
**HALOGEN SUBSTITUTED ADAMANTANONES.
STRUCTURAL STUDIES WITH LANTHANIDE SHIFT REAGENTS**

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Europium shift reagents (both FOD and DPM) have been used to study a series of halogen substituted adamantanones by ¹H NMR spectroscopy. Reliable correlations of molecular structure with the lanthanide induced shifts can be obtained only if certain precautions are taken. The source of atomic coordinates used to predict induced shifts with the pseudocontact equation is critical; coordinates obtained by X-ray crystallography can be unreliable for this purpose, while those from empirical force field calculations yield satisfactory results. Determination of the europium-oxygen bond length by optimization of the agreement factor is shown to be inadequate. Even with a restricted Eu—O bond length, calculation of the best lanthanide position is shown to be dependent on the step size by which the lanthanide is moved in the optimization procedure. All of the compounds studied were found to give complexes with approximately linear C—O—Eu arrays, and the distortions from linearity are consistent with steric effects.

Lanthanide shift reagents have become increasingly valuable aids in structure determination during the last decade¹. Previous studies in our laboratories have demonstrated that excellent correlations can be obtained between experimentally observed lanthanide induced shifts (LIS) and shifts that are predicted for the correct structure. Consequently, this comparison of observed and calculated LIS provides a reliable and sensitive method for evaluating structure and conformation of molecules in solution. We have shown that the LIS of many symmetric ketones can be accurately predicted on the basis of a one-site model in which the carbon-oxygen-lanthanide geometry is approximately linear²⁻⁵. Variations in the observed LIS that are observed upon substitution of a ketone in an unsymmetrical manner, seem to result from changes in both the coordination geometry^{2,5} and complexation energy⁶⁻⁸. We have undertaken the study of a series of halogen derivatives of adamantanone (*I*) in order to learn the origin and magnitude of substituent effects on interactions

of ketones with lanthanide shift reagents. Changes in the observed LIS of an adamantanone upon substitution could result from one or more of the following: 1) Distortion of the substrate carbon skeleton (or of its C—H bonds) as a result of steric interactions. 2) Changes in either or both of the association constants, K_1 and K_2 (for formation of the 1 : 1 and 1 : 2 lanthanide–substrate complexes, respectively). 3) Changes in the lanthanide–substrate coordination geometry as a result of steric and/or electronic influences of the substituent. The halogenated adamantanones selected for this study provide a range of both steric and electronic effects at the coordination site of the ketone. The relatively rigid framework of the adamantane skeleton minimizes the likelihood of distortion of the substrate geometry and allows direct and reliable comparison of the data for the various derivatives. In addition, by utilizing the bound shifts for the 1 : 1 complexes, we have eliminated the influence of changes in the association constants on the observed LIS. Consequently, any variations in the LIS for the adamantanone derivatives studied here, should arise almost entirely from changes in the lanthanide–substrate binding geometry.

EXPERIMENTAL

Substrates *I–V* were prepared^{6,9} in the Laboratory of Synthetic Fuels (Prague). All NMR studies were carried out using deuteriochloroform as solvent and tetramethylsilane as internal standard. Commercial europium shift reagents were sublimed and stored over phosphorous pentoxide prior to use.

Lanthanide induced shifts were obtained by two different procedures. First by incremental addition of the FOD (FOD is 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione) reagent to a 0.2 mol l^{-1} solution of substrate (*I*, *III-syn*, *III-anti*, or *V*) over the range from 0.05 to 2.0 of the L/S concentration ratio (ρ); and second, by incremental addition of the DPM reagent (DPM is 2,2,6,6-tetramethyl-3,5-heptanedione) to a solution of substrate *II–IV* over a range in ρ from 0.05 to 0.5.

The two-step model^{10–12} was used to calculate the relative bound shifts of the 1 : 1 adducts (for *I*, *III-syn*, *III-anti*, and *V*). LIS for the DPM experiments were calculated as slopes of the linear portions of plots of observed shift vs the L/S concentration ratio for the various hydrogens. The correlation coefficients were greater than 0.99 in all cases.

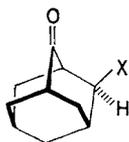
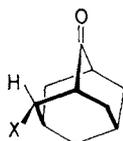
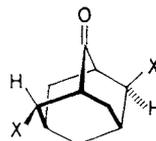
The assignment of bound shifts to particular hydrogen atoms was done on the basis of published data together with the use of the computer programs PSEUDO 1980 and BDSHIFT. These programs optimize the position of the lanthanide atom in the lanthanide–substrate adduct by minimization of the agreement factor between calculated and experimental LIS. Shift assignments for *V* were obtained from a 2D COSY experiment in which a sample of *V* was doped with a small amount of $\text{Eu}(\text{FOD})_3$.

Molecular mechanics calculations^{13,14} were employed to generate atomic coordinates for the different adamantanones.

¹H NMR spectra of *I–V* were recorded on Tesla BS 567 and Varian XL-100 NMR spectrometers. The 2D COSY experiment for *V* was carried out using a Nicolet 200 WB NMR spectrometer. The ¹H spectra of *V* with the FOD reagent were also obtained using a Varian XL-200 NMR spectrometer. Computations were performed on ADT 4 300 and IBM 3033N computers.

RESULTS AND DISCUSSION

Direct halogenation of adamantanone with the appropriate halogen in sulfuric acid afforded the *syn* and *anti*-4-halo-2-adamantanones *II–IV* as complex mixtures^{6,9}. Bromination of adamantanone afforded the dibromo derivatives *V* in addition to stereoisomers *III-syn* and *III-anti*. The individual components were isolated by preparative HPLC and structures were assigned on the basis of ¹³C NMR spectra. In the case of the dibromide *V*, the structure assignment was confirmed by single-

*syn**anti**V*, X = Br

II, X = Cl
III, X = Br
IV, X = I

-crystal X-ray crystallography. The crystallographic study was carried out by C. Piccinni-Leopardi and G. Germain.* The structure was solved by MULTAN 80 program¹⁵ and refined by the SHELX76 program¹⁶ on the basis of 1 366 observed reflections for which $I > 2.5\sigma(I)$. Incident radiation was $\text{CuK}\alpha$ ($\lambda = 1.54178 \text{ \AA}$). The final R value is 0.055. Crystal data: $\text{C}_{10}\text{H}_{12}\text{Br}_2\text{O}$ monoclinic, space group $P2_1$; cell dimensions: $a = 7.645(2)$, $b = 11.606(3)$, $c = 11.758(3) \text{ \AA}$, $\beta = 91.49(2)^\circ$; $V = 1\,042.9(5) \text{ \AA}^3$; $Z = 4$. Coordinates and molecular dimensions are available from the Cambridge Crystallographic Data Centre.**

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Association Constants

Shift reagent studies were carried out using $\text{Eu}(\text{FOD})_3$ in C^2HCl_3 . The association constants were also evaluated for adamantanone *I* and the three bromo derivatives *III-anti*, *III-syn*, and *V*. The experimental data for the latter compounds were analyzed by nonlinear regression analysis according to the two-step model of Eqs (A) and (B) where L and S stand for the lanthanide and substrate respectively¹⁰⁻¹²:



The association constants determined for these compounds are reported in Table I.

For each of the compounds the value of K_1 falls in a relatively narrow range between 26 and 63 l mol^{-1} , and the corresponding value of K_2 is somewhat smaller. The values for adamantanone are quite similar to those obtained previously^{2,4}. Previous work has demonstrated that there is considerable uncertainty in equilibrium measurements obtained in this manner so all the association constants in Table I should probably be considered the same within experimental error.

Atomic Coordinates

In order to confirm the structure of the dibromide *V*, a single-crystal X-ray crystallographic study was carried out. This provided a unique opportunity to assess various methods of obtaining atomic coordinates for LIS studies, because coordinates were available for two crystallographically unique enantiomers of the compounds *Va* and *Vb*. Previous studies have emphasized the importance of experimental errors on the LIS that can be caused by errors in the coordinates¹⁷⁻¹⁹ and it has been suggested that X-ray coordinates are inadequate¹⁷. In the present instance, three independent sets of coordinates are available: two from X-ray study and a third from empirical force field calculations. The X-ray crystal structure was determined

TABLE I
Association constants (l mol^{-1}) for haloadamantanones with $\text{Eu}(\text{FOD})_3$ in C^2HCl_3

Compound	<i>I</i>	<i>III-syn</i>	<i>III-anti</i>	<i>V</i>
K_1	63	45	26	55
K_2	8	11	14	4

for the purpose of verifying the positions of the bromine atoms on the adamantanone skeleton, so a high degree of refinement was not needed. The refinement involved only heavy atoms (C, O, and Br), and the positions of the hydrogen atoms were imposed on the carbon framework using standardized, uniform bond lengths and angles. Complete atomic coordinates for *V* were generated in two different ways. First, hydrogens were "added" to the carbon skeleton of the X-ray structure for each of the enantiomers, *Va* and *Vb*, using the appropriate routine in Allinger's MM2 program^{13,14}. Second, an approximate set of coordinates was fully optimized with empirical force field calculations again with the MM2 program. The resulting coordinates (identified as "X-ray" and "EFF optimized", respectively) were used to predict LIS for comparison with the experimental values. The results of the LIS calculations are reported in Table II. Also shown in Table II are the calculated steric energies of the X-ray and EFF optimized structures.

It comes as no surprise that the steric energy is lower for the EFF optimized structures. But the magnitude of the energy difference is quite large — the X-ray structures are higher in energy by some 120 kJ mol⁻¹. It was important to determine whether this discrepancy corresponds to a real structural difference between the solid state and (computed) gas phase molecules. Consequently, a separate calculation was performed. The coordinates of the heavy atoms only for the EFF optimized structure were used as the starting geometry, and the hydrogens were "added" in a manner identical to that which had been employed to generate the complete sets of X-ray coordinates. The steric energy of the structure generated in this manner is 116.4 kJ mol⁻¹, whereas the structures generated by adding hydrogen atoms to

TABLE II

Comparison of predicted and experimental LIS for dibromoadamantanone *V* using X-ray and EFF optimized geometries

Parameter	X-Ray		EFF Optimized
	Enantiomer <i>A</i>	Enantiomer <i>B</i>	
Agreement factor ^a	0.060	0.027	0.021
C—O—Eu Angle, deg	161	170	169
C—C—O—Eu Dihedral angle, deg	348	80	43
EFF Energy, kJ mol ⁻¹	222.8	275.5	98.3

^a For the structure with Eu—O = 2.5 Å, otherwise the position of the europium with respect to the substrate was optimized. Hydrogens on C-1 and C-3 were excluded from the analysis (see text).

the heavy atom X-ray coordinates are more than 80 kJ mol^{-1} higher in energy. The higher energy calculated for the X-ray structures is therefore mainly a consequence of distortion of the carbon skeleton. For example there are several carbon-carbon bonds in the X-ray structures that differ from the typical value of 1.54 \AA by as much as 0.1 \AA . Such large deviations presumably reflect the fact that only a partial refinement was needed in determining the crystal structure of *V*. We therefore conclude that the use of partially refined X-ray coordinates for LIS studies is inadvisable. The results reported in the remainder of this work are based on substrate coordinates that were fully optimized by EFF calculations. The optimized coordinates are quite similar for *I-V*.

This conclusion is further supported by the LIS studies. As clearly shown in Table II, the agreement factor²⁰ obtained using EFF optimized coordinates is considerably lower than for either of the two sets of X-ray coordinates. Others have argued that rigorous comparison of agreement factors requires the use of the Jackknife test²¹, but it is nevertheless clear that the X-ray coordinates for isomer *A* do not fit as well with the experimental data as either of the other two sets of coordinates. The latter two sets of coordinates (X-ray for isomer *B* and EFF) are very similar as shown by their respective agreement factors. The relatively good fit obtained with the X-ray *B* coordinates must nevertheless be considered as coincidence, because those for its isomer are unsatisfactory.

Although we felt that 2.5 \AA was a good approximation of the Eu-O bond length³, we attempted to learn if the LIS data would provide any additional information. Consequently, comparisons of experimental and predicted LIS were carried out where the LIS were predicted for an oxygen-europium distance ranging from 1.8 to 4.0 \AA . For each bond length the range of C-O-Eu bond angles from 120° to 180° and the complete range of C(1)-C(2)-O-Eu torsion angles from 0° to 360° were evaluated, and the geometry affording the lowest agreement factor was selected. These calculations were repeated for each of the three sets of coordinates discussed above, and the results are summarized in Fig. 1.

The data in Fig. 1 lead to several conclusions. First, the optimum bond length (in addition to the optimum agreement factor discussed above) is highly dependent upon the model used to obtain atomic coordinates. Second, multiple minima are observed in some cases. Third, both the optimum bond length and the optimum agreement factor obtained in these calculations are highly dependent upon the step size used in varying the C-O-Eu bond angle and C-C-O-Eu torsion angle. That the outcome of the calculations depends on the source of atomic coordinates is not surprising. We have already shown that erroneous agreement factors can result from inaccurate coordinates, and others have addressed this question as well¹⁷⁻¹⁹. Similarly, the data in Fig. 1 reaffirms our previous conclusion that bond lengths determined from LIS data are unreliable⁴.

The most important conclusion to be drawn from Fig. 1 concerns the dependence of the calculations on the step size. This is illustrated by the two curves depicting calculations with MM2 coordinates. When the bond angle and torsion angle are each varied in 10° steps, a clear minimum in the curve is found at 2.4 \AA (with an agreement factor of 0.0202). But reduction of the step size to 1° for each of the angles produces a much flatter curve with an optimum bond length of only 2.2 \AA (and an agreement factor of 0.0196). The importance of this result is not so much the different bond length found in the two calculations, since we have already concluded that bond lengths calculated from LIS data are unreliable. Instead, the conclusion is much more general: when the step size is too large, the true minimum may be missed entirely. This is easily seen by considering the calculations for a bond length of 1.8 \AA . The best agreement factor of 0.023 is missed entirely when a step size of 10° is employed. Instead, an "optimum" geometry with an agreement factor of 0.049 is found. The procedure that we employ for comparing predicted and experimental LIS employs a uniform step size over a specified range of bond angles and torsion angles. But other optimization algorithms (e.g. steepest descent) use a step size that changes during the course of the calculations. Our results now demonstrate that procedures which employ large or variable step sizes cannot be relied upon to give correct answers.

Geometry of LIS Complexes

The relative bond shifts for adamantanone *I* and the bromo derivatives *III-syn*, *III-anti*, and *V* are reported in Table III. Also shown for comparison are the relative LIS obtained for *I* and *V* by the gradient method. We have already demonstrated that the association constants and atomic coordinates for all four compounds are quite similar. Consequently, the small differences in LIS for these compounds must reflect differences in the coordination geometries of their lanthanide adducts.

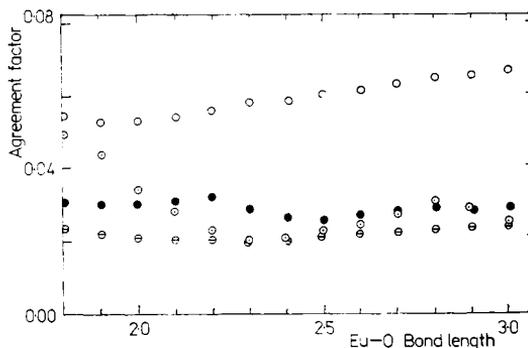


FIG. 1

Dependence of agreement factor on oxygen-europium bond length for dibromide *V*.
 ○ X-ray *A* (stepsizes: bond angle = 5° /torsion angle = 10°); ○ X-ray *B* ($5^\circ/10^\circ$); ● EFF ($10^\circ/10^\circ$); ⊙ EFF ($1^\circ/1^\circ$)

The position of the europium atom in the lanthanide-substrate complexes of *III-syn*, *III-anti*, and *V* was determined by finding the structures which afforded the lowest agreement factors when experimental LIS were compared with those values calculated with the pseudocontact equation:

$$\text{LIS} = k(3 \cos^2 \theta - 1)/r^3. \quad (1)$$

The agreement factors were calculated both by complete optimization of the lanthanide position and by partial optimization at a Eu—O bond length of 2.5 Å. The results of these computations are summarized in Table IV. Optimization of Eu—ligand bond lengths in agreement factor calculations had previously been shown to be unreliable⁴, and this is further supported by the data in Table IV. The optimized bond lengths vary by 1.5 Å, an unreasonable range for such closely related compounds. Similarly, the C—O—Eu bond angle of 158° for *III-anti* is not consistent

TABLE III

Experimental relative bound shifts in C^2HCl_3 at 37°C for hydrogens of adamantanone (*I*) and bromoadamantanones *III-syn*, *III-anti*, and *V*^a

Hydrogen ^b	Compound			
	<i>I</i> ^c	<i>III-syn</i>	<i>III-anti</i>	<i>V</i> ^c
1	4.25 (4.29)	4.02	5.09	3.85 (3.93)
3	4.25 (4.29)	4.56	5.05	4.33 (4.23)
4- <i>syn</i>	2.18 (2.20)	—	2.65	— (—)
4- <i>anti</i>	1.39 (1.41)	1.41	—	1.49 (1.36)
5	1.16 (—)	1.33	1.29	1.21 (1.20)
6- <i>syn</i>	1.00 (—)	1.00	1.13	1.01 (1.02)
6- <i>anti</i>	1.00 (—)	1.00	1.00	1.00 (1.00)
7	1.16 (—)	1.12	1.31	1.03 (0.99)
8- <i>syn</i>	2.18 (2.20)	2.10	2.70	2.02 (2.05)
8- <i>anti</i>	1.39 (1.41)	1.28	1.29	— (—)
9- <i>syn</i>	2.18 (2.20)	2.14	2.66	2.11 (2.09)
9- <i>anti</i>	1.39 (1.41)	1.28	1.90	1.31 (1.30)
10- <i>syn</i>	2.18 (2.20)	2.23	2.56	2.07 (2.05)
10- <i>anti</i>	1.39 (1.41)	1.39	1.75	1.37 (1.36)

^a The values shown are relative to the bound shift of hydrogen 6-*anti* for each compound. The following bound shifts for the 6-*anti* hydrogen were determined for the 1:1 lanthanide substrate complex by the two-step method^{1,2}: *I*, 3.22; *III-syn*, 2.51; *III-anti*, 2.22; *V*, 2.62. ^b *Syn* and *anti* relative to the carbonyl group; in the case of hydrogens on C-6 they are relative to C-1.

^c Values in parentheses for *I* and *V* were obtained by the gradient method.

with the results for the other compounds. Therefore we employed the value of 2.5 Å that was suggested earlier on the basis of known X-ray structures². This is slightly longer than the sum of the crystallographic ionic radii for europium and oxygen²², but it is well documented that bond lengths between lanthanide ions and neutral oxygen donor atoms are somewhat longer than those to anionic oxygens². Although we feel that optimization of the oxygen–europium bond length is not reliable, the results of those calculations are also reported for the sake of completeness.

The C—O—Eu bond angle, C—C—O—Eu torsion angle and the term k in the pseudocontact equation were optimized in each case. When the hydrogen atoms on C-1 and C-3 were included in these calculations, the agreement factor was always found to be larger. We believe that the LIS of these protons includes a significant contact contribution²³, but Eq. (1) calculates only pseudocontact shifts. The inclusion of experimental data with contact shifts results in a much poorer fit. This is in agreement with our earlier work³. Consequently we believe that the most reliable data in Table IV corresponds to the first entry for each compound, where the Eu—O bond length is 2.5 Å and the hydrogen atoms on C-1 and C-3 are excluded. Note, however, that the optimum geometry for the complexes is relatively independent of the procedure used. While the results are not identical, the optimum position of the

TABLE IV
Structural results for LSR–substrate complexes^a

Compound	Eu—O Bond length Å	C—O—Eu Angle deg	Eu—O—C—C Torsion angle deg	Agreement factor
Eu—O bond length optimized				
<i>III-syn</i>	3.2 (2.2)	164 (169)	38 (38)	0.039 (0.065)
<i>III-anti</i>	3.7 (2.2)	158 (178)	199 (146)	0.046 (0.063)
<i>V</i>	2.3 (2.2)	171 (169)	41 (43)	0.020 (0.049)
<i>V^b</i>	2.2 (2.2)	175 (171)	48 (51)	0.025 (0.056)
Eu—O bond length 2.5 Å				
<i>III-syn</i>	—	172 (165)	32 (35)	0.040 (0.068)
<i>III-anti</i>	—	174 (177)	180 (150)	0.055 (0.064)
<i>V</i>	—	169 (163)	43 (41)	0.021 (0.053)
<i>V^b</i>	—	172 (166)	49 (50)	0.026 (0.058)

^a Values in parentheses are data for all hydrogens; otherwise the hydrogens on C-1 and C-3 are excluded. ^b LIS were obtained by the gradient method.

europium in a particular complex is qualitatively similar no matter which computational procedure is employed.

The position of the europium ion in these complexes is summarized graphically in Fig. 2, as a composite projection of the lanthanide–adamantanone complexes viewed along the oxygen–carbon bond. The positions of key atoms in the structures are indicated. The most remarkable feature of the data is the absence of large deformations from linear geometries. Even the presence of a *syn*-bromo substituent (which is an axial substituent on the cyclohexanone ring) does not result in a large deformation. These results are again in accord with our previous work on alkyl-substituted adamantanones^{2,5}, and are consistent with steric effects. Repulsive steric interactions with the *syn*-bromine would result in movement of the europium away from the halogen, but at longer Eu–Br distances for the *anti*-bromo groups, attractive van der Waals forces would favor distortion of the europium toward the halogen. For all three compounds these distortions are small, however, and it is difficult to assess the influence of experimental errors on small variations in the computed optimum geometries.

An additional set of experiments was carried out using $\text{Eu}(\text{DPM})_3$ as the shift reagent. In this case we studied the chloro and iodo derivatives *II* and *IV* as well

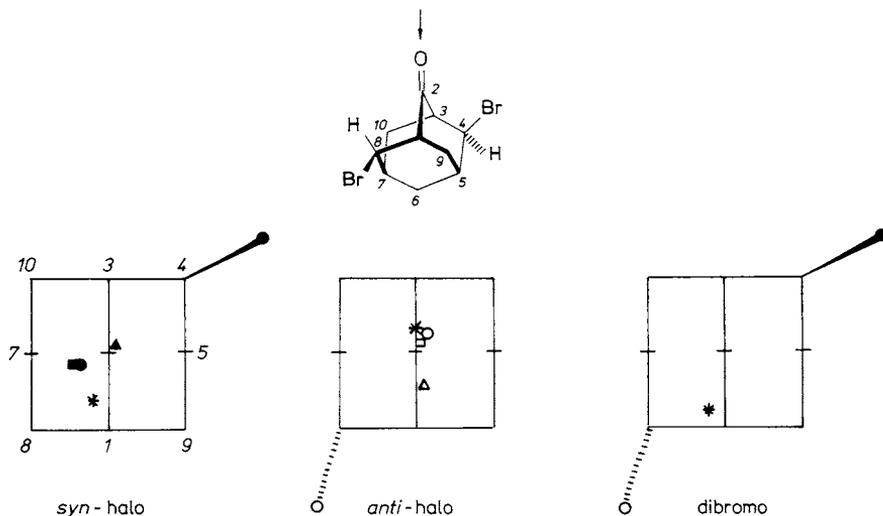


FIG. 2

Location of the europium nucleus in complexes of halogen substituted adamantanones. The drawing is a composite for the different ketones, *II*–*V*. The adamantanone is viewed along the C–O axis from above the oxygen atom as shown in the insert. (stars: Br, FOD; circles: Br, DPM; triangles: Cl, DPM; squares: I, DPM)

as the bromides *III*. These experiments are summarized in Table V, which shows both the relative LIS and the results of the structure optimizations. The gradient method²⁴ was employed for these experiments, because the lower solubility of Eu(DPM)₃ precluded high L/S concentration ratios. Since most of the data was obtained at low L/S concentration ratios where the spectra are not well-resolved, greater experimental error is present in the resulting data. This is reflected by the

TABLE V
Lanthanide induced shifts and results of structure evaluation for 4-halo-2-adamantanones with Eu(DPM)₃

Hydrogen ^a	<i>II-syn</i>	<i>II-anti</i>	<i>III-syn</i>	<i>III-anti</i>	<i>IV-syn</i>	<i>IV-anti</i>
Relative bound shifts for 1 : 1 complex ^a						
1	3.23	3.99	3.63	4.05	2.64	4.10
3	3.88	3.73	4.24	4.24	3.14	4.29
4- <i>syn</i>	—	1.96	—	2.11	—	2.21
4- <i>anti</i>	1.19	—	1.39	—	1.26	—
5	1.00	1.21	1.00	1.28	1.00	1.15
6- <i>anti</i>	1.00	1.16	1.00	1.00	1.00	1.00
6- <i>syn</i>	1.00	1.00	1.00	1.00	1.00	1.00
7	1.15	1.21	1.00	1.17	1.03	1.11
8- <i>syn</i>	1.81	2.08	1.78	1.71	1.49	2.05
8- <i>anti</i>	1.21	1.21	1.43	1.28	1.03	1.11
9- <i>syn</i>	1.84	2.08	1.97	1.71	1.69	2.05
9- <i>anti</i>	1.21	1.22	1.43	1.34	1.01	1.33
10- <i>syn</i>	1.81	1.73	1.78	1.71	1.49	2.05
10- <i>anti</i>	1.21	1.21	1.43	1.34	1.03	1.50
Results with Eu—O bond length optimized ^b						
Eu—O, Å	1.8	2.1	1.8	2.0	2.0	2.3
C—O—Eu, deg	174	174	172	174	169	174
C—C—O—Eu, deg	352	31	307	114	310	145
Agr. factor	0.068	0.077	0.073	0.118	0.082	0.077
Results with Eu—O 2.5 Å ^c						
C—O—Eu, deg	176	170	172	172	168	173
C—C—O—Eu, deg	147	18	286	127	285	160
Agr. factor	0.070	0.088	0.074	0.105	0.109	0.047

^a The assignments for H-1 and H-3 may be interchanged. Determined by the gradient method and normalized to the shift of hydrogen 6-*syn* for each compound. ^b All hydrogens were included in the calculations. ^c H-1 and H-3 were excluded from the calculations.

larger agreement factors reported in Table V. Although the $\text{Eu}(\text{DPM})_3$ data is less accurate, it reinforces our conclusions based on $\text{Eu}(\text{FOD})_3$ studies. The optimized position for the europium is similar to the calculated FOD complex. There is also an increasing distortion from linearity as a function of the steric bulk of the halogen. As in the case of alkyl substituents³, these results support the idea that the geometries of lanthanide-substrate complexes are largely determined by steric interactions.

CONCLUSIONS

The results we report here indicate that reliable structure correlations can be obtained with lanthanide induced shifts if certain precautions are taken. Reliable atomic coordinates are needed for the calculations, and X-ray coordinates from a partially refined structure are not always adequate. On the other hand, coordinates obtained by empirical force field afford very good results, so this is clearly the method of choice. Our data also demonstrates that considerable care must be exercised when searching for the best agreement factor by variation of the lanthanide position. Lanthanide-ligand bond lengths obtained by the method are quite unreliable, structurally similar compounds afforded quite different values. Moreover, the optimum structure that one obtains can be highly dependent on the computational procedure employed. If too large a step size is used when the location of the lanthanide nucleus is varied, minima in the agreement factor can be missed entirely.

All of the adamantanone derivatives studied were found to have coordination geometries with lanthanide shift reagents that are approximately linear. The distortions from linearity do not exceed 12° and are in all cases consistent with steric effects.

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