Conformation Ambiguity in Solid Cyclobutane-1,1-dicarboxylic Acid

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Summary X-Ray crystallographic analysis of cyclobutane-1,1-dicarboxylic acid shows the cyclobutane ring to be either statically or dynamically disordered.

THE ring-puckering vibration in cyclobutane derivatives has been observed in several compounds, most recently in 1,1-difluorocyclobutane,[1] in which the barrier to a planar ring has been measured as 241 ± 5 cm.$^{-1}$. In the solid state, a recently observed manifestation of the low barrier occurs in *trans*-cyclobutane-1,3-dicarboxylic acid, which has been shown to exist in both the planar and puckered forms depending upon its crystalline environment.[2] Cyclobutane derivatives previously studied by X-ray diffraction have carried substituents at two or more ring carbons. In cyclobutane-1,1-dicarboxylic acid (I) only one ring carbon atom is substituted (excluding hydrogen). One might expect that the substituents would have less effect on ring conformation and vibrations than in derivatives substituted at more than one ring carbon. We have determined the crystal structure of this molecule at room temperature. Our results are consistent with a large ring-puckering vibration or a disordered structure which has static molecules of different orientation or conformation.

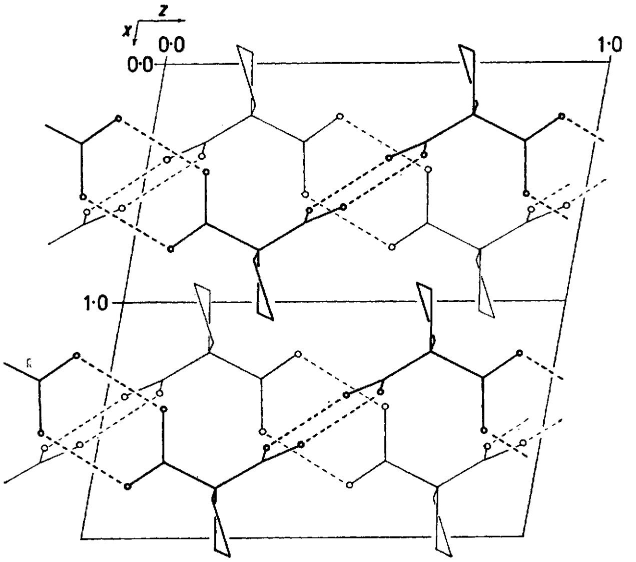

FIGURE 1. *The crystal structure viewed along* b.

Crystals of (I), $C_6H_8O_4$, are monoclinic, space group $P2_1/c$, $Z = 4$, $a = 6{\cdot}128 \pm 0{\cdot}002$, $b = 10{\cdot}536 \pm 0{\cdot}004$, $c = 11{\cdot}005 \pm 0{\cdot}003$ Å; $\beta = 99{\cdot}78 \pm 0{\cdot}15°$ (Cu-K_α radiation). The structure was determined from diffractometer data by direct methods and refined by full-matrix least-squares calculations to $R = 0{\cdot}05$ for 925 non-zero independent reflections.

In the crystal centrosymmetric hydrogen-bonds between carboxyl groups generate infinite zig-zag chains of molecules running in the z direction. The cyclobutane rings hang off these chains (Figure 1). During the least-squares refinement the anisotropic thermal parameters of C(3), the atom transannular to the carboxyl groups, refined to values indicating large thermal motion perpendicular to the plane of the other three ring carbon atoms. An electron-density map (Figure 2) illustrates this distortion of the electron cloud of C(3). A difference map showed a large peak near C(3) at a position corresponding to a ring puckered in the opposite way from the original. These observations are consistent with a large-amplitude ring puckering vibration. They are also consistent with a statically disordered crystal structure with some molecules puckered one way and some the other.‡ Since X-ray diffraction shows the electron density averaged over a long period of time over many molecules it alone cannot distinguish between dynamic and static effects.

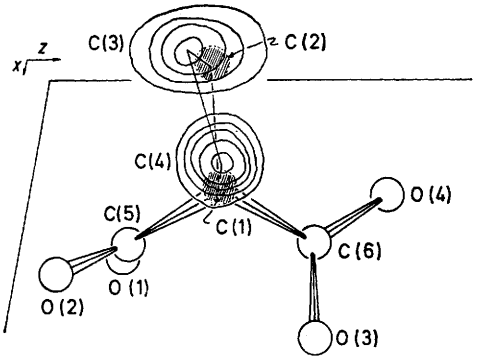

FIGURE 2. *One molecule viewed along* b. *Contours on* C(4) *provided for comparison with* C(3).

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‡ Such a disorder could reasonably arise here, because the molecule has a pseudo-twofold axis bisecting the angle C(2)–C(1)–C(4). Rotation of the molecule through 180° about this axis leaves the crystal structure essentially unchanged and translates C(3) in the direction of the electron-cloud distortion.

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[2] T. N. Margulis, and M. Fisher, *J. Amer. Chem. Soc.*, 1967, **89**, 223; E. Adman and T. N. Margulis, *ibid.*, 1968, **90**, 4517.