microanalyses, to Mr. Peter Ziegler for 220-MHz nmr spectra, and to The Rockefeller University Mass Spectrometry Laboratory for mass spectra. The 220-MHz nmr spectra were obtained on an instrument at The Rockefeller University and operated by a consortium supported in part by NSF Grant No. GB-12278 and grants from Research Corporation and the Alfred P. Sloan Foundation.

Lanthanide Shift Reagents. II.[1] (a) Photochemical Ring Expansion of a β-Lactam and Product Identification Using LSR Nmr Shifts and X-Ray Crystallography. (b) Probable Structure of an LSR–Substrate Complex in Solution. (c) Conformational Analysis Using LSR Nmr Data[2]

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Abstract: Irradiation of *exo*-3-aza-4-ketobenzotricyclo[4.2.1.$0^{2,5}$]non-7-ene (**6**) in methanol gave *exo*-2-methoxy-3-aza-4-keto-7,8-benzobicyclo[4.2.1]nonene (**7**) in 43% yield, a reaction which involved ring expansion of the β-lactam moiety in **6** plus the addition of the elements of methanol. The reaction mechanism is discussed. The structure of **7** was determined by nmr using the lanthanide shift reagents (LSR) $Eu(dpm)_3$ and $Pr(dpm)_3$, and by a single-crystal, X-ray diffraction analysis. A series of least-squares calculations was carried out to determine the "best" position of the Ln atom in the LSR–substrate complex, using the McConnell–Robertson pseudo-contact equation to provide a means of computing an nmr shift from an assumed LSR–substrate geometry. The procedure used the shift data for the 12 ring protons and minimized the function $\Sigma(R_{oi} - R_{ci})^2$, where the *R*'s are ratios of the Lanthanide-induced nmr shifts. The conformational minima of the methoxy group in **7** and the ethoxy group in the *exo*-2-ethoxy homolog of **7** were also determined from the nmr shift data for these substituents.

In 1969, Hinckley reported[4] that the addition of the dipyridinate of tris(dipivaloylmethanato)europium(III)[5] to a CCl_4 solution of cholesterol produced a substantial paramagnetic shift in the nmr spectrum of the compound with essentially no line broadening. This communication triggered an avalanche of scientific interest in the so-called "lanthanide shift reagents" (LSR), most of which has centered on the application of the reagents to the resolution of problems in molecular structure.[6] In this paper, we report (1) the photochemical ring expansion of a polycyclic β-lactam, (2) the use of lanthanide induced shifts (LIS) to produce a first-order nmr spectrum of the photoproduct and the identification of the material from these data, (3) a single-crystal X-ray diffraction determination of the structure of the photoproduct, (4) the determination of the probable structure of the lanthanide–photoproduct complex in solution, and (5) conformational analysis using the LIS nmr data.

Results and Discussion

Photochemical Ring Expansion. An investigation by Fisher[7] in 1968 of the photochemistry of β-lactams **1** revealed that ring cleavage occurred at essentially two points (dashed lines labeled A and B in structure **1**), and that the direction of cleavage depended on the degree of substitution at the 3 position. On the basis of these results plus an analysis of quantum yield data, Fisher suggested that the initial photochemical process involved cleavage of a C–N bond to a diradical intermediate (**2** or **3**) which subsequently underwent homolysis of the appropriate bond to form product.

The subsequent chemistry of these reactive fragments is of interest, but in the case of monocyclic β-lactams they tend to diffuse apart and the major products arise from reaction with solvent. However, if a polycyclic system were constructed, these fragments could be prevented from diffusing apart and their mutual reactions might be realized. We initiated a study of this

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(1) Part I: P. H. Mazzocchi, H. J. Tamburin, and G. R. Miller, *Tetrahedron Lett.*, 1819 (1971).

(2) (a) The partial support of this work by the Center for Materials Science, University of Maryland, and the National Science Foundation (GP-15791) is gratefully acknowledged. Computer time was generously provided through the facilities of the Computer Science Center, University of Maryland. (b) Presented in part before the Organic Division, 162nd National Meeting of the American Chemical Society, Washington D. C., Sept 1971, and the American Crystallographic Association, Winter Meeting, Albuquerque, N. M., April 1972.

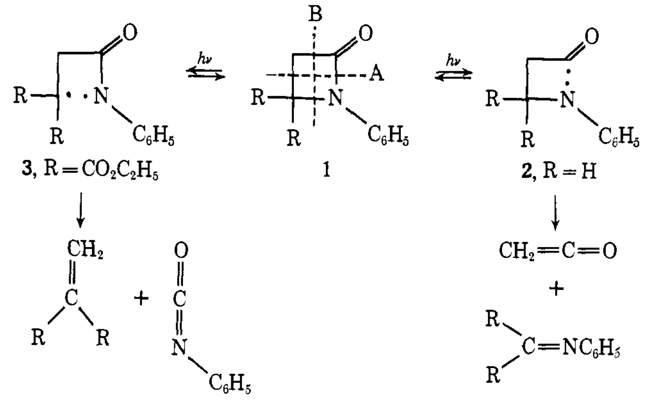
(3) (a) Department of Chemistry; (b) Department of Biophysics; (c) taken in part from the Ph.D. dissertation of W. J. Kopecky to be submitted to the Department of Biophysics, University of Maryland; (d) taken in part from the Ph.D. dissertation of H. J. Tamburin, University of Maryland, 1971.

(4) C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969).

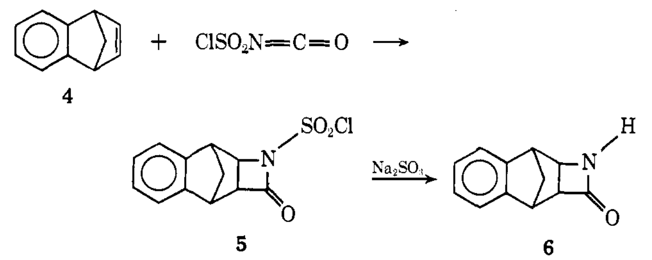
(5) $Eu(dpm)_3(py)_2$; Hdpm = 2,2,6,6-tetramethylheptane-3,5-dione; py = pyridine.

(6) For reviews and leading references, see (a) W. D. Horrocks and J. P. Sipe, *J. Amer. Chem. Soc.*, **93**, 6800 (1971); (b) R. von Ammon and R. D. Fischer, *Angew. Chem., Int. Ed. Engl.*, **11**, 675 (1972).

(7) M. Fisher, *Chem. Ber.*, **101**, 2669 (1968).



type using the polycyclic β-lactam, *exo*-3-aza-4-ketobenzotricyclo[4.2.1.0^{2,5}]non-7-ene (**6**), the preparation of which is outlined below.

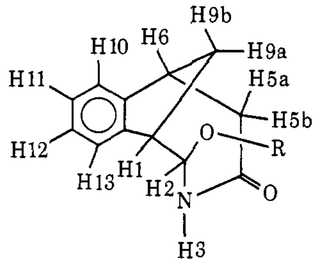


4
5
6

The reaction of benzonorbornadiene (**4**)[8] with chlorosulfonyl isocyanate gave an 80% yield of the *N*-chlorosulfonyl β-lactam (**5**),[9] which was then reduced with sodium sulfite[10] to the β-lactam **6**. The reduction of **5** was monitored using the disappearance of the 1810-cm^{-1} carbonyl band characteristic of **5** and the appearance of the 1740-cm^{-1} absorption of **6**. The yield of crude **6** was 90% and spectroscopic and analytical data from a pure sample were consistent with the assigned structure.

Irradiation of a sample of **6** in absolute methanol using a 450-W Hanovia medium-pressure lamp led to the isolation of a single photoproduct as a white crystalline solid in 43% yield. Mass spectral data and elemental analysis gave the molecular formula $C_{13}H_{15}NO_2$, which required the incorporation of 1 mol of methanol into the photoproduct. This was confirmed by the nmr spectrum which showed a sharp singlet characteristic of the OCH_3 group at δ 3.25. The ir spectrum indicated that the material, while still an amide [ir (CCl_4) 3350 (N—H) and 1650 (C=O) cm^{-1}], was no longer a β-lactam. The compound was tentatively assigned structure **7** on the basis of these and the following nmr data: ($CDCl_3$) δ 7.10 (s, 4 H, aromatic), 6.6–7.0 (1 H, N–H), 4.18 (t, 1 H, J = 5.0 Hz, HCO—), 3.1–3.7 (m, 2 H, bridgehead H1, H6), 3.25 (s, 3 H, CH_3O—), 2.82 (m, 2 H, —CH_2C=O) and 2.2–2.6 (m, 2 H, -CH_2-).

The complete resolution of the proton resonances in the nmr spectrum of **7** was achieved by the addition of the lanthanide shift reagent Eu(dpm)$_3$[6] to a $CDCl_3$ solution of **7**. The shifted spectrum showed important resonances at δ 13.13 (d, H5b), 10.68 (d, H5a), 6.43 (m, H6), 6.13 (t, H2), 5.26 (d, H9a, J = 18 Hz), 5.04 (t, H1), and 4.43 (m, H9b). Irradiation of the doublet at δ 10.68 (H5a) caused the doublet at 13.13 (H5b) to collapse to a broadened singlet with no change in the resonance due to H6 (6.43). Irradiation of H5b, in addition to causing the doublet at δ 10.68 to collapse to a singlet, also caused the multiplet at 6.43 (H6) to collapse to a broadened doublet. The H5a–H6 coupling was expected to be small because molecular models showed that the H5a–H6 dihedral angle was close to 90°. The irradiation of the multiplet at δ 6.43 (H6) caused, in addition to the sharpening of the doublet at 13.13 (H5b), the multiplet at 4.43 (H9b) to resolve to an approximate doublet of doublets. This operation had no effect on the doublet at δ 5.26 (H9a). The coincidences in the H1 and H9a chemical shifts could be removed by the simple expedient of increasing the concentration of **7** in the nmr sample. Irradiation of the resonances assigned to H1 and H9a caused the multiplet assigned to H9b to simplify. These experiments indicated that H1, H9a, and H6 were coupled to H9b, but neither H1 nor H6 is coupled to H9a. These results again were in accord with molecular model predictions of *ca.* 90° dihedral angles for H1–H9a and H6–H9a. The relatively large coupling constants for H1, H2, and H3 (J_{12} = J_{23} = 5.0 Hz) suggested that the methoxy group occupied the exo position.



7, R = CH_3
8, R = CH_3CH_2
9, R = $CH_3CH_2CH_2$

A reasonable mechanism for the photochemical reaction could involve the initial formation of diradical **10**, followed by rearrangement to ketene–imine **11**. **11** could then either collapse to the resonance stabilized **13** or addition of the imine across the ketene moiety could afford acylimine **12**. Alternatively, **13** could arise directly from **6b** *via* electrocyclic ring opening. Addition of primary alcohols to systems **12**[11] and **13**[12] has good analogy and would afford the observed product. It is known that acylimines react most efficiently with primary alcohols and that they do not react with tertiary alcohols.[13] As expected, **6** affords **8** and **9** with ethanol and propanol as solvent but none of the corresponding ring expanded material was obtained in *tert*-butyl alcohol. Suprisingly, starting material in the *tert*-butyl alcohol experiment was recovered in high yield. In the absence of a large solvent effect, this result suggests that there is a step in the reaction sequence after the initial photoprocess which can either revert to starting material or proceed to product. On the basis of this single experiment, we tentatively prefer intermediate **13** which can simply collapse back to starting material, over intermediate **12**. Additional experi-

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[8] G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958).

[9] See E. Moriconi and W. Crawford, *J. Org. Chem.*, **33**, 370 (1968).

[10] T. Durst and M. J. O'Sullivan, *ibid.*, **35**, 2043 (1970).

[11] W. von E. Doering and M. J. Goldstein, *Tetrahedron*, **5**, 53 (1959).

[12] A. Gomes and M. Jouille, *Chem. Commun.*, 935 (1967); W. T. Brady and E. D. Dorsey, *J. Org. Chem.*, **35**, 2732 (1970); H. B. Kagan and J. L. Luche, *Tetrahedron Lett.*, 3093 (1968).

[13] J. F. Banfield, G. M. Brown, F. H. Davey, N. Davies, and T. H. Ramsay, *Aust. J. Sci. Res., Ser. A*, 330 (1948).

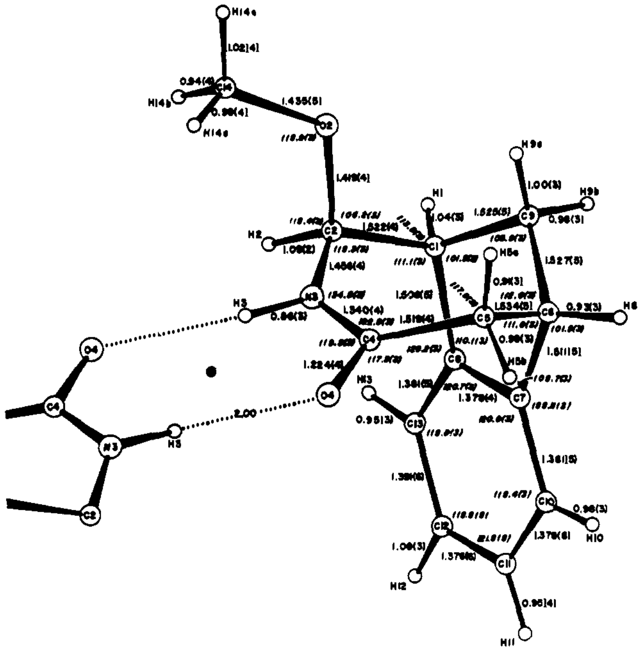
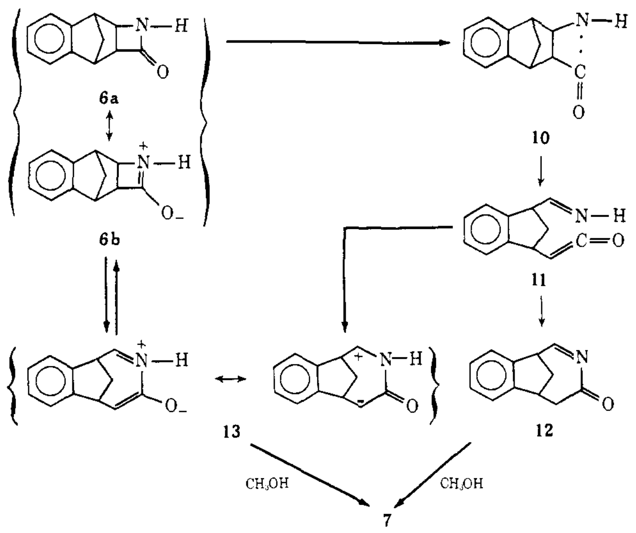


Figure 1. Bond lengths (Å) and angles (deg) for compound 7. The view is parallel to the crystallographic *a* axis. The angles to the hydrogen atoms are not shown. The interaction to form a hydrogen-bonded amide dimer across a crystallographic center of symmetry is also illustrated.



ments now in progress should clearly define the mechanism of the reaction.

The observed cleavage process corresponds to cleavage A in 1. Examination of the crude photochemical reaction mixture by nmr for the presence of 4 or its known[14] triplet photoproduct benzotetracyclo[3.2.0.-$0^{2,7}0.^{4,6}$]heptene was fruitless, indicating that B cleavage, if it occurred at all, was at best a minor process.

X-Ray Crystallographic Investigation. The preceding LIS nmr results and the fact that the photoproducts each contained 12 different protons linked to a rigid molecular frame suggested that 7–9 would make a good system for an investigation of the geometry of the LSR–substrate complex. Since the study would require an accurate knowledge of bond distances and angles, an X-ray crystallographic analysis of crystalline 7 was undertaken to provide the information. The crystal data and details of the intensity data measurements, structure solution, and refinement are given in the Experimental Section. The structure is shown in Figures 1 and 2 along with bond lengths and most of the angles; the lengths and angles all have normal values. The principal intermolecular interaction, *viz.*, the formation of a hydrogen-bonded amide dimer across a center of symmetry, is also illustrated in Figure 1. The view of the molecule given in Figure 2, from bridgehead atom to bridgehead atom (C6 to C1), can be likened to a "hobby horse." Several interplanar angles have been included in the drawing as an aid to understanding the overall molecular conformation.

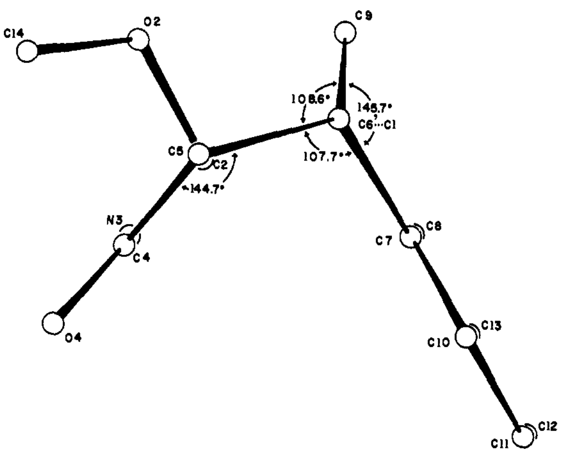


Figure 2. The "hobby horse": a view of compound 7 parallel to the C6 · · · C1 vector.

Two groups of atoms in the molecule form distinct planes: the amide function, N3–C4–C5–O4 (0.003 Å[15]), and the benzene ring with its two substituents, C1–C6–C7–C8–C10–C11–C12–C13 (0.001 Å[15]). The methyl group hydrogens are staggered relative to C2; dihedral angles (about C14–O2) are H14a–C2 = 179.9°, H14b–C2 = 55.4°, and H14c–C2 = 59.6°. The dihedral angles for the three pairs of adjacent hydrogen atoms, which coincide with small nmr coupling constants (*J*), are H5a–H6 = 74.8° (about C5–C6), H1–H9a = 81.0° (about C1–C9), and H6–H9a = 87.7° (about C6–C9). The H–H dihedral angles about C1–C2 and C2–N3 are H1–H2 = 48.2° and H2–H3 = 21.2°.

Studies on the Photoproduct Eu(dpm)$_3$ and Pr(dpm)$_3$ Complexes. The lanthanide induced nmr shifts for the methyl, ethyl, and *n*-propyl photoproducts (7–9) obtained with the Eu and Pr shift reagents are reported in Table I. The shifts, Δ_{Eu} and Δ_{Pr}, were obtained by extrapolation of plots of the nmr shift *vs.* the concentration of LSR, to 1 molar equiv of LSR.[16] Negative shifts are downfield and positive shifts are upfield. Note that in all cases the resonances of the alkoxy protons and the 12 protons attached to the benzobicyclononene nucleus shift in opposite directions (*vide infra*).

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(14) J. R. Edman, *J. Amer. Chem. Soc.*, **91**, 7103 (1969).

(15) This number gives the average deviations of the atoms from the least-squares plane of the group.

(16) Least-squares lines were calculated for the Eu LIS data for 7. The average of the 13 least-squares standard deviations was 0.07 ppm, and the maximum value was 0.13 ppm (for H_3); the corresponding values of the Pr LIS data for 9 are 0.10 and 0.29 ppm (for H_3). The reported shifts are equivalent to the slopes of the LIS *vs.* [LSR]/[substrate] lines: P. V. Demarco, P. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Amer. Chem. Soc.*, **92**, 5734 (1970).

Table I. Lanthanide Induced Shift Nmr Data for Photoproducts **7–9**

	7			**8**			**9**		
Proton	Δ_{Eu}	Δ_{Pr}	$\|\Delta_{Pr}/\Delta_{Eu}\|$[c]	Δ_{Eu}	Δ_{Pr}	$\|\Delta_{Pr}/\Delta_{Eu}\|$[d]	Δ_{Eu}	Δ_{Pr}	$\|\Delta_{Pr}/\Delta_{Eu}\|$
H1	−2.93	+3.67	1.25	−2.60	+3.60	1.38	−2.85	+4.03	1.41
H2	−3.02	+3.85	1.27	−2.98	+4.15	1.39	−3.20	+4.45	1.39
H3	−15.57	+18.90	1.21	−14.80	+18.66	1.26	−15.82	+18.65	1.18
H5a	−12.62	+16.48	1.30	−11.97	−15.92	1.33	−12.18	+16.65	1.36
H5b	−16.88	+22.98	1.36	−15.67	+22.03	1.40	−16.12	+22.82	1.41
H6	−5.30	+7.08	1.32	−4.73	+6.98	1.47	−5.05	+7.13	1.41
H9a	−4.50	+5.73	1.27	−4.30	+5.40	1.26	−4.52	+5.88	1.30
H9b	−3.30	+4.40	1.33	−3.00	+4.15	1.38	−3.22	+4.71	1.46
H10	−4.90	+6.60	1.34	−4.30	+5.43	1.26	−4.30	+5.25	1.22
H11	−1.90	+2.43	1.28	−1.70	+1.97	1.16	−1.67	+1.75	1.05
H12	−1.23	+1.35	1.10	−1.10	+1.27	1.16	−1.00	+1.28	1.28
H13	−1.90	+2.43	1.27	−1.70	+2.87	1.68	−1.88	+2.50	1.33
OCH_3	+2.25	−2.38	1.06						
OCH_2				+1.05, +1.93[a]	−2.33[b]		+0.58, +0.88[a]	−1.20[b]	
CCH_2C							+0.58	−0.75[b]	
CCH_3				+0.90	−1.13[b]		+0.57	−0.75[b]	

[a] Diastereotopic protons. [b] These data are crude estimates because the peaks partially coincide with those of the Pr LSR. [c] Δ_{Pr}/Δ_{Eu} for all protons = 1.28 (7). [d] Δ_{Pr}/Δ_{Eu} for protons 1–12 = 1.34 (14). [e] Δ_{Pr}/Δ_{Eu} for protons 1–12 = 1.31 (9).

There is a growing body of experimental evidence that the lanthanide induced shifts can be adequately correlated[6b,17] by the McConnell–Robertson pseudo-contact equation[6b,18,19]

$$\Delta H_i = K\left(\frac{3\cos^2\theta_i - 1}{r_i^3}\right)_{\text{av}}$$

where ΔH_i is the induced shift for the *i*th proton, *K* represents a collection of constants and may be assumed to be a scale factor for a given experimental set-up, θ_i is the angle between the lanthanide–proton vector and the symmetry axis of the paramagnetic LSR,[20] and r_i is the lanthanide–proton distance. The calculated shift must be averaged over all positions of the proton relative to the LSR for a conformationally mobile system.[21]

We have performed a series of calculations designed to investigate the relative geometries of the photoproducts and the LSR's in solution, using the McConnell–Robertson equation to provide the necessary link between an assumed LSR–substrate structure and the nmr shift data. In these calculations, the atomic positions determined in our X-ray diffraction study of **7** were used to specify the relative locations of the 12 benzobicyclononene protons (referred to as the "skeletal protons" below), the LSR was assumed to complex to the amide oxygen atom, and the orientation of the LSR symmetry axis was assumed to be parallel to the LSR–oxygen vector. The 12 X-ray proton locations were transformed to an orthonormal coordinate system with the amide oxygen at the origin (0, 0, 0) and all lanthanide atom positions were referenced to this point. For a fixed substrate geometry, and using the assumptions given above, a ΔH_i can be computed if *K*, the scale factor, and the coordinates (*x*, *y*, *z*) of the Ln atom are known. Since we wished to determine *x*, *y*, *z* from the observed nmr shifts, the scale factor was a troublesome extra variable. This difficulty was circumvented by using *ratios* of shifts rather than the shifts themselves: whereas ΔH_i and ΔH_j both require a knowledge of *K*, the ratio, $R_{ij} = \Delta H_i/\Delta H_j$, is independent of *K*.[22] The 12 protons gave 66 ratios, which then became our "experimental" data. The Ln coordinates were determined by the method of least squares minimizing the function $\Sigma_{i=1}^{66}[R_{oi} - R_{ci}(x,y,z)]^2$, where R_o and R_c are respectively the observed and calculated ratios.[23]

Since the pseudo-contact equation is not a linear function of the Ln coordinates, *x*, *y*, *z*, the R_c function was recast as a Taylor series using only first derivatives: $R_c(x,y,z) = R_c(x',y',z') + (\partial R/\partial x)(x - x') + (\partial R/\partial y)\cdot(y - y') + (\partial R/\partial z)(z - z')$, where *x*, *y*, *z* are the "best" values of the coordinates, x', y', z' are the "current" values, and $x - x'$, $y - y'$, and $z - z'$ are the differences between these two sets of coordinates. The partial derivatives are evaluated using the "current values" x', y', z'. Since R_c now is a linear function of the coordinate differences, it is these quantities which were determined in the least-squares calculations. Using this method requires the calculations to be "cycled"; that is, an initial guess for x', y', z' leads to a set of differences which give the "best" values, *x*, *y*, *z*; these quantities then become the "current" values for the next cycle. As the computations proceed from cycle to cycle, the differences become successively smaller until there is no significant difference between the "best" values and the "current values" in a cycle. This type of

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(17) See, for example, M. R. Willcott, R. E. Lenkinski, and R. E. Davis, *J. Amer. Chem. Soc.*, **94**, 1742 (1972); R. E. Davis and M. R. Willcott, *ibid.*, **94**, 1744 (1972).

(18) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958). The pseudocontact shifts are also referred to as dipolar shifts. A through-space rather than a through-bond (contact) mechanism is assumed.

(19) W. D. Horrocks and J. P. Sipe, *Science*, **177**, 994 (1972).

(20) The opposite signs for the LIS's of the alkoxy protons in **7–9** for the Eu data indicate that these protons are located in the shielding portion of the LSR field (the opposite occurs in the Pr case). In terms of the McConnell–Robertson equation, θ_i for these protons is greater than 54.7° (the term $3\cos^2\theta - 1$ goes through 0 at this angle).

(21) The three principal axes of the LSR paramagnetic anisotropy tensor (*x*, *y*, *z*) are defined with *z* parallel to the main symmetry axis (rotation) of the compound. Thus θ_i is the angle between the $Ln\cdots H_i$ vector and the *z* axis. Although any instantaneous form of the LSR–substrate complex probably would be totally unsymmetrical, the "average" solution complex could have the rotational symmetry required for use with the McConnell–Robertson equation.

(22) R_{ij} gives the ratio of the maximum LIS of proton *i* to the maximum LIS of proton *j*: $R_{ij} = \Delta^i\text{max}/\Delta^j\text{max}$; see D. R. Kelsey, *J. Amer. Chem. Soc.*, **94**, 1764 (1972).

(23) Willcott (ref 17) has recently reported a similar kind of investigation for a number of organic compounds. Using polar coordinates (*d*, ρ, ϕ) to specify the location of the lanthanide atom, he fixed the Ln–oxygen distance (*d*) and then computed a map in which an agreement factor ($[\Sigma(\Delta H_o - \Delta H_c)^2/\Sigma(\Delta H_o)^2]^{1/2}$) was evaluated as a function of the angles ρ and ϕ. These maps were computed for several values of *d*.

Table II. Lanthanide Atom Positions[a] Derived from the Nmr Shift Data

Compd	Lanthanide atom coordinates[b]	Residual factor[c]	Distance, Å[d]	Angle, deg[e]
7 (Eu)	1.317 (34), 0.409 (63), −2.014 (44)	0.060	2.44 (4)	33.7
8 (Eu)	1.218 (54), 0.660 (95), −2.078 (66)	0.083	2.50 (7)	32.6
9 (Eu)	1.137 (40), 0.907 (66), −2.083 (55)	0.075	2.54 (5)	30.1
7 (Pr)	1.313 (27), 0.313 (54), −1.806 (45)	0.069	2.25 (4)	35.1
8 (Pr)	1.193 (40), 0.722 (73), −1.703 (77)	0.084	2.20 (7)	26.8
9 (Pr)	1.159 (15), 0.766 (33), −1.435 (42)	0.045	2.00 (3)	21.8

[a] Relative to the amide oxygen atom at 0, 0, 0. The axes of the orthonormal coordinate system are parallel to the unit cell axes used in the X-ray diffraction study of **7**. [b] Estimated standard deviations ($\times 10^3$) are given in parentheses. [c] Residual factor = $\Sigma|R_{oi} - R_{ci}|/\Sigma R_{oi}$. [d] Lanthanide atom···amide oxygen atom distance. Estimated standard deviations ($\times 10^2$) are given in parentheses. [e] Angle between the O → Ln and C → O (amide carbonyl) vectors.

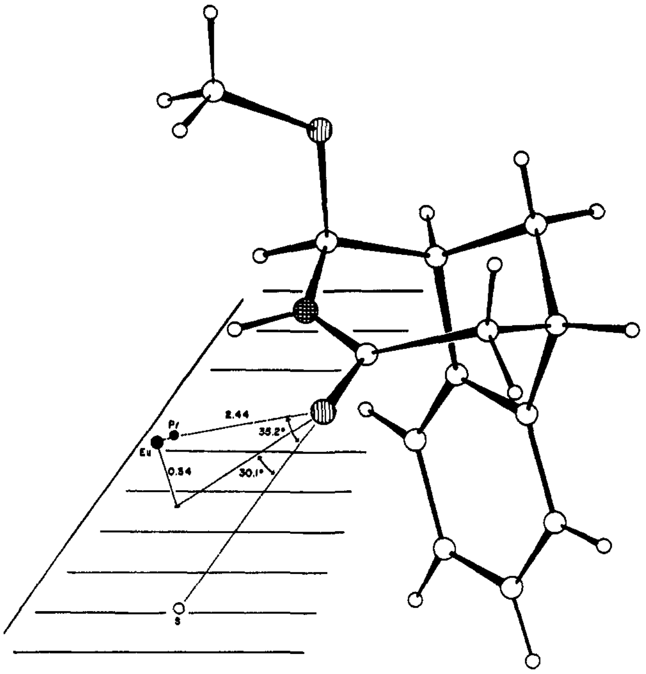

Figure 3. This drawing illustrates the positions of the Eu and Pr atoms obtained from calculations using the LIS data for compound **7**. Some distances (Å) and angles (deg) which clarify the position of the Eu atom are given. The plane shown in the drawing is the plane of the amide carbonyl group. "S" marks the starting Ln location for the least-squares calculations.

calculation can be unstable and substantial overestimates of the differences can occur if the initially selected "current" values deviate greatly from the final "best" values. Damping factors, ranging from 0.2 to 0.5, were used to reduce the computed differences and promote smooth convergence to the final values.

The least-squares computations were carried out for the six sets of LIS data reported in Table I using a point on the C=O vector 3 Å from the oxygen atom as the starting position for refinement of the Ln coordinates. The refinements converged rapidly to distinct minima, giving the Eu and Pr data recorded in Table II.[24] The Ln starting position and the Eu and Pr positions determined from the shift data of **7** are illustrated in Figure 3; the displacement of the Eu from the plane of the amide moiety and from the C=O vector have also been indicated in the figure.

The 2.49-Å average of the three Eu···O distances (Table II) is slightly longer than the mean Eu–O distance of 2.35 Å determined from a recent X-ray crystallographic study of Eu(dpm)$_3$(py)$_2$.[25,26] Since these distances should reflect the relative stabilities of the europium–oxygen connection, the solution Eu···O distance is expected to be larger than the solid state Eu–O length. The small change in Eu···O distance from **7** to **8** to **9** coincides with the anticipated increase in the steric requirement of the alkoxy substituents, methyl to ethyl to propyl, which should hinder the approach of the LSR. The decrease in the O···Ln–C=O angle from **7** to **9**, which was observed in the refinement of both the Eu and Pr LIS data, could also result from an increase in the steric requirements of the alkoxy groups since a decrease in the angle indicates that the lanthanide atom is moving away from the alkoxy portion of the molecule.[27]

X-Ray crystallographic studies of Pr$_2$(dpm)$_6$[28] and Pr$_2$(fod)$_6$·2H$_2$O[29] reported average Pr–O distances of 2.41 and 2.42 Å. Since the difference between these Pr–O values and the 2.35 Å Eu–O distance found in Eu(dpm)$_3$(py)$_2$[25] corresponds closely to the difference in the ionic radii of the two lanthanide atoms,[30] Pr···O distances in the 2.5–2.6 Å range were expected by analogy with the Eu···O results. The Pr···O distances actually obtained from the least-squares calculation range from 2.00 Å for the propyl compound **9** to 2.25 Å for the methyl derivative **7**. These data are inconsistent with the Eu results, in both the magnitude and trend of the Pr···O distances.

Although the internal agreement obtained in the Pr calculations is as good as that observed with the Eu data, the above differences may be partially due to errors in the Pr nmr shifts. The skeletal protons in **7–9** experience upfield shifts in the Pr LSR spectra and hence they must shift through the spectrum of the LSR itself. As a result, many of the Δ_{Pr} values have been extrapolated from only a few experimental points and

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[24] For each system a set of "ratio maps" was calculated to verify that the least-squares minimum obtained was indeed unique. At each point (x, y, z) in the ratio map, the factor $\Sigma(R_o - R_c)^2$ was evaluated as a function of the Ln coordinates (x, y, z). The maps were computed over a 4 × 4 × 4 Å^3 volume in 0.1-Å steps centered at the starting position for the LSR refinement.

[25] R. E. Cramer and K. Seff, *Chem. Commun.*, 400 (1972).

[26] The mean Eu–O distance is 2.40 Å in tris(acetylacetonato)-(1,10-phenanthroline)europium(III): W. H. Watson, R. J. Williams, and N. R. Stemple, *J. Inorg. Nucl. Chem.*, **34**, 501 (1972). The average (HO)···Eu and (CO)$_2$···Eu distances in Eu(HOCH$_2$CO$_2$)$_3$ are 2.62 and 2.45 Å, respectively: I. Grentle, *Acta Chem. Scand.*, **25**, 3347 (1971).

[27] The O···Ln and C=O vectors would be parallel at an angle of 0°. The distance from the Ln atom to the amide plane decreases from *ca.* 0.84 Å for the methyl compound **7** to *ca.* 0.35 Å for the propyl compound **9**.

[28] S. C. Eramus and J. C. A. Boeyens, *Acta Crystallogr., Sect. B*, **26**, 1843 (1970).

[29] Hfod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione: J. P. R. deVilliers and J. C. A. Boeyens, *ibid.*, **27**, 692 (1971).

[30] R. D. Shannon and C. T. Prewitt, *ibid.*, **25**, 925 (1969); D. G. Karraker, *J. Chem. Educ.*, **47**, 424 (1970).

they are intrinsically less accurate than the Δ_{Eu} data.

Other considerations, in addition to possible inaccuracies in the Pr LIS data, should be taken into account when comparing the outcome of the Eu and Pr calculations. For example, it should not be assumed that the geometries of the various LSR–substrate species are the same or that even identical shift mechanisms operate.[31] Furthermore, the similarities in the averages (*ca.* 1.3) of the Δ_{Pr}/Δ_{Eu} ratios listed for compounds **7–9** in Table I should not be interpreted as evidence for a simple multiplicative relationship between the Eu and Pr shifts. The shift ratio method used in our calculations should have given virtually identical results for the two LSR's had the shifts been related in such a straightforward fashion. This point is also illustrated by the ostensible inconsistencies in the Δ_{Pr}/Δ_{Eu} ratios reported for the C_5 to C_{15} cycloalkanones,[32] which range from about 1.0 to 1.8 and which alternate from the even to the odd-membered rings. In addition, there is a possibility that the short Pr···O distances reflect the presence of some amount of a Pr–Pr dimer–substrate complex in solution.[33] A proton in the environment of such a dimer would be shifted by both of the paramagnetic atoms in the dimer. Calculations for a system of this type should include complexation by both monomeric and dimeric LSR species and consider the possible orientations of the dimeric species relative to substrate. The complexity of the situation precluded our attempting to carry out this kind of analysis.[34]

In addition to the hydrogen atom positions found in the X-ray analysis of **7**, two additional hydrogen coordinate models were used to test the sensitivity of the calculations to variations in these quantities. The second model was constructed using ideal X–X–H angles and X–H lengths (N–H = 1.01, C(sp^2)–H = 1.05, C(sp^3)–H = 1.07 Å) to define the hydrogen locations while the third used the X-ray values for the X–X–H angles and the ideal X–H lengths. Although differences between the H locations and the original X-ray positions were small, their effect on the refined Eu and Pr coordinates was surprisingly large. In all cases, the Ln···O distances increased from the values observed using the X-ray H coordinate data, amounting to *ca.* 0.2 for the Eu data and *ca.* 0.3 Å for the Pr data. For example, the distances obtained using the X-ray angles–ideal lengths coordinate model were: Eu···O for **7**, **8**, and **9** = 2.64, 2.70, and 2.72 Å; Pr···O for **7**, **8**, and **9** = 2.50, 2.49, and 2.32 Å. The residuals associated with these refinements were in general 0.02–0.04 larger than the values reported in Table II. Note that the Pr···O distances for **7** and **8** are now longer than the Pr–O solid state values but that the length in **9** (2.32 Å) remains short. The relationship between the various H coordinate models and the Ln positions derived from them can be rationalized in terms of an expansion in scale. The X-ray derived X–H distances for 10 of the 12 skeletal hydrogen atoms are shorter than the ideal lengths used in the second and third model systems. By placing the atoms at the ideal X–H distances, one is essentially enlarging the scale of the H coordinate model. Thus the Ln···O distances determined from calculations based on the "expanded" H coordinate scale should also be "expanded"; that is, they should be longer than the distances obtained from the normal X-ray H coordinate scale.

As far as we have been able to determine, all of the published LSR research has assumed that the principal magnetic axis of the shift reagent is parallel to the vector from the Ln atom to the coordinating atom (X) in the substrate molecule. Although correlations based on the assumption have generally been good ones, the assumption may be invalid in some instances. It is probably unnecessary to consider deviations of the principal axis from the Ln···X vector in cases where X is connected by a conformationally mobile single bond to the remainder of the substrate (*e.g.*, the O in ROH). However, in the present system, the X–substrate bond is O═C, and such a deviation could be important in determining the best coordinates for the Ln atom. Our basic least-squares program was written to handle the refinement of *x*, *y*, *z* plus three angles to define the deviation of the principal axis from the Ln···O vector. For small angular increments (<90°), two angles suffice to specify the deviations, and all calculations were made using only two angles.

Starting with the final positional parameters given for Eu and Pr in Table II and allowing only the angles to vary, a best fit was obtained with maximum angular deviations of less than 2° from the initial values (0°). The residuals were slightly smaller than those obtained from the *x*, *y*, *z* computations, but this is to be expected since two additional parameters have been introduced to help fit the observed ratios. Simultaneous variation of *x*, *y*, *z* and the two angles gave similar results to those obtained from just the *x*, *y*, *z* calculations. However, in several cases, the parameters tended to oscillate about their final values. The oscillations were undoubtedly due to the fact that the position coordinates and angles were heavily dependent upon each other with correlation coefficients greater than 0.9.

Although it appears that for this system the principal magnetic axis can be satisfactorily assumed to coincide with the Ln···O vector, the dual coordinate-angle refinement can be useful if one makes a poor guess about the effective point of complexation (*i.e.*, atom X) of the substrate to the shift reagent. We tested this concept by referencing the H coordinates to the amide nitrogen instead of oxygen, the effect of which is to define the Ln···N vector as the direction of the LSR principal

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(31) A. M. Grotens, J. Smid, and E. DeBoer, *J. Magn. Resonance*, **6**, 612 (1972); B. Bleaney, C. M. Dobson, B. A. Levine, R. B. Martin, R. J. P. Williams, and A. V. Xavier, *Chem. Commun.*, 791 (1972).

(32) P. Kristiansen and T. Ledaal, *Tetrahedron Lett.*, 4457 (1971).

(33) M. K. Archer, D. S. Fell, and R. W. Jotham, *Inorg. Nucl. Chem. Lett.*, 7, 1135 (1971), have observed both monomeric, $Ln(dpm)_3$, and dimeric, $Ln_2(dpm)_6$, species in solutions of the Eu and Pr LSR's. The Eu and Pr dpm chelates are dimers in the solid state (ref 28). In the case of the Pr reagent, we have verified by an X-ray analysis that the LSR actually added to our nmr solutions was the same as the dimer reported in ref 28.

(34) Calculations using a Pr–Pr dimeric model (with a fixed Pr distance of 4.14 Å, ref 28), in conjunction with the Δ_{Pr} data for **9**, served merely to increase the Pr···O distance from 2.00 Å (Table II) to 2.06 Å (residual = 0.096). These calculations assumed that the Pr–Pr···O moiety was linear. A further investigation of the dimeric model used a total of five positional parameters and allowed the Pr–Pr vector to deviate from the Pr···O vector. Although this treatment gave a Pr···O distance of 2.57 Å (residual = 0.107), the refinement showed severe oscillations near the "best" minimum and very high correlations between several of the parameters. We have also tested the fit of a single Ln site to data generated from a Ln–Ln dimer, to determine if the best single Ln location would be found closer to O than the nearest Ln in the dimer. A set of perfect LIS data was computed using a linear Ln–Ln···O model with Ln–Ln and Ln···O distances of 4.0 and 2.6 Å. The best single Ln···O distance was 3.08 Å (residual = 0.028) and the angle between the Ln···O vector and the original Ln–Ln···O vector was 5.1°.

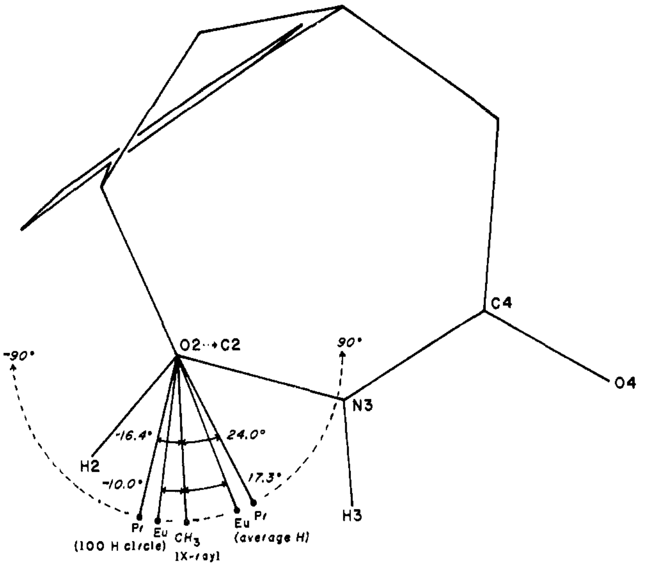

Figure 4. This figure contains a line drawing of compound **7** made parallel to the O2–C2 vector. It illustrates the various methyl group locations obtained from the X-ray data and from the LIS data using the 100 H circle and average H atom models. The area of search, defined by a rotation angle about O2–C2, was limited to the dashed hemicircle.

axis. Using the Eu LIS data for **7**, simultaneous variation of these five parameters gave an Eu position similar to that reported in Table II. In addition, the two angles directed the magnetic axis away from the Eu···N line to the Eu···O line.

The assumptions made in describing the geometry of the Ln–substrate complex and the form of the pseudo-contact equation used in the computations appear to be justified by the small values of the residual indices (0.045–0.084, Table II) and the close agreement between the experimental and calculated ratios.[17] A more general form of the pseudo-contact equation[18] than the one used in our studies contains a second term which is a function of θ_i, r_i and the orientation of the Ln···H$_i$ projection onto a plane normal to the LSR symmetry axis: that is, $\Delta H_i = \langle f(\theta_i,r_i) + g(\theta_i,r_i,\phi_i)\rangle_{\text{av}}$,[19,35,36] where ΔH, θ, and r have been previously defined and ϕ is the in-plane angle between the Ln···H projection and the magnetic x axis.[37] The excellent correlation of the nmr shifts by the single $f(\theta,r)$ term suggests that the $g(\theta,r,\phi)$ term is either negligible, identically equal to zero,[38] or effectively zero because of rotational symmetry in the "average" solution complex which would cause $\langle\cos 2\phi\rangle_{\text{av}} = 0$. Cramer and Seff have shown[36] that the pyridine nmr shifts in Eu(dpm)$_3$(py)$_2$ can be properly correlated only with the double term pseudo-contact equation. The superior binding strength of pyridine nitrogen is undoubtedly responsible for the formation of a tight LSR complex in solution with pyridine in a preferred ϕ orientation.

Conformational Analysis. A detailed analysis of lanthanide induced shift data with the McConnell–Robertson equation,[18] or a similar expression, which is a function of a particular spatial relationship between the Ln atom and the resonating nucleus, holds considerable promise for the determination of molecular conformation in solution.[39] However, it should be emphasized that the data contain information only on the (weighted) average Ln···nuclei geometries, and that the substrate conformation in an LSR complex could well differ from the conformation of the free substrate.[40] The agreement between the experimental and calculated shift ratios described above encouraged us to attempt to determine the methyl and ethyl group conformations in **7** and **8**. The system appeared to be a good candidate for this kind of analysis for the following reasons: (a) the 12 rigidly fixed skeletal protons served to specify the Ln···substrate geometry; (b) the location of the methyl group determined from the X-ray study of **7** was probably close to a minimum in the steric energy profile for rotation about C2–O2; (c) the two methylene protons adjacent to oxygen in the ethyl and propyl groups of **8** and **9** are diastereotopic and showed individual Eu shifts.

In each instance, our conformational analysis started by placing the Ln atom at the least-squares position computed from the LIS data for the 12 skeletal protons. Since only a single methyl group positional parameter could be specified by the methyl shift datum, it was assumed that the methyl C atom would be located on a circle defined by rotation of the CH$_3$–C2 vector about an axis parallel to the C2–O2 bond. The hypothetical circle was constructed using the X-ray values for the CH$_3$–O2 distance and CH$_3$–O2–C2 angle. The methyl group was assumed to be rotating rapidly about the CH$_3$–O2 bond and two models were used to treat the average position(s) of the methyl hydrogen atoms. Model A used a single H atom positioned along the O → CH$_3$ vector at a distance of 0.22 Å from the methyl C atom. This placed an "average H" in the center of the triangle formed by the three CH$_3$ H atoms.[41] Model B used a circle of 100 H atoms to approximate the rotating CH$_3$ moiety. The coordinates of the 100 H atoms were computed by taking a single methyl H position (defined by an H–C–O angle of 109.5° and H–C distance of 1.09 Å) and rotating it by 3.6° increments around an axis coincident with the CH$_3$–O bond. This process generated coordinates for a "100 H circle" in which each H–C–O angle and H–C distance had the standard values of 109.5° and 1.09 Å, and the H–C–H angle between adjacent H atoms was 3.6°. The scale factor (S) necessary to convert a calculated to an observed LIS was estimated from the experimental and calculated shifts of the 12 skeletal protons: $S = \Sigma_{i=1}^{12} \cdot \Delta H_{oi}/\Delta H_{ci}$. Each methyl H model was then rotated in 1° increments about an axis coincident with the C2–O2 bond. At each position, the new coordinates for the H atom(s) were computed and the agreement between the observed and calculated shifts evaluated.[42] Figure 4

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(35) G. N. La Mar, W. D. Horrocks, and L. C. Allen, *J. Chem. Phys.*, **41**, 2126 (1964); G. N. La Mar, *ibid.*, 43, 1085 (1965); W. D. Horrocks and E. S. Greenberg, *Inorg. Chem.*, 10, 2190 (1971); W. D. Horrocks and D. D. Hall, *ibid.*, 10, 2368 (1971).

(36) R. E. Cramer and K. Seff, *Acta Crystallogr.* (in press). Our thanks go to Drs. Cramer and Seff for a preprint of their work on the Eu(dpm)$_3$(py)$_2$ complex.

(37) The geometric part of g_i is $(\sin^2\theta_i \cos 2\phi_i)/r_i^3$.

(38) If the in-plane paramagnetic susceptibilities are equal (*i.e.*, $\chi_x = \chi_y$), $g = 0$.

(39) N. S. Angerman, S. S. Danyluk, and T. A. Victor, *J. Amer. Chem. Soc.*, **94**, 7137 (1972).

(40) An example of the perturbation of a conformational equilibrium with the addition of LSR's has been reported recently by W. G. Bentrude, H.-W. Tan, and K. C. Yee, *ibid.*, **94**, 3264 (1972).

(41) The locations of the three methyl H atoms were specified using H–C–O and H–C–H angles of 109.5° and a H–C distance of 1.09 Å: 0.22 Å = 1.09 Å × cos (180° − 109.5°).

(42) Only half of the total C2–O2 methyl circle was searched; the

illustrated the "best" methyl positions, corresponding to the smallest value of $\Delta H_o - S\Delta H_c$ obtained using the two methyl proton models and both the Eu and Pr LIS data for **7**. The minima for the two models are located on opposite sides of the X-ray methyl location by angular amounts ranging from −16.4 to +24.0°. In each case (Pr and Eu data), there was closer agreement between the observed and calculated shifts using the 100 H circle model than for the average H position approximation. Since the H circle should be nearer physical reality for the calculation of lanthanide induced shifts, the two left-most positions in Figure 4 (labeled Pr and Eu H circle) indicate the most probable methyl group locations in the Pr···**7** and Eu···**7** solution complexes.[43]

We have also performed a similar conformational analysis for the ethyl group in **8** using the Eu nmr data. As before, the Eu was located at the least-squares minimum obtained from the 12 skeletal proton shifts, and coordinates for the two diastereotopic methylene protons and for a circle of 100 methyl protons were constructed with the following data: C2–O–CH$_2$ = 114.0°; CH$_3$–CH$_2$–O = 111.0°; H–C(methyl)–CH$_2$ = 109.5°; H–C(methylene)–H = 109.5°; CH$_2$–O = 1.44 Å; CH$_3$–CH$_2$ = 1.51 Å; H–C(methyl) = 1.09 Å; H–C-(methylene) = 1.08 Å; H–C(methylene)–H plane bisected the C–C–O angle. The group was oriented with CH$_3$ and C2 eclipsed, and with the CH$_3$–CH$_2$–O–C2 moiety coplanar with the X-ray position for the CH$_3$–O–C2 group in **7**. Two degrees of conformational freedom were allowed: (a) a 180° rotation about the O–C2 bond (±90° from the starting location); (b) a 360° rotation about the CH$_2$–O connection. Two methods were used to assess the agreement between the observed and calculated ethyl shift data: (a) comparison of ratios of the three shifts, $\Sigma_{i=1}{}^{3}|R_{oi} - R_{ci}|$; (b) direct comparison of shifts, $\Sigma_{i=1}{}^{3}|\Delta H_{oi} - S\Delta H_{ci}|$ where $S = \Sigma_{i=1}{}^{3}\cdot\Delta H_{oi}/\Sigma_{i=1}{}^{3}\Delta H_{ci}$. The angular search increment for each rotation was 1°, a 360° CH$_2$–O rotation being performed for each 1° change in the O–C angle. Since the shift identities of the diastereotopic methylene protons were unknown, a shift-coordinate swap was made for each 1° CH$_2$–O increment, two observed *vs.* calculated shift comparisons were computed, and the smallest of these two values was recorded as the agreement parameter. The ratio and shift comparison methods gave identical results, each yielding two minima which are diagrammed in Figure 5. The two positions correspond to O–C, CH$_2$–O angle pairs of −3, 183 and −7, 208°. Although it is hardly significant, the better agreement was found for the −7, 208° conformation. The ethyl group O–C angles coincide with the −10° angle found for the methyl group in **7** (Eu data), and the CH$_2$–O angles indicate that a staggered conformation prevails for the CH$_3$ and two H atoms relative to C2 in the LSR–substrate complex. A conformational analysis for the *n*-propyl substituent in **9** was not attempted.

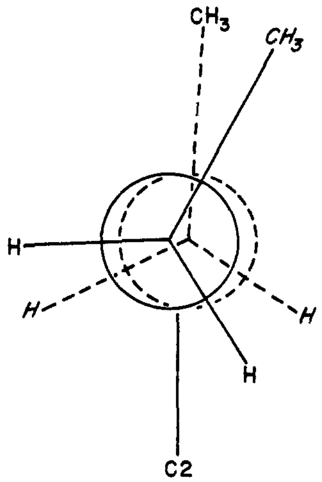

Figure 5. This figure illustrates the two best ethyl group conformations obtained from the Δ_{Eu} of compound **8**. The drawing is a Newman projection looking down the CH$_2$–O bond of the ethoxy group. The full and dashed circles show the two conformations. The relative rotation angles are: O–C2 = −3° and CH$_2$–O = 183° for the dashed-line conformation; O–C2 = −7° and CH$_2$–O = 208° for the full-line conformation.

The calculations used to determine the orientations of the methoxy and ethoxy groups suggest that similar procedures could be used in more complicated conformationally mobile systems.[39] The present system is a very favorable one for this kind of analysis because the 12 skeletal protons provide a rigid frame of reference for fixing the position of the lanthanide atom.

Experimental Section

All melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 337 spectrometer. Nmr spectra were taken on either Varian A-60D or Perkin-Elmer R20-A spectrometers; decoupling experiments were carried out on the latter instrument. Elemental analyses were performed by Dr. Franz Kasler, Department of Chemistry, University of Maryland.

Benzonorbornadiene (4). The procedure of Wittig and Knauss[8] was employed. The yield was 55%, bp 53–54° (2 mm).

***N*-Chlorosulfonyl-*exo*-3-aza-4-ketobenzotricyclo[4.2.1.0^{2,5}]non-7-ene (5).** A solution of 12 g (0.09 mol) of chlorosulfonyl isocyanate in 50 ml of anhydrous ether was added dropwise to a magnetically stirred solution of 12 g (0.09 mol) of freshly distilled benzonorbornadiene in 50 ml of anhydrous ether maintained at −40–60° *via* a Dry Ice–ethanol bath. The solution was allowed to warm to room temperature slowly and kept overnight. The solid was filtered from the cold ether solution and washed with cold ether to remove any traces of unreacted chlorosulfonyl isocyanate. The yield of crude product was 19.6 g (80%), mp 152–155° dec. Two recrystallizations from methylene chloride gave analytically pure material, mp 153–156° dec.

Anal. Calcd for $C_{12}H_{10}NSO_3Cl$: C, 50.80; H, 3.55; N, 4.94. Found: C, 50.54; H, 3.63; N, 4.81.

The nmr spectrum (CDCl$_3$) showed absorption at δ 7.42 (m, 4 H, aromatic), 4.03 (d, 1 H, J = 5.0 Hz, HCN), 4.00 (s, 1 H, bridgehead), 3.73 (s, 1 H, bridgehead), 3.43 (d, 1 H, J = 5.0 Hz, HCC=O), and 7.80 (s, 2 H, methylene). The infrared spectrum had characteristic bands at 3000, 2975 (saturated C–H stretch), 1810 (carbonyl stretch), 1495, and 1100 cm^{-1} (SO$_2$ stretch).

***exo*-3-Aza-4-ketobenzotricyclo[4.2.1.0^{2,5}]non-7-ene (6).** The reduction of **5** with sodium sulfite was accomplished by the procedure of Durst and O'Sullivan.[10] *N*-Chlorosulfonyl lactam **5** (17.7 g, recrystallized once from methylene chloride) in 150 ml of chloroform was added slowly to a magnetically stirred solution of 75 ml of 25% sodium sulfite and 35 ml of chloroform. The solution was stirred and kept at pH 7–9 by the addition of 10% potassium hydroxide over a period of 11 hr. The mixture was separated, and the chloroform solution after drying (MgSO$_4$) was evaporated leaving 11.0 g of a white powdery material. An infrared spectrum showed only one carbonyl band characteristic of a β-lactam (1740

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area corresponded to a 90° C2–O2 rotation on either side of the CH$_3$ X-ray location (see Figure 4). A shift for the 100 H circle model was computed as the average of 100 individual shifts.

(43) A shift computed using the average coordinates of *n* nuclear positions, and one calculated as an average of *n* shifts (using the *n* nuclear positions), will differ since the nuclear position cannot be factored out of the pseudo-contact expression. As an illustration of this point, consider the following: using the location of the Ln atom deduced from the Eu–LIS data for **7** and placing a methyl C atom at the X-ray position from **7**, the ratio of the calculated shifts for the 100 H circle and average H models of the methyl group was 1.2.

Table III. Atomic Fractional Coordinates[a] and Thermal Parameters (Å^2)[a,b] for Compound **7**

Atom	x	y	z	U or U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	0.1486 (4)	−0.1286 (2)	0.1316 (1)	4.6 (2)	4.8 (2)	4.1 (2)	−1.1 (2)	0.6 (2)	0.2 (2)
C2	0.2371 (4)	−0.1438 (3)	0.0705 (1)	4.2 (2)	4.7 (2)	4.2 (2)	−0.5 (2)	0.0 (2)	0.4 (2)
O2	0.2807 (3)	−0.2503 (2)	0.06789 (8)	7.0 (2)	4.6 (4)	4.9 (1)	0.0 (1)	0.5 (1)	−0.1 (1)
N3	0.3788 (3)	−0.0762 (2)	0.0583 (1)	3.9 (2)	6.0 (2)	2.6 (2)	−1.2 (2)	−0.1 (1)	0.6 (2)
C4	0.4999 (4)	−0.0347 (3)	0.0929 (1)	3.7 (2)	5.9 (2)	3.4 (2)	−0.5 (2)	−0.3 (2)	0.0 (2)
O4	0.6038 (3)	0.0220 (2)	0.06913 (9)	4.4 (1)	9.2 (2)	4.5 (1)	−2.9 (1)	−0.2 (1)	1.4 (1)
C5	0.5175 (4)	−0.0565 (4)	0.1611 (1)	4.2 (2)	6.5 (3)	4.1 (2)	0.6 (2)	−0.5 (2)	0.5 (2)
C6	0.3579 (4)	−0.0609 (3)	0.1993 (1)	5.3 (2)	6.6 (3)	2.6 (2)	0.4 (2)	−0.3 (2)	0.5 (2)
C7	0.2372 (4)	0.0241 (3)	0.1826 (1)	3.9 (2)	4.9 (2)	3.2 (2)	0.2 (2)	0.8 (2)	0.5 (2)
C8	0.1169 (4)	−0.0148 (2)	0.1437 (1)	3.2 (2)	4.6 (2)	3.7 (2)	−0.3 (2)	0.3 (2)	0.4 (2)
C9	0.2540 (5)	−0.1578 (3)	0.1872 (1)	6.6 (3)	5.0 (3)	4.1 (2)	0.4 (2)	1.3 (2)	1.2 (2)
C10	0.2385 (5)	0.1277 (3)	0.1984 (1)	5.0 (3)	6.0 (3)	4.5 (2)	0.0 (2)	0.1 (2)	−0.6 (2)
C11	0.1159 (6)	0.1911 (4)	0.1747 (2)	7.2 (3)	5.5 (3)	6.1 (3)	0.8 (3)	1.0 (2)	−0.9 (2)
C12	−0.0059 (5)	0.1531 (3)	0.1362 (2)	6.0 (3)	6.8 (3)	5.4 (2)	2.0 (3)	0.5 (2)	0.3 (2)
C13	−0.0062 (5)	0.0488 (3)	0.1202 (1)	3.9 (2)	7.7 (3)	4.6 (2)	−0.1 (2)	−0.1 (2)	−0.3 (2)
C14	0.3111 (7)	−0.2878 (4)	0.0069 (2)	7.7 (4)	7.7 (4)	5.3 (3)	0.8 (3)	0.2 (3)	−1.9 (3)
O2	0.2807 (3)	−0.2503 (2)	0.06789 (8)	7.0 (2)	4.6 (1)	4.9 (1)	0.0 (1)	0.5 (1)	−0.1 (1)
H1	0.037 (3)	−0.169 (2)	0.127 (1)	4.0 (8)					
H2	0.150 (3)	−0.129 (2)	0.033 (1)	3.7 (8)					
H3	0.384 (4)	−0.057 (2)	0.020 (1)	4.6 (1.0)					
H5a	0.571 (4)	−0.118 (2)	0.164 (1)	6.1 (1.2)					
H5b	0.584 (4)	0.003 (2)	0.177 (1)	4.5 (1.0)					
H6	0.382 (3)	−0.056 (2)	0.242 (1)	4.8 (9)					
H9a	0.322 (3)	−0.222 (2)	0.179 (1)	4.9 (1.0)					
H9b	0.183 (3)	−0.172 (2)	0.223 (1)	4.6 (9)					
H10	0.329 (4)	0.149 (2)	0.226 (1)	6.8 (1.1)					
H11	0.118 (4)	0.262 (3)	0.187 (1)	8.1 (1.3)					
H12	−0.103 (4)	0.204 (2)	0.121 (1)	8.1 (1.1)					
H13	−0.084 (4)	0.020 (2)	0.092 (1)	4.7 (1.0)					
H14a	0.342 (5)	−0.364 (3)	0.007 (2)	10.9 (1.6)					
H14b	0.220 (5)	−0.276 (3)	−0.020 (2)	12.5 (1.9)					
H14c	0.403 (5)	−0.248 (3)	−0.011 (2)	10.5 (1.7)					

cm^{-1}). The crude product was recrystallized from methanol–water to give 10.5 g (91%) of pure **6**, mp 142–144°. The mass spectrum showed a molecular ion at *m/e* 185.

Anal. Calcd for $C_{12}H_{11}NO$: C, 77.81; H, 5.99; N, 7.56. Found: C, 78.10; H, 6.15; N, 7.58.

The nmr spectrum showed absorption at δ 7.30 (broad s, 1 H, NH), 7.08 (m, 4 H, aromatic), 3.55 (d, 1 H, HCNH), 3.40 (s, 2 H, bridgehead), 3.00–3.20 (m, 1 H, HCC=O) and 1.70–2.30 (m, 2 H, methylene). The infrared spectrum had characteristic bands at 3400 (N–H stretch), 2960 (saturated C–H stretch), and 1740 cm^{-1} (carbonyl stretch).

Photolysis of 6 in Methanol. A sample of 1.5 g of **6** in 300 ml of anhydrous methanol was irradiated under nitrogen for a period of 47 hr with a 450-W Hanovia lamp through a Vycor filter. Solvent was removed *in vacuo* leaving a yellow oil which solidified on standing. Preliminary purification was effected by filtration of a chloroform solution of the product through silica gel. Evaporation of solvent and recrystallization of the resulting solid from chloroform gave 0.75 g of pure **7**, mp 168–171° dec. The mass spectrum showed a molecular ion at *m/e* 217.

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.44. Found: C, 71.88; H, 6.97; N, 6.17.

The nmr ($CDCl_3$) showed absorption at δ 7.10 (s, 4 H, aromatic), 6.60–7.00 (1 H, N–H), 4.18 (t, 1 H, J = 5.0 Hz, HCO–), 3.1–3.7 (m, 2 H, bridgehead), 3.25 (s, 3 H, OCH_3), 2.82 (m, 2 H, $-CH_2-C{=}O$), and 2.2–2.6 (m, 2 H, CH_2). The infrared spectrum (CCl_4) showed peaks at 3350 (N–H), 2950, 2900 (C–H), 1650 (C=O), and 1070 cm^{-1} (COC).

Photolysis of 6 in Ethanol. A sample of 2.55 g of **6** in 400 ml of absolute EtOH was photolyzed as above. After 26 hr, the solvent was removed by rotary evaporation depositing 25 g of residue which was chromatographed on 250 g of Woelm neutral alumina (activity grade I). The eluting solvent was benzene–chloroform (3:1); 250-ml fractions were taken. Evaporation of each fraction and analysis of the residue by nmr indicated that pure product had eluted in fractions 10–26 (0.7 g). Fractions 27–30 were combined (0.62 g). Integration of the nmr spectrum indicated that this sample contained a 1:1 mixture of **6** and **8**. The yield of **8** based on unreacted starting material was 41%. Recrystallization of the combined solids from fractions 10–26 from chloroform–hexane gave analytically pure material, mp 156–157°. The mass spectrum showed a molecular ion at *m/e* 231.

Anal. Calcd for $C_{14}H_{17}NO$: C, 72.70; H, 7.41; N, 6.05 Found: C, 72.60; H, 7.55; N, 5.72.

The nmr ($CDCl_3$) showed absorption at δ 7.10 (s, 4 H, aromatic), 6.53 (broad s, 1 H, N–H), 4.32 (t, 1 H, J = 5.0 Hz, HCO), *ca.* 3.60 (m, 1 H, bridgehead H1), *ca.* 3.23 (m, 1 H, bridgehead H6), 3.50 (m, 2 H, OCH_2CH_3), 2.83 (m, 2 H, methylene H5a, H5b), 2.40 (m, 2 H, methylene H9a, H9b), and 1.20 (t, 3 H, OCH_2CH_3, J = 7.0 Hz). The ir spectrum (CCl_4) had characteristic absorption at 3380 (N–H), 2960, 2925 (C–H), 1645 (C=O), and 1080 cm^{-1} (COC).

Photolysis of 6 in 1-Propanol. A sample of 3 g of **6** in 450 ml of *n*-propyl alcohol was photolyzed in the usual manner. After 26 hr, the solvent was removed *in vacuo* yielding 3.0 g of a residual oil. The oil was dissolved in $CHCl_3$ and deposited on a column containing 300 g of Woelm neutral alumina (activity grade I). The column was eluted with a 3:1 mixture of benzene–chloroform and 200-ml fractions were collected. Evaporation of the fractions and analysis of the residue showed that pure product had eluted in fractions 7–25 (0.8 g). The residues in fractions 26–36 were combined (0.8 g) and nmr integration indicated these fractions contained a 1:1 mixture of **6** and **9**. The yield of **9** was 36% based on unreacted starting material. Recrystallization of the combined solids from fractions 7–25 from ether gave analytically pure material, mp 118.5–119.5°. The mass spectrum showed a molecular ion at *m/e* 245.

Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.70. Found: C, 73.11; H, 7.81; N, 5.56.

The nmr spectrum ($CDCl_3$) showed absorption at δ 7.08 (s, 4 H, aromatic), 6.48 (1 H, N–H), 4.28 (t, 1 H, J = 5.0 Hz, HCO), 3.2–3.6 (m, 2 H, bridgehead), 3.38 (m, 2 H, OCH_2-), 2.82 (m, 2 H, $-CH_2C{=}O$), 2.2–2.6 (m, 2 H, CH_2), 1.58 (m, 2 H, J = 7.0 Hz, OCH_2CH_2-), and 0.92 (t, 3 H, J = 7.0 Hz, $OCH_2CH_2CH_3$). The infrared spectrum (CCl_4) showed peaks at 3250 (N–H), 2960, 2940 (C–H), 1660 (C=O), and 1080 cm^{-1} (COC).

Lanthanide Shift Reagent Procedure. The general procedure employed follows. An accurately weighed amount (~30–35 mg) of photoproduct was placed into a clean and dry nmr tube *via* a small tapered glass funnel. Dry $CDCl_3$ (0.4 ml, previously dried over preheated (120°) 4 Å molecular sieves[44]) was then added and the nmr spectrum was recorded at 1000-Hz sweep width.

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(44) The absolute magnitude of the Δ_{Eu} values is a function of the "dryness" of the solvent: J. M. Sanders and D. H. Williams, *J. Amer.*

Accurately weighed amounts of the Eu or Pr dpm shift reagents[45] were added in increments to the nmr tube. After each addition of shift reagent, the nmr tube was stoppered and vigorously shaken. In some cases, the nmr tube was placed into a beaker of warm tap water (40°) to effect solution. The spectrum was recorded after each addition of shift reagent, and the chemical shifts of all the protons were recorded (in Hz downfield from internal tetramethylsilane). The results of these experiments are listed in Table I.

X-Ray Crystal Structure of *exo*-2-Methoxy-3-aza-4-keto-7,8-benzobicyclo[4.2.1]nonene (7). The compound crystallized from methanol as colorless octagonal bipyramids in the orthorhombic space group *Pnaa*. A specimen with dimensions of *ca.* 0.1 × 0.1 × 0.2 mm, mounted parallel to the long crystal axis (*b*), was used for all space group work, cell parameter, and intensity measurements. The cell parameter and intensity data were obtained using a Siemens computer-controlled AED diffractometer with Ni-filtered Cu K radiation and the crystal was aligned to place *b* parallel to the diffractometer's ϕ axis. Unit cell parameters were obtained by the method of least squares from 21 2θ's determined automatically by a reflection centering program. The 2θ's ranged in magnitude from 19 to 79°, and the average difference between $2\theta_o$ and $2\theta_c$ was 0.036°. The cell parameters are $a = 8.010$ (5), $b = 12.904$ (8), and $c = 21.79$ (1) Å. The calculated crystal density assuming eight molecules per unit cell is 1.281 g cm^{-3}.

The intensity measurements covered the $h,k,\pm l$ octants of reciprocal space using the Siemens five-point scan technique.[46] A single standard, measured after every 20 reflections, was used to monitor and later correct for intensity fluctuations. In all, 2952 data were measured to a 2θ maximum of 100°. These measurements yielded 1375 unique data of which 1039 were 3σ above background and coded "observed"; the remaining data were coded "unobserved." All crystallographic calculations were performed with the X-ray System[47] on a UNIVAC 1108 computer.

The structure was solved by the routine application of direct methods. The phases of the 50 reflections with the largest $|E|$'s were automatically determined as functions of three origin-fixing phases by the X-ray system subprogram PHASE. An additional 107 phases (for reflections with $|E| > 1.0$) were determined from the first 50 known phases and an E map computed using these 157 terms (74 +, 83 −) clearly revealed the locations of 14 of the 16 heavy atoms. The two remaining atoms were located from a structure factor–electron density calculation. The residual (R)[48] based on these 16 atoms, which at this stage were all assigned carbon scattering factors,[49] was 0.31. The one nitrogen and two oxygen atoms were easily identified, following several cycles of structure refinement, by the magnitudes of their isotropic temperature factors. The remaining structure refinement proceeded normally using anisotropic temperature factors for C, N, and O and isotropic terms for H (initially located in a difference map). $1/\sigma$ (F) weights (ω) were used in the latter stage of refinement and the quantity minimized in the least-squares calculations was $\Sigma\omega^2(|F_o| - |F_c|)^2$. The "unobserved" data were included in the refinement only in those instances where $I_c > 3\sigma(I)$. The final R index was 0.037 and the weighted R index[50] was 0.029. The atomic fractional coordinates and thermal parameters are given in Table III.[51]

LSR–Substrate Calculations. The calculations used in this investigation were performed with a series of four Fortran IV programs written by the authors. The computations were carried out on a UNIVAC 1108 at the Computer Science Center, University of Maryland.

Chem. Soc., **93**, 641 (1971). Note that the values reported in ref 1 using undried CDCl$_3$ are smaller than those reported here.

(45) We recommend that the present convention of referring to these reagents as Eu(dpm)$_3$ and Pr(dpm)$_3$ be abandoned. These are empirical, not molecular, formulas. Even though the reagents may undergo complete dissociation in solution, the solid materials actually handled are Eu$_2$(dpm)$_6$ and Pr$_2$(dpm)$_6$ (ref 28 and 31).

(46) P. G. H. Trouton, *Siemens Rev.*, 37 (4), 22 (1970).

(47) "The X-ray System-Version of June 1972," Technical Report TR-192 of the Computer Science Center, University of Maryland, 1972.

(48) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

(49) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 24, 321 (1968).

(50) Weighted $R = (\Sigma w^2(|F_o| - |F_c|)^2/\Sigma|F_o|^2)^{1/2}$; $w = 1/\sigma(F)$.

(51) The calculated and observed structure factor table and a table giving the bond angles to hydrogen will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-1968. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.