

Evaluation of Contact and Dipolar Contributions to ^1H and ^{13}C Paramagnetic NMR Shifts in Axially Symmetric Lanthanide Chelates

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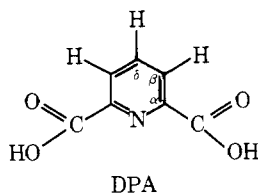
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Abstract: The lanthanide-induced isotropic shifts in ^{13}C and ^1H NMR spectra of axially symmetrical tris complexes of pyridine-2,6-dicarboxylate (DPA) and tris(4-methyl-2,6-pyridinedicarboxylate) (MDPA) are compared with the purely dipolar model using geometric factors calculated from crystallographic data. The ^1H shifts are consistent with the solid state structure and Bleaney's C_D constants. The ^{13}C shifts, however, contain deviations that cannot be explained if Fermi contact contributions are neglected. The latter are evaluated by difference and correlate well with Golding's (S_z) factors. Contact shift contributions are important even for carbons five bonds removed from the lanthanide. Variable temperature experiments also substantiate the relative contributions of contact and dipolar shifts computed for the various ^{13}C and ^1H via the difference procedure based on the solid state structure.

Considerable interest² continues to exist in the use of paramagnetic ions, particularly the lanthanides, as NMR shift probes for various organic molecules. Several assumptions have most often been made, either implicitly or explicitly, in deducing the solution structure of lanthanide shift reagent (LSR) adducts namely: (1) only one complex species exists in solution; furthermore it is axially symmetric and structurally rigid; (2) the principal magnetic axis has a known orientation, taken almost invariably as colinear with the lanthanide³ ligand atom bond; (3) the induced shifts are purely dipolar ("pseudocontact") in origin.

The validity of these assumptions is sometimes doubtful. For example, in the solid state, LSR have at most an axis of twofold symmetry^{3,4} with the result that conditions 1 and 2 no longer persist. Moreover, a few recent reports, mainly devoted to nuclei other than ^1H , seem to invalidate the third assumption. For instance, Gansow et al.⁵ found substantial contact contribution in the ^{13}C spectra of pyridine bases associated to various LSR. Very recently and after the present work was completed, Ajisaka and Kainosho⁶ reported large contact shifts induced by Gd and other LSR. In both of these studies the exact locations of the adduct relative to the lanthanide ion were not known a priori and the location was established by relying on the best least-squares fit between observed proton shifts and trial geometric factors.

In the present ^1H and ^{13}C NMR study, lanthanide chelates of axially symmetric structure were investigated in order to test with fewest assumptions the validity of the theory currently applied to the interpretation of LSR modified spectra. These ligands were selected because x-ray structural data and stability constants were available, hence affording a much firmer basis than is usually available concerning assumptions 1 and 2. The proton NMR study of 2,6-pyridinedicarboxylic acid (DPA) by Donato and Mar-



tin⁷ oriented our work toward this ligand. 4-Methyl-2,6-pyridinedicarboxylic acid (MDPA) was also investigated. DPA forms stable lanthanide complexes of known stability⁸

and their crystallographic structure has been extensively studied by Albertsson.⁹ The lanthanide ions are nine coordinate and are located at the center of a tricapped trigonal prism with the heterocyclic nitrogen atoms in the equatorial plane (Figure 1). MDPA was found to behave very much like DPA, suggesting similar structures and stability constants for this new ligand.

Experimental Section

Materials and Solutions. The DPA ligand was obtained from Aldrich Chemical Co. and MDPA was synthesized from chelidamic acid by the method of Koenigs and Jaeschke.¹⁰ The complexes were prepared by mixing equal volumes of 0.4 M solutions of ligand and 0.1 M solutions of lanthanide chloride in D_2O and adjusting the pH to around 10 with NaOD. As demonstrated by a computer analysis performed with the program COMICS,¹¹ only two species are present at significant concentration levels in these solutions: the tris complex and the excess free ligand.

Nuclear Magnetic Resonance Spectra. Proton spectra were determined on a Jeolco C-60 or a Bruker HFX-90. Carbon-13 spectra were recorded with a deuterium lock on a Bruker HFX-90 equipped with a Nicolet Fourier transform computer. Samples were spun in 10-mm tubes and proton noise decoupled spectra were obtained after 3–4 h of accumulation. The variable temperature accessories were calibrated either with an ethylene glycol sample (^1H) or with a thermometer directly placed in the solution (^{13}C). The paramagnetic shifts were referenced to the corresponding diamagnetic lanthanum chelate and a small amount of *tert*-butyl alcohol was used as an internal standard. DPA and MDPA peaks were assigned by comparison of the spectra of both ligands and from off-resonance proton decoupled spectra.

Calculations. A Fortran computer program CONF was used to calculate the dipolar geometric factors from the crystallographic coordinates. After axes transformations, the program adds the protons and performs symmetry operations, if necessary, to build the whole molecular complex. Orthogonal and stereoscopic projections along any direction (i.e., Figure 1) are plotted as a useful means to check the calculations. Finally the program computes the dipolar geometric factors with the magnetic axes automatically positioned in any selected orientation. To estimate the effect of a slight modification of the structure, the position of one ligand can be altered and new geometric factors computed.

Theory

Dipolar interaction is considered the main contributor to isotropic shifts induced by lanthanide ions.² Bleaney¹² proposed a theoretical treatment to account for the anisotropy in the magnetic susceptibility in a crystal field of axial symmetry. The paramagnetic shifts are expressed as function of

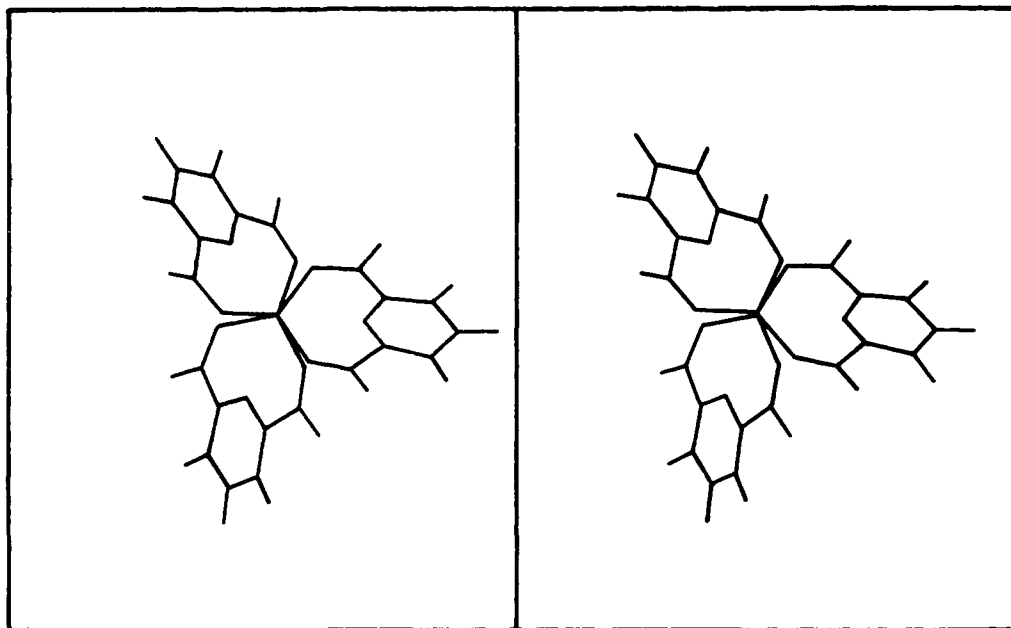


Figure 1. Stereoview of $\text{Ln}(\text{DPA})_3$ down the molecular threefold axis.

a constant C_D , for which only relative values can be obtained:

$$\frac{\Delta H}{H} = \frac{g^2 \beta^2}{60k^2 T^2} C_D \left\langle \frac{3 \cos^2 \theta - 1}{r^3} \right\rangle \quad (1)$$

where θ and r are polar coordinates of the nucleus under consideration. The constant C_D may be conveniently used as a scaling factor to be compared with dipolar shifts induced by a series of lanthanide ions in a ligand or an organic adduct.¹³ Although not strictly valid,^{14a} and a subject of some controversy,^{14b} the T^{-2} temperature dependence has recently been reported for a Yb shift reagent-acetone complex.¹⁵

Contact contributions involving some degree of covalency have sometimes been claimed to dominate the isotropic shifts for nuclei one or two bonds removed from the paramagnetic center. The contact interaction is a function of A , the hyperfine coupling constant, and of $\langle S_z \rangle$, the average of the z component of the lanthanide electron spin:

$$\Delta H = A \langle S_z \rangle / g_N \beta_N \quad (2)$$

Values of $\langle S_z \rangle$ have been computed by Golding and Halton¹⁶ and account very well for the ^{17}O shifts of hydrated lanthanides¹⁷ and indicate that the value of A is virtually identical for all lanthanides. In the simplest cases $\langle S_z \rangle$ has a T^{-1} dependence and the contact shifts follow Curie law behavior.

Isotropic Shifts in DPA and MDPA Complexes. Depending upon the method of preparation, solids of different crystallographic habits have been obtained⁹ with $\text{Ln}(\text{DPA})_3$. The coordination polyhedra are, however, little affected by the nature of the various crystallographic habits and an exact or nearly exact C_3 axis is maintained. As DPA and MDPA are strong and rigid chelating agents, their complexes probably maintain their solid state structure in solution. The geometric factors $G(\theta, r)$ computed from x-ray crystallographic results are given in Table I. A comparison of the various crystallographic structures⁹ as well as perturbed geometries achieved via computer calculations demonstrate that the $G(\theta, r)$ factor for the carboxylic carbon is very sensitive to slight distortion in placement of the ligand. For this reason this nucleus appears to be an unreliable probe for contact/dipolar analysis and will not be considered further.

Table I. Geometric Factors, $G(\theta, r)$, for $\text{Ln}(\text{DPA})_3$ and $\text{Ln}(\text{MDPA})_3$ [$G(\theta, r) = \langle (3 \cos^2 \theta - 1)/r^3 \rangle$]

		DPA ^a			
H_β	$-4.23 \times 10^{-3} \text{ \AA}^{-3}$	H_γ	$-3.82 \times 10^{-3} \text{ \AA}^{-3}$		
C_α	$-2.05 \times 10^{-2} \text{ \AA}^{-3}$	C_β	$-8.34 \times 10^{-3} \text{ \AA}^{-3}$		
C_γ	$-7.50 \times 10^{-3} \text{ \AA}^{-3}$	COO^-	$-6.96 \times 10^{-4} \text{ \AA}^{-3}$		
		MDPA ^b			
CH_3	$-2.50 \times 10^{-3} \text{ \AA}^{-3}$	CH_3	$-3.13 \times 10^{-3} \text{ \AA}^{-3}$		

^a Mean value for monoclinic $\text{Yb}(\text{DPA})_3$. ^b Computed with program CONF using standard geometries for CH_3 .

The exchange between free and coordinated ligand is slow on the NMR time scale and separate resonances for both species are observed. Moreover the ^1H and ^{13}C isotropic shifts of the nuclei common to DPA and MDPA are identical within the limit of experimental errors.

Only the heavier lanthanides induce proton shifts sufficiently large to allow accurate measurement of the H_β/H_γ or H_β/CH_3 NMR shift ratios (Figure 2).¹⁸ Prior to Albertsson's x-ray structure determination,⁹ Donato and Martin⁷ had deduced from the former ratio that DPA complexes exhibited D_3 symmetry, with the aromatic ring canted at an angle of 49° with respect to the equatorial plane containing the three nitrogens. Interestingly, this angle is quite close to the mean value of 52° subsequently computed from the x-ray crystallographic structure of $\text{Yb}(\text{DPA})_3$. Because of this agreement one may conclude that the solution structure is indeed very similar to that of the solid and also that contact contributions can be neglected in the interpretation of the proton NMR spectra. The same latter conclusion is reached for the MDPA chelates through the H_β/CH_3 ratio. Two additional arguments support this assignment of negligible contact contributions to the proton spectra. First, the sign and magnitude of the various ^1H shifts can be scaled to Bleaney's C_D constants¹² with good accuracy. Second a T^{-2} temperature dependence with zero intercept is observed for the proton shifts induced by Yb^{3+} and Tm^{3+} (Figure 3). In the temperature range investigated, separate resonances are observed for the complexed and for the free ligand and hence the exchange remains slow on the NMR time scale. These proton data for the complexed ligand are therefore quite reliable since they do not require the joint consideration of equilibrium constants and their

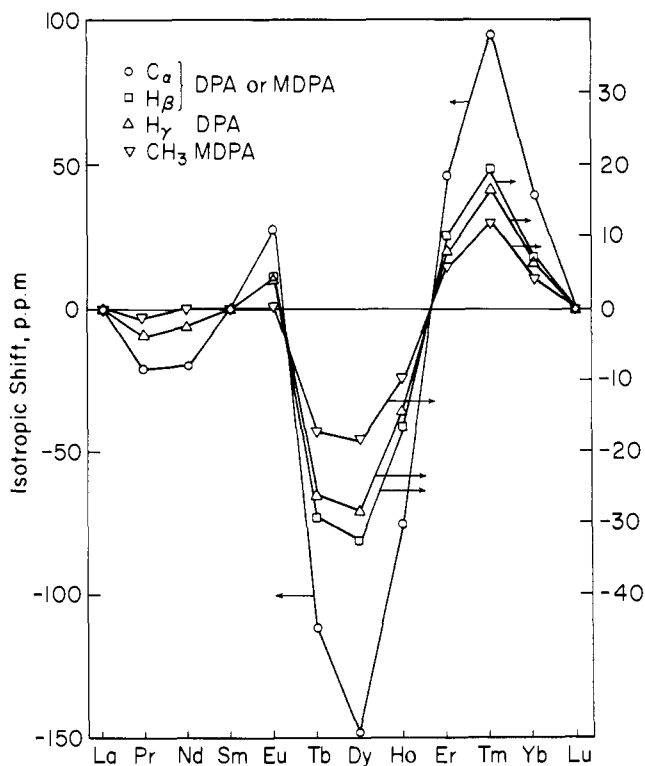


Figure 2. Variation of observed chemical shifts in $\text{Ln}(\text{DPA})_3$ and $\text{Ln}(\text{MDPA})_3$. The C_α and H_β have the same shifts in both complexes.

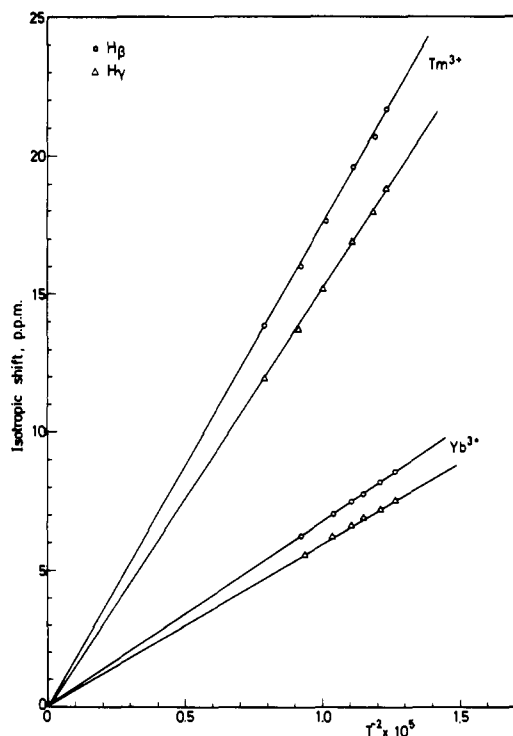


Figure 3. Temperature dependence of observed isotropic shifts for protons in $\text{Tm}(\text{DPA})_3$ and $\text{Yb}(\text{DPA})_3$.

temperature dependencies ordinarily needed in cases with rapid ligand exchange.

As shown in Figure 2, the large C_α shifts have signs and relative magnitudes comparable to those observed in the ^1H spectra. These shifts are consistent with Bleaney's C_D constants,¹² as illustrated in Figure 4. In contrast the other carbon spectra cannot be interpreted on such a simple basis and numerous discrepancies are found (Figure 5). Incorrect

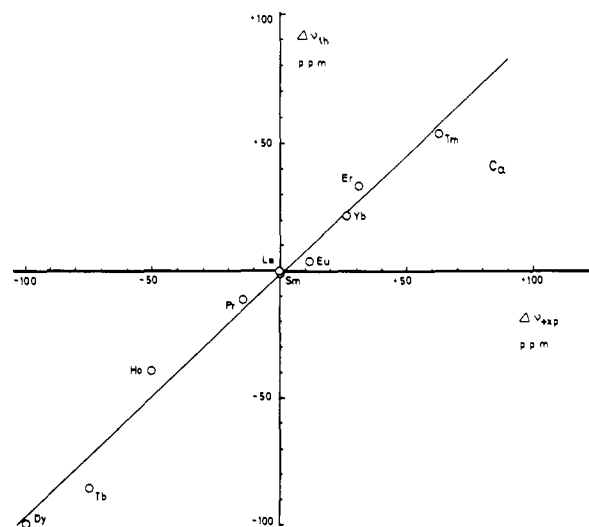


Figure 4. Correlation of observed C_α shifts for $\text{Ln}(\text{DPA})_3$ and $\text{Ln}(\text{MDPA})_3$ with Bleaney's dipolar C_D constants.¹² Each axis is scaled to -100 for the Dy^{3+} complexes.

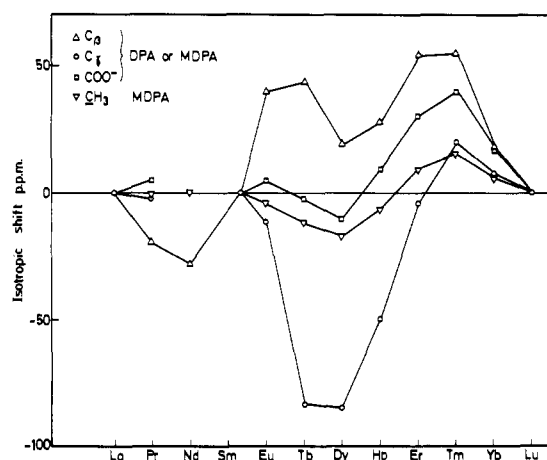
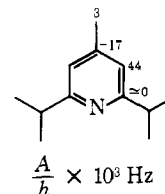


Figure 5. Variation of observed ^{13}C chemical shifts in $\text{Ln}(\text{DPA})_3$ and $\text{Ln}(\text{MDPA})_3$. The C_β , C_γ , and COO^- have the same shifts in both complexes.

signs are, for instance, obtained for the C_β shifts induced by most of the lanthanide ions and the relative magnitudes of these carbon shifts do not follow the regular C_D pattern.

These data point to a Fermi contact contribution in certain carbon spectra which appears to be absent in the proton spectra. Assuming purely dipolar ^1H shifts, the magnetic susceptibility term for each lanthanide complex was computed. Using the known geometric factors $G(\theta, r)$, estimations of the dipolar, and by difference the contact, contributions to the observed isotropic shifts were made. As illustrated in Figure 6, the large contact shifts calculated by this treatment vary linearly with $\langle S_z \rangle$ for all the carbon skeleton nuclei except C_α whose shifts are almost entirely dipolar in origin. The hyperfine coupling constants A can be calculated from these data and are essentially independent of the nature of the lanthanide ions. The constant A is particularly



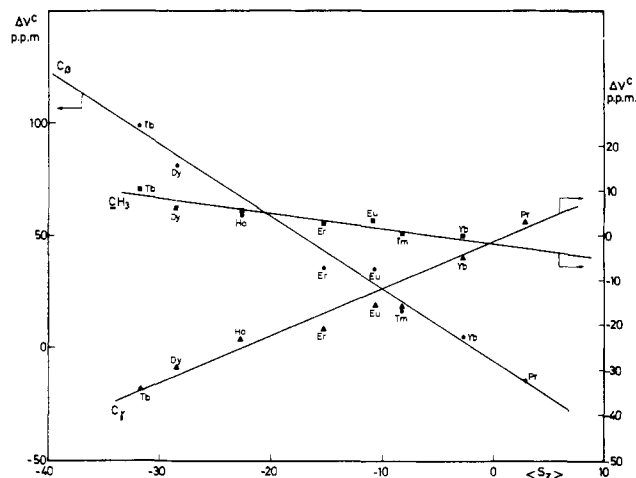


Figure 6. Correlation of the calculated C_β , C_γ , and CH_3 contact shifts with Golding's $\langle S_z \rangle$ function.¹⁶ See text.

large for C_β and decreases, with successive inversions of sign, for C_γ and for CH_3 . For most of the rare earths, the contact interaction at the C_β nuclei is larger than the dipolar interaction and of opposite sign. Unpaired spin density thus seems to account for the upfield C_β shifts. It is also of interest that contact shifts are not negligible for the methyl carbon although it is five bonds removed from the paramagnetic metal center (and 6.7 Å away).

Carbon-13 variable temperature measurements performed with a 0.08 M $\text{Yb}(\text{DPA})_3$ solution afford a completely independent proof of the significance of contact interactions. A T^{-2} temperature dependency is not followed by most of the carbon shifts, as nonlinear relationships and nonzero intercepts are obtained. The temperature data can be treated as the sum of a contact (eq 2) and a dipolar (eq 1) contribution, with the observed isotropic shift being expressed as:

$$\Delta H/H = (A/T) + (B/T^2) \quad (3)$$

A plot of $(\Delta H/H)T$ vs. T^{-1} allows computation of the constants A and B and consequently of the contact and dipolar contributions to the experimental shift at a given temperature. It is worth pointing out that, with this procedure, no prior assumption has to be made relative to the geometric structure or the origin of the ^1H shifts.

Large intercept values indicative of a substantial contact contribution are obtained for C_β and C_γ as shown in Figure 7. The contact and dipolar shifts computed on the basis of the solid state structure and on the basis of the temperature dependence are compared in Table II. The good agreement between the results obtained by the two independent approaches supports the validity of the relative contributions of the contact and dipolar shifts reported here.

Discussion

The DPA complexes appear to be ideal probes for the evaluation of recent theories proposed to interpret isotropic shifts induced by lanthanide ions. Through their use we were able to verify the main features of both the dipolar^{11,14} and the contact interactions¹⁶ on a reliable basis.

Our data show marked differences in the magnetic behavior of ^1H and of ^{13}C nuclei. The significance of contact interactions in the carbon spectra of some other organic molecules can now be inferred with greater confidence since suitable measurements (x-ray structures, magnetic susceptibility, and ^1H , ^{13}C NMR) are available in literature. For example, Horrocks and Sipe performed a detailed x-ray³ and magnetic susceptibility¹⁹ analysis of LSR adducts with

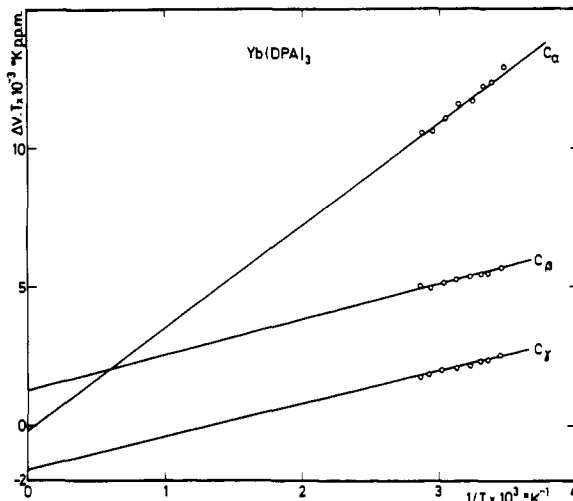


Figure 7. Temperature dependence of observed ^{13}C shifts of $\text{Yb}(\text{DPA})_3$ permitting separation of contact (intercept) and dipolar (slope) contributions.

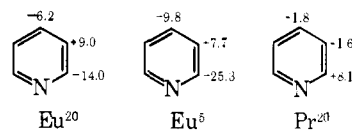
Table II. Contact and Dipolar Shifts in $\text{Yb}(\text{DPA})_3^a$

	Contact, ppm		Dipolar, ppm	
	$(\Delta H/H)_C^b$	$(\Delta H/H)_T^c$	$(\Delta H/H)_C^b$	$(\Delta H/H)_T^c$
C_α	≈ 0	≈ 0	+37.3	+34.8
C_β	+4.4	+3.6	+13.1	+14.2
C_γ	-5.1	-5.4	+12.8	+12.1

^a At 318 K in D_2O . ^b Computed from the geometrical model.

^c Computed from variable temperature measurements.

4-methylpyridine. They found no indication of a contact contribution for the methyl protons. The ^{13}C shifts of pyridine associated to $\text{Eu}(\text{thd})_3$ and $\text{Pr}(\text{thd})_3$ have been published^{5,20} and Gramer and Seff⁴ reported the crystal structure of $\text{Eu}(\text{thd})_3(\text{pyridine})_2$. We oriented the magnetic axes in this structure as suggested by Horrocks and Sipe¹⁹ and used their magnetic susceptibility data to compute the dipolar shifts in the pyridine ring. Using reported experimental shifts^{5,20} we compute that large contact shifts are induced by Eu^{3+} and that smaller shifts with opposite signs are present for the Pr^{3+} adduct, as could have been expected from a comparison of the $\langle S_z \rangle$ values. The computed ^{13}C contact shifts are:



Obviously contact shift contributions must be taken into account for LSR, particularly for ^{13}C spectral interpretation.

McGarvey and Kurland²¹ clearly outlined why contact contributions may be more significant in the ^{13}C spectra than in the ^1H spectra of paramagnetic complexes. The hyperfine coupling constant A depends on the square of the unpaired spin wave function $|\Psi_0|^2$ at the nucleus under consideration. The $|\Psi_0|^2$ function is much larger for nuclei heavier than ^1H , i.e., for nuclei of current interest in NMR such as ^{13}C , ^{19}F , and ^{31}P . Moreover, unpaired spin density at a carbon nucleus can reside in a p orbital and induce a ligand centered dipolar shift. This new contribution has not received much attention but Kurland and McGarvey²¹ point out that it may be significant even for a small amount of unpaired spin. Ligand-centered dipolar shifts are apparently of minor importance for lanthanide complexes of DPA

and MDPA as there was no need to introduce a third contribution in order to interpret the spectra.

From a more pragmatic viewpoint the present NMR data corroborate the various procedures used to separate ^{13}C contact and pseudocontact shifts where the assumption is made that ^1H shifts are purely of dipolar nature.^{5,22} This assumption should be checked through studies using several lanthanides, as contact contributions are not always negligible for protons.¹⁸ The Gd^{3+} induced shifts, recently reported for the first time by Ajisaka and Kainosho,⁶ afford in principle a new method of separation of the two forms of shifts; however, this ion leads to enormous line broadening for DPA complexes as well as for various LSR adducts and shifts are difficult or impossible to measure. Finally it should be pointed out that the variable temperature method outlined for $\text{Yb}(\text{DPA})_3$ has to be applied with reservation as the $\langle S_z \rangle$ factor of various lanthanides may follow a Curie-Weiss dependence instead of a simple T^{-1} law.

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^{13}C Nuclear Magnetic Resonance of Organophosphorus Compounds. X. Ring-Size Variation in Heterocyclic Phosphines, Phosphonium Salts, and Phosphine Oxides

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Abstract: ^{13}C chemical shifts and ^{13}C - ^{31}P nuclear spin couplings are reported for phosphorus heterocycles with exocyclic substitutions: phenyl, diphenyl, benzylphenyl, and phenyloxide. These saturated heterocycles extend from three-membered (only for the phosphine) through eight-membered rings, using di-*n*-butyl analogues as examples of unconstrained relatives. Sign determination for several of the ^{13}C - ^{31}P couplings in the phosphines has been made, including the only *positive* one-bond couplings yet observed for directly bonded ^{13}C - ^{31}P couplings in P(III) organophosphorus compounds. Dihedral angle dependence of two-bond ^{13}C - ^{31}P couplings in phosphines is observed, both in sign and magnitude. Proton chemical shifts for several of the phosphines were measured and assigned from data obtained from ^{13}C - $\{^1\text{H}\}$ double resonance data, cases in which this was impossible from direct observation of the proton NMR spectrum. A very large -39.7 Hz coupling was observed for the methylene carbon in the three-membered ring phenylphosphorinane, a coupling larger than the $(-38.7$ Hz coupling to the directly bonded phenyl carbon. This is in contrast to the near zero *positive* coupling to the corresponding methylene in a four-membered ring analogue, which yet has a very similar phenyl coupling. In addition to the ring size data, new results are reported for various ring methylation patterns of phenylphosphetanes and phenylbenzylphosphetanium salts.

Cyclic molecules have been traditionally interesting because of their restricted number of populated conformations. Variable temperature experiments have permitted estimates of these populations and uncovered stereochemical specificities in physical properties. Although the great majority of magnetic resonance work has been in ^1H NMR, the last decade has produced an accelerating number of ^{13}C NMR investigations in which the increased chemical shift dispersion has greatly extended the power of the NMR method. We have pursued²⁻⁸ the study of phosphorus het-

erocycles because of the attractive, multifaceted nature of phosphorus which provides stable compounds that can be studied in different oxidation states and a nuclear spin which allows an additional and very sensitive probe of molecular electronic structure through its couplings to the naturally abundant ^{13}C . In this work we systematically analyze the ^{13}C shifts and ^{13}C - ^{31}P couplings for four types of exocyclic phosphorus substitution: an oxide, two salts, and a phosphine. For each of these phosphorus substitutions a sizeable variation of (saturated) ring size is examined, using