

**1077. The Rôle of 3d-Orbitals in  $\pi$ -Bonds between (a) Silicon, Phosphorus, Sulphur, or Chlorine and (b) Oxygen or Nitrogen.**

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In the  $\text{XO}_4^{n-}$  tetrahedral ions ( $\text{X} = \text{Si}, \text{P}, \text{S}, \text{or Cl}$ ) two strong  $\pi$ -bonding molecular orbitals are formed with the  $3d_{x^2-y^2}$  and  $3d_{z^2}$  orbitals of  $\text{X}$  and the appropriate  $2p\pi$  and  $2p\pi'$ -orbitals of oxygen. This explains the contraction of the S-O bond, say, from the presumed 1.69 Å for a single bond to 1.49 Å in  $\text{SO}_4^{2-}$ . In ethyl sulphate the ester-oxygen still has a share in one  $\pi$ -orbital, which explains its intermediate S-O value of 1.60 Å. The ability of doubly linked oxygen and triply linked nitrogen to share in the  $\pi$ -bond systems generated by tetrahedrally co-ordinated  $\text{X}$  is widespread. An interpretation is given of the structures of  $[\text{S}_2\text{O}_7]^{2-}$ ,  $[\text{NH}(\text{SO}_3)_2]^{2-}$ ,  $[\text{CH}(\text{SO}_3)_2]^{2-}$ ,  $\text{SO}_3\text{NH}_3$ ,  $[\text{SO}_3\text{NH}_2]^-$ ,  $\text{SO}_2(\text{NH}_2)_2$ , and  $(\text{SO}_3)_\infty$  in terms of the  $\pi$ -bond systems. Structures with tetrahedral phosphorus and silicon are similarly discussed, with special attention to those with XOX angles of 140–180°. In ions containing hydroxyl groups, the bonds are intermediate in length between those for the ion without the proton and for the ion with R in place of H, apparently owing to hydrogen-bond formation. The use of  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals for  $\pi$ -bonding is of potential importance whenever  $\text{X}$  is tetrahedrally co-ordinated and must be considered in, say,  $\text{RSO}_3^-$ ,  $\text{R}_2\text{SO}_2$ , and  $\text{RSO}_2^-$ . X-F bonds and the  $\pi$ -bond systems in  $[\text{PNF}_2]_4$  and  $[\text{PN}(\text{CH}_3)_2]_4$ , etc., are also discussed.

THE single system of  $\pi$ -orbitals in planar aromatic molecules is well known. This paper presents evidence for a double system of  $\pi$ -orbitals in sulphates, phosphates, silicates, etc., the orbitals extending throughout the molecules. The discussion is restricted to molecules in which silicon, phosphorus, sulphur, or chlorine atoms are tetrahedrally co-ordinated. The bonding in the  $\text{XO}_4^{n-}$  ions is considered first, and the description is extended successively to molecules in which the oxygens are linked also to other atoms or to other tetrahedra, to molecules in which nitrogen and other atoms are ligands of  $\text{X}$ , and to molecules in which lone pairs of  $\text{X}$  occupy some of the tetrahedral positions. Thus, ions such as  $[\text{C}_2\text{H}_5\cdot\text{SO}_4]^-$ ,  $\text{P}_2\text{O}_7^{6-}$ ,  $\text{SO}\cdot\text{NH}_3^+$ , and  $\text{ClO}_3^-$  are discussed, but not  $\text{SO}_3$  or  $\text{SO}_2$ . The theme of the paper is thus summarised in its title. The  $\pi$ -orbital system is a double one in the sense that two  $d$ -orbitals of  $\text{X}$ ,  $d_{x^2-y^2}$  and  $d_{z^2}$ , are used simultaneously when  $\text{X}$  is tetrahedrally co-ordinated. The experimental evidences appealed to in this paper are the observed bond lengths in a large number of molecules, many of which have been recently determined or refined in this Department by X-ray crystallographic methods. The main features of the paper were reported<sup>1</sup> briefly at the Congress of the International Union of Crystallography at Cambridge in August, 1960.

Estimated standard deviations (e.s.d.'s) for the observed bond lengths quoted in this paper are shown in the style " $\pm 0.01$  Å." Some of these e.s.d.'s are larger than those quoted by the original authors. Such increases have been made to cover more recently discovered types of systematic error, etc. The rotational-oscillation effect,<sup>2</sup> in particular, has often altered bond lengths by 0.005–0.01 Å or even 0.03 Å. In a few instances no e.s.d.'s were quoted by the original authors and estimates have been made subjectively by the present writer. Some attention should be paid to the e.s.d.'s quoted for the observed results, as the analyses range from those with e.s.d.'s of 0.004 Å in the X-O bonds to others with e.s.d.'s of 0.03 Å or so. The results for some relevant structures have had to be excluded because their precision, judged by modern standards, is too uncertain.

This investigation arose out of the results of the X-ray crystal-structure analysis of nitronium perchlorate<sup>3</sup> in which the Cl-O bond length in the discrete  $\text{ClO}_4^-$  ion was

<sup>1</sup> Cruickshank, *Acta Cryst.*, 1960, **13**, 1033.<sup>2</sup> Cruickshank, *Acta Cryst.*, 1956, **9**, 757; 1961, **14**, 896.<sup>3</sup> Truter, Cruickshank, and Jeffrey, *Acta Cryst.*, 1960, **13**, 855.

determined as  $1.46 \pm 0.01 \text{ \AA}$ .<sup>\*</sup> This bond length is appreciably shorter than the  $1.685 \text{ \AA}$  expected<sup>7</sup> for a single bond or the  $1.70 \pm 0.02 \text{ \AA}$  found<sup>8</sup> in  $\text{Cl}_2\text{O}$ . The double-bond character of the bonds in the isoelectronic  $\text{SiO}_4^{4-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ , and  $\text{ClO}_4^-$  tetrahedral ions has been often stressed previously, but we shall consider it again here in more detail. In Table 1 we compare the observed bond lengths, whose e.s.d.'s are about  $0.01 \text{ \AA}$ , with the expected single-bond distances and we see that the shortenings increase from perhaps  $0.13 \text{ \AA}$  in  $\text{SiO}_4^{4-}$  to  $0.22_5 \text{ \AA}$  in  $\text{ClO}_4^-$ . The symmetrical stretching force constants<sup>9</sup> are also greater than for typical single bonds, though the sequence of values P-O 9.05, S-O 9.07, and Cl-O 8.24 mdyne/ $\text{\AA}$  does not indicate the Cl-O bond as the stiffest.

TABLE 1.  
Bond lengths in  $\text{XO}_4^{n-}$  ions  $\text{\AA}$ .

	Si-O	P-O	S-O	Cl-O
Single-bond value * .....	1.76	1.71	1.69	1.68 <sub>5</sub>
Observed .....	1.63 †	1.54 ‡	1.49 §	1.46
Contraction .....	0.13	0.17	0.20	0.22 <sub>5</sub>

\* Calculated by the Schomaker-Stevenson equation.<sup>7</sup> † Average derived from analyses of spurrite  $\text{Ca}_5(\text{SiO}_4)_2\text{CO}_3$  (Smith, Karle, Hauptman, and Karle, *Acta Cryst.*, 1960, **13**, 454), grossularite  $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$  (Abrahams and Geller, *ibid.*, 1958, **11**, 437), and  $\beta\text{-Ca}_2\text{SiO}_4$  (Midgeley, *ibid.*, 1952, **5**, 307; Cruickshank, unpublished work). ‡ Average from hydroxyapatite  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  (Posner, Perloff, and Diorio, *Acta Cryst.*, 1958, **11**, 308), and  $\text{LiMnPO}_4$  (Geller and Durand, *Acta Cryst.*, 1960, **13**, 325) with approximate rotational corrections considered. § From gypsum  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (Atoji and Rundle, *J. Chem. Phys.*, 1958, **29**, 1306).

*Nature of the  $\pi$ -Bonding in the  $\text{XO}_4^{n-}$  Ions.*—In the  $\text{XO}_4^{n-}$  ions, after electrons have been allotted to the inner shells, to four tetrahedral  $sp^3$   $\sigma$ -bonds, and to four  $\sigma$ -lone pairs at the back of each oxygen atom, there remain 16 electrons needing eight molecular orbitals. These orbitals may be built from the available atomic orbitals, which are the  $2p\pi$  and  $2p\pi'$  on each oxygen (so that the oxygens alone could provide the eight orbitals) and the five  $3d$ -orbitals of the central X atom. The combinations of the  $3d$ - and oxygen  $2p$ -orbitals are settled by group theory applied to the point group  $T_d$  (see Eyring *et al.*<sup>10</sup> for notation and methods; note, however, that their character table for  $T_d$  erroneously interchanges the characters for  $T_1$  and  $T_2$  representations). There prove to be two strongly  $\pi$ -bonding molecular orbitals in the representation  $E$ , three weakly  $\pi$ -bonding molecular orbitals in  $T_2$ , which are effectively lone-pair combinations, and three non-bonding combinations of oxygen orbitals in  $T_1$ , thus giving the eight desired orbitals.

One of the two strong  $\pi$ -bonding molecular orbitals uses the  $d_{x^2-y^2}$  orbital. The excellent overlap of this with the oxygen combination  $\frac{1}{2}(p_1 + p_2 + p_3 + p_4)$  is shown in Plate 1a. The other uses  $d_{z^2}$  with  $\frac{1}{2}(p_1' + p_2' + p_3' + p_4')$  and is shown in Plate 1b. Here  $p_1, p_2, p_3, p_4$  are the  $2p\pi$ -orbitals perpendicular to the  $z$ -axis of the tetrahedron and  $p_1', p_2', p_3', p_4'$  are the corresponding  $2p\pi'$ -orbitals on the four oxygen atoms. The models illustrated in the Plates are only schematic. For each atom the black and the white lobes represent regions in which the atomic wave functions are positive and negative. The  $d$ -orbitals should be thought of as much larger than the  $p$ -orbitals, since they actually diffuse well into the region of the latter. Further, in the  $d_{z^2}$  orbit the amplitude of the

\* This value is slightly larger than those reported in some other recent analyses, but in one of them, the room-temperature form<sup>4</sup> of  $\text{H}_3\text{O}^+\text{ClO}_4^-$  which M. R. Truter<sup>5</sup> has refined, a substantial rotational-oscillation correction<sup>2</sup> of  $0.027 \text{ \AA}$  satisfactorily increases the Cl-O length to  $1.452 \pm 0.005 \text{ \AA}$ . A good analysis<sup>6</sup> of the ordered low-temperature form of  $\text{H}_3\text{O}^+\text{ClO}_4^-$  gives a mean Cl-O length of  $1.462 \pm 0.004 \text{ \AA}$ .

<sup>4</sup> Lee and Carpenter, *J. Phys. Chem.*, 1959, **63**, 279.

<sup>5</sup> Truter, *Acta Cryst.*, 1961, **14**, 318.

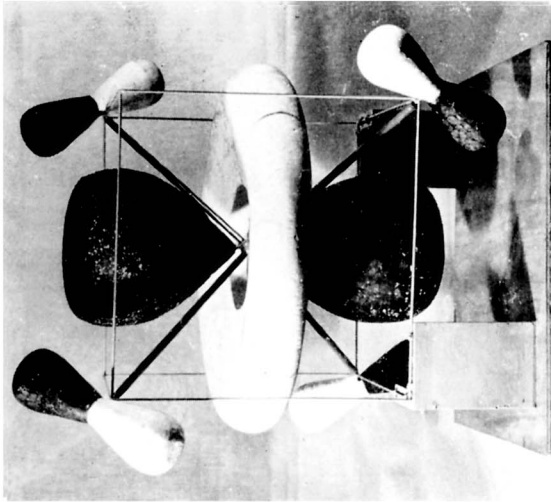
<sup>6</sup> Nordman, *Acta Cryst.*, 1960, **13**, 1030; private communication.

<sup>7</sup> Schomaker and Stevenson, *J. Amer. Chem. Soc.*, 1941, **63**, 37.

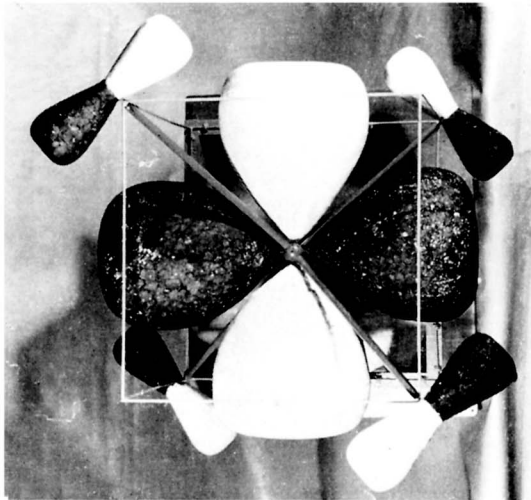
<sup>8</sup> Dunitz and Hedberg, *J. Amer. Chem. Soc.*, 1950, **72**, 3108.

<sup>9</sup> Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, Van Nostrand Co., Princeton, 1945.

<sup>10</sup> Eyring, Walter, and Kimball, "Quantum Chemistry," John Wiley, New York, 1944.



(b) Overlap of  $X(d_{z^2})$  with oxygen  $2p_z$ .



(a) Overlap of  $X(d_{x^2-y^2})$  with oxygen  $2p_x$  in  $XO_4^{2-}$

wave function along the  $\pm z$  axes is twice the amplitude at the equator for the same radius (which is why the conventional polar diagram shows only a small equatorial band). Since the maximum amplitude of  $\psi$  occurs at the same radius for both the equatorial band and the axial lobes, the model had been made with band and lobes of similar maximum radius in order to bring out the geometrical suitability of the  $d_{z^2}$ -orbital for  $\pi$ -bonding.

As shown in the Plates, the nodes of each  $3d$ -orbital pass through the oxygen positions, so that the positive and negative lobes of the  $p$ -orbitals lie nicely in the corresponding regions of the  $d$ -orbitals. The group overlap integrals for these two  $\pi$ -bonding molecular orbitals are identical and are  $(8/3)^{\frac{1}{2}} = 1.63$  times the maximum possible overlap of an X  $3d$ -orbital with one  $2p$ -orbital at the same internuclear distance. The absolute values of the overlap integrals are not easy to estimate. The arguments of Appendix I, based on self-consistent-field calculations for the first long row, suggest a value of 0.6 in the perchlorate ion. This Cl ( $3d$ ) : O(combination) group overlap is about twice that of adjacent  $p\pi$ -orbitals in benzene, so that it is not surprising that the Cl-O distance in the perchlorate ion is 0.22<sub>5</sub> Å shorter than a single bond.

The three orbitals in  $T_2$  are

$$(1/2)^{\frac{1}{2}} (d_{xz} - d_{yz}) \text{ with } (3/8)^{\frac{1}{2}}(p_1 - p_2) + (1/8)^{\frac{1}{2}}(p_3' - p_4')$$

$$(1/2)^{\frac{1}{2}} (d_{xz} + d_{yz}) \text{ with } (3/8)^{\frac{1}{2}}(p_3 - p_4) + (1/8)^{\frac{1}{2}}(p_1' - p_2')$$

$$d_{xy} \text{ with } (1/2)(-p_1' - p_2' + p_3' + p_4')$$

The overlaps of the X and oxygen combination orbitals of  $T_2$  symmetry are not as good as those of  $E$  symmetry; for example, with  $d_{xy}$ , while one lobe of each oxygen  $p$ -orbital dips into a lobe of  $d_{xy}$ , the other  $p$ -orbital lobe points away into a region where  $d_{xy}$  is of low density and wrong sign. If  $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$  had the same radial size as  $d_{x^2-y^2}$ , the three orbitals of  $T_2$  would have overlap integrals  $\sqrt{3}$  times lower than the orbitals of  $E$ . In fact these three  $d$ -orbitals will be more diffuse, partly because of repulsion by the  $\sigma$ -bonds and partly because the  $T_2$  orbitals will be of higher energy than the  $E$  orbitals; consequently the overlaps will be further reduced. Also these  $T_2$  molecular orbitals are probably very heteropolar,<sup>11</sup> since they have the highest energy of any filled orbitals which could be heteropolar. We may therefore infer that the orbitals of the  $T_2$  representation play a much smaller effective part in the  $\pi$ -bonding system of the  $XO_4^{n-}$  ions and that they can be treated as three weakly  $\pi$ -bonding orbitals.

In a previous application of group theory to these tetrahedral ions Wolfsberg and Helmholtz<sup>12</sup> obtained rather more cumbersome forms of the molecular orbitals than those given above and showed that the group overlaps for the  $E$  and  $T_2$  orbitals differed by a factor of  $\sqrt{3}$ . Strictly speaking, only their numerical values showed this factor; owing to a misprint their two analytical expressions were identical. By an uncritical use of the Slater screening constants, they concluded that  $3d$ -orbitals were not important in  $ClO_4^-$  though they were in  $MnO_4^-$ .

In an important paper Jaffé,<sup>13</sup> by working from electronegativities and the consequent charge shifts in the X-O  $\sigma$ -bonds, derived a value of 0.57 for the Cl-O group overlap of  $E$  symmetry, which is practically the same as the 0.6 given above. His values for the group overlap integrals in the four ions (Cl-O 0.57, S-O 0.52, P-O 0.46, Si-O 0.33) nicely parallel the bond shortenings (0.22<sub>5</sub>, 0.20, 0.17, and 0.13 Å). However, possibly misled by Wolfsberg and Helmholtz's misprint, which he repeats, he did not stress that only two of the five  $3d$ -orbitals lead to strong  $\pi$ -bonding.

The key point of the present discussion is the assertion that in the  $ClO_4^-$ ,  $SO_4^{2-}$ ,  $PO_4^{3-}$ , and  $SiO_4^{4-}$  ions two strongly  $\pi$ -bonding molecular orbitals are formed with the  $3d_{x^2-y^2}$  and

<sup>11</sup> Moffitt, *Proc. Roy. Soc.*, 1950, *A*, **200**, 409.

<sup>12</sup> Wolfsberg and Helmholtz, *J. Chem. Phys.*, 1952, **20**, 837.

<sup>13</sup> Jaffé, *J. Phys. Chem.*, 1954, **58**, 185.

$3d_z$  orbitals of the central atom. The assertion is supported by the light it seems to throw on the sulphate, phosphate, and silicate structures discussed below. Whenever chloride, sulphur, phosphorus, or silicon is (approximately) tetrahedrally surrounded by ligands, these two  $d$ -orbitals are always of potential importance for  $\pi$ -bonding.

In the  $XO_4$  ions each of the two  $3d$ -orbitals is  $\pi$ -bonded to four oxygens, so that in valence-bond language each X-O bond has a  $\pi$ -bond order of  $\frac{1}{4} + \frac{1}{4} = \frac{1}{2}$ . In molecular-orbital language the bond order is  $(\frac{1}{2})^{\frac{1}{2}} + (\frac{1}{2})^{\frac{1}{2}} = 1$ , provided the bond is exactly homopolar. For the molecules we shall now go on to consider, we shall quote only valence-bond bond orders, partly because these can often be written down very easily and partly because there is quite a good correlation of them with molecular-orbital bond orders for aromatic molecules,<sup>14</sup> which suggests that it is unnecessary to make both sets of calculations in an introductory survey of the present kind.

*Application of the Hypothesis to a Series of Sulphates, Sulphamides, etc.*—Consider now a series of sulphur-containing molecules. The basic member of the series is the  $SO_4^{2-}$  ion, in which the S-O length of valence-bond  $\pi$ -order  $\frac{1}{2}$  is observed as  $1.49 \pm 0.01$  Å. This is 0.20 Å shorter than the presumed single-bond length of 1.69 Å.

In the ethyl sulphate ion (Fig. 1) the original  $p\pi$ -orbit of the fourth oxygen O(C) is utilised in the  $\sigma$ -bond to the ethyl group and in a lone pair in the SOC plane, but the other

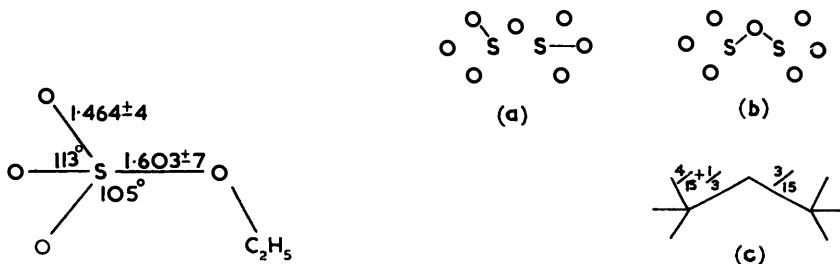


FIG. 1.  $[(C_2H_5)SO_4]^-$  in  $K(C_2H_5)SO_4$ .

FIG. 2. Valence-bond structures and bond orders for  $S_2O_7^{2-}$ . (a) One of the 15 possible structures; (b) the excluded structure; (c) bond orders.

$p\pi$ -orbit perpendicular to the SOC plane is still available for the  $\pi$ -system. If we assume that the energy of this orbit is unaltered when the ethyl group is attached, the  $\pi$ -bonding orbits may be written as

$$d \text{ with } \frac{1}{2} (p_1 + p_2 + p_3 + p_4)$$

and

$$d' \text{ with } (1/\sqrt{3}) (p_1' + p_2' + p_3')$$

The  $\pi$ -bond order of S-O(C) would then be  $\frac{1}{4}$ ; the length found by Jarvis and by Truter in potassium ethyl sulphate<sup>15</sup> is  $1.603 \pm 0.007$  Å, which is correctly intermediate between 1.49 and 1.69 Å. The other three S-O bonds should contract because the  $d'$ -orbit is shared with only three oxygens. Thus the S-O bond order is  $\frac{1}{3} + \frac{1}{4} = 0.58$  and the actual length of  $1.464 \pm 0.004$  Å is appropriately shorter than 1.49 Å. If we assume a linear bond-length-bond-order relation determined by 1.69 Å for a bond of  $\pi$ -order zero and 1.49 Å for order  $\frac{1}{2}$ , the theoretical lengths for ethyl sulphate are 1.59 and 1.46 Å.

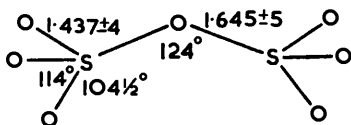
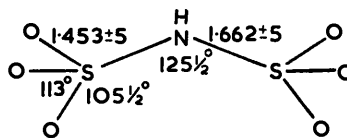
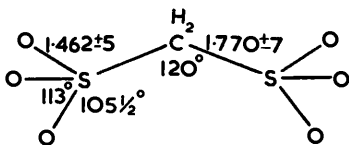
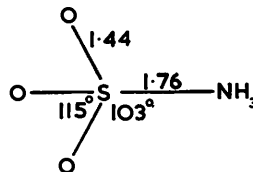
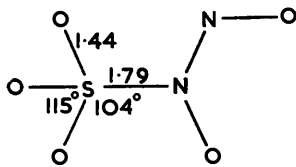
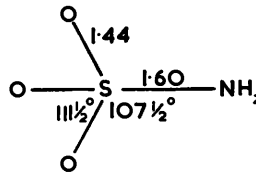
The above argument has assumed that the  $p_4$ -orbit is of the same energy in  $SO_4^{2-}$  and  $RSO_4^-$ . The formation of the  $\sigma$ -bond with R will draw electrons away from O(C), while the loss of the  $\pi$ -bond with S( $3d$ ) will increase the number of electrons on O(R). The balance of these effects cannot be estimated in a trivial approach, so it seems best to treat the actual S-O(C) bond length of 1.60 Å as evidence that the energy of  $p_4$  is not greatly

<sup>14</sup> Cruickshank and Sparks, *Proc. Roy. Soc.*, 1960, A, 258, 270.

<sup>15</sup> Jarvis, *Acta Cryst.*, 1953, 6, 327; Truter, *ibid.*, 1958, 11, 680.

altered and as an indication that this method of calculating bond orders may be reasonably applied to other sulphates.

In the  $S_2O_7^{2-}$  pyrosulphate ion the bridge oxygen has a  $p$ -orbit, perpendicular to the SOS plane, which can link with a  $d$ -orbit on each sulphur and so give a  $\pi$ -bonding system running throughout the molecule; the other  $\pi$ -system, which uses the  $d$ -orbitals, remains in two distinct halves. For the  $\pi$ -system running through the molecule  $4 \times 4 - 1 = 15$  valence-bond structures can be written if the one in which the bridge oxygen makes  $\pi$ -bonds to both sulphurs is excluded (Fig. 2). The bond orders are therefore S-O(bridge) =  $3/15 = 0.20$  and S-O =  $4/15 + 1/3 = 0.60$ , corresponding to lengths 1.61 and 1.45 Å. The observed lengths from an accurate study of  $K_2S_2O_7$  by Lynton and Truter<sup>16</sup> (Fig. 3) are  $1.645 \pm 0.005$  Å and  $1.437 \pm 0.004$  Å. These are correctly longer and shorter than the corresponding bonds in the ethyl sulphate. However, as a point

FIG. 3.  $S_2O_7^{2-}$  in  $K_2S_2O_7$ .FIG. 4.  $[NH(SO_3)_2]^{2-}$  in  $K_2[(SO_3)_2NH]$ .FIG. 5.  $[CH_2(SO_3)_2]^{2-}$  in  $K_2[(SO_3)_2CH_2]$ .FIG. 6.  $SO_3(NH_3)$  ( $\pm 0.02$  Å).FIG. 7.  $[SO_3N_2O_2]^{2-}$  in  $(NH_4)_2SO_3N_2O_2$   
( $\pm 0.02$  Å).FIG. 8.  $[SO_3 \cdot NH_2]^{-}$  in  $K[SO_3 \cdot NH_2]$   
( $\pm 0.03$  Å).

of detail, the S-O(bridge) bond of 1.645 Å is slightly longer than the 1.61 Å expected for a bond of  $\pi$ -order 0.20.

If the bridge oxygen is replaced by NH, similar  $\pi$ -bonding might be expected since the  $p$ -orbit of nitrogen perpendicular to the S·NH·S plane will be available for  $\pi$ -bonding. The dimensions found<sup>17</sup> (Fig. 4) for the iminodisulphonate ion, in  $K_2[(SO_3)_2NH]$ , are very similar to those in the pyrosulphate. Indeed since the S-N bond of  $1.662 \pm 0.005$  Å is only  $0.017 \pm 0.007$  Å longer than the S-O(bridge) bond, whereas it might have been expected to be at least 0.05 Å longer on account of the different covalent radii of oxygen and nitrogen, there is a sense in which the S-N bond can be regarded as a relatively stronger  $\pi$ -bond than the S-O(bridge) bond.

A study of the isomorphous  $K_2[(SO_3)_2CH_2]$  has just been completed by Dr. Mary R. Truter. On the present approach the carbon atom should have no  $p$ -orbit available for  $\pi$ -bonding and so the S-C bonds were expected to be pure single bonds of length at least

<sup>16</sup> Lynton and Truter, *J.*, 1960, 5112.

<sup>17</sup> Jeffrey and Jones, *Acta Cryst.*, 1956, 9, 283; Cruickshank and Jones, unpublished work.

1.77 Å. [1.77 Å is the value found for S-C(H<sub>3</sub>) by Wheatley and his collaborators<sup>18</sup> in a series of dimethyl sulphones; 1.81 Å is the Schomaker-Stevenson value<sup>7</sup> for the S-C single bond.] The dimensions found (Fig. 5) are S-C = 1.770 ± 0.007 Å, S-O = 1.462 ± 0.005 Å, and ∠S-C-S = 120°. The S-C bond is thus similar to that in the dimethyl sulphones. In conformity with subsequent discussions of phosphate and silicate structures, the opening out of the S-C-S angle beyond 109½° (or the 112° or so found for C-C-C angles in paraffin chains) may be interpreted as due to the electrostatic repulsions of the two SO<sub>3</sub><sup>-</sup> groups. Discussion of the S-O length of 1.462 Å will be deferred to a later section on structures in which X is not surrounded by four π-bonding ligands.

The view that the S-N bond of 1.662 Å in the iminodisulphonate is a partial double bond can be proved, not merely by comparison with the pyrosulphate and the methylenedisulphonate, but also from the observation<sup>19</sup> that S-N bond length is 1.76 ± 0.02 Å in sulphamic acid SO<sub>3</sub>(NH<sub>3</sub>), where the nitrogen has no orbitals available for π-bonding (Fig. 6). This value is close to the 1.74 Å for an S-N single bond given by the Schomaker-Stevenson rules.<sup>7</sup> A comparable S-N bond of 1.79 ± 0.02 Å is also found in the dinitrosulphite ion<sup>20</sup> [in (NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub>N<sub>2</sub>O<sub>2</sub>], where the *p*π-orbit of the nitrogen is needed in the π-bonding system of the N<sub>2</sub>O<sub>2</sub> group (Fig. 7). On the other hand, the results<sup>20</sup> for

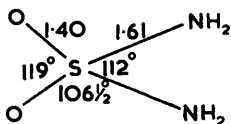


FIG. 9. SO<sub>2</sub>(NH<sub>2</sub>)<sub>2</sub> (±0.01 Å).

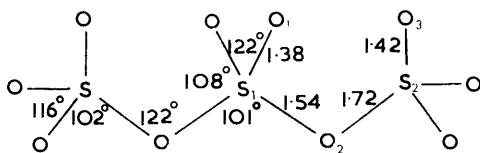


FIG. 11. S<sub>3</sub>O<sub>10</sub><sup>2-</sup> in (NO<sub>2</sub>)<sub>2</sub>S<sub>3</sub>O<sub>10</sub> (±0.05 Å).

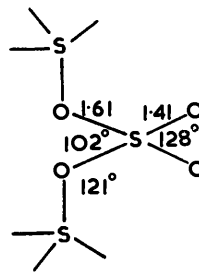


FIG. 10. (SO<sub>3</sub>)<sub>∞</sub> (±0.03 Å).

K[SO<sub>3</sub>·NH<sub>2</sub>], though not of great accuracy, show (Fig. 8) that the bonding in the sulphamate ion is analogous to that in the ethyl sulphate discussed above. (Jeffrey and Stadler, in their paper<sup>20</sup> on these last two structures, stressed that the large difference in S-N lengths showed that the bond in the sulphamate ion must have considerable double-bond character.)

In sulphonyl diamide, SO<sub>2</sub>(NH<sub>2</sub>)<sub>2</sub>, whose structure has been determined by Trueblood and Mayer,<sup>21</sup> the two nitrogen atoms each have only one *p*-orbital available for the π-systems. The problem is whether one molecular orbital embraces the two oxygens and both nitrogens and the other just the two oxygens, or whether both embrace the nitrogens separately. This depends on the relative orientations of the SNH<sub>2</sub> planes. Group theory shows that the general rule is that, if the normals to these two planes are related by a two-fold rotation about the bisector of the NSN angle, then the two *p*-orbitals on the nitrogens mate with the same *d*-orbital on the sulphur no matter what the relations of these normals to the OSO plane. To link with different *d*-orbitals one of the nitrogen *p*-orbitals must be rotated by 90° from these positions. Since in the actual crystal structure of sulphonyl diamide, the NH<sub>2</sub> groups are related by a two-fold axis through sulphur, both nitrogen *p*-orbitals mate with the same *d*-orbital. Thus the S-N bonds are of order ¼ and the S-O bonds are of order ¼ + ½ = ¾. With additions

<sup>18</sup> Wheatley, *Acta Cryst.*, 1954, **7**, 68; Wheatley and Bullough, *ibid.*, 1957, **10**, 233; Daly, *J.*, 1961, 2801.

<sup>19</sup> Sass, *Acta Cryst.*, 1960, **13**, 320.

<sup>20</sup> Jeffrey and Stadler, *J.*, 1951, 1467.

<sup>21</sup> Trueblood and Mayer, *Acta Cryst.*, 1956, **9**, 628.

of 0.01 Å as approximate rotational-oscillation corrections to the values given by Trueblood and Mayer,<sup>21</sup> the observed lengths (Fig. 9) are  $1.61 \pm 0.01$  Å for S-N, which is close to  $1.60 \pm 0.03$  Å in the sulphamate ion, and  $1.40 \pm 0.01$  Å for S-O. These S-O bonds are shorter than any others so far discussed and this is satisfactorily explained by their high bond order, which gives a theoretical length of 1.39 Å. The S-N bonds are within 0.01 Å of the S-O(C) bond of the same order in the ethyl sulphate. This very small difference parallels that discussed earlier between the S-N and S-O(bridge) bonds in  $(\text{SO}_3)_2\text{NH}$  and  $\text{S}_2\text{O}_7$ . As the  $p$ -orbit on the nitrogen will be larger than that on the oxygen, the S(3d)-N(2p) overlap will be larger than the S(3d)-O(2p) overlap and this may lead to a stronger S-N  $\pi$ -bond.

Bond lengths rather similar to those in the sulphonyl diamide are predicted and found<sup>22</sup> in  $(\text{SO}_3)_\infty$ , where each tetrahedron is linked to two others (Fig. 10). The geometry of the chain is such that the  $p$ -orbitals of the two bridging oxygens of each tetrahedron mate almost exactly (within 3°) with same  $d$ -orbital of the sulphur, so that a single  $\pi$ -system extends throughout the length of the molecule. The bond orders for the long and short

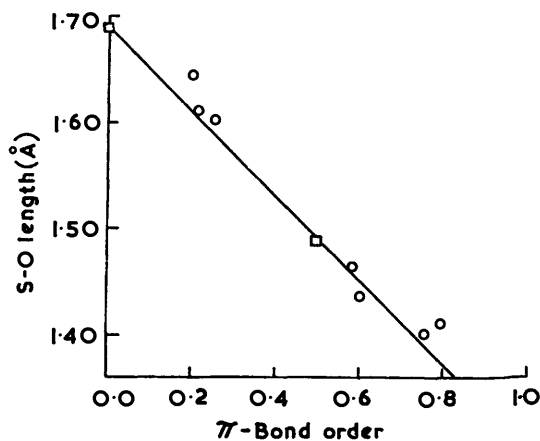


FIG. 12. S-O bond lengths and  $\pi$ -bond orders.

bonds are therefore  $3/14 = 0.21$  and  $4/14 + \frac{1}{2} = 0.79$ , which correspond to lengths of 1.61 and 1.37 Å. These are sufficiently close to the observed values of  $1.61 \pm 0.03$  and  $1.41 \pm 0.03$  Å.

A rather approximate set of dimensions, with e.s.d.'s of about 0.05 Å, is available<sup>23,24</sup> for the trisulphate ion in  $(\text{NO}_2)_2\text{S}_3\text{O}_{10}$  (Fig. 11). The  $\pi$ -bond orders are  $\text{S}_1\text{-O}_1$   $(16/56) + \frac{1}{2}$ ,  $\text{S}_1\text{-O}_2$   $12/56$ ,  $\text{S}_2\text{-O}_2$   $11/56$ ,  $\text{S}_2\text{-O}_3$   $(15/56) + 1/3$ . The predicted lengths in  $\text{S}_3\text{O}_{10}^{2-}$  are then 1.38, 1.60, 1.61, and 1.45 Å, which show some similarity with the rather rough observed values of 1.38, 1.54, 1.72, and 1.42 Å.

Fig. 12 summarises this discussion of S-O bond lengths by plotting all the observed lengths, except those for the rather inaccurate  $\text{S}_3\text{O}_{10}$ , against the  $\pi$ -bond orders. The observed values lie gratifyingly close to the straight line drawn through 1.69 Å for order zero and 1.49 Å for order  $\frac{1}{2}$ .

*Phosphates, Phosphoramides, etc.*—The hypothesis of double  $\pi$ -systems may be applied similarly to phosphates. Owing to an opening of the POP angle in some structures, the  $p$ -orbital lying in the POP plane has to be considered in addition to the perpendicular  $p$ -orbital. However, even when this is taken into account, the predictions of the hypothesis, though showing the right trends, are less satisfactory than with the sulphates. This discussion is hampered by the lack of an accurate analysis of an ion of the type  $\text{PO}_3(\text{OR})^{2-}$ ,

<sup>22</sup> Westrik and MacGillavry, *Acta Cryst.*, 1954, 7, 764.

<sup>23</sup> Eriks and MacGillavry, *Acta Cryst.*, 1954, 7, 430.

<sup>24</sup> Cruickshank, unpublished work.



whose place in the theoretical scheme corresponds to that of the ethyl sulphate ion. A surmise, based on the experimental results mentioned later for serine phosphate, is that the P-O(R) bond length in  $\text{PO}_4\text{R}^{2-}$  is probably 1.62—1.63 Å. This is indeed about half-way between the bond length in the isolated phosphate ion (order  $\frac{1}{2}$ ), which we shall take as 1.54<sub>5</sub> Å, and the P-O single bond, estimated by the Schomaker-Stevenson method (not of course observed), of 1.71 Å.

We note first that the S-N single bond of  $1.76 \pm 0.02$  Å in sulphamic acid is paralleled by the P-N single bond of  $1.77 \pm 0.02$  found in the  $\text{PO}_3^{2-}\text{NH}_3^+$  ion by Cruickshank's refinement<sup>24</sup> of Hobbs, Corbridge, and Raistrick's<sup>25</sup> results for sodium phosphoramidate (Fig. 13). The Schomaker-Stevenson estimate for the P-N single bond is 1.76 Å, which is close to the experimental value and so tends to support the value of 1.71 Å for the (hypothetical) P-O single bond.

The most likely dimensions of the  $\text{P}_4\text{O}_{10}$  molecule are shown in Fig. 14. These are optimum values derived from two gas-phase electron-diffraction studies<sup>26,27</sup> and from a new refinement<sup>24</sup> of the crystal structure data.<sup>28</sup> In this molecule each phosphate tetrahedron is joined to the three others, so that, since the three linked P-O bonds will have low bond orders, the unlinked P-O bond will have a high order and should be very short. This accords with the observed length of  $1.40 \pm 0.02$  Å.

A calculation of the bond orders along the lines used for  $\text{S}_2\text{O}_7$  is a little difficult because the symmetry of the molecule mixes the two systems of  $\pi$ -orbitals. For a molecule  $\text{R}_3\text{PO}_4$

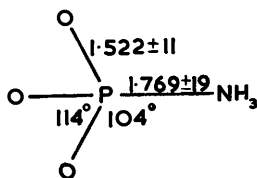


FIG. 13.  $[\text{PO}_3\cdot\text{NH}_3]^-$  in  $\text{Na}[\text{PO}_3\cdot\text{NH}_3]$ .

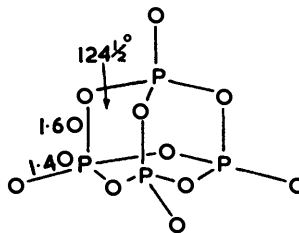


FIG. 14.  $\text{P}_4\text{O}_{10}$  ( $\pm 0.02$  Å).

with a three-fold axis of symmetry, the bond orders may be estimated as 0.8 for P-O and 0.4 for P-O(R), since the first oxygen has two  $p$ -orbitals available and the latter one. By analogy with  $\text{RSO}_4$  and  $\text{S}_2\text{O}_7$ , the effect of replacing the R by other tetrahedra will be to accentuate the difference between the two types of bond. Extrapolation from calculations for the pairs of molecules  $\text{RXO}_4$  and  $\text{X}_2\text{O}_7$ ,  $\text{R}_2\text{XO}_4$  and  $\text{X}_3\text{O}_9$ ,  $\text{R}_2\text{XO}_4$  and  $\text{X}_4\text{O}_{12}$  to the pair  $\text{R}_3\text{PO}_4$  and  $\text{P}_4\text{O}_{10}$  suggests that the short and the long bonds in  $\text{P}_4\text{O}_{10}$  will have a bond order ratio of roughly 3.0 : 1. Since the total bond order in any tetrahedron is 2.0, the bond orders are 1.00 and 0.33. If the P-O single bond is 1.71 Å and the bond of order  $\frac{1}{2}$  is 1.54<sub>5</sub> Å, the expected bond lengths in  $\text{P}_4\text{O}_{10}$  are therefore  $1.71 - 0.16_5 \times (1.0/0.5) = 1.38$  Å, and  $1.71 - 0.16_5 \times (0.33/0.5) = 1.60$  Å, which are close to the observed values of 1.40 and 1.60 Å. However, in the third form of phosphorus pentoxide,<sup>29</sup> which forms infinite sheets of  $(\text{P}_2\text{O}_5)_\infty$ , a new refinement<sup>24</sup> shows (Fig. 15) that the one unlinked and the three linked P-O bonds in each tetrahedron are  $1.49 \pm 0.02$  and  $1.56 \pm 0.02$  Å. The much smaller difference between the two types of bond is related to the opening of the POP bridging angles to an average of  $145^\circ$  as compared with  $124^\circ$  in  $\text{P}_4\text{O}_{10}$ . (This opening is caused at least partly by steric repulsions within a sheet.) Because of the opening, the P-O(bridge) bonds receive some  $\pi$ -character from the  $p$ -orbital in the POP plane as well as from the  $p$ -orbital perpendicular to the plane; the order of the unlinked P-O bond is then

<sup>25</sup> Hobbs, Corbridge, and Raistrick, *Acta Cryst.*, 1953, **6**, 621.

<sup>26</sup> Hampson and Stosick, *J. Amer. Chem. Soc.*, 1938, **60**, 1814.

<sup>27</sup> Akishin, Rambidi, and Zazorin, *Kristallografiya*, 1959, **4**, 360.

<sup>28</sup> de Decker and MacGillavry, *Rec. Trav. chim.*, 1941, **60**, 153.

<sup>29</sup> MacGillavry, de Decker, and Nijland, *Nature*, 1949, **164**, 448.

somewhat reduced. In the limit of  $\angle\text{POP} = 180^\circ$ , both  $p$ -orbitals on the oxygen perpendicular to the POP line would share fully in the two  $\pi$ -systems.

Fig. 16 shows the dimensions found<sup>24,30</sup> for the  $\text{P}_2\text{O}_7^{4-}$  pyrophosphate ion in  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ . The results are less accurate than those for the  $\text{S}_2\text{O}_7^{2-}$  ion (Fig. 3), but the POP angle of  $133\frac{1}{2}^\circ$  is definitely larger than the SOS angle of  $124^\circ$ . The simple theory with just the one  $p$ -orbital on the bridge oxygen predicts, from the bond orders of 0.60 and 0.20, bond lengths of 1.51 Å and 1.64 Å. The observed bridge length of 1.61 Å is perhaps significantly less than the predicted 1.64 Å, but it is evident from the discussion of  $\text{P}_4\text{O}_{10}$  and  $\text{P}_2\text{O}_5$  that the actual difference of 0.10 Å between the short and the long bonds, as compared with the expected 0.13 Å, is about what might be expected when the POP angle is opened to  $133\frac{1}{2}^\circ$ .

A slight opening also occurs in the  $(\text{PO}_3^-)_\infty$  chain (Fig. 17) in rubidium metaphosphate.<sup>24,31</sup> The general stereochemistry of the chain is very similar to that of the  $(\text{SO}_3)_\infty$  chain (Fig. 10); the mismatching of successive  $p$ -orbitals with the intermediate phosphorus  $p$ -orbital is again only  $3^\circ$ . The simple theory gives bond orders of 0.79 and 0.21 for the short and the long bonds. The expected lengths are then 1.45 and 1.64 Å, which differ appreciably more than the observed  $1.488 \pm 0.010$  and  $1.616 \pm 0.010$  Å. The slight opening of the POP angle to  $129^\circ$  presumably allows the second  $\pi$ -system to play some

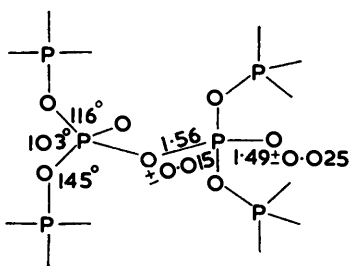


FIG. 15.  $(\text{P}_2\text{O}_5)_\infty$ .

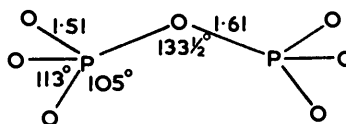


FIG. 16.  $\text{P}_2\text{O}_7^{4-}$  in  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$  ( $\pm 0.015$  Å).

part in the bridging bonds, but the two types of bond are more equal in length than can probably be explained by this factor alone.

Figs. 18 and 19 show two other structures which contain doubly linked phosphate tetrahedra. Both present problems in interpretation. The triphosphate ion, which has a two-fold axis through  $\text{P}_1$ , is from the analysis of  $\text{Na}_5\text{P}_3\text{O}_{10}$  by Davies and Corbridge<sup>32</sup> as refined by Cruickshank.<sup>24</sup> On the simple theory, with just one  $p\pi$ -orbital on oxygen, as in  $\text{S}_3\text{O}_{10}$ , the predicted lengths are 1.45, 1.64, 1.65, and 1.51 Å as compared with the observed 1.49, 1.61, 1.67, and 1.50 Å (e.s.d.'s  $\pm 0.02$  Å). The agreement in the outer tetrahedron is sufficiently close, but in the inner tetrahedron, whose dimensions are close to those in  $(\text{PO}_3)_\infty$ , the theory predicts too large a difference between the two bonds. It is no use appealing to an opening of the POP angle since this angle is only  $122^\circ$ . A conceivable explanation, which would apply to  $(\text{PO}_3)_\infty$  also, is that the  $\sigma$ -character of the two bonds is different; since the  $\text{O}_2'-\text{P}_1-\text{O}_2$  angle of  $99^\circ$  is halfway between  $109\frac{1}{2}^\circ$  and  $90^\circ$ , the  $\sigma$ -hybridisation of  $\text{P}_1-\text{O}_2$  may tend towards  $sp^3d^2$  from  $sp^3$ .

Two sets of dimensions (Fig. 19) are available for the  $\text{P}_4\text{O}_{10}^{4-}$  tetrametaphosphate ion, one from the analysis of  $(\text{NH}_4)_4\text{P}_4\text{O}_{12}$  by Romers, Ketelaar, and MacGillavry<sup>33</sup> as refined by Cruickshank<sup>24</sup> and the other from the analysis of  $\text{Na}_4\text{P}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$  by Ondik, Block, and MacGillavry.<sup>34</sup> In the ammonium salt the ion has  $2/m$  symmetry by space-group requirements; in the sodium salt it has practically the same symmetry although this is not forced

<sup>30</sup> MacArthur and Beevers, *Acta Cryst.*, 1957, **10**, 428.

<sup>31</sup> Corbridge, *Acta Cryst.*, 1956, **9**, 308.

<sup>32</sup> Davies and Corbridge, *Acta Cryst.*, 1958, **11**, 315.

<sup>33</sup> Romers, Ketelaar, and MacGillavry, *Acta Cryst.*, 1951, **4**, 114.

<sup>34</sup> Ondik, Block, and MacGillavry, *Acta Cryst.*, 1961, **14**, 555.

by the space group. The dimensions of the ions in the two crystals agree within experimental error. The most interesting feature is that the lengths of the two types of P-O(bridge) bonds in the ring are different: 1.58 and 1.65 Å in the ammonium salt and 1.584 and 1.635 Å in the sodium salt. As the differences are in the same sense in both structures, it is clear that they are definite. *Prima facie*, the present theory might well explain this difference as due to different bond orders resulting from differences in geometrical environment. However, on examination of the way in which the various *d*- and *p*-orbitals match up, the simple theory in fact suggests that one  $\pi$ -system is effectively continuous around the ring and that both P-O(bridge) bonds should have about the same bond order. Various possible refinements of the theory have proved equally unsuccessful.\*

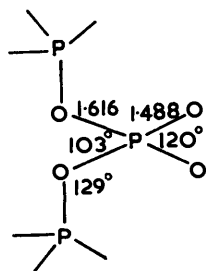


FIG. 17.  $(\text{PO}_3^-)_\infty$  in  $\text{RbPO}_3$  ( $\pm 0.010$  Å).

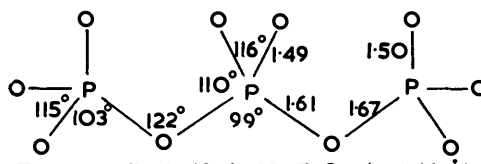
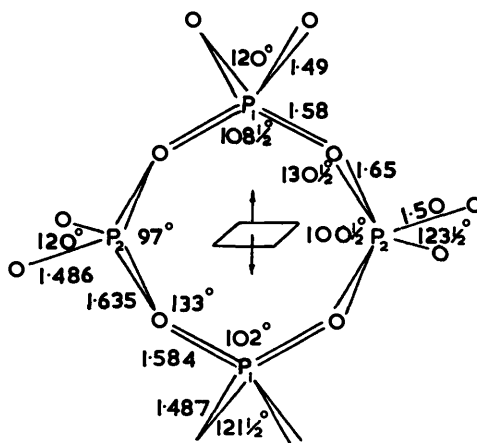


FIG. 18.  $(\text{P}_3\text{O}_{10})^{5-}$  in  $\text{Na}_5\text{P}_3\text{O}_{10}$  ( $\pm 0.02$  Å).

FIG. 19. The tetrametaphosphate ion. Dimensions at upper right from  $(\text{NH}_4)_2\text{P}_4\text{O}_{12}$  ( $\pm 0.03$  Å), at lower left from  $\text{Na}_4\text{P}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$  ( $\pm 0.016$  Å).



Leaving aside this difficulty, we note that the averages of 1.61 Å for the two P-O(bridge) bonds and 1.49 Å for the P-O(unlinked) bonds are practically the same as those for the corresponding bonds in the doubly linked tetrahedra in  $(\text{PO}_3)_\infty$  and  $\text{P}_3\text{O}_{10}$ . These lengths, together with linked and unlinked OPO angles of about  $100^\circ$  and  $120^\circ$ , are therefore consistent structural features. This consistency is not upset by the fact that in  $\text{P}_3\text{O}_{10}$  the bridging *d*-orbital is mainly  $d_{x^2-y^2}$  ( $0.98d_{x^2-y^2} + 0.18d_{z^2}$ ), while in  $(\text{PO}_3)_\infty$  it is largely  $d_{z^2}$  ( $0.38d_{x^2-y^2} + 0.93d_{z^2}$ ), where local axes have been chosen so that the *z*-axis is the bisector of the O(bridge)-P-O(bridge) angle and the *x*- and *y*-axes are at  $\pm 45^\circ$  to that plane.

Fig. 20 collects together all the results for the P-O bonds mentioned in this section, except those for  $(\text{P}_2\text{O}_5)_\infty$  in which the opening of the P-O-P angles has such a marked effect. Despite the difficulties in  $\text{P}_4\text{O}_{12}$  and the effects of the slight opening out of the P-O-P angles in some structures, the observed P-O lengths cluster quite close to the theoretical line based on unopened angles.

*Silicon-Oxygen Bonds.*—The chief difficulty in a discussion of the lengths of Si-O bonds is the paucity of accurate results. Though the crystal structures of many silicates have been worked out, the number of these with relatively pure chemical composition and with

\* See note added in proof at end of paper.

bond lengths accurate even to 0.05 Å is quite small. The most remarkable feature of the available results is that practically all the known Si-O distances are within 0.03 Å of 1.63 Å. The known spread of Si-O distances is thus much smaller than the spread of P-O or S-O distances, which are 1.40–1.67 and 1.40–1.64 Å, respectively. (The details of Si-O bonds in molecules in which silicon is not linked to four oxygens will be considered later, but even for these the distances are close to 1.63 Å.) Some reasons for this smaller spread will emerge shortly, but it is probable that the more varied Si-O bonds will be found in suitable structures.

No results are available for ions of the type  $\text{RSiO}_4^{3-}$ ,  $\text{R}_2\text{SiO}_4^{2-}$ , or  $\text{R}_3\text{SiO}_4^-$ , but an electron-diffraction study<sup>35</sup> of tetramethyl silicate gives  $\text{Si-O} = 1.64 \pm 0.03$  Å (and  $\angle \text{Si-O-C} = 113^\circ \pm 2^\circ$ ). Since each oxygen has only one *p*-orbit available for  $\pi$ -bonding, the Si-O bonds will be of order  $\frac{1}{2}$  and should therefore be, as they are, of similar length to those in a  $\text{SiO}_4^{4-}$  group.

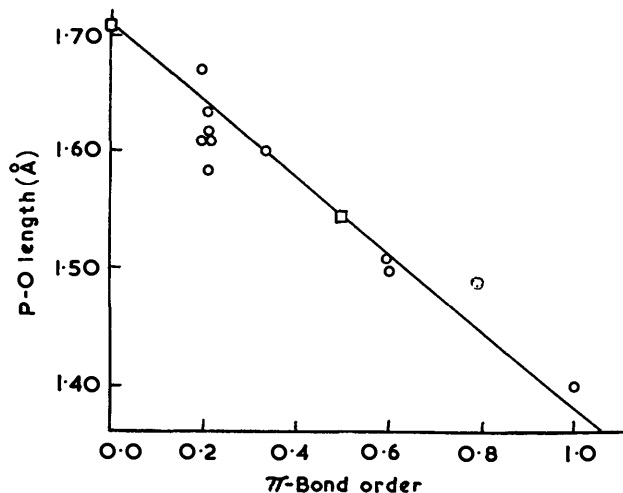
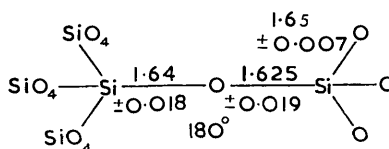


FIG. 20. P-O bond lengths and  $\pi$ -bond orders.

(The indication corresponding to  $\pi$ -bond order 0.8 is the superposition of three circles.)

FIG. 21.  $[\text{Si}_5\text{O}_{16}]^{12-}$  in zunyite.



The equalisation of bond orders in linking and non-linking X-O bonds by the opening of the X-O-X angles reaches a limit in some of the silicates. In thortveitite,<sup>36</sup>  $\text{Sc}_2\text{Si}_2\text{O}_7$ , the  $\text{Si}_2\text{O}_7$  pyrosilicate ion has a linear Si-O-Si bridge with an inner Si-O<sub>1</sub> bond of  $1.607 \pm 0.007$  Å and an outer Si-O<sub>2</sub> bond of  $1.626 \pm 0.012$  Å. These dimensions are similar to those reported in two-dimensional work on seidozerite<sup>37</sup> ( $\angle \text{Si-O-Si}$   $180^\circ$ , inner Si-O 1.63 Å, outer Si-O 1.635 Å) and are paralleled in Kamb's three-dimensional work on zunyite<sup>38</sup> where the  $\text{Si}_5\text{O}_{16}$  group (Fig. 21) has linear Si-O-Si links and Si-O lengths of  $1.64 \pm 0.018$ ,  $1.625 \pm 0.019$ , and  $1.65 \pm 0.007$  Å.

In pyrosilicate groups with  $\angle \text{Si-O-Si} = 180^\circ$ , the bridge oxygen O<sub>1</sub> will have two *p*-orbitals available for  $\pi$ -bonding and so may join fully in both  $\pi$ -systems. On the simple picture the  $\pi$ -bond orders are 2/5 for the inner bonds and 8/15 for the outer bonds. With 1.76 Å for a single bond and 1.63 Å for a bond of order  $\frac{1}{2}$ , the predicted lengths are 1.656

<sup>35</sup> Yamasaki, Kotera, Yokoi, and Ueda, *J. Chem. Phys.*, 1950, **18**, 1414.

<sup>36</sup> Cruickshank, Lynton, and Barclay, *Acta Cryst.*, in the press.

<sup>37</sup> Simonov and Belov, *Kristallografiya*, 1959, **4**, 163.

<sup>38</sup> Kamb, *Acta Cryst.*, 1960, **13**, 15.

and 1.621 Å. To a rough approximation the bonds ought to be of about equal length, which is what is observed, but in detail the inner bond ought to be slightly the longer, which is not correct for thortveitite. The observations cannot be explained either by reversion to a simple electrostatic picture of the old style, in which both the Si-O  $\pi$ -bonds and the partial covalent character of the inter-ionic Sc-O bonds are ignored. In such an approach, with the crystal treated as an array of discrete  $\text{Sc}^{3+}$  and  $\text{Si}_2\text{O}_7^{6-}$  ions and with 50% ionic character for the Si-O  $\sigma$ -bonds,<sup>39</sup> a simple electrostatic calculation for an isolated  $\text{Si}_2\text{O}_7^{6-}$  group suggests that, with reasonable force constants, the outer Si-O bonds should be of the order of 0.1 Å shorter than the inner bonds. However, as discussed by Cruickshank, Lynton, and Barclay,<sup>36</sup> some details of the packing together of the pyrosilicate groups in the crystal seem intelligible only with reduced formal charges on the outer oxygens. These reduced charges (and consequent reduced charges on the scandium and  $\text{Si}_2\text{O}_7$  ions) would fit with a slight covalent character for the Sc-O bonds and so with Pauling's electroneutrality principle. It would then be possible for the net charge on the inner oxygen (say, -0.8) to be greater than the charges (say, -0.5) on the outer oxygens, so that the near equality of the Si-O bonds in thortveitite could be explained by a balance of an electrostatic effect, tending to make the inner bonds the shorter, and the  $\pi$ -bond effect, tending to make the inner bonds the longer.

Although the details of some of the structures are a little doubtful, crystals with  $\text{Si}_2\text{O}_7$  groups show variations of the Si-O-Si angles from the 180° of thortveitite and seidozerite down to about 135° in hemimorphite<sup>40</sup> and lawsonite.<sup>41</sup> The evident dependence of the structure of the  $\text{Si}_2\text{O}_7$  group on crystal environment is in keeping with the above remarks on the importance of the partial covalent character of the inter-ionic bonds. (Indeed, with any plausible bending-force constant for oxygen, it is easily shown that, if an isolated  $\text{Si}_2\text{O}_7$  group has a total charge of -6, the electrostatic forces are sufficient to compel the Si-O-Si link to be linear.) The reported Si-O distances for the pyrosilicate groups in hemimorphite or lawsonite are not sufficiently accurate for comparison to be made with theoretical estimates of these distances.

Si-O-Si angles of around 135° have been found in several  $(\text{SiO}_3)_\infty$  chains, but unfortunately no really accurate result seems available. The two-dimensional least-squares studies of clinoenstatite and pigeonite by Morimoto, Appleman, and Evans,<sup>42</sup> together with the older results for diopside,<sup>43</sup> show that Si-O(bridge) bonds tend to be about 0.05 Å larger than Si-O(unlinked) bonds. If the Si-O-Si angles were about 120°, the bond orders quoted earlier for  $(\text{SO}_3)_\infty$  imply a difference of about 0.14 Å (1.70 and 1.56 Å). The smaller actual difference is presumably partly due to the opening of the Si-O-Si angles to about 135° and partly to the same (?electrostatic) effect as seems to operate for the inner and the outer bonds in thortveitite. In  $\text{Na}_2\text{SiO}_3$  the bonds are reported<sup>44</sup> as 1.68 and 1.57 Å, but the accuracy of these results cannot be high since the residual  $R$  is 27%. An accurate analysis of a structure of this type is very desirable.

Si-O bond lengths with e.s.d.'s of 0.01 or 0.02 Å have been obtained by Meier<sup>45</sup> for the  $\text{Si}_3\text{O}_{10}$  group in natrolite,  $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}$ . They all lie in the range 1.60—1.65 Å. In the crystal structure there are also numerous Al-O bonds of length about 1.75 Å, which are not very dissimilar in character to the Si-O bonds. Consequently the  $\text{Si}_3\text{O}_{10}$  group cannot be considered as separate an entity as an  $\text{S}_3\text{O}_{10}$  group and no simple predictions of its bond lengths can be made, though clearly all the Si-O bonds will tend to be approximately equal in length as every oxygen belongs either to two silicon tetrahedra or to one silicon and one aluminium tetrahedron.

<sup>39</sup> Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, 3rd edn., 1960.

<sup>40</sup> Barclay and Cox, *Z. Krist.*, 1960, **113**, 23.

<sup>41</sup> Rumanova and Skipetrova, *Doklady Akad. Nauk S.S.S.R.*, 1959, **124**, 324.

<sup>42</sup> Morimoto, Appleman, and Evans, *Z. Krist.*, 1960, **114**, 120.

<sup>43</sup> Warren and Bragg, *Z. Krist.*, 1928, **69**, 168.

<sup>44</sup> Grund and Pizy, *Acta Cryst.*, 1952, **5**, 837.

<sup>45</sup> Meier, *Z. Krist.*, 1960, **113**, 430.

Accurate results are available for two forms of silica  $(\text{SiO}_2)_\infty$ ,  $\alpha$ -quartz<sup>46</sup> and coesite.<sup>47</sup> In  $\alpha$ -quartz the Si-O-Si angle is  $144^\circ$ , in coesite there is one angle of  $180^\circ$  and four in the range  $139$ – $148^\circ$ . The spread of angles in this one structure may be compared with the similar spread in the various structures with pyrosilicate groups. In both  $\alpha$ -quartz and coesite the Si-O distances are all close to  $1.61 \text{ \AA}$ . In each structure the Si-O  $\pi$ -bond orders will be approximately  $\frac{1}{2}$ , irrespective of the details of the linking of the  $\pi$ -systems through the  $p$ -orbitals of the oxygens. The observed  $1.61 \text{ \AA}$  is close to the  $1.63 \text{ \AA}$ , which has been noticed both as the general average for Si-O distances and as the length of the bonds (also of order  $\frac{1}{2}$ ) in the  $\text{SiO}_4$  group itself, though perhaps there is again the tendency for an external bond, as in  $\text{SiO}_4$ , to be slightly longer than an internal bond of the same order.

The present  $\pi$ -bonding theory suggests an important difference between  $\alpha$ - and  $\beta$ -quartz. In  $\beta$ -quartz,<sup>48</sup> of which an accurate modern determination seems very desirable, each silicate tetrahedron has three two-fold axes of symmetry. Consequently, on the four oxygens the  $p$ -orbitals, which are normal to the Si-O-Si planes, all match the same silicon  $d$ -orbital, so that one  $\pi$ -system plays a dominant rôle in the structure. In  $\alpha$ -quartz, where each tetrahedron has a single two-fold axis, the geometry shows that the  $p$ -orbitals on the two independent types of oxygens are  $73^\circ$ , *i.e.*, nearly  $90^\circ$ , out of phase for overlapping the same silicon  $d$ -orbital. Consequently, both  $\pi$ -systems, using two essentially distinct  $d$ -orbitals, play an equal rôle in the structure of  $\alpha$ -quartz. In both systems a small part of the  $\pi$ -bonding will arise from the  $p$ -orbital which bisects the  $144^\circ$  Si-O-Si angle.

It was remarked earlier that the known spread of Si-O distances about  $1.63 \text{ \AA}$  is very small. This seems partly due to the accident that most of the structures studied have involved linked silicate tetrahedra, in which the opening of the Si-O-Si angles has tended to equalise the  $\pi$ -bond orders. A structure such as, say,  $\text{R}_2\text{SiO}_4^{2-}$  might therefore offer a better chance of finding more varied Si-O bonds. Here the  $\pi$ -bond orders will be  $\frac{1}{4}$  for Si-O(R) and  $\frac{3}{4}$  for Si-O.

*X-O Bonds when X is not Surrounded by Four  $\pi$ -Bonding Ligands.*—In many sulphones,  $\text{R}_2\text{SO}_2$ , S-O lengths close to  $1.43 \text{ \AA}$  (and O-S-O angles of about  $120^\circ$ ) have been found. The bonding in such systems has been discussed by Moffitt<sup>11,49</sup> but, as Jaffé has pointed out,<sup>13</sup> he did not realise that the sulphur  $d$ -orbital of  $a_1$ -symmetry, corresponding to the present  $d_{z^2}$ -orbital, can be involved in  $\pi$ -bonding to the oxygens. In any molecule where sulphur is surrounded by four ligands in an approximately tetrahedral arrangement,  $\pi$ -bonding can occur between suitable ligand orbitals and the sulphur orbitals,  $d_{xz}$ ,  $d_{yz}$  and  $d_{z^2}$  (with some admixture of  $d_{xy}$  if the angles are distorted), in the same kind of way as described for the sulphate ion. On a blind application of the present treatment to the sulphones, S-O bonds much shorter than the observed  $1.43 \text{ \AA}$  would be expected, since the bond orders are  $\frac{1}{2} + \frac{1}{2} = 1$ , which implies a length of about  $1.3 \text{ \AA}$ . The relatively small contraction from the  $1.49 \text{ \AA}$  of the sulphate ion may be ascribed to the smaller electronegativity of a group R than of oxygen and to the asymmetry of the  $\pi$ -bonding about sulphur, so that the effective nuclear charge  $Z_{\text{eff}}(3d)$  for the  $3d$ -orbitals is lowered with a loss of bonding strength. In the sulphonates,  $\text{R}\cdot\text{SO}_3^-$ , lengths of  $1.44 \pm 0.02$ ,  $1.462 \pm 0.005$ , and  $1.45 \pm 0.01 \text{ \AA}$  are reported for sulphamic acid,<sup>19</sup> methylenedisulphonate,<sup>50</sup> and sodium naphthionate.<sup>51</sup> These are intermediate between the  $1.49 \text{ \AA}$  of the sulphate ion and the  $1.43 \text{ \AA}$  of the sulphones.

If a group R in one of the tetrahedral positions of a sulphone is replaced by a lone pair to give  $\text{R}\cdot\text{SO}_2^-$ ,  $Z_{\text{eff}}(3d)$  should be considerably reduced and in sodium hydroxymethanesulphonate<sup>50,52</sup> the S-O bonds are duly found to be lengthened from  $1.43$  to  $1.51 \text{ \AA}$  (though

<sup>46</sup> Alexander and Smith, personal communication.

<sup>47</sup> Zoltai and Buerger, *Z. Krist.*, 1959, **111**, 129.

<sup>48</sup> Bragg and Gibbs, *Proc. Roy. Soc.*, 1925, *A*, **109**, 405.

<sup>49</sup> Koch and Moffitt, *Trans. Faraday Soc.*, 1951, **47**, 7.

<sup>50</sup> Truter, unpublished work.

<sup>51</sup> Brown and Corbridge, unpublished work.

<sup>52</sup> Truter, *J.*, 1955, 3064.

some of this lengthening might be due to a change in the  $\sigma$ -bond strength, since the S-C bond of 1.83 Å is also rather long).

In a similar way in the series  $\text{ClO}_4^-$ ,  $\text{ClO}_3^-$ ,  $\text{ClO}_2^-$ , and  $\text{ClO}^-$ , where lone pairs successively replace oxygens in the tetrahedron, the bond lengths<sup>3,53</sup> (1.46,  $1.46 \pm 0.01$  + some rotational correction,  $1.57 \pm 0.03$  Å, and ?) are a balance between the increasing bond order of the Cl-O bonds ( $\frac{2}{4}$ ,  $\frac{2}{3}$ ,  $\frac{2}{2}$ ,  $\frac{2}{1}$ ) and the successively lowered  $Z_{\text{eff}}$  for the Cl(3*d*) orbitals.

Some similarities to the sulphonates and sulphones can be observed in structures containing phosphorus. As compared with the 1.54<sub>5</sub> Å of  $\text{PO}_4^{3-}$ , values observed are about 1.52 Å for  $\text{R}\cdot\text{PO}_3^{2-}$  [ $1.52 \pm 0.01$  in<sup>24,25</sup>  $\text{PO}_3\text{NH}_3^-$ ,  $1.51 \pm 0.05$  in<sup>54</sup>  $\text{HPO}_3^{2-}$ , and a mean of  $1.53 \pm 0.02$  Å for P-O and P-O(H) in<sup>55</sup>  $\text{HPO}(\text{OH})_2$ ] and  $1.50 \pm 0.02$  Å for  $\text{R}_2\text{PO}_2^-$  [the hypophosphite ion<sup>55</sup> in  $\text{Ca}(\text{PO}_2\text{H}_2)_2$ ]. In  $\text{P}_4\text{O}_6$ , as compared with  $\text{P}_4\text{O}_{10}$ , the effect of replacing the four outer oxygens by lone pairs is to increase the P-O length<sup>26</sup> from 1.60 to  $1.65 \pm 0.02$  Å.

The closeness of Si-O lengths in silicates to 1.63 Å has already been noted. The same length ( $1.633 \pm 0.001$  Å) is found<sup>56</sup> in an accurate electron-diffraction study of disilyl ether,  $(\text{SiH}_3)_2\text{O}$ , where the Si-O-Si angle is  $144^\circ \pm 1^\circ$ . Similar, but much less accurate, dimensions had been found in earlier studies<sup>35</sup> of  $[(\text{CH}_3)_3\text{Si}]\text{O}$  and  $(\text{Cl}_3\text{Si})_2\text{O}$ . The opening of the Si-O-Si angle beyond  $109\frac{1}{2}^\circ$  necessarily implies  $\pi$ -bonding and/or electrostatic effects. On the present view, the oxygen *p*-orbitals perpendicular to the Si-O-Si plane will join in  $\pi$ -bonds, while the *p*-orbitals bisecting the angle will also play some part because the angle is so large. Lengths near to 1.63 Å are also found in the crystal structure<sup>57</sup> of  $(\text{C}_2\text{H}_5)_2\text{Si}(\text{OH})_2$  and in the -O-Si(CH<sub>3</sub>)<sub>2</sub>-O- groupings<sup>58-60</sup> in spiro-siloxane,  $[(\text{CH}_3)_2\text{SiO}]_4$ , and  $[(\text{CH}_3)_2\text{SiO}]_3$ . On the present approach, the approximate equality of all these Si-O distances is to be regarded as an accident of a balance of the varying  $\pi$ -bond orders with the varying  $Z_{\text{eff}}$ (3*d*) and electrostatic forces.

As Craig *et al.*<sup>61</sup> remarked, evidence of the ability of Si(3*d*) orbitals to form  $\pi$ -bonds with nitrogen may be found<sup>62</sup> from  $(\text{H}_3\text{Si})_3\text{N}$ , where the co-planar Si-N bonds of  $1.71 \pm 0.02$  Å are 0.06 Å shorter than the expected Si-N single-bond length.

*Effect of Attached Hydrogen.*—It seems to be a general rule for crystals that, when hydrogen is attached to sulphate or phosphate groups, the bond lengths are roughly halfway between those for the ion without the proton and for the ion with a group R attached. Thus in mercallite<sup>63</sup>  $\text{KHSO}_4$ , where the  $\text{OH} \cdots \text{O}$  hydrogen bonds are 2.62 Å long, an appreciable refinement<sup>24</sup> shows that the average dimensions from the two  $\text{HSO}_4^-$  ions are S-O(H) = 1.56 and S-O =  $1.47 \pm 0.015$  Å. The difference between the short and the long bonds is 0.09 Å, compared with the larger difference of 0.14 Å in ethyl sulphate.

In the low-temperature form<sup>64</sup> of  $\text{KH}_2\text{PO}_4$ , where the hydrogen bonds are 2.49 Å long, P-O(H) = 1.58 and P-O = 1.51 Å, with a difference of 0.07 Å; in phosphoric acid<sup>65</sup>  $\text{H}_3\text{PO}_4$ , with hydrogen bonds 2.50—2.59 Å long, the lengths are 1.57 and 1.52 with a difference of only  $0.05 \pm 0.02$  Å. The distinction between attached hydrogen and attached R is beautifully illustrated by the analysis of serine phosphate<sup>66</sup> (Fig. 22), where the phosphate group has both hydrogen and R attached, and the hydrogen bond is 2.55 Å

<sup>53</sup> Gillespie, Sparks, and Trueblood, *Acta Cryst.*, 1959, **12**, 867.

<sup>54</sup> Corbridge, *Acta Cryst.*, 1956, **9**, 991.

<sup>55</sup> Loopstra, Thesis, Amsterdam, 1958.

<sup>56</sup> Bastiansen and Traetteberg, personal communication.

<sup>57</sup> Kakudo and Watase, *J. Chem. Phys.*, 1953, **21**, 167.

<sup>58</sup> Roth and Harker, *Acta Cryst.*, 1948, **1**, 34.

<sup>59</sup> Peyronel, *Atti Accad. naz. Lincei, Rend.*, 1954, **16**, 231.

<sup>60</sup> Steinfink, Post, and Fankuchen, *Acta Cryst.*, 1955, **8**, 420.

<sup>61</sup> Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, **332**.

<sup>62</sup> Hedberg, *J. Amer. Chem. Soc.*, 1955, **77**, 6491.

<sup>63</sup> Loopstra and MacGillavry, *Acta Cryst.*, 1958, **11**, 349.

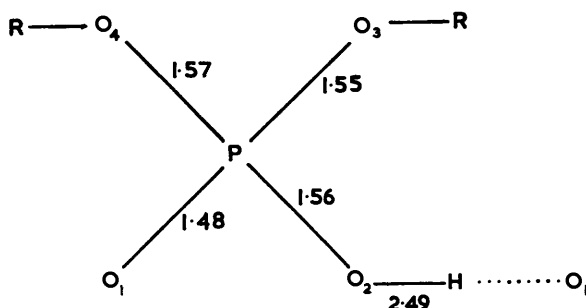
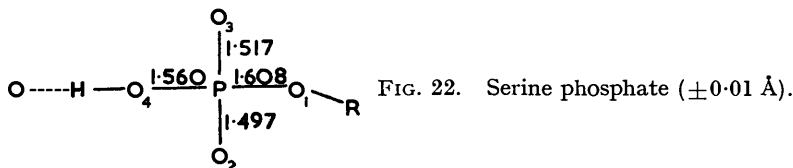
<sup>64</sup> Bacon and Pease, *Proc. Roy. Soc.*, 1955, **A**, **230**, 359.

<sup>65</sup> Furberg, *Acta Chem. Scand.*, 1955, **9**, 1557.

<sup>66</sup> McCallum, Robertson, and Sim, *Nature*, 1959, **184**, 1863.

long. Here  $P-O_1(R) = 1.61 \text{ \AA}$ , while the  $P-O_4(H)$  bond of  $1.56 \pm 0.01 \text{ \AA}$  is definitely shorter. An examination of the geometry of the molecule shows that the  $p$ -orbit of  $O_4(H)$  is about  $60^\circ$  out of alignment with that  $d$ -orbit of P which mates with the  $p$ -orbit of  $O_1(R)$ . Consequently the bond order of  $P-O(R)$  is somewhat less than  $\frac{1}{2}$ , which would be the value for an ion  $R_2PO_4^-$  with a two-fold axis of symmetry. It is for this reason that the  $P-O(R)$  bond length in  $R \cdot PO_4^{2-}$ , discussed earlier, is estimated as a little larger than  $1.61 \text{ \AA}$ , say  $1.62-1.63 \text{ \AA}$ .

The dimensions of dibenzyl hydrogen phosphate are shown in Fig. 23. These differ from those given by Dunitz and Rollett,<sup>67</sup> after their three-dimensional anisotropic SFLS



analysis, by the addition of rotation-oscillation corrections<sup>2</sup> ranging from  $0.006$  to  $0.015 \text{ \AA}$  which have been roughly estimated from the vibration parameters. The phosphorus  $d$ -orbit which matches the available  $p$ -orbit of  $O_3(C)$  is about  $75^\circ$  mismatched for the  $p$ -orbit of  $O_4(C)$ . Thus the  $p$ -orbitals of the two  $O(C)$  mate with essentially different  $d$ -orbitals, and for this reason alone the  $\pi$ -bond orders of the  $P-O(C)$  bonds are at least  $\frac{1}{3}$ . The  $p$ -orbit of  $O_2(H)$  is about  $52^\circ$  out of alignment for the  $d$ -orbit determined by  $O_4(C)$  and  $45^\circ$  out for  $O_3(C)$ . Thus the effect of the proton, which is involved in a  $2.49 \text{ \AA}$  hydrogen bond, will be to increase slightly the bond orders of each  $P-O(C)$  from the  $\frac{1}{3}$  already derived. The present approach, therefore, gives some explanation of why the average  $P-O(C)$  distance of  $1.56 \text{ \AA}$  in dibenzyl hydrogen phosphate is shorter than the  $1.61 \text{ \AA}$  in serine phosphate or the  $1.62-1.63 \text{ \AA}$  expected in  $R \cdot PO_4^{2-}$ .

That the shorter bond lengths for  $X-O(H)$  than for  $X-O(R)$  are due to the formation of short hydrogen bonds in *crystals* seems confirmed by the electron-diffraction study<sup>68</sup> of perchloric acid *vapour*, where the  $Cl-O(H)$  bond of  $1.64 \pm 0.02 \text{ \AA}$  is some  $0.2 \text{ \AA}$  longer than the three  $Cl-O$  bonds of  $1.42 \text{ \AA}$ . It is also interesting that in the ordered low-temperature crystal form<sup>6</sup> of  $H_3O^+ClO_4^-$  the three oxygens at the termini of the hydrogen bonds have  $Cl-O$  distances of  $1.468 \pm 0.004 \text{ \AA}$ , which are slightly longer than the  $Cl-O$  distances of  $1.443 \pm 0.006 \text{ \AA}$  for the oxygen entirely free from hydrogen bonds. Thus, even participation in the weak end of a hydrogen bond causes a very slight loss of double-bond character in the  $Cl-O(\cdots H)$  bonds.

*A Simple Empirical Rule.*—The average  $X-O$  distances in  $XO_4$  tetrahedra are about:

Si-O	P-O	S-O	Cl-O
1.63	1.54 <sub>5</sub>	1.49	1.46 $\text{\AA}$

<sup>67</sup> Dunitz and Rollett, *Acta Cryst.*, 1956, **9**, 327.

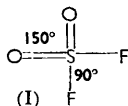
<sup>68</sup> Akishin, Rambidi, and Zazorin, *Kristallografiya*, 1959, **4**, 360.



X-O bonds which involve oxygen linked to another atom or to another tetrahedron may lengthen by amounts up to  $\sim 0.15$  Å but the other X-O bonds in the tetrahedron contract so as to preserve the average.

*Bonds to Fluorine.*—The tetrahedral molecule  $\text{SiF}_4$  is isoelectronic with the orthosilicate ion and has a Si-F bond length<sup>69</sup> of  $1.56 \pm 0.02$  Å. This is  $0.13$  Å shorter than the value predicted for a Si-F single bond by the Schomaker-Stevenson method; thus it seems that the fluorine  $2p\pi$ - and  $2p\pi'$ -orbitals engage in some  $\pi$ -bonding with the silicon  $d_{xz}$ - and  $d_{yz}$ -orbitals.

Sulphonyl fluoride,  $\text{SO}_2\text{F}_2$ , is isoelectronic with  $\text{SO}_4^{2-}$  and has the dimensions<sup>70</sup> S-O  $1.405$ , S-F  $1.530$  Å,  $\angle\text{O-S-O}$   $124^\circ$ ,  $\angle\text{F-S-F}$   $96^\circ$ . As compared with the sulphones,  $\text{R}_2\text{SO}_2$ , where R is a hydrocarbon residue, the effect of fluorine is to contract the S-O distance a little, from  $1.43$  to  $1.405$ , and to open the angle from  $120^\circ$ . We may regard the structure of sulphuryl fluoride as intermediate between that of an exactly tetrahedral molecule, in which fluorines participate in the  $\pi$ -bonding in a similar, but reduced, fashion to the oxygens, and one based on a sulphur atom with six octahedral ( $sp^3d^2$ )  $\sigma$ -orbitals, which would give the configuration (I) with the S=O double bonds formed from two bent  $\sigma$ -bonds. The Schomaker-Stevenson value from tetrahedral radii for the S-F single bond is  $1.625$  Å; an old study<sup>71</sup> of the octahedral molecule sulphur hexafluoride gives S-F  $1.58 \pm 0.03$  Å. The value of  $1.530$  Å in sulphuryl fluoride therefore indicates some double-bond character in the S-F bond.



The isoelectronic molecule  $\text{PF}_3\text{O}$  is even less distorted from the tetrahedral configuration. Here  $\angle\text{F-P-F}$  is reported<sup>72</sup> as  $106^\circ$ , P-F as  $1.52$  Å, and P-O as  $1.48$  Å. It is noticeable that both bonds are shorter than the  $1.54$  Å for the P-O in an orthophosphate ion and that the P-F bond is decidedly shorter than  $1.65$  Å for the Schomaker-Stevenson single bond.

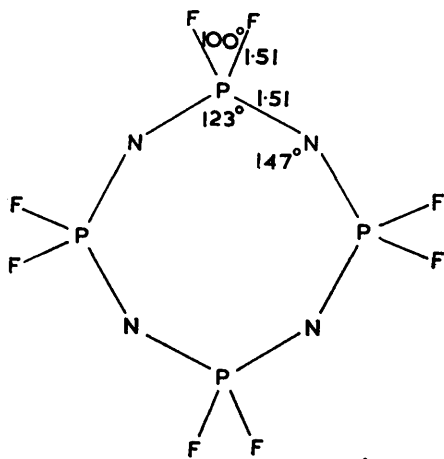


FIG. 24.  $[\text{PNF}_2]_4$  ( $\pm 0.01$  Å).

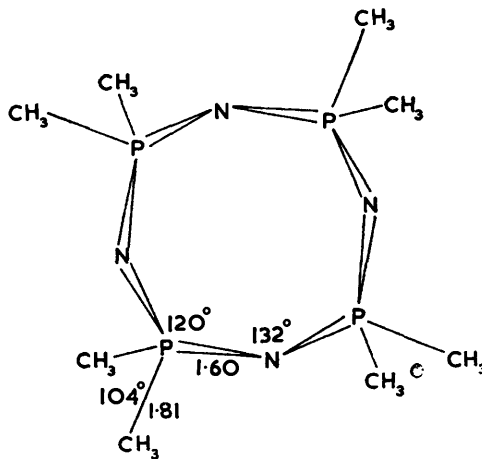


FIG. 25.  $[\text{PN}(\text{CH}_3)_2]_4$  ( $\pm 0.005$  Å).

We now turn to the isoelectronic pair of phosphonitrilic molecules  $[\text{PNF}_2]_4$  and  $[\text{PN}(\text{CH}_3)_2]_4$ , whose structures have been recently determined<sup>73</sup> with some precision by X-ray methods (Figs. 24 and 25). In the difluoro-tetramer, which has a planar eight-membered ring, the  $p$ -orbitals of the nitrogens perpendicular to the plane can match exactly with the phosphorus  $d_{xz}$ - $y$ -orbitals (these are the  $d_{xz}$ -orbitals in Craig's system of axes<sup>74</sup>),

<sup>69</sup> Atoji and Lipscomb, *Acta Cryst.*, 1954, **7**, 597.

<sup>70</sup> Lide, Mann, and Fristrom, *J. Chem. Phys.*, 1957, **26**, 734.

<sup>71</sup> Brockway and Pauling, *Proc. Nat. Acad. Sci. U.S.A.*, 1933, **19**, 68.

<sup>72</sup> Hawkins, Cohen, and Koski, *J. Chem. Phys.*, 1952, **20**, 528.

<sup>73</sup> McGeachin and Tromans, *J.*, in the press; Dougill, *J.*, 1961, 5471.

<sup>74</sup> Craig, *J.*, 1959, 997.

while owing to the large P-N-P angle of  $147^\circ$  some further  $\pi$ -bond character in the P-N bonds can be obtained from the matching of the  $p$ -orbit, which bisects the P-N-P angle, with the phosphorus  $d_{z^2}$ -orbitals (to which a little  $d_{xy}$  may be added to compensate for the distortions from tetrahedral angles). The P-F distance of  $1.51 \text{ \AA}$  in this tetramer is similar to the P-F distance of  $1.52 \text{ \AA}$  in  $\text{PF}_3\text{O}$ , so that it also shows some  $\pi$ -bond character.

When the fluorines of sulphuryl fluoride are replaced by methyl groups the S-O distance increases; it is therefore reasonable that the P-N distances in  $[\text{PN}(\text{CH}_3)_2]_4$  are longer than those in  $[\text{PNF}_2]_4$ , as is indeed found. However, the ring of the dimethyl-tetramer is considerably puckered and it might therefore seem that the  $\pi$ -bonding systems would be very different. The relevant point is the measure of mismatching between the  $p$ -orbitals on successive nitrogens, perpendicular to the P-N-P planes, and the intermediate  $d$ -orbitals. In the dimethyl-tetramer, which has  $\bar{4}$  symmetry, an orbital  $0.73 d_{x^2-y^2} + 0.69 d_{z^2}$  is only  $\pm 11\frac{1}{2}^\circ$  mismatched to the principal  $p$ -orbitals of the adjoining nitrogens. Thus the introduction of the  $d_{z^2}$ -orbital ( $d_{y^2}$  in Craig's axes) allows the principal  $\pi$ -bond system to retain much of its energy despite the puckering of the molecule. The increase of the P-N

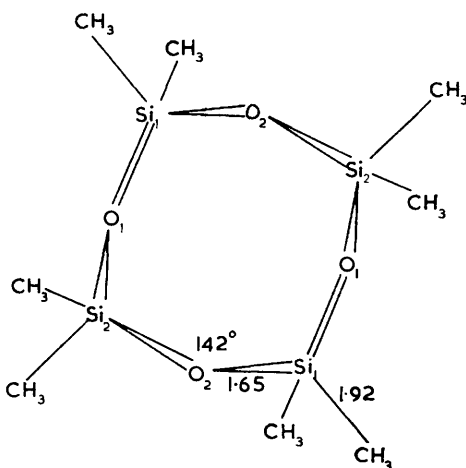


FIG. 26.  $[\text{SiO}(\text{CH}_3)_2]_4$  ( $\pm 0.03 \text{ \AA}$ ).

length from  $1.51 \text{ \AA}$  in the difluoro-tetramer to  $1.60 \text{ \AA}$  in the dimethyl-tetramer may therefore be correlated with (a) the inevitable direct increase of lengths due to the replacement of fluorine by methyl, (b) the closing of the P-N-P angle from  $147^\circ$  to  $132^\circ$ , with a consequent loss of strength in the minor  $\pi$ -bond system, and (c) the slight ( $\pm 11\frac{1}{2}^\circ$ ) mismatching of the principal  $p$ -orbitals. These effects are, of course, not independent, and the above account is not so much an explanation of the structure of the two molecules as an indication of some of the factors which will have to be considered in any full explanation.

It is perhaps appropriate here to mention the isoelectronic  $[\text{SiO}(\text{CH}_3)_2]_4$ , which is also heavily puckered<sup>60</sup> (Fig. 26). In this the orbital  $0.78 d_{x^2-y^2} + 0.63 d_{z^2}$  on  $\text{Si}_1$  is  $\pm 14^\circ$  mismatched to the adjacent oxygens, while the orbital  $-0.17 d_{x^2-y^2} + 0.98 d_{z^2}$  on  $\text{Si}_2$  is  $\pm 21^\circ$  to the adjacent oxygens. It is perhaps not surprising that these mismatches are a little greater than in  $[\text{PN}(\text{CH}_3)_2]_4$ , since the average Si-O-Si angle of  $142^\circ$  will allow the second  $\pi$ -system to play a proportionately larger rôle than in phosphonitrile tetramer with its P-N-P angle of  $132^\circ$ .

*Discussion.*—Apart from the initial discussion of bonding in the  $\text{XO}_4$  ions, the theory presented in this paper has been deliberately kept at a very low mathematical level. The reason for this has been that the simple geometrical ideas of the double  $\pi$ -bonding system seem to go a long way in explaining the general features of the structures. The simple picture has its obvious shortcomings, but it has seemed more important first to codify the experimental results and to see how they fit a simple scheme, than to embark

prematurely on a detailed theoretical treatment of a particular molecule. The details of the present semiempirical classification cannot possibly all be correct, but the overall correlation seems sufficiently compelling to indicate that some of the ideas must be integral features of any fuller theory.

It is not only the theoretical side which needs more attention; much vital experimental information is still lacking. Some of the wanted key structures have been mentioned at appropriate points. As one illustration of the need for further experimental work, consider the  $X_2O_7$  ions. We have quoted the dimensions of the  $Si_2O_7$  group<sup>36</sup> in thortveitite (inner X-O =  $1.607 \pm 0.007$  Å, outer X-O =  $1.626 \pm 0.012$  Å and  $\angle X-O-X = 180^\circ$ ), the  $P_2O_7$  group<sup>24</sup> in  $Na_4P_2O_7 \cdot 10H_2O$  ( $1.61 \pm 0.015$  Å,  $1.51 \pm 0.015$  Å,  $133\frac{1}{2}^\circ$ ), and the  $S_2O_7$  group<sup>16</sup> in  $K_2S_2O_7$  ( $1.645 \pm 0.005$  Å,  $1.437 \pm 0.004$  Å,  $124^\circ$ ). To these may be added the results of a recent Russian gas-electron-diffraction study<sup>68</sup> of  $Cl_2O_7$  ( $1.725 \pm 0.03$  Å,  $1.424 \pm 0.01$  Å,  $115 \pm 5^\circ$ ). It is tempting to be satisfied with noting that the differences of the inner and the outer bonds in these four groups are very close to 0.0, 0.1, 0.2, and 0.3 Å and to correlate this with the change of angle from  $180^\circ$  to  $133\frac{1}{2}^\circ$ ,  $124^\circ$ , and  $115^\circ$ , a correlation which can be related to the decreasing rôle of the second  $\pi$ -system in the inner bond as the X-O-X angle falls below  $180^\circ$ . To do only this is to oversimplify the situation. First, in the pyrosilicates the Si-O-Si angle can go as low as  $135^\circ$ , yet no accurate bond lengths are available for such structures (indeed the thortveitite results are not up to the best current X-ray standards). Secondly, in view of the variability of the Si-O-Si angles and of the difference between the P-O-P angles in  $P_4O_{10}$  and the third form of  $(P_2O_5)_\infty$ , study of many more pyrophosphate structures is needed. Thirdly, the results for  $Cl_2O_7$  are not up to the standard of the best current electron-diffraction work and they are considerably less accurate than the X-ray results for  $K_2S_2O_7$ . One surprising feature is that the mean Cl-O length in  $Cl_2O_7$  is 1.50 Å, which is 0.04 Å larger than in  $ClO_4^-$  and 0.025 Å larger than the mean in the simpler perchloric acid studied by the same authors.<sup>68</sup> An accurate re-examination of chlorine heptoxide would be most valuable.

Despite the variation in individual phosphate or silicate structures, there is a definite tendency for the X-O-X angles to get larger as X changes from chlorine to silicon. The most reasonable explanation is that the effect is primarily electrostatic, the forces between adjacent tetrahedra opening the angle beyond  $109\frac{1}{2}^\circ$ . Such forces will increase as we pass from chlorine to silicon, even though the nominal charges of groups such as  $Si_2O_7^{6-}$  are unlikely to be realized. The opening of the angle allows the second  $\pi$ -system to play an increasing part and so reduces the difference between the inner and the outer X-O bonds.

For the final point, we return to the  $XO_4$  ions and recall that the observed bond lengths are shorter than the expected single-bond distances by amounts which increase from 0.13 Å in  $SiO_4^{4-}$  to 0.22<sub>5</sub> Å in  $ClO_4^-$ . This was interpreted in terms of two  $\pi$ -bonding molecular orbitals, whose group overlaps Jaffé<sup>13</sup> showed to increase markedly from silicon to chlorine owing to the increasing effective nuclear charge for the X(3*d*) orbitals. There is no obvious reason why we should not carry on to the next member of the series, argon tetroxide, and we may therefore predict that, when the difficulties of preparation have been overcome, the neutral molecule  $ArO_4$  will be found to have an Ar-O bond of length about 1.45 Å.

(Note added October 27th, 1961). Dr. Helen M. Ondik (personal communication) has recently completed structure analyses of the triclinic form of  $Na_4P_4O_{12} \cdot 4H_2O$  and  $LiK_2P_3O_9 \cdot H_2O$ . In the  $P_4O_{12}$  ion the average lengths of the two kinds of P-O ring bonds are 1.608 Å and 1.594 Å ( $\pm 0.005$  Å), so that their difference is much smaller than in the two less accurate analyses discussed above. This agrees better with the present theory. In the  $P_3O_9$  ion the average bond lengths are 1.61 Å (ring) and 1.48 Å (external), and the average P-O-P angle is  $129^\circ$ .

Results for a structure of type  $PO_4R^{2-}$  have been given for calcium thymidylate (Trueblood, Horn, and Luzzati, *Acta Cryst.*, 1961, 14, 965). With approximate rotational

corrections of 0.01 Å, the lengths are P-O(R) = 1.60 Å and P-O = 1.50 Å ( $\pm 0.01$  Å). With the relation of Fig. 20 the predicted lengths are 1.63 and 1.52 Å. The difference between the two lengths is thus about right, but the average P-O length in this structure seems unusually low.

## APPENDIX

*The Chlorine-Oxygen 3d $\pi$ -2p $\pi$  Overlap Integral.*—No directly relevant self-consistent-field calculations are available, but comparison with s.c.f. wave functions<sup>75</sup> for atoms in the first long row shows that the Slater rules<sup>76</sup> seriously underestimate the effective nuclear charge for 3d-orbitals. For instance, in Ti<sup>+</sup>, with three 3d-electrons outside a complete 3s,3p-shell, the Slater rules give a screening number of  $18 + 2 \times 0.35 = 18.7$  and an effective nuclear charge of  $22 - 18.7 = 3.3$ , whereas the s.c.f. calculations correspond to a screening number of 15.6 and an effective nuclear charge of 6.4. This implies that the 3d-electrons considerably penetrate the 3s,3p-shell. As other s.c.f. results suggest a screening number of 0.3 from each other 3d-electron, we may roughly take the screening from each 3s,3p-electron in Ti<sup>+</sup> as  $(15.6 - 10 - 2 \times 0.3)/8 = 0.625$ . In the perchlorate ion this suggests a screening number of  $10 + 4 \times 0.625 + 2.2 \times 0.3 = 13.16$  for a 3d-electron, if the chlorine has a net charge of -0.2 (the precise charge is not important). For an oxygen with a charge of -0.2 the s.c.f. results suggest a screening number of about 4.0. With the appropriate effective nuclear charges of 3.84 and 4.0 and a Cl-O distance of 1.464 Å, Jaffé's tables<sup>77,13</sup> give the overlap integral for 3d $\pi$  with a single 2p $\pi$  as  $\sim 0.37$ , so that the group overlap in the E molecular orbital is  $\sim 1.63 \times 0.37 = 0.60$ . This estimate is obviously rather speculative, but it is supported by Jaffé's calculations with different assumptions.<sup>13</sup>

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<sup>75</sup> Hartree, "The Calculation of Atomic Structures," John Wiley, New York, 1957.

<sup>76</sup> Slater, *Phys. Rev.*, 1930, **36**, 57.

<sup>77</sup> Jaffé, *J. Chem. Phys.*, 1953, **21**, 258.