Primary and Secondary Binding Sites for Lanthanide Shift Reagents with Amides. Differential Behavior of *cis* vs *trans* Amide Isomers with LSR

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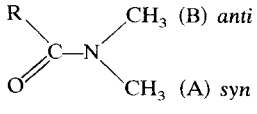
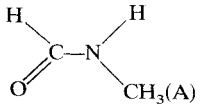
Lanthanide induced shifts (LIS) were measured for four dimethylamides, $RCON(CH_3)_2$, and four monomethyl amides, $RCONHCH_3$, R = H, CH_3, CF_3 and CCl_3, using $Eu(fod)_3$ in CCl_4 and benzene (C_6D_6) solution. Structural correlations for $HCON(CH_3)_2$ and $CH_3CON(CH_3)_2$ in both solvents yield a preferred binding site for the $Eu(fod)_3$ on one of the lone-pair orbitals of the oxygen atom, with a probable site of secondary importance on the other lone-pair orbital. The *cis* vs *trans* isomers of $HCONHCH_3$ and $CH_3CONHCH_3$ exhibit remarkably different chemical shift behavior upon addition of $Eu(fod)_3$.

INTRODUCTION

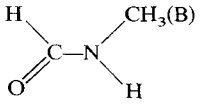
The barrier to internal rotation about the central C—N bond in many dimethylamides, $RCON(CH_3)_2$, is in the range 10–20 kcal mol^{-1}; separate NMR resonances are thus observed for *N*-methyl protons which are located *syn* or *anti* to the carbonyl oxygen atom.[1] (These are



labeled A and B protons, respectively). The dimethylamides studied in this work are R = H, dimethylformamide (DMF); R = CH_3, dimethylacetamide (DMA); R = CF_3, dimethyltrifluoroacetamide (DMTFA); R = CCl_3, dimethyltrichloroacetamide (DMTCA). In aliphatic monomethylamides, the energy barriers are within the same range[2] as the dimethylamides; these amides are, however, found to be almost entirely in the *trans* configuration (Ia)[1,3–5]



Ia *trans*



Ib *cis*

For the series of monomethylamides studied, R = H, CH_3, CF_3, CCl_3, only the first two show the presence of a measurable amount of *cis* isomer.[3,6] NMR studies show that pure *N*-methylformamide (NMF) contains about 8%[3] and an aqueous solution of *N*-methylacetamide (NMA) about 3% of the *cis* isomer.[6]

Infrared spectroscopic studies of *N*-methyltrifluoroacetamide (NMTFA) and *N*-methyltrichloroacetamide (NMTCA) in CCl_4 indicate that these molecules are predominantly in the *trans* configuration[5f–5h] (the *cis* configuration, which has unique N—H stretching frequencies, is apparently not present). An increase in stabilization has been postulated[5f,5g] for the *trans* as compared with the *cis* configuration in α-halosubstituted amides (such as NMTFA and NMTCA). This is attributed to the formation of a weak intramolecular hydrogen bond between a halogen atom and the nitrogen proton.[5f,5g]

The present work was undertaken in order to determine the usefulness of the lanthanide induced shift (LIS) method in distinguishing between *cis* and *trans* isomers in *N*-monosubstituted amides. Earlier NMR studies of the LIS of amides reveal that the LSR complexes with the oxygen atom of the amide,[7–10] and that in dimethylamides the *N*-methyl protons located *syn* to the carbonyl oxygen atom are shifted more than those located *anti*.[8–10] We also wished to study the difference, if any, in molecular structure LIS correlations between two solvents, one of which (CCl_4) is relatively inert to amides while the other (C_6D_6) interacts with amides causing an aromatic solvent induced shift (ASIS).[11] The ASIS causes the relative chemical shifts of the *N*-methyl protons to invert positions from those in CCl_4 solution.[12,13]

The slopes of the least squares plots of the induced shift vs L_0/S_0 yield $2\Delta_2$, where Δ_2 is the limiting shift of the 1:2 LSR–amide complex.[14] The treatment assumes the coexistence of 1:1 and 1:2 LSR–amide complexes in solution. The quantity $2\Delta_2$, measured for each proton in the amide, is referred to here as $(LIS)_i$, the magnitude of the shift of the i^{th} proton, expressed in ppm, and can be correlated with molecular geometry through the McConnell–Roberts equation[15]

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

where r_i is the vector between the lanthanide atom and the proton for which the LIS is being measured, θ_i is the angle between r_i and the z magnetic axis of the complex, and D is a constant whose value depends

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Table 1. Selected equilibrium constants

A. Amide–benzene interaction		$K(M^{-1})$		Temperature (°C)	Reference
DMF—C_6H_6 association		0.14		37	a
NMA—C_6H_6 association		0.25		26	b
B. Amide–amide hydrogen bonding		$K_{12}(M^{-1})$[c]	$K(M^{-1})$[d]		
Amide	Solvent				
NMF	C_6H_6	18.9	19.4	25	e
NMA	C_6H_6	6.1	13	25	e
NMA	CCl_4	1.5	23	30	f
NMTCA[g]	C_6H_6	0.75	2.5	25	e
Lactams (*cis*)	CCl_4	110–470		20	h
C. Shift reagent self-association		$K(M^{-1})$			
$Eu(fod)_3$ dimerization in CCl_4		100		37	i
$Eu(fod)_3$ dimerization in benzene solution		60		37	i
D. Carbamate[k]-shift reagent association					
1:1 TMC:$Eu(fod)_3$ complex[l]		1600		27	m
2:1 TMC:$Eu(fod)_3$ complex[l]		107		27	m

[a] A. A. Sandoval and M. W. Hanna, *J. Phys. Chem.* **70,** 1203 (1966). Value converted from kg mol^{-1}.
[b] K. R. Bhaskai and C. N. R. Rao, *Biochem. Biophys. Acta* **136,** 561 (1967).
[c] K_{12} is for 2 monomers$\rightleftharpoons$dimer.
[d] K is for n-mer+monomer$\rightleftharpoons(n+1)$-mer.
[e] Ref. 7. Values converted from mole fraction units.
[f] L. L. Graham and C. Y. Chang, *J. Phys. Chem.* **75,** 776 (1971). Values converted from mole fraction units.
[g] In order to compare the association of NMTFA with the other amides in this list for which K could be found, the degree of association in CCl_4 may be used. This value is 4.3 for NMTFA and 0.15 in NMTCA. See Ref. 5g.
[h] W. A. P. Luck, in *The Hydrogen Bond,* ed. by P. Schuster, G. Zundel and C. Sandorfy, North Holland, Amsterdam (1976).
[i] J. F. Desreux, L. F. Fox and C. N. Reilly, *Anal. Chem.* **44,** 2217 (1972).
[j] R. Porter, T. J. Marks and D. F. Shriver, *J. Am. Chem. Soc.* **95,** 3548 (1973).
[k] Amide-shift reagent equilibrium constants are not available; the carbamate was therefore used for comparison.
[l] TMC is methyl *N,N*-dimethylcarbamate, $CH_3O\overset{O}{\overset{\|}{C}}N(CH_3)_2$.
[m] See Ref. 20.

upon the magnetic anisotropy of the complex. Effective axial symmetry is apparently achieved in solution through time averaging of all possible orientations of the complex.[16,17] Self-association of $Eu(fod)_3$ is minimized in this work by limiting the concentration range to $0 \leq L_0/S_0 \leq 0.4$, the region in which the slopes, $2\Delta_2$, are determined.

Table 1 provides a comparison of the equilibrium constants for amide and LSR systems. For dimethylamides at low L_0/S_0 ratios, only the 2:1 amide–LSR complexes are significant and the slopes of the induced shift vs L_0/S_0 are expected to be linear. However, in the *N*-methylamide solution, both conformational changes and perturbation of the self-association through hydrogen bonding are possible, and curvature of the induced shift vs L_0/S_0 plot may result.

EXPERIMENTAL

NMF, NMA, DMF and DMA (Eastman Organic Chemicals) were dried and then fractionally distilled *in vacuo.* NMTCA and NMTFA were prepared by adding trichloroacetyl chloride or trifluoroacetyl chloride to a solution of monomethylamine in ether at 5 °C. The amides were purified by sublimation. DMTCA and DMTFA were prepared by adding trifluoroacetic anhydride or trichloroacetyl chloride to a solution of dimethylamine in ether at 5 °C. The amides were purified by fractional distillation *in vacuo.* All amides were kept in a desiccator after purification. DMTCA and DMTFA were kept in a cold room to prevent decomposition and/or evaporation.

About 20–50 mg of the lanthanide shift reagent, $Eu(fod)_3$-d_{27} (Stohler, Inc.) were weighed and dried immediately before each run *in vacuo* in a 1 dram vial. The vial was placed at an angle in a modified Abderholden drying apparatus with $Mg(ClO_4)_2$ in the pistol. Boiling xylene raised the temperature of the LSR to about 120 °C. After one minute at this temperature and pressure (0.2 Torr) the $Eu(fod)_3$ turned from pale to bright yellow. It was then allowed to cool to room temperature *in vacuo.* (Prolonged heating resulted in sublimation.) The vacuum was then released using dry nitrogen gas. This was followed immediately by inserting a micropipette through a small hole in a rubber cap which fitted tightly over the section of the drying apparatus containing the vial. (A fitted glass cover made a vacuum-tight seal over the rubber cap.) A volume of 0.5 ml of 0.1 M amide in CCl_4 or benzene solution was added to the LSR in the vial via the micropipette. Approximately 0.48 ml of this solution was transferred to an NMR tube. All

glass apparatus was baked overnight in an oven at 110 °C.

The initial molar ratio of $Eu(fod)_3$ (L_0) to amide (S_0) in these solutions therefore ranged from 0.4 to 1.0. Succeeding solutions were prepared by adding aliquots of a stock solution which was 0.1 M in amide. Between 7 and 25 dilutions were made for each amide except NMF and DMF; for these amides 50 dilutions spanned the range from $L_0/S_0 = 0.01$ to 1.0. After each dilution, the NMR tube remained in the probe for at least 5 min before the spectrum was recorded at 28 °C with a Varian A60-A NMR spectrometer.

RESULTS AND DISCUSSION

N,N-Dimethylamides

In the dimethylamides, it is the *N*-methyl group *syn* to the carbonyl oxygen atom, [labeled the *N*-CH_3 (A) group] which shows the greater downfield shift upon the addition of LSR[8–10](Fig. 1). The slopes of the least square best fits of the amide chemical shift vs the molar ratio of amide to $Eu(fod)_3$ are given in Table 2. Excluding DMTCA, the LIS of the *N*-methyl (A) protons are in the range 10–13 ppm and the LIS of the *N*-methyl (B) protons are in the range 5–7 ppm.

Table 2 also shows the ratio of LIS values for the *syn* *N*-methyl to *anti* *N*-methyl protons. The ratio for a given amide is the same in CCl_4 and in C_6D_6 (within experimental error). When the ratio is taken in this manner, the constant D [Eqn (1)] is cancelled, and the ratio of the LIS values becomes equal to the ratio of the geometric factors.

$$\frac{(LIS)_{syn}}{(LIS)_{anti}} = \frac{(3\cos^2\theta_A - 1)/r_A^3}{(3\cos^2\theta_B - 1)r_B^3} \qquad (2)$$

Although accidental coincidence of the values θ_A, θ_B, r_A and r_B could be responsible for the LIS ratios being the same in CCl_4 and C_6D_6, it is more likely that the geometric factors are the same for each *N*-methyl proton in each solvent. Further evidence of this is given in Table 3, which lists the computer-generated

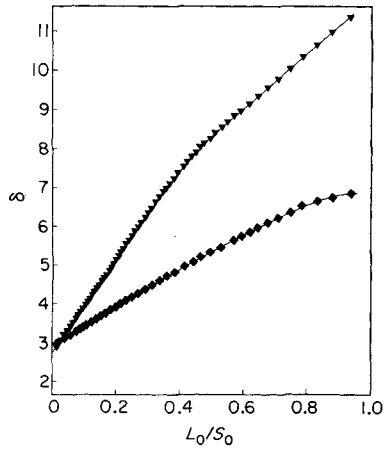


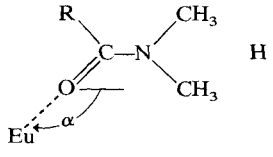
Figure 1. The chemical shift of the methyl protons in $HCON(CH_3)_2$ vs L_0/S_0 in CCl_4 solution. (▼) = A protons and (◆) = B protons. The peaks cross at $L_0/S_0 = 0.02$. For clarity, partially overlapping symbols were omitted from the graph.

Table 2. Values of the LIS[a,b]

	N-CH_3 (A)	*N*-CH_3 (B)	HCO or CH_3CO	R[c]
Disubstituted amides in CCl_4				
DMF	11.4	5.2	16.4	2.2
DMA	13.6	6.4	12.2	2.1
DMTFA	12.4	7.3		1.7
DMTCA		9.1[d]		
Disubstituted amides in benzene[e]				
DMF	11.3	5.3	17.8	2.1
DMA	11.2	5.6	12.3	2.0
DMTFA	10.5	6.0		1.7
DMTCA		12.4[d]		
Monosubstituted amides in CCl_4				
NMF	8.1	[f]	12.6	
NMA	10.7	[f]	12.2	
NMTFA	9.3			
NMTCA	8.9			
Monosubstituted amides in benzene[e]				
NMF	9.0	[f]	14.4	
NMA	10.4	[f]	12.6	
NMTFA	9.2			
NMTCA	7.8			

[a] Least square best fits not including the point at $L_0/S_0 = 0$.
[b] Concentrations of amides were all 0.1 M except for NMTCA, which was soluble in CCl_4 only to 0.076 M.
[c] R is the ratio of the LIS of *N*-CH_3(A) to *N*-CH_3(B).
[d] Due to rapid rotation about the C–N bond, only one peak is observed.
[e] Formamides were studied in deuterated benzene so that the formyl proton peak was detectable over a wider range.
[f] Peaks were observed, but slopes were not determined due to curvature. (See Fig. 2).

values of the angle α and D [Eqn (1)] for DMF and DMA in C_6D_6 and in CCl_4 solution. The use of



this computer program has been described.[7]

In the version of the program used for this work, the Eu—O axis is taken as the symmetry axis of the

Table 3. Values of α, *D* and *AF* for DMF and DMA in CCl_4 and C_6D_6[a–c]

	Primary binding site		
Amide/solvent	α	*D*	*AF*
DMF/CCl_4	175.9	904	0.0095
DMF/C_6D_6	176.3	997	0.0076
DMA/CCl_4	178.5	1104	0.0002
DMA/C_6D_6	178.6	1004	0.0056
	Secondary binding site		
Amide/solvent	α	*D*	*AF*
DMF/CCl_4	83.2	706	0.0827
DMF/C_6D_6	83.5	816	0.0688
DMA/CCl_4	83.6	891	0.0458
DMA/C_6D_6	83.6	817	0.0531

[a] LSR = $Eu(fod)_3$.
[b] Eu . . . O distance taken as 2.7 Å.
[c] α is defined in II, *D* is from Eqn 1 and *AF* is the agreement factor.

complex and the Eu—O distance is set at 2.7 Å. Only the DMF and DMA data supply a sufficient number of LIS values (three) for the determination of two unknowns (α and D). In order to insure that only one minimum was present the program was run with six different initial estimates of α. The results are shown in Table 3: when the initial value of α was 90°, 110° or 130°, $\alpha = 83°$ was obtained as the best value, with an agreement factor (AF) in the range 0.04–0.08. (See Ref. 7 for a discussion of a reasonable agreement factor.) However, when the initial value of α was 150°, 170° or 190°, the minimum occurred at $\alpha = 176$–$178°$ with an AF value below 0.01 in all cases. Although the AF value at 83° is large, it must be recognized that both solutions (83° and 178°) occur at chemically significant binding sites, namely, in the region usually associated with the lone-pair orbitals of the oxygen atom. A small percentage of the complex having Eu binding at the $\alpha = 83°$ position could easily coexist with the major portion of the complex having $\alpha = 176$–$178°$ with the AF value remaining reasonably low. Other workers[10,18] have considered that the LSR may bind on either side of the oxygen atom of amides. However, in these studies, the Eu—O—C angle was determined from previous work and it was assumed[10] that D is the same for either binding site. Our work indicates that D differs for each site both for DMF and DMA (Table 3), due possibly to different magnetic anisotropies for the complexes formed. It appears that the LSR may bind on either side of the oxygen atom of amides, with steric factors determining the primary binding site. Our earlier work, with *N,N*-diisopropylamides revealed bonding only at the $\alpha \sim 180°$ site;[7] these molecules were found to be very sterically hindered, and it is likely that the $\alpha = 83°$ site is unavailable for bonding in *N,N*-diisopropylamides.

The amide DMTCA was included in this series for comparison with the NMTCA LIS data. At 28 °C, it is rotating too rapidly about the central C—N bond for separate resonances to be observed for the *N*-methyl protons.[19] As Eu(fod)$_3$ is added to the DMTCA solution, the single *N*-methyl peak broadens, reaching a linewidth of about 20 Hz at $L_0/S_0 = 0.3$. The spectra are very similar to those published for methyl *N,N*-dimethylcarbamate as LSR is added.[20] A solvent effect was evident in the DMTCA spectra: the linewidth at half-height of the *N*-methyl peak in CCl_4 is 3.7 Hz, and in C_6D_6 it is 6.5 Hz (at $L_0/S_0 = 0.2$).

N-Methylamides

Both *trans* (Ia) and *cis* (Ib) isomers were observed for NMF and NMA in CCl_4 as well as in benzene solution. The observed induced shift, $\Delta\delta_c$, for the *cis* isomers, is given by

$$\Delta\delta_{cis} = \frac{1}{(S_0)_{cis}} \sum_{i=1}^{N} n_i C_i \Delta_i \qquad (3)$$

where $(S_0)_{cis}$ is the molar concentration of all *cis* isomers taken as monomer, n_i is the number of substrate molecules in a given complex, C_i is the molar concentration of that complex, Δ_i is the limiting LIS of the complex and the summation is over all forms of the *cis* isomer bonded to LSR. An equation similar to (3) may be written for $\Delta\delta_{trans}$, where $(S_0)_{cis} + (S_0)_{trans} = S_0$ = molar concentration of amide = 0.1 M. The values of $(S_0)_{cis}$ and $(S_0)_{trans}$ may be found from the integrated intensities of the methyl peaks of the *cis* and *trans* isomers.

For both NMF and NMA, an increasing L_0/S_0 causes an increasing value of $(S_0)_{cis}$. In the case of NMF, as L_0/S_0 increases from 0 to 0.5, the percentage of *cis* isomers increases from 8% to approximately 45%. It is apparent from Eqn (3) that unless the molar concentration of *cis* isomers bonded to LSR (C_i) also continues to increase over this concentration range, an increase in $(S_0)_{cis}$ could cause the value of $\Delta\delta_{cis}$ to increase initially, but then to decrease. This is in fact observed (Fig. 2). The slope of the plot of $\Delta\delta_{cis}$ is initially larger than that of $\Delta\delta_{trans}$ but only up to a concentration of $L_0/S_0 \sim 0.1$, after which the slope of $\Delta\delta_{cis}$ falls rapidly and becomes negative at $L_0/S_0 \sim 0.45$. Simultaneously, the plot of $\Delta\delta_{trans}$ vs L_0/S_0 shows an upward curvature (Fig. 2) as L_0/S_0 increases, which was not observed for the A methyl protons in the straight-line graphs of the dimethylamides (Fig. 1). The curvature is therefore a consequence of the change in $(S_0)_{cis}$ and $(S_0)_{trans}$ as the *cis* isomer becomes more favored upon the addition of L_0/S_0. This has been attributed to more favorable steric interactions in the *cis* LSR–amide complex. Apparently, the LSR has more space around the oxygen atom for complexation[21] in the *cis* amide (Ib vs Ia).

The *cis* *N*-methyl proton induced shift (Fig. 2) is, however, much smaller than the *trans*-induced shift. Referring to Eqn (3), and realizing that exchange among the various *cis* structures is fast on the NMR time scale, the integrated intensity of the *cis* peak yields the relative amount of c_n, $L \cdot c_n$, and any other species having the amide in the *cis* conformation, where c_n represents n monomer *cis* amide units self-associated through hydrogen bonding and $L \cdot c_n$ represents one c_n polymer bound to one LSR molecule, $n = 1, 2, 3 \ldots$. In a similar manner, the relative amounts of t_n, $L \cdot t_n$ and all other *trans* configurations are given by the integrated intensity of the *trans* peak. However, while all *cis* species contribute to the peak

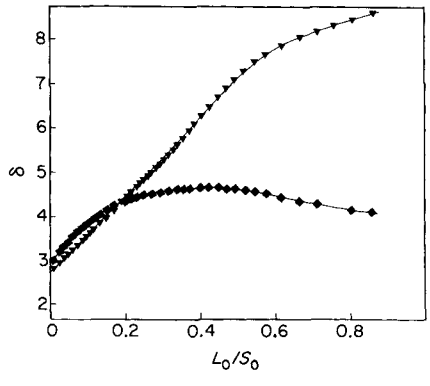


Figure 2. The chemical shift of the methyl protons in *cis* and *trans* $HCONHCH_3$ vs L_0/S_0 in CCl_4 solution. (▼) = A protons of the *trans* isomer and (◆) = B protons of the *cis* isomer. The peaks cross at $L_0/S_0 = 0.2$. Curvature is apparent in the plots of each isomer. For clarity, partially overlapping symbols were omitted from the graph.

area, only those species which are complexed with LSR will contribute to $\Delta\delta_{cis}$ of the *cis* isomer methyl protons. The same is true for the *trans* isomer; however, since the population of the *trans* isomer is larger than the *cis* isomer in this region, there may be more species contributing to $\Delta\delta_{trans}$, making the *trans*-induced shift larger than the *cis*.

Another factor which would contribute to a larger $\Delta\delta$ for *trans* vs *cis* structures would be a larger value for Δ_i, the limiting shift. However, these values may only be obtained by a detailed analysis of the entire dilution curve (in which the *cis*/*trans* ratio is constantly changing) and accompanying determination of all equilibrium constants for the various reactions involved, including hydrogen bonding of both *cis* and *trans* isomers. (The equilibria have been analyzed in detail and the results will be published elsewhere.)

Although qualitative, this discussion of the NMF equilibria points out the differences between the dimethylamide and the monomethylamide-LSR interactions and describes how the induced shift for *trans*-NMF can be larger than that of *cis*-NMF, even though the percentage of *trans*-NMF decreases as LSR is added.

The dilution curve for NMF in benzene was similar to that for CCl_4 (Fig. 2). The *cis* isomer was also detected in the NMA solutions; however, only 3% is present at $L_0/S_0 = 0$. The initial solution used for the NMA studies had a value of $L_0/S_0 = 0.3$, at which point the population of the *cis* isomer is 10%. The dilution curve for the *cis*-NMA isomer also showed the negative curvature obtained for the *cis*-NMF isomer.

Only one isomer peak could be found for NMTFA and NMTCA. IR studies[5f–5h] indicate that these molecules are in the *trans* configuration. The plot of δ vs L_0/S_0 for both NMTFA and NMTCA is a straight line to $L_0/S_0 = 0.4$, similar to that obtained for the *N*-methyl (A) protons of the dimethylamides.

We have considered the possibility that NMTCA is freely rotating about the central C—N bond at room temperature, in the same manner as DMTCA, due perhaps to a low free energy of activation for this process. Free rotation in NMTCA is unlikely for several reasons. When the concentration of $Eu(fod)_3$ relative to DMTCA reached $L_0/S_0 = 0.25$, the *N*-methyl proton resonance became extremely broad. The LSR, in binding to the amide, raises the free energy of activation for rotation about the central C—N bond.[22] A similar effect should occur for NMTCA when $Eu(fod)_3$ is added, if rotation is free on the NMR time scale; however, this is not observed. Furthermore, the resonance peak for DMTCA is significantly broader than the NMTCA doublet at all L_0/S_0 ratios, indicating that the rate of rotation about the C—N bond is significantly slower for NMTCA. The evidence thus far leans toward the conclusion that NMTCA as well as NMTFA is predominantly in the *trans* configuration.

Acknowledgements

We wish to thank Mrs Paulanne Rider, Mr Jack Hedstrom and Miss Catherine O'Brian for careful sample preparation and operation of the NMR spectrometer.

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Received 21 May 1979; accepted (revised) 27 September 1979