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QUANTITATIVE ESTIMATES OF π-CONTACT TERM CONTRIBUTIONS TO THE LANTHANIDE-INDUCED ^{1}H AND ^{13}C SHIFTS IN ANILINE AND p-TOLUIDINE

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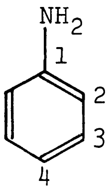
An attempt was made for the separation of contact term contributions from the Pr(FOD)$_3$- and Eu(FOD)$_3$-induced ^{1}H and ^{13}C shifts in aniline and p-toluidine, by using the contact shift pattern estimated theoretically. This suggested the transfer of negative and positive spin from the Eu ion and the Pr ion, respectively.

Although it has been reported by several workers that there is a contact shift (cs) contribution to the paramagnetic shifts induced by some β-diketone chelates of a lanthanide ion, most of the discussions on cs contributions are qualitative.$^{1)}$ Recently, the quantitative estimates of σ-cs terms for some aliphatic$^{2)}$ and pyridine type compounds$^{3)}$ have been carried out by several workers on the base that a true pattern of pseudo contact shifts (pcs) can be calculated from the inclusion of several atoms having almost only pcs in such the compounds. However, for the aromatic substrates with π-cs at almost all atoms, the quantitative separation of cs and pcs terms is generally very difficult. While the use of the Ni(AcAc)$_2$-induced shift pattern as a cs term has resulted in a much smaller cs for the pyridine- and toluidine-Eu(FOD)$_3$ systems,$^{4)}$ attempts for separation made by using the cs term estimated theoretically have been almost unsuccessful.$^{5)}$

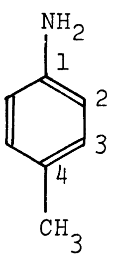
We report here on an attempt for quantitative estimates of cs contributions to the Eu- and Pr(FOD)$_3$-induced ^{1}H and ^{13}C shifts of aniline and p-toluidine by using the cs patterns estimated theoretically. The data used in the present investigation are those corrected for the complex formation shifts, which were observed by Kainosho et al.$^{6)}$ and Tori et al.$^{1e)}$ Firstly, the same geometry and stoichiometric relation were assumed for the complexes formed between aniline and Eu-, Pr-, and La(FOD)$_3$ in the solution. Since the spin induced into the N-lone pair orbital may be expected to delocalize predominantly through π-bonds,$^{7)}$ a π-spin density distribution obtained by the McLachlan's method$^{8)}$ was approximately used for the calculation of relative values of cs (R_{cs}), except for the shift at C_1 because of the inclusion of large σ-cs. There may be four possible R_{cs} patterns occurred from α- and β-spin in the highest occupied π-MO [h.o(α) and h.o(β)], and α- and β-spin in the lowest vacant π-MO [l.v(α) and l.v(β)]. The relative values of pcs (R_{pcs}) were calculated from the geometric factor, $(3\cos^2\theta-1)/r^3$,$^{9)}$ where two geometric parameters χ and r_N were varied in the range of 0°—90° and 2.2 Å—3.4 Å, respectively (Fig. 1). The effect of rotation about the N-C bond was not introduced into pcs calculations, on the base that the N-lone pair orbital could be expected to conjugate with the ring π-MO to great extent. With the reasonable assumption that $S_{cal} = a\cdot R_{pcs} + b\cdot R_{cs}$,10) a preliminary comparison of $S_{obs}(Eu)$11) and $S_{cal}(Eu)$ calculated with several combinations of appropriate values of r_N and χ for aniline showed that only R_{cs} due to h.o(β), $R_{cs}(\beta)$, is effective for correcting the R_{pcs} pattern, especially in explaining the observed relation $|S(\beta H)|<|S(\gamma H)|$ for aniline with $Eu(FOD)_3$. Then, $S_{cal}(Eu)$ was calculated with $R_{cs}(\beta)$ for an arbitrary combination of r_N and χ values in the above ranges by the least squares technique.

Table 1. The observed and calculated lanthanide-induced ^{1}H and ^{13}C shifts in aniline$^{a)}$

		$S_{obs}(Eu)^{b)}$	$S_{obs}(Pr)^{b)}$	R_{pcs}	$R_{cs}(\beta)$	$R_{cs}(\alpha)$	$S_{cal}(Eu)^{c)}$	$S_{cal}(Pr)^{d)}$
	2H	-16.07	+22.33	1.000	-1.000	+1.000	-15.79	+24.62
		(- 1.00)	(+ 1.00)				-15.98	+22.28
	3H	- 4.00	+ 6.90	0.326	+0.379	-0.379	- 4.63	+ 7.67
		(- 0.25)	(+ 0.31)				- 4.17	+ 6.99
	4H	- 5.23	+ 5.97	0.256	-1.131	+1.131	- 4.69	+ 6.74
		(- 0.33)	(+ 0.27)				- 5.38	+ 6.04
	1C	-73.8	+101.0	2.576	-32.844	+32.844	-63.07	+78.56
		(- 4.59)	(+ 4.52)					
	2C	-12.2	+28.0	1.220	+7.212	-7.212	-13.02	+25.82
		(- 0.76)	(+ 1.25)					
	3C	-15.5	+17.9	0.546	-7.188	+7.188	-13.54	+16.76
		(- 0.96)	(+ 0.80)					
	4C	- 3.2	+ 4.8	0.429	+8.468	-8.468	- 0.19	+ 6.11
		(- 0.20)	(+ 0.21)					

a) See Ref. 10. Negative signs designate shifts to lower field. The S_{cal} values for ^{1}H in the second line were calculated only with the terms for ^{1}H by the least-squares technique. b) The data from Ref. 6. c) $R_{C,H}$=0.139(a=15.05, b=0.74), R_H=0.020(a=14.51, b=1.47) d) $R_{C,H}$=0.099(a=24.12, b=0.50), R_H=0.005(a=21.89, b=0.39)

Table 2. The observed and calculated lanthanide-induced ^{1}H and ^{13}C shifts in p-toluidine$^{a)}$

		$S_{obs}(Eu)^{b)}$	$S_{obs}(Pr)^{b)}$	$R_{pcs}^{e)}$	$R_{cs}(\beta)$	$R_{cs}(\alpha)$	$S_{cal}(Eu)^{c)}$	$S_{cal}(Pr)^{d)}$
	2H	-15.0	+20.5	1.000	-1.000	+1.000	-15.52	+23.63
		(- 1.00)	(+ 1.00)				-14.91	+20.53
	3H	- 3.55	+ 6.17	0.302	+0.358	-0.358	- 4.09	+ 6.69
		(- 0.24)	(+ 0.30)				- 3.80	+ 6.03
	$4CH_3$	- 1.01	+ 2.92	0.164	+1.288	-1.288	- 1.24	+ 2.90
		(- 0.07)	(+ 0.14)				- 0.89	+ 2.99
	1C	-70.8	+97.8	2.696	-32.644	+32.644	-68.80	+83.77
		(- 4.72)	(+ 4.77)					
	2C	-10.4	+26.3	1.235	+7.060	-7.060	-11.70	+23.63
		(- 0.69)	(+ 1.28)					
	3C	-14.8	+16.5	0.526	-7.148	+7.148	-14.12	+16.87
		(- 0.99)	(+ 0.81)					
	4C	- 2.5	+ 3.3	0.406	+7.512	-7.512	+ 0.83	+ 4.29
		(- 0.17)	(+ 0.16)					
	$4CH_3$	- 5.4	+ 6.8	0.193	-2.670	+2.670	- 5.22	+ 6.22
		(- 0.36)	(+ 0.33)					

a) See Table 1. b) The data from Ref. 1e. c) $R_{C,H}$=0.102(a=14.62, b=0.90), R_H=0.020(a=13.84, b=1.07) d) $R_{C,H}$=0.113(a=22.96, b=0.67), R_H=0.007(a=20.27, b=0.26) e) Calculated with χ=43.

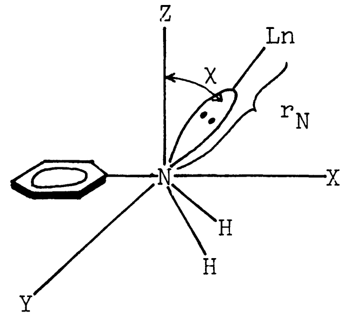


Fig. 1.

The shift values of C_1 were excluded in this technique, because of the possibility of inclusion of a much larger σ-cs contribution. Although a combination of r_N and χ values minimizing the agreement factor, R,[12)] was sought, the R value for this system could not clearly be minimized. So the Eu-N distance in the Eu(DPM)$_3$(Pyridine)$_2$ crystal, 2.65 Å,[13)] was adopted as a reasonable one, and the calculations with this distance led the smallest $R_{C,H}$[14)] value at $\chi=50°$ in the Eu(FOD)$_3$-aniline system (Table 1). R_H[14)] is much smaller at 50°. This angle is incidentally similar in magnitude to that decided so as to fit the ^{1}H pcs pattern to S_{obs}(Pr). A combination of $r_N=2.65$ Å and $\chi=40°$ giving the ^{1}H pcs pattern similar to that of the Yb(FOD)$_3$-induced ^{1}H shifts of aniline,[1h)] led larger R values ($R_{C,H}=0.172$, $R_H=0.024$), in spite of the general recognition that the Yb ion may produce the smallest cs into a ligand.[2b,3,15)] On the other hand, the S_{obs}(Pr) values, particularly for ^{13}C, were well explained by adding a small amount of $S_{cs}(\alpha)$ to S_{pcs}, as shown in Table 1. The result of application of this procedure to p-toluidine is shown in Table 2, where $r_N=2.65$ Å and $\chi=43°$ give the best result. Thus, while the R values for ^{1}H are satisfactorily small, those for ^{13}C are too large (See Tables 1 and 2). However, even with the variation of r_N and χ in the ranges of 2.4—2.8 Å and 20°—50°, respectively, the sign alternation characteristic of $R_{cs}(\alpha)$ and $R_{cs}(\beta)$ is considerably effective to correct the R_{pcs} patterns for both ^{1}H and ^{13}C. Therefore, the above results seem adequate to show that a small amount of negative and positive spin similar to that of positive spin in the Ni(AcAc)$_2$-aniline system[7)] may be transferred from the Eu ion and the Pr ion, respectively,[16)] but are still unsatisfactory for a strictly quantitative requirement. It is still under investigation whether the minimization of R cannot be essentially obtained in such the procedure containing MO calculations or the situation is improved by a reconsideration on the method of estimates of R_{cs}.

The above results for the Eu-complexes allow us to consider that whether an f-orbital unoccupied by an unpaired spin overlaps with the nitrogen lone pair orbital, and a pair of electrons in the resulted complex MO interacts via spin exchange with an unpaired spin in the other f-orbital, or there is no overlapping,[15b)] and a pair of electrons in the N-lone pair orbital is directly polarized by a spin in the Eu ion. These mechanisms are expected to produce a very small amount of negative spin at the nitrogen nucleus, and seem to be consistent with the fact that we need only about 10^{-3} negative spin in the ligand π-orbital to account for our observations. In the Pr complex, although one may consider the possibility that the f-orbital containing a spin directly interacts with the nitrogen lone pair orbital, the very small amounts of observed shifts show that this possibility may be not necessarily valid.[15b)]

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