Ring Inversion in Dispiro[2,2,2,2]decane

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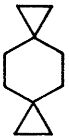
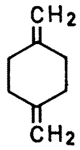
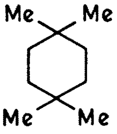
Summary The title compound (I), which contains a cyclohexane ring with spiro-bound cyclopropanes at either end, has been found to have a barrier (E_a) to ring inversion of 12·1 ± 0·4 kcal mol^{-1}; the axial–equatorial chemical-shift difference is 1·21 p.p.m., an unusually large value.

RING inversion has only recently been observed in spiro-compounds, particularly in certain cyclic ethers.[1] We report the first carbocyclic example, dispiro[2,2,2,2]decane (I). The molecule is of theoretical interest because the orbitals from the quaternary carbons into the six-membered ring may be closer to sp^2 than sp^3 hybridization. By analogy with the bis-(*exo*-methylene) compound (II),[2] the barrier to ring inversion should be lower than in cyclohexane (IV), whereas analogy with the tetramethyl compound (III)[3] would suggest a similar or slightly higher barrier for (I) than for (IV).


(I)


(II)


(III)


(IV)

Compound (I) was prepared by the multiple cyclopropanation of (II) with zinc and methylene iodide. The 60 MHz (Varian A-60) ^{1}H nuclear magnetic resonance spectrum in $C_6D_5\cdot CD_3$ consists of two equal-area singlets at room temperature (0·1 and 1·2 p.p.m. below Me_4Si). The cyclohexyl resonance passes reversibly through a coalescence at −40° to an AA′XX′ pattern ($\Delta\nu_{AB}$ = 72·5 Hz or 1·21 p.p.m.). The cyclopropyl resonance remains an unaltered singlet down to −80°, although at 90 MHz (Bruker HFX-10) it becomes an AA′BB′ spectrum at this temperature. Rates were measured from the cyclohexyl spectral changes for 25 data points ranging from +28° to −61° by a complete line-shape analysis. The following activation parameters were obtained: E_a = 12·1 ± 0·4 kcal mol^{-1}; log A = 13·8; $\Delta H^‡$ = 11·5 kcal mol^{-1}; $\Delta S^‡$ = 2·5 eu; $\Delta G^‡$ (25°) = 10·7 kcal mol^{-1}; correlation coefficient = 0·998.

The results are best interpreted by comparison with related compounds (see Table). Despite possible electronic and structural similarities, the spiro-compound and the *exo*-methylene compound differ significantly in barrier size. The barrier height for (I) is much closer to that for cyclohexane (IV) and its methylated derivative (III). This situation contrasts to the oxygen heterocycles reported previously,[1] in which the spirocyclopropyl derivatives have lower barriers than the non-spiro six-membered ring. The shape of the central ring in (I) is also much closer to that of cyclohexane than to that of (II), as indicated by their respective R values[5] [(I) 2·1; (IV) 2·2; (II) 1·4]. The spirocyclopropyl rings in (I) thus alter the structural properties of the central cyclohexane ring very little.

Ring reversal for dispiro[2,2,2,2]*decane and related compounds*

Compound	$\Delta\nu_{AB}$, p.p.m.	T_c, °	$\Delta G^‡(T)$	Source
(I)	1·21	−40[a]	10·7 (25)	This work
(II)	0·35	−118[b]	7·5 (−118)	Ref. 2
(III)	0·20[c]	−53[b]	11·6 (−53)	Ref. 3
(IV)	0·48	−67[a]	10·2 (−67)	Ref. 4

[a] Taken at 60 MHz.
[b] Taken at 100 MHz.
[c] Estimated from the spectra in ref. 3.

One of the most remarkable aspects of the n.m.r. spectrum of (I) is the axial–equatorial chemical-shift difference, 1·21 p.p.m. Compounds (II)—(IV) exhibit differences of no more than 0·48 p.p.m. The equatorial proton in (I) is positioned over the cyclopropane ring, whereas the axial proton is more nearly in the plane of that ring. The anisotropic three-membered ring will strongly shield the equatorial proton and possibly even deshield the axial proton. Since the usual axial–equatorial ordering is thereby reversed, the effect is even larger than indicated by the measured difference. The magnitude of the axial–equatorial chemical-shift difference in (I) may be the largest observed for a hydrocarbon six-membered ring.†

It has been assumed that (I) exists in a centrosymmetric chair conformation, rather than in the twist boat once suggested for (II).[6] These conformations may be differentiated by vibrational spectroscopy, since the C_{2h} chair should have few or no Raman–i.r. coincidences, but the C_2 twist boat should exhibit only coincidences. We observed 25 i.r. and 30 Raman bands, with only 8 coincidences. For liquid-phase comparisons, such a number is entirely consistent with the centrosymmetric chair and unequivocally excludes the various boat conformations.

We thank the National Science Foundation, the Petroleum Research Fund, and the Alfred P. Sloan Foundation for direct support of this research. We also thank the National Science Foundation for traineeship support of J. L. G. and L. G. G. and for an equipment grant to purchase the Bruker HFX-10.

(*Received, June 25th,* 1970; *Com.* 1006.)

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† Previously, large geminal chemical-shift differences have been observed in N-alkylpiperidines and in cyclohexanone oximes, but these effects are due to nitrogen lone-pair anisotropy.

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