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^{13}C CONTACT SHIFTS OF AROMATIC AMINES INDUCED BY GD(FOD)$_3$ AND SPIN DELOCALIZATION MECHANISM: EVIDENCE FOR THE OCCURRENCE OF DIRECT SPIN TRANSFER

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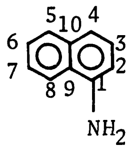
The ^{13}C contact shift patterns of several aromatic amines induced by Gd(fod)$_3$ have clearly been interpreted by the superposition of σ-type delocalization of positive spin transferred directly into C_1 from the Gd ion and π-type delocalization of the negative spin introduced into the N-lone pair orbital.

Although it has been theoretically predicted that the bonding of a lanthanoid metal to a ligand occurs primarily through the 6s metal orbital in lanthanoid complexes,[1)] detailed studies for actual complexes have not yet been carried out on the covalency of this bond and the spin delocalization into the ligand via this bond, in contrast to extensive works studied on the application of dipolar shifts to structural problems.

In order to investigate the nature of such a bond, we have measured ^{13}C contact shifts of several series of rigid aromatic substrates induced by Gd(fod)$_3$[2)] with an isotropic nature,[3)] and have compared the intramolecular ratios of these contact shifts with those of spin densities on the 2s orbital of carbon(ρ_{2s}) calculated by the INDO method[4)] for model radicals as a molecular fragment.

In this paper, we report on ^{13}C contact shifts of several substituted anilines and naphthylamines induced by Gd(fod)$_3$. The sample solutions were prepared by adding Gd(fod)$_3$ to the 0.8—2.2 M $CDCl_3$ solution of a substrate up to an Gd(fod)$_3$-to-substrate ratio(R) of 0.02—0.06. NMR spectra were measured on a Varian CFT-20 spectrometer at 25°C using TMS as an internal standard. Good linear relation was obtained between Gd-induced shifts and R for all the substrates studied. Since the slope(δ_{Gd}) of this linear relation can be regarded as proportional to the intrinsic shift of 1:1 adduct of a substrate with Gd(fod)$_3$,[5)] the δ_{Gd} values corrected for the diamagnetic shift induced by La(fod)$_3$[6)], δ'_{Gd}, were taken as the relative values of ^{13}C contact shifts. Benzyl and naphthylmethyl radicals were adopted as model radicals, since these are considered to be similar in electronic structure to aniline and naphthylamine complexed with an paramagnetic metal ion, respectively.[7)] The important geometric parameters of those used in MO calculations are the N-C bond length and the angle(θ) between the N-C bond and the NH_2 plane. The former was taken as 1.4 Å and the latter 60°, taking account of the pyramidal structure of nitrogen.[9)] Representative examples for aniline and α-naphthylamine are listed in Table 1 for comparisons of relative values of δ'_{Gd} to those of ρ_{2s}, where all the values are relative to the

Table 1. ^{13}C contact shifts and spin densities on the 2s orbitals of carbon

			relative		
		δ'_{Gd} a)	δ'_{Gd} b)	$\rho_{2s}(\pi)$ c)	$\rho_{2s}(\pi+\sigma)$ d)
aniline	1	-75.1 ± 7	-3.61 ± 0.3	-1.24	3.61
	2	26.8	1.29	1.13	-1.19
	3	-16.4	-0.79	-0.81	0.97
	4	20.8	1.00	1.00 (0.0106)	-1.02
α-naphthylamine	1	-93.4 ± 5	-3.08 ± 0.2	-1.30	3.06
	2	49.9 ± 2	1.65 ± 0.1	1.37	-1.57
	3	-30.8	-1.02	-0.85	1.07
	4	30.3	1.00	1.00 (0.0102)	-1.13
	5	6.5	0.21	0.41	-0.45
	6	-10.2	-0.34	-0.38	0.43
	7	7.8	0.26	0.41	-0.46
	8	-12.4	-0.41	-0.45	0.56
	9	33.7	1.11	0.71	-0.81
	10	-23.4	-0.77	-0.59	0.75

a) $Gd(fod)_3$-induced ^{13}C contact shifts corrected for $La(fod)_3$-induced shift in ppm. Lowfield shifts are denoted as negative signs. b) δ'_{Gd} relative to the position 4. c) Relative values of spin densities on the 2s orbital of carbon calculated by the INDO method for π-radicals(benzyl and α-naphthylmethyl radicals). Values in parentheses are spin densities. d) $-\alpha \cdot \rho_{2s}(\pi) + \beta \cdot \rho_{2s}(\sigma)$, where $\rho_{2s}(\sigma)$ is for the corresponding σ-radical(phenyl or α-naphthyl radical).

position 4, since accuracies of shift values of C_1 are fairly low owing to considerable broadening of resonance lines. Table 1 shows that the negative spin is introduced into amine molecules via the N-lone pair orbital from the Gd ion[10] and that the feature of sign alternation of spin is completely identical for theoretical and observed spin densities.

However, it was found that an anomalous component of shifts is included in the shifts of C_1 and its neighbours; considerably large lowfield shifts at C_1 and small highfield shifts at C_2 and C_9. The distribution of such anomalous components is very similar to that expected from the σ-type delocalization of the positive spin placed on C_1 into the ring. Then, an attempt was made to reproduce experimental shift patterns by the superposition of spin densities of the phenyl or naphthyl radical(σ-radical) to those of the benzyl or naphthylmethyl radical(π-radical). Thus, δ'_{Gd} is denoted as

$$\delta'_{Gd} = -\alpha \cdot \rho_{2s}(\pi) + \beta \cdot \rho_{2s}(\sigma)$$

where $\rho_{2s}(\pi)$ and $\rho_{2s}(\sigma)$ are spin densities of π- and σ-radicals, respectively. The factors α and β were determined so as to give a best fit of the intramolecular ratio of contact shifts to that of calculated spin densities. Fig. 1a shows the correlation of ρ_{2s} of the π-radical to the δ'_{Gd} value for several substituted anilines and α- and β-naphthylamines observed in this investigation, while in Fig. 1b the super-

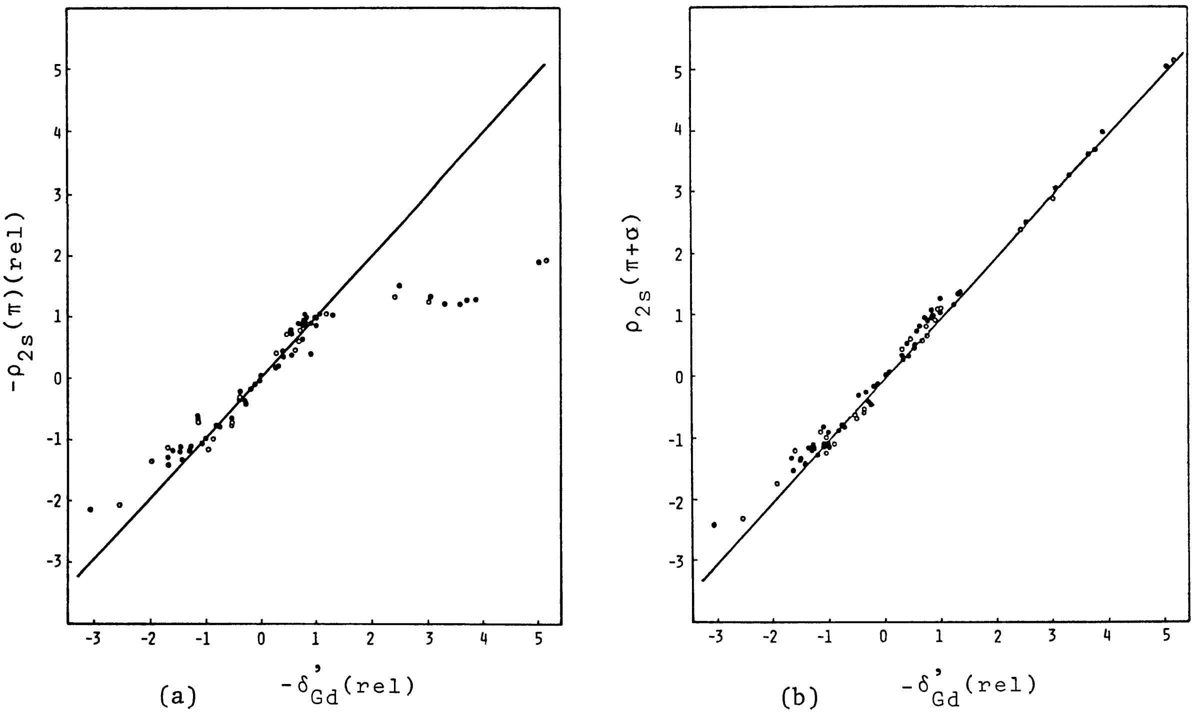


Fig. 1. Plots of $-\rho_{2s}(\pi)(\text{rel})$(a) and $\rho_{2s}(\pi+\sigma)$(b) vs. $-\delta'_{Gd}$ for aniline, o- and m-toluidines, p-n-butylaniline, 4-aminodiphenyl, and α- and β-naphthylamines. Open symbols imply data for aniline and α- and β-naphthylamines with $Gd(dpm)_3$ and $La(dpm)_3$.

position of spin densities, $\rho_{2s}(\pi+\sigma) = -\alpha\cdot\rho_{2s}(\pi) + \beta\cdot\rho_{2s}(\sigma)$, is compared with δ'_{Gd}. The linear relationship becomes excellent going from Fig. 1a to Fig. 1b, especially for 10 data points from C_1 in the right-hand side of the figures. This is because the spin density at C_1 in these σ-radicals is considerably larger than those at any other carbons. Thus, it is found that the addition of spin densities of a corresponding σ-radical to those of the π-radical is very effective for the reproduction of experimental contact shift patterns.

Such the spin density distributions of σ-radicals may be reproduced only by a σ-type delocalization of the positive spin induced directly into C_1 from the Gd ion. Then, we will propose the occurrence of direct transfer of the positive spin from the Gd ion into C_1 nearest to the Gd ion. It may be presumed in this mechanism that a spin-containing orbital in the Gd ion directly overlaps with the σ-orbital forming the N-C_1 bond, in view of the pyramidal structure of the NH_2 group[11] and the large ionic radius of lanthanoid ion. On the other hand, for pyridines and quinolines with $Gd(fod)_3$[12], these anomalous features of shifts have not been observed. One may consider that this is due to a relatively long distance of C_1 to the Gd ion in the linear C_1-N-Gd linkage. The ^{13}C contact shift pattern of aniline induced by Ni-$(acac)_2$[13] has been well interpreted solely by the spin densities of a π-radical, in contrast to that of the present system. This may be due to the small ionic radius of Ni^{2+}. The amount of negative spin transferred through the major mechanism is estimated to be about 7×10^{-4} and the contribution of the direct spin-transfer mechanism is 10—20 percent.

References and Notes

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7) It has been suggested by Morishima et al[8)] that the spin delocalization for N-containing molecules may be well reproduced by calculations on molecules in which nitrogen nucleus and its lone pair are replaced by a radical carbon. This idea was applied to the present systems.

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9) Although MO calculations were tentatively made in the range of 1.37—1.54 Å for the N-C bond and 0°—80° for θ, these results do not affect the conclusion of the discussion on the spin delocalization mechanism.

10) The is consistent with the negative sign in $\langle S_z \rangle$ of the Gd ion calculated by Golding et al.[1b)]

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