The averages of ν_A and ν_B for the compounds in Table I show a downfield shift trend as R becomes larger, in qualitative agreement with the series of hydrocarbons in which OH is replaced by H.[6,7] That the 1,5 interaction results in a downfield shift is especially interesting in view of the usual upfield shifts associated with steric effects.[3,4]

The degree of proximity of the isopropyl group to the asymmetric center on the magnitude of the shift difference $\nu_A - \nu_B$ has been examined for compounds of the type $(CH_3)_2CH(CH_2)_nCH(CH_3)C_2H_5$, and the results appear in Table II. The monotonic decline of $\nu_A - \nu_B$ with n presumably reflects attenuation of the steric effect with increasing distance. The largest isopropyl methyl group nonequivalence we have so far observed is 7.2 ppm for $(CH_3)_2CHCH(CH_3)C(CH_3)_3$.

Table II. Dependence of Isopropyl Group Nonequivalence on Proximity to the Asymmetric Carbon (Marked with an Asterisk)

Compound	$\nu_A{}^a$	$\nu_B{}^a$	$\nu_A - \nu_B$
$(CH_3)_2CH{*}CH(CH_3)CH_2CH_3$	174.7	172.5	2.2
$(CH_3)_2CHCH_2{*}CH(CH_3)CH_2CH_3$	170.3	169.3	1.0
$(CH_3)_2CHCH_2CH_2{*}CH(CH_3)CH_2CH_3$	170.1	169.9	0.2
$(CH_3)_2CHCH_2CH_2CH_2{*}CH(CH_3)CH_2CH_3$	170.0	169.9	0.1

[a] Shifts are in ppm relative to carbon disulfide. The assignments A and B are arbitrary.

The use of ^{13}C nmr should provide a powerful additional tool for the elucidation of structure and the determination of optical purity of diastereomers. The latter technique has been shown to be complicated when observing protons[8] by small shift differences, a difficulty which the present work shows should be significantly alleviated by use of ^{13}C spectra.

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The Direct Measurement of the Magnetic Susceptibility Tensor Elements in 1,3-Cyclohexadiene and Comparison with Benzene and Other Small-Ring Compounds

Sir:

We have observed the molecular rotational Zeeman effect in 1,3-cyclohexadiene at magnetic fields near 21,000 G which gives the molecular g values and magnetic susceptibility anisotropies. Our observations show that (1) the electric quadrupole moments of benzene and 1,3-cyclohexadiene are nearly equal; (2) the magnetic susceptibility anisotropies in benzene (and other aromatic compounds) are much larger than the values reported here for 1,3-cyclohexadiene; (3) the large anisotropy in benzene relative to 1,3-cyclohexadiene is strong evidence for a nonlocal contribution in benzene (ring currents). The previous estimates of local contributions to the magnetic susceptibility anisotropies in aromatic rings may be too large.

Ring currents[1,2] in molecules and their relation to observed molecular magnetic susceptibility anisotropies have been interesting subjects for speculation for some time. Ring currents were first postulated to explain the large directly measured[3] anisotropy in the magnetic susceptibility of the benzene molecule. A current induced in the benzene ring would lead to a larger diamagnetic susceptibility along the axis perpendicular to the ring than the equal in-plane susceptibilities. Later modifications[4] of the original classical ring-current theories have apparently indicated that the ring currents can only contribute about one-half of the observed magnetic susceptibility anisotropy in the benzene ring.[4-7] The remaining anisotropy is apparently due to local contributions.[5,8,9] Indeed, Musher[10] claims that the magnetic susceptibility anisotropies in benzene and other conjugated rings can be explained completely on the basis of local effects.[11]

One major problem in the above analyses is the lack of experimental magnetic susceptibility anisotropies in a system of small-ring compounds. The susceptibility anisotropies are either obtained for very large molecules by measurements[12] on single crystals or for small compounds from chemical shift effects which lead indirectly[9,13] to numbers which may or may not be correct.

Recently, we have developed theoretical[14] and experimental[15,16] methods of using gas-phase microwave spectroscopy to measure the magnetic susceptibility anisotropies in any molecule which has a microwave spectrum. Recently we have presented these methods and resultant magnetic susceptibilities for several small-ring compounds including fluorobenzene,[17] ethylene oxide,[18] ethylene sulfide,[19] thiophene,[20] furan,[20] and other compounds including formaldehyde[15] and formic acid.[21]

In this paper we report the measurements of the molecular g values, magnetic susceptibility tensor elements,

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and molecular quadrupole moments of 1,3-cyclohexadiene. These results are then compared with other small rings and planar molecules.

The microwave spectrum of 1,3-cyclohexadiene has been assigned previously,[22] and we observed the $1_{11} \rightarrow 2_{12}$, $1_{10} \rightarrow 2_{11}$, and $1_{01} \rightarrow 2_{02}$ $\Delta M = 0$ and $\Delta M = \pm 1$ rotational transitions (in the gas phase) at magnetic fields near 21,000 G. The high-field electromagnet which gives fields of up to 30,000 G over a 6-ft length and the phase-stabilized microwave spectrograph and frequency sweep system used in this work have also been described previously.[16] The spectra were recorded at about 230°K and the results are listed in Table I. A least-squares fit of the experimental data given in Table I gives the five independent Zeeman parameters (the molecular g values, g_{aa}, g_{bb}, g_{cc}, and the magnetic susceptibility anisotropies, $(2\chi_{aa} - \chi_{bb} - \chi_{cc})$ and $(2\chi_{bb} - \chi_{aa} - \chi_{cc})$) listed in Table II.[23] The molecular electric quadrupole moments, Q_{xx}, are directly related to the molecular g values and magnetic susceptibility anisotropies.[15] The resultant values of the quadrupole moments are listed in Table II. We note that the molecular quadrupole moments in 1,3-cyclohexadiene are nearly identical with the values in benzene.[20] The methods of determining the remaining numbers in Table II have all been explained previously.[14-21] Thus, using the approximate molecular structure[22] and the known bulk susceptibility[24] leads to the remaining numbers in Table II.

Table I. High-Field Frequency Shifts from ν^a of Several Rotational Transitions in 1,3-Cyclohexadienes

Transition	M_J	$\rightarrow M_J'$	$\Delta\nu$(obsd), kHz	$\Delta\nu$(calcd), kHz	$\Delta\Delta\nu$, kHz	H, G
$1_{11} \rightarrow 2_{12}$	1	2	−180	−162	−18	21,034
(13,167.43)	−1	−2	+262	252	10	
	−1	−1	−176	−154	−22	20,960
	0	0	−16	−11	−5	
	1	1	−16	9	−25	
$1_{01} \rightarrow 2_{02}$	1	2	−100	−124	24	21,015
(17,179.03)	−1	−2	+240	238	2	
	−1	−1	−164	−167	3	20,977
	0	0	4	−36	−40	
	1	1	4	48	−44	
$1_{10} \rightarrow 2_{11}$	0	1	−684	−672	−12	21,041
(17,888.67)	1	2	−500	−498	−2	
	−1	−2	496	511	−15	
	0	−1	496	501	−5	
	0	0	−19	−61	42	20,971

[a] The zero-field frequencies (ν_0) are given (in parentheses) in MHz directly under the transition designation. The calculated results are with the Zeeman parameters listed in Table II.

Table II. Molecular Zeeman Parameters, Molecular Quadrupole Moments, Magnetic Susceptibilities, and the Second Moment of the Electronic Charge Distribution in 1,3-Cyclohexadiene[a]

$g_{aa} = -0.0400 \pm 0.0024$	$\chi = {}^1/_3(\chi_{aa} + \chi_{bb} + \chi_{cc}) = -48.6$
$g_{bb} = -0.0433 \pm 0.0011$	$\chi_{aa} = -46.69 \pm 0.8$
$g_{cc} = -0.0062 \pm 0.0009$	$\chi_{bb} = -45.57 \pm 1.0$
$2\chi_{aa} - \chi_{bb} - \chi_{cc} = 5.73 \pm 1.6$	$\chi_{cc} = -53.54 \pm 1.2$
$2\chi_{bb} - \chi_{aa} - \chi_{cc} = 9.09 \pm 2.2$	$\chi_{aa}^{\mathrm{d}} = -331.66 \pm 1.7$
$Q_{aa} = 2.68 \pm 2.8$	$\chi_{bb}^{\mathrm{d}} = -330.12 \pm 1.3$
$Q_{bb} = 3.20 \pm 2.8$	$\chi_{cc}^{\mathrm{d}} = -565.55 \pm 2.0$
$Q_{cc} = -5.88 \pm 3.8$	$\langle a^2 \rangle = 66.45 \pm 0.7$
$\chi_{aa}^{p} = 284.97 \pm 1.3$	$\langle b^2 \rangle = 66.80 \pm 0.7$
$\chi_{bb}^{p} = 284.55 \pm 1.0$	$\langle c^2 \rangle = 11.34 \pm 0.7$
$\chi_{cc}^{p} = 512.01 \pm 1.0$	

[a] The a axis contains the electric dipole moment and the c axis is out of the molecular plane. χ is in units of 10^{-6} erg/G^2 mole, Q is in units of 10^{-26} esu cm^2, and $\langle a^2 \rangle$ is in units of 10^{-16} cm^2.

Table III. Values of the Magnetic Susceptibility Anisotropy (in units of 10^{-6} erg/G^2 mole) for a Wide Range of Small Molecules[a]

Molecule	$\chi_{zz} - {}^1/_2(\chi_{xx} + \chi_{yy})$	Ref
Benzene	−59.7	3
Fluorobenzene	−58.3 ± 0.8	17
Thiophene	−50.1 ± 1.0	20
Pyrrole	−42.4 ± 0.5	*b*
Furan	−38.7 ± 0.5	20
Cyclopropene	−17.0 ± 0.5	*c*
Ethylene sulfide	−15.4 ± 0.4	19
Ethylenimine	−10.9 ± 0.7	*b*
Ethylene oxide	−9.4 ± 0.4	18
1,3-Cyclohexadiene	−7.4 ± 2.2	This work

[a] The z axis is perpendicular to the molecular plane. [b] D. H. Sutter and W. H. Flygare, unpublished results. [c] R. C. Benson and W. H. Flygare, *J. Chem. Phys.*, in press.

The surprising result of this work is the extremely small magnetic susceptibility anisotropy in the 1,3-cyclohexadiene molecule. This large difference is put into proper perspective in Table III where the experimental values of $\chi_{zz} - {}^1/_2(\chi_{xx} + \chi_{yy})$ are listed for a series of ring compounds which have been recently determined.

The dramatic difference between the values of $\chi_{zz} - {}^1/_2(\chi_{xx} + \chi_{yy})$ for 1,3-cyclohexadiene and benzene (as well as the other aromatic ring compounds) leaves little doubt that a substantial ring current exists in aromatic compounds. Indeed, the magnetic susceptibility anisotropies listed in Table III may be useful in establishing a criterion for aromatic character.[25,26]

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

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Isomerization of *o*-Biphenylyl Isocyanide into 1-Azabenz[*b*]azulene and the Formation of Both from *o*-Biphenylyl Isothiocyanate[1]

Sir:

The formation of 1-azabenz[*b*]azulene[2] (**2**) by the irradiation of *o*-biphenylyl isocyanide (**1**) is a new reaction which reveals electrophilic carbenoid properties of the aromatic isocyanide group.[3] This appears to be

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