Acta Cryst. (1973). B29, 2057

$Ca(H_2PO_4)_2$, a Crystal Structure Containing Unusual Hydrogen Bonding

By B. Dickens, E. Prince, L. W. Schroeder* and W. E. Brown†

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234, *U.S.A.*

(*Received* 9 *January* 1973; *accepted* 30 *April* 1973)

$Ca(H_2PO_4)_2$ crystallizes in the triclinic unit cell $a=7{\cdot}5577$ (5), $b=8{\cdot}2531$ (6), $c=5{\cdot}5504$ (3) Å, $\alpha=109{\cdot}87$ (1)°, $\beta=93{\cdot}68$ (1)° and $\gamma=109{\cdot}15$ (1)° at 25°C with $Z=2$. The structure was determined by an automated $\sum_2$ method from X-ray data and refined by least-squares analysis to $R_w(F)=0{\cdot}048$, $R(F)=0{\cdot}020$ using 3678 observed X-ray data and to $R_w(F)=0{\cdot}055$, $R(F)=0{\cdot}048$ using 843 observed neutron data. Corrections were made for absorption, isotropic secondary extinction and anomalous dispersion in the X-ray case and for anisotropic secondary extinction in the neutron case. Least-squares refinements proceeded to the limits of the data sets in space group $P\bar{1}$. Rudimentary chains Ca···[P(1)O$_4$]-H(1)···[P(2)O$_4$]··· run parallel to [1$\bar{1}$0]. Adjacent chains are joined by Ca···O bonds on one side and by O(8)-H(5)-O(8′) hydrogen bonds on the other. Alternatively, the structure may be considered to contain hydrogen-bonded layers of PO_4 groups; these layers are held together by hydrogen bonds on one side and by Ca···O bonds on the other. There are two very strong hydrogen bonds in the structure; O(7)--H(4)--O(7′), O(7)···O(7′)= 2·434 (2) Å and O(8)--H(5)--O(8′), O(8)···O(8′)=2·423 (2) Å. These hydrogen bonds join the P(2)O$_4$ groups together to form an infinite chain. The very strong hydrogen bonds are across nominal centers of symmetry, and diffraction results indicate that each of the H(4) and H(5) protons is effectively centered in a broad symmetric potential well, possibly with a central barrier. A combination of diffraction and infrared spectral considerations suggests that the central barriers in the wells, if they exist, probably lie below the zero-point energy of the hydrogens.

Introduction

Our earlier studies of calcium phosphates have included refinements of the crystal structures of the hydrogen-containing salts $Ca(H_2PO_4)_2.H_2O$ (Dickens & Bowen, 1971) and $CaHPO_4$ (Dickens, Bowen & Brown, 1971*a*). Here we have extended our studies of hydrogen bonding in calcium phosphates and related compounds by determining and refining the crystal structure of $Ca(H_2PO_4)_2$ using both X-ray and neutron data. $Ca(H_2PO_4)_2$ alters to randomly oriented crystallites of $Ca(H_2PO_4)_2.H_2O$ in moist air (Smith, Lehr & Brown, 1955); perhaps because of this it has been studied comparatively little. It is an important constituent of freshly made superphosphate fertilizer.

Experimental details

Clear colorless platy crystals of $Ca(H_2PO_4)_2$ were prepared according to the method of Smith, Lehr & Brown (1955). An ellipsoidal crystal with axes of 0·15, 0·15 and 0·18 mm was the result of an attempt to grind a sphere. This crystal was mounted in a borate glass capillary with clear household cement and was used in the X-ray study. Crystal data are as follows: ideal formula: $Ca(H_2PO_4)_2$; cell at 25°C: triclinic with $a=7{\cdot}5577$ (5), $b=8{\cdot}2531$ (6), $c=5{\cdot}5504$ (3) Å, $\alpha=109{\cdot}87$ (1), $\beta=93{\cdot}68$ (1), $\gamma=109{\cdot}15$ (1)°, cell volume $=302{\cdot}01$ Å^3; space group $P\bar{1}$; cell contents $2[Ca(H_2PO_4)_2]$; calculated density 2·57 g cm^{-3}; observed density 2·546 g cm^{-3} (Bassett, 1908); linear absorption coefficient for Mo $K\alpha=14{\cdot}3$ cm^{-1}. Standard deviations are given in parentheses after the cell parameters, which were calculated by least-squares methods from 30 2θ values observed at 25°C on an X-ray diffractometer equipped with a highly oriented graphite monochromator. Care was taken to use only the $K\alpha_1$ peak in determining these 2θ values. The wavelength λ(Mo $K\alpha_1$)$=0{\cdot}709260$ was assumed.

The X-ray data were measured and processed as described by Dickens & Bowen (1971) with the exception that the diffractometer setting program used was written by Lenhert (1970). 12043 reflections (maximum $\sin\theta/\lambda=0{\cdot}907$ Å^{-1}) comprising two complete sets from one hemisphere and one set from the other hemisphere were measured and merged into a unique set of 3756. Of these, 3690 were greater than $2\sigma(I)$ above background and 66 were less than this threshold. The average disagreement between equivalent or remeasured reflections was 0·8%. Absorption corrections were applied for a sphere with a radius the average of the axes of the elliptical crystal. The *maximum* systematic effect on F due to the asphericity of the crystal, is estimated at 4%. Absorption due to the capillary was neglected.

The X-ray structure was solved by $\sum_2$ methods using the sequence *DATRDN-DATFIX-SIGMA2-PHASE-FOURR* in the XRAY 67 System of computer programs (Stewart, 1967). Seven E maps were calculated.

---

* Research Associate of the American Dental Association Research Unit at the National Bureau of Standards, Washington, D.C. 20234, U.S.A.

† Director, American Dental Association Research Unit at the National Bureau of Standards, Washington, D. C. 20234.

Calculations of distances between the three highest peaks (presumed to be one Ca ion and two P atoms) in these trial structures ruled out all but one. The oxygen atoms were found from a subsequent electron-density synthesis with phases based on the Ca and P atoms. The structure with hydrogens excluded was refined with isotropic temperature factors using the program *RFINE* (Finger, 1968) to $R_w=0{\cdot}077$ and $R=0{\cdot}064$ ($R_w=[\sum w(|F_o|-|F_c|)^2/\sum w(|F_o|^2)]^{1/2}$ and $R=\sum||F_o|-|F_c||/\sum|F_o|$). The maximum shift/error was $-6{\cdot}4$. The structure was then refined with anisotropic temperature factors to $R_w=0{\cdot}065$, $R=0{\cdot}037$ (maximum shift/error$=0{\cdot}90$). The scattering factors used were for Ca^{2+} and neutral P, O and H; they were taken from Cromer & Mann (1968) and Cromer & Liberman (1970) for Ca^{2+}, P and O and from Finger (private communication) for H. Only reflections greater than $2\sigma(I)$ were used in the refinements.

The neutron data were taken on a computer-controlled four-circle diffractometer at the National Bureau of Standards Research Reactor (Alperin & Prince, 1970) according to the procedure described by Prince (1972). The crystal was sealed with $CaCl_2$ in a silica-glass enclosure to protect it from moisture. With a wavelength of 1·232 Å and a limiting 2θ angle of 100°, 1212 independent reflections were accessible; of these 843 had integrated intensities greater than $2\sigma(I)$. The crystal was a plate with dimensions approximately $0{\cdot}5\times1{\cdot}0\times3{\cdot}0$ mm. The hydrogen positions were obtained from a Fourier synthesis based on the neutron data and signs determined from the X-ray parameters. The structure was then refined further.

In the X-ray refinement of the complete structure, consideration of isotropic secondary extinction was deemed adequate and the refinement on all parameters but the thermal parameters of hydrogen, which were fixed at 1 Å^2, gave $R_w=0{\cdot}033$ and $R=0{\cdot}023$. The isotropic secondary extinction factor, r, in the notation of Zachariasen (1967) was $0{\cdot}33(7)\times10^{-4}$ cm. The standard deviation of an observation of unit weight (SDOUW), 7·81, indicated that improper weights were being applied in the least-squares analysis, so that new weights, $(\sigma_c^2+0{\cdot}00058\ F_o^2)^{-1}$, were applied. Here σ_c is the standard deviation of F_o as estimated from counting statistics. The few reflections with extinction factors less than 0·95 were rejected from the final refinement. The final values are $R_w=0{\cdot}048$, $R=0{\cdot}020$, SDOUW$=1{\cdot}84$, $r=0{\cdot}74(5)\times10^{-4}$ cm. The largest peaks in a difference synthesis calculated after the last cycle of refinement were 0·63, 0·58 and 0·53 e Å^{-3}. The lowest value was $-0{\cdot}51$ e Å^{-3}. The first three are all halfway between P and O in PO_4 groups. The fourth is 0·1 Å from Ca.

In the neutron case, anisotropic secondary-extinction corrections were deemed necessary. The value of SDOUW, 6·87, showed that once again counting statistics were inadequate. New weights, given by $(\sigma_c^2+0{\cdot}00025F_o^2)^{-1}$ were applied. The structure was then refined to $R_w=0{\cdot}055$, $R=0{\cdot}048$, and SDOUW$=2{\cdot}50$. The scattering lengths used were Ca: 0·49; P: 0·51; O: 0·577; H: $-0{\cdot}372$ (The Neutron Diffraction Commission, 1969).

The components ($\times10^{10}$) of the extinction tensor, w (Coppens & Hamilton, 1970) in the neutron case are 0·29(5), 0·27(4), 0·42(6), $-0{\cdot}11(3)$, 0·24(4), 0·06(3), and indicate considerable anisotropy. This extinction tensor results from a type II treatment in which extinction is dominated by domain size. The principal axes ($\times10^4$) of the ellipsoidal domain are 0·128, 0·172 and 0·502 cm. One-third of their sum, $0{\cdot}435\times10^{-4}$ cm, is comparable with the isotropic value $0{\cdot}74\times10^{-4}$ cm given by the X-ray refinement.

Refinement using the type I treatment, where mosaic spread dominates, led to non-positive definite tensors and diverged even when starting from converged isotropic-extinction refinements. This can be understood by considering the isotropic extinction parameter for the X-ray case, which as given is equivalent to the mean radius of the domains in the crystal. However, the refined parameter can also represent a mosaic-spread parameter. Such a calculation leads to a mosaic spread of $\sim30''$, roughly a factor of ten larger than that usually obtained in cases where type I occurs (Coppens & Hamilton, 1970). Thus, our refinements suggest that extinction in $Ca(H_2PO_4)_2$ is dominated by the effect of the domain size.

The largest positive peaks in a difference synthesis with the neutron data were 27, 25 and 25 and the largest negative peaks were -27 and -27 on a scale on which the amplitude of a hydrogen peak is -600. The first four peaks are obviously artifacts, since they do not occupy chemically reasonable positions. The fifth, in a chemically reasonable position, is 1·03 Å from O(1) and 2·04 Å from O(7), and thus could be evidence for very slight disordering of the hydrogen atoms, but was not given serious consideration because it is comparable with the background in the map.

The appropriateness of the final weighting schemes was checked by comparisons of F_o, F_c and $\sigma(F_o)$ with a normal distribution as suggested by Abrahams & Keve (1971) using an unpublished program written by us. The comparison for the neutron data showed that there was little skewness in the fit of F_o and F_c, implying that the residuals followed a normal distribution. The value of the standard deviation of an observation of unit weight obtained from the least-squares refinement was confirmed in this comparison. A similar comparison of the X-ray data showed the F_o-F_c distribution to be somewhat skewed with F_c being a little smaller than F_o suggesting that the extinction correction may have been somewhat overestimated. Similar comparisons of the structural parameters from the X-ray and neutron refinement gave a least-squares line of $\delta p=-0{\cdot}10+1{\cdot}50x$ for the positional parameters and $\delta p=0{\cdot}01+1{\cdot}49x$ for the thermal parameters, where

$$\delta p_i=||p(1)_i|-|p(2)_i||/(\sigma^2p(1)_i+\sigma^2p(2)_i)^{1/2}$$

for the ith parameter ($1=$X-ray, $2=$neutron), and x is the expected quantile (Hamilton & Abrahams, 1972). Points with $x>1\cdot5$ were not included in the plots so that effects in the tails of the distributions were not overemphasized. The positional parameters and thermal parameters from the X-ray and neutron studies were compared in separate plots. Comparison of the goodness-of-fit for a least-squares line (0·11) and a least-squares quadratic (0·09) shows that the positional plot contains a slight curvature, which, taken with the non-zero intercept, indicates systematic differences between the X-ray and neutron parameters. The slope of $\sim1\cdot50$ suggests that the standard deviations of the positional parameters should be increased by 50%. The plot of the 66 common thermal parameters is essentially linear out to $x=1\cdot45$ and has a similar slope to the positional parameter plot. The largest discrepancies consist of B_{ii} for Ca and B_{33} for P(1), P(2) and O(3) to O(7). Some rationalization can be given. Each B_{ii} of Ca in the X-ray study is less than the corresponding quantity in the neutron study. This suggests that the X-ray scattering factor for Ca^{2+} does not adequately represent the electronic density of Ca in $Ca(H_2PO_4)_2$. The observation that the neutron value of B_{33} is more than 20% larger than the X-ray value for 8 of the 11 non-hydrogen atoms in the structure suggests an anisotropic effect. This may arise from our treatment of extinction or, in the case of the oxygen atoms, from the way we included hydrogen atoms in the X-ray study. It could also arise from systematic error in the X-ray absorption correction. Extinction is probably the largest effect. Both crystals came from the same crystallization batch but only refinements using the neutron data included anisotropic extinction corrections. The X-ray sample was obtained from a fragment of a crystal originally comparable in size with the one used in the neutron study. About 2% of the X-ray data had extinction factors less than 0·90, suggesting slight to moderate extinction which we treated as being isotropic. About 30% of the neutron data had extinction factors less than 0·90 and about 5% had extinction factors less than 0·60. A factor less than $\sim0\cdot6$ is beyond the range of the Zachariasen correction, which below this value tends to underestimate the correction as is shown by comparison with the exact results for an infinite plate (Zachariasen, 1967) and with the work of Cooper & Rouse (1971). This 5% of reflections was excluded from the refinements. We feel that a more detailed comparison of the X-ray and neutron models is not warranted until a better extinction correction can be applied to the 30% of the neutron data considerably affected by extinction. The importance of extinction is dramatically illustrated by Denne (1972) who shows the effect of anisotropic extinction on intensities measured from different crystals of the same compound.

In the neutron case, the largest correlation coefficient was 0·83 between components of the extinction tensor. Coefficients between the extinction parameters and the scale factor were in the range 0·56 to 0·69. Other coefficients in the range 0·56 to 0·69 involved the B's of H(5), but as Fig. 1 shows, the tensor is oriented with respect to the crystal coordinate system in such a way that fairly large correlations are expected. In the X-ray refinement the three largest coefficients were 0·64 to 0·65 between the scale factor and B_{ii} of Ca(1). The three next largest ($\sim0\cdot62$) were between B_{ii} of Ca(1) and the corresponding B_{ii} of P(1) and P(2). The correlation coefficient between the extinction parameter and the scale factor was 0·57. Both X-ray and neutron refinements proceeded satisfactorily to the limits of the data sets assuming space group $P\bar{1}$. There is therefore no indication from the diffraction data that the crystals are not centrosymmetric. Further-

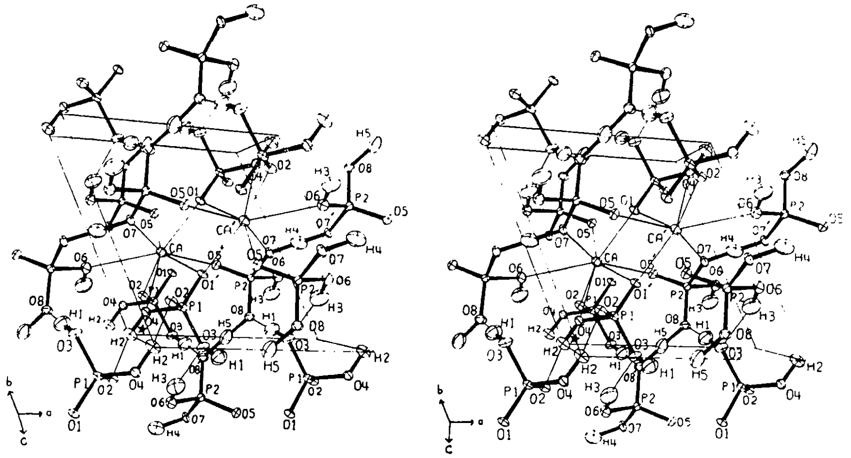

Fig. 1. A stereoscopic illustration of the $Ca(H_2PO_4)_2$ structure. The origin of the crystallographic coordinate system marked by *. $P(1)O_4$ groups hydrogen bonded into dimers may be seen at the lower left front corner. The $P(2)O_4$ hydrogen-bonded infinite chain passes near the centers of the bottom and right edges of the unit cell. The parameters from the neutron study were used in making the drawings.

more, similar crystals did not show any piezoelectric resonances when tested by the transmission method (Blume, 1962).

The structural parameters for $Ca(H_2PO_4)_2$ are given in Table 1. The observed and calculated structure factors are given in Table 2 for the X-ray data and in Table 3 for the neutron data.

Description of the structure

There are two formula units of $Ca(H_2PO_4)_2$ in a nominally centrosymmetric unit cell. There are five crystallographically different hydrogen bonds, two of which cross nominal centers of symmetry. If these hydrogen bonds are centered, all atomic sites would be fully occupied and there would be no positional disorder as there is for the hydrogen atoms in $CaHPO_4$ (Jones & Cruickshank, 1961; Curry, Denne & Jones, 1968; Dickens, Bowen & Brown, 1971*a*). The question of whether the hydrogen bonds in $Ca(H_2PO_4)_2$ are actually centered or not is discussed later.

There are several ways of describing the $Ca(H_2PO_4)_2$ structure. Many calcium phosphates can be described in terms of $Ca\cdots PO_4$ chains which are linked into sheets, usually puckered or corrugated but occasionally planar, and which are bonded to each other either directly or by some chemically different intermediate layer. In $Ca(H_2PO_4)_2$ (Fig. 1), rudimentary chains with the repeat unit $Ca\cdots[P(1)O_4]\text{–}H(1)\cdots[P(2)O_4]\cdots$ exist parallel to $[1\bar{1}0]$. A series of corrugated sheets may then be imagined parallel to (100). Adjacent chains are joined by $Ca\cdots O$ bonds on one side and by O(8)---H(5)---O(8′) bonds on the other. There is hydrogen bonding along the surfaces of the sheets involving H(3) between neighboring chains. The corrugated sheets are bonded together by hydrogen bonds involving H(2) and H(4).

An alternative description is that the PO_4 groups are held in layers parallel to (010) by hydrogen bonds. These layers are bonded to each other by hydrogen bonds on one side and by Ca ions on the other.

Two striking features of the structure are (i)

Table 1. *Atomic parameters in* $Ca(H_2PO_4)_2$

Figures in parentheses are standard deviations in the last digit(s) as estimated by least squares.
Thermal parameters are in Å^2 and have the form $\exp -[\frac{1}{4}(h^2a^{*2}B_{11}+k^2b^{*2}B_{22}+l^2c^{*2}B_{33}+2hka^*b^*B_{12}+2hla^*c^*B_{13}+2klb^*c^*B_{23})]$.

		x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ca	*a*	0·31392 (2)	0·41915 (2)	0·18764 (3)	0·835 (6)	0·767 (6)	0·597 (6)	0·219 (4)	0·088 (4)	0·233 (4)
	b	0·3139 (6)	0·4190 (5)	0·1877 (6)	1·0 (1)	1·0 (1)	0·9 (1)	0·2 (1)	0·3 (1)	0·3 (1)
P(1)	*a*	0·25687 (3)	0·15967 (3)	0·51764 (4)	0·693 (7)	0·590 (7)	0·534 (7)	0·124 (5)	0·073 (5)	0·209 (5)
	b	0·2569 (5)	0·1596 (5)	0·5171 (5)	1·8 (1)	0·7 (1)	0·7 (1)	0·1 (1)	0·14 (8)	0·18 (9)
O(1)	*a*	0·42553 (8)	0·31905 (8)	0·5122 (1)	0·80 (2)	0·83 (2)	0·91 (2)	0·05 (1)	0·09 (1)	0·38 (1)
	b	0·4259 (4)	0·3189 (4)	0·5122 (5)	0·8 (1)	0·8 (1)	1·1 (1)	−0·08 (8)	0·20 (8)	0·37 (9)
O(2)	*a*	0·17951 (9)	0·18764 (8)	0·76582 (1)	1·04 (2)	1·02 (2)	0·63 (2)	0·14 (1)	0·25 (1)	0·20 (1)
	b	0·1802 (4)	0·1888 (4)	0·7671 (5)	1·0 (1)	1·0 (1)	0·7 (1)	0·1 (1)	0·3 (1)	0·1 (1)
O(3)	*a*	0·2902 (1)	−0·02827 (9)	0·4366 (1)	1·72 (2)	0·84 (2)	0·96 (2)	0·63 (2)	0·22 (2)	0·32 (1)
	b	0·2906 (4)	−0·0270 (4)	0·4384 (6)	1·8 (2)	0·9 (1)	1·2 (1)	0·6 (1)	0·38 (9)	0·3 (1)
O(4)	*a*	0·10443 (9)	0·12477 (9)	0·2801 (1)	0·98 (2)	1·08 (2)	0·95 (2)	0·11 (1)	−0·17 (1)	0·49 (1)
	b	0·1035 (4)	0·1237 (4)	0·2795 (5)	0·9 (1)	1·1 (1)	1·3 (1)	0·1 (1)	−0·1 (1)	0·5 (1)
H(1)	*a*	0·306 (3)	−0·053 (3)	0·566 (5)	1·00					
	b	0·3239 (9)	−0·0622 (8)	0·586 (1)	2·8 (3)	2·1 (3)	2·3 (2)	1·1 (2)	−0·0 (2)	0·7 (2)
	c	0·317	−0·064	0·587						
H(2)	*a*	0·021 (4)	0·038 (3)	0·235 (5)	1·00					
	b	−0·0152 (8)	0·0123 (8)	0·237 (1)	1·5 (2)	1·5 (2)	2·4 (2)	−0·1 (2)	−0·1 (2)	0·5 (2)
	c	−0·013	0·011	0·236						
P(2)	*a*	0·73538 (3)	0·31138 (3)	0·17145 (4)	0·651 (7)	0·650 (7)	0·624 (7)	0·210 (5)	0·029 (5)	0·211 (5)
	b	0·7356 (4)	0·3116 (5)	0·1710 (6)	0·6 (1)	0·8 (1)	1·1 (1)	0·3 (1)	0·3 (1)	0·4 (1)
O(5)	*a*	0·60344 (9)	0·37118 (9)	0·04075 (9)	1·10 (2)	1·05 (2)	0·94 (2)	0·50 (1)	0·05 (1)	0·47 (1)
	b	0·6026 (4)	0·3708 (4)	0·0403 (5)	1·1 (1)	1·1 (1)	1·3 (1)	0·6 (1)	0·2 (1)	0·5 (1)
O(6)	*a*	0·91733 (9)	0·32349 (9)	0·0360 (1)	1·12 (2)	1·26 (2)	1·01 (2)	0·47 (2)	0·47 (1)	0·26 (2)
	b	0·9167 (4)	0·3234 (5)	0·0351 (6)	1·1 (1)	1·4 (1)	1·3 (1)	0·4 (1)	0·6 (1)	0·4 (1)
O(7)	*a*	0·82615 (8)	0·44107 (9)	0·4552 (1)	0·63 (2)	1·16 (2)	0·67 (2)	0·20 (1)	−0·01 (1)	−0·09 (1)
	b	0·8261 (4)	0·4407 (4)	0·4553 (5)	0·5 (1)	1·3 (1)	0·9 (1)	0·2 (1)	0·1 (1)	−0·1 (1)
O(8)	*a*	0·6416 (1)	0·11232 (8)	0·1612 (1)	1·24 (2)	0·71 (2)	1·19 (2)	0·05 (1)	−0·23 (1)	0·46 (1)
	b	0·6411 (4)	0·1126 (4)	0·1610 (6)	1·3 (1)	0·8 (1)	1·3 (1)	0·1 (1)	−0·2 (1)	0·5 (1)
H(3)	*a*	0·899 (3)	0·248 (3)	−0·103 (5)	1·00					
	b	0·882 (1)	0·233 (1)	−0·140 (1)	3·6 (3)	2·7 (3)	2·3 (3)	1·6 (3)	1·1 (2)	0·4 (2)
	c	0·888	0·230	−0·147						
H(4)	*a*	1·000	0·500	0·500	1·00					
	b	1·000	0·500	0·500	3·1 (4)	2·1 (4)	1·3 (3)	0·7 (3)	0·4 (3)	0·1 (2)
	c	0·969	0·490	0·493						
H(5)	*a*	0·500	0·000	0·000	1·00					
	b	0·500	0·000	0·000	2·5 (3)	2·7 (4)	2·8 (3)	1·4 (3)	0·7 (3)	1·7 (3)
	c	0·526	0·033	0·020						

(*a*) X-ray values.
(*b*) Neutron values.
(*c*) Calculated hydrogen positions as described in text.

$H_2P(2)O_4$ ions linked into infinite chains by centered hydrogen bonds involving H(4) and H(5) (Fig. 4) and (ii) pairs of $H_2P(1)O_4$ ions linked into dimers across centers of symmetry by the O(4)–H(2)···O(2) hydrogen bond (Fig. 3). The latter feature may also be seen at the lower left front corner of Fig. 1.

The Ca *ion environment*

The Ca ion is coordinated (Table 4 and Fig. 2) to eight oxygen atoms including the [O(1′), O(4)] edge of the P(1)O_4 group. This edge and the PO_4 apexes O(1), O(5), and O(6) are arranged in an approximate pentagon about Ca. Oxygen atom O(7) and the mid-

Table 2. *Calculated and observed X-ray structure factors for* $Ca(H_2PO_4)_2$

Columns are l, $10F_o$, $10F_c$ and $10\sigma(F_o)$. Unobserved reflections are those with intensity less than $2\sigma(I)$ and are marked by *.

5,0,L			
-1	194	191	4
0	220	223	5
1	53	51	1
2	239	241	5
3	127	124	3
4	97	97	2
5	126	128	3
6	67	59	2
7	95	95	2
5,1,L			
-9	59	55	1
-8	105	106	2
-7	17	14	5
-6	97	99	2
-5	250	252	5
-4	155	157	3
-3	26	25	1
-2	380	393	9
-1	342	351	9
0	31	31	1
1	337	337	9
2	394	399	9
3	109	110	2
4	140	141	3
5	286	297	7
6	34	33	1
-6	39	39	1
-5	75	75	2
-4	144	145	3
-3	95	95	2
-2	152	150	3
-1	11	7	2
0	113	111	3
1	155	155	4
5,10,L			
-7	125	123	3
-6	55	55	1
-5	42	41	1
-4	92	90	3
-3	9	2	1
-2	74	75	2
-1	111	110	3
0	36	35	1
5,11,L			
-5	13	12	1
-4	24	27	1
-3	79	79	2
-2	90	91	2
5,-14,L			
0	100	101	2
1	12	12	2
2	177	105	3
3	99	100	2

Table 2 (*cont.*)

point of the O(5′)···O(2) vector occupy apical positions of an approximate pentagonal bipyramid. Bipyramidal coordination of Ca is common in calcium phosphates. As judged from the Ca···O distances (Table 4) six of these Ca···O bonds are strong; those to O(4) and O(6) are weaker.

In the 'normal' Ca···O coordination in sheet-containing calcium phosphates the shortest distances are from Ca to oxygen atoms in neighboring chains, the intermediate ones are to oxygens in the same chain but with no covalently attached hydrogen, and the longest are to oxygens covalently bonded to hydrogen (Dickens, Bowen & Brown, 1971*a*). While vestiges of this pattern persist in $Ca(H_2PO_4)_2$, strong hydrogen bonding has apparently modified it, as is the case in $CaHPO_4$ (Dickens, Bowen & Brown, 1971*a*). The two oxygens O(4) and O(6), which are covalently bonded to hydrogen atoms in 'normal' hydrogen bonds (see

Table 3. *Calculated and observed neutron structure factors for* $Ca(H_2PO_4)_2$

Columns are h, $100F_o$, $100F_c$ and $100\sigma(F_c)$. Unobserved reflections are those with intensity less than $2\sigma(I)$ and are marked by *.

H,-1,-5			
0	134*	-126	70
1	135*	-37	68
2	111	-138	10
3	79*	59	39
4	82*	-76	41
H,0,-6			
0	196	195	5
1	202	-220	5
2	116	-139	8
3	131*	107	66
4	135*	-51	68
H,1,-6			
0	120*	31	60
1	123	-143	7
2	122*	89	61
3	287	296	5
4	101	107	10
5	134*	119	69
H,2,-6			
0	309	-309	5
1	226	229	5
2	113*	-90	59
3	143	152	6
4	124*	-39	64
5	168	-173	7
H,3,-6			
1	182	-179	4
2	117*	61	59
3	243	242	5
4	142	-147	7
H,4,-6			
1	342	321	5
2	179	177	6
3	139	-155	7
4	107	95	10
H,5,-6			
1	107	95	8
2	191	199	5
3	161	150	7
H,6,-6			
1	215	-224	6
2	134*	-25	69
H,7,-6			
1	192	168	7
H,-4,-5			
2	133	-128	9
3	143*	-58	71
4	193	194	7
H,-3,-5			
0	133*	-74	65
1	154	157	7
2	205	-200	6
3	138	-149	7
4	150	159	7
5	279	-285	6
H,-2,-5			
0	277	284	5
1	83	-84	10
2	164	-172	6
3	203	215	5
4	179	-194	6
5	292	291	5
6	144*	123	72
H,-1,-5			
0	114*	-41	57
1	117*	0	59
2	236	-235	5
3	119*	-69	59
4	116	125	7
5	131	-141	7
6	165	180	7
H,0,-5			
0	114*	16	57
1	115*	11	57
2	233	-237	5
3	113*	21	56
4	295	293	5
5	120*	-9	60
6	133*	-40	65
H,1,-5			
0	324	-315	5
1	383E	364	5
2	115	118	7
3	151	153	5
4	63	-75	12
5	216	224	5
6	167	-159	6
H,2,-5			
0	293	-290	5
1	119*	73	59
2	113*	54	56
3	111*	40	55
4	363E	352	5
5	123*	-128	60
6	171	-181	6
H,3,-5			
1	258	283	5
2	114*	-17	57
3	493E	-450	9
4	133	-140	4
5	120*	-69	60
6	239	-226	6
H,4,-5			
1	420E	415	7
2	114*	-49	57
3	56*	-53	28
4	79	-82	10
5	126*	32	63
H,5,-5			
1	432E	-409	7
2	71*	-13	35
3	155	-159	6
4	126*	-25	63
H,6,-5			
1	231	-270	5
2	122*	-47	61
3	128*	-106	64
4	139*	1	70
H,7,-5			
1	130*	84	65
2	147	-145	7
3	167	160	7
H,8,-5			
1	139*	-24	70
H,-5,-4			
0	230	219	6
1	276	-264	6
2	133*	47	66
3	134*	-85	67
4	217	-223	6
5	149	179	8
6	262	262	6
H,-4,-4			
0	328	-323	6
1	207	-208	5
2	225	-216	5
3	103	105	8
4	158	-169	6
5	129*	99	65
6	137*	21	68
7	129	-101	10
H,-3,-4			
0	118*	-64	59
1	396E	-364	6
2	175	166	5
3	78	79	10
4	145	-157	6
5	196	206	5
6	130*	13	65
7	186	-211	7
H,-2,-4			
0	373E	-353	6
1	159	-164	5
2	408E	375	7
3	297	289	5
4	292	-286	5
5	119*	-37	59
6	159	164	6
7	254	-257	6
H,-1,-4			
0	166	-135	5
1	215	201	5
2	396E	-344	6
3	161	139	5
4	71	95	11
5	91	-94	10
6	193	192	5
7	132*	-58	66
H,0,-4			
0	359E	336	6
1	122	120	5
2	107	112	6
3	307	-287	5
4	457E	-425	7
5	114*	-63	57
6	155	-174	6
7	73*	5	36
H,1,-4			
0	105*	34	53
1	102*	-41	51
2	104*	3	52
3	225	222	5
4	176	178	5
5	209	-215	5
6	103	-119	8
7	139	-163	7
H,2,-4			
1	361E	-334	5
2	364E	-349	5
3	125	119	6
4	114*	-5	56
5	240	-249	5
6	201	206	5
7	192	175	5
H,3,-4			
1	364E	-337	6
2	114*	117	57
3	119*	-40	59
4	324	-329	6
5	93	78	9
6	282	-299	5
H,4,-4			
1	57	-73	12
2	127*	48	63
3	124*	-11	62
4	222	-240	5
5	157	-152	5
6	279	289	5
H,5,-4			
1	139	-96	6
2	121*	13	60
3	123	111	7
4	71*	-49	35
5	74*	37	37
H,6,-4			
1	71*	-79	36
2	450E	-441	7
3	124*	38	62
4	131*	32	65
H,7,-4			
1	129*	5	60
2	123*	16	62
3	215	226	6
H,8,-4			
1	92	-118	11
2	169	-163	7
H,-7,-3			
2	141*	-32	71
3	140*	-49	70
4	143*	93	71
5	144*	-9	72
H,-6,-3			
0	137*	-103	68
1	129*	-5	64
2	123*	7	62
3	124*	49	62
4	102	-99	9
5	92	-104	11
6	159	172	7
7	155*	69	77
H,-5,-3			
0	122*	86	61
1	109	-109	7
2	71*	94	36
3	252	247	5
4	219	-220	5
5	234	248	5
6	133	-151	7
7	139*	40	70
H,-4,-3			
0	253	249	5
1	311	307	5
2	431E	-362	7
3	293	-282	5
4	279	265	5
5	175	172	5
6	111	120	9
7	131*	-69	66
8	147*	-31	73
H,-3,-3			
0	155	153	5
1	256	243	5
2	62	-52	11
3	91	79	9
4	112	-62	7
5	299	-290	5
6	166	-169	5
7	233	-239	5
8	141*	-127	70
H,-2,-3			
0	161	162	4
1	118	107	4
2	327	-303	5
3	460E	412	8
4	359E	345	6
5	107	65	8
6	379E	-374	6
7	122*	-98	61
8	132*	-35	66
H,-1,-3			
0	160	-156	4
1	146	142	4
2	197	-197	4
3	239	-230	4
4	134	129	5
5	364E	-344	6
6	122*	-14	61
7	371	353	6
8	132*	15	66
H,0,-3			
0	318	-296	5
1	273	261	5
2	248	245	4
3	361E	-335	6
4	223	-231	4
5	114*	-83	57
6	136	-137	6
7	120*	47	60
8	133	149	8
H,1,-3			
0	84*	31	42
1	429E	385	7
2	153	-151	4
3	144	-136	4
4	224	-214	4
5	152	137	5
6	119*	69	59
7	152	168	6
8	117	-97	10
H,2,-3			
1	133	-134	4
2	83	91	4
3	336E	-326	5
4	327	322	6
5	381E	407	6
6	159	-153	5
7	122*	21	61
H,3,-3			
1	90*	12	45
2	191	-182	4
3	297	-311	5
4	152	133	6
5	330	345	6
6	154	-150	4
7	270	-255	6
H,4,-3			
1	100*	43	50
2	119	125	5
3	466E	494	9
4	125*	-52	63
5	117*	-81	59
6	125*	-73	62
H,5,-3			
1	82	-89	8
2	220	216	5
3	57*	-57	29
4	115*	72	57
5	120*	91	60
6	222	-216	5
H,6,-3			
1	395E	360	5
2	216	227	5
3	121*	-10	60
4	306	-309	5
5	209	-213	6
H,7,-3			
1	232	235	5
2	122*	54	61
3	124*	1	62
4	174	-150	7
H,8,-3			
1	126*	-6	63
2	134*	-57	67
3	260	-263	6
H,9,-3			
1	145*	-56	72
H,-9,-2			
2	144*	149	72
3	141*	-65	70
4	141*	-32	70
5	351	346	6
H,-7,-2			
0	135*	36	68
1	156	153	6
2	206	-197	5
3	71*	22	36
4	127*	-103	63
5	335	339	6
6	174	219	7
7	152	-175	9
H,-6,-2			
0	159	173	6
1	316	-307	5
2	249	249	6
3	498E	393	7
4	117*	109	58
5	221	-229	6
6	257	-269	5
7	135*	-55	69
8	249	-247	7
H,-5,-2			
0	119*	97	59
1	72	37	11
2	119*	39	60
3	360	331	5
4	253	239	5
5	92	115	8
6	122*	22	61
7	129*	-112	64
8	69*	54	34
H,-4,-2			
0	191	-177	5
1	315	292	5
2	67*	-66	33
3	194	191	4
4	391E	-359	6
5	392E	-351	6
6	306	323	5
7	196	214	5
8	132*	67	66
9	201	190	7
H,-3,-2			
0	278	260	5
1	90*	12	45
2	362E	324	5
3	129	-115	4
4	295	-299	5
5	120*	-19	60
6	127*	3	63
7	174	175	5
8	337	-332	6
9	234	233	6
H,-2,-2			
0	92*	39	46
1	341E	307	6
2	94	-95	4
3	85	-81	5
4	167	169	4
5	101*	9	51
6	150	137	5
7	118*	97	59
8	124*	-55	62
9	141	-123	9
H,-1,-2			
0	399E	-347	7
1	206	-161	4
2	227	-209	4
3	89*	2	44
4	263	249	4
5	345E	344	6
6	175	162	5
7	131	-116	6
8	123	128	8
9	376	343	7
H,0,-2			
0	177	164	3
1	315E	-276	5
2	161	149	3
3	69	-72	6
4	157	-157	4
5	181	186	4
6	259	-246	5
7	354	341	6
8	124*	3	62
H,1,-2			
1	156	-151	3
2	211	189	4
3	495E	466	8
4	217	235	4
5	213	-220	4
6	123*	58	62
7	133	116	6
8	130	117	8
H,2,-2			
1	36	47	7
2	103	103	4
3	64*	49	32
4	130	-132	3
5	231	216	5
6	239	231	5
7	117*	0	58
8	135*	-2	68
H,3,-2			
1	117	-103	3
2	179	193	3
3	366E	406	6
4	287	-314	5
5	115*	-5	57
6	116*	31	58
7	125*	46	62
H,4,-2			
1	95*	-30	47
2	154	-152	4
3	186	205	5
4	188	192	5
5	121*	-53	60
6	200	194	5
H,5,-2			
1	319E	335	5
2	208	-220	5
3	119*	-11	60
4	165	168	5
5	107	-122	8
6	135*	-46	67
H,6,-2			
1	126*	28	63
2	237	-229	5
3	177	198	5
4	178	-184	6
5	138*	-103	69
H,7,-2			
1	228	236	5
2	121*	31	60
3	66	-70	7
4	315	295	6
H,8,-2			
1	133	-136	7
2	280	-286	6
H,9,-2			
1	147*	53	73
H,-9,-1			
3	264	264	6
4	305	305	6
H,-8,-1			
0	158	157	7
1	132*	39	66
2	204	217	6
3	127*	35	64
4	124	-125	7
5	424E	402	7
6	135*	-94	69
7	155	147	9
H,-7,-1			
0	72*	-2	36
1	72*	124	36
2	69*	16	34
3	67*	42	33
4	171	-159	5
5	324	-316	6
6	171	162	5
7	135*	67	68
8	155*	43	78
H,-6,-1			
0	226	234	5
1	272	274	5
2	121*	-9	60
3	103	-36	7
4	114*	-20	57
5	77	88	10
6	118*	-42	59
7	243	-253	5
8	142*	-100	71
H,-5,-1			
0	71	-95	10
1	253	264	4
2	114	-114	5
3	103*	23	52
4	110*	40	55
5	322	312	6
6	219	-241	5
7	73*	-74	37
8	207	213	6
9	131	124	10
H,-4,-1			
0	233	-241	4
1	121	-126	4
2	215	-207	4
3	239	-225	4
4	192	196	4
5	103*	22	51
6	249	233	5
7	120*	81	60
8	123*	48	62
9	506E	444	8
H,-3,-1			
0	63	-64	6
1	294	259	5
2	83*	4	41
3	243	-234	4
4	76	-66	6
5	156	-165	4
6	248	-240	5
7	334	332	6
8	328	309	6
9	243	-238	6
H,-2,-1			
0	54	55	4
1	121	115	2
2	123	-116	2
3	310E	288	5
4	163	168	3
5	306E	317	5
6	113*	-51	56
7	111*	71	55
8	110*	56	55
9	193	-177	6
H,-1,-1			
0	328E	-294	5
1	211	-191	4
2	276E	257	5
3	320E	-302	5
4	46	-60	8
5	279	281	5
6	253	253	5
7	93	100	8
8	259	-258	5
9	82*	10	41
H,0,-1			
0	65	-62	2
1	125	-112	2
2	95	90	2
3	280E	290	5
4	88	98	4
5	60	61	9
6	194	-180	5
7	234	-197	5
8	120*	-15	60
H,1,-1			
1	224E	214	4
2	82	-76	3
3	179	181	3
4	194	-196	4
5	285	291	5
6	126*	-9	63
7	390	-356	6
8	130*	83	65
H,2,-1			
1	229E	230	4
2	285E	314	5
3	197	-220	4
4	72	-80	7
5	113	-73	5
6	203	-189	4
7	116	135	7
8	222	209	6
H,3,-1			
1	149	161	3
2	162	-256	4
3	64*	47	32
4	239	-235	5
5	239	-234	5
6	152	143	5
7	109	-99	9
H,4,-1			
1	281E	324	5
2	208	-228	4
3	117*	-2	58
4	81	84	10
5	117*	70	58
6	123*	72	62
H,5,-1			
1	299E	-364	5
2	195	-194	5
3	293	-289	5
4	149	153	6
5	218	210	5
H,6,-1			
1	127*	-32	63
2	212	229	5
3	121*	5	60
4	187	-191	6
5	139*	-66	70
H,7,-1			
1	87	107	10
2	170	160	6
3	133*	153	66
H,8,-1			
1	107	-139	9
2	350	329	6
H,-9,0			
1	146*	-115	73
2	242	264	6
3	132*	22	66
4	136*	-116	68
5	137*	44	68
6	149*	15	75
H,-8,0			
0	228	-238	5
1	121*	-71	60
2	124*	16	62
3	190	205	5
4	173	-190	5
5	124*	-60	62
6	133*	80	66
7	150	-187	9
H,-7,0			
0	249	248	5
1	120*	3	60
2	363E	-446	6
3	151	153	6
4	293	-291	5
5	290	-308	5
6	286	299	5
7	171	175	6
8	148*	16	74
H,-6,0			
0	220	220	5
1	55	61	13
2	109*	-11	55
3	209	-218	4
4	113*	-43	56
5	271	-276	5
6	254	-263	5
7	309	314	6
8	136*	-91	68
9	132	82	11
H,-5,0			
0	115	-130	5
1	113	-126	4
2	309E	-352	5
3	193	197	4
4	244	262	4
5	114*	36	56
6	338	326	6
7	125*	49	62
8	333	-315	6
9	159	-148	9
H,-4,0			
0	330E	-399	5
1	248E	-299	4
2	232	-236	4
3	84	108	4
4	85	-102	5
5	165	-165	4
6	195	185	5
7	231	240	5
8	211	-207	5
9	131	-134	9
H,-3,0			
0	69*	26	34
1	193	-221	3
2	102	103	3
3	77	48	4
4	248	254	4
5	74	84	7
6	477E	-445	8
7	146	144	5
8	247	-239	5
9	141*	-71	70
H,-2,0			
0	160	-183	3
1	223E	226	4
2	170	187	3
3	62*	-9	31
4	219	-226	4
5	88*	-53	44
6	138	137	6
7	212	-214	5
8	72*	-37	36
9	83*	-90	41
H,-1,0			
0	126E	-150	2
1	120	139	2
2	82*	14	41
3	80*	24	40
4	107	-111	4
5	135	-132	4
6	273	-254	5
7	122*	35	61
8	167	162	6
H,0,0			
1	117	-131	2
2	270E	-315	5
3	62*	-33	31
4	214	-209	4
5	92*	-38	46
6	315	-288	5
7	70*	66	35
8	144	-158	7
H,1,0			
1	50	-17	3
2	204	-219	3
3	73*	24	36
4	159	149	4
5	115	-121	6
6	58	64	13
7	172	-158	5
8	182	168	6
H,2,0			
1	222E	-266	4
2	358E	-404	6
3	65	-61	7
4	127	-121	5
5	239	-227	5
6	122	128	4
7	210	194	4
H,3,0			
1	77*	-63	38
2	77	87	6
3	232	232	4
4	301	-292	5
5	201	-206	5
6	165	-157	6
7	197	184	6
H,4,0			
1	212	229	4
2	89	-88	6
3	297	-288	5
4	391E	372	6
5	121*	51	60
6	130*	4	65
H,5,0			
1	105*	25	52
2	119	-89	7
3	173	-182	5
4	142	-126	6
5	155	142	7
H,6,0			
1	127*	-96	64
2	230	-242	5
3	72*	18	36
4	78*	63	39
H,7,0			
1	72*	66	36
2	74*	27	37
3	82*	-51	41
H,8,0			
1	209	-218	6
H,-10,1			
3	230	-235	7
4	153*	-42	77
H,-9,1			
0	95	-81	12
1	189	215	5
2	108	-103	9
3	132*	-129	66
4	132*	10	66
5	136*	4	68
6	239	-243	7
7	199	-174	8
H,-8,1			
0	127*	-7	63
1	205	-225	5
2	284	-303	5
3	121*	86	60
4	97	90	9
5	227	220	5
6	130*	42	65
7	222	235	6
8	193	-154	8
H,-7,1			
0	362E	-427	6
1	122*	-82	61
2	127	-100	7
3	215	-196	5
4	127*	94	64
5	272	-267	5
6	124*	21	62
7	132*	98	66
8	149*	110	74
H,-6,1			
0	314E	-366	5
1	332E	364	6
2	216	205	4
3	322	-297	5
4	105	107	7
5	308	288	5
6	243	-249	5
7	122	-126	7
8	71	-97	15
H,-5,1			
0	227	-236	4
1	159	166	4
2	336	301	5
3	96*	-4	48
4	362E	-327	6
5	269	277	5
6	69	-26	12
7	125*	-34	62
8	133*	-94	66
9	181	-188	8
H,-4,1			
0	160	-166	3
1	86*	-15	43
2	133	122	3
3	384E	-335	6
4	282	282	5
5	188	198	4
6	330	-315	6
7	187	-193	5
8	127*	14	64
9	144*	105	72
H,-3,1			
0	250E	246	4
1	108	102	3
2	77*	-51	39
3	121	-111	3
4	207	-210	4
5	175	168	4
6	308	-294	5
7	310	-286	5
8	130*	75	65
9	212	-194	7
H,-2,1			
0	182	-167	3
1	319E	-269	5
2	180	170	3
3	352E	335	6
4	324E	-345	5
5	171	170	4
6	87	-59	10
7	251	-266	5
8	210	219	5
H,-1,1			
0	50	54	2
1	237E	-209	4
2	75*	27	37
3	220	-218	4
4	267E	-302	4
5	305	-322	5
6	132	94	7
7	246	263	5
8	130*	-76	65
H,0,1			
1	169	157	3
2	133	149	3
3	213	233	4
4	310E	-368	5
5	104*	-58	52
6	157	175	6
7	264	-258	5
8	146	153	7
H,1,1			
1	163	159	3
2	277E	-275	5
3	158	-170	4
4	66	-81	8
5	409E	371	7
6	325	349	6
7	154	-170	6
H,2,1			
1	275	-265	5
2	58	-80	6
3	110	-109	5
4	134	125	6
5	119*	-56	59
6	99	84	8
7	264	237	6
H,3,1			
1	116	114	4
2	190	-190	4
3	100	90	7
4	240	239	5
5	112*	15	56
6	278	-273	5
H,4,1			
1	250	250	4
2	270	272	5
3	285	293	5
4	118*	38	59
5	139	-136	7
H,5,1			
1	417E	-439	7
2	338	346	6
3	92	67	9
4	263	-257	5
H,6,1			
1	317	323	5
2	122*	-27	61
3	149	-156	7
H,7,1			
1	74*	-31	37
2	81*	10	40
H,-10,2			
2	119	-131	11
3	198	202	7
4	342	-309	7
5	178	-157	8
H,-9,2			
0	135*	6	67
1	120	104	8
2	252	263	6
3	145	-162	7
4	132*	34	66
5	94	104	11
6	200	216	7
H,-8,2			
0	125*	-34	63
1	125*	-18	63
2	212	-205	5
3	316	309	5
4	125*	129	62
5	124*	-49	62
6	226	217	6
7	141*	38	71
H,-7,2			
0	122*	70	61
1	129	87	7
2	323	-291	6
3	128*	28	64
4	321	300	5
5	203	206	5
6	161	-181	6
7	132	-133	8
8	146*	-74	73
H,-6,2			
0	258	274	5
1	96	-91	6
2	323	297	5
3	174	166	4
4	117*	67	58
5	196	-187	5
6	318	-328	5
7	235	251	5
8	226	-245	6
H,-5,2			
0	83	97	6
1	179	-171	4
2	66	59	7
3	519E	433	8
4	108*	-61	54
5	260	-242	5
6	71	197	12
7	126*	27	63
8	147	156	7
H,-4,2			
0	274	264	5
1	314E	289	5
2	149	-147	4
3	80	-73	6
4	289	-276	5
5	249	-249	5
6	77*	-52	39
7	312	319	5
8	136*	119	69
H,-3,2			
0	413E	364	7
1	120	-112	3
2	134	122	3
3	181	179	3
4	182	-189	4
5	204	223	4
6	132*	69	66
7	123*	-28	62
8	177	-183	6
H,-2,2			
0	70*	-40	35
1	141	136	3
2	473E	-408	8
3	96	-98	4
4	191	191	4
5	100	123	7
6	398E	405	7
7	116*	11	58
8	129*	-17	65
H,-1,2			
0	153	166	3
1	129	140	3
2	430E	-407	7
3	216	224	4
4	319E	347	5
5	143	-155	6
6	164	-182	5
7	239	241	5
8	203	197	6
H,0,2			
1	233	222	4
2	89*	8	44
3	144	129	4
4	178	207	4
5	181	173	5
6	256	-264	5
7	124*	-17	62
H,1,2			
1	385E	356	6
2	200	190	4
3	256	260	4
4	392E	409	6
5	341	-330	6
6	141	131	6
7	369	330	6
H,2,2			
1	94*	3	47
2	137	-139	4
3	93	-95	8
4	120*	45	60
5	117	115	7
6	127*	-96	63
H,3,2			
1	469E	445	8
2	257	243	5
3	237	-236	5
4	114	-114	7
5	237	235	5
H,4,2			
1	124*	-43	62
2	181	190	5
3	84	-73	9
4	216	217	5
5	110	67	10
H,5,2			
1	115*	62	57
2	117*	-35	59
3	122*	-66	61
H,6,2			
1	127*	109	63
2	170	-167	7
H,7,2			
1	144*	-2	72
H,-10,3			
2	151*	-59	76
3	150	-145	9
4	265	250	6
H,-9,3			
0	193	-182	6
1	241	237	5
2	213	215	6
3	234	224	6
4	164	152	7
5	203	-193	6
6	265	-260	6
H,-8,3			
0	126*	135	63
1	122*	23	61
2	114	135	9
3	98	108	9
4	125*	-49	63
5	205	190	6
6	137*	-107	68
7	152*	141	76
H,-7,3			
0	258	-259	5
1	374E	351	5
2	319	299	6
3	471E	-417	8
4	61	-85	8
5	126*	-53	63
6	130*	-42	65
7	138*	10	69
H,-6,3			
0	122*	22	61
1	60	-89	12
2	152	150	5
3	120	81	7
4	210	-180	5
5	356	341	6
6	124*	15	62
7	165	-178	7
8	150*	-73	75
H,-5,3			
0	48*	-37	24
1	51	-59	11
2	114	-115	5
3	111	-121	6
4	245	-225	5
5	351	343	6
6	126*	-21	63
7	129*	54	65
8	372E	363	6
H,-4,3			
0	130	-123	4
1	95*	24	47
2	65	52	7
3	141	-146	5
4	204	199	5
5	121*	-20	60
6	84	-87	10
7	125*	9	62
8	200	211	6
H,-3,3			
0	92*	-123	46
1	94*	56	47
2	185	175	4
3	264	249	5
4	294	-300	5
5	217	217	5
6	242	264	5
7	120	-119	8
8	142*	4	71
H,-2,3			
0	250	-243	4
1	45	-37	9
2	101	-101	5
3	367E	355	6
4	175	190	5
5	119*	72	59
6	164	182	6
7	215	227	5
H,-1,3			
1	186	-187	4
2	76	83	6
3	287	-287	5
4	57	9	14
5	125*	129	62
6	151	162	6
7	131*	-48	66
H,0,3			
1	351E	327	6
2	430E	403	7
3	228	231	5
4	179	-186	4
5	109*	27	54
6	118*	-57	59
H,1,3			
1	155	-146	4
2	104*	52	52
3	242	232	5
4	107*	25	53
5	110*	15	55
6	123*	-51	62
H,2,3			
1	123	-125	6
2	336	325	6
3	292	-286	5
4	223	-226	5
5	125*	77	62
H,3,3			
1	117*	3	58
2	220	-224	5
3	116*	89	58
4	153	-146	6
H,4,3			
1	315	-296	5
2	122*	-82	61
3	212	212	5
H,5,3			
1	405E	-403	7
2	148	-143	7
H,6,3			
1	133	124	9
H,-9,4			
0	192	205	7
1	165	-175	7
2	122	122	9
3	141*	-83	70
4	163	172	8
5	145*	-14	72
H,-8,4			
0	162	-141	6
1	156	134	6
2	74*	-97	37
3	140	-140	7
4	227	-209	6
5	138*	52	69
6	142	-132	9
H,-7,4			
0	132	123	7
1	124*	3	62
2	188	-190	5
3	127*	-60	64
4	127*	-105	64
5	129*	21	64
6	68	-115	12
H,-6,4			
0	379E	349	6
1	416E	-375	7
2	126*	-13	63
3	112	129	8
4	162	-174	6
5	91	93	10
6	134*	61	67
7	218	235	6
H,-5,4			
0	169	-157	5
1	121	-109	7
2	516E	-454	8
3	234	224	5
4	304	292	5
5	125*	58	62
6	177	198	5
7	70	-121	17
H,-4,4			
0	111*	1	55
1	109*	-28	55
2	197	-190	5
3	133	97	7
4	190	-212	5
5	74	-81	11
6	128*	133	64
7	141*	-70	70
H,-3,4			
0	108	-105	6
1	109*	78	55
2	331	313	6
3	360E	341	6
4	126*	72	63
5	103	-124	8
6	274	-288	5
7	140*	-49	70
H,-2,4			
0	141	-144	5
1	380E	381	6
2	370E	-365	6
3	174	-150	5
4	280	300	5
5	227	-250	5
6	126*	59	63
H,-1,4			
1	316	306	5
2	90	-25	8
3	335	-314	6
4	185	-199	5
5	121*	12	60
6	244	-270	6
H,0,4			
1	116*	-22	58
2	315	-312	5
3	189	-187	5
4	114*	53	57
5	122*	39	60
H,1,4			
1	114	-117	7
2	124	-135	6
3	115*	-72	57
4	167	170	6
5	170	-159	7
H,2,4			
1	227	-211	5
2	155	-149	5
3	122*	-90	61
4	132*	-89	66
H,3,4			
1	70*	92	35
2	138	144	7
3	129	136	8
H,4,4			
1	130*	43	65
2	139*	28	70
H,-9,5			
1	299	-281	6
2	149*	-79	74
3	152*	93	75
H,-8,5			
0	170	-184	7
1	342	-336	6
2	136*	-94	68
3	141*	62	70
4	136	-159	9
H,-7,5			
0	234	-225	5
1	138	-143	7
2	209	203	5
3	115	126	8
4	222	-223	6
5	323	-314	6
H,-6,5			
0	168	-158	6
1	83	92	10
2	119	121	7
3	357	345	6
4	127*	-79	63
5	154	164	7
H,-5,5			
0	120*	27	60
1	320	312	6
2	281	-274	5
3	167	-158	6
4	125*	-78	63
5	132*	52	66
6	159	149	8
H,-4,5			
0	121*	5	60
1	121*	-6	60
2	135	124	6
3	164	-168	6
4	122*	37	61
5	209	-258	6
H,-3,5			
0	129	128	7
1	111	138	8
2	276	-303	5
3	121*	87	60
4	123*	68	61
5	111	-129	9
H,-2,5			
0	266	-290	5
1	176	-172	5
2	118*	95	59
3	95	120	8
4	59*	-81	29
5	169	-157	7
H,-1,5			
1	367	-343	6
2	282	288	5
3	353	-345	6
4	237	-244	5
H,0,5			
1	88	97	9
2	113*	19	56
3	197	191	5
4	279	-288	5
H,1,5			
1	223	-234	5
2	146	-153	6
3	120	-127	8
H,2,5			
1	74*	-97	37
2	77*	27	38
H,3,5			
1	198	-190	5
H,-7,6			
0	245	252	6
1	66*	19	33
2	130	-141	9
3	247	237	6
H,-6,6			
0	161	169	6
1	226	227	6
2	133*	58	66
3	138*	-31	69
H,-5,6			
0	362	-347	6
1	216	218	5
2	74*	-21	37
3	97	106	11
4	82*	-8	41
H,-4,6			
0	123*	-2	62
1	125*	95	62
2	127*	62	63
3	343	-338	6
4	275	-268	6
H,-3,6			
0	176	176	5
1	152	152	6
2	125*	44	62
3	164	-150	7
H,-2,6			
1	122*	-54	61
2	117	-123	8
3	272	-274	6
H,-1,6			
1	122*	-30	61
2	106	109	9
H,0,6			
1	194	-179	6

later), have the largest Ca···O distances, 2·665 and 2·826 Å respectively, in some agreement with the normal pattern. The Ca···O(7) distance, 2·429 Å, is relatively short for an oxygen covalently bonded to hydrogen. Oxygens O(3) and O(8), which are also bonded to hydrogens, are not within the primary coordination of Ca.

The PO_4 *groups and their environments*

The details of the two unique PO_4 groups and their environments are given in Table 4 and shown in Figs. 3 and 4. The longest P–O distances in the phosphate groups are those where the oxygen has a covalently bonded hydrogen. The P(2)–O(7) and P(2)–O(8) distances are intermediate in length, which is consistent

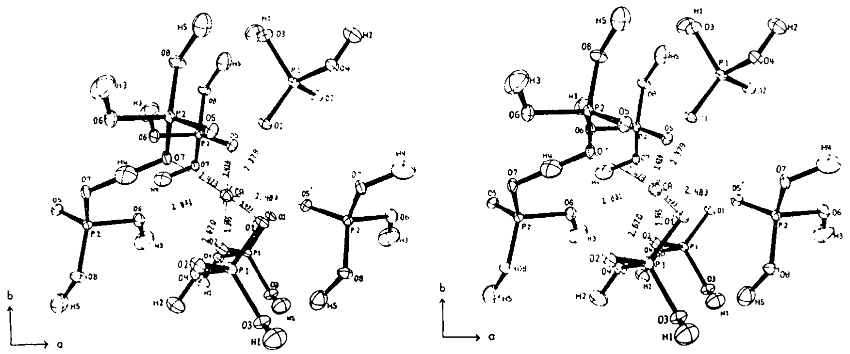

Fig. 2. The Ca ion environment in $Ca(H_2PO_4)_2$ as obtained in the neutron study.

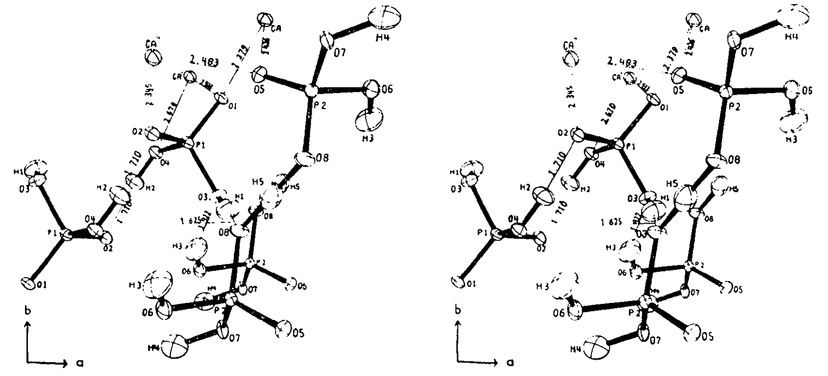

Fig. 3. The $H_2P(1)O_4$ ion environment in $Ca(H_2PO_4)_2$ as obtained in the neutron study. Note the $(H_2P(1)O_4)_2$ dimeric configuration.

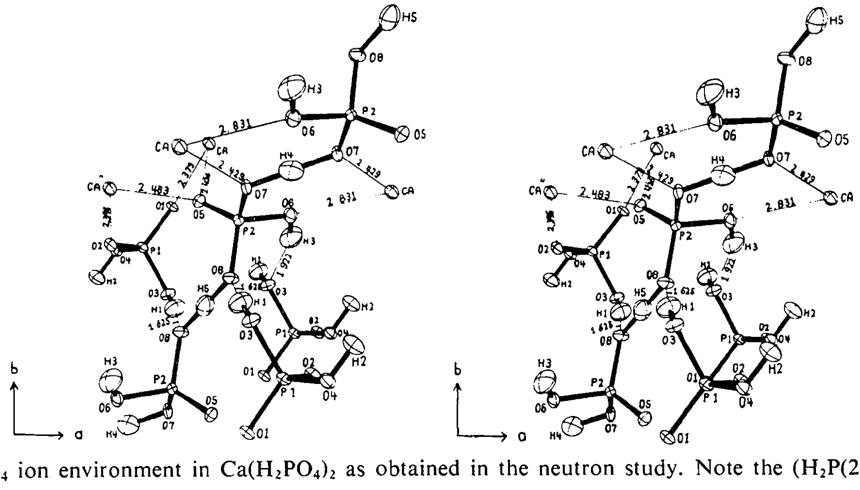

Fig. 4. The $H_2P(2)O_4$ ion environment in $Ca(H_2PO_4)_2$ as obtained in the neutron study. Note the $(H_2P(2)O_4)_n$ infinite chain.

with the 'half' hydrogens found to be associated with O(7) and O(8). The P–O bond lengths are expected to be in some proportion to the strength of the interaction of each oxygen with its environment. In some instances this expectation is realized but in others it is not.

The O–P–O angles in the unusually distorted $P(1)O_4$ group may be explained as follows. The smallest angle, O(1)–P(1)–O(4) (102·07°), is in accord with Pauling's (1960) rule since the O(1)–O(4) edge is coordinated to Ca. The O(3)–P(1)–O(4) angle (103·17°) is expected to be small because O(3) and O(4) are both covalently bonded to hydrogen and P(1)–O(3) and P(1)–O(4) are both long (see, for example, Table 11 of Baur & Khan, 1970). Conversely, the O(1)–P(1)–O(2) angle is expected to be large (the observed value is 117·59°) because P(1)–O(1) and P(1)–O(2) are both short. In the $P(2)O_4$ group, the angles involving O(5) are the largest, as expected because P(2)–O(5) is the shortest P–O distance in this group. However, it is not clear why the O(6)–P(2)–O(7) angle (102·41°) is considerably different from the O(6)–P(2)–O(8) angle (108·42°), or why the O(5)–P(2)–O(7) angle is different from the O(5)–P(2)–O(8) angle.

The O(1)–O(4) edge and the O(1) and O(2) apexes

Table 4. *Structural details in* $Ca(H_2PO_4)_2$

Figures in parentheses are standard deviations from least squares and do not include errors in cell dimensions. They should not be taken as implying the mean bond distance is known to this precision. The range of thermal motion corrections for Ca–O and O–O distances is 0·001 Å (max. correlated in-phase displacements) to 0·02 Å (max. correlated out-of-phase displacements).

Ca environment	Distance, or angle			
	X-ray		Neutron	
Ca, O(2)	2·3547 (6) Å		2·345 (4) Å	
Ca, O(1)	2·3795 (6)		2·379 (5)	
Ca, O(5)	2·4238 (6)		2·426 (4)	
Ca, O(7)	2·4284 (6)		2·423 (5)	
Ca, O(1′)	2·4316 (6)		2·433 (4)	
Ca, O(5′)	2·4874 (7)		2·483 (4)	
Ca, O(4)	2·6647 (6)		2·670 (4)	
Ca, O(6)	2·8262 (7)		2·831 (4)	
$H_2P(1)O_4$ group				
P(1), O(1)	1·5125 (6)	1·5157 (6)^R	1·513 (4)	1·515 (4)^R
P(1), O(2)	1·5061 (6)	1·5105 (6)^R	1·512 (4)	1·515 (4)^R
P(1), O(3)	1·5709 (6)	1·5770 (6)^R	1·563 (4)	1·569 (4)^R
P(1), O(4)	1·5742 (6)	1·5791 (6)^R	1·576 (4)	1·579 (4)^R
O(1), O(2)	2·5818 (9)		2·581 (4)	
O(1), O(3)	2·5773 (9)		2·569 (4)	
O(1), O(4)	2·4003 (8)		2·409 (4)	
O(2), O(3)	2·4849 (9)		2·482 (4)	
O(2), O(4)	2·5533 (9)		2·560 (4)	
O(3), O(4)	2·4643 (9)		2·463 (4)	
O(1), P(1), O(2)	117·59 (3)°		117·2 (3)°	
O(1), P(1), O(3)	113·40 (4)		113·3 (3)	
O(1), P(1), O(4)	102·07 (3)		102·5 (3)	
O(2), P(1), O(3)	107·69 (4)		107·6 (3)	
O(2), P(1), O(4)	111·95 (4)		112·0 (3)	
O(3), P(1), O(4)	103·17 (4)		103·4 (3)	
O(3), H(1)	0·82 (2) Å		1·000 (8) Å	1·016 (8)^R
O(4), H(2)	0·73 (2)		1·000 (8)	1·011 (8)^R
P(1), O(3), H(1)	110 (1)°		115·9 (4)°	
P(1), O(4), H(2)	117 (1)		117·0 (3)	
$H_2P(2)O_4$ group				
P(2), O(5)	1·4959 (6) Å	1·4997 (6)^R	1·499 (4) Å	1·502 (4)^R
P(2), O(6)	1·6001 (6)	1·6057 (6)^R	1·596 (4)	1·601(4)^R
P(2), O(7)	1·5266 (6)	1·5308 (6)^R	1·528 (4)	1·532 (4)^R
P(2), O(8)	1·5401 (6)	1·5461 (6)^R	1·540 (4)	1·545 (4)^R
O(5), O(6)	2·5292 (9)		2·530 (4)	
O(5), O(7)	2·5341 (8)		2·540 (4)	
O(5), O(8)	2·5389 (9)		2·535 (4)	
O(6), O(7)	2·4372 (9)		2·439 (4)	
O(6), O(8)	2·5473 (9)		2·547 (4)	
O(7), O(8)	2·4869 (9)		2·484 (4)	

$H_2P(2)O_4$ group (cont.)	Distance, or angle	
	X-ray	Neutron
O(5), P(2), O(6)	109·52 (4)°	109·6 (3)°
O(5), P(2), O(7)	113·95 (4)	114,1 (3)
O(5), P(2), O(8)	113·49 (4)	113·0 (3)
O(6), P(2), O(7)	102·41(3)	102·7 (3)
O(6), P(2), O(8)	108·42 (4)	108·6 (3)
O(7), P(2), O(8)	108·38 (3)	108·1 (3)
O(6), H(3)	0·78 (2) Å	0·957 (8) Å 0·985 (8)^R
O(7), H(4)	1·2171 (5)	1·218 (3)
O(8), H(5)	1·2116 (6)	1·210 (3)
P(2), O(6), H(3)	116 (1)°	111·7 (5)°
P(2), O(7), H(4)	113·75 (4)	113·6 (2)
P(2), O(8), H(5)	121·59 (5)	121·9 (2)
H_2PO_4 environments		
O(1), Ca	2·3795 (6)	2·379 (4)
O(1), Ca′	2·4316 (6)	2·433 (4)
O(2), Ca	2·3547 (6)	2·346 (4)
O(2), H(2)	1·70, 1·98 (2)‡	1·710 (6)
O(2), O(4)	2·6778 (9)§	2·677 (5)§
O(3), O(8)	2·6210 (9)§	2·620 (4)§
H(1), O(8)	1·62, 1·80 (2)‡	1·625 (7)
O(3), H(1), O(8)	177°, 175 (1)°‡	173·6 (6)°
O(3), H(3)	1·90, 2·11 (2) Å‡	1·922 (8) Å
O(3), O(6)	2·8101 (9)§	2·817 (4)§
O(4), Ca	2·6647 (6)	2·671 (5)
O(4), O(2)	2·6778 (9)§	2·677 (5)§
H(2), O(2)	1·70, 1·98 (2)‡	1·710 (6)
O(4), H(2), O(2)	164, 161 (2)°‡	162·8 (6)°
O(5), Ca	2·4238 (6) Å	2·426 (4) Å
O(5), Ca″	2·4874 (7)	2·483 (4)
O(6), Ca	2·8262 (7)	2·831 (4)
O(6), O(3)	2·8101 (9)§	2·817 (4)§
H(3), O(3)	1·90, 2·11 (2)‡	1·922 (8)
O(6), H(3), O(3)	150, 150 (2)°‡	154·5 (6)°
O(7), Ca	2·4284 (6) Å	2·429 (4) Å
O(7), O(7′)	2·434 (1)§	2·434 (5)§
H(4), O(7′)	1·43, 1·217 (5)‡	1·217 (3)
O(7), H(4), O(7′)	180, 180°‡	180°
O(8), O(8′)	2·423 (1)§	2·419 (6) Å§
H(5), O(8′)	1·44, 1·216 (6)‡	1·210 (3)
O(8), H(5), O(8′)	167, 180°‡	180°
O(8), O(3)	2·6210 (9)§	2·620 (4)§
O(8), H(1)	1·62, 1·80 (2)‡	1·625 (7)

‡ First value from calculated hydrogen position,O–H distance of 1·000Å, P–O–H angle of 114° assumed, as described in text, second value from X-ray results.
§ These O···O distances involve hydrogen bonds.
^{R} Riding-model correction (Busing & Levy, 1964).

in the P(1)O_4 group and the O(5), O(6) and O(7) apexes in the P(2)O_4 group are coordinated to Ca. No edge in the H_2P(2)O_4 ion is coordinated to Ca.

The hydrogen bonds

In our X-ray studies of calcium phosphates, the positions of the hydrogen atoms are known only imprecisely owing to known systematic error in the scattering factors of hydrogen. It has become our practice to calculate 'ideal hydrogen positions'. In Table 1 we report similarly calculated hydrogen positions for comparison with the positions from the neutron-diffraction results. The calculated positions were obtained by assuming that the O–H distance is 1·000 Å and the P–O–H angle is 114°, averages of the values found by neutron diffraction here and in $CaHPO_4.2H_2O$ (Jones, 1970). The calculated positions for H(1), H(2) and H(3) are close to those found by neutron diffraction, and justify the procedure for use in cases of non-centered hydrogen bonds if neutron studies may be unavailable.

The variation of the O–H distance with the O···O distance for the non-centered hydrogen bonds is consistent with the curve given by Pimentel & McClellan (1971; Fig. 4, therein). The O(6)–H(3) distance of 0·97 Å is the value expected for an O···O distance of 2·82 Å. Likewise, the O(3)–H(1) and O(4)–H(2) distances of ~1·03 Å are those expected for O···O distances of 2·62 and 2·68 Å.

While the precision of our neutron study does not equal that of our X-ray work, the orientations of the ellipsoids representing the vibrational motion of H(1) and H(2) are reasonable in that the smallest principal axis is in each case approximately parallel to the O–H bond, and the largest amplitude of motion is perpendicular to the P–O–H···O plane. This is to be expected since motion of the hydrogen out of this plane (derived from OH libration about the P–O bond) is known to be of low frequency (~950 cm^{-1}) and thus of relatively large amplitude (Chapman & Thirlwell, 1964).

The orientation of the thermal ellipsoid for H(3) is not as easily understood as those of H(1) and H(2). The large errors (~20°) in the orientation angles for H(3) suggest that the motion of this hydrogen may not be adequately described by the usual thermal ellipsoid.

Hydrogen atoms H(4) and H(5) are both involved in very short hydrogen bonds, the O···O distances being 2·434 and 2·423 Å respectively, and link P(2)O_4 groups together to form a chain with the repeating unit -H(4)---O(7)P(O_2H)O(8)---H(5)- (see Figs. 1 and 4). The apparent positions of these protons on centers of symmetry may be examined in terms of three models. (i) The protons could be ordered in a chain so that each one is associated with only one PO_4 group. Thus, H(4) and H(5) would not be on centers of symmetry, but the sense of neighboring chains would be random to give an average picture of two half-hydrogens about the center. This situation is very unlikely in view of the very short O···O distances; asymmetric distributions have been found only for O···O distances greater than 2·54 Å (Pimentel & McClellan, 1971). (ii) Each proton could be located in a symmetrical double-minimum potential with the very short O···O distance implying a low central barrier and consequently a high tunneling rate. (iii) Each proton could be in a potential well with a central barrier, if any, below the zero-point energy.

The difficulty of deciding from diffraction data alone whether the potential has a single or double minimum has been discussed by Hamilton & Ibers (1968). Using the neutron data on $Ca(H_2PO_4)_2$, we carried out a series of refinements in which H(4) and H(5) were displaced off center along the O(7)···O(7′) and O(8)···O(8′) vectors respectively in steps of 0·05 Å and only the vibrational amplitudes of the protons and associated oxygens O(7) and O(8) were allowed to vary. The

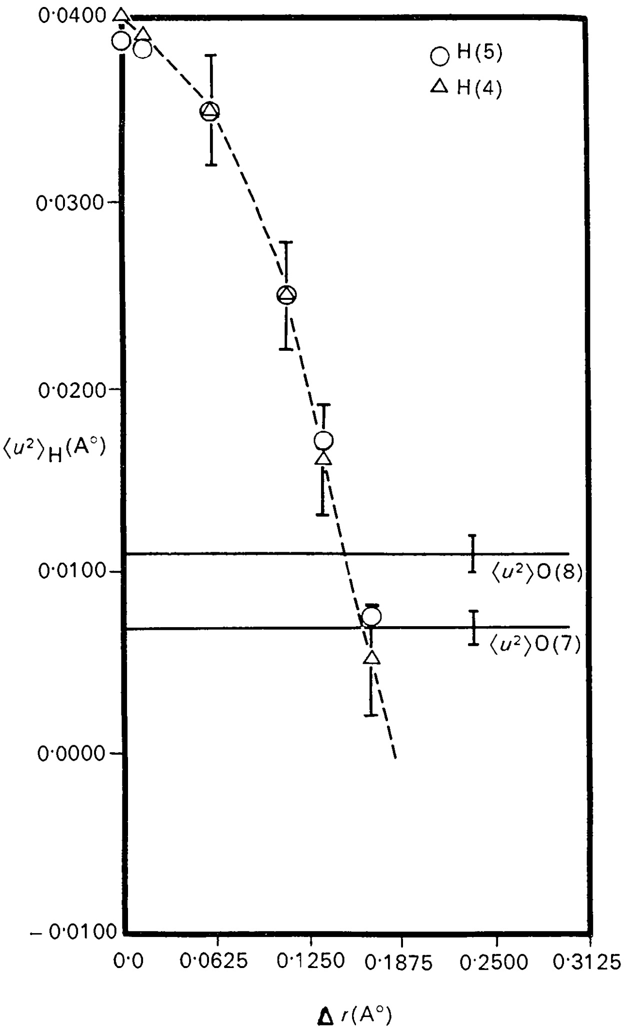

Fig. 5. The variation of the mean-square amplitudes of hydrogen atoms H(4) and H(5) with displacement from the centers of symmetry along the O(7)···O(7′) and O(8)···O(8′) vectors in $Ca(H_2PO_4)_2$.

apparent amplitudes of vibration for H(4) and H(5) along the O···O vectors decreased as the protons were moved further off center while the corresponding amplitudes for O(7) and O(8) remained constant. No significant change in the value of R_w occurred until the protons were 0·17 Å off center, when negative amplitudes of vibration were obtained for both protons. Fig. 5 gives the results of these refinements and shows that an upper bound for the off-center distances is ~0·15 Å assuming the proton vibrational amplitude along the O···O vector must be at least that of the oxygens. This is a good assumption since the only motions where the proton does not move with the oxygen atoms are modes in which the oxygen motions maintain the center of symmetry and these optic modes are known to have very small amplitudes. This reasoning restricts the protons to within 0·15 Å of the centers.

More insight into the nature of these short hydrogen bonds can be gained by considering both spectroscopic and diffraction information. The exact frequency of the OH stretching vibration for very short (~2·45 Å) hydrogen bonds is still under discussion, but is generally associated with absorptions in the range 600–1500 cm^{-1} (Hadzi, 1965). The infrared spectrum of $Ca(H_2PO_4)_2$ in the range 400–4000 cm^{-1} is shown in Fig. 6. Our spectrum confirms an earlier one by Lehr, Brown, Frazier, Smith & Thrasher (1967). Although we do not intend to delve into detailed assignments, some absorption bands can be assigned by analogy with other phosphates (Chapman & Thirlwell, 1964) and $Ca(H_2PO_4)_2 . H_2O$ (Berry, 1967). The absorptions at 3450 and 3320 cm^{-1} are O–H stretching frequencies expected for an O···O distance of ~2·82 Å (Pimentel & McClellan, 1971), while absorption at 2950 cm^{-1} is similarily expected for O···O distances of ~2·6 Å. This leaves open the question of the OH stretching frequency for the very short (~2·45 Å) hydrogen bonds, which are expected to absorb in the 500–1700 cm^{-1} region (Hadzi, 1965). However, many absorptions including in-plane and out-of-plane OH bends, which hinder assignments *via* deuterium shifts, absorb in this region and make it difficult to uniquely assign the OH stretching frequencies associated with the short hydrogen bonds. The spectrum indicates that the highest stretching frequency the OH vibrations in the centered hydrogen bonds could have is ~1400 cm^{-1}, assuming the absorption at ~1400 cm^{-1} is due to OH stretching rather than to OH in-plane bending. One can construct an approximate double-minimum potential for these protons using both spectroscopic and diffraction data. As the extreme case, we can take an upper bound to the OH stretching frequency as 1400

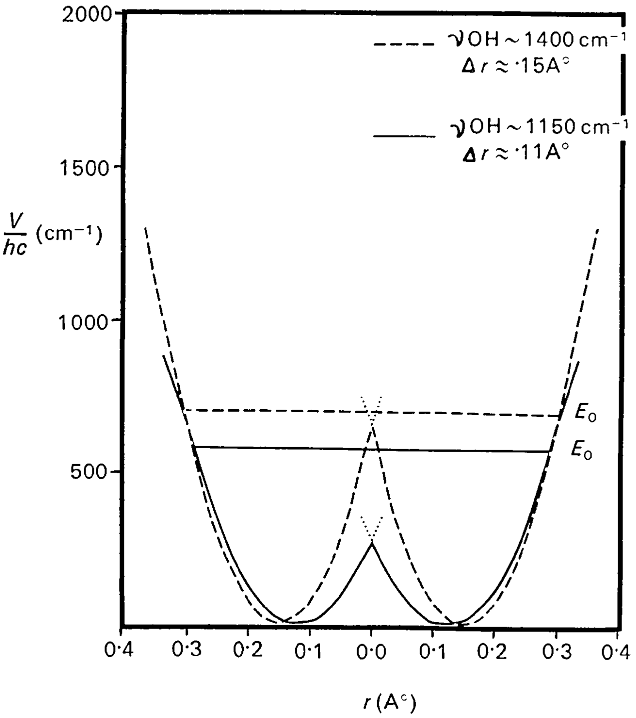

Fig. 7. A comparison of the zero-point energy, E_0, and the central barrier of two combined harmonic potential wells for an extreme case (dotted lines) and a more probable case (lines) solid for hydrogens H(4) and H(5) in $Ca(H_2PO_4)_2$.

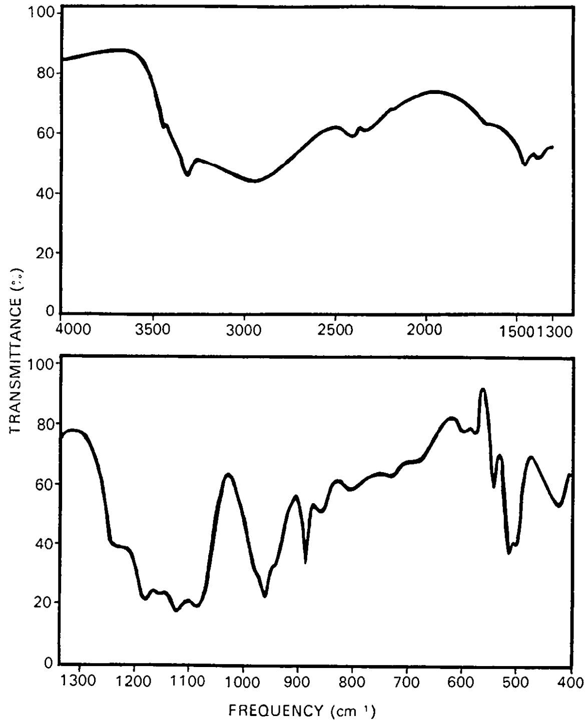

Fig. 6. Top: infrared spectrum of $Ca(H_2PO_4)_2$ in the region 1300 to 4000 cm^{-1} taken from a halocarbon oil mull smeared between KBr plates. Particle sizes under 10 μm. Bottom: spectrum in the 400 to 1300 cm^{-1} region taken from a Nujol mull. Spectra were run on a grating spectrophotometer using the standard slit program and a scan speed of 33 cm^{-1} min^{-1}. Frequencies were checked against a standard 0·05 mm polystyrene film.

cm^{-1}, and using the relationship (Hamilton & Ibers, 1968)

$$\langle u^2\rangle = \frac{h}{8\pi^2 mcv}$$

for the harmonic oscillator in the ground state, we obtain $\langle u^2\rangle \simeq$ 0·012 Å^2, where $\langle u^2\rangle$ is the mean-square amplitude of vibration in Å^2 and v is the frequency in cm^{-1}. If we make the assumption that the total mean-square amplitude of each proton is at least that of the bonded oxygens, the potential minimum could be 0·15 Å off center (Fig. 5). Fig. 7 shows that in this extreme case (highest OH stretching frequency, no allowance for other vibrational modes, *i.e.*, no oxygen motion considered, harmonic potential), the central barrier is below the ground state vibrational level, *i.e.*, the zero-point energy. Allowance for the anharmonity associated with hydrogen bonds would lower the barrier.

A more reasonable potential might be one constructed assuming $\nu_{\mathrm{OH}} \sim$ 1150 cm^{-1} because the spectrum shows intense absorption characteristic of hydrogen bonding in this region. (This assignment is not unique because PO_4^{3-} vibrations also absorb in this region.) Then $\langle u^2\rangle$ would be 0·015 Å^2, $\langle u^2\rangle_{\mathrm{O}}$ as estimated from the diffraction results is 0·009 Å^2, and the total mean-square amplitude, $\langle u^2\rangle_{\mathrm{O}} + \langle u^2\rangle_{\mathrm{H}}$ would be approximately 0·015 + 0·009 = 0·024 Å^2. This puts the potential minimum 0·11 Å off center (Fig. 5) and Fig. 7 shows the central barrier would again be much lower than the ground-state vibrational level.

One might assume a value for the OH stretching frequency lower than that given here, but this leads to a larger mean-square-amplitude of vibration and thus the separation of the potential minima must be smaller to fit the diffraction data. Hence, the central barrier would be still lower. Thus, we conclude that the H(4) and H(5) atoms in $Ca(H_2PO_4)_2$ are in centered hydrogen bonds. The conclusion that the central barrier lies below the ground-state vibrational level for these hydrogen bonds agrees with the prediction that the proton displays a centrosymmetric distribution when R(O···O) < 2·47 Å (Pimentel & McClellan, 1971), and is supported by recent *ab initio* calculations on short hydrogen bonds (O···O ~2·45 Å) in $H_5O_2^+$ and $H_3O_2^+$ (Kollman & Allen, 1970; Newton & Ehrenson, 1971). These calculations indicate that the central barriers in the potential wells are significantly below the zero-point energies (~700 cm^{-1}) for O···O separations up to 2·487 Å. It therefore appears best to consider the delocalized proton in hydrogen bonds of this type as a 'particle in a box' since the proton moves in a rather broad and flat potential exhibiting considerable anharmonicity.

General discussion

The general details found in the structure of $Ca(H_2PO_4)_2$ are also present in $Ca(H_2AsO_4)_2$ (Ferraris, Jones & Yerkess, 1972), which was investigated independently. The overall structural type is expected to be uncommon because the great excess of anions over cations will make three-dimensional bonding unavailable for most combinations of ions. Possible candidates for this type of structure will probably consist chiefly of anions with at least one and more probably two hydrogens (*i.e.*, $H_2PO_4^-$, $H_2AsO_4^-$, $H_2VO_4^-$, HSO_4^-, $HCrO_4^-$, *etc.*) with which to form hydrogen bonds. If an acid molecule (with zero net charge) derived from a tetrahedral anion can be induced to crystallize in the structure, the cation need not be more than monovalent. Salts of the type $Ca[BF_2(OH)_2]_2$ are also possibilities although BF_4 salts themselves are not because they have no way of forming significant bonds between anions. The salts $Sr(H_2PO_4)_2$ and $Ba(H_2PO_4)_2$ are known to crystallize in two forms each (Lehr *et al.*, 1967). The reduced cells (Mighell, Santoro & Donnay, 1969) of their triclinic forms, together with a permutation of the cell of $Ca(H_2PO_4)_2$, are:

	a	b	c	α	β	γ
$Ca(H_2PO_4)_2$	5·550 Å	8·253 Å	7·558 Å	109·15°	93·68°	109·87°
$Sr(H_2PO_4)_2$	6·70	7·10	7·84	104·7	96·9	109·3
$Ba(H_2PO_4)_2$	7·03	7·24	8·10	105·0	96·2	108·6

While the Sr and Ba salts appear to be structurally related to each other, they do not seem to be simply related to the Ca salt. Perhaps Ca is not able to sustain the large cation coordinations undoubtedly required in the Sr and Ba structures, and a relationship of distortion obtains similar to the relationship between the $Ba_3(PO_4)_2$ (Zachariasen, 1948) or $Ba_3(VO_4)_2$ (Süsse & Buerger, 1970) type structures and β-$Ca_3(PO_4)_2$ (Gopal & Calvo, 1971; Dickens, Bowen & Brown, 1971*b*). In the apatite series, Ca is just within the stability field which includes Ba and Sr. For cations with ionic radii less than that of Ca, the wagnerite (Mg_2PO_4F) structure is preferred (Kreidler, 1967).

The linking of PO_4 groups through symmetrical hydrogen bonds to form chains running throughout the crystal is one of the more novel features of the structure of $Ca(H_2PO_4)_2$. To our knowledge this is one of only two examples of such extended linkages involving centered hydrogen bonds, the arsenate analog, $Ca(H_2AsO_4)_2$ (Ferraris *et al.*, 1972), apparently being a similar case. Such linkages suggest possible ferroelectric behavior especially in view of the fact that other salts of $H_2PO_4^-$, *e.g.*, KH_2PO_4, are well known ferroelectrics. Present theories of hydrogen-bonded ferroelectrics (Kobayashi, 1968) emphasize the ordering of the protons in a double well. In general, these theories lead to the result that the higher the tunneling rate (*i.e.* the lower the barrier), the lower the temperature of the phase transition, which is often second order.

In the case of $Ca(H_2PO_4)_2$, our unsuccessful attempt to reduce extinction in the crystal used for neutron diffraction by dipping it in liquid nitrogen indicates that there is probably no first-order phase change in $Ca(H_2PO_4)_2$ between room temperature and ~77°K, although there is still the possibility of a second-order phase transition. However, the barriers are seemingly well below the zero-point energies even at room temperatures, and contraction on cooling would be expected to decrease the barriers by more overlapping of the component potential wells. Thus, we conclude that the existence of a ferroelectric phase of $Ca(H_2PO_4)_2$ is unlikely.

The existence of hydrogen-bonded dimers of $H_2PO_4^-$ groups in $Ca(H_2PO_4)_2$ may have some bearing on species present in aqueous solutions of phosphates. The existence of a dimeric species $[H_4(PO_4)_2]^{2-}$ in fairly dilute aqueous solutions of alkali metal orthophosphates has been suggested (Childs, 1969, 1970) on the basis of studies of ionic equilibria. Similar postulates have been made for solutions of H_3PO_4 more concentrated than 0·1 m (Elmore, Hatfield, Dunn & Jones, 1965). The presence of the ion pairs $[CaHPO_4]^\circ$ and $[CaH_2PO_4]^+$ has been suggested (Moreno, Gregory & Brown, 1966) *via* solubility studies of calcium phosphates. Our observation of $H_2P(1)O_4$ ions linked into dimers and $H_2P(2)O_4^-$ ions linked together by symmetrical hydrogen bonds to form polymeric chains suggests that the possibility that small polymers of phosphate ions exist in aqueous solution be given serious consideration. The related case of the hydration of $H^+.nH_2O$ to $H^+.(n+1)H_2O$ has been studied by Kerbale, Searles, Zolla, Scarborough & Arshadi (1967) who showed by mass spectrometry that no unique value of n dominates. Indeed, in the crystal structure studies of $(H^+.nH_2O)\ X^-$ compounds (Lundgren & Olovsson, 1968), $H_5O_2^-$ and higher complexes were found. Thus, further investigations into the existence of dimeric, trimeric, *etc.*, species involving $H_2PO_4^-$ seems warranted. The dissociation constants of H_3PO_4, $10^{-2\cdot12}$, $10^{-7\cdot21}$ and $10^{-12\cdot67}$, reveal considerable affinity of the PO_4 group for its second and especially its third hydrogens. Thus phosphates, being polybasic, might be expected to contain unusual but chemically important hydrogen bonds which result in the formation of unusual complexes.

We thank J. S. Bowen and P. B. Kingsbury for technical help. Figs. 1, 2, 3 and 4 were drawn using the *ORTEP* program of C. K. Johnson. This investigation was supported in part by research grant DE00572 to the American Dental Association, General Research Support Grant RR05689 funds made available to the American Dental Association, and by contract NIDR-02 to the National Bureau of Standards from the National Institute of Dental Research.

References

ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* **A27**, 157–165.

ALPERIN, H. & PRINCE, E. (1970). *J. Res. Natl. Bur. Stand.* **74C**, 89–95.

BASSETT, H. (1908). *Z. anorg. Chem.* **59**, 1–55.

BAUR, W. H. & KHAN, A. A. (1970). *Acta Cryst.* **B26**, 1584–1596.

BERRY, E. E. (1968). *Spectrochim. Acta*, **24A**, 1727–1734.

BLUME, R. J. (1962). *Rev. Sci. Instrum.* **22**, 598–599.

BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142–146.

CHAPMAN, A. C. & THIRLWELL, L. E. (1964). *Spectrochim. Acta*, **20**, 937–947.

CHILDS, C. W. (1969). *J. Phys. Chem.* **73**, 2956–2960.

CHILDS, C. W. (1970). *Inorg. Chem.* **9**, 2465–2469.

COOPER, M. J. & ROUSE, K. D. (1971). *Acta Cryst.* **A27**, 622–628.

COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* **A26**, 71–83.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

CURRY, N. A., DENNE, W. A. & JONES, D. W. (1968). *Bull. Soc. Chim. Fr.* pp. 1748–1750.

DENNE, W. A. (1972). *Acta Cryst.* **A28**, 192–201.

DICKENS, B. & BOWEN, J. S. (1971). *Acta Cryst.* **B27**, 2247–2255.

DICKENS, B., BOWEN, J. S. & BROWN, W. E. (1971*a*). *Acta Cryst.* **B28**, 797–806.

DICKENS, B., BOWEN, J. S. & BROWN, W. E. (1971*b*). Abstract G3, American Crystallographic Association winter meeting, Columbia, S. C.

ELMORE, K. L., HATFIELD, J. D., DUNN, R. L. & JONES, A. D. (1965). *J. Phys. Chem.* **96**, 3520–3525.

FERRARIS, G., JONES, D. W. & YERKESS, J. (1972). *Acta Cryst.* **B28**, 209–214.

FINGER, L. W. (1968). Carnegie Institute of Washington, unpublished.

GOPAL, R. & CALVO, C. (1971). *Canad. J. Chem. Soc.* **49**, 1036–1046.

HAMILTON, W. C. & ABRAHAMS, S. C. (1973). *Acta Cryst.* **A28**, 215–218.

HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids*, Chap. 3. New York: Benjamin.

HADZI, D. (1965). *Pure Appl. Chem.* **11**, 435–453.

JONES, D. W. (1970). Private communication.

JONES, D. W. & CRUICKSHANK, D. W. J. (1961). *Z. Kristallogr.* **116**, 101–125.

KERBALE, P., SEARLES, S. K., ZOLLA, A., SCARBOROUGH, J. & ARSHADI, M. (1967). *J. Amer. Chem. Soc.* **89**, 6393–6399.

KOBAYASHI, K. K. (1968). *J. Phys. Soc. Japan*, **24**, 497–508.

KOLLMAN, P. A. & ALLEN, L. C. (1970). *J. Amer. Chem. Soc.* **92**, 6101–6107.

KREIDLER, E. R. (1967). Ph. D. Thesis, Penn. State Univ. Dissertation 68-3549, University Microfilms, Ann Arbor, Mich.

LEHR, J. R., BROWN, E. H., FRAZIER, A. W., SMITH, J. P. & THRASHER, R. D. (1967). *Crystallographic Properties of Fertilizer Compounds; Chem. Eng. Bull.* 6, TVA, p. 118.

LENHERT, P. G. (1970). Abstract M8, American Crystallographic Association winter meeting, New Orleans, La., March.

LUNDGREN, J. O. & OLOVSSON, I. (1968). *J. Chem. Phys.* **49**, 1068–1074, and references therein.

MIGHELL, A. D., SANTORO, A. & DONNAY, J. D. H. (1969). *International Tables for X-ray Crystallography*, Vol. I. p. 534.: Birmingham Kynoch Press.

MORENO, E. C., GREGORY, T. M. & BROWN, W. E. (1966). *J. Res. Natl. Bur. Stand.* **70A**, 545–552.

Newton, M. D. & Ehrenson, S. (1971). *J. Amer. Chem. Soc.* **93**, 4971–4990.

Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 559. Ithaca: Cornell Univ. Press.

Pimentel, G. C. & McClellan, A. L. (1971). *Ann. Rev. Phys. Chem. 'Hydrogen Bonding'* **22**, 347–385.

Prince, E. (1972). *J. Chem. Phys.* **56**, 4352–4355.

Smith, J. P., Lehr, J. R. & Brown, W. E. (1955). *Amer. Min.* **40**, 893–899.

Stewart, J. M. (1967). XRAY 67 System of Computer Programs, Technical Report 67-58. Univ. of Maryland, College Park, Maryland 20742.

Süsse, P. & Buerger, M. J. (1970). *Z. Kristallogr.* **131**, 161–174.

The Neutron Diffraction Commission (1969). *Acta Cryst.* A**25**, 391–392.

Zachariasen, W. H. (1948). *Acta Cryst.* **1**, 263–265.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1973). B**29**, 2070

The Crystal and Molecular Structure of Dibenzofuran

By Asok Banerjee

X-ray Laboratory, Presidency College, Calcutta-12, India

(*Received* 22 *January* 1973; *accepted* 25 *April* 1973)

Dibenzofuran, $C_{12}H_8O$, forms colourless orthorhombic crystals with four molecules in the unit cell of dimensions $a = 7{\cdot}65 \pm 0{\cdot}02$, $b = 5{\cdot}90 \pm 0{\cdot}01$, $c = 19{\cdot}32 \pm 0{\cdot}02$ Å. The intensity-statistics test decided in favour of space group *Pnam* rather than $Pna2_1$. The gross structure was solved by the method of the weighted reciprocal lattice combined with trial-and-error procedures taking advantage of the analogy with similar structures. The parameters were refined by three-dimensional least-squares methods utilizing 539 observed reflexion intensities obtained photographically with Cu *K* radiation, to a final *R* index of 0·092. The bond lengths and bond angles of the molecule show no abnormalities; they have estimated standard deviations of about 0·007 Å and 0·45° respectively for non-hydrogen atoms. The individual five or six-membered rings are planar but the six-membered rings make a significant dihedral angle (1·2°) with the five-membered ring. A crystallographic mirror plane normal to the *c* axis passes through the oxygen atom of the molecule. Some physical properties of the compound are compared with those of fluorene and carbazole. A theoretical calculation has been made to account for the lengthening of the C(6)–C(6′) contact bond, a characteristic feature of this type of molecule with a phenanthrenoid arrangement of rings.

Introduction

The investigation of the crystal and molecular structure of dibenzofuran, $C_{12}H_8O$, is part of a programme of research on heterocyclic compounds in our laboratory being carried out because of their important uses as drugs, dyes and because many of the cancer-arresting substances are heterocyclic. The objects of the present investigation were twofold: (*a*) to explain the physical properties such as cleavage, melting point, *etc.* in relation to crystal structure and (*b*) to obtain molecular dimensions of sufficient accuracy to form a basis for discussion and comparison with theories of molecular structure. Extensive theoretical calculations have been done from the standpoint of π-electron delocalization to account for the irregular deviations of bond lengths within a ring from the values of standard conjugated distances. Preliminary results on the crystal structure analysis of this compound were reported by Banerjee (1971, 1972). Thereafter a comprehensive three-dimensional least-squares refinement was carried out with anisotropic temperature factors and hydrogen-atom contributions and the results are presented here.

Experimental

Repeated crystallizations by sufficiently slowing down the rate of evaporation of the solvent at room temperature (27°C) from a solution in alcohol yielded colourless transparent crystals lath-like in habit, platy on the (001) face, with lengths parallel to the shortest crystallographic axis, **b**. The crystals exhibited a perfect cleavage parallel to the (001) plane and displayed extinction parallel to their length. The cell dimensions were determined from single-crystal oscillation and Weissenberg photographs about the *a* and *b* axes using a good crystal. Diffraction effects show the following systematic absences: $h0l$ absent if $h = 2n+1$ and $0kl$ absent if $k+l = 2n+1$. This X-ray data and dimensional considerations indicate that the four molecules in the unit cell must either occupy general positions in space group $Pna2_1$ or lie across the mirror planes in the space group *Pnam*. This ambiguity in space group was resolved in favour of *Pnam* by the statistics test of Wilson (1949). The crystal density was measured by flotation in an aqueous solution of $ZnSO_4$. The crystal data are given in Table 1. The integrated intensities of 539 reflexions were visually estimated from zero and