The Crystal Structure of the Hexahydrated Calcium Salt of Hexacyanoisobutylene

By D. A. Bekoe*, P. K. Gantzel†, and K. N. Trueblood

Department of Chemistry,‡ University of California, Los Angeles, California 90024, U.S.A.

$CaC[C(CN)_2]_3.6H_2O$ forms hexagonal crystals with $a_0 = 10.82$, $c_0 = 7.335$ Å, and two formula units in the unit cell. The structure has been determined three-dimensionally and refined chiefly by full-matrix least-squares methods. A good fit to the data has been obtained in space group $P\bar{3}m1$ with a model in which there is twofold disorder of columns of non-planar anions, each column having symmetry 3. The hexacyanoisobutylene anion is propeller-shaped, with approximate symmetry 32, the three $C(CN)_2$ arms being rotated by 24° from the completely planar conformation. The four central carbon atoms are coplanar, and there are no significant differences in the three independent C–C distances (e.s.d. 0.006 Å), which are the same as that in graphite (1.42 Å). Adjacent anions in any stack are enantiomorphous (R, S); the energy involved in interconversion of R and S anions is considered in an Appendix. The different stacks of anions are held together by coordination of one set of nitrogen atoms to the calcium ions and hydrogen bonding of the other set with the water molecules. The calcium ion has ninefold coordination, with its neighbors in an approximately face-centered trigonal prismatic arrangement.

Hexacyanoisobutylene (2-dicyanomethylene-1,1,3,3-tetracyanopropane, $(NC)_2C = C[CH(CN)_2]_2$) is a strong dibasic acid, comparable in strength to sulfuric acid (Middleton, Little, Coffman & Engelhardt, 1958). This unusual strength arises from the stability of the anion, $C[C(CN)_2]_3^{2-}$, which has usually been assumed to be planar because this conformation would give maximum p-orbital overlap and resonance stabilization. The present study has in fact established that, at least in its hydrated calcium salt, the anion is propeller-shaped (Fig. 1), presumably as a consequence of intramolecular steric repulsion.

* On leave from the department of Chemistry, University of Ghana, Legon, Ghana.

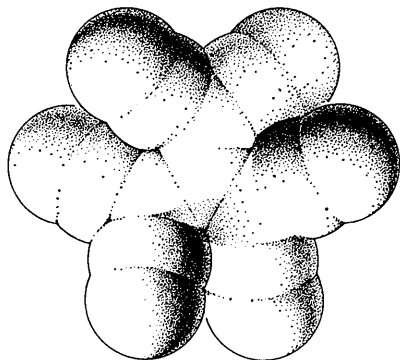† Present address: General Atomic, San Diego, California, U.S.A.

Fig. 1. One of the propeller-shaped enantiomorphic forms of HCB^{2-}. The radii used are about 1·6 Å for carbon and 1·5 Å for nitrogen.

Experimental

We examined a number of different salts containing the anion of hexacyanoisobutylene (HCB^{2-}) in an effort to find one suitable for detailed study. Crystals of the hexahydrated barium salt were kindly provided by Dr E. L. Little. The other salts were prepared by adding a hot aqueous solution of an equivalent amount of the sulfate of the other cation to a hot solution of $BaHCB.6H_2O$, removing the barium sulfate precipitate by filtration, and cooling (or evaporating) the resulting solution. The barium and calcium salts crystallize as hexahydrates, with two molecules in a trigonal unit cell, as discussed further below. These crystals are stable in our normal laboratory air unless the relative humidity is unusually low; on the other hand, $MgHCB.6H_2O$, which forms monoclinic needles with a four-molecule unit cell, effloresces rapidly under normal conditions. The guanidinium salt crystallizes as handsome needles, with pronounced basal cleavage; however, whether grown from water or methanol, all of our samples displayed an abundance of superlattice reflections superimposed on a relatively small hexagonal unit. The anilinium salt forms highly birefringent triclinic plates with two molecules in the unit cell.

The calcium salt forms needles elongated along **c**, exhibiting good (001) cleavage, and these crystals seemed suitable for structure analysis. The dimensions of the hexagonal unit cell, measured on a Weissenberg photograph calibrated with a CeO_2 powder pattern ($a_0 = 5·411$ Å) and taken with Cu $K\alpha$ radiation ($\lambda = 1·5418$ Å), are $a_0 = 10·82 \pm 0·01$ and $c_0 = 7·335 \pm 0·007$ Å. The density of the crystals, measured by flotation, is 1·56 g.cm^{-3}; that calculated for two formula units of $CaC_{10}N_6.6H_2O$ in the unit cell is 1·572 g.cm^{-3}. X-ray

photographs show diffraction symmetry $\bar{3}m1$ and there are no systematic extinctions; the possible space groups are $P321$, $P3m1$, and $P\bar{3}m1$. An additional possibility is that the crystals are actually twinned, with the correct space group $P\bar{3}$ and the twinning plane (110). This possibility is discussed below.

Three-dimensional photographic intensity data were collected with Cu $K\alpha$ radiation by the equi-inclination Weissenberg method. Two crystals were used, each cleaved to an approximate needle-like shape parallel to **a**, one with a diameter about 0·16 mm and the other about 0·25 mm. Layers $h=0$ to 6 were recorded, estimated visually, converted to F^2 values and correlated by comparison of symmetry-equivalent reflections. Despite the relatively large absorption coefficient for Cu $K\alpha$, 3·9 mm^{-1}, the smallness of the crystals made absorption corrections unnecessary. Of the approximately 680 unique reflections within the copper sphere, 646 (95%) were accessible, and 560 of these were strong enough to be measured. The 86 'unobserved' reflections were included in the least-squares refinements with $F=F_{\min}/\sqrt{3}$, where $F_{\min}$ is the minimum observable structure factor amplitude in the corresponding region of reciprocal space; this value is also that listed for these reflections (marked with a U) in Table 4.

Crystals of the barium salt were not investigated in detail, chiefly because the high atomic number of barium would prevent precise determination of the geometry of the anion. However, the crystal seems to be isostructural with the calcium salt, at least in projection down **c**, and indeed the latter structure was solved with the help of the former. The axes of BaHCB.6H$_2$O are $a_0=11\cdot04\pm0\cdot01$ and $c_0=7\cdot57\pm0\cdot02$ Å, the former measurement having been made on a CeO$_2$-calibrated Weissenberg photograph and the latter from a rotation photograph about **c**. The structure was solved, as discussed below, in the (001) projection based on 55 integrated intensities measured with a Baird Atomic Model CB densitometer.

All calculations were made on an IBM 7094 with programs written in this laboratory. The least-squares program was that of Gantzel, Sparks and Trueblood (ACA No. 317), which minimizes $\Sigma\,\omega(\Delta|F|)^2$; Hughes (1941) weights were used. The form factors for carbon, nitrogen, and oxygen were those of Hoerni & Ibers (1954), that for the calcium ion was taken from Freeman (1959), and that for the barium ion was obtained by appropriate modification of Thomas & Umeda's (1957) curve for the barium atom.

Determination and refinement of the structure

A planar HCB^{2-} would have ideally point symmetry $3m$, and even if the entire ion were not planar, the atoms of the individual C(CN)$_2$ arms would presumably remain coplanar, these arms merely being rotated about the bonds to the central carbon atom so as to yield a propeller-shaped anion, with, ideally, symmetry 32. Models suggest, in fact, that this propeller shape

is likely in order to relieve otherwise abnormally short intramolecular $C\cdots C$ and $N\cdots N$ contacts between the arms. Furthermore, consideration of the intensities of the $00l$ reflections indicated that some non-planarity of the ion must exist. For these reasons, we initially concluded that of the three possible space groups, the correct one was probably $P321$, with the anion having point symmetry 3 or 32. However, regardless of which space group is correct, both the calcium ion and the central carbon atom of the HCB anion must lie in special positions having (x,y) coordinates $(0,0)$, $(\frac{1}{3},\frac{2}{3})$ or $(\frac{2}{3},\frac{1}{3})$. The two highest peaks in a sharpened three-dimensional Patterson function were at $(0,0,0\cdot50)$ and $(0\cdot33, 0\cdot67, 0\cdot26)$, with the former about 50% higher than the latter. Although a projection of the electron density down **c**, phased with the calcium ions at the origin and carbon atoms at $(\frac{1}{3},\frac{2}{3})$ and $(\frac{2}{3},\frac{1}{3})$, was not readily interpretable, the peak at $(\frac{1}{3},\frac{2}{3})$ was much higher than that at the origin, suggesting that the metal ions were probably at the former position. A projection calculated with the $hk0$ data of the barium salt, phased with the barium ions at $(\frac{1}{3},\frac{2}{3})$ and $(\frac{2}{3},\frac{1}{3})$, gave an immediately interpretable pattern, with R, the usual discrepancy index, equal to 0·25. An unanticipated feature of the pattern was that the arrangement of the water molecules about the barium ion was trigonal prismatic rather than octahedral; the anion, centered at the origin, was clearly discernible. The strong Patterson peak at $(0,0,0\cdot50)$ is due to the superposition of the six $O\cdots O$ interactions along the parallel edges of the two trigonal prisms in the unit cell.

Table 1. *Final parameters* $(\times 10^4)^*$

	x		y		z	
Ca	6667		3333		1297,	2
C(1)	0		0		2489,	6
C(2)	1229,	5	1383,	4	2488,	5
C(3)	2586,	4	1643,	4	1878,	5
C(4)	1192,	8	2588,	4	3156,	4
N(3)	3697,	4	1972,	8	1381,	4
N(4)	1228,	6	3595,	5	3742,	6
O(1)	5714,	2	1428,	3	3623,	4
O(2)	5717.	2	1434	3	−0993,	4

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ca	76	76	101	76	0	0
C(1)	43	43	84	43	0	0
C(2)	48	45	116	35	3	7
C(3)	50	64	111	40	16	15
N(4)	141	65	165	101	−8	−22
O(1)	94	116	204	116	48	96
O(2)	100	108	219	108	−47	−94
C(4)	2·30					
N(3)	3·20					

* B's of C(4) and N(3) are in Å^2. The number following each position parameter, set off by a comma, is the corresponding e.s.d.; Ca, C(1), O(1), and O(2) are in special positions. The e.s.d.'s of the B_{ii} average about 2% for Ca, about 3% for the oxygen atoms, and about 7% for C(1), C(2), C(3), and N(4). The e.s.d.'s of the isotropic B's for C(4) and N(3) are about 0·08 Å^2.

The anisotropic temperature factor is expressed as:

$$\exp\,[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)].$$

One difference-Fourier refinement cycle led to an R value of 0·13. The parameters from the projection of the barium salt structure were then used in phasing the corresponding projection of the calcium salt, which was refined by two successive difference maps, R falling from 0·25 to 0·16.

The apparent symmetry of the projection of the barium salt was $P6m$, corresponding to $P\bar{3}m1$ in three dimensions; this space group is compatible with a non-planar anion only if the arrangement of the anions in the unit cell is a disordered one. The initial full-matrix least-squares refinement was based on such a model, the z parameters of the atoms being found by consideration of the three-dimensional Patterson function. Two of the atoms, one carbon and one nitrogen, were refined with isotropic temperature factors inasmuch as

Table 2. *Molecular geometry of the anion**

Distances, Å		HMO π-Bond order†	Angles	
C(1)–C(2)	1·424, 5 (1·420)	0·52	C(2)′–C(1)–C(2)	120·0°
C(2)–C(3)	1·426, 6 (1·422)	0·48	C(1) –C(2)–C(3)	122·6, 4
C(2)–C(4)	1·416, 6 (1·412)	0·48	C(1) –C(2)–C(4)	121·9, 4
C(3)–N(3)	1·15, 1 (1·130)	0·81	C(3) –C(2)–C(4)	115·5, 4
C(4)–N(4)	1·17, 1 (1·154)	0·81	C(2) –C(3)–N(3)	174·0, 5
			C(2) –C(4)–N(4)	176·5, 5

Deviations from least-squares plane‡
$$0{\cdot}3629X-0{\cdot}1808Y+0{\cdot}9141Z=1{\cdot}660$$

C(1)	0·009 Å	C(3)	0·014 Å	C(4)	−0·022 Å
C(2)	−0·015	N(3)	−0·003	N(4)	0·017

* The number separated by a comma immediately following each experimental value is its e.s.d., in units of the last place of the value itself. The distances in parentheses are before corrections for anisotropic thermal motion of the atoms; these corrections are negligible for all but the C–N distances (see text).

† The π-bond orders were calculated with simple HMO theory, assuming the resonance integrals to be $0{\cdot}95\beta_0$ for all C–C bonds and $1{\cdot}25\beta_0$ for the C–N bonds, and the coulomb integrals for the nitrogen atoms to be $0{\cdot}5\beta_0$ greater than for the carbon atoms. The C–N bonds have, of course, an additional orthogonal π-bond. The π-bond order for graphite, with distance 1·421 Å, is 0·50, and thus the experimental values for this anion agree with expectation (far better than justified by the approximations of HMO theory). Consideration of resonating unexcited valence bond structures suggests too that graphite is a good model for comparison, for there is just one-third double bond character to each C–C bond (as in graphite) if one restricts the negative charge to positions on the nitrogen atoms. The HMO calculation suggests that there may be significant negative charge on C(2) also, the calculated charges being: C(1), +0·08; C(2), −0·25; C(3) and C(4), +0·14; N(3) and N(4), −0·36.

‡ Plane through the C–C(CN)₂ group of Table 1. X, Y, Z are coordinates in Å parallel to **a**, **b***, and **c**.

Table 3. *Short non-bonded distances**

Intramolecular

C(1)···C(3)	2·49 Å		C(3)···N(4)	3·40 Å
C(1)···C(4)	2·48		C(3)···N(4), C	3·29
C(3)···C(4)	2·40			
C(2)···C(2), B	2·46		C(4)···N(3)	3·36
C(2)···C(3), B	2·93		C(4)···N(3), B	3·33
C(2)···C(4), C	2·92			
C(3)···C(4), C	2·83			

Others

Ca···O(1)	2·47 Å		O(1)···O(1), B	3·09 Å
O(2)	2·45		O(1), D, (101)	3·35
N(3)	2·79		O(2), D, (100)	3·30
			O(2)	3·39
N(3)···O(1)	3·01		O(2)···O(2), B	3·08
O(1), C, (110)	2·88		O(2), D, (100)	3·06
O(2)	3·07			
O(2), C, (110)	2·93		C(2)···C(3), F	3·53
			C(4), E, (001)	3·51
N(4)···O(1), E, (011)	2·92†		N(3)···C(4), E	3·49
O(2), E, (010)	2·98†		N(4)···C(3), F, (001)	3·36
O(1), B	3·31		C(4), F, (001)	3·55
O(1), F, (001)	3·52		C(2), F, (001)	3·55
O(2), F	3·56			

* Atoms other than those of Table 1 are given by their equivalent position, with the unit translations if any, as follows: B, $-y,x-y,z$; C, $y-x,-x,z$; D, $-x,-y,-z$; E, $y,y-x,-z$; F, $x-y,x,-z$. The parameters used in these calculations have not been corrected for the effects of thermal motion, which might increase the Ca···N and Ca···O distances by 0·01−0·02 Å. All distances shorter than 3·4 Å have been listed, and some others of interest are also given.

† Possible hydrogen bond; see text.

Table 4. *Observed and calculated structure factors*

The three columns list, respectively, k, F_o, and F_c. Unobserved reflections, marked with a U, are given $F_o = 0.57 F_{min}$, with F_{min} the minimum observable F in that region of reciprocal space. (010) may have been partially blocked by the layer-line screen.

```
H= 0, L= 0          10  2.0U  -1.3      8 10.4 -11.0      8 15.8  16.0     H= 0, L= 4       H= 0, L= 5        8 10.6  -9.7     1  4.5  -4.7
 1  9.2  17.7                           9  4.6   3.9      9  2.0U  0.6      0 68.4 -69.1      0 13.4 -13.2      9  3.1  -3.3     2  6.5  -6.5
 2 18.1 -21.7     H= 3, L= 1           10  5.2  -4.2     10  4.7  -5.0      1 48.8  47.4      1 26.2  27.5                      3  3.1   3.5
 3 32.9 -27.5      0  6.1   6.8        11  1.2U -1.4     11  4.2  -3.6      2 38.3  38.7      2  9.4  -9.2     H= 1, L= 6        4  4.4   4.6
 4 59.1 -60.2      1 27.1 -25.6                                            3 18.2  17.7      3  2.9   3.4      0 11.8 -11.5     5  2.8  -2.7
 5 11.3  10.9      2 10.1  10.7        H= 2, L= 2        H= 1, L= 3         4 19.7  20.0      4  8.1   8.0      1  7.5  -7.6     6  4.8   4.9
 6 14.6  12.8     10  5.3  -5.6         0 55.5  53.0      0 14.5  11.9      5 16.4 -18.0      5  2.3  -3.0      2  6.5   6.8
 7 25.3  26.9      3 18.4  18.3         1 70.6  66.2      1 17.7 -17.2      6  8.3  -8.3      6  6.2  -6.6      3 17.7 -17.4    H= 4, L= 7
 8  9.3   8.9      4 13.5 -14.0         2 14.5 -13.5      2 14.2 -14.8      7 11.2  10.7      7  8.3   8.8      4  3.8   3.9     0  7.3  -7.1
 9 17.2  18.3      5  5.6   4.9         3 37.0 -37.9      3 21.4  22.3      8 11.1  11.8      8  2.0U -1.1      5  5.8   5.4     1  9.6   9.1
10 11.5 -11.0      6  3.4   3.5         4  9.3  -9.2      4 15.8 -15.4      9  8.0  -7.4      9  8.0  -8.1      6 19.6 -19.5     2  1.4U -1.6
11  1.5U -1.7      7 11.2 -11.6         5  1.5U -1.0      5  1.5U  0.5     10 13.0  11.4     10  7.4   6.5      7  4.4   3.9     3  2.5  -2.1
12  6.8   7.8      8  2.5  -2.8         6 20.3 -21.9      6 13.4  13.6                                         8  1.5U  1.9     4  4.8   5.3
                   9  1.5U  1.6         7  4.2   3.3      7  9.5  -9.4     H= 1, L= 4       H= 1, L= 5                          5  2.5   2.6
H= 1, L= 0                              8  8.0   8.2      8  2.4U -0.7      0 26.2  25.4      0  9.7 -10.5     H= 2, L= 6
 1 38.2  37.1     H= 4, L= 1            9  7.9  -7.3      9  2.8   2.9      1  6.4  -6.3      1 11.2 -11.7      0  7.5  -8.3    H= 5, L= 7
 2 16.7 -15.3      0  8.9  -9.0        10  3.3   2.8     10  6.5  -5.9      2 19.5  19.5      2 11.5  11.7      1 15.9 -16.4     0  6.7   6.8
 3 38.5  36.2      1 14.0  14.0                                            3  9.1  -8.9      3  7.5  -7.4      2  8.7   9.2     1  6.8  -6.2
 4  9.5   8.8      2 24.3 -25.6        H= 3, L= 2        H= 2, L= 3         4 11.2 -11.2      4  1.5U -0.5      3 19.4  19.3     2  1.5U  0.5
 5  3.9   4.1      3  7.3   7.8         0 37.9 -33.0      0  4.7   5.1      5  2.2  -0.8      5 11.7  12.1      4  2.6  -2.0     3  3.9  -3.6
 6 14.6 -15.4      4 14.0  14.2         1 25.1 -25.0      1 21.2  21.8      6 22.3  23.2      6  2.0U  0.9      5  9.0 -10.2     4  7.0  -7.3
 7 18.7  20.7      5 18.0 -16.9         2 14.5  14.8      2 20.4 -22.2      7  3.2   3.5      7  7.2  -7.2      6  2.0U -2.4
 8 10.3  10.9      6  1.5U -0.5         3  6.5  -6.5      3  6.8  -7.6      8  2.2U  1.7      8  6.2   6.3      7  6.4  -6.5    H= 6, L= 7
 9 10.4 -10.9      7  4.1   4.3         4  6.6   7.1      4 10.6  11.0      9  8.1   8.2      9  3.8  -3.7      8  3.1  -3.3     0 10.6  10.0
10 13.8  12.9      8  5.6  -5.5         5  1.5U -0.9      5  4.0  -4.3     10  6.0  -6.1                                        1  3.4   2.9
11  1.5U -0.7      9  1.8   0.7         6  3.4  -2.9      6  2.0U -1.5                     H= 2, L= 5        H= 3, L= 6         2  6.6  -6.8
                                        7 11.5 -12.5      7  5.9   6.3     H= 2, L= 4       0 11.9  11.1      0 14.5  15.1     3  3.3   3.5
H= 2, L= 0       H= 5, L= 1             8 11.0  10.8      8  8.8  -8.3      0  2.5   2.8      1  1.5U -0.2      1 13.2  13.3
 2 57.2  59.3      0 13.8 -14.4         9  4.8  -4.2      9  2.0U  0.4      1  2.5  -2.5      2  7.5  -7.6      2  7.6  -7.5    H= 7, L= 7
 3 16.5 -15.3      1  2.8   2.3                         10  7.7   8.5      2 25.4 -26.3      3 18.1  18.2      3  4.7   5.2     0 10.2  -9.5
 4 14.0 -13.5      2  3.8  -2.7        H= 4, L= 2                          3 18.9  19.4      4  3.2  -2.8      4  2.6  -2.3     1  5.7   6.2
 5 24.7  25.4      3 14.7 -14.8         0 38.5  38.6     H= 3, L= 3         4  8.9   9.1      5  8.2  -8.9      5 12.2 -12.1
 6  2.0U -0.5      4  4.1   4.5         1 16.8 -16.9      0 24.3 -24.7      5  9.8  -9.4      6  4.1   4.3      6  1.5U -0.6    H= 8, L= 7
 7 11.2  12.0      5  5.4   5.7         2  3.7   3.5      1  9.1   9.9      6 17.4  17.0      7  4.6  -4.7      7  6.6   6.6     0  1.1U -0.4
 8  5.3   5.5      6  5.0  -5.5         3  6.6  -6.5      2 21.3  21.2      7  2.3U  1.4      8  2.0U  0.3
 9 10.4U -9.7      7  3.1   2.4         4  3.8   3.4      3  5.0  -4.9      8  4.8  -4.7      9  6.8   7.7     H= 4, L= 6       H= 0, L= 8
10  2.0U -1.2      8  3.9   4.0         5 12.2 -13.1      4  7.3  -6.9      9  9.3   8.7                       0 16.6 -16.3     0 15.5  15.7
                                        6  8.0   7.9      5  6.8   7.5                     H= 3, L= 5        1  1.5U -0.9     1  6.1  -7.1
H= 3, L= 0       H= 6, L= 1             7 10.8  10.6      6  9.1  -9.1     H= 3, L= 4       0 10.4 -10.6      2  1.5U  0.6     2  2.0U -0.1
 3 53.7  55.9      0 20.3  20.5         8 11.8 -11.4      7  3.8  -3.6      0 17.2 -17.0      1  9.1   9.3      3  1.5U -0.5     3  9.8   9.4
 4 16.4 -17.1      1 13.4 -13.8         9  3.4   3.4      8 11.6  11.1      1 13.2 -12.7      2 10.8 -11.1      4  2.9  -2.9     4  4.5  -4.4
 5 15.7 -15.3      2  2.0U -0.2                          9  3.2  -2.0      2 14.8  15.4      3 13.7 -14.4      5  4.1   3.9     5  5.9   6.5
 6 11.5  12.1      3 11.8  11.6        H= 5, L= 2                          3 22.5 -23.3      4 14.6  14.4      6  3.1  -3.1     6 10.4  11.0
 7  7.2  -7.1      4  9.1  -9.1         0 26.3 -26.4     H= 4, L= 3         4 14.1  14.8      5  5.4  -4.5
 8  1.5U  0.0      5  2.0U  2.6         1 10.1  11.1      0 18.5  18.7      5 14.6  16.0      6  2.5   2.0     H= 5, L= 6       H= 1, L= 8
 9  6.8   5.9      6  4.7   4.7         2  1.5U  1.1      1 13.4 -13.2      6  2.8  -2.4      7  5.8   6.0      0  3.1  -3.5     0  2.0U -0.4
10  4.6   4.6      7  8.0  -7.8         3  3.4   3.6      2  7.3   6.9      7  3.4   2.6      8  2.6  -2.7      1 16.2 -16.1     1 12.3  12.1
                                        4 11.2  11.0      3  4.5   5.1      8  2.0  -2.0                       2  2.0U  0.2     2  1.5U  0.5
H= 4, L= 0       H= 7, L= 1             5  4.9  -5.0      4  8.8  -9.4      9  2.6  -2.4     H= 4, L= 5        3  2.8   2.5     3  1.5U  0.3
 4 25.7  28.1      0 14.5  15.0         6 10.1 -10.9      5  3.5  -3.3                       0  5.7   6.2      4  6.6  -6.3     4  3.5   3.5
 5 14.0 -13.9      1  9.7   9.0         7  3.2   3.2      6 13.1  13.6     H= 4, L= 4       1 11.5 -12.1      5  5.1   4.6     5  2.0   1.8
 6 11.5  12.0      2  5.3  -2.5         8  3.2  -2.8      7  1.2U -0.3      0 32.4  32.7      2 13.2  13.7
 7  3.1   3.1      3  3.8   4.2                          8  1.2U  0.1      1  3.7  -2.4      3  8.0  -8.7     H= 6, L= 6       H= 2, L= 8
 8  5.9  -5.5      4  3.1   3.0        H= 6, L= 2                          2 13.5  13.0      4  9.5  -9.4      0  6.2  -6.0     0  2.0U  1.3
 9  1.8   0.4      5  6.3  -7.1         0  1.8  -1.6     H= 5, L= 3         3  2.8   2.1      5  8.9   8.3      1  7.3   7.2     1  3.4   4.2
                   6  1.5U  0.9         1 32.9 -34.0      0 15.2 -14.7      4 19.1 -19.7      6  5.1  -4.4      2  9.0  -8.6     2  7.4   6.8
H= 5, L= 0                              2 11.0  12.2      1 15.3  15.8      5 13.4  14.1      7  3.3  -3.6      3  1.5U -1.1     3 14.0 -13.8
 5 14.2  14.6     H= 8, L= 1            3  4.3  -5.5      2  4.7  -4.5      6  6.2  -6.8                       4  4.3   3.8     4  2.9  -3.5
 6  1.7U -2.1      0 17.5 -17.8         4 11.8 -12.2      3  2.5   1.4      7  5.4  -5.2     H= 5, L= 5                        5 10.1  11.6
 7  3.3  -3.4      1  2.3U  1.3         5  7.0   7.3      4 14.5  15.4      8  7.3   6.2      0  7.0   7.3     H= 7, L= 6
 8  7.6   7.3      2 16.0  15.7         6  1.5U  0.4      5  5.1  -5.3                       1  4.8  -5.3      0 11.8 -12.0    H= 3, L= 8
                   3  2.9  -2.6         7  3.3  -3.1      6  2.0U -1.9     H= 5, L= 4       2  2.0U  1.7      1  5.0  -5.0     0  9.7   9.5
H= 6, L= 0         4  3.6   3.9                          7  5.3   5.1      0  9.0   8.7      3 12.5  12.0      2  2.0U  2.1     1  3.2  -3.0
 6  5.5   6.1      5  5.8   5.3        H= 7, L= 2         8  5.9  -5.9      1  6.8   7.4      4  4.1  -4.4      3  4.7  -9.9     2  9.3  -9.3
 7  5.9  -5.6                           0  4.9   3.3                       2 16.3 -17.1      5  5.9  -6.5                      3  2.8   2.5
                 H= 9, L= 1             1  2.3U  1.1     H= 6, L= 3         3  5.9   6.4      6  1.2U  0.5     H= 8, L= 6       4  1.8  -1.5
H= 0, L= 1         0  5.7  -5.4         2 16.5 -17.0      0 12.3 -11.8      4  7.2   7.8                       0  5.4   5.2
 0 29.9  28.2      1  9.5  -9.6         3  7.2   8.2      1  5.9  -5.9      5  7.9  -7.7     H= 6, L= 5        1  9.1  -9.3    H= 4, L= 8
 1 41.4 -41.5      2  5.9   6.5         4 12.7 -12.2      2  4.4   4.2      6  1.5U  1.7      0  5.7  -6.3      2  1.1U -1.2     0  5.3  -5.6
 2 12.1  11.1      3  6.5   6.7         5  1.5U -0.9      3 11.6 -12.4      7  2.9   2.7      1  6.6   7.3                      1  6.5   6.0
 3 17.7  15.6      4  1.5  -1.3         6  3.1   2.6      4  4.0   3.6                       2  2.3   3.2     H= 9, L= 6       2  4.8  -4.4
 4  8.4  -8.4                                            5  4.8   5.9     H= 6, L= 4       3  4.5  -3.8      0  3.7  -3.8     3  1.8   1.9
 5 21.3  19.6     H= 10, L= 1          H= 8, L= 2         6  1.5U -2.3      0  2.9   2.4      4  6.0   5.9
 6  9.7  10.3      0  4.0  -3.4         0 32.2 -31.1      7  1.1U -0.7      1 16.8  18.1      5  2.8  -2.9     H= 0, L= 7       H= 5, L= 8
 7 24.5 -24.2      1  3.2   2.3         1  4.5  -4.0                       2  3.6   3.4                       0  2.0U  2.2     0  2.3   2.8
 8  4.8  -4.0      2  9.0  -8.6         2 10.8 -11.9     H= 7, L= 3         3  7.1  -7.1     H= 7, L= 5        1  2.0U  0.2     1  2.8   3.1
 9 10.8  10.5      3  1.1U  1.4         3  7.6  -6.9      0 25.4  23.9      4  1.5U  0.7      0 15.8 -14.8      2 13.2 -13.4     2  8.6   9.6
10  2.8   2.4                           4 11.8  11.9      1  9.5 -10.0      5  3.9   3.9      1  2.2U -3.1      3  6.5   6.4
11 10.8   9.7     H= 11, L= 1           5  1.1U -0.2      2 10.6 -11.0      6  4.0  -4.4      2  6.8   7.6      4  3.1   2.3    H= 6, L= 8
                   0  8.6  -8.5                           3  4.2   3.3                       3  6.5   5.9      5 10.1  -9.5     0  9.9  10.0
H= 1, L= 1         1  2.0  -1.3        H= 9, L= 2         4 10.4 -10.1     H= 7, L= 4       4  1.5   0.7      6 10.3   9.9
 0 12.6  11.9                           0  7.1  -7.1      5  1.5U -0.2      0  2.0U  1.6                       7  4.0  -3.7    H= 0, L= 9
 1 24.9  24.9     H= 0, L= 2            1  3.6  -3.7      6  4.7   5.2      1  2.3U  0.8     H= 8, L= 5        8  4.0  -5.4     0  4.1   4.0
 2 24.2 -22.3      0 66.1 -72.0         2 11.5   9.8                       2  4.6   5.6      0  6.8   6.7                      1  8.7  -8.7
 3 11.7  11.9      1 53.7 -57.5         3  3.2   2.4     H= 8, L= 3         3 12.3  12.5      1  1.9U -2.5     H= 3, L= 7       2  4.1   3.9
 4 14.3  15.0      2 49.2 -48.5         4  8.0  -7.6      0  3.8   4.8      4  1.8  -0.6      2  7.5  -6.8      0 12.0  11.5     3  0.9U  0.6
 5 14.2 -15.1      3 45.5  43.8                           1  7.6   8.3      5  2.5   2.1      3  6.1   6.2
 6  2.0U  0.1      4 29.7 -29.7        H= 10, L= 2        2  9.9  -9.7                                                        H= 1, L= 9
 7  7.5   8.5      5 31.1  31.9         0  4.1   4.0      3  3.2  -3.3     H= 8, L= 4       H= 9, L= 5                         0  5.3   5.4
 8 10.1  -9.8      6 12.2 -12.4         1  5.2   4.4      4  0.9U  1.3      0 14.0  13.0      0  1.5U -1.8                      1  3.8   3.9
 9  3.7   4.2      7 26.6 -27.6         2  4.8  -4.4      5  3.5  -4.0      1  7.1   6.6      1  6.6   6.3                      2  4.8  -5.2
10  9.7   8.7      8  4.3   2.6                                            2  2.0U  1.3      2  4.0  -5.4
11  2.9  -2.8      9  2.0U -1.7        H= 11, L= 2       H= 9, L= 3         3  2.8   2.9                                      H= 2, L= 9
                  10  3.9  -3.4         0  1.5U  0.6      0  2.2   1.6      4  2.5   2.8     H= 10, L= 5                        0  5.4  -4.9
H= 2, L= 1        11  3.6  -3.6         1  2.5  -1.3      1  2.0U  1.7                       0  2.5  -2.5                       1  1.1U  0.9
 0 29.4 -29.0                                            2  9.0   8.1     H= 9, L= 4                                          2  2.2   2.4
 1  5.4   4.8     H= 1, L= 2           H= 0, L= 3        3  6.7  -6.3      0  2.0U -1.6     H= 0, L= 6
 2 22.3  20.4      0 38.7 -31.1         0  9.3  -8.0                       1 10.7  10.7      0  3.7   4.9                     H= 3, L= 9
 3 31.2 -30.6      1 11.4 -10.7         1  3.8  -4.0     H= 10, L= 3        2  5.0   4.3      1  3.6   4.0                      0  3.4   3.3
 4  1.2   0.5      2 65.4 -63.6         2 29.6  29.9      0  2.3   2.1      3  7.2  -7.3      2 17.4 -16.6
 5 14.6  14.6      3 30.7  29.5         3 12.1 -12.3      1  2.0U -2.3                       3 21.4 -22.5
 6  4.0  -3.8      4 12.3  12.0         4 13.8 -14.4      2  1.5U  1.7     H= 10, L= 4       4  9.0   9.5
 7  9.7   9.0      5 10.8 -11.1         5 10.9  10.2                       0  5.3   4.6      5  6.3  -6.3
 8  2.3U  0.8      6 18.8  18.8         6 24.7 -24.6     H= 11, L= 3        1 11.8 -11.6      6  2.0U -0.7
 9 15.3 -14.1      7 29.9 -30.7         7  3.8   2.8      0  2.5  -2.4                       7  2.0U  0.5
```

they were too near their mirror-related counterparts for anisotropic temperature factors to be applicable. The refinement converged quickly to a final discrepancy index, R, of 0·062; all of the bond distances and other intra- and inter-molecular features of the structure seemed plausible. The parameters of this structure, and data derived from them, are given in Tables 1–3; the structure factors are listed in Table 4.

Attempts were also made to fit an ordered structure in space group $P321$ to the data. Full-matrix least-squares refinement was carried out, starting from a set of parameters close to those of the final structure in $P\overline{3}m1$; anisotropic temperature factors were used for all atoms. The discrepancy index R converged only to about 0·12 after four cycles; the largest shift in a position parameter in the last cycle was 0·001 Å. Furthermore, certain of the resulting bond distances were inconsistent and unreasonable; for example, the two independent C–CN distances were 1·32 and 1·42 Å, and the two C–N distances were about 0·1 Å longer than usual, 1·22 and 1·27 Å. Quite clearly, the disordered $P\overline{3}m1$ model, for which the final sum of the weighted squares of the residuals was one fourth as great (although the number of parameters is actually smaller because two atoms are isotropic) and for which the molecular structure is more plausible, is to be preferred, and we consider only it hereafter.

Discussion

We shall discuss first the geometry of the anions themselves, then the crystal structure, including the hydrogen bonding, the calcium coordination, and the disorder, and finally the interconversion of anions of opposite chirality.

The anion

The individual anions have symmetry 3 (but very nearly 32); a typical anion is represented in Fig. 1 and its geometry is given in Fig. 2 and Table 2. The arms are rotated 24° from the completely planar conformation. The bond distances are quite in accord with ex-
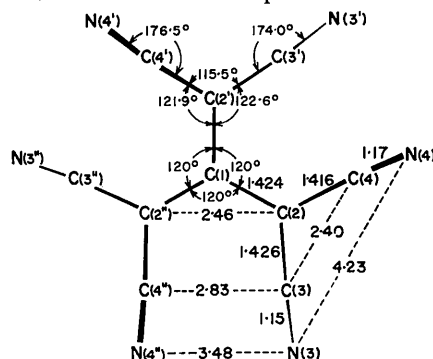
Fig. 2. Distances and angles in the HCB²⁻ anion. Some non-bonded contacts are also shown (see Table 3). Bond distances include estimated corrections for thermal vibration. Atoms designated with ′ and ″ correspond, respectively, to positions B and C of Table 3.

pectation if one considers possible resonance structures or the predictions of simple Hückel molecular orbital (HMO) theory (Table 2); π-overlap is reduced less than 9% by the tilt of 24°, while the repulsions between cyano groups in adjacent arms are considerably diminished. Even after the rotation of the arms, $C \cdots C$ contacts (with at least two intervening bonded atoms) of 2·83, 2·92, and 2·93 Å remain, but the shortest of these probably contributes only about 1 kcal.mole⁻¹ to the strain energy (Gantzel & Trueblood, 1965). Similar contacts, in the range 2·92–3·00 Å, are numerous in 15,15′-dehydro-β-carotene (Sly, 1964) and are apparently responsible for the overall conformation and the slight departures from planarity of the conjugated system of that molecule. However, the steepness of the repulsive interaction curve in this region is manifested in the apparently significantly increased strain in a molecule for which the shortest non-bonded contacts are only about 2·7 Å (Laing, 1964).

The four central atoms are precisely coplanar [as indicated by the essentially identical z parameters of C(1) and C(2)] and there is no indication of significant pyramidal character around C(2) either (Table 2). It has been reported that the $C(CN)_3^-$ ion (Desiderato & Sass, 1965) and the $N-C(CN)_2$ group in pyridinium dicyanomethylide (Bugg & Sass, 1965) are slightly pyramidal, the central carbon atom being about 0·13 Å above the plane of the three nitrogen atoms in the cyanoform carbanion and comparably displaced in the other compound. Because $\sigma(z)$ and B_{33} are quite normal for C(1) and C(2) in the present structure, we believe the apparent absence of pyramidal character in HCB²⁻ is meaningful. (Prof. R. Sass pointed out to us that if the z parameter of C(2) were changed to $(\frac{1}{2}-z)$, the anion would be slightly pyramidal. This possibility seemed worth examining and we did full-matrix least-squares refinements on two modified sets of parameters, one with this change in z of C(2) and the other with the same change in z of both C(1) and C(2). In each instance the atoms returned in one cycle to substantially the original position with no other significant shifts in these or other atoms).

The small deviations from planarity of the $CC(CN)_2$ groups and from linearity of the CCN groups seem reasonable in view of the short non-bonded interactions between adjacent arms of the anion. The coordination of N(3) to the calcium ion and presumed hydrogen bonding of N(4) to the water molecules (both discussed below) may play a role as well.

Very small corrections were made to the C–C distances (Table 2) as a consequence of differing thermal vibrations of the atoms; the assumptions were the same as those of Bekoe & Trueblood (1960) which are equivalent to the 'riding motion' case of Busing & Levy (1964). The corrections to the C–N bonds are, however, significant, at least 0·02 Å, just as in tetracyanoethylene (TCNE; Bekoe & Trueblood, 1960, 1964) and tetracyanoquinodimethane (TCNQ; Long, Sparks & Trueblood, 1965). The C–CN bond length (1·421 Å,

e.s.d. 0·006) borders on being significantly shorter than those in TCNQ and TCNE, which are 1·441 Å (e.s.d. 0·004). If this difference is real, it reflects the fact that the bond order of these bonds is calculated to be greater by about 0·1 in the present molecule.

It is noteworthy that the angles around C(2) are very similar to those in TCNQ; the NC–C–CN angle in TCNE is about 2° larger, perhaps as a result of the absence of the short intramolecular non-bonded contacts provided by the hydrogen atoms of TCNQ and the other arms of HCB^{2-}.

Structure and packing

The structure contains columns of the propeller-shaped anions, the different columns held together by coordination of N(3) to Ca^{2+} and by hydrogen bonds to N(4) from the two water molecules. Each water molecule apparently forms (in an ordered region) only one hydrogen bond. The most plausible structural model of the disorder seems the following: any *given* stack of anions is ordered and has symmetry $P\bar{3}$, but the different stacks in the structure are not all in the same orientation, being (presumably randomly) related by a twofold rotation along **a** (or **b**, or [110], these being equivalent). Because of the center of symmetry, these twofold rotations are equivalent to the mirror planes of $P\bar{3}m1$, e.g. (110). Fig.3 gives a view down **c** of ordered and disordered regions of the structure. Since the different columns of anions are in contact only with water molecules and calcium ions, it is these contacts which are affected by the disordering, and therefore we will first consider these contacts in detail.

In any given column of anions, both R and S anions are present, that is, both right-handed and left-handed

propellers. [The R and S notation is that of Cahn, Ingold & Prelog (1966)]. Adjacent anions along **c** are of opposite hand, rotated by 60° relative to one another so that they mesh well (Fig.3). The anions are almost equally spaced along the columns (because the z parameter of C(1) is so near 0·25), with a few contacts between the tilted arms of around 3·4–3·5 Å (Table 3). The columns of anions are cemented together by the calcium ions; each calcium is surrounded by a trigonal prism of water molecules and, projecting out from near the center of each side face of the prism, three N(3) atoms, one from each of three different anions. Each anion is thus coordinated to three different calcium, and each calcium to three different anions. The ninefold coordination of calcium is similar to that in $CaCl_2.6H_2O$ (or $SrCl_2.6H_2O$) and $Nd(BrO_3)_3.9H_2O$ (Jensen, 1940; Helmholz, 1939).

It seems likely that N(4), which is not coordinated to the calcium ions, is linked by a hydrogen bond to each of the two water molecules. Thus, N(4) is 2·92 Å from O(1) and 2·98 Å from O(2), and in a difference-Fourier synthesis calculated with the final parameters, peaks of heights 0·45 and 0·42 $e.Å^{-3}$ respectively were found about 1 Å from the oxygen atoms and near these O···N lines. There are other short contacts between N(3) and the water molecules (Table 3) but it is doubtful whether they should be regarded as potential hydrogen bonds for they lie near edges of the coordination polyhedron of the calcium ion (Templeton, 1960; Clark, 1963). Furthermore, no peaks were found along these lines in the difference map, although one additional rather diffuse peak of height about 0·3 $e.Å^{-3}$ was found about 1 Å from O(1), and might represent the second hydrogen atom of that water molecule, or one possible position for this atom.
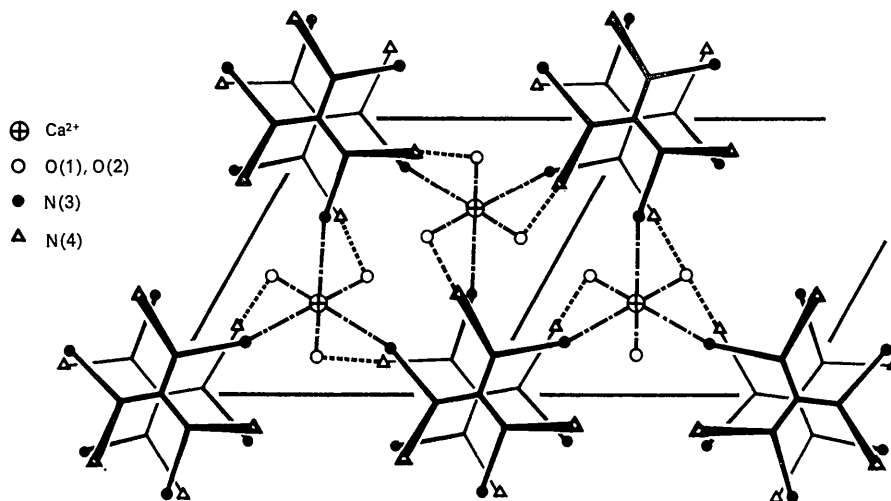
Fig. 3. View of the structure along **c**. Only the skeletons of the anions are shown; Fig. 2 gives the positions of the individual atoms. The darker anion is nearer and in each individual anion the tapered arms project toward the viewer, the others project away. The two water molecules are superimposed in this projection; their positions are indicated by the circles. Hydrogen bonds to them (. . . .) also superimpose; because N(4) lies between coordination polyhedra along **c**, the hydrogen bonds link different polyhedra together. An ordered portion of the structure is shown at the left; the column of anions in the lower right is disordered relative to the other four.

If a stack of anions is rotated by 180° about **a** to produce the observed disorder, there is no effect on the coordination of N(3) to the calcium ion, for this rotation merely has the effect of moving N(3) by 0·27 Å across the mirror plane ($1\bar{2}0$) and does not affect its relation to the Ca^{2+} which lies on this plane. The presumed hydrogen bonds from the water molecules to N(4) are changed by the disordering only in that *one* of the three water molecules of each type [O(1) and O(2)] in any coordination group around the Ca^{2+} will now form *two* hydrogen bonds to two different N(4) atoms, while one of the other two water molecules of each type will form no hydrogen bonds (lower right part of Fig. 3). Because these two hydrogen bonds from O(1) or O(2) to N(4) are equivalent, and correspond to the ones we found in the $P3m1$ difference-Fourier map, this would explain why only one good (unique) hydrogen peak was found for each water molecule. The angles between these bonds are 97° at O(1) and 94° at O(2), so that it is entirely reasonable that the two hydrogen atoms of a given water molecule could lie along these directions. Furthermore, these directions are pointed away from the calcium ion, which is also reasonable.

It seems worthy of note that with such a propeller-shaped non-planar anion, space group $P321$ would imply spontaneous resolution in the crystal, since this space group is non-centrosymmetric; each individual crystal would have to contain either all R or all S anions. However, as discussed below, even if such crystals did exist, and could be separated, we believe the anions would probably racemize rapidly in solution at ordinary temperatures.

Because of impossibly close contacts, no individual column of anions can have symmetry $P3m1$. Our disordered model seems to us the most plausible way to achieve this diffraction symmetry with individual columns having symmetry $P\bar{3}$ but an alternative possibility is that the crystal is really a twin, with individual regions of symmetry $P\bar{3}$ twinned on (110). We never observed any crystals of the calcium salt with diffraction symmetry other than $\bar{3}m1$, although several crystals mounted about both **a** and **c** were examined. However, we made an attempt to see whether a twinned $P\bar{3}$ model is at least consistent with the data. This was done by using the final parameters of Table 1 in the calculation of F^2 values in $P\bar{3}$ for both hkl and $kh\bar{l}$ which are no longer equivalent, and averaging the resulting F^2 values for hkl and $kh\bar{l}$. Comparison of these average values with the observed F^2 showed many large discrepancies, particularly when the signs of the individual structure factors differed. Thus the twinned model seems an unlikely one. Fortunately, however, for a given parameter set the detailed nature of the disorder (or twinning) does not significantly affect the discussion of the anions because the individual columns in any plausible structure have symmetry only $P\bar{3}$, and the columns are related only through the calcium coordination polyhedra. Thus most of the dis-

cussion of the structural features could apply as well to an ordered structure in $P\bar{3}$.

The existence of distinct R and S anions in the crystal raises the question of the barrier between them. The interconversion of these species must involve rotation of each arm either through the conformation in which it is coplanar with the central carbon atoms or through the position in which it lies in a plane normal to the central plane. Even if the arms move in non-concerted fashion, two pairs of arms will be nearly eclipsed at some stage; a concerted rotation through the completely planar conformation would involve eclipsing of all arms with one another, with some very short (*ca.* 2·5 Å) contacts. An approximate calculation (see Appendix) suggests that steric and electrostatic repulsions and bond-angle deformations might contribute to the barrier about 4 kcal.mole^{-1} for each pair of coplanar arms, or 12 kcal.mole^{-1} for the completely planar anion. The actual barrier, measured relative to the equilibrium conformation found in the crystal, is presumably appreciably smaller; the calculations in the Appendix suggest that resonance stabilization offsets most of the steric and electrostatic barrier, the net barrier thus being only a few kcal.mole^{-1}. If this is correct, then the completely planar conformation might exist in some complexes of this anion. In any event, however, even if there were a concerted rotation of the arms and no offsetting delocalization energy effect, a barrier of 12 kcal.mole^{-1} is so small that the rate of interconversion would be extremely high and there would be no possibility of isolating the anions of opposite configuration except by stabilizing them in some fashion similar to that provided by their environment in this crystal. It seems likely that the loss in resonance energy when one of the arms turns through the perpendicular conformation is sufficiently great that this mode of interconversion is of minor importance.

Appendix

The approximate barrier to rotation of the arms from the equilibrium conformation to the completely co-planar conformation (ignoring at first the effects of resonance energy) was estimated as follows: (1) the non-electrostatic interaction of all non-bonded atoms was represented by the potential function of Kitajgorodskij (1965), $U(r) = -0.148\,[1/z^6 - 0.46\exp(13 - 13z)]$ with $z = r/r_0$ and $r_0 = 3.8$ Å for C–C, 3.4 Å for N–N, and 3.6 Å for C–N; negligibly different results were obtained with $r_0 = 3.6$ Å for N–N, corresponding to a harder nitrogen atom; (2) calculations of the energy of electrostatic interactions were based on the admittedly questionable assumption that a point-charge distribution corresponding to that of the Hückel molecular-orbital calculation (Table 2) was valid for both the equilibrium and coplanar conformations; (3) the energies of deformation of valence angles were assumed to be $8.4 \times 10^{-3}(\delta)^2$ kcal.mole^{-1} for the C–C–C angle (V. Dashevskij, private communication) and 7.6×10^{-3} $(\delta)^2$ kcal.mole^{-1} for the C–C≡N angle, with δ the deviation in degrees from the ideal values of $120°$ and $180°$ respectively. The constants in these expressions are only about half those frequently assumed because part of the angle-deformation potential has already been included in the expression for non-bonded interactions; (4) bond distances were assumed to remain unchanged, and the approximate minimum-energy conformation for the completely coplanar anion (of symmetry $3m$) was calculated as a function of two parameters, the C–C–C angle and the C–C≡N angle. The barrier was then estimated by comparing the energy of this conformation with that of the equilibrium conformation actually found in the crystal. The results of these calculations are summarized in Table 5.

The calculations thus indicate that the barrier is about 12 kcal.mole^{-1}; the figures for the 'ideal' planar model are included because they illustrate the enormous relief of steric and electrostatic strain that a relatively inexpensive degree of valence-angle deformation can provide

There are several obvious shortcomings of this calculation; the most glaring is that the enhanced stabilization of the coplanar form due to delocalization energy is ignored. This problem is considered below. Other doubtful features include: the approximations in the potential functions used, the assumptions concerning the charge distribution, and the fact that no account has been taken of any intrinsic barrier to rotation about each C–C bond, which might add a few kcal.mole^{-1} to the total barrier between the equilibrium and coplanar conformations.

There are several possible approaches to the calculation of the resonance energy. For a non-cyclic heteroatomic anion such as the present one, direct quantum-chemical calculations involve a great many well-known uncertainties. An alternative approach, perhaps no more reliable but giving an independent empirical estimate of at least the order of magnitude of the energy, is to assume that the only force tending to oppose the increase of the twist angle arises from the variation of the delocalization energy and that this variation is a known function of the angle. If the resonance energy is represented by D and the twist angle by φ, then $dD/d\varphi$ at $\varphi = 24°$ can be evaluated, because it must be just equal to the rate of change of the steric and electrostatic energies with φ at this equilibrium angle. (It is assumed that the effects of the crystalline environment on the equilibrium angle are of minor importance; the variation in the valence-angle bending energy is so small that it can safely be ignored.) For the present anion, the derivatives of the steric and electrostatic energies with φ can be readily calculated from the known geometry and potential functions. Such calculations yield the values 25 and 18 kcal.radian^{-1} (at $\varphi = 24°$) for the derivatives of the steric and electrostatic energies, respectively. Most of the former arises from the C(3)–C(4″) interaction (Fig. 2), with small contributions from C(2)–C(4″) and C(3)–N(4″); the chief contributions to the electrostatic derivative arise from the interactions of N(3) with N(4″) and C(3) with N(4″), which have opposite signs.

Thus a very approximate estimate of $dD/d\varphi$ at $\varphi = 24°$ is 43 kcal.radian^{-1}. Several different empirical functions have been used for the dependence of resonance energy on twist angle in conjugated system; Adrian's (1958) calculations for triphenylmethyl radical suggest that $\cos^3\varphi$ is a good approximation, with slightly higher power dependence for biphenyl and some related systems, while Goodwin & Morton-Blake (1963) indicate that for biphenyl a $\cos^2\varphi$ dependence is appropriate. If we let D_0 be the total resonance energy and D_e that remaining in the equilibrium conforma-

Table 5. *Relative energies of different models*[a]

Model	Twist	Angles C–C–C	C–C≡N	Steric	Energies (kcal.mole^{-1}) Electro-static	Angle bending	Total
Actual	24°	116°	175°	0*	0*	2	2
Minimum-energy planar[b]	(0)	110	175	7	3	4	14
Ideal planar	(0)	(120)	(180)	19	11	0	30

[a] Angles in parentheses are a necessary consequence of the assumed model; energies identified by * are taken as arbitrary zero-points for present purposes.

[b] The minima for the angles are rather flat and the values are only approximate; C–C–C probably lies in the range 109–113° and C–C≡N in the range 173–177°.

tion, then the gain in stabilization in going from $\varphi = 24°$ to $\varphi = 0°$ is $(D_0 - D_e)$; if it is assumed that D varies as $\cos^n\varphi$, $(D_0 - D_e)$ is fortuitously almost independent of the exponent (at least for $n = 1, 2,$ or 3), because $\cos 24°$ is not far from unity. $(D_0 - D_e)$, the gain in stabilization on returning to the planar form, is calculated to be about 10 kcal.mole^{-1}; if this estimate is at all reasonable, it indicates that the *net* barrier to rotation is only about 2 kcal.mole^{-1}, which is less than the uncertainties introduced by many of the assumptions. In any event, the net barrier would seem to be very small indeed. The value of the resonance energy itself, D_0, depends on the function assumed for the variation of D with φ; with a $\cos^2\varphi$ dependence, it is about 57 kcal.mole^{-1}, and with $\cos^3\varphi$ about 42 kcal.mole^{-1}. These numbers should be regarded, however, with considerable skepticism.

References

ADRIAN, F. J. (1958). *J. Chem. Phys.* **28**, 608.
BEKOE, D. A. & TRUEBLOOD, K. N. (1960). *Z. Kristallogr.* **113**, 1.
BEKOE, D. A. & TRUEBLOOD, K. N. (1964). Abstracts of the Bozeman A. C. A. Meeting, p.87.
BUGG, C. & SASS, R. (1965). *Acta Cryst.* **18**, 591.
BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142.
CAHN, R. S., INGOLD, C. & PRELOG, V. (1966). *Angew. Chemie (Internat.)*, **5**, 385.
CLARK, J. R. (1963). *Rev. Pure Appl. Chem.* **13**, 50.
DESIDERATO, R. & SASS, R. (1965). *Acta Cryst.* **18**, 1.
FREEMAN, A. J. (1959). *Acta Cryst.* **12**, 261.
GANTZEL, P. K. & TRUEBLOOD, K. N. (1965). *Acta Cryst.* **18**, 958.
GOODWIN, T. & MORTON-BLAKE, D. (1963). *Theor. Chim. Acta*, **1**, 458.
HELMHOLZ, L. (1939). *J. Amer. Chem. Soc.* **61**, 1544.
HOERNI, J. A. & IBERS, J. A. (1954). *Acta Cryst.* **7**, 744.
HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
JENSEN, A. T. (1940). *K. Danske Vidensk. Selsk.* **17**, no.9, 27; *Structure Reports*, **8**, 133.
KITAJGORODSKIJ, A. I. (1965). *Acta Cryst.* **18**, 587.
LAING, M. (1964). *Proc. Chem. Soc.* p.343.
LONG, R. E., SPARKS, R. A. & TRUEBLOOD, K. N. (1965). *Acta Cryst.* **18**, 932.
MIDDLETON, W. J., LITTLE, E. L., COFFMAN, D. D. & ENGELHARDT, V. A. (1958). *J. Amer. Chem. Soc.* **80**, 2795.
SLY, W. G. (1964). *Acta Cryst.* **17**, 511.
TEMPLETON, D. (1960). *Acta Cryst.* **13**, 684.
THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 239.

The Crystal Structure and Phase Transformation of α-Cu2P2O7

BY B. E. ROBERTSON AND C. CALVO

McMaster University, Hamilton, Ontario, Canada

α-Cu$_2$P$_2$O$_7$ is found to be of monoclinic symmetry with $a = 6.876$ (5), $b = 8.113$ (5), $c = 9.162$ (5) Å, $\beta = 109.54$ (6)° and $Z = 4$. The structure has been refined in space groups Cc and $C2/c$, and the latter is the preferred choice. The anion possesses a twofold axis and a P–O–P bond angle of 157°. The inner and outer P–O bonds of the anion are 1.58 and 1.53 Å respectively. A phase transformation is found to begin at 70°C and extends to above 100°C. The reflexions with their l index odd show diffuse temperature dependent streaks directed along [100] in this temperature range. The transformation thus appears to proceed by a positional disordering of bent pyrophosphate ions.

Introduction

Copper pyrophosphate is one of a series of crystallographically related pyro-compounds which have isostructural high temperature phases (called β) and related low temperature phases (called α). These compounds have the generalized formula M$_2$X$_2$O$_7$ with M the cation and X an element showing a disposition for tetrahedral coordination with oxygen atoms. This series of compounds includes the mineral thortveitite, which is a pyrosilicate of Y and Sc (Cruickshank, Lynton & Barclay, 1962), the analogous Sc pyrogermanate (Goldschmidt, 1931), the pyroarsenates of Zn and Mg (Calvo & Neelakantan, 1967), the pyrovanadate of Cd (Au & Calvo, 1967) and a number of pyrophosphates. Among the pyrophosphates Mn (Lukaszewicz & Smaj-

kiewicz, 1961), Cu (Lukaszewicz & Nagler, 1961), Mg (Calvo, 1965a, 1967) and Zn (Calvo, 1965b) have been investigated crystallographically. Each of these pyrophosphates, except Mn$_2$P$_2$O$_7$, displays a reversible phase transformation and in each case the room temperature form is the α phase. The unit cell volume of the α phase is roughly double, quadruple and sextuple that of the conjugate β phase for Cu, Mg and Zn salts respectively. Further, in each case, the c axis is roughly doubled with a c-glide plane replacing the mirror plane of the β phase while the a axis is unchanged, doubled and tripled in the respective α phases. Details of the α–β Cu$_2$P$_2$O$_7$ transition have not previously been reported although Roy, Middleswarth & Hummel (1948) suggested some evidence existed for a phase transformation. The α–β Mg$_2$P$_2$O$_7$ transformation, however,