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The Pseudorotation of Cycloheptane.
II.* The Crystal Structure of Calcium Cycloheptanecarboxylate Pentahydrate

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The orthorhombic crystals of calcium cycloheptanecarboxylate pentahydrate, $(C_7H_{13}COO)_2Ca.5H_2O$, have a unit cell with $a = 33 \cdot 122$ (3), $b = 20 \cdot 094$ (2) and $c = 6 \cdot 649$ (4) Å. The space group is *Aba*2 or *Abam*, with a preference for the noncentrosymmetric description. There are eight formula units per unit cell. The structure consists of (i) hydrophilic layers (perpendicular to **a**) of Ca ions surrounded by five water molecules and four O atoms belonging to the carboxylate ions, alternating with (ii) hydrophobic layers in which the two cycloheptane rings occupy disordered positions. A reasonable interpretation of the X-ray diffraction pattern is obtained by the assumption of four pseudorotational conformers contributing to the regions (2 + 2) assigned to the cycloheptane rings. The unweighted and weighted reliability indices of the refined model are $R = 9 \cdot 10$ and $R_w = 9 \cdot 79\%$. Below −78°C a second phase with space group $P2_1/b$ is observed.

Introduction

Theoretical considerations and potential-energy calculations by Hendrickson (1967) indicated that among the medium-sized rings cycloheptane should display pseudorotation, the principal symmetrical conformers being the chair (*C*) and the twist-chair (*TC*) in the *C*/*TC* itinerary, and the boat (*B*) and the twist-boat (*TB*) in the *B*/*TB* pathway (see Fig. 1). Hendrickson calculated that the *C*, *TB* and *B* forms have relative energies of 1·4, 2·4 and 2·6 kcal mol^{-1} with respect to the most stable *TC* conformation. Recent calculations of Bocian, Pickett, Rounds & Strauss (1975), however, point to the boat as the most stable form.

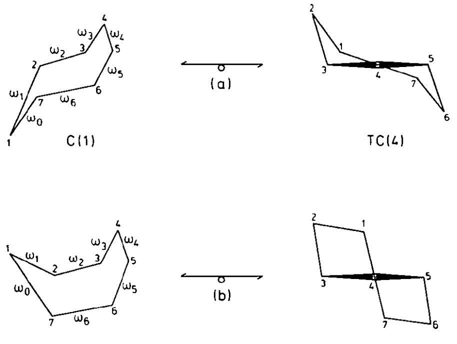

Fig. 1. Symmetrical C_s and C_2 forms in (*a*) the chair/twist-chair family and (*b*) the boat/twist-boat family.

Elsewhere Flapper & Romers (1975) (hereafter FR) introduced the empirical relationship

$$\omega_i = A \sin \varphi_j + B \sin 3\varphi_j + C \sin 5\varphi_j + D \sin 7\varphi_j \,; \quad (1)$$
$$\varphi_j = \Delta/2 + j\delta/2; \delta = 4\pi/7;$$
$$i = 2j + 4, \bmod 7; \quad j = 0, 1, \ldots 6,$$

which allows the calculation of all endocyclic torsion angles ω_i for *any* phase angle of pseudorotation Δ, the parameters *A*, *B*, *C* and *D* being angles defining the 'degree' of chair or boat character. Numerical values of these parameters are to be found in FR. Since *C* and *D* are negligible in practical cases, this representation attains to describe any conformation by only three parameters *A*, *B* and Δ, rather than the full set of torsional angles.

We wish to present crystallographic evidence for pseudorotation. The Ca salt of cycloheptanecarboxylic acid was chosen, other cycloheptane derivatives being liquid or polycrystalline. The diffraction study of this salt was hampered by apparent disorder of the cycloheptane rings. This phenomenon seems to be related to pseudorotation and induced us to postulate equation (1).

Experimental

Metallic Ca was added to a benzenic solution of cycloheptanecarboxylic acid and after filtration the salt was recrystallized from water in the form of colourless orthorhombic needles elongated along [001]. Absent X-ray reflexions *hkl* for *k* + *l* odd, 0*kl* for *k*(*l*) odd and *h*0*l* for *h*(*l*) odd indicate the space groups *Aba*2 and *Abam* (Nos. 41 and 64 in *International Tables for X-ray Crystallography*, 1965).

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* Part I: Flapper & Romers (1975).

The lattice constants at room temperature (Table 1) were measured manually with a three-circle diffractometer and Cu $K\alpha$ radiation ($\lambda = 1{\cdot}54178$ Å). The density, determined by means of the flotation method with chlorobenzene/bromobenzene mixtures, of 1·24 g cm^{-3} indicates eight molecules per unit cell and is in excellent agreement with the calculated value (1·238 g cm^{-3}) if one assumes the presence of five water molecules per formula $(C_7H_{13}COO)_2.Ca$. The Patterson analysis (see next section) confirms that the salt is indeed a pentahydrate.

The reflexion intensity data were collected on a Nonius CAD 3 diffractometer* with Cu $K\alpha$ radiation and the $\theta/2\theta$ scan, between glancing angles $\theta = 4$ and $\theta = 67°$. A total of 3479 reflexions were measured with a crystal 0·50 × 0·22 × 0·11 mm. The number of recorded symmetry-independent reflexions was 2091, of which 1726 with intensities larger than twice the standard deviations were used during the refinement. The crystal suffered from radiation damage. After each group of 29 reflexions, one of three standard reflexions (131, 211 and 211) was measured. With these reflexions, a fifth-order polynomial function of the exposure time (4 d) was determined in order to correct the intensities for loss in scattering power of the crystal. The ultimate decrease in scattering power was about 10%. The intensities were also corrected for absorption using the Monte Carlo method described by de Graaff (1973). The transmission factors vary between 0·52 and 0·73. Finally the intensities were reduced to structure factors in the usual way.

Table 1. *Crystal data for calcium cycloheptane-carboxylase pentahydrate*

Estimated standard deviations are given in terms of the last decimal.

Molecular composition: $CaC_{16}H_{36}O_9$, $M_r = 412{\cdot}5$
M.p. > 300 °C (under decomposition)
Transition point: −78 °C

20 °C	−90 °C
$a = 33{\cdot}122\,(3)$ Å	$a = 32{\cdot}2$ Å
$b = 20{\cdot}094\,(2)$	$b = 20{\cdot}2$
$c = 6{\cdot}649\,(4)$	$c = 6{\cdot}8$
	$\alpha \simeq 90°$
$V = 4425{\cdot}3$ Å^3	$V = 4423$ Å^3
*Aba*2 or *Abam*	$P2_1/b$ (unique *a* axis)
$d_{\mathrm{exp}} = 1{\cdot}24$ g cm^{-3}	
$d_x = 1{\cdot}238$	$d_x = 1{\cdot}24$ g cm^{-3}
$Z = 8$	$Z = 8$
$\mu(\mathrm{Cu}\ K\alpha) = 31{\cdot}2\ \mathrm{cm}^{-1}$	

Patterson search and Fourier maps

The positions of the Ca and O atoms were derived from a sharpened Patterson synthesis. A solution was obtained in space group *Abam* with Ca, O(1) and O(2) in special position 8(*f*) (mirror plane), O(3) in 8(*e*) (twofold axis) and O(4), O(5) and O(6) in general position 16(*g*).

Fourier maps also reveal well-defined maxima for the carboxylic atoms C(*P*0) and C(*K*0) and for the first ring atoms C(*P*1) and C(*K*1), all positions being 8(*f*). The adjuncts *P* and *K* designate the two *different* cycloheptane rings to be located in different regions of the unit cell. If *Abam* is the correct space group and if disorder is absent, then these rings must be C_s forms with their mirror planes coinciding with the crystallographic mirror plane. If the second condition is violated (as happens to be the case) then mixtures of equal amounts of enantiomorphic forms are present in space group *Abam*, or mixtures of arbitrary forms in space group *Aba*2. For technical reasons it was advantageous to shift to the noncentrosymmetric space group halfway through the analysis; the correct space group was determined after the final stage (see below). Disregarding atoms C(*P*1) and C(*K*1), the moiety located forms the 'hydrophilic' part of the structure. This part was refined by minimization of least squares taking the scattering factors of Ca, O and C from *International Tables for X-ray Crystallography* (1962). The Ca and O atoms were refined anisotropically, and the C atoms C(*P*0) and C(*K*0) isotropically. This way an *R* value of 21·1% was obtained. The weighted and unweighted reliability indices R_w and R are defined as: $R_w = [\Sigma\ w(|F^{\mathrm{obs.}}| - |F^{\mathrm{calc.}}|)^2/\Sigma\ w(F^{\mathrm{obs.}})^2]^{1/2}$ and $R = \Sigma||F^{\mathrm{obs.}}| - |F^{\mathrm{calc.}}||/\Sigma|F^{\mathrm{obs.}}|$, where $w = [\sigma(F^{\mathrm{obs.}})]^{-2}$.†

Fourier sections based upon this refinement display diffuse electron-density regions which (in width) extend over more than 4 Å in the direction [010]. Attempts to introduce reasonable models in accordance with conformations predicted by Hendrickson were not successful. Although an ordered noncentrosymmetric structure containing cycloheptane rings *P* and *K* was refined anisotropically to an *R* value of 8·5%; the resulting rings are too flat, while the C—C bond lengths and the valency angles show unrealistic values between 1·2 and 1·8 Å and 100 and 130° respectively. Moreover, several tensor components U_{ij} of the temperature factor: $\exp[-2\pi^2\,\Sigma_{i,j}\,h_i h_j a_i^* a_j^*\,U_{ij}]$, $i, j = 1, 2, 3$, attained very high values of $\sim 0{\cdot}25$ Å^2. These features clearly demonstrate that the 'hydrophobic' part is disordered and possibly displays large thermal motions.

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* A full account of the measurements of two other data sets, one photographic and the other diffractometric, which were collected four years earlier, is given in Flapper (1976) (hereafter FL).

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31952 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Refinement with slack constraints

In agreement with earlier experiences (Stam, 1972; de Wolf, Verschoor & Romers, 1972) it is useless, unless constraints can be applied, to refine disordered structural fragments containing atoms whose separations are smaller than 0·5 Å. After several trials with rigid models and strict constraints which resulted in $R = 14{\cdot}5$ and $R_w = 17{\cdot}8\%$ for two K and two P rings in space group *Abam* (for details consult FL), we resorted to the rarely applied method of slack constraints (Waser, 1963). This procedure enables a model to include subsidiary conditions which, to a certain extent, are governed by the weighting factors chosen.

Defining seven endocyclic C–C bond distances (we chose 1·520 and not 1·537 Å in order to account for thermal-motion effects) and seven 1–3 distances (at 2·578 Å, *i.e.* fixing the bond angles at 116°, see Table 1 of FR) with one degree of freedom, the phase angle Δ can still be chosen at will. Accordingly for each ring the residual $\Sigma_v w_v (r_v^{\text{obs.}} - r_v^{\text{calc.}})^2$ is added to the least-squares residual $\Sigma\, w_h \| F_h^{\text{obs.}} | - | F_h^{\text{calc.}} \|^2$. The weights w_v are calculated from $w_v = \Sigma\, w_h \| F_h^{\text{obs.}} | - | F_h^{\text{calc.}} \|^2 / \sigma_v^2 (M - N)$, where M is the number of observations and N the number of parameters. The standard error (σ_v) was estimated to be 0·02 Å for both types of distances. Altogether 72 constraints were introduced in the refinement which, adopting space group *Aba*2, converged after 25 cycles to the minimum R and R_w values of 9·20 and 9·79%.

The resulting geometries of the four rings are given in Table 2.

Table 2. *Bond lengths* (Å), *valency angles* (°) *and torsion angles* (°) *resulting from slack constraints*

Included are calculated torsion angles [applying equation (1)], and parameters A, B and phase Δ(°); d_j = distance between atom j and $j+1$; θ_j = angle between atoms $j-1$, j and $j+1$; ω_j is the dihedral angle between the plane of atoms $j-1, j, j+1$ and the plane of atoms $j, j+1$ and $j+2$.

	j	d_j	θ_j	ω_j	ω(calc.)	A	B	Δ
Ring 1*K*	1	1·53	113	−84	−80	77·7	36·7	246
	2	1·51	119	54	53			
	3	1·51	119	−41	−43			
	4	1·51	117	70	71	$\langle d \rangle = 1{\cdot}517$		
	5	1·51	118	−76	−77	$\langle \theta \rangle = 117{\cdot}3$		
	6	1·52	118	14	17	*C–TC* conformation		
	7	1·52	117	57	59	Multiplicity 0·594		
Ring 2*K*	1	1·51	119	−35	−37	67·8	47·0	298
	2	1·51	121	24	24			
	3	1·52	120	−67	−65			
	4	1·53	115	84	82	$\langle d \rangle = 1{\cdot}518$		
	5	1·53	114	−19	−20	$\langle \theta \rangle = 116.9$		
	6	1·52	115	−61	−65	*C–TC* conformation		
	7	1·52	115	81	80	Multiplicity 0·406		
Ring 1*P*	1	1·50	121	46	45	75·1	30·0	701
	2	1·51	119	−69	−64			
	3	1·52	116	76	72			
	4	1·51	118	−26	−26	$\langle d \rangle = 1{\cdot}508$		
	5	1·51	120	−41	−44	$\langle \theta \rangle = 119{\cdot}0$		
	6	1·50	120	71	74	*TC* conformation		
	7	1·50	119	−53	−58	Multiplicity 0·543		
Ring 2*P*	1	1·50	122	18	20	14·0	57·7	371
	2	1·51	120	54	49			
	3	1·51	120	−60	−55			
	4	1·51	118	−12	−18	$\langle d \rangle = 1{\cdot}505$		
	5	1·51	118	59	65	$\langle \theta \rangle = 120{\cdot}6$		
	6	1·50	123	−18	−21	*B–TB* conformation		
	7	1·49	123	−41	−40	Multiplicity 0·457		

We wish to remark that our structural model explaining the observed disorder in the regions of the rings is approximate in the sense that we cannot exclude the presence of minor amounts of other seven-ring conformers. The tabulated entities have to be judged with care. The rings may well be too flat. This appears to be the case for ring 2*P* whose average endocyclic bond angle (120·6°) is conspicuously large. A composite drawing of a number of sections of the electron density containing two *P* rings is given in Fig. 2.

The coordinates and their estimated standard deviations are in Table 3. The e.s.d.'s of the C atoms were taken from a 'free' refinement in which no constraints were applied. They are twice as large as the corresponding e.s.d.'s resulting from the slack constraints. Table 3 also includes the multiplicities and isotropic B values of the ring C atoms.

Finally the anisotropic thermal U_{ij} values and corresponding e.s.d.'s of Ca, O and C atoms C(*P*0) and C(*K*0) are listed in Table 4. Since the structure is approximately centrosymmetric (see below) it is likely that the U_{11}, U_{22}, U_{33} and U_{12} values of pairs such as O(4′) and O(4) are the same, while corresponding U_{23} and U_{31} values are equal and opposite in sign. By constraining the U_{ij} values in this manner, the possible correlation of thermal and positional parameters was avoided.

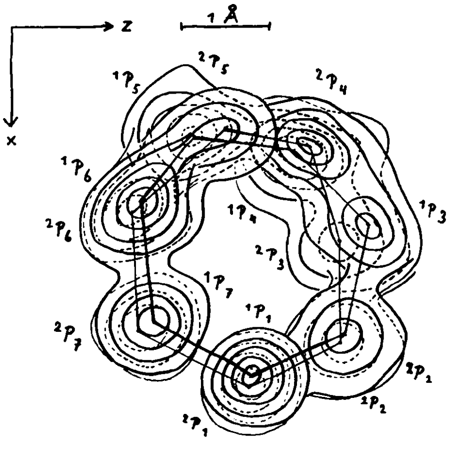

Fig. 2. Composite electron-density sections containing rings *P*. The contour lines are drawn at arbitrary equal intervals. The phases of the Fourier coefficients were calculated from the final model. The atomic positions indicated are taken from the same model.

Table 3. *Fractional coordinates* (×10⁴) *of all atoms* (*except* H) *and multiplicities and B values* (Å²) *of the ring* C *atoms*

Estimated standard deviations (10^{-3} Å) are given in parentheses.

	x	*y*	*z*	*m*	*B*
Ca	2739 (1)	3635 (1)		1	
O(1)	3312 (5)	2897 (6)	−2 (15)	1	
O(2)	2884 (7)	4794 (6)	26 (16)	1	
O(3)	2513 (15)	2726 (5)	2511 (15)	1	
O(4)	2905 (17)	813 (10)	2104 (15)	1	
O(4′)	2920 (16)	859 (10)	−2044 (15)	1	
O(5)	2074 (11)	3908 (10)	1577 (11)	1	
O(5′)	2074 (11)	3868 (10)	−1729 (11)	1	
O(6)	1804 (11)	2046 (11)	1720 (13)	1	
O(6′)	1766 (11)	2108 (11)	−1594 (13)	1	
C(*P*0)	1889 (7)	3956 (8)	−58 (15)	1	
C(1*P*1)	1420 (13)	3963 (16)	216 (32)	0·543	2·90
C(1*P*2)	1290 (40)	4414 (32)	1897 (40)	0·543	5·00
C(1*P*3)	844 (35)	4498 (37)	2301 (26)	0·543	7·78
C(1*P*4)	608 (26)	4872 (27)	695 (25)	0·543	6·53
C(1*P*5)	508 (46)	4511 (43)	−1228 (46)	0·543	7·30
C(1*P*6)	771 (27)	3947 (28)	−1952 (29)	0·543	5·40
C(1*P*7)	1222 (18)	3997 (21)	−1814 (19)	0·543	3·42
C(2*P*1)	1472 (16)	4257 (20)	−125 (47)	0·457	2·86
C(2*P*2)	1338 (34)	4680 (35)	1606 (37)	0·457	6·62
C(2*P*3)	923 (40)	4984 (43)	1604 (38)	0·457	8·93
C(2*P*4)	555 (58)	4546 (52)	1312 (57)	0·457	6·44
C(2*P*5)	524 (29)	4152 (33)	−622 (37)	0·457	6·52
C(2*P*6)	812 (40)	4319 (41)	−2312 (45)	0·457	8·23
C(2*P*7)	1261 (38)	4287 (30)	−2111 (38)	0·457	4·49
C(*K*0)	1605 (8)	2039 (8)	83 (18)	1	
C(1*K*1)	1125 (17)	2050 (18)	219 (43)	0·594	5·16
C(1*K*2)	1036 (26)	1372 (29)	1176 (29)	0·594	8·38
C(1*K*3)	638 (43)	1274 (41)	2255 (44)	0·594	10·00
C(1*K*4)	249 (40)	1422 (38)	1150 (41)	0·594	8·42
C(1*K*5)	242 (32)	2035 (37)	−160 (78)	0·594	10·00
C(1*K*6)	490 (44)	2032 (42)	−2067 (42)	0·594	9·19
C(1*K*7)	943 (23)	2125 (26)	−1872 (25)	0·594	5·78
C(2*K*1)	1154 (21)	1900 (22)	−114 (54)	0·406	5·16
C(2*K*2)	956 (37)	1730 (39)	1861 (38)	0·406	5·06
C(2*K*3)	517 (65)	1527 (61)	1946 (61)	0·406	5·75
C(2*K*4)	315 (29)	1232 (31)	104 (71)	0·406	8·84
C(2*K*5)	268 (62)	1714 (72)	−1654 (68)	0·406	6·83
C(2*K*6)	643 (50)	1770 (56)	−2981 (47)	0·406	10·00
C(2*K*7)	1032 (32)	1527 (31)	−2001 (37)	0·406	4·11

The hydrophilic part

An illustration of the hydrophilic part of the structure is given in a projection along [001] (Fig. 3). The atoms are located in slabs perpendicular to [100] and at positions $x = \pm\frac{1}{4}$. Fig. 4 shows the slab at $x = \frac{1}{4}$ in a projection along [100]. The Ca ion is surrounded by eight O atoms forming an undecahedron (see FL). The Ca—O distances (Table 5) observed in the range 2·313–2·608

Table 5. *The coordination of Ca*

	Symmetry operation	Distances (Å)
O(1)	$x,\ y,\ z$	2·405
O(2)	$x,\ y,\ z$	2·378
O(3)	$x,\ y,\ z$	2·581
O(3)	$\frac{1}{2}-x,\ y,\ -\frac{1}{2}+z$	2·608
O(5)	$x,\ y,\ z$	2·499
O(5)	$\frac{1}{2}-x,\ y,\ -\frac{1}{2}+z$	2·420
O(5′)	$x,\ y,\ z$	2·531
O(5′)	$\frac{1}{2}-x,\ y,\ -\frac{1}{2}+z$	2·313

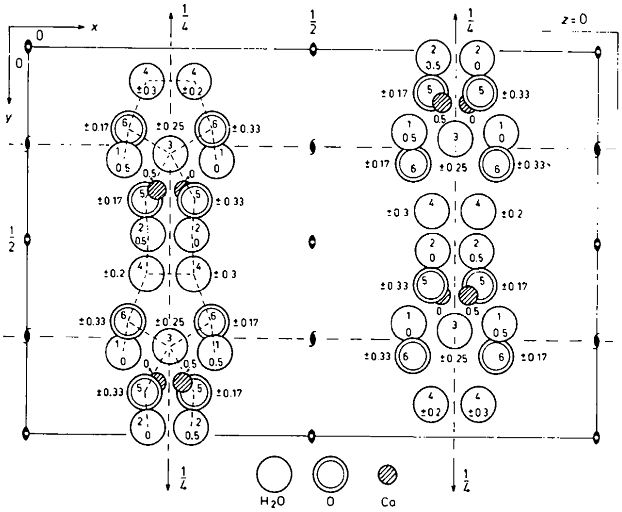

Fig. 3. Projection of the hydrophilic structure along [001]. The fractional *z* coordinates are indicated in the figure. The representation is in *Abam*.

Table 4. *Thermal parameters* U_{ij} (10^{-3} Å²) *for* Ca, C(*P*0), C(*K*0) *and* O

E.s.d.'s (10^{-3} Å²) are given in parentheses.

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{13}$	$2U_{31}$
Ca	31 (1)	37 (1)	22 (1)	2 (1)	−3 (2)	−1 (2)
O(1)	43 (3)	57 (3)	33 (4)	8 (3)	18 (8)	−5 (9)
O(2)	128 (6)	35 (3)	38 (5)	−13 (3)	−16 (8)	18 (12)
O(3)	35 (3)	40 (3)	43 (3)	−15 (7)	−8 (7)	1 (3)
O(4)	101 (4)	56 (3)	52 (4)	−10 (3)	7 (2)	−4 (3)
O(4′)	101 (4)	56 (3)	52 (4)	−10 (3)	−7 (2)	4 (3)
O(5)	41 (2)	51 (2)	19 (3)	8 (2)	2 (2)	−5 (2)
O(5′)	41 (2)	51 (2)	19 (3)	8 (2)	−2 (2)	5 (2)
O(6)	49 (3)	56 (3)	41 (3)	−5 (2)	−2 (2)	−6 (2)
O(6′)	49 (3)	56 (3)	41 (3)	−5 (2)	2 (2)	6 (2)
C(*P*0)	41 (4)	45 (4)	26 (6)	1 (3)	9 (11)	−20 (10)
C(*K*0)	55 (5)	40 (4)	39 (7)	−7 (4)	4 (11)	1 (13)

Å fully cover the reported values (compare *International Tables*, 1962). The undecahedra share faces of O atoms O(3), O(5) and O(5′) (see Fig. 4) and form columns in the direction [001]. The carboxylate ion containing atoms O(6) and O(6′) is not coordinated to the Ca ion; this group is hydrogen-bonded to O(1), O(3) and O(4′), and possibly to O(4).

The hydrogen-bond lengths and a possible scheme of donor and acceptor atoms are presented in Table 6, and are also suggested by double (full H atoms) or single (half H atoms) arrows in Fig. 4. Alternative schemes are, however, possible. One is given in parentheses in Table 6. Attempts to verify the proposed schemes by means of difference Fourier syntheses resulted in about seven peaks which are partly common to both systems. The former scheme is questionable for three reasons: (1) The angle O(5′)· · ·O(2)· · ·O(4) (see Fig. 4) has the large value of 173°. (2) The artifact to introduce disordered H positions about O(3). (3) The relatively small cohesion between O(4), O(4′) layers and O(6), O(6′) layers, which are connected by only one hydrogen bond. The last presents the difficulty that (1) the shortest-but-one O· · ·O distance [2·72 Å, *viz.* the distance between O(3) and O(5′)] is empty, (2) the longest O· · ·O distance (2·95 Å) between O(4) and O(6′) is considered to be a hydrogen bond.

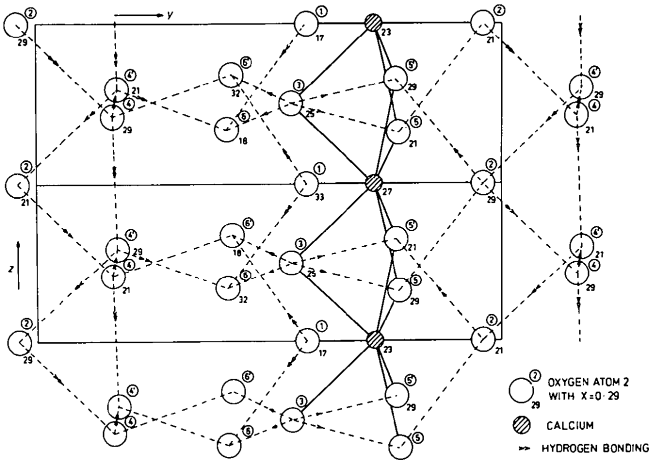

Fig. 4. A part of the hydrophilic structure in a view along [100] in the noncentrosymmetric representation *Aba*2. The dashed lines indicate possible hydrogen bonds. The double and single arrows indicate full- or half-donated H atoms.

The schemes given are in agreement with the noncentrosymmetric space group. *Abam* requires a large disordered distribution of H atoms and equal lengths of several bond pairs, *e.g.* of O(4′)· · ·O(6) and O(4)· · ·O(6′), which are 2·68 and 2·95 Å in the noncentrosymmetric structure. The difference in length between these two bonds is highly significant. Further arguments in favour of the noncentrosymmetric structure are given below.

The choice of space group

Although the hydrophilic part is approximately centrosymmetric, the distribution of H atoms over the various hydrogen bonds can be better described by means of the space group *Aba*2, while the already mentioned difference (0·263 Å) between O(4′)—O(6) and O(4)· · ·O(6′) is a strong indication that the centrosymmetric structure must be rejected. The Hamilton (1965) test leads to the same conclusion. The R and R_w indices are 9·10 and 9·79% for *Aba*2, and 9·56 and 11·33% for *Abam*. With 1726 reflexions and 359 or 303 parameters for *Aba*2 and *Abam* respectively, the ratios $R(Abam)/R(Aba2)$ and $R_w(Abam)/R_w(Aba2)$ are 1·05 and 1·16. On a significance level of 0·5% the theoretical value of the $\mathcal{R}$-factor ratio $\mathcal{R}(56, 1423, 0{\cdot}005)$ is 1·031.

The low-temperature phase

Applying X-ray diffraction and DTA, a low-temperature phase of $Ca(C_7H_{13}COO)_2.5H_2O$ was found. The DTA diagram indicates a sharp transition, apparently of the first order, at −78 °C. The unit-cell constants at −90 °C (Table 1) were roughly determined by photographic methods. A close inspection of oscillation and Weissenberg diagrams reveals: (1) The diffraction symmetry appears to be *mmm*. (2) Extinctions $h00$ for h odd and $0kl$ for k odd point to the monoclinic space group $P2_1/b$ (C_{2h}^5), with unique axis a. (3) The reflexions with $k + l$ odd are weak. (4) On cooling, the crystal invariably fragments into at least two pieces. (5) The cell dimensions at 20 and −90 °C are approximately equal.

These characteristics are possible if the positions of the Ca ions correspond to the position 8(*f*) of *Abam*, irrespective of the total structure being centro-

Table 6. *Hydrogen bonds* (Å) *per asymmetric unit in* $Ca(C_7H_{13}COO)_2.5H_2O$

A scheme of donors and acceptors is given in column four. An alternative scheme is given in parentheses.

Bond	Position of second atom	Distance (Å)	Function of first atom	
O(1)· · ·O(6)	$\frac{1}{2}-x,\ y,\ -\frac{1}{2}+z$	2·80	Donor	1 (1, *d*)
O(1)· · ·O(6′)	$\frac{1}{2}-x,\ y,\ \frac{1}{2}+z$	2·78	Donor	1 (1, *d*)
O(2)· · ·O(4)	$x,\ \frac{1}{2}+y,\ -\frac{1}{2}+z$	2·82	Donor	1 (1, *d*)
O(2)· · ·O(4′)	$x,\ \frac{1}{2}+y,\ \frac{1}{2}+z$	2·90	Acceptor	1 (1, *a*)
O(2)· · ·O(5)	$\frac{1}{2}-x,\ y,\ -\frac{1}{2}+z$	2·91	Empty	0 (0, *e*)
O(2)· · ·O(5′)	$\frac{1}{2}-x,\ y,\ \frac{1}{2}+z$	2·85	Donor	1 (0, *e*)
O(3)· · ·O(5)	$x,\ y,\ z$	2·86	Donor	$\frac{1}{2}$ (0, *e*)
O(3)· · ·O(5′)	$\frac{1}{2}-x,\ y,\ \frac{1}{2}+z$	2·72	Donor	$\frac{1}{2}$ (0, *e*)
O(3)· · ·O(6)	$x,\ y,\ z$	2·77	Donor	$\frac{1}{2}$ (1, *d*)
O(3)· · ·O(6′)	$\frac{1}{2}-x,\ y,\ \frac{1}{2}+z$	2·75	Donor	$\frac{1}{2}$ (1, *d*)
O(4)· · ·O(4′)	$x,\ y,\ z$	2·76	Donor	1 (1, *d*)
O(4)· · ·O(4′)	$\frac{1}{2}-x,\ y,\ \frac{1}{2}+z$	2·81	Donor	1 (1, *a*)
O(4)· · ·O(6′)	$\frac{1}{2}-x,\ y,\ \frac{1}{2}+z$	2·95	Empty	0 (1, *d*)
O(4′)· · ·O(6)	$\frac{1}{2}-x,\ y,\ -\frac{1}{2}+z$	2·68	Donor	1 (1, *d*)

symmetric or noncentrosymmetric. A small shift, $\pm(\Delta y + \Delta z)$, of the Ca ions in the plane $z = \frac{1}{2}$ induces a change to space group $P2_1/b$, and we note that the latter is a subgroup of the former. Since this shift can be introduced in several ways, disorder or a twinning with (001) as twinning plane seems to be unavoidable. Concomittant with this shift the angle α becomes $90 \pm \delta°$; this rationalizes why the crystal splits into two or more fragments.

In view of the postulated pseudorotation, the existence at room temperature of a dynamic equilibrium of pseudorotating cycloheptane rings might be preferred to a statistical distribution of different conformers (disorder) in a number of domains in the crystal. Unfortunately, X-ray diffraction at room temperature cannot discriminate between these alternatives. However, the large values of the thermal B parameters of the ring C atoms (between 6 and 10 Å^2) might be indicative of large thermal motions at room temperature. The observed phase transition can then be considered as a collapse of pseudorotation below −78 °C. Preliminary wide-line solid-state PMR experiments above and below −78 °C (Berendsen, 1976) confirm the transition and are indicative of certain changes in the CH_2 proton signals. A definite answer to this problem has, however, to await more extensive diffraction and NMR studies.

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