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Molecular g Values, Magnetic Susceptibility Anisotropies, Second Moment of the Charge Distribution, and Molecular Quadrupole Moments in Ethylenimine and Pyrrole

D. H. Sutter¹ and W. H. Flygare

Contribution from the Noyes Chemical Laboratory, University of Illinois,
Urbana, Illinois. Received June 9, 1969

Abstract: The high-field first- and second-order Zeeman effect has been observed in ethylenimine and pyrrole. Only the relative signs of the molecular g values are obtained experimentally. However, the absolute signs are conclusively assigned in both molecules by an analysis of the second moment of the charge distributions or molecular quadrupole moments. For ethylenimine the b axis bisects the CNC angle and lies at an angle of $4^\circ 45'$ from the CNC plane (see Figure 1). The a axis also lies nearly in the CNC plane and the c axis is approximately perpendicular to the CNC plane. The measured g values and magnetic susceptibility anisotropies are $g_{aa} = -(0.0422 \pm 0.008)$, $g_{bb} = 0.0229 \pm 0.0009$, $g_{cc} = 0.0539 \pm 0.0010$, $2\chi_{aa} - \chi_{bb} - \chi_{cc} = (16.5 \pm 0.7) \times 10^{-6}$ erg/(G² mol), and $2\chi_{bb} - \chi_{cc} - \chi_{aa} = (4.6 \pm 0.8) \times 10^{-6}$ erg/(G² mol). The molecular quadrupole moments are $Q_{aa} = (1.3 \pm 0.6)$, $Q_{bb} = -(2.6 \pm 0.6)$, and $Q_{cc} = (1.3 \pm 1.0)$ all in units of 10^{-26} esu cm². Using the known molecular structure allows a determination of the diagonal elements in the paramagnetic susceptibility tensor and the anisotropies in the second moment of the charge distribution. These numbers are $\chi_{aa}^p = 66.6 \pm 1.6$, $\chi_{bb}^p = 77.0 \pm 1.6$, and $\chi_{cc}^p = 90.5 \pm 1.6$ all in units of 10^{-6} erg/(G² mol) and $\langle a^2 \rangle - \langle b^2 \rangle = 2.2 \pm 0.6$, $\langle b^2 \rangle - \langle c^2 \rangle = 6.4 \pm 0.6$, and $\langle c^2 \rangle - \langle a^2 \rangle = -(8.6 \pm 0.6)$ all in units of 10^{-16} cm². All of the above results in ethylenimine are remarkably similar to recent results obtained for ethylene oxide. For pyrrole the a axis bisects the CNC angle and lies in the molecular plane. The b axis also lies in the molecular plane. The measured g values and magnetic susceptibility anisotropies are $g_{aa} = -(0.0895 \pm 0.0010)$, $g_{bb} = -(0.0643 \pm 0.0010)$, $g_{cc} = (0.0752 \pm 0.0010)$, $2\chi_{aa} - \chi_{bb} - \chi_{cc} = (50.2 \pm 1.0) \times 10^{-6}$ erg/(G² mol), and $2\chi_{bb} - \chi_{cc} - \chi_{aa} = (34.6 \pm 1.8) \times 10^{-6}$ erg/(G² mol). The molecular quadrupole moments are $Q_{aa} = 6.6 \pm 1.2$, $Q_{bb} = 5.8 \pm 1.6$, and $Q_{cc} = -(12.4 \pm 2.3)$ in units of 10^{-26} esu cm². Using the known molecular structure allows a determination of the diagonal elements in the paramagnetic susceptibility tensor and the anisotropies in the second moment of the charge distribution. These numbers are $\chi_{aa}^p = 163.8 \pm 1.0$, $\chi_{bb}^p = 160.6 \pm 1.0$, and $\chi_{cc}^p = 253.0 \pm 1.0$ in units of 10^{-6} erg/(G² mol) and $\langle a^2 \rangle - \langle b^2 \rangle = 0.5 \pm 0.4$, $\langle b^2 \rangle - \langle c^2 \rangle = 31.2 \pm 0.6$, and $\langle c^2 \rangle - \langle a^2 \rangle = -(31.7 \pm 0.6)$ in units of 10^{-16} cm². Combining the above data with the known bulk magnetic susceptibility for pyrrole gives the diagonal elements in the total magnetic susceptibility tensor which are $\chi_{aa} = -(31.9 \pm 0.9)$, $\chi_{bb} = -(37.0 \pm 1.1)$, and $\chi_{cc} = -(76.8 \pm 1.5)$ in units of 10^{-6} erg/(G² mol). Also available are the individual elements of the second moment of the charge distribution which are $\langle a^2 \rangle = 39.1 \pm 0.7$, $\langle b^2 \rangle = 38.6 \pm 0.7$, and $\langle c^2 \rangle = 7.5 \pm 0.7$ all in units of 10^{-16} cm². The results on pyrrole are compared to the recent values for furan. The magnetic susceptibilities for several ring compounds are discussed in light of local and ring-current anisotropies.

The search for appropriate criteria for aromatic character of small ring compounds has been the subject of active research for many years.² The inter-

pretation of the anisotropy in the magnetic susceptibility of ring compounds in terms of ring currents has led to quite controversial criteria for the determination of aromaticity. Elvidge and Jackman³ have attempted to equate ring current to aromaticity.

(1) Deutsche Forschungsgemeinschaft Postdoctoral Fellow.
(2) See A. J. Jones, *Rev. Pure Appl. Chem.*, **18**, 253 (1968), for a current review.

(3) J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 859 (1961).

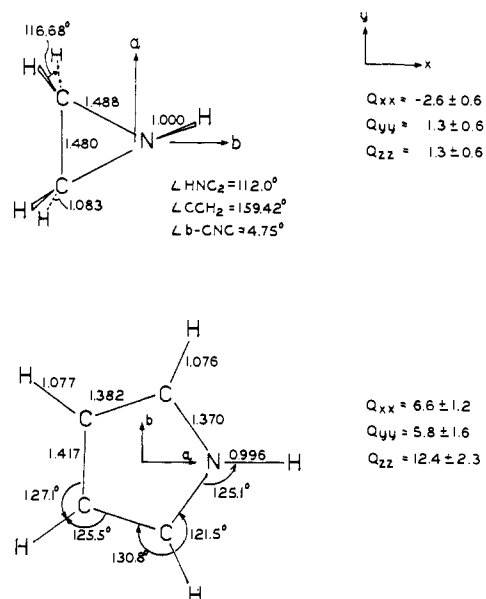


Figure 1. The structures of ethylenimine and pyrrole used in this work. The a , b , and c axes are the principal inertial axes in the molecule. Also listed are the molecular quadrupole moments (in units of 10^{-26} esu cm^2) obtained from this work.

Ring currents⁴ were first postulated to explain the large directly measured⁵ anisotropy in the magnetic susceptibility of the benzene molecule. A current induced in the magnetic benzene ring would lead to a larger diamagnetic susceptibility along the axis perpendicular to the ring than the equal in-plane susceptibilities. Later modification⁶ of the original classical ring-current theories have shown that the ring currents can only contribute about one-half of the observed magnetic susceptibility anisotropy in the benzene ring.⁶⁻⁸ The remaining anisotropy is apparently due to local contributions.^{7,9,10}

There have been several attempts to interpret the magnetic susceptibility anisotropy of the five-membered furan, pyrrole, and thiophene rings in terms of ring currents relative to the benzene molecule. However, up until now the actual experimental magnetic susceptibility anisotropies have not been known. Instead, the magnetic susceptibilities are inferred from the magnetic shielding of the protons in the above three molecules.^{7,10,11} This indirect interpretation of magnetic shielding in terms of the inferred magnetic susceptibility anisotropy has led to various interpretations of the ring current in furan, pyrrole, and thiophene relative to benzene. Abraham, *et al.*, indicate, on the basis of proton chemical shifts, that the ring currents in benzene, furan, and thiophene are equivalent.¹² However, Elvidge has

also interpreted the proton chemical shielding on the above molecules as well as pyrrole.¹³ Elvidge concludes that the ring currents are decreasing in the series benzene, thiophene, pyrrole, and furan.¹³ This latter conclusion agrees with the theoretical calculation of relative ring currents in these molecules by Davies¹⁴ and by Black, *et al.*¹⁵

Because of the lack of experimental measurements of the magnetic susceptibility anisotropies in small ring compounds, we have initiated a program of measurement of the anisotropies by using high-resolution microwave spectroscopy to observe the rotational Zeeman effect in high magnetic fields. The first-order Zeeman effect in diamagnetic molecules leads to a measurement of the molecular g values in the principal inertial axis system.¹⁶ If the molecular structure is known, the molecular g values lead to a direct determination of the diagonal elements in the paramagnetic susceptibility tensor in the principal inertial axis system.¹⁷ The second-order molecular Zeeman effect leads to a direct measurement of the anisotropies in the total magnetic susceptibility tensor elements.^{18,19} The anisotropies in the total magnetic susceptibility can be combined with the first-order determined paramagnetic susceptibility elements to yield the anisotropies in the ground-state second moment of the electronic charge distribution. Furthermore, if the bulk or average magnetic susceptibility is known, each element in the total susceptibility and each diagonal element of the second moment of the electronic charge distribution can be obtained. The first-order determined molecular g values can be combined with the second-order determined magnetic susceptibility anisotropies to obtain a direct measurement of the molecular quadrupole moments.¹⁹

We have previously reported the molecular g values, magnetic susceptibility anisotropies, and molecular quadrupole moments in fluorobenzene,²⁰ furan,²¹ thiophene,²¹ ethylene sulfide,²² and ethylene oxide.²³ In this paper we report the similar results for ethylenimine and pyrrole. The spectra in both ethylenimine and pyrrole are complicated by the presence of the ¹⁴N nuclear quadrupole coupling. The magnetic susceptibility anisotropy results on these various ring compounds are discussed in terms of localized and delocalized effects. The molecular quadrupole moments and second moments of the electronic charge distributions in ethylenimine and pyrrole are also compared with other molecules.

Experimental and Data Analysis

The microwave spectrometer and the 72-in. high-field electromagnet have been described previously.^{24,25}

- (4) (a) L. Pauling, *J. Chem. Phys.*, **4**, 673 (1933); (b) F. London, *J. Phys. Radium*, **8**, 397 (1937).
 (5) J. Hoarau, N. Lumbroso, and A. Pacault, *Compt. Rend.*, **242**, 1702 (1956).
 (6) J. S. Waugh and R. W. Fessenden, *J. Amer. Chem. Soc.*, **79**, 846 (1957); **80**, 6697 (1958).
 (7) B. P. Dailey, *J. Chem. Phys.*, **41**, 2304 (1964).
 (8) D. W. Davies, *Trans. Faraday Soc.*, **57**, 2081 (1961).
 (9) J. Hoarau, *Ann. Chim. (Paris)*, **1**, 560 (1956).
 (10) A. F. Ferguson and J. A. Pople, *J. Chem. Phys.*, **42**, 1560 (1965), and references cited therein.
 (11) See also J. A. Pople, W. G. Schneider, and J. H. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, for a discussion relating group magnetic susceptibility anisotropy to nuclear magnetic shielding.
 (12) R. J. Abraham, R. C. Sheppard, W. A. Thomas, and S. Turner, *Chem. Commun.*, **43** (1965).

- (13) J. A. Elvidge, *ibid.*, **160** (1965).
 (14) D. W. Davies, *ibid.*, **258** (1965).
 (15) P. J. Black, R. D. Brown, and M. L. Heffernan, *Aust. J. Chem.*, **20**, 1305 (1967).
 (16) J. R. Eshbach and M. W. P. Strandberg, *Phys. Rev.*, **85**, 24 (1952).
 (17) W. H. Flygare, *J. Chem. Phys.*, **42**, 1563 (1965).
 (18) W. Hüttner and W. H. Flygare, *ibid.*, **47**, 4137 (1967).
 (19) W. Hüttner, M. K. Lo, and W. H. Flygare, *ibid.*, **48**, 1206 (1968).
 (20) W. Hüttner and W. H. Flygare, *ibid.*, **50**, 2863 (1969).
 (21) D. H. Sutter and W. H. Flygare, *J. Amer. Chem. Soc.*, **91**, 4063 (1969).
 (22) D. H. Sutter and W. H. Flygare, *Mol. Phys.*, **16**, 153 (1969).
 (23) D. H. Sutter, W. Hüttner, and W. H. Flygare, *J. Chem. Phys.*, **50**, 2869 (1969).
 (24) W. H. Flygare, W. Hüttner, R. L. Shoemaker, and P. D. Foster, *ibid.*, **50**, 1714 (1969).

The zero-field microwave spectra of both ethylenimine^{26,27} and pyrrole^{28,29} have been observed previously in detail and the samples are readily available commercially. Very good structures are also available for both ethylenimine²⁷ and pyrrole.³⁰ The structures are shown in Figure 1,

The theory of the rotational Zeeman effect in an asymmetric top has been given by Hüttner and Flygare.¹⁸ In the case of ethylenimine and pyrrole, the Zeeman effect is complicated by the presence of the ¹⁴N nuclear quadrupole coupling with the rotational motion. Following the work of Jen³¹ and Hüttner and Flygare,¹⁸ Pochan, Stone, and Flygare³² have given the first-order energy levels which describe the Zeeman effect in the presence of a quadrupole nucleus on the symmetry axis of a symmetric top. Equation 1 in Pochan, Stone, and Flygare's study³² for a symmetric top is easily converted to the appropriate equation for an asymmetric top. The resultant first-order equation is

$$E(J, M_J) = -\frac{1}{2}\chi H^2 - \frac{\mu_0 M_J H}{J(J+1)} \sum_g g_{\theta\theta} \langle J_{\theta}^2 \rangle - \mu_0 H M_J g_I - H^2 \left[\frac{3M_J^2 - J(J+1)}{(2J-1)(2J+3)} \right] \left[\frac{1}{J(J+1)} \right] \times \sum_g (\chi_{\theta\theta} - \chi) \langle J_{\theta}^2 \rangle + \frac{h[J(J+1) - 3M_J^2][I(I+1 - 3M_I^2)]}{2J(J+1)(2J+3)(2J-1)I(2I-1)} \sum_{\theta} \chi_{\theta\theta}^N \langle J_{\theta}^2 \rangle \quad (1)$$

$\chi = 1/3(\chi_{aa} + \chi_{bb} + \chi_{cc})$ is the average magnetic susceptibility with χ_{aa} , χ_{bb} , and χ_{cc} being the components along the principal inertial axes in the molecule. H is the external magnetic field, μ_0 is the nuclear magneton, J and M_J are the rotational quantum numbers, $g_{\theta\theta}$ is the molecular g value along the g th principal inertial axis, and $\langle J_{\theta}^2 \rangle$ is the average value of the squared rotational angular momentum (in units of \hbar^2) along the g th principal inertial axis. The $-1/2\chi H^2$ term will cancel out in our observation of an energy difference. Thus, we can measure the absolute values of the three g values and two independent magnetic anisotropy parameters. The magnetic anisotropy components are

$$\begin{aligned} \chi_{aa} - \chi &= \frac{1}{3}(2\chi_{aa} - \chi_{bb} - \chi_{cc}) \\ \chi_{bb} - \chi &= \frac{1}{3}(-\chi_{aa} + 2\chi_{bb} - \chi_{cc}) \\ \chi_{cc} - \chi &= \frac{1}{3}(-\chi_{aa} - \chi_{bb} + 2\chi_{cc}) \end{aligned} \quad (2)$$

Only two of these equations are independent. We have written our least-squares program to give the values of $2\chi_{aa} - \chi_{bb} - \chi_{cc}$ and $2\chi_{bb} - \chi_{cc} - \chi_{aa}$. The third an-

(25) S. G. Kukolich and W. H. Flygare, *J. Amer. Chem. Soc.*, **91**, 2433 (1969).

(26) R. D. Johnson, R. J. Myers, and W. D. Gwinn, *J. Chem. Phys.*, **21**, 1425 (1953).

(27) T. E. Turner, V. C. Fiora, and W. M. Kendrick, *ibid.*, **23**, 1966 (1955).

(28) W. S. Wilcox and J. H. Goldstein, *ibid.*, **20**, 1656 (1952).

(29) R. Bak, D. Christensen, L. Hansen, and J. Rastrup-Anderson, *ibid.*, **24**, 720 (1956).

(30) L. Nygaard, J. T. Nielsen, J. Kirchheiner, G. Maltesen, J. Rastrup-Andersen, and G. O. Sorensen, private communication.

(31) C. K. Jen, *Phys. Rev.*, **76**, 1494 (1949).

(32) J. M. Pochan, R. G. Stone, and W. H. Flygare, *J. Chem. Phys.*, in press.

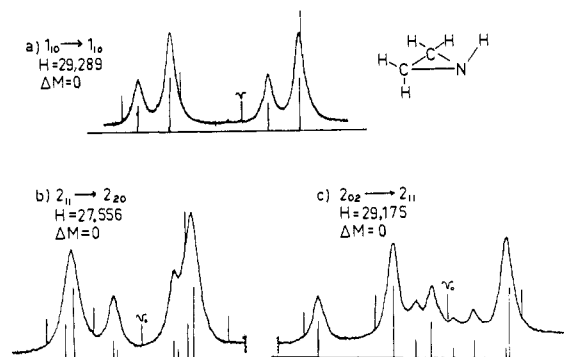


Figure 2. Traces of three low J transitions in ethylenimine at high magnetic fields. The zero-field frequencies are marked with ν_0 and the frequency increases from left to right. The markers are every MHz. The specific transitions are (a) the $1_{01} \rightarrow 1_{10}$ $\Delta M_J = 0$, $\Delta M_I = 0$, transition at 29,289 G, $\nu_0 = 9352.9$ MHz; (b) the $2_{11} \rightarrow 2_{20}$ $\Delta M_J = 0$, $\Delta M_I = 0$ transition at 27,556 G, $\nu_0 = 11,103.3$ MHz; (c) the $2_{02} \rightarrow 2_{11}$ $\Delta M_J = 0$, $\Delta M_I = 0$ transition at 29,175 G, $\nu_0 = 23,634.5$ MHz. The sticks under the experimental spectra are the calculated components which are identified and assigned in Table I. There are four components in a and eight components in each of b and c.

isotropy component is the negative sum of the first two as the trace of the $\chi_{\theta\theta} - \chi$ tensor is zero. h is Planck's constant, I and M_I are the nuclear quantum numbers, g_I is the g value of the nucleus with nuclear angular momentum I , and $\chi_{\theta\theta}^N$ is the nuclear quadrupole coupling constant along the g th principal inertial axis. The last term in eq 1 arises from the evaluation of the standard Hamiltonian, describing the nuclear quadrupole coupling, in the uncoupled $\langle J, M_J, I, M_I \rangle$ basis.

The selection rules depend on the orientation of the wave guide absorption cell with respect to the magnetic vector. If the magnetic field vector is parallel to the electric vector of the radiation, the selection rules are $\Delta I = 0$, $\Delta M_I = 0$, $\Delta J = 0, \pm 1$, and $\Delta M_J = 0$. If the two fields are perpendicular, the selection rules are $\Delta I = 0$, $\Delta M_I = 0$, $\Delta J = 0, \pm 1$, and $\Delta M_J = \pm 1$.

A large number of rotational transitions were observed at zero and high magnetic fields in both ethylenimine and pyrrole. We will list the experimental data for ethylenimine in detail to illustrate the experimental technique. A briefer description will be given for pyrrole as the methods used to extract the data in the two systems are identical.

Three $\Delta M_J = 0$, $\Delta M_I = 0$ Q-branch transitions in ethylenimine are shown in Figure 2. The $1_{01} \rightarrow 1_{10}$ $\Delta M = 0$ transition is shown in Figure 2a as four completely resolved components. The frequency shifts from the zero-field frequency, ν_0 , are listed in Table I. In the absence of any nuclear coupling the $1_{01} \rightarrow 1_{10}$ $\Delta M_J = 0$ transition would appear as a doublet composed of $M_J = 1 \rightarrow M_J = 1$ and $M_J = -1 \rightarrow M_J = -1$ components. In the presence of the ¹⁴N nuclear quadrupole coupling ($I = 1$), in a high field where the ¹⁴N nucleus is uncoupled from J ($h\chi^N < \mu_0 H g_I$, see eq 1), each of the $\Delta M_J = 0$ components will be further split into the $M_I = 0$ and $M_I = \pm 1$ sets of lines. Thus, the two strong components forming one doublet in Figure 2a arise from the degenerate $M_I = \pm 1$ set and the weak doublet is the $M_I = 0$ set.³³ These assignments are listed in Table I.

(33) The uncoupled spectra is described in detail in ref 32.

Table I. The Rotational Zeeman Splitting in Ethylenimine^a

Transition	$M_L \rightarrow M_U$	$\Delta\nu_{\text{exp}}$, MHz	$\Delta\nu_{\text{calcd}}$, MHz	$\Delta\nu_{\text{exp}} - \Delta\nu_{\text{calcd}}$, MHz	M_I
$0_{00} \rightarrow 1_{11}$	0 +1*	-0.170	0.197	+0.027	± 1
36,119.3 MHz	0 -1		0.029	+0.041	± 1
25,320 G	0 +1	+0.070	0.128	-0.058	0
	0 -1*	+0.36	0.356	+0.004	0
$1_{01} \rightarrow 1_{10}$	-1 0*	-0.853	-0.853	0.0	± 1
9,352.9 MHz	0 -1		-0.269		0
25,212 G	-1 0		-0.099		0
	0 -1*	-0.078	-0.047	-0.031	± 1
	0 +1		+0.099		0
	0 +1*	+0.322	+0.322	0.0	± 1
	+1 0*	+0.647	+0.623	+0.024	± 1
	+1 0*	+1.397	+1.377	+0.020	0
$1_{01} \rightarrow 1_{10}$	-1 -1*	-1.679	-1.695	+0.016	0
9,352.9 MHz	-1 -1*	-1.166	-1.164	-0.002	± 1
29,289 G	+1 +1*	+0.456	0.449	+0.007	0
	+1 +1*	+0.986	0.980	+0.006	± 1
$2_{11} \rightarrow 2_{20}$	-2 -2	-1.419	-1.470	+0.051	0
11,103.3 MHz	-2 -2*		-1.358	-0.061	± 1
27,556 G	-1 -1*	-0.529	-0.560	+0.031	± 1
	-1 -1		-0.504	-0.025	0
	+1 +1*	+0.716	+0.679	+0.037	± 1
	+1 +1		0.734	-0.018	0
	+2 +2	+1.148	1.008	+0.140	0
	+2 +2*		1.119	+0.029	± 1
$2_{11} \rightarrow 2_{20}$	-1 -2*	-1.535	-1.541	+0.006	0
11,103.3 MHz	-2 -1*	-1.045	-1.041	-0.004	± 1
25,579 G	-1 -2*	-0.715	-0.732	+0.017	± 1
	0 -1		-0.307		0
	-1 0		-0.298		± 1
	-2 -1		-0.288		0
	0 -1		-0.130		± 1
	-1 -0		+0.046		0
	+1 +2		+0.086		0
	0 +1		+0.171		0
	0 +1		+0.347		± 1
	+1 0		+0.374		± 1
	+1 0		+0.718		0
	+2 +1		+0.781		± 1
	+1 +2		+0.895		± 1
	+2 +1*	+1.515	+1.534	+0.019	0
$2_{02} \rightarrow 2_{11}$	-2 -2	-1.733	-1.817	+0.084	0
23,634.5 MHz	-2 -2	-0.698	-0.776	+0.078	± 1
29,175 G	-1 -1	-0.418	-0.463	+0.045	± 1
	+2 +2	-0.208	-0.116	-0.092	0
	-1 -1		+0.058		0
	+1 +1	+0.352	+0.388	-0.036	± 1
	+1 +1	+0.836	+0.908	-0.072	0
	+2 +2		+0.925	-0.089	± 1
$2_{12} \rightarrow 2_{21}$	-2 -2	-2.967	-3.022	+0.055	0
28,058.2 MHz	-2 -2	-2.227	-2.263	+0.036	± 1
29,208 G	-1 -1	-0.977	-1.015	+0.038	± 1
	-1 -1	-0.647	-0.636	-0.011	0
	+1 +1	+1.143	+1.132	+0.011	± 1
	+2 +2		+1.272	-0.129	0
	+1 +1		+1.511		0
	+2 +2	(+1.883)	+2.030	-0.147	± 1

^a The first column on the left identifies the ΔM_J transition and the last column on the right identifies the M_I component. The calculated frequencies are with eq 1 and the parameters in Table II. The data used in the least-squares analysis to yield the five new Zeeman parameters are listed marked with an asterisk. The zero-field frequencies (ν_0) are listed under the rotational transition designation.

According to eq 1, the high-field Zeeman spectra will be a function of seven parameters. These parameters are the three g values (g_{aa} , g_{bb} , and g_{cc}), the two magnetic susceptibility anisotropies ($(2\chi_{aa} - \chi_{bb} - \chi_{cc})$ and $(2\chi_{bb} - \chi_{aa} - \chi_{cc})$), and two of the three independent nuclear quadrupole coupling constants (χ_{aa}^N and χ_{bb}^N). In ethylenimine the nuclear quadrupole coupling constants are known to be^{34,35}

$$\begin{aligned}\chi_{aa}^N &= 685 \pm 5 \text{ kHz} \\ \chi_{bb}^N &= 2170 \pm 5 \text{ kHz}\end{aligned}\quad (3)$$

We have used these ¹⁴N nuclear quadrupole coupling constants to reduce eq 1 to a standard five-parameter problem that we have discussed previously in our work on furan,²¹ thiophene,²¹ ethylene oxide,²³ and fluorobenzene.²⁶ The only difference in the present analysis is that all of the $\Delta M_J = 0$ and ± 1 spectra are doubled into $M_I = 0$ and $M_I = \pm 1$ components where the

(34) W. M. Tolles and W. D. Gwinn, *J. Chem. Phys.*, **42**, 2253 (1965).

(35) M. K. Kemp and W. H. Flygare, *J. Amer. Chem. Soc.*, **90**, 6267 (1968).

Table II. Zeeman Parameters, Molecular Quadrupole Moments, and Second Moment of the Charge Distributions in Ethylenimine and Pyrrole^c

	Ethylenimine	Pyrrole
g_{aa}	-0.0422 ± 0.008	-0.0895 ± 0.0010
g_{bb}	$+0.0229 \pm 0.0009$	-0.0643 ± 0.0010
g_{cc}	$+0.0539 \pm 0.0010$	$+0.0752 \pm 0.0010$
$2\chi_{aa} - \chi_{bb} - \chi_{cc}$	16.5 ± 0.7	50.2 ± 1.0
$2\chi_{bb} - \chi_{cc} - \chi_{aa}$	4.6 ± 0.8	34.6 ± 1.8
Q_{aa}	1.3 ± 0.6	6.6 ± 1.2
Q_{bb}	-2.6 ± 0.6	5.8 ± 1.6
Q_{cc}	1.3 ± 1.0	-12.4 ± 2.3
χ_{aa}^p	66.6 ± 1.6	163.8 ± 1.0
χ_{bb}^p	77.0 ± 1.6	160.6 ± 1.0
χ_{cc}^p	90.5 ± 1.6	253.0 ± 1.0
$\langle a^2 \rangle - \langle b^2 \rangle$	2.2 ± 0.6	0.5 ± 0.4
$\langle b^2 \rangle - \langle c^2 \rangle$	6.4 ± 0.6	31.2 ± 0.6
$\langle c^2 \rangle - \langle a^2 \rangle$	$-(8.6 \pm 0.6)$	-31.7 ± 0.6
$\chi = 1/3(\chi_{aa} + \chi_{bb} + \chi_{cc})$	-36.5^a	48.6
χ_{aa}	-31.0^a	-31.9 ± 0.9
χ_{bb}	-35.0^a	-37.0 ± 1.1
χ_{cc}	-43.6^a	-76.8 ± 1.5
χ_{aa}^d	-97.6^a	-195.7 ± 1.1
χ_{bb}^d	-107.0^a	-197.6 ± 1.3
χ_{cc}^d	-134.1^a	-329.8 ± 0.2
$\langle a^2 \rangle$	16.9^b	39.1 ± 0.6
$\langle b^2 \rangle$	14.7^a	38.6 ± 0.6
$\langle c^2 \rangle$	8.3^a	7.4 ± 0.6

^a Calculated using $\langle a^2 \rangle = 16.9$. ^b From H. Basch, M. B. Robin, N. A. Kuebler, C. Baker, and D. W. Turner, *J. Chem. Phys.*, **51**, 52 (1969). We are indebted to Dr. Basch for sending us this result prior to publication. ^c Only the absolute values of the g values are obtained experimentally. The signs listed here are obtained by other arguments which are given in the text. The a and b axes are in the plane in pyrrole and nearly in the plane in ethylenimine. The a axis bisects the CNC angle in pyrrole and the b axis bisects the CNC angle in ethylenimine (see Figure 1). The magnetic susceptibilities are listed in units of 10^{-6} erg/(G² mol). The quadrupole moments are in units of 10^{-26} esu cm² and the values of $\langle a^2 \rangle$ are in units of 10^{-16} cm².

$M_J = \pm 1$ components are twice as strong as the $M_J = 0$ components. It is evident by the near-perfect symmetry of the $1_{01} \rightarrow 1_{10}$ at 29,289 G as shown in Figure 2a and Table I that the ¹⁴N nucleus is completely uncoupled in this transition. Therefore, the off-diagonal nuclear quadrupole coupling ($\Delta M_J = \pm 1$, $\Delta M_I = \pm 1$) that was necessary in the analysis of the $J = 0 \rightarrow J = 1$ transition in H₃CC¹⁴N is not needed here.³² All of our analyses on both ethylenimine and pyrrole were satisfactorily completed with the first-order expression in eq 1.

Two different $J = 2 \rightarrow J = 2$ $\Delta M = 0$ transitions in ethylenimine are shown in Figures 2b and 2c. Both rotational transitions are composed of four original $M_J = \pm 1 \rightarrow M_J = \pm 1$ and $M_J = \pm 2 \rightarrow M_J = \pm 2$ transitions which are doubled into eight components due to the $M_J = 0$ and ± 1 first-order nuclear quadrupole corrections. The assignments in Figures 1b and 1c are shown in Table I. Several additional rotational transitions were observed in ethylenimine in both of the $\Delta M = 0$ and ± 1 absorption cells. The data from some of our observations are listed in Table I.

The values of $\langle J_a^2 \rangle$, $\langle J_b^2 \rangle$, and $\langle J_c^2 \rangle$ needed in eq 1 are evaluated by standard techniques using the rotational assignments in the literature. The rotational constants (MHz) for ethylenimine are^{26,27} $A = 22,736.1$, $B = 21,192.3$, and $C = 13,383.3$. The resultant least-squares fit of the data for ethylenimine is given in Table II.

A similar analysis was performed on the high-field Zeeman data in pyrrole. The $0_{00} \rightarrow 1_{01}$, $1_{10} \rightarrow 2_{11}$, $2_{12} \rightarrow 2_{11}$, $3_{12} \rightarrow 3_{13}$, $4_{32} \rightarrow 4_{31}$, and $5_{23} \rightarrow 5_{42}$ rotational transitions were observed under high resolution at magnetic fields from 25,000 to 29,400 G. The spectra are not shown or recorded here as no new Zeeman features

arose above the description given above for the ethylenimine spectra. The values of $\langle J_a^2 \rangle$, $\langle J_b^2 \rangle$, and $\langle J_c^2 \rangle$ were computed from the known rotational constants^{28,29} (MHz) in pyrrole of $A = 9130.61$, $B = 9001.34$, and $C = 4532.08$. As the ¹⁴N nuclear quadrupole coupling constants in pyrrole had not been measured previously, we extracted accurate values for χ_{aa}^N and χ_{bb}^N from the zero-field spectra. The numbers have also been recently given by Nygaard, *et al.*^{30,36} These values for pyrrole are

$$\begin{aligned}\chi_{aa}^N &= 1.45 \pm 0.02 \text{ MHz} \\ \chi_{bb}^N &= 1.21 \pm 0.02 \text{ MHz}\end{aligned}\quad (4)$$

The least-squares treatment of the remaining five-parameter problem for pyrrole gave the g values and magnetic susceptibility anisotropies listed in Table II.

Molecular Quadrupole Moments

Hüttner, Lo, and Flygare¹⁹ have given a general expression relating the molecular quadrupole moments to the parameters in Table II. This equation is

$$\begin{aligned}Q_{zz} &= \frac{|e|}{2} \sum_n Z_n (3z_n^2 - r_n^2) - \frac{|e|}{2} \langle 0 | \sum_i (3z_i^2 - r_i^2) | 0 \rangle = \\ &= -\frac{\hbar |e|}{8\pi M} \left[\frac{2g_{zz}}{G_{zz}} - \frac{g_{zz}}{G_{zz}} - \frac{g_{yy}}{G_{yy}} \right] - \\ &= \frac{2mc^2}{|e|N} (2\chi_{zz} - \chi_{zz} - \chi_{yy})\end{aligned}\quad (5)$$

$|e|$ is the electronic charge, Z_n is the charge on the n th nucleus, and z_n and z_i are the nuclear and electronic

(36) We are indebted to Dr. Nygaard for sending the structural and χ_{aa}^N and χ_{aa}^N results given in ref 30 prior to publication.

center of mass coordinates summed over all n nuclei and i electrons. $\langle 0||0\rangle$ indicates the ground electronic state average value. M is the proton mass, \hbar is Planck's constant divided by 2π , G_{zz} is the rotational constant along the z th principal inertial axis, c is the speed of light, m is the electron mass, and N is Avogadro's number. Direct substitution from Table II into eq 5 gives two sets of Q for either choice of the signs of the g values; see Figure 1 for the orientation of the a , b , and c principal inertial axes in ethylenimine and pyrrole. The molecular quadrupole moments (in units of 10^{-26} esu cm^2) for ethylenimine are shown in eq 6 and 7, and those for pyrrole in eq 8 and 9.

Ethylenimine

g_{aa} negative, g_{bb} and g_{cc} positive

$$\begin{aligned} Q_{aa} &= 1.3 \pm 0.6 \\ Q_{bb} &= -2.6 \pm 0.6 \\ Q_{cc} &= 1.3 \pm 1.0 \end{aligned} \quad (6)$$

g_{aa} positive, g_{bb} and g_{cc} negative

$$\begin{aligned} Q_{aa} &= -20.0 \pm 0.6 \\ Q_{bb} &= -2.6 \pm 0.6 \\ Q_{cc} &= 22.6 \pm 1.0 \end{aligned} \quad (7)$$

Pyrrole

g_{aa} and g_{bb} negative, g_{cc} positive

$$\begin{aligned} Q_{aa} &= 6.6 \pm 1.2 \\ Q_{bb} &= 5.8 \pm 1.6 \\ Q_{cc} &= -12.4 \pm 2.3 \end{aligned} \quad (8)$$

g_{aa} and g_{bb} positive, g_{cc} negative

$$\begin{aligned} Q_{aa} &= -63.4 \pm 1.2 \\ Q_{bb} &= -45.0 \pm 1.6 \\ Q_{cc} &= 108.4 \pm 2.3 \end{aligned} \quad (9)$$

The molecular quadrupole moments for several ring compounds have been recently determined, and the results are listed in Table III. It is striking to compare the nearly equal set of quadrupole moments for ethylene oxide with the results in eq 6 for ethylenimine. The values in eq 7 appear to be unreasonably large. Thus, we assign the signs of the g values in ethylenimine as shown in eq 6 and Table II. This choice of signs of g_{aa} negative and g_{bb} and g_{cc} positive in ethylenimine also parallels the signs along the equivalent axes in ethylene oxide.²³

There appears to be little doubt in assigning the molecular quadrupole moments in eq 8 to pyrrole when a comparison is made with furan and thiophene in Table III. It is interesting to note that the quadrupole moment along the x axis (Table III) in pyrrole has a large positive number. In furan and thiophene the value of Q_{xx} is small. The larger Q_{xx} in pyrrole is probably due to the proton on the nitrogen which makes the entire periphery of the molecule positively charged, leading to positive in-plane quadrupole moments as demonstrated in the benzene molecule.

Anisotropies of the Second Moment of the Electronic Charge Distribution

The anisotropies in the center of mass average values of x^2 , y^2 , and z^2 for the electronic charge distribution are also directly available from the experimental results in Table II and the known molecular structure of both molecules.^{27,30}

The total magnetic susceptibility, χ_{xx} , along any axis is a sum of diamagnetic, χ_{xx}^d , and paramagnetic, χ_{xx}^p , components defined by

$$\begin{aligned} \chi_{xx} &= \chi_{xx}^p + \chi_{xx}^d \\ \chi_{xx}^d &= -\frac{e^2 N}{4mc^2} \langle 0 | \sum_i (y_i^2 + z_i^2) | 0 \rangle \end{aligned} \quad (10)$$

$$\chi_{xx}^p = -\frac{e^2 N}{2mc^2} \left[\frac{\hbar g_{xx}}{8\pi G_{xx} M} - \frac{1}{2} \sum_n Z_n (y_n^2 + z_n^2) \right]$$

We now define the average values of the second moment of the electronic charge distributions as

$$\begin{aligned} \langle x^2 \rangle &= \langle 0 | \sum_i x_i^2 | 0 \rangle \\ \langle y^2 \rangle &= \langle 0 | \sum_i y_i^2 | 0 \rangle \\ \langle z^2 \rangle &= \langle 0 | \sum_i z_i^2 | 0 \rangle \end{aligned} \quad (11)$$

Returning to eq 11 we can relate the anisotropies of the second moments in eq 11 to the observables in Table II and the known molecular structures. The appropriate equation is

$$\begin{aligned} \langle y^2 \rangle - \langle x^2 \rangle &= \sum_n Z_n (y_n^2 - x_n^2) + \\ &\frac{\hbar}{4\pi M} \left(\frac{g_{yy}}{G_{yy}} - \frac{g_{xx}}{G_{xx}} \right) + \frac{4mc^2}{3e^2 N} [(2\chi_{yy} - \\ &\chi_{xx} - \chi_{zz}) - (2\chi_{zz} - \chi_{yy} - \chi_{xx})] \end{aligned} \quad (12)$$

The values of $\sum_n Z_n x_n^2$, $\sum_n Z_n y_n^2$, and $\sum_n Z_n z_n^2$ for the nuclei in ethylenimine²⁷ and pyrrole³⁰ are given in eq 13 and 14 (in units of 10^{-16} cm^2). The experimental

Ethylenimine

$$\begin{aligned} \sum_n Z_n a_n^2 &= 13.05 \pm 0.22 \\ \sum_n Z_n b_n^2 &= 10.30 \pm 0.22 \\ \sum_n Z_n c_n^2 &= 4.46 \pm 0.10 \end{aligned} \quad (13)$$


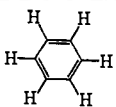
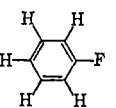
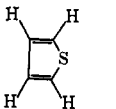
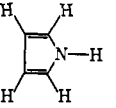
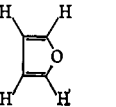
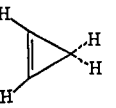
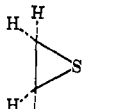
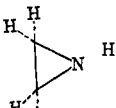
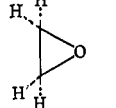
Pyrrole

$$\begin{aligned} \sum_n Z_n a_n^2 &= 34.25 \pm 0.01 \\ \sum_n Z_n b_n^2 &= 33.69 \pm 0.01 \\ \sum_n Z_n c_n^2 &= 0.00 \end{aligned} \quad (14)$$

uncertainties are from the structures given in ref 27 and 30.

Substituting the experimental g values and magnetic susceptibility anisotropies into eq 12 along with the nuclear squared coordinates in eq 13 and 14 gives the anisotropies in the second moment of the electronic charge distributions which are listed in Table II. Substituting the nuclear squared coordinates in eq 13 and 14

Table III. Zeeman Parameters and Molecular Quadrupole Moments for Several Ring Compounds

Molecule 	$(\chi_{xx} - \chi_{yy})^b$	$\chi_{zz} - \frac{1}{2}(\chi_{xx} + \chi_{yy})^b$	$\begin{matrix} (xx) \\ Q^c (yy) \\ (zz) \end{matrix}$	$\langle z^2 \rangle$	Ref
	0	-59.7	$\begin{matrix} 2.8 \pm 1.6 \\ 2.8 \pm 1.6 \\ -5.6 \pm 2.8 \end{matrix}$	7.5 ± 1.6	5, d
	-3.6 ± 0.6	-58.3 ± 0.8	$\begin{matrix} -1.9 \pm 0.8 \\ 5.1 \pm 1.0 \\ -3.2 \pm 1.0 \end{matrix}$	8.4 ± 0.6	20
	-0.1 ± 0.6	-50.1 ± 1.1	$\begin{matrix} 1.7 \pm 1.6 \\ 6.6 \pm 1.5 \\ -8.3 \pm 2.2 \end{matrix}$	8.5 ± 1.2	21
	5.2 ± 0.5	-42.4 ± 0.5	$\begin{matrix} 6.6 \pm 1.2 \\ 5.8 \pm 1.6 \\ -12.4 \pm 2.5 \end{matrix}$	7.5 ± 0.7	This work
	2.8 ± 0.4	-38.7 ± 0.5	$\begin{matrix} 0.2 \pm 0.4 \\ 5.9 \pm 0.3 \\ -6.1 \pm 0.4 \end{matrix}$	6.8 ± 0.7	21
	-6.6 ± 0.5	-17.0 ± 0.5	$\begin{matrix} -0.4 \pm 0.4 \\ 2.4 \pm 0.3 \\ -2.0 \pm 0.6 \end{matrix}$	5.82	a
	-2.2 ± 0.4	-15.4 ± 0.4	$\begin{matrix} -0.5 \pm 0.7 \\ 1.2 \pm 0.8 \\ -0.7 \pm 0.7 \end{matrix}$	8.0 (est)	22
	-4.0 ± 0.5	-10.6 ± 0.7	$\begin{matrix} -2.6 \pm 0.6 \\ 1.3 \pm 0.6 \\ 1.3 \pm 0.6 \end{matrix}$		This work
	-5.8 ± 0.4	-9.4 ± 0.4	$\begin{matrix} -4.3 \pm 0.5 \\ 2.5 \pm 0.4 \\ 1.8 \pm 0.8 \end{matrix}$	6.8 ± 0.4	23

^a See R. C. Benson and W. H. Flygare, *J. Chem. Phys.*, in press. ^b In units of 10^{-6} erg/(G² mol). ^c In units of 10^{-26} esu cm². ^d R. L. Shoemaker and W. H. Flygare, *J. Chem. Phys.*, in press.

and the molecular g values into χ_{xx}^p in eq 10 gives the diagonal elements of the paramagnetic susceptibility tensor which are also listed in Table II.

Magnetic Susceptibility and Individual Elements in the Second Moment of the Charge Distribution

Each of the individual elements of the second moment of the electronic charge distribution can be obtained by using the bulk magnetic susceptibility. The bulk magnetic susceptibility for pyrrole is³⁷

$$\chi = \frac{1}{3}(\chi_{aa} + \chi_{bb} + \chi_{cc}) = -(48.6) \times 10^{-6} \text{ erg/(G}^2 \text{ mol)} \quad (15)$$

(37) Landolt-Börnstein, "Physikalisch-Chemische Tabellen," Vol. 2, Part 10, Springer-Verlag, Berlin, 1951.

The above bulk value can be combined with the experimental anisotropies in Table II to yield the individual components in pyrrole. The results are listed in Table II. Also listed in Table II are the diagonal elements in the diamagnetic susceptibility tensor of pyrrole. The bulk magnetic susceptibility is apparently not known for ethylenimine.

We can now compute the individual elements in the second moment of the electronic charge distribution given by

$$\begin{aligned} \langle 0 | \sum_i x_i^2 | 0 \rangle = \langle x^2 \rangle = & -\frac{2mc^2}{e^2 N} [\chi_{yy}^d + \chi_{zz}^d - \chi_{xx}^d] = \\ & -\frac{2mc^2}{e^2 N} [(\chi_{yy}^p + \chi_{zz}^p - \chi_{xx}^p)] \quad (16) \end{aligned}$$

Rewriting eq 16 in terms of the molecular g values and molecular structure (see eq 10) gives

$$\langle x^2 \rangle = -\frac{2mc^2}{e^2N}[(\chi_{yy} + \chi_{zz} - \chi_{xx}) + \sum_n Z_n x_n^2] - \frac{\hbar}{8\pi M} \left(\frac{g_{yy}}{G_{yy}} + \frac{g_{zz}}{G_{zz}} - \frac{g_{xx}}{G_{xx}} \right) \quad (17)$$

The results for pyrrole are listed in Table II.

We can estimate the remaining quantities for ethylenimine by using a calculated value of $\langle a^2 \rangle$ from a reliable molecular wave function composed of a large set of Gaussian orbitals.³⁸ The result given by Basch, *et al.*,³⁸ in ethylenimine is

$$\langle a^2 \rangle = 16.9 \times 10^{-16} \text{ cm}^2 \quad (18)$$

Using this number and the experimental results listed in Table II, we have computed the values of χ , χ_{aa} , χ_{bb} , χ_{cc} , χ_{aa}^d , χ_{bb}^d , χ_{cc}^d , $\langle b^2 \rangle$, and $\langle c^2 \rangle$ for ethylenimine. All of the results are listed in Table II.

Conclusion and Discussion

The molecular Zeeman effect has been observed in ethylenimine and pyrrole. The presence of the N¹⁴ nuclear coupling with the rotational motion doubles the Zeeman components, making an analysis more difficult. The three molecular g values and the two magnetic susceptibility anisotropy components are extracted for both molecules. The molecular g values in ethylenimine are of the same sign and relative magnitude as in ethylene oxide. The molecular g values of pyrrole are of the same sign and magnitude as in furan.

The magnetic susceptibility anisotropies in the molecular ring ($\chi_{zz} - \chi_{yy}$) of ethylenimine and pyrrole are easily computed from the results in Table II and are listed along with the results for other ring systems in Table III. The magnetic susceptibility anisotropies perpendicular to the rings relative to the average in-plane values are also listed in Table III as $\chi_{zz} - 1/2(\chi_{xx} + \chi_{yy})$. The values of $(\chi_{xx} - \chi_{yy})$ and $\chi_{zz} - 1/2(\chi_{xx} + \chi_{zz})$ in ethylenimine and ethylene oxide are nearly identical. The corresponding comparison between pyrrole and furan shows that the $(\chi_{xx} - \chi_{yy})$ values are nearly identical, but $\chi_{zz} - 1/2(\chi_{xx} + \chi_{yy})$ in pyrrole is significantly

(38) H. Basch, M. Robin, N. A. Kuebler, C. Baker, and D. W. Turner, *J. Chem. Phys.*, **51**, 52 (1969).

larger in magnitude than in furan. We also note that the values of $\chi_{zz} - 1/2(\chi_{xx} + \chi_{yy})$ in the series furan-pyrrole-thiophene increase in magnitude at a rate *faster* than the corresponding values of $\chi_{zz} - 1/2(\chi_{xx} + \chi_{yy})$ in the ethylenimine-ethylene oxide-ethylene sulfide series. We feel that these trends in the five-membered rings compared to the corresponding three-membered rings support the concept of increasing ring currents in the furan-pyrrole-thiophene series.^{3,12-15} Furthermore, the increase in magnitude of $\chi_{zz} - 1/2(\chi_{xx} + \chi_{yy})$ in the three-membered ring-five-membered ring-six-membered ring series indicates an appreciable increase in the ring currents between these series. The result for cyclopropene indicates an enhancement in the magnitude of $\chi_{zz} - 1/2(\chi_{xx} + \chi_{yy})$ relative to the saturated three-membered rings. This may indicate that the ring current in cyclopropene is larger than in the other three-membered rings.

There is still the question of the actual existence of ring currents in these molecules as opposed to strictly local effects.³⁹ There is no doubt about the reality of the magnetic susceptibility anisotropies as listed in Table IV. We feel that the above discussion in comparing the relative rates of increase in the values of $\chi_{zz} - 1/2(\chi_{xx} + \chi_{yy})$ in the five-membered ring series leaves little alternative to the concept of the existence of ring currents in the five-membered and six-membered rings in Table IV. In order to obtain a breakdown into ring-current and local contributions to $\chi_{zz} - 1/2(\chi_{xx} + \chi_{yy})$, we must establish a set of local group anisotropies. This work is now in progress in our laboratory. We have discussed the molecular quadrupole moments of ethylenimine and pyrrole relative to similar molecules in the Molecular Quadrupole Moments section.

We have also listed the out-of-plane values of $\langle z^2 \rangle$ for the ring compounds in Table IV. A systematic variation in these numbers is evident. Each first-row atom in the molecular plane and each out-of-plane proton contributes about one unit of $\langle z^2 \rangle$. Each in-plane proton contributes about 0.25 unit and the second row in-plane atoms (S) contribute approximately 2.7 units to $\langle z^2 \rangle$.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged.

(39) J. I. Musher, *J. Chem. Phys.*, **43**, 4081 (1965); J. M. Gaidis and R. West, *ibid.*, **46**, 1218 (1967); J. I. Musher, *ibid.*, **46**, 1219 (1967).