The dimensions of the tetraphenylarsonium cation are similar to those found in other crystal structure analyses. The ranges of bond lengths and angles are as follows:

As–C 1·90 (1)–1·92 (1) Å; C–As–C 106·2 (6)–113·2 (6)°; C–C 1·34 (2)–1·47 (2) Å; C–C–C 116·5 (15)–124·7 (15)°.

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The Prediction of the Stereochemistry of Polysulphate and Hydrogen Sulphate Ions

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The angles in nine polysulphate and hydrogen sulphate ions are predicted to within 1·5° using two empirical relations, one involving the lengths of the bonds which define the angle, the other involving the configuration of the bonds around the bridging oxygen atom. Using, in addition, the bond strength relations of Brown & Shannon it is possible to predict *a priori* the complete geometry of the $S_2O_7^{2-}$ ion to an accuracy of 0·013 Å and 0·8°. The variations in angle can be understood equally well by assuming that they are caused by O–O repulsion or by variation in the strengths of the S–O bonds.

In most crystals the sulphate ion, SO_4^{2-}, shows a remarkable regularity, variations from $\bar{4}3m$ (Td) symmetry usually being quite small, but in the polysulphate and hydrogen sulphate ions much larger variations are found. The bond lengths can range from 1·36 to 1·83 Å and the angles from 97 to 128°. This paper shows that it is possible to make quantitative predictions of these effects.

The variations in bond length in SO_4 groups have been discussed in terms of π bonding by Cruickshank (1961), but they can also be understood in terms of the bond strength or bond valence theory by which it is assumed that the formal valence of an atom is shared among the bonds it forms. Thus in a regular SO_4^{2-} ion the valence, 6, of sulphur is shared equally between the four S–O bonds, each having a bond strength of 1·5 valence units (v.u.). The oxygen atoms have a valence of 2 and consequently form additional bonds with a total strength of 0·5 v.u. to other atoms in the crystal. Where the sulphur valence is shared unequally between the bonds the effect is manifest in the unequal lengths of the S–O bonds. Brown & Shannon (1973) have recently determined an empirical relationship between bond length (R) and bond strength (s) of the form:

$$s=(R/R_0)^{-N} \qquad (1)$$

where $R_0=1{\cdot}622$ and $N=4{\cdot}290$ for S–O bonds.

This relationship can be used either to determine bond strengths when the bond lengths are known or, if an *a priori* estimate of the bond strengths can be made, it can be used to predict the bond lengths. The regularity of most SO_4^{2-} ions arises because the very weak bonds ($s\sim0{\cdot}15$) formed between most metallic cations and oxygen cause only small variations in the S–O bond strengths.

In the case of the polysulphate and hydrogen sulphate ions, at least one of the oxygen atoms (here designated as bridging) is bonded to two sulphur atoms or one sulphur and one hydrogen atom. Consequently its valence is more nearly equally shared between these two bonds giving rise to bonds of strength close to 1 v.u. with lengths of about 1·62 Å. The remaining oxygen atoms (here designated as terminal) are correspondingly more strongly bound with the bond-length shortening from the normal 1·47 to 1·43 Å. The effect is less marked in the hydrogen sulphate ions since the O–H bond typically has a bond strength of 0·85 v.u. (Brown & Shannon, 1973) so that the strength of the S–O bond will be 1·15 v.u. corresponding to a length of 1·57 Å.

Two different theories have been offered to explain the wide range of angles found in the SO_4 group. Baur (1970) assumes that the contact repulsion between the O atoms is sufficiently large to ensure that the oxygen atoms remain at the corners of a regular tetrahedron and the variation in angle is the result of the sulphur atom moving away from the centre of the tetrahedron. Thus the shortening of an S–O bond results in the increase of the angles between it and neighbouring bonds. On the other hand Louisnathan & Gibbs (1972) associate the increase in O–S–O angle with an increase

Table 1. *Predicted bond lengths and angles for* $S_2O_7^{2-}$ *and values observed in* $K_2S_2O_7$ (*Lynton & Truter*, 1960)

(*a*) Calculation of bond lengths.

	Bond strength (v.u.) assumed	Bond length (Å) calculated	Bond length (Å) observed
S–O(*b*)	1·00	1·622	1·645 (5)
S–O(*t*1)	1·67	1·440	1·428 (7)
S–O(*t*2)	1·67	1·440	1·438 (7)
S–O(*t*3)	1·67	1·440	1·447 (7)

Standard deviation 0·013 Å

(*b*) Calculation of bond angles (equation 2).

	Bond length effect (°)	Correction for configuration effect (°)	Angle (°) predicted	Angle (°) observed
O(*b*)—S–O(*t*1)	104·6	−3·2	101·4	101·3 (4)
O(*b*)—S–O(*t*2)	104·6	+1·6	106·2	106·1 (4)
O(*b*)—S–O(*t*3)	104·6	+1·6	106·2	106·2 (4)
O(*t*1)–S–O(*t*2)	114·8	+0·6	115·4	115·5 (4)
O(*t*1)–S–O(*t*3)	114·8	+0·6	115·4	113·6 (4)
O(*t*2)–S–O(*t*3)	114·8	−1·2	113·6	112·8 (4)

Standard deviation 0·8°

(*c*) Calculation of bond angles (equation 3).

	Bond length effect (°)	Correction for configuration effect (°)	Angle (°) predicted	Angle (°) observed
O(*b*)—S–O(*t*1)	104·4	−3·2	101·2	101·3 (4)
O(*b*)—S–O(*t*2)	104·4	+1·6	106·0	106·1 (4)
O(*b*)—S–O(*t*3)	104·4	+1·6	106·0	106·2 (4)
O(*t*1)–S–O(*t*2)	114·6	+0·6	115·2	115·5 (4)
O(*t*1)–S–O(*t*3)	114·6	+0·6	115·2	113·6 (4)
O(*t*2)–S–O(*t*3)	114·6	−1·2	113·4	112·8 (4)

Standard deviation 0·7°

Table 2. *Agreement between observed and calculated* O–S–O *angles in polysulphates and hydrogen sulphates*

	P (Å)	s_0 (v.u.)	σ (°)	$\langle\theta_{obs}-\theta_{calc}\rangle_{rms}$		$\langle\theta_{obs}-\theta_{calc}\rangle_{rms}/\sigma$		Reference
				eqn 2	eqn 1,3	eqn 2	eqn 1,3	
$H_3OH.SO_4$	2·41	1·52	0·2	1·0	1·1	5·0	5·5	*a*
$NaHSO_4.H_2O$	2·43	1·47	1·7	0·6	1·3	0·4	0·8	*b*
$KHSO_4$	2·43	1·47	2·0	1·8	1·1	0·9	0·6†	*c*
	2·43	1·46	2·0	1·7	1·8	0·8	0·9	
NH_4HSO_4	2·38	1·60	0·4	1·2	1·1	3·0	2·7	*d*
	2·41	1·53	0·4	1·5	1·2	3·8	3·0	
$RbHSO_4$	2·40	1·54	1·4	1·5	1·5	1·1	1·1	*e*
	2·39	1·57	1·4	1·2	1·5	0·9	1·1	
$K_2S_2O_7$*	2·43	1·49	0·8	1·3	1·1	1·6	1·4	*f*
$Se_4(HS_2O_7)_2$	2·44	1·50	2·0	1·5	1·4	0·8	0·7	*g*
	2·46	1·42	2·0	1·6	1·7	0·8	0·8	
$K_2S_5O_{16}$	2·44	1·48	1·4	0·8	1·7	0·6	1·2	*h*
	2·46	1·45	1·1	1·6	1·3	1·5	1·2	
	2·48	1·48	0·9	3·8	1·4	4·2	1·5	
γ-S_3O_9	2·46	1·46	2·0	1·8	1·9	0·9	1·0	*i*
	2·47	1·43	2·0	1·8	2·4	0·9	1·2	
	2·45	1·50	2·0	2·3	1·8	1·1	0·9	

P = O–O distance expected for a regular SO_4 ion having an S–O distance equal to the observed average S–O distance.

s_0 = mean of the bond strengths calculated from the observed S–O distances.

σ = standard error in $\langle\theta_{obs}-\theta_{calc}\rangle_{rms}$ calculation from the experimental errors in both observed and calculated angles.

References: (*a*) Taesler & Olovsson (1968), (*b*) Pringle & Broadbent (1965), (*c*) Cruickshank (1964), (*d*) Nelmes (1971), (*e*) Ashmore (1971), (*f*) Lynton & Truter (1960), (*g*) Brown, Crump & Gillespie (1971), (*h*) De Vries & Mijlhoff (1969), (*i*) McDonald & Cruickshank (1967).

† This group has the configuration shown in Fig. 1(*b*).

* Angles calculated from the observed (not the predicted) bond lengths.

in the π bonding. Using extended Hückel molecular orbital theory, they show that an increase in the angles formed between a bond and its neighbours results in a larger overlap population for the bond. Both theories account moderately well for the observed variations in O–S–O angles with S–O bond lengths (the bond-length effect).

There is, however, a second smaller variation in angle that is associated only with the *configuration* of the SO_4 ion (the configuration effect). It is observed that even when allowance has been made for the bond-length effect, all the S–O bonds move towards the SO_4 ion's pseudo $\bar{4}$ axis* [the z axis in Fig. 1(*a*)] which lies in the plane defined by the S–O(bridging)–S (or H) atoms, the terminal S–O bonds moving by 0·6° and the bridging S–O bond moving by 2·6°. When more than one oxygen atom is bridging, as in the $S_5O_{16}^{2-}$ ion, this angular effect is applied successively for each bridging bond treating the other three bonds as terminal.

It is possible to calculate the individual angles expected in polysulphate and hydrogen sulphate groups from these two effects, the bond length and the configuration effect. The configuration effect can be applied using the empirical correction described above and the bond length effect can be applied in one of two ways depending on whether one assumes that the effect is the result of O–O repulsion or improved bonding overlap.

If the oxygen atoms are assumed to be in contact in the form of a regular tetrahedron, then the relationship between the S–O bond lengths, R_1 and R_2, and the included angle, θ_{12}, is given by the geometrical relation (cosine rule)

$$\cos\theta_{12}=(R_1^2+R_2^2-P^2)/2R_1R_2 \qquad (2)$$

where P is the O–O distance calculated for a regular tetrahedron having the observed average S–O bond length.

On the other hand, if the variation of angle is the result of improved bonding, the correct expression to use cannot be so easily derived. One can assume that the bond strengths of Brown & Shannon (1973) give a proper measure of the strength of bonding and that the relationship between bond strength and angle is linear. If this is true, the expression for θ_{12} will be of the form

$$\theta_{12}=109{\cdot}5+k(s_1+s_2-2s_0) \qquad (3)$$

where k is an empirical constant equal to 15·3°/v.u., s_1 and s_2 are the strengths (calculated from equation 1) of the bonds defining the angle and s_0 is the mean bond strength for the particular SO_4 group (s_0 normally lies close to 1·50 v.u.).

In certain cases, such as the $S_2O_7^{2-}$ ion, it is possible to make an *a priori* prediction of the bond strengths and hence predict the bond lengths as well as the angles. One can assume that the S–O (bridging) bonds have a strength of 1·00 v.u., that the S–O (terminal) bonds have a strength of 1·67 v.u. each and that the configuration is that shown in Fig. 1(*a*) for both halves of the ion. The resulting predictions of the bond lengths (using equation 1) and angles (using equation 2 or 3 and correcting for the configuration effect in each case) deviate from the observed values in $K_2S_2O_7$ (Table 1) by 0·013 Å and 0·8° respectively, being only twice the indicated standard error in the observed values.

In cases where one cannot make an unambiguous *a priori* assignment of bond strength one can calculate the angles from the observed bond lengths. Angles for

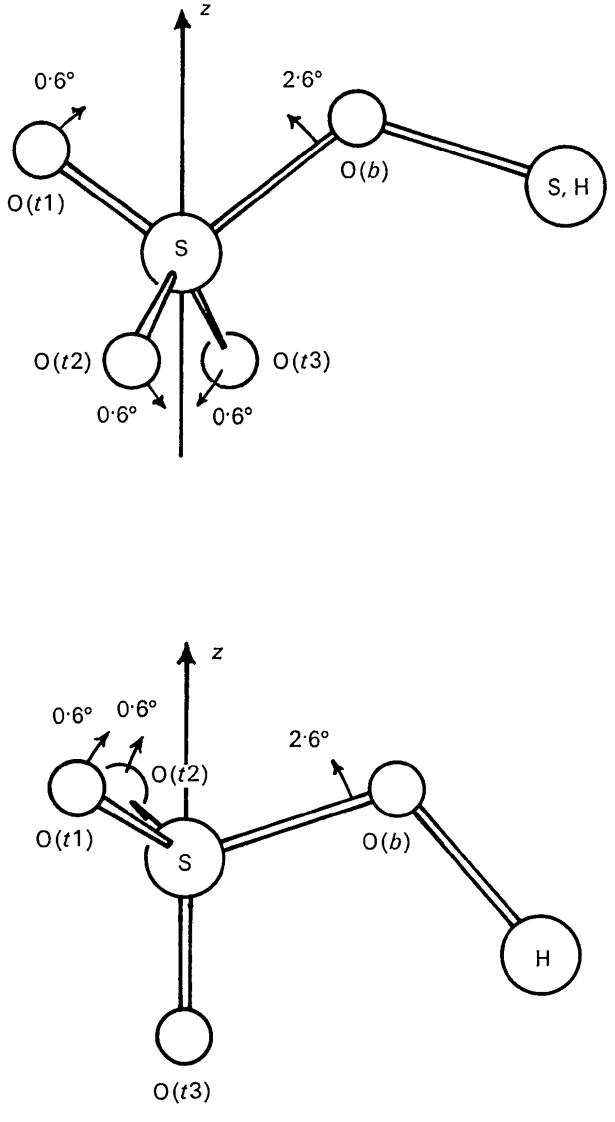

Fig. 1. The effect of configuration on O–S–O angles in sulphates: (*a*) normal configuration, (*b*) configuration observed in one of the HSO_4 groups in $KHSO_4$.

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* This observation applies for the normal configuration found [Fig. 1(*a*)]. The configuration shown in Fig. 1(*b*) is found for one of the HSO_4 groups in $KHSO_4$. Here the z axis is a pseudo-threefold axis.

nine polysulphate and HSO_4 groups have been calculated using both the bond-length and configuration effects. The bond-length effect has been calculated in two ways: using either equation 2 or equations 1 and 3. The results of the two calculations are plotted in Figs. 2 and 3 respectively and are summarized in Table 2. The standard deviation between the observed and calculated angles is 1·6° in the first case and 1·5° in the second and is the same as the standard error in most of the experimental measurements. Both methods give an equally good fit, except that equation 2 predicts values about 6° too large for the angles between the terminal bonds in the last sulphate group of the $S_5O_{16}^{2-}$ chain. Since the bridging S–O bond in this case is extremely long (1·83 Å) the average O–O distance is also longer (2·48 Å) than usual. However, the observed O–O distances corresponding to these anomalously small angles are still as large as those found in other SO_4 groups (2·42 Å) indicating that little relief from anion repulsion would occur by keeping the O_4 tetrahedron regular. Thus it is not possible using evidence from the sulphates to discriminate between the two theories represented by equations 2 and 3.

If anion repulsion is the cause for the variations, the effect should become progressively less marked for phosphates, silicates and aluminates in that order, since the O–O distances become progressively larger. Louisnathan & Gibbs (1972) show this to be the case but they also show that the variation of bond overlap populations becomes less sensitive to angle in the same progression. However, the remarkable uniformity of the angles in the dichromate ions (Brown & Calvo, 1970) even though the range of bond strengths matches that in the sulphates, suggests that the bond-length effect results from anion repulsion. The shortest O–O distance found in the dichromates (2·6 Å) is much larger than that (2·4 Å) normally found in the sulphates.

The configuration effect is itself a combination of two effects, a movement of all atoms towards the *z* axis by 0·6° and a further tilting of the S–O(*b*) bond in the same sense by 2°. The latter effect has been observed in Cl_2O_7 by Beagley (1965), in $(CH_3)_2O$ by Blukis, Kasai & Meyers (1963) and in $(CH_3)_2S$ by Pierce & Hayashi (1961). Blukis *et al.* (1963) attribute the effect to repulsion between the atoms on opposite sides of the bridge but the fact that it is observed for C–O–C (C–O ~ 1·41 Å), C–S–C (C–S ~ 1·80 Å), Cl–O–Cl (Cl–O ~ 1·71 Å) and S–O–S (S–O ~ 1·62 Å) bridges but not for C–C–C (C–C ~ 1·54 Å) and C–Si–C (C–Si ~ 1·87 Å) bridges (Pierce & Hayashi, 1961) suggests that the effect is related to the presence of unpaired electrons on the bridging atom.

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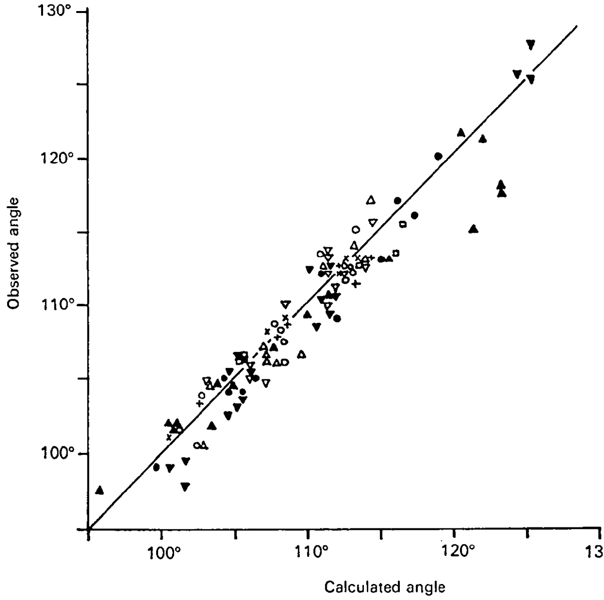

Fig. 2. A plot of the observed (vertical axis) *vs.* the calculated (horizontal axis) O–S–O angles assuming anion repulsion (equation 2). For key to symbols, see Fig. 3.

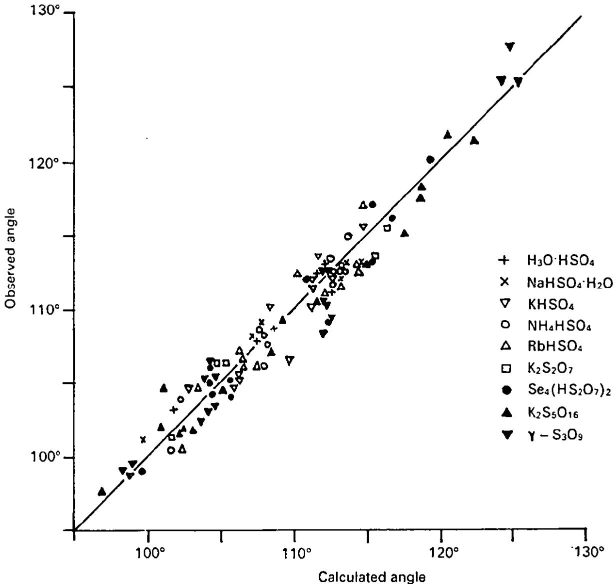

Fig. 3. A plot of the observed (vertical axis) *vs.* the calculated (horizontal axis) O–S–O angles assuming improved bonding (equations 1 and 3).

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Effect of Neglect of Dispersion in Centrosymmetric Structures: Results for OsO_4

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The 0·03 Å difference between the Os–O bond lengths reported for crystalline and gaseous OsO_4 is shown not to be caused by neglect of anomalous dispersion corrections in the crystallographic refinement of a centrosymmetric structure. Small shifts in the scale factor and vibration parameters caused by anomalous dispersion are explained by a simple theory.

The crystal structure of OsO_4 (space group $C2/c$) was determined and refined by Ueki, Zalkin & Templeton (1965), who showed that it contains nearly tetrahedral molecules OsO_4, with average Os–O bond distance $1·74 \pm 0·02$ Å, uncorrected for the thermal motion. The same molecule was studied by gas electron diffraction (Seip, 1967) and the bond distance R_g was $1·712 \pm 0·002$ Å. We have examined whether this disagreement could be due to the lack of allowance in the X-ray investigation for the anomalous dispersion of Os ($\Delta f' = -1·55$ and $\Delta f'' = 8·60$ for Mo $K\alpha$ radiation). Despite the theoretical arguments (Cruickshank & McDonald, 1967) that no significant shifts in atomic positions are to be expected for a centrosymmetric structure, we thought it worth while to undertake actual refinement in a case with a very large anomalous contribution.

Refinement

The cell dimensions of OsO_4 are $a = 9·379$, $b = 4·515$, $c = 8·632$ Å, $\beta = 116·6°$. The data used were the observed structure factors of Ueki, Zalkin & Templeton, with unit weight assigned to each of the 479 reflexions as in the original paper. The refinement was carried out with the *CRYLSQ* program of F. A. Kundell, in which the anomalous dispersion terms are included in all structure-factor and derivative calculations. Four different full-matrix refinements of two cycles each were carried out, starting from the original parameters:

(1) without any dispersion term. The maximum shift/error in the refinement was 0·1 with no change in R. The reference parameters in the first column of Table 1 are from this refinement;
(2) correcting only for $\Delta f'' = 8·60$ on Os;
(3) correcting only for $\Delta f' = -1·55$ on Os;
(4) correcting for $\Delta f''$ and $\Delta f'$ on Os.

The results are shown in Table 1. No significant shifts in coordinates occur for the three refinements with dispersion correction. Thus lack of correction for dispersion cannot explain the difference between the X-ray and electron-diffraction values of the Os–O bond length. (The individual lengths from the fourth refinement are 1·760 and 1·715 Å. The mean is $1·738 \pm 0·020$ Å, to which a rotational correction of about 0·02 Å must be added. The difference from the electron-diffraction value of $1·712 \pm 0·002$ Å would be significant at between the 5% and 1% levels if the rotational correction were reliable.)

The only noticeable changes in the refinements are to the scale factor and the vibration parameters of the heavy atom. Moreover, in this structure, the error produced by neglecting $\Delta f''$ is about the same, and in the opposite direction, as the error produced by neglecting $\Delta f'$.

Scale and vibration-parameter errors

The small shifts in the scale factor and vibration parameters can be explained by simple theoretical considera-