S–O bonds of about 0·05 Å. Owing to the pseudosymmetry of the structure this is likely to be an underestimate, an impression which is confirmed by the fact that the three equivalent S–O bonds of the S(2) tetrahedron are all much shorter than those of the S(2′) tetrahedron. Accurate dimensions can probably be obtained only with full three-dimensional data, which would minimize the effects of the pseudosymmetry. The best course for the present is to average the chemically equivalent bonds and angles; these averages are shown in Fig. 2. The precise details are probably not very reliable, but the general features of the $S_3O_{10}^{2-}$ ion are similar to those of the isoelectronic $P_3O_{10}^{5-}$ ion (Davies & Corbridge, 1958; Cruickshank, 1964). The angles all correspond within 6° and the four distinct bond lengths show the same sequence, though the evidence from the much more accurate $P_3O_{10}^{5-}$ suggests that the difference between the lengths of S(1)–O(1) and S(2)–O(1) should be appreciably less. The angles between the planes S(2)–O(1)–S(1) and S(2′)–O(1′)–S(1) and the plane O(1)–S(1)–O(1′) are about 13° and 10° respectively, so that the five atoms S(2), O(1), S(1), O(1′) and S(2′) are roughly coplanar (indeed this is a plane of a pseudosymmetry for the whole ion) and the $p\pi$ orbitals on O(1) and O(1′) belong to essentially the same π-orbital system (Cruickshank, 1961).

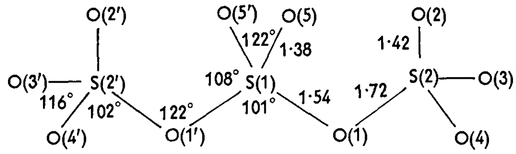

Fig. 2. Averaged dimensions of the $S_4O_{10}^{2-}$ ion.

The four N–O bonds in the nitronium ions average 1·12 Å, which is sufficiently close to the expected 1·14 Å (Truter, Cruickshank & Jeffrey, 1960). Both O–N–O angles are 166°; despite the rather large probable errors this is probably significantly different from 180° and agrees with Gerding & Eriks's (1952) interpretation of the Raman spectra in terms of slightly bent NO_2^+ ions.

One unsatisfactory feature of the interionic contacts obtained by Eriks & MacGillavry was the short 2·34 Å distance for the O(3)–N and O(3′)–N′ approaches. With the revised coordinates the minimum contact distance is 2·54 Å between O(4′) and N′. Further the original structure had a contact of 2·70 Å between an O(5) and an O(5′) of neighbouring $S_3O_{10}^{2-}$ ions; this has satisfactorily lengthened to 3·14 Å with the revised coordinates.

The main interionic contacts are between nitronium ions and oxygen atoms of the terminal sulphate groups. N is approached by five oxygen atoms from four $S_3O_{10}^{2-}$ ions: O(3) (2·93 Å) and O(4) (2·87 Å) of the same molecule, another O(4) (2·76 Å), an O(3) (2·68 Å) and an O(2) (2·75 Å). N′ is similarly approached by five oxygen atoms: O(3′) (2·92 Å) and O(4′) (2·96 Å), another O(4′) (2·54 Å) an O(3′) (2·56 Å) and an O(2′) (2·57 Å). These sulphate oxygen atoms also approach one or both of the nitronium oxygen atoms at distances down to 2·62 Å. There are also several contacts of about 3 Å between a terminal sulphate oxygen atom and the terminal oxygen atom only of a nitronium ion. As mentioned, O(5) and O(5′) of neighbouring ions approach to within 3·14 Å. In addition O(5) lies between the ends O(6) (2·75 Å) and O(6′) (2·89 Å) of two nitronium ions, and O(5′) between O(6) (2·84 Å) and O(6′) (2·80 Å) of other ions.

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Refinements of Structures Containing Bonds between Si, P, S or Cl and O or N. X. β–Ca_2SiO_4

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The crystallographic data given by Midgley (1952) have been used in a structure refinement. The revised bond length in the orthosilicate ion is $Si-O = 1{\cdot}62 \pm 0{\cdot}02$ Å.

The crystal structure of β dicalcium silicate, Ca_2SiO_4, was determined by Midgley (1952) from the three principal Fourier syntheses. Owing to overlapping, the orthosilicate tetrahedron was assumed to be nearly regular. Because of this and of the paucity of values for the Si–O bond lengths in orthosilicates, it

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appeared worth while refining the structure by least squares.

The space group is $P2_1/n$, with cell dimensions $a=5{\cdot}48$, $b=6{\cdot}76$, $c=9{\cdot}28$ Å and $\beta=94°\,33'$. All atoms are in general positions. The crystal structure consists of isolated orthosilicate ions and two kinds of calcium ions, one of which serves to link the tetrahedra in strings and the other of which fills the holes between tetrahedra. The structure is very similar to that of orthorhombic β-K_2SO_4.

The data used in the refinement were the 196 non-zero $|F_o|$ listed by Midgley. Four cycles of least-squares refinement were carried out. These produced coordinate shifts of up to 0·04 Å for calcium, 0·06 Å for silicon and 0·15 Å for oxygen. The residual R dropped from Midgley's 19% to a final 12·6%. The revised atomic coordinates and their nominal e.s.d.'s are given in Table 1. Anisotropic vibrations were allowed for Ca and Si (though the anisotropy had little effect on the residual) and isotropic vibrations for O. The final vibration parameters are given in Table 2. The e.s.d.'s are about 0·003 Å^2 for Ca, 0·004 Å^2 for Si and 0·006 Å^2 for O. The $|F_o|$ scale factor determined by the LS process was 0·97 ± 0·02. The weighting scheme used was

$$w = 1/(30+|F_o|+|F_o|^2/107)\,,$$

without the factor 0·97 applied to the $|F_o|$.

Table 1. *Atomic coordinates and e.s.d.*'s

Atom	x	y	z
Ca_{I}	1·45 ± 0·01 Å	2·32 ± 0·01 Å	3·99 ± 0·01 Å
Ca_{II}	1·52 ± 0·01	−0·01 ± 0·01	−2·78 ± 0·01
Si	1·36 ± 0·01	−1·49 ± 0·01	3·88 ± 0·01
O_{I}	1·67 ± 0·03	0·08 ± 0·03	4·03 ± 0·03
O_{II}	0·17 ± 0·03	−1·70 ± 0·03	2·87 ± 0·02
O_{III}	2·69 ± 0·04	−2·28 ± 0·04	3·36 ± 0·03
O_{IV}	0·89 ± 0·04	−2·20 ± 0·04	5·32 ± 0·03

The Si–O bond lengths are Si–O_{I} = 1·61, Si–O_{II} = 1·51, Si–O_{III} = 1·67 and Si–O_{IV} = 1·70 Å, with individual e.s.d.'s of about 0·04 Å. The O–Si–O bond angles are all within 5° of the regular tetrahedral value. The difference in the vibration amplitudes of the oxygen and silicon atoms implies a small bond length correction of about 0·006 Å, which is negligible in comparison with the e.s.d.'s. The main result of the refinement is therefore that the average Si–O bond length in the orthosilicate ion is 1·62 ± 0·02 Å.

Table 2. *Mean-square vibration amplitudes* (Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Ca_{I}	0·005	0·008	0·010	−0·007	0·002	0·002
Ca_{II}	0·006	0·009	0·006	0·002	0·000	−0·003
Si	0·009	0·009	0·008	−0·006	−0·004	0·003

	U
O_{I}	0·015
O_{II}	0·007
O_{III}	0·025
O_{IV}	0·020

Table 3. *Interatomic distances*

Atom	Number of neighbours	Neighbour	Distance
Ca_{I}	6 nearest	O_{I}	2·24 Å
		O_{II}	2·64
		O_{III}	2·26, 2·60
		O_{IV}	2·34, 2·69
	6 next nearest	O_{I}	3·53, 3·56
		O_{II}	3·08, 3·20
		O_{III}	3·19
		O_{IV}	3·15
Ca_{II}	8	O_{I}	2·49, 2·69
		O_{II}	2·35, 2·41*
		O_{III}	2·51, 2·71
		O_{IV}	2·42, 2·54

* There is also a Ca_{II}–O_{I} contact of 3·33 Å between the ions which have this 2·41 Å contact.

The revised distances between the calcium and oxygen atoms are given in Table 3. As indicated by Midgley, there is also a short O(1)–O(1) contact which is now 2·39 ± 0·06 Å. This is a shared edge of two Ca_{II} polyhedra and is probably not much different from the shared-edge lengths of 2·5 Å found in the aluminum octahedra of aluminosilicates.

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