

## The Rate of Interconversion of the Conformations of a Derivative of *cis*-Decalin

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THE proton magnetic resonance spectra of *trans*-decalin<sup>1</sup> (down to  $-115^\circ$ )<sup>2</sup> and of cyclohexane (below  $-66^\circ$ )<sup>3</sup> show broad unresolved absorption bands consistent with a substantial difference (0.48 p.p.m. in cyclohexane) between the chemical shifts of axial and equatorial protons. In contrast, *cis*-decalin shows a single *relatively* narrow absorption band<sup>1</sup> (down to  $-121^\circ$ )<sup>2</sup> which has been compared to the *sharp* absorption line of cyclohexane at room temperature. This observation may be explained in three ways. Moniz and Dixon<sup>2</sup>

supposed that *cis*-decalin undergoes rapid ring inversion between enantiomeric two-chair conformations even at  $-121^\circ$ . They estimated that the free energy of activation,  $\Delta F^\ddagger$ , for this inversion is  $<6.4$  kcal./mole; it was assumed that the difference in chemical shifts for axial and equatorial protons is the same in *cis*-decalin and in cyclohexane ( $\Delta F^\ddagger = 10.3$  kcal./mole).<sup>3</sup> Since the interconversion of the two-chair conformations of *cis*-decalin must take place through a conformation with *both* rings in boat forms strain in the

<sup>1</sup> J. Musher and R. E. Richards, *Proc. Chem. Soc.*, 1958, 230.

<sup>2</sup> W. B. Moniz and J. A. Dixon, *J. Amer. Chem. Soc.*, 1961, **83**, 1671.

<sup>3</sup> F. A. L. Anet, M. Ahmad, and L. D. Hall, *Proc. Chem. Soc.*, 1964, 145; F. A. Bovey, F. P. Hood, E. W. Anderson, and R. L. Kornegay, *loc. cit.*, p. 146.

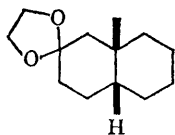
ground state<sup>2</sup> of *cis*-decalin, which is only 2.7 kcal./mole less stable than *trans*-decalin,<sup>4</sup> does not adequately explain the supposed high rate of interconversion. Geneste and Lamaty<sup>5</sup> have suggested that the preferred conformation of *cis*-decalin may be a double twisted boat form, which has not been considered by Davis and Hassel<sup>6</sup> and which is therefore not excluded by electron-diffraction studies, where there is no distinction between axial and equatorial protons. This explanation was supported by calculations of strain energies but no allowance was made for relief of strain by change of bond angles. Such calculations not only exaggerate strains<sup>7</sup> but may also change the predicted relative stabilities. The third possibility is that the preferred conformation is the accepted two-chair form but that the

protons have accidentally nearly equal chemical shifts so that little or no change in the spectrum occurs at low temperatures even when the interconversion of the conformations has become slow. This interpretation is supported by a study of a derivative (I) of *cis*-decalin.

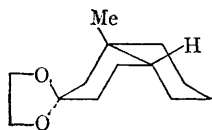
The spectrum of the compound (I) (10% w/w in chloroform) showed a relatively sharp singlet for the methyl group at room temperature. As the temperature was lowered the methyl group resonance broadened and below  $-42^\circ$  separated into two lines of very nearly equal intensity which were 4.1 c./sec. apart but still somewhat broadened at the lowest temperature reached ( $-67^\circ$ ). The free energy of activation is estimated to be 12.5 kcal./mole from the coalescence temperature and an estimated maximum separation of  $4.1 \pm 0.1$  c./sec. between the two methyl group resonances.<sup>8</sup> It may be predicted that the two-chair conformations (Ia) and (Ib) will be very nearly equal in stability and that the methyl group in conformation (Ia) (but not in Ib) will be deshielded by the nearer oxygen atom. In contrast, the methyl group and the nearer of the two oxygen atoms are never very close in the twisted boat conformations and there appears to be no reason to suppose that, apart from a very improbable coincidence, two of these conformations would have equal stability and be separated by a large energy barrier.

The spectra were measured on a Varian A60 spectrometer.

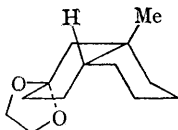
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(I)



(Ia)



(Ib)

<sup>4</sup> N. L. Allinger and J. L. Coke, *J. Amer. Chem. Soc.*, 1959, **81**, 4080.

<sup>5</sup> P. Geneste and G. Lamaty, *Bull. Soc. chim. France*, 1964, 2439.

<sup>6</sup> M. I. Davis and O. Hassel, *Acta Chem. Scand.*, 1964, **18**, 813, and references cited therein.

<sup>7</sup> F. H. Westheimer, "Steric Effects in Organic Chemistry," ed. M. S. Newman, J. Wiley and Sons, New York, 1956, pp. 524-555.

<sup>8</sup> J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959, pp. 218-225.