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Summary. We have shown how the energies and shapes of the frontier molecular orbitals of 2-substituted norbornadienes, derived from a combination of experimental and theoretical evidence, rationalize the selectivities observed in carbene cycloadditions to these species. These quantities should be useful in predicting the course of other electrophilic, as well as nucleophilic, and radical reactions.

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Registry No. Norbornadiene, 121-46-0; 2-methoxynorbornadiene, 74437-38-0; 2-(trimethylsiloxy)norbornadiene, 68364-22-7; 2-chloronorbornadiene, 2294-41-9; 2-cyanonorbornadiene, 39863-20-2; 2-(methoxycarbonyl)norbornadiene, 3604-36-2; 2-phenylnorbornadiene, 74437-39-1; norbornene, 498-66-8; 2-methoxynorbornene, 17190-90-8; 2-(trimethylsiloxy)norbornene, 57722-40-4.

Magnetic Susceptibility Anisotropy, Molecular *g* Values, and Other Molecular Properties of Cyclopropane As Determined from Rotational Zeeman Studies of the Cyclopropane–$H^{35}Cl$ and Cyclopropane–$HC^{15}N$ Complexes

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Abstract: A pulsed, Fourier-transform microwave spectrometer has been used to observe the rotational Zeeman effect with the cyclopropane–HCl and cyclopropane–HCN complexes. The molecular *g* values and magnetic susceptibility anisotropies have been determined for the cyclopropane–HCl complex and have been used to obtain the molecular quadrupole moment, magnetic susceptibility tensor elements as well as the paramagmetic and diamagnetic contributions, and the second moment of the electronic charge distribution. Certain Zeeman parameters along with zero-field rotational constants have been obtained for cyclopropane–$HC^{15}N$. The Zeeman constants for both complexes have then been used to extract various magnetic properties of cyclopropane.

Introduction

Microwave Zeeman experiments have been shown to be quite effective in the determination of certain molecular information. The molecular quadrupole moment, molecular *g* values, magnetic susceptibility anisotropies, and the sign and magnitude of the electric dipole moment can all be obtained by this means.[1,2] The molecular quadrupole moment and electric dipole moment give important information regarding charge distribution. The molecular *g* values can be combined with magnetic susceptibility anisotropies, structural information, and bulk susceptibility to give the second moments of the electronic charge distribution as well as the diamagnetic and paramagnetic contributions to the magnetic susceptibilities. In the case of ring compounds, the magnetic susceptibilities can be compared to localized semiempirical models to give a criterion for aromaticity and delocalization.[3] Obtaining this information from microwave Zeeman experiments is, however, contigent upon the molecule having a permanent electric dipole moment, thus allowing rotational transitions to be observed. In the case of a nonpolar molecule it is conceivable that weak complexation with a dipolar molecule might, however, indirectly give information about the nonpolar binding partner through Zeeman studies. The development of pulsed, Fourier-transform microwave spectroscopy with gas pulsed into a Fabry–Perot cavity,[4] and more recently, Zeeman microwave studies under the same conditions[5–7] make this sort of experiment feasible. Recently, this laboratory has been involved in Zeeman studies of many linear hydrogen-bound complexes with the aim of determining the effects of weak complexation upon the molecular properties of the substituent molecules.[7] The results have shown that if proper account is taken of changes in centers of mass and bending modes introduced upon complexation, the molecular quadrupole moments, magnetic susceptibility anisotropies, and *g* values are all to a good approximation resultants of the corresponding properties in the substituent molecules. It then seems plausible to study the aforementioned molecular properties of cyclopropane by obtaining the same molecular properties for cyclopropane complexed with a dipolar binding partner and subtracting out the effects of the binding partner. By complexing cyclopropane with two very magnetically different molecules, $H^{35}Cl$ and $HC^{15}N$, the ability of the projection equations to subtract out the effects of the binding partners can be tested.

Cyclopropane has been the object of much study and speculation. Values are not known for the molecular quadrupole moment. In addition, proton shieldings by cyclopropyl groups have pointed to cyclopropane as having an unexpectedly large magnetic susceptibility anisotropy possibly arising from the presence of ring currents.[8–12] Bulk susceptibility measurements of cyclopropane have caused similar speculations.[13] Ring currents have been attributed to many aromatic compounds.[3,14,15] and though there is disagreement[16–18] it is thought that many ring compounds not

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(1) C. H. Townes, G. C. Douismanis, R. L. White, and R. F. Schwarz, *Discuss. Faraday Soc.*, **19**, 56 (1955).

(2) W. H. Flygare, *Chem. Rev.*, **74**, 653 (1974).

(3) T. G. Schmalz, C. L. Norris, and W. H. Flygare, *J. Am. Chem. Soc.*, **95**, 7961 (1973).

(4) T. J. Balle and W. H. Flygare, *Rev. Sci. Instrum.*, **52**, 33 (1981).

(5) W. G. Reed and E. J. Campbell, *Phys. Rev. Lett.*, **49**, 1146 (1982).

(6) E. J. Campbell and W. G. Reed, *J. Chem. Phys.*, in press.

(7) W. G. Reed and E. J. Campbell, *J. Chem. Phys.*, in press.

(8) K. P. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961).

(9) J. Burke and P. Lauterbur, *J. Am. Chem. Soc.*, **86**, 1870 (1964).

(10) C. Poulter, R. Boiken, J. Braumm, and S. Winstein, *J. Am. Chem. Soc.*, **94**, 2291 (1972).

(11) R. C. Hahn and P. C. Howard, *J. Am. Chem. Soc.*, **94**, 3143 (1972).

(12) D. J. Patel, M. H. Howden, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3218 (1963).

(13) J. R. Lacher, J. W. Pollock, and J. D. Park, *J. Chem. Phys.*, **20**, 1047 (1952).

(14) L. Pauling, *J. Chem. Phys.*, **4**, 673 (1936).

(15) C. Johnson and F. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

(16) J. Musher, *J. Chem. Phys.*, **43**, 4081 (1965).

(17) J. Musher, *J. Chem. Phys.*, **46**, 1219 (1967).

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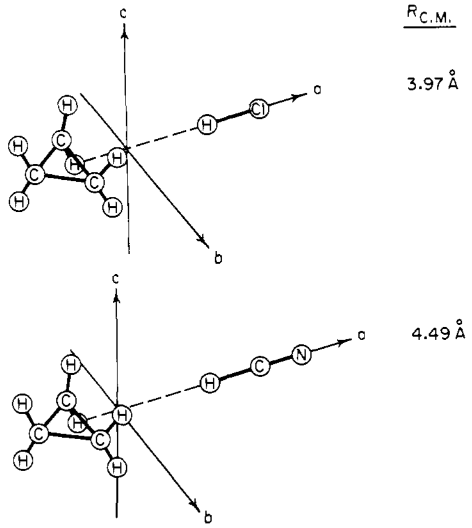

Figure 1. Equilibrium structures for the cyclopropane–HCl and cyclopropane–HC^{15}N complexes with respect to their principal axes and center of mass separations.

traditionally thought of as aromatic have some degree of electron delocalization and thus ring current.[19,20] The Coulson–Moffitt theory of cyclopropane predicts a certain amount of σ electron delocalization as a result of resonance,[21] and the conjugative ability of the cyclopropyl group has been evidenced by various spectroscopic means. The electronic absorption of carbonyl groups occurs at longer wavelengths with the attachment of cyclopropyl groups as is the case with conjugation.[22,23] Similar bathochromic shifts occur in the absorption spectrum of double bonds conjugated with cyclopropyl groups.[24,25] NMR spectra of phenyl protons of phenylcyclopropane have been interpreted as giving this molecule an optimum conformation for conjugation with the benzene ring.[26] Other works have shown that while cyclopropyl groups can extend conjugation, they are unable to serve as central transmitters of conjugation.[22,27,28] Because of the ambiguous understanding of electron delocalization in cyclopropane, it becomes important to obtain an accurate value for the magnetic susceptibility anisotropy. This coupled with a value for the bulk susceptibility can then give the out-of-plane susceptibility tensor element which is strongly influenced by the presence of ring currents due to electron delocalization.

The zero-field rotational spectra for various isotopic species of cyclopropane–HCl have been obtained previously,[29,30] and the structure is well determined. Structural information as well as zero-field spectroscopic parameters will be used freely in this paper. The zero-field spectrum of cyclopropane–HC^{14}N has been recently studied;[31] however, the cyclopropane–HC^{15}N rotational transitions are presented here for the first time. Rotational constants for this isotopic species are also presented. Both complexes are shown in Figure 1 with respect to their principal axes. In both complexes the HX (X = Cl, CN) subunit lies on the *a* principal axis of the complex on average where this axis is also a C_2 symmetry axis. In this paper we report for cyclopropane–H^{35}Cl the *g* values along with the two independent magnetic susceptibility anisotropies, $2\chi_{aa} - \chi_{bb} - \chi_{cc}$ and $2\chi_{bb} - \chi_{aa} - \chi_{cc}$. Using other information we also report the individual magnetic susceptibility tensor elements, along with the paramagnetic and diamagnetic contributions, and the second moments of the electronic charge distribution. For the cyclopropane–HC^{15}N complex we report $g_{bb} + g_{cc}$ and $2\chi_{aa} - \chi_{bb} - \chi_{cc}$ along with the rotational constants. Projection equations are also presented to give the Zeeman parameters of a general asymmetric top complex in terms of the corresponding values of the substituent molecules. These equations are then used to derive the Zeeman parameters of cyclopropane from those of the complexes and the binding partners. The values obtained are shown to be internally consistent, as, for example, the magnetic susceptibility anisotropy of cyclopropane, $\chi_{\parallel} - \chi_{\perp}$, can be determined from any of the three anisotropies obtained for the complexes. In addition, the magnetic susceptibility tensor elements and the second moments of the charge distribution for cyclopropane are compared with various ab initio and semiempirical calculations as well as rough experimental determinations.

Experimental Section

The rotational Zeeman effect was observed for the $2_{02} \rightarrow 3_{03}$ and $2_{12} \rightarrow 3_{13}$ nuclear quadrupole-split rotational transitions of the cyclopropane–H^{35}Cl complex and also the $2_{02} \rightarrow 3_{03}$ rotational transition of the cyclopropane–HC^{15}N complex. For cyclopropane–HCl, transitions were observed at field strengths of 25 104 and 30 098 G while the cyclopropane–HC^{15}N Zeeman transitions were observed at 30 098 G where the field is determined by calibrating the solenoid current using the Zeeman splitting of the $J = 0 \rightarrow 1$ transition of OCS and known Zeeman parameters.[32] Also six zero-field rotational transitions were observed for cyclopropane–HC^{15}N to establish the rotational constants of this complex. Zeeman spectra were obtained using a pulsed, Fourier-transform microwave spectrometer with a Fabry–Perot cavity located in the bore of a superconducting solenoid magnet. This spectrometer was built and described previously.[5-7] Zero-field spectra were obtained using the original pulsed, Fourier-transform spectrometer developed by Balle and Flygare.[4] With both spectrometers a mixture of ~2% cyclopropane and ~2% of either HCl or HC^{15}N with argon is pulsed into a tuned Fabry–Perot cavity kept under high vacuum by a diffusion pump. All transitions within the ~2 MHz cavity bandwidth are then polarized by ~1.50–3.0 μs power pulse from a phase-locked microwave oscillator. The free induction decay is then detected by a superheterodyne detector, mixed down to near DC, and digitized at 0.5 μs per point; 20–30 signals are taken at a rate of 1 Hz with every alternate signal, which is taken with no gas in the cavity, subtracted from the average to eliminate any coherent noise. The signal is then Fourier transformed to give a 0.5- or 1-MHz spectrum (with half-widths at half-height from 5 to 15 kHz) representing the offset of molecular resonances from the excitation frequency. Observed transitions then consist of six to ten measurements taken at different excitation frequencies. All transitions lie in the 8–11 GHz region. With the Zeeman spectrometer gas is pulsed through a piezoelectric valve with the axis of the gas flow approximately parallel to the static field. The microwave polarization pulse is oriented perpendicular to the static field in the present experiment to allow $\Delta M = \pm 1$ transitions.

Determination of Spectroscopic Constants for Cyclopropane–H^{35}Cl and Cyclopropane–HC^{15}N

The Hamiltonian describing the interactions present in the rotational Zeeman experiment is given by

$$\mathcal{H} = \mathcal{H}_{\text{rot}} + \sum_i \mathbf{Q}_i{:}\mathbf{V}_i - \frac{\mu_0}{\hbar}\boldsymbol{H}\cdot\mathbf{g}\cdot\boldsymbol{J} - \tfrac{1}{2}\boldsymbol{H}\cdot\chi\cdot\boldsymbol{H} - \frac{\mu_0}{\hbar}\sum_i g_i \boldsymbol{I}_i\cdot(1 - \sigma_i)\cdot\boldsymbol{H} \quad (1)$$

The first term is the rotational energy term described in terms of the rotational and centrifugal distortion constants. The second term is the nuclear quadrupole interaction and is necessary for the Cl nucleus in cyclopropane–HCl. $\mathbf{Q}_i$ is the nuclear quadrupole tensor for the *i*th nucleus and $\mathbf{V}_i$ is the electric field gradient tensor. The third term describes the interaction of the external magnetic field vector, $\boldsymbol{H}$, with the rotationally induced magnetic dipole moment, $(\mu_0/\hbar)\mathbf{g}\cdot\boldsymbol{J}$, where $\mathbf{g}$ is the molecular *g* value tensor and $\boldsymbol{J}$ is the rotational angular momentum vector for the molecule.

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(18) J. M. Gaidis and R. West, *J. Chem. Phys.*, **46**, 1218 (1967).

(19) D. H. Sutter and W. H. Flygare, *J. Am. Chem. Soc.*, **91**, 6895 (1969).

(20) W. H. Flygare and R. L. Shoemaker, *Symp. Faraday Soc.*, **3**, 119 (1969).

(21) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949).

(22) E. Trachtenberg and G. Odian, *J. Am. Chem. Soc.*, **80**, 4018 (1958).

(23) J. Roberts and C. Green, *J. Am. Chem. Soc.*, **68**, 214 (1946).

(24) H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

(25) A. E. Gillam and E. Stern, "An Introduction to Electronic Absorption in Organic Chemistry", 2nd ed., Edward Arnold, London, 1960.

(26) G. L. Closs and H. B. Klinger, *J. Am. Chem. Soc.*, **87**, 3265 (1965).

(27) R. Eastman, *J. Am. Chem. Soc.*, **76**, 4115 (1954).

(28) R. Eastman and S. Freeman, *J. Am. Chem. Soc.*, **77**, 6642 (1955).

(29) A. C. Legon, P. D. Aldrich, and W. H. Flygare, *J. Am. Chem. Soc.*, **102**, 7584 (1980).

(30) A. C. Legon, P. D. Aldrich, and W. H. Flygare, *J. Am. Chem. Soc.*, **104**, 1486 (1982).

(31) S. G. Kukolich, *J. Chem. Phys.*, **78**, 4832 (1983).

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

Table I. Measured Zeeman Transitions for Cyclopropane-H^{35}Cl

$J_{K_{-1}K_{+1}} \rightarrow J'_{K'_{-1}K'_{+1}}$	field (G)	$F,M_F \rightarrow F'M'_F$	measured frequency (MHz)	$\nu_{obsd} - \nu_{calcd}$ (kHz)
$2_{02} \rightarrow 3_{03}$	25 104	3/2,−3/2 → 5/2,−5/2	8927.2271	−2.0
		7/2,−5/2 → 3/2,−3/2	8927.7657	1.0
		7/2,−1/2 → 9/2, 1/2	8928.3078	5.0
		7/2, 1/2 → 5/2, 3/2	8928.6471	4.4
		3/2, 3/2 → 5/2, 5/2	8929.1232	−2.5
		7/2, 3/2 → 9/2, 5/2	8929.3277	−0.3
		3/2, 1/2 → 5/2,−1/2	8929.4647	0.7
		1/2, 1/2 → 3/2, 3/2	8929.6403	−7.0
		7/2, 5/2 → 9/2, 7/2	8929.9730	8.2
		5/2,−5/2 → 7/2,−7/2	8930.3228	7.1
		5/2,−3/2 → 7/2,−5/2	8930.3637	2.3
		5/2, 3/2 → 7/2, 5/2	8930.7793	−0.9
		7/2, 7/2 → 9/2, 9/2	8930.8579	−3.6
		7/2,−7/2 → 9/2,−9/2	8931.0226	3.2
		5/2,−5/2 → 5/2,−3/2	8931.2086	−0.6
		5/2, 3/2 → 7/2, 1/2	8931.6172	−0.6
		5/2, 1/2 → 7/2, 1/2	8931.6614	−1.8
		7/2,−5/2 → 9/2,−7/2	8931.7324	−11.0
		5/2, 5/2 → 7/2, 7/2	8931.7808	2.4
		7/2,−3/2 → 3/2,−1/2	8932.0144	6.4
		7/2,−3/2 → 9/2,−5/2	8932.1172	1.2
		1/2,−1/2 → 3/2, 1/2	8932.3398	−12.8
	30 098	7/2,−1/2 → 9/2, 1/2	8928.2566	−2.3
		7/2, 1/2 → 5/2, 3/2	8928.5342	1.8
		3/2,−1/2 → 7/2,−3/2	8929.0610	5.7
		3/2, 3/2 → 5/2, 5/2	8929.1275	−10.8
		5/2, 1/2 → 7/2, 3/2	8929.1675	6.0
		7/2, 3/2 → 9/2, 5/2	8929.2630	1.1
		3/2, 1/2 → 5/2,−1/2	8929.5520	−3.8
		1/2, 1/2 → 3/2, 3/2	8929.8149	6.8
		7/2, 7/2 → 9/2, 9/2	8930.8560	5.1
		7/2,−7/2 → 9/2,−9/2	8931.0393	−1.0
		5/2,−5/2 → 5/2,−3/2	8931.2531	1.0
		5/2, 3/2 → 7/2, 1/2	8931.6275	2.8
$2_{12} \rightarrow 3_{13}$	25 104	5/2,−5/2 → 7/2,−7/2	8827.3879	−6.8
		5/2,−3/2 → 5/2,−5/2	8827.9165	1.8
		3/2, 3/2 → 5/2, 5/2	8827.9999	−0.2
		5/2, 5/2 → 7/2, 7/2	8828.9068	−5.0
		7/2, 3/2 → 9/2, 5/2	8829.1328	3.4
		7/2, 5/2 → 9/2, 7/2	8829.2133	1.1
		5/2, 1/2 → 5/2,−1/2	8820.3281	5.4
		5/2,−1/2 → 7/2,−3/2	8829.3606	−11.1
		3/2,−1/2 → 5/2,−3/2	8829.4139	−0.4
		7/2, 1/2 → 7/2,−1/2	8829.5881	0
		7/2,−1/2 → 9/2,−3/2	8829.8671	7.8
		3/2,−3/2 → 3/2,−1/2	8830.1339	11.4
		7/2, 7/2 → 9/2, 9/2	8830.7700	−2.7
		7/2,−7/2 → 9/2,−9/2	8830.9073	2.9
		1/2, 1/2 → 3/2, 3/2	8831.3783	−1.5
	30 098	3/2, 3/2 → 5/2, 5/2	8827.9623	−3.8
		7/2,−1/2 → 9/2,−3/2	8828.8150	−3.3
		3/2,−1/2 → 5/2,−3/2	8829.6635	−1.2
		7/2, 7/2 → 9/2, 9/2	8829.7805	1.9
		7/2,−7/2 → 9/2,−9/2	8830.9424	5.7
		1/2, 1/2 → 3/2, 3/2	8831.3516	5.3

Table II. Molecular Properties of the Substituent Molecules

	cyclopropane	H^{35}Cl	HC^{15}N
A (MHz)	20 093 (5)[a]		
B (MHz)	20 093 (5)[a]	312 989.297[b]	43 027.7[c]
C (MHz)	12 522 (9)[a]		
P_b (amu Å^2)	4.97 (1)		
P_c (amu Å^2)	20.17 (1)		
μ (D)		1.1086 (3)[d]	2.985[e]
$\alpha_{\parallel}$ (Å)^3		2.81[f]	3.1[g]
$g_{\perp}$		0.459 35 (9)[h]	−0.0904 (3)[i]
$\chi_{\parallel} - \chi_{\perp}$ (erg/G^2·mol)		$-0.19\,(7) \times 10^{-6}$[h]	$7.2\,(4) \times 10^{-6}$[i]
$\bar{\chi}$ (erg/G^{2}mol)	$-39.2\,(8) \times 10^{-6}$[j]	$-22.1\,(5) \times 10^{-6}$[k]	
σ_{av} (ppm)		740 (24)[h]	
$\sigma_{\parallel} - \sigma_{\perp}$ (ppm)		300 (200)[h]	

[a] See ref 37. [b] F. C. DeLucia, P. Helminger, and W. Gordy, *Phys. Rev. A*, 3, 1849 (1971). [c] B. Senitzky, *J. Chem. Phys.*, **45**, 409 (1966). [d] E. U. Kaiser, *ibid.*, **53**, 1686 (1970). [e] A. G. Maki, *J. Chem. Phys. Rev. Data*, 3, 221 (1974). [f] N. J. Bridge and A. D. Buckingham, *Proc. R. Soc. London, Ser. A*, **295**, 334 (1966). [g] K. G. Denbigh, *Trans. Faraday Soc.*, 36, 936 (1940). [h] See ref 35. [i] See ref 36. [j] See ref 45. [k] V. P. Ehrlich, *Z. Anorg. Allg. Chem.*, 249, 219 (1947).

The fourth term takes into account the response of the electrons to an external magnetic field leading to an induced magnetic dipole moment proportional to the field strength. χ is the magnetic susceptibility tensor describing this response and has both paramagnetic and diamagnetic contributions. The rotationally invariant trace of χ can be factored out to give an energy contribution of $-\mathrm{Tr}(\chi)H_z^2$ which is, of course, unobservable with rotational transitions. For an asymmetric top then, this term is parameterized by the two independent susceptibility anisotropies, $2\chi_{aa} - \chi_{bb} - \chi_{cc}$ and $2\chi_{bb} - \chi_{aa} - \chi_{cc}$. The last term in eq 1 is the nuclear Zeeman interactions whereby an electronically shielded nuclear moment interacts with the external magnetic field. This term involves a summation over all nuclei with $I > 0$; however, in the present work only the Cl nucleus is coupled to the molecular rotation and thus other nuclei need not be considered. σ is the nuclear shielding tensor and is made up of a diamagnetic contribution involving ground-state electronic wave functions and a paramagnetic contribution involving ground- and excited-state wave functions.

The Zeeman splitting of the $2_{03} \rightarrow 3_{03}$ and $2_{12} \rightarrow 3_{13}$ transitions of cyclopropane–HCl was observed at two field strengths with 55 lines being observed. Initial assignments were made using matrix elements of the Hamiltonian in eq 1 calculated in the uncoupled $|JKM_JIM_I\rangle$ basis with matrix elements off-diagonal in J being neglected. This proved to be computer efficient in deconvoluting the extremely rich spectrum and gives transition frequencies differing from an exact treatment by less than 5 kHz in almost all cases. Final fitting involved correcting the observed frequencies by the difference between the above first-order treatment and an infinite order treatment and improved the fit slightly. As the chlorine nucleus is expected to have its nuclear spin strongly coupled to the angular momentum of the nuclear framework, the observed frequencies for cyclopropane–HCl are reported in Table I in the coupled $|JKI_{Cl}FM_F\rangle$ basis. The rotational and nuclear quadrupole parameters were provided from the previous zero-field study performed in this laboratory,[29,30] and adjustments were made so that they exactly reproduced the measured zero-field frequencies. The effects of shielding of the chlorine nucleus on the spectrum are slight, only amounting to 2 kHz or less for σ_{av} ranging from 0 to 1000 ppm. Furthermore, the effect of the magnetic susceptibility anisotropy of cyclopropane on the chlorine nuclear shielding can be shown to be less than 0.1% using the McConnell equation presented later. For this reason the chlorine nuclear shielding anisotropies were set equal to their free HCl value given in Table II and projected into the axis system of the complex taking into account vibrational averaging effects. This projection, which is completely analogous to the projection of HCl magnetic susceptibility anisotropy into the principal axis system of the complex that is discussed later, gives $2\sigma_{aa} - \sigma_{bb} - \sigma_{cc} = 484$ ppm and $2\sigma_{bb} - \sigma_{aa} - \sigma_{cc} = 242$ ppm while σ_{av} is unaffected by projection. Including these shielding values led to a slightly better fit without addition of new parameters. Final values for the Zeeman parameters for cyclopropane–HCl are reported in Table III. The sign of the molecular g values are determined relative to the nuclear g value of Cl^{33} leading to positive values for all three.

For the zero-field study of cyclopropane–HC^{15}N, only the first term of eq 1 was necessary and is given explicitly by

$$\mathcal{H}_{rot} = (2\pi/\hbar)[J_A^2 + J_B^2 + J_C^2] - D_J(J+1)^2 - D_{JK}J(J+1)K_p^2 \quad (2)$$

where K_p represents the K quantum number in the prolate limit. As indicated by eq 2, centrifugal distortion was treated in the symmetric top limit as the asymmetry parameter κ is −0.994 and

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(33) W. Hüttner and W. H. Flygare, *J. Chem. Phys.*, **41**, 4137 (1967).

Table III. Molecular Zeeman Constants for Cyclopropane-$H^{35}Cl$

g_{aa}	0.0301 (8)
g_{bb}	0.0011 (2)
g_{cc}	0.0071 (1)
$2\chi_{aa} - \chi_{bb} - \chi_{cc}$ (erg/G²·mol)	$8.77\ (28) \times 10^{-6}$
$2\chi_{bb} - \chi_{aa} - \chi_{cc}$ (erg/G²·mol)	$10.39\ (61) \times 10^{-6}$
Q_{aa}	$-1.83\ (26) \times 10^{-26}$
Q_{bb}	$0.06\ (47) \times 10^{-26}$
Q_{cc}	$1.77\ (44) \times 10^{-26}$
χ_{aa} (erg/G²·mol)	$-58\ (1) \times 10^{-6\ a}$
χ_{bb} (erg/G²·mol)	$-58\ (1) \times 10^{-6\ a}$
χ_{cc} (erg/G²·mol)	$-68\ (1) \times 10^{-6\ a}$
χ^{p}_{aa} (erg/G²·mol)	$74\ (1) \times 10^{-6\ a,b}$
χ^{p}_{bb} (erg/G²·mol)	$762\ (1) \times 10^{-6\ a,b}$
χ^{p}_{cc} (erg/G²·mol)	$788\ (1) \times 10^{-6\ a,b}$
χ^{d}_{aa} (erg/G²·mol)	$-132\ (1) \times 10^{-6\ a,b}$
χ^{d}_{bb} (erg/G²·mol)	$-820\ (1) \times 10^{-6\ a,b}$
χ^{d}_{cc} (erg/G²·mol)	$-855\ (1) \times 10^{-6\ a,b}$
$\langle a^2 \rangle$ (Å²)	$181.9\ (3)^{a,b}$
$\langle b^2 \rangle$ (Å²)	$19.8\ (3)^{a,b}$
$\langle c^2 \rangle$ (Å²)	$11.4\ (3)^{a,b}$

[a] Calculated using $\overline{\chi}^{\nabla\text{-HCl}} = -61.3 \times 10^{-6}$ erg/G²·mol. See text. [b] Calculated using structural information or rotational constants for cyclopropane–HCl from ref 30.

Table IV. Measured Rotational Transitions for Cyclopropane-$HC^{15}N$

$J_{K_{-1}K_{+1}} \rightarrow J'_{K'_{-1}K'_{+1}}$	measured (MHz)	$\nu_{obsd} - \nu_{calcd}$ (kHz)
$2_{12} \rightarrow 3_{13}$	7 827.265 9	−3.0
$2_{02} \rightarrow 3_{03}$	7 906.976 3	−0.0
$2_{11} \rightarrow 3_{12}$	7 986.862 1	2.8
$3_{13} \rightarrow 4_{13}$	10 436.068 8	2.1
$3_{03} \rightarrow 4_{04}$	10 541.947 5	0.1
$3_{12} \rightarrow 4_{13}$	10 648.851 6	−2.1

Table V. Molecular Constants for Cyclopropane-$HC^{15}N$

A (MHz)	20 081 (468)
B (MHz)	1344.529 (2)
C (MHz)	1291.332 (2)
D_J (kHz)	1.42 (7)
D_{JK} (kHz)	49 (2)
P_a (amu Å²)	371.04 (29)
P_b (amu Å²)	20.32 (29)
P_c (amu Å²)	4.84 (29)
R_{CM} (Å)	4.495 (3)
$g_{bb} + g_{cc}$	−0.012 83 (2)
$2\chi_{aa} - \chi_{bb} - \chi_{cc}$ (10^{-6} erg/G²·mol)	−4.31 (6)

D_K dependence is not necessary for *a*-dipole-type transitions. The six zero-field transitions in Table IV were used to obtain the rotational parameters given in Table V. These rotational parameters were used to form the rotational part of the Zeeman Hamiltonian to study cyclopropane–$HC^{15}N$ at 30 kG. Matrix elements for the three necessary terms of eq 1 were calculated in the $|JKM_J\rangle$ basis. The four Zeeman lines in Table VI were then fit to $g_{bb} + g_{cc}$ and $2\chi_{aa} - \chi_{bb} - \chi_{cc}$. Analysis showed that these transitions are essentially independent of g_{aa}, $g_{bb} - g_{cc}$, and $2\chi_{bb} - \chi_{aa} - \chi_{cc}$. Attempts to fit any or all of these parameters had little effect on the values of $g_{bb} + g_{cc}$ and $2\chi_{aa} - \chi_{bb} - \chi_{cc}$ that are reported in Table V. The sign of $g_{bb} + g_{cc}$ for cyclopropane–$HC^{15}N$ was determined by arguments to be given later.

Results

A. Consideration of Vibrational Averaging Effects. In order to calculate the contribution of each of the substituent molecules to the Zeeman parameters of the complex, it is necessary to account for the effects of zero-point bending motions introduced upon complexation. Motions involving cyclopropane can be safely ignored. Comparison of P_b and P_c for cyclopropane–HCl, cyclopropane–$HC^{15}N$, and free cyclopropane where

$$P_g = \sum_i m_i g_i^2 \qquad g = a, b, c \tag{3}$$

shows these values to be equal within experimental error,[29,30] indicating that bending motions involving cyclopropane in the complex are small. The zero-point bending motions of $H^{35}Cl$ from its average position in the complex are, however, relatively large in amplitude as indicated by the noticeable decrease of the ^{35}Cl nuclear quadrupole coupling constant in the complex from free $H^{35}Cl$. Similar conclusions can be made regarding the $HC^{15}N$ motion by consideration of the cyclopropane–$HC^{14}N$ isotopic species[31] where ^{15}N isotopic substitution is expected to have only a slight effect on the amplitude of the bending motions. If small electronic effects at the ^{35}Cl and ^{14}N nuclear sites which occur upon complexation are ignored, the nuclear quadrupole coupling constants, eQq_{gg}/h ($g = a, b, c$), in the cyclopropane–$H^{35}Cl$ and cyclopropane–$HC^{14}N$ complexes are given by eq 4. Here eQq_0/h

$$\begin{aligned} \frac{eQq_{aa}}{h} &= \langle \tfrac{3}{2} \cos^2 \beta \cos^2 \alpha - \tfrac{1}{2} \rangle \frac{eQq_0}{h} \\ \frac{eQq_{bb}}{h} &= \langle \tfrac{3}{2} \sin^2 \beta \cos^2 \alpha - \tfrac{1}{2} \rangle \frac{eQq_0}{h} \\ \frac{eQq_{cc}}{h} &= \langle \tfrac{3}{2} \sin^2 \alpha - \tfrac{1}{2} \rangle \frac{eQq_0}{h} \end{aligned} \tag{4}$$

is the nuclear quadrupole coupling constant of ^{35}Cl or ^{14}N in free $H^{35}Cl$ or $HC^{14}N$, Q is the nuclear quadrupole moment, q_{gg} (g = *a*, *b*, *c*) is the electric field gradient at the quadrupolar nuclei, and e and h have their usual meaning. α and β are the Euler angles required to project $H^{35}Cl$ or $HC^{14}N$ from their instantaneous displacement off the *a* axis of the complex first into the *ab* plane and then onto the *a* axis (see Figure 2), and the brackets indicate averaging over the zero-point motion. Information regarding the angle, θ, that the HCl or HCN subunit makes with the *a* axis of the complex is contained in the first of eq 4 as $\cos \theta = \cos \alpha \cos \beta$.

Table VI. Measured Zeeman Transitions for the $2_{02} \rightarrow 3_{03}$ Rotational Transition of Cyclopropane-$HC^{15}N$

30 kG $M_J \rightarrow M'_J$	measured (MHz)	$\nu_{obsd} - \nu_{calcd}$ (kHz)
2 → 3	7906.8203	0.0
−1 → −2	7907.1007	−0.3
−2 → −3	7907.1173	0.5
1 → 0	7907.1438	−0.2

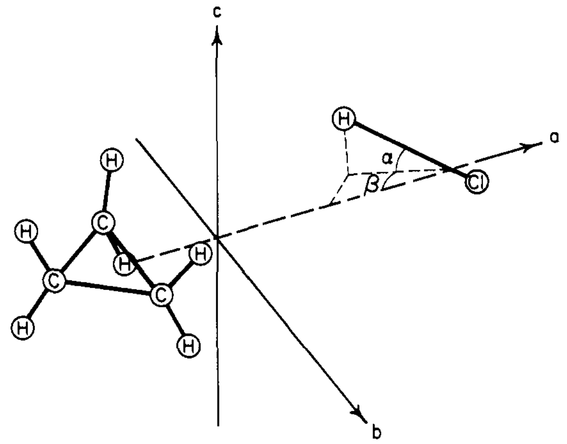

Figure 2. Euler angles describing instantaneous displacement of HCl in the cyclopropane–HCl complex.

Small perturbations at the ^{35}Cl and ^{14}N nuclear sites upon complexation are ignored in the present treatment. As the molecular quadrupole moment of cyclopropane is later shown to be small, calculations described elsewhere[34] show that if higher molecular moments are less important, the nuclear quadrupole coupling constants are better than 99% determined by projection.

From the measured values of the ^{35}Cl and ^{14}N nuclear quadrupole coupling constants in cyclopropane–HX (X = ^{35}Cl, $C^{14}N$) along with the free $H^{35}Cl$ and $HC^{14}N$ values, all given in Table

Table VII. Operational Angles θ, α, and β for Cyclopropane-$H^{35}Cl$ and Cyclopropane-$HC^{15}N$

	θ (deg)[a]	α (deg)	β (deg)
cyclopropane-$H^{35}Cl$	21.15 (1)[b]	15.35 (5)[b]	15.25 (5)[b]
cyclopropane-$HC^{15}N$	12.4 (1)[c]	8.9 (6)[c]	8.9 (6)[c]

[a] Angle obtained from $eQq_{aa}/h = \langle 3\cos^2\theta - 1\rangle(eQq_0/2h)$.
[b] Obtained from $eQq_{aa}/h = -54.41$ (2) MHz and $eQq_{bb}/h = 27.25$ (7) MHz in ref 30 for cyclopropane-$H^{35}Cl$ and $eQq_0/h = -67.618$ MHz for $H^{35}Cl$ in E. W. Kaiser, *J. Chem. Phys.*, **53**, 1686 (1970).
[c] Obtained from $eQq_{aa}/h = -4.38$ (1) MHz and $eQq_{bb}/h = 2.19$ (3) for the cyclopropane-$HC^{14}N$ isotopic species in ref 31 and $eQq_0/h = -4.709$ (1) for $HC^{14}N$ in F. DeLucia and N. W. Gordy, *Phys. Rev.*, **187**, 58 (1969).

Table VIII. Molecular Properties of Cyclopropane

$Q_{\parallel}$ (esu cm^2)	$1.04\ (40) \times 10^{-26}$
$Q_{\perp}$ (esu cm^2)	$-0.52\ (30) \times 10^{-26}$
$g_{\parallel}$	0.067 (1)
$g_{\perp}$	0.026 (1)[a] 0.024 (1)[b]
$\chi_{\parallel} - \chi_{\perp}$ (erg/G^2·mol)	$-9\ (1) \times 10^{-6}$ [c] $-10\ (1) \times 10^{-6}$ [d] $-9\ (1) \times 10^{-6}$ [e]
$\chi_{\parallel}$ (erg/G^2·mol)	$-45\ (1) \times 10^{-6}$ [f]
$\chi_{\perp}$ (erg/G^2·mol)	$-36\ (1) \times 10^{-6}$ [f]
$\chi_{\parallel}^{p}$ (erg/G^2·mol)	$101\ (1) \times 10^{-6}$ [f,g]
$\chi_{\perp}^{p}$ (erg/G^2·mol)	$75\ (1) \times 10^{-6}$ [f,g]
$\chi_{\parallel}^{d}$ (erg/G^2·mol)	$-147\ (1) \times 10^{-6}$ [f,g]
$\chi_{\perp}^{d}$ (erg/G^2·mol)	$-111\ (1) \times 10^{-6}$ [f,g]
$\langle a^2\rangle$, $\langle b^2\rangle$ (Å^2)	17.3 (2)[f,g]
$\langle c^2\rangle$ (Å^2)	8.8 (2)[f,g]

[a] Calculated using g_{aa} for cyclopropane-HCl. [b] Calculated using g_{bb} for cyclopropane-HCl. [c] Calculated using $2\chi_{aa} - \chi_{bb} - \chi_{cc}$ for cyclopropane-HCl. [d] Calculated using $2\chi_{bb} - \chi_{aa} - \chi_{cc}$ for cyclopropane-HCl. [e] Calculated using $2\chi_{aa} - \chi_{bb} - \chi_{cc}$ for cyclopropane-$HC^{15}N$. [f] Calculated using $\bar{\chi}^{\triangledown} = -39.2 \times 10^{-6}$ erg/G^2·mol. See ref 42. [g] Calculated using structural information or rotational constants for cyclopropane. See ref 37.

VII, operational values of α, β, and θ can all be assigned and are given by eq 5. The operational values for α, β, and θ are given

$$\alpha = \arctan\left(\frac{q_{cc} + q_0/2}{q_{aa} + q_0/2}\right)^{1/2}$$
$$\beta = \arccos\left(\frac{q_{aa} + q_0/2}{q_{aa} + q_{bb} + q_0}\right)^{1/2} \qquad (5)$$
$$\theta = \arccos\left(\frac{2q_{aa}}{3q_0} + \tfrac{1}{3}\right)^{1/2}$$

in Table VII for the two complexes and will be used in projection equations for the Zeeman parameters of the complexes.

The distance between the centers of mass of the subunits, R_{CM}, in cyclopropane-$HC^{15}N$, can be determined from the rotational constants of the complex and subunits and consideration of vibrational averaging effects. By redefining P_a for the complex in terms of displacements of the atoms from the centers of mass of the subunits, we have

$$P_a^{\triangledown-HCN} = P_a^{\triangledown} + I^{HCN}\langle\cos^2\theta\rangle + \frac{M^{\triangledown}M^{HCN}}{M^{\triangledown} + M^{HCN}}R_{CM}{}^2 \qquad (6)$$

where $M^{\triangledown}$ and M^{HCN} are the masses of the substituents. Using values $P_a{}^{\triangledown}$ and I^{HCN} in Table II along with $P_a^{\triangledown-HCN}$ in Table V and θ from Table VII, we obtain $R_{CM} = 4.495$ (3) Å. The effect of errors in θ in this determination are small with R_{CM} changing by 0.004 Å for θ ranging from 0 to 13°.

B. Molecular *g* Values. Recent studies by Read and Campbell[7] indicate that for weakly bound linear complexes of similar binding strength as the present ones, certain molecular properties of the complex, such as *g* values, magnetic susceptibilities, and molecular quadrupole moments, are to a good approximation resultants of the corresponding properties in the substituent molecules. In these studies, unlike the present one, the properties of the substituent molecules were known while those of the complex were determined. The success of using projection equations which relate the molecular property of the complex to those of the substituent molecules could then be determined by taking into account vibrational effects which are introduced upon complexation and changes of centers of mass. The intuition that weak complexation would little alter these properties in the substituent molecules was shown to be correct for these linear, hydrogen-bound complexes. We will use a similar approach with the present asymmetric tops to obtain *g* values for cyclopropane.

The molecular *g* values of the complexes are a sum of nuclear and electronic terms and are given by[2]

$$\mathbf{g} = M_P\sum_{\alpha}(r_\alpha{}^2\mathbf{1} - \boldsymbol{r}_\alpha\boldsymbol{r}_\alpha)\cdot\mathbf{I}^{-1} + \frac{2M_P}{m}\mathbf{I}^{-1}\cdot\sum_{k>0}\frac{\langle 0|\boldsymbol{L}|k\rangle\langle k|\boldsymbol{L}|0\rangle}{E_0 - E_k} \qquad (7)$$

The first summation is over all nuclei in the complex, $\mathbf{I}^{-1}$ is the inverse moment of inertia tensor of the complex, and the summation in the electronic term involves matrix elements of the angular momentum operator between ground and excited molecular electronic states of the complex where $\boldsymbol{L} = \sum_i \boldsymbol{r}_i \times \boldsymbol{p}_i$. Angular momentum and displacements are defined in terms of the centers of mass of the complex. The nuclear term is easily separated into two terms by redefining the displacements of a given nucleus with respect to the center of mass of the substituent molecule with which it is associated. The electronic term can be similarly separated into two terms by approximating the molecular electronic wave function of the complex as a product of electronic wave functions of the substituent molecules and ignoring the interaction energy of the substituent molecules (~500 cm^{-1}) as compared to the much higher electronic excitation energies of the free molecules. Redefining the angular momenta of the electrons with respect to the centers of mass of the substituents and various manipulations leads to eq 8, where $\langle g_{xx}^{HX}I_{xx}^{HX}\rangle$ refers to the value

$$\begin{aligned} g_{xx}^{\triangledown-HX}I_{xx}^{\triangledown-HX} = {} & \langle g_{xx}^{\triangledown}I_{xx}^{\triangledown}\rangle + \langle g_{xx}^{HX}I_{xx}^{HX}\rangle \\ & + 2M_pY^{\triangledown}[\sum_{\alpha(\triangledown)} Z_\alpha y_\alpha - \langle 0_{CP}|\sum_{i(\triangledown)} y_i|0_{CP}\rangle] \\ & + 2M_pZ^{\triangledown}[\sum_{\alpha(\triangledown)} Z_\alpha z_\alpha - \langle 0_{CP}|\sum_{i(\triangledown)} z_i|0_{CP}\rangle] \\ & + 2M_pY^{HX}[\sum_{\alpha(HX)} Z_\alpha y_\alpha - \langle 0_{HX}|\sum_{i(HX)} y_i|0_{HX}\rangle] \\ & + 2M_pZ^{HX}[\sum_{\alpha(HX)} Z_\alpha z_\alpha - \langle 0_{HX}|\sum_{i(HX)} z_i|0_{HX}\rangle] \end{aligned} \qquad (8)$$

$$X = Cl,\ CN$$

of $g_{xx}^{HX}I_{xx}^{HX}$ as defined in the axis system of the complex and averaged over zero-point motions. $Y^{\triangledown}$, etc., and Y^{HX}, etc. refer to displacements of the center of mass of the complex relative to the centers of mass of the substituents. Consideration of vibrational averaging effects leads to the expressions in eq 9. By using the

$$g_{aa}^{\triangledown-HX} = \frac{1}{I_{aa}{}^{\triangledown-HX}}[g_{\perp}^{\triangledown}I_{aa}^{\triangledown} + g_{\perp}^{HX}I^{HX}\langle\sin^2\beta + \cos^2\beta\sin^2\alpha\rangle]$$

$$g_{bb}^{\triangledown-HX} = \frac{1}{I_{bb}{}^{\triangledown-HX}}\left[g_{\perp}^{\triangledown}I_{bb}^{\triangledown} + g_{\perp}^{HX}I^{HX}\langle\cos^2\beta + \sin^2\beta\sin^2\alpha\rangle + \frac{2M_pA^{HX}}{|e|}\mu_z^{HX}\langle\cos\alpha\cos\beta\rangle\right]$$

$$g_{cc}^{\triangledown-HX} = \frac{1}{I_{cc}{}^{\triangledown-HX}}\left[g_{\parallel}^{\triangledown}I_{cc}^{\triangledown} + g_{\perp}^{HX}I^{HX}\langle\cos^2\alpha\rangle + \frac{2M_pA^{HX}}{|e|}\mu_z^{HX}\langle\cos\alpha\cos\beta\rangle\right] \qquad (9)$$

$$X = Cl,\ CN$$

molecular *g* values for cyclopropane-HCl in Table III, free cyclopropane and HCl molecular parameters in Table II, along with the rotational constants given in Table V and ref 30, and the vibrational angles in Table VII, the molecular g values can be calculated for cyclopropane using eq 9. Since cyclopropane is an oblate symmetric top, there are two independent g values, $g_\perp$ and $g_\parallel$, and these are reported in Table VIII. $g_\perp$ for cyclopropane can be calculated independently from g_{aa} and g_{bb} of the complex. Both values, which are in excellent agreement, are reported and reflect the accuracy of the projection equations. If we take their average value as the true one, the standard deviation is $\sigma = 0.0014$ putting the uncertainty at 6%. The calculated $g_\parallel$ and $g_\perp$ values of cyclopropane can now be used to predict a value for $g_{bb} + g_{cc}$ for the cyclopropane–HC^{15}N complex. This will determine the sign of the experimental value, and also comparison of the relative magnitudes of the calculated and observed values could serve as additional confirmation of the accuracy of the projection equations. Using free cyclopropane and HC^{15}N parameters given in Table II, structural information obtained from the rotational constants of cyclopropane–HC^{15}N along with $g_\parallel$ and $g_\perp$ just obtained for cyclopropane, -0.014 is calculated for $g_{bb} + g_{cc}$ using eq 9 as compared with our experimentally determined value of ± 0.013. In summary then, both $g_\parallel$ and $g_\perp$ values for cyclopropane have been checked in some independent manner and are expected to be fairly accurate.

C. Magnetic Susceptibility Anisotropy. The magnetic susceptibility tensor elements are given by[2]

$$\chi = \frac{-e^2}{4c^2m}\langle 0|\sum_i(r_i^2\mathbf{1} - \boldsymbol{r}_i\boldsymbol{r}_i)|0\rangle - \frac{e^2}{2m^2c^2}\sum_{k>0}\frac{\langle 0|\boldsymbol{L}|k\rangle\langle k|\boldsymbol{L}|0\rangle}{E_0 - E_k} \quad (10)$$

where the first term is the diamagnetic response of the molecule and the second term involving excited electronic states is the paramagnetic response of the molecule. The individual tensor elements for cyclopropane–HCl are given in Table **III**. These were obtained by using the susceptibility anisotropies also reported in Table III and the bulk susceptibility, $\bar{\chi}^{\nabla\text{-HCl}}$, for cyclopropane–HCl where

$$\bar{\chi}^{\nabla\text{-HCl}} = \tfrac{1}{3}(\chi_{aa} + \chi_{bb} + \chi_{cc}) \quad (11)$$

$\bar{\chi}^{\nabla\text{-HCl}}$ is obtained by taking the sum of the bulk susceptibilities for cyclopropane and HCl which are given in Table II. This is justified by the linear hydrogen-bond Zeeman studies[7] which show that the susceptibility anisotropy of the substituent molecules project to give the value for the complex along with the invariance of $\bar{\chi}^{\nabla\text{-HCl}}$ to vibrational motions of the substituent molecules introduced upon complexation. χ_{aa} and χ_{bb} are equal within experimental error as would be expected since the a and b directions are equivalent in cyclopropane and the susceptibility anisotropy of HCl is only -0.19×10^{-6} erg/G^2·mol.[35]

The paramagnetic contributions of the susceptibility tensor elements can be obtained from the molecular g values, the structure, and the rotational constants of the complex. From the paramagnetic contributions and the total magnetic susceptibilities, the diamagnetic contributions are then derived as well as the second moments of the electronic charge distribution, $\langle a^2\rangle$, etc., where

$$\langle a^2\rangle = \langle 0|\sum_i a_i^2|0\rangle \quad (12)$$

These constants are all reported in Table III.

It is now of interest to obtain the magnetic susceptibility anisotropy of cyclopropane. Various estimates of this quantity presently in the literature vary by as much as 100% and will be discussed in more detail later. We will again use projection equations to subtract out the effects of the two different binding partners and then check this assumption as the susceptibility anisotropy will be determined from any of the three susceptibility anisotropies obtained for the complexes. The appropriate equations for either complex will be

$$(2\chi_{aa} - \chi_{bb} - \chi_{cc})^{\nabla\text{-HX}} = (\chi_\perp - \chi_\parallel)^\nabla + \langle 3\cos^2\beta\cos^2\alpha - 1\rangle(\chi_\parallel - \chi_\perp)^{\text{HX}} \quad (13)$$

$$(2\chi_{bb} - \chi_{aa} - \chi_{cc})^{\nabla\text{-HX}} = (\chi_\perp - \chi_\parallel)^\nabla + \langle 3\sin^2\beta\cos^2\alpha - 1\rangle(\chi_\parallel - \chi_\perp)^{\text{HX}} \quad (14)$$

Using the three measured anisotropies for the complexes in Tables III and V, $\chi_\parallel - \chi_\perp$ for H^{35}Cl and HC^{15}N given in Table II, and values for α and β given in Table VII, we obtain independently three values for $\chi_\parallel - \chi_\perp$ for cyclopropane. These are listed in Table VII. The uniformity of the values is striking, especially when considering that the magnetic susceptibility anisotropy of the binding partner has changed considerably in going from HCl (-0.19×10^{-6} erg/G^2·mol) to HCN (7.2×10^{-6} erg/G^2·mol).[36] We take this as strong evidence that the projection equations are accurately subtracting out the effects of the binding partner and that the average of the three values is good to better than 10%. This uncertainty would also be consistent with the findings of Read et al. for linear hydrogen-bound complexes regarding the accuracy of projection equations for susceptibility anisotropy.

Using the bulk susceptibility of cyclopropane, $\bar{\chi}^\nabla$, given in Table II, the individual tensor elements of the magnetic susceptibility for cyclopropane can be obtained and these are reported in Table VIII using the average of the three $(\chi_\parallel - \chi_\perp)^\nabla$ values in Table VIII. The use of eq 13 and 14 assumes that χ_{aa} and χ_{bb} are equal for cyclopropane in the complex as they must be for free cyclopropane. To prove this is the case, this restraint can be lifted by using $(2\chi_{aa} - \chi_{bb} - \chi_{cc})^{\nabla\text{-HCl}}$ and $(2\chi_{bb} - \chi_{aa} - \chi_{cc})^{\nabla\text{-HCl}}$ to obtain $(2\chi_{aa} - \chi_{bb} - \chi_{cc})^\nabla$ and $(2\chi_{bb} - \chi_{aa} - \chi_{cc})^\nabla$ where these later two quantities replace $(\chi_\perp - \chi_\parallel)^\nabla$ in eq 13 and 14, respectively. These two cyclopropane anisotropies can then be combined with $\bar{\chi}^\nabla$ to obtain $\chi_{aa}{}^\nabla = 36.2\ (8)$ and $\chi_{bb}{}^\nabla = 35.7\ (8)$ which are equal within error and serve to confirm the method.

The diamagnetic and paramagnetic contributions were obtained using the g values calculated earlier and the structure and rotational constants for cyclopropane[37] and are reported in Table VIII along with the second moments of the electronic charge distribution. The diamagnetic susceptibilities and second moments of the electronic charge distribution for cyclopropane are in excellent agreement with those calculated using various methods. Maksić et al.[38] showed how calculation of these properties is relatively insensitive to the quality of the wave function used and utilizing STO wave functions with optimized exponents calculated values remarkably close to the present values. Values obtained by Snyder and Basch[39] from an SCF calculation in a double-ζ Gaussian basis set are also very close to the present values. These comparisons are illustrated in Table IX along with the excellent agreement between the value obtained in this work for $\langle c^2\rangle$ and that obtained using a semiempirical method.[40] The value of $\langle c^2\rangle$ obtained for cyclopropane (8.8 Å^2) is smaller than that for the complex (11.4 Å^2) in accord with the extra contribution in the complex due to the chlorine lone pairs.

D. Molecular Quadrupole Moments. The molecular quadrupole moment is in general given by

$$Q_{gg} = (e/2)\sum_\alpha z_\alpha(3g_\alpha{}^2 - r_\alpha{}^2) - (e/2)\langle 0|\sum_i(3g_\text{i}{}^2 - r_\text{i}{}^2)|0\rangle \quad (15)$$

$g = a, b, c$ where $g_\alpha{}^2$ and $r_\alpha{}^2$ have been averaged over molecular vibrations. From the definition of the molecular g-value tensor elements and the magnetic susceptibility tensor elements given in eq 7 and 10, it is evident that

$$Q_{aa} = \frac{2mc^2}{e}(\chi_{bb} + \chi_{cc} - 2\chi_{aa}) + \frac{e}{2M_\text{p}}(g_{bb}I_{bb} + g_{cc}I_{cc} - 2g_{aa}I_{aa}) \quad (16)$$

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[34] P. D. Aldrich, S. G. Kukolich, and E. J. Campbell, *J. Chem. Phys.*, **78**, 3521 (1983).

[35] F. H. DeLeeuw and A. Dymanus, *J. Mol. Spectrosc.*, **48**, 427 (1973).

[36] S. L. Hartford, W. C. Allen, C. L. Norris, E. F. Pearson, and W. H. Flygare, *Chem. Phys. Lett.*, **18**, 153 (1973).

[37] B. Rubin, S. R. Polo, and T. K. McCubbin, *J. Mol. Spectrosc.*, **84**, 487 (1980); R. J. Butcher and W. J. Jones, *ibid.*, **47**, 64 (1973).

[38] Z. B. Maksić and J. E. Bloor, *Chem. Phys. Lett.*, **13**, 571 (1972).

[39] L. C. Snyder and H. Basch, "Molecular Wavefunctions and Properties", Wiley, New York, 1972.

[40] R. P. Blickensderfer, J. H. Wong, and W. H. Flygare, *J. Chem. Phys.*, **51**, 3196 (1969).

Table IX. Comparison of Values Obtained for the Diamagnetic Susceptibility and Second Moment of the Electronic Charge Distribution for Cyclopropane in This Work with Previous Calculated Values

	present work	calcd[a]	calcd[b]	calcd[c]
$\chi_{\parallel}{}^{d}$ (erg/G^2·mol)	-147×10^{-6}	-145×10^{-6}	-149×10^{-6}	
$\chi_{\perp}{}^{d}$ (erg/G^2·mol)	-111×10^{-6}	-112×10^{-6}	-112×10^{-6}	
$\langle a^2 \rangle$ (Å^2)	17.3	17.2	17.6	
$\langle b^2 \rangle$ (Å^2)	17.3	17.2	16.6	
$\langle c^2 \rangle$ (Å^2)	8.8	9.1	8.9	9

[a] See ref 38. [b] See ref 39. [c] See ref 40.

and cyclical permutations for Q_{bb} and Q_{cc}. The values obtained for Q_{aa}, Q_{bb}, and Q_{cc} in the cyclopropane–HCl complex are given in Table III along with their uncertainties. The positive value for Q_{cc} indicates that most of the electron density is located near the plane containing the heavy atoms. The molecular quadrupole moments for cyclopropane are similarly obtained using average values for $\chi_{\parallel} - \chi_{\perp}$ and $g_{\perp}$ and the value determined for $g_{\parallel}$. Though the uncertainties of the cyclopropane molecular quadrupole moments reported in Table III are high, they are in qualitative agreement with intuition. The positive value obtained for Q_{cc} is expected as only hydrogen atoms project out of plane and is in agreement with the sign of Q_{cc} predicted by a semiempirical method[41] for calculating quadrupole moments though quantitative agreement is poor.

Discussion

The magnetic susceptibility tensor elements obtained for cyclopropane become especially significant in light of the body of literature concerning the supposed high susceptibility anisotropy of cyclopropane and various ring current theories utilized to account for it.[8-13] Early measurements[13,42] of the bulk susceptibility of cyclopropane showed values enhanced over predictions from semiempirical methods,[43-45] prompting speculation about delocalized p_z electrons giving rise to an enhanced susceptibility normal to the ring. The NMR proton shift in cyclopropane has been noted to occur at unusually high field (9.78 ppm with reference to tetramethylsilane) relative to normal methylene protons and has been taken to be evidence of ring currents.[8-10,12] Also, various studies[10,11,46] of shieldings of other protons by cyclopropyl groups have obtained values of $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$ consistent with ring current effects by relating $\Delta\chi$ of the cyclopropyl group to long-range shielding effects. $\Delta\chi$ can be obtained in this way be observing the change in the shielding experienced by a proton with the introduction of a cyclopropyl group using the McConnell equation[47]

$$\sigma = (\Delta\chi/3R^3)\langle 1 - 3\cos^2\gamma \rangle \qquad (17)$$

Here σ is the shielding at a given proton due to the magnetic susceptibility anisotropy of the cyclopropyl group, R is the distance btween the proton and the center of the ring, γ is the angle between R and the symmetry axis of cyclopropane, and averaging is over all internal motion. This equation assumes a point magnetic dipole for the cyclopropyl group and is most accurate[48] when the cyclopropyl group is 3 Å or more from the proton.

Table X compares the value obtained in this work for $\Delta\chi$ for cyclopropane with those obtained by other means. In three cases the values are obtained by a best fit of eq 17 to many cyclopropyl compounds. The variability is large, ranging over $11-21 \times 10^{-6}$ erg/G^2·mol and is an indication of the crudeness of this method.[2,49,50] The value obtained from magnetic birefrigence measurements[51] is contingent on assumptions regarding certain higher polarizability terms which give this value a certain amount of uncertainty.[2,50,52] The value obtained by Flygare was obtained by reasoning that $\Delta\chi$ for cyclopropane must lie between $\chi_{zz} - {}^1/_2(\chi_{xx} + \chi_{yy})$ for ethylenimine (-10.9×10^{-6} erg/G^2·mol) and ethylene oxide (-9.5×10^{-6} erg/G^2·mol). As the error in $\Delta\chi$ presented in this work is estimated to be less than 10%, the large error to be expected with the other methods can be seen from Table X.

Table X. Values Obtained for $\chi_{\parallel} - \chi_{\perp}$ for Cyclopropane Using Various Methods

$\chi_{\parallel} - \chi_{\perp}$ (erg/G^2·mol)	method
-9.7×10^{-6}	present work
-10.0×10^{-6} [a]	comparison with chemically similar systems
-13.6×10^{-6} [b]	semiempirical CNDO
-19.2×10^{-6} [c]	magnetic birefringence
-21.0×10^{-6} [d]	NMR shieldings
-15.0×10^{-6} [e]	NMR shieldings
-11.0×10^{-6} [f]	NMR shieldings

[a] R. C. Benson and W. H. Flygare, *J. Chem. Phys.*, **51**, 3087 (1969). [b] See ref 53. [c] See ref 51. [d] See ref 57. [e] See ref 46. [f] See ref 11.

Table XI. Susceptibility Tensor Elements for Cyclopropane[a]

		semiempirical CNDO[c]		
	localized model[b]	local contribution only	includes nonlocal contribution	present work
χ_{aa}	-34×10^{-6}	-31×10^{-6}	-30×10^{-6}	-36×10^{-6}
χ_{bb}	-34×10^{-6}	-31×10^{-6}	-30×10^{-6}	-36×10^{-6}
χ_{cc}	-34×10^{-6}	-33×10^{-6}	-44×10^{-6}	-45×10^{-6}

[a] In units of ergs/G^2·mol. [b] See ref 3. Assume sp^3 hybridization for the carbon atoms. [c] See ref 53.

That the present results could be indicative of ring current can best be seen by considering semiempirical methods for predicting the individual magnetic susceptibility tensor elements. In the absence of ring currents the localized magnetic susceptibility method of Flygare[3] is quite accurate. By assuming sp^3 hybridization on the carbon atoms for the moment, χ_{aa}, χ_{bb}, and χ_{cc} are calculated for cyclopropane by this method and presented in Table XI. Also given are values obtained in this work. The agreement between calculated and observed in-plane components is striking; however, the measured χ_{cc} value is clearly enhanced over prediction as would be expected by ring currents in the plane of the carbon atoms. Also included in Table XI are semiempirical CNDO results by Bley for cyclopropane[53] where nonlocal contributions are calculated by including selected two center integrals. With the exclusion of these nonlocal contributions the values for these calculated magnetic susceptibility tensor elements are in relative agreement with the values using Flygare's method and with χ_{aa} and χ_{bb} determined in this work. However, with the inclusion of nonlocal effects, Bley's calculated χ_{cc} value becomes almost identical with the measured value with little change in χ_{aa} or χ_{bb}.

Though the above comparisons may seem indicative of ring current, legitimate questions may be raised regarding the use of sp^3 hybridization in the semiempirical calculation. From the fact that the $J_{^{13}\mathrm{CH}}$ spin–spin coupling constant is, within certain limits, proportional to the s character of the carbon atom,[54,55] the hybridization of the carbon atom in cyclopropane has been found to be sp^2–sp$^{2.5}$.[12,54,56] Coulson and Moffitt reached similar con-

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(41) T. D. Gierke, H. L. Tigelaar, and W. H. Flygare, *J. Am. Chem. Soc.*, **94**, 330 (1972).

(42) C. Buster, R. G. Meisenheimer, and D. P. Stevenson, *J. Phys. Chem.*, **64**, 1312 (1960).

(43) P. Pascal, "Chimi generale"; Masson et Cie, Paris, 1959.

(44) P. Pascal, *C. R. Acad. Sci.*, **181**, 656 (1925).

(45) J. Farqaharson and M. Sastri, *Trans. Faraday Soc.*, **33**, 1474 (1937).

(46) S. Forsẽn and T. Norin, *Tetrahedron Lett.*, **39**, 2848 (1964).

(47) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

(48) J. R. Didrey and J. Guy *C. R. Acad. Sci.*, **253**, 422 (1961).

(49) J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961).

(50) R. Ditchfield, *MTP Int. Rev. Sci.*; *Phys. Chem.*, *Ser. One*, **2**, 91 (1972).

(51) A. D. Buckingham, W. H. Pritchard, and D. H. Whiffen, *Trans. Faraday Soc.*, **63**, 1057 (1967).

(52) W. H. Flygare, R. L. Shoemaker, and W. Hüttner, *J. Chem. Phys.*, **50**, 2414 (1969).

(53) W. R. Bley, *Mol. Phys.*, **20**, 491 (1971).

(54) N. Muller and D. Pritchard, *J. Chem. Phys.*, **31**, 768 (1959).

(55) C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2198 (1962).

clusions regarding carbon hybridization in the carbon–hydrogen bond by parameterizing the energy of the carbon–carbon valence bonds in cyclopropane in terms of the hybridization of the carbon atoms.[21] Mimimization led to $sp^{2.28}$ hybridization for orbitals associated with carbon–hydrogen bonds and $sp^{4.12}$ hybridization for orbitals associated with carbon–carbon bonds. It has been suggested by Tori and Kitahonoki[57] that the change in hybridization of the orbitals in cyclopropane changes the susceptibility anisotropy associated with the carbon–carbon bond so that shieldings by cyclopropyl groups can be explained without resorting to ring currents. In this study a modified McConnell equation was used to predict the additional proton shift observed in a number of molecules with the introduction of a cyclopropyl group. By ignoring the carbon–hydrogen bond anisotropy, the additional shift is then given by

$$\Delta\sigma = \frac{\Delta\chi}{3}\sum_{i}^{3}\frac{3\cos^2\theta_i - 1}{R_i^3} \qquad (18)$$

where $\Delta\chi$ is now the anisotropy of the carbon–carbon bond and this bond is treated as a point dipole. A more recent study,[11] however, has shown the failure of eq 18 in predicting certain proton shifts due to cyclopropyl groups. This study considered 18 proton shifts with a wide variety of orientations of the cyclopropyl group with respect to the protons including six shifts where the group anisotropy theory described by eq 17 predicts opposite signs for the additional shift as bond anisotropy theory utilizing eq 18. The study concluded that group anisotropy was strongly superior in its predictions and in the six cases mentioned predicted the correct sign while bond anisotropy theory did not. While this is not proof of ring current in cyclopropane it does seem to indicate the importance of nonlocal effects in explaining the susceptibility anisotropy of cyclopropane as do results for other three-member rings.[20,58]

The magnetic susceptibility due to ring current is given in a simple picture by[14]

$$\chi_{zz} = -(Ne^2/4mc^2)\rho^2 \qquad (19)$$

where ρ is the assumed radius of the ring, N is the number of circulating electrons, and the z direction is normal to the ring. If in the present case we attribute most of our determined magnetic susceptibility anisotropy to ring current as would be suggested by the semiempirical calculations as well as Bley's results, we obtain ca. three electrons for a radius of 0.88 Å (the centroid to carbon distance). Burke and Lauterbur[9] observed that in order to account for the ratio and magnitude of carbon and hydrogen shieldings in cyclopropane relative to those in central methylene groups in long alkanes it was necessary to have 3.5 electrons flow in a 1.10-Å radius. A more recent study[10] of 52 proton shieldings influenced by cyclopropyl groups utilized the more sophisticated Johnson and Bovey technique[59] to show that 4.5 electrons circulating in a 0.88-Å radius optimized agreement between experiment and calculation. Other ring current models for cyclopropane utilize three to six electrons.[11,20]

Conclusions

The rotational Zeeman effect has been observed experimentally with two complexes involving cyclopropane. Using information about vibrational motion of the binding partners of cyclopropane in the complex and their known magnetic properties, the magnetic properties of cyclopropane have been determined. The g values, paramagnetic and diamagnetic susceptibilities, second moments of the electronic charge distribution, and molecular quadrupole moments have all been determined for both the complexes and free cyclopropane. Numerous self-consistency checks have been employed in obtaining these constants for cyclopropane and indicate that the values obtained are quite accurate. Furthermore, the ground electronic state properties obtained such as the diamagnetic susceptibilities and second moments of the electronic charge distribution agree remarkably well with various calculations. These properties have been shown to be easily calculable with good accuracy, and thus these comparisons serve as additional confirmation of the present technique.

The magnetic susceptibility anisotropy obtained here for cyclopropane has been compared to less accurately determined values. Values obtained from NMR proton shieldings show great variability and cannot be expected to be more than a rough method of determining this quantity. Semiempirical CNDO calculations by Bley give a value for the anisotropy very close to the present value as does an estimate by Flygare et al. The discrepancy between the present value and that obtained from magnetic birefringence experiments points to the limitations of that technique when ignoring electronic distortion anisotropy ($\Delta\eta$). In these experiments the Cotton–Mouton constant is obtained which is related to the magnetic susceptibility anisotropy, the electric polarizability anisotropy ($\Delta\alpha$), and $\Delta\eta$ by[51]

$${}_{\mathrm{m}}C = \frac{2}{135}\pi N\left[\Delta\eta + \left(\frac{2}{3kT}\right)\Delta\alpha\Delta\chi\right] \qquad (20)$$

η is a fourth rank tensor describing the variation in the electric polarizability with an applied magnetic field, and often spherical distortion ($\Delta\eta = 0$) is assumed. The results of Buckingham et al. along with the present results allow us to determine $\Delta\eta$ to be 207×10^{-42} emu for cyclopropane. This is about one-fourth of the value calculated for benzene[2] though opposite in sign.

The value obtained for the magnetic susceptibility anisotropy in cyclopropane is consistent with the possibility of ring currents in cyclopropane. The in-plane susceptibility tensor element is in good agreement while the out-of-plane tensor element is significantly enhanced. NMR shielding evidence points to this enhancement as being more consistent with ring current effects than due to odd hybridization of the carbon atoms.

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Registry No. Cyclopropane, 75-19-4; cyclopropane–HCl, 75956-59-1; cyclopropane–$HC^{15}N$, 86335-62-8.

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(56) P. Lazlo, *Bull. Soc. Chim. Fr.*, 558 (1966).

(57) K. Tori and K. Kitahonoki, *J. Am. Chem. Soc.*, **87**, 386 (1965).

(58) R. Benson and W. H. Flygare, *Chem. Phys. Lett.*, **4**, 141 (1969).

(59) C. Johnson and F. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).