268. *The Structure of Brushite,* $CaHPO_4,2H_2O$.

By D. W. JONES and J. A. S. SMITH.

The *X*-ray crystal structure proposed by Beevers for calcium hydrogen phosphate dihydrate, $CaHPO_4,2H_2O$, has been refined three-dimensionally by the method of least squares, with allowance for anisotropic thermal motion of the calcium and phosphorus atoms. In agreement with the piezoelectricity observed in the crystals, there is improved correlation between observed and calculated *X*-ray data after refinement in the non-centrosymmetric space group *Ia* rather than in *I*2/*a*. A surprisingly close approach of 2·63 Å in the original structure between the oxygen atoms of neighbouring water molecules is increased to 2·84 ± 0·11 Å, thus removing an inconsistency with the nuclear resonance data. The P–O lengths are insufficiently precise to permit assignment of the acid hydrogen atom to an oxygen of the phosphate group, but a distribution of hydrogen positions is possible.

BRUSHITE,[1] $CaHPO_4,2H_2O$, the only well-established hydrate of calcium hydrogen phosphate,[2] has applications in the fertiliser and animal-food industries.[3] Its crystal structure was determined by Beevers [4] from Patterson and Fourier projections and refined by two-dimensional difference syntheses in which no allowance was made for the thermal motion of individual atoms. If the space group is *I*2/*a*, as Beevers assumed, the calcium and phosphorus lie in special positions, and the asymmetric unit also contains, apart from hydrogen, two distinct oxygen atoms, O_1 and O_2, of the phosphate group and one oxygen atom, O_3, of a water molecule. Chains, each formed of alternating calcium and phosphate ions, run parallel to the [101] axis and are arranged in corrugated sheets in the (010) plane.

One surprising conclusion from the original *X*-ray analysis of brushite was the close approach (2·63 Å) between the water-oxygen atoms O_3, as compared with that (3·47 Å) in the related structure of gypsum, $CaSO_4,2H_2O$.[5] This led Beevers,[4] on the evidence of the heavy-atom positions, to suggest that the anionic hydrogen atom, H_5, lies midway between these O_3 atoms on a two-fold axis. This would mean that H_5 is contained in a short and crystallographically symmetrical hydrogen bond roughly parallel to the *c*-axis. The two-fold symmetry would be preserved, without recourse to a statistical structure, if H_5 was sited elsewhere on the axis so as to form a bent hydrogen bond. In the crystal structures of the orthophosphates monetite, $CaHPO_4$, and calcium bis(dihydrogen phosphate) monohydrate, $Ca(H_2PO_4)_2,H_2O$, centres of inversion rather than two-fold axes occur in the middle of what are believed to be hydrogen-bonding distances.[6] On the other hand, a recent proton magnetic resonance study of a single crystal of brushite [7] showed that H_5 could not occupy a site on a two-fold axis between the two water-oxygen atoms; the presence of H_3O^+ or OH^- was also excluded. Attachment of H_5 to oxygen O_2 was suggested as most likely.

A second crystallographic property which might offer guidance about the position of H_5 is the length of the P–O bonds. Cruickshank [8] has shown that a P–O bond which has hydrogen attached to the oxygen atom should be detectably longer than a P–O bond which has not. Such an effect had been noticed earlier in, for example, potassium dihydrogen phosphate,[9] for which the two distances are 1·58 and 1·51 Å. This difference arises from

---

[1] Moore, *Amer. J. Sci.*, 1865, II, **39**, 43; Dana, *ibid.*, p. 45.
[2] Bassett, *Proc. Chem. Soc.*, 1906, **22**, 315.
[3] Lutz and Pratt in Sauchelli's " Chemistry & Technology of Fertilisers," Reinhold, New York, 1960, p. 333.
[4] Beevers, *Acta Cryst.*, 1958, **11**, 273.
[5] Atoji and Rundle, *J. Chem. Phys.*, 1958, **29**, 1306.
[6] Jones and (in part) Cruickshank, *Z. Krist.*, 1961, **116**, 101
[7] Jones and Smith, *Trans. Faraday Soc.*, 1960, **56**, 638.
[8] Cruickshank, *Acta Cryst.*, 1960, **13**, 1033.
[9] Bacon and Pease, *Proc. Roy. Soc.*, 1955, *A*, **230**, 359.

the variation in π-bonding between the $2p$-orbitals of the oxygen and the $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals of the phosphorus[10] but may be difficult to measure if on an average only one half of a hydrogen atom is available per oxygen atom. A spread of P–O distances, attributed to π-bonding effects, has been found in two calcium orthophosphates: 1·51—1·58 Å with $\sigma = 0{\cdot}015$ Å in $CaHPO_4$; and 1·48—1·62 Å with $\sigma = 0{\cdot}025$ Å in calcium bis(dihydrogen phosphate) monohydrate.[6] In the original brushite structure, however, these lengths are all the same to within the estimated standard deviation of 0·03 Å quoted for the oxygen positions;[4] we believe this to be an underestimate of the error.

Symmetry of Brushite Crystals.—Systematic absences in the *X*-ray reflexions (*hkl*) with $h + k + l$ odd indicate that the space group of brushite is either *I*2/*a* or *Ia* according to whether a centre of inversion is present or not. If the space group is *Ia*, there are no symmetry restrictions within the formula unit $CaHPO_4,2H_2O$, and H_5 need no longer be even statistically distributed about a two-fold axis. Beevers[4] noted the apparent centrosymmetry of small crystals and was able to carry out his two-dimensional *X*-ray analysis on the basis of the space group *I*2/*a* as far as a disagreement index $R = \sum|(|F_o| - |F_c|)|/\sum|F_o|$ of about 0·26 in each projection (the overall disagreement is rather higher). Evidently the positions of at least the heavier atoms in the structure must conform closely to those required for space group *I*2/*a*. Recently, however, Beevers[11] observed a positive piezo-electric effect, in agreement with an earlier report by Terpstra.[12] Further, the large single crystal used by us[7] was of unsymmetrical appearance and exhibits a very pronounced piezo-electric effect,[13] which implies that the space group is *Ia*; the departure of atoms from centrosymmetric positions need not be large.

In an attempt to resolve the problems of the symmetry, the close $O_3 \cdots O_3'$ approach, and the P–O lengths in the crystal structure of brushite, we have refined Beevers's data three-dimensionally by the method of least squares, with allowance for anisotropic thermal motion, first in the space group *I*2/*a* and then in the space group *Ia*.

METHODS

Refinement in Space Group I2/a.—The *X*-ray intensity data available were the 176 non-zero reflexions recorded photographically and (for the *h*0*l* planes) by counter diffractometry by Beevers[4] from Cu-K_α and Mo-K_α radiation. Of these 002, 200, 220, and 408 were excluded from the main refinement because of suspected secondary extinction. The set of atomic positions found by Beevers[4] was taken as the starting point for our centrosymmetric three-dimensional refinement; hydrogen-atom contributions to the structure factors were disregarded. Atomic scattering factors tabulated by Tomiie and Stam[14] were used for phosphorus and those listed by Berghuis *et al.*[15] for the other atoms. Individual isotropic temperature factors,

TABLE 1.

*I*2/*a* refinement: final sets of monoclinic atomic co-ordinates (*x*, *y*, and *z*), their minimum e.s.d.'s (σ), and the corresponding orthogonal co-ordinates (*Y* parallel to *b*, *X* the projection of *a* on plane perpendicular to *B*, *Z* perpendicular to *X* and *Y*), all in Å; and isotropic thermal parameters, *U* and their e.s.d.'s in Å².

Atom	*x*	*y*	*z*	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	*X*	*Y*	*Z*	*U*
Ca ...	1·453	12·527	0·000	0·012	0·008	0·012	1·453	12·527	0·000	—
P	1·453	4·933	0·000	0·012	0·011	0·012	1·453	4·933	0·000	—
O_1 ...	1·365	5·815	1·301	0·053	0·024	0·033	0·786	5·815	1·165	0·013 ± 0·005
O_2......	2·837	4·103	0·583	0·035	0·030	0·034	2·578	4·103	0·522	0·017 ± 0·006
O_3......	0·961	14·159	1·667	0·043	0·033	0·039	0·219	14·159	1·493	0·020 ± 0·006

---

[10] Cruickshank, *J.*, 1961, 5486.

[11] Beevers, personal communication, 1960.

[12] Terpstra, *Z. Krist.*, 1937, **97**, 229.

[13] Perdok, personal communication, 1960.

[14] Tomiie and Stam, *Acta Cryst.*, 1958, **11**, 126.

[15] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

TABLE 2.

Final sets of anisotropic mean square vibration tensor components, U_{ii}, parallel to a^*, b^*, and c^*, and their e.s.d.'s in Å^2: (*a*) after *I*2/*a* refinement; (*b*) after *Ia* refinement.

Atom	U_{11}	U_{22}	U_{33}
Ca (*a*)	" 0 " ± 0·003	0·003 ± 0·003	0·006 ± 0·003
(*b*)	" 0 " ± 0·002	" 0 " ± 0·002	0·007 ± 0·002
P (*a*)	" 0 " ± 0·004	0·002 ± 0·004	0·003 ± 0·004
(*b*)	" 0 " ± 0·003	0·008 ± 0·003	" 0 " ± 0·003

TABLE 3.

Comparison of observed structure factors with final sets of calculated structure factors: (*a*) for *I*2/*a* refinement; and (*b*) for *Ia* refinement.

l	$\lvert F_o \rvert$	F_c (a)	F_c (b)	$\lvert F_c \rvert \cos\alpha$	$\lvert F_c \rvert \sin\alpha$
00*l*					
2	25	35	35	34	−11
4	93	87	95	95	3
6	34	32	30	28	−9
8	47	39	44	41	−15
10	59	36	28	28	−4
20*l*					
$\overline{10}$	34	−34	28	−27	4
$\overline{8}$	55	−35	46	−45	11
$\overline{6}$	64	−68	58	−58	9
$\overline{4}$	114	−118	116	−116	0
$\overline{2}$	55	−33	44	−35	26
0	97	−122	108	−108	−5
2	25	−28	40	−40	−3
4	81	−84	74	−73	12
6	59	−50	47	−47	8
8	42	−37	34	−32	11
40*l*					
$\overline{10}$	51	51	42	41	−7
$\overline{8}$	17	35	43	39	−19
$\overline{6}$	55	52	59	53	−27
$\overline{4}$	51	50	56	56	5
$\overline{2}$	81	71	84	80	−26
0	102	103	96	93	−24
2	64	67	65	63	16
4	47	48	46	46	−7
6	38	38	37	37	6
60*l*					
$\overline{10}$	34	−33	31	−30	7
$\overline{8}$	55	−33	45	−43	15
$\overline{6}$	64	−63	58	−57	13
$\overline{4}$	72	−74	74	−74	−1
$\overline{2}$	59	−61	59	−52	27
0	51	−51	59	−59	−2
2	42	−50	43	−42	−9
4	64	−43	40	−39	7
6	42	−43	35	−35	−2
80*l*					
$\overline{10}$	21	36	27	27	−3
$\overline{8}$	85	49	61	55	−25
$\overline{6}$	47	35	40	36	−18
$\overline{4}$	64	53	61	60	−12
$\overline{2}$	47	45	41	40	−10
0	59	60	55	55	3
2	64	50	40	40	7
100*l*					
$\overline{8}$	59	−41	51	−49	14
$\overline{6}$	30	−35	37	−33	15
$\overline{4}$	64	−63	57	−57	3
$\overline{2}$	59	−40	43	−39	19
0	47	−47	43	−43	−2
0*k*0					
2	72	−89	91	−91	0
4	42	−47	40	−40	0
6	25	14	31	31	0
8	72	−52	54	−54	0
10	17	−72	15	−15	0
12	55	46	40	40	0
14	55	−52	46	−46	0
16	34	31	25	25	0
18	42	47	29	29	0
20	47	−62	50	−50	0
22	25	18	28	28	0
24	17	56	11	11	0
26	47	−23	36	−36	0
28	34	23	27	27	0
0*k*2					
2	136	−108	109	−108	−5
4	25	23	22	22	1
6	110	109	96	96	12
8	68	−55	58	−58	−2
10	13	−3	11	11	−1
12	64	62	62	61	−9
14	68	61	66	−64	17
16	13	−24	10	5	−9
18	38	24	33	33	2
20	51	−42	43	−42	−6
22	68	40	22	22	5
24	13	13	13	13	3
26	30	−39	30	−29	−5
28	21	25	21	21	−2
0*k*4					
2	13	−12	18	−16	8
4	42	−48	45	−45	2
6	72	58	60	59	−14
8	64	−66	60	−60	6
10	9	1	10	−7	7
12	38	46	41	40	−3
14	42	−50	44	−44	6
16	30	30	31	28	−14
18	34	31	27	21	18
20	42	−48	47	−47	1
22	25	13	28	26	−11
0*k*6					
2	25	−27	29	−29	2
4	25	−25	19	−18	−3
6	51	66	59	59	2
8	42	−40	42	−40	15
10	13	6	16	8	−14
12	42	38	42	41	−4
14	51	−54	58	−56	15
18	30	22	28	27	−6
20	30	−36	33	−33	−2
22	13	23	16	16	3
0*k*8					
2	25	−21	22	−18	12
4	13	−9	14	−13	4
6	38	38	38	36	−11
8	34	−42	38	−38	2
12	38	38	34	33	7
14	30	−33	30	−30	−3
20	25	−38	39	−38	9
0*k*1					
3	4	6	5	5	4
5	34	2	26	−3	−26
7	30	26	32	27	−17
9	42	−37	40	−40	6
11	42	27	41	19	36
13	13	−11	5	5	2
15	17	5	17	−14	−10
0*k*3					
1	17	34	22	21	5
3	30	−25	29	−28	−9
5	17	−11	15	−10	11
7	34	−1	31	16	26
9	30	6	22	−5	−22
11	9	−1	6	1	−6
13	13	−5	15	7	−14
15	17	−3	15	−15	4
17	13	17	13	11	6
21	17	−11	23	−19	12
0*k*5					
3	13	−3	11	3	−10
5	25	30	20	18	9
7	17	−9	13	−10	−9
9	25	−1	18	−10	−14
11	25	−4	28	−3	28
13	21	18	17	17	6
15	13	−17	23	−22	−7
0*k*7					
1	13	14	14	10	10
3	34	−10	26	−13	−22
5	13	−6	17	−6	16
7	9	−4	10	9	4
9	9	5	9	4	−7
2*k*0					
2	9	−1	19	17	9
4	72	101	100	97	−26
6	76	−82	92	−92	−4
8	64	64	54	53	6
10	9	−12	9	−9	2
12	42	−40	43	−42	10
14	68	62	54	53	12
16	25	−33	27	−27	−3
18	13	−32	19	−19	−3
4*k*0					
2	68	67	67	−67	−4
4	34	−23	29	−28	6
6	59	55	63	62	13
8	34	−23	26	−24	−9
10	21	5	16	6	15
12	34	35	34	34	0
14	47	−60	52	−50	−15
6*k*0					
2	30	31	32	30	11
4	25	34	32	29	−14
6	42	−65	58	−58	2
8	34	33	37	34	15
1*k*0					
1	13	−8	10	−10	3
3	13	2	4	−1	4
5	47	40	38	37	10
7	55	54	46	46	0
9	42	−29	27	−19	20
11	47	−44	42	−42	−6
13	21	−1	17	16	5
15	30	11	16	5	−16
17	21	6	16	−16	4
19	25	2	22	21	−8
3*k*0					
1	17	2	14	14	−3
3	30	31	33	33	6
5	21	−9	13	8	10
7	25	−26			
9	13	7	11	8	−8
11	34	19	23	17	−16
13	21	−8	22	−20	10
15	9	−9	10	−9	2
17	30	2	21	20	5
5*k*0					
1	13	−14	13	−12	−2
3	25	−18	15	−15	1
5	9	−11	13	−7	−11
7	17	17	16	14	−9
9	4	−2	8	4	7
11	9	−4	15	−14	

corresponding initially to Debye B factors of 1·2 Å^2, were assigned to the oxygen atoms and, after preliminary isotropic cycles, anisotropic coefficients, U_{ij}, in the form

$$\exp\{-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots)\}$$

and equivalent initially to isotropic B factors of 1·0 Å^2, were applied to the calcium and the phosphorus atoms. Since all these thermal factors became variables in the least-squares minimization, the total number of parameters was 28, including scale and overall temperature factors, and so the excess of data over variables was six-fold. All the least-squares calculations were made on the Leeds University Pegasus Computer with programmes developed by Cruickshank, Pilling, *et al.*[16]

After four cycles of structure-factor calculations and least-squares minimization of the residual $R' = \sum_{hkl} w(|F_o| - |F_c|)^2$ according to the weighting scheme $w = 1/|F_o|$, the disagreement index R fell from 0·347 to 0·227 over 176 planes, and the scale of $|F_o|$ was raised by 6%. Since the maximum oxygen O_1 co-ordinate shift was one-fifth of an estimated standard deviation and all other co-ordinate and vibration parameter shifts were proportionately smaller than this; refinement under centrosymmetric conditions was evidently complete. Atomic co-ordinates and thermal parameters at this stage are given in Tables 1 and 2. Entries of " 0 " for U_{ii} in Table 2 indicate that slightly negative values were predicted for these tensor components; positive working values for all U_{ii} were maintained during the least-squares refinement by addition of an average $U = 0{\cdot}010$ to all U_{iso} and U_{ii}. Table 3 lists the observed and calculated structure factors in this and the subsequent non-centrosymmetric analyses. From column (2) in Table 4, it will be seen that the co-ordinate shifts of oxygens O_1 and O_2 have made the two P–O lengths unequal in a sense which suggests that the hydrogen is attached to O_1 rather than O_2. On the other hand, the unusually close $O_3 \cdots O_{3'}$ distance between the water molecules found in the earlier analysis remains (Table 5).

TABLE 4.

Bond lengths and their minimum e.s.d.'s in Å at various stages in the analyses: initial (1) and final (2) values for *I*2/*a* refinement; initial (3) and final (4) values for *Ia* refinement (the dashed atoms of *Ia* degenerate to the corresponding undashed atoms in *I*2/*a*).

Bond	(1)	(2)	(3)	(4)
$P–O_1$	1·53	1·61 ± 0·04	1·53	1·69 ± 0·03
$P–O_1'$	1·53	1·61 ± 0·04	1·53	1·58 ± 0·04
$P–O_2$	1·54	1·49 ± 0·04	1·59	1·34 ± 0·05
$P–O_2'$	1·54	1·49 ± 0·04	1·49	1·69 ± 0·07

TABLE 5.

Close intermolecular oxygen separations and their e.s.d.'s (in Å) before (1) and after (2) the *I*2/*a* refinement.

Bond	Description	(1)	(2)
$O_3 \cdots O_{3'}$	Across two-fold axis	2·63	2·63 ± 0·08
$O_3 \cdots O_1$	Within (010) sheet	2·63	2·51 ± 0·05
$O_3 \cdots O_1$	Between (010) sheets	2·82	2·85 ± 0·05
$O_2 \cdots O_2$	Along [201]	2·79	2·86 ± 0·05
$O_3 \cdots O_2$	Between (010) sheets	3·09	3·06 ± 0·05
$O_2 \cdots O_1$	—	3·20	2·17 ± 0·05
$O_2 \cdots O_1$	Along [001]	3·16	3·18 ± 0·05

Refinement in Space Group Ia.—In view of the limited extent to which centrosymmetric refinement could be pursued, even with allowance for anisotropic thermal motion, it was thought that artificial symmetry restrictions might be responsible for the short apparent $O_3 \cdots O_3'$ distance and possibly for other erroneous oxygen positions. Accordingly, further refinement was undertaken in space group *Ia*. The same structure amplitudes as for *I*2/*a* are still valid in this space group, but now the asymmetric unit embraces a complete $CaHPO_4,2H_2O$ formula

---

[16] Cruickshank, Pilling, and (in part) Bujosa, Lovell, and Truter in Pepinsky, Robertson, and Speakman's " Computing Methods and the Phase Problem in *X*-ray Analysis," Pergamon, London, 1960, p. 32.

unit instead of half of one, and the two-fold axis in the trial structure disappears. Consequently, the water molecules are crystallographically different and the anionic hydrogen can be assigned to one of the four independent oxygen atoms of the phosphate group. Now the discussion of the proton magnetic resonance data [7] predicted an elongation of the average P–O_2 bond, whereas our *X*-ray crystallographic refinement in *I*2/*a* led to the extension of the average P–O_1 length [column (2) in Table 4]. For the *Ia* trial structure, it was decided [column (3) in Table 4] to retain the original co-ordinates [4] for the two O_1-like oxygens, designated O_1 and O_1' so that P–O_1 and P–O_1' are each 1·53 Å; to extend P–O_2, in the same direction as had been predicted, to 1·59 Å; and to use the co-ordinates as refined in *I*2/*a* for the other O_2-type oxygen (P–O_2' = 1·49 Å). In order to enable the $O_3 \cdots O_3'$ distance to be increased without appreciable departure from the approximate two-fold axis relationship indicated by the proton magnetic resonance measurements, O_3' was differentiated from O_3 by shifting its *y*-co-ordinate 0·11 Å from its *I*2/*a* position. This assumption of two crystallographically distinct kinds of water molecule does not correspond to the distinction [17] between strongly and weakly bound water molecules.

At first, temperature parameters—isotropic for the five oxygen atoms and anisotropic for calcium and phosphorus—were retained at the values found for *I*2/*a* and, as before, potentially negative-going coefficients were avoided by the device of applying an average *U* of 0·010 to the listed temperature parameters. The number of variables was now about one-quarter of the number of observed reflexions. A Hughes weighting scheme was used in the early stages, but in later cycles this routine was modified to one of the form $w = \{8 + |F_o| + |F_o|^2/|F_{\max}|\}^{-1}$ in order to achieve a more nearly constant value for $w|\Delta F|^2$ averaged over groups of increasing $|F_0|$ and $\sin\theta/\lambda$. The tendency of the *x* co-ordinates of the calcium and phosphorus atoms (which are fixed by symmetry in the *I*2/*a* case) to oscillate in opposite directions during successive cycles became insignificant when only one-third of the predicted shifts were applied in each cycle.

Ten successive structure-factor–least-squares cycles with the diagonal matrix approximation reduced the *R* index from 0·243 over 175 reflexions to 0·163 over 172 reflexions. In the later cycles, convergence was slow and the refinement was stopped when the average co-ordinate shift was one-seventh of a standard deviation. The maximum parameter shift between cycles was now 0·04 Å in the *y*-co-ordinate of O_4, which was two-thirds of a standard deviation. This atom shows the largest amount of thermal motion (Table 6) and is the least accurately determined atom so that the estimated standard deviation of P–O_4 is large [column (4) Table 4]. It was noticed that during the refinement the *x*-co-ordinate of calcium always remained close to its centrosymmetric value of 1·453 Å and indeed tended to make small oscillations about it, whereas the *x*-co-ordinate of phosphorus was always above its centrosymmetric value. The *z*-co-ordinates of calcium and phosphorus, both at 0·000 in space group *I*2/*a*, went to essentially their final values (Table 6) after the first two or three cycles; for the phosphorus atom, the change in *z* from the centrosymmetric value is very significant. Of the phosphorus–oxygen distances between stages (3) and (4) of Table 5, P–O_1 soon became long and nearly constant; P–O_2 (initially the longest) fluctuated slightly but became consistently short; P–$O_{1'}$ changed very slowly after an early extension; and P–O_2' (initially the shortest) steadily increased in length. Final structure factor agreement may be seen from Table 3.

TABLE 6.

Ia refinement: final sets of monoclinic atomic co-ordinates, their e.s.d.'s and the corresponding orthogonal co-ordinates (axes as in Table 2), in Å; and isotropic thermal parameters, *U* and their e.s.d.'s in Å².

Atom	*x*	*y*	*z*	σ(*x*)	σ(*y*)	σ(*z*)	*X*	*Y*	*Z*	*U*
Ca ...	1·459	12·552	0·028	0·019	0·006	0·012	1·447	12·552	0·025	—
P	1·477	4·878	−0·080	0·021	0·008	0·013	1·512	4·878	−0·072	—
O_1......	1·317	5·552	1·396	0·030	0·020	0·029	0·696	5·552	1·250	"0" ± 0·004
O_2......	2·765	4·198	0·559	0·062	0·039	0·056	2·517	4·198	0·501	0·019 ± 0·008
O_3......	1·469	5·929	−1·265	0·068	0·036	0·044	2·032	5·929	−1·133	0·016 ± 0·007
O_4......	−0·089	3·967	−0·541	0·078	0·056	0·091	0·152	3·967	−0·485	0·055 ± 0·019
O_5......	0·923	14·068	1·583	0·051	0·031	0·045	0·219	14·068	1·418	0·012 ± 0·006
O_6......	2·281	14·384	4·738	0·072	0·049	0·061	0·173	14·384	4·243	0·020 ± 0·011

---

[17] Lecomte, Boullé, and Lang-Dupont, *Compt. rend.*, 1955, **241**, 1927.

RESULTS AND DISCUSSION

The value of 0·227 for the disagreement index R after the centrosymmetric refinement may be compared with that of 0·164 after an analogous three-dimensional refinement[6] of principal zone data for calcium bis(dihydrogen phosphate) monohydrate. For this, the ratio, 5·2, of independent observations to unknown parameters was slightly less favourable than in brushite, the proportion of calcium-plus-phosphorus atoms to oxygen atoms was the same, but the structure is centrosymmetric since this salt does not exhibit a piezoelectric effect.[13] After the non-centrosymmetric refinement of brushite, R was reduced to 0·163, which is about the same proportion of its random value of 0·586 as was the case in the $I2/a$ refinement (random value 0·828). The improved structure factor agreement in Ia is taken as confirmation of the lower symmetry of the brushite structure. The surprisingly distinct X-ray pattern[18] exhibited by ardealite, $CaSO_4,CaHPO_4,4H_2O$, may be a consequence of the difference in symmetry between gypsum, which is not piezoelectric[19] and had its $I2/a$ symmetry confirmed by neutron diffraction,[5] and brushite. Certainly, the $CaSO_4$ and $CaPO_4$ sheets in gypsum and brushite, respectively, are very similar, and the two salts form solid solutions.[20]

Two consequences of the refinement in Ia have been the expansion of the $O_3 \cdots O_3'$ length from 2·62 to 2·84 ± 0·07 Å and the production of differences among the four P–O lengths within the phosphate ion [column (4) of Table 4]. How meaningful these changes are depends on the significance attached to the apparent e.s.d.'s quoted in Tables 4 and 6. These are minimum values taken directly from the least-squares calculations with the diagonal approximation. In a non-centrosymmetric structure, this approximation and the lack of complete three-dimensional X-ray intensity data could lead to a serious underestimation for the e.s.d.'s of the lighter atoms. If, for the present, the e.s.d.'s of column (4) in Table 4 are taken at their face value, $P–O_1$ is significantly long compared with a P–O length of, say, 1·50 Å to an isolated oxygen atom; $P–O_2$ is significantly shorter than 1·50 Å and so cannot carry a hydrogen, and $P–O_2'$ is barely significantly longer than 1·50 Å. If, as is more probable the e.s.d.'s of the lighter atoms should be increased[21] by a factor of about 1·6, one can conclude only that the anionic hydrogen is somewhat more likely to be on O_1 than on the other phosphate-oxygen atoms. In support of this, the average of the $O_1–P–O$ bond angles is 12° less than the average of the bond angles which do not include O_1. The occurrence of more than one long P–O bond in brushite would be consistent with the occupation by H_5 of alternative sites, as appears to be the case[6] for one of the two crystallographically different phosphate groups in monetite, $CaHPO_4$. No evidence is available from these calcium orthophosphates of ferro-electricity arising from disordering of the protons.

If the e.s.d. in the $O_3 \cdots O_3'$ distance is similarly increased, the change to 2·84 ± 0·11 Å is probably significant. This larger separation between the water molecules removes an anomaly in the original X-ray structure analysis since it is no longer necessary to assume that O_3 and O_3' are symmetrically hydrogen-bonded or even hydrogen-bonded at all. It also reduces the intermolecular broadening expected in the proton magnetic resonance spectra, so diminishing a discrepancy between the observed and the calculated second moments.

Apart from the main O–H doublet of 3150—3270 cm.$^{-1}$, the infrared spectrum of brushite [Fig. 1(b) of ref. 6] shows an absorption band near 2350 cm.$^{-1}$ and a faint shoulder at 2900 cm.$^{-1}$ (compare monetite, $CaHPO_4$, which has two peaks at 2784 and 2403 cm.$^{-1}$). These are at similar positions to the pairs of peaks near 2800 and 2360 cm.$^{-1}$ common to several hydrogen phosphates and regarded by Blinc and Hadži[22] as characteristic of

[18] Halla, *Z. Krist.*, 1931, **80**, 349.

[19] Egli, *Amer. Min.*, 1948, **33**, 622.

[20] Baynham and Raistrick in Sauchelli's "Chemistry & Technology of Fertilisers," Reinhold, New York, 1960, p. 566.

[21] Lippert and Truter, *J.*, 1960, 4996.

[22] Blinc and Hadži, *Spectrochim Acta*, 1960, **16**, 852.

short hydrogen bonds with proton tunnelling at room temperature and a proton magnetic resonance transition to a " frozen state " at low temperatures. Between 77° and 300°K, however, we have been unable to detect any such transition in either brushite or monetite, so that apparently these two structures do not fit Blinc and Hadži's classification.

Despite its moderate accuracy, the present analysis has produced atomic parameters in better agreement both with the *X*-ray data and with what would be expected from similar structure analyses of other orthophosphates. If O_4 is excluded (Table 6), the isotropic thermal vibration parameters for oxygen and the anisotropic U_{ii} values for calcium and phosphorus [Table 2(b)] are about the same as those found in monetite and calcium bis(dihydrogen phosphate) monohydrate.[6] In all three structures, the motions of the calcium and phosphorus atoms appear rather small compared with the cation and phosphorus vibrations [23] in potassium dihydrogen phosphate; possibly this difference is due to inadequate absorption corrections in the data from the calcium salts.

We are grateful to Dr. C. A. Beevers for encouragement, Dr. D. W. J. Cruickshank for advice, and Dr. W. G. Perdok for kindly making piezo-electric measurements. We also thank Miss M. Jowett and Mrs. B. Hawkshaw of the Leeds University Electronic Computing Laboratory for help with calculations.

Department of Chemical Technology, Institute of Technology, Bradford, 7.
Department of Inorganic & Structural Chemistry,
The University, Leeds, 2.

[*Received, October 9th,* 1961.]

---

[23] Bacon and Pease, *Proc. Roy. Soc.*, 1953, *A*, **220**, 397.