

Refinement of the Crystal Structure of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$

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$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ crystallizes in space group $P\bar{1}$ in the triclinic unit cell $a = 5.6261$ (5), $b = 11.889$ (2), $c = 6.4731$ (8) Å, $\alpha = 98.633$ (6), $\beta = 118.262$ (6), and $\gamma = 83.344$ (6)° at 25°C with $Z = 2$. The structure was refined with 3401 observed reflections measured on a diffractometer to $R_w = 0.033$, $R_o = 0.069$. Corrections were made for absorption, anomalous dispersion, and isotropic secondary extinction. The structure contains $\text{Ca}(\text{H}_2\text{PO}_4)^+$ chains which form corrugated layers. Between these layers are layers of $(\text{H}_2\text{PO}_4)^-$ ions and water molecules. Hydrogen atoms have been located approximately; ideal positions for the hydrogen atoms have been calculated. The two sets of hydrogen positions differ by ~ 0.28 Å. One hydrogen bond, in which the water molecule is the donor, is apparently bifurcated. All other hydrogen atoms form normal hydrogen bonds, with each hydrogen site seemingly fully occupied. The disorder of one hydrogen atom between the centrosymmetrically related atoms O(1) and O(1') was postulated by earlier workers. The P–O and O...O distances and electron-density maps obtained here show that there is no hydrogen atom in this position.

Introduction

The presence of a corrugated $[\text{CaH}_2\text{PO}_4]^+$ sheet in $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ was suggested by Smith, Lehr & Brown (1955) by analogy with the structural features then known to be in $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Wooster, 1936) and $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (Beever & Raistrick, 1954). The presence of the corrugated sheet in $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ was confirmed by the determination of the general features of the crystal structure by MacLennan & Beevers (1956), who refined the structure to $R = 0.235$ using the $h0l$, $hk0$ and $0kl$ reflections. Positions for the hydrogen atoms were not reported.

Jones & Cruickshank (1961) allowed for anisotropic thermal motion in their least-squares refinement of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ to 0.164 over 341 reflections. They used the original photographic X-ray data of MacLennan & Beevers, uncorrected for considerable absorption. Hydrogen atoms were provisionally placed, by Jones & Cruickshank from considerations of covalent P–O bond lengths and O...O distances.

The corrugated sheet is an important structural type among calcium phosphates. Similar sheets are present in $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (Beever, 1958; Jones & Smith, 1962; Curry & Jones, 1970), in the related $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Atoji & Rundle, 1958), in CaHPO_4 (MacLennan & Beevers, 1955; Jones & Cruickshank, 1961; Dickens & Bowen, 1971) and probably in $\text{Ca}_2(\text{NH}_4)\text{H}_7(\text{PO}_4)_4 \cdot 2\text{H}_2\text{O}$, $\text{Ca}_2\text{KH}_7(\text{PO}_4)_4 \cdot 2\text{H}_2\text{O}$, and $\text{CaCl}(\text{H}_2\text{PO}_4) \cdot \text{H}_2\text{O}$ (Brown, Smith, Lehr & Frazier, 1958). However, $\text{CaBr}(\text{H}_2\text{PO}_4) \cdot \text{H}_2\text{O}$ and $\text{CaI}(\text{H}_2\text{PO}_4) \cdot 4\text{H}_2\text{O}$, appear to contain planar $\text{Ca}-\text{PO}_4$ sheets (Brown *et al.*, 1958). Our refinement of the $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ structure was

prompted by our interest in the factors that contribute to the stability of the corrugated sheet and the nature of the hydrogen bonding in calcium phosphates. New X-ray data from a single crystal of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ were collected. Hydrogen atoms were located approximately.

Data collection and structure refinement

The crystal used in the data collection is an approximately square, flat plate of thickness ~ 0.04 mm and width ~ 0.1 mm, grown from aqueous solution at 25°C (conditions for precipitation given by Elmore & Farr, 1940). It was attached to a thin borate glass fiber using clear household cement; the fiber was attached to the insert in the goniometer head using epoxy cement. Crystal data are as follows:

Formula (ideal): $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$
Cell: triclinic

$a = 5.6261$ (5) Å
 $b = 11.889$ (2)
 $c = 6.4731$ (8)
 $\alpha = 98.633$ (6)°
 $\beta = 118.262$ (6)
 $\gamma = 83.344$ (6)

Volume = 376.55 Å³

Space-group $P\bar{1}$; cell contents $2[\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}]$; calculated density 2.231 g.cm⁻³; observed density 2.22 g.cm⁻³ (Bassett, 1908).

Standard deviations are given in parentheses after the cell parameters, which were calculated by least-squares methods from twelve 2θ values observed at 25°C on a diffractometer equipped with a highly oriented graphite monochromator. The wavelength $\lambda(\text{Mo } K\alpha_1)$

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$=0.70926 \text{ \AA}$ was assumed. Care was taken to use only the $K\alpha_1$ peak in determining the 2θ values for cell refinement.

Data were measured by $\theta-2\theta$ scans, using a scintillation counter on a Picker* 4-circle single-crystal diffractometer automated by a PDP 8/I computer through a Picker FACS-1 interface. The diffractometer controlling programs were those of Busing, Ellison, Levy, King & Roseberry (1968) as adapted by Picker Nuclear Corporation. Values for F_{hkl} , $\sigma(F_{hkl})$, and β (used in the extinction correction and calculated at the same time as the absorption corrections) were obtained using the following equations:

$$I = [P - (T/2T_B)(B_L + B_H)] (\text{SRC})/A$$

$$\sigma(I) = \{P + (B_L + B_H) [T/(2T_B)]^2\}^{1/2}/A$$

$$F_{hkl} = [(AF)(LP)(I)]^{1/2}$$

$$\sigma(F_{hkl}) = \{[\sigma(I)/2](LP/I)\}^{1/2}$$

$$LP = 2 \sin 2\theta_c / (\cos^2 2\theta_m + \cos^2 2\theta_c)$$

$$\beta = (-1.58883) (10^6) \lambda^2 (\cos^2 2\theta_m + \cos^4 2\theta_c) dA/d\mu / [AV^2 \sin^2 \theta_c (\cos^2 2\theta_m + \cos^2 2\theta_c)]$$

I = integrated intensity
 P = counts during 2θ scan
 B_L = background counts at lower 2θ
 B_H = background counts at higher 2θ
 T = scan time = $(1.4 + 0.692 \tan \theta_c / 0.5)$ (scan speed was $0.5^\circ/\text{min}$)
 λ = 0.70926 \AA (Mo $K\alpha_1$ radiation)
 T_B = time spent counting each background (40 secs here)
 SRC = scan range correction, calculated by table look-up method from values recommended by Smith & Alexander (1962)
 A = transmission factor in the absorption correction (max = 0.994, min = 0.962)

* Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

$\sigma(I)$ = standard deviation of integrated intensity
 F_{hkl} = structure factor
 AF = attenuator factor (attenuators were layers of 0.025 mm Nb)
 LP = Lorentz-polarization correction
 $\sigma(F_{hkl})$ = standard deviation of structure factor
 θ_c = Bragg angle for reflection under consideration
 θ_m = Bragg angle for monochromator (6.005° here)
 μ = linear absorption correction (12.5 cm^{-1} here)
 $dA/d\mu$ is in mm
 V = volume of unit cell

A total of 8834 reflections (maximum $\sin \theta/\lambda = 0.907 \text{ \AA}^{-1}$) were collected from the hkl and $\bar{h}\bar{k}l$ hemispheres and were merged, using the program described in Dickens & Bowen (1971), into a unique set of 4705 reflections. Of these, 3401 were 'observed' and 1304 were 'unobserved' (unobserved reflections are those less than $2\sigma(I)$ above background). The R value $\sum |F_{hkl}^i - F_{hkl}^j| / \sum F_{hkl}^i$ between equivalent reflections F_{hkl}^i and F_{hkl}^j , where $i < j$ and i and j are the orders of the reflections in the reflection list, is 0.046 calculated over 2173 observed reflections. The structure as given by Jones & Cruickshank was refined isotropically to $R_w = 0.060$ and $R = 0.092$; it was then refined anisotropically to $R_w = 0.048$ and $R = 0.073$ using the X-ray 67 system of computer programs (Stewart, 1967). Hydrogen atoms were not included at this stage. The value R_w is defined as $[\sum w(|F_o| - |F_c|)^2 / \sum w(|F_o|)^2]^{1/2}$; R is defined as $\sum ||F_o| - |F_c|| / \sum |F_o|$. The neutral atom scattering factors in *International Tables for X-ray Crystallography* (1962) were used in the X-ray 67 refinements. These refinements included unobserved reflections for which F_{hkl} was calculated higher than $2\sigma(F_{hkl})$ above background. Reflections were assigned weights of $[1/\sigma(F_{hkl})]^2$. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$.

Hydrogen atoms were found as unambiguous peaks in a difference electron-density synthesis in which the coefficients were weighted by the least-squares weights. Heights of the hydrogen atoms ranged from about 1.5 to 2.3 e. \AA^{-3} ; the highest background was about 1 e. \AA^{-3} . These hydrogen atoms were included with variable

Table 1. Atomic parameters in $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$

	x	y	z	B_{11}^*	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ca	0.73260 (9)	0.10247 (4)	0.77263 (8)	0.85 (1)	0.96 (1)	0.90 (2)	-0.01 (1)	0.50 (1)	0.12 (1)
P(1)	0.7463 (1)	0.09747 (5)	0.2771 (1)	0.82 (2)	1.06 (2)	0.84 (2)	-0.02 (1)	0.52 (1)	0.15 (2)
O(1)	0.5810 (3)	0.0332 (1)	0.3406 (3)	1.17 (6)	1.27 (6)	1.19 (6)	-0.39 (4)	0.70 (5)	0.13 (5)
O(2)	0.9168 (3)	0.0338 (1)	0.1730 (3)	1.21 (6)	1.46 (6)	1.19 (6)	0.37 (5)	0.88 (5)	0.24 (5)
O(3)	0.9207 (3)	0.1719 (1)	0.5143 (3)	1.26 (6)	1.80 (7)	1.37 (7)	-0.66 (5)	0.82 (6)	-0.43 (5)
O(4)	0.5661 (3)	0.1808 (2)	0.0864 (3)	1.30 (7)	1.98 (7)	1.78 (8)	0.70 (5)	0.95 (6)	-1.06 (6)
P(2)	0.3483 (1)	0.37290 (5)	0.6128 (1)	1.14 (2)	0.93 (2)	1.26 (2)	-0.04 (1)	0.57 (2)	0.25 (2)
O(5)	0.3804 (3)	0.2451 (1)	0.6034 (3)	1.24 (6)	0.89 (5)	1.86 (7)	0.05 (4)	0.78 (6)	0.28 (5)
O(6)	0.1903 (4)	0.4121 (2)	0.7587 (4)	3.02 (9)	1.98 (7)	2.41 (8)	1.06 (7)	2.02 (8)	0.81 (6)
O(7)	0.6345 (4)	0.4207 (2)	0.7581 (4)	1.78 (8)	2.24 (8)	2.49 (9)	-0.77 (6)	0.13 (7)	1.07 (7)
O(8)	0.1984 (3)	0.4191 (1)	0.3761 (3)	1.49 (7)	1.38 (6)	1.56 (7)	0.05 (5)	0.62 (6)	0.58 (5)
O(9)	0.0624 (4)	0.2541 (1)	-0.0025 (3)	1.75 (7)	1.20 (6)	1.34 (7)	-0.07 (5)	0.67 (6)	0.09 (5)

Figures in parentheses are standard deviations calculated in the final least-squares refinement.

* Thermal parameters are in \AA^2 , and have the form $\exp -[a^2 h^2 B_{11} + b^2 k^2 B_{22} + c^2 l^2 B_{33} + 2a^* b^* h k B_{12} + 2a^* c^* h l B_{13} + 2b^* c^* k l B_{23}]$.

Table 2. Observed and calculated structure factors for Ca(H₂PO₄)₂ · H₂O

Columns are I, 10F_o, 10F_c. Values F_o and F_c are on an absolute scale. These values do not include corrections for extinction or anomalous dispersion. 'Unobserved' reflections are marked by *.

Table with multiple columns containing numerical data for structure factors. The data is organized into rows and columns, with some cells containing asterisks to denote unobserved reflections. The table is dense and spans the majority of the page.

Table 2 (cont.)

3-11L	→ 113 125	3-31L	6 399 88	-3 66 65	-6 50 50	2 73 76	0 214 -215	*12L	-3 107 -107	-1 170 165	n 101 -76	-5 116 120	5 19L
-4 147 143	→ 131 131	-11 30 9	3 10L	-2 185 -179	-5 304 -33	3 56 49	1 119 128	-2 42 -42	-6 37 42	0 42 -42	-1 36 -28	-4 229 -228	-6 121 111
-7 54 -56	-1 21 14	-10 85 84	-10 102 -104	0 112 94	-3 29 -31	5 37 -64	5 122 -111	0 81 -56	0 80 83	1 36 -105	5 2L	-2 241 -240	-6 121 111
-10 106	-1 170 178	-5 82 -87	-10 102 -104	1 37 -30	-2 150 -187	6 39 -14	-9 125 -125	-9 125 -125	0 103 108	3 41 19	-11 30 -21	-1 143 -147	-10 101 -103
-5 30 36	-1 104 110	-8 52 -57	3 2L 19	2 34 -19	0 109 113	7 -22	6 59 58	-10 107 -110	6 32 9	5 52 -52	-9 72 106	2 34 34	-2 82 79
-12 121	2 133 -134	-7 29 -5	5 19L	0 109 113	7 -22	6 59 58	-10 107 -110	6 32 9	5 52 -52	-9 72 106	2 34 34	-2 82 79	-1 37 36
-2 23 -23	2 201 204	-5 307 307	-4 44 -44	-7 54 43	3 23 11	-11 30 36	7 45L	-4 53 84	5 -5L	-6 35 33	6 77 96	6 -15L	3 50 34
-1 31 -35	3 311 -311	-3 127 -127	-3 127 -127	-6 147 -149	3 23 11	-11 30 36	7 45L	-4 53 84	5 -5L	-6 35 33	6 77 96	6 -15L	3 50 34
0 137 202	6 138 -143	-3 127 -127	-3 127 -127	-5 30 31	3 23 11	-11 30 36	7 45L	-4 53 84	5 -5L	-6 35 33	6 77 96	6 -15L	3 50 34
-1 20 -20	2 240 -240	-2 616 516	-3 152 151	-5 30 31	3 23 11	-11 30 36	7 45L	-4 53 84	5 -5L	-6 35 33	6 77 96	6 -15L	3 50 34
2 60 -60	1 152 152	-2 616 516	-3 152 151	-5 30 31	3 23 11	-11 30 36	7 45L	-4 53 84	5 -5L	-6 35 33	6 77 96	6 -15L	3 50 34
3 36 6	0 15 -15	-1 63 61	-1 63 61	-2 39 23	-2 39 23	-2 39 23	-2 39 23	-2 39 23	-2 39 23	-2 39 23	-2 39 23	-2 39 23	-2 39 23
4 30 24	3 310 310	2 100 100	2 100 100	-2 39 23	-2 39 23	-2 39 23	-2 39 23	-2 39 23	-2 39 23	-2 39 23	-2 39 23	-2 39 23	-2 39 23
5 31 57	3 310 310	2 100 100	2 100 100	-2 39 23	-2 39 23	-2 39 23	-2 39 23	-2 39 23	-2 39 23	-2 39 23	-2 39 23	-2 39 23	-2 39 23
6 50 -24	-1 36 -36	3 101 100	2 27 16	0 124 100	9 324 21	-1 154 -147	-5 150 151	4 40 -3	0 70 -67	4 79 77	1 284 2	-9 97 74	6 -14L
7 84 -7	-10 87 73	4 235 230	6 55 -56	-8 160 167	-3 44 39	-4 235 -221	3 304 24	2 26 20	2 26 20	-2 173 -172	2 226 25	-8 228 -225	6 -14L
8 30 19	-7 72 -86	4 37 3	3 11L	-4 53 -59	-5 118 102	-10 103	0 235 -238	*15L	-3 124 -111	-1 37 36	4 195 194	-6 271 270	-6 224 -2
9 101 101	-5 82 -86	4 37 3	3 11L	-4 53 -59	-5 118 102	-10 103	0 235 -238	*15L	-3 124 -111	-1 37 36	4 195 194	-6 271 270	-6 224 -2
10 35 10	-7 77 85	3 11L	3 11L	-3 37 24	-2 151 -148	3 65 66	2 100 101	-1 162 156	-7 37 30	4 27 4	5 3L	-1 30 61	-1 30 61
11 171 170	-5 82 -86	4 37 3	3 11L	-3 37 24	-2 151 -148	3 65 66	2 100 101	-1 162 156	-7 37 30	4 27 4	5 3L	-1 30 61	-1 30 61
12 90 -92	-2 194 -198	-11 42 42	-10 85 -70	-2 36 23	-1 46 -57	4 85 84	3 294 17	7 39 50	-6 59 42	3 27 4	4 27 4	-3 50 -61	-1 30 61
13 210 199	-1 90 -2	-10 31 30	-10 151 141	-1 37 -13	0 333 334	5 34 -47	7 216 -216	-1 139 -145	5 34 -47	5 42 64	-11 40 16	-1 30 61	-1 30 61
14 123 -131	0 112 116	0 334 44	-7 126 116	1 142 -128	6 159 -151	5 32 -30	6 32 -30	-2 23 -17	4 66 74	5 35 3	-10 33 -14	1 57 59	1 84 159
15 250 -9	1 126 -124	-6 260 -264	-6 77 -78	3 214 159	4 123 -164	6 159 -151	5 32 -30	-2 23 -17	4 66 74	5 35 3	-10 33 -14	1 57 59	1 84 159
16 20 -20	2 137 -136	-1 36 13	-5 55 57	4 55 61	5 68 60	-4 55 61	5 68 60	-4 55 61	5 68 60	-4 55 61	5 68 60	-4 55 61	5 68 60
17 51 63	5 97 99	-5 21 12	-3 01 97	-4 35 29	0 32 -23	-11 36 4	-11 82 69	0 29 19	1 37 4	-11 36 20	-6 44 37	-9 30 4	-9 30 4
18 30 24	-1 36 -36	3 101 100	2 27 16	0 124 100	9 324 21	-1 154 -147	-5 150 151	4 40 -3	0 70 -67	4 79 77	1 284 2	-9 97 74	6 -14L
19 7 84	-10 87 73	4 235 230	6 55 -56	-8 160 167	-3 44 39	-4 235 -221	3 304 24	2 26 20	2 26 20	-2 173 -172	2 226 25	-8 228 -225	6 -14L
20 32 19	-7 72 -86	4 37 3	3 11L	-4 53 -59	-5 118 102	-10 103	0 235 -238	*15L	-3 124 -111	-1 37 36	4 195 194	-6 271 270	-6 224 -2
21 101 101	-5 82 -86	4 37 3	3 11L	-4 53 -59	-5 118 102	-10 103	0 235 -238	*15L	-3 124 -111	-1 37 36	4 195 194	-6 271 270	-6 224 -2
22 35 10	-7 77 85	3 11L	3 11L	-3 37 24	-2 151 -148	3 65 66	2 100 101	-1 162 156	-7 37 30	4 27 4	5 3L	-1 30 61	-1 30 61
23 171 170	-5 82 -86	4 37 3	3 11L	-3 37 24	-2 151 -148	3 65 66	2 100 101	-1 162 156	-7 37 30	4 27 4	5 3L	-1 30 61	-1 30 61
24 90 -92	-2 194 -198	-11 42 42	-10 85 -70	-2 36 23	-1 46 -57	4 85 84	3 294 17	7 39 50	-6 59 42	3 27 4	4 27 4	-3 50 -61	-1 30 61
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26 123 -131	0 112 116	0 334 44	-7 126 116	1 142 -128	6 159 -151	5 32 -30	6 32 -30	-2 23 -17	4 66 74	5 35 3	-10 33 -14	1 57 59	1 84 159
27 250 -9	1 126 -124	-6 260 -264	-6 77 -78	3 214 159	4 123 -164	6 159 -151	5 32 -30	-2 23 -17	4 66 74	5 35 3	-10 33 -14	1 57 59	1 84 159
28 20 -20	2 137 -136	-1 36 13	-5 55 57	4 55 61	5 68 60	-4 55 61	5 68 60	-4 55 61	5 68 60	-4 55 61	5 68 60	-4 55 61	5 68 60
29 51 63	5 97 99	-5 21 12	-3 01 97	-4 35 29	0 32 -23	-11 36 4	-11 82 69	0 29 19	1 37 4	-11 36 20	-6 44 37	-9 30 4	-9 30 4
30 30 24	-1 36 -36	3 101 100	2 27 16	0 124 100	9 324 21	-1 154 -147	-5 150 151	4 40 -3	0 70 -67	4 79 77	1 284 2	-9 97 74	6 -14L
31 7 84	-10 87 73	4 235 230	6 55 -56	-8 160 167	-3 44 39	-4 235 -221	3 304 24	2 26 20	2 26 20	-2 173 -172	2 226 25	-8 228 -225	6 -14L
32 32 19	-7 72 -86	4 37 3	3 11L	-4 53 -59	-5 118 102	-10 103	0 235 -238	*15L	-3 124 -111	-1 37 36	4 195 194	-6 271 270	-6 224 -2
33 101 101	-5 82 -86	4 37 3	3 11L	-4 53 -59	-5 118 102	-10 103	0 235 -238	*15L	-3 124 -111	-1 37 36	4 195 194	-6 271 270	-6 224 -2
34 35 10	-7 77 85	3 11L	3 11L	-3 37 24	-2 151 -148	3 65 66	2 100 101	-1 162 156	-7 37 30	4 27 4	5 3L	-1 30 61	-1 30 61
35 171 170	-5 82 -86	4 37 3	3 11L	-3 37 24	-2 151 -148	3 65 66	2 100 101	-1 162 156	-7 37 30	4 27 4	5 3L	-1 30 61	-1 30 61
36 90 -92	-2 194 -198	-11 42 42	-10 85 -70	-2 36 23	-1 46 -57	4 85 84	3 294 17	7 39 50	-6 59 42	3 27 4	4 27 4	-3 50 -61	-1 30 61
37 210 199	-1 90 -2	-10 31 30	-10 151 141	-1 37 -13	0 333 334	5 34 -47	7 216 -216	-1 139 -145	5 34 -47	5 42 64	-11 40 16	-1 30 61	-1 30 61
38 123 -131	0 112 116	0 334 44	-7 126 116	1 142 -128	6 159 -151	5 32 -30	6 32 -30	-2 23 -17	4 66 74	5 35 3	-10 33 -14	1 57 59	1 84 159
39 250 -9	1 126 -124	-6 260 -264	-6 77 -78	3 214 159	4 123 -164	6 159 -151	5 32 -30	-2 23 -17	4 66 74	5 35 3	-10 33 -14	1 57 59	1 84 159
40 20 -20	2 137 -136	-1 36 13	-5 55 57	4 55 61	5 68 60	-4 55 61	5 68 60	-4 55 61	5 68 60	-4 55 61	5 68 60	-4 55 61	5 68 60
41 51 63	5 97 99	-5 21 12	-3 01 97	-4 35 29	0 32 -23	-11 36 4	-11 82 69	0 29 19	1 37 4	-11 36 20	-6 44 37	-9 30 4	-9 30 4
42 30 24	-1 36 -36	3 101 100	2 27 16	0 124 100	9 324 21	-1 154 -147	-5 150 151	4 40 -3	0 70 -67	4 79 77	1 284 2	-9 97 74	6 -14L
43 7 84	-10 87 73	4 235 230	6 55 -56	-8 160 167	-3 44 39	-4 235 -221	3 304 24	2 26 20	2 26 20	-2 173 -172	2 226 25	-8 228 -225	6 -14L
44 32 19	-7 72 -86	4 37 3	3 11L	-4 53 -59	-5 118 102	-10 103	0 235 -238	*15L	-3 124 -111	-1 37 36	4 195 194	-6 271 270	-6 224 -2
45 101 101	-5 82 -86	4 37 3	3 11L	-4 53 -59	-5 118 102	-10 103	0 235 -238	*15L	-3 124 -111	-1 37 36	4 195 194	-6 271 270	-6 224 -2
46 35 10	-7 77 85	3 11L	3 11L	-3 37 24	-2 151 -148	3 65 66	2 100 101	-1 162 156	-7 37 30	4 27 4	5 3L	-1 30 61	-1 30 61
47 171 170	-5 82 -86	4 37 3	3 11L	-3 37 24	-2 151 -148	3 65 66	2 100 101	-1 162 156	-7 37 30	4 27 4	5 3L	-1 30 61	-1 30 61
48 90 -92	-2 194 -198	-11 42 42	-10 85 -70	-2 36 23	-1 46 -57	4 85 84	3 294 17	7 39 50	-6 59 42	3 27 4	4 27 4	-3 50 -61	-1 30 61
49 210 199	-1 90 -2	-10 31 30	-10 151 141	-1 37 -13	0 333 334	5 34 -47	7 216 -216	-1 139 -145	5 34 -47	5 42 64	-11 40 16	-1 30 61	-1 30 61
50 123 -131	0 112 116	0 334 44	-7 126 116	1 142 -128	6 159 -151	5 32 -30	6 32 -30	-2 23 -17	4 66 74	5 35 3	-10 33 -14	1 57 59	1 84 159
51 250 -9	1 126 -124	-6 260 -264	-6 77 -78	3 214 159	4 123 -164	6 159 -151	5 32 -30	-2 23 -17	4 66 74	5 35 3	-10 33 -14	1 57 59	1 84 159
52 20 -20	2 137 -136	-1 36 13	-5 55 57	4 55 61	5 68 60	-4 55 61	5 68 60	-4 55 61	5 68 60	-4 55 61	5 68 60	-4 55 61	5 68 60
53 51 63	5 97 99	-5 21 12	-3 01 97	-4 35 29	0 32 -23	-11 36 4	-11 82 69	0 29 19	1 37 4	-11 36 20	-6 44 37	-9 30 4	-9 30 4
54 30 24	-1 36 -36	3 101 100	2 27 16	0 124 100	9 324 21	-1 154 -147	-5 150 151	4 40 -3	0 70 -6				

0.50–0.70 for all atoms other than hydrogen. The coefficients for pairs of the first kind are about 0.50.

The extinction parameter, r , where $F^2 = F_{\text{unc}}^2(1 + \beta r |F_{\text{unc}}|^2)^{1/2}$ in the notation of Zachariasen (1967), was later refined to $5(1) \times 10^{-9}$ cm in three cycles. All parameters but the thermal parameters of hydrogen were varied in these cycles and corrections for anomalous dispersion were applied using the program *RFINE* written by L. W. Finger of the Carnegie Institute of Washington. Scattering factors for the neutral atoms were taken from Cromer & Mann (1968) and from Cromer (1965). Only 'observed' reflections were used. Structural parameters obtained in these refinements are given in Table 1. Observed and calculated structure factors are given Table 2. In the final refinement, $R_w = 0.033$, $R = 0.069$, the average shift/error = 0.05 and the standard deviation of an observation of unit weight, defined as $[\sum w(|F_o| - |F_c|)^2 / (4705 - 128)]^{1/2}$, is 1.04.

Three sets of hydrogen positions from the electron-density difference synthesis, least-squares refinements, and calculations to idealize the water geometry (see later), are given in Table 3. Calculated hydrogen positions were used to calculate interatomic distances mentioned in Table 4 and in the text. The positions in the 2nd and 3rd sets of hydrogen positions differ by 0.28 Å on the average.

Table 4. *Interatomic distances and angles in*
 $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$

Figures in parentheses are standard deviations in the last digit of the interatomic distances and angles, and were calculated from standard deviations in the atomic positional parameters and unit-cell parameters. They include terms from the variance-covariance matrix. Distances and angles involving hydrogen were obtained with the calculated hydrogen positions.

P(1)–O(1)	1.496 (1) Å
P(1)–O(2)	1.496 (1)
P(1)–O(3)	1.571 (2)
P(1)–O(4)	1.578 (2)
O(1)–P(1)–O(2)	119.71 (9)°
O(1)–P(1)–O(3)	103.09 (9)
O(1)–P(1)–O(4)	112.13 (9)
O(2)–P(1)–O(3)	111.74 (9)
O(2)–P(1)–O(4)	102.11 (9)
O(3)–P(1)–O(4)	107.81 (10)
O(1)–O(2)	2.587 (2) Å
O(1)–O(3)	2.403 (2)
O(1)–O(4)	2.549 (2)
O(2)–O(3)	2.540 (2)
O(2)–O(4)	2.390 (2)
O(3)–O(4)	2.544 (2)
P(2)–O(5)	1.505 (2)
P(2)–O(6)	1.570 (2)
P(2)–O(7)	1.555 (2)
P(2)–O(8)	1.511 (2)
O(5)–P(2)–O(6)	105.89 (9)°
O(5)–P(2)–O(7)	107.82 (10)
O(5)–P(2)–O(8)	115.31 (9)
O(6)–P(2)–O(7)	107.17 (12)
O(6)–P(2)–O(8)	109.29 (10)
O(7)–P(2)–O(8)	110.96 (9)

Table 4 (*cont.*)

O(5)–O(6)	2.454 (2) Å
O(5)–O(7)	2.473 (2)
O(5)–O(8)	2.548 (2)
O(6)–O(7)	2.515 (3)
O(6)–O(8)	2.513 (2)
O(7)–O(8)	2.527 (2)
O(3)–H(1)	1.00 Å
O(4)–H(2)	1.00
O(6)–H(3)	0.99
O(7)–H(4)	1.00
O(1)–Ca	2.309 (1)
O(1')–Ca	2.538 (2)
O(1)–O(1')	2.855 (3)
O(2)–Ca	2.326 (1)
O(2')–Ca	2.521 (2)
O(2)–O(2')	2.794 (3)
O(3)–Ca	2.625 (2)
O(3)–O(5)	2.596 (2)*
O(3)–O(9)	2.870 (2)
O(4)–Ca	2.627 (2)
O(4)–O(9)	2.668 (2)*
O(4)–O(5)	2.982 (2)
O(5)–Ca	2.393 (2)
O(5)–O(3)	2.596 (2)*
O(5)–H(1)	1.62
O(5)–O(4)	2.982 (2)
O(6)–O(8)	2.697 (2)*
O(6)–O(9)	2.969 (2)*
O(6)–H(6)	2.24
O(7)–O(8)	2.636 (2)*
O(7)–O(9)	2.920 (3)*
O(7)–H(6)	2.16
O(8)–O(7)	2.636 (2)*
O(8)–O(6)	2.697 (2)*
O(8)–O(9)	2.771 (2)*
O(8)–H(3)	1.72
O(8)–H(4)	1.66
O(8)–H(5)	1.81
H(1)–O(5)	1.62
O(3)–H(1)–O(5)	165°
H(2)–O(9)	1.70 Å
O(4)–H(2)–O(9)	163°
H(3)–O(8)	1.72 Å
O(6)–H(3)–O(8)	168°
H(4)–O(8)	1.66 Å
O(7)–H(4)–O(8)	163°
O(9)–Ca	2.475 (2) Å
H(5)–O(8)	1.81
H(6)–O(7)	2.16
H(6)–O(6)	2.24
O(9)–H(5)–O(8)	180° (assumed)
O(9)–H(5)–O(6)	132
O(9)–H(5)–O(7)	135

* Hydrogen bond between these two oxygen atoms.

Description of the structure

The structure of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ contains $[\text{CaH}_2\text{PO}_4]^+$ chains (shown nearly end-on in Fig. 1) along [001]. In these chains, opposite edges of the $\text{P}(1)\text{O}_4$ group are coordinated to Ca ions. The chains are inter-coordinated through the O(1) and O(2) apexes of the $\text{P}(1)\text{O}_4$ group, which bond to Ca ions in adjacent chains. The chains form corrugated layers parallel to (010), with O(1) and O(2) inside the layer. Apexes

O(3) and O(4) are on the outside of the layer and are the donors in two hydrogen bonds, one to water-oxygen O(9), and the other to O(5) of the P(2)O₄ group. Oxygen atoms O(5) and O(9) are coordinated to Ca ions, thus providing a bridge between next nearest Ca-PO₄ chains. This bridging may be a major factor in stabilizing the sheets in their 'corrugated' form. Between the corrugated sheets, the [H₂P(2)O₄]⁻ ions form a hydrogen-bonded network. The only direct bonding between this network and the corrugated sheet is the hydrogen bond O(5)···H(1)-O(3) and the Ca coordination to O(5) noted above.

The general features of the corrugated sheets in Ca(H₂PO₄)₂ · H₂O and CaHPO₄ · 2H₂O, the only two examples which are well known, are similar. The sheet is narrower in CaHPO₄ · 2H₂O, and a hydrogen bond O(1)-H···O(4) is formed between chains on opposite surfaces of the sheet. Also, the water molecules in CaHPO₄ · 2H₂O are hydrogen-bonded to both sheets. In Ca(H₂PO₄)₂ · H₂O, the water molecule hydrogen-bonds only to the interlayer H₂P(2)O₄ group. The water molecule is bonded to Ca and is the acceptor in the hydrogen bond O(4)-H(2)···O(9) from the corrugated layer. Also it is the donor in hydrogen bonds to O(6), O(7), and O(8) of the P(2)O₄ group and thus provides bridging between the corrugated layer and the P(2)O₄ network.

The Ca ion environment

The Ca ion is coordinated (Table 4) to 8 oxygen atoms, including two PO₄ edges [O(1', 3) and O(2', 4)], three PO₄ apices [O(1), O(2), and O(5)] and the oxygen atom O(9) of the water molecule, with Ca···O distances of 2.310 (2) to 2.627 (2) Å, which are in the normal range. The two PO₄ edges bonded to a given Ca are essentially perpendicular to one another, since they are opposite edges of P(1)O₄ groups related by the cell translation along *c*. The three apex oxygen atoms and the water oxygen atom form a distorted square about Ca approximately perpendicular to the P-Ca-P direc-

tion. The shortest Ca···O bonds are those that bond to neighboring CaH₂P(1)O₄ chains; the longest are those that bond to the P(1)O₄ edges in the same chains as the Ca atom, in accord with Pauling's rule on the sharing of polyhedron corners, edges, and faces (Pauling, 1960).

The PO₄ groups and their environments

Details of the two unique PO₄ groups and their environments are given in Table 4. The O-P-O angles associated with the edges coordinated to Ca are 102.11 and 103.09°; they allow greater separation of Ca and P, in accord with Pauling's rule, than tetrahedral angles do. Similar distortions of PO₄ groups have been observed in Ca₇Mg₉(Ca, Mg)₂(PO₄)₁₂ (Dickens & Brown, 1971). The P-O bond distances (Table 4) unequivocally support the assignment of covalently bonded hydrogen atoms to O(3), O(4), O(6), and O(7). In particular, the P(1)-O(1) distance and the O(1)···O(1') separation, reported by Jones & Cruickshank (1961) to be 1.62 (3) and 2.67 (5) Å, respectively, have refined to the significantly different values 1.496 (1) and 2.854 (3) Å, respectively. Thus, they no longer require the assignment of a hydrogen atom to O(1) and subsequent disordering of this hydrogen atom about the center of symmetry in the hydrogen bond O(1)-H···O(1'), O(1)···H-O(1'). The P-O distances in the P(1)O₄ group are self-consistent, with average values of 1.575 Å when H is covalently bonded to the oxygen atom, and 1.496 Å when there is no covalently bonded H. None of the oxygen atoms in the P(1)O₄ group is the acceptor of a hydrogen bond. In the P(2)O₄ group, the overriding effect on the P-O distance of a hydrogen atom covalently bonded to oxygen is shown by P(2)-O(6) and P(2)-O(7) which are the longest bonds. The fact that P(2)-O(6) is much longer than P(2)-O(7) may be the effect of stronger hydrogen-bonding from H(6) to O(6). Atom O(5) is the only oxygen atom bonded to Ca and is the acceptor in the hydrogen bond from H(1) on O(3) of the P(1)O₄ group.

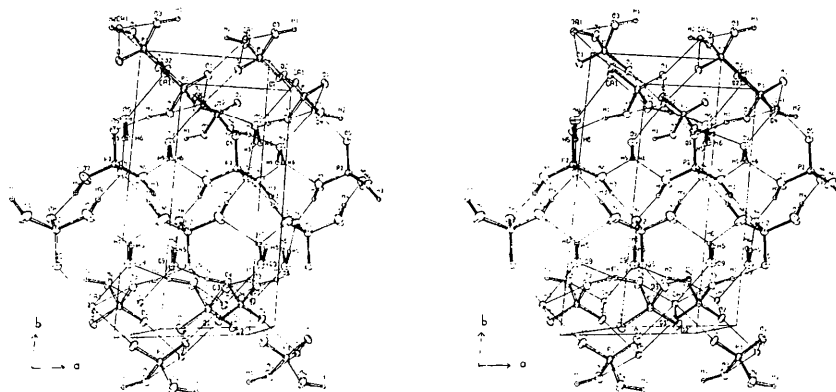


Fig. 1. Stereo illustration of the crystal structure of Ca(H₂PO₄)₂ · H₂O. Origin of the crystallographic coordinate system is in the bottom-left rear corner. Atomic labels are referred to in Table 4.

This is apparently the strongest hydrogen bond in the structure, and it may lengthen the P(2)–O(5) bond to the observed value of 1.505 Å, if this is indeed really significantly different from the corresponding average value of 1.496 Å observed in the P(1)O₄ group. The longest bond distance in the structure for an oxygen atom without a covalently attached hydrogen atom is P(2)–O(8) and may reflect the effect of O(8) being the acceptor of three hydrogen bonds: H(3) and H(4) from neighboring P(2)O₄ groups, and H(5) from the water molecule. These three hydrogen atoms and P(2) are approximately tetrahedrally arranged about O(8).

The water molecule

The environment of the water molecule is given in Table 4. The water-oxygen atom O(9) is bonded to Ca and is the acceptor in the hydrogen bond involving H(2) on O(4) of the P(1)O₄ group. Atom O(9) is the donor in the hydrogen bonding of H(5) to O(8) of the P(2)O₄ group, and in the apparently bifurcated hydrogen-bonding of H(6) to O(7) and O(6) in a different P(2)O₄ group.

The hydrogen positions

The hydrogen atoms were located in difference electron-density syntheses. Because hydrogen positions as determined by X-ray diffraction are known to be too close to the atom to which hydrogen is covalently bonded, probable positions of the hydrogen atoms were calculated. For the hydrogen atoms attached to oxygen atoms of the PO₄ groups, the O–H distance and P–O–H angle were assumed to be 0.992 Å and 112.36°, respectively, as found in a recent neutron diffraction study of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ by Curry & Jones (1970). The hydrogen atom was placed in the plane of the P, O_D, O_A atoms where O_D and O_A are the donor and acceptor oxygen atoms in the hydrogen bond. Thus, the hydrogen bond O_D–H···O_A was made as linear as possible; the calculated O_D–H···O_A angles are all reasonable. The water molecule was assumed to have the geometry of free water, *i.e.*, O–H=0.958 Å and angle H–O–H=104.5°. Because the distance O(9)···O(8) is significantly shorter than O(9)···O(6) and O(9)···O(7), the hydrogen bond O(9)–H(5)···O(8) was assumed to be linear. The water molecule was then rotated 360° in 3° steps about the O(9)···O(8) vector and the distances were calculated from the remaining hydrogen atom, H(6), to all the oxygen atoms closer to O(9) than 3 Å. In the present hydrogen-bonding scheme, O(4) already has a whole hydrogen atom, H(2), which is hydrogen-bonded to O(9). If H(6) were hydrogen-bonded to O(3), it would be in the edge of the coordination polyhedron of Ca. Atom H(6) could be bonded to either O(6) or O(7), which are on the side of O(9) remote from the Ca ion, or it could form an apparently satisfactory bifurcated hydrogen bond to both.

The water molecule was rotated over this range of interest in 1° steps; the position for H(6) given in

Table 3 was selected as having equally good bonding to both O(6) and O(7) simultaneously. The bifurcated hydrogen bond agrees with the difference synthesis results, although H(6) is a little smeared out there and is probably undergoing oscillations about the O(9)···O(8) vector. The distances from H(5) and H(6) to O(6), O(7), and O(8) are in satisfactory accord with the distances from O(9), to O(6), O(7), and O(8), with the strong hydrogen bond corresponding to the shortest O···O distance. Angles O(9)–H(6)···O(6) and O(9)–H(6)···O(7) are just within what Donohue (1968) considers the reasonable range. If H(6) were hydrogen-bonded only to O(7), H(6)···O(7) would be ~1.97 Å, and H(6)···O(6) would be ~2.67 Å. For H(6) hydrogen-bonded only to O(6), the corresponding distances are H(6)···O(6) ~2.03 Å, H(6)···O(7)=2.62 Å.

The factors contributing to the bifurcation of H(6) may be: (i) reduced repulsions because of the resulting near-tetrahedral arrangement of the positively charged Ca, H(2), H(5), and H(6) about O(9), (ii) stability enhancement by the formation of two hydrogen bonds instead of one, and (iii) bonding to the lone pairs of the water-oxygen atom by H(2) and Ca. In view of the many examples where the third factor has not been satisfied, the first two are probably more important.

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The Crystal Structure of 2,3-Dimethylbenzoic Acid

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The crystal structure of 2,3-dimethylbenzoic acid has been determined from three-dimensional X-ray data. The triclinic unit cell of dimensions $a=6.895$, $b=9.018$, $c=6.846$ Å, $\alpha=97^\circ 22'$, $\beta=110^\circ 50'$, $\gamma=95^\circ 40'$ contains two molecules. The space group is $P\bar{1}$. Positions of some atoms in the molecule deviate from a planar configuration owing to molecular overcrowding. The carboxyl group is somewhat distorted from the benzene ring.

Introduction

The determination of the crystal structure of 2,3-dimethylbenzoic acid was undertaken as a continuation of previous studies (Anca, Martínez-Carrera & García-Blanco, 1967; Florencio & Smith, 1970; Cano, Martínez-Carrera & García-Blanco, 1970) to

investigate existing interactions between methyl groups and the carboxyl group in these derivatives of benzoic acid. In the present paper we paid attention to the effect of the position of the methyl groups on the bond lengths and bond angles in the case of an asymmetric molecule.

Experimental

A purified specimen of 2,3-dimethylbenzoic acid was kindly supplied by Dr Colomina of this Institute. Single crystals were obtained by slow evaporation in ethyl alcohol.

Unit-cell parameters were derived by a least-squares fit to the 2θ values of 30 high-order reflexions measured, using a single crystal, on a General Electric XRD-6 diffractometer with Co $K\alpha$ radiation ($\lambda=1.7902$ Å).

Parameters of the triclinic cell are:

$a=6.895$ Å	$\alpha=97^\circ 22'$	$D_m=1.25$ g.cm ⁻³
$b=9.018$	$\beta=110^\circ 50'$	$D_x=1.27$ g.cm ⁻³
$c=6.846$	$\gamma=95^\circ 40'$	$Z=2$

The molecule was assumed to be planar and centrosymmetric based on the structures of other analogous benzoic acids. Therefore, the space group chosen was

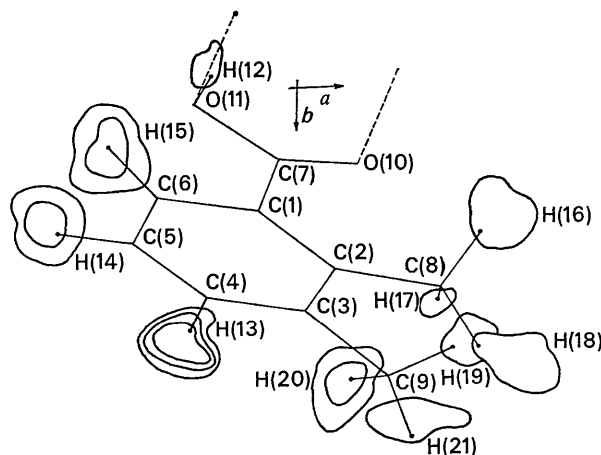


Fig. 1. Difference electron-density map showing hydrogen atoms contoured at intervals of 0.1 e.Å⁻³ beginning at 0.3 e.Å⁻³.