Solid State Conformation of *trans*-Cyclohexane-1,2-Dicarboxylic Acid

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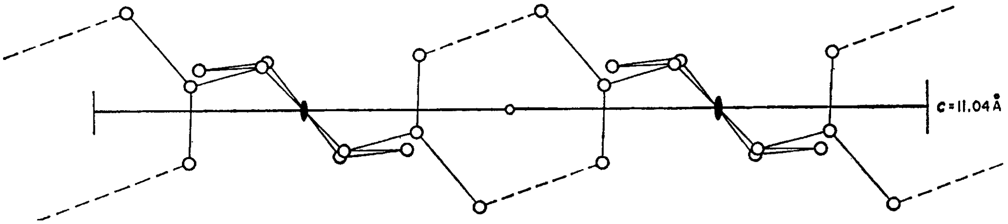
Two different conformers can exist for *trans*-cyclohexane-1,2-dicarboxylic acid, that is, either both carboxy-groups are axial or both equatorial. The conformation in solution has long been the subject of discussion. From the rates of acid-catalysed esterification, Smith *et al.*[1] concluded without clear evidence that the diaxial form would be favoured. Other authors[2] confirmed this result from the difference and the ratio between the first and second ionization constants as compared with those of the corresponding 1,2-*cis*-isomer. On the other hand, it has been suggested[3] that the *trans*-acid should be di-equatorial on the basis of the acidity constants of a series of analogous alicyclic compounds. In order to establish the conformation in the solid state we have examined, by means of X-ray diffraction, single crystals of the racemic and optically active forms of *trans*-cyclohexane-1,2-dicarboxylic acid.

(±)-*trans*-Cyclohexane-1,2-dicarboxylic acid: $a = 5{\cdot}65 \pm 0{\cdot}01$, $b = 13{\cdot}94 \pm 0{\cdot}03$, $c = 11{\cdot}04 \pm 0{\cdot}03$ Å, $\beta = 113° 16' \pm 10'$, $n = 4$, Space group $C2/c$; (the centrosymmetry has been reasonably established at the end of the structure determination). The intensities of 657 nonzero independent reflections were collected with a Picker four-circles automatic diffractometer, by use of Cu-K_α radiation.

The hypothesis of a C_2 symmetry of the molecule and of the presence of hydrogen-bonded molecules forming long rows in the crystal lattice enabled us to solve the structure by means of the close-packing criteria we have applied for analogous compounds.[4] Refinement of the structure was carried out by anisotropic full-matrix least-squares analysis and difference-Fourier synthesis. The final discrepancy factor R is 0·066. The diacid molecules indeed form rows hydrogen-bonded between carboxy-groups of molecules related by centres of symmetry in the direction of the c axis (Figure). The carboxy-groups are found to be diequatorial, thus establishing this conformation in the solid state for the compound studied. The more



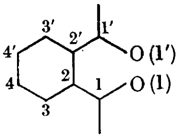
FIGURE

relevant internal rotation angles in the molecule are shown in the Table. The bond lengths and angles found in this study are in agreement with those reported in the literature for analogous alicyclic compounds.[5]

TABLE

Internal rotation angles of the molecule (± 1°)
(*gauche*-conform. = ± 60°, *trans*-conform. = 180°)

C(1)–C(2)–C(2′)–C(1′) = +70°
C(4)–C(3)–C(2)–C(C2′) = +50°
C(3)–C(2)–C(2′)C(3′) = −47°
C(2)–C(3)–C(4)–C(4′) = −56°
C(3)–C(4)–C(4′)–C(3′) = +59°
O(1)–C(1)–C(2)–C(3) = +112°



The shortest nonbonded O····O distance within the same molecule is 3·26 Å [O(1)····O(1′)].

The crystal structure of the optically active form, that is (+)-*trans*-cyclohexane-1,2-dicarboxylic acid, is currently being studied in our laboratory. It shows similarities to that of the racemic material, and it is likely that the di-equatorial conformation will be found there also.

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

[2] H. Christol and M. Gaignon, *J. Chem. Phys.*, 1960, **57**, 707; E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, New York, 1964, p. 242.

[3] J. Sicher, F. Šipoš and J. Jonas, *Coll. Czech. Chem. Comm.*, 1961, **26**, 262; E. L. Eliel, N. L. Allinger, S. L. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, 1966, p. 187.

[4] P. Corradini, P. Ganis, C. Pedone and G. Diana, *Makromol. Chem.*, 1963, **61**, 242; E. Martuscelli, E. Benedetti, P. Ganis, and C. Pedone, *Acta Cryst.*, 1967, **23**, 747; P. Ganis, P. A. Temussi, M. G. Northolt, and L. E. Alexander, *J. Chem. Phys.*, in the press.

[5] J. D. Dunitz and P. Strickler, *Helv. Chim. Acta*, 1966, **49**, 2505.