

## Nuclear Magnetic Resonance Shift Reagents: Abnormal $^{13}\text{C}$ Shifts Produced by Complexation of Lanthanide Chelates with Saturated Amines and *n*-Butyl Isocyanide

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**ABSTRACT** Lanthanide-induced shifts of  $^{13}\text{C}$  nuclear magnetic resonances are reported for several amines and *n*-butyl isocyanide. Contact contributions to such shifts, especially of  $\beta$  carbons, are clearly important for the chelates of  $\text{Eu}^{+3}$  and  $\text{Pr}^{+3}$ . The importance of contact terms is shown to change in a rather predictable manner with the structure of the amine.

There have been indications (1) of contact-shift contributions to the changes in nuclear magnetic resonance (NMR) chemical shifts produced by lanthanide-shift reagents but, so far, the most compelling evidence for contact contributions have been the very large "wrong-way"  $^{14}\text{N}$ -shift changes reported by Witanowski and coworkers (2) with amines. These results are contrary to the generally accepted idea (1) that the action of the lanthanide-shift reagents can be attributed to the dipolar part of the general shift equation (1).

In the course of an attempt to use the shift changes induced on  $^{13}\text{C}$  and proton resonances of europium chelates to determine the conformations of hydrocarbon chains in solution, we encountered the large "wrong-way" (upfield) shift on the 2-carbon signal of *n*-butylamine (Table 1) that has also been discovered by Cushley and coworkers (3). This abnormal shift, which occurs both with  $\text{Eu}(\text{DPM})_3$  (DPM, dipivaloylmethanato) and  $\text{Eu}(\text{FOD})_3$  (europium chelate of tris-1,1,1,2,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione), is all the more striking in that the shifts of all of the other carbons and protons are downfield, while the carbon and proton shifts are all upfield with praseodymium chelates\*.

On the basis of the dipolar effect and collinearity of the effective magnetic dipole and the N-Eu coordination bond (1, 4), it is not possible to have the C2 resonance go upfield and the C1 downfield in the observed ratio unless the C-N-Eu (<CNM; carbon-nitrogen-metal) bond angle is around  $80^\circ$ , a chemically unreasonable value. The only way that the ratio of the C1/C2 shifts can have the correct sign and magnitude with reasonable values of RNM (distance of nitrogen to metal) and <CNM is with the angle  $\phi$  drastically different from zero (4). This, in turn, is unreasonable itself because it would cause sizable deviations from the normal pattern of the shifts of some of the other atoms. Thus, if C2 were to fall in the region where  $(3 \cos^2 \chi - 1)$  is strongly negative, some of the hydro-

gens or other atoms of the chain must as well. The abnormal shift is therefore likely to be the result of a contact-interaction contribution (1, 3, 4). That the effect is opposite in sign to the normal europium-induced shifts is in agreement with the results obtained with isoborneol (4).

The question of the magnitude of the effect is difficult to answer for a conformationally flexible system of uncertain average geometry because the dipolar contribution cannot be readily assessed. A more quantitative assessment for the rigid system of *exo*-norbornylamine has been made elsewhere (5). We confine our attention here to a qualitative survey of abnormal lanthanide-chelate shifts of the  $^{13}\text{C}$  resonances of amines.

The most astonishing aspect of the abnormal  $^{13}\text{C}$  shifts is their chelate and structural specificity (see Table 1). First, as noted before, no "wrong-way"  $^{13}\text{C}$  shifts have so far been observed with amines and alcohols with praseodymium chelates, although this should not be taken, as has been pointed out (5), that contact-shift contributions are absent for complexes of amines and praseodymium chelates. They are almost surely important, but less important than the dipolar contributions.

Second, the contact-shift contributions with europium chelates and amines are probably small for proton resonances and diminish drastically as the substitution on nitrogen increases (Table 1). Tertiary amines appear to give a pattern of carbon shifts that corresponds qualitatively to expectations based on dipolar effects alone. This pattern may be the result of sufficiently rapid amine-metal chelate exchange to wash out the contact contribution (1) or specific structural influences. The first alternative is in agreement with the fact that the magnitude of the shifts of all of the carbons is much smaller for tertiary than for primary amines.

The very striking difference of 35-39 ppm between the two  $\beta$ -carbon shifts of 2-butylamine and those of *exo*-norbornylamine (4) with europium chelates argues strongly for a larger  $\beta$ -contact contribution for more highly substituted carbons. This is to be expected for hyperconjugative-type interactions I.

We postulate that Ia is much more important than Ib—that is, that an electron can be accommodated on carbon more easily than a hydrogen†. Also, that the more highly sub-

Abbreviations: DPM, dipivaloylmethanato; FOD, tris-1,1,1,2,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione; CNM, carbon-nitrogen-metal; RNM, distance of nitrogen to metal.

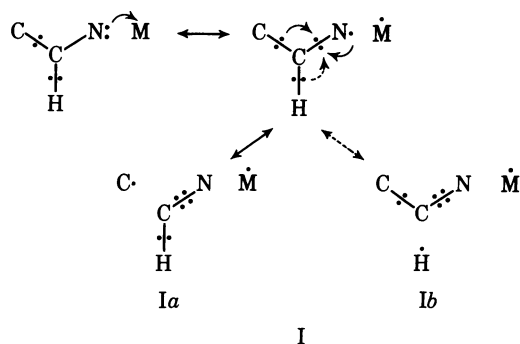
\* Similar, but smaller, effects of this type have recently been noted by Johnson, B. F. G., Lewis, J., McArdle, P. & Norton, J. R. (1972) *Chem. Commun.* 535.

† See Random, L., Pople, J. A., Buss, V. & Schleyer, P.v.R. *J. Amer. Chem. Soc.* 92, 6380-6382, for discussion of the relative importance of C-C against C-H hyperconjugation in carbonium ions.

TABLE 1.  $^{13}\text{C}$  NMR shifts induced by lanthanide chelates of amines and an isocyanide

Compound	Chelate	Shifts in ppm <sup>a</sup>				
		1	2	3	4	1'
1-Butylamine	Eu(DPM) <sub>3</sub>	-98.5	+12.2	-9.8	-7.3	—
	Eu(FOD) <sub>3</sub>	-94.5	+25.4	-5.3	-5.3	—
		(-34.1) <sup>b</sup>	(-22.4) <sup>b</sup>	(-13.8) <sup>b</sup>	(-7.3) <sup>b</sup>	—
	Pr(DPM) <sub>3</sub>	+134.4	+34.5	+22.7	+13.0	—
2-Butylamine	Eu(DPM) <sub>3</sub>	-24.2	-90.2	+11.0	-14.4	—
	Eu(FOD) <sub>3</sub>	-12.7	-81.9	+23.6	-8.9	—
	Pr(DPM) <sub>3</sub>	+54.5	+121.0	+34.6	+23.9	—
	Pr(FOD) <sub>3</sub>	+49.9	+111.0	+27.7	+23.6	—
1-Butyl(methyl)amine	Eu(DPM) <sub>3</sub>	-107.9	+2.7	-6.6	-4.0	-107 <sup>c</sup>
1-Butyl(dimethyl)amine	Eu(DPM) <sub>3</sub>	-8.8	-2.1	-1.7	~0	-9.7
<i>t</i> -Butylamine	Eu(DPM) <sub>3</sub>	-69.6	-16.0	—	—	—
1-Aminoadamantane	Eu(DPM) <sub>3</sub>	-54.6	-13.2	-8.2	-7.6	—
Isopropylbenzylamine	Eu(DPM) <sub>3</sub>	-49.8 <sup>d</sup>	-22.4 <sup>d</sup>	(-6.9 <sup>e</sup>	-7.3 <sup>f</sup> )	-57.5 <sup>g</sup>
<i>n</i> -Butyl isocyanide	Pr(FOD) <sub>3</sub>	+8.7	+4.5	+2.2	+1.7	-69.9 <sup>h</sup>
	Eu(FOD) <sub>3</sub>	-2.2	-10.0	-4.0	-2.2	+815.3 <sup>h</sup>

<sup>a</sup> Determined as described previously (5) for 1 M solutions of the amines in  $\text{DCCl}_3$ . <sup>b</sup> Shifts of protons attached to the numbered carbons. <sup>c</sup> Methyl group. <sup>d</sup> Isopropyl group. <sup>e</sup> C1 of phenyl group. <sup>f</sup> C2,6 of phenyl group. <sup>g</sup>  $\text{CH}_2$  of benzyl group. <sup>h</sup> Isonitrile carbon.



stituted the  $\beta$  carbon is, the more easily it can accommodate an electron. Strong support for these postulates comes from the contact shifts observed with amines complexed to  $\text{Co}(\text{AcAc})_2$  and  $\text{Ni}(\text{AcAc})_2$  (6).

An apparently normal pattern of shifts is observed with europium chelates and *t*-butylamine and 1-adamantylamine (Table 1). However, the symmetry of these molecules makes it especially easy to evaluate the dipolar effect, and it turns out that, for reasonable lanthanide-amine geometry (5), the dipolar contribution predicts a ratio of C1/C2 shifts of about 2.2, whereas 4.1 to 4.3 is observed. Again, an important "wrong-way" contribution to the shifts is evident. That the  $\beta$  shift of C1' of the phenyl of isopropylbenzylamine is small may again be due to a sizable contact-shift contribution (Table 1).

If there is any doubt that the praseodymium chelates can produce sizable contact interactions, this should be dispelled by the "wrong-way" shift of  $-70$  ppm of the isonitrile carbon of *n*-butyl isocyanide with  $\text{Pr}(\text{FOD})_3$ . The corresponding abnormal shift with  $\text{Eu}(\text{DPM})_3$  is  $+818$  ppm!

The present results provide strong evidence for contact contributions to  $^{13}\text{C}$  shifts with amines complexed with europium chelates and a rationale for the effect of  $\beta$ -substitution on such contributions.

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