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THE STRUCTURE OF SQUARIC ACID (3,4-DIHYDROXY-3-CYCLOBUTENE-1,2-DIONE)

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Diketocyclobutenediol (squaric acid), a stable colourless crystalline solid, was first synthesized by Cohen, Lacher and Park (1) by a two step hydrolysis of dichlorotetrafluorocyclobutene. Spectroscopic investigations of squaric acid in the crystalline state suggest the presence of strong hydrogen bonds (2.5 Å) (2), slightly longer than those observed for symmetrical hydrogen bonds. The solid state interactions, mainly due to hydrogen bonding, are strong enough to limit the solubility in water to 2% despite the fact that the molecule is a strong acid having pK values of 0.6 and 3.5 (3). A favourable arrangement in the crystalline state would also explain the unusually high melting point (290 ^{o}C) observed for this compound. Crystals grown from aqueous solutions were almost invariably twinned. The present determination was carried out with the only single crystal found.

The crystal data are as follows: Squaric acid, $C_4H_2O_4$, monoclinic, space group $P2_{1/m}$(assumed). Cell dimensions: a = 6.129(3) Å; b = 5.273(2) Å; c = 6.140(3) Å; β = 90.00(1)^{o}; Z = 2. The structure was determined from a three dimensional Patterson based upon 920 unique observed reflections recorded on diffractometer (MoK_{α} radiation, graphite crystal monochromator) and is so far refined to an agreement factor of 0.048 for 700 high order reflections. The hydrogen atoms have been included in the refinement.

Bond lengths (uncorrected for thermal motion) at this stage of the refinement are given in Fig 1, which shows the molecule as viewed along the b-axis. Estimated standard deviations are 0.001 Å for bond lengths and 0.1^{o} for bond angles. The molecule (exluding hydrogen atoms) possesses approximately C_{2v} symmetry with good agreement between chemically equivalent bonds. Although

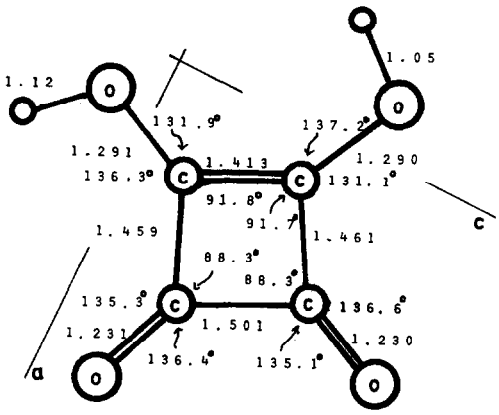

Fig 1. Bond lengths and angles in squaric acid

single and double bonds can easily be recognized, the degree of conjugation in the π-electron system of the present compound is considerably larger than in the related 3.4-dimethylene-cyclobutene system (4). Bond angles also conform to the approximate C_{2v} symmetry with the exception of the bond angles involving the hydroxylic oxygen atoms. These angles are distorted to give a more favourable hydrogen bonding arrangement. The crystal structure is pseudotetragonal (I 4/m) and consists of layers of molecules at y = 1/4 and y = 3/4. The molecules within each layer are hydrogen bonded. The two hydrogen bonds are fairly short, being 2.55 Å. The protons are located asymmetrically with O-H---O angles both close to 180°. A full account of the structure will be published elsewhere.

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