The structure was solved by the heavy atom (S) method and refined by full matrix least squares. The R factor is 0.04.

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Addition of Hydrogen Chloride and Deuterium Chloride to 2-*exo*-Methoxy-5-norbornene

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Additions of hydrogen chloride and deuterium chloride to bicyclic bridge compounds have been very extensively studied.[1-4] In this work the reaction of 2-*exo*-methoxy-5-norbornene (I) with hydrogen chloride in methylene chloride at room temperature has been investigated and found to give two main products, 2-*endo*-methoxy-5-*exo*-chloronorbornane (IIIA) and 2-*exo*-methoxy- 5-*exo*-chloronorbornane (IVA). Addition of deuterium chloride to I under similar reaction conditions also gave two main products, 2-*endo*-methoxy-5-*exo*-chloro-7-*anti*-deuterionorbornane (IIIB) and 2-*exo*-methoxy-5-*exo*-chloro-6-*exo*-deuterionorbornane (IVB). The results were verified by NMR and mass spectroscopy.

Dehydronorbornyl methyl ether (I) was prepared by acid-catalyzed addition of methanol to norbornadiene.[5] The reaction yielded a mixture of I and *exo*-3-methoxy-

nortricyclene (V) in the ratio 1:2. The methyl ethers (I) and (V) were separated by preparative gas chromatography.

exo-Dehydronorbornyl methyl ether (I) was treated with dry, gaseous hydrogen chloride in methylene chloride at room temperature for 24 h. Gas chromatographic analysis showed that the reaction had proceeded almost to completion. The reaction gave a mixture of IIIA and IVA in the ratio 52:48, as measured by the retention times and peak heights. Separation of IIIA and IVA was carried out by preparative gas chromatography.

The reaction of I with deuterium chloride was performed as above, using the labelled, dry gas prepared by the method of Dewar and Fahey.[6] In this case the reaction time was 48 h. The reaction gave a mixture of IIIB and IVB in the ratio 47:53. The stereochemical structure of IIIA, IIIB, IVA, and IVB could be deduced from the NMR spectra of the products of the reactions of I with hydrogen chloride and deuterium chloride. The correspondence of the product ratios reflects the mechanism for the stereochemical course of the additions of hydrogen chloride and deuterium chloride to I. It seems plausible that reaction proceeds *via* the "asymmetrically bridged" cation route:[7-9]
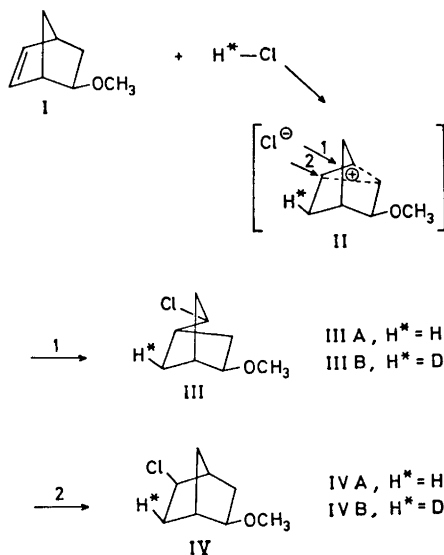
The proton resonance spectrum of 2-*endo*- methoxy-5-*exo*- chloronorbornane
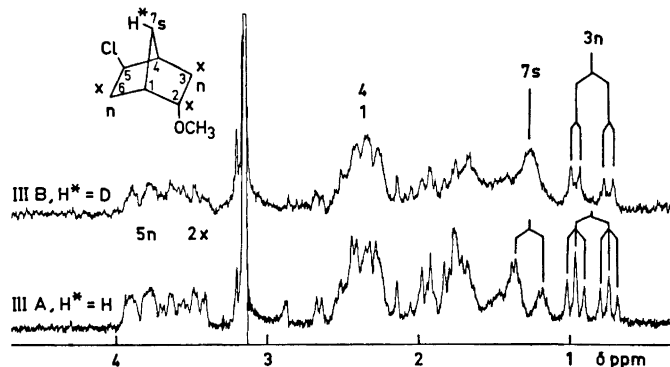
Fig. 1. Proton resonance spectrum of 2-endo-methoxy-5-exo-chloronorbornane (IIIA) and 2-endo-methoxy-5-exo-chloro-7-anti-deuterionorbornane (IIIB) in carbon tetrachloride measured with 60 Mc Perkin-Elmer R 12 B spectrometer. The following coupling constants (cps) were measured and confirmed by double resonance experimentents: $J_{3n3x}=13.5$, $J_{3n2x}= 3.7$, $J_{3x2x}=10.0$, $J_{5n6n}=7.9$, $J_{6x6n}=13.5$, $J_{7a7s}=10.5$.
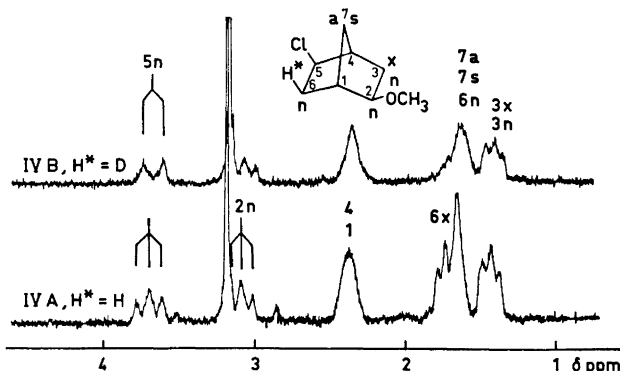

Fig. 2. Proton resonance spectrum of 2-exo-methoxy-5-exo-chloronorbornane (IVA) and 2-exo-methoxy-5-exo-chloro-6-exo-deuterionorbornane (IVB) in carbon tetrachloride recorded with a Perkin-Elmer Model R 12 B 60 Mc spectrometer. The signals of 5n and 2n in the spectrum of IVA appear as triplets, indicating a virtual coupling.[13] The signal of 5n in the spectrum of IVB is a doublet with $J=8.0$ cps. It arises from the endo-5-H and endo-6-H coupling.[3]

(IIIA) in CCl_4 (Fig. 1) shows the signals of the norbornane skeleton protons. The CH-signals at the lowest field arise from the α-protons (closest to chlorine and the methoxy group). In all the compounds studied the signal of the α-proton closest to chlorine appears at a lower field than that of the α-proton closest to the methoxy group. Accordingly, the 5n signal in the spectrum of IIIA in CCl_4 is at a lower

field than the 2x signal. This was confirmed by using trifluoroacetic acid as solvent. All signals in the spectrum of IIIA in CF_3COOH move to a lower field compared to solution in CCl_4, and the signal of 2x moves much more (0.34 ppm) than the signal of 5n (0.17 ppm). Because the 2x proton is nearest the oxygen of the methoxy group, this solvent effect of CF_3COOH causes more deshielding of the

$2x$ signal than of the $5n$. Interpretation of other signals and couplings was verified by double resonance experiments, and comparing them with the NMR data of norbornadiols [10,13] and norbornatriols.[11,12] The results are presented in Figs. 1 and 2.

The mass spectra of IIIA and IVA ($C_8H_{13}ClO$) were quite similar; M^+ peaks at m/e 160 and 162 were detected. The base peak at m/e 66 can be attributed to the cyclopentadienyl cation ($C_5H_6^+$), as in the case of starting compound (I). The other characteristic peaks in the mass spectrum of IIIA and IVA were at m/e 124, 93, 92, 91, 79, 58, 45, and 36. M^+ peaks were at m/e 161 and 163 in the mass spectra of IIIB and IVB. In each case the base peak was at m/e 67 and was due to the cation ($C_5H_5D^+$). The other characteristic peaks in mass spectra of IIIB and IVB were at m/e 125, 94, 93, 92, 80, 67, 58, 45, and 36 (run with a Perkin-Elmer gas chromatograph mass spectrometer Model 270).

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A Comparison of *ab initio* and Semi-empirical Calculations on Li+(NH3)

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The comparison between the *ab initio* and CNDO/2 method on the hydration of Li$^+$ is reported in a separate paper.[1] The ammonia molecule is now substituted for the water molecule to investigate whether the *ab initio* calculations on Li$^+$(NH$_3$) compared to the CNDO/2 method gives results similar to those found for the Li$^+$(H$_2$O) and Li$^+$(H$_2$O)$_2$ systems.

During the calculations the geometry of the ammonia molecule was kept constant at the experimental values: $R_{N-H} = 1.01$ Å and $\angle$ HNH $= 107°$. The three hydrogens lie in the xy-plane and N$-$Li lies on a line perpendicular to the xy-plane.

For the *ab initio* calculations the program IBMOL [2,3] was used. This program uses gaussian type functions

$$g = Nx^l y^m z^n e^{-\alpha r^2} \qquad (1)$$

where α is the orbital exponent and N is a normalisation constant. The calculations were performed with the following basis set:

(H|4) contracted to $\langle$H|2$\rangle$
(N|7,3) contracted to $\langle$N|4,2$\rangle$
(Li|7,2) contracted to $\langle$Li|4,2$\rangle$

Orbital exponents and contraction coefficients are tabulated in Table 1. R_{Li-N} was varied to find the distance corresponding to minimum energy.

The semi-empirical calculations are based on the CNDO theory as developed by Pople and co-workers.[4-6] The computations were performed with the QCPE program.[7] All parameters were taken from the original papers without any modification.

The results are given in Table 2. The calculated ammoniation energies (ΔE) for the reaction

$$Li^+ + NH_3 = Li^+(NH_3) \qquad (2)$$
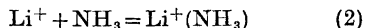
are also listed here.

The ΔE for the CNDO/2 calculation is much greater than for the *ab initio*. The ΔE for *ab initio* calculation is sensitive to the basis set.[1] No experimental ΔE value is available for the Li$^+$(NH$_3$) system.