Experimental Determination of Short Transannular H · · · H Distances in a Cyclodecane Derivative

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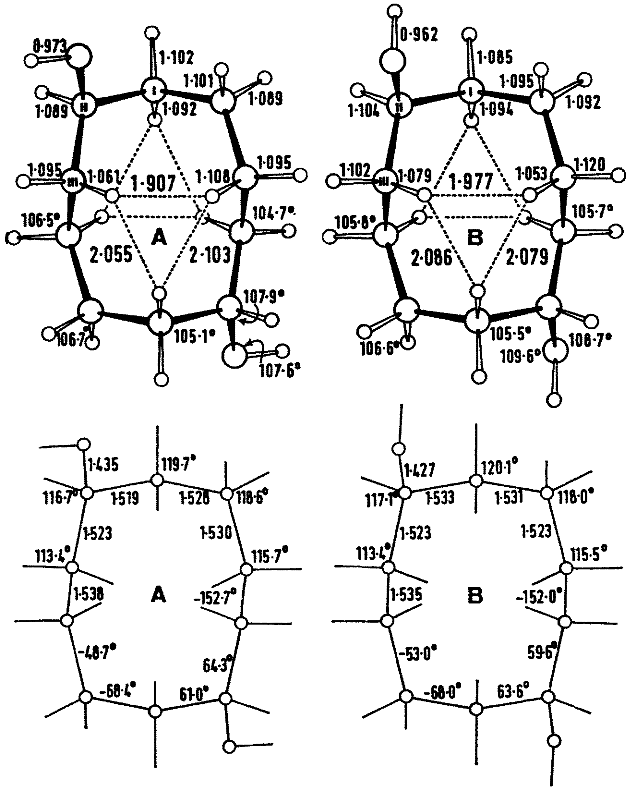
Summary The shortest transannular H · · · H distances in the two independent molecules occurring in the crystal of *trans*-cyclodecane-1,6-diol are 1·91 and 1·98 (both ±0·01) Å, respectively.

THE occurrence of short transannular H · · · H distances in cyclodecane derivatives has been inferred from the results of several X-ray crystallographic studies and supported by various strain-minimization calculations.[1] The hydrogen positions obtained from X-ray data have large standard deviations (at best *ca.* 0·05 Å) and are affected by the characteristic bias towards too short C–H distances, while those estimated from stereochemical considerations based on the heavy-atom skeleton depend on assumptions that cannot be strictly correct. Distances estimated from strain-minimization calculations likewise depend on arbitrary choices of empirical parameters in various potential functions.[2] We have now carried out an X-ray and neutron diffraction study of *trans*-cyclodecane-1,6-diol in order to obtain an accurate experimental measurement of these short transannular H · · · H distances.



FIGURE

The compound was crystallized from acetone as large, thick prisms. *Crystal data*: $a = 11{\cdot}168$, $b = 11{\cdot}728$, $c = 8{\cdot}072$ Å, $\beta = 110{\cdot}86°$, monoclinic, $P2_1/c$. The unit cell contains four centrosymmetric molecules, the asymmetric unit consisting of two crystallographically independent "half molecules." The crystal structure was solved by direct methods from X-ray data (Mo-K_α radiation) and refined by full-matrix least-squares analysis to give an R factor of 0·072 based on 1411 diffractometer-measured F-values. Neutron-diffraction data ($\lambda = 0{\cdot}9958$ Å) were measured at the Brookhaven National Laboratory High Flux Beam Reactor (Upton, Long Island, N.Y.). After correction for absorption (linear absorption coefficient $\mu = 2{\cdot}84\ \text{cm}^{-1}$) the data were likewise refined by full-matrix least-squares analysis ($R = 0{\cdot}053$; 1276 reflections). The resulting interatomic distances, bond angles and torsion angles in the two crystallographically independent molecules are shown in the Figure.

The main difference between the two molecules lies in the partial conformation about the C(II)–O bond, the O–H bond being, respectively, antiplanar and synclinal to the C(III)–C(II) bond (Figure). This difference is associated with small but statistically significant differences in torsion angles and transannular H · · · H distances.

The shortest transannular H · · · H distance occurs, as expected, between type III atoms, and is 1·907 ± 0·008 Å in molecule A and 1·977 ± 0·009 Å in molecule B. These distances are substantially longer than those (1·80 and 1·92 Å) calculated from the carbon framework with the usual assumptions (local C_{2v} symmetry of methylene groups, C–H = 1·10 Å, ∠HCH = 106°). The observed deviations from local C_{2v} symmetry at the type I and III methylene groups are all such as to reduce overcrowding in the intra-annular region. The largest deviations occur at type I atoms and consist essentially of a rocking of the CH_2 group whereby the HCH bisector is rotated by 3·5° (molecule A) and 4·5° (molecule B) out of the CCC plane. The corresponding angles at type III atoms are in the range 1—2°.

The vibrational amplitudes are in general somewhat smaller and less anisotropic for the intra-annular H-atoms than for the extra-annular ones, suggesting that they are better described in terms of rigid-body vibrations rather than framework vibrations. At any rate they suggest that the observed atomic positions correspond to a fairly well defined equilibrium structure and not to one where dynamic averaging over a set of multiple energy minima has to be invoked.

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