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. In this work the reaction of 2-endo-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-endo-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-endo-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. The reaction yielded a mixture of I and exo-3-methoxy-

H^+—Cl

H^+—Cl

H^+—Cl

The proton resonance spectrum of 2-endo-methoxy-5-exo-chloronorbornane

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Fig. 1. Proton resonance spectrum of 2-endo-methoxy-5-exo-chloronorbornane (III A) and 2-endo-methoxy-5-exo-chloro-7-anti-deuteronorbornane (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 experiments: $J_{3,12}=13.5$, $J_{3,13}=3.7$, $J_{2,12}=10.0$, $J_{2,13}=7.9$, $J_{4,13}=13.5$, $J_{3,22}=10.5$.

Fig. 2. Proton resonance spectrum of 2-exo-methoxy-5-exo-chloronorbornane (IVA) and 2-exo-methoxy-5-exo-chloro-6-exo-deuteronorbornane (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. 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.

(IIIA) in CCl$_4$ (Fig. 1) shows the signals of the norbornane skeleton protons. The CH-signals at the lowest field arise from the $\alpha$-protons (closest to chlorine and the methoxy group). In all the compounds studied the signal of the $\alpha$-proton closest to chlorine appears at a lower field than that of the $\alpha$-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$_3$COOH 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$_3$COOH causes more deshielding of the

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A Comparison of ab initio and Semi-empirical Calculations on Li\(^+\)(NH\(_3\))

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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 \(\angle HNH = 107^\circ\). 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\(^15\) was used. This program uses gaussian type functions

\[ g = N\alpha^\gamma r^{\alpha-\gamma} \]  

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

- \(\text{H}(4)\) contracted to \(\text{H}(2)\)
- \(\text{N}(7,3)\) contracted to \(\text{N}(4,2)\)
- \(\text{Li}(7,2)\) contracted to \(\text{Li}(4,2)\)

Orbital exponents and contraction coefficients are tabulated in Table 1. \(R_{\text{Li-N}}\) 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.\(^4,5\) 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 (\(\Delta E\)) for the reaction

\[ \text{Li}^+ + \text{NH}_3 = \text{Li}^+(\text{NH}_3) \]  

\(\Delta E\) are also listed here.

The \(\Delta E\) for the CNDO/2 calculation is much greater than for the ab initio. The \(\Delta E\) for ab initio calculation is sensitive to the basis set.\(^1\) No experimental \(\Delta E\) value is available for the Li\(^+\)(NH\(_3\)) system.