there are no other contacts between the two $-PO_3$ groups corresponding to standard van der Waals distances, though the 23° twist of each $-PO_3$ group may be caused by repulsions O(2′)–O(2), O(2′)–O(4), O(4′)–O(2) and O(4)–O(4′), which are considerably relieved in the twisted configuration to give a nearly staggered structure with O(2′)–O(2) = 3·34 and O(2′)–O(4) = O(4′)–O(2) = 3·37 Å.

Similar tilts of the $-SO_3$ groups relative to the S–O (bridge) directions occur in crystalline $K_2S_2O_7$ (Lynton & Truter, 1960), $K_2NH(SO_3)_2$ (Cruickshank & Jones, 1963) and $K_2CH_2(SO_3)_2$ (Truter, 1962). Lacking the results for gaseous Cl_2O_7, these authors did not appreciate that the distortions were of intramolecular origin. Hirshfeld (1964) would consider that such tilts indicate bent X–O(bridge) bonds, and on his recipe the 'valency angles' in the bisulphates are 118° when O is the bridge atom, 119° for NH and 114° for CH_2, as compared with geometrical S–A–S angles of 124°, 126° and 120°. In Cl_2O_7 the reduction is to 109° from 119°. These 'valency angles' are more acceptable than the geometrical angles. The corresponding 'valency angle' for sodium pyrophosphate is 127°.

Of the three bond lengths in the $-PO_3$ group, P–O(3) = 1·512 Å is slightly the shortest. This seems to correlate with the involvement of O(3) in the smallest O–P–O(1) angle, since a similar effect occurs in the above three sulphates.

One of us (W.S.M.) thanks the Science Research Council for a Studentship.

References

Beagley, B. (1965). *Trans. Faraday Soc.* **61**, 1821.
Calvo, C. (1965*a*). *Canad. J. Chem.* **43**, 1139.
Calvo, C. (1965*b*). *Canad. J. Chem.* **43**, 1147.
Calvo, C. (1966). In the press.
Corbridge, D. E. C. (1957). *Acta Cryst.* **10**, 85.
Cruickshank, D. W. J. (1964). *Acta Cryst.* **17**, 672.
Cruickshank, D. W. J. & Jones, D. W. (1963). *Acta Cryst.* **16**, 877.
Hirshfeld, F. L. (1964). *Israel J. Chem.* **2**, 87.
Lynton, H. & Truter, M. R. (1960). *J. Chem. Soc.* p. 5112.
MacArthur, D. M. & Beevers, C. A. (1957). *Acta Cryst.* **10**, 428.
Robertson, B. E. & Calvo, C. (1966). In the press.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
Truter, M. R. (1962). *J. Chem. Soc.* p. 3393.
Webb, N. C. (1966). *Acta Cryst.* **21**, 942.

Acta Cryst. (1967). **22**, 48

A Refinement of the Structure of S_3O_9

By W. S. McDonald and D. W. J. Cruickshank
Chemistry Department, University of Glasgow, Glasgow W.2, *Scotland*

(*Received* 8 *June* 1966)

After refinement with the data of Pascard & Pascard-Billy (1965) the molecular dimensions are S–O (ring) 1·626 ± 0·007 Å, S–O(axial) 1·371 ± 0·013 Å, and S–O(equatorial) 1·430 ± 0·013 Å. Owing to the polar space group, it was found necessary to correct for the imaginary component of the anomalous scattering of S and O.

Introduction

The γ form of sulphur trioxide was examined by Westrik & MacGillavry (1941), who showed that it contained cyclic S_3O_9 molecules. Pascard & Pascard-Billy (1965) obtained fresh three-dimensional data and carried out a refinement of the structure. Their published molecular dimensions, however, showed anomalies as there were some large differences between the lengths of chemically equivalent bonds. Thus the six S–O bonds of the ring ranged from 1·53 to 1·65 Å, and the three equatorial S–O bonds were 1·40, 1·33 and 1·40 Å, all with quoted standard deviations of 0·016 Å. Because of these rather implausible dimensions, the published data of Pascard & Pascard-Billy were used for a new least-squares refinement.

Cell dimensions

The space group is $P2_1nb$ with 4 molecules in the cell. The cell dimensions given by Pascard & Pascard-Billy are $a = 5{\cdot}13 \pm 0{\cdot}05$, $b = 10{\cdot}82 \pm 0{\cdot}02$, $c = 12{\cdot}40 \pm 0{\cdot}02$ Å, corresponding to 5·3, 10·7 and 12·3 Å given by Westrik & MacGillavry. At a late stage of our refinement we wondered whether the unusually short bond-lengths of the axial S–O bonds were really due to an error in the *a*-axis dimension. Mr Kreuger and Dr C. Stam of the University of Amsterdam were then kind enough to make measurements of a new *h*0*l* Weissenberg photo-

---

* Present address: Chemistry Department, University of Leeds, Leeds 2, England.

graph. A least-squares calculation with 13 reflexions, having θ ranging from 44 to 84°, gave $a=5\cdot191\pm0\cdot009$ and $c=12\cdot384\pm0\cdot006$ Å in satisfactory agreement with the Pascards' dimensions. These more accurate values, together with $b=10\cdot82$ Å, were used in our calculations of the molecular dimensions.

Least-squares refinement

The data used were the observed structure factors of Pascard & Pascard-Billy. An initial structure-factor calculation, using their final parameters, indicated that the observed and calculated values for the 032 reflexion were incorrectly given in Table 3 of their paper, and that the $30l$ reflexions had been listed as $31l$. The 032 reflexion was omitted, and refinement of the scale factor, coordinates and vibration parameters was then carried out with the KDF9 program of J. G. F. Smith and D. W. J. Cruickshank. The weighting scheme was

$$w=1/(7+|F_o|+0\cdot02|F_o|^2)\ .$$

Two cycles of full-matrix isotropic refinement reduced the R value to 0·142, and four cycles of block-diagonal anisotropic refinement led to convergence at an R value of 0·117.

Further refinement was carried out with allowance for the real and imaginary components of the anomalous scattering of sulphur. As the space group is polar, neglect of the small imaginary component effect ($\Delta f''=0\cdot6$) could give rise to rather large coordinate errors (Ueki, Zalkin & Templeton, 1966). The lengths of the axial S–O bonds, which are approximately parallel to the polar axis, are particularly affected by such errors. Assuming that the experimental data were hkl rather than $hk\bar{l}$, on completion of the new refinement the mean axial S–O bond length increased from 1·353 to 1·373 Å. When the anomalous scattering of oxygen ($\Delta f''=0\cdot1$) was also included, the mean length became 1·365 Å, showing that even the very small effect for oxygen produced appreciable errors in molecular dimensions.

Table 1. *Final fractional coordinates and e.s.d.'s*

	x	y	z
S(1)	0·2090 (22)	0·1304 (6)	0·0819 (4)
S(2)	0·0407 (24)	0·3055 (6)	−0·0731 (4)
S(3)	0·0000 (0)	0·3590 (6)	0·1487 (4)
O(1)	0·1261 (52)	0·0074 (18)	0·1029 (15)
O(2)	0·4537 (53)	0·1754 (23)	0·0835 (17)
O(3)	0·0706 (45)	0·1623 (12)	−0·0321 (11)
O(4)	−0·1469 (61)	0·2940 (24)	−0·1585 (14)
O(5)	0·2737 (51)	0·3648 (21)	−0·0817 (14)
O(6)	−0·1138 (38)	0·3608 (16)	0·0270 (12)
O(7)	0·2327 (42)	0·4165 (18)	0·1483 (13)
O(8)	−0·2069 (48)	0·3889 (18)	0·2174 (15)
O(9)	0·0254 (56)	0·2112 (14)	0·1619 (11)

The final scale factor for Pascard's $|F_o|$ data was 0·964, and the R value was 0·114. The final coordinates and e.s.d.'s are given in Table 1, and the vibration parameters in Table 2.

Molecular dimensions

A rigid-body molecular vibration analysis was carried out by the method of Cruickshank (1956), with coordinate corrections obtained according to Cruickshank (1961*a*). The calculations were performed on a KDF9 computer, using a program written by K. W. Muir and W. S. McDonald. The principal values of the vibration tensor $\mathbf{T}$ are 0·0391, 0·200 and 0·0295 Å², and of the libration tensor, $\boldsymbol{\omega}$, 24·7, 10·3 and 14·9 deg². The direction of maximum vibration is approximately in the crystallographic y direction (direction cosines −0·143, 0·990, 0·001). The axis of maximum libration has direction cosines −0·241, 0·761, 0·603, and is approximately parallel to the S(3)···O(3) direction.

The corrections to the bond lengths are quite small, ranging from 0·004 to 0·008 Å. Table 3 gives the cor-

Table 3. *Bond lengths*

Bond	Uncorrected length	Corrected length	e.s.d.
S(1)–O(3)	1·621 Å	1·629 Å	0·016 Å
S(1)–O(9)	1·629	1·635	0·020
S(2)–O(3)	1·637	1·645	0·014
S(2)–O(6)	1·593	1·599	0·016
S(3)–O(6)	1·619	1·627	0·015
S(3)–O(9)	1·612	1·619	0·016
S(1)–O(1)	1·423	1·428	0·021
S(2)–O(4)	1·443	1·448	0·024
S(3)–O(8)	1·409	1·413	0·021
S(1)–O(2)	1·361	1·367	0·025
S(2)–O(5)	1·374	1·380	0·024
S(3)–O(7)	1·359	1·365	0·020

Table 2. *Vibration tensor components and e.s.d.'s* (Å²)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
S(1)	0·039 (5)	0·041 (3)	0·034 (3)	0·003 (5)	−0·008 (5)	0·007 (8)
S(2)	0·049 (5)	0·040 (3)	0·021 (2)	0·007 (4)	−0·006 (5)	0·001 (7)
S(3)	0·029 (4)	0·056 (4)	0·028 (2)	−0·017 (5)	−0·011 (5)	0·005 (7)
O(1)	0·071 (18)	0·036 (9)	0·060 (10)	0·018 (17)	0·011 (24)	−0·006 (19)
O(2)	0·054 (23)	0·073 (14)	0·055 (12)	−0·016 (21)	−0·040 (20)	0·023 (27)
O(3)	0·062 (16)	0·025 (8)	0·028 (7)	−0·003 (12)	−0·026 (16)	0·001 (17)
O(4)	0·075 (18)	0·104 (17)	0·032 (9)	0·003 (18)	−0·027 (24)	−0·036 (30)
O(5)	0·041 (17)	0·065 (13)	0·052 (10)	0·025 (19)	0·008 (20)	−0·005 (23)
O(6)	0·018 (11)	0·058 (11)	0·033 (8)	0·015 (14)	−0·027 (15)	0·009 (19)
O(7)	0·032 (13)	0·056 (11)	0·049 (9)	−0·017 (16)	−0·007 (17)	−0·045 (20)
O(8)	0·047 (16)	0·054 (11)	0·056 (11)	−0·010 (18)	−0·005 (21)	−0·015 (19)
O(9)	0·059 (13)	0·042 (9)	0·026 (6)	−0·016 (13)	0·013 (19)	−0·014 (22)

rected and uncorrected bond lengths, with their e.s.d.'s. The bond angles and the principal non-bonded intramolecular contacts (uncorrected) are given in Tables 4 and 5 respectively.

Table 4. *Bond angles*

Angle		e.s.d.
O(3)–S(1)–O(9)	99·0°	1·0
O(3)–S(2)–O(6)	99·3	0·8
O(6)–S(3)–O(9)	97·8	0·8
O(1)–S(1)–O(2)	127·9	1·5
O(4)–S(2)–O(5)	125·3	1·2
O(7)–S(3)–O(8)	125·1	1·2
O(1)–S(1)–O(3)	103·0	1·0
O(1)–S(1)–O(9)	102·4	1·1
O(4)–S(2)–O(3)	102·1	1·2
O(4)–S(2)–O(6)	105·2	1·3
O(8)–S(3)–O(6)	106·4	1·0
O(8)–S(3)–O(9)	103·2	1·1
O(2)–S(1)–O(3)	110·5	1·1
O(2)–S(1)–O(9)	110·2	1·3
O(5)–S(2)–O(3)	112·5	1·3
O(5)–S(2)–O(6)	109·2	1·0
O(7)–S(3)–O(6)	108·4	0·9
O(7)–S(3)–O(9)	112·5	1·2
S(1)–O(3)–S(2)	120·9	0·9
S(2)–O(6)–S(3)	122·4	1·1
S(3)–O(9)–S(1)	121·2	1·1

Table 5. *Intramolecular non-bonded contacts*

O(1)···O(2)	2·501 Å	O(3)···O(6)	2·462 Å
O(4)···O(5)	2·502	O(6)···O(9)	2·435
O(8)···O(7)	2·456	O(9)···O(3)	2·471
O(1)···O(9)	2·381	O(2)···O(9)	2·457
O(1)···O(3)	2·385	O(2)···O(3)	2·454
O(4)···O(3)	2·399	O(5)···O(3)	2·508
O(4)···O(6)	2·414	O(5)···O(6)	2·421
O(8)···O(6)	2·427	O(7)···O(6)	2·420
O(8)···O(9)	2·371	O(7)···O(9)	2·474
O(2)···O(5)	3·043	S(1)···S(2)	2·834
O(5)···O(7)	2·910	S(2)···S(3)	2·814
O(7)···O(2)	2·961	S(3)···S(1)	2·824
S(1)···O(6)	3·079	S(1)···O(5)	3·263
S(2)···O(9)	3·084	S(1)···O(7)	3·205
S(3)···O(3)	3·110	S(2)···O(2)	3·215
		S(2)···O(7)	3·155
		S(3)···O(2)	3·185
		S(3)···O(5)	3·188

The anomalies between chemically equivalent bond lengths reported by Pascard & Pascard-Billy have disappeared, and the molecule does not deviate appreciably from $3m$ symmetry. The averaged dimensions are shown in Fig. 1. The mean S–O bond length in the ring is 1·626 ± 0·007 Å, and the mean axial and equatorial bond lengths are 1·371 and 1·430 ± 0·013 Å respectively. The difference in length between the ring and non-ring bonds is to be expected (see below), but the difference of 0·06 Å between the two types of peripheral bond is surprising. It is not predicted on a simple version of the π-bonding theory based on regular tetrahedral angles. There is also a significant difference between the mean angle O(bridge)–S–O(axial) = 110·6° and the angle O(bridge)–S–O(equatorial) = 103·7°, but though this could be correlated through hybridization effects with a greater σ- and π-bond strength for S–O(axial) it does not reveal the cause of the difference in length.

For the infinite chain $(SO_3)_\infty$ Cruickshank (1961*b*) calculated π-bond orders of 0·21 for the bridge bonds and 0·79 for the peripheral bonds. Similar π-bond orders would be expected for S_3O_9 and on the linear order/length relation given by Cruickshank the expected lengths are 1·61 and 1·37 Å. These are slightly smaller than the observed 1·626 and (mean) 1·400 Å: the discrepancies are chiefly a consequence of the unusually large average of 1·513 Å in S_3O_9 as compared with the 1·48–1·49 Å typical of most sulphates.

Gillespie & Robinson (1963*a*, *b*) have measured the stretching frequencies and have calculated a peripheral S–O force-constant of $11{\cdot}89 \times 10^5$ dyne.cm^{-1}. On their relation

$$kr^{7\cdot4} = 1{\cdot}41 \times 10^7$$

the S–O bond length comes out as 1·396 Å, in very close agreement with our mean of 1·400 Å. Following Lehmann (1961) they had averaged two frequencies, described as symmetric and asymmetric stretches, but if these frequencies (1250 and 1502 cm^{-1}) are assigned to the individual stretches of two distinct bonds, the above relation yields lengths 1·361 and 1·430 Å, which are remarkably close to the actual 1·371 and 1·430 Å. However, this assignment of individual frequencies is very dubious, since similar frequencies are found in SO_2F_2 where there is no question of inequality in the S–O bonds. The S–O(axial) bond of 1·371 ± 0·013 Å is thought to be the shortest S–O bond on record; it is regrettable that we can offer no explanation why it should be shorter than S–O(equatorial).

We have already commented (McDonald & Cruickshank, 1966) on the patterns among the O···O distances in the tetrahedral oxyions of Si, P, S and Cl. The mean distance between the two bridge oxygen atoms of a tetrahedron in S_3O_9 is 2·46 Å, which is

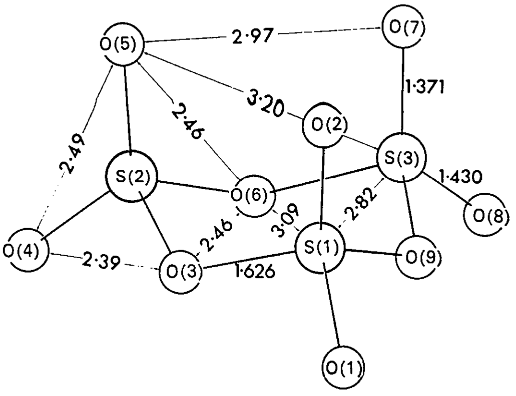

Fig. 1. Averaged dimensions of S_3O_9.

Table 6. *Intermolecular contacts*

x, y, z to $1+x, y, z$ and
$x-1, y, z$ to x, y, z

O(7)–O(8)	3·047 Å
O(2)–O(6)	3·091
O(2)–O(9)	3·146
O(5)–O(4)	3·246
O(2)–O(8)	3·346
O(5)–O(6)	3·453

x, y, z to $x-\frac{1}{2}, 1-y, -z$ and
$\frac{1}{2}+x, 1-y, -z$ to x, y, z

O(6)–O(5)	3·101
O(8)–O(5)	3·152
O(4)–O(7)	3·197
S(3)–O(5)	3·317
O(6)–O(7)	3·340
O(7)–O(5)	3·457

x, y, z to $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$ and
$x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$ to x, y, z.

O(9)–O(4)	2·801 Å
O(2)–O(4)	3·255
O(7)–O(4)	3·362
S(1)–O(4)	3·401
S(3)–O(4)	3·435

x, y, z to $\frac{1}{2}+x, -y, -z$ and
$x-\frac{1}{2}, -y, -z$ to x, y, z.

O(1)–O(3)	3·076
O(2)–O(1)	3·168
S(1)–O(1)	3·485

x, y, z to $x, y-\frac{1}{2}, \frac{1}{2}-z$ and
$x, y+\frac{1}{2}, \frac{1}{2}-z$ to x, y, z.

O(1)–O(8)	3·096
O(1)–O(7)	3·282

x, y, z to $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$ and
$x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$ to x, y, z.

O(3)–O(8)	3·356
O(4)–O(8)	3·390

almost the same as the 2·49 Å between the axial and equatorial peripheral atoms. Thus the O–S–O angles of 98·7 and 126·1° are consistent with their being determined by an equalization of the non-bonded contacts.

The axial oxygen atoms in neighbouring tetrahedra are 2·97 Å apart while the sulphur atoms are separated by only 2·82 Å; thus the S–O(axial) bonds are not parallel but diverge slightly. However, since the 2·97 Å is on the long side for a van der Waals contact and is much larger than the O···O distances within tetrahedra, it is unlikely that the divergence [and hence the tilt of, say, the O(4)S(2)O(5) group relative to the O(6)S(2)O(3) plane] is caused by a repulsion between axial oxygen atoms; it might just be caused by S···O repulsions.

The equations of the various planes in the molecule may be expressed as

$$0{\cdot}914X+0{\cdot}406Y-0{\cdot}010Z=d\,,$$

where X, Y, Z are coordinates in Å, and d is 0·643 Å for the equatorial oxygen atoms, 1·039 Å for the ring oxygen atoms, 1·551 Å for the sulphur atoms, and 2·912 Å for the axial oxygen atoms. The greatest displacements of any atoms from these planes are about two e.s.d.'s (for the three axial oxygen atoms). These displacements could be real distortions arising from packing forces.

In phosphates the differences between the lengths of bridge and peripheral bonds are rather smaller than in sulphates, thus in $Na_3P_3O_9$ (Ondik, 1965) the means are P–O(bridge) = 1·615 and P–O(peripheral) = 1·484 Å. However neither in this structure, nor in two other less accurate structures with $P_3O_9^{3-}$ groups (Eanes & Ondik, 1962), is there any evidence that P–O(axial) is shorter than P–O(equatorial). Both the triphosphate and the trisulphate have the chair configuration, so that the difference in S_3O_9 between the axial and equatorial lengths is particularly puzzling. In $Na_3P_3O_9$ there is a small difference between the angles O(bridge)–P–O(axial) = 109·7° and O(bridge)–P–O(equatorial) = 107·3°, which is in the same sense as in S_3O_9.

The molecular packing

Each molecule makes contacts of less than 3·4 Å with twelve neighbouring molecules. The molecules are arranged in a distorted hexagonal close-packed array, with the 'hexagonal' axis parallel to the crystallographic *b* axis. All intermolecular distances (calculated from the uncorrected coordinates) of less than 3·5 Å are listed in Table 6. Each molecule makes a total of 48 contacts of less than 3·5 Å with atoms of its 12 neighbours.

References

Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 754.

Cruickshank, D. W. J. (1961*a*). *Acta Cryst.* **14**, 896.

Cruickshank, D. W. J. (1961*b*). *J. Chem. Soc.* p. 5486.

Eanes, E. D. & Ondik, H. M. (1962). *Acta Cryst.* **15**, 1280.

Gillespie, R. J. & Robinson, E. A. (1963*a*). *Spectrochim. Acta*, **19**, 741.

Gillespie, R. J. & Robinson, E. A. (1963*b*). *Canad. J. Chem.* **41**, 2074.

Lehmann, W. J. (1961). *J. Mol. Spectroscopy*, **7**, 1.

McDonald, W. S. & Cruickshank, D. W. J. (1966). *Acta Cryst.* **22**, 37.

Ondik, H. M. (1965). *Acta Cryst.* **18**, 226.

Pascard, R. & Pascard-Billy, C. (1965). *Acta Cryst.* **18**, 830.

Ueki, T., Zalkin, A. & Templeton, D. H. (1966). *Acta Cryst.* **20**, 836.

Westrik, R. & MacGillavry, C. H. (1941). *Rec. Trav. chim. Pays-Bas*, **60**, 794.