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NATURAL ABUNDANCE NITROGEN - 15 NUCLEAR MAGNETIC RESONANCE
STUDIES OF SOME TWIN - SITE DONORS

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ABSTRACT

The natural abundance ^{15}N -NMR chemical shifts of 1,10-phenanthroline, pyridazine and 7-azaindole have been measured as a function of the nature of the solvent. Hydrogen bonding and protonation result in upfield shift of both the pyridine type nitrogens in

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1,10-phenanthroline and pyridazine whereas in 7-aza-indole, the effect is larger at the pyridine ring nitrogen. The chemical shifts due to protonation far exceeded those from hydrogen bonding. In addition to identifying the site of donation, the ^{15}N -NMR data establishes the mechanism of charge transfer and hydrogen bonded complex formation.

INTRODUCTION

Nitrogen - 15 NMR spectroscopy¹ offers several advantages over other forms of NMR spectroscopy for the study of problems connecting nitrogen compounds of biological interest. Furthermore unlike carbon and hydrogen, nitrogen is very often the donating site in metal complexes, hydrogen bonding etc., and nitrogen - 15 NMR spectral study can be expected to be very sensitive probe for the study of the nature of bonding involving nitrogen. It has recently been demonstrated¹⁻³ that it is possible to obtain ^{15}N -NMR spectra at natural abundance level of this isotope although the technique is somewhat complex. The importance of ^{15}N -NMR data in elucidating the effects of hydrogen bonding and protonation in amines⁴, diazoles⁵⁻⁷ has been clearly demonstrated. In the case of imidazoles and pyrazoles, the site of donation for hydrogen bonded complexes and protonation is shown to be at the pyridine type nitrogen^{4,6}.

In this laboratory work is in progress⁹ to study the donor properties of twin-site donors with the donor sites N,S,O under different chemical environments. Multifunctionality poses many problems such as the nature and extent of the interaction between sites in the ground state of the donor and the effect of the complexation at one site on the reactivity of the uncomplexed sites. While studying the donor properties of some twin site donors such as 1,10-phenanthroline and pyridazine using iodine, phenols and alcohols as acceptors employing UV-visible and proton NMR techniques, the assignment of the site of donation was not possible. It was felt that ¹⁵N-NMR spectral data would yield useful information on this aspect. In this paper, we present our study of the natural abundance Nitrogen - 15 NMR spectral data of some selected twin-site donors.

EXPERIMENTAL

The twin-site donors chosen for the study are

- a) 1,10-phenanthroline,
- b) pyridazine,
- c) 7-azaindole.

The ¹⁵N-NMR spectral data of these three compounds in non-polar (carbontetrachloride), hydrogen bonding (ethanol), and protonating (0.1N HCl) solvents were studied.

1,10-Phenanthroline, 7-azaindole and pyridazine were of Aldrich pure grade. 1,10-Phenanthroline and 7-azaindole were recrystallised from carbontetrachloride three times, pyridazine was further purified by distillation. Spectrograde carbontetrachloride and ethanol were dried and distilled. Solutions of 0.05M concentrations were used in all cases.

The ^{15}N -NMR spectra were taken with Bruker-WM 400 spectrometer operating at 40.56 MHz. All shifts reported are relative to NO_3^- in ammonium nitrate dissolved in D_2O . The reference was contained in a 5 mm NMR tube held in the centre of the sample by means of a Teflon plug. The deuterium in the reference provided the field frequency lock signal. The temperature of the probe was maintained at 304°K. Because of the long relaxation times and small unfavourable nuclear Overhauser effects (NOE) of the pyridine ring nitrogens in the compounds selected for the study, a pulse width of about 20-25 μ sec was used. Proton noise decoupling was done only during data acquisition with an average of 5000 scans at a sweep width of 7 KHz. Spectra were recorded using the inverse gated decoupling technique and in conditions where the NOE was negative.

RESULTS AND DISCUSSION

This is the first reported attempt to study the donor behaviour of twin-site donors based on ^{15}N -NMR

spectral data. ^{15}N -NMR chemical shifts of 1,10-phenanthroline, pyridazine and 7-azaindole in carbon tetrachloride, ethanol and 0.1M hydrochloric acid, are given in Table I. Both 1,10-phenanthroline and pyridazine show only a single ^{15}N -resonance in all the solvents, indicating that both the nitrogens are in the identical chemical environments in all the situations. The chemical shifts of both the nitrogens in pyridazine is 92.8 ppm downfield from that of 1,10-phenanthroline. This is probably due to the -I effect of each nitrogen on the other. In ethanol, the ^{15}N -resonances of both the compounds shift upfield to a smaller extent, whereas in protonating solvents the shifts are significantly larger (Table II).

The nature of the bonding in the two twin-site donors can be of two types:

- a) donation is only from one nitrogen
- b) donation is from both the nitrogens, wherein the hydrogen is fast exchanging between the two nitrogens (Fig. Ia, b).

It is known^{7,8} that both the donors form only 1:1 hydrogen bonded complexes and only monoprotonated species under these experimental conditions. If only one nitrogen were donating, we should necessarily get two ^{15}N -resonances for the two compounds in hydrogen

TABLE I

¹⁵N-NMR SPECTRAL DATA IN VARIOUS SOLVENTS

S.No.	Donor	¹⁵ N-Chemical shift, in ppm		
		Carbon Tetrachloride	Ethanol	0.1M HCl
1	1,10-Phenanthroline	-61.57	-74.43	-136.80
2	Pyridazine	+31.31	+14.01	-48.43
3	7-Azaindole			
	N ₁ -(Pyridine type)	-117.36	-119.30	-210.15
	N ₂ -(Pyrrole type)	-237.35	-239.93	-241.68

TABLE II

S.No.	Name of the Donor	$\Delta\delta^a$ of Hydrogen bonding (ppm)	$\Delta\delta^b$ of Protonation (ppm)
1	1,10-Phenanthroline	12.86	75.23
2	Pyridazine	17.30	79.74



Figure 1

bonding and protonating solvents, which is not experimentally observed. Structure I (a,b) can be assumed to explain the experimental data.

In a previous study in this laboratory, the donor properties of 1,10-phenanthroline and pyridazine have been studied using iodine, phenols etc., as acceptors and employing UV-visible and proton NMR spectral data. Structure I (a,b) have been assumed to explain the high equilibrium constant values compared to 2,2'-bipyridine, pyrazine etc., and also to explain broad Lewis acid-OH peaks appeared in proton NMR spectra of hydrogen bonded complexes between these two donors and Lewis acids. Thus, it can be assumed that the two nitrogens are participating in donation in these two donors. Further, ^{15}N -NMR spectral studies at low temperatures may confirm this mechanism.

In contrast, the ^{15}N -NMR spectrum of 7-azaindole, in carbontetrachloride (Table I) indicates that the nitrogens (pyrrole and pyridine types) are experiencing large downfield shifts from their normal posi-

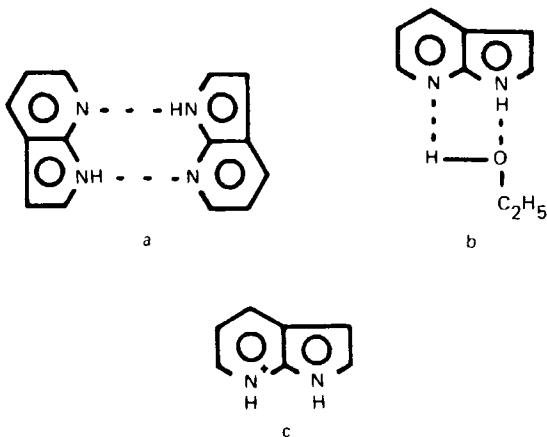


figure II

tions. This behaviour can be explained on the basis of the property of dimer formation of this compound as suggested by fluorescence studies¹⁰ (Fig.IIa). Further, the difference in the chemical shifts of both the nitrogens of 7-azaindole in carbontetrachloride and alcohol is small, which could be attributed to the following two possibilities.

- The dimer formed remains undisturbed.
- The hydrogen bonded complex of ethanol and 7-azaindole is very similar to the dimer structure (Fig.IIb).

In the case of protonation, the pyridine nitrogen is protonated as is evident from the large up field shift of the pyridine nitrogen and there is little effect on pyrrole type nitrogen, which can be explained by assuming that the uncomplexed pyrrole type donor

site would stabilize the dative form of the complex formed through donation of the pyridine nitrogen.

The ^{15}N -NMR spectral data of 7-azaindole which is similar to reported data of N-methylimidazole and N-methyl pyrazole further confirm this (Fig. IIc).

In this laboratory, work has been done¹¹ on the donor properties of 7-azaindole with acceptors like iodine, chloranil etc., and some Lewis acids employing UV-visible and proton NMR studies. The data now obtained conclusively establishes that the pyridine ring nitrogen is the donating site.

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