12:88 ratio by derivatization of the parent thiane[3] with methyl iodide followed by anion exchange with a Dowex 1X8-100 resin (hydroxide form) followed by neutralization with perchloric acid and were separated by crystallization from water: predominating isomer, mp 149–150°, minor isomer, mp 173–174°.[8] Configuration was assigned on the basis of cmr spectra; isomer 2 of mp 149–150°, formed in major amount has the downfield S-methyl (25.48 ppm from TMS) and 3,5-methylene (25.10 ppm) groups whereas the more compressed axial isomer 1 displayed the upfield methyl (16.61 ppm) and 3,5-methylene (19.04 ppm) signals, as might be expected on the basis of analogy with methylcyclohexanes.[9] The configurations were proved beyond the shadow of a doubt by X-ray crystallographic analysis of both isomers.

Crystals of 1 are orthorhombic, space group $P2_12_12_1$ (D_2^4), $a = 11.02 \pm 0.01$, $b = 13.57 \pm 0.01$, $c = 9.25 \pm 0.01$ Å, $Z = 4$. Isomer 2 crystallizes in the orthorhombic system, space group $Pbca$ (D_{2h}^{15}), $a = 13.25 \pm 0.01$, $b = 12.59 \pm 0.01$, $c = 17.22 \pm 0.01$ Å, $Z = 8$. Intensity data were recorded on an Enraf-Nonius CAD-3 diffractometer operating in the θ–2θ scanning mode with Zr-filtered Mo Kα (λ 0.7107 Å) radiation. Both structures were solved by the heavy-atom approach and the atomic parameters (anisotropic C, Cl, O, S; fixed H contributions) were refined by full-matrix least-squares calculations to $R = 0.063$ over 875 observed reflections [$I > 2\sigma(I)$] for 1 and $R = 0.104$ over 890 reflections for 2.

In addition to verifying isomer assignments the X-ray investigations provide details of the molecular dimensions which reveal no significant differences between the isomers *except* around C(2),C(6) where the mean value (assuming C_s molecular symmetry) of the C–C–S angle is $106.8 \pm 1.0°$ for 2 and $115.3 \pm 0.6°$ for 1. Associated mean endocyclic dihedral angles C(6)SC(2)C(3) and SC(2)C(3)C(4) are 64 and 69°, respectively, for 2 in contrast to substantially smaller values of 46 and 59° in 1, the differences being a measure of the ring flattening which occurs at sulfur in the axial methyl isomer 1 in order to relieve overcrowding with the syn-axial hydrogens.

Equilibration of the two isomers at 100° in chloroform-*d* for 57 hr led to identical equilibrium mixtures as shown by pmr; the ratio of the area of the methyl signal of 2 (3.03 ppm) to that of 1 (2.93 ppm) was 1.42. The composition was confirmed by a quantitative ^{13}C analysis of the mixture on a Varian XL-100 instrument with Fourier transform using gated decoupling and a 60-sec pulse delay time to minimize effects of nuclear Overhauser enhancement and of possibly unequal relaxation times of corresponding carbon nuclei; the ratio of the S-methyl signals of the two isomers was 1.48 and that of the 3,5-methylene signals 1.45. We thus conclude that $K = 1.45 \pm 0.05$ at 100° and $\Delta G°_{100} = -0.275$ kcal/mol favoring the equatorial isomer. The equilibrium position of the unbiased S-methylthianium perchlorate (3) is probably very similar, since the 4-*tert*-butyl group does not usually cause a major disturbance in the direct equilibration method.[10] Accordingly, the

S-methyl ^{13}C resonance of 3 was found at 22.10 ppm (calcd δ 22.06 ppm from $\delta = \delta_a/(K + 1) + K\delta_e/(K + 1)$ and $K^{25}_{calcd} = 1.592$ assuming $\Delta G_{25}° = \Delta G_{100}°$).

In the case of sulfoxides, it has been calculated[11] that the axial isomer is preferred because of a dominating O/H attraction. In the S-methylthianium salts, there is a slight net axial repulsion, but much smaller in magnitude than that in axial methylcyclohexane. If one constructs a model of the axial isomer 1 with the equatorial ring geometry (which might be considered the "natural" geometry of the thianium ring) one finds that the CH$_3$/H(3,5) distance d is nearly the same in the sulfur compound as in axial methylcyclohexane, as a result of a compensation of the increased ring-CH$_3$ bond length (which increases d) and the increased ring puckering (which decreases d). The large change of torsion angles in 1 (as compared to 2) indicates, however, that there is a very facile (*i.e.*, energetically cheap) flattening of the ring which greatly increases d and thus diminishes the energy of the axial form 1. An energetically cheap deformation of comparable magnitude is not possible in axial methylcyclohexane, presumably due to steric problems caused by the geminal equatorial hydrogen on the ring atom bearing the methyl group.[12] In the sulfonium salt 1 this hydrogen atom is replaced by an unshared electron pair, which evidently offers much less resistance to strain relief of the axial methyl group by torsional deformation.

(11) N. L. Allinger, J. A. Hirsch, M. A. Miller, and I. J. Tyminski, *J. Amer. Chem. Soc.*, **91**, 337 (1969).
(12) D. H. Wertz and N. L. Allinger, *Tetrahedron*, in press.

Ernest L. Eliel,* Rodney L. Willer

*W. R. Kenan, Jr., Laboratories of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27514*

Andrew T. McPhail, Kay D. Onan

*Paul M. Gross Chemical Laboratory, Duke University
Durham, North Carolina 27706*

Lanthanide Shift Reagents. A Model Which Accounts for the Apparent Axial Symmetry of Shift Reagent Adducts in Solution

Sir:

Insofar as nuclear resonance displacements induced by lanthanide shift reagents (LSR's) are dipolar in origin, they hold the promise of supplying valuable information about the geometries and conformations of substrate molecules in solution.[1] Equation 1 gives the

(8) Both isomers were of correct elemental composition. The minor isomer was isolated in pure form from an equilibrated mixture (see below); it is the less soluble.
(9) D. K. Dalling and D. M. Grant, *J. Amer. Chem. Soc.*, **94**, 5318 (1972).
(10) *Cf.* E. L. Eliel, *Chem. Ztg.*, **97**, 582 (1973).

(1) For current reviews see (a) R. E. Sievers, Ed., "Nuclear Magnetic Resonance Shift Reagents," Academic Press, New York, N. Y., 1973; (b) W. D. Horrocks, Jr., in "NMR of Paramagnetic Molecules; Principles and Applications," G. N. LaMar, W. DeW. Horrocks, Jr., and R. H. Holm, Ed., Academic Press, New York, N. Y., 1973, Chapter 12; (c) J. Reuben, *Progr. Nucl. Magn. Resonance Spectrosc.*, **9**, 1 (1973).

$$\frac{\Delta H^{\mathrm{dip}}}{H} = -\frac{1}{3N}\left[\chi_z - \frac{1}{2}(\chi_x + \chi_y)\right]\left\langle\frac{3\cos^2\theta - 1}{r^3}\right\rangle - \frac{1}{2N}[\chi_x - \chi_y]\left\langle\frac{\sin^2\theta\cos 2\phi}{r^3}\right\rangle \quad (1)$$

general form of the expression for dipolar shifts, $\Delta H^{\mathrm{dip}}/H$, where the χ's are the principal molecular magnetic susceptibilities and r, θ, and ϕ are the usual spherical polar coordinates of the resonating nucleus in the coordinate system of the principal magnetic axes. Most workers have chosen to ignore the second term in eq 1, and, indeed, there is compelling evidence from studies[2-6] on a variety of rigid substrate molecules that the first term of eq 1 satisfactorily accounts for the observed shift ratios and in some cases yields chemically reasonable lanthanide–substrate bond distances. It now appears that the most serious discrepancies between the data and the first term of eq 1 are often due to nonnegligible contact contributions to the observed shifts.[7-10] The success of this simple approach has been a puzzle to us[11,12] and others[13-15] because all of the available evidence from X-ray studies[16] shows that LSR adducts do not possess axial symmetry in the solid state. Moreover, our single-crystal studies[12] on the $\mathrm{Ln(dpm)_3(4\text{-}pic)_2}$[17] series reveal them to have highly nonaxial magnetic properties. Briggs, et al.,[18] pointed out that if a substrate molecule is freely rotating[19] about an axis which passes through the lanthanide ion, then the shifts will conform to an equation of the form of the first term of eq 1, where θ now refers to the angle made by the radius vector with the axis of rotation rather than the symmetry axis. This model does not appeal to us as being a realistic general explanation for the apparent axial symmetry observed in LSR experiments. A careful analysis of the solid state structural results for $\mathrm{Ho(dpm)_3(4\text{-}pic)_2}$ reveals that in the course of rotation of the picoline ligand about the Ho–N bond axis the ortho hydrogen and three of the carbonyl oxygen atoms would approach to a minimum distance of 1.9 Å, which is 0.7 Å less than the sum of their van der Waals radii.

(2) R. E. Davis and M. R. Willcott, *J. Amer. Chem. Soc.*, **94**, 1744 (1972).
(3) G. E. Hawkes, C. Marzin, S. R. Johns, and J. D. Roberts, *J. Amer. Chem. Soc.*, **95**, 1661 (1973).
(4) P. H. Mazzocchi, H. L. Ammon, and C. W. Jameson, *Tetrahedron Lett.*, 573 (1973).
(5) R. M. Wing, T. A. Early, and J. J. Uebel, *Tetrahedron Lett.*, 4153 (1972).
(6) R. M. Wing, J. J. Uebel, and K. K. Anderson, *J. Amer. Chem. Soc.*, **95**, 6046 (1973).
(7) G. E. Hawkes, C. Marzin, S. R. Johns, and J. D. Roberts, *J. Amer. Chem. Soc.*, **95**, 1661 (1973).
(8) C. Marzin, D. Liebfritz, G. E. Hawkes, and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, **70**, 562 (1973).
(9) B. F. G. Johnson, J. Lewis, P. McArdle, and J. R. Norton, *J. Chem. Soc., Chem. Commun.*, 535 (1972).
(10) A. A. Chalmers and K. G. R. Pachler, *Tetrahedron Lett.*, 4033 (1972).
(11) W. D. Horrocks, Jr., J. P. Sipe, III, and J. R. Luber, *J. Amer. Chem. Soc.*, **93**, 5258 (1971).
(12) W. D. Horrocks, Jr., and J. P. Sipe, III, *Science*, **177**, 994 (1972).
(13) R. E. Cramer and K. Seff, *J. Chem. Soc., Chem. Commun.*, 400 (1972).
(14) R. E. Cramer and K. Seff, *Acta Crystallogr., Sect. B*, **28**, 3281 (1972).
(15) J. J. Uebel and R. M. Wing, *J. Amer. Chem. Soc.*, **94**, 8910 (1972).
(16) See, for instance, Dyer, *et al.*, in ref 1a, pp 33–40, and references cited therein.
(17) Abbreviations: dpm = 2,2,6,6-tetramethylheptanedionate ion; 4-pic = 4-picoline; Ln = lanthanide ion.
(18) J. M. Briggs, G. P. Moss, E. W. Randall, and K. D. Sales, *J. Chem. Soc., Chem. Commun.*, 1180 (1972).
(19) Or is confronted with an n-fold barrier, where $n \geq 3$.

That such a rotation would take place with no energy barrier is unrealistic. Similar steric constraints are expected to occur in most other LSR–substrate adducts.

It is the purpose of this communication to offer an alternative, physically reasonable model, which is capable of accommodating the experimental facts from both solid state and solution nmr studies. Our model assumes that LSR adducts exist in solution as an ensemble of many rapidly interconverting geometrical isomers. The stereochemical lability of such seven- and eight-coordinate species is well established, and interconversions between isomers are expected to be rapid on the nmr time scale.[20] Each individual isomer has its own distinctive magnetic properties[21] (susceptibility tensor) and none of them are necessarily, or even very likely to be, axially symmetric. There may or may not be energetically significant barriers to isomer interconversions. With two additional provisos: (1) the number of interconverting isomers or fluctional forms is of the order 30 or more; (2) the substrate, through its influence on the ligand field in the individual isomers, exhibits a statistical bias to lie in proximity to an axis of maximum or minimum susceptibility, it is our contention that this model will lead to net shifts whose ratios conform reasonably well to the first term of eq 1.

A computer program was written to calculate dipolar shifts for two representative substrate ligands, namely, cyclohexanol (**1**) and isoquinoline (**2**), using the full

1   2
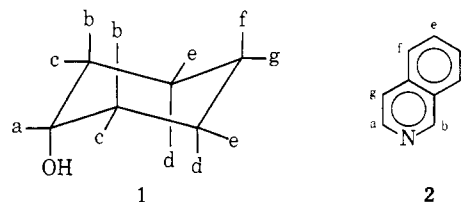
form of eq 1. The axes of the susceptibility tensor were randomly oriented with respect to the substrate molecule by choosing eulerian angles with the aid of a random number routine. The substrate was constrained to lie randomly within an arbitrary preset angle, β, of an extremum susceptibility axis. The magnitudes of the principal susceptibilities were themselves allowed to fluctuate, again randomly, by $\pm 20\%$ of the values determined experimentally[12] on the Ln-$(dpm)_3(4\text{-}pic)_2$ complexes. When the results of many calculations were averaged, it was found that the averaged shift ratios and magnitudes did not change significantly after 30–50 iterations. The average shift ratios for 20 runs on cyclohexanol[22] using different sets of randomly chosen parameters were for protons a–g (see structure **1**) respectively: 1.000, 0.392 (13), 0.579 (32), 0.658 (25), 0.307 (14), 0.284 (10), 0.273 (11).[23] These may be compared with the axial[24] ratios calculated from the model employed: 1.000, 0.387,

(20) See E. L. Muetterties, *Inorg. Chem.*, **12**, 1963 (1973), and references therein.
(21) The extremely short electronic spin–lattice relaxation times assure us that the magnetic properties will instantaneously follow the nuclear displacements involved in the isomer interconversions.
(22) Chair conformation, hydroxyl group axial, Ln–O = 2.7 Å, $\angle$Ln–O–C = 130°, C–O = 1.43 Å, C–C = 1.54 Å, C–H = 1.1 Å, all substrate angles tetrahedral, $\beta = 45°$.
(23) Standard deviations of the least significant figures are given in parentheses.
(24) The axis in question is that axis, rotation of the ligand about which, will not change the *aspect* of the ligand which is presented to the lanthanide ion in the various complexes.

0.568, 0.650, 0.302, 0.281, 0.271. In order to obtain a comparison with the expectations of the axial model with the same LSR-substrate distance used in the simulation, the converged average ratios for *each* of the 20 computer runs were treated as *observed* ratios and R values[2] were calculated. These ranged from 9.8 to 0.6% and averaged 4.4%.[25] In most cases closer agreement with an axial model could be obtained by allowing the Ln–O distance to vary from that employed in the simulation. Insofar as the present model may represent reality, this finding implies that LSR-substrate distances determined from nmr experiments by *assuming* an axial model may not reliably reflect the actual values of these quantities and deviations up to 0.5 Å and more are not unlikely. The average shift ratios for 20 runs on isoquinoline[26] were, for protons a–g (see structure **2**) respectively: 1.000, 1.000,[27] 0.252 (4), 0.144 (6), 0.154 (8), 0.248 (13), 0.439 (19). These may be compared with the axial ratios calculated from the model employed: 1.000, 1.000, 0.250, 0.141, 0.150, 0.243, 0.432. The R values calculated as described above ranged from 9.9 to 0.7% and averaged 4.6%.

An alternative model,[12,28] which assumes that shift reagent adducts in solution largely maintain the structure and properties found in the solid state, has certain inadequacies which are overcome by the present model. Although the earlier model accounted[12] quite well for the 4-methyl shifts of 4-picoline in the Ln-(dpm)₃(4-pic)₂ systems, it predicted 2- and 3-proton

shifts which were too large.[29] In addition, even the 4-methyl resonance shift was in poor agreement for the thulium system. Using a particular random number sequence and the experimental susceptibility tensors[12] for the Ln(dpm)₃(4-pic)₂ series, Ln = Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, and Yb, we calculate the following shifts for the 1-proton (a) of isoquinoline in the above sequence: 30.2, 14.5, 2.2, −12.7, 203.6, 244.9, 110.7, −42.0, −139.8, −31.7 ppm (298°K, β = 45°). The calculated negative Tm shift is larger than that of the Er and Yb systems, as is observed experimentally.[30] It should be noted that in its prediction of effective axial symmetry[24] the present model is completely independent of adduct stoichiometry.

While it is obvious that (with the qualification of a slight bias) an *infinite* number of randomly chosen isomers (a biased uniform distribution of substrate ligands with respect to the principal magnetic axes) would conform exactly to the expectations of axial symmetry, we have demonstrated that a dynamic equilibrium between a relatively small number of interconverting forms will lead to shift ratios which will approximate, but in general do *not exactly equal*, those derived from an axial model. Many of the details of the simulation are not necessarily realistic, *viz.*, unit weights for all contributing isomers, arbitrary angular constraints, and choice of susceptibility tensor components. However, the major finding, that resonance shift ratios will, within reasonably broad limits, conform to an axial[24] model, can be expected to be independent of the parameters employed.

(25) It should be noted that the ratios for the simulated individual contributing forms depart markedly from the expectations of axial symmetry. For example, in a run which yielded an R value of 0.6% the ratios for protons b–g respectively fell in the following ranges: −0.502 to 0.600, −1.698 to 0.827, −1.114 to 1.072, −0.693 to 0.541, −0.458 to 0.365, −0.398 to 0.431, while the converged average values were respectively: 0.389, 0.573, 0.653, 0.304, 0.282, 0.272.

(26) Ln–N = 2.53 Å, coordination along nitrogen lone pair axis, β = 45°.

(27) For each iteration a C₂ rotation of the substrate was performed and the results were averaged; this accounts for the identity of the calculated a and b proton shifts.

(28) R. E. Cramer and R. Dubois, *J. Amer. Chem. Soc.*, **95**, 3801 (1973).

(29) J. P. Sipe, III, Ph.D. Thesis, The Pennsylvania State University, 1973. For instance using eq 1, the susceptibility tensor data for Eu-(dpm)₃(4-pic)₂ of ref 12 (η = 18°) and geometric factors were calculated from the solid state structural data; dipolar shifts for the 4-picoline protons 2-H, 3-H, and 4-CH₃ were calculated to be −18.0, −5.4, and −2.5 ppm, respectively, at 298°K, when the nonequivalent 2-H and 3-H shifts are averaged. Variation of the η parameter failed to improve the agreement with the room temperature solution shift data (−12.0, −4.2, −3.0 ppm).

(30) W. D. Horrocks, Jr., and J. P. Sipe, III., *J. Amer. Chem. Soc.*, **93**, 6800 (1971).

William DeW. Horrocks, Jr.

*The Grover Cleveland Chandlee Laboratory
Department of Chemistry, The Pennsylvania State University
University Park, Pennsylvania 16802*

Received October 9, 1973

Book Reviews

Organic Chemistry. Third Edition. By R. T. MORRISON and R. N. BOYD. Allyn and Bacon, Inc., Boston, Mass. 1973. ix + 1258 pp. $17.95.

The third edition of this textbook is a result of a conservative and effective expansion, with a few deletions and modifications, of the second edition. The previous editions of this textbook have traditionally been well liked by students because of their clarity and organization. You will find no radically different methods for presentation of fundamental material in the third edition. The basic organization and approach have not been altered.

There must, however, be some changes in a new edition, and I will try to briefly mention those which came to my attention. (a) The initial discussion of resonance is presented much earlier in Chapter 6 on alkenes. As a result, the discussion of allyl radical

stability and 1,4-addition reactions of conjugated dienes can be presented to the student much more easily and in a clearer manner. In the previous edition, resonance was not initially introduced until Chapter 10 in the discussion of aromaticity. (b) Some of the chapters in the earlier edition have been combined. Ethers and epoxides are discussed together in Chapter 17, and the discussion of glycols is now included in the chapter on alcohols. The small chapter on diazonium salts in the second edition has been incorporated into one of the chapters on amines. The chapter on dicarboxylic acids is now included in Chapter 18 on carboxylic acids, and the separate chapter on keto acids has been deleted.

Slight feelings of nostalgia set in when one realizes that Körner's method of absolute orientation of benzene, balancing oxidation-reduction equations, and classical molecular weight determination