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The Stereochemistry of Subgroup VI_b of the Periodic Table

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Laboratory for Insulation Research
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April, 1956

The Stereochemistry of Subgroup VI_b of the Periodic Table

by

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THE STEREOCHEMISTRY OF SUBGROUP VI_b
OF THE PERIODIC TABLE

by

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1.1 Introduction

The properties of the elements in subgroup VI_b of the periodic table, oxygen, sulfur, selenium, tellurium and polonium, undergo striking transitions as the group is ascended. The chemical behavior of the group passes from that of the typical nonmetals oxygen and sulfur, to the typical metal polonium. Also systematic change is 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 sulfur are insulators, selenium and tellurium are semiconductors (about 10^{-5} ohm cm⁻¹) and polonium shows metallic conduction. The interrelation between structure and conductivity has been discussed by von Hippel (1948).

Within this subgroup, 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 subgroup VI_b has become available. The present review is an attempt to bring together the most important information, at present scattered throughout the literature,

concerning the geometrical and electronic configuration of these atoms in their different bonded states.

2.1 Divalent oxygen

The electronic configuration of the oxygen atom in the ground state may be written as $(1s)^2(2s)^2(2p_x)(2p_y)(2p_z)^2$. The two unshared p electrons are available for bond formation, and the simplest wave-mechanical theory would predict that in the formation of two covalent bonds it is these electrons that are engaged. The resulting bonds will then be at right angles, the angle between p orbitals. Bond formation of this kind may be illustrated by considering the case of the water molecule, for which it has been suggested that the available 1s electrons of the hydrogen atoms will combine with the $2p_x$ and $2p_y$ oxygen orbitals. The bond angle is observed to be not 90° as this theory would predict, but $104^\circ 31'$ (Table 1).

The 14.5° discrepancy between observation and the p-orbital prediction for the oxygen bond angle in water may be only partly reduced by taking into account the previously neglected Coulombic repulsion between the hydrogen atoms, for the hydrogen-hydrogen interaction would result merely in opening this angle to about 95° . A more reasonable explanation for the bonding mechanism does not presuppose pure p orbitals for the oxygen atoms, but instead will allow for a combination of s and p orbitals. Hybridization of this kind would allow larger angles than 90° to be predicted, the size depending upon the extent of the s, p admixture. A consequence of the s, p hybridization would be a substantial dipole moment possessed by the resulting lone pairs of oxygen electrons. Repulsion between these lone pairs will tend to result in a contraction of the angle between bonding orbitals, as in Fig. 1. A full account of the nature of the binding in the water molecule, with

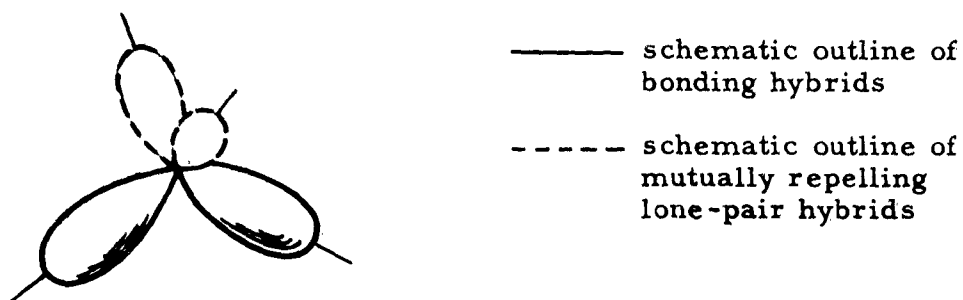


Fig. 1. Schematic representation of hybridization in divalent oxygen.

reference to the earlier literature, is given by Coulson (1952).

A mechanism similar to that just described for water is probably generally applicable to divalent oxygen. The amount of s character will in part be determined by the nature of the bonding atoms, and could vary from small percentages to that required for sp^2 hybridization. The experimental values found for the oxygen valency angle in a variety of molecules are collected in Table 1.

An examination of Table 1 reveals that the measured values for the oxygen valency angle fall into two fairly distinct groups. With the exception of ozone, the angle is 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 possible that in these non-aromatic molecules, use is made of the oxygen 2s orbitals to approach sp^3 (tetrahedral) hybridization. Where an aromatic group is involved, the hybridization appears to be sp^2 (trigonal). Both in the case of ozone and of the aromatic ethers, various ionic canonical forms are likely to contribute to the final electronic structure, e.g.,

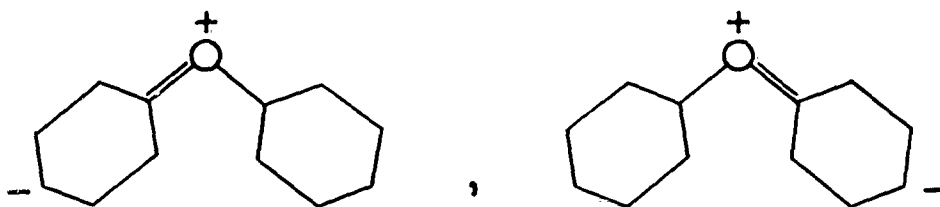


Table 1. Oxygen valency angle.

Molecule	Angle	Method	Reference
Ethylene oxide	$61.6 \pm 0.1^\circ$	microwave	Cunningham et al. (1951)
Trimethylene oxide	$94.5 \pm 3^\circ$	E. D.	Shand (Allen and Sutton, 1950)
Mercury diethylene oxide	$96 \pm 6^\circ$	x-ray	Grdenić (1952)
Fluorine monoxide	$\begin{cases} 101.5 \pm 1.5^\circ \\ 103.8 \pm 1.5^\circ \end{cases}$	$\begin{cases} \text{spectros.} \\ \text{E. D.} \end{cases}$	$\begin{cases} \text{Bernstein and Powling (1950)} \\ \text{Ibers and Schomaker (1953)} \end{cases}$
Hydrogen deuterio-oxide	$104.0 \pm 0.5^\circ$	spectros.	Strandberg (1949)
Water	$\begin{cases} 104.5 \pm 0.1^\circ \\ 105.1 \pm 0.1^\circ \end{cases}$	$\begin{cases} \text{spectros.} \\ \text{spectros.} \end{cases}$	$\begin{cases} \text{Darling and Dennison (1940)} \\ \text{Herzberg (1945)} \end{cases}$
Dimethyl peroxide	$105 \pm 3^\circ$	E. D.	Shand (Allen and Sutton, 1950)
Furan	108.1°	E. D.	Almenningen et al. (1955)
Divinyl ether	$\begin{cases} 107 \pm 3^\circ \\ 112 \pm 2^\circ \end{cases}$	$\begin{cases} \text{E. D.} \\ \text{E. D.} \end{cases}$	$\begin{cases} \text{Barricelli and Bastiansen (1949)} \\ \text{LuValle (Allen and Sutton, 1950)} \end{cases}$
Diethyl ether	$108 \pm 3^\circ$	E. D.	Schomaker (Allen and Sutton, 1950)
Chlorine monoxide	$110.8 \pm 1^\circ$	E. D.	Dunitz and Hedberg (1950)
Dimethyl ether	110°	dipole mom.	Gibbs (1954)
p-Dioxane	$\begin{cases} 108 \pm 5^\circ \\ 112 \pm 5^\circ \end{cases}$	$\begin{cases} \text{E. D.} \\ \text{E. D.} \end{cases}$	$\begin{cases} \text{Hassel and Viervoll (1947)} \\ \text{Shand (Allen and Sutton, 1950)} \end{cases}$
Benzofurazane	$112 \pm 12^\circ$	x-ray	Luzzati (1951)
Potassium ethyl sulfate	$114 \pm 4^\circ$	x-ray	Jarvis (1953)
Ozone	$116.8 \pm 0.5^\circ$	microwave	Trambarulo et al. (1953)
Dimethoxybenzene	$121 \pm 2^\circ$	x-ray	Goodwin et al. (1950)
Di-p-bromophenyl ether	$123 \pm 1^\circ$	x-ray	Toussaint (1952)*
Di-p-iodophenyl ether	$\begin{cases} 123 \pm 2^\circ \\ 123 \pm 1^\circ \end{cases}$	$\begin{cases} \text{x-ray} \\ \text{x-ray} \end{cases}$	$\begin{cases} \text{Plieth (1947)} \\ \text{Toussaint (1946)} \end{cases}$
Diphenyl ether	$124 \pm 5^\circ$	dipole mom.	Coop and Sutton (1938)

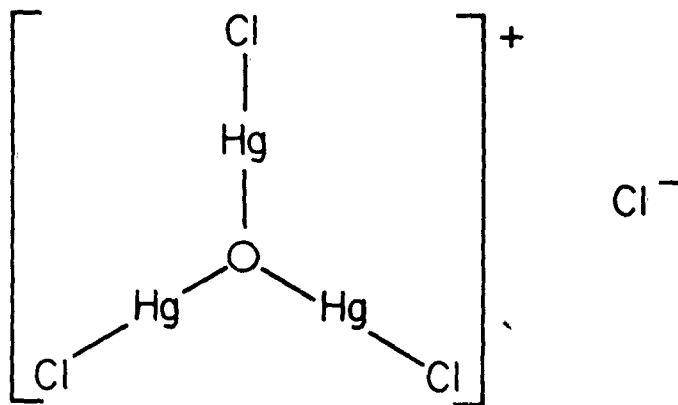
* A number of references to earlier determinations are given in this paper.

Ethylene oxide appears to be an example of strain, in the classical sense. Cunningham et al. (1951) have assumed p^2 hybridization in the oxygen atom, and hence "bent" bonds lying along the arc tangents to the carbon and oxygen orbitals.

2.2 Higher valencies of oxygen

Very few reports may be found in the literature giving critical measurements of molecular dimensions for compounds containing oxygen exhibiting a valency higher than two. Recently, the crystal structure of trichloromercury oxonium chloride has been solved by Šćavničar and Grdenić (1955), and shown to consist of the two ions:

The planar trichloromercury oxonium ion possesses trigonal symmetry, the O-Hg-Cl group being nearly linear (Cl-Hg-O is 175°) with $r_{\text{O-Hg}} = 2.03\text{\AA}$.



The structure of this molecule has also been reported by Weiss, Nagorsen and Weiss (1955). The two studies are essentially in complete agreement, except for small, probably not significant differences in the atomic parameters, e.g., Weiss et al. obtain $r_{\text{O-Hg}} = 2.06\text{\AA}$. In addition, the oxonium ion OH_3^+ has been studied by Ferriso and Hornig (1955), using infrared spectroscopy, and shown to possess C_3 symmetry, with angles very 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.

An example of oxygen with four attached bonds is provided by basic beryllium acetate. This compound forms a cubic crystal at room temperature

(Pauling and Sherman, 1934), in which the oxygen atom is crystallographically tetrahedrally co-ordinated to four beryllium atoms ($r_{\text{Be-O}} = 2.14\text{\AA}$, compared with the Be-O distance in BeO of $1.72\text{\AA}$). Other examples of 4-co-ordinated oxygen may be found in oxides with the zinc-blende structure, but in none of these cases can the oxygen be described as purely 4-covalent, although the bond distribution is tetrahedral, and corresponds to sp^3 hybridization.

2.3 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, respectively, each of the other oxygen valency bonds. A discussion of this angle (ϕ in Fig. 2) was given for the case of H_2O_2 by Penney and Sutherland in 1934, who assumed that only oxygen p orbitals were used in bonding.

They showed that the predominant steric factor governing the dihedral angle is neither the interaction between hydrogen atoms, nor between OH bonds. Instead, it 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. Penney and Sutherland calculated the potential energy of the hydrogen peroxide molecule for ϕ from 0° through 180° (Fig. 3).

The position of minimum energy was found to be about 100° . Lassettre and Dean (1949) took into additional account the interaction between the two OH bonds, between the OH bonds and the unshared pairs of electrons on opposite

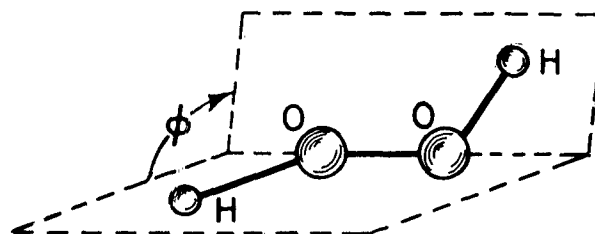


Fig. 2. Structure of the hydrogen peroxide molecule.

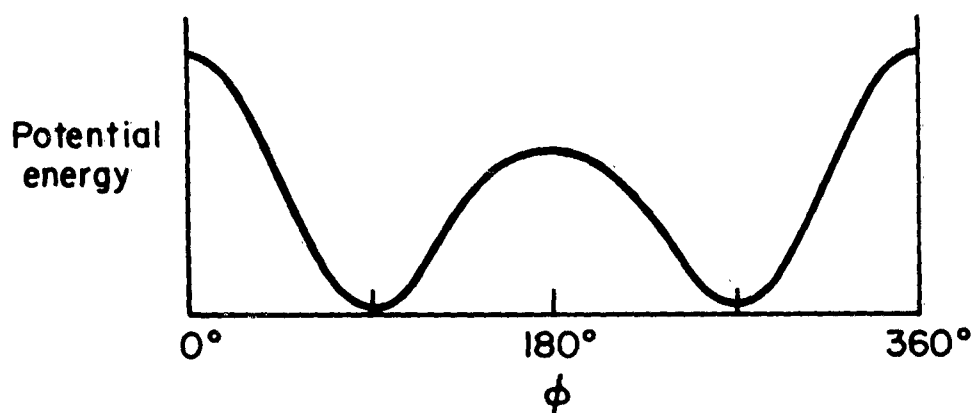


Fig. 3. Potential function for the H_2O_2 molecule.

oxygen atoms, and also between the unshared pairs on each oxygen. They did not make the assumption that p orbitals alone would be used, and found that the combined effect of all the interaction energies resulted in an equilibrium dihedral angle that lay in the range 94° to 113° .

A crystallographic study of the hydrogen peroxide-urea addition complex by Lu, Hughes and Giguère (1941) led to the assignment of $106 \pm 2^\circ$ for the dihedral angle, and a later x-ray study of solid hydrogen peroxide at -20°C by Abrahams, Collin and Lipscomb (1951) gave $\phi = 94 \pm 1.5^\circ$. In 1954, Giguère quoted the value $80 \pm 20^\circ$ for hydrogen peroxide, based upon a spectroscopic study. A microwave study of hydrogen peroxide by Massey and Bianco (1954) gave the height of the potential barrier as 113 cm^{-1} (0.3 kcal/mole), using a sinusoidal approximation for the hindering potential, while a subsequent paper by Massey and Hart (1955) showed that the presently available microwave data were equally applicable to a model in which there is a high cis- and low trans-barrier to internal rotation, such as 2800 cm^{-1} and 214.5 cm^{-1} (8 and 0.6 kcal/mole), respectively.

Luft (1953) says the energy barrier V_0 is $6 < V_0 < 18 \text{ kcal/mole}$. This compares with Penney and Sutherland's (1934) prediction of about 6 and 10 kcal/mole for the barrier at 180° and 0° , respectively.

The peroxide dihedral angle has also been measured in the molecule disulfur decafluoro dioxide (or peroxide) by Harvey and Bauer (1954) using the electron diffraction method. They showed the molecule to have a peroxide structure, with the sulfur-oxygen-oxygen bond angle $105 \pm 3^\circ$ and the dihedral angle $107 \pm 5^\circ$.

The predicted values for this angle have thus been accurately confirmed by experiment, and it is interesting that the dihedral angle in $F_5S-O-O-SF_5$ lies well within the limits given by Lassettre and Dean (1949) for hydrogen peroxide.

2.4 The oxygen-oxygen bond

The oxygen-oxygen bond has now been extensively studied under a variety of different circumstances. It is convenient to start this section by considering the case of the oxygen molecule O_2 . In the normal state, this molecule may be expected to contain a double bond, with the structure $\ddot{O} = \ddot{O}$. However, the ground state is $^3\Sigma_g^-$, and the molecule must hence contain two unpaired electrons (Pauling, 1940). The electronic configuration may thus be represented by Fig. 4, where each arrow signifies an electron, each circle an orbital. A recent microwave study of the magnetic hyperfine structure (Miller, Townes and Kotani, 1953) has confirmed that the unpaired electrons are primarily in the $2p\Pi$, rather than in $2p\sigma$ orbits. This study suggests that the wave function, which is predominantly $p\Pi$, has approximately a 2.5 percent s character.

The length of the oxygen-oxygen bond in the ground state for O_2 is given in Table 2, and corresponds very closely to a pure double bond. Greenhow and Smith (1951), however, have made molecular orbital calculations which show that a model with 5 to 10 percent s, p hybridization for O_2 gives a calcu-

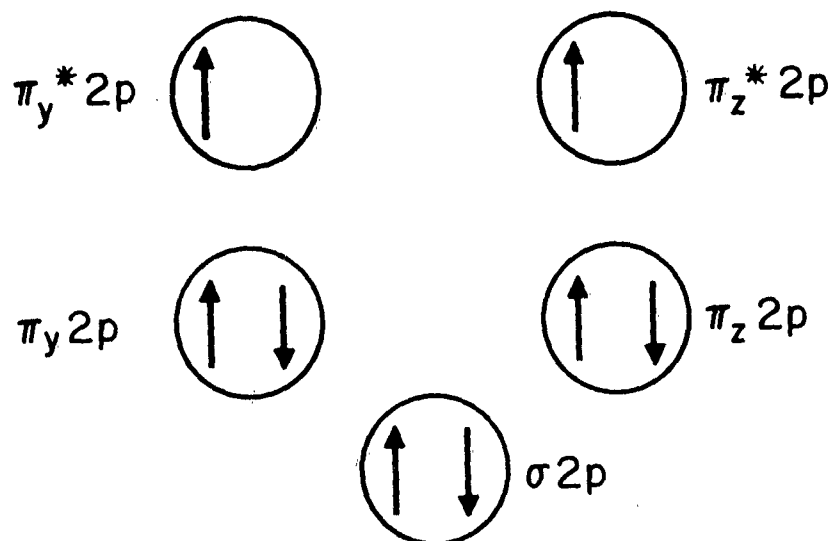


Fig. 4. Representation of valence electrons in the oxygen molecule (after Coulson, 1952).

lated quadrupole moment agreeing best with that deduced from the microwave line-broadening data.

It is possible to use Fig. 4 in deriving the electronic configuration of various O_2 ions. Thus, if one of the nonbonding $p\pi^*$ orbitals has an extra electron added, the O_2^- ion will be formed, and if a second electron is added to the remaining $p\pi^*$ orbital, the O_2^{2-} ion will result. Similarly, O_2^+ may be formed by the removal of one of the electrons in Fig. 4. The lengths of the oxygen-oxygen bonds in all of these ions, as well as in ozone, have been measured and are collected in Table 2.

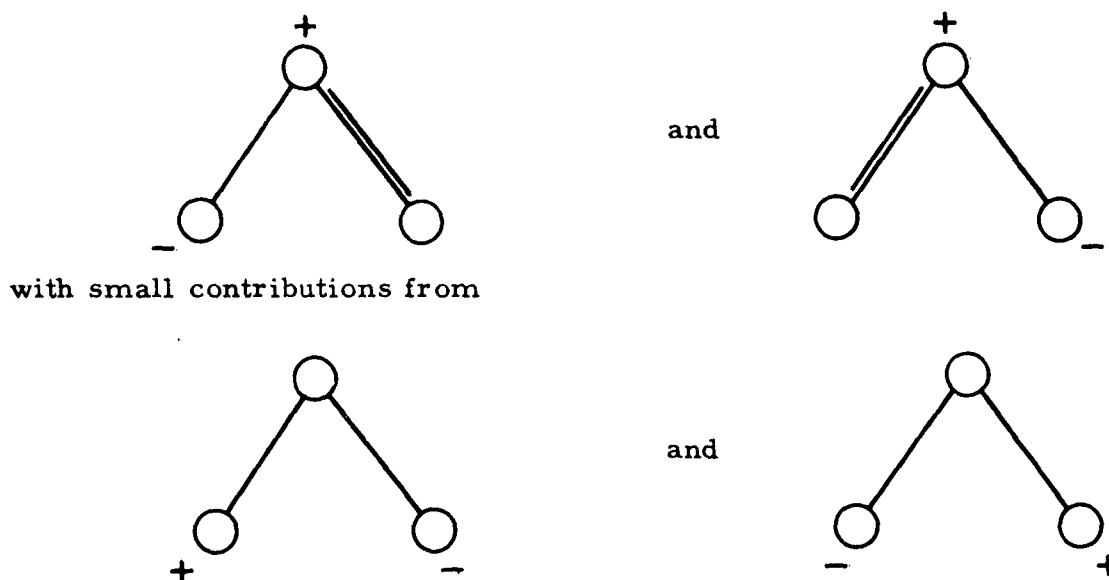
Bond-type (e) may be regarded, at 1.49A, as a standard single bond. The identity of bond-types (d) and (e) has been shown by Neiding and Kazarnovskii (1950), on the basis of the magnetic susceptibilities: -18×10^{-6} for O_2^- in Na_2O_2 and -17.7×10^{-6} for H_2O_2 . This conclusion is also strengthened by the identity in bond length (Table 2). It is further indicated by a consideration of Fig. 4; both antibonding $p\pi^*$ orbitals are likely to be filled in

Table 2. Oxygen-oxygen bond types and lengths.

Case	Bond	Example	Bond length (Å)	Reference
(a)	O-O	O ₂	1.2074±0.0001	Babcock and Herzberg (1948)
(b)	-O-O	O ₃	1.278±0.003	Trambarulo et al. (1953)
(c)	[O-O] ⁻	HO ₂	1.30	Giguère (1954)
		β-NaO ₂	1.33±0.06	Templeton and Dauben (1950)
			1.31±0.03	Zhdanov and Zvonkova (1952)
		α-KO ₂	1.28±0.07	Kasatochkin and Kotov (1937)
(d)	[O-O] ⁼		1.28±0.02	Abrahams and Kalnajs (1955)
		BaO ₂	1.47	Butuzov (1947)
			1.49±0.04	Abrahams and Kalnajs (1954)
		CaO ₂ ·8H ₂ O	1.48	Harr (1952)
		SrO ₂ ·8H ₂ O	1.49	
		BaO ₂ ·8H ₂ O	1.48	
		Li ₂ O ₂	1.3±0.1	Fehér, von Wilucki and Dost (1953)
(e)	-O-O-	H ₂ O ₂	1.47±0.02	Giguère and Schomaker (1933)
			1.49±0.02	Abrahams, Collin and Lipscomb (1951)
			1.49±0.01	Giguère (1954, b)
		SF ₅ ·O ₂ ·F ₅ S	1.47±0.03	Harvey and Bauer (1954)
(f)	[O-O] ⁺	O ₂ ⁺	1.1227±0.0001	Herzberg (1950)

each of these two cases, which thus contain two single bonds apiece. Thus 1.49A may be regarded as the length of a simple electron-pair single bond.

On filling only one of the Π^* 2p orbitals in Fig.4, the resulting ion is O_2^- . The superoxide ion is found to have a bond length of 1.28A. This linkage has been demonstrated to contain a 3-electron bond by magnetic susceptibility measurements (Klemm and Sodomann, 1935) and hence verifies the electronic arrangement just proposed, which corresponds to 50 percent double bond character. The oxygen-oxygen bond length in the HO_2 radical was determined using Badger's rule, and has been taken as indicating a bond similar to that observed in the superoxide ion. The bond found in ozone, also of 1.28A length, has been suggested to possess 50 percent double-bond character by Trambarulo et al. (1953), on the basis of the following canonical structures being most important:



Fischer-Hjalmars (1955) has made a partial molecular orbital study of the ozone molecule, and has found that a 2s, 2p approximation for the atomic orbitals agrees better with experiment (e.g., with respect to the sign of the dipole moment) than a 2p approximation.

The preparation of several alkali ozonides has been reported by Whaley and Kleinberg (1951), although no structural information was given. Giguère and Harvey (1954) have now claimed that the ozonide ion does not exist. The bond in O_2^+ of length 1.12 Å in the ${}^2\Pi_g$ state, can be considered to possess approximately 150 percent double-bond character, for it has only one electron in an antibonding orbital. A smooth bond-order vs. bond-length curve (Fig. 5) may now be constructed, on the basis of the available information, which passes through each point, within the experimental error.

Complementary information is available from bond strength studies. Glocker (1951) has estimated the O-O bond energy in H_2O_2 as 47.0 kcal/mole, in O_3 as 70.6 kcal/mole and in O_2 (${}^3\Sigma_g^-$ state) as 117.2 kcal/mole. These bond

energies are ascribed to the O-O bond as it exists in these molecules in their normal state. Giving these bonds the amount of double-bond character assigned above results in a smooth bond-order vs. energy curve.

2.5 Other atom-oxygen bonds

Bond length and related information is now available for bonds between oxygen and many other atoms. However, apart from the oxygen-oxygen bond,

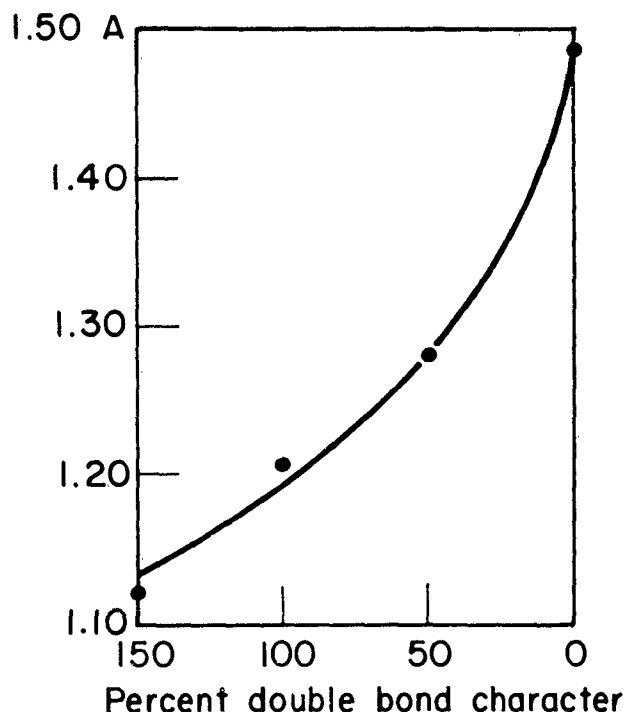


Fig. 5. Variation of the oxygen-oxygen bond length with bond character.

the only bonds for which enough data are known to establish bond-length vs. bond-order relations are probably the sulfur-oxygen, and carbon-oxygen bonds. Of these the sulfur-oxygen bond is discussed in Section 3.10 and only the carbon-oxygen bond will be treated here in detail.

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 (1951) have summarized the data for twenty-two different molecules containing single carbon-oxygen bonds, and find the mean carbon-oxygen distance to be 1.437A. The corresponding double-bond distance, based on determinations for 11 different molecules, results in a mean C=O value of 1.185A. Cox and Jeffrey suggest taking 1.44A as the standard single carbon-oxygen bond length, but feel that 1.19A for the standard double-bond length is less reliable, in view of Walsh's (1947) postulate that the double-bond length may vary with the polarity of the bond.

Vaughan and Donohue (1952) find that satisfactory agreement is obtained between their observed bond lengths in urea ($C-N = 1.335 \pm 0.009A$ and $C-O = 1.262 \pm 0.011A$) and those calculated on the basis of Pauling's (1940) equation relating bond order and length, if they take $C-O = 1.42A$ and $C=O = 1.20A$. Applying these same values to bond-length data for 12 carboxylic acids they find excellent correlation between the calculated and observed bond distances.

Recent carbon-oxygen bond-length determinations are in good agreement with the value 1.43A for a single bond, and with the smaller value of about 1.17A 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, as given in Fig. 6.

Skinner (1945) has given seven sets of related observed bond lengths

Table 3. Recent carbon-oxygen bond-length determinations.

Molecule	Bond length	Method	Reference
Carbon monoxide	$1.131 \pm 0.005 \text{ \AA}$	microwave	Gilliam, Johnson and Gordy (1950)
Phosgene	$\left\{ \begin{array}{l} 1.166 \pm 0.002 \\ 1.15 \pm 0.02 \end{array} \right.$	$\left\{ \begin{array}{l} \text{microwave} \\ \text{x-ray} \end{array} \right.$	$\left\{ \begin{array}{l} \text{Robinson (1953)} \\ \text{Zaslow, Atoji and Lipscomb (1952)} \end{array} \right.$
Anthraquinone	1.15 ± 0.02	x-ray	Sen (1948)
Carbonyl selenide	1.1588 ± 0.0001	microwave	Strandberg et al. (1949, a)
Carbonyl sulfide	1.1637 ± 0.0005	microwave	Strandberg et al. (1949, b)
Isocyanic acid	$\left\{ \begin{array}{l} 1.17 \pm 0.01 \\ 1.184 \pm 0.02 \end{array} \right.$	$\left\{ \begin{array}{l} \text{microwave} \\ \text{x-ray} \end{array} \right.$	$\left\{ \begin{array}{l} \text{Jones et al. (1950)} \\ \text{von Dohlen and Carpenter (1955)} \end{array} \right.$
Methyl isocyanate	1.18 ± 0.03	E.D.	Eyster et al. (1940)
Acetone	$\left\{ \begin{array}{l} 1.22 \pm 0.03 \\ 1.23 \pm 0.03 \\ 1.24 \pm 0.03 \end{array} \right.$	$\left\{ \begin{array}{l} \text{E.D.} \\ \text{E.D.} \\ \text{E.D.} \end{array} \right.$	$\left\{ \begin{array}{l} \text{Allen et al. (1952)} \\ \text{Bauer (1953)} \\ \text{Kimura and Kurita (1951)} \end{array} \right.$
p-Methoxybenzene	1.36 ± 0.02	x-ray	Goodwin et al. (1950)
Furan	1.377	E.D.	Almenningen et al. (1955)
Diketene	$\left\{ \begin{array}{l} 1.24 \pm 0.06 \\ 1.39 \pm 0.06 \end{array} \right.$	$\left\{ \begin{array}{l} \text{x-ray} \end{array} \right.$	$\left\{ \begin{array}{l} \text{Katz and Lipscomb (1952)} \end{array} \right.$
Ethyl ether	1.43 ± 0.02	E.D.	Schomaker (Allen and Sutton, 1950)
p-Dioxane	1.44 ± 0.03	E.D.	Shand (Allen and Sutton, 1950)
Methyl ether	1.46 ± 0.03	E.D.	Shand (Allen and Sutton, 1950)
Methanol	$\left\{ \begin{array}{l} 1.42 \pm 0.03 \\ 1.434 \pm 0.008 \\ 1.44 \pm 0.01 \\ 1.48 \pm 0.04 \end{array} \right.$	$\left\{ \begin{array}{l} \text{x-ray} \\ \text{microwave} \\ \text{E.D.} \\ \text{E.D.} \end{array} \right.$	$\left\{ \begin{array}{l} \text{Tauer and Lipscomb (1952)} \\ \text{Ivash and Dennison (1953)} \\ \text{Lu and Schomaker (Allen and Sutton, 1950)} \\ \text{Kimura (1950)} \end{array} \right.$
Ethanol	1.48 ± 0.04	E.D.	Kimura (1950)

and energies for the carbon-oxygen bond, and from these has suggested the empirical relationship $E r^n = A$, where E is the bond energy, A and n are bond constants, and r the bond length.

Among other atom-oxygen bonds, Dunitz and Hedberg (1950) report the length of the single chlorine-oxygen bond as $1.701 \pm 0.02 \text{ \AA}$ in chlorine monoxide, and of the double bond as $1.491 \pm 0.014 \text{ \AA}$ in chlorine dioxide.

In the latter molecule, a structure analogous with SO_2 was postulated, the chlorine atoms being assumed to use their d orbitals in bond formation.

The nitrogen-oxygen bond has often been measured, but there has always been doubt about the value of the multiplicity of these bonds. Thus in the nitro group in p -dinitrobenzene, the distance is $1.21 \pm 0.03 \text{ \AA}$ (Abrahams, 1950), while in the nitrite group it is $1.236 \pm 0.014 \text{ \AA}$ in the sodium salt (Carpenter, 1955). In N_2O (Coles, Elyash and Gorman, 1947) it is $1.191 \text{ \AA}$; in N_2O_5 (Grison, Eriks and de Vries, 1950) it is $1.243 \pm 0.01 \text{ \AA}$ in the NO_3^- ion and $1.154 \pm 0.010 \text{ \AA}$ in the NO_2^+ ion; and in NO_2 it is $1.28 \pm 0.03 \text{ \AA}$ (Harris and King, 1940). The total variation in the length of this bond is not large, and a bond-order vs. length relation must await further measurements and bond-order assignments. Earlier references to other nitrogen-oxygen bonds may be found in the papers here cited.

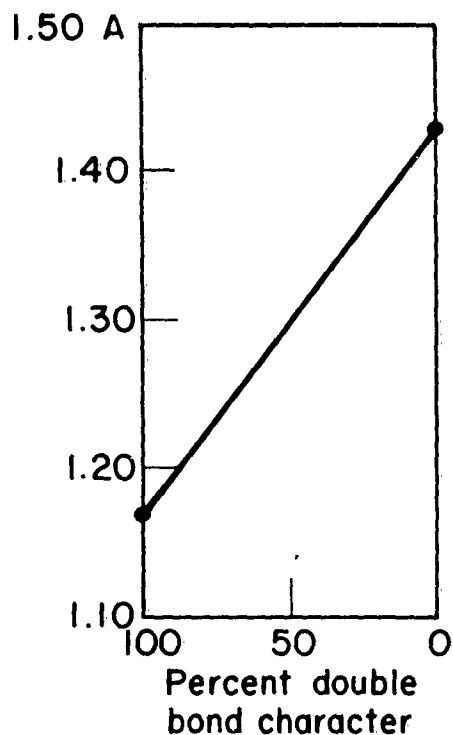


Fig. 6. Variation of the carbon-oxygen bond length with bond character.

3.1 Divalent sulfur

Sulfur, in common with all the elements of subgroup VI_b, has the valency electron configuration $(ns)^2(np_x)(np_y)(np_z)^2$, where $n = 3$ for sulfur. Unlike oxygen however, the 3d orbitals are available for sulfur bond formation, in an expansion of the outer octet to a decet, or even a duodecet of electrons. Thus, energy considerations show that sulfur will more readily promote its 3p electrons into its 3d levels than lose them altogether (Moffitt, 1950).

The experimental values for the sulfur 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 angles for sulfur in this table and for oxygen in Table 1 indicates that the bond mechanism for sulfur can not be very dissimilar from that described for oxygen in Section 2.1. Thus, in the case of the sulfur-sulfur-sulfur bond angle, the measured values vary only from 103° to 108° , with a mean value of 106° (diiododiethyl trisulfide is an exception). The angular range used is suggestive of a considerable s admixture in the sulfur bonds, with an approach to sp^3 hybridization. The bond structure in S_8 has been discussed by Dehmelt (1953) on the basis of nuclear quadrupole resonance measurements. Assuming that the observed angle of 107.8° is also the angle between the axes of the two orbitals originating at the sulfur atoms, he estimates about 20 percent s character in the bond. However, the energy required to promote a 3s electron, about 40 kcal/mole, is so high that Dehmelt suggests that it is unlikely to occur in view of the small resulting (14 percent) increase in bond strength of the sp hybrid as compared with the pure p orbitals. An alternative view proposed is that if the bond angle is not identical with the interorbital angle, then nearly pure p orbitals could be used, and the increased size of the bond

Table 4. Sulfur valency angle.

A. Sulfur linked only to two other sulfur atoms				
Compound	Value	Method	Reference	
(CF ₃) ₂ S ₃	103.8+3 ^o	E. D.	Bowen (1954)	
BaS ₄ O ₆ ·2 H ₂ O	103+2 ^o	x-ray	Foss et al. (1954)	
BaSeS ₄ O ₆ ·2 H ₂ O	103+2 ^o	x-ray	Foss and Tjomsland (1954)	
CH ₃ ·SO ₂ ·S·S·SO ₂ ·CH ₃	104+3 ^o	x-ray	Sørum (1953)	
CH ₃ ·S ₃ ·CH ₃	104+5 ^o	E. D.	Donohue and Schomaker (1948)	
BaS ₅ O ₆ ·2 H ₂ O (ortho-rhombic)	104+2 ^o	x-ray	Foss and Zachariasen (1954)	
BaS ₄ ·H ₂ O	104.5+1 ^o	x-ray	Abrahams (1954)	
C ₆ H ₅ ·SO ₂ ·S·SO ₂ ·C ₆ H ₅	106.5+1 ^o	x-ray	Mathieson and Robertson (1949)	
BaS ₅ O ₆ ·2 H ₂ O (triglinic)	107+3 ^o	x-ray	Foss and Tjomsland (1955)	
S ₈	107.8+0.5 ^o	x-ray	Abrahams (1955)	
Cs ₂ S ₆	108.8+2 ^o	x-ray	Abrahams and Grison (1953)	
I·C ₂ H ₅ ·S ₃ ·C ₂ H ₅ ·I	113+2 ^o	x-ray	Dawson and Robertson (1948)	
B. Sulfur linked only to two other atoms				
Compound	Angle	Value	Method	Reference
C ₂ H ₄ S	C-S-C	65.8+0.1 ^o	microwave	Cunningham et al. (1951)
H ₂ S	H-S-H	92.1+0.2 ^o	microwave	Burrus and Gordy (1953)
HDS	H-S-D	93.3+0.2 ^o	microwave	Bird and Townes (1954)
(I·C ₂ H ₅) ₂ S ₃	S-S-C	98+10 ^o	x-ray	Donohue (1950)
CH ₃ SH	C-S-H	99.4+0.5 ^o	microwave	Solimene and Dailey (1953)
As ₄ S ₆	As-S-As	100 +2 ^o	E. D.	Lu and Donohue (1944)

Table 4 (cont.)

Compound	Angle	Value	Method	Reference
SCl_2	Cl-S-Cl	100.3°	Raman	Stammreich et al. (1955)
As_4S_4	As-S-As	$102+3^\circ$	x-ray	Ito, Morimoto and Sadanaga (1952)
S_4N_4	N-S-N	$102+3^\circ$	x-ray	Clark (1952)
P_4S_3	P-S-P	$102+3^\circ$	x-ray	van Houten, Vos and Wiegers (1955)
$(\text{p-CH}_3\cdot\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{S})_2\text{Te}$	S-S-Te	$103+3^\circ$	x-ray	Foss and Öyum (1955)
$\text{BaSeS}_4\text{O}_6\cdot 2\text{H}_2\text{O}$	S-S-Se	$103+3$	x-ray	Foss and Tjomsland (1954)
$(\text{CH}_3)_2\text{S}_3$	S-S-C	$104+5$	x-ray	Donohue and Schomaker (1948)
$(\text{C}_6\text{H}_5\cdot\text{SO}_2\text{S})_2\text{Te}$	S-S-Te	$104+2^\circ$	x-ray	Öyum and Foss (1955)
$(\text{NH}_4)_2\cdot(\text{S}_2\text{O}_3)_2\text{Te}$	S-S-Te	104°	x-ray	Foss and Larsen (1954)
$\text{Se}(\text{SCN})_2$	Se-S-C	$104+5^\circ$	x-ray	Ohlberg and Vaughan (1954)
P_4S_7	P-S-P	$104+1^\circ$	x-ray	Vos and Wiebenga (1955)
S_2Cl_2	S-S-Cl	$104.5+2.5^\circ$	E. D.	Guthrie (Allen and Sutton, 1950)
$(\text{CH}_3\cdot\text{SO}_2\cdot\text{S})_2\text{Te}$	S-S-Te	$105+3^\circ$	x-ray	Foss and Vihovde (1954)
$(\text{CF}_3)_2\text{S}_2$	S-S-C	$105.4+3^\circ$	E. D.	Bowen (1954)
$(\text{CF}_3)_2\text{S}$	S-S-C	$105.6+3^\circ$	E. D.	Bowen (1954)
$(\text{p-Br}\cdot\text{C}_6\text{H}_4)_2\text{S}_2$	S-S-C	$107+1^\circ$	x-ray	Toussaint (1945)
$(\text{CH}_3)_2\text{S}_2$	S-S-C	$107+3^\circ$	E. D.	Stevenson and Beach (1938)
$(\text{p-CH}_3\cdot\text{C}_6\text{H}_4)_2\text{S}$	C-S-C	$109+2^\circ$	x-ray	Blackmore and Abrahams (1955, b)
P_4S_{10}	P-S-P	$109+1^\circ$	x-ray	Vos and Wiebenga (1945)
$(\text{p-Br}\cdot\text{C}_6\text{H}_4)_2\text{S}$	C-S-C	$109.5+1^\circ$	x-ray	Toussaint (1945)
$\text{C}_2\text{H}_5\text{SH}$	C-S-H	$113+2^\circ$	E. D.	Roualt and Gallagher (1949)
SO_2	O-S-O	$119.5+0.5^\circ$ $119.0+0.5^\circ$	microwave microwave	Sirvetz (1951) Crable and Smith (1951)

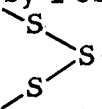
angle over 90° could be attributed to a pivoting of the p orbitals. One interesting difference between the behavior of sulfur and oxygen is that, in general, the 2-bonded sulfur valency angle never exceeds 109.5° , even when aromatic groups are linked to the sulfur atom. In the case of oxygen, in a similar environment, the oxygen bond angle generally increases to about 120° as in Table 1.

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 (1953) have suggested that this angle as well as the nuclear couplings, can be accounted for by postulating roughly equal (ca. 15 percent of each) s and d contributions to the bonding orbitals (since the amount of energy required to promote a 3s electron to a 3p orbital is about the same as that needed to promote a 3p to a 3d orbital). In addition to the s and d contributions to the bonding orbitals, they assume one nonbonding pair in a pure p orbital normal to the molecular plane, and the other in an sp hybrid lying along the symmetry axis. The admixture of both s and d orbitals tends to have a cancelling effect on the bond angle, but adds up to produce the observed asymmetry in the molecular electric field.

In the case of HDS, Bird and Townes (1954) assume 4 percent ionic character in the S-H bond, and about 14.6 percent of s character in s, p hybridization. However, such s, p hybridization would result in an angle of about 100° , whereas 93.3° is found. As in the case for sulfur itself, this difficulty can be met either by assigning some d hybridization, or else by assuming that the localization of a bond along the internuclear line is a poor approximation for very light molecules.

3.2 Polysulfur chains

An outstanding characteristic which distinguishes the behavior of sulfur from that of oxygen is the ability to form long chains. Thus, the stable state of elementary sulfur (orthorhombic form) consists of S_8 rings, while compounds such as $S_{100}Cl_2$ are known (Fehér and Baudler, 1952). A precise knowledge of the geometry of several kinds of long-chain sulfur compounds is now available. Together with our present sulfur-sulfur bond length (Table 5), the corresponding dihedral angle (Table 6) and the sulfur-sulfur-sulfur bond angle (Table 4) information, accurate prediction of the shape of other long-chain sulfur compounds is now possible.

There has been no confirmed report of a branched polysulfur chain, although rings, helices, and other nonbranched forms are well established. A review of the x-ray, electron diffraction and spectroscopic data has been given both by Foss (1950) and by Woodrow, Carmack and Miller (1951), who show that  formation is very unlikely (cf. also Minoura, 1952). The only cases in which sulfur forms a single (one only) bond appear to be in ions such as $[O_3S-S]^=$, and as terminal members of polysulfide chains. In orthorhombic sulfur (Abrahams, 1955) the puckered, eight-membered ring has the symmetry $\bar{8}2m$ within the limits of experimental error. In the $S_6^{=}$ ion (Abrahams and Grison, 1953) the chain is helical, while the $[S_5O_6]^=$ ion (Foss and Zachariasen, 1954) possesses a plane of symmetry passing through the middle atom of the sulfur chain. The sulfur chain in this ion is hence equivalent to an S_8 ring with three linked sulfur atoms missing.

The length of the sulfur-sulfur bond (Table 5) varies in the range 1.89 to 2.39A and attempts have been made (e.g., Abrahams, 1955) to establish a bond-order vs. length curve from some of these data for this bond. The

length chosen for a single bond by Pauling (1940) was 2.08A, and indeed, this value is identical with the average of the 41 bond lengths given in Table 5. If 2.08A is accepted as a single-bond length, the measured value in the element, as in orthorhombic sulfur (S_8), is short, and this bond must hence possess some double-bond character. This suggestion had previously been made by Powell and Eyring (1943) to account for the small heat of reaction of opening the S_8 ring, S_8 (ring) $\rightarrow S_x$ (chain), $\Delta H = 27.5 \pm 5$ kcal, as compared with the energy of the S-S bond in some alkyl disulfides of about 70-73 kcal/mole (Franklin and Lumpkin, 1952), or the heat of dissociation of a sulfur chain of 50 ± 5 kcal (Gee, 1952). Koch (1949) has proposed that in addition to the conventional single and various excited intermediate bonded canonical forms which can contribute to the structure of the S_8 molecule, an alternating no-bond, double-bond structure might be important. A similar explanation would also be required to account for the other shorter bonds, such as in dimethyl trisulfide.

The only sulfur-sulfur bonds which have been measured as significantly longer than 2.08A, the value proposed as a standard single-bond length, are in decafluoro disulfide and sodium dithionite. Dunitz (1956) has discussed the $S_2O_4^{2-}$ ion sulfur-sulfur bond length in terms of Pauling's (1947) relationship, $-\Delta R(n) = 0.353 \log n$, for which n is 0.36. He then suggests that the extra electrons due to the ionic charge will occupy antibonding Π orbitals, which will have a large amount of d character. In consequence, the sulfur-sulfur bond will possess a considerable proportion of $d\Pi-d\Pi$ bonding, which is weaker than the usual $p\sigma$ bond, and hence is longer. In the case of $F_5S \cdot SF_5$, n is 0.69. Both bonds are hence substantially less than single bonds. Huggins (1953), however, has recently calculated the length of the sulfur-sulfur single bond to be $2.053 \pm 0.02A$ on the basis of a

Table 5. Sulfur-sulfur bond lengths.

A. Without bond-length variations			
Compound	Bond length	Method	Reference
S_2	1.887A	spectros.	Ikenoue (1953)
$Na_2S_2O_3 \cdot 5H_2O$	1.97 ± 0.06	x-ray	Taylor and Beevers (1952)
S_8	2.037 ± 0.005	x-ray	Abrahams (1955)
$(CH_3)_2S_3$	2.04 ± 0.02	E.D.	Donohue and Schomaker (1948)
$C_{10}N_4O_6H_{18}S_2 \cdot 2H_2O^*$	2.04 ± 0.005	x-ray	Yakel and Hughes (1954)
H_2S_2	2.05 ± 0.02	E.D.	Stevenson and Beach (1938)
$(I \cdot C_2H_5)_2S_3$	2.05 ± 0.04	x-ray	Dawson and Robertson (1948)
$(CF_3)_2S_2$	2.053 ± 0.019	E.D.	Bowen (1954)
$(CF_3)_2S_3$	2.065 ± 0.016	E.D.	Bowen (1954)
$(C_6H_5 \cdot SO_2)_2S$	2.07 ± 0.02	x-ray	Mathieson and Robertson (1949)
Cl_2S_2	2.07 ± 0.10	E.D.	Guthrie (Allen and Sutton, 1950)
$(C_6H_5 \cdot SO_2 \cdot S)_2Te$	2.08 ± 0.03	x-ray	Öyum and Foss (1955)
$NaK_5Cl_2(S_2O_6)_2$	2.08 ± 0.04	x-ray	Stanley (1953)
$NaK_6Cl_5(S_2O_6)$	2.08 ± 0.04	x-ray	Stanley (1953)
$(CH_3 \cdot C_6H_4 \cdot SO_2 \cdot S)_2Te$	2.11 ± 0.04	x-ray	Foss and Öyum (1955)
$(NH_4)_2TeS_4O_6$	2.11 ± 0.03	x-ray	Foss and Larsen (1954)
$BaSeS_4O_6 \cdot 2H_2O$	2.13 ± 0.04	x-ray	Foss and Tjomsland (1954)
$(CH_3 \cdot SO_2 \cdot S)_2Te$	2.14 ± 0.03	x-ray	Foss and Vihovde (1954)
$F_5S \cdot SF_5$	2.21 ± 0.03	E.D.	Harvey and Bauer (1953)
$Na_2S_2O_4$	2.389 ± 0.010	x-ray	Dunitz (1956)
* N, N'-diglycyl-L-cystine dihydrate.			

Table 5 (cont.)

B. With variations in the bond length			
Compound	Bond length	Method	Reference
$\text{BaS}_4 \cdot \text{H}_2\text{O}$	2.02, 2.07, 2.02 $\pm 0.025\text{A}$	x-ray	Abrahams (1954)
Cs_2S_6	1.99, 2.10, 2.03, 2.12, 2.03 ± 0.03	x-ray	Abrahams and Grison (1953)
$\text{BaS}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$	2.10, 2.02, 2.13 ± 0.03	x-ray	Foss et al. (1954)
$\text{BaS}_5\text{O}_6 \cdot 2\text{H}_2\text{O}$ (triclinic)	2.12, 2.04, 2.04, 2.10 ± 0.04	x-ray	Foss and Tjoms- land (1955)
$\text{BaS}_5\text{O}_6 \cdot 2\text{H}_2\text{O}$ (orthorhombic)	2.14, 2.04, 2.04, 2.14 ± 0.03	x-ray	Foss and Zachari- asen (1954)
$\text{CH}_3 \cdot \text{SO}_2 \cdot \text{S} \cdot \text{S} \cdot \text{SO}_2 \cdot \text{CH}_3$	2.10, 2.06, 2.10 ± 0.03	x-ray	Sbrum (1953)

newly derived relation between bond energies and radii.

The sulfur-sulfur bond length in S_2 in the $^3\Sigma_g^-$ (ground) state has been spectroscopically determined to be 1.887A. As in the case of O_2 in the ground state, this bond corresponds fairly closely to a double bond. Intermediate points for the sulfur-sulfur bond-order vs. bond-length curve, between 2.08A and 1.89A corresponding to single and double bonds, respectively, can be obtained from a consideration of Table 5B. It may first be noted that variation in bond lengths along polysulfur chains has been measured only if four or more linked sulfur atoms are present. In the variation for the six examples reported, the sulfur-sulfur bonds are alternately short and long, with chemically equivalent bonds of identical length (within the

experimental error), for a chain containing an odd number of such bonds. The outermost bonds are the short bonds, except when oxygen atoms are linked to the terminal sulfur atoms. In this case, it is the outer sulfur-oxygen bonds that are short. If an even number of sulfur-sulfur bonds are present in the chain, the two central bonds appear to be of equal length, and the equivalent of a mirror plane of symmetry is introduced into the chain.

In the case of the four ions S_4^+ , S_6^{2-} , $S_4O_6^{2-}$, and $S_5O_6^{2-}$, the electrons gained from the cation may perhaps be considered as occupying molecular orbitals with local electron concentrations in the neighborhood of the short bonds. With this hypothesis, the polysulfide short bonds, of length about 2.02 Å, correspond to about 50 to 33 percent double-bond character. The distribution of ionic electrons in the polythionates is less easy to judge, although the outermost sulfur-oxygen bonds are also rather short (see Section 3.10), indicating some double-bond character there, as well as in the short sulfur-sulfur bonds.

An approximate bond-order vs. length relationship (Fig. 7) can hence be established, but it is apparent that more careful experimental and theoretical work is necessary if this relation is to be confirmed and extended.

3.3 Dihedral sulfur angle

The dihedral angle in sulfur, as in oxygen, is determined primarily by the

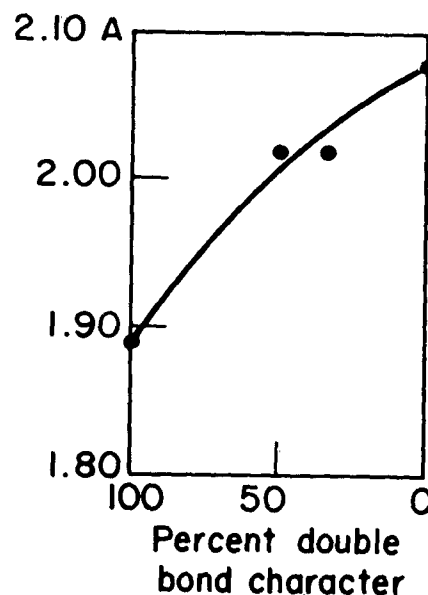


Fig. 7. Variation of the sulfur-sulfur bond length with bond character.

pπ electron repulsion, with the greatest repulsion between the unshared pairs of electrons on adjacent sulfur atoms. Pauling (1949) has estimated the potential barrier to internal rotation about a sulfur-sulfur bond at about 5 kcal/mole. He has also deduced a relationship between the dihedral angle and the valency angle in sulfur rings for various numbers of sulfur atoms in the ring, namely, $\sin^2 \frac{\phi}{2} = (\cos \frac{2}{n} + \cos \alpha) \div (1 + \cos \alpha)$, where ϕ is the dihedral angle, n is the number of atoms in the ring and α is the bond angle. For orthorhombic sulfur, Pauling's relationship predicts a dihedral 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 sulfur 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 78° to 110° , and hence are distributed on both sides of 90° .

The establishment of the sulfur dihedral angle at about 90° leads to the result that pentasulfide chains, or groups such as X-S-S-S-Y, may possess two isomeric forms. Foss (1953) has pointed out that if the isomer is of the cis form, i. e., with the two terminal S-S or 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. Thus, for example, sulfur, selenium and tellurium dimethane thiosulfonates (isomorphous crystals) are of the helix or trans type, while barium pentathionate dihydrate and the isomorphous selenopentathionate dihydrate are of the cis form. Ammonium telluropentathionate, however, crystallizes in the trans form.

Table 6. Sulfur dihedral angle.

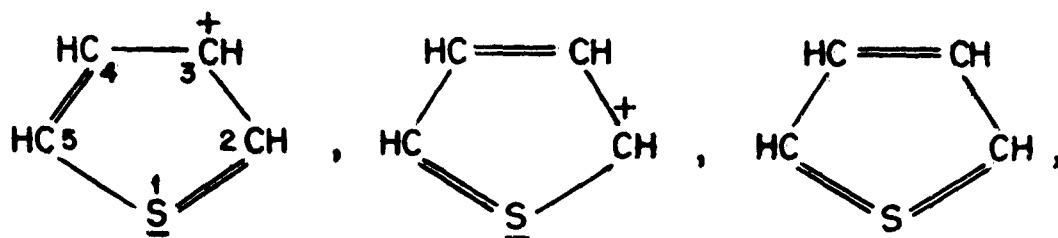
Compound	Dihedral angle	Method	Reference
Cs_2S_6	73.8°	x-ray	Abrahams and Grison (1953)
$\text{BaS}_4 \cdot \text{H}_2\text{O}$	75.6°	x-ray	Abrahams (1954)
$(\text{I} \cdot \text{C}_2\text{H}_5)_2\text{S}_3$	82°	x-ray	Donohue (1950)
H_2S_2	ca. 90°	spectros.	Wilson and Badger (1949)
$(\text{CH}_3\text{SO}_2)_2\text{S}_2$	ca. 90°	x-ray	Sørum (1953)
$\text{BaS}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$	90°	x-ray	Foss et al. (1954)
Cl_2S_2	92°	E. D.	Guthrie (Allen and Sutton, 1950)
$(\text{CH}_3)_2\text{S}_3$	93°	E. D.	Donohue and Schomaker (1948)
S_8	99.3°	x-ray	Abrahams (1955)
$\text{C}_{10}\text{N}_4\text{O}_6\text{H}_{18}\text{S}_2 \cdot 2\text{H}_2\text{O}^*$	101°	x-ray	Yakel and Hughes (1954)
$\text{BaS}_5\text{O}_6 \cdot 2\text{H}_2\text{O}$ (triclinic)	106.5°	x-ray	Foss and Tjomsland (1955)
$\text{BaS}_5\text{O}_6 \cdot 2\text{H}_2\text{O}$ (orthorhombic)	110°	x-ray	Foss and Zachariasen (1954)
* N, N'-diglycyl-L-cystine dihydrate.			

Of the compounds in Table 6, it is interesting to note that those crystallizing in the cis forms (S_8 and S_5O_6^-) have dihedral angles greater than 90° while those in the trans form (S_6^{2-} and diiododiethyl trisulfide) have dihedral angles less than 90° .

3.4 Heterocyclic sulfur

The valency angle of 2-bonded sulfur with no restraints is not necessarily the same as when constraints are placed, such as when the sulfur

atom forms part of a ring molecule. One of the earliest sulfur heterocycles to be investigated was thiophene (Schomaker and Pauling, 1939) and here the carbon-sulfur-carbon angle is not ca. 105° , as might be expected on the basis of Table 4B, but 91° (see Table 7A). These authors suggested that some of the sulfur 3d orbitals might be used in valence-bond structures of the form



etc. Longuet-Higgins (1949) extended this argument, employing the molecular orbital method. He found that by taking the sulfur 3d orbitals into account in Π conjugation, three pd hybrid orbitals could be formed, of which two have the symmetry and energy suitable for conjugation with the carbon atoms, the third being in too high an energy state. This molecular orbital treatment allowed the mobile-bond orders in thiophene to be computed as $C-S = 0.59$, $C_2-C_3 = 0.73$ and $C_3-C_4 = 0.61$. Using the bond-order vs. length curve of Fig. 8, the predicted carbon-sulfur bond length is then 1.73A, in excellent agreement with the experimental value of 1.74A. 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 was described by Abrahams and Lipscomb (1952). Direct calculation of the C-S bond order in thiophene has also been reported by de Heer (1954), who obtained the value 0.58.

A spectroscopic and thermodynamic study of tri-, tetra- and hexamethylene sulfide (Scott et al., 1953) indicates that these molecules are all coplanar, in contrast with the corresponding heterocyclic selenides (see Section 4.4).

Table 7A. Sulfur valency angle and carbon-sulfur bond length in heterocyclic molecules.

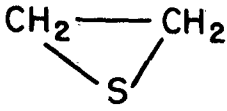
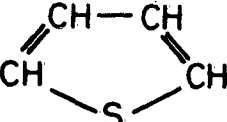
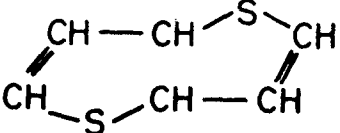
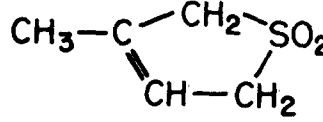
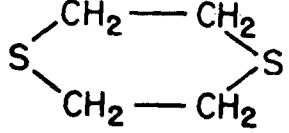
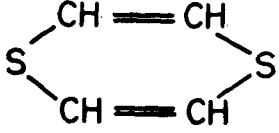
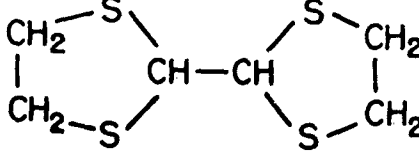
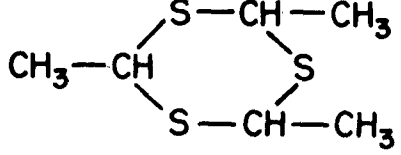
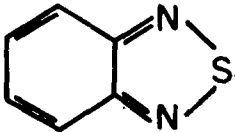
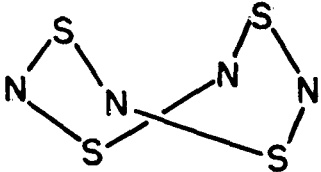
Molecule	Valency angle	C-S bond length	Method	Reference
	65.8°	1.819±0.001A	M.W.	Cunningham et al. (1951)
	91°	1.74±0.03	E.D.	Schomaker and Pauling (1939)
	91.2°	1.73±0.013	x-ray	Cox et al. (1949)
	98.3°	1.752±0.017	x-ray	Jeffrey (1951)
	99.0°	1.810±0.010	x-ray	Marsh (1955)
	101°	1.78±0.05	x-ray	Howells, Curtis and Lipscomb (1954)
	104°	1.85±0.07	x-ray	Brahde (1954)
	106.5°	1.81±0.03	E.D.	Hassel and Vier-voll (1947)

Table 7B. Sulfur valency angle and nitrogen-sulfur bond length in heterocyclic molecules.

Molecule	Valency angle	N-S bond length	Method	Reference
	102°	1.60±0.05A	x-ray	Luzzati (1951)
	102°	1.60±0.05	x-ray	Clark (1953)

There have not yet been any systematic attempts to explain the variations in the sulfur valency angle (Table 7A) from 91° to 101° in the system =CH-S-CH=, and from 65.8° to 106.5° in the system -CH₂-S-CH₂-. Indeed, in the present state of our understanding of the kind of hybridization used in these sulfur-carbon bonds, views concerning this variation are likely to be somewhat speculative. The values given for the sulfur valency angle in Table 7B, as well as the nitrogen-sulfur bond length, show no variation.

The interesting case of the ethylene sulfide molecule, with a sulfur bond angle of 65.8°, has been compared by Cunningham et al. (1951) with cyclopropane, for which Coulson and Moffitt (1949) suggested that the bonds are bent, and lie along the arc tangents to the bonding orbitals. The view that the bonds are also bent in ethylene oxide and sulfide was taken by Cunningham et al. Assuming p² hybridization for the group VI_b atom in both molecules, in the oxide case the internuclear carbon-oxygen distance of 1.436A becomes 1.45A measured along the arc tangent. Although it is not possible to measure the arc tangent in the case of the sulfide, since the angle made by the carbon-

sulfur line with the carbon orbital is different from that made with the sulfur orbital, the length along the arc tangent will be appreciably more than 1.819A, i.e., longer than a single bond (see Section 3.5).

3.5 The carbon-sulfur bond

Enough reliable experimental and theoretical work is now available to derive a bond-order vs. bond-length curve for the carbon-sulfur bond.

Cox and Jeffrey (1951) obtained a mean value of 1.812A for a single carbon-sulfur bond length from a list of eleven molecules containing a formal single bond. This value is also the sum of the Pauling (1940) covalent radii of sulfur and carbon. Huggins (1953) has proposed a new systematization of interatomic distances, based on the bond energies, and has calculated the C-S single bond to be of length $1.83 \pm 0.02A$. The mean of the first six entries in Table 8, all of which should be close to formal single carbon-sulfur bonds involving only two bonds to the sulfur atom, is 1.83A. The weighted mean of all these bond lengths is 1.82A, and this value may hence be taken as the length of a carbon-sulfur bond of bond order 1.0.

The determination of the length of a pure double carbon-sulfur bond offers greater difficulty. The sum of the Pauling radii is 1.61A, and amongst the recent data in Table 8, there is no molecule with an unambiguous double carbon-sulfur bond, e.g., in $O=C=S$, the molecule is assumed (Townes and Dailey, 1949) to have the resonance forms, $O=C=S$, $O-C \equiv S$, $O \equiv C-S$ with a respective importance of 58, 14 and 28 percent. Cox and Jeffrey (1951) used the results of the careful x-ray analysis of thiophthene (Cox, Gillot and Jeffrey, 1949) to provide intermediate points on this bond-length vs. bond-order curve. The molecular orbital calculations of Evans and de Heer (1949) showed that the experimental carbon-sulfur bond lengths of 1.72 and 1.74A correspond to a

Table 8. The carbon-sulfur bond length (see also Table 7A).

Molecule	C-S bond length	Method	Reference
CH ₃ SH	1.808A	M. W.	Solimene and Dailey (1953)
(CH ₃ S) ₄ C	1.81±0.02	x-ray	Perdok and Terpstra (1943)
(CF ₃) ₂ S	1.828±0.015	E. D.	Bowen (1954)
(CF ₃) ₂ S ₂	1.829±0.017	E. D.	Bowen (1954)
(CF ₃) ₂ S ₃	1.848±0.015	E. D.	Bowen (1954)
(IC ₂ H ₄) ₂ S ₃	1.86±0.05	E. D.	Donohue (1950)
TeCS	1.557±0.010	M. W.	Hardy and Silvey (1954)
HNCS	1.557±0.010	M. W.	Beard and Daily (1950)
	1.561±0.002	M. W.	Dousmanis et al. (1953)
OCS	1.5586±0.0005	M. W.	Strandberg et al. (1949, b)
CS ₂	1.56±0.02	E. D.	Hassel and Viervoll (1947)
[Hg(SCN) ₄] [Cu(en) ₂] [*]	1.57±0.10	x-ray	Scouloudi (1953)
NH ₄ SCN	1.59	x-ray	Zvonkova and Zhdanov (1949)
(NH ₂ C=S) ₂	1.663	x-ray	Long, Markey and Wheatley (1954)
$ \begin{array}{c} \text{CH} \text{---} \text{NH} \\ \diagup \quad \diagdown \\ \text{CH} \quad \text{C}=\text{S} \\ \diagdown \quad \diagup \\ \text{CH} = \text{CH} \end{array} $	1.68±0.02	x-ray	Penfold (1953)
$ \begin{array}{c} \text{CH}_2 \text{---} \text{NH} \\ \quad \diagdown \\ \text{CH}_2 \text{---} \text{NH} \quad \text{C}=\text{S} \end{array} $	1.708±0.008	x-ray	Wheatley (1953)
(CH ₃ SO ₂) ₂ C=C=N·CH ₃	$ \begin{cases} 1.726 \pm 0.007 \\ 1.770 \pm 0.009 \end{cases} $	x-ray	Wheatley (1954)

* en = ethylene diamine.

Table 8 (cont.)

Molecule	C-S bond length	Method	Reference
$(p\text{-CH}_3 \cdot \text{C}_6\text{H}_4)_2\text{S}$	$1.75 \pm 0.03\text{A}$	x-ray	Blackmore and Abrahams (1955, c)
$(p\text{-Br} \cdot \text{C}_6\text{H}_4)_2\text{S}$	1.75 ± 0.03	x-ray	Toussaint (1945)
$(\text{C}_6\text{H}_5)_2\text{SO}$	1.760 ± 0.015	x-ray	Abrahams and Gren- ville-Wells (1955)
$(\text{C}_6\text{H}_5 \cdot \text{SO}_2)_2\text{S}$	1.76 ± 0.02	x-ray	Mathieson and Robertson (1949)
$(\text{C}_6\text{H}_5 \cdot \text{SO}_2)_2\text{Se}$	1.77 ± 0.05	x-ray	Furberg and Öyum (1954)
$(\text{CH}_3 \cdot \text{SO}_2)_2\text{S}_2$	1.77 ± 0.05	x-ray	Sörum (1953)
$\text{CH}_3 \cdot \text{CO} \cdot \text{SH}$	1.78 ± 0.02	E.D.	Gordy (1946)
$(\text{CH}_3)_2\text{SO}_2$	1.80 ± 0.02	E.D.	Lister and Sutton (1939)
$(\text{CH}_3 \cdot \text{SO}_2 \cdot \text{S})_2\text{Te}$	1.80 ± 0.06	x-ray	Foss and Vihovde (1954)
$(p\text{-Br} \cdot \text{C}_6\text{H}_4)_2\text{S}_2$	1.80 ± 0.04	x-ray	Toussaint (1945)
$(\text{CH}_3)_2\text{SO}$	1.82	E.D.	Bastiansen and Vier- voll (1948)
$\text{Na} \cdot \text{SO}_2 \cdot \text{CH}_2\text{OH}$	1.838 ± 0.011	x-ray	Truter (1955)
$(p\text{-Br} \cdot \text{C}_6\text{H}_4)_2\text{SO}_2$	1.84 ± 0.04	x-ray	Toussaint (1945)
N, N'-diglycyl-L-cystine dihydrate	1.87 ± 0.017	x-ray	Yakel and Hughes (1954)

bond order of 1.54 and 1.49, respectively. By assuming a single-bond length of 1.81A, and a linear bond-order vs. length relation, the length of a double bond was thus demonstrated to be about 1.65A. The entries in Table 8, however, suggest that the Pauling value of 1.61A might be closer to the length of a pure double carbon-sulfur bond. It is clearly very desirable to measure this bond length in a well-defined double bond.

Taking 1.61Å for the double, 1.82Å for the single, and the data based on thiophene for the intermediate carbon-sulfur bond lengths as in Fig. 8, the results in Table 8 yield some interesting information. Thus, di-p-tolyl and di-p-bromo phenyl sulfide each possess about 40 percent double-bond character in the C-S bond. The environment for the sulfur atom in these molecules is similar to that in thiophene or thiophene, namely =CH-S-CH= , for which p, d hybridization was assumed (Section

3.4). Related evidence in support of 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 sulfide, the angle between the normals to the two benzene rings is only 56° , resulting in a 3.19Å contact between the nearest carbon atoms in the different benzene rings. If this angle were 90° the closest contact of this kind would be 3.99Å, demonstrating that the C-S bond here cannot be single, with cylindrical symmetry. Similarly, in the case of di-p-bromophenyl sulfide, 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 72° .

A similar effect is found in the sulfoxides, for dimethyl sulfoxide has a pure single bond on the basis of the length-order relationship derived, while diphenyl sulfoxide, in which the sulfur atom has a thiophene-like environment, again has about 35 to 40 percent double-bond character. In the case of the

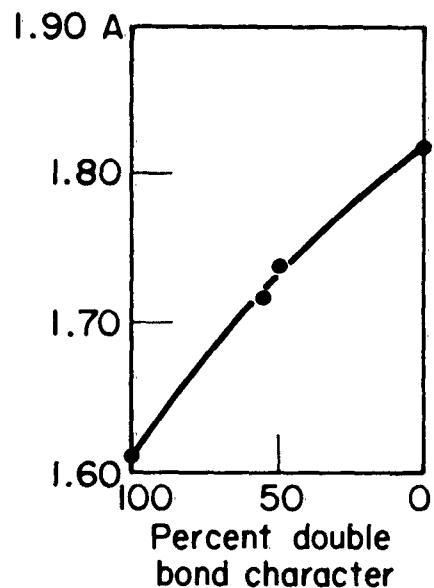


Fig. 8. Variation of the carbon-sulfur bond length with bond character.

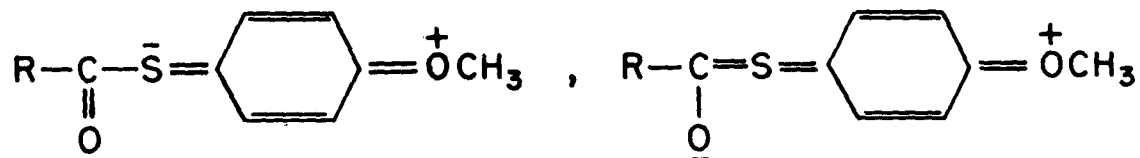
sulfones, no such effect appears, for the C-S bond length in the dimethyl, and the di-p-bromophenyl sulfones are equal, within the error of observation, to a single bond.

The case of di-methane-sulfonyl disulfide, $\text{CH}_3 \cdot \text{SO}_2 \cdot \text{S} \cdot \text{S} \cdot \text{SO}_2 \cdot \text{CH}_3$ is interesting, for the C-S bond is again shorter than single (ca. 30 percent double-bond character), although the sulfur atom is in different environment from the examples just cited. However, in this molecule, the sulfur-sulfur bond lengths vary as shown in Table 5B, and the short carbon-sulfur 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-sulfur bond in divalent sulfur compounds has been given by Tarbell and Harnish (1951).

3.6 Expansion of the sulfur valency-electron octet

In Section 3.5, reference was made to the need for postulating the use of available sulfur 3d orbitals in p,d hybridization, in the grouping >C-S-C< . There is also considerable additional evidence, based largely upon ultraviolet-absorption spectral measurements, which support this postulate. Thus, Cilento and Walter (1954) state that in some thioesters, such as p-anisyl thiolacetates, electronic transitions to the following excited states are indicated:



Rothstein (1953) has suggested that sulfones are able to utilize their d orbitals, but not sulfoxides nor sulfonium salts, by adding electrons from an external atom into the vacant orbitals. Similar suggestions have also been made by

Table 9. Dimensions in the sulfoxide group.

Molecule	X-S-O	X-S-X	r _{S-O}	Method	Reference
F ₂ SO	106.8 $\pm$ 0.1°	92.8 $\pm$ 0.1°	1.412 $\pm$ 0.001A	Micro-wave	Ferguson (1954)
Cl ₂ SO	106 $\pm$ 1°	114 $\pm$ 2°*	1.45 $\pm$ 0.02	E.D.	Palmer (1938)
Br ₂ SO	108 $\pm$ 2°	96 $\pm$ 2°	1.45 (assumed)	E.D.	Stevenson and Cooley (1940)
(CH ₃) ₂ SO	107 $\pm$ 5°	100 $\pm$ 5°	1.47 $\pm$ 0.03	E.D.	Bastiansen and Viervoll (1948)
	106 $\pm$ 6°	-	1.47 $\pm$ 0.03	E.D.	Rundle (Allen and Sutton, 1950)
(C ₆ H ₅) ₂ SO	106.2 $\pm$ 0.7°	97.3 $\pm$ 1.0°	1.473 $\pm$ 0.015	x-ray	Abrahams and Grenville-Wells (1955)
* Angles smaller than 106° were not used in the models tried.					

Eastman and Wagner (1949), Price and Morita (1953), Bordwell and Andersen (1953), Jaffé (1954), Mangani and Passerini (1954) and many others.

3.7 3-Bonded sulfur

The stereochemistry of sulfur in the sulfoxide grouping, >S-O , once a matter for much debate, is now relatively well established. The three sulfur bonds form a shallow pyramid, and the molecular dimensions of the measured sulfoxides are given in Table 9.

The nature of the orbitals used by sulfur in the sulfoxide group have not yet been determined. However, Koch's (1949) proposal for the electronic structure of diphenyl sulfone (see also Section 3.8) is in good agreement with the known molecular structure of diphenyl sulfoxide. Koch suggested that the sulfur 3d and the carbon 2p orbitals overlap to a large extent (cf. Price and

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Morita, 1953), with the result that the two benzene rings would be perpendicular to the C-S-C plane. In diphenyl sulfoxide (Abrahams and Grenville-Wells, 1955) the angle between the benzene rings and the C-S-C plane is 81.9° . It is interesting to notice that the F-S-F angle in thionyl fluoride of 92.8° is smaller than the F-O-F angle in fluorine monoxide of 102.6° (Table 1), although it is nearly identical with the sulfur valency angle in H_2S (Table 4B). However, the Cl-S-Cl angle in thionyl chloride of 114° is much larger than the corresponding angle in SCl_2 (Table 4B), and possibly is in error (see footnote to Table 9).

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 sulfides, this variation in X-S-X angle has been in part correlated (Section 3.1) with the change in admixture of s, p and possible d orbitals. The presence of the nonorthogonal pyramidal arrangement, in itself, appears to be sufficient evidence for some hybridization rather than pure p orbitals being used by sulfur in the sulfoxide group. A definite assignment of the actual hybridization used must await further work.

In the case of SO_3 , the arrangement of the 3-bonded sulfur atom is quite different. In the gas state, this molecule has zero dipole moment, suggesting a flat molecule with a trigonal arrangement of oxygen atoms. This model has been confirmed by electron diffraction methods (Palmer, 1938), which show the oxygen-sulfur-oxygen bond angle to be $120 \pm 2^\circ$. Both in the ice- and asbestos-like forms of sulfur trioxide (Westrik and MacGillavry, 1941 and 1954) the molecules are linked together through S-O-S groups, and the resulting four sulfur bonds are arranged approximately tetrahedrally.

It is reported (Grdenić, private communication) that an x-ray determination of the crystal structure of $S(CH_3)_3^+ Br^-$ is at present in progress. On

completion, this will allow a comparison with the oxonium ion (Section 2.2) to be made. Siebert has shown that the group symmetry for the $(\text{CH}_3)_3\text{S}^+$ ion is C_{3v} , using Raman spectra, i. e., is pyramidal in shape, with the sulfur atom at the apex.

3.8 4-Bonded sulfur

An excellent review of the preparative chemistry of 4-covalent sulfur has been given by Suter (1944). In the 4-bonded state, sulfur is very stable and may be observed in many different groupings. One of the most common examples is the sulfate group, and Wells (1945) has summarized the earlier investigations demonstrating the tetrahedral configuration of the four sulfur-oxygen bonds. A recent confirmation of this model has been made by Jarvis (1953) for potassium ethyl sulfate, in which the mean O-S-O angle is 109° .

A similar arrangement is found in the thiosulfate group, and Taylor and Beevers (1952) have shown this ion to have the structure $\left[\begin{array}{c} \text{O} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{S} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{S} \end{array} \right]^-$ in $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, with the bond angles in the range 104° to 115° . References may also be found in this paper, and in Phillips, Hunter and Sutton (1945), to older work on the S_3O_9^- , S_3O_6^- , S_2O_5^- and S_2O_6^- ions, all of which have a tetrahedral distribution for the sulfur bonds. Other recent work on the S_2O_6^- ion (Stanley, 1953), the $\text{S}_3\text{O}_{10}^-$ ion (Eriks and MacGillavry, 1953) and the SO_4^- ion (Larson and Helmholz, 1954) has confirmed the earlier assignment of a tetrahedral bond distribution for sulfur.

A related bond arrangement for 4-bonded sulfur is found in the sulfones. The molecular structure of several sulfones has now been elucidated, and the results are summarized in Table 10.

With the exception of β -isoprene sulfone, the carbon (or halogen-) sulfur-oxygen angle has very nearly the same constant value of about 107° in

the sulfoxides and in the sulfones. The fluorine-sulfur-fluorine bond angle is identical at 92.8° in thionyl and sulfonyl fluoride, and a strong similarity also exists between other corresponding pairs of angles in the sulfones and sulfoxides (Tables 9 and 10). It may be noticed that the oxygen-sulfur-oxygen angle in the sulfone group is invariably the largest sulfur bond angle in a given molecule, and also is always greater than the tetrahedral value of 109.5° , in contrast with the oxygen-sulfur-oxygen angle in the $S_2O_4^{=}$ ion (Dunitz, 1956) of 108.2° and in the $[HO \cdot CH_2 \cdot SO_2]^-$ ion of 108.5° (Truter, 1955). The range in the carbon-sulfur-carbon angle, from 98 to 115° , conflicts with the prediction made by Lüttringhaus and Buchholz (1939) on the basis of ring-closure experiments, that the limits for this angle were 75° and 90° .

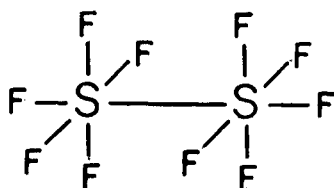
The sulfone and sulfoxide groups are indeed sufficiently similar (Abrahams and Silverton, 1956) for diphenyl sulfoxide to dissolve in proportions up to 90 percent in diphenyl sulfone to form a continuous series of solid solutions, which retain the diphenyl sulfone crystal structure. At this concentration the bonds to nine in every ten pairs of sulfone oxygen atoms are replaced by one sulfur-oxygen bond and a lone pair of electrons, which latter hence appears to have very nearly the same orientation as the sulfur-oxygen bond. Koch and Moffitt (1951) have suggested that the most likely structure for diphenyl sulfone has the normals to the aromatic rings lying in the C-S-C plane (cf. the structure of diphenyl sulfoxide, Section 3.7).

The dipole moment of the interesting molecule $(C_6H_5)_2 \cdot SI_2$ has been measured by Jensen (1943) as 4.4D. The analogous molecules $(p-CH_3 \cdot C_6H_4)_2 SeX_2$, where X is Br and Cl, have been shown by McCullough (Section 4.6) to possess an unusual bond distribution, and it would be valuable to know if a similar bond distribution can also be exhibited by the central sulfur atom.

3.9 6-Bonded sulfur

There have been very few compounds examined containing 6-valent sulfur and their molecular shape subsequently determined. In the case of SF_6 , a very stable molecule, the shape is reported to be that of a regular octahedron, with $\text{S-F} = 1.58 \pm 0.03 \text{ \AA}$ (Brockway, 1936), based on electron diffraction experiments. Senent (1951) has suggested that the sulfur atom has the arrangement $3s3p^34s3d$ leading to a tetragonal bipyramidal, almost regular octahedral bond structure. Duffey (1950) points out that there are no unshared electrons in the sulfur 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. Duncan (1952) has computed the lowest energy or ionization potential in SF_6 to be about 20.1 ev based on a LCAO molecular orbital treatment. In this, he assumed a sp^3d^2 configuration for the sulfur atom.

Another example of 6-valent sulfur is disulfur decafluoride, and Harvey and Bauer (1953) have determined this structure to be



in which all bond angles except those formed by the linear F-S-S-F axis are right angles, and $\text{S-F} = 1.56 \pm 0.02 \text{ \AA}$. The remaining example is disulfur decafluorodioxide (Harvey and Bauer, 1954). Here again all bond angles are right angles except S-O-O , which is 105° (cf. Table 1), with $\text{S-F} = 1.56 \pm 0.02 \text{ \AA}$.

3.10 The sulfur-oxygen bond

The nature of the sulfur-oxygen bond in various molecules has been the subject of much discussion, largely centering around the question of whether

the bond is a covalent double bond, or a co-ordinate link, or whether both types contribute. A review of much of the work in this field up to 1945 is given by Phillips, Hunter and Sutton (1945). On the basis of the relatively small dipole moments of a number of sulfoxides and sulfones, the relative constancy of the sulfur-oxygen bond length at about 1.45A, and a consideration of the thermal data, these authors regard the sulfur-oxygen bond as primarily double in nature. Wells (1949) has shown that these dipole moment data may be interpreted in terms of a small charge separation equally well as in terms of a short bond length. He also points out that the departures from additivity in covalent radii are large enough to throw doubt on this concept, especially as applied to this bond, and concludes that at the time of writing, there was no satisfactory explanation for this short bond.

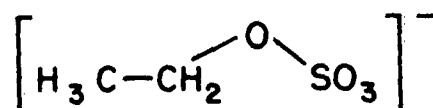
Moffitt (1950) has used a molecular orbital method to analyze the electronic structure of this bond. He finds, in agreement with Phillips, Hunter and Sutton, that the oxygen-sulfur bond is largely double in character, and that the 3d orbitals of the sulfur atom are important in the formation of this bond. Moffitt's self-consistent LCAO treatment, in addition, can satisfactorily explain the variation in the physical properties of these bonds. Table 11 gives the bond orders derived by Moffitt for several sulfur-oxygen bonds, and these may be used in conjunction with the observed sulfur-oxygen bond lengths in Tables 9, 10 and 12 to provide a bond-order vs. bond-length relationship in the region close to a double bond (corresponding to an order of 1.0). Jeffrey and Stadler (1951) have tabulated the values of reliable S-O distances in oxides, oxy-acids and acid salts of sulfur, and show that this bond length appears to be very constant at about 1.43A, which could be taken as the standard double-bond distance.

A sulfur-oxygen bond that may be regarded as close to a single bond has

Table 11. Some LCAO-derived sulfur-oxygen bond orders.

Molecule	Bond order	Molecule	Bond order
Dialkyl sulfoxides	0.82	$\text{SO}(^3\Sigma_g^-)$	0.98
Cl_2SO	ca. 0.9	Cl_2SO_2	ca. 1.0
Dialkyl sulfones	0.89	SO_3	1.08
SO_2	0.93	F_2SO	1.12
		F_2SO_2	1.14

been measured in potassium ethyl sulfate, the anion of which has been shown to have the structure



If this bond, of 1.60Å length, is selected as a standard single bond and the value 1.43Å as a double-bond length, the points obtained from $(\text{CH}_3)_2\text{SO}$, $(\text{CH}_3)_2\text{SO}_2$, Cl_2SO , Cl_2SO_2 , SO_2 , F_2SO , and F_2SO_2 lie, within the experimental error, on the resulting straight line, except for F_2SO_2 which deviates by 0.04Å from this line (see Fig. 9).

Vogel et al. (1952) have used bond-refraction measurements, and Price and Gillis (1953) have made independent bond refraction and infrared observations on sulfides, sulfoxides and sulfones, which are claimed to support the view that the sulfur-oxygen bonds in these compounds are not covalent double bonds. In addition, Amstutz et al. (1951) have suggested, on the basis of infrared studies, that sulfones have the canonical forms

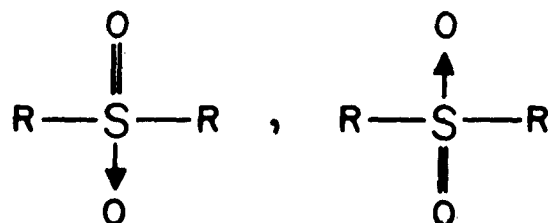


Table 12. Sulfur-oxygen bond lengths (see also Tables 9 and 10).

Compound	Bond length	Method	Reference
SO ₃ (ice form)	$\begin{cases} 1.40 \pm 0.05A \\ 1.60 \pm 0.05 \end{cases}$	$\begin{matrix} \text{x-ray} \\ \text{x-ray} \end{matrix}$	Westrik and MacGillavry (1941)
(C ₆ H ₅ SO ₂) ₂ Se	1.41 ± 0.05	x-ray	Furberg and Öyum (1954)
BaS ₄ O ₆ · 2H ₂ O	1.41 ± 0.04	x-ray	Foss et al. (1954)
SO ₃ (asbestos form)	$\begin{cases} 1.41 \pm 0.04 \\ 1.63 \pm 0.04 \end{cases}$	$\begin{matrix} \text{x-ray} \\ \text{x-ray} \end{matrix}$	Westrik and MacGillavry (1954)
(NH ₄) ₂ TeS ₄ O ₆	1.43 ± 0.04	x-ray	Foss and Larson (1954)
(CH ₃ · SO ₂ · S) ₂ Te	1.43 ± 0.06	x-ray	Foss and Vihode (1954)
BaS ₅ O ₆ · 2H ₂ O	1.43 ± 0.04	x-ray	Foss and Zachariasen (1954)
SO ₂	$\begin{cases} 1.4321 \pm 0.0005 \\ 1.432 \pm 0.005 \\ 1.43 \pm 0.015 \end{cases}$	$\begin{matrix} \text{microwave} \\ \text{microwave} \\ \text{x-ray} \end{matrix}$	$\begin{matrix} \text{Crable and Smith (1951)} \\ \text{Sirvetz (1951)} \\ \text{Post, Schwartz and Fankuchen (1952)} \end{matrix}$
CH ₃ · C ₄ H ₅ · SO ₂	1.436 ± 0.017	x-ray	Jeffrey (1951)
(NH ₄) ₂ SO ₃ · N ₂ O ₂	1.44 ± 0.01	x-ray	Jeffrey and Stadler (1951)
K ₂ SO ₃ · NH ₂	1.44 ± 0.03	x-ray	Jeffrey and Stadler (1951)
KC ₂ H ₅ · SO ₄	$\begin{cases} 1.46 \pm 0.03 \\ 1.60 \pm 0.03 \end{cases}$	$\begin{matrix} \text{x-ray} \\ \text{x-ray} \end{matrix}$	Jarvis (1953)
HSO ₃ · NH ₂	1.48 ± 0.03	x-ray	Kanda and King (1951)
(CH ₃ · SO ₂) ₂ S ₂	1.48 ± 0.05	x-ray	Sörrum (1953)
NaK ₆ Cl ₅ S ₂ O ₆	1.48 ± 0.04	x-ray	Stanley (1953)
NaK ₅ Cl ₂ (S ₂ O ₆) ₂	1.48 ± 0.05	x-ray	Stanley (1953)
Na ₂ S ₂ O ₃ · 5H ₂ O	1.48 ± 0.06	x-ray	Taylor and Beevers (1952)
NaSO ₂ · CH ₂ OH	1.50 ± 0.01	x-ray	Truter (1955)
Li ₂ SO ₄ · H ₂ O	1.50 ± 0.02	x-ray	Larson and Helmholz (1954)
Na ₂ S ₂ O ₄	1.505 ± 0.017	x-ray	Dunitz (1956)

contributing to their structure, although Varsányi and Ladik (1953) believe that in organic sulfones, sulfonic acids and sulfoxides, the sulfur atoms are not donors, in agreement with Moffitt (1950), but instead form double bonds with the oxygen atoms on the basis of the uv.-absorption spectra of diphenyl sulfone and benzene sulfonic acid and of the infrared spectra of diethyl sulfone.

A discussion of the nature of the sulfur-oxygen bond has very recently been given by Simon and Kriegsmann (1955), based on Raman spectra observations. The length of the single bond is computed to be 1.69Å. These authors also list the vibrational frequencies of this bond in a wide variety of compounds.

4.1 Divalent Selenium

The general resemblance in bond formation between 2-bonded oxygen and sulfur (3.1) is paralleled by an even greater similarity between sulfur and selenium. Both elements show marked allotropy, eight-membered rings and long chains being formed. Hexagonal selenium, however, has an important characteristic not yet found in a sulfur allotrope, being a semiconductor, whereas sulfur behaves as an insulator. An interesting variation of electrical conductivity with crystalline direction has been demonstrated by Billig (1952), who finds that the conductivity is about 10 times greater along

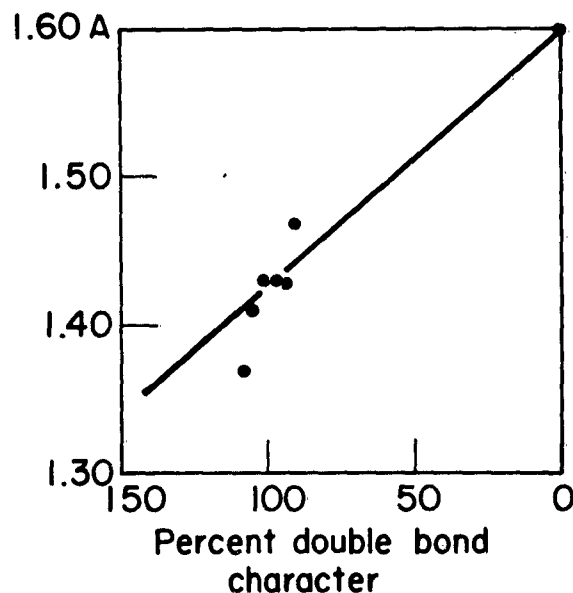


Fig. 9. Variation of the sulfur-oxygen bond length with bond character.

Table 13. Selenium valency angle.

Compound	Angle	Method	Reference
H ₂ Se	91°	spectros.	Palik (1955)
SeO ₂	$\begin{cases} 90 \pm 0.5^\circ \\ 98 \pm 2^\circ \end{cases}$	x-ray	McCullough (1937)
(CH ₃) ₂ Se	98 $\pm$ 10°	E.D.	Goldish et al. (1955)
BaSeS ₄ O ₆ · 2H ₂ O	101 $\pm$ 3°	x-ray	Foss and Tjomsland (1954)
(p-Cl · C ₆ H ₄) ₂ Se ₂	101 $\pm$ 1°	x-ray	Marsh, Kruse and McCullough (1953)
Se(SeCN) ₂	101 $\pm$ 2°	x-ray	Aksnes and Foss (1954)
Se(SCN) ₂	101 $\pm$ 3°	x-ray	Ohlberg and Vaughan (1954)
Hexagonal Se	103.6 $\pm$ 2°	x-ray	Grison (1951)
(CF ₃) ₂ Se	104.4 $\pm$ 5°	E.D.	Bowen (1954)
(C ₆ H ₄ · SO ₂) ₂ Se	105.1 $\pm$ 2°	x-ray	Furberg and Öyum (1954)
α-Se ₈	105.3 $\pm$ 2.3°	x-ray	Burbank (1951)
β-Se ₈	105.7 $\pm$ 0.8°	x-ray	Marsh, Pauling and McCullough (1953)
(p-CH ₃ · C ₆ H ₄) ₂ Se	106 $\pm$ 2°	x-ray	Blackmore and Abrahams (1955, b)
(C ₆ H ₅) ₂ Se ₂	106 $\pm$ 2°	x-ray	Marsh (1952)

the helix direction in hexagonal selenium, than across the helices.

The angle between the bonds linking a selenium atom with two other atoms varies over a rather small range. The selenium-selenium-selenium bond angle has a mean value of 103.9° (Table 13) as compared with the corresponding average sulfur angle of 106.2°. The angle in H₂Se of 91° can probably be accounted for by a mechanism similar to that applied to the 92.1° angle in H₂S, where an admixture of s and d orbitals with the sulfur p orbitals

has been proposed (Burrus and Gordy, 1953). The bond angles measured in the remaining compounds have an average value of about 104° (except for SeO_2 and $(\text{CH}_3)_2\text{Se}$, where the experimental errors are probably rather large), and in no case does this angle exceed the tetrahedral bond angle of 109.5° .

4.2 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 average selenium-selenium bond length in the elementary allotropes (Table 14) may be regarded as corresponding to a pure single bond, for there are no data which indicate the presence of double-bond character in the Se_8 ring molecule (cf. Section 3.2). The Se_2 molecule, with bond length 2.19A, can tentatively be taken as containing a standard double bond (Fig. 10). In this case, the molecules $\text{Se}(\text{SeCN})_2$ and $(\text{CF}_3)_2\text{Se}_2$ appear to contain normal single selenium-selenium bonds. In contrast, diphenyl diselenide, with bond length 2.29A, has a significant percentage (ca. 35) of double-bond character in the selenium-selenium bond, although the selenium-carbon bond in this molecule, 1.93A, is close to the value expected for a normal single bond (see Section 4.9). Another short Se-Se bond length, 2.31A, has also been reported in the related molecule p,p'-dichlorodiphenyl diselenide.

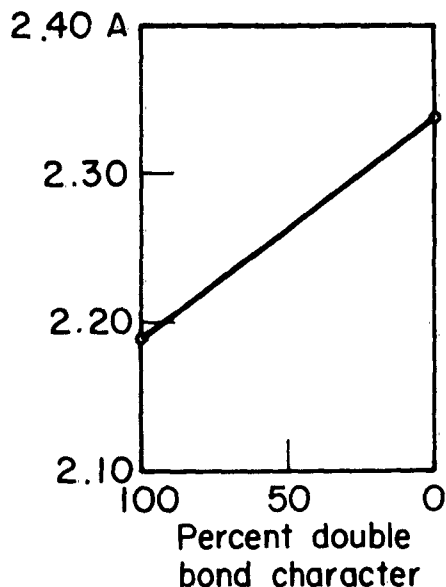


Fig. 10. Variation of the selenium-selenium bond length with bond character.

Table 14. Selenium-selenium bond length.

Molecule	Bond length	Method	Reference
Se ₂	2.19 $\pm$ 0.03A	E.D.	Maxwell and Mosley (1940)
(C ₆ H ₅) ₂ Se ₂	2.29 $\pm$ 0.01	x-ray	Marsh (1952)
(p-Cl·C ₆ H ₄) ₂ Se ₂	2.31	x-ray	Marsh, Kruse and McCullough (1953)
Se(SeCN) ₂	2.33 $\pm$ 0.03	x-ray	Aksnes and Foss (1954)
(CF ₃) ₂ Se ₂	2.335 $\pm$ 0.032	E.D.	Bowen (1954)
α -Se ₈	2.34 $\pm$ 0.02	x-ray	Burbank (1951)
β -Se ₈	2.34 $\pm$ 0.014	x-ray	Marsh, Pauling and McCullough (1953)
Hexagonal Se	2.36 $\pm$ 0.04	x-ray	Grison (1951)

4.3 Dihedral selenium 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 15 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 p π -electron repulsion, as appears to be the case for oxygen (2.3) and sulfur (3.3).

The dihedral angle for the mixed selenium-sulfur bond in BaSeS₄O₆·2H₂O (Foss and Tjomsland, 1954) has been determined as 109°, and in Se(SCN)₂ (Ohlberg and Vaughan, 1954) it is 79°.

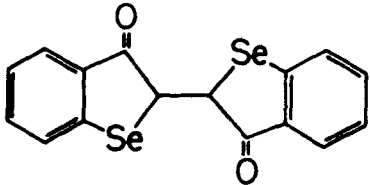
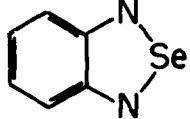
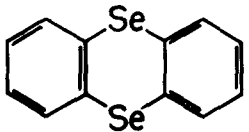
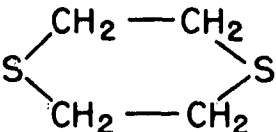
4.4 Heterocyclic selenium

A review of the organic chemistry of selenium has been given by Campbell, Walker and Coppinger (1952). Measurements of the molecular constants have been reported for very few heterocyclic selenium compounds, and these data are summarized in Table 16.

Table 15. Selenium dihedral angle.

Compound	Dihedral angle	Method	Reference
$(p\text{-Cl}\cdot\text{C}_6\text{H}_4)_2\text{Se}_2$	74°	x-ray	Marsh, Kruse and McCullough (1953)
$(\text{C}_6\text{H}_5)_2\text{Se}_2$	82°	x-ray	Marsh (1952)
$(\text{C}_2\text{H}_5)_2\text{Se}_2$	83°	elec. mom.	Rogers and Campbell (1952)
$\text{Se}(\text{SeCN})_2$	94°	x-ray	Aksnes and Foss (1954)
Hexagonal Se	101°	x-ray	Grison (1951)
$\alpha\text{-Se}_8$	102°	x-ray	Burbank (1951)
$\beta\text{-Se}_8$	102°	x-ray	Marsh, Pauling and McCullough (1953)

Table 16. Selenium valency angle and Se-C bond length in selenium heterocycles.

Molecule	Se valency angle	Se-C bond length	Method	Reference
	$80\pm 7^\circ$	$1.86\pm 0.10\text{\AA}$	x-ray	von Eller (1954)
	$95\pm 4^\circ$	1.83 ± 0.04 (Se-N length)	x-ray	Luzzati (1951)
	96°	1.96	x-ray	Wood and Williams (1942)
				
	$97.6\pm 3.5^\circ$	2.01 ± 0.03	x-ray	Marsh and McCullough (1951)

The Raman spectrum of selenophene, C_4H_4Se , has been studied by Gerding, Milazzo and Rossmark (1953). This study appears to indicate that, unlike thiophene, the selenophene molecule is not coplanar, but bent, with a single plane of symmetry present passing through the selenium atom and the single carbon-carbon bond. Similarly, selenanthrene is not coplanar, but bent about the Se-Se axis as the line of fold, through an angle of 127° (Wood and Williams). Gerding, Milazzo and Rossmark conclude that there is only a weak tendency for conjugation between the carbon π electrons, and the nonbonding electrons of the selenium atom, in contrast with sulfur in a similar atomic environment (see Section 3.4).

4.5 Three-valent selenium

In those 3-bonded selenium compounds for which molecular constants are available, the data suggest that the three selenium bonds form a pyramid, somewhat similar to the configuration of sulfur in the sulfoxides (Table 9). The possibility of a pyramidal bond arrangement of this nature had previously been discounted (Gaythwaite, Kenyon and Phillips, 1928) since, although organic sulfoxides had been optically resolved, separation into enantiomorphs had not been achieved with compounds of the form R_1R_2SeO .

A pyramidal configuration was described for solid SeO_2 (McCullough, 1937) in which the oxygen-selenium-oxygen bond angles were reported to be 90° , 98° , 98° in each group. In F_2SeO , Rolfe and Woodward (1955) 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. Section 3.7). The structure of H_2SeO_3 is reported by Wells and Bailey (1949) also to consist of pyramidal SeO_3 groups, with a mean oxygen-selenium-oxygen bond angle of $100 \pm 10^\circ$ joined together by hydrogen bonds

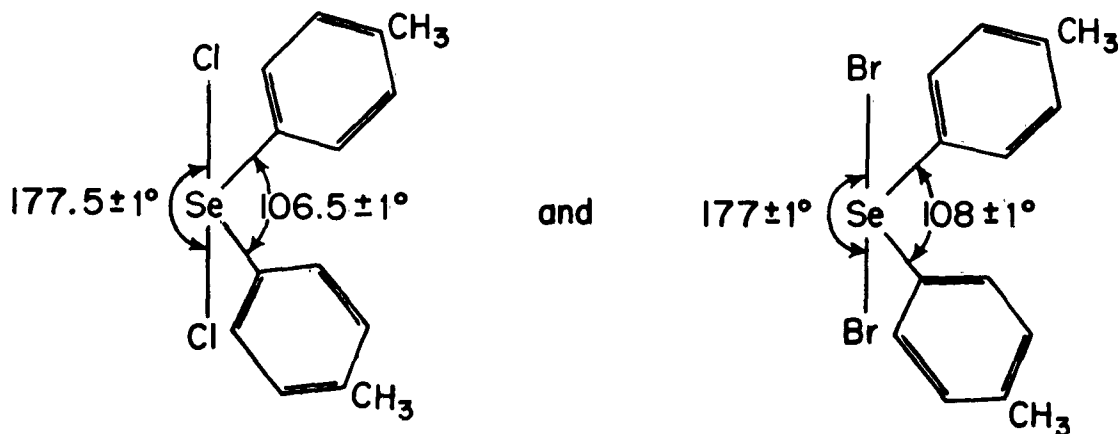
(4 such bonds per SeO_3 group).

Bryden and McCullough (1954) have recently established the crystal structure of benzene seleninic acid, and this too is found to have a pyramidal structure, with an oxygen-selenium-oxygen bond angle of $103.5 \pm 0.7^\circ$ and the carbon-selenium-oxygen bond angles equal to $98.7 \pm 0.9^\circ$.

The crystal structure of diphenyl selenoxide is isomorphous with that of diphenyl sulfoxide (Abrahams and Grenville-Wells, 1955) which is known to have pyramidal configuration (Table 9), hence it may be predicted that in this molecule, the selenium atom again has a pyramidal bond distribution.

4.6 Four-valent selenium

The distribution of the bonds from a selenium atom linked to four other atoms can be entirely different from the shape of a 4-bonded sulfur atom (Section 3.8). The best determinations of molecules of this type (McCullough and Marsh, 1950) are of di-p-tolyl selenium dichloride and dibromide, which have the molecular constants



In the dichloride, the dihedral angle between the carbon-selenium-carbon plane and the chlorine-selenium-chlorine plane is $85 \pm 2^\circ$; in the dibromide the corresponding angle is $87 \pm 2^\circ$. Along the selenium-halogen bonds, the selenium radius is 1.40A, which is close to the octahedral covalent radius assigned to

this atom (Pauling, 1940). However, the selenium-carbon bonds of 1.93 and 1.95A in the two molecules (Table 18) are close to the normal single-bond radius for selenium (1.17A). McCullough has therefore suggested that while the selenium-carbon bond is of the $4s4p^2$ type (although the C-Se-C bond angle is intermediate between 120° , as this suggestion would predict, and 90° , which is indicative of a higher p admixture or a combination of d with the s, p hybrid), that the selenium-halogen bond probably involves 5s orbitals. Pauling has further suggested that 4d and 5s orbitals may enter equally into hybridization with the 4p electrons in forming this axial bond, while Palmer (1953) has proposed the use of sp^3d^2 hybridization.

There is a striking resemblance between the structure of the two molecules just described and di-p-tolyl selenide (Blackmore and Abrahams, 1955b) if the halogen atoms are disregarded. Thus, the carbon-selenium-carbon valency angles are nearly identical (cf. Table 13), the selenium-carbon bond distances are identical at 1.93A, and the dihedral angle between the plane of the benzene rings and of the carbon-selenium-carbon plane is 35 to 40° for both structures.

There are no other unequivocal determinations of the structure of 4-bonded selenium compounds of this type. Lister and Sutton (1941) proposed that $SeCl_4$ has a tetrahedral bond distribution, but recognized that the available electron-diffraction data were not decisively in favor of this model. However, in the solid state, $SeCl_4$, $SeBr_4$ and $TeBr_4$ are isomorphous (Brink, 1954). 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 (Jensen, 1943). 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 Spectra (Gerding and

Houtgraaf, 1954a).

An electron-diffraction investigation of SeF_4 (Bowen, 1953) has indicated C_{2v} symmetry, with 4 angles of $104 \pm 5^\circ$ (Lachman, 1953) and two of $120 \pm 10^\circ$. The Raman spectra of SeF_4 (Rolfe, Woodward and Long, 1953) is also reported to agree with C_{2v} symmetry, and it is concluded that the Raman spectra is most consistent with a trigonal bipyramidal arrangement, the lone pair of electrons occupying an equatorial position. An x-ray study of the crystal structure of TeBr_4 (Brink, Lavine and Abrahams, 1956) is under way, but the molecular constants have not yet been reported.

In the case of selenic acid, H_2SeO_4 , Bailey and Wells (1951) report the structure to consist of tetrahedral SeO_4 groups (mean oxygen-selenium-oxygen bond angle is $110 \pm 5^\circ$) linked together by a system of O-H-O bonds, with four such bonds per SeO_4 unit. In this structure, the $\text{SeO}_4^{=}$ ion appears to have an identical bond distribution with the $\text{SO}_4^{=}$ ion (3.8).

4.7 Six-valent selenium

The only 6-bonded selenium molecule for which the molecular parameters have been determined is SeF_6 (Maxwell, 1940), which like SF_6 has an octahedral bond configuration. Palmer (1953) has suggested that sp^3d^2 orbitals are used in hybridization in this molecule, as in SF_6 .

4.8 The selenium-oxygen bond

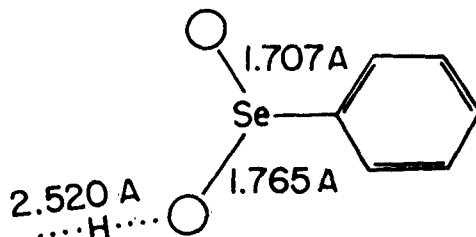
There are, at present, insufficient data for a bond-length vs. bond-order relation to be constructed. Table 17 summarizes the available measurements on this bond.

The difference in the two observed Se-O bond lengths in benzene seleninic acid is significant (4 times the standard deviation in these bonds) and is

Table 17. Selenium-oxygen bond lengths.

Compound	Bond length	Method	Reference
H_2SeO_4	$1.61 \pm 0.05 \text{ \AA}$	x-ray	Bailey and Wells (1951)
$\text{C}_6\text{H}_5\text{SeO}_2\text{H}$	$\begin{cases} 1.707 \pm 0.015 \\ 1.765 \pm 0.015 \end{cases}$	x-ray	Bryden and McCullough (1954)
H_2SeO_3	1.74 ± 0.02	x-ray	Wells and Bailey (1949)
SeO_2	$\begin{cases} 1.76 \pm 0.08 \\ 1.61 \pm 0.03 \end{cases}$	$\begin{matrix} \text{x-ray} \\ \text{E. D.} \end{matrix}$	$\begin{matrix} \text{McCullough (1937)} \\ \text{Palmer and Elliot (1938)} \end{matrix}$

caused by one of the oxygen atoms being bonded to the hydrogen atom:



It is thus obvious that the selenium-oxygen bond can possess some double-bond character, but no reliable assignment has yet been made.

4.9 The selenium-carbon bond

A considerable variation in the length of the selenium-oxygen bond has been reported (Table 18). As in the case of the selenium-oxygen bond, it appears clear 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 vs. bond-length curve to be proposed, although the value 1.96 Å for a single bond and 1.71 Å for the double bond allows a reasonable interpretation for the data in Table 18.

Table 18. Selenium-carbon bond lengths (see also Table 16).

Molecule	Bond length	Method	Reference
OCS _e	1.7090 $\pm$ 0.0001A	microwave	Strandberg et al. (1949, a)
Se(SeCN) ₂	1.83 $\pm$ 0.10	x-ray	Aksnes and Foss (1954)
(p-Cl·C ₆ H ₄) ₂ Se ₂	1.86 $\pm$ 0.04	x-ray	Marsh, Kruse and McCullough (1953)
C ₆ H ₅ ·SeO ₂ H	1.903 $\pm$ 0.021	x-ray	Bryden and McCullough (1954)
(p-CH ₃ ·C ₆ H ₄) ₂ Se	1.93 $\pm$ 0.03	x-ray	Blackmore and Abrahams (1955, b)
(C ₆ H ₅) ₂ Se ₂	1.93 $\pm$ 0.05	x-ray	Marsh (1952)
(p-CH ₃ ·C ₆ H ₄) ₂ SeCl ₂	1.93 $\pm$ 0.03	x-ray	McCullough and Marsh (1950)
(CF ₃) ₂ Se ₂	1.934 $\pm$ 0.018	E. D.	Bowen (1954)
(p-CH ₃ C ₆ H ₄) ₂ SeBr ₂	1.95 $\pm$ 0.03	x-ray	McCullough and Marsh (1950)
(CF ₃) ₂ Se	1.958 $\pm$ 0.022	E. D.	Bowen (1954)
(CH ₃) ₂ Se	1.977 $\pm$ 0.012	E. D.	Goldish et al. (1955)

5.1. Divalent tellurium

In the elementary state, tellurium does not exhibit the structural complexity observed in sulfur and 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 19.

With the exception of TeO₂^{*}, the tellurium valency angle involving two bonds is remarkably constant, with a value of about 102 $\pm$ 2°. There is little direct information regarding the electronic configuration of 2-bonded tellurium,

*

Te is not divalent here.

Table 19. Tellurium bond angle.

Compound	Bond angle	Method	Reference
TeBr_2	$98 \pm 3^\circ$	E.D.	Rogers and Spurr (1947)
$(\text{CH}_3 \cdot \text{SO}_2 \cdot \text{S})_2\text{Te}$	$100 \pm 3^\circ$	x-ray	Foss and Vihovde (1954)
$(p\text{-CH}_3 \cdot \text{C}_6\text{H}_4)_2\text{Te}$	$101 \pm 2.7^\circ$	x-ray	Blackmore and Abrahams (1955, a)
$(\text{NH}_4)_2\text{TeS}_4\text{O}_6$	$103 \pm 3^\circ$	x-ray	Foss and Larssen (1954)
Hexagonal Te	$103.7 \pm 2^\circ$	x-ray	Grison (1951)
TeO_2	$132 \pm 5^\circ$	x-ray	Stehlík and Balak (1949)

but the overall resemblance to the angular value of 2-bonded selenium suggests a very similar hybridization (Section 4.1). This close similarity is further instanced by the formation of continuous series of solid solutions of selenium in tellurium (Grison, 1951).

5.2 The tellurium-tellurium bond

The scanty data concerning the length of this bond hardly warrant any conclusions being drawn. These data are contained in Table 20.

Tunell and Pauling (1952) in a study of three different gold-silver ditellurides, report a large variety of tellurium-tellurium bond distances, involving the well-defined Te_2 groups of sylvanite (AuAgTe_4) (Table 20), endless chains with a 3.19Å Te-Te separation in calaverite, and other arrangements. They use a single-bond radius for tellurium of 1.348Å to calculate the bond orders of the various tellurium-tellurium, tellurium-gold and tellurium-silver contacts, with the equation $D(n) = D(1) - 0.600 \log n$, where $D(n)$ is the interatomic distance, $D(1)$ is the sum of the single-bond radii for the two bonded atoms, and n is the bond number.

Table 20. Tellurium-tellurium bond length.

Compound	Bond length	Method	Reference
FeTe ₂	2.90 $\pm$ 0.03A	x-ray	Grønvold, Haraldsen and Vihovde (1954)
AuAgTe ₄ *	2.87 $\pm$ 0.10	x-ray	Tunell and Pauling (1952)
Hexagonal Te	2.82 $\pm$ 0.02	x-ray	Grisson (1951)
Te ₂	2.59 $\pm$ 0.02	E.D.	Maxwell and Mosley (1940)
* Sylvanite.			

5.3 Dihedral tellurium angle

A summary of the values of those dihedral angles involving tellurium which have been measured is given in Table 21. This angle, like the corresponding angles for oxygen, sulfur and selenium, is close to 90°, and in the present case the variation from 90° is $\pm 10^\circ$.

5.4 Higher valencies of tellurium

The stereochemistry of three-bonded tellurium does not yet appear to have been investigated. Jensen (1943) has measured the dipole moment of di-p-tolyl telluroxide as 3.93D and suggests this indicates a semipolar Te-O bond.

An electron-diffraction study on TeCl₄ by Stevenson and Schomaker (1940) was reported to be compatible with a distorted trigonal bipyramid, with the chlorine-tellurium-chlorine angle equal to $93 \pm 3^\circ$. Lachman (1954) has pointed out that if five of the six angles in this molecule are $93 \pm 3^\circ$, then the sixth angle will be $171 \pm 9^\circ$, suggesting that the participating electrons in the σ bonds here are d^3p , dp^3 , d^4 or d^2sp . A similar suggestion for the

Table 21. Dihedral tellurium angle.

Compound	Atoms defining angle	Value	Reference
$(C_6H_5 \cdot SO_2 \cdot S)_2Te$	SSTe, STeS	79°	Öyum and Foss (1955)
$(CH_3 \cdot SO_2 \cdot S)_2Te$	SSTe, STeS	81°	Foss and Vihovde (1954)
$(CH_3 \cdot C_6H_4 \cdot SO_2 \cdot S)_2Te$	SSTe, STeS	86°	Foss and Öyum (1955)
$(NH_4)_2TeS_4O_6$	SSTe, STeS	$86, 95^\circ$	Foss and Larssen (1954)
Hexagonal Te	TeTeTe, TeTeTe	101°	Grison (1951)

electron configuration in $TeCl_4$ had previously been made by Dyatkina (1945).

A Raman spectra study of solid $TeCl_4$ by Gerding and Houtgraaf (1954, a) is reported to suggest strongly the presence of $[TeCl_3]^+$ ions (cf. $SeCl_4$, Section 4.6), as does also a corresponding study on $TeCl_4 \cdot AlCl_3$ (Gerding and Houtgraaf, 1954, b).

The crystal structure of α -dimethyltellurium dichloride has very recently been reported by McCullough (1955) to have a structure similar to that of the diarylselenium dihalides (Section 4.6). In this molecule the chlorine-tellurium-chlorine bond angle is close to 180° , the carbon-tellurium-carbon bond angle is near 110° and the C-Te-C plane is normal to the Cl-Te-Cl axis. The crystal structure of diphenyltellurium dibromide (Christofferson and McCullough, 1955) and of tellurium tetrabromide (Brink, Lavine and Abrahams, 1956) are known to be in the process of final refinement, but molecular constants have not yet been reported.

McCullough (1953) has suggested that in compounds of the type $R_2(S, Se, Te)X_2$, the structure should be 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. The X-M-X bond angle should be

nearly linear and the M-X distance longer than the sum of the normal single covalent bond radii (M is S, Se or Te).

Tellurium hexafluoride, like the sulfur and selenium analogues, has an octahedral bond distribution. Brockway (1936) reports the Te-F bond distance to be $1.82 \pm 0.03\text{\AA}$. Kimball (1940) and also Eastman and Wagner (1949) point out that although SF_6 and SeF_6 are very inert, and stable to hydrolysis, TeF_6 is easily hydrolysed. It is suggested that this is due to the possibility of the tellurium atom accepting a pair of oxygen electrons in a vacant 4f orbital. An octahedral bond distribution has also been reported for tellurium in the anion of Cs_2TeBr_6 (Bagnall, D'Eye and Freeman, 1955, b).

5.5 The tellurium-carbon bond

The tellurium-carbon bond length appears to have been reported only in the two following cases. In $(p\text{-CH}_3 \cdot \text{C}_6\text{H}_4)_2\text{Te}$ the length is $2.05 \pm 0.05\text{\AA}$ (Blackmore and Abrahams, 1955, a) and in TeCS the length is measured as $1.904 \pm 0.010\text{\AA}$ (Hardy and Silvey, 1954) in a microwave determination. These two bond lengths probably correspond fairly closely to single and double bonds, respectively.

6.1 Polonium

Polonium is a soft, low-melting, grey metal, like lead, and exhibits no covalent bonding in the elementary state. Beamer and Maxwell (1949) 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 also is indicated by its other physical properties, such as hardness, density, electrical resistance, etc. The transformation of the cubic α - to the rhombohedral β -form occurs at 36°C (Goode, 1955, a).

The crystal structures of several polonium compounds have now been determined. Martin (1954) has demonstrated the formation of the oxide PoO_2 , and Bagnall and D'Eye (1954) have confirmed this formula, and also measured the Po-O distance as 2.44A, corresponding to an ionic contact between Po^{4+} and O^{2-} . Zinc polonide, ZnPo , has a face-centered cubic structure of the zinc-blende type (Fauble, 1955) and lead polonide, PbPo , belongs to the NaCl structure type (Brocklehurst and Vassamillet, 1955). Platinum polonide, PtPo_2 , has been shown to crystallize in the hexagonal system, with the $\text{Cd}(\text{OH})_2$ structure type (Goode and Timma, 1955), and NiPo also is hexagonal (Goode, 1955b).

Some polonium halides have been investigated, such as PoCl_2 and PoCl_4 (Joy, 1954a and Bagnall, D'Eye and Freeman, 1955a) and PoBr_2 and PoBr_4 (Joy, 1954b, and Bagnall, D'Eye and Freeman, 1955b). The only polonium halide for which the crystal structure is known is the tetrabromide. Bagnall, D'Eye and Freeman (1955b) have shown that in this crystal, the polonium is in octahedral co-ordination with bromine, the Po-Br distance being about 2.8A.

The stereochemistry of polonium in some complex ions has also been reported. Thus, the crystal structure of ammonium hexachloropolonite (Bagnall, D'Eye and Freeman, 1955a) is isomorphous with $(\text{NH}_4)_2\text{PtCl}_6$, with a Po-Cl distance of 2.38A, indicating this bond to be largely covalent, for the radius of the Po^{4+} ion is 1.04A (Bagnall and D'Eye, 1954) and of Cl^- is 1.81A (Pauling, 1940). Similarly, ammonium hexabromopolonite is isostructural with the chloro complex (Bagnall, D'Eye and Freeman, 1955b), with a Po-Br separation of 2.60A, again corresponding primarily to a covalent bond. Cesium hexabromopolonite, Cs_2PoBr_6 , has been found isostructural with Cs_2TeBr_6 (Bagnall, D'Eye and Freeman, 1955b) and the Po-Br and Te-Br distances are, respectively, 2.64 and 2.61A.

In general, the stereochemical behavior of polonium is primarily that of a typical metal, covalent bond formation being negligible. However, in complex ions such as $(\text{PoHal}_6)^{2-}$, an octahedral bond distribution is observed, with a corresponding bond radius of about 1.45A.

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