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.

Geoffrey E. Hawkes,[11] Dieter Leibfritz[12]
Donald W. Roberts, John D. Roberts*
Contribution No. 4482
Gates and Crellin Laboratories of Chemistry
California Institute of Technology
Pasadena, California 91109

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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]

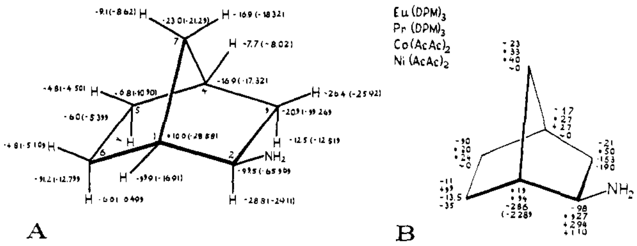

Figure 1. (A) Calculated (in parentheses) and observed ^{13}C and ^1H shifts for *exo*-norbornylamine with Eu(DPM)$_3$. The values are in ppm, calculated for 1 *M* concentrations of amine and lanthanide in CDCl$_3$. (*B*) Summary of ^{13}C shifts produced by various metal chelates in downward order Eu(DPM)$_3$,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

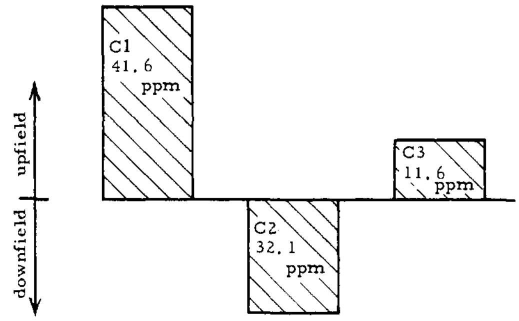

Figure 2. Estimated deviations from dipolar shifts due to contact interactions for *exo*-norbornylamine and Eu(DPM)$_3$.

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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[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.

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[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.

Authentic contact contributions to the carbon shifts of *exo*-norbornylamine are produced by cobalt and nickel acetylacetonates (Figure 1B) which reflect the trends previously observed.[6,8,9] It will be seen that the deviations from the carbon shifts which we have observed with Eu(DPM) and *exo*-norbornylamine as well as those with borneol and isoborneol and lanthanide chelates[4] fit the idea that the contact contributions for these cases are *opposite in sign* for the α and β carbons, and are larger for the more highly substituted carbon.[6b] Furthermore, the evidence is that the praseodymium contact contributions are *opposite in sign* to the europium contact contributions. This is most clearly seen for the borneol–isoborneol carbon shifts[4] but can also be qualitatively inferred from the difference between the C-1 and C-2 praseodymium-induced shifts shown in Figure 1B.

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(9) The sizable downfield shift of C-6 produced by $Ni(AcAc)_2$, which contrasts to the very small shifts at C-4, C-5, and C-7, may represent a special long-range stereospecific contact contribution; see also S. R. Johns, R. A. Smith, G. E. Hawkes, and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, in press.

(10) NATO Postdoctoral Fellow, 1970–1972.

Geoffrey E. Hawkes,[10] Claude Marzin
S. R. Johns, John D. Roberts*
Contribution No. 4484
Gates and Crellin Laboratories of Chemistry
California Institute of Technology
Pasadena, California 91109

Received June 27, 1972

Dynamics of Axial Ligation in Metalloporphyrins. II. Porphyrin "Inversion" and Halogen Exchange in High-Spin Iron Complexes

Sir:

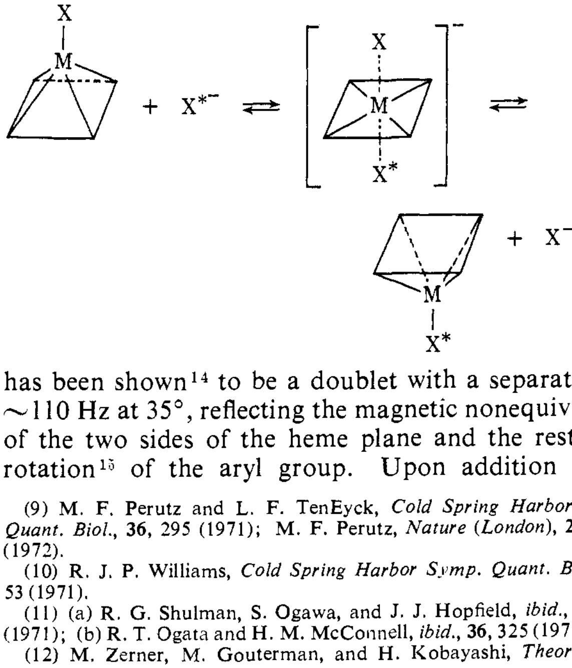
The systematic characterization of the stereochemistry[1] of iron porphyrins has led to the elucidation of the interrelation of a number of their structural and magnetic features which not only describe the behavior of the simple inorganic model compounds but also reflect some important biological functions[2] of various classes of heme proteins. Thus structural[1] and magnetic data[3] have revealed that high-spin, HS, forms of iron porphyrins suffer significant displacements of the iron atom out of the porphyrin plane. These displacements, which should be larger for the ferrous[4] (~0.75 Å) than the ferric[5,6] ion (~0.4–0.5 Å), reflect the inability of the tetrapyrrole "hole" to accommodate[1] these sizable HS ions. Hence five-coordinate geometry is common in the HS complexes. Upon addition of a sixth ligand, the spin multiplicity of the ground state decreases, generally yielding diamagnetic ferrous and spin-doublet ferric species,[1,3] whose reduced ionic radii are easily accommodated within the porphyrin plane.[7,8]

This conversion of iron(II) from an out-of-plane HS to an in-plane diamagnetic, six-coordinate species upon oxygenation is typical of the heme proteins, myoglobin and hemoglobin.[2,4,9,10] The latter tetraheme protein exhibits cooperativity among its subunits with respect to oxygenation, which has been the subject of considerable recent interest.[1,4,5–11] The biochemical trigger[1,4,9,10] which precipitates this cooperativity is thought to originate precisely from the sizable rearrangement imposed on the protein chain of the globin molecule by reducing the distance between the F-8 histidine and the heme plane[4,9] by some ~0.75 Å upon oxygenation of one subunit.

There is, therefore, considerable interest in the thermodynamic and kinetic parameters describing the motion of an iron atom relative to the porphyrin plane. Although calculations[12] have confirmed the stabilizing effect of the out-of-plane displacement of the iron in HS species, little is known about the magnitude of this stabilization. Furthermore, since it has been proposed[10] that iron–heme moieties exist in some form of mobile equilibrium with respect to the position of the iron relative to the porphyrin plane, an estimate of the possible rate constants for such mobility could be of value.

One approach is to monitor the rate of porphyrin "inversion," where the metal moves from one side of the porphyrin plane to the other. The activation energy for such a process would be related to this stabilization energy and would also reflect the "mobility"[10] of the HS iron atom. High-spin, five-coordinate ferrous porphyrin complexes have not been characterized; however, the HS ferric analogs of both natural and synthetic porphyrins are well characterized.[6,13,14]

We report here on the porphyrin "inversion" for the HS complexes of tetra-*p*-tolylporphyrin, *p*-CH_3-TPPFeCl, and octaethylporphyrin, OEPFeCl, where the "inversion" is induced by facile halogen exchange according to (A). The *m*-H signal in *p*-CH_3TPPFeCl has been shown[14] to be a doublet with a separation of ~110 Hz at 35°, reflecting the magnetic nonequivalence of the two sides of the heme plane and the restricted rotation[15] of the aryl group. Upon addition of in-



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