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PREFERRED ROTATIONAL CONFORMATION OF CARBOXYL GROUPS ON THE CYCLOHEXANE RING

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Recent speculations (1, 2) about the preferred rotational conformation of carboxyl groups on the cyclohexane ring prompt us to describe some recent crystal structure results that bear on this problem.

In crystals of cyclohexane-1, 4-*trans*-dicarboxylic acid (3) the carboxyl groups are equatorial. The keto and hydroxyl oxygen atoms are easily identified by bond length criteria (C=O, 1.25 A; C-OH, 1.30 A) and the keto oxygen is found to occur in the syn-planar position with respect to one of the α, β-bonds of the ring ($\tau(C_\beta - C_\alpha - C{=}O) = 5^o$).

An axial carboxyl group occurs in the crystal structure of cyclohexane-1-aminomethyl-4-*cis*-carboxylic acid hydrobromide, recently described by Groth and Hassel (4). These authors did not discuss the rotational conformation of the carboxyl group, but calculations based on their published coordinates lead to a torsion angle $\tau(C_\beta - C_\alpha - C{=}O) = 0.3^o$. Thus the keto group (C=O, 1.25 A; C-OH, 1.31 A) is again syn-planar with one of the α, β-bonds of the ring.

These results do not altogether agree with the preferred conformations assumed (1, 2) in order to explain the pK_a differences between variously substituted cyclohexanecarboxylic acids, and it seems somewhat premature to propose a general rule with any confidence from them. Nevertheless, the common features of the rotational conformation observed for both equatorial and axial carboxyl groups with those observed in a whole range of straight chain acids (5) encourage us to believe that the preferred orientation is indeed that with the keto group syn-planar to one of the two α, β-bonds of the ring. However, the energy barrier separating the two such equivalent orientations is probably rather low. It seems unlikely that the same preferred rotation conformation holds for the more symmetrical carboxylate anion.

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