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STUDIES OF THE NITROGEN INVERSION BY NMR SPECTROSCOPY. I.
AMINE-LEWIS ACID COMPLEXES WITH DIASTEREOTOPIC PROTON SYSTEMS

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It has been demonstrated by many authors that a nitrogen atom can be a chiral centre which gives rise to anisochronism of the geminal proton systems. In such cases however, NMR spectroscopy gives signals attributable to isochronic protons unless the nitrogen configuration is made relatively stable in the NMR time scale. When the nitrogen inversion is hampered owing to such structural factors as:

(1) ring strain in aziridine and azetidine derivatives,
(2) steric hindrance,
(3) bonding of the nitrogen with atoms carrying electron lone pairs, e.g. in derivatives of hydroxylamine, hydrazine or difluoroamine,

resolution of the geminal proton signals can be obtained by taking the spectra at low temperatures [1,2].

Methyldibenzylamine ($T_c \cong -140°C$ in $CH_2{=}CHCl$) is the only hitherto reported example of acyclic tertiary amine for which the above method gives satisfactory results[3,4]. In similar cases the best effects were obtained by protonation of the nitrogen lone pair (NMR spectra recorded in solutions of trifluoroacetic[5] or formic acids[6], or in aqueous solutions of sufficiently low pH values[7]). The restricted inversion of nitrogen was also observed by NMR spectroscopy of amine hydrochlorides[8] and quarternary ammonium compounds[9] in organic solvents.

Harris and Spragg[10] have demonstrated the possibility of stabilizing the nitrogen configuration by involving its lone pair in a bond with a sulphur dioxide molecule. In this communication we would like to report the use of aluminium organic compounds as the species coordinating with the nitrogen.

As it is shown in Fig.1 and Table 1, in the spectrum of an approximately equimolar mixture (1:1·1) of methylaluminiumdichloride (A_1) and methylisopropylphenylamine (B) in benzene the two methyls of the isopropyl group appear as a pair of doublets thus giving evidence of the restricted inversion. While the B:A ratio increases a gradual averaging of the C-methyl signals occurs. This is presumably due to the exchange of the amine molecules in

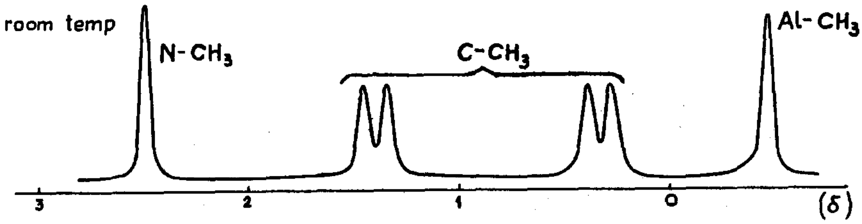

Fig.1. i-PrN(Me)Ph:MeAlCl$_2$ = 1:1·1 in benzene

the complex and rapid nitrogen inversion within the free amine. An additional support of such interpretation is provided with the low-temperature (-79°C) spectrum in toluene (Fig.2) in which the free amine, present in the sample in a considerable excess, and the complexed amine give separate signals of the isopropyl group. Broadening of the resonance lines is here probably due to the still operative amine exchange and poor resolution (high viscosity of the solution).

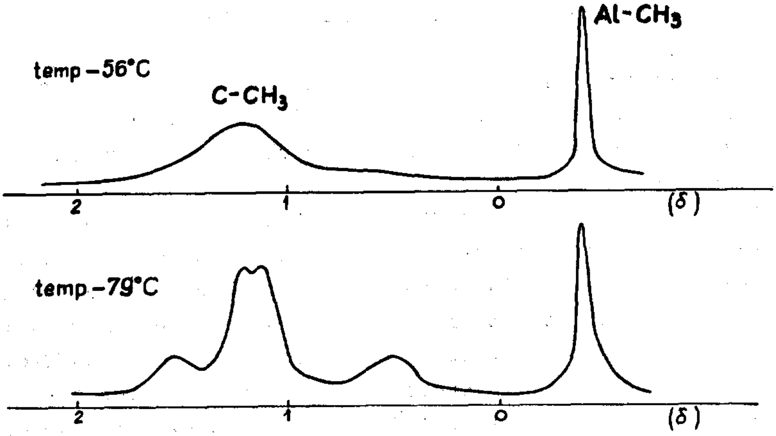

Fig.2. i-PrN(Me)Ph:MeAlCl$_2$ = 1:0·5 in toluene

Similar exchange reactions have been shown earlier to proceed either by the S_N1 mechanism [as in systems containing $(CH_3)_3N$ and $(CH_3)_3B$[11] or by the S_N1 and S_N2 mechanisms simultaneously [as in systems containing $(CH_3)_2O$, $(C_2H_5)_2O$ and BF_3[12]]. In our case the life-time of the B-A_1 complex depends on concentration of B; consequently it seems that in the presence of the free amine in excess the exchange takes place rather by S_N2 than S_N1 mechanism. The weaker and bulkier Lewis acid dimethylaluminiumchloride(A_2) gives with B a less stable complex. In this case the Al-methyl and C-methyl signals appear at room temperature, independently of the A_2:B ratio, as a sharp singlet and a somewhat broadened doublet respectively (Fig.3).

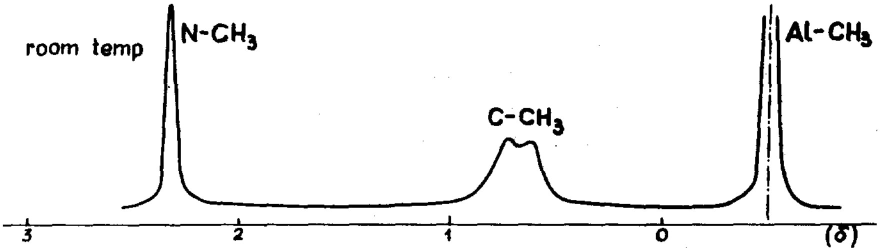

Fig.3. i-PrN(Me)Ph:Me_2AlCl = 1:2 in benzene

At -50°C the life-time of the A_2-B complex increases and the diastereotopic C-methyl and Al-methyl groups become anisochronous (Fig.4).

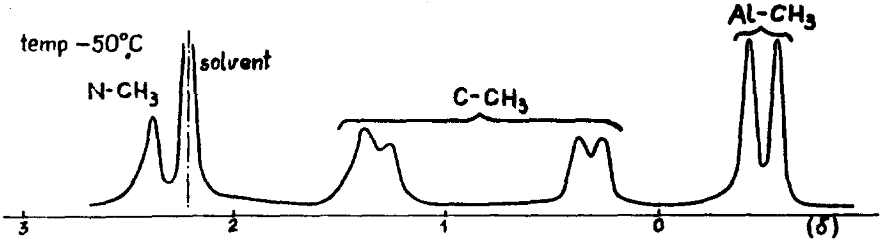

Fig.4. i-PrN(Me)Ph:Me_2AlCl = 1:1 in toluene

In our opinion further investigations on the amine-Lewis acid complexes with diastereotopic proton systems should give much information on the nitrogen inversion as well as the mechanism of formation and reactions of the complexes.

Table 1

Compound	Solvent	Temperature (°C)	Chemical shifts(δ)[a]		
			CH_3-C[b]	CH_3-N	CH_3-Al
i-PrN(Me)Ph	Benzene	ambient	0.90	2.44	-
$MeAlCl_2$	"	"	-	-	-0.35
i-PrN(Me)Ph:$MeAlCl_2$=1:1·1	"	"	0.38;1.37	2.50	-0.53
Me_2AlCl	Toluene	-50	-	-	-0.31
i-PrN(Me)Ph:Me_2AlCl=1:1	"	-50	0.27;1.29	2.33	-0.63;-0.49

a. The benzene peak(δ 7.15) and Me toluene peak (δ 2.15) were used as internal references

b. Doublets J≅ 6.8 cps

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