Conformational Rigidity in [2,2](2,5)Pyrrolofuranophane[1]

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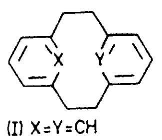
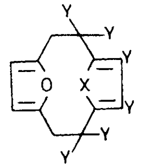
Summary A variable temperature n.m.r. study of a hexadeuterio-analogue of [2,2](2,5)pyrrolofuranophane (IVb) defines a lower limit of 27 kcal/mol for the barrier to ring inversion in the title compound.

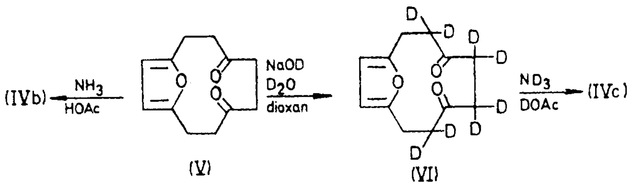
In recent years, variable temperature nuclear magnetic resonance (v.t.n.m.r.) studies of *meta*-bridged cyclophanes and their heterocyclic analogues have provided information regarding non-bonded interactions between π-clouds,



(I) X=Y=CH
(II) X=CH,Y=N:
(III) X=Y=N:



(IV) a, X=O, Y=H
b, X=NH, Y=H
c, X=NH, Y=D



hydrogen atoms, and non-bonding electron pairs during the ring inversion processes in these systems. It has been demonstrated, for example, that the aromatic rings in [2,2]metacyclophane (I)[2] and [2,2](2,6)pyridinometacyclophane (II)[3] are rigid on the n.m.r. time scale ($E_{\text{act}} > 27$ kcal/mol), while those in [2,2](2,6)pyridinophane (III)[4] and [2,2](2,5)furanophane (IVa)[4] are freely rotating at temperatures close to ambient (E_{act} 15—17 kcal/mol). [2,2](2,5)-Pyrrolofuranophane (IVb) is an interesting addition to the series, since the van der Waals radii of the interacting nuclei in (IVb) and (II) are similar. We have recently reported the synthesis and v.t.n.m.r. study of (IVb).[1] However, the complexity of the n.m.r. signals associated with the bridging protons (ABCD pattern) prevented interpretation of data in terms of conformational mobility. We now report v.t.n.m.r. results on the hexadeuterio-analogue (IVc) which was synthesized to facilitate analysis of the rotational process by n.m.r.

The cyclophane (IVc) was prepared from the diketone (V) *via* (VI) by the Paal–Knorr route. Mass spectral analysis indicates $> 70\%$ deuteriation in the bridge positions α to the pyrrole ring and $< 1\%$ deuteriation on nitrogen.†

The n.m.r. spectrum of (IVc) at 60 MHz exhibits a deuterium broadened AB quartet [in contrast to the complicated ABCD pattern in (IVb)] for the bridge protons α to the furan ring. The deuterium decoupled 100 MHz spectrum of (IVc) shows the AB quartet more clearly. The separation (δ) between the A and B resonances is calculated[5] to be 12·7 Hz based on the coupling constant (J_{AB}) of 13·6 Hz as obtained from the deuterium decoupled spectrum. This deuterium decoupled spectrum remains unchanged upon heating the sample to 190°. For a minimum detectable line broadening of 0·5 Hz, the above data represent a rate constant for conformational inversion in (IVc) of $< 1\ \text{s}^{-1}$ with an associated Arrhenius energy of activation greater than 27 kcal/mol.

Thus, like the sterically similar [2,2](2,6)pyridinometacyclophane (II), (IVb) is conformationally rigid on the n.m.r. time scale.

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† The mass spectrum shows a total of 90% hexa- and penta-deuteriated isomers. The effect of the penta-deuteriated isomers on the n.m.r. spectrum is negligible.

[1] For previous papers in this series see: J. F. Haley, jun., and P. M. Keehn, *Tetrahedron Letters*, 1973, 4017; S. Rosenfeld and P. M. Keehn, *ibid.*, p. 4021.

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[3] J. R. Fletcher and I. O. Sutherland, *Chem. Comm.*, 1969, 1504.

[4] I. Gault, B. J. Price, and I. O. Sutherland, *Chem. Comm.*, 1967, 540.

[5] L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance in Organic Chemistry,' Pergamon Press, New York, 1969, p. 129.