure of α-dimethyltellurium dichloride was reported [189] to be similar to that of the diarylselenium dihalides (XXX) and (XXXI). In this molecule the Cl–Te–Cl bond angle is about 172°, the C–Te–C bond angle is near 110°, and the C–Te–C plane is normal to the Cl–Te–Cl axis. McCullough [226] has suggested that in compounds of the type $R_2(S,Se,Te)Hal_2$, the structure is that of a trigonal bipyramid with the halogen atoms at the apices, the three equatorial positions being occupied by the R groups and the unshared electron pair.

Tellurium hexafluoride, like the sulphur and the selenium analogue, has an octahedral bond distribution. Brockway [175] reports the Te–F bond distance to be 1·82 ± 0·03 Å. Although SF_6 and SeF_6 are very inert, and stable to hydrolysis, TeF_6 is easily hydrolysed. It is suggested [227, 159] that this is due to the possibility of the tellurium atoms' accepting a pair of oxygen electrons in a vacant 4*f* orbital. An octahedral bond distribution has also been reported [228] for tellurium in the anion of Cs_2TeBr_6.

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[222] Stevenson and Schomaker, *J. Amer. Chem. Soc.*, 1940, **62**, 1267.
[223] Lachmann, *J. Chem. Phys.*, 1954, **22**, 1459.
[224] Blackmore, Abrahams, and Kalnajs, *Acta Cryst.*, 1956, **9**, 295.
[225] Gerding and Houtgraaf, *Rec. Trav. chim.*, 1954, **73**, 759.
[226] McCullough, *Acta Cryst.*, 1953, **6**, 746.
[227] Kimball, *J. Chem. Phys.*, 1940, **8**, 188.
[228] Bagnall, D'Eye, and Freeman, *J.*, 1955, 3959.

(e) *The Tellurium–Carbon Bond.*—The tellurium–carbon bond length appears to have been reported only in the three following cases. In $(p\text{-Cl}\cdot C_6H_4)_2Te_2$ it is 2·16 ± 0·14 Å,[189] in $(p\text{-CH}_3\cdot C_6H_4)_2Te$ 2·05 ± 0·05 Å,[218] and in TeCS the length is measured [144] as 1·904 ± 0·010 Å in a microwave determination.

The Stereochemistry of Polonium

Polonium is a soft, low-melting, grey metal, like lead, and exhibits no covalent bonding in the elementary state. Beamer and Maxwell [229] first measured the lattice constants of α- and β-polonium, and pointed out that the simple cubic structure has the symmetrical properties associated with true metallic bonding, as is also indicated by its other physical properties.

The crystal structures of several polonium compounds have now been determined. The formation of the oxide PoO_2 has been confirmed,[230] and the Po–O distance measured [231] as 2·44 Å, corresponding to an ionic contact between Po^{4+} and O^{2-}. Zinc polonide, ZnPo, has a face-centred cubic structure of the zinc blende type,[232] and lead polonide, PbPo, belongs to the NaCl structure type.[232] Platinum polonide, $PtPo_2$, has been shown [232] to crystallise in the hexagonal system, with the $Cd(OH)_2$ structure type, and NiPo also is hexagonal.[232]

Some polonium halides have been investigated, such as $PoCl_2$ and $PoCl_4$,[233, 234] and $PoBr_2$ and $PoBr_4$.[235, 228] The only polonium halide for which the crystal structure is known is the tetrabromide. In this crystal,[228] the polonium is in octahedral co-ordination with bromine, the Po–Br distance being about 2·8 Å.

The stereochemistry of polonium in some complex ions has also been reported. Thus the crystal structure of ammonium hexachloropolonite [234] is isomorphous with that of $(NH_4)_2PtCl_6$, with a Po–Cl distance of 2·38 Å, indicating this bond to be largely covalent, for the radius of the Po^{4+} ion is [231] 1·04 Å and of Cl^- is [111] 1·81 Å. Similarly, ammonium hexabromopolonite is isostructural with the chloro-complex,[228] the Po–Br separation of 2·60 Å again corresponding primarily to a covalent bond. Cæsium hexabromopolonite, Cs_2PoBr_6, has been found [228] isostructural with Cs_2TeBr_6 and the Po–Br and Te–Br distances are respectively 2·64 and 2·61 Å.

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[229] Beamer and Maxwell, *J. Chem. Phys.*, 1949, **17**, 1293.

[230] Martin, *J. Phys. Chem.*, 1954, **58**, 911.

[231] Bagnall and D'Eye, *J.*, 1954, 4295.

[232] Unpublished results by the Mound Laboratory, Monsanto Chemical Co., Miamisburg, Ohio, U.S.A.

[233] Joy, 125th Amer. Chem. Soc. Meeting, Kansas City, 1954.

[234] Bagnall, D'Eye, and Freeman, *J.*, 1955, 2320.

[235] Joy, 126th Amer. Chem. Soc. Meeting, New York, 1954.