For mass spectrometric measurements the samples were introduced into the evacuated tube, shown in Figure 5c, by dipping the capillary tip into the sample and opening the Teflon stopcock. Aliquots of the gas phase above the aqueous solution were taken through the metal valve at the top. After condensation in a liquid nitrogen trap, the H_2 was pumped away and the sample was warmed and examined with the mass spectrometer. For detailed analyses, samples were distilled into an open tube column (91.5 m long and 0.25 mm i.d., coated with Apiezon L). The column was developed in a stream of He and detected and analyzed by the time-of-flight mass spectrometer.[10]

The nonvolatile but benzene-extractable dimers consisting of the group of compounds $C_{12}H_{14}\cdots C_{12}H_{22}$ were separated on a Perkin-Elmer 900 gas chromatograph programmed 10 min at 80°, then 2°/min to 110° on a 1.5% OV-17 on Chromosorb W column. They were also separated at 130–140° on a stainless steel open tube column 91.5 m long and 0.25 mm i.d., coated with Apiezon L. The dimers were then detected and identified by mass spectrometry.[10]

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The Molecular and Crystal Structure of (±)-*trans*-1,2-Cyclohexanedicarboxylic Acid

Ettore Benedetti, Paolo Corradini, Carlo Pedone, and Ben Post

Contribution from the Physics and Chemistry Departments,
Polytechnic Institute of Brooklyn, Brooklyn, New York.
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Abstract: The crystal structure of (±)-*trans*-1,2-cyclohexanedicarboxylic acid has been determined. The unit cell is monoclinic with $a = 5.65$, $b = 13.34$, $c = 11.04$ Å; $\beta = 113°\ 16'$. The space group is C2/c with four molecules per unit cell. The crystal structure was determined by the application of close-packing criteria in the hypothesis that the molecules are assembled in hydrogen-bonded rows and that the C_2 symmetry of the molecule is retained as a crystallographic symmetry element. In the crystalline state the preferred conformation of carboxyl groups is diequatorial. The mode of packing of rows is discussed.

Each molecule of the (±)-*trans*-1,2-cyclohexanedicarboxylic acid possesses two asymmetric centers having the same chirality. As far as the conformation is concerned, two conformers are possible; *i.e.*, either both carboxyls are in axial positions, or both are equatorial. Studies of rate of acid-catalyzed esterification led Smith and Byrne[1] to describe that the diaxial form would predominate in the *trans* acid since the carboxyl groups are more widely separated. Other authors[2,3] confirmed that the *trans* acid should exist as diaxial from considerations of the dissociation constants as compared with those of the *cis* isomer and from the fact that the intermolecular polymeric anhydride tends to be formed from the *trans* acid. On the other hand, it has been suggested[4] that the *trans* acid exists as diequatorial on the basis of acidity constants of a series of analogous alicyclic compounds. In order to establish the conformation in the solid state for the *trans*-1,2-cyclohexanedicarboxylic acid, we have examined single crystals of this compound by means of X-ray diffraction.

Experimental Section

Crystals suitable for X-ray analysis were obtained by slow evaporation of aqueous solution (mp 232–233°). On the basis of Weissenberg's photograph taken with Cu Kα radiation, the crystals were found to belong to the monoclinic system. The extinctions of hkl reflections for $h + k = 2n + 1$ and $h0l$ for $h = 2n + 1$, and $l = 2n + 1$ indicate two possible space groups: the centrosymmetric C2/c, or the acentric Cc. A small crystal was carefully centered on a Picker automatical four-circle diffractometer equipped with a PDP-8 digital computer. The determination of the lattice constants was carried out by a least-squares refinement of the setting angles of 12 reflections using Cu Kα radiation (λ 1.5418 Å). The parameters obtained are reported in Table I. The density calculated, $d = 1.43$ g/cm^3, on the basis of the molecular weight (mol wt = 172.18) with assuming four molecules per unit cell agreed reasonably with the experimental value of $d = 1.41$ g/cm^3 obtained by flotation method. The intensity data were collected using the 2θ scan mode of the diffractometer with Ni-filtered Cu Kα radiation. The take-off angle of the tube was 3.0° and a counter aperture, 4.0 × 4.0 mm, was placed 30 cm from the crystal. A scan angle of 1.50° was found to be sufficient for all reflections over the range (0–130°) of 2θ examined. The scan speed was 1°/min. Two stationary-crystal–stationary-counter background counts of 10 sec were taken at each end of each scan.

Table I. Unit Cell Dimensions

(±)-*trans*-1,2-Cyclohexanedicarboxylic acid: $C_8O_4H_{12}$	
Mol wt = 172.18	F(000) = 368
Monoclinic, space group C2/c	
$a = 5.65 \pm 0.01$ Å	
$b = 13.34 \pm 0.03$ Å	$\beta = 113°\ 16' \pm 10'$
$c = 11.04 \pm 0.03$ Å	
$D_{X-R} = 1.43$ g/cm^3	$Z = 4$

Structure Determination and Refinement

The structure of the (±)-*trans*-1,2-cyclohexanedicarboxylic acid was determined by a relatively straightforward application of close-packing criteria.[5] At the

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[1] H. A. Smith and F. P. Byrne, *J. Am. Chem. Soc.*, 72, 4406 (1950).

[2] H. Christol and M. Gaignon, *J. Chem. Phys.*, 57, 707 (1960).

[3] Y. Nishimura, Dissertation Thesis, Polytechnic Institute of Brooklyn, 1965.

[4] J. Sicher, F. Sipos, and J. Jonas, *Collect. Czech. Chem. Commun.*, 26, 262 (1961); E. L. Eliel, N. L. Allinger, S. L. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1966, p 187.

start, we made the reasonable hypothesis that the molecules are assembled in hydrogen-bonded rows, the hydrogen bonds being formed across symmetry centers between carboxylic groups of different molecules. If the space group is C2/c, the C_2 symmetry of the molecule must be retained in the structure as a crystallographic symmetry, and this occurrence dictates in turn that the translation c coincides with the identity period of the row. The length of the c axis is only compatible with a diequatorial model of the molecule, when reasonable values of the internal coordinates are assumed for the molecules.

Under the above conditions, a given hydrogen-bonded row of diequatorial substituted molecules can be positioned in the unit cell in only two ways. One of them was immediately discarded because of unfavorable van der Waals distances between atoms of neighboring molecules, while the other one appeared immediately very promising as a starting trial model. Using the model resulting from these assumptions, after few cycles of full-matrix isotropic least-squares refinement, the reliability factor R defined as

$$R = \frac{\sum||F_c| - |F_o||}{\sum|F_o|}$$

dropped from 0.35 to 0.16. Upon the introduction of anisotropic temperature factors R decreased to 0.12. At this point an electron density difference map was computed. The positions of all six hydrogen atoms in the asymmetric unit of the structure were revealed. Two additional least-squares cycles in which the hydrogen atoms were included brought the reliability factor to 0.066 for 657 nonzero reflections.[6] (An isotropic temperature factor of 3.5 Å^2 was assigned to the hydrogen atoms.)

Result and Discussion

Accuracy of the Structure. Refinement of the structural parameters was continued until the changes in the positional parameters of nonhydrogen atoms between successive least-squares cycles were less than 5% of their standard errors (for the hydrogen atoms these changes were about 10%). Standard errors of parameters were computed by inversion of the least-squares matrices. Standard deviations of any other parameter reported in this manuscript were computed from the least-squares variance–covariance matrix, taking into account the standard errors of the unit cell constants. The final values of the positional and thermal parameters are listed in Table II. The root-mean-square amplitudes of the thermal ellipsoids along the principal axes (1, 2, 3) are given in Table III.

Molecular Conformation and Packing. The bond distances and angles are shown on the molecular model of the diacid molecule reported in Figure 1. The average C–H bond distance is 1.09 ± 0.07 Å, and the angles involving the H atoms are near the tetrahedral value. The main aspects of the molecular conformation and mode of packing of the molecules (Figure 2) that we assumed at the outset have been confirmed.

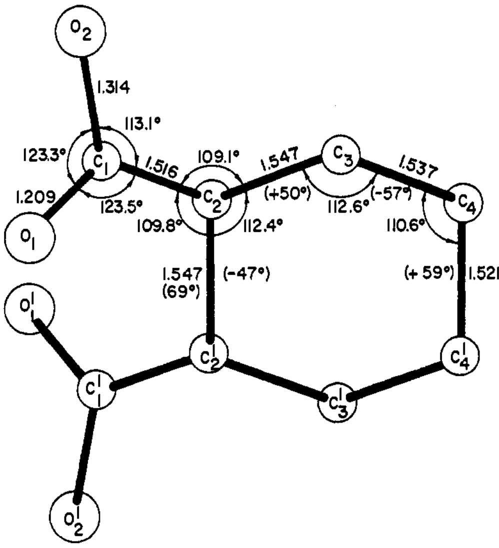

Figure 1. Molecular model for (±)-*trans*-1,2-cyclohexanedicarboxylic acid; bond distances and angles are reported together with the internal rotation angles of the cyclohexane ring. Standard deviations are 0.004 Å per bond length and 0.3 or 0.6°, respectively, for bond angles and internal rotation angles.

In the crystalline state, the preferred conformation of the carboxyl groups in the molecule of (±)-*trans*-1,2-

Table II. Final Structure Parameters

A. Positional Parameters

Atom	x	y	z
C_1	0.0607 (6)	0.1005 (2)	0.1274 (3)
C_2	0.1044 (6)	0.1846 (2)	0.2211 (3)
C_3	0.1051 (7)	0.2789 (2)	0.1470 (3)
C_4	0.1132 (7)	0.3690 (2)	0.2294 (4)
O_1	−0.1328 (5)	0.0521 (2)	0.0882 (2)
O_2	0.2505 (5)	0.0881 (1)	0.0888 (2)
H_1O_2[a]	0.210	0.021	0.023
H_1C_2	0.294	0.170	0.303
H_1C_3	−0.071	0.278	0.064
H_2C_3	0.254	0.285	0.121
H_1C_4	0.307	0.361	0.321
H_2C_4	0.100	0.448	0.170

B. Anisotropic Thermal Parameters $(10^4)^b$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C_1	375 (17)	26 (2)	54 (4)	16 (4)	86 (7)	9 (2)
C_2	318 (16)	26 (2)	53 (4)	−5 (4)	66 (7)	1 (2)
C_3	408 (17)	30 (2)	73 (4)	−14 (5)	92 (7)	3 (2)
C_4	451 (20)	28 (2)	106 (5)	−7 (5)	110 (8)	−5 (2)
O_1	399 (13)	40 (1)	105 (3)	−46 (3)	124 (5)	−28 (2)
O_2	385 (12)	46 (1)	114 (4)	−18 (3)	145 (6)	−23 (2)

[a] The hydrogen atom notation is in the form H_nX_m, where n is a progressive number and m is the number assigned to the atom X to which the hydrogen is bonded. [b] Temperature factor = exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Root-Mean-Square Amplitudes of Vibration (Å)

Atom	Axis 1	Axis 2	Axis 3
C_1	0.136	0.165	0.229
C_2	0.152	0.164	0.208
C_3	0.159	0.188	0.238
C_4	0.165	0.219	0.252
O_1	0.159	0.190	0.275
O_2	0.157	0.205	0.275

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(5) P. Corradini, P. Ganis, C. Pedone, and G. Diana, *Makromol. Chem.*, 61, 242 (1963).

(6) A list of the calculated and observed structure factors has been deposited as Document No. NAPS-00328 with the ASIS National Auxiliary Publication Science, c/o CCM Information Science Inc., 22 West 34 St., New York, N. Y. 10001. A copy may be secured by citing the document number and by remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

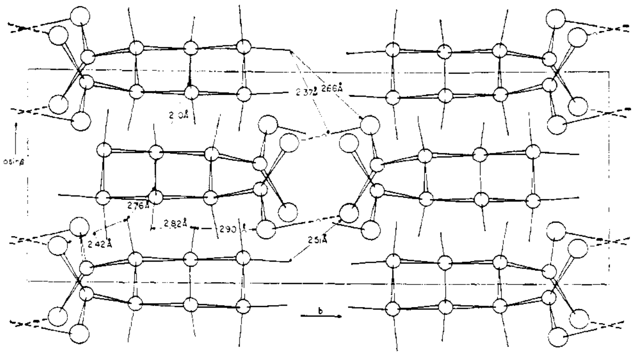

Figure 2. Intermolecular packing viewed along (010)

cyclohexanedicarboxylic acid is evidently the diequatorial. No unfavorable interactions between nonbonded atoms are apparent within any given molecule, apart from the dipole–dipole interactions. The shortest contact between atoms separated by more than three bonds is the distance between the ketonic oxygens, which are 3.26 Å apart (O_1–$O_{1'}$).

Table IV

A. Internal Rotation Angles (esd = 0.6°) (*trans* conformation = 180°)	
C_1–C_2–$C_{2'}$–C_3	−168.6°
C_1–C_2–C_3–C_4	−172.6°
O_1–C_1–C_2–C_3	−112.1°[a]
O_2–C_1–C_2–C_3	+65.2°
O_1–C_1–C_2–$C_{2'}$	+11.5°
O_2–C_1–C_2–$C_{2'}$	−172.5°
B. Hydrogen Bond Parameters[b]	
$O_1 \cdots O_2$	2.65 ± 0.01
$O_1 \cdots H_1O_2$	1.51 ± 0.01
$O_2 \cdots H_1O_2$	1.15 ± 0.01
C_1—O_2—H_1O_2	109 ± 2
H_1O_2—$O_2 \cdots O_1$	7 ± 1
C_1—$O_2 \cdots O_1$	110 ± 2
C_1—$O_1 \cdots O_2$	127 ± 2
O_2—$H_1O_2 \cdots O_1$	167 ± 2

[a] The sign of this angle has been previously given as +. [b] Distances in Å, angles in degrees.

The internal rotation angles (Table IV) of the carboxylic group are such that the ketonic oxygen is almost "eclipsed" with respect to one of the carbon–carbon single bonds of the ring, in accordance with similar observations.[7] The mode of packing may deserve a short discussion. The structure of a molecular row is determined by the formation of hydrogen bonds (Table IV) and dictates the direction and length of the **c** axis and the direction of the **b** axis. In the plane perpendicular to **b**, the direction and length of the **a** axis is determined by the side-by-side packing of rows, with the shortest inter-row distance ($= a \sin \beta$), while maintaining the contact distances between nonbonded atoms in a comfortable range (H–H never lower than 2.44 Å, H–O never lower than 2.66 Å) except for one close distance H–H of 2.1 Å ± 0.1 (Figure 2). Similar contact distances are observed between atoms of rows, displaced by the translation vector $|{}^1/_2a + {}^1/_2b| = 7.5$ Å (H–H never lower than 2.37 Å, H–O never lower than 2.51 Å). In the classification of the possible symmetries of molecular rows, given by one of us,[8] the symmetry of the molecular rows in this crystal is *t i c*, which allows the repetition of alternately enantiomorphous molecules, having C_2 symmetry. The monoclinic space groups which are compatible with the maintenance of this symmetry are P2/c and C2/c.

Molecule rows of *t i c* symmetry are present in the monoclinic crystal lattice of a polymer (1,4-*cis*-polybutadiene),[9] of (±)-α,α′-dimethylglutaric acid,[10] and of (±)-α,α′-dimethylsuccinic acid.[11] The first two substances crystallize in the C2/c space group; the third one crystallizes in space group P2/c.

From the results of this study, as well as from preliminary results of our investigations of similar substances, such as the (±)- and the (+)-*trans*-1,2-cyclopentanedicarboxylic acids and the *trans*-1,2-cyclobutanedicarboxylic acid,[12] we believe that one of the most convenient ways of close-packing layers of rows having 2/c (≡*t i c*) symmetry is indeed by centering the "*c*" face in a monoclinic unit cell (**b** unique axis).

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