X-ray and Neutron Investigation of the Structure and Disorder in Dicalcium Barium Acrylate

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Abstract

In the room-temperature modification of dicalcium barium hexaacrylate, $Ca_2Ba(C_2H_3CO_2)_6$, two out of the four independent acrylate molecules are flip-flop disordered: their vinyl end groups perform 180° jumps about intramolecular C—C bonds. One of the disordered molecules lies on a mirror plane which relates the two flip-flop positions. From Fourier density maps we deduce a translational–librational motion of the whole molecule. This is the result of a structure analysis of X-ray and neutron data sets taken at 300 K ($R_{X-ray} = 7.6\%$, $R_{neutron} = 9.1\%$). The space group found is *Pnma* and the lattice parameters are $a = 12.496$, $b = 12.845$ and $c = 18.298$ Å. Hydrogen atomic distances between neighbouring molecules have been determined from the neutron data. They point out the important role of the hydrogen–hydrogen interaction as the origin of the molecular disorder.

1. Introduction

In the last few years, the interest in dicalcium-*M*-propionates $Ca_2M(C_2H_5CO_2)_6$, with M = Ba, Sr, Pb, has grown because of the occurrence and anomalous behaviour of some physical properties, such as ferroelectricity, ferroelasticity and phase transitions. Ferroelectricity was reported for dicalcium strontium propionate (hereafter abbreviated DSP) for the first time by Matthias & Remeika (1957) and for dicalcium lead propionate (DLP) by Takashige, Iwamura, Hirotsu & Sawada (1976). In addition, ferroelectricity was also detected in dicalcium barium propionate (DBP) under an applied hydrostatic pressure (Sawada, Kikugawa & Ishibashi, 1978; Gesi & Ozawa, 1975). The structure of DBP, which crystallizes at room temperature in the cubic space group

Fd3m, seems to be the prototype phase for this family. Structural analysis of DBP by Stadnicka & Glazer (1980) and the measurements of the diffuse X-ray scattering by Singh & Glazer (1981) have revealed molecular disorder of the propionate molecules and of the cation framework. Partial molecular disorder was reported for the DSP structure in the paraelectric room-temperature phase with the space group $P4_12_12$ or $P4_32_12$ (Glazer, Stadnicka & Singh, 1981; Itoh, Mishima & Nakamura, 1981; Machida & Yagi, 1988), as well as in the ferroelectric phase with $P4_1$ or $P4_3$ (Stadnicka, Glazer, Singh & Sliwinski, 1982; Mishima, Itoh & Nakamura, 1982; Mishima, 1984; Machida & Yagi, 1988).

The phase transition from the para- to the ferroelectric phase is an improper one. This matches well with the critical scattering of a deuterated DSP crystal found with neutrons (Yagi, Chou & Shapiro, 1990), where the correlation length of the critical scattering was found to be too small for a long range dipole–dipole interaction, which occurs in proper ferroelectric phase transitions. The deuteration of DSP has no influence on the phase transition temperature, thus indicating that the molecular motion cannot be regarded as the origin of the phase transition, as suggested by Matthias & Remeika (1957). The critical scattering of deuterated DBP shows a correlation length still smaller, but of the same order of magnitude as in DSP and the deuteration also produces a secondary effect on the phase transition temperature in DBP (Hofstätter, 1992). Thus, the origin of the phase transitions occurring in these compounds seems to be quite complex and is not completely understood.

Stadnicka & Glazer (1982) have reported the crystallization of a new class of compounds, $Ca_2M(C_2H_3CO_2)_6$, where the acrylic ion replaces the propionic group. The space group for dicalcium barium acrylate (DBA) at room temperature is *Pnma* as a result of the present investigation, and $P2_12_12_1$ for DSA and DLA. DBA shows a second-order

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phase transition at ca 382 K to the prototype cubic phase Fd3m, which has been confirmed by optical birefringence and X-ray powder investigations (Stadnicka & Glazer, 1982).

No structural analyses of any of these new compounds are available at the moment. Our main interests are in the molecular motion of the organic group in comparison to the already known molecular motion of the propionate compounds. To elucidate the molecular disorder in DBA and to obtain a better understanding of the origin of the phase transitions occurring in this crystal family, we have investigated the dicalcium barium acrylate compound with X-rays and with neutron radiation.

Fig. 1 shows the geometry of the acrylic molecule: it is planar in contrast to the propionic one. NMR studies have shown that the terminal methyl group of the propionic molecule rotates almost freely about the C2—C3 axis. This kind of disorder cannot occur in DBA because of the rigid π-bond between C2 and C3. Therefore, it should be possible to detect the H atoms by neutron investigations, which is quite complicated in the case of DBP because of the multiple disorder of the organic group, which results in an overlap of the scattering density distribution for the D atoms.

2. Experimental

Crystals were grown from aqueous solutions of the acrylate salts in stoichiometric proportions. The crystals for the X-ray investigation were grown by slow evaporation of the solution. The larger crystals for the neutron investigations were made by heating the solution in a closed glass container from 303 to
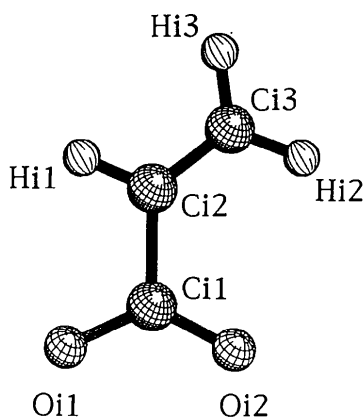

Fig. 1. The geometry of the acrylate molecule and the numbering system used throughout in this paper. Cn atoms (n = 1,2,3) belonging to the molecule i (i = 1,...4) are marked Cin, with the corresponding O atoms. In the case of the flip-flop disordered molecules i = 2,4, the atoms related by the 180° rotation are marked Cin and Cin' (cf. Fig. 2) drawn with the program SCHAKAL88 (Keller, 1989).

Table 1. Experimental data and R factors

	X-ray	Neutrons
Crystal shape	Sphere	Octahedron
Crystal size	$\varnothing$ 0.4 mm	$V = 35$ mm^3
Wavelength (Å)	Mo $K\alpha$ 0.709	0.834
Scan modus	$\omega/2\theta$	ω, PSD*
θ_{max} (°)	32	30
Collected reflections	11 264	3299
Unit reflections		
used in the analysis;	5632	2262
all F's with $\sigma(F)/F \leq 0.25$	3938	1782
Data R factor	0.014	0.024
Intensity correction	Lorentz–polarization	Lorentz
Absorption coefficient (cm^{-1})	16.3	1
Lattice constants a (Å)	12.496 (2)	—
b (Å)	12.845 (3)	—
c (Å)	18.298 (2)	—
Number of parameters	178	290
R	0.0761	0.0912
R_w	0.0561	0.0698
R_G	0.0513	0.0596
GOF	4.57	3.82

* Position Sensitive Detector.

$$R = (\Sigma|F_o - F_c|)/\Sigma F_o; \quad R_w = [\Sigma w^{1/2}(|F_o - F_c|)]/\Sigma w^{1/2}F_o; \quad R_g = \{[\Sigma w(F_o - F_c)^2]/\Sigma wF_o^2\}^{1/2}; \quad w = k/[\sigma^2(F_{obs})]; \quad GOF = w\sigma^2(F_{obs}).$$

318 K with a heating rate of 1 K/day: this procedure is appropriate because the solubility decreases with increasing temperature. The crystals obtained are clear and octahedral in shape. The X-ray data were collected on a CAD-4 diffractometer, the neutron data at the diffractometer D9 of the Institute Laue–Langevin in Grenoble. In the X-ray case, Friedel pairs were measured at 300 K. A total of 3299 reflections were measured in the neutron case, 1718 at two equivalent positions and the remaining reflections only once. Further experimental details are given in Table 1.

3. Data analysis

3.1. X-ray data, Pnma

Due to the disorder of the acrylate ions, which was anticipated but unknown in detail, the crystal structure analysis had to be performed stepwise. Two space groups are compatible with the observed extinction rules: Pnma and Pn2₁a. The calculations were started with the centrosymmetric space group Pnma. We used SHELX76 (Sheldrick, 1976), scattering factors for neutral atoms [International Tables for X-ray Crystallography (1974, Vol. IV; anomalous contributions were taken into account] and a first guess of the structure containing only the cations at the positions known approximately from the cubic parent structure of DBP. This first refinement gave $R = 22\%$ and the Fourier map calculated with the phase factors computed from this model showed that two out of the four independent molecules in the unit cell are well ordered. From the

other two molecules, all atoms with the exception of Ci3′ (Fig. 1) could be localized. After a second step, difference Fourier maps show the split nature of the atoms C23/C23′ and C43/C43′ belonging to molecules (2) and (4), respectively. Figures showing the electron densities have been deposited; nuclear scat-

tering density plots are given in Fig. 2. The split positions observed can be transformed one into the other by 180° rotations about the molecular axis Ci1—Ci2: this is the type of disorder called "flip-flop" in the present paper. The electronic density of the atoms C22 and C42 turned out to be anoma-
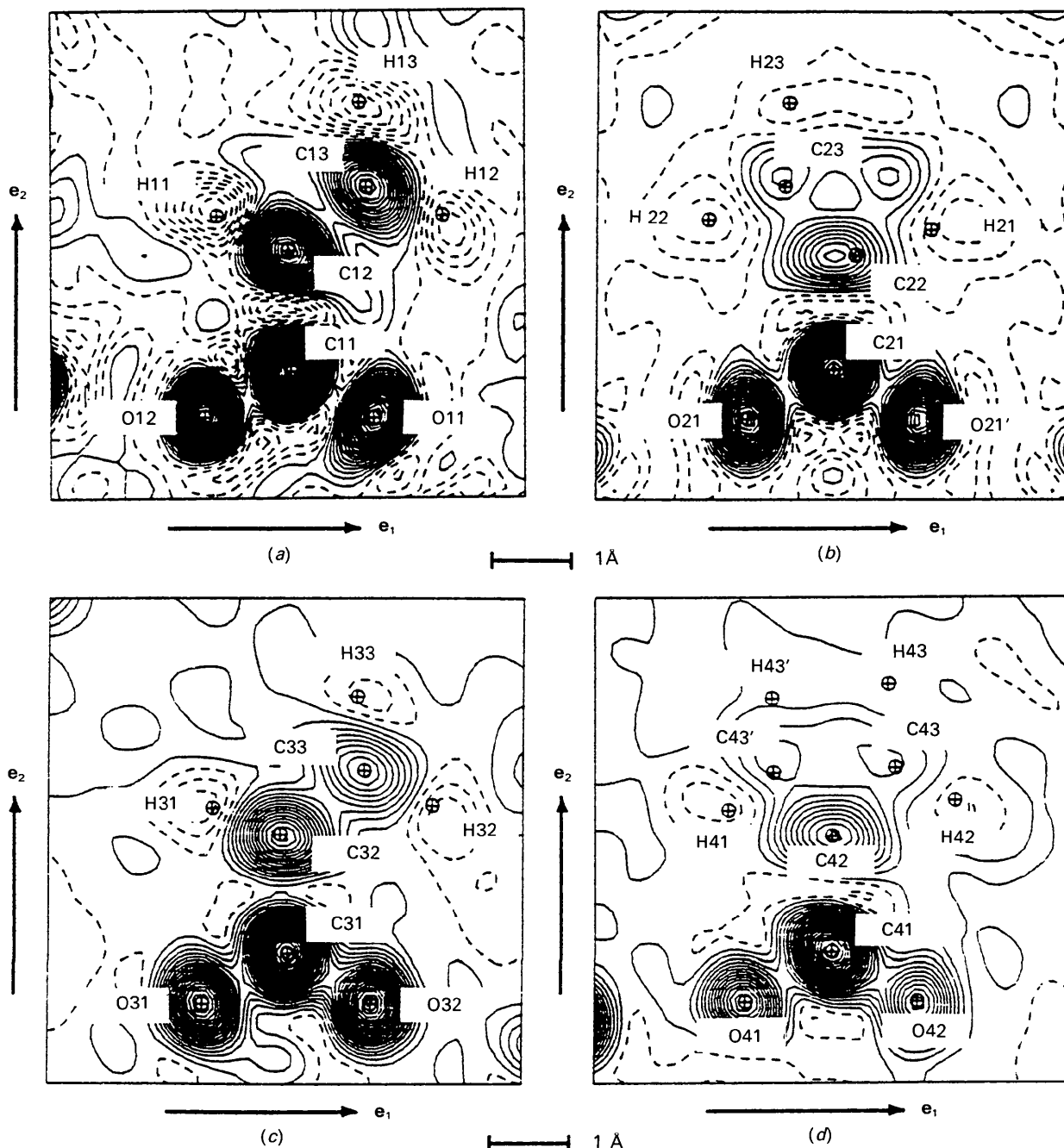

Fig. 2. Observed scattering density distribution of the four independent molecules in DBA, calculated from the refinement of the neutron data set. Projection into the molecular plane with an integration depth $\delta = \pm 1$ Å. (a) and (c) show the ordered molecules (1) and (3), (b) the disordered molecule $i = 2$ occupying a symmetric site and (d) the disordered molecule $i = 4$ which occupies a general site.

lously widely spread out and, therefore, split positions were also tentatively introduced for these atoms. This suggestion was supported by the data, in the final refinement, for the C22's, but not for the C42's, which remained single.*

An attempt to repeat this analysis with the non-centrosymmetric space group $Pn2_1a$ resulted in high correlations among the parameters and the fitting procedure did not converge. In addition, the statistical test performed using $SHELX76$ indicates that the structure is centrosymmetric. We thus conclude that the average disordered structure of $Ca_2Ba(C_2H_3CO_2)_6$ at 300 K has the space group $Pnma$.

3.2. Neutron data

The final parameters for Ba, Ca, C and O from the X-ray analysis were used as the starting values. Fig. 2 shows the scattering density distribution of the four independent molecules, referred in each case to a local coordinate system, of which the two basis vectors e_1 and e_2 lie in the plane of the molecule. Broken lines refer, due to the negative scattering length, to hydrogen nuclei. In the case of the disordered molecules (2) and (4), the densities of the protons Hi1 and Hi2 overlap heavily. For the mirror symmetric density of molecule (2), only one of the two positions of H21 and H22 is shown in Fig. 2. Complete lists of the parameters have been deposited.* A summary of R values and the numbers of parameters and GOF's is included in Table 1.

The mean-square amplitudes of the C and O atoms derived from X-ray and neutron data, respectively, are given in Table 2 and are discussed in §4.

4. Discussion

4.1. Description of the structure

We start our description from the well known DBP parent structure (Stadnicka & Glazer, 1980), which is face-centred cubic with a lattice constant $a_c \approx 18$ Å. The Ba ions are distributed over the sites of a diamond structure and each Ba ion is coordinated tetrahedrally along body diagonals by four Ca ions. Along the $\pm x$, $\pm y$, $\pm z$ directions, on the other hand, the Ba ions have six propionate ions as neighbours, with two O atoms of each propionate group pointing towards Ba. The Ca^{2+} ions are surrounded by six O atoms belonging to six different propionate molecules: the O atoms form a trigonal antiprism. The Ca ions are thus linked together by (O—C—O) bridges from the carboxylic group.

* Lists of anisotropic displacement parameters, H-atom coordinates and complete geometry and electron-density diagrams have been deposited with the IUCr (Reference: SE0115). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Thermal parameters $\langle u^2 \rangle$ (Å²) of the C and O atoms in the molecular coordinate system e_1, e_2, e_3*

	X-ray			Neutrons		
	$\langle u^2 \rangle_{e_1}$	$\langle u^2 \rangle_{e_2}$	$\langle u^2 \rangle_{e_3}$	$\langle u^2 \rangle_{e_1}$	$\langle u^2 \rangle_{e_2}$	$\langle u^2 \rangle_{e_3}$
C11	0.083 (6)	0.075 (6)	0.092 (6)	0.047 (2)	0.043 (2)	0.097 (2)
C12	0.156 (3)	0.059 (3)	0.105 (3)	0.109 (5)	0.052 (5)	0.163 (5)
C13	0.274 (9)	0.164 (9)	0.162 (9)	0.186 (9)	0.094 (9)	0.166 (9)
O11	0.088 (5)	0.199 (5)	0.142 (5)	0.055 (4)	0.101 (4)	0.153 (4)
O12	0.083 (4)	0.079 (4)	0.124 (4)	0.049 (3)	0.050 (3)	0.122 (3)
C21	0.072 (6)	0.061 (6)	0.209 (6)	0.057 (3)	0.042 (3)	0.117 (3)
C22	0.19 (1)	0.04 (1)	0.45 (1)	0.12 (2)	0.04 (2)	0.37 (2)
C23	0.28 (1)	0.07 (1)	0.72 (1)	0.14 (1)	0.11 (1)	0.61 (1)
O21	0.058 (3)	0.091 (3)	0.235 (3)	0.052 (2)	0.079 (2)	0.148 (2)
C31	0.094 (5)	0.067 (5)	0.136 (5)	0.179 (7)	0.053 (7)	0.407 (7)
C32	0.216 (8)	0.115 (8)	0.309 (8)	0.11 (2)	0.07 (2)	0.41 (2)
C33	0.319 (9)	0.145 (9)	0.326 (9)	0.18 (2)	0.29 (2)	0.22 (2)
O31	0.075 (4)	0.094 (4)	0.173 (4)	0.085 (3)	0.089 (3)	0.148 (3)
O32	0.064 (3)	0.090 (3)	0.165 (3)	0.074 (2)	0.058 (2)	0.127 (2)
C41	0.088 (5)	0.094 (5)	0.187 (5)	0.060 (2)	0.043 (2)	0.099 (2)
C42	0.256 (8)	0.139 (8)	0.598 (8)	0.128 (4)	0.041 (4)	0.230 (4)
C43	0.174 (9)	0.176 (9)	0.530 (9)	0.23 (1)	0.11 (1)	0.27 (1)
C43'	0.228 (9)	0.171 (9)	0.215 (9)	0.053 (3)	0.068 (3)	0.129 (3)
O41	0.094 (3)	0.119 (3)	0.195 (3)	0.043 (3)	0.064 (3)	0.130 (3)
O42	0.090 (3)	0.087 (3)	0.179 (3)	0.064 (2)	0.046 (2)	0.135 (2)

Topologically, the orthorhombic structure of DBA is derived from DBP by doubling the primitive volume $a_c^3/4$ of the face-centred cubic cell and setting $a_o \approx (a_c + b_c)/2$, $b_o \approx (a_c - b_c)/2$ and $c_o \approx c_c$. The octahedron of the acrylate molecules around Ba is heavily deformed, whereas the oxygen octahedron surrounding Ca stays essentially undistorted with,
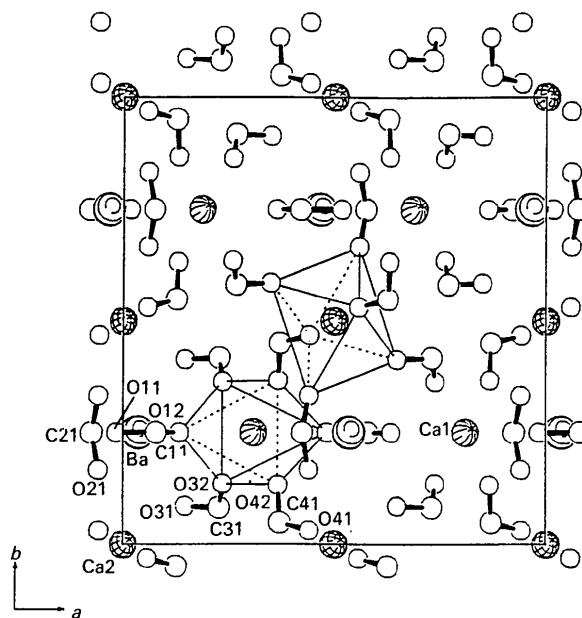

Fig. 3. Projection of the structure (one unit cell) of DBA along c. Beyond the cations only the atoms of the carboxylic groups are drawn. Molecules (1) and (2) lie with their molecular planes on and perpendicular to mirror planes, respectively. Molecules (3) and (4) occupy general sites. One octahedron with O atoms around Ca(1) and one around Ca(2) are drawn, using the program $SCHAKAL88$ (Keller, 1989).
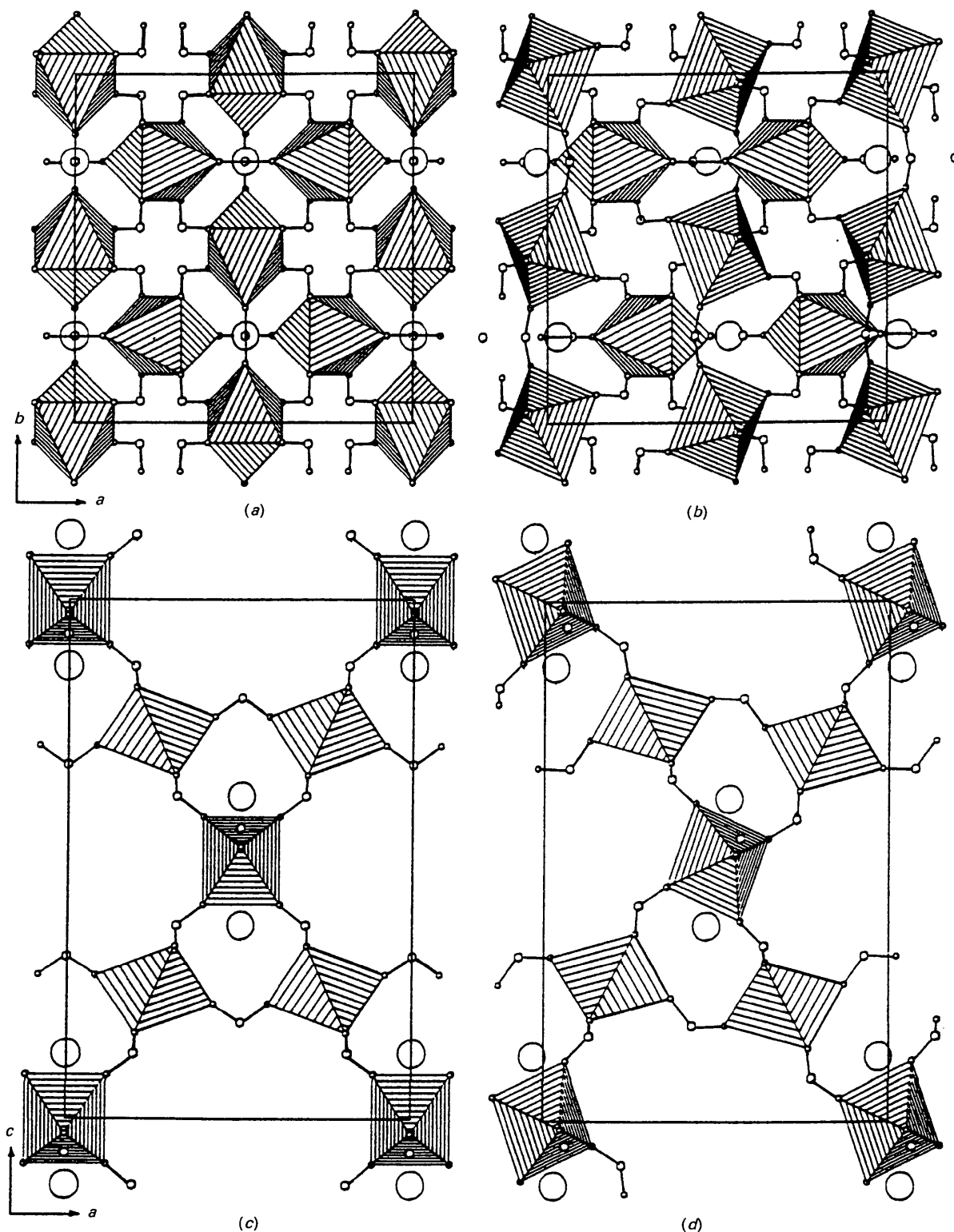
$Ca_2Ba(C_2H_3CO_2)_6$

Fig. 4. The rotation and shift of the O octahedra around Ca caused by the transition from the cubic (represented by the DBP compound) to the orthorhombic (represented by the DBA compound) symmetry. The octahedra are linked by Ci1 of the carboxylic groups. (a) and (c) show the arrangement in the pseudo-cubic symmetry, (b) and (d) in the orthorhombic symmetry. The Ba atoms are marked by large circles. Drawn using the program STRUPLO (Fischer, 1985).

Table 3. *Intramolecular bond distances* (Å) *and angles*
(°) *of the* C, O *backbone in DBA*

	X-ray	Neutrons
C11—C12	1.47 (1)	1.488 (8)
C12—C13	1.27 (2)	1.27 (1)
O11—C11	1.18 (1)	1.192 (6)
O12—C11	1.25 (1)	1.257 (7)
C21—C22	1.49 (2)	1.44 (2)
C22—C23	1.21 (4)	1.22 (3)
C21—O21	1.227 (7)	1.218 (5)
C31—C32	1.49 (2)	1.475 (8)
C32—C33	1.31 (2)	1.33 (1)
O31—C31	1.22 (1)	1.256 (5)
O32—C31	1.23 (1)	1.224 (6)
C41—C42	1.47 (2)	1.45 (1)
C42—C43	1.24 (3)	1.19 (3)
C42—C43'	1.10 (3)	1.11 (3)
O41—C41	1.25 (1)	1.227 (6)
O42—C41	1.21 (1)	1.231 (5)
O11—C11—O12	126 (1)	125 (1)
O11—C11—C12	122 (1)	120 (1)
O12—C11—C12	112 (1)	115 (1)
C11—C12—C13	125 (1)	127 (1)
O21—C21—O21'	121 (0)	121 (0)
O21—C21—C22	127 (2)	130 (1)
O21'—C21—C22	111 (2)	109 (1)
C21—C22—C23	118 (2)	123 (2)
O31—C31—O32	122 (1)	121 (0)
O31—C31—C32	113 (1)	115 (0)
O32—C31—C32	125 (1)	124 (1)
C31—C32—C33	117 (1)	123 (1)
O41—C41—O42	122 (1)	122 (0)
O41—C41—C42	119 (1)	119 (1)
O42—C41—C42	120 (1)	120 (1)
C41—C42—C43	128 (2)	135 (2)
C41—C42—C43'	133 (3)	134 (3)

Table 4. *Intramolecular bond distances* (Å) *and angles*
(°) *in DBA*

C12—H11	1.03 (2)
C13—H12	1.04 (3)
C13—H13	1.04 (2)
C22—H21	1.07 (7)
C23—H22	1.18 (6)
C23—H23	1.02 (4)
C32—H31	0.96 (2)
C33—H32	0.98 (3)
C33—H33	0.92 (2)
C42—H42	1.61 (3)
C42—H41	1.33 (3)
C43—H42	0.86 (4)
C43—H43	1.09 (6)
C43'—H41	0.78 (4)
C43'—H43'	0.94 (5)
C11—C12—H11	117 (1)
H11—C12—C13	117 (1)
H12—C13—H13	114 (3)
C21—C22—H21	118 (3)
H21—C22—C23	118 (4)
H22—C23—H23	113 (4)
C31—C32—H31	114 (1)
H31—C32—C33	123 (2)
H32—C33—H33	122 (3)
C41—C42—H42	106 (1)
C41—C42—H41	103 (1)
H42—C42—C43'	113 (2)
H41—C42—C43	118 (2)
H43—C43—H42	121 (6)
H41—C43'—H43'	131 (8)

however, a shift and a rotation with respect to the cubic arrangement. The final structure is shown in Fig. 3 and a comparison between the orientation of the polyhedra in the cubic parent form and the actual structure is given in Figs. 4(*a–d*).

The distances between the cations and the O atoms have been deposited.* The Ba—O distances vary from 2.833 to 3.045 Å, with the exception of Ba—O(11), which is 3.66 Å. All these distances exceed the sum of the pure ion radii of Ba and O [$r_{Ba}(1.35)$ + $r_O(1.4) = 2.75$ Å]. The Ca—O distances are generally slightly less (2.274–2.331 Å) than the sum of the ionic radii [$r_{Ca}(0.99) + r_O(1.4) = 2.39$ Å]. This points out the dominant role of the Ca—O bond for the stability of the structure in the compounds of this family.

The intramolecular bond distances, as given in Tables 3 and 4, for the ordered molecules are in good agreement with those found in crystalline acrylic acid (Higgs & Sass, 1963; Chatani, Sakata & Nitta, 1963), whereas those for the disordered molecules differ, in part remarkably, from the expected ones.

4.2. Thermal parameters and molecular disorder

Due to the heavy disorder and the overlap of the electron densities, the thermal parameters derived

* See deposition footnote.

from X-ray data cannot be interpreted in terms of oscillations about equilibrium positions. Neutrons see the point-like nuclei: thermal data calculated from neutron observations are, therefore, more accessible for analysis. As a general feature (Table 2), we find appreciable-to-strong anisotropy of all the C atoms, C*im*: the out-of-plane motion along e_3 surpasses the in-plane motion. This observation also applies for the O atoms. This means that the carboxylic groups bridging Ca—Ca pairs oscillate anisotropically and preferentially along directions which are at the same time perpendicular to the bond direction and to the molecular plane.

There is a characteristic difference among the two disordered molecules (2) and (4). For molecule (2), the mean-square amplitudes $\langle u^2 \rangle_{e_3}$ of the C atoms increase monotonically with their distance from the carboxylic group. This is an indication that all parts of the molecule perform large amplitude angular in-phase oscillations in the e_2–e_3 plane, combined with the flip-flop 180° jumps of the H22—C23—H23 end groups. In molecule (4), on the other hand, the intermediate C42 atom is spread out along e_3 (Table 2) as wide as the end group C43 atom and less wide than C43'. We conclude, therefore, that the end group of molecule (4) is more restricted in space than the end group of molecule (2) and that, in contrast to the in-phase angular oscillation of molecule (2), C42 and C43 may move anti-phase along e_3 when the flip-flop jump occurs. This interpretation is supported by Fourier sections (Hofstätter, 1992) show-

ing the scattering density distributions of molecules (2) and (4) in the local e_1–e_3 planes. From these densities it also becomes clear that the actual motions are highly anharmonic: the contours of equal probability density deviate strongly from the elliptical form expected for harmonic oscillations.

Because of the exceptional occurrence of ordered and disordered molecules (two molecules are in an ordered state, one is disordered in a symmetrical position and one is disordered in a general position), one can simulate the flip-flop motion of the vinyl groups, by reflecting the scattering density distribution of the ordered molecules (1) and (3) at a pseudo-mirror plane, which lies in the e_2–e_3 plane of the molecular coordinate system and passes through Ci1 (Fig. 5). A comparison of these pseudo-disordered molecules with the actual disordered molecules (Fig. 2) shows that the Ci3—Ci3' distances differ from one another: they are larger for the pseudo-disordered molecules. This means that the flip-flop motion conserves the centre of mass of the molecule.

4.3. Origin of the molecular disorder: frustration of hydrogen bonds

In order to obtain a better understanding of the origin of the flip-flop motion, which is coupled with a librational motion around an axis perpendicular to the molecular plane, we look at six neighbouring molecules pointing with their vinyl end groups towards the empty centre of a distorted octahedron

(Fig. 6). The distances between H atoms belonging to molecules (1) and (3) are generally larger than twice the van der Waals' radius (2.4 Å) of H atoms. However, some hydrogen distances between molecules (2) and (4) become smaller than the van der Waals' distance, for every molecular arrangement.

In Fig. 6, molecules A, B and E are of the ordered type ($i = 1,3$) and molecules C, D and F belong to the disordered types ($i = 2,4$). Suggesting molecule C ($i = 4$) is, at a given time, in one of its two possible configurations, denoted by black circles in Fig. 6, then molecule F ($i = 2$) is forced to occupy the sites which are also denoted by black circles. As a consequence, molecule D ($i = 4$) cannot occupy any of its two possible configurations in such a way that steric hindrance would be avoided either between molecules D and F or between molecules D and C. This results in a frustration of the orientations of molecules D, F and C caused by steric hindrance between H atoms of neighbouring molecules. It is well known from other frustrated systems, e.g. the spin glasses, that this kind of topological disorder gives rise to relaxational changes of local configurations which appear, for instance, in the quasielastic neutron scattering.

In passing, we arrive at the following conclusions. The room-temperature phase of $Ca_2Ba(C_2H_3CO_2)_6$ is unusual with respect to the molecular order/disorder: out of the four symmetrically independent molecules in the unit cell, two are well ordered, one shows a
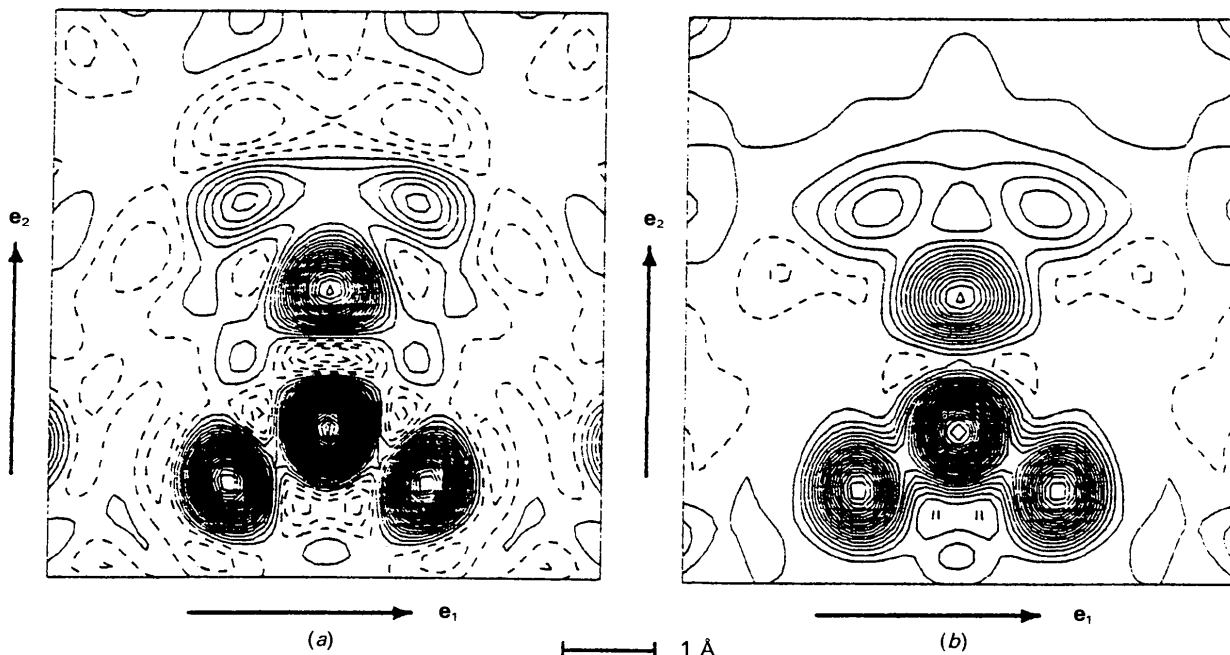

Fig. 5. Simulation of a 180° rotation of the vinyl group around the molecular axis, generated from the density distribution of the ordered molecules (a) (1) and (b) (3). Scaling of contours as in Fig. 2.
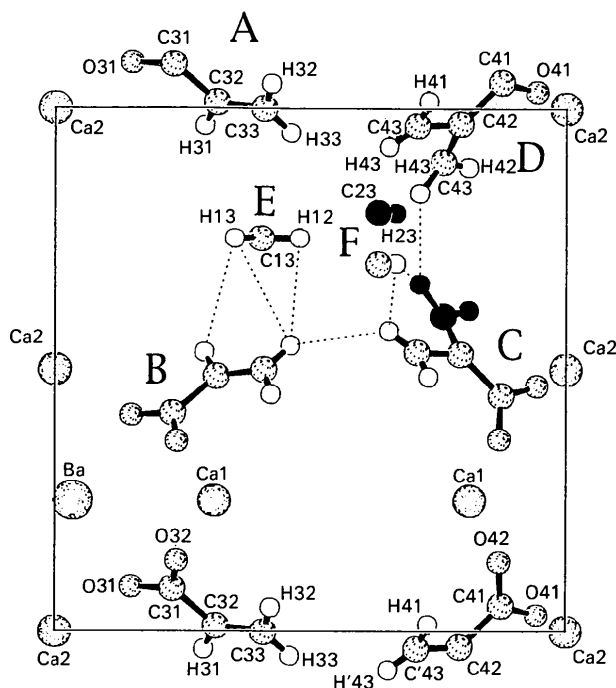
Fig. 6. Six nearest acrylate molecules point with their vinyl groups towards the empty centre of a distorted octahedron. Molecules A, B and E are in an ordered state. No arrangement of the disordered molecules C, D and F is possible without steric hindrance. Further explanations are given in the text. Drawn using the program *SCHAKAL*88 (Keller, 1989).

mirror symmetric combined flip-flop librational disorder and the fourth is disordered in the same way, but without the mirror symmetry.

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Structure of *trans,trans*-4,4′-Di(methoxycarbonylimino)dicyclohexylmethane: a Model for *trans,trans*-4,4′-Diisocyanatodicyclohexylmethane/1,4-Butanediol-Based Units in Polyurethane Hard Segments

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Abstract

$C_{17}H_{30}N_2O_4$, monoclinic, $P2_1/n$, $a = 17.963\,(4)$, $b = 6.290\,(2)$, $c = 18.214\,(4)$ Å, $\beta = 116.59\,(3)°$, $V = 1840.3\,(8)$ Å^3, $Z = 4$, $D_m = 1.16$, $D_x = 1.178$ Mg m^{-3}, $T = 173$ K, $F(000) = 712$, final weighted $wR = 0.039$ for 3231 observed independent reflections. The bridge C—CH$_2$—C angle of the V-shaped title compound is 116.1 (2)°. Both cyclohexyl rings have

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