Conformation of a Cyclo-octane Derivative

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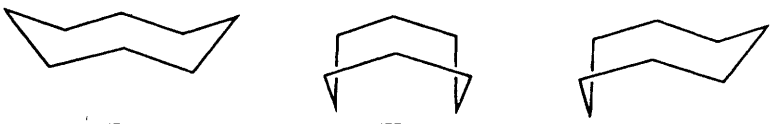
ALTHOUGH the stable conformation of cyclo-octane is generally assumed[1] to be that of a stretched or twisted crown (I), there has been no really compelling evidence for this, or for the alternative "saddle" conformation (II), which has also been proposed.[2] Strain energy minimization calculations[3,4] suggest that no one form of the cyclo-octane ring is clearly favoured energetically, so that a conformational mixture may be expected at ordinary temperatures. However, infrared and Raman evidence has been interpreted in favour of a single conformation.[5] We have now established by *X*-ray analysis the conformation of a cyclo-octane derivative and find that the ring is represented by neither (I) nor (II) but by (III), corresponding to what Hendrickson[3] has called the "boat–chair" form.



(I) (II) (III)

The compound studied is cyclo-octane-1,2-*trans*-dicarboxylic acid, kindly supplied by Dr. J. Sicher. The crystals are monoclinic, space group $C2/c$, $a = 14{\cdot}76$ Å, $b = 11{\cdot}89$ Å, $c = 12{\cdot}98$ Å, $\beta = 111{\cdot}25°$, with 8 molecules in the cell. The structure has been determined by direct methods and refinement of the parameters is in progress. The Figure shows the spatial arrangement of the carbon and oxygen atoms in the molecule, as derived from the second Fourier synthesis based on about 1000 F_o-values. Already at this stage ($R = 0{\cdot}22$) it is clear that the CCC-bond angles tend to be greater than in paraffin-chain molecules, the average value being close to 116°. The same tendency has been noted for the CCC angles in cyclononane[6] and cyclodecane[7] rings. Since both carboxyl groups appear to be engaged in intermolecular hydrogen bonds, it is unlikely that the conformation found is stabilized by intramolecular hydrogen-bond formation.

An earlier *X*-ray study of azacyclo-octane hydrobromide has been interpreted[8] in terms of a crown form for the eight-membered ring. The crystal structure is disordered, however, and the results appear to be about equally compatible with (III), which has also been found in the heterocyclic compound, 5-methyl-1-thia-5-azacyclo-octane 1-oxide perchlorate.[9]

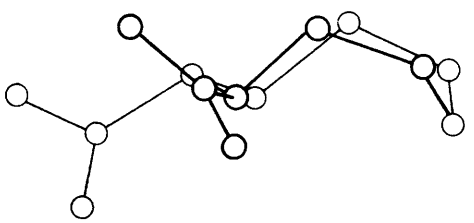


FIGURE. *Arrangement of atoms in cyclo-octane*-1,2-trans-*dicarboxylic acid.*

Investigations are in progress to determine the conformation of the cyclo-octane ring in other derivatives.

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