to alkanes, the magnitude of this term is not expected to be unusually small. If this is the case, the positive g values imply that, on the average, the electrons are considerably closer to the center of mass than the nuclei. In other words, the positive g values suggest a concentration of electronic charge below the bridgehead. Moreover, the molecular quadrupole moments indicate the electronic charge will be elongated along the b axis.

This distribution of electronic charge in bicyclobutane would account for the chemical reactivity of the bridgehead bond. Furthermore, electrophilic attack would be expected to occur from below, which has been observed by Pomerantz, *et al.*, in the reaction of benzyne with labeled bicyclobutanes.[6,7] Finally, the molecular dipole moment would be along the c axis with its positive end pointing up through the bridgehead in agreement with the calculation of Schulman and Fisanick.[15]

Conclusion

The molecular rotational Zeeman effect has been measured at high fields in bicyclobutane and the molecular g values, magnetic susceptibility anisotropies, and quadrupole moments were obtained. The molecular g values were found to be all positive, and the correlation between this result and the chemical properties of bicyclobutane was discussed.

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Molecular Zeeman Effect in Formamide and the α-Proton Chemical Shift in Poly(L-alanine)

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Abstract: The molecular Zeeman effect has been observed in $^{15}NH_2COH$, leading to the molecular g values of $g_{aa} = -(0.2843 \pm 0.0011)$, $g_{bb} = -(0.0649 \pm 0.0004)$, and $g_{cc} = -(0.0117 \pm 0.0004)$ and the two independent values of the magnetic susceptibility anisotropies of $2\chi_{aa} - \chi_{bb} - \chi_{cc} = 2.2 \pm 0.7$ and $2\chi_{bb} - \chi_{aa} - \chi_{cc} = 8.0 \pm 0.5$ in units of 10^{-6} erg/(G^2 mol). The b axis nearly bisects the NCO angle, and the a axis is also in the molecular plane. The molecular quadrupole moments and second moments of the charge distribution are also reported. Using the above-measured magnetic susceptibility of the amide link and McConnell's theory, the α-proton chemical shift due to the reorientation of the amide planes in poly(L-alanine) during the helix to random coil transition has been calculated. It is shown that the predicted shift is opposite to the observed shift, thus indicating that the shift is caused by solvation affects and is not due to the amide group anisotropy shielding.

The proton nmr spectrum of several low molecular weight polypeptides shows two peaks for the α proton in helix-breaking solvents such as $CDCl_3$–trifluoroacetic acid mixtures.[1-6] The upfield peak has been assigned to the α protons in the helical form. There has been some controversy, however, over the assignment of the downfield peak. Some groups[1-3] have argued that this peak is due to α protons in the random-coil form, the shift being caused by reorientation of the adjacent amide planes in going from helix to coil.

Others[4,5] argue that while the amide planes do have some effect, the shift is largely due to solvation of the amide planes in the acidic media. Recent experimental results by Tam and Klotz[6] strongly support this latter argument.

In this paper we report the measurement of the molecular Zeeman effect in formamide-^{15}N. These measurements yield the molecular g values, magnetic susceptibility anisotropies, and molecular quadrupole moments. By using the known bulk magnetic susceptibility, the diagonal elements in the magnetic susceptibility tensor and the second moments of the electronic charge distribution are computed.

Using the measured value of the magnetic susceptibility anisotropy for the amide planes we have calculated the expected shift caused by the helix–coil transition in poly(L-alanine). Our results predict a small upfield shift in contrast to the downfield shift seen in experiments, thus supporting the view that the downfield shift is caused by solvation of the amide planes.

Experimental Section

Formamide-^{15}N was used in the Zeeman experiments to avoid the complexity in the spectra caused by the naturally occurring ^{14}N nuclear quadrupole coupling. The sample was obtained from the International Chemical and Nuclear Corp. Spectra were taken using the high-resolution microwave spectrograph and high-field electromagnet described previously.[7]

Analysis of the Data

The rotational transitions and high-field shifts that were measured are listed in Table I. The molecular Zeeman effect in an asymmetric top has been described

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Table I. The Measured and Calculated Frequency Shifts in ^{4}NH$_2$COH at High Magnetic Fields

Transition	$M_l - M_u$	$\Delta\nu_{\text{exptl}}$, kHz	$\Delta\nu_{\text{calcd}}$, kHz	$\Delta\nu_{\text{exptl}} - \Delta\nu_{\text{calcd}}$, kHz
$0_{00} \longrightarrow 1_{01}$	$0 \longrightarrow 0$	−25	−17	−8
$\nu_0 = 20{,}644.37$				
$H = 21{,}143$				
$0_{00} \longrightarrow 1_{01}$	$0 \longrightarrow 1$	620	624	−4
$\nu_0 = 20{,}644.37$	$0 \longrightarrow -1$	−600	−608	8
$H = 21{,}102$				
$1_{11} \longrightarrow 2_{12}$	$-1 \longrightarrow -1$	+1280	1262	18
$\nu_0 = 39{,}824.21$	$0 \longrightarrow 0$	28	5	23
$H = 21{,}094$	$1 \longrightarrow 1$	−1355	−1376	21
$1_{11} \longrightarrow 2_{12}$	$-1 \longrightarrow 0$	1885	1864	21
$\nu_0 = 39{,}824.22$	$0 \longrightarrow 1$	885	876	9
$H = 17{,}002$	$1 \longrightarrow 2$	−175	−191	16
	$-1 \longrightarrow -2$	235	223	12
	$0 \longrightarrow -1$	−825	−835	10
	$1 \longrightarrow 0$	−1975	−1973	−2
$3_{13} \longrightarrow 3_{12}$	$-3 \longrightarrow -3$	−1400	−1400	0
$\nu_0 = 8{,}786.69$	$-2 \longrightarrow -2$	−860	−857	−3
$H = 21{,}173$	$2 \longrightarrow 2$	+905	857	47
	$3 \longrightarrow 3$	+1150	1172	−22
$5_{10} \longrightarrow 5_{14}$	$-5 \longrightarrow -5$	−2280	−2278	−2
$\nu_0 = 21{,}957.87$	$-4 \longrightarrow -4$	−1765	−1770	5
$H = 21{,}220$	$-3 \longrightarrow -3$	−1270	−1279	9
	$-2 \longrightarrow -2$	−790	−806	16
	$2 \longrightarrow 2$	+920	911	9
	$3 \longrightarrow 3$	+1310	1297	13
	$4 \longrightarrow 4$	+1670	1664	6
	$5 \longrightarrow 5$	+2018	2015	3
$3_{13} \longrightarrow 4_{04}$	$-1 \longrightarrow -1$	145	163	−18
$\nu_0 = 24{,}470.35$	$0 \longrightarrow 0$	40	38	2
$H = 21{,}113$	$1 \longrightarrow 1$	−105	−109	4
	$2 \longrightarrow 2$	−270	−279	9
	$3 \longrightarrow 3$	−455	−471	16

in detail by Hüttner and Flygare.[8] The energy of any rotational state is given by

$$E(J, \tau, M) = -\mu_0 \left[\frac{MH}{J(J+1)}\right] \times$$
$$[g_{aa}\langle J_a{}^2\rangle + g_{bb}\langle J_b{}^2\rangle + g_{cc}\langle J_c{}^2\rangle] -$$
$$\frac{H^2}{3}\left\{\frac{3M^2 - J(J+1)}{(2J-1)(2J+3)}\right\}[J(J+1)]^{-1} \times$$
$$[(2\chi_{aa} - \chi_{bb} - \chi_{cc})(\langle J_a{}^2\rangle - \langle J_c{}^2\rangle) +$$
$$(2\chi_{bb} - \chi_{aa} - \chi_{cc})(\langle J_b{}^2\rangle - \langle J_c{}^2\rangle)] \quad (1)$$

where μ_0 = the nuclear magneton, H = the magnetic field, g_{gg} = the molecular g value components along the gth principal inertial axis, J and M = the rotational quantum numbers (in $\hbar$), χ_{gg} = the magnetic susceptibility components along the gth principal inertial axis, and $\langle J_g{}^2\rangle$ = the average value of the squared rotational angular momentum (in $\hbar$) along the gth principal inertial axis.

The $\langle J_g{}^2\rangle$'s were computed with standard methods[9,10] using the rotational assignment of Costain and Dowling (A = 72448.61, B = 11054.40, C = 9589.93 MHz).[11] The transitions in Table I were least squares fit with eq 1 to give the three components of the molecular g value (g_{aa}, g_{bb}, and g_{cc}) and the two magnetic susceptibility anisotropies ($2\chi_{aa} - \chi_{bb} - \chi_{cc}$ and $2\chi_{bb} - \chi_{aa} - \chi_{cc}$). The third anisotropy, $2\chi_{cc} - \chi_{aa} - \chi_{bb}$, is linearly dependent upon the other two.

The Zeeman parameters were determined to be

$$g_{aa} = \pm 0.2843 \pm 0.0011$$
$$g_{bb} = \pm 0.0649 \pm 0.0004$$
$$g_{cc} = \pm 0.0117 \pm 0.0004 \quad (2)$$
$$2\chi_{aa} - \chi_{bb} - \chi_{cc} = (2.2 \pm 0.7) \times 10^{-6}\ \text{erg/(G}^2\ \text{mol)}$$
$$2\chi_{bb} - \chi_{aa} - \chi_{cc} = (8.0 \pm 0.5) \times 10^{-6}\ \text{erg/(G}^2\ \text{mol)}$$

where the b axis bisects the NCO angle, the a axis is also in the molecular plane, and the c axis is perpendicular to the molecular plane.

The signs of the g values cannot be determined experimentally, but will be shown to be negative.

A general expression relating the above five parameters to the molecular quadrupole moments has been given by Hüttner, Lo, and Flygare[9]

$$Q_{cc} = -\frac{\hbar|e|}{8\pi M}\left(\frac{2g_{cc}}{C} - \frac{g_{aa}}{A} - \frac{g_{bb}}{B}\right) - \frac{2mc^2}{|e|N}(2\chi_{cc} - \chi_{aa} - \chi_{bb}) \quad (3)$$

where A, B, and C = rotational constants, M = the proton mass, m = the electron mass, and N = Avogadro's number.

Using Costain and Dowling's[11] rotational constants the molecular quadrupole moments were determined. For g negative values, $Q_{aa} = -0.3 \pm 0.5$, $Q_{bb} = 3.4 \pm 0.4$, and $Q_{cc} = -3.1 \pm 0.8$; for g positive values, $Q_{aa} = -2.1 \pm 0.5$, $Q_{bb} = -12.5 \pm 0.4$, and $Q_{cc} = +14.6 \pm 0.8$ (all in units of 10^{-26} esu cm^2).

The positive g values give quadrupole moments that are too large when compared to those of other molecules of similar structure.[12,13] In addition, the out-of-plane quadrupole moment, Q_{cc}, calculated with the positive g values is larger than one would expect for a near-planar molecule. Therefore, the negative g values are the correct ones and will be used in subsequent calculations. A summary is given in Table II.

Using the known structure of formamide[11] and eq 4 and 5, the components of the paramagnetic susceptibility and the anisotropies in the second moments of the electronic charge distribution were calculated.[13] These results are reported in Table II.

$$\chi_{aa}{}^{\text{p}} = \left(-\frac{e^2N}{2mc^2}\right)\left[\frac{\hbar g_{aa}}{8\pi AM} - \frac{1}{2}\sum_n Z_n(b_n{}^2 + c_n{}^2)\right] \quad (4)$$

where Z_n = the nuclear charge, b_n and c_n = the coordinates of the nth nucleus.

$$\langle b^2\rangle - \langle a^2\rangle = \sum_n Z_n(b_n{}^2 - a_n{}^2) + \frac{\hbar}{4\pi M}\left(\frac{g_{bb}}{B} - \frac{g_{aa}}{A}\right) + \frac{4mc^2}{3e^2N}[(2\chi_{bb} - \chi_{aa} - \chi_{cc}) - (2\chi_{aa} - \chi_{bb} - \chi_{cc})] \quad (5)$$

where $\langle a^2\rangle = \langle 0|\Sigma_i a_i{}^2|0\rangle$.

$\chi = {}^1/_3\,(\chi_{aa} + \chi_{bb} + \chi_{cc})$ has been measured to be $-22.04 \pm 0.02 \times 10^{-6}$ erg/(G^2 mol).[14] Combining

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Table II. The Molecular Zeeman Parameters in $^{15}NH_2COH$

g_{aa}	-0.2843 ± 0.0011
g_{bb}	-0.0649 ± 0.0004
g_{cc}	-0.0117 ± 0.0004
$2\chi_{aa} - \chi_{bb} - \chi_{cc}$	2.2 ± 0.7
$2\chi_{bb} - \chi_{aa} - \chi_{cc}$	8.0 ± 0.5
Q_{aa}	-0.3 ± 0.5
Q_{bb}	3.4 ± 0.4
Q_{cc}	-3.1 ± 0.8
χ_{aa}	-21.3 ± 0.3
χ_{bb}	-19.4 ± 0.2
χ_{cc}	-25.4 ± 0.4
$\chi_{aa}{}^{p}$	31.5 ± 0.8
$\chi_{bb}{}^{p}$	117.9 ± 2.7
$\chi_{cc}{}^{p}$	130.6 ± 2.7
$\chi_{aa}{}^{d}$	-52.8 ± 1.1
$\chi_{bb}{}^{d}$	-137.3 ± 2.9
$\chi_{cc}{}^{d}$	-156.0 ± 3.1
$\langle a^2\rangle - \langle b^2\rangle$	19.9 ± 0.9
$\langle b^2\rangle - \langle c^2\rangle$	4.4 ± 0.4
$\langle c^2\rangle - \langle a^2\rangle$	-24.3 ± 0.8
$\langle a^2\rangle$	28.3 ± 0.9
$\langle b^2\rangle$	8.4 ± 0.9
$\langle c^2\rangle$	4.0 ± 0.9

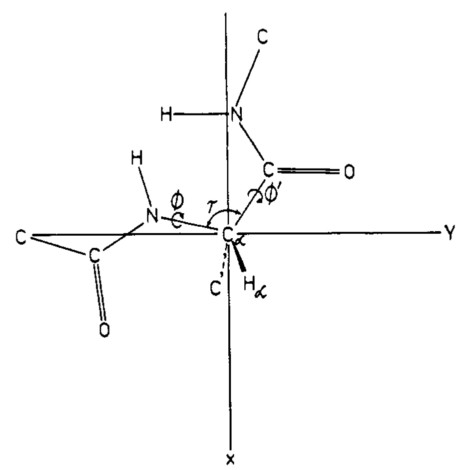

Figure 1. The orientation of the two amide groups adjacent to the α-proton in poly(L-alanine). τ = 110° and, according to ref 18, the limits on ϕ and ϕ' are ϕ = 22–127° and ϕ' = 92–179 and 300–320°.

this result with the anisotropies allows the evaluation of the individual diagonal components of the susceptibility tensor, χ_{aa}, χ_{bb}, and χ_{cc}. By subtracting the paramagnetic components the diamagnetic parts, $\chi_{aa}{}^{d}$, $\chi_{bb}{}^{d}$, and $\chi_{cc}{}^{d}$ can also be determined. These are also listed in Table II.

The sums of the second moments of the electronic charge distributions, $\langle b^2\rangle + \langle c^2\rangle$, $\langle a^2\rangle + \langle b^2\rangle$, and $\langle a^2\rangle + \langle c^2\rangle$, are related to the diamagnetic susceptibilities by

$$\chi_{aa}{}^{d} = -\left(\frac{e^2N}{4mc^2}\right)(\langle b^2\rangle + \langle c^2\rangle) \qquad (6)$$

Knowing the sums and differences of the second moments gives the individual components of the electronic charge distribution. For negative g values, $\langle a^2\rangle = 28.3 \pm 0.9$, $\langle b^2\rangle = 8.4 \pm 0.9$, and $\langle c^2\rangle = 4.0 \pm 0.9$; and for g positive values, $\langle a^2\rangle = 26.7 \pm 0.9$, $\langle b^2\rangle = 8.8 \pm 0.9$, and $\langle c^2\rangle = -0.3 \pm 0.9$.

These values can be accurately predicted using the methods given by Gierke, Tigelaar, and Flygare.[15] The predicted values are $\langle a^2\rangle = 28.2$, $\langle b^2\rangle = 9.0$, and $\langle c^2\rangle = 4.1$. The values calculated with the negative g values overlap these predictions within experimental error, again supporting the choice of the negative signs. All of the Zeeman parameters are summarized in Table II.

Chemical Shift Calculation

McConnell's[16] equation for the magnetic shielding at a nucleus caused by induced magnetic dipole moments of distant groups in a molecule is given for an axially symmetric group by

$$\sigma_n{}^{G} = \frac{\Delta\chi_G}{3R^3N}\langle 1 - 3\cos^2\theta\rangle_{av} \qquad (7)$$

where $\sigma_n{}^{G}$ = the shielding at nucleus N caused by group G; $\Delta\chi_G$ = the molar susceptibility anisotropy of group G; N = Avogadro's number; θ = the angle between the axis of axial symmetry and the vector from nucleus N to a point in group G, usually chosen to be the electrical center of gravity; and R = the length of vector from N to the point.

Formamide is almost axially symmetric with respect to its magnetic susceptibility components about the out-of-plane c axis. $\Delta\chi_G$ was, therefore, taken to be $\chi_{cc} - {}^1/_2(\chi_{aa} + \chi_{bb}) = -5.1 \pm 0.60$ cm^3.

Benson and Flygare[17,18] have shown that magnetic susceptibility anisotropies of planar molecules can be predicted by assuming that the total anisotropy is composed of localized group contributions. In this scheme, the formamide anisotropy would be predicted by summing the contributions from a sp^2 carbon, sp^2 oxygen, and sp^3 nitrogen. Since hydrogens make a negligible contribution to shielding anisotropies and group anisotropies are not strongly dependent upon the groups they are bonded to, we believe that $\Delta\chi$ for the amide group in a polypeptide will be very nearly that of formamide. The origin of the moment of $\Delta\chi_G$ in eq 7 was located midway between the positive and negative electrical centers of gravity of the formamide molecule. Only the amide planes immediately preceding and following the α carbon were included in the calculations, since the $1/R^3$ term in eq 7 causes the contribution from others to be at least an order of magnitude lower. The amide planes above and below the α carbon in the α helix contributed at most a 0.05-ppm shift and were consequently ignored.

For the random-coil case, the amide planes were allowed to rotate about the bonds connecting them to the α carbon. $(1 - 3\cos^2\theta)/R^3$ was calculated at 1° intervals and then averaged (see Figure 1). The structure used was determined by Arnott and Dover.[19]

Ramakrishnan and Ramachandran[20] have shown that not all orientations of the amide planes are stereochemically allowed. The limits that ϕ and ϕ' were allowed to rotate through in our calculation were those determined by Ramachandran and Ramakrishnan for τ 110° (see Figure 1). The helix values for $(1 - 3\cos^2\theta/$

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R^3 were obtained when $\phi = 123°$ and $\phi' = 313°$ ($\psi = 133°$), as given by Arnott and Dover.[19]

The results of the calculation, given in Table III, show that an upfield shift of about 0.1 ppm should occur in going from helix to coil. The largest uncertainty in the calculation is in the choice of where to locate the origin of the induced dipole in eq 7. When allowed to vary by 0.4 Å about our center of charge, it was found that the shift changed from a 0.05-ppm upfield shift to a 0.18-ppm upfield shift.

Table III. The Calculated α-Proton Magnetic Shielding in the Helical and Random-Coil Forms of Poly(L-alanine) Due to the Induced Magnetic Moment of the Amide Group Using the Measured Magnetic Susceptibility Anisotropy of Formamide[a]

	ϕ	ϕ'	Shielding
Helical form	123°	312°	−0.43 ppm
Random-coil form	22–127°	92–179° and 300–320°	−0.33 ppm

[a] The angles and limits are illustrated in Figure 1.

Conclusion

The molecular Zeeman effect has been observed in formamide-^{15}N, and the relevant magnetic parameters and molecular quadrupole moments are reported.

The chemical shift at the α proton in the random-coil and helix forms of poly(L-alanine) was calculated using the measured magnetic susceptibility anisotropy of the amide group.

Our calculation predicts a small upfield shift of approximately 0.1 ppm due to the reorientation of the amide planes when poly(L-alanine) undergoes the helix to coil transition. Experimentally, a downfield shift of 0.3–0.4 ppm is observed. We therefore conclude that the shift is not caused by the reorientation of these amide planes and support the view that solvation of the amide planes causes the observed shift. Tam and Klotz[6] have measured the shift of the α proton in poly(L-alanine) (helix) and poly(DL-alanine) (random coil) in $CDCl_3$ and found them to be the same which agrees quite well with our prediction of a small shift.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged. We also wish to thank Dr. Paul Schmidt for his helpful discussions concerning the chemical shift calculation.

An Approximate Treatment of the Conformational Characteristics of the Cyclic Hexa-L-peptides (Pro-Ser-Gly-Pro-Ser-Gly) and (Ser-Pro-Gly-Ser-Pro-Gly)

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Abstract: Several conformations for the cyclic hexa-L-peptides (Pro-Ser-Gly-Pro-Ser-Gly) and (Ser-Pro-Gly-Ser-Pro-Gly), which are consistent with conformation dependent information obtained in recently reported nmr investigations of these same cyclic hexapeptides, are presented. Deduction of these several conformations from the myriad of possible cyclic conformations is achieved by eliminating from consideration all conformations having a high intramolecular conformational energy. The intramolecular conformational energies of both cyclic hexapeptides are estimated by summing the independent residue energies which have been calculated previously by others using approximate potential functions to account for the intrinsic torsional potentials about the backbone bonds and the nonbonded steric (6–12 potential) and electrostatic (monopole–monopole) interactions solely dependent upon one or both of the backbone residue rotations φ and ψ about the N–C^α and C^α–C bonds, respectively. A search for the presence of intramolecular hydrogen bonds is made in each cyclic conformation generated, and, when present, their stabilizing effect is accounted for by adding their negative energies to the previously determined sum of residue energies. Comparisons of the magnitudes of the vicinal coupling constants between N–H and C^α–H^α in the serine and glycine residues and comparison of the presence of the appropriate intramolecular hydrogen bonds with the nmr findings are used to test the consistency of the generated conformations with experiment. The averaging of a "Karplus-like" relation connecting the dihedral angle φ' and vicinal coupling $J_{N\alpha}$ between N–H and C^α–H^α over all of the low-energy cyclic conformations generated makes the comparison between the predicted and experimentally observed vicinal coupling constants possible. The hexa-L-peptide (Pro-Ser-Gly-Pro-Ser-Gly) flips *via* small rotations about φ_{Gly} between two Gly-Gly hydrogen-bonded conformations, both of which have all-trans peptide bonds and minimum C prolines ($\varphi_{\mathrm{Pro}} \approx 300°$). Cyclic (Ser-Pro-Gly-Ser-Pro-Gly) adopts at least two conformations, one with trans, the other with cis imide bonds, but both containing minimum C prolines and non-α-helical serines ($\varphi_{\mathrm{Ser}} \approx 330°$). The trans peptide bond conformation possesses strong internal Ser-Ser hydrogen bonds.

The conformational characteristics of polypeptides in solution and in the crystal have been successfully described by approximate intramolecular potential energy calculations.[1–8] Residues separated by planar

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