as the CF_2 group, of both **1** and $\cdot CF_2CONH_2$, is bent 10° out-of-plane ($\Delta = 0.0002$). Thus, the a^F values will increase as the geometry becomes tetrahedral. Based on $a^F = 51.4$ for planar **1**, an isotropic $a^F = 62.6$ G is calculated for a 10° out-of-plane bend by INDO.[23] This calculated value (62.6) for nonplanar **1** can be compared to the experimentally observed a^F of 72 G for nonplanar $\cdot CF_2CONH_2$ where less withdrawal of spin density takes place.[18,20] This difference reflects the greater withdrawal of spin density by phenyl. Thus, the a^F (51.4) observed for **1** is still consistent with the planar geometry calculated by INDO.

The magnitude of all the $a^{F, H, \text{ or } ^{13}C}$ values varied only slightly, going from the symmetrical to the quinoid geometries in **1** and **2**.[24] Progressively rotating the CF_2 plane out of the phenyl ring's plane in **1** and **2** resulted in moderate increases in the calculated $a_F^{CF_2}$ and $a_{^{13}C}^{CF_2}$ splittings while the $a_{H_{o,m,p}}$ and a_{F_p} splittings decrease.[25] An 18 kcal/mol^{-1} barrier to this rotation is predicted in **1**.

In summary, the experimental and theoretical results support all-planar geometries for **1** and **2**.

(23) An unequivocal experimental or calculated value of isotropic fluorine splittings for planar 1, which explicitly defines the effect of spin density withdrawal on a^F, is desired. The discrepancy between the experimental and calculated hyperfine couplings for 1 and 2 was similar to that found previously for the benzyl radical, and ring geometry optimization improved the agreement; *i.e.*, see J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, **90**, 4021 (1968). The effects of new sets of spin coupling parameters, *Q*, in *ab initio* calculations of a_F as a function of geometry have been discussed (see H. Konishi and K. Morokuma, *ibid.*, **94**, 5603 (1972)), and the failure of expressions such as $a^F = Q_{eff}\,\rho\pi$ to predict experimental a^F values, even in a structurally related series of radicals, has been discussed (see M. Iwasaki, S. Noda, and K. Toriyama, *Mol. Phys.*, **18**, 201 (1970), and references therein).

(24) Very small absolute increases occurred for the values of $a_{H_{o,m,p}}$ while small decreases were observed for $a_F^{CF_2}$ and $a_C^{CF_2}$. These results are similar in magnitude and direction to those recently observed when the geometry of the benzyl radical was optimized; see D. L. Beveridge and E. Guth, *J. Chem. Phys.*, **55**, 458 (1971).

(25) The changes in the calculated hyperfine splittings going from the planar-quinoid geometry of 1 to that where the CF_2 plane is rotated 90° out-of-plane (and with a symmetrical ring) were a_{H_p} -5.61 to -0.16, a_{H_m} 3.29 to 2.08, a_{H_o} -5.83 to -1.75, $a_F^{CF_2}$ 39.9 to 44.4, and $a_{^{13}C}^{CF_2}$ 29.9 to 35.0. These results are entirely consistent with similar calculations on the benzyl radical; see J. A. Pople and D. L. Beveridge, *J. Chem. Phys.*, **49**, 4725 (1968).

(26) Undergraduate summer research participant, 1972.

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Nuclear Magnetic Resonance Shift Reagents. The Question of the Orientation of the Magnetic Axis in Lanthanide–Substrate Complexes[1]

Sir:

The utility of nmr shift reagents which function predominantly by the dipolar mechanism for structural and stereochemical problems is becoming abundantly clear.[2] After a brief flurry of reports[2a] which indicated that the magnitude of the shifts induced by lanthanide chelates could be satisfactorily correlated by distance factors alone, the importance of angular factors, as predicted by the expected proportionality of the shifts to $(3\cos^2\chi - 1)/r^3$, which would lead to either upfield or downfield shifts with the same reagent–substrate complex, has been clearly established.[2] The $(3\cos^2\chi - 1)/r^3$ dependence, where χ is the angle between the principal magnetic axis of the complex and the vector of length, *r*, connecting the metal atom and nucleus under consideration, is justified strictly only for axially symmetric, or effectively axially symmetric, complexes. Nonetheless, excellent fits have been obtained following $(3\cos^2\chi - 1)/r^3$ proportionality with complexes of shift reagents and alcohols which can hardly be expected to be strictly axially symmetric and, furthermore, with the assumption that χ is, in fact, the angle between the vector *r* and the O–metal bond of the complex.[2b,3]

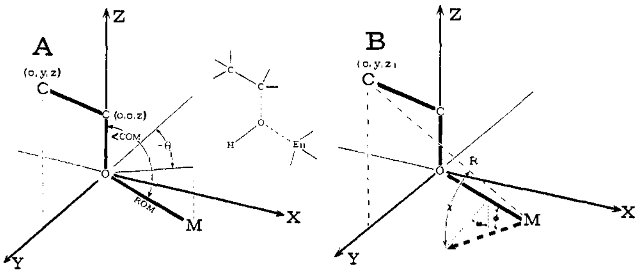

Figure 1. (A) Conventions for geometric parameters of metal atom in lanthanide chelate–alcohol complexes. (B) Parameters locating the principal magnetic axis with respect to the O–M bond. The angle ω is a dihedral angle for locating the magnetic dipole with respect to the O–C bond. It is defined as zero when the dipole lies in the plane determined by C–O–M and is on the opposite side of O–M from O–C.

This assumption might well be justified on the basis that it works, but it seems imperative to know the limits which should be placed on it. To this end, we have undertaken the correlation of lanthanide-induced shifts of rigid alcohols without assuming that the O–M bond of the complex is necessarily collinear with the magnetic axis. The metal atom is defined in space with respect to the oxygen, C-1, and C-2 of the alcohol by the distance ROM, and the angles ∠COM and θ (Figure 1A), while the orientation of the effective magnetic axis is defined by the angles φ and ω (Figure 1B). A computer program (CHMSHIFT) was used to find the best fit between observed lanthanide shifts and the five geometric and magnetic parameters for the metal atoms. The procedure involved maximizing the correlation coefficient for a least-squares fit of experimental[4] and calculated values of the shifts of both protons and ^{13}C resonances induced by praseodymium and europium chelates. No restrictions were placed on the values of

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(1) Supported by the National Science Foundation and the Public Health Service, Research Grant No. GM-11072 from the Division of General Medical Sciences.

(2) (a) *Cf.* W. D. Horrocks, Jr., J. P. Sipe, III, and J. R. Luber, *J. Amer. Chem. Soc.*, **93**, 5258 (1971), and W. D. Horrocks, Jr., and J. P. Sipe, III, *ibid.*, **93**, 6800 (1971), for extensive references to earlier studies; (b) M. R. Willcott, III, R. E. Lenkinski, and R. E. Davis, *ibid.*, **94**, 1742 (1972), and R. E. Davis and M. R. Willcott, III, *ibid.*, **94**, 1744 (1972).

(3) (a) J. Briggs, F. A. Hart, and G. P. Moss, *Chem. Commun.*, 1506 (1970); (b) J. Briggs, G. H. Frost, F. A. Hart, G. P. Moss, and M. L. Staniforth, *ibid.*, 749 (1970); (c) J. Briggs, F. A. Hart, G. P. Moss, and E. W. Randall, *ibid.*, 364 (1971); (d) the problem of the location of the principal magnetic axis has been considered very recently in a theoretical way by C. L. Honeybourne, *Tetrahedron Lett.*, 1095 (1972). See also the papers of H. Huber, *ibid.*, 3559 (1972); J. M. Briggs, G. P. Moss, E. W. Randell, and K. D. Sales, *J. Chem. Soc., Chem. Commun.*, 1180 (1972).

(4) The experimental shifts were determined on 1 *M* solutions of substrate in deuteriochloroform with five or six concentrations of lanthanide chelate. The shifts were strictly linear with concentration (correlation coefficient >0.99). The shifts reported here in parts per million are extrapolated from the least-squares fit and represent hypothetical shifts at 1 *M* chelate concentration.

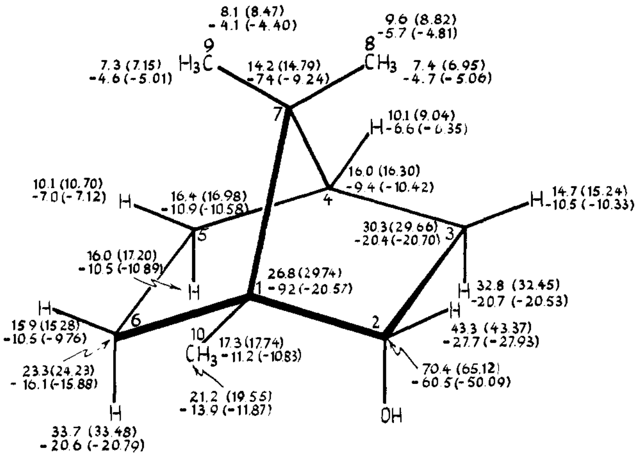

Figure 2. Calculated (in parentheses) and observed ^{13}C and ^{1}H shifts for lanthanide chelates and borneol. The values are in ppm, calculated for 1 *M* concentrations of alcohol and lanthanide chelate in $CDCl_3$: upper numbers for $Pr(FOD)_3$; lower numbers for $Eu(FOD)_3$.

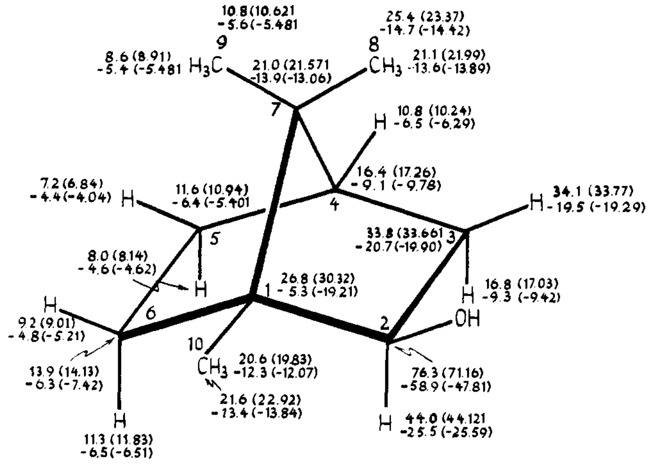

Figure 3. Calculated (in parentheses) and observed ^{13}C and ^{1}H shifts for lanthanide chelates and isoborneol. The values are in ppm, calculated for 1 *M* concentrations of alcohol and lanthanide chelate in $CDCl_3$: upper numbers for $Pr(FOD)_3$; lower numbers for $Eu(FOD)_3$.

the variables, save for ROM, which was restrained to the chemically reasonable range of 1–3.5 Å. The borneols were chosen for study because the coordinates of the substrate atoms can be rather accurately inferred from X-ray diffraction studies[5] and, except for the possibility (here neglected) of different rotational isomers about the C–O bond, are not complicated by conformational equilibria.[6] The experimental shifts for the protons and the carbons of borneol and isoborneol are shown in Figures 2 and 3 and agree well with those reported elsewhere.[3a] The ^{13}C chemical-shift assignments used for borneol were identical with the literature values.[7] However, the best fit between experimental and calculated shifts for isoborneol was obtained by interchanging the ^{13}C assignments[7a] for C-8 and C-10. This interchange is much more satisfactory than the alternative exchanges proposed elsewhere.[8]

In attempting the correlations, it became obvious almost at once that the C-1 and C-2 carbon shifts of borneol and isoborneol were subject to more than a dipolar influence. This was suspected previously[3] for C-2 and is in line with the large contact shifts produced with saturated amines and transition-metal chelates.[9] The proton shifts were much more amenable and produced excellent agreements between calculated and observed (correlation coefficient >0.99, $R \leq 0.026$)[2b] with gratifyingly reasonable geometric parameters (Table I). The O–M distances are similar to what has been found by X-ray diffraction for this general type of complex,[2a] ∠COM is wholly reasonable, and the dihedral angle θ is such as to have the metal in sterically favorable positions. The limits of significance of the geometric parameters, such as the difference between ROM for the Eu and Pr complexes, will be discussed in later papers. At present, we believe the values reported are good to perhaps better than 10%.

Table I. Geometric and Magnetic Parameters Calculated from Shift Data

Substrate	Shift reagent	∠COM, deg	ROM, Å	θ, deg[a]	ϕ, deg[a]	ω, deg[b]
Borneol	$Pr(FOD)_3$	132.8	2.71	91.1	2.4	23.3
Borneol	$Eu(FOD)_3$	134.5	2.38	90.0	0.2	0.0
Isoborneol	$Pr(FOD)_3$	129.5	2.70	266.6	1.6	140.7
Isoborneol	$Eu(FOD)_3$	129.6	2.51	276.5	0.04	80.4

[a] The angle θ is defined in such a way that C-3 is in the y,z plane; *cf.* Figure 1A. [b] The angle ω is ill-defined for small values of ϕ.

The carbon shifts were measured with a different spectrometer at somewhat different temperatures and are expected to have a different complexation equilibrium, but should have the *same* geometry. The geometries determined by the proton shifts gave excellent correlations (>0.99) of the carbon shifts, except for C-1 and C-2, with slightly different slopes than for the protons. That the shifts of C-1 and C-2 fail to be correlated by the dipolar equation suggests a contact interaction contribution to these shifts, a matter which is considered in more detail in other communications.[9b,10]

The most important finding of the present study is that the best correlations are obtained with quite small values of ϕ (*cf.* Table I), even though the shifts are much more sensitive for ϕ than any other variable. This result justifies the assumption[2b,3] that the effective magnetic axes of alcohol-chelate complexes are essentially collinear with the O–M bonds. For the compounds we have run, the maximum value of χ encountered for the favored geometries was 40°. This means that effective axial symmetry must be involved if the $(3\cos^2\chi - 1)/r^3$ relation gives a satisfactory fit, because the correction term for nonaxial symmetry in-

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(5) The coordinates were derived from those given for the camphane derivative by G. Ferguson, C. J. Fritchie, J. M. Robertson, and G. A. Sim, *J. Chem. Soc.*, 1976 (1961).

(6) The hydrogens of the methyl groups were considered to have an average location at the center of the circle described by the protons in a freely rotating methyl group. Separate calculations indicated that this would introduce less than a few per cent error for the hydrogens of C-10, as long as $(3\cos^2 - 1) > 0$.

(7) (a) E. Lippmaa, T. Pehk, J. Paasivirta, N. Belikova, and A. Plate, *Org. Mag. Resonance*, 2, 581 (1970); (b) H. J. Schneider and W. Bremser, *Tetrahedron Lett.*, 5197 (1970); (c) see ref 3c.

(8) O. A. Gansow, R. M. Willcott, III, and R. E. Lenkinski, *J. Amer. Chem. Soc.*, 93, 4295 (1971).

(9) (a) I. Morishima, K. Okada, T. Yonezawa, and K. Goto, *ibid.*, **93**, 3922 (1971); (b) S. R. Johns, G. E. Hawkes, and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, in press.

(10) G. E. Hawkes, C. Marzin, S. R. Johns, and J. D. Roberts, *ibid.*, **95**, 1661 (1973).

volves, among other things, $\sin^2 \chi$ which, for $\chi = 40°$, will hardly be negligible.

Further experience will be needed to tell whether ϕ is close to zero or is actually zero; in any case, it appears that the complexes investigated here are effectively axially symmetric, with the magnetic axis essentially collinear with the O–M bond.

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(11) NATO Postdoctoral Fellow, 1970–1972.

(12) Deutsche Forschungsgemeinschaft Postdoctoral Research Fellow, 1970–1971.

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Nuclear Magnetic Resonance Shift Reagents. Quantitative Estimates of Contact Contributions to Lanthanide-Induced Chemical-Shift Changes for *exo*-Norbornylamine[1]

Sir:

The possibility of contributions from contact interactions to the predominantly dipolar-induced changes in chemical shifts produced by lanthanide-shift reagents has been widely recognized.[2] Such contributions might be expected to be especially large at the substrate atom directly coordinated to the lanthanide[3] and, in general, be confined with saturated substrates at least to carbons and hydrogens in the immediate vicinity of the coordination site. Nonetheless, there is no firm basis for the prediction of the direction or magnitude of contact contributions to lanthanide-induced shifts on carbon or proton spectra.

In an accompanying communication[4] and elsewhere, it has been shown (1) that ^{13}C resonances appear to be more sensitive to contact contributions than proton resonances involving the same number of intervening bonds to the site of the metal–atom coordination, and (2) that such contributions are important with both alcohols and amines using lanthanide chelates, specifically those of europium and praseodymium. The magnitude and direction of the contact corrections are considered here for the specific case of *exo*-norbornylamine which has the advantage over the aliphatic amines studied previously of being stereochemically rigid.[5]

The procedure used to obtain quantitative estimates of the contact-shift corrections of the carbon resonances was similar to that used for borneol and isoborneol,[4] namely, to determine the geometric and magnetic parameters of the complexes from the proton shifts, and to determine the deviations of the carbon shifts from those expected for the dipolar contributions. Allowance was made for the possibility of effects arising from the slightly different conditions used for measuring the ^1H and ^{13}C shifts by making a separate least-squares analysis for the ^{13}C shifts. The proton and carbon shifts used for this purpose were determined as described earlier[4] and are shown in Figure 1. Here again, it will be seen that a β carbon (C-1 but not C-3) shows an *upfield* shift with a europium chelate.[6]

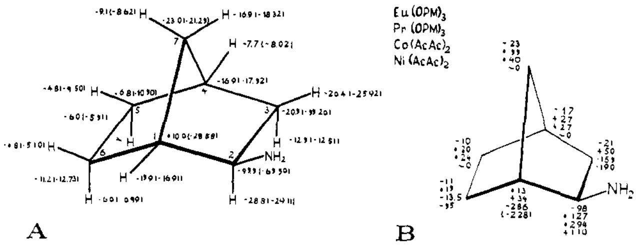

Figure 1. (A) Calculated (in parentheses) and observed ^{13}C and ^1H shifts for *exo*-norbornylamine with Eu(DPM)$_3$. The values are in ppm, calculated for 1 *M* concentrations of amine and lanthanide in CDCl$_3$. (B) Summary of ^{13}C shifts produced by various metal chelates in downward order Eu(DPM)$_3$, Pr(DPM)$_3$, Co(AcAc)$_2$, and Ni(AcAc)$_2$.

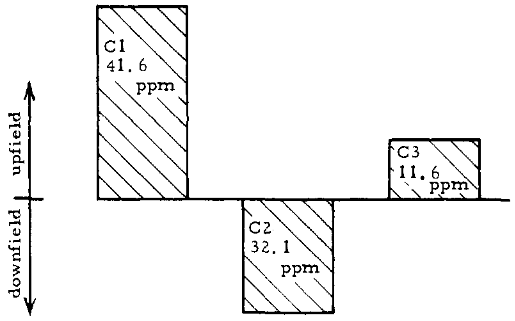

Figure 2. Estimated deviations from dipolar shifts due to contact interactions for *exo*-norbornylamine and Eu(DPM)$_3$.

For Eu(DPM)$_3$, an excellent fit (correlation coefficient = 0.997, R = 0.036) could be obtained for the proton resonances with RNM at 3.10 Å, which was rather longer than expected. However, the goodness of fit is not very sensitive to RNM, and with RNM held constant at 2.50 Å and the other parameters allowed to vary to obtain the best fit, the proton shifts gave a correlation coefficient of 0.997, R = 0.039, with $\angle$CNM = 137°, θ = 259°, ϕ = 4°, and ω = 74°.[4,7] With the geometry of the complex determined by the proton shifts, carbons 4, 5, 6, and 7, but *not* C-1, C-2, and C-3, give an excellent correlation (correlation coefficient = 0.987) with expectations of the dipolar contributions. Figure 2 shows the pattern of the deviations observed for C-1, C-2, and C-3 which, we believe, are best ascribed to contact contributions to the shifts.[6] It is possible that the contact interaction with lanthanide chelates extends farther along the carbon chain to C-6 and C-7, but so far we have no consistent evidence for this.

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(1) Supported by the National Science Foundation and the Public Health Service, Research Grant No. GM-11072 from the Division of General Medical Sciences.

(2) For references see W. D. Horrocks, Jr., J. P. Sipe, III, and J. R. Luber, *J. Amer. Chem. Soc.*, 93, 5258 (1971), and W. D. Horrocks, Jr., and J. P. Sipe, III, *ibid.*, 93, 6800 (1971).

(3) Very large contact shifts have been observed for the resonances of ^{14}N coordinated to lanthanide chelates by M. Witanowski, L. Stefanik, M. Janusewski, and Z. W. Wolkowski, *Tetrahedron Lett.*, 1653 (1971); *Chem. Commun.*, 1573 (1971). These shifts are all the more impressive in that they are opposite in direction to expected dipolar shifts of perhaps 200 ppm.

(4) G. E. Hawkes, D. Leibfritz, D. W. Roberts, and J. D. Roberts, *J. Amer. Chem. Soc.*, **95**, 1659 (1973).

(5) Studies of a very similar nature and purpose have been carried out by O. A. Gansow, P. A. Loeffler, R. E. Davis, M. R. Willcott, III, and R. E. Lenkinski, *J. Amer. Chem. Soc.*, in press.

(6) (a) R. J. Cushley, D. R. Anderson, and S. R. Lipsky, *J. Amer. Chem. Soc., Chem. Commun.*, 636 (1972); (b) C. Marzin, D. Leibfritz, G. E. Hawkes, and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, in press; (c) see also, M. Kainosho and K. Ajisaka, *Chem. Lett.*, 1061 (1972).

(7) The values of ω are not very well defined when ϕ is small. Angle θ is defined[4] so that C-3 lies in the y–z plane, and for 185°, the metal is located so as to be about 28° short of trans to the C-1–C-2 bond.