

THE IMPORTANCE OF NON-AXIAL SYMMETRY IN THE INTERPRETATION OF LANTHANIDE-INDUCED SHIFTS FOR KETONES

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Abstract—Pr(dpm)₃-induced shifts in the PMR spectrum of camphor are significantly better explained if the McConnell–Robertson expression is extended to include a term with non-axial symmetry, which contributes between 1% and 40% to the individual shifts. Complexes of six other ketones provide further evidence. Good agreement with observed shifts was obtained without any optimisation of lanthanide–oxygen bond lengths or angles. The success of the extended expression suggests that complexes of ketones with shift reagents may exist in two preferred rotational conformations.

INTRODUCTION

It is commonly assumed that the McConnell–Robertson expression (Eq 1) is adequate for predicting the effect of lanthanide shift reagents on PMR spectra.¹⁻³

$$(\Delta H/H_0) = K r_i^{-3} (3 \cos \theta_i - 1) \quad (1)$$

where $\Delta H/H_0$ is the lanthanide-induced shift (LIS), r_i is the distance from the lanthanide atom to the i 'th proton of the ligand, θ_i is the angle between the vector \bar{r}_i and the lanthanide–ligand bond, and K is a constant characteristic of the magnetic susceptibility anisotropy.

Agreement between observed and calculated shifts is conveniently expressed as an "agreement factor",^{4,6} R , analogous to the crystallographic R -factor.⁷ Typical values are scattered over the range $R = 0.03$ to 0.09 . Agreement factors at the lower end of this range can be explained by random experimental errors, but those at the upper end are somewhat large, suggesting that systematic errors may also be present. This is not surprising, since the McConnell–Robertson expression was originally derived for a magnetic susceptibility tensor with axial symmetry,⁸ and X-ray crystallographic studies of shift-reagent complexes show no evidence for axial symmetry, in the solid state at least.⁹⁻¹² If the magnetic susceptibility tensor does not have axial symmetry, then a more general expression should be used;¹³

$$(\Delta H/H_0)_i = K_1 r_i^{-3} (3 \cos^2 \chi_i - 1) + K_2 r_i^{-3} \sin^2 \chi_i \cos 2\Omega_i \quad (2)$$

Here the polar coordinates of the i 'th proton are (r_i, χ_i, Ω_i) , measured from the principal axes of the magnetic susceptibility tensor.

Use of the McConnell–Robertson expression could still be justified, in a special case; averaging Eq 1 over at least 3 rotational conformations, each with the same population, eliminates any term that does not have axial symmetry about the axis of rotation.¹⁴ Since there is no direct evidence for the existence of three or more conformations, this simplification can be justified only by its apparent success in a number of applications,¹⁻⁵ and it may not be generally valid.

The general expression, Eq 2, would be of little practical use, since there are 5 unknowns; K_1 , K_2 and the three angles which define the orientation of the principal axes of the susceptibility tensor. On the other hand, the McConnell–Robertson expression contains only one unknown, namely K . This paper considers evidence in favor of an intermediate expression, derived by averaging the induced shifts over two rotational conformations.

An extension of the McConnell–Robertson expression. The general expression, Eq 2, must be used if the complex exists as one unique rotational conformation.¹³ Averaging over three or more rotamers yields Eq 1.¹⁴ This leaves an intermediate case (two rotamers) which has not yet been considered. It can be shown that the appropriate expression for this case has the same form as the McConnell–Robertson expression, with an additional term to correct for non-axial symmetry. An outline of the derivation is given here, for the special case of a magnetic susceptibility tensor which has axial symmetry (but not about the lanthanide–ligand bond). The general case ($K_2 \neq 0$) may be treated by a similar procedure, but the full derivation is outside the scope of the present discussion.

Suppose that the symmetry axis, \bar{m} , of the magnetic susceptibility tensor lies at an angle α from the lanthanide–ligand bond. Rotation of the

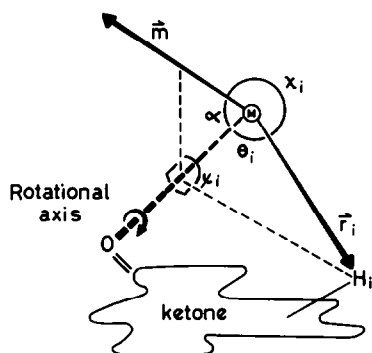


Fig 1. Illustrating some of the angles used in this paper.

ligand about this bond can be described by an angle ψ_i , shown in Fig 1. The four angles of Fig 1 are related by Eq 3;

$$\cos \chi_i = \cos \alpha \cos \theta_i + \sin \alpha \sin \theta_i \cos \psi_i. \quad (3)$$

Suppose that the probability of any given rotational conformation is expressed by the function $f(\psi_i)$, and that this function is symmetric on either side of two (equally probable) preferred conformations, at $\psi_i = \phi_i$ and $\psi_i = \phi_i + \pi$. The observable shift is obtained by substituting Eq 2 into Eq 3 and averaging over a complete revolution ($\psi_i = \phi_i$ to $\psi_i = \phi_i + 2\pi$), using $f(\psi_i)$ as a weighting factor. For an axially symmetric susceptibility tensor (i.e. $K_2 = 0$) the result is;

$$\langle \Delta H/H_0 \rangle_i = K r_i^{-3} (3 \cos^2 \theta_i - 1) + K' r_i^{-3} \sin^2 \theta_i \cos 2\phi_i \quad (4)$$

where;

$$K = \frac{1}{2} K_1 (3 \cos^2 \alpha - 1),$$

$$K' = 3 K_1 (\langle \cos^2 \gamma \rangle_{av} - \frac{1}{2}) \sin^2 \alpha,$$

$$\gamma = \psi_i - \phi_i$$

and

$$\langle \cos^2 \gamma \rangle_{av} = \int_0^{2\pi} f(\phi_i + \gamma) \cos^2 \gamma \, d\gamma.$$

Eq 4 has the same form as Eq 2, with χ_i replaced by θ_i and Ω_i by ϕ_i . In other words, the derivation outlined above leads to an "effective" magnetic susceptibility tensor with non-axial symmetry, but with a principal axis along the lanthanide-ligand bond. Eq 4 can also be regarded as an extension of Eq 1. In this intermediate case, there are three unknowns: K , K' and the angle defining the reference plane from which ϕ_i is to be measured. The relative magnitude of the coefficient K' could vary widely, and could be positive or negative depending on the magnitude of the angle α . If α approaches 54.7° , the non-axial term would dominate over the first term. If the restriction on free rotation is lifted,

$f(\psi_i)$ becomes constant and $\langle \cos^2 \gamma \rangle_{av} = \frac{1}{2}$; hence the nonaxial term vanishes, as expected.¹⁴

The general case, $K_2 \neq 0$, leads to a much more complicated expression, but it still reduces to the same functional form as Eq 4, with ϕ_i replaced by $(\phi_i - \phi_0)$. The angle ϕ_0 defines a new plane from which ϕ_i must now be measured.

The lanthanide-ligand bond. It has been assumed, almost without exception, that the lanthanide-ligand bond length and bond angles can be treated as adjustable parameters.¹⁻⁵ This approach certainly improves the agreement factor, but it is disturbing to note the wide variation of lanthanide-ligand bond lengths which must be assumed in order to minimise the agreement factor; e.g., Demarco *et al*⁴ found it was necessary to assume that the Eu-O bond length varies from 2.1 Å for adamantanone/Eu(dpm)₃, to 3.9 Å for camphor/Eu(dpm)₃. To take a more extreme example; Eu(fod)₃-induced shifts for an amine have been interpreted by assuming a Eu-N bond length of 4.6 Å.⁵ This means that the bond would have to be stretched by almost 2 Å, compared with the Eu-N bond in crystalline Eu(dpm)₃(py)₂ which is 2.65 Å long.⁹

Adding a further adjustable parameter will always result in an improvement of the agreement factor, regardless of whether or not the additional variable has any significance. This is particularly true in the interpretation of lanthanide-induced shifts, where there are typically as few as five to ten measurable shifts to begin with. Thus the improvement gained by adjusting the lanthanide atom coordinates should be viewed with caution. In the present study, the number of variables was kept low by considering the extension of Eq 1 to Eq 4 as an alternative to adjustment of the lanthanide coordinates, rather than as an additional assumption.

RESULTS AND DISCUSSION

Camphor. Camphor (1) was chosen as a model substrate for a detailed study of the possible sources of systematic errors, and particularly the possibility of a non-axial susceptibility tensor. This particular ketone was chosen because of its rigid conformation, and because ten widely-differing Pr-(dpm)₃-induced shifts can be measured from the PMR spectra, even at 60 MHz. These shifts are tabulated in Table 1. An accuracy of $\pm 2\%$ was aimed for in these measurements, so that the agreement factor would be sufficiently sensitive to the model used.

First, a model for the binding-site geometry must be chosen. No structural data is available for complexes of shift reagents with ketones; however, the shift reagents themselves are β -diketone complexes (dpm = dipivaloylmethane). The crystal structure of a shift-reagent dimer, [Pr(dpm)₃]₂, has been published,¹⁵ and this data was used to estimate the binding-site geometry for a ketone ligand. The

average bond angle, C—O—Pr, was 135° . The O—Pr bond lengths ranged from 2.38 \AA to 2.44 \AA , except for the oxygen atoms involved in bridging the dimer (2.59 \AA). This longer distance was considered more appropriate for an estimate of the ketone-praseodymium bond length, since in a ketone complex in solution the ketone is not as strongly bound as the β -diketone ligands themselves. The praseodymium might be expected to lie in the plane of each CO group,¹⁵ but in practice it is displaced out of these planes by small amounts. However, this is probably the result of strains imposed by formation of the dimer. If the strain is released, e.g. by formation of a seven-coordinate monomer, the praseodymium may return to the carbonyl plane; this behaviour has been observed for $\text{Dy}(\text{dpm})_3(\text{H}_2\text{O})_9$.

Thus the model chosen for the binding-site geometry placed the praseodymium in the plane of the carbonyl group, 2.6 \AA from the oxygen, with a bond angle (C—O—Pr) of 135° . For an initial trial, this model was used along with Eq 1, and only the coefficient K was optimised. The result was $R = 0.265$, which is quite unacceptable.

The next step was to allow the symmetry axis of the magnetic susceptibility tensor to deviate from the O—Pr bond.¹⁴ The best fit was obtained when the symmetry axis was deflected through 5.6° away from the O atom, in the direction of C-2. The agreement factor then dropped to $R = 0.090$. This is still not as low as would be expected from consideration of experimental uncertainties. An accuracy of $\pm 0.1 \text{ \AA}$ in measuring proton coordinates, along with an accuracy of $\pm 2\%$ in the observed shifts, would lead one to expect an agreement factor in the region of $R = 0.05$.

Thirdly, the three coordinates of the lanthanide atom were treated as variables, following the commonly accepted procedure.¹⁻³ The best fit ($R = 0.083$) was obtained for a bond length of 3.5 \AA . The praseodymium coordinates were then; $x_0 = -1.1 \text{ \AA}$, $y_0 = 2.2 \text{ \AA}$, $z_0 = 2.5 \text{ \AA}$. This fit is not a significant improvement over that described in the preceding paragraph, since it was obtained by varying four parameters (K , x_0 , y_0 , z_0), while $R = 0.090$ was obtained by varying only three parameters (K , and the two angles defining the orientation of the axis of axial symmetry).

The fourth approach used Eq 4. When the angles ϕ , were measured from the yz plane, the agreement factor dropped to $R = 0.035$, for $K'/K = 0.64$. This is below the criterion ($R = 0.05$) fixed by experimental uncertainties, so any further improvement would not be significant. Thus there was no search for a better choice of a reference plane for the angles ϕ . It should be noted that the sign of K'/K has not been determined, since ϕ , could equally well have been measured from a perpendicular plane, giving $K'/K = -0.64$.

The contribution of the non-axial term is tabu-

lated in Table 1. Note that the protons of the methylene group adjacent to the CO are affected far more than any other protons. It could perhaps be argued that these protons may be subject to a contact shift,¹ since they are separated from the praseodymium by only four bonds. Certainly, Eq 1 gives a better agreement factor if these protons are omitted; R drops from 0.265 to 0.095 . However, the agreement factor drops even further on addition of the non-axial correction term ($R = 0.048$ for $K'/K = 0.62$). This optimum value of K'/K is not significantly different from the optimum value found when the adjacent methylene group was included; thus non-axial symmetry remains the better explanation.

It is unreasonable to expect that the complex of a shift reagent with a ketone must form with only one unique geometry. There are lone pairs of electrons on either side of the CO, each capable of forming a bond with the electrophilic shift reagent, so two isomers are possible.⁴ These have been labelled "A" and "B" in Fig 2. The possibility of isomers was incorporated in the computer program by taking the weighted mean of the shifts for each isomer. It was assumed that K'/K would not vary significantly between the two isomers. The agreement factor did not improve; it rose from $R = 0.035$ to $R = 0.052$ on addition of 5% isomer B. If the interpretation is correct, then very little of the camphor/ $\text{Pr}(\text{dpm})_3$ complex can be present in the form of the second isomer, presumably because of steric interactions between the shift reagent and the 10-Me group.

To summarise the results for camphor; adjusting the lanthanide atom coordinates does improve the agreement factor, but this improvement is not unique. Similar improvement can be obtained by adjusting the orientation of the susceptibility tensor, or by ignoring protons separated from the praseodymium by only four bonds. Even better agreement can be obtained by assuming instead that the "effective" magnetic susceptibility tensor does not have axial symmetry. Yet it is still possible to assume that a principal axis of this tensor lies along the Pr—O bond. This corresponds to the situation described by Eq 4, rather than Eq 1 or Eq 2. In this interpretation, the non-axial term is not simply a minor correction term. Table 1 shows that the non-

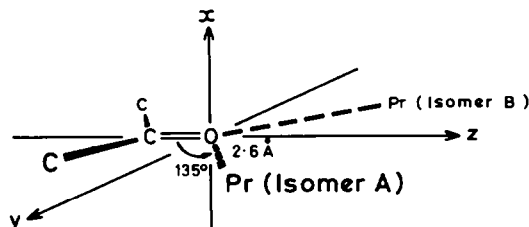


Fig 2. The binding-site geometry used for calculating $\text{Pr}(\text{dpm})_3$ -induced shifts.

axial term would account for as much as 40% of the praseodymium-induced shift for protons close to the binding site.

Other ketones. Eq 4 was tested further by using published lanthanide-induced shifts for five ketones,^{4,16} chosen because they have rigid conformations, with only one functional group, and with five or more lanthanide-induced shifts reported for each. It was assumed that the binding site geometries for these ketone complexes would be the same as the geometry assumed for the complex of Pr(dpm)₃ with camphor, apart from a small decrease in bond length resulting from the lanthanide contraction. The bond lengths used were; Eu-O 2.5 Å, Yb-O 2.4 Å. The results are tabulated in Table 2. Three agreement factors are given for each ketone; the first was obtained using Eq 1, optimising only K and the percentage of isomer B. The second corresponds to optimisation of the lanthanide atom coordinates, following the accepted procedure.¹⁻⁵ The third was obtained using Eq 4 and optimising the contribution of the non-axial term. Both of the latter two procedures result in substantial reductions of the agreement factor, but Eq 4 gives the better agreement. It should be stressed that the more successful use of Eq 4 cannot be dismissed as being the result of increasing the number of parameters. In fact, the number of adjustable parameters was reduced from four (K, x₀, y₀, z₀) to three (K, K', % isomer B).

Table 2 also shows the wide range of lanthanide-oxygen bond lengths which must be assumed if Eq 1 is used. On the other hand, Eq 4 is not sensitive to the lanthanide coordinates chosen. Trial values for the bond length can be varied over ±0.5 Å, and the bond angle can be varied by ±10°, before any increase in the agreement factor becomes significant. Thus Eq 4 cannot be used to deduce an improved model for the binding-site geometry of the complexes in solution.

The improved fit for adamantanone can, to some extent, be attributed to averaging the calculated shifts over two isomers ("A" and "B" in Fig 1). In the original interpretation⁴ the shifts were calculated for a single "time-averaged" geometry, although the authors recognised that this was an over-simplification.

Practical applications. To test whether Eq 4 could be used in routine stereochemical analysis, the modified computer program was used as an aid in the interpretation of Eu(dpm)₃-induced shifts for two ketones of uncertain structure. The ketones were obtained by photolysis of pinocarvone; details of preparation and properties will be published elsewhere.¹⁷ The PMR spectra were compatible with structures 2 and 3a. Tables 3 and 4 compare the observed and calculated Eu(dpm)₃-induced shifts. The vinyl group of 2 was omitted from the analysis, since it is free to rotate. The agreement factors were;

$$2/\text{Eu(dpm)}_3; R = 0.052 \text{ for } K'/K \\ = 0.7 \text{ and } 0\% \text{ isomer B,}$$

$$3a/\text{Eu(dpm)}_3; R = 0.063 \text{ for } K'/K \\ = 1.1 \text{ and } 1\% \text{ isomer B.}$$

The agreement factors are acceptable, considering the experimental uncertainties; thus the LIS's have yielded strong evidence in favour of the proposed structures.

The PMR spectrum of 3a also appears compatible with two further structures (3b and 3c). The resonances were re-assigned for each model, and the agreement factors were minimised by treating K, K' and % isomer B as variables: R = 0.118 for 3b, R = 0.131 for 3c. The significance of these increases in R can be tested statistically;⁶ in this case, there are seven degrees of freedom (ten LIS's, less three parameters). Comparing 3a and 3b gives an agreement-factor ratio:

$$R = 0.118/0.063 = 1.87.$$

Statistical tables⁷ show that this ratio is large enough for structure 3b to be rejected, in favour of 3a, at the 0.5% confidence level. Similarly, 3c can be rejected; this time the rejection is even more conclusive.

It is interesting to compare these rejections with the results of statistical testing using Eq 1, and treating the europium coordinates as variables. The results for each trial structure were:

$$3a: R = 0.093 \text{ for Eu-O} = 3.7 \text{ \AA,} \\ 3b: R = 0.183 \text{ for Eu-O} = 4.2 \text{ \AA,} \\ 3c: R = 0.138 \text{ for Eu-O} = 1.8 \text{ \AA.}$$

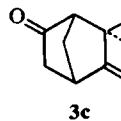
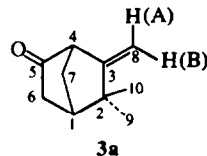
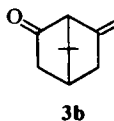
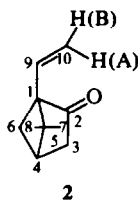
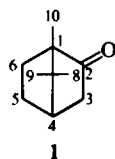


Table 1. Observed and calculated Pr(dpm)₃-induced shifts for camphor

The observed lanthanide-induced shifts are expressed relative to the sum of the shifts of the three Me resonances. Calculated shifts are compared for two interpretations

Proton	<i>exo</i> -3	<i>endo</i> -3	4	<i>exo</i> -5	<i>endo</i> -5	<i>exo</i> -6	<i>endo</i> -6	8-Me	9-Me	10-Me
Observed (relative) LIS	0.620	0.597	0.232	0.186	0.217	0.289	0.430	0.294	0.186	0.520
Calculated LIS; Eq 1, lanthanide coord.'s optimised	0.630	0.608	0.215	0.180	0.244	0.256	0.443	0.349	0.187	0.450
Calculated LIS; Eq 4, K'/K optimised	0.622	0.596	0.217	0.193	0.250	0.275	0.440	0.282	0.187	0.510
Contribution of the non-axial term in Eq 4	0.256	0.256	0.056	0.017	0.027	-0.003	-0.028	-0.029	0.004	0.004

Table 2. Agreement factors and best-fit parameters for five ketones

Ref	Ketone	Shift reagent	No. of LIS's measured	R (Eq 1) (Lanthanide coordinates fixed)	R (Eq 1) (Lanthanide coordinates optimised)	Best-fit bond length	R (Eq 4) (K'/K optimised)	Best-fit parameters	
								K'/K	% isomer B
16	1-Indanone	Yb(dpm) ₃	6	0.172	0.029	3.5 Å	0.029	0.63	15%
16	4- <i>t</i> -Butylcyclo- hexanone	Yb(dpm) ₃	6	0.269	0.058	3.5 Å	0.055	0.73	50%
4	Adamantanone	Eu(dpm) ₃	5	0.138	0.046	2.1 Å	0.013	0.34	50%
4	Norcamphor	Eu(dpm) ₃	10	0.142	0.073	2.7 Å	0.034	0.90	9%
4	Camphor	Eu(dpm) ₃	10	0.210	0.027	3.9 Å	0.029	0.61	9%

Table 3. Eu(dpm)₂-induced shifts for ketone 2

Proton	<i>exo</i> -3	<i>endo</i> -3	4	<i>exo</i> -6	<i>endo</i> -6	7-Me	8-Me	9	10(A)	10(B)
Relative LIS	1.06	1.06	0.44	0.50	0.76	0.62	0.38	1.13	0.62	0.33
Calculated LIS (Eq 4)	1.06	1.06	0.46	0.53	0.81	0.54	0.36	—	—	—

Table 4. Eu(dpm)₂-induced shifts for ketone 3a

Proton	1	4	<i>exo</i> -6	<i>endo</i> -6	<i>syn</i> -7	<i>anti</i> -7	8(A)	8(B)	9-Me	10-Me
Relative LIS	0.71	2.07	1.91	1.91	1.09	0.71	0.72	0.54	0.57	0.43
Calculated LIS (Eq 4)	0.72	2.06	1.91	1.91	1.14	0.84	0.72	0.40	0.42	0.40

There are four parameters (K , x_0 , y_0 , z_0) to be determined from ten shifts, leaving six degrees of freedom. Structure 3b can be rejected at the 1% confidence level, but structure 3c can be rejected only at the 5% confidence level. Thus the accepted procedure for interpretation of LIS's would leave some doubt about the correct structure.

CONCLUSION

Some simplifying assumptions are necessary if LIS's are to be used in structural chemistry. However, the common assumption of an axially symmetric magnetic susceptibility tensor seems inappropriate. For the ketone complexes studied here, better results were obtained by permitting non-axial symmetry and assuming instead that variations in the lanthanide-ligand bond lengths and bond angles can be ignored. The consistent success of Eq 4 in predicting lanthanide-induced shifts for seven different ketones suggests that complexing by these ketones may involve two preferred rotational conformations. Eq 4 can be used to predict the shifts induced by any magnetic susceptibility tensor, whether axially symmetric or not, provided the complex exists in two preferred rotational conformations with equal populations.

The procedure described uses only three parameters, compared with the four parameters required by the accepted procedure. This reduction in the number of parameters means that the new procedure uses considerably less computing time; the improved agreement also makes the procedure more sensitive to details of molecular structure.

The procedure could prove equally useful if applied to other rigid functional groups; e.g. epoxides, cyclic ethers and sulphoxides. A similar interpretation of LIS's for alcohols and amines could present problems, since internal rotation about the C—O and C—N bond would introduce further parameters.

EXPERIMENTAL

PMR spectra were obtained at 60 MHz (22°C) on a Varian DA 60-IL NMR spectrometer. Solid Pr(dpm)₃ was added to 0.8 M dl-camphor in CCl₄ along with 5% benzene (internal lock) and a drop of TMS (internal reference). Solid Eu(dpm)₃ was added to dilute solns of 2 and 3 in CCl₄, using TMS as an internal lock. The chemical

shift of each proton was plotted against the sum of the shifts of the three Me groups, since this procedure¹⁸ gives better linearity than plotting shifts against the weight of shift reagent added. Relative LIS's (gradients of the plots) were determined by linear least-squares fitting. Resonances for camphor were assigned following Demarco *et al.*¹⁹

Proton coordinates were measured directly off a molecular model of each ketone. The axes used are shown in Fig 2. The positive y-axis was placed in the direction of the adjacent methylene group, except for adamantanone for which symmetry makes the choice of directions irrelevant. Induced shifts for Me protons were averaged over 6 rotational conformations. Agreement factors for each interpretation were calculated using computer programs written in BASIC for use on a HP2100A mini-computer.

REFERENCES

- ¹J. Briggs, F. A. Hart and G. P. Moss, *Chem. Commun.* 1506 (1970)
- ²S. Farid, A. Ateya and M. Maggio, *Ibid.* 1285 (1971)
- ³M. R. Willcott, R. E. Lenkinski and R. E. Davis, *J. Am. Chem. Soc.* **94**, 1742 (1972)
- ⁴P. V. Demarco, B. J. Cerimele, R. W. Crane and A. L. Thakkar, *Tetrahedron Letters* 3539 (1972)
- ⁵M. Ochiai, E. Mizuta, O. Aki, A. Morimoto and T. Okada, *Ibid.* 3245 (1972)
- ⁶R. E. Davis and M. R. Willcott, *J. Am. Chem. Soc.* **94**, 1744 (1972)
- ⁷W. C. Hamilton, *Acta Crystallogr.* **18**, 502 (1965)
- ⁸H. M. McConnell and R. E. Robertson, *J. Chem. Phys.* **29**, 1361 (1958)
- ⁹C. S. Erasmus and J. C. A. Boeyens, *J. Cryst. Mol. Struct.* **1**, 83 (1971)
- ¹⁰J. J. Uebel and R. M. Wing, *J. Am. Chem. Soc.* **94**, 8910 (1972)
- ¹¹R. E. Cramer and K. Seff, *J. Chem. Soc. Chem. Commun.* 400 (1972)
- ¹²W. De W. Horrocks Jr, J. P. Sipe III and J. R. Lueber, *J. Am. Chem. Soc.* **93**, 5258 (1971)
- ¹³B. Bleaney, *J. Mag. Res.* **8**, 91 (1972)
- ¹⁴J. M. Briggs, G. P. Moss, E. W. Randall and K. D. Sales, *J. Chem. Soc. Chem. Commun.* 1180 (1972)
- ¹⁵C. S. Erasmus and J. C. A. Boeyens, *Acta Crystallogr., Sect B*, **26**, 1843 (1971)
- ¹⁶Z. W. Wolkowski, *Tetrahedron Letters* 821 (1971)
- ¹⁷T. D. R. Manning, to be published
- ¹⁸J. A. Peters, J. D. Remijnse, A. van der Wiele and H. van Bekkum, *Tetrahedron Letters* 3065 (1971)
- ¹⁹P. V. Demarco, D. Doddrell and E. Wenkert, *Chem. Commun.* 1418 (1969)