Determination of the Molecular Geometry of Eu(fod)$_3$ Complexes with Amides and Diamides and Its Conformational Significance

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Paramagnetic shifts, induced in the nmr spectra of some amides and diamides by Eu(fod)$_3$, have been used to assign configurational isomers in these compounds. The observed Eu-induced shifts agree well with values calculated on the basis that their origin is of pseudocontact nature, and have been used to determine the molecular geometries of the corresponding Eu(fod)$_3$–amide complexes. Remarkably, all the structures could be fitted by the same pseudocontact constant (eq 1, $K = 900 \pm 100$), Eu–O distance (3.0 Å), and average Eu–O–C angle (120°). The spatial location of the Eu ion in the complexes seems always to correspond with an orientation of amide molecule which has minimal intramolecular steric interaction with the other ligands. Consequently, the Eu–O–C–N dihedral angle (see Figure 4 in the text) varies appreciably in the amides studied. Finally, evidence is presented that, according to steric hindrance factors, diamides investigated form two distinct kind of complexes.

Convincing evidence has been recently presented[1-12] for a number of oxygenated compounds, that the shifts in the nmr signals induced by association of organic molecules with paramagnetic lanthanide chelates, are entirely or predominantly due to pseudocontact interaction according to eq 1[13] where χ is the O–Ld–H

$$\Delta\nu_{\text{obsd}} = K(3\cos^2\chi - 1)/r^3 \qquad (1)$$

internuclear angle and r is the corresponding Ld–H distance. $\Delta\nu_{\text{obsd}}$ is usually taken as the slope in a plot of the induced chemical shifts *vs.* [Ld]/[S], where [Ld] and [S] are the respective molar concentrations of lanthanide and substrate.

Although nmr lanthanide shifts have been recently reported for two simple amides,[14] the geometry of the complexes and their pseudocontact constants (K in eq 1) were not investigated.

To explore this point, and its implications in the conformational analysis of more complex organic molecules containing amide groups, we have measured the Eu(fod)$_3$ induced shifts[15] for a series of amides and diamides reported in Table I.

These data, besides providing configurational assignments for the rotamers possessing a defined identity on the nmr time scale, have been used by us to determine the geometries of the complexes.

Remarkably, all the structures could be fitted by the same pseudocontact constant ($K = 900 \pm 100$), Eu–O distance (3.0 Å), and average Eu–O–C angle (120°). The latter two values appear to be in agreement with the most reliable values found for these parameters in a number of lanthanide complexes with alcohols[1-4,12] and ketones.[10]

The spatial location of the Eu ion in the complexes seems always to correspond with an orientation of amide molecule which has minimal intramolecular steric interactions with the other ligands. Finally, we have obtained evidence that, according to steric hindrance factors, diamides in Table I form two distinct kinds of complexes.

Experimental Section

Syntheses and characteristics of the amides used in this study were previously described.[16-18]

Induced Shift Measurements.—Eu(fod)$_3$ (Sievers reagent)[15] obtained from Alfa Inorganic (N. J.), was used without further purification. A concentrated (0.32 *M*) CDCl$_3$ solution of Eu(fod)$_3$ was used throughout this work. Spectra of 10% CDCl$_3$ solutions containing 0–0.50 mol of Eu(fod)$_3$/mol of amide were obtained at 60 MHz (Varian Associates A-60 and T-60 analytical spectrometers). In general, each signal could be followed in these spectra and the shift to lower field was for all signals directly proportional to the Eu(fod)$_3$: amide ratio present. An example is shown in Figure 1.

However, a marked upward curvature in the $\Delta\nu$ *vs.* [Ld]/[S] plot was observed for the methylene signals of the (conformationally mobile; see below) rotamer IIIc in Table I.

The Eu-induced shifts were found largely independent of the absolute concentration of amide, contrary to what was observed in the case of some alcohols[19a] and sulfoxides.[19b]

The population of the various amides rotamers was not found to vary appreciably with the Eu(fod)$_3$ concentration.[20]

Eu Location and Distance Measurements.—A Hewlett-Packard 9100 B computer was used to determine the optimal Eu spatial location for monoamides I and II in Table I, and metal–hydrogen distances were analytically calculated from amide interatomic distances and bond angles deduced from pertinent literature data.[21]

For diamides IV–IX in Table I, the eq 1 parameters could be measured on Dreiding models, once R and φ were fixed at their optimal values (see text).

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(1) J. Briggs, F. A. Hart, and G. P. Moss, *Chem. Commun.*, 1506 (1970), and references therein.

(2) J. Briggs, F. A. Hart, G. P. Moss, and E. W. Randall, *ibid.*, 364 (1971).

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(6) B. L. Shapiro, I. R. Hlubucek, G. R. Sullivan, and L. F. Johnson, *ibid.*, **93**, 3821 (1971), and references therein.

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(11) R. F. Fraser and Y. Y. Wigfield, *Chem. Commun.*, 1471 (1970).

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(13) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).

(14) C. Beauté, Z. W. Wolkowski, and N. Thoai, *Chem. Commun.*, 700 (1971). However, for some studies on thioamides, see W. Walter, R. F. Becker, and J. Thiem, *Tetrahedron Lett.*, 1971 (1971).

(15) R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, **93**, 1522 (1971).

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(17) C. G. Overberger, G. Montaudo, Y. Nishimura, J. Sebenda, and R. A. Veneski, presented in IUPAC Symposium, Budapest, 1969.

(18) Y. Miron, B. R. Garvey, and H. Morawetz, *Macromolecules*, **2**, 154 (1969).

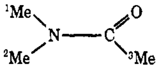
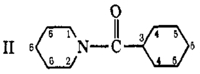
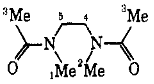
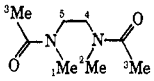
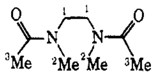
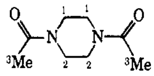
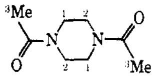
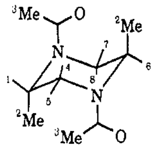
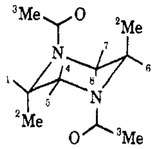
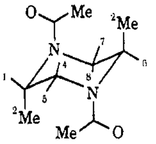
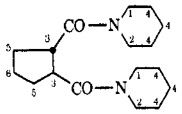
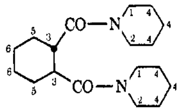
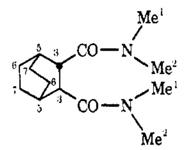
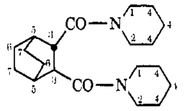
(19) (a) I. Armitage, G. Dunsmore, L. D. Hall, and A. G. Marshall, *Chem. Commun.*, 1281 (1971); (b) K. K. Andersen and J. J. Uebel, *Tetrahedron Lett.*, 5253 (1970).

(20) For a discussion on the implications of this result, see M. R. Vegar and R. J. Wells, *Tetrahedron Lett.*, 2847 (1971).

(21) J. M. Robertson in "Organic Crystals and Molecules," Cornell University Press, Ithaca, N. Y. 1953, pp 219–246 and references therein.

TABLE I

EFFECT OF Eu(fod)$_3$ ON THE 60-MHz NMR SPECTRA OF SOME AMIDES AND MOLECULAR GEOMETRY PARAMETERS OF THE CORRESPONDING COMPLEXES[a]

No.	Compd	1	2	3	4	5	6	7	8	R, Å	φ, deg	ω, deg	Eu–Eu, Å	*K*
I		*3.06* 8.1 (8.1)	*3.16* 3.8 (3.8)	*2.17* 9.2 (9.2)						3.0	110	80		890
II		*3.67* 8.4 (8.3)	*3.67* 4.3 (3.7)	2.47 6.2 (6.2)	1.67 5.9 (5.6)					3.0	110	90		910
IIIa		*3.14* 7.7	*3.14* 7.7	*2.17* 10.0	*3.67* 6.9	*3.67* 6.9								
IIIb		*3.14* 6.5	*3.14* 6.5	*3.67* 10.0	*3.67* 10.0	*3.67* 10.0								
IIIc		*3.67* [b]	*3.14* 4.2	*2.17* 6.5										
IVa		*3.70* 18.1 (17.4)	*3.70* 10.4 (7.3)	*2.30* 11.9 (11.8)						3.0	120	60	11.0	1040
IVb		*3.70* 13.8 (14.8)	*3.70* 7.7 (7.2)	*2.30* 13.5 (10.6)						3.0	120	60	11.3	940
Va[c]		*4.03* 5.2 (5.0)		*2.20* 6.5 (6.4)	*3.45* 5.8 (6.0)	*3.45* 5.8 (5.0)	*4.90* 12.5 (12.5)	*4.37* 12.8 (12.5)	*2.95* 5.8 (5.7)	3.0	120	50	11.0	850
Vb[d]		*4.03* 5.2 (4.9)		*2.20* 6.5 (5.9)	*3.05* 5.8 (5.8)	*4.23* 10.9 (10.9)	*4.03* 5.2 (5.7)	*4.23* 10.9 (10.8)	*3.05* 5.8 (6.0)	3.0	120	50	11.3	790
Vc[d]		*4.90* 12.5 (11.2)		*2.20* 6.5 (5.8)	*3.45* 5.8 (6.9)	*3.45* 5.8 (6.1)	*4.90* 12.5 (12.8)	*3.45* 5.8 (4.9)	*3.45* 5.8 (4.8)	3.0	120	50	11.0	860
VI		*3.66* 3.4 (2.5)	*3.66* 3.4 (2.5)	*3.66* 10.4 (10.2)		*1.90* 4.3 (3.9)	*1.90* 2.3 (1.9)			3.0	120	80	3.0	870
VII		*3.66* 2.0 (2.2)	*3.66* 2.0 (2.2)	3.22 6.2 (6.2)		*1.66* 2.5 (2.5)				3.0	120	80	0	940
VIII		*3.23* 2.5 (2.7)	*3.00* 2.5 (2.7)	3.77 12.3 (12.3)		*1.79* 4.6 (4.6)				3.0	120	80	3.0	1020
IX		*3.66* 1.8 (1.5)	*3.66* 1.8 (1.5)	*3.84* 11.2 (11.1)		*1.66* 4.4 (3.8)				3.0	120	80	3.0	850

[a] Only clearly detectable signals are reported; figures in the first row, in italics, indicate chemical shifts of the undoped spectra; figures in the second row indicate observed molar induced shifts; figures in the third row in parentheses indicate calculated molar induced shifts. [b] Deviates from linearity in the Δν *vs.* [Ld]/[S] plot. [c] Both enantiomers contribute to the nmr spectrum. [d] This form has an inversion center.

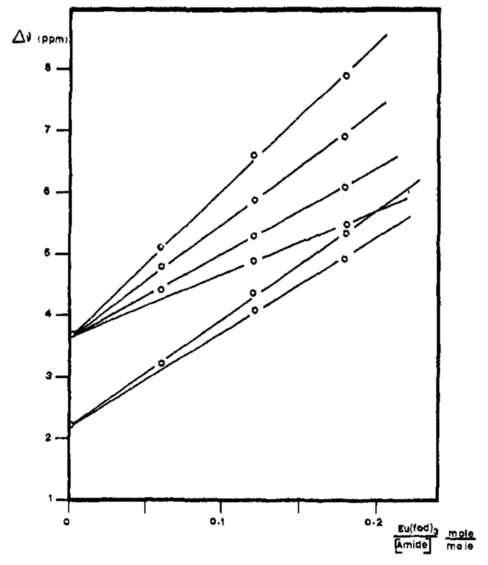


Figure 1.—Variation of induced shifts with molar ratio [Eu(fod)$_3$]/[substrate] for *N*,*N*′diacetylpiperazine, IV.

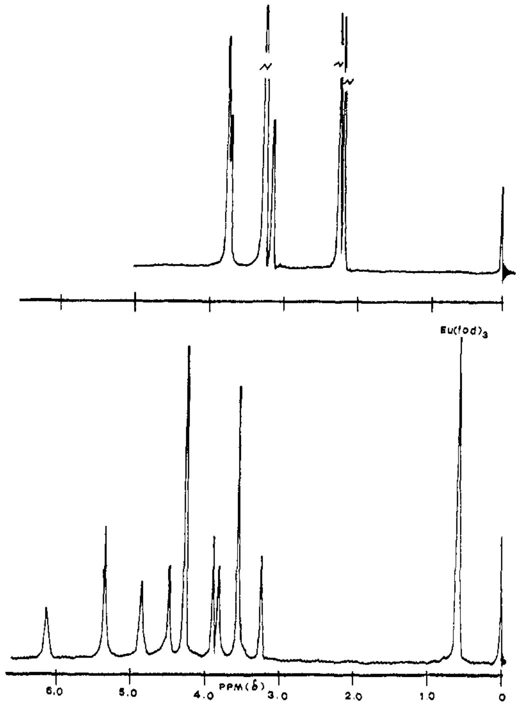


Figure 2.—60-MHz spectra (CDCl$_3$) of *N*,*N*′-diacetyldimethylethylenediamine, III: above, no Eu(fod)$_3$; below, [Eu(fod)$_3$]/[amide] = 0.12 mol/mol.

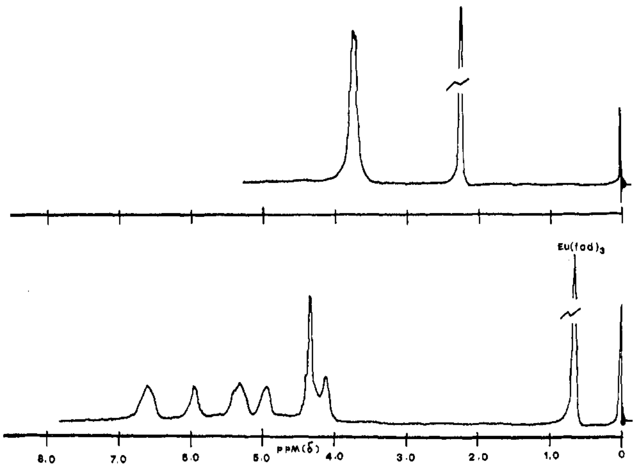


Figure 3.—60-MHz spectra (CDCl$_3$) of *N*,*N*′-diacetylpiperazine, IV: above, no Eu(fod)$_3$; below, [Eu(fod)$_3$]/amide] = 0.12 mol/mol.

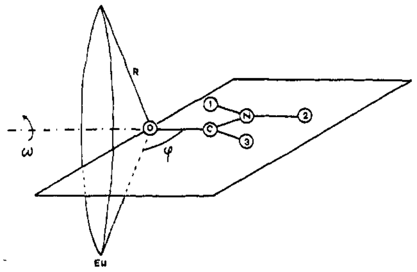


Figure 4.—Possible locations of the Eu ion in the space around the (planar) amide unit. *R* represents the Eu–O distance; φ is in the Eu–O–C internuclear angle; the dihedral angle Eu–O–C–N, ω, is 90° for the (perpendicular) configuration indicated in the figure. Varying *R*, φ, and ω, all the Eu possible spatial locations can be explored.

Results

General.—Kinetically restricted rotation around the C–N amide bonds does not produce nmr distinguishable rotamers for compounds I, II, VI–IX, in Table I. Previous work has shown[16] that in diamide V the piperazine conformational equilibrium is strongly biased towards forms containing diaxial methyl groups (nearly equipopulated mixture of the four rotamers possible), and has provided[16] the relative configurational assignments (see Table I).

On the other side, diamide III (Table I) is predicted[18] to exist as three isomers (cis–cis; cis–trans; trans–trans).

The Eu-induced shifts (Figure 2) allow, for the first time, direct detection of the three isomers and of their relative population (2:6:2). If the most populated rotamer (IIIb, Table I) is assigned to a cis–trans configuration, the ratio 2:6:2 speaks for the presence in equal amounts of cis and trans amide units in the mixture, indicating that the two amide moieties in diamide III behave as independent units.

N,*N*′-Diacetylpiperazine IV (Table I) exists[18] in two forms (trans and cis). The Eu-induced shifts (Figure 3) allow, also in this case, the first direct detection of the two isomers and of their relative population (6:4).

Eu(fod)$_3$–Monoamide Complexes.—The molecular geometries of the Eu(fod)$_3$ complexes of monoamides I and II (Table I) were obtained determining the optimal location of the Eu ion in the space around the amide oxygen atom. A computer program was used to explore all the possible Eu spatial locations, defined in Figure 4 by polar coordinates *R*, φ, ω, where *R* is the Eu–O distance, φ is the Eu–O–C angle, and ω is the Eu–O–C–N dihedral angle. *R* was allowed to vary between 2.5 and 3.5 Å; φ was varied between 90 and 270° (values of φ between 0 and 90° are highly improbable); ω was varied over the entire 360° range. A reasonable agreement between the measured shifts (Table I) and $(3 \cos^2 \chi - 1)r^{-3}$, according to eq 1, was found only for a limited set of *R*, φ, and ω values centered in the space around $R = 2.8 \pm 0.4$ Å, $\varphi = 110° \pm 20$; $\omega = 80° \pm 10$. The set of *R*, φ, and ω values which gave the best correlation in the Δν *vs.* $(3 \cos^2 \chi - 1)r^{-3}$

plot for both amides I and II (Figure 5), was selected to represent the optimal molecular geometry of these Eu(fod)$_3$ complexes.[22] Pertinent data are collected in Table I.

Eu(fod)$_3$–Diamide Complexes.—Lanthanide shift reagents have already been used with a number of bifunctional compounds,[23,24] but no diamides have been hitherto reported.

Eu-induced shifts for diamides III, IV, and V in Table I are considerably higher with respect to those of monoamides I and II. This seems to imply that two molecules of Eu(fod)$_3$ are involved in the complexes, each proton being subject to the deshielding effect of two Eu ions.

As far as diamide III is concerned the conformational mobility of its three isomers prevents any attempt to assess a reasonable average geometry for the corresponding Eu(fod)$_3$ complexes.[10,20]

Although both rotamers of diamide IV experience rapid chair–chair interconversion of the piperazine ring,[18] this conformational mobility does not prevent the determination of a reasonably accurate geometry for the Eu(fod)$_3$ complexes, if the piperazine ring is taken in the average planar position.[20]

In the case of diamide V, as discussed above the piperazine conformational equilibrium is strongly biased towards forms containing diaxial methyl groups,[16] so that the conformers detectable in the spectrum can be regarded as rigid structures on the nmr time scale.

According to these considerations, only the geometries of complexes corresponding to diamides IV and V have been investigated.

The method used to locate the Eu ions in the space around each amide unit is similar to that described in the case of monoamide complexes. However, to reduce the computing work involved, R and φ (Figure 4) were fixed at their optimal values determined in the case of monoamide complexes (Table I), and only ω was allowed to vary.[25]

The deshielding effects of the two Eu ions on each proton were computed for each pair of spatial locations of the Eu ions around the diamide molecule.

A reasonable agreement between the measured shifts and $(3\cos^2\chi - 1)r^{-3}$ was found only for a restricted number of cases in which the two Eu ions are in *identical spatial positions* with respect to each amide unit in the molecule. The optimal molecular geometry chosen for each complex (Table I) is the one which gave the best correlation of experimental and calculated shifts.

The pseudocontact constant (K, eq 1) was selected to allow direct comparison with observed shifts, and it is gratifying that the values found in this way come very close to the value obtained for the monoamides (Table I). Recent work,[16,26] based on nmr data, dipole moments, and *priori* conformational energy estimates, has shown that diamides VI–IX (Table I) all exist in a preferred conformation, where the two diamide carbonyls lay close to each other, being almost eclipsed to the C$_1$–C$_2$ bond (Figure 6).

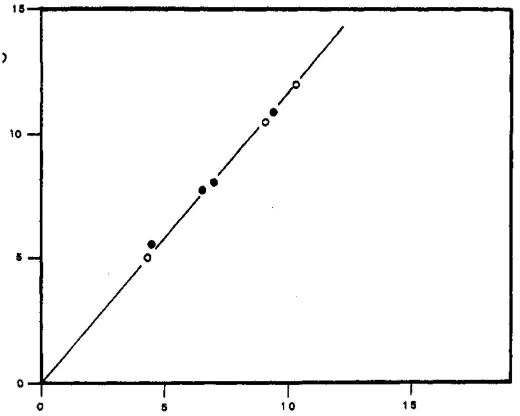


Figure 5.—Plot of measured shifts (Δν) against the pseudocontact geometric factor for N,N'-dimethylacetamide, I (open circles), and amide II (closed circles).

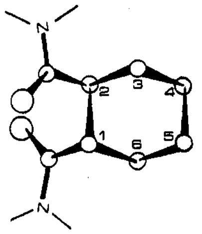


Figure 6.—Preferred conformation of diamide VII. The piperidine rings are omitted for clarity and only the cyclohexane ring is shown. The two C–O bonds are both almost eclipsed with respect to the C$_1$–C$_2$ bond.

The Eu-induced shifts of the N-methylene protons for diamides VI–IX are *much lower* with respect to the corresponding shifts observed for the other diamides (Table I). Furthermore, they are *equally shifted* (contrary to all other cases in Table I), implying that the Eu(fod)$_3$ complexes are different from the cases hitherto considered. Inspection of molecular models shows that only one Eu(fod)$_3$ molecule can possibly come in contact with the two carbonyls, for diamides VI–IX in their preferred conformation (depicted in Figure 6 for diamide VII).

Assuming the same R and φ values used for the other diamides (Table I) and allowing only ω to vary, appropriate geometries for 2:1 Eu(fod)$_3$–diamide complexes could be obtained. In these complexes the Eu ion is considered *alternatively bound* to one oxygen atom, so that an average deshielding effect of the Eu ion on each proton has to be computed. In Figure 7 is shown, as an example, the spatial arrangement of this complex in the case of diamide VII.

The distance between the two Eu alternative locations (labeled Eu–Eu in Table I) is close to zero in this particular case; for diamides VI, VIII, and IX a finite value is found (3.0 Å).

A reasonable agreement exists between the measured shifts and those calculated for diamides VI–IX ac-

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[22] The cyclohexane ring in amide II was assumed biased in the chair conformation with the amide group in the equatorial position, and the tertiary atom placed in the most distant position with respect to the Eu ion (*i.e.*, the carbonyl bisects the cyclohexane ring).

[23] (a) H. Hart and G. M. Love, *Tetrahedron Lett.*, 625 (1971); (b) C. C. Hinckley, M. R. Klotz, and F. Patil, *J. Amer. Chem. Soc.*, **93**, 2417 (1971).

[24] (a) H. Van Brederode and W. C. B. Anysmans, *Tetrahedron Lett.*, 1695 (1971); (b) I. Fleming, S. W. Hanson, and J. K. M. Sanders, *ibid.*, 3733 (1971).

[25] The more rigorous analytical method used to determine the Eu location in monoamide complexes was not followed here because of the amount of computer work involved. Instead, simple Dreiding model measurements were used, which enabled us to assess tentative geometries for the complexes that could be later optimized to the degree of approximation needed.

[26] C. G. Overberger, G. Montaudo, and P. Finocchiaro, *Macromolecules*, submitted for publication.

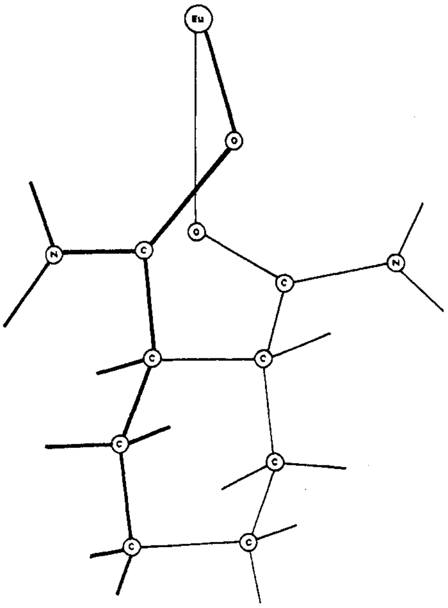

Figure 7.—Molecular geometry of the Eu(fod)$_3$–diamide VII complex. Diamide VII is represented in its preferred conformation (see also Figure 6). Only one Eu ion is involved in the formation of this complex (2:1 type).

cording to the molecular geometries defined by the R, φ, and ω parameters in Table I.[27] The pseudocontact constant (K), selected to allow direct comparison with observed shifts, was found also in this case very close to the value obtained for other amides in Table I.

Discussion

Although the molecular geometry of some lanthanide–substrate complexes has been already carefully investigated,[1-3] most of the work presented to date on the lanthanide shift reagents has been somewhat different in scope.

We have concerned ourselves with the determination of the molecular geometry of a series of Eu(fod)$_3$–amide complexes and it seems appropriate to discuss shortly the basis and limitations of the method, and the assumptions involved.

The exchange of lanthanide ions is a fast process on the nmr time scale and the shifted spectrum represents an averaged spectrum of free and complexed substrate.[1]

Accordingly, if there are several possible locations of the lanthanide in the complex, the observed shifts ($\Delta\nu_{\text{obsd}}$) are given by eq 2 where x_i is the mole fraction

$$\Delta\nu_{\text{obsd}} = \Sigma_i x_i \Delta\nu_i \qquad (2)$$

of the ith species of complexed substrate molecule and $\Delta\nu_i$ is the corresponding induced shift.

If this is the case, only an *averaged* molecular geometry can be found for these complexes and this geometry does not necessarily possess a physical identity.

On the other side, if it is assumed that there is *one* preferred lanthanide location in the complex (see below) eq 2 becomes eq 3 where x is the mole fraction of complexed substrate molecules and $\Delta\nu$ the corresponding induced shifts.

When this assumption is verified and it is possible to detect *one* preferred lanthanide location in the complex, eq 1 and 3 can be applied, and the best fit of the

$$\Delta\nu_{\text{obsd}} = x\Delta\nu \qquad (3)$$

experimental data can be approximately described as *the* molecular geometry of the complex.

At least two other conditions should be fulfilled in order to make the above analysis possible.

First, the substrate conformation should be rigid, or should remain unchanged by the lanthanide addition.[20] Second, if there are conformational isomers which owe their identity to a process slow on the nmr time-scale, their relative population should not vary appreciably with the lanthanide addition. Any failure under this respect should result in the deviation of the $\Delta\nu$ *vs.* [Ld]/[S] plots from linearity, so that it should be possible to verify experimentally if the above conditions are fulfilled.[20]

Diamide III is a conformationally mobile system in which some interconversions are fast compared to the nmr time scale (ethylene units) and some are not (amide units).

Accordingly, curved $\Delta\nu$ *vs.* [Ld]/[S] plots are expected, and found (Table I), for this compound. Linear plots are observed for other amides in Table I, enabling one to carry further the analysis of the data.

In general, our results support the idea that there is one preferential location of the Eu ion in the complex and, furthermore, seem to provide a common molecular model for the Eu(fod)$_3$–amide complexes. The optimal values found for the Eu–O distance (3.0 Å) and Eu–O–C angle (120°) in these complexes seem to correspond to chemical bond requirements, as ascertained by X-ray diffraction studies.[28,29] The Eu–O–C–N dihedral angle (Figure 4) is found to vary between 50 and 90° according to the steric requirements in each complex. Incidentally, it should be noted that the variation of the dihedral angle is an energetically favored process with respect to the variation of the Eu–O distance and Eu–O–C angle. This implies that the existence of one preferential Eu location in the complex is due to the minimum conformational energy requirements relative to the molecular architecture of each complex.

An important corollary of the common molecular model discussed above for the Eu(fod)$_3$–amide complexes is that the Eu ion binds itself to the amide units with a strength largely independent from the rest of the molecule to which the amide unit belongs. If this is true, the mole fraction of complexed substrate (eq 3) should remain roughly constant for this class of compounds. Our results strikingly confirm this expectation; K values in Table I are nearly constant for all the amides investigated.

A possible extention of the present work is in the structural and conformational analysis of complex organic molecules.

A long-range goal in our research is to apply this

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[27] It should be stressed that there is no way to obtain agreement between measured shifts and those calculated on alternative hypotheses.

[28] P. A. Cunningham, D. E. Sands, W. F. Wagner, and M. F. Richardson, *Inorg. Chem.*, **8**, 22 (1969).

[29] S. Dahl and P. Groth, unpublished results quoted in ref 12.

technique to the study of the conformational properties and processes of appropriate macromolecules.

Registry No.—I, 127-19-5; I–Eu(fod)$_3$ complex, 35208-59-4; II, 7103-46-0; II–Eu(fod)$_3$ complex, 35208-60-7; III, 24768-60-3; IV, 18940-57-3; IV–Eu(fod)$_3$ complex, 35238-57-4; V, 35168-21-9; V–Eu(fod)$_3$ complex, 35208-61-8; VI, 35211-97-3; VI–Eu(fod)$_3$ complex, 35208-62-9; VII, 35168-20-8; VII–Eu(fod)$_3$ complex, 35208-63-0; VIII, 35212-03-4; VIII–Eu(fod)$_3$ complex, 35208-64-1; IX, 35212-04-5; IX–Eu(fod)$_3$ complex, 35238-58-5; Eu(fod)$_3$, 17631-68-4.

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Intramolecular Oxygen–Nitrogen Benzoyl Migration of 6-Aroyloxyphenanthridines[1,2]

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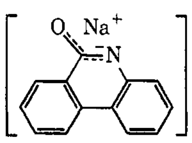
The sodium salt (**1**) of 6(5*H*)-phenanthridinone reacts with benzoyl chloride to give, under kinetically controlled conditions, the O-substituted product, 6-benzoyloxyphenanthridine (**2a**). When heated alone the *O*-benzoyl compound rearranges to the crystalline *N*-benzoyl isomer, *N*-benzoyl-6(5*H*)-phenanthridinone (**3a**), to the extent of at least 99%. This rearrangement also occurs in hexane or tetrahydrofuran solution but approaches an equilibrium with the ratio **3a**:**2a** of about 5:1. The approach to equilibrium in hexane is first order in **2a** or **3a** and is relatively insensitive to change in solvent polarity. The benzoylations with *p*-methoxybenzoyl chloride and with *p*-chlorobenzoyl chloride have been found to proceed in a similar fashion and the rate and equilibrium constants for reactions of the variously substituted compounds are compared. The effect of the crystalline state on the position of the equilibrium is discussed and other cases are reviewed where crystallization has been utilized to achieve isolation in the pure state of substances which are in mobile equilibrium in solution.

The ready 1,3 rearrangement of acyl groups between oxygen and/or nitrogen atoms[3] may be anticipated to have an important bearing on the chemistry of N- and O-acylated heterocyclic compounds. In a preliminary communication[4] the sodium salt (**1**) of 6(5*H*)-phenanthridinone was reported to undergo O-benzoylation in tetrahydrofuran to give 6-benzoyloxyphenanthridine (**2a**); when heated alone or in methylene chloride solution **2a** was found to rearrange to the *N*-benzoyl isomer **3a**. This paper presents a more detailed study of the equilibrium between **2a** and **3a** as well as rates of isomerization of **2a** and **3a** and their para-substituted analogs.



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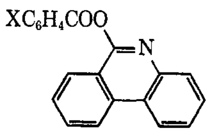
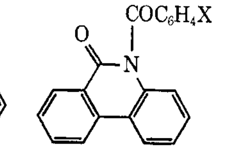


2a, **X** = H
b, **X** = CH_3O
c, **X** = Cl



3

Experimental Section

Melting points were determined on a calibrated micro hot-stage melting point apparatus. Infrared spectra were determined with a Perkin-Elmer Model 521 spectrophotometer, uv spectra with a Cary Model 14 spectrophotometer, and nmr spectra by Mr. R. Thrift and his associates with a Varian Model A-56/60 and HA-100 spectrometer. Microanalyses were performed by Mr. J. Nemeth and his associates. Reproductions of the principal spectra are contained in the thesis[1] available from University Microfilms, Ann Arbor, Mich.

Unless otherwise indicated, solvents were purified as follows. Methylene chloride was spectral grade stored over molecular sieves. Pentane and petroleum ether (bp 90–120°) were treated with concentrated H_2SO_4, then with $NaHCO_3$ solution, dried with molecular sieves, and distilled from NaH. Tetrahydrofuran (THF) was freshly distilled from lithium aluminum hydride for each use. Benzene and toluene were reagent grade and were dried by passage through a column of molecular sieves. Glassware was dried in an oven at 120°.

Benzoylation of the Sodium Salt (1) of Phenanthridone. 6-Benzoyloxyphenanthridine (2a).—The sodium salt **1** was prepared from phenanthridinone (5.12 g) which had been purified by recrystallization from pyridine, washed with dilute HCl and water, and dried in a vacuum desiccator for 8 hr, by treatment in 200 ml of THF with 2.0 g of 57% NaH in mineral oil. After reaction the infrared maxima (THF solution) at 1678 and 1609 cm^{-1} had been replaced by absorptions at 1621, 1584, 1515, and 1474 cm^{-1}. The mixture was cooled in a Dry Ice bath and 3.66 g of benzoyl chloride was added. After several hours at −20° the mixture was filtered and the filtrate was evaporated to dryness. Extraction with pentane at −20° left an insoluble residue which was extracted with 250 ml of toluene at room temperature. Filtration of the toluene solution, evaporation at 0° under reduced pressure of the toluene solution to a volume of 100 ml, addition of 100 ml of pentane, and cooling to −20° gave 2.46 g (32% based on benzoyl chloride) of crude **3** as tan crystals. Three recrystallizations from toluene–pentane gave 0.55 g of white crystals: mp 119° (resolidified almost immediately and remelted at 189–193.5°); ir (CH_2Cl_2) 1743 (s), 1621 (m), 1593 (m), 1467 cm^{-1} (m); nmr ($CDCl_3$) δ 7.14–8.15 (m); uv (hexane–0.3% THF) λ_{max} 240 nm (ϵ 46,200), 249 (46,300).

Anal. Calcd for $C_{20}H_{13}NO_2$: C, 80.3; H, 4.4; N, 4.7. Found: C, 80.4; H, 4.3; N, 4.5.

A similar reaction mixture from which aliquots were withdrawn a few minutes after addition of the benzoyl chloride showed, in addition to the absorption at 1656 cm^{-1} attributed to unreacted phenanthridone, the development of the absorption at 1742 cm^{-1} of the benzoyloxyphenanthrene **2**. No absorption was observed at 1733 or 1656 cm^{-1} where the *N*-benzoyl isomer **3** absorbs.

***N*-Benzoyl-6(5*H*)-phenanthridinone (3). A. Room Temperature Benzoylation of the Sodium Salt 1.**—A reaction starting with 4.45 g of phenanthridinone, 1.70 g of 50% NaH, 200 ml of THF, and 6.0 g of benzoyl chloride carried out at room temperature for several minutes was completed by evaporation of the THF, extraction with pentane, and finally with boiling toluene. Filtration and partial evaporation of the toluene extracts gave upon

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[1] Taken in part from the Ph.D. Thesis of J. H. E., University of Illinois, Urbana, Ill., 1969.

[2] We are very much indebted to the National Science Foundation for a grant which provided substantial support of this work.

[3] D. Y. Curtin and L. L. Miller, *J. Amer. Chem. Soc.*, **89**, 637 (1967).

[4] D. Y. Curtin and J. H. Engelmann, *Tetrahedron Lett.*, 3911 (1968).