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

**Ettore Benedetti, Paolo Corradini, and Carlo Pedone**

*Contribution from the Polymer Research Institute, Department of Chemistry, 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 $a = 5.58$, $b = 10.62$, $c = 7.34$ Å; $\beta = 107° 41'$. The space group is $P2_1$ and there are two molecules per unit cell. The crystals are usually twinned. The crystal structure has been derived from that of the corresponding racemic compound. The carboxyl groups are found to be in the diequatorial conformation. Positional disorder between carboxyl and hydroxyl oxygens is indicated by the fact that the C–O distances as well as the C–C–O angles of each carboxyl group appear almost identical. A model for the mechanism of twinning is presented.

We have reported earlier[1] on the crystal structure of the racemic form of the *trans*-1,2-cyclohexanedicarboxylic acid where the carboxyl groups were found to be diequatorial. Continuing our studies on the stereochemistry of small molecules, we undertook the present investigation in order to determine similarities and differences between the molecular conformation and mode of packing of the racemic and the optically active *trans*-1,2-cyclohexanedicarboxylic acids.

## Experimental Section

Crystals of (+)-*trans*-1,2-cyclohexanedicarboxylic acid were obtained by slow evaporation from aqueous as well as from acetone or dioxane solutions (mp 181–183°). On the basis of Weissenberg and rotating photographs taken with Cu K$\alpha$ radiation along the *a* and *b* axes, the crystals were found to belong to the monoclinic system. We prepared crystals from different solvents and we always observed the occurrence of twinning. More precisely, while the $0kl$ Weissenberg photographs do not show any evidence of twinning, the $h0l$ and $hk0$ photographs clearly demonstrate the presence of two individuals in twin orientation. For the crystal we chose for the collection of the intensities data, the ratio of the intensities of corresponding reflections was approximately 3:1. The systematic extinctions of the $0k0$ reflections with $k$ odd indicate as most probable the acentric space group $P2_1$ with two molecules per unit cell. The small twinned crystals chosen (0.2 × 0.4 × 0.2 mm) were aligned along the *a* axis and carefully centered on a Picker four-circle automated diffractometer.

The unit cell constants are reported in Table I. Using a procedure given before,[1] the intensity data collection was carried out for the two individuals of the twin. While the *a* axis has the same orientation for the two individuals, the *b* axes have opposite directions and, as a result, the *c* axes are at an angle of $2(180° - \beta)$ (Figure 1). The $0k$ reflections were found to be coincident for the two orientations of the twin; then their use in the crystal determination required that their intensities be corrected by an appropriate factor. The $5kl$ reciprocal lattice points of one crystal are practically coincident for geometrical reasons with the reciprocal lattice points $\bar{5}\bar{k}(+4)$ of the other crystal. Therefore, the corresponding intensities were not taken into consideration in the refinement. For the other classes of reflections, it is possible to see that under the conditions used for collecting the data no overlapping of reflections of the differently oriented crystals occurs. The intensities of 750 nonzero independent reflections were collected in the range (0–130°) of $2\theta$ examined.

**Table I.** Unit Cell Constants

| | |
|---|---|
| (+)-*trans*-1,2-Cyclohexanedicarboxylic acid: $C_8O_4H_{12}$ | |
| Mol wt = 172.18 | $F(000) = 184$ |
| Monoclinic, space group $P2_1$ | |
| $a = 5.584 \pm 0.005$ Å | |
| $b = 10.624 \pm 0.008$ Å | $\beta = 107° 41'$ |
| $c = 7.337 \pm 0.005$ Å | |
| $D_{X-R} = 1.38$ g/cm$^3$ | $Z = 2$ |

## Determination of the Structure

While the unit cell constants of (+)-*trans*-1,2-cyclohexanedicarboxylic acid appear at first glance to be quite different from those of the racemic form ($a = 5.65$ Å, $b = 13.94$ Å, $c = 11.04$ Å, $\beta = 113° 16'$, space group $C2/c$), it is possible to observe that the intensities of the $0kl$ reflections of the two different forms are practically identical (if we compare the $0kl$ of the optically active compound with the $0,l/2,K$ of the racemic one). This observation suggests that some analogy between the two structures should arise from a comparison of the unit cell constants of the racemic compound as reported above with those of the optically active one, transformed into those of a centered space group ($C2_1$, *c* unique axis, $a = 5.58$ Å, $b = 13.94$ Å, $c = 10.25$ Å, $\gamma = 95°$). Figure 2A shows the mode of packing of the molecule of the racemic compound as seen along the *b* axis. Since the structure of the optically active compound should look very close to that of the racemic one as seen along the *a* axis, it was reasonable to assume that a preliminary model of the mode of packing of the optically active compound could be derived as shown in Figure 2B. The shortening of the row axis (10.25 *vs.* 11.04 Å) is clearly related to the need of repeating isomorphous molecules through the operation of a twofold screw axis, instead of repeating enantiomorphous molecules through the combined operation of a glide plane and symmetry centers. In comparing the respective $C2/c$ and $C2_1$ structures, this model satisfactorily predicts the shortening of the row axis *c*, as discussed above, the change of the $\beta$ angle from 113 to 90°, and the practical invariance of the length of the *a* and *b* axes. We used this model as a starting model for the refinement. The disagreement factor $R$ was 0.40 and dropped after two cycles of isotropic full-matrix least-squares refinement to 0.17. Two more cycles of anisotropic refinement reduced $R$ to 0.10. At this point a

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[1] E. Benedetti, P. Corradini, C. Pedone, and B. Post, *Chem. Commun.*, 1626 (1968); *J. Am. Chem. Soc.*, 91, 4072 (1969).

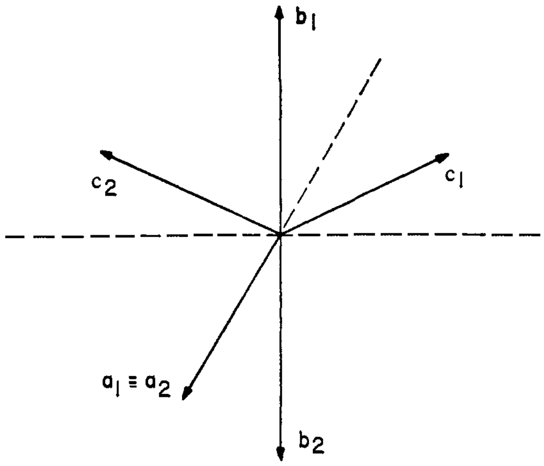

Figure 1. Orientations of the two individuals of the twin.

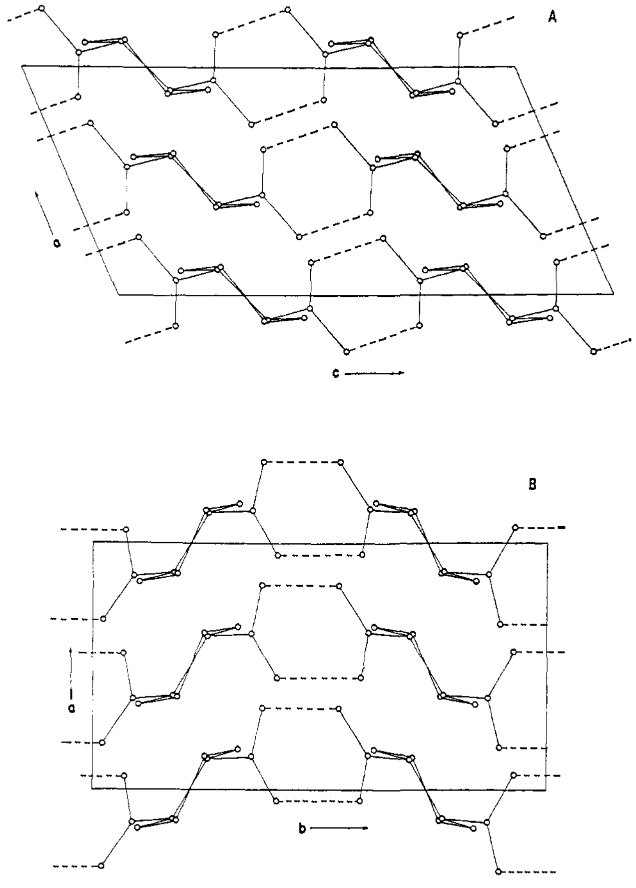

Figure 2. (A) Mode of packing of the racemic *trans*-1,2-cyclohexanedicarboxylic acid along the (010) projection. (B) Mode of packing of the optically active (+)-*trans*-1,2-cyclohexanedicarboxylic acid along the (001) projection (see text) as derived from the mode of packing of the racemic compound.

difference synthesis disclosed the approximate position of 10 of the 12 hydrogen atoms present in the asymmetric unit, the two missing atoms being those involved in hydrogen bonds. Two final cycles of full-matrix least-squares, including the refinement of the positional parameters of the hydrogen atoms, were now performed and the final disagreement factor was[2]

$$R = \frac{\sum||F_o| - |F_c||}{\sum|F_o|} = 0.056$$

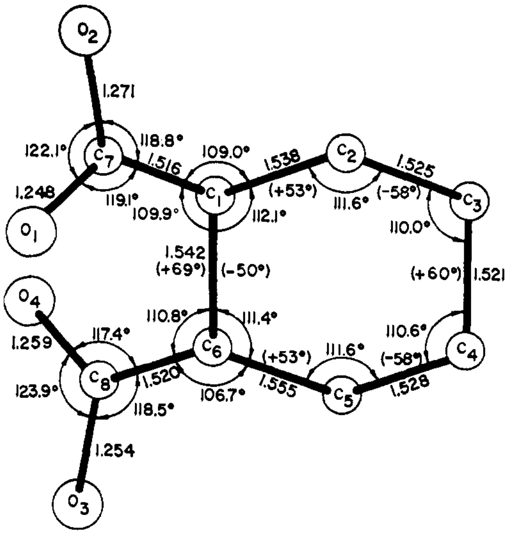

Figure 3. Molecular model of the optically active *trans*-1,2-cyclohexanedicarboxylic acid (in parentheses are reported the internal rotation angles in the ring). Bond lengths and bond angles are indicated. Their standard deviations are, respectively, 0.008 Å and 0.5°

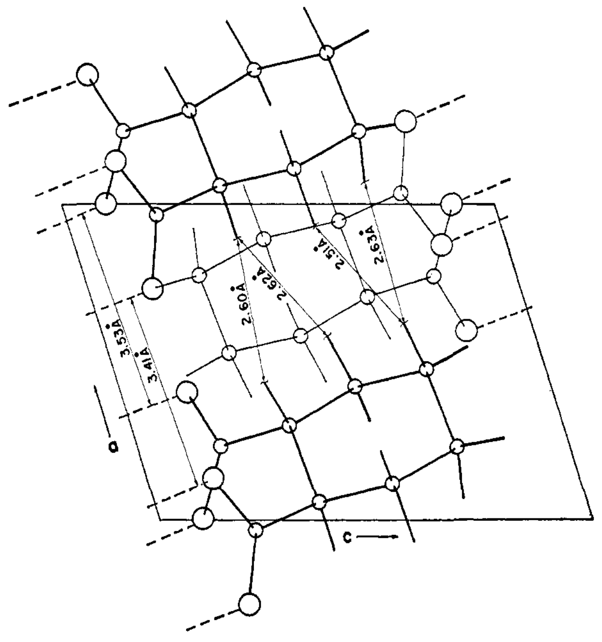

Figure 4. Mode of packing along the (010) projection.

Table II gives the final positional and thermal parameters of the atoms.

## Discussion of the Structure

A molecular model of the optically active compound is given in Figure 3 together with bond lengths and angles.[3] A list of the internal rotation angles and the hydrogen bond parameters are reported in Table III.

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(2) A list of the observed and calculated structure factor has been deposited as Document No. NAPS-00328 with the ASIS to 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.

(3) The average C–H distance is 1.09 ± 0.08 Å, and the bond angles involving H atoms are close to the tetrahedral value.

**Table II**

A. Final Positional Parameters

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| $C_1$ | 0.2944 (12) | 0.3223 (9) | 0.3633 (8) |
| $C_2$ | 0.4204 (15) | 0.2466 (10) | 0.5460 (8) |
| $C_3$ | 0.4724 (15) | 0.3285 (10) | 0.7246 (9) |
| $C_4$ | 0.2287 (16) | 0.3861 (10) | 0.7372 (9) |
| $C_5$ | 0.1091 (16) | 0.4686 (10) | 0.5627 (8) |
| $C_6$ | 0.0566 (13) | 0.3917 (9) | 0.3742 (7) |
| $C_7$ | 0.2281 (13) | 0.2337 (9) | 0.1933 (8) |
| $C_8$ | −0.0342 (13) | 0.4848 (9) | 0.2103 (8) |
| $O_1$ | 0.0026 (10) | 0.2193 (8) | 0.0987 (7) |
| $O_2$ | 0.4035 (10) | 0.1734 (8) | 0.1551 (7) |
| $O_3$ | −0.2653 (10) | 0.5073 (7) | 0.1466 (7) |
| $O_4$ | 0.1302 (10) | 0.5407 (7) | 0.1552 (7) |
| $H_1C_1$[a] | 0.430 | 0.382 | 0.339 |
| $H_1C_2$ | 0.577 | 0.203 | 0.517 |
| $H_2C_2$ | 0.309 | 0.170 | 0.556 |
| $H_1C_3$ | 0.615 | 0.401 | 0.704 |
| $H_2C_3$ | 0.544 | 0.235 | 0.837 |
| $H_1C_4$ | 0.064 | 0.318 | 0.716 |
| $H_2C_4$ | 0.253 | 0.471 | 0.854 |
| $H_1C_5$ | −0.071 | 0.503 | 0.571 |
| $H_2C_5$ | 0.208 | 0.563 | 0.559 |
| $H_1C_6$ | −0.105 | 0.322 | 0.380 |

B. Thermal Parameters[b]

| | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| $C_1$ | 299 (29) | 50 (6) | 117 (11) | −1 (10) | 15 (14) | −12 (7) |
| $C_2$ | 416 (38) | 69 (7) | 135 (13) | 12 (12) | 9 (16) | 13 (8) |
| $C_3$ | 406 (36) | 104 (9) | 110 (12) | 20 (15) | −16 (16) | 7 (9) |
| $C_4$ | 526 (42) | 102 (8) | 111 (13) | 3 (17) | 68 (17) | 4 (10) |
| $C_5$ | 506 (38) | 74 (7) | 111 (12) | 22 (14) | 61 (16) | −9 (8) |
| $C_6$ | 332 (31) | 55 (6) | 102 (11) | −11 (11) | 33 (14) | 2 (7) |
| $C_7$ | 382 (36) | 58 (6) | 134 (12) | −4 (13) | 28 (16) | 10 (8) |
| $C_8$ | 339 (32) | 58 (6) | 111 (11) | 0 (12) | 38 (15) | −19 (7) |
| $O_1$ | 341 (26) | 133 (7) | 260 (12) | 11 (10) | −13 (14) | −96 (8) |
| $O_2$ | 372 (27) | 112 (6) | 224 (11) | 47 (11) | 71 (13) | −44 (7) |
| $O_3$ | 313 (26) | 108 (6) | 199 (10) | 40 (9) | 34 (12) | 35 (7) |
| $O_4$ | 379 (26) | 116 (6) | 243 (12) | 9 (11) | 106 (14) | 76 (7) |

[a] The notation of the hydrogen atoms is in the form $H_nC_m$, where $n$ is a progressive number and $m$ is the number assigned to the carbon atom to which the hydrogen is bounded (see Figure 3). [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**

| A. Internal Rotation Angles (*trans* conformation = ±180°) | |
|---|---|
| $C_7$–$C_1$–$C_6$–$C_5$ | −171.7 ± 0.6° |
| $C_8$–$C_6$–$C_1$–$C_2$ | −169.0 ± 0.6° |
| $O_1$–$C_7$–$C_1$–$C_2$ | −117.3 ± 0.7° |
| $O_1$–$C_7$–$C_1$–$C_6$ | +6.0 ± 0.9° |
| $O_2$–$C_7$–$C_1$–$C_2$ | +60.6 ± 0.9° |
| $O_2$–$C_7$–$C_1$–$C_6$ | −176.1 ± 0.6° |
| $O_3$–$C_8$–$C_6$–$C_1$ | −149.3 ± 0.6° |
| $O_3$–$C_8$–$C_6$–$C_5$ | +89.2 ± 0.7° |
| $O_4$–$C_8$–$C_6$–$C_1$ | +35.1 ± 0.7° |
| $O_4$–$C_8$–$C_6$–$C_5$ | −86.4 ± 0.8° |
| **B. Hydrogen Bond Parameters** | |
| $O_1$–$O_4$ | 2.60 ± 0.01 Å |
| $O_2$–$O_3$ | 2.75 ± 0.01 Å |
| $C_7$–$O_2$–$O_3$ | 117 ± 0.5° |
| $C_7$–$O_1$–$O_4$ | 120 ± 0.5° |
| $C_8$–$O_4$–$O_1$ | 120 ± 0.5° |
| $C_9$–$O_3$–$O_2$ | 118 ± 0.5° |

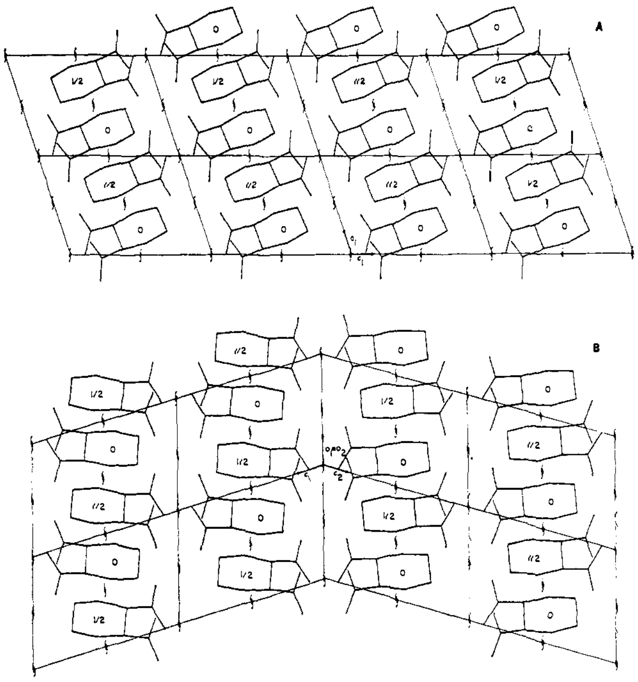

Figure 5. Models of (A) nontwinned and (B) twinned crystals (the coordinate of the center of the cyclohexane ring is indicated).

The mode of packing of the molecules has been discussed before for the preliminary model, and we believe that only a few additions are needed at this point. The packing between adjacent hydrogen-bonded rows of molecules is similar to that of the racemic compound, the main changes having been brought by the absence of symmetry centers; as expected it is determined by van der Waals contacts between nonbonded atoms (distances H–H never lower than 2.51 Å, H–O never lower than 2.70 Å, O–O never lower than 3.41 Å). Figure 4 shows the mode of packing along the *b* axis. A mechanism of twinning is proposed in Figure 5 which is self-explanatory and should be compared with Figure 1. The departure of the internal rotation angles of the ring from 60° is probably due to the need of relaxing the nonbonded interactions between carboxyl groups, by increasing the internal rotation angle $C_7$–$C_1$–$C_6$–$C_8$ from 60 to 70°. The major difference in the internal coordinates of the molecule of *trans*-1,2-cyclohexanedicarboxylic acid in the two crystalline structures is in the C–O distances. In fact, in the optically active compound the two C–O distances as well as the C–C–O angles of each carboxyl group appear almost identical at the end of the refinement. We take this observation together with the fact that we could not detect the positions of the hydrogen atoms bonded to the carboxyl groups in the difference Fourier synthesis as an indication of positional disorder between the carbonyl and hydroxyl oxygens.

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