Selection of Dipivalomethanate Chelates as Shift Reagents for Nitrogen-14 Nuclear Magnetic Resonance

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Summary Comparative studies of the effects of lanthanide and actinide dipivalomethanate (DPM) chelates on the ^{14}N n.m.r. spectrum of pyridine show that Dy(DPM)$_3$ is by far the best high-field shift reagent for ^{14}N whilst Yb (DPM)$_3$ is the best low-field shift reagent.

WE have recently reported[1] appreciable ^{14}N n.m.r. shifts induced by Eu(DPM)$_3$ and Yb(DPM)$_3$, in a number of organic molecules. These shifts are particularly useful in structure assignments. We now report the properties of other lanthanide and actinide (DPM) chelates in order to find the most suitable shift reagent *i.e.* one which causes maximum chemical shift with minimum signal broadening. We have not studied the nature of the interactions resulting in spectral expansion. Such a study would require ^{14}N n.m.r. and ^{1}H n.m.r.[2] data for a large number of chelated metals.

Pyridine was chosen for the comparison of the effects of lanthanide and actinide (DPM) complexes on ^{14}N n.m.r. spectra because of its high sensitivity to chemical shifts.[1] Comparable induced shifts have been observed[1] in the spectra of aliphatic amines, but the rigid molecule of pyridine constitutes a better model.

The results (see Table) suggest that Dy(DPM)$_3$ is by far the best shielding shift reagent for ^{14}N nuclei. It combines the highest absolute value of the induced resonance displacement with the least broadening for a given chelate: solute molar ratio. Ho(DPM)$_3$ is probably the next best shielding reagent.

The selection of a deshielding reagent must be based on the broadening effects since all chelates in this group (La, Ce, Pr, Ne, Sm, and Yb) are about equally active. Yb(DPM)$_3$ is the best reagent.

There are considerable differences between the relative effects of various lanthanide (DPM) chelates on ^{14}N and ^{1}H n.m.r. spectra.[2] However, the maximum absolute displacement occurs with Dy and the neighbouring elements in the rare-earth sequence. The (DPM) complexes of the latter, however, cause a substantial increase in signal width[2] in ^{1}H n.m.r. spectra and the signs of the shift are different for ^{1}H and ^{14}N n.m.r. for at least half the number of lanthanides.

Effect of lanthanide and actinide DPM-Chelates on ^{14}N magnetic resonance of pyridine[a]

Chelate	Concentration of pyridine in CCl_4, mol l^{-1}	Chelate : pyridine molar ratio	^{14}N Chemical* shift, p.p.m.	Resonance half-height width, Hz	Induced shift* for 1 : 1 molar ratio, p.p.m .
La(DPM)$_3$	2·60	0	+ 58 ± 2	175 ± 10	− 380 ± 30
		0·00586	+ 56 ± 2	250 ± 20	
		0·00912	+ 54·5 ± 2	300 ± 30	
		0·01303	+ 53 ± 3	350 ± 30	
Ce(DPM)$_3$	2·52	0	+ 58 ± 2	175 ± 10	− 290 ± 50
		0·00496	+ 57 ± 2	300 ± 20	
		0·00733	+ 56 ± 2	380 ± 30	
		0·01032	+ 55 ± 3	470 ± 50	
Pr(DPM)$_3$	2·42	0	+ 58 ± 2	175 ± 10	−450 ± 300
		0·00558	+ 56 ± 2	450 ± 30	
		0·00782	+ 54 ± 3	520 ± 50	
		0·01080	+ 50 ± 4	700 ± 60	
Nd(DPM)$_3$	2·74	0	+ 58 ± 2	175 ± 10	− 360 ± 300
		0·00586	+ 56 ± 3	400 ± 50	
		0·00825	+ 55 ± 3	600 ± 50	
Sm(DPM)$_3$	2·65	0	+ 58 ± 2	175 ± 10	− 540 ± 50
		0·00461	+ 55 ± 2	280 ± 20	
		0·00810	+ 54 ± 2	370 ± 30	
		0·01048	+ 52 ± 3	550 ± 50	
Eu(DPM)$_3$	2·05	0	+ 58 ± 2	175 ± 10	+1500 ± 200
		0·01688	+ 79 ± 3	360 ± 30	
		0·02898	+ 100 ± 5	600 ± 50	
Gd(DPM)$_3$	2·60	0	+ 58 ± 2	175 ± 10	+2900 ± 500
		0·00415	+ 71 ± 2	300 ± 20	
		0·00674	+ 78 ± 3	410 ± 30	
		0·00889	+ 84 ± 3	520 ± 40	
Dy(DPM)$_3$	2·80	0	+ 58 ± 2	175 ± 10	+ 4000 ± 300
		0·01050	+ 98 ± 2	260 ± 20	
		0·01424	+ 112 ± 3	330 ± 30	
		0·01697	+ 128 ± 3	390 ± 30	
Ho(DPM)$_3$	2·88	0	+ 58 ± 2	175 ± 10	+ 2100 ± 200
		0·00630	+ 72 ± 2	260 ± 20	
		0·01082	+ 82 ± 3	320 ± 30	
		0·01703	+ 93 ± 3	450 ± 30	
Er(DPM)$_3$	2·60	0	+ 58 ± 2	175 ± 10	+870 ± 100
		0·00498	+ 62 ± 2	220 ± 10	
		0·01079	+ 67 ± 2	270 ± 20	
		0·01824	+ 74 ± 3	320 ± 30	
Yb(DPM)$_3$	3·19	0	+ 58 ± 2	175 ± 10	−425 ± 20
		0·02002	+ 49 ± 2	310 ± 10	
		0·03701	+ 43 ± 3	400 ± 20	
		0·05728	+ 34 ± 4	700 ± 50	
Th(DPM)$_3$	2·92	0	+ 58 ± 2	175 ± 10	0 ± 100
		0·00441	+ 58 ± 2	230 ± 20	
		0·00778	+ 58 ± 2	300 ± 30	
		0·01101	+ 58 ± 2	350 ± 40	
U(DPM)$_3$	2·58	0	+ 58 ± 2	175 ± 10	0 ± 300
		0·00410	+ 58 ± 2	200 ± 10	

[a] All measurements carried out at 32°; 15 mm o.d. sample tubes; Varian HA-60IL, HR mode, 4·33 MHz, audio-modulation 2 kHz, field-sweep. Increasing field direction taken as positive.

The ^{14}N shifts measured in the present work were all referred to nitromethane as an internal standard.[3] In order to exclude the possibility of a contribution to the shifts of displacements of the reference resonance itself, we carried out two series of measurements with coaxial sample tubes containing dilute CCl_4 solutions of nitromethane, one tube with a lanthanide chelate added and the other without. For a 10 : 1 nitromethane : chelate molar ratio, there were no observable shifts for either the chelate in the inner compartment or in the outer tube, respectively. The only exception was Dy(DPM)$_3$ which gave a shift of about 5 p.p.m. to higher fields in the latter case, and about the same but in the opposite direction (as reckoned from different line-widths) in the former. In a system of non-spinning coaxial tubes, the spectrum should consist[4] of a single signal from the inner tube and a double, broad signal from the annulus. In our experiments, where the difference between the inner and the outer diameter of the inner tube was very small as compared with the mean radius of the annulus, an interchange of liquids in the compartments should result in a change in the sign of the dulk-susceptibility correction. This suggests that the observed shift is almost all due to the latter effect and that the possible induced shift in the reference is practically zero if the magnitude of the induced shifts and the experimental errors are considered. Thus, it seems that nitromethane is a suitable internal standard in the presence of ^{14}N shift reagents.

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