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EFFECT OF Yb(DPM)$_3$ AND Eu(DPM)$_3$ ON NITROGEN-14 MAGNETIC RESONANCE

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The expansion of n.m.r. chemical shifts of protons induced by tris-(dipivalomethanato) europium, Eu(DPM)$_3$, and by other lanthanide chelates is a subject of growing interest (1)(2). So far no such attempt has been made at nitrogen magnetic resonance shifts. Apart from possible practical applications of such effects to ^{14}N spectral assignments, the results for ^{14}N nuclei may throw some light on the nature of the interactions which induce the shifts. Proton resonance spectra (2) suggest nitrogen lone electron pairs as important ligands in the formation of associates responsible for the shifts.

The results of ^{14}N resonance measurements for some organic molecules involving various types of nitrogen valence states are given in Tables I and II. While both Yb(DPM)$_3$ and Eu(DPM)$_3$ (2) induce paramagnetic shifts in proton resonance spectra, the former acting 2.0±0.1 times stronger with fivefold line broadening relative to the latter, the effects on the ^{14}N shifts are different, since Eu(DPM)$_3$ induces a diamagnetic shift which is about 3 times as large as the Yb - induced paramagnetic shift. The induced nitrogen shifts extrapolated to an equimolar ratio of chelate to solute seem to be related to the basicity of the nitrogen lone electron pair and steric effects. Alkylamines and pyridine show the largest induced shifts (about -400 ppm for Yb, about +1500 ppm for Eu). The relatively large shift for pyridine may be due to steric effects since the planar molecule may offer the least hindrance to association with the chelate. The nitrogen atom with the lone electron pair which lies within the plane of the ring of N-methylimidazole shows an induced ^{14}N shift of about -200 ppm for Yb, and about +1400 ppm for Eu, and the effect on the resonance of acetonitrile is still smaller (about -130 ppm for Yb, about +500 ppm for Eu). If the lone electron pair is involved in a delocalised π-electron system, like in N,N-dimethylformamide or the other

Table I. Effect of Yb(DPM)$_3$ on ^{14}N Resonance in Organic Molecules

Substance	Concentration in CCl$_4$ (mole/l)	Molar ratio Yb(DPM)$_3$ to solute	Chemical shift ref. to internal MeNO$_2$ (ppm)	Resonance half-height width (Hz)	Induced shift for 1:1 molar ratio (ppm)
	12.00 (neat)	–	+ 345±3	290±30	
Pyrrolidine	3.86	0	+ 339±2	200±20	– 410±20
	3.86	0.009173	+ 335±2	310±30	
	3.86	0.023182	+ 330±3	380±40	
	3.86	0.044788	+ 321±3	590±50	
	12.14 (neat)	–	+ 359±1	85±5	
n-Propylamine	2.34	0	+ 355±1	110±10	– 340±20
	2.34	0.019400	+ 349±2	250±20	
	2.34	0.038701	+ 342±3	360±30	
	12.37 (neat)	–	+ 63±2	175±10	
Pyridine	3.19	0	+ 58±2	170±10	– 425±20
	3.19	0.020021	+ 49±2	310±10	
	3.19	0.037005	+ 43±3	400±20	
	3.19	0.057277	+ 34±4	700±50	
	12.62 (neat)	–	+ 221±1 (NMe) + 123±2	150±5 325±10	– 10±10 (NMe)
N-Methylimidazole	3.38	0	+ 218±1 (NMe) + 116±3	125±5 300±20	
	3.38	0.019202	+ 218±1 (NMe) + 112±3	170±20 380±50	– 205±20
	3.38	0.039558	+ 217.5±1 + 108±3	210±20 500±80	
Acetonitrile	19.58 (neat)	–	+ 137±1	88±2	– 135±5
	3.08	0	+ 130±1	120±5	
	3.08	0.017889	+ 127.5±1	160±10	
	3.08	0.037159	+ 125±1	200±10	
	12.92 (neat)	–	+ 276±1	135±3	
Dimethylformamide	2.22	0	+ 277±1	196±4	– 30±30
	2.22	0.014008	+ 276.5±1	220±5	
	2.22	0.028171	+ 276±1	255±5	

Table II. Effect of Eu(DPM)$_3$ on ^{14}N Resonance in Organic Molecules

Substance	Concentration in CCl$_4$ (mole/l)	Molar ratio Eu(DPM)$_3$ to solute	Chemical shift ref. to internal MeNO$_2$ (ppm)	Resonance half-height width (Hz)	Induced shift for 1:1 molar ratio (ppm)
Pyrrolidine	12.00 (neat)	-	+ 345±3	290±30	+1500±200
	2.61	0	+ 337±2	200±20	
	2.61	0.008176	+ 343±3	250±20	
	2.61	0.013919	+ 355±3	280±30	
	2.61	0.020292	+ 367±4	410±50	
n-Propylamine	12.14 (neat)	-	+ 359±1	85±5	+1600±200
	1.96	0	+ 353±1	98±5	
	1.96	0.013136	+ 374±2	230±20	
	1.96	0.019530	+ 385±3	280±40	
Pyridine	12.37 (neat)	-	+ 63±2	175±10	+1500±200
	2.05	0	+ 57±2	170±10	
	2.05	0.016885	+ 79±3	360±30	
	2.05	0.028977	+ 100±5	600±50	
N-Methylimidazole	12.62 (neat)	-	+ 221±1 (NMe) + 123±2	150±5 325±10	+80±50 (NMe) +1400±300
	2.81	0	+ 218±1 (NMe) + 116±3	125±5 300±20	
	2.81	0.018146	+ 218±1 (NMe) + 137±4	150±20 400±50	
	2.81	0.023034	+ 219±1 (NMe) + 148±5	200±30 500±100	
	2.81	0.037876	+ 221±1 (NMe)	250±30	
Acetonitrile	19.58 (neat)	-	+ 137±1	88±2	+490±100
	2.83	0	+ 130±1	120±5	
	2.83	0.008957	+ 133±1	130±5	
	2.83	0.021335	+ 141±1	150±5	
Dimethylformamide	12.92 (neat)	-	+ 276±1	135±3	+50±30
	2.26	0	+ 277±1	196±4	
	2.26	0.021683	+ 277.5±1	200±5	
	2.26	0.038236	+ 279±1	240±5	

nitrogen atom in N-methylimidazole, the induced ^{14}N shift is the smallest, almost negligible for Yb and less than +100 ppm for Eu.(4) Since all chemical shifts measured in this work are referred to internal CH_3NO_2, there may be a contribution from possible induced shifts in the resonance of the standard. However, the resonance of nitromethane did not show any appreciable broadening even at the highest concentrations of the lanthanide chelates used in the measurements, in spite of the fact that the molar ratio of chelate to nitromethane was generally 10-20 times as large as that of chelate to solute. It seems that the eventual contribution of the induced shift of the standard is far within the experimental error.

These preliminary results indicate that the role of the induced ^{14}N shifts seems to be promising due to the characteristic values of such shifts for various types of bonding at the nitrogen atom in molecules. They may have a considerable diagnostic value in spectral assignments of nitrogen resonance signals. The induced ^{14}N shifts have much less importance for setting apart overlapping signals because of the loss in resolution due to signal broadening. The effective range of measurements is up to about 4 mole % of the chelate relative to the substance examined. Beyond that the broadening of the ^{14}N resonance practically precludes any accurate measurements. It is also of prime importance that the shifts should be measured at the same concentration of the substance. The results in Tables show that appreciable dilution shifts relative to neat samples may occur at low concentrations of the solute.

Experimental techniques in ^{14}N resonance measurements employed in this work were the same as described elsewhere (3).

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