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Calculation of NMR Shift in Paramagnetic System when the Threefold Axis is Chosen as the Quantization Axis (III). The NMR Shift for $3d^2$ System in a Strong Crystal Field of Octahedral Symmetry

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A general expression using the nonmultipole expansion method is derived for the NMR shift arising from 3d electron angular momentum and the 3d electron spin dipolar-nuclear spin angular momentum interactions for a $3d^2$ system in a strong crystal field environment of octahedral symmetry when the threefold axis is chosen as the quantization axis. The NMR shift is separated to the contribution of constant, $1/R^5$ and $1/R^7$ terms and compared with the multipolar terms. We find that $1/R^5$ term contributes dominantly to the NMR shift but the contribution of $1/R^7$ term may not be negligible. It is also found that the exact values of the NMR shift are in agreement with the multipolar results for distances larger than 0.35 nm.

Introduction

Since 1960, a great deal of interest has been centered on the nuclear magnetic resonance of paramagnetic molecules.¹ Effects of paramagnetism on the characteristics of nuclear resonances have been investigated by the various methods. In this work, we investigate the NMR shift arising from the electron angular momentum and the electron spin dipolar-nuclear spin angular momentum interactions for a $3d^2$ system in a strong crystal field environment of octahedral symmetry when the threefold axis is chosen as the quantization axis. For a $3d^1$ system a few methods have been developed to investigate the pseudo contact contribution to the NMR shift when the fourfold axis is chosen as the quantization axis.²⁻⁷ Recently, the nonmultipole expansion method has been developed by Golding and Stubbs⁸ and this method was applied to investigate the NMR shift for a $3d^1$ system in a strong crystal field of octahedral, tetragonal and trigonal symmetries when bonding with the paramagnetic center was included.⁹ The nonmultipole expansion method was also applied to elucidate the NMR shift for a $4f^1$ and $4f^{13}$ systems when the fourfold axis is chosen to be our axis of

quantization.¹⁰ More recently we have investigated the NMR shift for a $3d^1$ system in a strong crystal field of octahedral, and trigonal symmetries and the exact solution^{11,12} for the NMR shift was compared with the multipolar terms.^{13,14}

The magnetic moments for a $3d^2$ system were calculated theoretically using the axial wave functions when threefold axis is chosen as the quantization axis.¹⁵ In that work, the dipolar shift was also calculated adopting the paramagnetic susceptibility. No attempt has been made theoretically to investigate the NMR shift for a $3d^2$ system as far as we are aware.

Theory

For a $3d^n$ system in a strong crystal field environment of octahedral symmetry, the appropriate hamiltonian representing the various interactions is given by

$$\mathcal{H} = \sum_{i=1}^n \left\{ -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i} \right\} + \sum_{i>j} \frac{e^2}{r_{ij}} + \sum_{i=1}^n V(r_i) + \sum_{i=1}^n \zeta_i \mathbf{l}_i \cdot \mathbf{s}_i + \sum_{i=1}^n \mathcal{H}_B(\mathbf{l}_i + 2\mathbf{s}_i) \cdot \mathbf{B} + \mathcal{H}_b \quad (1)$$

where

$$V = \sum_{i=1}^n V(r_i) = a_4 \left\{ \frac{1}{3} \sqrt{\frac{7}{3}} Y_{40}(\theta, \phi) - \frac{1}{3} \sqrt{\frac{10}{3}} [Y_{4-3}(\theta, \phi) \right.$$

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$$-Y_{43}(\theta, \phi)] \quad (2)$$

and

$$\mathcal{H}_{hy} = \frac{\mu_0}{4\pi} g_N \mu_B \mu_N \left\{ \frac{2L_N \cdot I}{r_N^3} + g_s \left[\frac{3(r_N \cdot s) r_N \cdot I}{r_N^5} - \frac{s \cdot I}{r_N^3} \right] \right\} \quad (3)$$

Here r_i and r_N are the electron radius vectors about the electronbearing atom and the nucleus with nuclear spin angular momentum I , respectively. The quantity B is the applied magnetic field, V is the crystal field potential of octahedral symmetry and a_4 is the required crystal field parameter for the 3d electron system. The other symbols have their usual meaning. The ground state for a 3d² system in a strong crystal field of octahedral symmetry is ³T₁, which is originated from both (*t*₂²) and (*e*¹, *t*₂¹) electron configurations.¹⁷ Since the contribution of (*e*¹, *t*₂¹) to the ground state (³T₁) is negligibly small, we may neglect the contribution of (*e*¹, *t*₂¹) to the ground state wavefunctions for a 3d² system in a strong crystal field environment of octahedral symmetry.¹⁵ When the threefold axis is chosen as the quantization axis, the two electron wavefunctions resulting from the spin-orbit coupling interactions for a 3d² system in a strong octahedral crystal field, adopting $|\phi_i^{ms}\rangle$ notation, is given by^{18,19}

$$\begin{aligned} \chi_1 &= \frac{1}{\sqrt{2}} |\phi_0^+ \phi_2^+| \\ \chi_3 &= \frac{1}{\sqrt{2}} |\phi_0^- \phi_1^-| \\ \chi_3 &= \frac{1}{\sqrt{2}} |\phi_0^+ \phi_1^+| \\ \chi_4 &= \frac{1}{\sqrt{2}} |\phi_0^- \phi_2^-| \\ \chi_5 &= \frac{1}{2} \{ |\phi_1^- \phi_2^+| + |\phi_1^+ \phi_2^-| \} \\ \chi_6 &= \frac{1}{\sqrt{2}} |\phi_1^+ \phi_2^+| \\ \chi_7 &= \frac{1}{2} \{ |\phi_0^+ \phi_2^-| + |\phi_0^- \phi_2^+| \} \\ \chi_8 &= \frac{1}{2} \{ |\phi_0^+ \phi_1^-| + |\phi_0^- \phi_1^+| \} \\ \chi_9 &= \frac{1}{\sqrt{2}} |\phi_1^- \phi_2^-| \end{aligned} \quad (4)$$

where

$$\begin{aligned} |\phi_1 \phi_2| &\equiv \begin{vmatrix} \phi_1(1) \phi_1(2) \\ \phi_2(1) \phi_2(2) \end{vmatrix}, \\ \phi_0 &= |3d_z^2\rangle, \quad \phi_1 = \sqrt{\frac{3}{2}} |3d_x^2\rangle - \sqrt{\frac{1}{3}} |3d_{-1}\rangle \end{aligned}$$

and

$$\phi_2 = \sqrt{\frac{2}{3}} |3d_{-2}\rangle + \sqrt{\frac{1}{3}} |3d_1\rangle. \quad (5)$$

To determine the NMR shift for a 3d² system in a strong crystal field of octahedral symmetry, the magnetic field interaction is added and treated as a perturbation to yield new eigenfunctions, $|\psi_n\rangle$, and corresponding eigenvalues, E_n . The principal values of the NMR shielding tensor σ are determined by considering the magnetic field as parallel to the *x*, *y* and *z* axes and then averaged by using a Boltzmann distribution. The contribution to the NMR shift, ΔB , is given by

$$\Delta B = \frac{1}{3} B (\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) \quad (6)$$

where

$$\sigma_{\alpha\alpha} = \left[\frac{\partial^2}{\partial \mu_\alpha \partial B_\alpha} \left(\frac{\sum_i \langle \phi_i | \mathcal{H}_{hy} | \phi_i \rangle \exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)} \right) \right]_{\mu=B=0}$$

and

$$\mu = g_N \mu_N I$$

To evaluate the hyperfine interaction matrix elements, $\langle \phi_i | \mathcal{H}_{hy} | \phi_i \rangle$, we adopt the hyperfine interaction integrals.^{8,11} In a strong crystal field environment of octahedral symmetry, the NMR shift, $\Delta B/B$, for a 3d² system when the threefold axis is chosen as the quantization axis is given by

$$\frac{\Delta B}{B} = \frac{2}{3} \frac{\mu_0}{4\pi} \frac{\mu_B^2}{kT} \left\{ \frac{\sum_{i=1}^3 (B_i + A_i kT/\zeta) \exp(-E_i/kT)}{\sum_{i=1}^3 d_i \exp(-E_i/kT)} \right\} \quad (7)$$

where $E_1 = -\zeta/2$, $E_2 = \zeta/2$, $E_3 = \zeta$, $d_1 = 5$, $d_2 = 3$, $d_3 = 1$ and ζ is the spin-orbit coupling constant.

In equation (7), A_i and B_i are expressed as a function of spherical harmonics as given in the following,

$$\begin{aligned} A_1 &= -22/55(\pi)^{\frac{1}{2}} Y_{00}(\theta, \phi) A_1(t) \\ &+ 16128/t^5(\pi/21)^{\frac{1}{2}} [1/3(7/3)^{\frac{1}{2}} Y_{40}(\theta, \phi) \\ &\mp 1/3(10/3)^{\frac{1}{2}} \{ Y_{4-3}(\theta, \phi) - Y_{43}(\theta, \phi) \}] S_1(t) \\ &+ 1382400/t^7(\pi/26)^{\frac{1}{2}} [4/9(2)^{\frac{1}{2}} Y_{60}(\theta, \phi) \\ &\pm 1/9(35/3)^{\frac{1}{2}} \{ Y_{6-3}(\theta, \phi) - Y_{63}(\theta, \phi) \} \\ &+ 1/9(77/6)^{\frac{1}{2}} \{ Y_{6-6}(\theta, \phi) + Y_{66}(\theta, \phi) \}] M(t) \end{aligned} \quad (8)$$

$$\begin{aligned} A_2 &= -18/35(\pi)^{\frac{1}{2}} Y_{00}(\theta, \phi) A_2(t) \\ &- 16218/t^5(\pi/21)^{\frac{1}{2}} [1/3(7/3)^{\frac{1}{2}} Y_{40}(\theta, \phi) \\ &\mp 1/3(10/3)^{\frac{1}{2}} \{ Y_{4-3}(\theta, \phi) - Y_{43}(\theta, \phi) \}] S_2(t) \\ &- 4147200/t^7(\pi/26)^{\frac{1}{2}} [4/9(2)^{\frac{1}{2}} Y_{60}(\theta, \phi) \\ &\mp 1/9(35/3)^{\frac{1}{2}} \{ Y_{6-3}(\theta, \phi) - Y_{63}(\theta, \phi) \} \\ &+ 1/9(77/6)^{\frac{1}{2}} \{ Y_{6-6}(\theta, \phi) + Y_{66}(\theta, \phi) \}] M(t) \end{aligned} \quad (9)$$

$$\begin{aligned} A_3 &= 8/7(\pi)^{\frac{1}{2}} Y_{00}(\theta, \phi) P(t) \\ &+ 10752/t^5(\pi/21)^{\frac{1}{2}} [1/3(7/3)^{\frac{1}{2}} Y_{40}(\theta, \phi) \\ &\mp 1/3(10/3)^{\frac{1}{2}} \{ Y_{4-3}(\theta, \phi) - Y_{43}(\theta, \phi) \}] S_3(t) \\ &+ 2764800/t^7(\pi/26)^{\frac{1}{2}} [4/9(2)^{\frac{1}{2}} Y_{60}(\theta, \phi) \\ &\pm 1/9(35/3)^{\frac{1}{2}} \{ Y_{6-3}(\theta, \phi) - Y_{63}(\theta, \phi) \} \\ &+ 1/9(77/6)^{\frac{1}{2}} \{ Y_{6-6}(\theta, \phi) + Y_{66}(\theta, \phi) \}] M(t) \end{aligned} \quad (10)$$

$$\begin{aligned} B_1 &= 34/105(\pi)^{\frac{1}{2}} Y_{00}(\theta, \phi) A_3(t) \\ &- 6272/t^5(\pi/21)^{\frac{1}{2}} [1/3(7/3)^{\frac{1}{2}} Y_{40}(\theta, \phi) \\ &\mp 1/3(10/3)^{\frac{1}{2}} \{ Y_{4-3}(\theta, \phi) - Y_{43}(\theta, \phi) \}] W_1(t) \\ &- 345600/t^7(\pi/26)^{\frac{1}{2}} [4/9(2)^{\frac{1}{2}} Y_{60}(\theta, \phi) \\ &\pm 1/9(35/3)^{\frac{1}{2}} \{ Y_{6-3}(\theta, \phi) - Y_{63}(\theta, \phi) \} \\ &+ 1/9(77/6)^{\frac{1}{2}} \{ Y_{6-6}(\theta, \phi) + Y_{66}(\theta, \phi) \}] M(t) \end{aligned} \quad (11)$$

$$B_2 = 8/105(\pi)^{\frac{1}{2}} Y_{00}(\theta, \phi) A_4(t)$$

$$\begin{aligned}
& + 896/t^5 (\pi/21)^{\frac{1}{2}} [1/3(7/3)^{\frac{1}{2}} Y_{40}(\theta, \phi) \\
& \mp 1/3(10/3)^{\frac{1}{2}} \{Y_{4-3}(\theta, \phi) - Y_{43}(\theta, \phi)\}] W_2(t) \\
& + 345600/t^7 (\pi/26)^{\frac{1}{2}} [4/9(2)^{\frac{1}{2}} Y_{60}(\theta, \phi) \\
& \pm 1/9(35/3)^{\frac{1}{2}} \{Y_{6-3}(\theta, \phi) - Y_{63}(\theta, \phi)\} \\
& + 1/9(77/6)^{\frac{1}{2}} \{Y_{6-6}(\theta, \phi) + Y_{66}(\theta, \phi)\}] M(t) \quad (12)
\end{aligned}$$

$$B_3=0$$

where

$$\begin{aligned}
A_1(t) &= \beta^3 \exp(-t) \left(8/99 t^4 / 4! + \sum_{n=0}^3 t^n / n! \right) \\
A_2(t) &= \beta^3 \exp(-t) \left(-8/27 t^4 / 4! + \sum_{n=0}^3 t^n / n! \right) \\
A_3(t) &= \beta^3 \exp(-t) \left(2/51 t^4 / 4! + \sum_{n=0}^3 t^n / n! \right) \\
P(t) &= \beta^3 \exp(-t) \left(-4/45 t^4 / 4! + \sum_{n=0}^3 t^n / n! \right) \\
S_1(t) &= \beta^3 \left\{ 1 - \exp(-t) \left(4/33 t^9 / 9! + \sum_{n=0}^8 t^n / n! \right) \right\} \\
S_2(t) &= \beta^3 \left\{ 1 - \exp(-t) \left(16/11 t^9 / 9! + \sum_{n=0}^8 t^n / n! \right) \right\} \\
S_3(t) &= \beta^3 \exp(-t) (-16/11 t^9 / 9!) \\
W_1(t) &= \beta^3 \left\{ 1 - \exp(-t) \left(44/27 t^9 / 9! + \sum_{n=0}^8 t^n / n! \right) \right\} \\
W_2(t) &= \beta^3 \left\{ 1 - \exp(-t) \left(24/11 t^9 / 9! + \sum_{n=0}^8 t^n / n! \right) \right\} \\
M(t) &= \beta^3 \left(1 - \exp(-t) \sum_{n=0}^{11} t^n / n! \right) \\
A_4(t) &= \beta^3 \exp(-t) \left(-1/6 t^n / 4! + \sum_{n=0}^3 t^n / n! \right)
\end{aligned}$$

and $t=2\beta R$.

Since this expression for $\Delta B/B$ is applicable for all values of R , we may readily determine from eq. (7) the case when $R \rightarrow 0$

$$\begin{aligned}
\Delta B/B \rightarrow & 2/315 \beta^3 \frac{\mu_0}{4\pi} \frac{\mu_B^2}{kT} \\
& \left\{ \frac{(17-33kT/\zeta) \exp(\zeta/2kT) + (4-27kT/\zeta) \exp(-\zeta/2kT)}{5 \exp(\zeta/kT) + 3 \exp(-\zeta/2kT) + \exp(-\zeta/kT)} \right. \\
& \left. + 60kT/\zeta \exp(-\zeta/kT) \right\} \quad (13)
\end{aligned}$$

When R is large, the term in eqs. (8-12) involving the polar coordinates of the NMR may be expressed in terms of $1/R^5$ and $1/R^7$,

$$\begin{aligned}
A_1 &= 1/R^5 [504/\beta^2 (\pi/21)^{\frac{1}{2}} (1/3(7/3)^{\frac{1}{2}} Y_{40}(\theta, \phi) \\
& \mp 1/3(10/3)^{\frac{1}{2}} \{Y_{4-3}(\theta, \phi) - Y_{43}(\theta, \phi)\}) \\
& + 1/R^7 [10800/\beta^4 (\pi/26)^{\frac{1}{2}} (4/9(2)^{\frac{1}{2}} Y_{60}(\theta, \phi) \\
& \pm 1/9(35/3)^{\frac{1}{2}} \{Y_{6-3}(\theta, \phi) - Y_{63}(\theta, \phi)\} \\
& + 1/9(77/6)^{\frac{1}{2}} \{Y_{6-6}(\theta, \phi) + Y_{66}(\theta, \phi)\})] \quad (14)
\end{aligned}$$

$$\begin{aligned}
A_2 &= 1/R^5 [-504/\beta^2 (\pi/21)^{\frac{1}{2}} (1/3) (7/3)^{\frac{1}{2}} Y_{40}(\theta, \phi) \\
& \mp 1/3(10/3)^{\frac{1}{2}} \{Y_{4-3}(\theta, \phi) - Y_{43}(\theta, \phi)\}) \\
& + 1/R^7 [-32400/\beta^4 (\pi/26)^{\frac{1}{2}} (4/9(2)^{\frac{1}{2}} Y_{60}(\theta, \phi) \\
& \pm 1/9(35/3)^{\frac{1}{2}} \{Y_{6-3}(\theta, \phi) - Y_{63}(\theta, \phi)\} \\
& + 1/9(77/6)^{\frac{1}{2}} \{Y_{6-6}(\theta, \phi) + Y_{66}(\theta, \phi)\})] \quad (15)
\end{aligned}$$

$$\begin{aligned}
A_3 &= 1/R^7 [21600/\beta^4 (\pi/26)^{\frac{1}{2}} (4/9(2)^{\frac{1}{2}} Y_{60}(\theta, \phi) \\
& \pm 1/9(35/3)^{\frac{1}{2}} \{Y_{6-3}(\theta, \phi) - Y_{63}(\theta, \phi)\})
\end{aligned}$$

$$+ 1/9(77/6)^{\frac{1}{2}} \{Y_{6-6}(\theta, \phi) + Y_{66}(\theta, \phi)\})] \quad (16)$$

$$\begin{aligned}
B_1 &= 1/R^5 [-196/\beta^2 (\pi/21)^{\frac{1}{2}} (1/3(3/7)^{\frac{1}{2}} Y_{40}(\theta, \phi) \\
& \mp 1/3(10/7) \{Y_{4-3}(\theta, \phi) - Y_{43}(\theta, \phi)\}) \\
& + 1/R^7 [-2700/\beta^4 (\pi/26)^{\frac{1}{2}} (4/9(2)^{\frac{1}{2}} Y_{60}(\theta, \phi) \\
& \pm 1/9(35/3)^{\frac{1}{2}} \{Y_{6-3}(\theta, \phi) - Y_{63}(\theta, \phi)\} \\
& + 1/9(77/6)^{\frac{1}{2}} \{Y_{6-6}(\theta, \phi) + Y_{66}(\theta, \phi)\})] \quad (17)
\end{aligned}$$

$$\begin{aligned}
B_2 &= 1/R^5 [28/\beta^2 (\pi/21)^{\frac{1}{2}} (1/3(7/3)^{\frac{1}{2}} Y_{40}(\theta, \phi) \\
& \mp 1/3(10/3)^{\frac{1}{2}} \{Y_{4-3}(\theta, \phi) - Y_{43}(\theta, \phi)\}) \\
& + 1/R^7 [2700/\beta^4 (\pi/26)^{\frac{1}{2}} (4/9(2)^{\frac{1}{2}} Y_{60}(\theta, \phi) \\
& \pm 1/9(35/3)^{\frac{1}{2}} \{Y_{6-3}(\theta, \phi) - Y_{63}(\theta, \phi)\} \\
& + 1/9(77/6)^{\frac{1}{2}} \{Y_{6-6}(\theta, \phi) + Y_{66}(\theta, \phi)\})] \quad (18)
\end{aligned}$$

In eqs. (8-12), the symmetry of the 3d² system is reflected in the analytical form for $\Delta B/B$, so that only those combinations of the spherical harmonics, $Y_{lm}(\theta, \phi)$, that transform as the irreducible representation $A_1 a_1$ of the octahedral group occur. This is also the case for 3d¹ system.²⁰

Results and Discussion

The calculated NMR shifts along the x , y and z axes for a 3d² system in a strong crystal field environment of octahedral symmetry are listed in Table 1. Here we choose $\beta=1.55/a_0$.

TABLE 1: $\Delta B/B$ (ppm) for Specific R -values for a 3d² System along the x , y and z Axes in a Strong Crystal field Environment of Octahedral Symmetry When the Three fold Axis is chosen to be our Axis of Quantization

R (nm)	$\Delta B/B$		
	(100) axis	(010) axis	(001) axis
0.05	-382.944	-359.735	-331.038
0.10	-107.548	-53.336	-9.966
0.15	-22.763	10.086	33.343
0(20)	-4.478	8.058	17.327
0.25	-0.741	3.369	6.942
0.30	-0.015	1.340	2.827
0.35	0.093	0.580	1.266
0.40	0.084	0.277	0.628
0.45	0.061	0.145	0.339
0.50	0.042	0.082	0.197

TABLE 2: $\Delta B/B$ (ppm) for Specific R -values for a 3d² System in a Strong Crystal Field Environment of Octahedral Symmetry when the Threefold Axis is Chosen to be our Axis of Quantization

R (nm)	$\Delta B/B$		
	(100) axis	(110) axis	(111) axis
0.05	-382.944	-371.339	-367.429
0.10	-107.548	-80.442	-52.971
0.15	-22.763	-6.339	22.821
0.20	-4.478	1.790	21.498
0.25	-0.741	1.314	13.546
0.30	-0.015	0.663	8.629
0.35	0.093	0.335	5.961
0.40	0.084	0.180	4.468
0.45	0.061	0.103	3.584
0.50	0.042	0.062	3.040

TABLE 3: A Comparison of the Exact Values of $\Delta B/B$ (ppm) Using eq. (7) with the Multipolar Terms for Specific R -values (a) Along the (100) Axis

R (nm)	$\Delta B/B$			
	$1/R^5$	$1/R^7$	Sum of all multipolar terms	from eq.(7)
0.05	16.585	-14.618	1.967	-832.947
0.10	24.544	-34.147	-9.603	-107.548
0.15	13.058	-20.691	-7.633	-22.763
0.20	5.220	-7.896	-2.676	-4.478
0.25	2.031	-2.589	-0.558	-0.741
0.30	0.855	-0.853	0.002	-0.015
0.35	0.399	-0.306	0.094	0.093
0.40	0.205	-0.122	0.084	0.084
0.45	0.114	-0.053	0.061	0.061
0.50	0.067	-0.026	0.042	0.042

(b) Along the (010) Axis

R (nm)	$\Delta B/B$			
	$1/R^5$	$1/R^7$	Sum of all multipolar terms	From eq. (7)
0.05	16.585	8.590	25.175	-359.735
0.10	24.544	20.066	44.609	-53.336
0.15	13.058	12.159	25.217	10.086
0.20	5.220	4.640	9.860	8.058
0.25	2.031	1.522	3.553	3.369
0.30	0.855	0.502	1.357	1.340
0.35	0.399	0.180	0.579	0.578
0.40	0.205	0.071	0.277	0.277
0.45	0.114	0.031	0.145	0.145
0.50	0.067	0.015	0.082	0.082

(c) Along the (001) Axis

R (nm)	$\Delta B/B$			
	$1/R^5$	$1/R^7$	Sum of all multipolar terms	from eq. (7)
0.05	44.228	9.645	53.872	-331.038
0.10	65.450	22.530	87.979	-99.657
0.15	34.821	13.652	48.473	33.343
0.20	13.919	5.210	19.129	17.327
0.25	5.417	1.708	7.125	6.942
0.30	2.281	0.563	2.844	2.827
0.35	1.066	0.202	1.268	1.266
0.40	0.548	0.080	0.628	0.628
0.45	0.304	0.035	0.339	0.339
0.50	0.180	0.017	0.197	0.197

the spin-orbit coupling constant, ζ , as 210 cm^{-1} . These parameter values are similar to those for V^{3+} ion. The temperature is taken as $T=300\text{K}$. As shown in Table 1, the calculated NMR shift values for specific R -values along the x , y and z axes are not equal when the threefold axis is chosen as the quantization axis, which is different from the case when the fourfold axis is chosen to be our axis of quantization. It is found that $\Delta B/B$ (ppm) decreases in magnitude rapidly as R increases and along the (010), (001), (110) and (111) axes, the NMR shift changes in sign to positive around $R \approx 0.10 \text{ nm}$. However, along the (100) axis $\Delta B/B$ (ppm) changes in sign to positive around $R \approx 0.35 \text{ nm}$. We find that the sign of linear combinations of spherical harmonics, $(Y_{4-3}(\theta, \phi) - Y_{43}(\theta, \phi))$ and $(Y_{6-3}(\theta, \phi) - Y_{63}(\theta, \phi))$, is negative or

TABLE 4: A Comparison of the Exact values of $\Delta B/B$ (ppm) Using eq. (7) with the Multipolar Terms for Specific R -Values (a) Along the (110) Axis

R (nm)	$\Delta B/B$			
	$1/R^5$	$1/R^7$	Sum of all multipolar terms	from eq. (7)
0.05	16.585	-3.014	13.571	-371.339
0.10	24.544	-7.041	17.503	-80.442
0.15	13.058	-4.266	8.792	-6.339
0.20	5.220	-1.628	3.592	1.790
0.25	2.031	-0.534	1.497	1.314
0.30	0.855	-0.176	0.679	0.663
0.35	0.400	-0.063	0.337	0.335
0.40	0.205	-0.025	0.180	0.180
0.45	0.114	-0.011	0.103	0.103
0.50	0.067	-0.005	0.062	0.062

(b) Along the (111) axis

R (nm)	$\Delta B/B$			
	$1/R^5$	$1/R^7$	Sum of all multipolar terms	from eq. (7)
0.05	17.549	-0.067	17.482	-367.429
0.10	47.269	-2.295	44.794	-52.971
0.15	41.175	-3.223	37.952	22.821
0.20	25.519	-2.219	23.300	21.498
0.25	14.916	-1.186	13.730	13.546
0.30	9.251	-0.605	8.646	8.629
0.35	6.288	-0.325	5.963	5.961
0.40	4.658	-0.190	4.468	4.468
0.45	3.706	-0.121	3.584	3.584
0.50	3.123	-0.084	3.040	3.040

positive according to the previous report¹¹. The negative sign is adequate to (111), (-1-1-1), (-11-1) and (1-11) axes, while the positive sign is adequate to (-1-11), (11-1), (1-1-1) and (-111) axes (refers to Figure 3 or reference (11)). We separate the NMR shift, $\Delta B/B$, to the contributions of constant, $1/R^5$ and $1/R^7$ terms and compare the exact value of $\Delta B/B$ calculated using eq. (7) with the corresponding multipolar terms. As shown in Table 3 and 4, along the (100), (010), (001), (110) and (111) axes the sign of $1/R^5$ term is positive for all values of R . However, $1/R^7$ term along the (100), (110) and (111) axes is negative in sign, while along the (010) and (001) axes, the sign of $1/R^7$ term is opposite. We also find from Table 1 and 2 that the exact values given by eq. (7) are exactly in agreement with the multipolar results for distances larger than 0.35 nm. It is stressed that as shown in Table 3 and 4, $1/R^5$ term has the dominant contribution to the NMR shift but the contribution of $1/R^7$ term may not be negligible. This work may be applied to investigate the NMR shift for $3d^n$ systems when the threefold axis is chosen as the quantization axis.

References

- (1) D. R. Eaton and W. D. Philips. *Adv. in Quantum Chem.*, **1**, 103 (1965).
- (2) G. A. Webb. *Ann. Rept. on NMR Spectroscopy*, **3**, 211 (1970).

- (3) A. F. Cockerill, G. O. Davis, R. C. Harden and D. M. Rackham, *Chem. Rev.*, **73**, 553 (1973).
- (4) O. Hofer, *Topics in Stereochem.*, **9**, 111 (1976).
- (5) G. A. Webb, *Ann. Rept. NMR Spectroscopy*, **6A**, 1 (1975).
- (6) M. Gerloch, *prog. Inorg. Chem.*, **26**, 1 (1979).
- (7) G. A. Webb, *Ann. Rept. NMR Spectroscopy*, **10A**, Academic Press, New York (1980).
- (8) R. M. Golding and L. C. Stubbs, *proc. Roy. Soc.*, **A354**, 223 (1977).
- (9) R. M. Golding and L. C. Stubbs, *J. Magn. Reson.*, **33**, 627 (1979).
- (10) R. M. Golding, R. O. Pascual and S. Ahn, *J. Magn. Reson.*, **46**, 406 (1982).
- (11) S. Ahn, E. Park and K. H. Lee, *Bull. Korean Chem. Soc.*, **4**, 103 (1983).
- (12) S. Ahn, E. Park and K. H. Lee, *Bull. Korean Chem. Soc.*, in press.
- (13) P. J. Stiles, *Mol. Phys.*, **27**, 1271 (1974).
- (14) P. J. Stiles, *Mol. Phys.*, **29**, 1271 (1975).
- (15) S. Ahn, H. C. Suh and J. S. Ko, *Bull. Korea Chem. Soc.*, **3**, 104 (1982).
- (16) J. S. Griffith, "The Theory of Transition Metal Ion", Cambridge Univ. press, Cambridge, 1961.
- (17) H. L. Schaffer and G. Glimann, "Basic Principles of Ligand Field Theory," Wiley-Interscience, 1969.
- (18) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, 1962.
- (19) T. M. Dunn, D. S. McClure and R. G. Pearson, "Some aspects of Crystal Field Theory," Harper & Row, 1965
- (20) L. C. Stubbs, Unpublished Ph. D. Thesis (The Univ. of New South Walse, 1978)

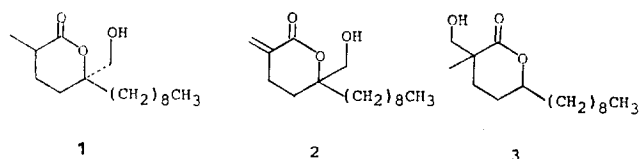
Malyngolide Analogues. Synthesis of (\pm)-Dehydromalyngolide and (\pm)-Isomalyngolide

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Two novel malyngolide analogues, (\pm)-dehydromalyngolide and (\pm)-isomalyngolide, of ($-$)-malyngolide antibiotic have been synthesized by application of our previously developed synthetic sequence for the synthesis of (\pm)-malyngolide. Dehydromalyngolide was synthesized from the known lactone (4) in a 55 % overall yield in six steps, while isomalyngolide was synthesized from the readily available keto ester (11) in a 56 % overall yield in four steps.

($-$)-Malyngolide (1), an antibiotic active against *Mycobacterium smegmatis* and *Streptococcus pyogenes*, was isolated from a shallow water variety of the blue-green alga *Lyngbya majuscula* Gomont and its structure was originally determined by Clardy.¹ In view of its biological properties and to further confirm the assigned structure, many reports on the synthesis of malyngolide have been appeared.²⁻¹⁰ We have prepared two closely related analogues with malyngolide which we designate hereim (\pm)-dehydromalyngolide (2) and (\pm)-isomalyngolide (3). Our interest in dehydromalyngolide stemmed from the observation that the α -methylene lactone and ketone functional groups are the active functionality in a great number of natural products with antitumor and anticancer activity.¹¹⁻¹⁴ Furthermore, the synthesis of isomalyngolide would allow further exploration of its relative biological properties and structureactivity relationship. Since our previous synthesis of (\pm)-malyngolide⁸ is very efficient in terms of the high yield, the few steps required, the use of readily available starting material, and the versatility for the



synthesis of its analogues, we adopted the similar synthetic scheme for the synthesis of dehydromalyngolide and isomalyngolide.

Results and Discussion

The known lactone ester (4), which was prepared in a high yield from readily available 2-(carbomethoxy)-cyclopentanone in two steps,⁸ was hydrolyzed with lithium iodide in pyridine at reflux for 6 hrs to afford the acid (5) in 95 % yield. Reduction of the acid (5) with equimolar amounts of borane-tetrahydrofuran in tetrahydrofuran or borane-dimethyl sulfide complex in methylene chloride resulted in 30-40 % of the triol, resulting from overreduction of the δ -lactone ring, along with the hydroxy lactone (6) and the original acid. Thus, the acid (5) was converted to the mixed anhydride with equimolar amounts of ethyl chloroformate

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