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# The Crystal and Molecular Structure of *trans*-1,2-Bis-(2-carboxymethyl-2-propyl)cyclohexane

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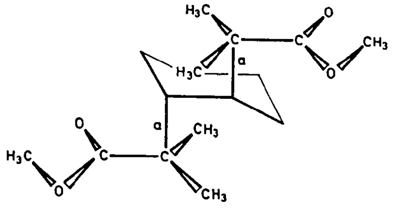
The crystal structure of *trans*-1,2-bis-(2-carboxymethyl-2-propyl)cyclohexane, $C_{16}H_{28}O_4$, has been determined from three-dimensional X-ray diffraction data. The crystals are orthorhombic, space group *Pbcn*, with unit-cell dimensions $a=9{\cdot}944$, $b=8{\cdot}361$, $c=18{\cdot}951$ Å. With $Z=4$ and a measured density $D_m=1{\cdot}21$ g cm$^{-3}$ the molecules must lie on twofold axes. The structure was solved by direct methods and refined by full-matrix least-squares calculations with anisotropic thermal parameters for the heavy atoms and isotropic thermal parameters for the hydrogen atoms to a residual of 5·5% for the 1307 observed structure factors. The cyclohexane rings form strings along the [110] direction. The strings are held together by non-bonding contacts between the 2-carboxymethyl-2-propyl groups. The six-membered ring is a strongly distorted chair. The axial substituents are bent outwards from the centre of the ring. The exocyclic CCCC torsion angle is 134·5° and the mean endocyclic torsion angle is 48·5°. The $C_\alpha(C_\beta)$COOC-fragment is planar, the carbonyl oxygen being nearly eclipsed with a $C_\beta$ atom: $\angle C_\beta C_\alpha = 6{\cdot}2°$. The $C(1)C_\alpha$ bond distance $= 1{\cdot}576$ Å. The C(1)C(2) ring bond distance is 1·562 Å.

## Introduction

The effects of an equatorial substituent on the shape of the cyclohexane ring have been well studied (Altona & Sundaralingam, 1970; Remijnse, 1971; van Koningsveld, 1972).

The impact of an axial group differs appreciably from that of an equatorial group (Allinger, Miller, Van-Catledge & Hirsch, 1967). Strong evidence in favour of a twist form is reported for *trans*-1,3-di-t-butylcyclohexane and for *cis*-1,4-di-t-butylcyclohexane (Allinger & Freiberg, 1960; van Bekkum, Hoefnagel, de Lavieter & van Veen, 1967; Allinger, Hirsch, Miller, Tyminski & Van-Catledge, 1968; Remijnse, 1971).

N.m.r. and infrared spectroscopy measurements of *trans*-1,2-bis(2-carboxymethyl-2-propyl)cyclohexane (=TRANS) show that the compound in solution does not exist in a diequatorial chair conformation but exists, at least partly, in a twist conformation (van de Graaf, 1972).



TRANS

The conformation of TRANS in the crystal is reported here.

## Experimental

A sample of the compound, $C_{16}H_{28}O_4$, was kindly provided by A. van Wijk from this laboratory.

Rhombohedral crystals of TRANS were obtained by recrystallization from petroleum spirit (60–80°) at room temperature. The unit-cell dimensions, deduced from measurements on a Nonius-automatic single-crystal diffractometer (Cu $K\alpha_1=1{\cdot}54051$ Å) are $a=9{\cdot}944$ (3), $b=8{\cdot}361$ (3) and $c=18{\cdot}951$ (5) Å. The systematic extinctions ($0kl$ for $k$ odd, $h0l$ for $l$ odd and $hk0$ for $h+k$ odd) are consistent with the space group *Pbcn*. The only reasonable calculated density is for $Z=4$, *viz.* 1·202 g cm$^{-3}$, the molecules thus lie on twofold axes. The density measured by flotation is $D_m=1{\cdot}21$ g cm$^{-3}$.

Three-dimensional intensity data were collected with the diffractometer using Cu $K\alpha$ radiation and the $\theta/2\theta$ scan mode with a maximum $\theta$-value of 69·47°. High intensities were reduced by nickel filters. The background intensity was measured at each side of a reflexion for half the scan time. Depending on the intensity the reflexions were scanned from 1 to 10 times, thereby approaching fixed-count strategy. The intensities of two standard reflexions, collected after every 25 reflexions, remained constant throughout the data collection. From the 1478 measured reflexions 161 had intensities smaller than $2{\cdot}85\sigma(I)$ (Stout & Jensen, 1968) and were left out during the whole refinement.

The crystal had approximate dimensions of $0{\cdot}5\times0{\cdot}6\times0{\cdot}4$ mm and was mounted about the $b$ axis. In the reduction of intensities to structure factors no correction for absorption was made. [$\mu$(Cu $K\alpha$) = 6·9 cm$^{-1}$].

## Structure determination and refinement

All computations were made using the computer programs from *X-RAY*70 (Stewart, Kundell & Baldwin, 1970). The atomic scattering factors used were those of C, O, H, as given in *International Tables for X-ray crystallography* (1969). The calculations were carried out attributing equal weights to all observed reflexions.

An overall temperature factor ($B = 3{\cdot}6$ Å$^2$) and scaling factor were determined by Wilson's (1942) method.

The structure was solved by the direct phase determining method based on the symbolic addition method for centrosymmetrical structures (Karle & Karle, 1966). Normalized structure factor computations, $\sum_2$ relations and the symbolic addition procedure were performed and the resulting $E$-map revealed all the heavy atoms in the asymmetric unit.

A full-matrix least-squares refinement of the coordinates and anisotropic temperature factors of the

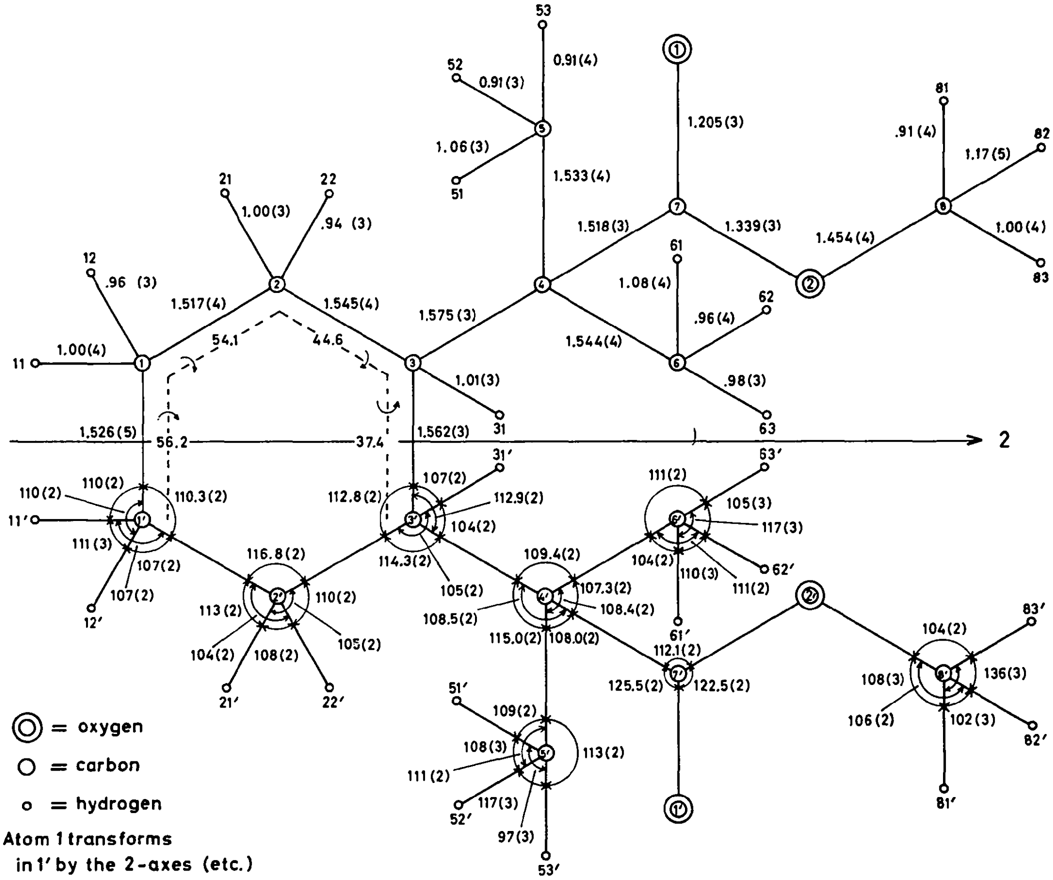


Fig. 1. Bond lengths, bond angles and ring torsion angles in TRANS with e.s.d.'s in brackets.

Table 1. *Final parameters with e.s.d.'s in parentheses*

The fractional atomic coordinates are multiplied by $10^4$ for the non-hydrogen atoms and by $10^3$ for the hydrogen atoms. The expression for the anisotropic thermal parameters (Å$^2 \times 10^3$) is:

$$\exp\left[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+a^*b^*hkU_{12}+b^*c^*klU_{23}+c^*a^*lhU_{31})\right].$$

The isotropic factors ($U$) are in Å$^2 \times 10^3$

| | $x/a$ | $y/b$ | $z/c$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| C(1) | 383 (3) | 256 (3) | 2151 (2) | 59 (2) | 31 (2) | 58 (2) | 3 (1) | 6 (2) | −6 (1) |
| C(2) | 1232 (3) | 1758 (3) | 2088 (1) | 36 (1) | 38 (1) | 39 (1) | 7 (1) | 3 (1) | 0 (1) |
| C(3) | 495 (2) | 3372 (3) | 2180 (1) | 24 (1) | 30 (1) | 28 (1) | 0 (1) | 0 (1) | 0 (1) |
| C(4) | −161 (2) | 4043 (3) | 1484 (1) | 28 (1) | 36 (1) | 28 (1) | 0 (1) | −4 (1) | 0 (1) |
| C(5) | −1544 (3) | 3344 (4) | 1303 (2) | 35 (1) | 63 (2) | 40 (2) | −9 (1) | −10 (1) | 3 (2) |
| C(6) | −296 (3) | 5878 (3) | 1540 (1) | 45 (2) | 39 (2) | 38 (1) | 9 (1) | 3 (1) | 6 (1) |
| C(7) | 779 (3) | 3695 (3) | 871 (1) | 40 (1) | 38 (1) | 28 (1) | 0 (1) | −3 (1) | 0 (1) |
| C(8) | 3002 (3) | 4012 (5) | 432 (2) | 51 (2) | 67 (2) | 38 (2) | 0 (2) | 19 (1) | −4 (2) |
| O(1) | 512 (2) | 2877 (3) | 367 (1) | 60 (1) | 77 (2) | 40 (1) | −9 (1) | −5 (1) | −25 (1) |
| O(2) | 1980 (2) | 4395 (2) | 954 (1) | 39 (1) | 49 (1) | 36 (1) | −7 (1) | 11 (1) | −11 (1) |

Table 1 (*cont.*)

| | *x* | *y* | *z* | *U* |
|---|---|---|---|---|
| H(11) | 101 (3) | −68 (4) | 212 (2) | 38 (9) |
| H(12) | −23 (3) | 27 (4) | 176 (2) | 27 (9) |
| H(21) | 170 (3) | 185 (3) | 162 (2) | 17 (7) |
| H(22) | 189 (3) | 164 (3) | 244 (2) | 20 (8) |
| H(31) | 123 (3) | 418 (3) | 229 (1) | 11 (7) |
| H(51) | −184 (3) | 375 (3) | 80 (2) | 25 (8) |
| H(52) | −217 (3) | 367 (4) | 162 (2) | 26 (9) |
| H(53) | −152 (3) | 228 (5) | 119 (2) | 35 (10) |
| H(61) | −65 (4) | 623 (5) | 103 (2) | 63 (13) |
| H(62) | 56 (4) | 637 (4) | 164 (2) | 34 (10) |
| H(63) | −86 (3) | 617 (3) | 194 (2) | 19 (8) |
| H(81) | 269 (4) | 435 (5) | 0 (2) | 60 (13) |
| H(82) | 299 (5) | 263 (6) | 37 (2) | 95 (17) |
| H(83) | 371 (5) | 486 (6) | 50 (2) | 72 (14) |

heavy atoms, using the 1317 observed (non-zero) reflexions, converged to $R(=\sum||F_o|-|F_c||/\sum|F_o|\times 100)=$ 13·2%. At this stage in the refinement, hydrogen atom positions were obtained from peaks on an $F_o-F_c$ Fourier synthesis; these parameters together with isotropic temperature factors from the parent heavy atoms were included and refined in subsequent cycles. Inspection of the structure factors revealed that 10 very strong low-order reflexions were subject to extinction or to experimental errors. Continued refinement with omission of these 10 reflexions reduced *R* to 5·5%. The ratios of the shifts to the estimated standard deviations in the last least-squares cycle, including all parameters refined, were less than 0·1. A final difference synthesis showed a residual density between −0·24 and +0·24 e $Å^{-3}$.

The final atomic coordinates, the temperature factors and their standard deviations as calculated from the full-matrix least-squares refinement are given in Table 1. A list of $F_o$ and final $F_c$ values is available from the laboratory.

## Results

Atomic numbering, bond angles, bond distances, endocyclic CCCC torsion angles, e.s.d.'s and the orientation of the twofold axes are shown in Fig. 1. Bond lengths and angles were calculated without correcting for anisotropic thermal motion.

The geometry rather strongly deviates from an ideal chair; the C(3)C(3′) and C(3)C(4) bond distances are lengthened (Fig. 1) and the substituents are bent outwards from the centre of the ring: the C(4)C(3)C(3′)-C(4′) torsion angle is 134·5° [Fig. 2(*a*)]. The Newman

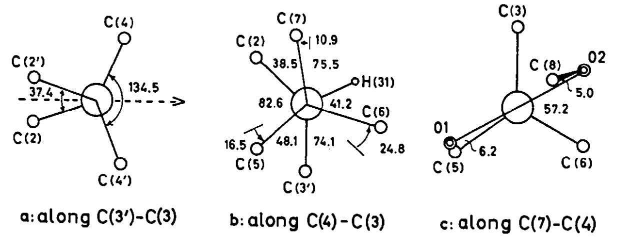


Fig. 2. Newman projections (*a*) along C(3)C(3′) showing exocyclic CCCC torsion angle, (*b*) along C(4)C(3) showing the orientation of the 't-Bu' group, (*c*) along C(7)C(4) showing the orientation of the carboxymethyl group.

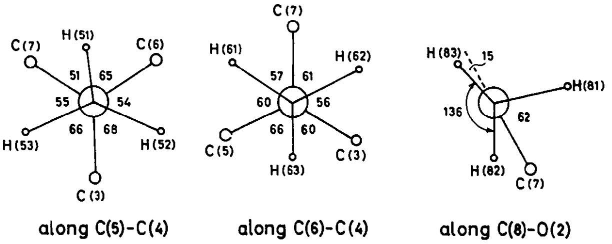


Fig. 3. Newman projections (*a*) along C(5)C(4), (*b*) along C(6)C(4), (*c*) along C(8)O(2), showing the orientation of the methyl groups.

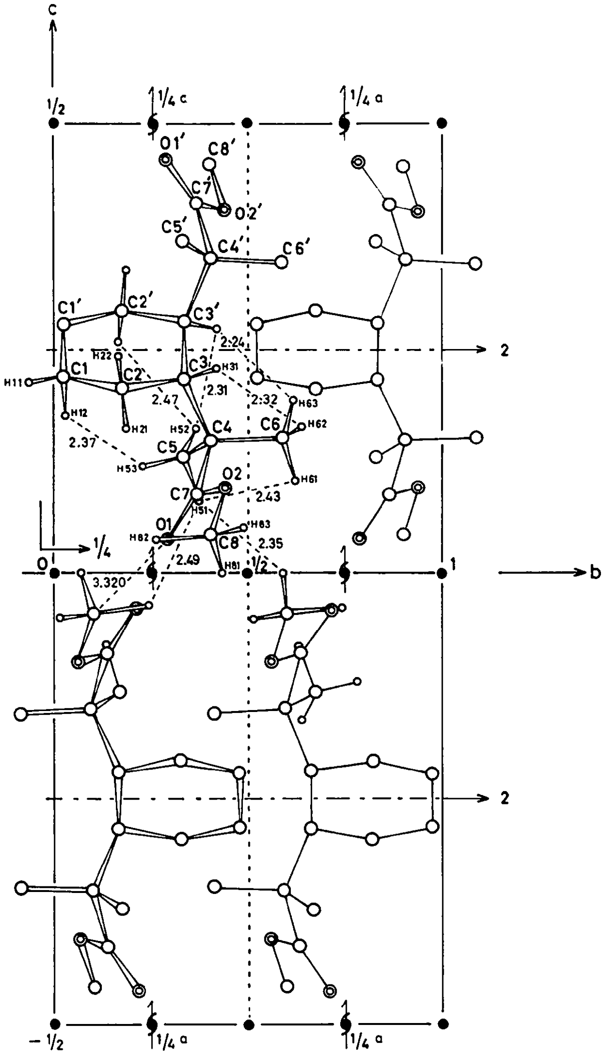


Fig. 4. Projection of the crystal structure along a showing the packing of the molecules. Some short hydrogen–hydrogen distances (< 2·5 Å) are given.

projection of the C(5)C(6)C(7)-moiety (the 't-Bu' group) along the C(4)C(3) bond is given in Fig. 2(*b*). An average twist from the perfectly staggered position of 17·4° is observed.

The molecular strain is relieved by an overall flattening of the chair and not by adopting a 'twist' conformation. The distortion of the ring and the observed twist of the 't-Bu' group may be due to nonbonded contacts between the methyl-hydrogen atoms and ring-hydrogen atoms. Relevant contacts, smaller than 2·50 Å, are shown in Fig. 4. As far as we know this is the first 1,2-diaxially substituted cyclohexane chair thus far reported.

The C(4)C(7)O(1)O(2)-group is planar within experimental error. The atoms C(5) and C(8) are 0·155 and 0·128 Å at either side from this plane. The C=O and C(4)–C(5) bonds deviate 6·2° from being eclipsed [Fig. 2(*c*)]. This orientation is in excellent agreement with the situation usually found in aliphatic carboxylic acids (Kanters, Kroon, Peerdeman & Schoone, 1967) and with the conformation of an axial carboxyl group in cyclohexanecarboxylic acids (van Koningsveld, 1972 and references cited therein). The orientation of the methyl groups is shown in Fig. 3. The large H(82)C(8)H(83) angle (136°) cannot be conclusively explained.

The packing of the molecules in the crystal is illustrated in Fig. 4. The cyclohexane rings form strings along the [110] direction. The strings are held together by non-bonding contacts between the 2-carboxymethyl-2-propyl groups. Some short hydrogen-hydrogen distances (<2·50 Å) are given in the figure.

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# An X-ray Study of Two Phases of BaFeO$_{3-x}$

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BaFeO$_{3-x}$ shows several phases depending upon the iron valence. In α-BaFeO$_{2\cdot5}$, which is orthorhombic, with $a = 5\cdot911 \pm 0\cdot003$, $b = 16\cdot450 \pm 0\cdot008$, $c = 11\cdot037 \pm 0\cdot006$ Å, the iron atom is strictly trivalent. BaFeO$_{2\cdot67}$, which is hexagonal with $a = 5\cdot683 \pm 0\cdot002$, $c = 13\cdot916 \pm 0\cdot005$ Å, space group $P6_3/mmc$, is isomorphous with BaTiO$_3$.

## Introduction

The compound BaFeO$_{3-x}$, barium orthoferrate, has been examined by many authors (Erchak, Fankuchen & Ward, 1946; Malinofsky & Kedesdy, 1954; Brisi, 1955; Gallagher, MacChesney & Buchanan, 1965; MacChesney, Potter, Sherwood & Williams, 1965; Mori, 1966) to determine its phase equilibrium diagram and structural properties.

The valence of the iron atom and the crystal structure of barium orthoferrate depend upon temperature, firing atmosphere and cooling rate.

The present investigation was undertaken to ascertain the isomorphism between hexagonal BaFeO$_{3-x}$ and BaTiO$_3$, suggested by Malinofsky & Kedesdy (1954), Brisi (1955), Gallagher *et al.* (1965), MacChesney *et al.* (1965), and Mori (1966) and to determine the crystal data of a phase quenched at