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Gd(fod)₃-Induced Contact Shifts. A Versatile New Method to Estimate Contact and Pseudocontact Shift Contributions to Observed Lanthanide-Induced Shifts

Katsumi Ajisaka and Masatsune Kainosho*

Contribution from the Central Research Laboratories, Ajinomoto Co., Inc., Kawasaki, Japan.
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Abstract: A new method to separate the lanthanide-induced shifts into contact, pseudocontact, and complex formation contributions is described. We propose that the Gd(fod)₃-induced ¹³C shifts are a versatile measure of the contact contributions for shifts induced by lanthanide shift reagents other than Gd(fod)₃. We also suggest that shifts due to the complex formation between shift reagents and substrates should be quite small in cases of aliphatic compounds. On the other hand, in cases of aromatic compounds, the complex formation shifts were found to be significant. The interpretation is strongly supported by comparison of the evaluated contact shifts and pseudocontact shifts with theoretical values.

Chemical shifts induced by lanthanide shift reagents have been assumed to be dominated by the pseudocontact interaction. This assumption has been supported by the well-documented facts that for ¹H nmr the observed shifts nicely coincide with the calculated values based upon the simple axially symmetric pseudocontact equation.¹⁻³ However, recent observations of many anomalous lanthanide-induced shifts, mainly for other nuclei than ¹H, cannot easily be explained by pseudocontact shifts. This questions the assumption concerning the origin of the induced shifts for these nuclei.³⁻⁸

These abnormal shifts might be caused partly by contact interaction and partly by complex formation between lanthanide chelate and substrate⁹ since the induced shifts may contain three contributions, *i.e.*, pseudocontact shifts (PCS), contact shifts (CS), and complex formation shifts (CFS). We have previously indicated that caution must be exercised in the application of lanthanide shift reagents, because the CFS term as well as the CS term are sometimes too large to be ignored in the lanthanide-induced shifts.^{10,11} As it seems to be quite essential to have a better knowledge about the relative values of these terms when applying shift reagents to structural analysis, we describe here a new experimental method to separate the lanthanide-induced shifts into the three terms.

Results and Discussion

Several attempts to estimate the ¹³C CS contribution

* Address correspondence to this author at the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, Calif. 91109.

quantitatively have been reported so far. Among them, the procedure by Gansow, *et al.*, seems to be worth mentioning.⁶ Assuming the lanthanide-induced shifts in ¹H resonance to be almost entirely composed of PCS, they deduced the best fit for the geometry of the lanthanide metal-substrate adduct, with which they in turn calculated the possible ¹³C PCS values. The CS contributions to the observed shifts were readily estimated by comparing the calculated PCS with the observed ¹³C shifts. It is not necessarily valid, however, that the differences of these two values represent the CS contribution only.

Estimation of the CFS Term. As the first step to explain the curious aspects of the shifts induced in ¹³C resonances by complexes, we decided to eliminate the CFS contribution from the observed shifts. Such correction can be made using the shift values (*S* values)¹² induced by diamagnetic La(fod)₃ or Lu(fod)₃¹³ assuming that the CFS terms are the same for all the other lanthanide shift reagents. This assumption might be reasonable, because the CFS induced by La(fod)₃, the lightest lanthanide, and by Lu(fod)₃, the heaviest lanthanide, are usually very similar.¹⁰ In previous work, CFS terms as high as 10 ppm for pyridine *N*-oxide and related aromatic compounds were found.¹⁰ In contrast, for aliphatic compounds, as can be seen in Table I, La(fod)₃- and Lu(fod)₃-induced shifts are quite small, so it might be concluded that the CFS is not a major contribution to the abnormality of the ¹³C lanthanide shifts for these compounds.

Gd(fod)₃ Induced Shifts as a Measure of the CS Term. Previous reports have suggested the Gd complexes as useful

Table I. Lanthanide-Induced ^{13}C Shifts for Various Compounds

| Substrates | $\text{Ln}(\text{fod})_3$ | α factor ^a | Carbon position relative to the complexing site | | | | | | | | |
|---------------------------|---|---|---|---------|----------|----------|------------|---------|--------|----------|-------|
| | | | α | β | γ | δ | ϵ | ζ | η | θ | |
| γ -Picoline (1) | ^{13}C Chemical shift ^b | | -149.3 | -124.4 | -146.7 | -20.9 | | | | | |
| | Calcd N-PCS ^c | | 1.00 | 0.41 | 0.32 | 0.15 | | | | | |
| | La S value ^d | | +0.9 | | -2.2 | | | | | | |
| | Pr S value | | +111 | +25.0 | +30.8 | +11.6 | | | | | |
| | CS | -0.13 | +13.8 | -15.1 | +5.4 | -1.6 | | | | | |
| | PCS | | +96.2 | +40.1 | +28.8 | +13.2 | | | | | |
| | N-PCS | | 1.00 | 0.42 | 0.30 | 0.14 | | | | | |
| | Nd S value | | +62.3 | -2.1 | +17.2 | +4.8 | | | | | |
| | CS | -0.17 | +18.0 | -19.7 | +7.1 | -2.0 | | | | | |
| | PCS | | +43.3 | +17.6 | +13.5 | +6.8 | | | | | |
| | N-PCS | | 1.00 | 0.41 | 0.31 | 0.16 | | | | | |
| | Eu S value | | -83.5 | +19.2 | -33.6 | -3.2 | | | | | |
| | CS | -0.34 | -36.0 | +39.4 | -14.1 | +4.1 | | | | | |
| | PCS | | -48.5 | -20.2 | -16.1 | -7.3 | | | | | |
| | N-PCS | | 1.00 | 0.42 | 0.33 | 0.15 | | | | | |
| | Gd S value | | 1.00 | -105 | +116 | -45 | +12 | | | | |
| | CS | | | -106 | +116 | -41.6 | +12 | | | | |
| | Ho S value | | | +251 | +173 | +68.6 | +50.6 | | | | |
| | CS | 0.45 | | -47.7 | +52.2 | -18.7 | +5.4 | | | | |
| | PCS | | | +297.7 | +120.8 | +90.9 | +45.2 | | | | |
| | N-PCS | | | 1.00 | 0.41 | 0.31 | 0.15 | | | | |
| | Yb S value | | | +251 | +173 | +68.6 | +50.6 | | | | |
| | CS | 0.05 | | -5.3 | +5.8 | -2.1 | +0.6 | | | | |
| | PCS | | | -143.7 | -59.9 | -44.0 | -21.9 | | | | |
| | N-PCS | | | 1.00 | 0.42 | 0.31 | 0.15 | | | | |
| | Lu S value | | | +1.0 | | -4.6 | | | | | |
| | CFS ^e | | | +1.0 | | -3.4 | | | | | |
| | 1-Adamantane-carbonitrile (2) | ^{13}C Chemical shift ^b | | -124.8 | -30.1 | -39.9 | -27.1 | -35.7 | | | |
| | | Calcd N-PCS ^f | | 1.00 | 0.38 | 0.23 | 0.12 | 0.10 | | | |
| | | La S value ^g | | | -1.0 | | | | | | |
| Pr ^h S value | | | +19.6 | +17.8 | +18.1 | +7.5 | +5.8 | | | | |
| CS | | -0.45 | -40.2 | -2.5 | +2.1 | +0.8 | | | | | |
| PCS | | | +59.8 | +20.3 | +16.0 | +6.7 | +5.8 | | | | |
| N-PCS | | | 1.00 | 0.34 | 0.27 | 0.11 | 0.10 | | | | |
| Eu ^h S value | | | +57.8 | -4.3 | -11.3 | -4.5 | -2.9 | | | | |
| CS | | 0.95 | +84.8 | +5.3 | -4.4 | -1.7 | | | | | |
| PCS | | | -27.0 | -9.6 | -6.9 | -2.8 | -2.9 | | | | |
| N-PCS | | | 1.00 | 0.36 | 0.26 | 0.10 | 0.11 | | | | |
| Gd S value | | | 1.00 | +89.3 | +5.6 | -4.6 | -1.8 | | | | |
| Yb S value | | | | -27.1 | -12.3 | -7.4 | -4.4 | -3.5 | | | |
| CS | | 0.05 | | +4.5 | +0.3 | -0.2 | -0.1 | | | | |
| PCS | | | | -31.6 | -12.6 | -7.2 | -4.3 | -3.5 | | | |
| N-PCS | | | | 1.00 | 0.40 | 0.22 | 0.13 | 0.11 | | | |
| Lu S value ^g | | | | +1.3 | | | | | | | |
| n -Octyl alcohol (3) | | ^{13}C Chemical shift ^b | | -62.8 | -32.9 | -25.8 | -29.5 | -29.3 | -31.9 | -22.9 | -14.1 |
| | | La S value ^g | | | | | | | | | |
| | | Pr S value | | +79.9 | +32.1 | +18.9 | +10.4 | +6.3 | +3.5 | +1.9 | +2.0 |
| | CS | -0.10 | +2.4 | -3.2 | -0.4 | | | | | | |
| | PCS | | +77.5 | +35.3 | +18.9 | +10.4 | +6.3 | +3.5 | +1.9 | +2.0 | |
| | N-PCS | | 1.00 | 0.46 | 0.26 | 0.13 | 0.08 | 0.05 | 0.02 | 0.02 | |
| | Eu S value | | -58.0 | -9.7 | -7.8 | -5.0 | -2.5 | -1.9 | -1.3 | -1.5 | |
| | CS | 0.41 | -9.9 | +13.1 | +1.5 | | | | | | |
| | PCS | | -48.2 | -22.8 | -9.3 | -5.0 | -2.5 | -1.9 | -1.3 | -1.5 | |
| | N-PCS | | 1.00 | 0.47 | 0.19 | 0.10 | 0.05 | 0.04 | 0.03 | 0.03 | |
| | Gd S value | | 1.00 | -24.0 | +32.0 | +3.6 | | | | | |
| | Yb S value | | | -132 | -60.7 | -33.7 | -18.0 | -10.5 | -6.4 | -4.0 | -2.5 |
| | CS | 0.05 | | -1.2 | +1.6 | +0.2 | | | | | |
| | PCS | | | -130.8 | -62.3 | -33.9 | -18.0 | -10.5 | -6.4 | -4.0 | -2.5 |
| | N-PCS | | | 1.00 | 0.48 | 0.26 | 0.14 | 0.08 | 0.05 | 0.03 | 0.03 |
| | Lu S value ^g | | | +1.3 | | | | | | | |
| | n -Octylamine (4) | ^{13}C Chemical shift ^b | | -42.3 | -33.9 | -26.9 | -29.5 | -29.3 | -31.9 | -22.7 | -14.1 |
| | | La S value ^g | | +1.0 | | | | | | | |
| | | Pr S value | | +98.0 | +12.8 | +13.7 | +9.5 | +5.5 | +3.3 | +1.9 | +1.5 |
| | | CS | -0.15 | +18.8 | -22.8 | -3.1 | -0.9 | | | | |
| PCS | | | +79.2 | +35.6 | +16.8 | +10.4 | +5.5 | +3.3 | +1.9 | +1.5 | |
| N-PCS | | | 1.00 | 0.45 | 0.21 | 0.13 | 0.07 | 0.04 | 0.02 | 0.02 | |
| Nd S value | | | +43.4 | -4.0 | +4.2 | +3.4 | +1.8 | +1.2 | +0.6 | +0.7 | |
| CS | | -0.11 | +13.8 | -16.7 | -2.3 | -0.7 | | | | | |
| PCS | | | +29.6 | +12.7 | +6.5 | +4.1 | +1.8 | +1.2 | +0.6 | +0.7 | |
| N-PCS | | | 1.00 | 0.43 | 0.22 | 0.14 | 0.06 | 0.04 | 0.02 | 0.02 | |
| Sm S value | | | +5.9 | +5.2 | +2.1 | +1.1 | | | | | |
| CS | | 0.01 | -1.5 | +1.8 | +0.3 | +0.1 | | | | | |
| PCS | | | +7.4 | +3.4 | +1.8 | +1.0 | | | | | |
| N-PCS | | | 1.00 | 0.46 | 0.24 | 0.14 | | | | | |

Table I (Continued)

| Substrates | Ln(fod) ₃ | α factor ^a | Carbon position relative to the complexing site | | | | | | | |
|------------|----------------------|-----------------------|---|-------|-------|-------|-------|-------|-------|-------|
| | | | α | β | γ | δ | ε | ζ | η | θ |
| Eu | S value | 0.29 | -83.6 | +22.9 | -4.2 | -4.6 | -2.6 | -2.0 | -1.6 | -0.9 |
| | CS | | -36.3 | +44.1 | +6.1 | +1.8 | | | | |
| | PCS | | -47.3 | -21.2 | -10.3 | -6.4 | -2.6 | -2.0 | -1.6 | -0.9 |
| | N-PCS | | 1.00 | 0.45 | 0.22 | 0.14 | 0.06 | 0.04 | 0.03 | 0.02 |
| Gd | S value | 1.00 | -125 | +152 | +20.9 | +6.1 | | | | |
| Tb | S value | 0.80 | +395 | +358 | +132 | +68.3 | +41.3 | +25.0 | +15.9 | +13.3 |
| | CS | | -100 | +122 | +17 | +4.9 | | | | |
| | PCS | | +495 | +236 | +115 | +63.4 | +41.3 | +25.0 | +15.9 | +13.3 |
| | N-PCS | | 1.00 | 0.38 | 0.23 | 0.13 | 0.08 | 0.04 | 0.03 | 0.02 |
| Dy | S value | 0.47 | +542 | +355 | +151 | +78.8 | +48.7 | +30.2 | +19.6 | +14.0 |
| | CS | | -58.8 | +71.4 | +9.8 | +2.9 | | | | |
| | PCS | | +601 | +284 | +141 | +75.9 | +48.7 | +30.2 | +19.6 | +14.0 |
| | N-PCS | | 1.00 | 0.47 | 0.23 | 0.13 | 0.08 | 0.05 | 0.03 | 0.02 |
| Ho | S value | 0.38 | +195 | +170 | +62.1 | +31.4 | +19.0 | +11.4 | +7.1 | +5.6 |
| | CS | | -47.5 | +57.8 | +7.9 | +2.3 | | | | |
| | PCS | | +243 | +112 | +54.2 | +29.1 | +19.0 | +11.4 | +7.1 | +5.6 |
| | N-PCS | | 1.00 | 0.47 | 0.22 | 0.12 | 0.08 | 0.05 | 0.03 | 0.02 |
| Er | S value | 0.28 | -202 | -38.3 | -38.7 | -24.5 | -15.0 | -9.5 | -6.4 | -4.0 |
| | CS | | -35.0 | +42.6 | +5.9 | +1.7 | | | | |
| | PCS | | -167 | -89.9 | -44.6 | -26.2 | -15.0 | -9.5 | -6.4 | -4.0 |
| | N-PCS | | 1.00 | 0.48 | 0.27 | 0.16 | 0.09 | 0.06 | 0.04 | 0.02 |
| Tm | S value | 0.10 | -306 | -121 | -75.2 | -44.0 | -28.5 | -17.7 | -12.3 | -7.8 |
| | CS | | -12.5 | +15.2 | +2.1 | +0.6 | | | | |
| | PCS | | -293 | -136 | -77.3 | -44.6 | -28.5 | -17.7 | -12.3 | -7.8 |
| | N-PCS | | 1.00 | 0.46 | 0.26 | 0.15 | 0.09 | 0.06 | 0.04 | 0.02 |
| Yb | S value | 0.05 | -151 | -62.1 | -33.2 | -19.4 | -11.8 | -7.4 | -4.9 | -3.0 |
| | CS | | -6.3 | +7.6 | +1.1 | +0.3 | | | | |
| | PCS | | -145 | -69.7 | -34.3 | -19.7 | -11.8 | -7.4 | -4.9 | -3.0 |
| | N-PCS | | 1.00 | 0.48 | 0.24 | 0.14 | 0.08 | 0.05 | 0.03 | 0.02 |
| Lu | S value ^g | | +2.0 | | | | | | | |

^a Ratios relative to the CS induced by Gd(fod)₃ (see text). ^b Parts per million from internal TMS. ^c ¹³C shifts calculated from McConnell-Robertson equation, assuming a lanthanide-nitrogen distance of 2.6 Å along the C₂ axis which is an average of the Eu-N distance (2.651 Å)³⁰ and the Ho-N distance (2.533 Å)³¹ as determined by X-ray crystallography. There is good agreement with the lanthanide-induced ¹H shifts assuming this geometry. In each case, the calculated ¹³C PCS is normalized to that of the α carbon. ^d See ref 21. The estimated accuracy is ±1 ppm, and the values close to 1 ppm may not be significant. Negative and positive signs denote downfield and upfield shifts, respectively. ^e CFS = ¹/₃(S values (La) + S values (Lu)). ^f ¹³C PCS calculated similarly to γ-picoline (see footnote c to this table). The best-fit location of lanthanide ion is 2.6 Å away from the nitrogen along the C₃ axis, which agrees well with the ¹H shift induced by Eu(fod)₃. ^g The diamagnetic shifts for aliphatic compounds were too small to allow estimation of the CFS. Thus CFS contributions for 2-4 were ignored. ^h These data were measured for deuteriobenzene solutions.

"relaxation reagents" since it has generally been assumed that these complexes cause only line broadening.¹⁴ This aspect makes it difficult to observe the induced shifts, but using Gd(fod)₃, we could observe quite large shifts of the ¹³C resonances for various amines, nitriles, and alcohols. This is the first reported observation of such shifts. As the g tensor of Gd³⁺ has been predicted to be isotropic,^{9,15} the Gd-induced shifts should not contain any PCS term, which is assumed to originate in the anisotropic nature of the g tensor. The shifts induced by Gd(fod)₃ should therefore consist only of the CS term and CFS term, which allows the CS term induced by Gd(fod)₃ to be calculated directly by subtracting the CFS term. The contact contributions were found to fall off abruptly as one proceeds away from the site of complexation in agreement with theoretical considerations¹⁶ (Table I). Since these calculations do not involve the complexing metal, we assume, as a first approximation, that the profile of the shift attenuation^{16,17} is independent of the type of lanthanide ion. We therefore proceeded to assume that CS values induced by any lanthanide fod chelates could be evaluated by multiplying the CS values induced by Gd(fod)₃, CS_{Gd}, by an appropriate factor α. An appropriate α value was found by making the pseudocontact shift values (the observed shift, corrected for CFS, minus the α-CS_{Gd} term) satisfy the geometric factors of each nucleus in question. The sign of the α factor was found to be positive for Sm, Eu, Tb, Dy, Ho, Tm, and Yb and negative for Pr and Nd. This agrees with the prediction by Golding, *et al.*,¹⁸ Figure 3.

Using the procedures outlined above, we successfully estimated the CFS, CS, and PCS terms separately for various substrates. The values for two substrates with rigid molecular structure [γ-picoline (**1**) and 1-adamantanecarbonitrile (**2**)] and two with flexible molecular structure [*n*-octyl alcohol (**3**) and *n*-octylamine (**4**)] are listed in Table I. To facilitate comparison we introduced a new term, "N-PCS," which is a normalized PCS value relative to the PCS of the α carbon. The N-PCS value would be constant for the *i*th carbon regardless of the nature of the shift reagents, if the geometry of the substrate-shift reagent adduct was invariant.

Attempts to Separate CS from PCS. From ¹H resonance shifts by Eu(fod)₃, which are assumed to be predominantly due to PCS contributions, the best fit for the location of the lanthanide ion in the adduct with rigid compounds can easily be computed. Calculation of geometric factors was thus made for **1**, the distance between the lanthanide metal and the nitrogen atom being 2.6 Å along the C₂ axis (see footnote c, Table I). It should be noted that the CFS contributions for the C_γ of γ-picoline are too large to be ignored, and therefore Gansow's procedure to evaluate the CS contributions by subtracting the estimated PCS from the observed shifts would be inadequate.¹⁹ Similarly the geometric factors of **2** were calculated (see footnote f, Table I). For this compound, the CFS terms were found to be negligible as for **3** and **4**. Then the CS of **2** can be easily estimated (Table I). Marked CS contributions, which are opposite in sign, are evident for Eu(fod)₃- and Pr(fod)₃-induced ¹³C

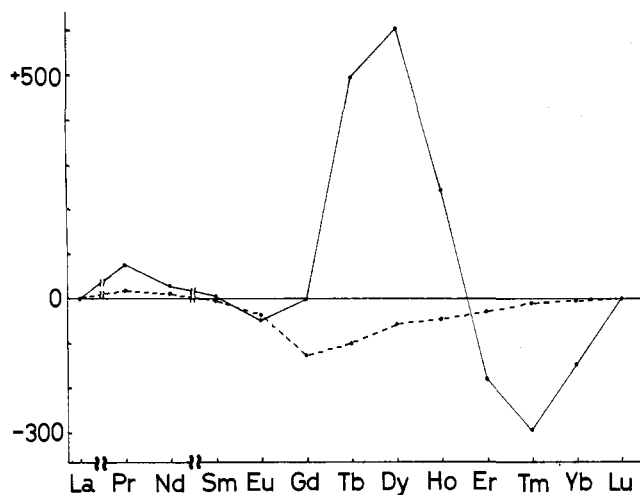
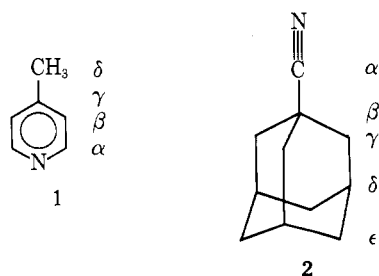


Figure 1. ^{13}C contact shift (broken line) and pseudocontact shift (solid line) of the α carbon of **4** plotted against the type of lanthanide shift reagent. Ce and Pm are not included. Vertical scale is given in parts per million and positive sign denotes upfield shifts.



shifts. These observations are in agreement with our previous findings.²⁰ Analogous treatments were applied to the flexible molecules **3** and **4**. In these cases, although a unique conformation could not be given for the shift reagent-substrate adduct, the ^{13}C PCS would be expected to fall off monotonically with distance from the site of the complexation, as has been found for the ^1H case of similar substrates.^{3,20} The CS ratio for each lanthanide chelate was adjusted to afford constant N-PCS values for all the shift reagents by trial and error computation varying the α factors.²¹ These results are also listed in Table I.

Some Features of the Results. The PCS and CS terms of the α carbon of **4** were plotted as a function of the atomic number of the lanthanide ion, as is shown in Figure 1. The PCS curve (solid line) shows the same features found for the lanthanide-induced ^1H shifts of γ -methyl protons of **1**,²² which also supports our estimations. In aliphatic compounds **2-4**, the $\text{La}(\text{fod})_3$ - and $\text{Lu}(\text{fod})_3$ -induced shifts are small relative to the other two terms, and as anticipated the CFS should be totally negligible. In this situation, our method is practically equivalent to that given by Gansow, *et al.*,⁶ except that their method needs the best-fit location of the lanthanide ion. Such locations are usually quite difficult to obtain for flexible substrates. Also evident from Figure 1 is that the maximum upfield PCS was obtained for $\text{Dy}(\text{fod})_3$ and the maximum downfield PCS by $\text{Tm}(\text{fod})_3$, so that $\text{Dy}(\text{fod})_3$, and also $\text{Tb}(\text{fod})_3$, may be chosen if only an "expanded" spectrum is needed. Generally, $\text{Tm}(\text{fod})_3$ should be the most suitable shift reagent for ^{13}C nmr.²³ $\text{Eu}(\text{fod})_3$ and $\text{Pr}(\text{fod})_3$, which have been the most popular shift reagents in ^1H nmr spectroscopy, are evidently not suited for ^{13}C spectroscopy.

Comparison with Theories. The deduced PCS values for

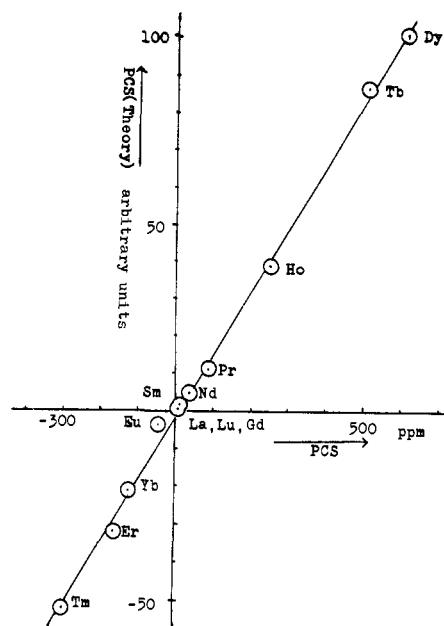


Figure 2. Comparison of theoretical⁹ and experimental pseudocontact shifts for α carbon of **4**. A linear relation ($r = 0.998$) was computed by performing a least-squares analysis.

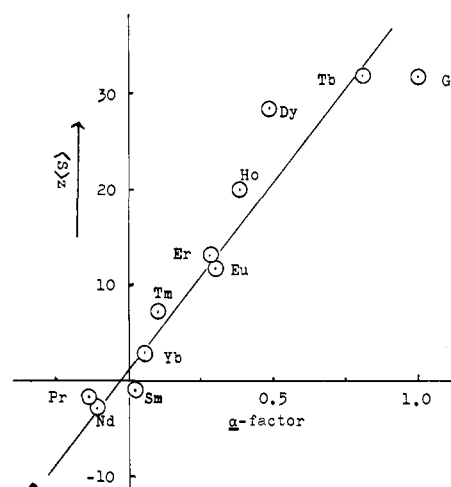


Figure 3. The weighted average of the Z component of the lanthanide electron spin, $\langle S_z \rangle$,¹⁸ compared with the α factor for **4**. A linear plot ($r = 0.95$) was also obtained by computation.

each carbon nucleus of **4** could be correlated linearly with the theoretically predicted values by Bleaney, *et al.*²⁴ The linearity (correlation coefficient $r = 0.998$) is illustrated in Figure 2 for the α carbon. The Eu -induced PCS were found to deviate considerably from the expected value (observed -47.4 ppm, calculated -19.4 ppm), which may be attributed to the ambiguity existing in calculating the Eu^{3+} -induced dipolar shifts.^{9,25,26} The CS values were also compared with the theoretical values for the weighted average of the Z components of the lanthanide electron spin, $\langle S_z \rangle$.¹⁸ In this case, the α factor for **4** (Table I) and all five sets of $\langle S_z \rangle$ in the table of Golding's paper¹⁸ were used. Correlation coefficients in each case were in the range 0.94–0.95 (Figure 3), which, considering the rather simplified theoretical treatment in their paper, can be regarded as a reasonable fit. Our method to separate the CS and PCS from the observed lanthanide shifts, thus, is supported by the theoretical considerations.²⁷ Furthermore, the ratios of the CS to the PCS for the α carbon of the four compounds in Table

Table II. The Normalized Ratio of CS to PCS for Various Lanthanide Shift Reagents^{a,b}

| Ln(fod) ₃ | Substrates | | | | Gansow, <i>et al.</i> ^c |
|----------------------|------------|------|-------------------|-------------------|---------------------------------------|
| | 1 | 2 | 3 | 4 | |
| Pr | 0.19 | 0.22 | 0.15 | 0.31 | 0.19 |
| Nd | 0.57 | | | 0.61 | 0.88 |
| Sm | | | | (-)0.25 | |
| Eu | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| Tb | | | | (-)0.26 | 0.26 |
| Dy | | | | (-)0.13 | 0.16 |
| Ho | (-)0.22 | | | (-)0.26 | 0.24 |
| Er | | | | 0.27 | 0.31 |
| Tm | | | | 0.05 | |
| Yb | 0.05 | 0.04 | 0.05 ^c | 0.05 ^c | 0.06 |

^a Shift values for the α carbon were used, although Gansow, *et al.*, used average values for the five carbons in the nitrogen ring of isoquinoline. ^b All values were arbitrarily normalized with respect to the Eu values. This normalization eliminates differences between the geometric factors for various substrates. Also the CS-PCS ratios eliminate a possible difference in the equilibrium constant for association of shift reagent and substrate. The difference in equilibrium constants may directly affect the α factor as is evident by the α factors for **2** with Eu(fod)₃ and Pr(fod)₃ which were obtained in benzene solutions. ^c These values are arbitrarily fixed (see ref 21).

I were compared with those given by Gansow, *et al.*,⁶ for the nitrogen ring carbons of isoquinoline (Table II). For all the compounds **1-4**, the agreement between the two procedures is reasonable.²⁸

The applicability of the present method, especially to compounds where the coordinated structure is unknown, demonstrates its usefulness as compared with previous methods. Accordingly, the ¹³C PCS deduced by this method could safely be applied to the structural examination of organic compounds.

Experimental Section

¹³C (25.2 MHz) and ¹H (100.1 MHz) nmr spectra were measured on a Varian XL-100 with an FT accessory. All chemical shifts were determined with reference to internal TMS. The solvent except as noted in Table I was deuteriochloroform dried over molecular sieves. The samples were 1 M in substrate with Ln(fod)₃ varying from 0.0 to 0.3 M, except with Gd(fod)₃ which was varied from 0.0 to 0.15 M. Usually 8K data points were sampled for ¹³C FT nmr; however, in cases with severely broadened lines due to the added shift reagents, as few as 1K data points were used for FT to give the best results. The spectral window was 5 kHz for **1** and 2.5 kHz for the other substrates. Assignments of ¹³C nmr were completed for the lanthanide shifted spectra using off-resonance coherent wave decoupling. All shift reagents, except La(fod)₃ and Lu(fod)₃, were commercially available. La(fod)₃ and

Lu(fod)₃, and some of the other chelates, were synthesized by the usual method²⁹ and were fully characterized by elemental analysis and mass spectra.

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