

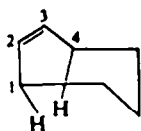
## THE CONFORMATION OF A CYCLOHEPTENE

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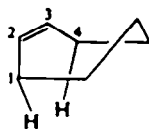
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**Abstract**—Spectroscopic studies on 2,3-benzocyclohepten-1,4-diol show that the cycloheptene ring is in the chair conformation.

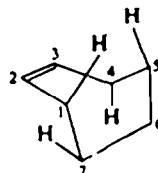
CYCLOHEPTENE resembles cyclohexane inasmuch as it can be depicted in the chair Ia, boat Ib or twist-boat Ic conformations, but even an intuitive estimate of their relative energies is difficult. Although the boat incorporates none of the eclipsed butane conformations of the cyclohexane boat, "prow" interaction will be severe<sup>1</sup> and both boat and chair have objectionable (ca. 2 Å) H<sub>1</sub>-H<sub>4</sub> interactions. Similarly the twist-boat Ic has two pairs of repulsions, H<sub>1</sub>-H<sub>5</sub> and H<sub>4</sub>-H<sub>7</sub>. A more sophisticated



Ia



Ib



Ic

calculation<sup>2</sup> has suggested that the boat would be marginally preferred, but experimental observations<sup>3</sup> favour the chair conformation. We present here, further evidence in favour of the chair conformation.

The *cis*-diol II, which was available to us,<sup>4</sup> is particularly suitable for study, since the substituents do not, of themselves, forbid any of the above conformations. In CCl<sub>4</sub> solution, it showed strong intramolecular hydrogen bonding ( $\nu_{\text{OH}}$  3600, 3508 cm<sup>-1</sup>-ratios unchanged on dilution) and must therefore be represented as IV with axial OH groups. In DMSO the IR spectrum shows one broad OH band (3300 cm<sup>-1</sup>) due to hydrogen bonding with the solvent, and here the OH groups, which have no reason to remain axial, are probably equatorial V. These assignments can be corroborated from the NMR spectrum of the diol (see Figs. 1 and 2).

In CDCl<sub>3</sub> solution, the aromatic protons of the diol appear as a clean singlet (2.7  $\tau$ ) but in DMSO the same protons show up as an A<sub>2</sub>B<sub>3</sub> system centered at 2.6  $\tau$ . due to the influence of the equatorial oxygen atoms on the two adjacent aromatic protons. The possibility that this might be a solvent effect was considered but was

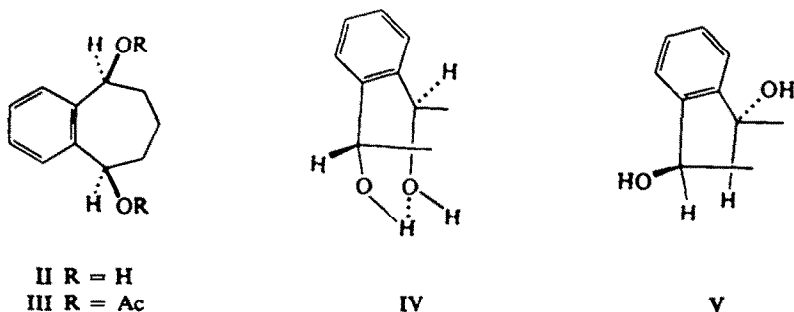
<sup>1</sup> N. Allinger and W. Szkrybalo, *J. Org. Chem.* 27, 722 (1962) footnote 11.

<sup>2</sup> R. Pauncz and D. Ginsburg, *Tetrahedron* 9, 40 (1960).

<sup>3</sup> S. Kabuss, H. Friebolin and H. Schmid, *Tetrahedron Letters* 469 (1965). These authors neglected to consider the boat conformation.

<sup>4</sup> G. L. Buchanan, *J. Chem. Soc.* 1060 (1954).

excluded by observing that the aromatic signal of tetralin appeared as a clean singlet in either solvent. That it is an effect of structure rather than of solvent is also demonstrated by Fig. 3 in which the diacetate III is seen to give the same  $A_2B_2$  pattern in  $CDCl_3$  solution. It can therefore be inferred that in the diacetate III and in a DMSO solution of the diol II, the oxygen substituents are equatorial.



An examination of molecular models reveals that in cycloheptene, an equatorial  $C_1-H$  will be at approximately  $90^\circ$  to one of the adjacent  $C-H$  bonds in either the boat or chair conformation. It is therefore not surprising that in Fig. 1, the  $5.2 \tau$  signal is only a doublet ( $J$  6 c/s). However, this is not true of an axial  $C_1-H$ . Such a bond subtends an angle of  $90^\circ$  with one of the adjacent  $C-H$  bonds *only* if the ring is in the chair conformation VI. In the boat conformation neither of these angles is  $90^\circ$  (they are in fact  $15^\circ$  and  $150^\circ$ ) and so multiple coupling should be observed. Thus the appearance of the  $4.05 \tau$  signal as a doublet ( $J$  9 c/s) in Fig. 3, and the  $5.3 \tau$  signal as a

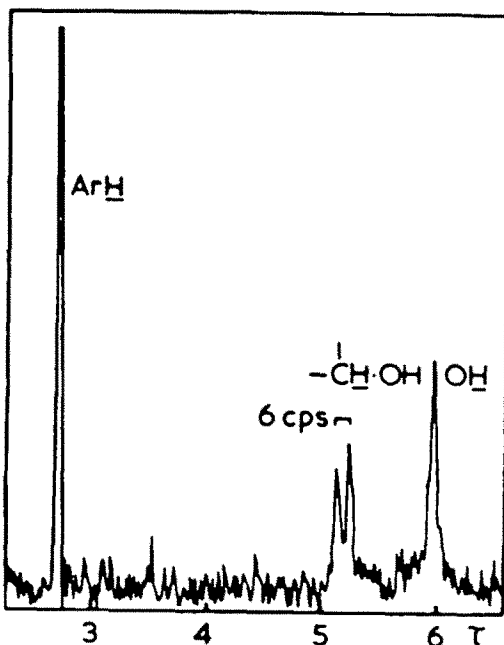


FIG. 1. NMR of diol II in  $CDCl_3$ .

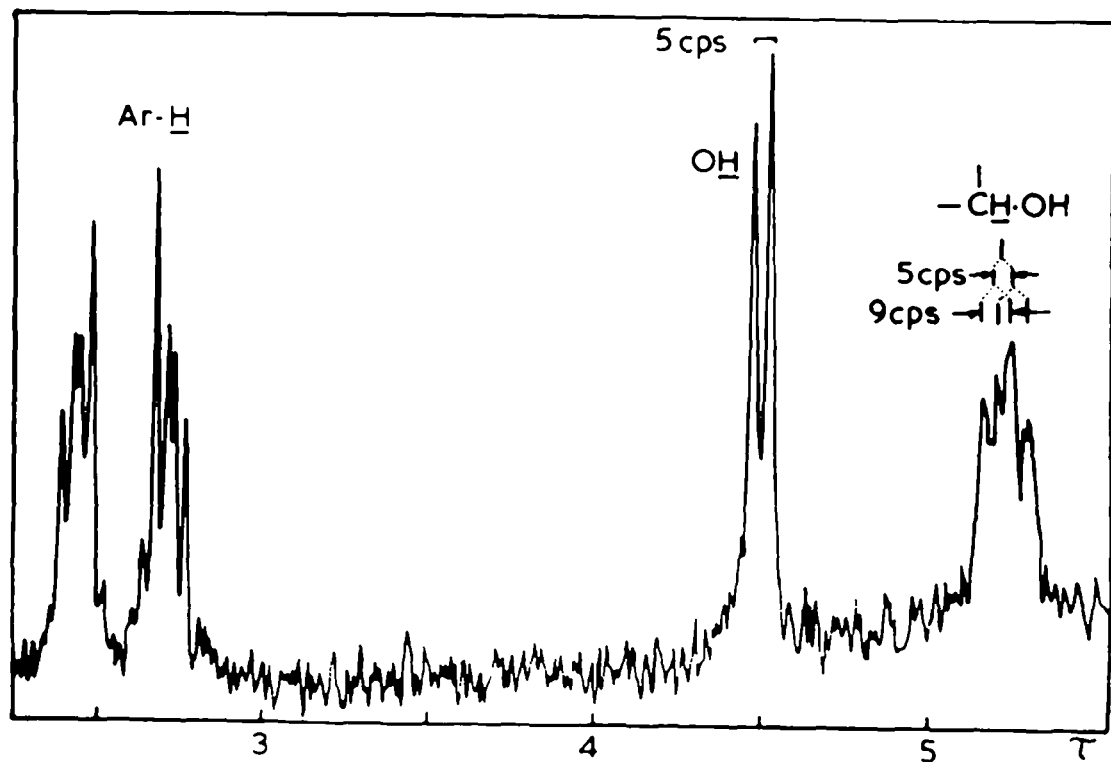


FIG. 2. NMR of diol II in DMSO.

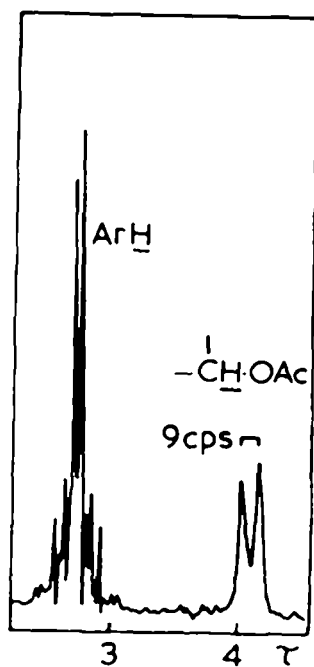
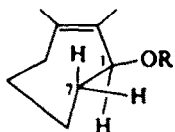
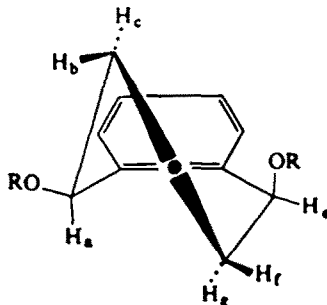


FIG. 3. NMR of diacetate III in  $\text{CDCl}_3$ .



VI



VII

quartet<sup>5</sup> ( $J_{H_1-H_2}$ , 9 c/s) in Fig. 2 excludes the boat conformation but is fully consistent with the chair conformation VI in which the dihedral angles are  $90^\circ$  and  $115^\circ$ .<sup>6</sup>

The twist-boat conformation VII presents a slightly more complicated picture, for here one of the benzylic C—H bonds will be pseudo-equatorial and the other pseudo-axial; but it appears from models that each will show significant coupling with only one of the adjacent protons (Angles  $H_bH_c$  and  $H_eH_f = 90^\circ$ :  $H_aH_c = 150^\circ$ :  $H_dH_f = 30^\circ$ ). Pseudorotation produces the mirror image structure involving identical angles. These conformations as such, are incompatible with the observed spectra, for the two benzylic protons would have different chemical shifts and the aromatic protons signal would not be symmetrical. However, rapid interconversion could conceivably make the benzylic protons appear equivalent, and account for the simplicity of the NMR signal. In an attempt to overcome this objection, the spectrum of the diacetate III has been recorded on a 100 mc instrument at  $-30^\circ$ ,  $-60^\circ$  and  $-85^\circ$ . No change of any sort was observed. There is therefore no evidence for the "slowing down" of this interconversion, and the most rational deduction is that the cycloheptene ring is in the chair conformation VI.

#### EXPERIMENTAL

IR spectra: by Mrs. F. Lawrie on a Unicam S. P. 100 spectrophotometer and the NMR spectra: Mr. J. Gall on Perkin-Elmer 60 mc and Varian HA 100 instruments. Microanalysis: by Mr. J. M. L. Cameron. Low temp NMR spectra: by Dr. W. McCrae, Cambridge University.

*cis*-1,4-Diacetoxy-2,3-benzocycloheptene. The diol<sup>4</sup> II (150 mg.) in dry pyridine (3.5 ml.) was treated with  $Ac_2O$  AR (1.5 ml.) and left at room temp for 3 days. It was then poured into ice-water, and the precipitated diacetate was recrystallized from EtOH, m.p.  $122-123^\circ$ . (Found: C, 68.7; H, 7.0.  $C_{18}H_{18}O_4$  requires: C, 68.7; H, 6.9%).  $\nu_{CO}^{CCl_4}$   $1735\text{ cm}^{-1}$ .

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<sup>5</sup> In DMSO further coupling with the hydroxyl proton is observed. [O. L. Chapman and R. W. King, *J. Amer. Chem. Soc.* **86**, 1257 (1964).]

<sup>6</sup> The coupling constant is also of the order expected from the Karplus relationship [M. Karplus, *J. Amer. Chem. Soc.* **85**, 2870 (1963)].