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Molecular Zeeman Effect of Cyclopentadiene and Isoprene and Comparison of the Magnetic Susceptibility Anisotropies

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Abstract: The rotational Zeeman effect has been observed in cyclopentadiene and isoprene. The molecular g values, magnetic susceptibility anisotropies, and molecular quadrupole moments were obtained for both molecules. The a and b axes are in the molecular plane. The b axis in cyclopentadiene bisects the CCC angle along the symmetry axis. The b axis in isoprene is near the C–CH_3 bond. The magnetic susceptibility anisotropies which are given below are listed in units of 10^{-6} erg/(G^2 mol), and the molecular quadrupole moments are in units of 10^{-26} esu cm^2. The results for cyclopentadiene are: $g_{aa} = -0.0700 \pm 0.0003$, $g_{bb} = -0.0827 \pm 0.0003$, and $g_{cc} = +0.0385 \pm 0.0002$; $2\chi_{aa} - \chi_{bb} - \chi_{cc} = 30.7 \pm 0.3$ and $-\chi_{aa} + 2\chi_{bb} - \chi_{cc} = 37.8 \pm 0.3$; $Q_{aa} = +1.4 \pm 0.4$, $Q_{bb} = +3.7 \pm 0.4$, and $Q_{cc} = -5.1 \pm 0.5$. All of the above results for cyclopentadiene are very similar to those for furan. The results for isoprene are: $g_{aa} = -0.0621 \pm 0.0013$, $g_{bb} = -0.0339 \pm 0.0016$, and $g_{cc} = +0.0080 \pm 0.0016$; $2\chi_{aa} - \chi_{bb} - \chi_{cc} = +16.7 \pm 1.2$ and $-\chi_{aa} + 2\chi_{bb} - \chi_{cc} = +19.2 \pm 1.0$; $Q_{aa} = +1.7 \pm 2.2$, $Q_{bb} = +3.3 \pm 2.3$, and $Q_{cc} = -5.0 \pm 3.2$. Of the above results for both molecules, only the magnetic susceptibility anisotropies are markedly different, the values for isoprene being only one-half those of cyclopentadiene. In light of these results, local and nonlocal (ring current) contributions to the magnetic susceptibility anisotropies are discussed.

For the last several years, there has been a great deal of controversy regarding the interpretation of the experimentally observed magnetic susceptibility anisotropy in ring compounds. The interpretation of this anisotropy, which is the difference between the magnetic susceptibility value along the axis perpendicular to the ring, χ_{zz}, and the average value along the in-plane axes, $^1/_2(\chi_{xx} + \chi_{yy})$, has been in terms of nonlocal (ring currents) and/or local effects.[1] Originally, ring currents were postulated to totally account for the anisotropy,[2] but later modifications attribute only one-half of the anisotropy to ring currents.[3-5] The remaining one-half is attributed to local contributions.[4,6,7] Furthermore, Musher has recently proposed that the anisotropy in conjugated systems can be explained entirely by local effects.[8]

In order to experimentally verify (or refute) the above theories, there have been direct magnetic susceptibility measurements of large molecules in the crystalline state[9] and indirect measurements of small molecules on the basis of proton chemical shifts.[10] However, the results for small molecules have been variously interpreted. Abraham, *et al.*, indicate that ring currents in the five-membered rings furan and thiophene

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[1] See A. J. Jones, *Rev. Pure Appl. Chem.*, **18**, 253 (1968), for a current review.

[2] (a) L. Pauling, *J. Chem. Phys.*, 4, 673 (1936); (b) F. London, *J. Phys. Radium*, **8**, 397 (1937).

[3] J. S. Waugh and R. W. Fessenden, *J. Amer. Chem. Soc.*, **79**, 846 (1957); **80**, 6697 (1958).

[4] B. P. Dailey, *J. Chem. Phys.*, **41**, 2304 (1964).

[5] D. W. Davies, *Trans. Faraday Soc.*, **57**, 2081 (1961).

[6] J. Hoarau, *Ann. Chim. (Paris)*, **1**, 560 (1956).

[7] A. F. Ferguson and J. A. Pople, *J. Chem. Phys.*, **42**, 1560 (1965), and references cited therein.

[8] (a) J. I. Musher, *ibid.*, **43**, 4081 (1965); (b) J. M. Gaidis and R. West, *ibid.*, **46**, 1218 (1967); (c) J. I. Musher, *ibid.*, **46**, 1219 (1967).

[9] See a review in A. A. Bothner-By and J. A. Pople, *Annu. Rev. Phys. Chem.*, **16**, 43 (1965).

[10] A summary of this method is given in J. A. Pople, W. G. Schneider, and J. H. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959. For more current work, see ref 4 and 6.

are the same as that in benzene.[11] On the other hand, Elvidge has interpreted the proton chemical shifts of the above molecules and pyrrole, and concludes that the ring currents decrease in the series benzene, thiophene, pyrrole, and furan.[12] This latter conclusion is in agreement with the theoretical calculation of relative ring currents in these molecules by Davies[13] and by Black, *et al.*[14]

Cyclopentadiene was not included in the above studies, but cyclic delocalization *via* hyperconjugative σ–π overlap of the methylene C–H bonds with the π system has been predicted.[15] This is expected to result in a magnetic susceptibility anisotropy for cyclopentadiene which is similar to that of furan,[16] thiophene,[16] and pyrrole.[17]

An additional approach to the determination of nonlocal contributions to the anisotropy is diamagnetic susceptibility exaltation, defined as the difference between the measured bulk susceptibility and the predicted susceptibility which is estimated for the identical, but noncyclically delocalized, structure using a revised Pascal system.[18] Since the bulk value is $^1/_3(\chi_{xx} + \chi_{yy} + \chi_{zz})$, in cyclically delocalized systems the bulk value is increased by one-third the augmentation in χ_{zz}, the out-of-plane component. These exaltation values for cyclopentadiene and benzene predict the ring current in the former to be about one-half that of benzene.[18] The exaltation values, which depend on nonlocal effects, are probably more qualitative than quantitative, especially for small molecules. This is because they depend on estimates, not direct measurements, of the bulk susceptibility values in the noncyclically delocalized system.

In contrast to the above methods, quite accurate susceptibility anisotropies in small-ring and nonring compounds can be obtained directly from observations of the rotational Zeeman effect. In the past two years several three-, four-, five-, and six-membered ring molecules have been studied in our laboratory. These include ethylene oxide,[19] ethylenimine,[17] ethylene sulfide,[20] cyclopropene,[21] trimethylene oxide,[22] trimethylene sulfide,[22] cyclobutanone,[23] pyrrole,[17] furan,[16] thiophene,[16] 1,3-cyclohexadiene,[24] pyridine,[25] and fluorobenzene.[26] From these molecular Zeeman measurements, $\chi_{zz} - {}^1/_2(\chi_{xx} + \chi_{yy})$ values for the five-membered rings decrease in the series thiophene, pyrrole, and furan. Although this agrees with the results of ref 12–14 discussed above, this anisotropy is not entirely due to nonlocal effects, but also depends on local effects.

In order to separate local and nonlocal effects, we are measuring the magnetic susceptibility anisotropies in ring and open-ring analogs. If the values of $\chi_{zz} - {}^1/_2(\chi_{xx} + \chi_{yy})$ are essentially the same in ring and open-ring analogs, then local effects are dominant. If the values are markedly different, then there must be some nonlocal contribution due to the presence of the ring. Measurements have recently been completed on the cyclopropene and propene,[27] ethylene oxide and dimethyl ether,[28] and ethylene sulfide and dimethyl sulfide[28] pairs, where the anisotropy was found to be significantly different between the ring and open-ring analog. However, the comparison assumes no change in carbon hybridization as the ring is closed. (This point will be discussed further in the last section.)

The present paper on cyclopentadiene and its open-ring analog, isoprene, is a continuation of the study to determine the magnitude of the local contributions to $\chi_{zz} - {}^1/_2(\chi_{xx} + \chi_{yy})$. This will be discussed in conjunction with other ring molecules. In addition to the magnetic susceptibility anisotropies, the molecular g values and molecular quadrupole moments are also obtained for both molecules. In the case of cyclopentadiene, individual elements of the diamagnetic and paramagnetic (and hence total) susceptibility tensors and the second moments of the electronic charge distribution are also obtained.

Experimental Section

The microwave spectrometer and high-field electromagnetic used in the Zeeman studies reported here have been described previously.[29] The 12 × 72 in. flat poles were used for the present work.

The zero-field microwave spectra of cyclopentadiene[30] and isoprene[31] have been studied previously. Cyclopentadiene was obtained from its dimer (Matheson Coleman and Bell) by simple distillation. Isoprene was obtained from Chemical Samples Co.

The theory of the rotational Zeeman effect for an asymmetric top has been given by Hüttner and Flygare.[32] In the absence of nuclear spin, they have derived the following expression for the rotational energy levels in the presence of a magnetic field

$$E(J,M_J) = -{}^1/_2\chi H^2 - \frac{\mu_0 M_J H}{J(J+1)}\sum_g g_{gg}\langle J_g{}^2\rangle - H^2\left[\frac{3M_J{}^2 - J(J+1)}{J(J+1)(2J-1)(2J+3)}\right]\sum_g(\chi_{gg} - \chi)\langle J_g{}^2\rangle \quad (1)$$

$\chi = {}^1/_3(\chi_{aa} + \chi_{bb} + \chi_{cc})$ is the average magnetic susceptibility; χ_{aa}, χ_{bb}, and χ_{cc} are the individual components along the principal inertial axes of the molecule; H is the external magnetic field; μ_0 is the nuclear magneton; J and M_J are the rotational quantum numbers (in units of $\hbar$); g_{gg} is the molecular g value along the gth principal inertial axis; and $\langle J_g{}^2\rangle$ is the average value of the squared rotational angular momentum (in units of $\hbar$) along the gth principal inertial axis. Since only energy differences are observed, the $-{}^1/_2\chi H^2$ term cancels out. There are only two linearly independent magnetic susceptibility anisotropies and they are arbi-

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[23] H. L. Tigelaar and W. H. Flygare, *ibid.*, in press.

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[31] D. R. Lide and M. Jen, *ibid.*, 40, 252 (1964).

[32] W. Hüttner and W. H. Flygare, *ibid.*, **47**, 4137 (1967).

Table I. Molecular Zeeman Splittings in Cyclopentadiene[a]

	$M_l \rightarrow M_u$	$\Delta\nu_{\mathrm{exptl}}$,[b] kHz	$\Delta\nu_{\mathrm{calcd}}$, kHz	$\Delta\nu_{\mathrm{exptl}} - \Delta\nu_{\mathrm{calcd}}$, kHz
$0_{00} \rightarrow 1_{11}$	$0 \rightarrow -1$	−103	−113	+10
ν_0 = 12697 560 MHz	$0 \rightarrow 1$	392	397	−5
H = 21224 G				
$1_{11} \rightarrow 2_{02}$	$1 \rightarrow 0$	. . .	−760	
ν_0 = 21032.498 MHz	$-1 \rightarrow 0$	. . .	−252	
H = 21162 G	$1 \rightarrow 2$	−28	−31	+3
	$0 \rightarrow 1$	92	100	−8
	$0 \rightarrow -1$		101	−9
	$-1 \rightarrow -2$	476	478	−2
$1_{01} \rightarrow 2_{12}$	$1 \rightarrow 0$	−827	−840	+13
ν_0 = 21240.397 MHz	$-1 \rightarrow 0$	−113	−126	+13
H = 21200 G	$1 \rightarrow 2$		−112	−1
	$0 \rightarrow 1$	44	43	+1
	$0 \rightarrow -1$		50	−6
	$-1 \rightarrow -2$	609	616	−7
$1_{10} \rightarrow 2_{21}$	$0 \rightarrow -1$	−1293	−1303	+10
ν_0 = 29549.691 MHz	$1 \rightarrow 0$	. . .	−811	
H = 21170 G	$-1 \rightarrow -2$	−421	−420	−1
	$0 \rightarrow 1$	459	441	+18
	$1 \rightarrow 2$	606	604	+2
	$-1 \rightarrow 0$	. . .	1653	
$2_{12} \rightarrow 3_{03}$	$2 \rightarrow 1$	. . .	−839	
ν_0 = 29678.259 MHz	$-2 \rightarrow -1$	. . .	−538	
H = 21200 G	$2 \rightarrow 3$	−269	−297	+28
	$-1 \rightarrow 0$	. . .	−248	
	$1 \rightarrow 0$	. . .	−241	
	$1 \rightarrow 2$	−129	−127	−2
	$0 \rightarrow 1$		−111	−18
	$0 \rightarrow -1$	221	203	+18
	$-1 \rightarrow -2$	*c*	495	
	$-2 \rightarrow -3$	651	632	+19
$0_{00} \rightarrow 1_{11}$				
ν_0 = 12697.563 MHz	$0 \rightarrow 0$	−280	−284	+4
H = 21192 G				
$1_{11} \rightarrow 2_{02}$	$1 \rightarrow 1$	−574	−579	+5
ν_0 = 21032.493 MHz	$0 \rightarrow 0$	−74	−82	+8
H = 21182 G	$-1 \rightarrow -1$		−70	−4
$1_{11} \rightarrow 2_{02}$	$1 \rightarrow 1$	−652	−652	0
ν_0 = 21032.501 MHz	$0 \rightarrow 0$	−103	−103	0
H = 22840 G	$-1 \rightarrow -1$		−96	−7
$1_{01} \rightarrow 2_{12}$	$1 \rightarrow 1$	−730	−737	+7
ν_0 = 21240.396 MHz	$0 \rightarrow 0$	−150	−159	+9
H = 22868 G	$-1 \rightarrow -1$	+29	+41	−12
$1_{10} \rightarrow 2_{21}$	$0 \rightarrow 0$	−411	−406	−5
ν_0 = 29549.688 MHz	$1 \rightarrow 1$	−8	6	−14
H = 22850 G	$-1 \rightarrow -1$	789	783	+6
$2_{12} \rightarrow 3_{03}$	$2 \rightarrow 2$	−769	−759	−10
ν_0 = 29678.257 MHz	$1 \rightarrow 1$	−325	−326	+1
H = 22876 G	$-2 \rightarrow -2$	−62	−96	+34
	$0 \rightarrow 0$		−71	+9
	$-1 \rightarrow -1$	−2	6	−8
$2_{02} \rightarrow 3_{13}$	$2 \rightarrow 2$	−761	−765	+4
ν_0 = 29685.863 MHz	$1 \rightarrow 1$	−329	−330	+1
H = 22876 G	$-2 \rightarrow -2$	−69	−88	+19
	$0 \rightarrow 0$		−72	+3
	$-1 \rightarrow -1$	+9	+8	+1
$3_{03} \rightarrow 3_{12}$	$-3 \rightarrow -3$	−3150	−3145	−5
ν_0 = 20239.702 MHz	$-2 \rightarrow -2$	−1687	−1680	−7
H = 22830 G	$-1 \rightarrow -1$	−504	−465	−39
	$1 \rightarrow 1$	*c*	1215	
	$2 \rightarrow 2$	1688	1680	+8
	$3 \rightarrow 3$	1890	1895	−5
$3_{13} \rightarrow 3_{22}$	$-3 \rightarrow -3$	−3137	−3125	−12
ν_0 = 20276.615 MHz	$-2 \rightarrow -2$	−1675	−1668	−7
H = 22886 G	$-1 \rightarrow -1$	*c*	−460	
	$1 \rightarrow 1$	1215	1208	+7
	$2 \rightarrow 2$	1705	1668	+37
	$3 \rightarrow 3$	1859	1878	−19

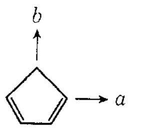
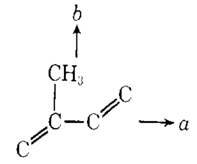
[a] The second column on the left identifies the ΔM_J transition. The magnetic field (in G) and the zero-field frequencies are listed under the rotational transition designation. The calculated splittings are obtained using the g and χ parameters of Table III and eq 1. [b] The experimental splittings are the average of several scans; the errors in $\Delta\nu_{\mathrm{exptl}}$ range from 5 to 60 kHz. [c] Obscured by the Stark effect.

Table II. Molecular Zeeman Splittings in Isoprene[a]

	$M_l \rightarrow M_u$	$\Delta\nu_{\text{exptl}}$,[b] kHz	$\Delta\nu_{\text{calcd}}$, kHz	$\Delta\nu_{\text{exptl}} - \Delta\nu_{\text{calcd}}$, kHz
$1_{01} \rightarrow 2_{12}$	$1 \rightarrow 0$	. . .	−465	
ν_0 = 17083.49 MHz	$0 \rightarrow -1$	. . .	−143	
H = 21210 G	$-1 \rightarrow 0$	. . .	−46	
	$-1 \rightarrow -2$	−20	−6	−14
	$0 \rightarrow 1$	230	202	+28
	$1 \rightarrow 2$		266	−36
$1_{10} \rightarrow 2_{21}$	$0 \rightarrow -1$	−970	−962	−8
ν_0 = 28433.20 MHz	$-1 \rightarrow -2$	−660	−656	−4
H = 21170 G	$1 \rightarrow 0$	. . .	−551	
	$0 \rightarrow 1$	520	514	+6
	$1 \rightarrow 2$	740	746	−6
	$-1 \rightarrow 0$	. . .	998	
$1_{11} \rightarrow 2_{20}$	$-1 \rightarrow -2$	−1300	−1312	+12
ν_0 = 30014.84 MHz	$0 \rightarrow -1$	. . .	−569	
H = 21200 G	$1 \rightarrow 0$	. . .	−384	
	$-1 \rightarrow 0$	. . .	490	
	$1 \rightarrow 2$	940	917	+23
	$0 \rightarrow 1$		983	−43
$1_{01} \rightarrow 2_{12}$	$1 \rightarrow 1$	−211	−224	+7
ν_0 = 17083.468 MHz	$-1 \rightarrow -1$	−150	−144	−6
H = 22838 G	$0 \rightarrow 0$	−82	−78	−4
$2_{02} \rightarrow 3_{13}$	$2 \rightarrow 2$	−340	−277	−63
ν_0 = 22236.31 MHz	$1 \rightarrow 1$	−170	−171	+1
H = 21165 G	$0 \rightarrow 0$		−84	−86
	$-1 \rightarrow -1$	20	−18	38
	$-2 \rightarrow -2$		28	−8

[a] See footnote *a*, Table I. [b] See footnote *b*, Table I.

Table III. The Experimental Molecular *g* Values, Magnetic Susceptibility Anisotropies, and Molecular Quadrupole Moments for Cyclopentadiene and Isoprene[a]

		
g_{aa}	−0.0700 ± 0.0003	−0.0621 ± 0.0013
g_{bb}	−0.0827 ± 0.0003	−0.0339 ± 0.0016
g_{cc}	+0.0385 ± 0.0002	+0.0080 ± 0.0016
$2\chi_{aa} - \chi_{bb} - \chi_{cc}$	+30.7 ± 0.3	+16.7 ± 1.2
$2\chi_{bb} - \chi_{aa} - \chi_{cc}$	+37.8 ± 0.3	+19.2 ± 1.0
Q_{aa}	+1.4 ± 0.4	+1.7 ± 2.2
Q_{bb}	+3.7 ± 0.4	+3.3 ± 2.3
Q_{cc}	−5.1 ± 0.5	−5.0 ± 3.2

[a] The magnetic susceptibilities are in units of 10^{-6} erg/(G^2 mol) and the molecular quadrupole moments are in units of 10^{-26} esu cm^2.

trarily chosen to be $2\chi_{aa} - \chi_{bb} - \chi_{cc}$ and $-\chi_{aa} + 2\chi_{bb} - \chi_{cc}$. Thus, two magnetic susceptibility parameters and the absolute values and relative signs of three *g* values are directly measured.

The values of $\langle J_g{}^2 \rangle$ are calculated using the rotational constants from the previous assignments. The rotational constants for cyclopentadiene are[30] A = 8426.09, B = 8225.63, and C = 4271.44 MHz; and for isoprene they are[31] A = 8526.95, B = 4175.22, and C = 2852.14 MHz.

The rotational Zeeman effect was observed on several rotational transitions in cyclopentadiene. Since the lines were quite strong, the analysis was straightforward, and the observed splittings are listed in Table I. In isoprene, however, the line strengths were extremely weak and only a few rotational transitions were measured. Although the zero-field rotational spectrum of isoprene is complicated by the presence of internal rotation of the methyl group, the A–E splittings are very small (less than 10 kHz) for the transitions observed here.[33] Thus, the internal rotation splittings were not resolved and they did not complicate the Zeeman spectrum. The Zeeman splittings observed for isoprene are listed in Table II.

The observations of Tables I and II were then least-squares fit to give the five Zeeman parameters (three *g* values and two magnetic susceptibility anisotropies) for both molecules.[34,35] Only the stronger lines were observed; weak lines are denoted in Tables I and II by . . . . These parameters are listed in Table III. Although only relative signs of the *g* values can be determined experimentally, it will be shown in the next section that the signs given in Table III are correct.

Molecular Quadrupole Moments

A general expression relating the five parameters in Table III to the molecular quadrupole moments has been given by Hüttner, Lo, and Flygare[35]

$$Q_{zz} = {}^1\!/_2|e|\sum_n Z_n(3z_n{}^2 - r_n{}^2) - {}^1\!/_2|e|\langle 0|\sum_i(3z_i{}^2 - r_i{}^2|0\rangle = -\frac{\hbar|e|}{8\pi M}\left[\frac{2g_{zz}}{G_{zz}} - \frac{g_{xx}}{G_{xx}} - \frac{g_{yy}}{G_{yy}}\right] - \frac{2mc^2}{|e|N}(2\chi_{zz} - \chi_{xx} - \chi_{yy}) \quad (2)$$

where $|e|$ is the electronic charge; Z_n is the charge on the *n*th nucleus; z_n and z_i are the nuclear and electronic 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; 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.

Substituting the five parameters from Table III into eq 2 gives two sets of quadrupole moments, one set for each choice of the signs of the *g* values. The *a* and

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(33) S. L. Hsu, M. K. Kemp, J. M. Pochan, R. C. Benson, and W. H. Flygare, *J. Chem. Phys.*, 50, 1482 (1969).

(34) The least-squares analysis is described in ref 19 and 35.

(35) W. Hüttner, M. K. Lo, and W. H. Flygare, *J. Chem. Phys.*, **48**, 1206 (1968).

b axes are in the molecular plane. The *b* axis in cyclopentadiene bisects the CCC angle along the symmetry axis. The *b* axis in isoprene makes a small angle with the C–CH$_3$ bond. The two sets of Q (in units of 10^{-26} esu cm^2) are listed below for both molecules. For cyclopentadiene, g_{aa} and g_{bb} negative; g_{cc} positive

$$\begin{aligned} Q_{aa} &= +1.4 \pm 0.4 \\ Q_{bb} &= +3.7 \pm 0.4 \\ Q_{cc} &= -5.1 \pm 0.5 \end{aligned} \qquad (3)$$

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

$$\begin{aligned} Q_{aa} &= -36.1 \pm 0.4 \\ Q_{bb} &= -46.5 \pm 0.5 \\ Q_{cc} &= +82.6 \pm 0.5 \end{aligned} \qquad (4)$$

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

$$\begin{aligned} Q_{aa} &= +1.7 \pm 2.2 \\ Q_{bb} &= +3.3 \pm 2.3 \\ Q_{cc} &= -5.0 \pm 3.2 \end{aligned} \qquad (5)$$

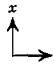
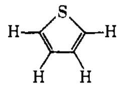
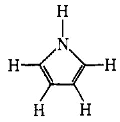
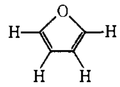
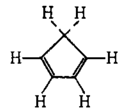
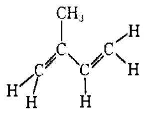
g_{aa} and g_{bb} positive; g_{cc} negative

$$\begin{aligned} Q_{aa} &= -20.6 \pm 2.2 \\ Q_{bb} &= -25.0 \pm 2.3 \\ Q_{cc} &= +45.6 \pm 3.2 \end{aligned} \qquad (6)$$

The results of eq 4 and 6 are unreasonably large. It is expected that the molecular quadrupole moments along the in-plane axes, *a* and *b*, would be positive due to the protons, and that the value along the *c* axis would be negative due to the two π bonds. Thus, the values of eq 3 and 5 and the corresponding *g* values are favored.

The molecular quadrupole moments for the five-membered ring molecules studied so far are listed, along with those of isoprene, in Table IV. Similarities are readily apparent. In all cases, the in-plane values are all positive due to the presence of protons along these axes, with Q_{xx} in thiophene and furan less positive because of the sulfur and oxygen atoms along the *x* axis. And in all cases, Q_{zz} is negative due to the π electrons. The presence of two out-of-plane protons in cyclopentadiene and isoprene is reflected in the lower value for Q_{zz}. Possibly the most striking similarity is the nearly identical values for isoprene and cyclopentadiene, which may indicate a similar electronic charge distribution at the periphery of the molecule.

Table IV. Molecular Quadrupole Moments for Some Five-Membered Ring Compounds and Isoprene

	Q_{xx}, Q_{yy}, Q_{zz}, 10^{-26} esu cm^2
	1.7 ± 1.6 6.6 ± 1.5 −8.3 ± 2.2
	6.6 ± 1.2 5.8 ± 1.6 −12.4 ± 2.5
	0.2 ± 0.4 5.9 ± 0.3 −6.1 ± 0.4
	+3.7 ± 0.4 +1.4 ± 0.4 −5.1 ± 0.5
	3.3 ± 2.3 1.7 ± 2.2 −5.0 ± 3.2

Second Moments of the Electronic Charge Distribution and Magnetic Susceptibilities

The total magnetic susceptibility, χ_{xx}, along any axis is a sum of diamagnetic, $\chi_{xx}{}^{\mathrm{d}}$, and paramagnetic, $\chi_{xx}{}^{\mathrm{p}}$, components defined by[16,26]

$$\begin{gathered} \chi_{xx} = \chi_{xx}{}^{\mathrm{p}} + \chi_{xx}{}^{\mathrm{d}} \\ \chi_{xx}{}^{\mathrm{d}} = -(e^2N/4mc^2)\,\langle 0|\sum_i(y_i{}^2 + z_i{}^2)|0\rangle \\ \chi_{xx}{}^{\mathrm{p}} = -(e^2N/2mc^2)[(\hbar g_{xx}/8\pi G_{xx}M) - {}^1/_2\sum_n Z_n(y_n{}^2 + z_n{}^2)] \end{gathered} \qquad (7)$$

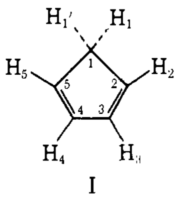
The average value of the second moment of the electronic charge distribution along any axis, *x*, is defined as

$$\langle x^2\rangle = \langle 0|\sum_i x_i{}^2|0\rangle \qquad (8)$$

The anisotropies of the second moments are related to the observables in Table III and the known molecular structure according to the following expression[16,26]

$$\langle y^2\rangle - \langle x^2\rangle = \sum_n Z_n(y_n{}^2 - x_n{}^2) + \frac{\hbar}{4\pi M}\left(\frac{g_{yy}}{G_{yy}} - \frac{g_{xx}}{G_{xx}}\right) + \frac{4mc^2}{3e^2N}[(2\chi_{yy} - \chi_{xx} - \chi_{zz}) - (2\chi_{xx} - \chi_{yy} - \chi_{zz})] \qquad (9)$$

The molecular structure of isoprene has not been determined and the calculations cannot be carried any further. For cyclopentadiene, only the carbon ring structure was determined by Scharpen and Laurie.[30] Using this ring structure, a proton structure was determined which is in agreement with the rotational constants. The proton structure parameters are (see I for labeling of the atoms): $r(\mathrm{C_2H_2}) = r(\mathrm{C_3H_3}) = 1.08$ Å, $r(\mathrm{C_1H_1}) = 1.09$ Å, $\angle\mathrm{H_1C_1H_1'} = 110°$, $\angle\mathrm{C_1C_2H_2} = 120°$, and $\angle\mathrm{C_4C_3H_3} = 125°$. The values of $\Sigma_n Z_n x_n{}^2$, $\Sigma_n Z_n y_n{}^2$, and $\Sigma_n Z_n z_n{}^2$ were then calculated and are given below (in units of 10^{-16} cm^2); the uncertainties are based on the uncertainties in the carbon structure given in ref 30, and in the above proton structure the errors in the *cm* coordinates for the protons were estimated to be 0.05 Å.



I

$$\begin{aligned} \sum_n Z_n a_n{}^2 &= 36.4 \pm 0.7 \\ \sum_n Z_n b_n{}^2 &= 36.3 \pm 0.9 \\ \sum_n Z_n c_n{}^2 &= 1.6 \pm 0.2 \end{aligned} \qquad (10)$$

Substituting the above values, the measured *g* values, and the measured magnetic susceptibility anisotropies for cyclopentadiene into eq 9 gives the anisotropies in the second moment of the electronic charge distribution which are $\langle a^2 \rangle - \langle b^2 \rangle = 0.4 \pm 1.7$, $\langle b^2 \rangle - \langle c^2 \rangle = 33.5 \pm 1.2$, and $\langle c^2 \rangle - \langle a^2 \rangle = -33.9 \pm 1.0$, all in units of 10^{-16} cm^2. Similarly, the individual elements in the paramagnetic susceptibility are obtained using eq 7. Since the bulk susceptibility is known[36] [$\chi = -44.7 \pm 1.0 \times 10^{-6}$ erg/(G^2 mol)], the individual elements of the diamagnetic (and hence total) susceptibility tensors can be obtained. These values are [in units of 10^{-6} erg/(G^2 mol)]: $\chi_{aa}^{\mathrm{p}} = 178.5 \pm 4.7$, $\chi_{bb}^{\mathrm{p}} = 182.7 \pm 3.9$, $\chi_{cc}^{\mathrm{p}} = 289.4 \pm 3.9$, $\chi_{aa}^{\mathrm{d}} = -213.0 \pm 5.8$, $\chi_{bb}^{\mathrm{d}} = -214.8 \pm 5.0$, $\chi_{cc}^{\mathrm{d}} = -356.9 \pm 5.1$, $\chi_{aa} = -34.5 \pm 1.1$, $\chi_{bb} = -32.1 \pm 1.1$, and $\chi_{cc} = -67.5 \pm 1.2$. Similarly, the individual elements of the second moment of the electronic charge distribution are determined: $\langle a^2 \rangle = 42.3 \pm 2.2$, $\langle b^2 \rangle = 41.8 \pm 2.2$, and $\langle c^2 \rangle = 8.4 \pm 2.2$ (all in units of 10^{-16} cm^2).

Discussion

Values of the magnetic susceptibility anisotropy for several ring compounds and some open-ring analogs are listed in Table V. It should be noted that the in-plane average, $^1/_2(\chi_{xx} + \chi_{yy})$, is invariant to rotation about the z axis. The open-ring compounds propene, dimethyl sulfide, dimethyl ether, and isoprene have significantly lower (in magnitude) anisotropies than the respective ring analogs cyclopropene, ethylene sulfide, ethylene oxide, and cyclopentadiene. This change in the anisotropy must be due to the nonlocal effects if there is no appreciable change in carbon hybridization as the ring is closed. As mentioned in the introduction, for the three-membered rings there is, indeed, a change in carbon hybridization. For example, the vinyl carbon atoms in propene apparently have near sp^2 hybridization as determined from the $J_{\mathrm{H}^{13}\mathrm{C}}$ spin–spin coupling constants,[37,38] while in cyclopropene the hybridization is more nearly sp. It is quite probable that this change in hybridization could account for most, if not all, of the difference in the anisotropies in the small strained rings. Thus, in the case of the three-membered ring molecules, there is doubt as to whether any nonlocal effects are present.

Table V. Values of the Magnetic Susceptibility Anisotropy [10^{-6} erg/(G^2 mol)]

Molecule	$\chi_{zz} - {}^1/_2(\chi_{xx} + \chi_{yy})$	Ref
Benzene	-59.7	*a*
Fluorobenzene	-58.3 ± 0.8	26
Pyridine	-57.4 ± 0.7	25
Thiophene	-50.1 ± 1.0	16
Pyrrole	-42.4 ± 0.5	17
Furan	-38.7 ± 0.5	16
Cyclopentadiene	-34.3 ± 0.3	This work
Cyclopropene	-17.0 ± 0.5	21
Ethylene sulfide	-15.4 ± 0.4	20
Ethylenimine	-10.9 ± 0.7	17
Ethylene oxide	-9.4 ± 0.4	19
1,3-Cyclohexadiene	-7.4 ± 2.2	24
Cyclobutanone	-2.1 ± 1.0	23
Trimethylene oxide	$+16.8 \pm 0.7$	22
Trimethylene sulfide	$+22.8 \pm 1.0$	22
Isoprene	-18.0 ± 1.1	This work
Propene	-6.3 ± 0.4	27
Dimethyl sulfide	$+3.5 \pm 0.7$	28
Dimethyl ether	$+4.6 \pm 0.5$	28

[a] J. Hoarau, N. Lumbroso, and A. Pacault, *C. R. Acad. Sci.*, **242**, 1702 (1956).

In isoprene and cyclopentadiene, however, the hybridization is essentially the same (one sp^3 and four sp^2 carbon atoms), implying that the difference in the anisotropies is due to nonlocal effects in cyclopentadiene which arise from the presence of the ring.

A more dramatic effect is seen by comparing benzene and 1,3-cyclohexadiene, where the anisotropy for the latter is only about 12% that of benzene. This is due not only to a probable nonlocal effect in benzene, but also due to two factors which affect the local contributions. In benzene there are six sp^2 carbon atoms that contribute to the local anisotropy, while in cyclohexadiene there are four sp^2 and two sp^3 carbon atoms that contribute. There is probably a marked difference in the local anisotropies for sp^2 and sp^3 carbon atoms which is apparent when comparing the four-membered rings (cyclobutanone, trimethylene oxide, and trimethylene sulfide) with isoprene. The sp^3 carbon atoms in the four-membered rings undoubtedly contribute a positive amount to the anisotropy, while the sp^2 carbon atoms, as in isoprene, contribute a negative amount. Thus in cyclohexadiene, the presence of two sp^3 carbon atoms is estimated to contribute about 10–15 positive units [1 unit = 10^{-6} erg/(G^2 mol)] to the anisotropy. The second factor which may affect the local contributions is the slight nonplanarity of the ring in 1,3-cyclohexadiene. We believe the change in carbon hybridization is quite small, but certainly no larger than the effect of two sp^3 carbon atoms discussed above. So as a conservative upper limit, we estimate the effect of nonplanarity to be no more than 10 positive units. These considerations result in an estimate of the local contribution in benzene to be no more than 30 negative units, one-half (or less) of the observed anisotropy.

Returning specifically to the cyclopentadiene–isoprene molecules studied here, it is interesting to compare the experimental anisotropies with the values computed from the local (exclusively) contributions suggested by Musher.[5a] Musher assigns an anisotropy of $\chi_{\perp} - \chi_{\parallel} = -9.5$ to each carbon atom in a single aromatic ring. We would like to use this number to compare our experimental anisotropies for cyclopentadiene and isoprene. If we assume that the above value of $\chi_{\perp} - \chi_{\parallel}$ is a *local* effect, as suggested by Musher, we should be able to use this number in both cyclopentadiene and isoprene. Thus, according to $\chi_{\perp} - \chi_{\parallel} = -9.5$ for a vinyl carbon atom, we would predict the following anisotropies: cyclopentadiene, $\Delta\chi = -38 + \Delta\chi_{\mathrm{CH_2}}$; experimental, -34.3 ± 0.3; isoprene, $\Delta\chi = -38 + \Delta\chi_{\mathrm{CH_3}}$; experimental, -18.0 ± 1.0.

Accordingly, the anisotropies needed for the CH$_2$ group in cyclopentadiene and the CH$_3$ group in isoprene would be different by 20 units in order to agree with the experimental results. Thus, we think the above comparison of numbers shows that Musher's local

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(36) J. Hoarau, *Bull. Soc. Chim. Fr.*, **17**, 1153 (1950); J. Farquharson, *Trans. Faraday Soc.*, **32**, 219 (1936). The value used is the average.

(37) See C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2198 (1962), and references cited therein.

(38) P. Lazlo, *Bull. Soc. Chim. Fr.*, 558 (1966), and references cited therein.

anisotropies cannot explain the small (in magnitude) anisotropy in isoprene relative to cyclopentadiene.

According to the above discussions, we conclude that the anisotropies in the ring molecules listed in Table V from cyclopentadiene to benzene must be described in terms of *both* local and nonlocal contributions. From the isoprene–cyclopentadiene study, the local effects and the ring current contribute roughly an equal amount to the anisotropy. If this is true in general, it lends support to the modified ring-current theories.[3–5]

We are trying to develop a set of local group anisotropies in order to determine with more confidence the magnitude of the nonlocal effects, but refinements, along with more data, are necessary. For example, in isoprene there is the possibility that the anisotropy might change depending on the location of the methyl group or that the methyl and methylene carbon atoms in isoprene and cyclopentadiene have a different anisotropy even though both carbon atoms have sp^3 hybridization. The first possibility is easy to test by measuring the anisotropies in *cis*- and *trans*-1,3-pentadiene. We are presently trying to do this, but the line strengths are extremely weak. As another example, the anisotropies of acrolein and crotonaldehyde would give the anisotropy of the methyl group. (The anisotropy for acrolein is very close to that for isoprene.[39]) But at the present time, we feel that these effects will be small (less than 5 units) and will not explain the factor of 2 between the anisotropies of isoprene and cyclopentadiene.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged. We would also like to thank J. Musher for some interesting comments on magnetic susceptibilities which stimulated much of the work in the present paper.

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[39] R. C. Benson and W. H. Flygare, unpublished results.

Molecular Orbital Calculations on the 2-Phenylethyl → Phenonium Cation Transformation

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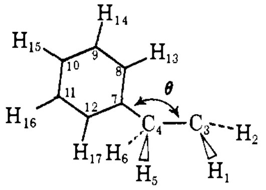
Received May 9, 1970

Abstract: The reaction coordinate for the transformation, classical 2-phenylethyl → phenonium cation, has been mapped using CNDO/2 calculations. That the results of such calculations must be quantitatively grossly incorrect was shown by the results of similar calculations for the corresponding radical species. We show that CNDO/2 has a built-in bias for three-membered ring formation, at least for the Pople and Wiberg parametrizations. Extended Hückel calculations on the same problem give results which are the qualitative inverse of those of CNDO. However, known experimental data demonstrate that the EHT results are also quantitatively incorrect. Thus neither semiempirical calculation gives results which can be trusted.

The nature of the 2-phenylethyl cation remains a question of current interest.[2] To assist in the structural formulation, we have employed semiempirical molecular orbital calculations to construct the potential energy surface for the equilibrium

$$C_6H_5CH_2CH_2^+ \rightleftharpoons {}^+CH_2CH_2C_6H_5$$

Results would be most valid for the gas-phase reaction, but remain meaningful for the condensed phase provided that the solvation energy of species along the reaction coordinate does not change significantly. When this work was performed, the CNDO SCF MO treatment of Pople[3] seemed the best compromise between relevant quantum-mechanical completeness and computational manageability. Using parameters suggested by Wiberg,[4] the energy of the 2-phenylethyl cation was calculated as a function of the angle θ.



For every value of θ the geometry of the cation was optimized to minimize the *total* energy (electronic + nuclear repulsive). This optimization procedure was continued until all bond distances and angles were within 0.02 Å and 2°, respectively, of the structure corresponding to the absolute minimum energy geometry. Coordinates of the various nuclei were calculated sub-

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[1] All computational work was performed at the University of Connecticut. The basic program obtained from the Quantum Chemistry Program for Exchange was modified somewhat, including the addition of a subroutine for bond index calculations. Because the prediagonalization feature of the original program sometimes caused errors to mount, resulting in divergence in the SCF-iteration sequence, it was omitted in most calculations. Address correspondence to the author at Kraftco Corp., Research and Development Division, Glenview, Ill. 60025.

[2] P. v. R. Schleyer, *et al.*, *J. Amer. Chem. Soc.*, **91**, 4291, 4294, 4296, 4297, 7508 (1969); S. Winstein, *et al.*, *ibid.*, 90, 6546 (1968); **91**, 4300 (1969); J. L. Coke, *et al.*, *ibid.*, 91, 1154, 4284 (1969); R. J. Jablonski and E. I. Snyder, *ibid.*, **91**, 4445 (1969); J. E. Nordlander and W. G. Deadman, *ibid.*, **90**, 1590 (1968); G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969). For a viewpoint significantly different from those expressed above, see S. L. Loukas, M. R. Velkou, and G. A. Gregoriou, *Chem. Commun.*, 251 (1970), and references cited therein.

[3] J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, S136 (1965); **44**, 3289 (1966).

[4] K. B. Wiberg, *J. Amer. Chem. Soc.*, **90**, 59 (1968).