Molecular Zeeman Effect and Electronic Charge Distribution in Bicyclobutane

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Abstract: The high magnetic field molecular Zeeman effect has been observed in bicyclobutane yielding the molecular g values of $g_{aa} = 0.0593 \pm 0.0002$, $g_{bb} = 0.0025 \pm 0.0002$, and $g_{cc} = 0.0412 \pm 0.0002$ and the magnetic susceptibility anisotropies of $2\chi_{aa} - \chi_{bb} - \chi_{cc} = (-5.9 \pm 0.3) \times 10^{-6}$ erg/(G^2 mol) and $2\chi_{bb} - \chi_{aa} - \chi_{cc} = 21.1 \pm 0.3 \times 10^{-6}$ erg/(G^2 mol). The molecular quadrupole moments are $Q_{aa} = 1.3 \pm 0.2$, $Q_{bb} = -(2.6 \pm 0.3)$, and $Q_{cc} = 1.3 \pm 0.4$ in units of 10^{-26} esu cm^2. The magnetic parameters are interpreted in terms of the electron distribution in the molecule.

The bonding and chemical properties of small hydrocarbons with strained rings have been the subject of many investigations.[1] Among these molecules, bicyclobutane is especially interesting,[2] since the dipole moment (0.675 ± 0.020),[3] the bridgehead $J_{^{13}C-H}$ coupling constant (205 Hz),[2,4] and the strain energy (64 kcal/mol)[5] are all unusually large. The derivative, 3-methylbicyclobutane-1-carboxylate, has a uv extinction coefficient (λ_{max} 210, ϵ 6800) which is more similar to that of an α,β-unsaturated ester than to that of methyl cyclopropanecarboxylate.[5] Moreover, bicyclobutanes readily undergo many reactions which lead to addition across the bridgehead bond,[5-8] suggesting that the bridgehead protons are highly acidic.[2]

With these observations, it is tempting to regard the bridgehead bond as ethylenic or even acetylenic;[9] however, bicyclobutanes do not undergo facile Diels–Alder reactions,[10] and the measured length of the bridgehead bond[11] (1.497 ± 0.03 Å) is considerably larger than that of a standard ethylenic bond (1.34 Å).

In order to elucidate the type of bonding in bicyclobutanes, several theoretical investigations have been conducted.[12-15] Of these, the *ab initio* SCF calculation of Schulman and Fisanick suggests a bonding model which is the most consistent with the observed physical and chemical properties.[15] In this model, the bridgehead bond is described by a dominant σ interaction between two unhybridized p orbitals with an accumulation of electron density behind and below the bridgehead bond, thus accounting for both the chemical reactivity and length of that bond. An interesting result of this model is that the molecular dipole moment has its positive end directed *up* through the bridgehead.

To provide further insight into the bonding in this interesting molecule, it would be desirable to obtain direct experimental information about its electronic charge distribution. This information can be obtained by measuring the molecular Zeeman effect in the rotational spectra.[16] Several small-ring molecules have already been studied in this laboratory. These include cyclopropene,[17] methylenecyclopropane,[18] cyclobutene,[18] and bicyclo[2.1.0]pent-2-ene.[19] In this paper we report the result of the molecular Zeeman measurements on bicyclobutane.

Experimental Section

Bicyclobutane was prepared by the method of Wiberg, *et al.*,[2] and identified by its nmr spectrum. The microwave spectrometer and high-field electromagnet used for the Zeeman study have been described previously.[20] The spectra were taken at −50°.

The theory of the rotational Zeeman effect in diamagnetic molecules has been given by Hüttner and Flygare.[16] For an asymmetric rotor in the presence of a static external magnetic field, the energy levels are described by

$$E(J, M_J) = -\frac{1}{2}\chi H^2 - \left[\frac{\mu_0 M_J}{J(J+1)}\right] H \sum_g g_{gg}\langle P_g^2\rangle - H^2 \frac{[3M_J^2 - J(J+1)]}{[J(J+1)(2J-1)(2J+3)]}\sum_g (\chi_{gg} - \chi)\langle P_g^2\rangle \quad (1)$$

In this expression J and M_J are the rotational quantum numbers in units of $\hbar$, $\chi = {}^1/_3(\chi_{aa} + \chi_{bb} + \chi_{cc})$ is the average magnetic susceptibility and χ_{gg} is the element of the magnetic susceptibility tensor along the gth principle inertial axis of the molecule, H is the static magnetic field, μ_0 is the nuclear mageton, g_{gg} is the molecular g value along the gth principle axis, and $\langle P_g^2\rangle$ is the average of the squared rotational angular momentum along the gth axis. The values of $\langle P_g^2\rangle$ were calculated[21,22] using the rotational constants of Harmony and Cox[3] (A = 17,311.98; B = 9313.51; C = 8393.52 MHz).

Experimentally, only energy differences are observed and the ${}^1/_2\chi H^2$ term in eq 1 cancels out. Of the three susceptibility anisotropies in eq 1, only two will be linearly independent. These were chosen as $(\chi_{aa} - \chi)$ and $(\chi_{bb} - \chi)$. Thus, the two sus-

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(1) K. B. Wiberg, *Advan. Alicyclic Chem.*, **2**, 59 (1968).

(2) K. B. Wiberg, G. M. Lampman, R. R. Ciula, D. S. Conner, P. Schertler, and J. Lavanish, *Tetrahedron*, 21, 2749 (1965).

(3) M. D. Harmony and K. Cox, *J. Amer. Chem. Soc.*, **88**, 5049 (1966).

(4) K. Wüthrich, S. Meiboom, and L. C. Snyder, *J. Chem. Phys.*, **52**, 230 (1970).

(5) K. B. Wiberg, *Rec. Chem. Progr.*, **26**, 143 (1965).

(6) M. Pomerantz, *J. Amer. Chem. Soc.*, **88**, 5349 (1966).

(7) M. Pomerantz, G. W. Gruber, and R. N. Wilke, *ibid.*, **90**, 5040 (1968).

(8) K. B. Wiberg and Günter, *ibid.*, **92**, 571 (1970).

(9) M. Pomerantz and E. W. Abrahamson, *ibid.*, **88**, 5049 (1966).

(10) E. P. Blanchard and A. Cairncross, *ibid.*, **88**, 489 and 496 (1966).

(11) K. W. Cox, M. D. Harmony, G. Nelson, and K. B. Wiberg, *J. Chem. Phys.*, 50, 1976 (1969).

(12) Z. Maksic, L. Klasinc, and M. Randic, *Theor. Chim. Acta*, **4**, 273 (1966).

(13) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

(14) T. Yonezawa, K. Simizu, and H. Kato, *Bull. Chem. Soc. Jap.*, **41**, 2336 (1968).

(15) J. M. Schulman and G. J. Fisanick, *J. Amer. Chem. Soc.*, **92**, 6653 (1970).

(16) W. Hüttner and W. H. Flygare, *J. Chem. Phys.*, **47**, 4137 (1967).

(17) R. C. Benson and W. H. Flygare, *ibid.*, **51**, 3087 (1969).

(18) R. C. Benson and W. H. Flygare, *ibid.*, **53**, 4470 (1970).

(19) S. L. Hsu, H. A. Andrist, T. D. Gierke, R. C. Benson, W. H. Flygare and J. E. Baldwin, *J. Amer. Chem. Soc.*, **92**, 5250 (1970).

(20) W. H. Flygare, W. Hüttner, R. L. Shoemaker, and P. D. Foster, *J. Chem. Phys.*, **50**, 1714 (1969).

(21) W. Hüttner and W. H. Flygare, *ibid.*, **50**, 2863 (1969).

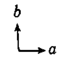
(22) W. Hüttner, M. K. Lo, and W. H. Flygare, *ibid.*, **48**, 1206 (1968).

Table I. Experimental Frequency Shifts from ν_0 in Several *c*-Dipole Transitions in Bicyclobutane in High Magnetic Fields

	$M_l - M_u$	$\Delta\nu_{\text{exptl}}$, kHz	$\Delta\nu_{\text{calcd}}$,[a] kHz	$\Delta\nu_{\text{exptl}} - \Delta\nu_{\text{calcd}}$, kHz
$0_{00} \longrightarrow 1_{10}$	$0 \longrightarrow 0$	+133	133	0.0
$\nu_0 = 26{,}625.57$				
$H = 22{,}814$				
$1_{10} \longrightarrow 2_{02}$	$-1 \longrightarrow -1$	−91[b]	−60	−31
$\nu_0 = 26{,}420.70$	$0 \longrightarrow 0$	−91[b]	−109	+18
$H = 22{,}804$	$1 \longrightarrow 1$	+212	+217	−5
$2_{11} \longrightarrow 2_{21}$	$-2 \longrightarrow -2$	+1158	+1156	+2
$\nu_0 = 23{,}995.40$	$-1 \longrightarrow -1$	+407	+410	−3
$H = 22{,}800$	$0 \longrightarrow 0$		−172	
	$1 \longrightarrow 1$	−572	−578	+6
	$2 \longrightarrow 2$	−818	−820	+2
$2_{12} \longrightarrow 2_{20}$	$-2 \longrightarrow -2$	+199[b]	+205	−6
$\nu_0 = 26{,}830.19$	$-1 \longrightarrow -1$	+199[b]	+174	+25
$H = 22{,}752$	$0 \longrightarrow 0$			
	$1 \longrightarrow 1$	−106	−102	−4
	$2 \longrightarrow 2$	−354	−346	−8
$3_{12} \longrightarrow 3_{22}$	$-3 \longrightarrow -3$	+1133	+1132	+1
$\nu_0 = 22{,}664.24$	$-2 \longrightarrow -2$	+643	+649	−6
$H = 22{,}770$	$-1 \longrightarrow -1$		+227	
	$0 \longrightarrow 0$			
	$1 \longrightarrow 1$		−423	
	$2 \longrightarrow 2$	−652	−649	−4
	$3 \longrightarrow 3$	−808	−814	+6
$0_{00} \longrightarrow 1_{10}$	$0 \longrightarrow 1$	−553	−555	+2
$\nu_0 = 26{,}625.57$	$0 \longrightarrow -1$	+440	+440	0
$H = 21{,}127$				
$1_{10} \longrightarrow 2_{02}$	$-1 \longrightarrow 0$	−445[b]	−421	−24
$\nu_0 = 26{,}420.70$	$0 \longrightarrow 1$	−445[b]	−474	+29
$H = 21{,}170$	$1 \longrightarrow 2$	−195	−205	+10
	$-1 \longrightarrow -2$	+277[b]	+279	−2
	$0 \longrightarrow -1$	+277[b]	+266	+11
	$1 \longrightarrow 0$		+587	
$2_{11} \longrightarrow 2_{21}$	$-2 \longrightarrow +1$	+231[b]	+256	−25
$\nu_0 = 23{,}995.41$	$1 \longrightarrow 0$	+231[b]	+208	+23
$H = 21{,}033$	$-1 \longrightarrow 0$	−373	−382	+9
	$0 \longrightarrow 1$	−882	−878	−4
	$1 \longrightarrow 2$	−1249	−1231	−18
	$-1 \longrightarrow -2$	+1187	+1182	+3
	$0 \longrightarrow -1$	+617	+623	−6
	$2 \longrightarrow 1$	−41	−64	+23
$2_{12} \longrightarrow 2_{20}$	$-2 \longrightarrow -1$	−583[b]	−561	−18
$\nu_0 = 26{,}830.18$	$-1 \longrightarrow 0$	−583[b]	−586	+3
$H = 21{,}070$	$0 \longrightarrow 1$		−670	
	$1 \longrightarrow 2$	−788	−800	+12
	$-1 \longrightarrow -2$		+958	
	$0 \longrightarrow -1$	+807	+805	−2
	$1 \longrightarrow 0$	+627	+627	0
	$2 \longrightarrow 1$	+402	+387	+15

[a] $\Delta\nu_{\text{calcd}}$ values were obtained using the results in Table II and eq 1. [b] Unresolved.

Table II. The Experimental Molecular *g* Values and Magnetic Susceptibility Anisotropies[a]

	
g_{aa}	$\pm 0.0593 \pm 0.0002$
g_{bb}	$\pm 0.0025 \pm 0.0002$
g_{cc}	$\pm 0.0412 \pm 0.0002$
$2\chi_{aa} - \chi_{bb} - \chi_{cc}$	-5.9 ± 0.3
$-\chi_{aa} + 2\chi_{bb} - \chi_{cc}$	$+21.1 \pm 0.3$

[a] Susceptibility in units of 10^{-6} erg/(G^2 mol). The positive *g* values are favored (see text).

ceptibility anisotropies and the magnitude and relative signs of the three *g* values are determined from the measured rotational Zeeman effect.

Results

The observed Zeeman transitions are listed in Table I. These data were least squares fit to eq 1[21,22] to give the Zeeman quantities in Table II. The absolute signs of the *g* values are not experimentally determined, but arguments will be given later which indicate that the positive *g* values are correct. The transitions calculated with these Zeeman parameters are listed with the observed transitions in Table I for comparison.

The susceptibility anisotropies and molecular *g* values may be used to calculate the molecular quadrupole moments. The appropriate expression is[22]

$$Q_{xx} = \frac{1}{2}\,|e|\,\sum_n Z_n(3x_n^{\,2} - r_n^{\,2}) - \frac{1}{2}\,|e|\,\langle 0|\sum_i (3x_i^{\,2} - r_i^{\,2})|0\rangle = -\frac{\hbar|e|}{8\pi M} \times \left[\frac{2g_{xx}}{G_{xx}} - \frac{g_{yy}}{G_{yy}} - \frac{g_{zz}}{G_{zz}}\right] - \frac{2mc^2}{|e|N}(2\chi_{xx} - \chi_{yy} - \chi_{zz}) \quad (2)$$

In this expression $|e|$ is the protonic charge; Z_n is the charge on the *n*th nucleus; x_n and x_i are the nuclear and electronic center of mass coordinates, respectively; $\langle 0||0\rangle$ indicates the ground electronic state average value; M is the proton mass; G_{xx} is the rotational constant along the *x* principle axis; *c* is the speed of light; *m* is the mass of the electron; and *N* is Avogadro's number. The resultant molecular quadrupole moments are given in Table III for both signs of the molecular *g* values.

Table III. Molecular Quadrupole Moments, Anisotropies in the Second Moment of Charge Distribution, and Individual Elements in the Paramagnetic Susceptibility Tensor[a]

Quantity	+*g* value	−*g* value
Q_{aa}	$+1.3 \pm 0.2$	$+5.4 \pm 0.4$
Q_{bb}	-2.6 ± 0.3	-21.4 ± 0.3
Q_{cc}	$+1.3 \pm 0.4$	$+16.0 \pm 0.4$
$\langle 0\|a^2 - b^2\|0\rangle$	$+15.7 \pm 0.2$	$+12.5 \pm 0.2$
$\langle 0\|b^2 - c^2\|0\rangle$	$+2.1 \pm 0.2$	$+6.8 \pm 0.2$
$\langle 0\|c^2 - a^2\|0\rangle$	-17.8 ± 0.2	-19.3 ± 0.2
χ_{aa}^{p}	$+76.8 \pm 0.4$	$+91.4 \pm 0.4$
χ_{bb}^{p}	$+152.6 \pm 0.6$	$+153.7 \pm 0.6$
χ_{cc}^{p}	$+149.5 \pm 0.6$	$+170.4 \pm 0.6$

[a] Quadrupole moments, second moments, and anisotropies are in units of 10^{-26} (esu cm^2), 10^{-16} cm^2, and 10^{-6} erg/(G^2 mol), respectively.

The total magnetic susceptibility χ_{xx} along any axis *x* may be written as a sum of a diamagnetic component χ_{xx}^{d} and a paramagnetic component χ_{xx}^{p}.[21,22]

$$\begin{aligned} \chi_{xx} &= \chi_{xx}^{\text{d}} + \chi_{xx}^{\text{p}} \\ \chi_{xx}^{\text{d}} &= -\left(\frac{e^2N}{4mc^2}\right)\langle 0|\sum_i (y_i^{\,2} + z_i^{\,2})|0\rangle \\ \chi_{xx}^{\text{p}} &= -\left(\frac{e^2N}{2mc^2}\right)\left[\frac{\hbar g_{xx}}{8\pi G_{xx}M} - \frac{1}{2}\sum_n Z_n(y_n^{\,2} + z_n^{\,2})\right] \end{aligned} \quad (3)$$

The average value of the second moment of electronic charge distribution along any axis *x* is defined as

$$\langle x^2\rangle = \langle 0|\sum_i x_i^{\,2}|0\rangle \quad (4)$$

and the anisotropies in these second moments are related to the observables in Table II by[21,22]

$$\langle y^2\rangle - \langle x^2\rangle = \sum_n Z_n(y_n^2 - x_n^2) + \frac{\hbar}{4\pi M}\left(\frac{g_{yy}}{G_{yy}} - \frac{g_{xx}}{G_{xx}}\right) + \frac{4mc^2}{3e^2N}[(2\chi_{yy} - \chi_{xx} - \chi_{zz}) - (2\chi_{xx} - \chi_{yy} - \chi_{zz})] \quad (5)$$

The values for the nuclear second monents

$$\sum_n Z_n x_n^2 \qquad \sum_n Z_n y_n^2 \qquad \sum_n Z_n z_n^2$$

needed in eq 3 and 5 may be calculated with the available structure and are given below. Uncertainties are based on uncertainties in the structure.[11]

$$\begin{aligned}\sum_n Z_n a_n^2 &= 26.97 \pm 0.07\\ \sum_n Z_n b_n^2 &= 10.71 \pm 0.03 \qquad (6)\\ \sum_n Z_n c_n^2 &= 9.11 \pm 0.07\end{aligned}$$

The resultant paramagnetic susceptibilities and anisotropies in the electronic second moments are listed in Table III.

Finally, if the bulk susceptibility is known, it may be combined with the susceptibility anisotropies to yield the individual elements of the total (and hence diamagnetic) susceptibility tensor. The diamagnetic elements can then be combined with the anisotropies in the electronic second moments to give the individual second moments. Unfortunately, the bulk susceptibility of bicyclobutane has not been measured. However, one may estimate the bulk susceptibility according to a model proposed by Gierke, Tigelaar, and Flygare[23] in the previous paper. The second moments of the electronic charge distribution are evaluated by rules based on a model where molecular charge distributions are estimated by collections of polarized atoms. According to eq 22 and Table II of ref 23, the second moments of electronic charge in bicyclobutane are $\langle a^2\rangle = 31.9$, $\langle b^2\rangle = 16.4$, and $\langle c^2\rangle = 14.0$ in units of 10^{-16} cm². These numbers, combined with eq 3 and 5 of this paper, give the remaining pertinent numbers which are listed in Table IV. Results similar to those shown in Table IV are obtained by using another empirical method for estimating χ.[24]

Table IV. Evaluation of the Magnetic Parameters in Bicyclobutane According to the Values of $\langle a^2\rangle$, $\langle b^2\rangle$, and $\langle c^2\rangle$ Which Are Obtained from the Methods Described in Ref 23 and the Experimental Results in Tables II and III[a]

$\langle a^2\rangle$	+31.9
$\langle b^2\rangle$	+16.4
$\langle c^2\rangle$	+14.0
$\langle a^2\rangle - \langle b^2\rangle$	+15.5
$\langle b^2\rangle - \langle c^2\rangle$	+2.4
$\langle c^2\rangle - \langle a^2\rangle$	−17.9
χ_{aa}^{d}	−130
χ_{bb}^{d}	−195
χ_{cc}^{d}	−205
χ_{aa}	−53
χ_{bb}	−42
χ_{cc}	−55
χ	−50

[a] $\langle a^2\rangle$, $\langle b^2\rangle$, and $\langle c^2\rangle$ in units of 10^{-16} cm². χ values in units of 10^{-6} erg/(G² mol).

Comparing the results in Table IV with the experimental results in Table III indicates that the positive molecular *g* values are correct. Furthermore, the molecular quadrupole moments for negative *g* values seem unreasonably large when compared with the results for a large number of similar molecules[25] (see also Table V). Thus we will exclude the negative *g* values and consider only the numbers derived from the positive *g* values.

Discussion

The molecular *g* values, magnetic susceptibility anisotropies, and quadrupole moments of bicyclobutane are compared with the results for similar small-ring systems in Table V. The molecular quadrupole moments in the small-ring compounds listed in Table V are all very small, indicating a near-spherical charge distribution as measured by the second moments of electronic charge.

The magnetic susceptibility anisotropies in bicyclobutane are also quite small. These results indicate that there are no unusual ring current or delocalized electron effects in bicyclobutane as compared to similar molecules.[18,19] Apparently cyclopentadiene and possibly cyclopropene contain some nonlocal contribution to their magnetic susceptibility anisotropies.[26] It is interesting to note that the *g* values of bicyclobutane are all positive, while the *g* values of other molecules are predominantly negative. Furthermore, it is interesting to speculate on a possible connection between the chemical properties and the positive *g* values of bicyclobutane. The molecular *g* value is directly related to the rotationally induced magnetic moment of a molecule and can be described as the near cancellation of a large positive nuclear contribution and a large negative electronic contribution[25,27]

$$g_{xx} = \frac{M_{\mathrm{p}}}{I_{xx}}\left[\sum_n Z_n(y_n^2 + z_n^2) + \frac{2}{m}\sum_{k>0}\frac{|\langle 0|L_x|k\rangle|^2}{E_0 - E_k}\right] \quad (7)$$

where I_{xx} is the *x*th component of the principal inertial moment tensor, L_x is the total electronic angular momentum along the *x* axis, and $|k\rangle$ is the *k*th excited electronic state. As $E_k > E_0$, a positive *g* value implies that the nuclear term dominates. However, this is difficult to interpret, since the second term contains both the electronic angular momentum due to the rotating molecular frame and the momentum with respect to this frame.

In order to interpret the molecular *g* values, we will transform the electronic angular momentum into terms at the individual atomic origins. This type of transformation is discussed in detail in the preceding paper. Using the notation in the preceding paper, we can write the total electronic angular momentum as a sum over atomic terms.

$$\mathbf{L} = \sum_i \mathbf{r}_i \times \mathbf{p}_i = \sum_n \sum_{i_n=1}^{Z_n} \mathbf{r}_{i_n} \times \mathbf{p}_{i_n} \quad (8)$$

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(23) T. D. Gierke, H. L. Tigelaar, and W. H. Flygare, *J. Amer. Chem. Soc.*, **94**, 330 (1971), previous paper.

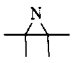
(24) H. F. Hameka, *J. Chem. Phys.*, **34**, 1996 (1961); P. S. O'Sullivan and H. F. Hameka, *J. Amer. Chem. Soc.*, **92**, 29 (1970).

(25) R. C. Benson and W. H. Flygare, *Mol. Phys.*, **20**, 225 (1971), and references therein.

(26) R. C. Benson and W. H. Flygare, *J. Amer. Chem. Soc.*, **92**, 7523 (1970).

(27) W. H. Flygare, *J. Chem. Phys.*, **42**, 1563 (1965).

Table V. Comparison of the *g* Values, Magnetic Susceptibility Anisotropies, and Molecular Quadrupole Moments in Bicyclobutane with Other Strained-Ring Compounds[a]

Molecule 	g_{aa} g_{bb} g_{cc}	Q_{aa} Q_{bb} Q_{cc}	$2\chi_{aa} - \chi_{bb} - \chi_{cc}$ $2\chi_{bb} - \chi_{aa} - \chi_{cc}$ $\chi_{cc} - \frac{1}{2}(\chi_{aa} + \chi_{bb})$	Ref
	$+0.0593 \pm 0.0002$ $+0.0025 \pm 0.0002$ $+0.0412 \pm 0.0002$	$+1.3 \pm 0.2$ -2.6 ± 0.3 $+1.3 \pm 0.4$	-5.9 ± 0.3 $+21.1 \pm 0.3$ -7.6 ± 0.4	This work
	-0.0046 ± 0.0019 -0.0342 ± 0.0011 -0.0218 ± 0.0012	-1.9 ± 1.5 $+2.7 \pm 1.7$ -0.8 ± 2.4	-14.9 ± 1.1 $+7.8 \pm 1.5$ $+3.5 \pm 1.5$	19
	-0.0516 ± 0.0007 -0.0663 ± 0.0006 -0.0219 ± 0.0006	-0.3 ± 0.6 $+1.6 \pm 0.7$ -1.3 ± 1.0	-0.9 ± 0.5 $+5.0 \pm 0.7$ -2.1 ± 0.7	18
	-0.0827 ± 0.0003 -0.0700 ± 0.0003 $+0.0385 \pm 0.0002$	$+3.7 \pm 0.4$ $+1.4 \pm 0.4$ -5.1 ± 0.5	$+37.8 \pm 0.3$ $+30.7 \pm 0.3$ -34.3 ± 0.4	*b*
	-0.0320 ± 0.0008 -0.0218 ± 0.0010 -0.0184 ± 0.0011	-1.2 ± 1.1 -1.1 ± 2.0 $+2.3 \pm 2.4$	-6.4 ± 0.5 $+4.3 \pm 1.7$ $+1.1 \pm 1.5$	18
	-0.0672 ± 0.0007 -0.0231 ± 0.0004 $+0.0244 \pm 0.0004$	-0.7 ± 0.5 $+0.9 \pm 0.6$ -0.2 ± 0.9	$+18.3 \pm 0.5$ $+14.9 \pm 0.6$ -16.6 ± 0.6	18
	-0.0897 ± 0.0009 -0.1492 ± 0.0002 $+0.0536 \pm 0.0002$	-0.4 ± 0.4 $+2.4 \pm 0.3$ -2.0 ± 0.6	$+7.1 \pm 0.6$ $+26.8 \pm 0.4$ -17.0 ± 0.6	17
	-0.0422 ± 0.0008 $+0.0229 \pm 0.0009$ $+0.0539 \pm 0.0010$	$+1.3 \pm 0.6$ -2.6 ± 0.6 $+1.3 \pm 0.6$	$+16.5 \pm 0.7$ $+4.6 \pm 0.8$ -10.6 ± 0.8	*c*
	-0.0946 ± 0.0004 $+0.0189 \pm 0.0003$ $+0.0318 \pm 0.0006$	$+2.5 \pm 0.5$ -4.3 ± 0.4 $+1.8 \pm 0.8$	$+18.1 \pm 0.6$ $+0.8 \pm 1.0$ -9.5 ± 1.0	*d*

[a] The units are the same as in Tables II and III. [b] R. C. Benson and W. H. Flygare, *J. Amer. Chem. Soc.*, **92,** 7523 (1970). [c] D. H. Sutter and W. H. Flygare, *ibid.*, **91,** 6895 (1969). [d] D. H. Sutter, W. Hüttner, and W. H. Flygare, *J. Chem. Phys.*, **50,** 2869 (1969).

where the sum over i_n is over all electrons in the nth free atom and the sum over n is over all of the atoms in the molecule. Now using

$$\mathbf{r}_{i_n} = \mathbf{r}_n + \boldsymbol{\varrho}_{i_n} \tag{9}$$

as discussed in the preceding paper (see Figure 1 in preceding paper for the coordinate system), we can rewrite eq 8 as

$$\mathbf{L} = \sum_n \sum_{i_n=1}^{Z_n} (\mathbf{r}_n + \boldsymbol{\varrho}_{i_n})(\mathbf{p}_n + \mathbf{P}_{i_n}) \tag{10}$$

where $\mathbf{p}_n$ is the linear momentum of the nth free atom with respect to the CM and $\mathbf{P}_{i_n}$ is the linear momentum of the ith electron in the nth atom with respect to the origin at the nth nucleus. Substituting eq 10 into the second part of eq 8 and applying the Born–Oppenheimer approximation for a rigid rotor give[23,28,29]

$$\frac{2}{m}\sum_{k>0}\frac{|\langle 0|L_x|k\rangle|^2}{E_0 - E_k} = -\sum_n Z_n(y_n^2 + z_n)^2 - 2\sum_n[y_n\langle 0|\sum_i^{Z_n} Y_i|0\rangle + z_n\langle 0|\sum_i^{Z_n} Z_i|0\rangle] + \frac{2}{m}\sum_n\left[\sum_{k>0}\left(\frac{|\langle 0|L_x'|k\rangle|^2}{E_0 - E_k}\right)\right] \tag{11}$$

where L_x' is the component of the electronic angular momentum about the nth nucleus along the x axis of the molecular frame. Upper case Y_i and Z_i indicate origins at the atomic nuclei. Thus, the electronic part of the molecular g value has three contributions when referred to the atomic origin. The first term represents the contribution to the magnetic moment which would result if the electronic charge distribution about each nucleus were a point charge centered at that nucleus. The second term represents the alteration to this magnetic moment if the Z_i center of electronic charge is displaced from the nucleus by

$$\langle 0|\sum_i^{Z_i} R_i|0\rangle$$

Finally the third term represents the contribution to the magnetic moment which results from the second order term involving the electronic angular momentum at the atomic origins. Substituting eq 11 into eq 7 gives

$$g_{xx} = \frac{M_\mathrm{p}}{I_{xx}}\left[-2\sum_n(y_n\langle 0|\sum_i^{Z_n} Y_i|0\rangle + z_n\langle 0|\sum_i^{Z_n} Z_i|0\rangle) + \frac{2}{m}\sum_n\sum_{k>0}\left(\frac{|\langle 0|L_x'|k\rangle|^2}{E_0 - E_k}\right)\right] \tag{12}$$

The first term in eq 12 is usually positive since the center of electronic charge about each nucleus is shifted into the bond and consequently towards the center of mass. Highly electronegative atoms like oxygen and fluorine can, however, give negative contributions to this term.[23] The term involving the excited electronic states must always be less than or equal to zero and because the excited states in bicyclobutane are relatively close to the ground state,[5,14] as compared

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(28) W. H. Flygare, *J. Chem. Phys.*, 41, 793 (1964); see Appendix.

(29) See eq 27 in M. K. Lo, V. W. Weiss, and W. H. Flygare, *ibid.*, 45, 2439 (1966).

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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(1) J. Ferretti, *Chem. Commun.*, 1030 (1967).

(2) E. M. Bradbury, C. Crane-Robinson, H. Goldman, and H. W. E. Rattle, *Nature (London)*, 217, 812 (1968).

(3) J. A. Ferretti and L. Paolillo, *Biopolymers*, 7, 155 (1969).

(4) J. H. Bradbury and M. D. Fenn, *Aust. J. Chem.*, 22, 357 (1969).

(5) J. H. Bradbury, M. D. Fenn, and A. G. Moritz, *ibid.*, 22, 2443 (1969).

(6) J. W. V. Tam and I. M. Klotz, *J. Amer. Chem. Soc.*, **93**, 1313 (1971).

(7) W. H. Flygare, W. Hüttner, R. L. Shoemaker, and P. D. Foster, *J. Chem. Phys.*, 50, 1714 (1969).