

The Crystal Structure of Calcium Terephthalate Trihydrate

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The crystals of calcium terephthalate trihydrate are monoclinic with the unit-cell dimensions, $a = 7.11$, $b = 21.67$, $c = 6.59$ Å, $\beta = 92.3^\circ$. The space group is $P2_1/c$ containing four structure units in a cell. The crystal structure was solved by the symbolic addition method and refined by the block-matrix least-squares method allowing anisotropic thermal vibrations for each atom. The final R value was 0.135 for 1311 observed structure factors derived from the visually estimated intensity data to which due corrections had been applied for the twinning of the crystal. Each carboxyl group of the molecule twists by about 5° from the plane of the benzene ring. The calcium ion takes eightfold coordination: four oxygen atoms of three terephthalic acid ions and four oxygen atoms of water molecules.

Introduction

The crystal structure of calcium terephthalate trihydrate has been determined to elucidate the spatial arrangement of the terephthalic acid ions and calcium ions, the coordination system around the calcium ion and the mode of hydrogen bonding.

Experimental

An aqueous solution of calcium acetate was gently added to an aqueous solution of potassium hydroxide and terephthalic acid, so that two layers were formed. The layers were allowed to mix by diffusion and the crystals of calcium terephthalate trihydrate were obtained after standing the solution for 24 hours.

The crystals were twinned and it was not possible to find an untwinned crystal. The present investigation was therefore carried out with a twinned crystal which showed the lowest degree of twinning.

The unit-cell dimensions were determined from Weissenberg photographs taken with $\text{Cu } K\alpha$ radiation using copper powder as an internal standard. The density was measured by the flotation method in a benzene-tetrabromoethane solution. The number of water molecules in a chemical unit was calculated to be three, assuming four chemical units in a cell.

Crystal data

Calcium terephthalate trihydrate, $\text{C}_8\text{H}_4\text{O}_4\text{Ca} \cdot 3\text{H}_2\text{O}$

Monoclinic

$P2_1/c$, $Z = 4$

$a = 7.11 \pm 0.01$, $b = 21.67 \pm 0.02$, $c = 6.59 \pm 0.01$ Å,

$\beta = 92.3 \pm 0.2^\circ$

$U = 1014.4$ Å³

$D_m = 1.69$, $D_x = 1.690$ g.cm⁻³

$\mu(\text{Cu } K\alpha) = 57.8$ cm⁻¹

$F(000) = 536$.

The intensity data were collected from equi-inclination Weissenberg photographs taken with $\text{Cu } K\alpha$ radiation by use of the multiple-film method. The layers from $hk0$ to $hk5$ for the c axis and from $h0l$ to $h2l$ for the b axis were recorded. Intensities were measured by visual comparison with a calibrated intensity scale.

Since the crystal was twinned on the (001) twin plane, the correction for twinning was applied to $0kl$ reflexions. The intensities of a pair of reflexions having the same index, each of which was diffracted from each component of the twinned crystal, were measured for twenty pairs on the $h0l$ Weissenberg photograph. The ratio of the contribution of the main component to that of the whole crystal was determined to be 0.937 and the intensities of $0kl$ reflexions were multiplied by this value.

After correction for Lorentz and polarization factors, the structure factors on various layers were correlated and scaled to a common base. No absorption correction was applied. 1600 structure factors were finally obtained in which 289 reflexions were too weak to be observed. A Wilson plot gave the value of B as 2.64 Å². Normalized structure factors were then calculated. The statistical values are:

	Observed	Theoretical (for centrosymmetric structures)
$\langle E ^2 \rangle$	1.007	1.000
$\langle E \rangle$	0.843	0.798
$\langle E^2 - 1 \rangle$	0.860	0.968

Determination of the structure

The structure was solved by the symbolic addition method (Karle & Karle, 1966). The specification of the

Table 1. Observed and calculated structure factors

h	k	l	F _o	F _c	Phase
1	0	0	1000	1000	0
2	0	0	4000	4000	0
3	0	0	9000	9000	0
4	0	0	16000	16000	0
5	0	0	25000	25000	0
6	0	0	36000	36000	0
7	0	0	49000	49000	0
8	0	0	64000	64000	0
9	0	0	81000	81000	0
10	0	0	100000	100000	0
11	0	0	121000	121000	0
12	0	0	144000	144000	0
13	0	0	169000	169000	0
14	0	0	196000	196000	0
15	0	0	225000	225000	0
16	0	0	256000	256000	0
17	0	0	289000	289000	0
18	0	0	324000	324000	0
19	0	0	361000	361000	0
20	0	0	400000	400000	0
21	0	0	441000	441000	0
22	0	0	484000	484000	0
23	0	0	529000	529000	0
24	0	0	576000	576000	0
25	0	0	625000	625000	0
26	0	0	676000	676000	0
27	0	0	729000	729000	0
28	0	0	784000	784000	0
29	0	0	841000	841000	0
30	0	0	900000	900000	0
31	0	0	961000	961000	0
32	0	0	1024000	1024000	0
33	0	0	1089000	1089000	0
34	0	0	1156000	1156000	0
35	0	0	1225000	1225000	0
36	0	0	1296000	1296000	0
37	0	0	1369000	1369000	0
38	0	0	1444000	1444000	0
39	0	0	1521000	1521000	0
40	0	0	1600000	1600000	0
41	0	0	1681000	1681000	0
42	0	0	1764000	1764000	0
43	0	0	1849000	1849000	0
44	0	0	1936000	1936000	0
45	0	0	2025000	2025000	0
46	0	0	2116000	2116000	0
47	0	0	2209000	2209000	0
48	0	0	2304000	2304000	0
49	0	0	2401000	2401000	0
50	0	0	2500000	2500000	0
51	0	0	2601000	2601000	0
52	0	0	2704000	2704000	0
53	0	0	2809000	2809000	0
54	0	0	2916000	2916000	0
55	0	0	3025000	3025000	0
56	0	0	3136000	3136000	0
57	0	0	3249000	3249000	0
58	0	0	3364000	3364000	0
59	0	0	3481000	3481000	0
60	0	0	3600000	3600000	0
61	0	0	3721000	3721000	0
62	0	0	3844000	3844000	0
63	0	0	3969000	3969000	0
64	0	0	4096000	4096000	0
65	0	0	4225000	4225000	0
66	0	0	4356000	4356000	0
67	0	0	4489000	4489000	0
68	0	0	4624000	4624000	0
69	0	0	4761000	4761000	0
70	0	0	4900000	4900000	0
71	0	0	5041000	5041000	0
72	0	0	5184000	5184000	0
73	0	0	5329000	5329000	0
74	0	0	5476000	5476000	0
75	0	0	5625000	5625000	0
76	0	0	5776000	5776000	0
77	0	0	5929000	5929000	0
78	0	0	6084000	6084000	0
79	0	0	6241000	6241000	0
80	0	0	6400000	6400000	0
81	0	0	6561000	6561000	0
82	0	0	6724000	6724000	0
83	0	0	6889000	6889000	0
84	0	0	7056000	7056000	0
85	0	0	7225000	7225000	0
86	0	0	7396000	7396000	0
87	0	0	7569000	7569000	0
88	0	0	7744000	7744000	0
89	0	0	7921000	7921000	0
90	0	0	8100000	8100000	0
91	0	0	8281000	8281000	0
92	0	0	8464000	8464000	0
93	0	0	8649000	8649000	0
94	0	0	8836000	8836000	0
95	0	0	9025000	9025000	0
96	0	0	9216000	9216000	0
97	0	0	9409000	9409000	0
98	0	0	9604000	9604000	0
99	0	0	9801000	9801000	0
100	0	0	10000000	10000000	0

Table 2. Final atomic parameters and their standard deviations ($\times 10^4$)

Temperature factors are of the form

$$T = \exp \{ -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl) \}.$$

W(1), W(2) and W(3) denote the oxygen atoms of water molecules.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca	1648 (3)	2141 (1)	9945 (3)	141 (4)	10 (0)	53 (5)	-2 (1)	22 (3)	-0 (1)
W(1)	-351 (12)	1266 (4)	1-0024 (13)	161 (18)	17 (2)	76 (20)	-10 (5)	21 (15)	-0 (5)
W(2)	-937 (11)	2506 (4)	7471 (13)	115 (14)	11 (2)	123 (21)	1 (4)	-44 (13)	3 (4)
W(3)	4823 (14)	1771 (6)	9967 (15)	182 (22)	43 (4)	132 (24)	19 (8)	29 (18)	-0 (8)
O(1)	2722 (12)	-1399 (3)	3313 (11)	211 (20)	9 (2)	67 (20)	-2 (4)	14 (15)	-8 (4)
O(2)	2578 (12)	-1394 (3)	6679 (11)	187 (18)	10 (2)	66 (20)	2 (4)	24 (14)	5 (4)
O(3)	2274 (12)	1838 (3)	6616 (11)	198 (19)	8 (1)	56 (18)	3 (4)	39 (14)	-6 (4)
O(4)	2508 (11)	1844 (3)	3290 (10)	169 (17)	8 (1)	46 (18)	0 (4)	20 (13)	4 (4)
C(1)	2608 (15)	-432 (5)	4967 (16)	113 (20)	13 (2)	68 (27)	-1 (6)	30 (17)	1 (6)
C(2)	2351 (18)	-101 (5)	6781 (17)	199 (29)	10 (2)	83 (30)	7 (6)	29 (22)	2 (6)
C(3)	2284 (17)	536 (5)	6743 (17)	202 (28)	10 (2)	60 (29)	2 (6)	20 (22)	9 (6)
C(4)	2508 (15)	869 (5)	4945 (18)	97 (19)	11 (2)	123 (32)	1 (5)	40 (18)	-4 (6)
C(5)	2780 (16)	537 (5)	3159 (18)	159 (26)	11 (2)	109 (33)	3 (6)	34 (22)	-10 (7)
C(6)	2833 (17)	-101 (5)	3161 (17)	183 (27)	8 (2)	106 (31)	4 (6)	50 (22)	3 (6)
C(7)	2638 (16)	-1122 (5)	4956 (17)	111 (21)	17 (3)	82 (30)	-4 (6)	34 (19)	-1 (7)
C(8)	2420 (15)	1554 (5)	4944 (17)	92 (19)	10 (2)	106 (30)	1 (5)	4 (17)	4 (6)

origin and the assignment of symbols were as follows:

<i>h</i>	<i>k</i>	<i>l</i>	<i>E</i>	Phase
1	9	0	3.27	+
$\bar{6}$	1	5	3.16	+
4	1	0	1.85	+
0	21	5	4.02	<i>a</i>
1	15	4	3.33	<i>b</i>
0	24	4	3.19	<i>c</i>
$\bar{1}$	15	2	3.13	<i>d</i>
$\bar{2}$	25	3	3.12	<i>e</i>

The signs of the reflections 006 and $\bar{2}06$ were found to be + and - respectively from the Σ_1 formula. On the basis of the phases of these ten reflexions, the signs of 47 out of 58 reflexions having *E* values greater than 2.0 were assigned by use of the Σ_2 formula, $s(E_h) \approx s(E_k) \cdot s(E_{h-k})$. During the application of the Σ_2 relationship it became apparent that $b = -c = -d = -e$. Therefore, four possible combinations of the signs of *a* and *b* were examined. In the case of $a = -$ and $b = -$, the signs of 168 out of the 183 reflexions of $|E| \geq 1.4$ could be determined, and the *E* map gave a reasonable structure.

Refinement of the structure

The parameters obtained from the *E* map were refined by three cycles of block-matrix least-squares calculations with individual isotropic temperature factors. The *R* value was reduced from 0.35 to 0.20. A difference Fourier synthesis was then calculated and it showed that the site of one water molecule was incorrect. After the correction of the parameters of the water molecule, six cycles of block-matrix least-squares refinement with individual anisotropic temper-

ature factors were carried out using 1311 observed reflections. In the last three cycles the following weighting system was adopted:

$$\begin{aligned} \sqrt{w} &= 20/|F_o| && \text{when } |F_o| > 20 \\ \sqrt{w} &= 1 && \text{when } 20 \geq |F_o| \geq 5 \\ \sqrt{w} &= 0.7 && \text{when } 5 > |F_o| \end{aligned}$$

The atomic scattering factors for C, O and Ca were taken from *International Tables for X-ray Crystallography* (1962).

The final *R* value for 1311 observed reflexions was 0.135. A comparison of the observed and calculated structure factors is given in Table 1. The final atomic parameters and their standard deviations are listed in Table 2.

Discussion of the structure

Terephthalic acid ion

The bond lengths and angles are shown in Fig. 1. These values agree well with those found in terephthalic acid (Bailey & Brown, 1967) and diethyl terephthalate (Bailey, 1949).

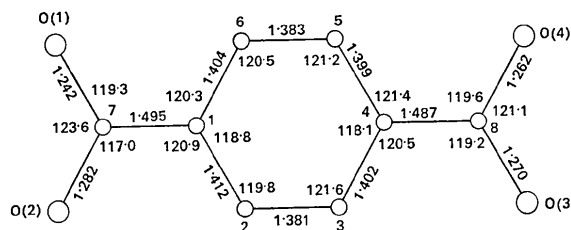


Fig. 1. Bond lengths (Å) and angles (°). E.s.d.'s are ± 0.015 Å and $\pm 1.0^\circ$.

Table 3. Coordination around the calcium ion

Distances		Ca-O(3) I(000)		Ca-W(1) I(000)		Ca-O(4) I(000)	
		2.350 Å		2.372 Å		2.533	
		2.503		2.395		2.642	
		2.539					
		(0.008)					
Angles A-Ca-B							
B atom	W(2)	W(2)	W(3)	O(3)	O(3)	O(4)	O(4)
A atom	I(000)	III(001)	I(000)	I(000)	III(001)	I(001)	III(001)
W(1)	81.0°	77.6°	107.3°	86.2°	142.5°	83.9°	148.9°
I(000)							
W(2)		79.1	140.1	69.3	96.8	147.4	68.6
I(000)							
W(2)			140.6	146.3	65.4	69.5	101.9
III(001)							
W(3)			72.4	98.2	72.1	72.1	92.9
I(000)							
O(3)					128.4	138.3	77.5
I(000)							
O(3)						78.2	51.9
III(001)							
O(4)							125.5
I(001)							
e.s.d.	(0.3)						

The terephthalic acid ion also has a certain amount of quinonoid character, as was found in the terephthalic acid molecule. The C–C bonds parallel to the substituent groups are about 0.02 Å shorter than the mean of the remaining four bonds in the ring.

The terephthalic acid ion is composed of three planes: carboxyl group I [formed by the atoms C(1), C(7), O(1) and O(2)], carboxyl group II [C(4), C(8), O(3) and O(4)] and the benzene ring [C(1), C(2), C(3), C(4), C(5) and C(6)]. The equations of the least-squares planes are: $0.999X + 0.015Y + 0.046Z = 1.984$, $0.996X + 0.039Y + 0.076Z = 2.089$ and $0.989X + 0.028Y + 0.144Z = 2.272$ respectively, where X , Y and Z are the coordinates (in Å) referred to the orthogonal axes, $X \parallel a^*$, $Y \parallel b$ and $Z \parallel c$. The atoms do not deviate more than 0.007 Å from the respective planes. The angles between the normals to the planes are 5.7° between the benzene ring and carboxyl group I, 4.0° between the benzene ring and carboxyl group II and 2.2° between the two carboxyl groups. The twistings around the bonds C(1)–C(7) and C(4)–C(8) occur as if the terephthalate ion possessed a centre of symmetry. A similar effect was also found in form I of terephthalic acid in which the molecule has an exact centre of symmetry and the angle of twist was 5.25° .

Crystal structure

The projections of the crystal structure along the a axis and the c axis are shown in Figs. 2 and 3. The figures were drawn by the plotter program of Johnson (1965). The surface of each ellipsoid encloses the region in which the center of the atom is found with probability 50%.

Terephthalic acid ions lie at $x \approx \frac{1}{4}$ and $\frac{3}{4}$ with their planes parallel to the (100) plane and stacked along

the a axis. The manner of stacking resembles that found in the form I crystal of terephthalic acid. The

Table 4. *The lengths and angles associated with hydrogen bonds*

Lengths		
$W(1)I(000)$ – $O(1)II(\bar{1}00)$		2.732 Å
$W(1)I(000)$ – $O(2)II(\bar{1}01)$		2.753
$W(2)I(000)$ – $O(1)II(\bar{1}00)$		2.753
$W(2)I(000)$ – $O(2)IV(\bar{1}01)$		2.722
$W(3)I(000)$ – $O(1)II(000)$		2.944
$W(3)I(000)$ – $O(2)II(001)$		2.939
e.s.d.		(0.010)
Angles		
$O(1)II(\bar{1}00)$ – $W(1)I(000)$ – $O(2)II(\bar{1}01)$		105.6°
$O(1)II(\bar{1}00)$ – $W(2)I(000)$ – $O(2)IV(\bar{1}01)$		127.1
$O(1)II(000)$ – $W(3)I(000)$ – $O(2)II(001)$		95.9
e.s.d.		(0.4)

Table 5. *Packing distances shorter than 3.5 Å*

From atom of I(000)	To atom	Distance
$W(1)$	C(3)I(000)	3.319 Å
$W(1)$	C(5)I(001)	3.369
$W(1)$	O(3)I(000)	3.225
$W(1)$	O(4)I(001)	3.159
$W(1)$	$W(2)I(000)$	3.189
$W(1)$	$W(2)III(001)$	3.147
$W(2)$	C(8)III(001)	3.491
$W(2)$	O(3)I(000)	2.780
$W(2)$	O(4)III(001)	2.858
$W(2)$	$W(2)III(000)$	3.295
$W(3)$	O(3)I(000)	2.804
$W(3)$	O(4)I(001)	2.796
Ca	C(8)III(001)	2.879
C(1)	C(5)II(000)	3.465
C(4)	C(7)II(000)	3.493
O(3)	O(4)III(001)	3.064
e.s.d.		(0.015)

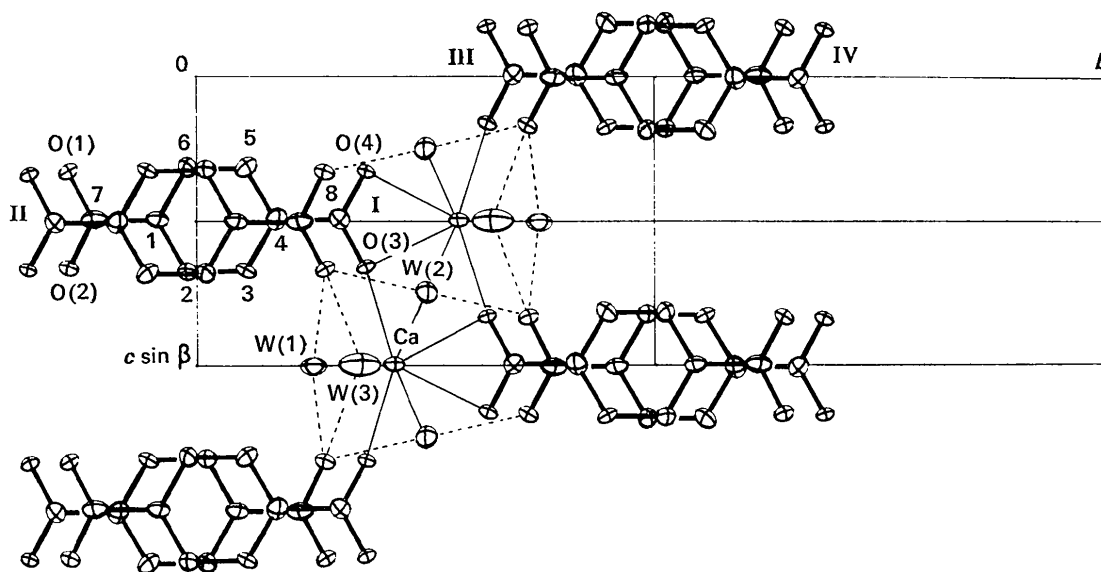


Fig. 2. Projection of the crystal structure along the a axis. Roman numerals denote the symmetry operations I: x, y, z ; II: $1-x, -y, 1-z$; III: $x, \frac{1}{2}-y, -\frac{1}{2}+z$; IV: $1-x, \frac{1}{2}+y, \frac{1}{2}-z$. Broken lines indicate hydrogen bonds and solid thin lines indicate coordinations around calcium ions.

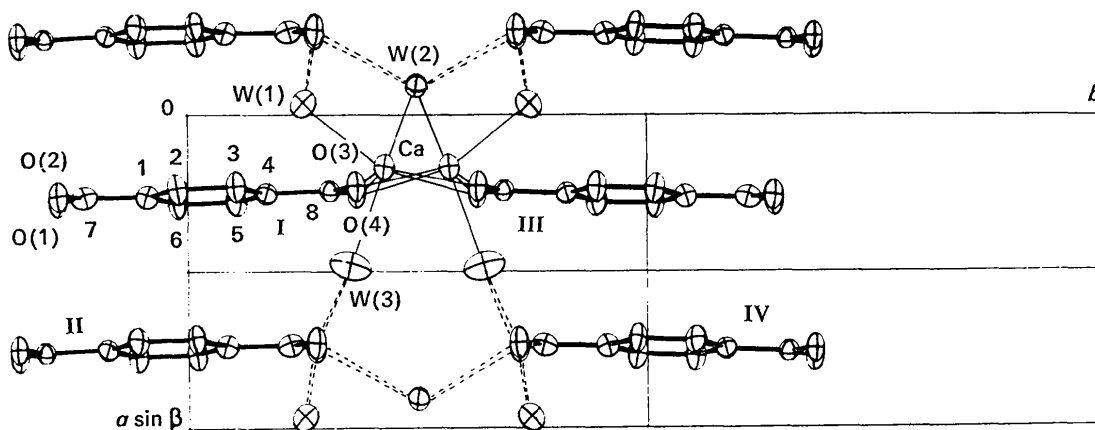
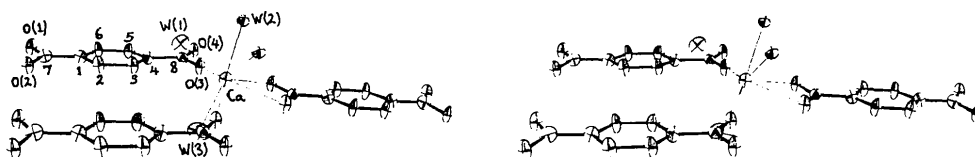
Fig. 3. Projection of the crystal structure along the *c* axis.

Fig. 4. Stereoscopic drawing of the crystal structure showing the coordination of the oxygen atoms around the calcium ion.

distances between the successive planes of the benzene rings are 3.39 and 3.60 Å, the shortest contact being 3.465 Å between C(1)I(000) and C(5)II(000) where the Roman numbers denote the symmetry operations listed in Figs. 2 and 3, followed by the components of translation vectors in parentheses.

As seen in Fig. 2, the stacked units are packed parallel to each other in the *c* direction, resembling the packing found in the form II crystal of terephthalic acid. The arrangement of the stacked units in the *b* direction, however, differs from the form II. In the latter structure, they are arranged in the *b* direction so as to present their carboxyl groups to each other, forming a chain of hydrogen bonds along *b*. In the present structure on the other hand, the neighbouring units in *b* are displaced by *c*/2, disconnecting the hydrogen bonds and leaving room between the stacked units. The calcium ions and water molecules are located in this space and complete the eight-coordinated systems around the calcium ions and the network of hydrogen bonds between the carboxyl groups and water molecules.

A stereoscopic drawing of the coordination around a calcium ion is given in Fig. 4. It is seen that the four oxygen atoms of three terephthalic acid ions and the four oxygen atoms of water molecules are coordinated to the calcium ion to form distorted bipyramidal coordination. The atoms O(3)I(000), O(4)I(001), W(1)I(000) and W(3)I(000) form one square and the atoms

O(3)III(001), O(4)III(001)I, W(2)I(000) and W(2)I(001) form another square. The interatomic distances and angles involved in the coordinated group are listed in Table 3.

As the hydrogen atoms of the water molecules are presumed to be at the opposite side of the calcium ion, the hydrogen bonds were assigned as shown by dotted lines in Figs. 2 and 3. In Table 4, the lengths and angles associated with hydrogen bonds are shown. The two carboxyl groups of a terephthalic acid ion are in quite different situations. Carboxyl group II is coordinated to the calcium ions while carboxyl group I is connected to water molecules by the hydrogen bonds. The closest approaches of atoms other than in hydrogen bonds, with distances less than 3.5 Å are listed in Table 5.

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References

- BAILEY, M. (1949). *Acta Cryst.* **2**, 120.
 BAILEY, M. & BROWN, C. J. (1967). *Acta Cryst.* **22**, 387.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 JOHNSON, C. K. (1965). *ORTEP*. ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
 KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849.