Busing, W. R., Martin, K. O. & Levy, H. A. (1964). ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Cruickshank, D. W. J., Pilling, D. E., Bujosa, A., Lovell, F. M. & Truter, M. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. Oxford: Pergamon Press.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Knop, O. & Giguère, P. A. (1959). *Canad. J. Chem.* **37**, 1794.

Maas, O. & Hatcher, W. H. (1922). *J. Amer. Chem. Soc.* **44**, 2472.

Mironov, K. E. (1959). *Zh. Neorgan. Khim.* **4**, 153.

Olovsson, I. (1960). *Ark. Kemi*, **16**, 437.

Olovsson, I. & Templeton, D. H. (1959). *Acta Cryst.* **12**, 827.

Olovsson, I. & Templeton, D. H. (1960). *Acta Chem. Scand.* **14**, 1325.

Pimentel, G. C. & McClellan, A. L. (1960). *The Hydrogen Bond*. San Francisco & London: W. H. Freeman.

Simon, A. & Kriegsmann, H. (1955). *Naturwissenschaften*, **42**, 14.

Simon, A. & Marchand, M. (1959). *Z. anorg. Chem.* **262**, 191.

Simon, A. & Uhlig, U. (1952). *Chem. Ber.* **85**, 977.

Tables of Interatomic Distances and Configuration in Molecules and Ions (1958). London: The Chemical Society.

Acta Cryst. (1966). **21**, 942

The Crystal Structure of β-$Ca_2P_2O_7$

By Ned C. Webb

The Procter & Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239, *U.S.A.*

(*Received* 31 *January* 1966 *and in revised form* 1 *May* 1966)

Crystals of β-$Ca_2P_2O_7$ are tetragonal, space group $P4_1$, with 8 formula units in a unit cell with $a=b=6{\cdot}684$, $c=24{\cdot}144$ Å. Each of the two independent pyrophosphate groups is in an essentially eclipsed configuration. The mean values for the bond lengths in the pyrophosphate groups are P–O (bridge) = $1{\cdot}615 \pm 0{\cdot}017$ Å and P–O = $1{\cdot}518 \pm 0{\cdot}021$ Å, and the P–O–P angles are 131 and 138°. Of the four independent calcium atoms two have seven nearest neighbor oxygen atoms, one has eight and one has nine. The structure exhibits a local, non-crystallographic center of symmetry.

Introduction

One of the objectives of the determination of the structure of sodium pyrophosphate decahydrate (MacArthur & Beevers, 1957; Cruickshank, 1964) was to establish the geometry of the pyrophosphate ion and, in particular, to determine the P–O–P angle. The P–O–P angle was found to be 134°, which is quite different from the value of 180° reported in cubic ZrP_2O_7 by Levi & Peyronel (1935). In ZrP_2O_7 the central oxygen atom lies on a center of symmetry, and in $Na_4P_2O_7.10H_2O$ it lies on a twofold axis. In the β phase of calcium pyrophosphate, β-$Ca_2P_2O_7$, all atoms are in general positions, thereby providing an opportunity for studying the geometry of pyrophosphate groups free of symmetry restrictions. In other investigations of structures containing a pyro-group, X_2O_7, the X–O–X angle has been found to be 128° in Cl_2O_7 (Fonteyne, 1938), 124° in $K_2S_2O_7$ (Lynton & Truter, 1960) and 180° in $Sc_2Si_2O_7$ (Zachariasen, 1930; Cruickshank, Lynton & Barclay, 1962). In β-$Mg_2P_2O_7$ and β-$Zn_2P_2O_7$ the P–O–P group appears to be linear because of a thermal averaging of the position of the central oxygen atom (Calvo, 1965*a*, *b*).

Experimental

Heating dicalcium phosphate dihydrate to approximately 750 °C produces β-$Ca_2P_2O_7$ which melts at approximately 1350 °C:

$$2\,CaHPO_4.2H_2O \xrightarrow[-4H_2O]{\sim 120°C} 2\,CaHPO_4 \xrightarrow[-H_2O]{\sim 450°C} \gamma\text{-}Ca_2P_2O_7 \xrightarrow{\sim 750°C} \beta\text{-}Ca_2P_2O_7 .$$

A sample of $CaHPO_4.2H_2O$ in a Vycor crucible was placed in a muffle oven and heated to ~1400 °C. The oven was turned off but left closed to allow slow cooling of the melt. The solidified melt obtained in this way had a glassy appearance, but on shattering, the melt yielded small single crystals in the shape of rectangular solids. One of these crystals ($0{\cdot}25 \times 0{\cdot}17 \times 0{\cdot}10$ mm) was mounted with its long axis (later found to be *a*) coincident with the axis of rotation.

Corbridge (1957) reported β-$Ca_2P_2O_7$ to crystallize in the tetragonal space group $P4_1$. We observed systematic absences ($00l$, $l \neq 4n$) on Weissenberg photographs indicating either space group $P4_1$ or $P4_122$, but the relationship observed in the intensity data, $|F(hkl)| \neq |F(h\bar{k}l)|$, eliminated $P4_122$ as a possibility. Precise values of the cell parameters *b* and *c* were obtained by least-squares refinement on data for seventeen $0kl$ reflections taken from measurements of a Straumanis-type rotation photograph. In adjusting the cell parameters to give the best fit between observed and calculated $\sin^2\theta$ values no allowance was made for eccentricity or absorption effects; each observational equation was weighted with $\sqrt{w} = 1/\sin 2\theta$, and λ(Cu $K\alpha_1$) was taken as 1·5405 Å. The results obtained here are listed in Table 1 along with those obtained by Corbridge (1957) and Keppler (1962); the standard deviations estimated from the least-squares treatment seemed unrealistically small and hence were multiplied by three before listing in Table 1. (Multiplying by three raises the confidence level to 99%). The density was measured by the flotation method with solutions of carbon tetrachloride and tin tetrabromide; the calculated densities are based on eight units of $Ca_2P_2O_7$ per unit cell.

Table 1. *Unit-cell dimensions and densities of* β-$Ca_2P_2O_7$ *as found by Corbridge* (1957) *and Keppler* (1962) *and as determined in this work*

	Corbridge	Keppler	This work
a (Å)	6·66	6·685 ± 0·01	6·684 ± 0·006
c (Å)	23·86	24·154 ± 0·05	24·144 ± 0·015
ϱ_o (g.cm^{-3})	3·1	3·119 ± 0·01	3·120 ± 0·005
ϱ_c (g.cm^{-3})	3·19	3·127	3·128

Weissenberg photographs were recorded for the zero through fifth layer lines about **a** using Cu $K\alpha$ radiation and employing the equi-inclination multiple-film technique. A striking feature of the photographs was that there were intense reflections all the way to the edge of the film. Intensities were estimated by visual comparison with a calibrated strip prepared from one reflection of the crystal used throughout this investigation. Intensities were corrected for Lorentz-polarization and absorption effects. The absorption corrections were made with the aid of a program for the IBM 1620 computer written by Craven (1963), who used a procedure suggested by Busing & Levy (1957). In practice, the absorption corrections were not made until the need was indicated in the refinement process; when the need became apparent, the raw data were reprocessed. Corrected intensities from different layers were correlated by using the relationship $|F(h\bar{k}l)| = |F(khl)|$. In all, 1150 independent reflections (89%) were estimated out of a possible 1296 in the Cu $K\alpha$ sphere. Of the 1150 total estimated reflections, 80 were estimated as being less than a minimum observable intensity.

In all of the structure-factor calculations the scattering factors used were for Ca^{2+}, P and an average of O and O^- as given in *International Tables for X-ray Crystallography* (1962).

Structure determination

With space group $P4_1$ and 8 units of $Ca_2P_2O_7$ in the unit cell there must be 4 Ca and 4 P atoms in the asymmetric unit. The positions of these heavy atoms were deduced from a three-dimensional Patterson map, relying heavily on the Harker sections at $w = \frac{1}{4}$ and $\frac{1}{2}$, and from electron-density maps calculated on the basis of 4 out of 8 and then 6 out of 8 of the heavy atoms. The trial model for the heavy atoms was derived with some scepticism because the eight heavy atoms occur in pairs in four layers in the **c** direction and the vector relating the atoms in any one pair is essentially the same as that relating the atoms within the other pairs. Nearly identical Ca–P vectors also made me feel uneasy about the trial solution. An early clue to the layered nature of the heavy atoms was the high intensity of the 008 reflection, which indicated layers separated by approximately $\frac{1}{8}$ along **c**; this indication is substantiated by the final results.

After location of the heavy atoms the oxygen atoms were found in two subsequent Fourier syntheses. Expected P–O distances were consulted in making judicious choices of oxygen positions from the excess of possible positions indicated in the electron-density maps. From the first map 10 of the 14 oxygen atoms were located, and while the positions of the remaining oxygen atoms could be predicted, the electron densities at these positions were barely above background, and another Fourier synthesis was carried out with the 4 oxygen atoms omitted; in the resulting map the missing atoms were readily apparent.

The refinement

A structure-factor calculation based on the trial positions of all eight heavy atoms showed reasonably good agreement between observed and calculated values as indicated by $R = 0{\cdot}35$, where R is the usual agreement index. (In the early stages of seeking a solution only the low order 60% of the data were used.) After a complete trial structure had been obtained and with unit weights and estimated fixed temperature factors, three cycles of least-squares brought R to 0·19. At this stage some of the observed P–O distances were not close to expected values. Consequently five of the oxygen atoms were shifted to give satisfactory P–O distances, and the next structure-factor calculation showed an agreement index of 0·147 which dropped to 0·127 in three cycles. At this point individual isotropic temperature factors were introduced into the refinement over all of the data rather than just the low order 60%. The first structure-factor calculation showed $R = 0{\cdot}135$ and a few least-squares cycles lowered R, but all of the heavy atoms and some of the oxygen atoms had negative temperature factors. By comparing lists of F_o's and F_c's it was apparent that the data were suffering from absorption effects. As indicated above, absorption corrections were made and the first structure-factor calculation showed $R = 0{\cdot}095$. In all subsequent refinement the weighting function (similar to Hughes, 1941) was taken as

$$\sqrt{w} = \frac{1}{S(F_o + K)} \text{ for } F_o > 4\,F_{\min}$$

$$\text{and} \sqrt{w} = \frac{1}{S(4\,F_{\min} + K)} \text{ for } F_o \le 4\,F_{\min}$$

where $4\,F_{\min} = 31{\cdot}7$ and $K = 7{\cdot}9$. Usually the value of S was inversely proportional to the square root of the number of times the intensity was estimated, with slight variations depending on a subjective evaluation of the accuracy of the estimation. S was assigned a much larger value than usual for the 008 reflection because it probably suffers from extinction, and for the 004

Table 2. *Observed and calculated structure factors*

The five columns within each group contain the values l, $10F_o$, $10F_c$, $10A_c$ and $10B_c$.

[illegible]

reflection because it was near the beam stop. Throughout, full-matrix least-squares refinement cycles were used in minimizing the quantity $\Sigma\, w(|F_o|-|F_c|)^2$. Three cycles in which all the positional parameters, isotropic temperature factors and the scale factor were varied reduced R to 0·068; in the last two cycles the shifts were less than the standard deviations. Two additional cycles did not reduce R and the shifts were all less than one-fifth the estimated standard deviations for the coordinates and all less than one-third for the temperature factors. The final fractional coordinates and isotropic temperature factors are listed in Table 3. The above value for R does not include the 'less-than' reflections; out of the total of 80 'less-thans', only 3 had $F_c > F_{\rm min}$ and none of these by more than 9%. If the 008 reflection, which appears to be suffering from extinction, is disregarded, the agreement index is 0·065.

In the final electron-density map, in which the 'less-than' reflections were given half weight, the ranges in peak height in electrons per cubic Å are 61 to 65 for Ca, 49 to 52 for P and 18 to 20 for O, and the extremes in background are found in ripples around the heavy atoms and ranged from 5 e.Å^{-3} to -5 e.Å^{-3}; the ripples are not symmetric and probably are indicative of anisotropic thermal motion of the heavy atoms.

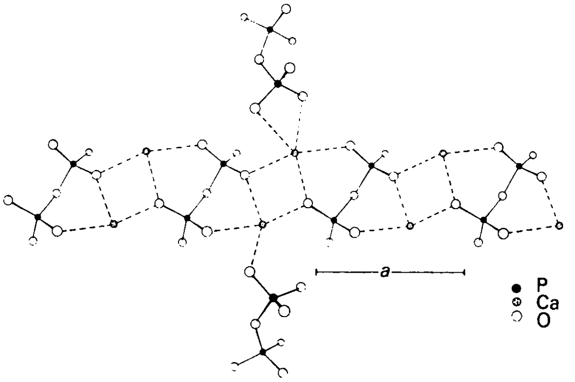


Fig. 3. An illustration of the infinite chains based on the chelate-like rings. This drawing shows the chain formed by pyrophosphate group I [P(1) and P(2)] and Ca(3) and Ca(4). The view is along **b**.

Description of the structure

One layer of the structure is illustrated in Fig. 1; a few oxygen atoms have been added where necessary to show complete coordination shells around the Ca atoms. The heavy atoms occur in pairs of like atoms in planes at $z=0$, 0·02, 0·12 and 0·14 in the order Ca, P, P, and Ca. Oxygen atoms of the pyrophosphate groups extend above and below the sheets of Ca atoms to provide bonding between adjacent sheets. Packed around each Ca atom are 6 PO_4 tetrahedra with P atoms at the vertices of a distorted octahedron. There is a pseudo-center of symmetry at $x=0{\cdot}456$, $y=0{\cdot}520$ and $z=0{\cdot}067$, which are the mean values of the coordinates of centers relating Ca(1)–Ca(4), Ca(2)–Ca(3), P(1)–P(4), P(2)–P(3), O(5)–O(8) and so on for all appropriate pairs; the ranges in values are 0·44–0·47, 0·51–0·53 and 0·063–0·074. This pseudo-center holds within one layer of the structure as shown in Fig. 1, but atoms above a layer do not have centrosymmetrically related atoms below the layer. That is, the fourfold screw symmetry does not preserve the center.

Each pyrophosphate group is linked in all directions to surrounding groups by commonly shared Ca atoms. As one might expect, there are infinite chains running throughout the structure. In Fig. 3 is illustrated a pyrophosphate–Ca chain running parallel to **a** and perpendicular to the chains which are above and below and are parallel to **b**, giving a matted effect when viewed down **c**. Within a layer there are two such chains parallel to each other, being related by the pseudo-

Table 3. *Fractional atomic coordinates with standard deviations* ($\times 10^4$) *in parentheses and isotropic temperature factors with standard deviations* ($\times 10^2$) *in parentheses*

	x	y	z	B(Å^2)
Ca(1)	−0·2101 (4)	0·2656 (4)	0·0	0·35 (4)
Ca(2)	0·5449 (4)	0·1583 (4)	0·1454 (1)	0·55 (4)
Ca(3)	0·3619 (4)	−0·1061 (4)	0·0026 (1)	0·50 (4)
Ca(4)	0·1391 (4)	−0·2314 (4)	0·1379 (1)	0·56 (4)
P(1)	−0·1327 (5)	0·7449 (5)	0·0134 (1)	0·26 (4)
P(2)	−0·3782 (5)	0·6929 (5)	0·1141 (1)	0·38 (5)
P(3)	0·2893 (5)	0·3544 (5)	0·0171 (1)	0·43 (5)
P(4)	0·0467 (5)	0·2850 (5)	0·1194 (2)	0·42 (4)
O(1)	−0·1012 (13)	0·5912 (13)	−0·0313 (3)	0·52 (13)
O(2)	−0·2615 (13)	0·9166 (14)	−0·0096 (4)	0·63 (13)
O(3)	0·0529 (13)	0·8224 (13)	0·0427 (3)	0·63 (13)
O(4)	−0·2612 (14)	0·6186 (14)	0·0593 (4)	0·86 (14)
O(5)	0·5338 (15)	0·5072 (17)	0·1369 (4)	1·30 (16)
O(6)	0·4610 (14)	0·8407 (14)	0·0951 (4)	0·92 (15)
O(7)	−0·2256 (13)	0·7986 (14)	0·1509 (4)	0·60 (13)
O(8)	0·3460 (13)	0·5469 (13)	−0·0105 (3)	0·64 (14)
O(9)	0·4627 (14)	0·2274 (14)	0·0356 (4)	0·87 (14)
O(10)	0·1481 (14)	0·2252 (14)	−0·0201 (4)	0·94 (15)
O(11)	0·1595 (14)	0·4055 (15)	0·0704 (4)	0·78 (15)
O(12)	0·0222 (15)	0·4458 (14)	0·1624 (4)	0·89 (14)
O(13)	0·1892 (15)	0·1198 (15)	0·1382 (4)	1·01 (15)
O(14)	−0·1492 (14)	0·2105 (14)	0·0942 (4)	0·74 (14)

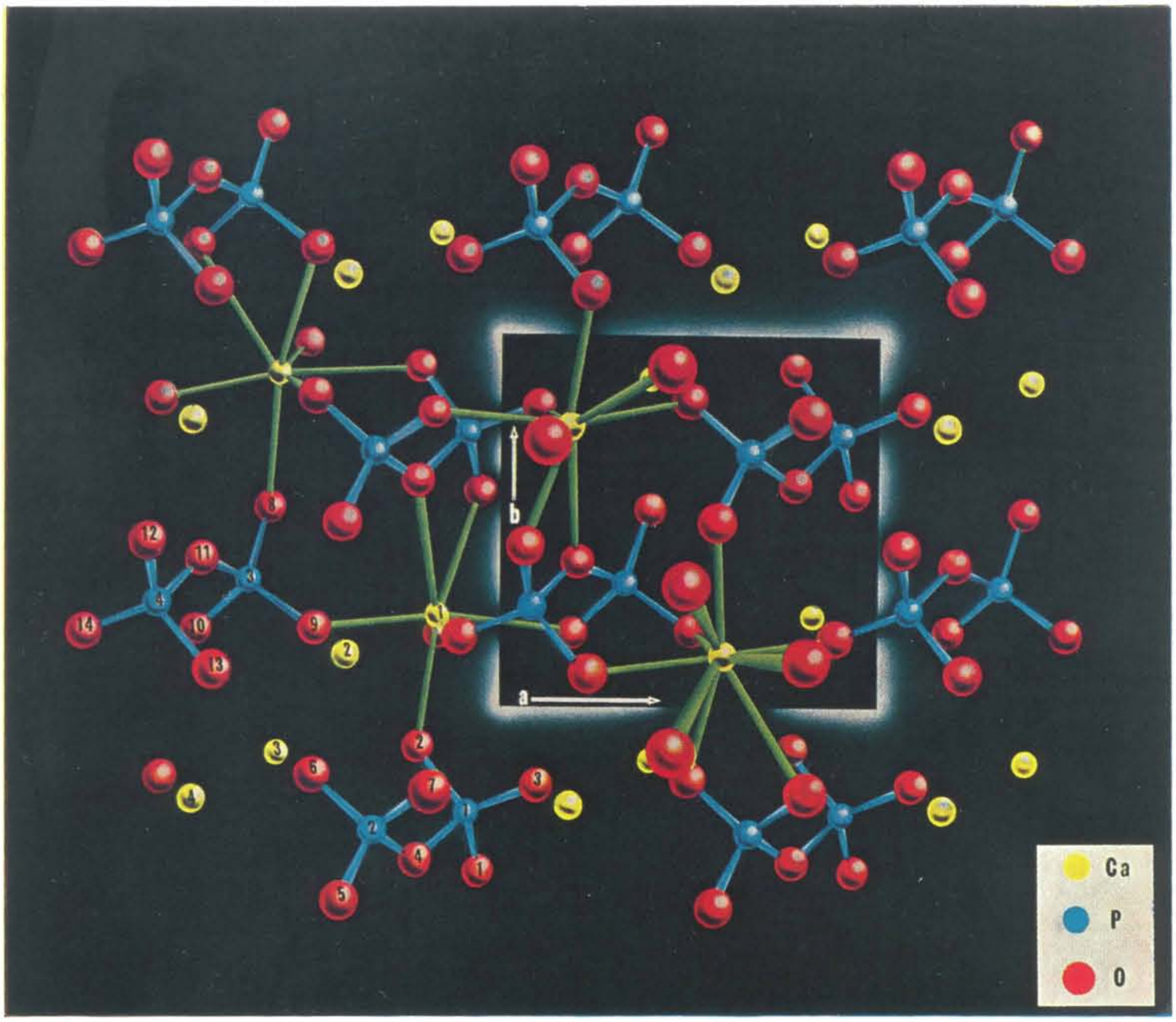


Fig. 1. Illustration of the structure of β-$Ca_2P_2O_7$ viewed along **c**, but including the cell contents between approximately $z=0$ and $z=0{\cdot}20$ only. The complete coordination shells around the four independent calcium ions are shown only once; these shells contain some oxygen atoms which are either above or below the general level shown.

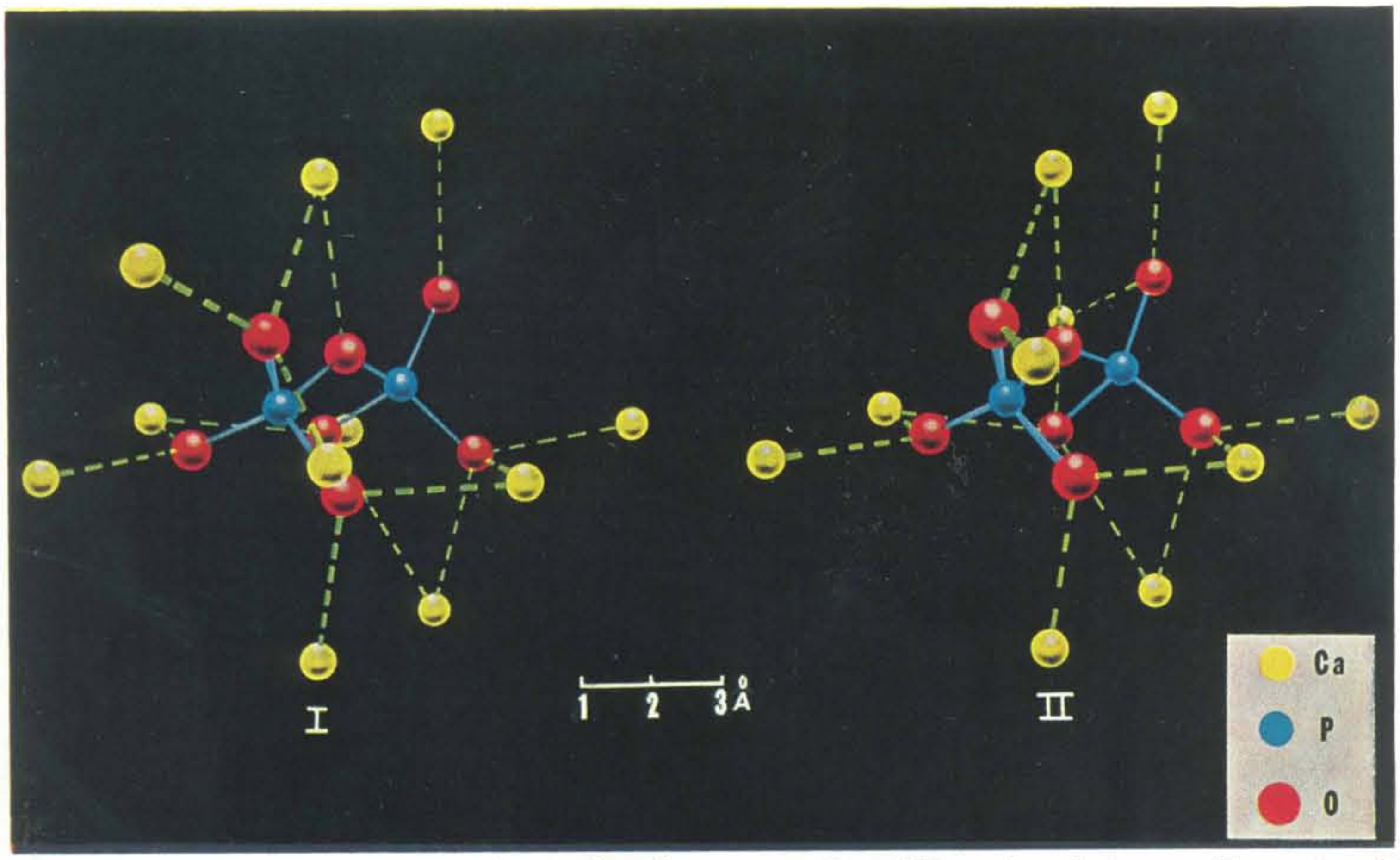


Fig. 2. The arrangement of calcium atoms around pyrophosphate groups I and II as viewed along **c**. Group I and its cluster of calcium atoms have been inverted through the pseudo-center. See text.

center. Around a fourfold screw axis each set of pyrophosphate groups forms an infinite spiral held together by ionic bonds to Ca atoms.

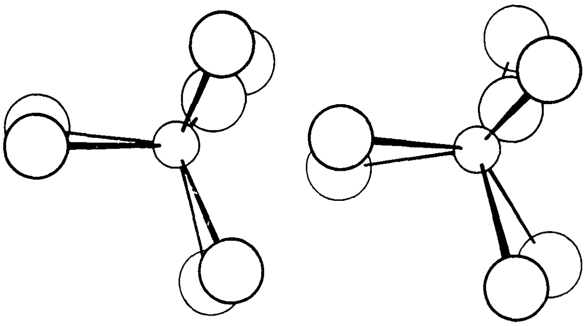
The shortest Ca–Ca distance is 3·69 Å, Ca(3)–Ca(4). In $CaHPO_4.2H_2O$ (Beevers, 1958) there are Ca–Ca distances of 3·8 Å. The four shortest intermolecular O–O distances in β-$Ca_2P_2O_7$ are O(12)–O(2′) = 2·75 Å, O(5)–O(8′) = 2·76 Å, O(6)–O(13) = 2·80 Å and O(13)–O(1′) = 2·85 Å.

The pyrophosphate groups

Viewed down the P–P axis, each crystallographically independent group is essentially in an eclipsed configuration as shown in Fig. 4, whereas the group in $Na_4P_2O_7.10H_2O$ is staggered. Group I has eleven Ca atoms in its first shell of interaction and group II has ten. All Ca atoms considered to be within the first shell of a group are within 2·65 Å of at least one oxygen atom of that group. In order to raise the number of Ca atoms in the first shell around group II to eleven, one would have to consider a Ca–O distance of 3·67 Å as constituting a significant interaction. The clustering of Ca atoms around each of the groups is shown in Fig. 2; in that figure group I has been inverted through the pseudo-center to bring out the structural similarities between the two groups. Each group forms two chelate-like rings which demand an eclipsed configuration, and surprisingly, perhaps, the bridge oxygen atoms take part in coordination of the calciums. The bridge oxygen atoms O(4) and O(11), and O(5) are bonded to only one Ca atom each, five oxygen atoms are bonded to two Ca atoms each, and six are bonded to three (here only Ca–O distances of less than 3·10 Å have been considered as constituting a bond or as indicating a significant degree of coordination – this will be discussed later).

The bond distances in the pyrophosphate groups are shown in Fig. 5. If the pyrophosphate groups had ideal *mm* symmetry, there would be three structurally independent P–O bonds. On looking at the distances in Fig. 5 it is obvious that the 4 P–O_B (O_B designates a bridge oxygen atom) bonds are longer than the others, and it is suggested that the 4 P–O bonds that are essentially coplanar with their respective P–O_B–P bridges are shorter than the other 8 P–O bonds. The distances for these three types of bond are 1·497 ± 0·011 Å, 1·529 ± 0·016 Å and 1·615 ± 0·019 Å; the standard deviation based on uncertainties in the least-squares coordinates is approximately ± 0·010 Å for all P–O bonds. If the first two groups are put together we find the P–O distance to be 1·518 ± 0·021 Å; the mean value for all P–O bonds is 1·543 Å, which is not different from the 1·545 Å predicted by Cruickshank (1961). It may be that the bonds in the P–O_B–P plane are slightly contracted by enhanced delocalization and overlap through the oxygen 2*pπ* and phosphorus 3*d* orbitals of the atoms in the plane. Those bonds may also be shorter because, in general, judging from the number and length of the Ca---O bonds the in-plane oxygen atoms are not as strongly bonded to neighboring calcium atoms as are the other oxygen atoms.

The oxygen-to-oxygen distances within each pyrophosphate group are shown in Fig. 6. In the same way that we have considered categorical differences in the P–O distances we may select groups of O–O distances and of O–P–O angles (Table 4). Within PO_4 tetrahedra it seems that the distances between the bridge oxygen atom and the oxygen atoms in the P–O_B–P plane (2·450 ± 0·037 Å) are shorter than the remaining distances (2·527 ± 0·032 Å); the mean expected standard deviation for an O–O distance is ± 0·013 Å. On examining the angles and distances one gets a picture of PO_4 groups distorted from perfect tetrahedra by flaring of the oxygen atoms in the faces opposite the bridge atoms, that is, by a flattening of those PO_3 pyramids. In both β-$Ca_2P_2O_7$ and $Na_4P_2O_7.10H_2O$ the O–P–O



(I) (II)

Fig. 4. A view of each pyrophosphate group along its P–P axis. For group I, P(1) is toward the viewer; for group II, P(3).

Table 4. *Oxygen–phosphorus–oxygen angles*

e.s.d. ± 0·5°*

O–P–O			
4–1–1	101·9°	11–3–8	108·3°
4–2–5	103·8	11–4–12	101·6
	103·9° ± 3·1°		
4–1–2	109·6°	11–3–9	107·5°
4–1–3	106·7	11–3–10	104·7
4–2–6	106·9	11–4–13	106·6
4–2–7	107·2	11–4–14	105·8
	106·9° ± 1·4°		

1–1–2	109·2°	8–3–9	115·0°
1–1–3	116·9	8–3–10	111·9
2–1–3	111·8	9–3–10	108·9
5–2–6	111·9	12–4–13	112·3
5–2–7	113·4	12–4–14	114·5
6–2–7	110·2	13–4–14	115·0
	112·6° ± 2·5°		

* The estimated standard deviation is based on the mean values of the least-squares deviations of coordinates.

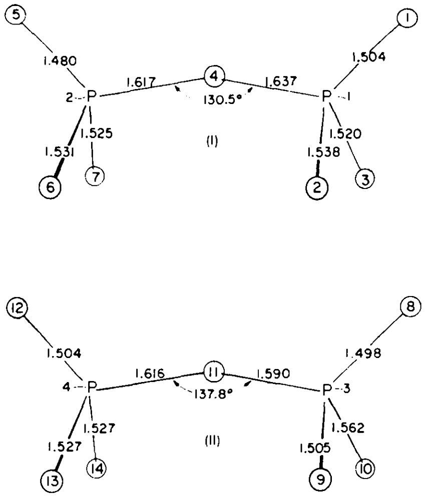


Fig. 5. Bond distances and P–O–P angles in the pyrophosphate groups.

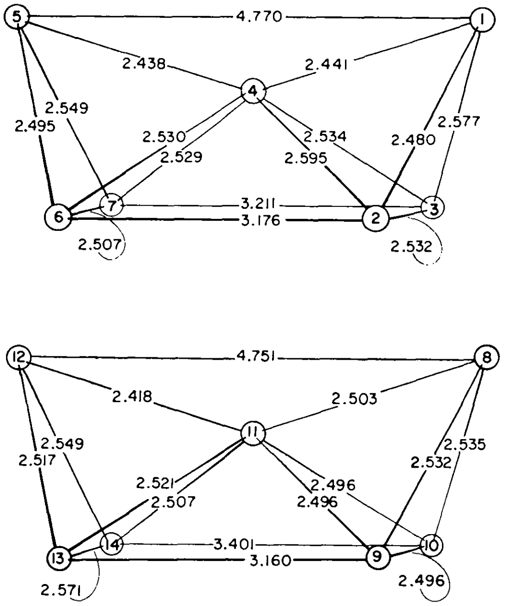


Fig. 6. Oxygen to oxygen distances in the pyrophosphate groups.

angles are 113° as compared with 105° for the O–P–O_B angles. In the $S_2O_7^{2-}$ anion the structurally similar angles are 114 and 105°, and this distortion has been attributed to repulsion between the charged oxygen atoms (Lynton & Truter, 1960). In Table 5 are some of the dimensions of the pyrophosphate group as found here and as found by Cruickshank in $Na_4P_2O_7.10H_2O$.

Table 5. *Comparison of dimensions of pyrophosphate group as found in* $Na_4P_2O_7.10H_2O$ *with those found in this work*

	$Na_4P_2O_7.10H_2O$	β-$Ca_2P_2O_7$
P–O_{outer}	1·51 ± 0·015 Å	1·518 ± 0·021 Å
P–O_{Bridge}	1·61 ± 0·015	1·615 ± 0·017
P–O_B–P	133·6°	134·2°
O_B–P–O	105	105·4
O–P–O	113	112·6

Pyrophosphate group II is distorted; the O(10)–O(14) separation (3·401 Å) is significantly larger than the other three of its kind (~3·18 Å). This is because Ca(1) is jammed into the side of the anion – as indicated by its approach to the bridge oxygen, 3·14 Å, which is close in comparison to the three other similar Ca–O_B approaches of 3·41, 3·43 and 3·56 Å. In addition, the two pyrophosphate groups significantly differ in their P–P separation, 2·955 and 2·991 Å, both ± 0·005 Å; this is, of course, reflected in the P–O_B–P angles of 130·5 and 137·8°, both ± 0·8°. The differences and distortions are probably due to differences in unsymmetrical environments.

Calcium coordination

Of the four independent calcium atoms in the structure two exhibit a coordination number of 7, one of 8 and one of 9. These coordination numbers reflect a judgment of which oxygen atoms are in the first shell, that is, the nearest neighbors. For these nearest neighbors the longest Ca–O distance is 2·93 Å, but Ca–O distances up to 3·7 Å have been listed in Table 6.

The coordination polyhedra are shown in Fig. 7 (and also in Fig. 1). The coordination shell around Ca(3)

Table 6. *Interatomic distances in the calcium–oxygen coordination polyhedra*
The fourfold screw operations carry atom O(1″) to O(1) to O(1′)

	Ca(1)		Ca(2)		Ca(3)		Ca(4)
O		O		O		O	
14	2·340 Å	5	2·342 Å	12″	2·318 Å	12	2·370 Å
9	2·364	13	2·397	3	2·330	13	2·371
2	2·369	14	2·414	8	2·343	3	2·397
7″	2·409	6	2·509	6	2·356	6	2·435
1	2·416	10′	2·557	9	2·462	7	2·466
10	2·457	1′	2·640	2	2·539	2′	2·510
4	2·780	8′	2·668	10	2·692	1′	2·794
11	3·141	9	2·745	13″	3·250	11	2·927
8	3·522	7	2·855	4	3·407	5	3·165
5″	3·582	11	3·555			4	3·431
3	3·596					14	3·681
12″	3·669						

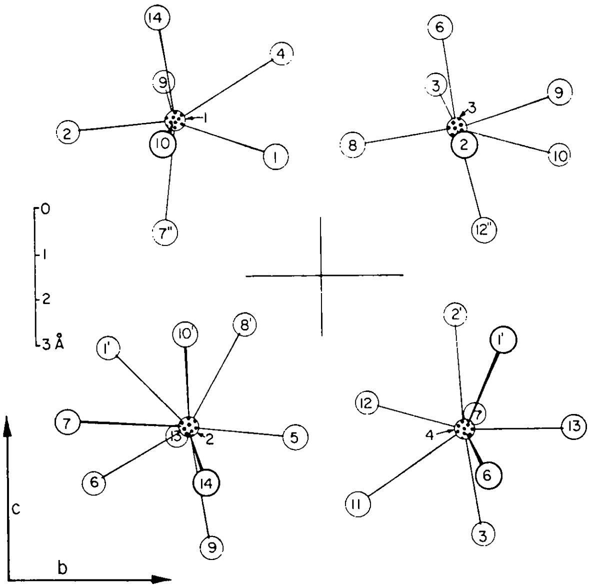


Fig. 7. Calcium–oxygen coordination shells viewed along **a**. Compare with view along **c** in Fig. 1.

can be pictured as a distorted pentagonal bipyramid, as a distorted NbF_7^{2-} configuration (Hoard, 1939) or, perhaps more descriptively, as an octahedron distorted by the approach of O(10) a little farther out than the others. The same description could apply to Ca(1) where O(4) is the distorting atom. Likewise the shell around Ca(4) can be described as an octahedron with two oxygen atoms jammed into edges, O(1') and O(11). The coordination polyhedron around Ca(2) is a distorted one; it can be pictured as a pentagonal bipyramid with an apical atom replaced by three atoms.

We are indebted to Dr James Stewart for providing us with and instructing us in the use of X-ray 63, the system of crystallographic programs for the IBM 7094 computer developed at the Universities of Washington and Maryland; with the exception of the absorption corrections, this system was used throughout this work. The assistance given by Dr J. S. Cantrell in using X-ray 63 and the many discussions with Dr A. J. Mabis are greatly appreciated. The air-brush art work of Mr H. Thomas Brown is gratefully acknowledged.

References

Beevers, C. A. (1958). *Acta Cryst.* **11**, 273.
Busing, W. & Levy, H. A. (1957). *Acta Cryst.* **10**, 180.
Calvo, C. (1965*a*). *Canad. J. Chem.* **43**, 1139.
Calvo, C. (1965*b*). *Canad. J. Chem.* **43**, 1147.
Corbridge, D. E. C. (1957). *Acta Cryst.* **10**, 85.
Craven, B. M. (1963). Private communication.
Cruickshank, D. W. J. (1961). *J. Chem. Soc.* p. 5486.
Cruickshank, D. W. J. (1964). *Acta Cryst.* **17**, 672.
Cruickshank, D. W. J., Lynton, H. & Barclay, G. A. (1962). *Acta Cryst.* **15**, 491.
Fonteyne, R. (1938). *Natuurw. Tijdschr.* **20**, 275.
Hoard, J. L. (1939). *J. Amer. Chem. Soc.* **61**, 1252.
Hughes, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
International Tables for X-ray Crystallography (1962). Vol. III, Table 3.3.1A. Birmingham: Kynoch Press.
Keppler, U. (1962). *Naturwissenschaften*, **49**, 446.
Levi, G. R. & Peyronel, G. (1935). *Z. Kristallogr.* **92**, 190.
Lynton, H. & Truter, M. R. (1960). *J. Chem. Soc.* p. 5112.
MacArthur, D. M. & Beevers, C. A. (1957). *Acta Cryst.* **10**, 428.
Zachariasen, W. H. (1930). *Z. Kristallogr.* **73**, 1.

Acta Cryst. (1966). **21**, 948

Molecular Structure of Xylerythrin, a Fungus Pigment

By Sixten Abrahamsson and Maureen Innes

Crystallography Group, Department of Medical Biochemistry, University of Göteborg, Sweden

(*Received* 3 *May* 1966)

The molecular structure of the red fungus pigment xylerythrin has been determined by X-ray single-crystal analysis of the bisbromoacetate derivative. The *R* value is 10·6% for the 1745 independent observed reflexions.

Introduction

Xylerythrin ($C_{26}H_{15}O_5$) is the main component of the red pigments present in wood infected by the fungus *Peniophora sanguinea* Bres. It has been isolated and studied chemically by Gripenberg (1965). He showed that the compound contained two hydroxyl groups, a lactone group, a conjugated carbonyl group and at least one monosubstituted benzene ring. A single-crystal X-ray analysis was undertaken to provide detailed information about the structure.

Experimental

The bisbromoacetate of xylerythrin ($C_{30}H_{18}O_7Br_2$) was prepared by Prof. Gripenberg who provided us with