Contact-Only and Dipolar-Only NMR Shift Reagents

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Contact-Only and Dipolar-Only Mixtures of Lanthanide NMR Shift Reagents

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Two new types of NMR shift reagents, one giving dipolar-only and the other giving contact-only shifts, can be prepared simply by mixing two appropriate $Ln(fod)_3(Ln = Pr, Nd, Eu, and Yb)$ reagents in certain ratios. The ^{1}H and ^{13}C NMR spectra of pyridine-type substrates, quinoline and isoquinoline, whose paramagnetic shifts are normally a composite of contact and dipolar contributions with single lanthanide shift reagents, show the feasibility of this approach.

Introduction

Considerable interest has recently been shown in ^{1}H and ^{13}C NMR shifts, induced in a wide range of organic molecules by the lanthanide shift reagents.[1,2] These induced shifts $\Delta\delta_{ij}$'s are a combination of dipolar (or pseudocontact) and contact shifts caused by coordination of the organic molecule to the lanthanide shift reagent, according to eq. 1[3]

$$\Delta\delta_{ij} = G_i C_j^D + F_i <Sz>_j \qquad (1)$$

where C_j^D and $<Sz>_j$ depend upon the lanthanide ion j being used and have been calculated by Bleaney[4,5] and Golding.[6,7] G_i and F_i depend upon the geometric location and electron spin density of the substrate nucleus i, respectively.

In the previous work[8] we demonstrated the applicability of contact-only and dipolar-only mixtures of the lanthanide shift reagents whose effective net C^D or $<Sz>$ values were zero, to determine F_i and G_i values of the nuclei in 4-picoline. The F_i and G_i values obtained directly by the contact-only and the dipolar-only reagents, which were appropriate mixtures of $Pr(fod)_3$ and $Eu(fod)_3$, agreed well with those values obtained by experiments using individual $Ln(fod)_3$ reagents. But F_i and G_i values obtained directly by the contact-only and the dipolar-only reagents, which were mixtures of $Nd(fod)_3$ and $Yb(fod)_3$, deviated from the expected values. It was supposed that the deviation was due to the behavior of the ytterbium complex.

We report here the applicability of contact-only and dipolar-only mixtures of lanthanide shift reagents to determine F_i and G_i values for more complicate pyridine-type

Table 1. Mole Ratios of $Ln(fod)_3$ for Contact-only (COM) and for Dipolar-only (DOM) Mixtures[a]

mixture	mole ratio		net $<Sz>$	net C^D
	$Eu(fod)_3/Pr(fod)_3$	$Yb(fod)_3/Nd(fod)_3$		
COM 1	2.75	—	−7.04	0
COM 2	—	0.191	3.36	0
DOM 1	0.278	—	0	−7.73
DOM 2	—	1.73	0	12.4

[a] Computed from Bleaney's data(5) scaled to Dy value and from Golding's data (6) scaled to −100 for Dy.

substrates (quinoline and isoqunoline), which provide informations about electron spin densities and geometries.

Experimental

Materials. The substrates, quinoline and isoquinoline were purchased from Aldrich Chemical Co., distilled, and stored over Molecular Sieve 4A. The lanthanide shift reagents, $Ln(fod)_3(Ln = Pr, Eu, and Yb; fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)$ were commercial chemicals from Norell Inc. $Nd(fod)_3$ were synthesized as described by Sievers *et al.*[9] Contact-only and dipolar-only lanthanide shift reagents were prepared as described in the previous work.[8] Table 1 shows the mole ratios of $Ln(fod)_3$ used to prepare contact-only (COM 1 and COM 2) and dipolar-only (DOM 1 and DOM 2) reagents.

NMR Spectra. ^{1}H and ^{13}C NMR spectra were obtained

Table 2. Observed Lanthanide-Induced Shifts of Quinoline

nucleus	lanthanide-induced shift (ppm)[a]							
	Pr(fod)₃	Nd(fod)₃	Eu(fod)₃	Yb(fod)₃	COM 1	COM 2	DOM 1	DOM 2
C_2	-136.75	-87.19	128.98	107.05	50.36	-60.59	-82.65	32.28
C_3	-35.37	-11.41	-0.30	38.80	-9.31	-4.46	-28.87	19.81
C_4	-31.63	-19.55	36.55	36.99	16.29	-11.81	-18.36	14.97
C_5	-19.54	-10.80	11.59	23.42	2.76	-6.21	-13.56	10.06
C_6	-15.03	-9.09	12.04	18.64	4.31	-5.40	-9.80	7.85
C_7	-24.92	-19.19	26.33	24.17	11.32	-13.44	-14.79	7.51
C_8	-75.02	-55.58	73.86	64.41	29.94	-39.88	-46.03	18.31
C_9	-95.61	-53.17	60.02	111.88	15.38	-30.77	-65.05	46.50
C_{10}	-29.83	-2.58	-11.73	42.65	-14.17	3.78	-23.49	25.30
H_2	-81.04	-37.23	29.64	74.26	-0.35	-22.31	-56.40	17.46
H_3	-23.14	-10.68	11.24	27.82	1.69	-9.70	-16.22	6.59
H_4	-18.33	-9.45	12.19	26.62	3.57	-4.83	-11.68	6.69
H_5	-13.85	-7.39	8.38	21.01	2.24	-3.83	-8.91	5.31
H_6	-10.37	-6.94	8.42	14.46	2.89	-5.45	-6.46	3.08
H_7	-12.16	-9.66	7.29	13.71	2.11	-5.03	-8.24	2.54
H_8	-66.33	-53.64	41.03	84.00	11.51	-34.82	-42.68	17.31

[a] positive downfield.

Table 3. Observed Lanthanide-Induced Shifts of Isoquinoline

nucleus	lanthanide-induced shift (ppm)[a]							
	Pr(fod)₃	Nd(fod)₃	Eu(fod)₃	Yb(fod)₃	COM 1	COM 2	DOM 1	DOM 2
C_1	-112.07	-64.66	96.14	184.38	42.78	-26.06	-71.22	83.51
C_3	-108.51	-64.50	84.35	190.63	35.55	-26.27	-70.48	84.68
C_4	-26.62	-1.23	-14.61	68.56	-17.18	9.36	-25.12	40.09
C_5	-11.87	-4.63	4.19	26.63	0.25	0.26	-9.01	14.57
C_6	-10.18	-5.14	13.04	21.10	7.01	-1.05	-5.66	10.90
C_7	-6.69	-0.92	0.72	18.85	-0.98	2.17	-5.52	10.86
C_8	-16.65	-7.63	11.63	31.26	4.55	-1.68	-11.32	16.29
C_9	-23.59	2.93	-25.74	61.09	-24.50	11.84	-25.46	37.69
C_{10}	-32.63	-19.84	29.46	55.47	13.88	-8.10	-20.73	26.72
H_1	-61.27	-26.14	27.83	103.71	4.64	-5.58	-40.20	49.77
H_3	-60.23	-29.87	34.35	133.65	9.28	-4.07	-38.22	62.92
H_4	-20.90	-9.25	20.49	41.43	2.28	-0.51	-13.47	21.05
H_5	-12.23	5.61	8.15	19.95	2.50	1.54	7.61	10.35
H_6	-6.91	-3.18	3.98	11.06	0.99	-0.89	-4.39	6.31
H_7	-7.31	-3.64	4.10	9.91	1.21	-1.09	-4.80	5.75
H_8	-13.31	-6.88	7.04	19.65	1.71	-1.76	-8.55	10.31

[a] positive downfield.

on a Varian XL-100 FT NMR spectrometer. The spectrometer was run at 100 MHz for ^{1}H spectra and at 25.2 MHz for ^{13}C spectra. NMR samples were prepared as described in the previous work.[8]

Results and Discussion

Lanthanide shift reagents are well known to induce the NMR shifts in the NMR spectra of π-deficient heterocyclic compounds such as quinoline and isoquinoline.[10-16] The aromatic amines may be expected to show substantial contact and dipolar shifts, and ^{1}H and ^{13}C assignments are available. Also quinoline and isoquinoline are the structurally rigid molecules which possess hard nitrogen suitable for relatively tight chelation to Ln(fod)₃ hard acid. If rapid equilibrium between Ln(fod)₃ and substrate occurs in the solution and adduct formation is nearly complete, the effective net C_D or $<S_z>$ values for the binary Ln(fod)₃ mixtures employed are expected to be zero.

^{1}H spectra, unlike ^{13}C spectra, exhibit little contact interactions because electron in the 1s orbital of hydrogen has only a small spin density at the proton nucleus. Thus, the ^{13}C shift data are a more decisive test. Also the ^{13}C chemical shifts are measured with ease and greater accuracy than the ^{1}H values

Table 4. F_i and G_i Values Obtained from Observed Lanthanide-Induced Shifts of Quinoline

nucleus	F_i[a]			INDO[b] (quinoline[c])	G_i[c]			Yb(fod)	calc'd G_i[d]
	Ln(fod)_3	COM 1	COM 2		Ln(fod)_3	DOM 1	DOM 2		
C_2	-9.10	-7.16	-18.06		10.02	10.69	1.99		
	(3.70)	(3.09)	(5.13)	(1.96)	(4.53)	(4.49)	(2.12)	(2.89)	(2.88)
C_3	1.08	1.32	-1.33		3.53	3.73	1.22		
	(-0.44)	(0.57)	(0.38)	(-1.58)	(1.60)	(1.57)	(1.30)	(1.05)	(1.27)
C_4	-2.46	-2.32	-3.52		2.21	2.38	0.94		
	(1.00)	(1.00)	(1.00)	(1.00)	(1.00)	(1.00)	(1.00)	(1.00)	(1.00)
C_5	-0.67	-0.39	-1.85		1.61	1.75	0.62		
	(0.27)	(0.17)	(0.53)	(0.14)	(0.73)	(0.73)	(0.66)	(0.63)	(0.66)
C_6	-0.80	-0.61	-1.61		1.16	1.27	0.50		
	(0.33)	(0.26)	(0.46)	(-0.23)	(0.52)	(0.53)	(0.53)	(0.50)	(0.50)
C_7	-2.22	-1.61	-4.01		1.69	1.91	0.47		
	(0.90)	(0.69)	(1.14)	(0.33)	(0.76)	(0.80)	(0.50)	(0.65)	(0.59)
C_8	-6.10	-4.26	-11.89		5.24	5.95	1.09		
	(2.48)	(1.84)	(3.38)	(-1.03)	(2.37)	(2.50)	(1.16)	(1.74)	(1.54)
C_9	-3.54	-2.19	-9.17		7.79	8.42	2.82		
	(1.44)	(0.94)	(2.61)	(1.65)	(3.52)	(3.54)	(3.00)	(3.02)	(2.46)
C_10	2.19	2.02	1.13		2.94	3.04	1.62		
	(-0.89)	(-0.87)	(-0.32)	(-1.96)	(1.33)	(1.28)	(1.72)	(1.15)	(1.22)
H_2	-0.74	0.05	-6.65		7.20	7.30	1.41		
	(1.16)	(0.10)	(4.61)	(2.15)	(3.26)	(3.07)	(1.50)	(2.01)	(2.28)
H_3	-0.39	-0.24	-2.89		2.00	2.10	0.53		
	(0.61)	(0.47)	(2.01)	(0.83)	(0.91)	(0.88)	(0.56)	(0.75)	(0.75)
H_4	-0.64	-0.51	-1.44		1.50	1.51	0.54		
	(1.00)	(1.00)	(1.00)	(1.00)	(0.68)	(0.63)	(0.57)	(0.72)	(0.62)
H_5	-0.46	-0.32	-1.14		1.14	1.15	0.43		
	(0.72)	(0.63)	(0.79)	(0.80)	(0.52)	(0.48)	(0.46)	(0.57)	(0.46)
H_6	-0.65	-0.41	-1.62		0.78	0.84	0.25		
	(1.02)	(0.80)	(1.13)	(-0.06)	(0.35)	(0.35)	(0.27)	(0.39)	(0.30)
H_7	-0.77	-0.30	-1.50		0.92	1.07	0.21		
	(1.20)	(0.59)	(1.04)	(0.10)	(0.42)	(0.45)	(0.22)	(0.37)	(0.25)
H_8	-4.40	-1.64	-10.38		4.98	5.52	1.39		
	(6.86)	(3.22)	(7.21)	(0.42)	(2.25)	(2.31)	(1.48)	(2.27)	(1.45)

[a] The values in parentheses are normalized to 1.00 at C_4 position for carbon nuclei and to 1.00 at H_4 position for proton nuclei. [b] Calculated quinoline radical spin density in C_2, or H_2, obtained by INDO calculations. [c] The values in parentheses are normalized to 1.00 at C_4 position. [d] Calculated in this work, assuming a Ln-nitrogen disitance of 3.63Å and ρ = 9.60°.

which are obtained by first-order analysis. The ^1H spectra are complicated by spin-spin coupling to other protons and accurate chemical shift data require numerous computer simulations for the systems. The broadening of the ^1H spectra was much greater than that of ^{13}C, leading to less accurate evaluation of the lanthanide-induced shifts. The greater broadening is expected when controlled by electron dipole/ nuclear dipole relaxation in the lanthanide-substrate complex. The equation of Solomon[17] and Bloembergen[18] for the effect of paramagnetic species on relaxation times shows that the broadening of ^1H spectra will be 15.8 times greather than for ^{13}C.

The observed lanthanide-induced shifts of quinoline and isoquinoline are summarized in Table 2 and 3. These values

were obtained by extrapolating linearly the observed chemical shifts to a value corresponding to a 1:1 mole ratio of lanthanide reagent/substrate ($\Delta\delta_{ij}$). From $\Delta\delta_{ij}$'s F_i and G_i values of nuclei in the substrates were determined by using eq. 2

$$\Delta\delta_{ij}/<Sz>_j = F_i + G_i (C_j^p/<Sz>_j)\qquad (2)$$

where the intercept and the slope gave F_i and G_i, individually. To determine F_i and G_i values, data and parameters for three Ln(fod)_3(Ln = Pr, Nd, and Eu) reagents were used. In determining F_i and G_i values from the observed shifts Yb(fod)_3 data were excluded for the reason of the large discrepancy of the data. In Table 4 and 5 F_i and G_i values determined from Ln(fod)_3 data are compared to those obtained directly from the

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Table 5. F_i and G_i Values Obtained from Observed Lanthanide-Induced Shifts of Isoquinoline

nucleus	F_i [a]			INDO[a,b] (isoquinoline[c])	G_i [c]			Yb(fod)₅	calc'd G_i [c,d]
	Ln(fod)₃	COM 1	COM 2		Ln(fod)₃	DOM 1	DOM 2		
C₁	-6.06 (-2.34)	-6.08 (-2.49)	-7.77 (-2.78)	(-2.27)	8.57 (2.75)	9.21 (2.83)	6.73 (2.08)	(2.69)	(2.37)
C₃	-5.53 (-2.14)	-5.05 (-2.07)	-7.83 (-2.80)	(-1.59)	8.42 (2.70)	9.12 (2.81)	6.83 (2.11)	(2.78)	(2.26)
C₄	2.59 (1.00)	2.44 (1.00)	2.80 (1.00)	(1.00)	3.12 (1.00)	3.25 (1.00)	3.23 (1.00)	(1.00)	(1.00)
C₅	-0.00 (-0.00)	-0.04 (-0.02)	0.08 (0.03)	(0.59)	1.08 (0.35)	1.17 (0.36)	1.18 (0.37)	(0.39)	(0.42)
C₆	-0.74 (-0.29)	-1.00 (-0.41)	-0.31 (-0.11)	(-0.34)	0.72 (0.23)	0.73 (0.22)	0.88 (0.27)	(0.31)	(0.29)
C₇	0.30 (0.12)	0.14 (0.06)	0.65 (0.23)	(0.41)	0.68 (0.22)	0.71 (0.22)	0.88 (0.27)	(0.27)	(0.29)
C₈	-0.50 (-0.19)	-0.65 (-0.27)	-0.50 (-0.18)	(-0.20)	1.38 (0.44)	1.46 (0.45)	1.31 (0.41)	(0.46)	(0.48)
C₉	3.58 (1.38)	3.48 (1.43)	3.53 (1.26)	(0.89)	3.11 (1.00)	3.29 (1.01)	3.04 (0.94)	(0.89)	(1.01)
C₁₀	-1.97 (-0.76)	-1.97 (-0.81)	-2.41 (-0.86)	(-0.64)	2.44 (0.78)	2.68 (0.82)	2.15 (0.67)	(0.81)	(0.81)
H₁	-0.68 (2.05)	-0.66 (2.04)	-1.66 (11.07)	(2.01)	5.39 (1.73)	5.20 (1.60)	4.01 (1.24)	(1.51)	(1.41)
H₃	-1.60 (4.85)	-1.32 (4.07)	-1.21 (8.07)	(2.32)	5.06 (1.62)	4.94 (1.52)	5.07 (1.55)	(1.95)	(1.37)
H₄	-0.33 (1.00)	-0.32 (1.00)	-0.15 (1.00)	(1.00)	1.81 (0.58)	1.74 (0.54)	1.70 (0.53)	(0.60)	(0.56)
H₅	-0.34 (1.04)	-0.36 (1.11)	-0.46 (3.07)	(-0.13)	1.02 (0.33)	0.99 (0.30)	0.83 (0.26)	(0.29)	(0.32)
H₆	-0.15 (0.47)	-0.14 (0.43)	-0.27 (1.00)	(0.23)	0.59 (0.19)	0.57 (0.18)	0.51 (0.16)	(0.16)	(0.20)
H₇	-0.19 (0.57)	-0.17 (0.52)	-0.33 (2.13)	(0.17)	0.62 (0.20)	0.62 (0.19)	0.46 (0.14)	(0.14)	(0.19)
H₈	-0.32 (0.96)	-0.24 (0.74)	-0.53 (3.47)	(0.23)	1.13 (0.36)	1.11 (0.34)	0.83 (0.26)	(0.29)	(0.34)

[a] The values in parentheses are normalized to 1.00 at C_4 position for carbon nuclei and to 1.00 at H_4 position for proton nuclei. [b] Calculated isoquinoline radical spin density in C_{2i} or H_i, obtained by INDO calculations. [c] The values in parentheses are normalized to 1.00 at C_4 position. [d] Calculated in this work, assuming a Ln-nitrogen disitance of 2.85Å and $\rho = 3.25°$.

experimental shifts using contact-only (COM 1 and COM 2) and dipolar-only (DOM 1 and DOM 2) mixtures. The F_i and G_i values obtained by COM 1 and DOM 1, which consisted of Pr(fod)₃ and Eu(fod)₃ mixtures, agreed well with those determined by individual Ln(fod)₃(Ln = Pr, Nd, and Eu) reagents. However, F_i and G_i values obtained by COM 2 and DOM 2 differed much more widely. When a plot of $\Delta\delta/<Sz>$ against $C^D/<Sz>$ according to eq. 2 was made, the points corresponding to Yb(fod)₃-induced shifts deviated substantially from the straight line which passed through the points corresponding to other Ln(fod)₃-induced shifts. It is supposed that the deviation of Yb(fod)₃ data comes from one or more of the following sources; (1) stoichiometry of substrate-lanthanide shift reagent adducts, (2) structural changes, and (3) degree of covalency.[a] Thus, COM 2 and DOM 2, which consist of

Yb(fod)₃ and Nd(fod)₃ mixtures, might not be contact-only and dipolar-only, respectively for pyridine-type substrate.

Contact Shifts. The sign of the unpaired electron spin density on the carbon atoms of the substrates, which is proportional to the F_i values determined from the observed Ln(fod)₃-induced shifts is as shown in Figure 1. The sign alter-

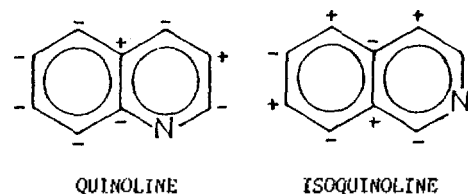QUINOLINE   ISOQUINOLINE

Figure 1. Sign of electron spin densities in Ln(fod)₃-substrate.

nations in isoquinoline ring is identical with the pattern of those predicated by a dominant spin polarization mechanism. In the quinoline substrate a strong σ–spin delocalization through π–bond may occur as well and as a result the alternate sign change is not observed at C_5 and C_8 atoms. The smaller F_i value observed at C_5 in isoquinoline could be taken as being indicative of σ–spin delocalization mechanism. For pyridine-type substrates the unperturbed cation radical appeared to be the best model for the INDO calculation of the net unpaired electron spin density distribution in the substrate bound to lanthanide complex.[3] As shown in Table 4 and 5, F_i values of proton and carbon nuclei obtained by COM 1 or Ln(fod)₃ reagents agreed roughly with the INDO–calculated s–orbital spin densities of the cation radical for isoquinoline. But the observed F_i values agreed less well with the calculated spin densities for quinoline. A serious discrepancy between the observed and the calculated spin density existed at H_8 only, the proton closest to the lanthanide, for quinoline.

Dipolar Shifts. The substrates examined in this study have rigid chemical frameworks and all substrate–Ln(fod)₃ complexes might have the same structure. A computer program was used to determine the best-fit location of Ln in the substrate–Ln(fod)₃ complex. For ease in calculation, a molecule is described with respect to an internal Cartesian coordinate systems with nitrogen at the origin and the principal axis passes through the center of the heterocyclic ring. The atomic coordinates for the substrate molecules are derived from standard bond lengths and bond angles.[19] The lanthanide is then moved incrementally over the surface of a sphere of radius d, the assumed Ln–N distance. The location of Ln on the sphere is described in terms of the two angles, ρ and φ. At each lanthanide position, the variable term

$$(3\cos^2\theta_i - 1)/r_i^3 \qquad (3)$$

in the dipolar equation[20] is evaluated for all i nuclei. In eq. 3 r_i is the distance from Ln to nucleus i and θ_i is the angle between the nucleus–Ln vector and the principal axis. This set of numbers is then scaled by least squares against the relative observed shifts, $\Delta\delta_{i(o)}$ to yield a set of calculated shifts $\Delta\delta_{i(c)}$. The best-fit lanthanide is taken as the minimum of the agreement factor R,[21]

$$R = [\frac{\sum_i (\Delta\delta_{i(o)} - \Delta\delta_{i(c)})}{\sum_i \Delta\delta_{i(o)}^2}]^{1/2} \qquad (4)$$

The best-fit location of lanthanide determined from Ln(fod)₃ (Ln = Pr, Nd, and Eu) G_i values is at d = 3.63Å, ρ = 9.60° for quinoline and at d = 2.85Å, ρ = 3.25° for isoquinoline, as shown in Figure 2. In these structures the lanthanide ion is displaced slightly away from the center line, as might be expected on the steric ground. Also the Ln–N distance of quinoline complex is greater than that of isoquinoline complex because of more steric effect.

Geometric factors G_i's give us the valuable information about the geometries of substrate molecules in solution. In Table 5 and 6 we compared the G_i values obtained by DOM 1 or Ln(fod)₃(Ln = Pr, Nd, and Eu) with those calculated from the geometry of the complexes. The observed G_i values agreed well with those calculated for quinoline and isoquinoline. Because of the large $C^D/\langle Sz\rangle$ values for ytterbium, the observed lanthanide–induced shifts obtained from Yb(fod)₃ data
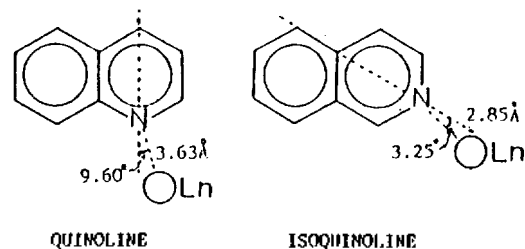

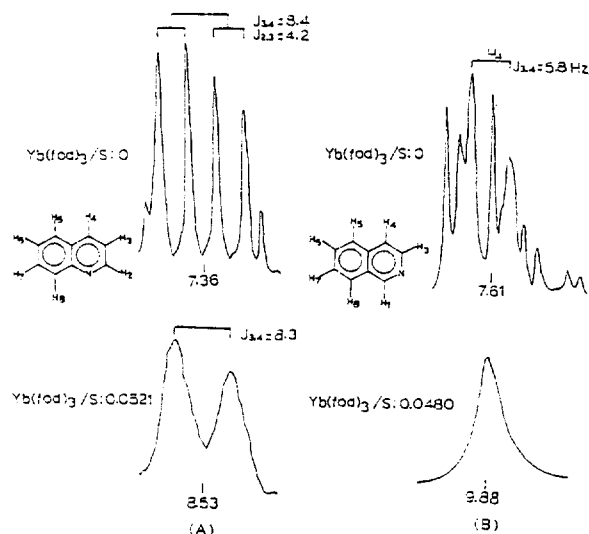**Figure 2.** Best–fit location of lanthanide ion in Ln(fod)₃–substrate.

Figure 3. Spin-decoupling upon addition of Yb(fod)₃ in (A) H_3 resonance of quinoline and (B) H_4 resonance of isoquinoline. In the quinoline spectra, the resonance for H_4 are indicated; the remaining resonances shown occur in the chemical shift range of H_6 and H_7 and matched an ABCD computer simulation for $H_5H_6H_7H_8$.

should be principally dipolar. Thus, the relative shift values corresponding to this reagent are tabulated in Table 4 and 5.

Chemical Exchange Spin Decoupling. As a result of the enhancement of the proton longitudinal relaxation rate, $1/T_1$, some proton nuclei were found to be effectively decoupled from other nuclei. With increasing Ln(fod)₃concentration, the initial effect(in addition to shifting) is a broadening followed at higher concentrations by a collapse of the multiplet pattern. Figure 3 illustrates this phenomenon for quinoline and isoquinoline using Yb(fod)₃ as the shift reagent. In the case of quinoline H_3 is initially spin coupled to H_4 and to H_2; upon addition of shift reagent the lifetime of H_2 in a given state can be shortened and eventually decoupled, leaving H_3 coupled only to H_4. This occurs when $1/T_1(H_2) > 2\pi J_{2,3}/\sqrt{2}$. This phenomenon formally resembles the case where the broadening and collapse are caused by chemical exchange[22,23] and has been termed "chemical exchange spin decoupling". This chemical exchange spin decoupling was also found in isoquinoline where the initial doublet for H_4 was collapsed to a singlet by addition of Yb(fod)₃ which shortened T_1 for H_3.

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Characterization of Korean Clays and Pottery by Neutron Activation Analysis (III). A Classification Rule for Unknown Korean Ancient Potsherds

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A number of Korean potsherd samples has been classified by Fisher's discriminant method for the training set of Kyungki, Koryung and Kyungnam groups. The Koryung samples have been further classified for the training set of Koryung A, B and C subgroups. The training sets have been used to define classification of unknown samples and clay samples so as to find out some similarity between clay samples and certain potsherd groups.

Introduction

The pattern recognition (PR) approach can be stated as follow,[1-3] "Given a set of objects and a list of measurements made on them, it is possible to find or predict a property of the objects, that is not directly measurable but is known to be related to the measurements via some unknown relationship." Archaeology is one of the major beneficiaries of such a PR approach,[4,5] the other notable area of application being environmental science,[6] forensic science[7] and diagnostic classification.[8]

In pattern recognition, two different situations can be considered according to whether the calsses into which individual samples must be classified are known or not. In the first instance, one speaks of supervised learning and in the second of unsupervised learning. Only supervised learning is of interest here. Supervised learning means that a learning or training set, *i.e.,* a number of classified individuals or samples, is developed, and this is used to define a classification rule which is subsequently applied to the classification of unknown samples.[8]

In the previous work, some classification had been tried