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The Crystal Structure of Bicyclo[4.4.1]undecane-1,6-diol

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$C_{11}H_{20}O_2$ is tetragonal, space group $P4_32_12$ or $P4_12_12$, with $a = 11{\cdot}73$, $c = 15{\cdot}47$ Å, $Z = 8$. The structure was solved with *MULTAN* and 1087 independent reflexions refined to $R = 3{\cdot}8\%$. The cycloheptane rings adopt the minimum-energy twist-chair conformation and the ten-membered ring resembles a low-energy cyclodeca-1,6-diene conformer.

X-ray analysis has proved to be useful in defining the minimum-energy conformations (MEC's) of medium ring compounds (Dunitz, 1968). The results are of intrinsic chemical interest and provide useful reference structures for the development of force fields used in molecular-mechanics calculations (Ermer & Lifson, 1973). Although the structures calculated by the latter technique correspond to the gas phase, major conformational differences between condensed and non-condensed phases are the exception rather than the rule (Huler & Warshel, 1974). There are, however, cases where characterization of a single MEC by X-ray analysis has proved difficult because of the existence of several conformations which are approximately iso-energetic (Bixon *et al.*, 1967; Dunitz & Shearer, 1960), and cycloheptane falls into this category.

Hendrickson (1967) calculated that the conformations of cycloheptane belong to two families: the chair/twist-chair and boat/twist-boat, with a potential-energy barrier of *ca* 8 kcal mol^{-1} between the two families. Within each family the boat or chair conformations are energy maxima 1–2 kcal mol^{-1} above the twist minima. On this basis Hendrickson predicted that cycloheptane pseudorotates in the gas phase at room temperature, and the disordered crystal structures of calcium cycloheptanecarboxylate pentahydrate (Flapper & Romers, 1975) and 1-aminocycloheptane-1-carboxylic acid hydrobromide monohydrate (Chacko, Srinivasan & Zand, 1971) suggest that this process may also take place in the solid when the hydrocarbon is lightly or non-substituted. On the other hand, the cycloheptane rings in 8,9,17,18-tetraoxadispiro-[6.2.6.2]octadecane (Groth, 1967) are ordered (presumably as a consequence of the very bulky substituents) but do not correspond to the minimum-energy twist-chair conformation (C_2 symmetry), being displaced along the pseudorotational itinerary from this point. Presumably the crystal packing can be optimized by this deformation at an extremely modest cost in energy. Cycloheptane rings fused to cyclopentane and γ-lactone rings are common features of sesquiterpenoid natural products. X-ray studies have characterized conformations from both the chair and boat families, but in all cases there are appreciable departures from symmetric forms (McPhail & Sim, 1973).

The foregoing arguments suggest that the MEC of cycloheptane is only likely to be fortuitously observed in the crystal of a suitable derivative, unless the seven-membered ring can be locked into the C_2 twist-chair MEC. Dreiding models show that two MEC cycloheptane rings can be 1,3-fused to form bicyclo[4.4.1]-undecane with minimal changes in the individual seven-membered-ring conformations. The cycloheptane rings will be locked into the C_2 symmetric twist-chair forms and, barring the introduction of any serious steric compression by 1,3-fusion, this hybrid conformation should also be the MEC of bicyclo[4.4.1]undecane.

A structure analysis of bicyclo[4.4.1]undecane-1,6-diol, therefore, provides not only details of the MEC of the parent hydrocarbon but also structural details of the MEC of cycloheptane. One might also expect that the conformation of the ten-membered ring would correspond to one of the previously studied possibilities for cyclodecane (Hendrickson, 1967).

Experimental

Crystal data

Bicyclo[4.4.1]undecane-1,6-diol, $C_{11}H_{20}O_2$, $M_r = 184{\cdot}3$; tetragonal, $a = 11{\cdot}73$, $c = 15{\cdot}47$ Å, $U = 2125$ Å^3, $Z = 8$, $D_c = 1{\cdot}15$, $D_x = 1{\cdot}17$ g cm^{-3}, $F(000) = 816$, space group $P4_32_12$ or $P4_12_12$, μ(Mo $K\alpha$) = 0·83 cm^{-1}.

Crystallographic measurements

Cell dimensions determined from precession photographs were optimized by least squares from the setting angles for a number of reflexions measured on a Hilger & Watts Y290 four-circle computer-controlled diffractometer. The intensities were obtained by the ω–2θ step scan procedure with background measurements at each end of the scan and periodic monitoring of two standard reflexions. 1087 intensities with $I \geq 3\sigma(I)$ were obtained by irradiating a crystal, $0{\cdot}8 \times 0{\cdot}5 \times 0{\cdot}3$ mm, with Mo $K\alpha$ radiation.

Structure analysis

All C and O atoms were located from an E map calculated with the set of phases having the highest FOM produced by *MULTAN* for the space group $P4_32_12$. Full-matrix least-squares adjustment of the positional and anisotropic thermal parameters converged at $R = 12{\cdot}4\%$. The H atoms were located in a difference map and least-squares refinement continued with the positional and isotropic thermal parameters of the H atoms included. A weighting scheme, $\sqrt{w} = 1/\sigma(|F_o|)$, was employed and the refinement converged at $R = 3{\cdot}8\%$.* No correction was made for absorption.

Results and discussion

The structure is shown in Figs. 1 and 2 and the atomic coordinates and molecular dimensions in Table 1 and Fig. 3. The mean C–O, C–C and C–H lengths are 1·450, 1·530 and 0·990 Å, the latter result showing the usual foreshortening observed in X-ray analyses. The mean C–C–C angle is 114·7° corresponding to values characteristic of medium ring alkanes (Dunitz, 1968).

Bicyclo[4.4.1]undecane-1,6-diol approximates fairly closely to C_2 symmetry, the axis passing through C(11) normal to the plane of least inertia. Molecular-mechanics calculations, with our alkene force field (White & Bovill, 1975, 1976*a*,*b*) and a two-stage Newton–Raphson minimization procedure (White & Ermer, 1975), have been used to derive the molecular geometries and steric energies of a number of plausible conformations of bicyclo[4.4.1]undecane. The gas-phase MEC appears to be an exactly C_2 symmetric structure corresponding closely to that in the solid state and the calculated geometry has been appended to Fig. 3. Torsion angles and relative energies for the other calculated conformations are given in Table 2. The shortest observed transannular H···H contacts are 2·15 and 2·14 Å between H(21)···H(91) and H(42)···H(71) (C–H vectors corrected to a length of 1·08 Å) and the calculated values are 2·21 Å. We have shown that correct prediction of short H···H distances in strained molecules can be a useful test of empirical valence force fields (White & Bovill, 1976*b*) but the

* Lists of structure factors and thermal parameters and Table 3 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32623 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

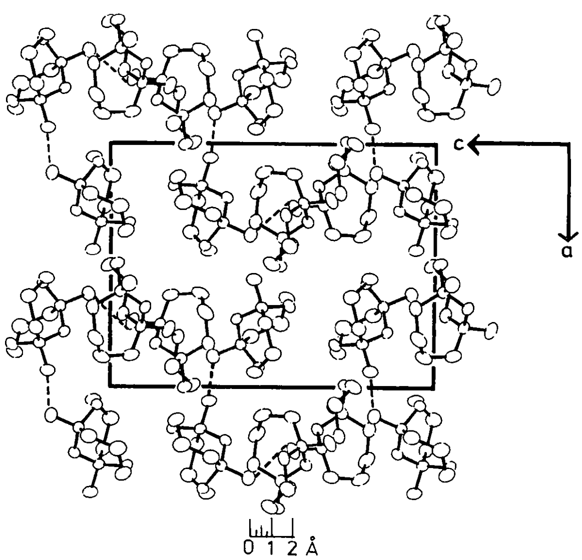

Fig. 1. The crystal packing viewed down **b**. Intermolecular hydrogen bonds are indicated by broken lines.

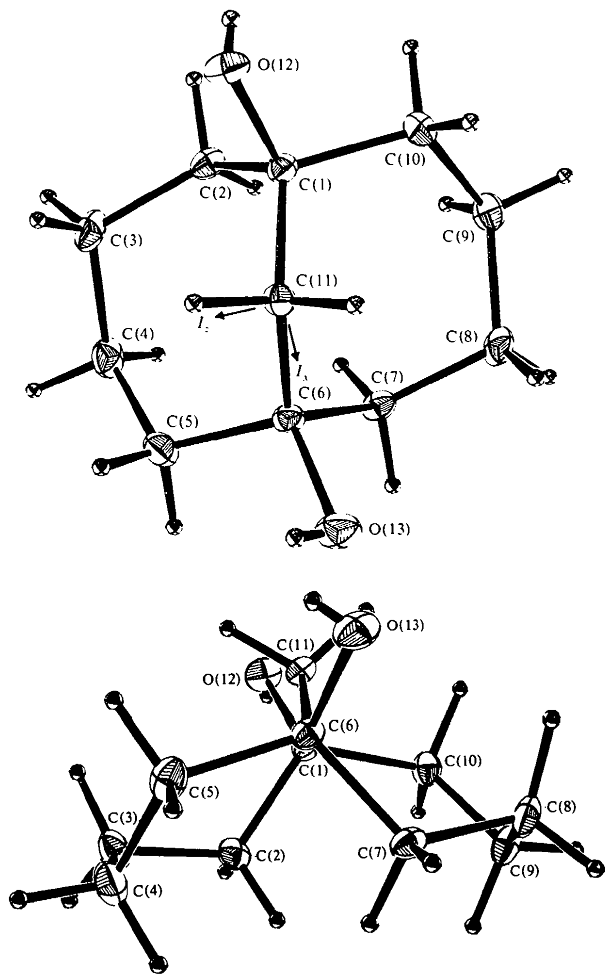

Fig. 2. Two views of the molecule in approximately perpendicular directions.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *with e.s.d.'s* ($\times 10^4$) *in parentheses*

	x	y	z
C(1)	8238 (2)	8897 (2)	2191 (2)
C(2)	8303 (3)	8231 (3)	3038 (2)
C(3)	8606 (3)	6967 (3)	2948 (2)
C(4)	7584 (3)	6193 (3)	2770 (2)
C(5)	7070 (3)	6269 (3)	1854 (2)
C(6)	6720 (2)	7460 (2)	1540 (2)
C(7)	5782 (2)	7968 (3)	2101 (2)
C(8)	5575 (3)	9237 (3)	1981 (2)
C(9)	6339 (3)	9980 (3)	2540 (2)
C(10)	7606 (3)	10036 (2)	2302 (2)
C(11)	7771 (2)	8232 (2)	1417 (2)
O(12)	9387 (2)	9210 (2)	1933 (2)
O(13)	6225 (3)	7343 (3)	0687 (2)
H(21)	7617 (28)	8312 (26)	3379 (18)
H(22)	8852 (29)	8635 (27)	3426 (20)
H(31)	9224 (36)	6863 (34)	2502 (26)
H(32)	8922 (26)	6742 (26)	3438 (19)
H(41)	7784 (30)	5379 (33)	2847 (22)
H(42)	6996 (30)	6384 (31)	3212 (22)
H(51)	6384 (29)	5800 (27)	1803 (19)
H(52)	7599 (30)	5982 (28)	1434 (20)
H(71)	5917 (25)	7814 (24)	2724 (18)
H(72)	5088 (29)	7527 (30)	1959 (20)
H(81)	4802 (30)	9367 (27)	2145 (20)
H(82)	5654 (30)	9401 (29)	1298 (23)
H(91)	6277 (28)	9653 (27)	3148 (22)
H(92)	6084 (28)	10764 (28)	2593 (21)
H(101)	7980 (27)	10445 (26)	2829 (18)
H(102)	7722 (30)	10443 (28)	1699 (21)
H(111)	7606 (25)	8786 (26)	0947 (18)
H(112)	8371 (27)	7761 (27)	1215 (19)
H(12)	9577 (34)	9480 (33)	2182 (24)
H(13)	6548 (33)	7100 (36)	0558 (27)

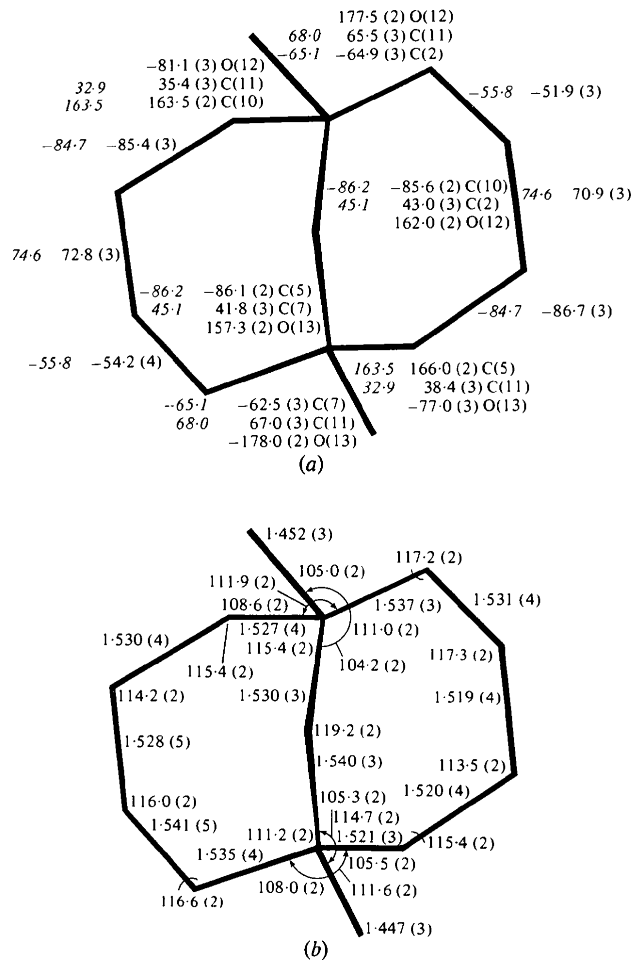

Fig. 3. (*a*) The observed torsion angles (°) with e.s.d.'s ($\times 10$) in parentheses. Calculated values are shown in italics. Multiple torsion angles around one bond are distinguished by appending the label of the fourth atom to the value. (*b*) The bond lengths (Å) with e.s.d.'s ($\times 10^3$), and bond angles (°) with e.s.d.'s ($\times 10$).

comparison in this instance is hampered by the limited precision of the experimental result. However, there is no evidence of anomalous methylene scissoring modes in the IR spectrum of solid bicyclo[4.4.1]undecane (Martin, 1964; Mackenzie, MacNicol, Mills, Raphael, Wilson & Zabkiewicz, 1972) and so, by analogy with 9-thiabicyclo[3.3.1]nonane-2,6-dione where the effect is also absent and the distance in question is known to be 2·07 Å (Cox, Guy, Hardy, McCabe & Sim, 1977), it seems reasonable to conclude that the actual distances in bicyclo[4.4.1]undecane are, at least, greater than 2·07 Å.

The conformation of the ten-membered ring in bicyclo[4.4.1]undecane-1,6-diol appears to be representative of a class which has so far escaped attention. The low-energy conformations of cyclodecane studied by Hendrickson (1967) and others (Ermer, 1976) are either asymmetric or have mirror planes/twofold axes bisecting bonds and/or passing through atoms. In the present instance the sole symmetry element is a twofold axis passing through the centre of the ring and the conformation resembles a *trans,trans*-cyclodeca-1,6-diene variant which we have previously described (White & Bovill, 1975). The

Table 2. *Torsion angles* (°) *and steric energies relative to the MEC* (kcal mol^{-1}) *for some low-energy conformations of bicyclo*[4.4.1]*undecane*

	(I)	(II)	(III)	(IV)
ω(10,1,2,3)	−56	−162	−151	−156
ω(1,2,3,4)	−59	73	72	68
ω(2,3,4,5)	−8	−6	−13	0
ω(3,4,5,6)	70	−69	−64	−68
ω(4,5,6,7)	57	170	168	155
ω(5,6,7,8)	−120	−108	−53	−156
ω(5,6,11,1)	60	50	51	64
ω(6,7,8,9)	58	49	−34	68
ω(7,8,9,10)	−87	−88	−33	0
ω(8,9,10,1)	63	70	76	−68
ω(9,10,1,2)	85	78	60	155
ω(10,1,11,6)	75	76	68	64
E_s	4·88	4·34	6·43	8·26

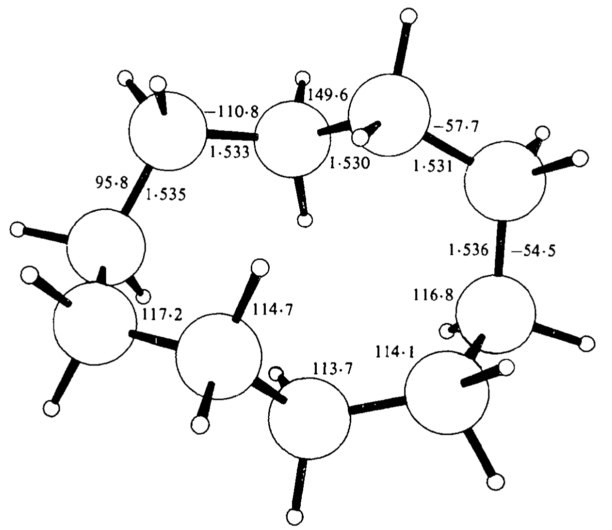

Fig. 4. The calculated cyclodecane conformation derived from the ten-membered ring of bicyclo[4.4.1]undecane. The steric energy is 2·4 kcal mol^{-1} above the global minimum-energy (BCB) conformation.

results of a strain-minimization calculation of cyclodecane starting from the observed ten-membered-ring conformation are shown in Fig. 4.

We have used a recently derived algorithm (Cremer & Pople, 1975) in order to compare the various observed and calculated cycloheptane structures with the calculated C_2 symmetric twist-chair MEC which is characterized by the amplitudes $q_2 = 0{\cdot}499$, $q_3 = 0{\cdot}673$ Å and phase angles $\varphi_2 = 270$, $\varphi_3 = 270°$. This geometry is not significantly different from that calculated by Flapper & Romers (1975) and therefore forms a valid reference point for the following discussion. The amplitudes and phase angles for the two observed seven-membered rings of bicyclo[4.4.1]undecane are 0·512, 0·644 Å, 273, 271° and 0·535, 0·630 Å, 271, 270°, and the corresponding calculated values are 0·512, 0·656 Å, 276, 272°. Although the values of q_2 and q_3 vary slightly from seven-membered ring to seven-membered ring, the value of $Q = (\Sigma_m q_m^2)^{1/2}$ for each ring is nearly constant at $0{\cdot}83 \pm 0{\cdot}01$ Å, so that 1,3-fusion appears to have little effect on the total puckering amplitude. The differences between the calculated q and φ values for cycloheptane and bicyclo-[4.4.1]undecane indicate a small amount of distortion consequent upon fusion of the two twist-chair seven-membered rings to form the bicyclic molecule, so that the observed conformations probably do not correspond exactly to the MEC of cycloheptane although the deviation is small. Differences between the two observed seven-membered rings amount to $\langle \Delta l \rangle = 0{\cdot}008$ Å, $\langle \Delta\theta \rangle = 0{\cdot}5°$ and $\langle \Delta\omega \rangle = 1{\cdot}5°$, compared with $3\langle \sigma(l) \rangle = 0{\cdot}012$ Å, $3\langle \sigma(\theta) \rangle = 0{\cdot}6°$ and $3\langle \sigma(\omega) \rangle = 1{\cdot}5°$, so that, with one exception, the departures of bicyclo[4.4.1]undecane-1,6-diol from C_2 molecular symmetry are probably not significant in the solid state. The exception concerns the orientation of the O–H vectors (Fig. 2) which might be expected to vary independently in order that the intermolecular hydrogen bonding is optimized.

Analysis of the thermal vibrations (Schomaker & Trueblood, 1968) indicates that the carbon skeleton at least behaves as a rigid body as evidenced by the reasonable agreement between the r.m.s. $\sigma(U_{ij}^o)$ of 0·0015 Å^2 and the calculated value of $\langle (U_{ij}^o - U_{ij}^c)^2 \rangle^{1/2}$ of 0·0024 Å^2. The calculated **L**, **T** and **S** tensors are given in Table 3.* The eigenvector corresponding to the largest eigenvalue of the **L** tensor is almost exactly parallel to the vector between the two O atoms, so that the intermolecular hydrogen bonds are minimally perturbed by this librational mode. A similar orientation of the **L** eigenvectors has been observed in cyclodecane-1,6-diol (Ermer, Dunitz & Bernal, 1973).

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* See previous footnote.

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A Neutron Diffraction Refinement of the Crystal Structures of β-L-Arabinose and Methyl β-D-Xylopyranoside*

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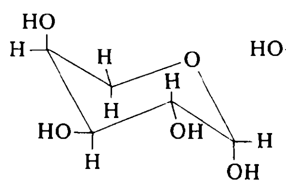
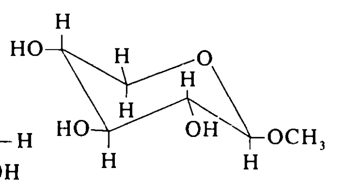
The crystal structures of β-L-arabinose, $C_5H_{10}O_5$, and methyl β-D-xylopyranoside, $C_6H_{12}O_5$, have been refined using neutron diffraction data. In the β-arabinose structure, the hydrogen bonding consists of infinite chains of strong bonds, with H···O distances of 1·735 and 1·801 Å, attached to which are very weak bonds for which H···O is 2·201 Å. There is also a single link from the anomeric hydroxyl to a ring oxygen with H···O 1·820 Å. The hydrogen bonding in the methyl β-xylopyranoside structure is a single finite chain with H···O distances of 1·785 and 1·885 Å, terminating in a weak bond to a ring oxygen (2·088 Å).

Introduction

The crystal structures of β-L-arabinose (I) and methyl β-D-xylopyranoside (II) were determined by Hordvik (1961) and by Brown, Cox & Llewellyn (1966), respectively, using X-ray diffraction film methods. The main purpose of this refinement was to obtain a more precise description of the hydrogen bonding in these structures.



(I)



(II)

Four pyranose monosaccharide crystal structures have been examined by neutron diffraction: α-D-glucose (Brown & Levy, 1965), methyl α-D-altropyranoside (Poppleton, Jeffrey & Williams, 1975), and methyl α-D-glucopyranoside and methyl α-D-mannopyranoside (Jeffrey, McMullan & Takagi, 1977). Definite rules governing hydrogen-bond geometry are not generally observed (*cf.* Hopfinger, 1973); however, a comparison of the hydrogen-bond H···O distances in these four carbohydrate structures revealed two interesting correlations. One was a connection between the hydrogen-bond H···O lengths and the type of hydroxyl-to-oxygen interaction. The other was the observation that the anomeric hydroxyl in α-D-glucose is a stronger hydrogen-bond donor and weaker hydrogen-bond acceptor than the other hydroxyl groups (Jeffrey, Gress & Takagi, 1977). There are theoretical reasons why this might be so, as shown by Tse & Newton (1977), and good supporting evidence from X-ray studies (Jeffrey & Lewis, 1977). Nevertheless, further experimental evidence relating to both these observations is necessary and this work is part of a program to obtain this information.

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Experimental

Transparent crystals, with well developed faces, of both compounds were obtained by slow evaporation of 95% ethanol–water solutions at room temperature. The crystal and experimental data and the structure-refinement parameters are given in Table 1. The unit-cell dimensions were determined by least-squares refinement of the setting angles of 29 reflections, which were centered automatically on the neutron diffractometer using the *NEXDAS* program of McMullan (1976).