Carbon-13 Contact Shifts and Spin Delocalization Mechanism for Substituted Anilines complexed with Gadolinium(III) Chelates

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The Gd(fod)$_3$-induced ^{13}C shifts for a series of aniline derivatives in CDCl$_3$ were measured. These shifts were well interpreted by the superposition of the spin density distributions of the carbon 2*s*-orbitals of the aniline cation radical and the corresponding phenyl radical. This may imply two kinds of contact shift contributions due to a through-bond delocalization of β-spin and a through-space transfer of α-spin from Gd^{3+} to aniline. Furthermore, the tentative addition of a third contribution to the observed shifts, relative pseudo-contact shifts, led to a better fit to the experimental shift patterns, and thus, this result suggests the possibility that Gd^{3+} complexes are magnetically anisotropic.

SINCE the *g*-tensor of Gd^{3+} has been theoretically predicted to be isotropic,[1] paramagnetic shifts induced in ligand molecules by this ion should be expected to consist only of a contact term. Thus, Gd(fod)$_3$ †-induced shifts have been successfully used to separate the lanthanoid-induced shifts (LIS) due to any analogous shift reagents [Ln(fod)$_3$] into contact (c.s.) and pseudo-contact shifts (p.c.s.).[2] This situation corresponds well to the successful separation of paramagnetic shifts for a number of Co^{2+} complexes to c.s. and p.c.s. contributions using the c.s. pattern of a corresponding isotropic Ni^{2+} complex. For such complexes of the first-row transition metals, particularly octahedral Ni^{2+} complexes of an isotropic nature, the spin delocalization mechanism has been extensively studied, while for Gd^{3+} or the other lanthanoid complexes this sort of investigation has scarcely been reported.[3] This may be ascribed to difficult observation of Gd-induced shifts due to a considerable line broadening, particularly in ^{1}H resonances.

The present paper reports on a spin delocalization mechanism in Gd complexes investigated through ^{13}C paramagnetic shifts induced in ligand substrates. We chose a series of aniline derivatives complexed with Gd(fod)$_3$ or Gd(dpm)$_3$,‡ because line broadening may be avoidable to some extent due to fast exchange of a ligand molecule on the n.m.r. time scale, the chemical equilibria are well known,[4] and molecular structures are rigid, which are convenient for calculations of the p.c.s. and c.s. terms.

EXPERIMENTAL

Liquid substrates were used after distillation and drying over molecular sieves and solid ones were purified by recrystallization. CDCl$_3$ used as solvent was stored over molecular sieves. Gd(fod)$_3$ and La(fod)$_3$ and Gd(dpm)$_3$ and La(dpm)$_3$ were synthesized by literature procedures [5,6] and dried over P$_2$O$_5$ in a vacuum desiccator. After the addition of an appropriate amount of a lanthanoid shift reagent (LSR) to a CDCl$_3$ solution of a substrate (S) (1.3—1.7M) in the sample tube, the n.m.r. spectrum was measured at 25 °C. With a Gd chelate, this was repeated 4—7 times up to an LSR : substrate ratio [L$_0$] : [S$_0$] (ρ) of 0.03—0.07 until shifts could not be measured owing to line broadening. With a La chelate, ρ was ⩽ *ca.* 0.3. N.m.r. spectra were measured on a Varian CFT-20 spectrometer (20 MHz) using tetramethylsilane as an internal standard. MO calculations were carried out on a Hitachi 8800/8700 computer of The Computer Center of the University of Tokyo, using the library program Y4CB04 [7] collected in the Center.

RESULTS AND DISCUSSION

All the ^{13}C LIS observed in this study show that chemical exchange is rapid on the n.m.r. time scale under the present experimental conditions, as well as ^{1}H data for the same system studied previously,[4] and that the LIS–ρ plot is excellently linear. The present system is well described by the two-step equilibria (1) and (2) where the *K* values, δ_{LS}, and δ_{LS_2} are equilibrium constants and intrinsic shifts of adducts LS and LS$_2$, respectively.[4b,c] If values of δ_{LS} and δ_{LS_2} are approximately identical and further, if $K_1 \gg 1$, the slope ($\delta_{obs.}$) of an LIS–ρ plot in the range of sufficiently low ρ values can be formulated as approximation (3) where [S$_0$] is the total concentration of a substrate. Equation (3) has been found to hold for the present system.[4b,c] Thus, the ratios of $\delta_{obs.}$ values will be regarded as those for δ_{LS}. The values of $\delta_{obs.}$ are summarized in Table 1. Correlation coefficients for all the LIS–ρ plots are >0.999, except for those for the resonance lines of C-1 which rapidly broaden with increasing ρ and for very small shifts such as those induced by La^{3+}. It has been generally recognized that the diamagnetic shifts of organic substrates arising from complex formation with a lanthanoid chelate are equal in magnitude along the lanthanoid series.[8] In accord with this situation, Gd(fod)$_3$- or Gd(dpm)$_3$-induced shifts were corrected for those

$$1 + \mathrm{S} \rightleftharpoons \mathrm{LS_2}\ K_1,\ \delta_{LS} \qquad (1)$$

$$\mathrm{LS} + \mathrm{S} \rightleftharpoons \mathrm{LS_2}\ K_2,\ \delta_{LS_2} \qquad (2)$$

$$\delta_{obs.} \approx \delta_{LS}\,\frac{1 + 2K_2[\mathrm{S_0}]}{1 + K_2[\mathrm{S_0}]} \qquad (3)$$

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† fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionato.

‡ dpm = dipivaloylmethanato.

TABLE 1

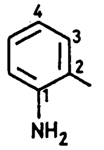
$Gd(fod)_3$-induced ^{13}C shifts for substituted anilines[a]

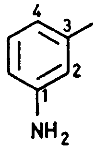
Substrate	Position	$\delta_{\text{obs.}}$[b]	$\delta_{\text{obs.}}$(La)[c]	$\delta'_{\text{obs.}}$[d]
Aniline	1	69 ± 7	−6.1	75.1 ± 7
	2	−19.2	7.6	−26.8
	3	17.9	1.5	16.4
	4	−13.6	7.2	−20.8
Aniline[e]	1	35 ± 4	−2.1	37.1 ± 4
	2	−16.6	2.8	−19.4
	3	10.2	−0.7	10.9
	4	−10.8	1.4	−12.2
o-Toluidine	1	40 ± 4	−3.4	43.4 ± 4
	2	−23.4	5.7	−29.1
	3	14.8	0.7	14.1
	4	−10.3	6.8	−17.1
	5	14.8	0.5	14.3
	6	−16.5	6.9	−23.4
	CH_3	8.8	−0.8	9.6
m-Toluidine	1	64 ± 7	−5.7	69.7 ± 7
	2	−20.0	7.2	−27.2
	3	17.5	1.1	16.4
	4	−13.6	7.4	−21.0
	5	15.6	~0	15.6
	6	−21.0	6.5	−27.5
	CH_3	−3.8	−0.3	−3.5
p-n-Butylaniline	1	105 ± 7	−6.1	111.1 ± 7
	2	−34.6	7.8	−42.4
	3	26.0	1.1	24.9
	4	−21.0	8.9	−29.9
	α	11.0	1.1	9.9
	β	−13.4	0.7	−14.1
	γ	0.8	0.7	0.1
	δ	~0	0.1	−0.1
p-Phenylaniline	1	68 ± 8	−5.2	73.2 ± 8
	2	−17.6	5.9	−23.5
	3	18.1	1.0	17.1
	4	−10.6	7.8	−18.4
	1′	7.6	−0.4	8.0
	2′	−4.9	0.9	−5.8
	3′	2.0	0.5	1.5
	4′	~0	2.2	−2.2

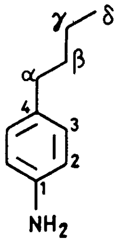
[a] In p.p.m. Negative signs denote highfield shifts. [b] Values of LIS obtained from the extrapolation of ρ to unity. [c] $\delta_{\text{obs.}}$ with $La(fod)_3$. [d] $\delta_{\text{obs.}}-\delta_{\text{obs.}}$(La). [e] With $Gd(dpm)_3$ and $La(dpm)_3$ instead of $Gd(fod)_3$ and $La(fod)_3$. The ^{13}C n.m.r. assignments refer to 'Satler Standard ^{13}C NMR Spectra' for aniline, *o*- and *m*-toluidines, and E. M. Schulman, K. A. Christensen, and D. M. Grant, *J. Org. Chem.*, 1974, **39**, 2686, for *p*-phenylaniline. The assignment of the n-butyl group was made by analogy with the spectrum of n-butylbenzene (L. F. Johnson and W. C. Jankowski, '^{13}C NMR Spectra.'

induced by $La(fod)_3$ or $La(dpm)_3$, respectively, the corrected values being denoted as $\delta'_{\text{obs.}}$ in Table 1.

For discussion of a spin delocalization mechanism, we must content ourselves with a 'relative method,' because MO calculations for the whole adduct containing a lanthanoid metal cannot be carried out so far. The INDO MO calculations [7] of spin densities on carbon 2*s*-orbitals (ρ_{2s}) were then carried out for appropriate molecular fragments, since ^{13}C contact shifts are predicted to be proportional to ρ_{2s}, and the INDO method is so far considered to be the best available owing to the inclusion of spin polarization effects. The aniline cation radical was adopted as the most suitable model for a ligand moiety, which reproduces spin delocalization comparatively well in these paramagnetic adducts. The calculated ρ_{2s} values of this radical [$\rho_{2s}(An^+)$] are listed in Table 2, together with the MO parameters used. The following standard geometries were used with 120° or tetrahedral bond angles: C–H(methyl and n-butyl), 1.10 Å; C–H(aromatic), 1.08 Å; C–C(aromatic), 1.40 Å; C–CH_3, 1.54 Å; C–N, 1.37 Å. It is known that aniline has a pyramidal structure at nitro-







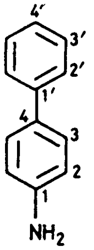


TABLE 2

Comparisons of the observed and calculated ratios of Gd^{3+}-induced shifts for aniline[a]

						Relative[e]			
Position	Relative $\delta'_{\text{obs.}}$	$\rho_{2s}(An^+)$[c]	ρ_{2s}(Ph)	GF[d]		$\delta^{I}_{\text{calc.}}$	$\delta^{II}_{\text{calc.}}$	$\delta^{III}_{\text{calc.}}$	$\delta^{IV}_{\text{calc.}}$
1	3.61[b]	−0.0060	0.1845	0.0375		0.662	3.725	0.970	3.725
2	−1.29	0.0092	−0.0058	0.0158		−1.016	−1.334	−0.915	−1.241
3	0.79	−0.0074	0.0131	0.0058		0.817	1.206	0.881	0.749
4	−1.00	0.0119	−0.0032	0.0042		−1.314	−1.657	−1.311	−1.124
					A	−110.4	−135.0	−112.9	−80.1
					B		15.8		22.4
					C			7.8	−23.7
					r[f]	0.7740	0.9862	0.8410	0.9992
1	3.04[g]					0.720	3.268	1.156	3.231
2	−1.59					−1.104	−1.353	−0.930	−1.422
3	0.89					0.888	1.199	0.961	0.774
4	−1.00					−1.428	−1.693	−1.389	−1.275
					A	−120.0	−138.7	−120.8	91.3
					B		13.2		20.5
					C			11.5	−29.3
					r[f]	0.8411	0.9803	0.8944	0.9944

[a] Negative signs denote upfield shifts. [b] With $Gd(fod)_3$. [c] Calculated with θ 45° and N–C 1.37 Å. [d] Geometric factors calculated with χ 30°. [e] Relative calculated shifts. See text. [f] Correlation coefficients between $\delta'_{\text{obs.}}$ and $\delta_{\text{calc.}}$. [g] With $Gd(dpm)_3$.

gen, and that on complexing with $Ni(acac)_2$ the angle between the N–C bond and the NH_2 plane (θ) becomes slightly larger than that of free aniline (*ca.* 60°).[9] On the other hand, analyses of the ^1H LIS of the aniline–$Ln(fod)_3$ system gave 130—140° as the $C\text{-}\widehat{N}\text{-}Ln$ angle(χ).[4a] This information caused us to calculate ρ_{2s} values with θ in the range 0—60°. The result showed that although the variation of θ within this range causes a relatively large change of ρ_{2s} at each position, this does not significantly affect the intramolecular ratios of ρ_{2s}. Indeed, this variation does not give a significant change in the correlation coefficients (*r*) between $\delta'_{obs.}$ and $\delta_{calc.}$ described later. Values of $\rho_{2s}(An^+)$ calculated using $\theta = 45°$ are shown in Table 2. Since the accuracy of $\delta_{obs.}$ at C-1 was less than that at the other carbons owing to line broadening, $\delta_{obs.}$ and $\delta'_{obs.}$ are presented relative to the values for position 4, in order to facilitate comparisons of observed and calculated shift patterns. The calculated relative shifts ($\delta^{I}_{calc.}$) were obtained by the least-squares method from comparisons with $\delta'_{obs.}$ using equation (4) where *A* is a constant. *r* was used as the

$$\delta^{I}_{calc.} = A \cdot \rho_{2s}(An^+) \qquad (4)$$

criterion for the least-square fits; the agreement is very poor (*r* 0.7740). However, it is found that the sign alternation in $\delta^{I}_{calc.}$ is completely identical with that in $\delta'_{obs.}$, and that a β-spin is required, which is delocalized into the HOMO (π-type) of this radical. (Lowfield shifts of carbons correspond to plus signs of ρ_{2s}.) The latter result is consistent with the minus sign of $\langle S_z \rangle$ estimated for Gd^{3+}.[10]

The pattern of $\delta^{I}_{calc.}$ shows that a particularly larger correction for the $\rho_{2s}(An^+)$ pattern at C-1 is required than for the other carbons. The spin density distribution required for this correction leads us to expect that some α-spin might be delocalized into one orbital with σ-symmetry. The contribution of α-spin delocalized into the LUMO of aniline was tentatively added to the above

TABLE 3

Observed and calculated shifts induced by $Gd(fod)_3$ [a]

			Calculated			
			C.s.			
Substrate	Position	$\delta'_{obs.}$	An^+	Ph	P.c.s.	Total [b]
Aniline	1	75.1	10.01	85.96	−18.49	77.48
	2	−28.8	−15.32	−2.70	−7.79	−25.81
	3	16.4	12.34	6.10	−2.86	15.58
	4	−20.8	−19.82	−1.49	−2.07	−23.38
						(0.9992)
Aniline [c]	1	37.1	6.68	46.14	−13.40	39.42
	2	−19.4	−10.25	−1.45	−5.65	−17.35
	3	10.9	8.23	3.28	−2.07	9.44
	4	−12.2	−13.26	−0.80	−1.50	−15.56
						(0.9944)
m-Toluidine	1	69.7	8.19	87.40	−23.07	72.52
	2	−27.2	−11.59	−3.22	−9.72	−24.53
	3	16.4	10.97	5.46	−3.57	12.86
	4	−21.0	−21.32	−1.65	−2.58	−25.55
	5	15.6	12.82	6.34	−3.57	15.59
	6	−27.5	−15.92	−2.85	−9.72	−28.49
	CH_3	−3.5	−2.32	0.43	−1.35	−3.24
						(0.9972)
o-Toluidine	1	43.4	6.67	51.3	−9.01	48.96
	2	−29.1	−18.84	−1.17	−3.80	−23.81
	3	14.1	15.31	3.60	−1.39	17.52
	4	−17.1	−19.62	−0.68	−1.01	−21.31
	5	14.3	8.83	3.35	−1.39	10.79
	6	−23.4	−10.60	−1.50	−3.80	−15.90
	CH_3	9.6	2.16	1.88	−1.20	2.84
						(0.9759)
p-n-Butylaniline	1	111.1	5.18	144.90	−29.59	120.49
	2	−42.4	−20.41	−4.78	−12.47	−37.66
	3	24.9	16.14	10.10	−4.58	21.66
	4	−29.9	−35.94	−2.35	−3.31	−41.60
	α	9.9	9.14	1.17	−1.26	9.05
	β	−14.1	−10.36	−0.39	−0.95	−11.70
						(0.9933)
p-Phenylaniline	1	73.2	2.13	119.05	−26.42	94.76
	2	−23.5	−6.19	−3.99	−11.13	−21.31
	3	17.1	5.03	8.24	−4.07	9.20
	4	−18.4	−10.16	−1.87	−2.96	−14.99
	1′	8.0	3.68	1.09	−1.20	3.57
	2′	−5.8	−3.97	−0.32	−0.70	−4.99
	3′	1.5	1.94	0.13	−0.35	1.72
	4′	−2.2	−2.61	−0.13	−0.28	−3.02
						(0.9744)

[a] In p.p.m. Negative signs denote upfield shifts. [b] Shifts calculated using the superposition of three components of relative shifts ($\delta^{IV}_{calc.}$) (see text). Numbers in parentheses are correlation coefficients. [c] With $Gd(dpm)_3$.

distribution of $\rho_{2s}(\text{An}^+)$ by using ρ_{2s} values for the aniline anion radical, but resulted in poor fits to the experimental data. This is perhaps because LUMO is of π-symmetry.

Although the 19th orbital (lowest unoccupied) in the aniline cation radical was confirmed to be of σ-type, we cannot so far calculate correctly any excited states by the INDO˙ MO method. The phenyl radical was then considered, as it is expected to have a similar distribution of electron spin to that in a σ-type orbital. The superposition of the ρ_{2s} pattern of the phenyl radical [$\rho_{2s}(\text{Ph})$] on that of $\rho_{2s}(\text{An}^+)$ resulted in good fits to $\delta'_{\text{obs.}}$, for both Gd(dpm)_3 and Gd(fod)_3 (see Table 2 for *r* values). α-Spin for a $\rho_{2s}(\text{Ph})$ pattern is required in contrast to the β-spin of the $\rho_{2s}(\text{An}^+)$ pattern. Thus, $A < 0$ and $B > 0$ in equation (5) where A and B are constants. This

$$\delta^{\text{II}}_{\text{obs.}} = A\,.\,\rho_{2s}(\text{An}^+) + B\,.\,\rho_{2s}(\text{Ph}) \qquad (5)$$

result suggests the possibility that through-space transfer of α-spin directly occurs into the ligand from a spin-containing orbital of Gd^{3+}, in addition to through-bond transfer of β-spin *via* the nitrogen lone pair.

Furthermore, in order to examine the possible contribution of p.c.s. to Gd-induced shifts, the relative p.c.s. values were further superimposed on the above two c.s. patterns. Assuming that the approximation of axial symmetry can be applied to the present system, geometric factors were calculated using several geometric parameters estimated in our previous investigation.[4a] The C–N and N–Ln bond lengths are 1.37 and 2.65 Å, respectively, and the $\text{C–}\widehat{\text{N}}\text{–Ln}$ angle (χ) is 120—140°. This attempt resulted in further better fits to $\delta'_{\text{obs.}}$, which was unexpected (see Table 2 for *r* values) and moreover, relatively large amounts of p.c.s. are required, as seen from Table 3. It may be noticed that small variations of the N–C and N–Ln bond lengths and χ within a reasonable range have no serious influence on the effectiveness of p.c.s. contributions. These p.c.s. terms are upfield ones, which have the same direction as those obtained with Pr(fod)_3 and Nd(fod)_3, *etc.*, *i.e.* $C < 0$ in equation (6) where GF is a geometric factor.

$$\delta^{\text{IV}}_{\text{calc.}} = A\,.\,\rho_{2s}(\text{An}^+) + B\,.\,\rho_{2s}(\text{Ph}) + C\,.\,\text{GF} \qquad (6)$$

$\rho_{2s}(\text{An}^+)$ corrected only for a p.c.s. pattern led to poor fits, as expected previously ($\delta^{\text{III}}_{\text{calc.}}$ in Table 2).

The same results were obtained for four aniline derivatives, *i.e.*, $\delta^{\text{II}}_{\text{calc.}}$ fits $\delta'_{\text{obs.}}$ better than $\delta^{\text{I}}_{\text{calc.}}$, and $\delta^{\text{IV}}_{\text{calc.}}$ best correlates with $\delta'_{\text{obs.}}$ (Table 3). For the MO and p.c.s. calculations of *p*-phenylaniline cation radical, 1.49 Å and 41.6° were taken as the bond length and twisting angle between the two phenyl rings, respectively.* For toluidine cation radicals, two spin density patterns obtained from two typical conformations of the methyl group were averaged. The conformations are those in which one C–H bond is perpendicular or coplanar to the molecular plane. The shifts of the γ- and δ-carbons in the n-butyl group were neglected in the least-square fits because they are very small. It was found that ρ_{2s} of the β-carbon varies considerably with rotation about the C_α–C-4 bond. Taking into account only the zigzag conformations of the n-butyl group, we adopted the average of two patterns of the spin density distribution obtained from two conformations in which the plane of the σ-skeleton of the n-butyl group is perpendicular and coplanar to the molecular plane. The effectiveness of a p.c.s. contribution to all the substrates studied here implies that this result is at least not insignificant. Thus, one can consider the possibility that some Gd^{3+}-complexes include a dipolar contribution to the paramagnetic shifts. This situation, which is against theoretical predictions for Gd^{3+}, can be ascribed to anisotropy arising from some distortion of the purely octahedral symmetry of a ligand field.

[0/1373 *Received, 5th September, 1980*]

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* These values were determined by electron diffraction for the biphenyl crystal.

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