Planar Cyclobutanes: Structure of 2,2,4,4-Tetramethylcyclobutane-*trans*-1,3-diol

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X-RAY diffraction studies of simple,† planar cyclobutanes have been made exclusively in compounds with only one kind of substituent besides hydrogen attached to the cyclobutane ring. The five planar rings of known structure are *cis,trans,cis*-1,2,3,4-tetraphenylcyclobutane;[1,2] *cis,trans,cis*-1,2,3,4-tetracyanocyclobutane;[3] octahydroxycyclobutane;[4] and cyclobutane-*trans*-1,3-dicarboxylic acid[5]‡ and its dianion.[6] These molecules are centrosymmetric, and in each case the centre of the molecule coincides with a crystallographic centre of symmetry. The rings are either square or rectangular with C–C bonds 0·01—0·03 Å longer than normal C–C single bonds. We know of no examples of a planar ring in an acentric molecule. We report the results of an X-ray diffraction study of 2,2,4,4-tetramethylcyclobutane-*trans*-1,3-diol which has two types of substituents on a planar cyclobutane ring.

A Picker full-circle manual diffractometer with scintillation counter and pulse-height analyser was used to obtain cell dimensions and intensities. A single crystal with no dimension greater than 0·15 mm. was grown from toluene and used for all X-ray work. Cu-K_α radiation (λ 1·5418 Å) was used to measure 322 independent non-zero intensities which were converted into structure factors without correction for absorption.

The crystals are trigonal, space group C_{3i}^{2}–$R\bar{3}$. The dimensions of the hexagonal unit cell containing nine molecules are a 19·521 ± 0·01, c 6·397 ± 0·003 Å. The calculated density is 1·02 g./cm.^{3}. The structure was determined by a trial-and-error procedure carried out on an IBM 7094 computer, and then successfully refined by full-matrix least-squares calculations. In the final cycles of least-squares, hydrogen atoms (located in a difference map) were refined with isotropic temperature factors while anisotropic temperature factors were used for carbon and oxygen. The final value of R is 0·044.

The crystal structure consists of a three-dimensional network of hydrogen bonds. Each oxygen atom is hydrogen-bonded to two other oxygen atoms so that each molecule is hydrogen-bonded to four other molecules. The O–O distance is 2·737 Å, comparable to other values for hydrogen bonding in alcohols.§ Molecular dimensions are shown in the Figure. The cyclobutane ring is planar and diamond-shaped with equal C–C bond lengths but unequal C–C–C bond angles. The transannular distances of 2·16 ± 0·01 and 2·21 ± 0·01 Å, respectively, further illustrate the departure from rectangular shape. The C–C–C angle of 91·2° *is the* largest angle yet found in a planar cyclobutane. As indicated in the Figure, the methyl groups are arranged so as to give an approximate mirror plane through C-1, C-1′, H-1, H-1′, O,

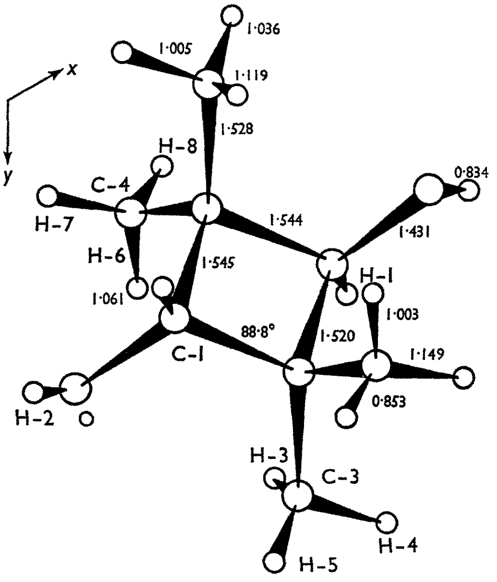

FIGURE. *One molecule of* 2,2,4,4-*tetramethylcyclobutane*-trans-1,3-*diol viewed along* c. *Estimated standard deviations are* 0·005 *Å for* C–C *and* C–O *bonds and* 0·1 *Å for* C–H *and* O–H *bonds.*

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† By simple, we mean molecules in which the ring is not part of another ring and is not conjugated.

‡ Cyclobtuane-*trans*-1,3-dicarboxylic acid also exists with a puckered ring. See ref. 6.

§ The details of the hydrogen-bonding will be reported elsewhere.

O′, H-2, and H-2′. This conformation, although eclipsing many pairs of hydrogen atoms, leaves the oxygen atom relatively free to receive a hydrogen bond. The C–C single bonds within the cyclobutane ring are only slightly (and not necessarily significantly) longer than "normal" C–C single bonds, in contrast to other cyclobutanes where accurate values above 1·56 Å have been reported.[6] The shortness of the ring–methyl bonds is almost certainly due to thermal motion. A correction, based on Busing and Levy's "riding" model makes these bonds 1·545 and 1·549 Å, respectively.[7]

Proof of structure of a cyclobutane in the solid state does not necessarily mean that the ring will have the same conformation in other phases. There is no clear-cut evidence yet for a truly planar cyclobutane except in the solid state. The existing data on simple cyclobutanes may be summarized: rings which are not centrosymmetrically substituted are puckered; rings which are, may be planar. However, centrosymmetrically substituted cyclobutanes can also be puckered (*e.g.*, cyclobutane[8] itself, octachlorocyclobutane,[2,9] and cyclobutane-*trans*-1,3-dicarboxylic acid in the sodium salt).[6]

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