The Molecular g Values, Magnetic Susceptibility Anisotropies, Second Moment of the Charge Distribution, and Molecular Quadrupole Moments in Furan and Thiophene[1a]

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Abstract: The high-field first- and second-order Zeeman effect has been observed in furan and thiophene. The a coordinate is in the molecular plane and bisects the COC or CSC angle, and the b axis is also in the molecular plane. Using these coordinates, the molecular parameters for both molecules are listed below. 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 distribution or molecular quadrupole moments. For furan the measured g values and magnetic susceptibility anisotropies are $g_{aa} = -0.0911 \pm 0.0007$, $g_{bb} = -0.0913 \pm 0.0002$, $g_{cc} = 0.0511 \pm 0.0001$, $2\chi_{aa} - \chi_{bb} - \chi_{cc} = (43.04 \pm 0.24) \times 10^{-6}$ erg/(G^2 mole), and $2\chi_{bb} - \chi_{cc} - \chi_{aa} = (34.39 \pm 0.20) \times 10^{-6}$ erg/(G^2 mole). The molecular quadrupole moments are $Q_{aa} = (0.2 \pm 0.4)$, $Q_{bb} = (5.9 \pm 0.3)$, and $Q_{cc} = -(6.1 \pm 0.4)$, all in units of 10^{-26} esu cm^2. 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 $\chi_{aa}{}^{p} = 159.0 \pm 0.4$, $\chi_{bb}{}^{p} = 149.2 \pm 0.2$, and $\chi_{cc}{}^{p} = 243.3 \pm 0.2$, all in units of 10^{-6} erg/(G^2 mole) and $\langle a^2 \rangle - \langle b^2 \rangle = -(1.6 \pm 0.2)$, $\langle b^2 \rangle - \langle c^2 \rangle = 31.0 \pm 0.2$, and $\langle c^2 \rangle - \langle a^2 \rangle = -(29.4 \pm 0.2)$, all in units of 10^{-16} cm^2. Combining the above data with the known bulk susceptibility for furan gives the diagonal elements in the total magnetic susceptibility which are $\chi_{aa} = -(30.5 \pm 1.6)$, $\chi_{bb} = -(33.3 \pm 1.6)$, $\chi_{cc} = -(70.6 \pm 1.6)$ in units of 10^{-6} erg/(G^2 mole). Also available are the individual elements of the second moment of the charge distribution which are $\langle a^2 \rangle = 36.2 \pm 0.7$, $\langle b^2 \rangle = 37.8 \pm 0.7$, and $\langle c^2 \rangle = 6.8 \pm 0.7$, all in units of 10^{-16} cm^2. For thiophene the measured g values and magnetic susceptibility anisotropies are $g_{aa} = -0.0862 \pm 0.0023$, $g_{bb} = -0.0662 \pm 0.0006$, $g_{cc} = 0.0501 \pm 0.0005$, $2\chi_{aa} - \chi_{bb} - \chi_{cc} = (49.6 \pm 1.1) \times 10^{-6}$ erg/(G^2 mole), and $2\chi_{bb} - \chi_{cc} - \chi_{aa} = (50.6 \pm 1.3) \times 10^{-6}$ erg/(G^2 mole). The molecular quadrupole moments are $Q_{aa} = 1.7 \pm 1.6$, $Q_{bb} = 6.6 \pm 1.5$, and $Q_{cc} = -(8.3 \pm 2.2)$ in units of 10^{-26} esu cm^2. 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 $\chi_{aa}{}^{p} = 184.8 \pm 2.0$, $\chi_{bb}{}^{p} = 244.3 \pm 1.5$, and $\chi_{cc}{}^{p} = 347.3 \pm 1.6$ in units of 10^{-6} erg/(G^2 mole) and $\langle a^2 \rangle - \langle b^2 \rangle = 13.9 \pm 1.0$, $\langle b^2 \rangle - \langle c^2 \rangle = 36.1 \pm 0.7$, and $\langle c^2 \rangle - \langle a^2 \rangle = -(50.0 \pm 0.8)$ in units of 10^{-16} cm^2. Combining the above data with the known bulk magnetic susceptibility for thiophene gives the diagonal elements in the total magnetic susceptibility tensor which are $\chi_{aa} = -(40.9 \pm 1.2)$, $\chi_{bb} = -(40.5 \pm 1.3)$, and $\chi_{cc} = -(90.8 \pm 1.7)$ in units of 10^{-6} erg/(G^2 mole). Also available are the individual elements of the second moment of the charge distribution which are $\langle a^2 \rangle = 58.6 \pm 1.3$, $\langle b^2 \rangle = 44.6 \pm 1.2$, and $\langle c^2 \rangle = 8.5 \pm 1.2$, all in units of 10^{-16} cm^2.

Bulk magnetic susceptibility data have been available for several molecules for some time. However, very little data are available on the individual elements of the paramagnetic, diamagnetic, and total magnetic susceptibility tensors. We report here experimental data which lead to the individual diagonal elements in the susceptibility tensors in furan and thiophene. These data also lead to the experimental determination of the molecular quadrupole moments and the second moment of the charge distribution in these two molecules. The results are compared to similar molecules.

The experimental technique which is used to obtain the magnetic susceptibility information is to observe the rotational Zeeman effect by combining high magnetic fields with high-resolution microwave spectroscopy. The first-order Zeeman effect in diamagnetic molecules leads to a measurement of the molecular g values in the principal inertial axis system. 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. The second-order molecular Zeeman effect leads to a direct measurement of the anisotropies in the total magnetic susceptibility tensor elements. 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.

The Experiment and Data Analysis

The microwave spectrometer and the 72-in. high-field electromagnet have been described previously.[2,3]

The zero-field microwave spectra of both furan[4a] and thiophene[4b] are well known.

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[1] (a) This work was partially supported by the Advanced Projects Agency Grant SD-131 to the Materials Research Laboratory at the University of Illinois. (b) Deutsche Forschungsgmeinschaft Postdoctorate Fellow.

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

[3] S. G. Kukolich and W. H. Flygare, *J. Am. Chem. Soc.*, in press.

[4] (a) B. Bak, D. Christensen, W. B. Dixon, L. Hansen-Nygaard, J. Rastrup-Anderson, and M. Schottländer, *J. Mol. Spectry.*, **9**, 124 (1962); (b) B. Bak, D. Christensen, L. Hansen-Nygaard, and J. Rastrup-Anderson, *ibid.*, 7, 58 (1961).

The theory of the rotational Zeeman effect in an asymmetric top has been given by Hüttner and Flygare.[5] The rotational energy levels of furan and thiophene are expected to be governed by eq 28 in ref 5 which is

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

$\chi = {}^1/_3(\chi_{aa} + \chi_{bb} + \chi_{cc})$ 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 the nuclear magneton, J and M_J are the rotational quantum numbers, 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 $\hbar^2$) along the gth 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

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

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 anisotropy component is the negative sum of the first two as the trace of the tensor $\chi_{gg} - \chi$ is zero.

The values of $\langle J_a^2\rangle$, $\langle J_b^2\rangle$, $\langle J_c^2\rangle$ are evaluated by standard techniques using the previous rotational assignments. The rotational constants for furan are[4a] A = 9446.96, B = 9246.61, and C = 4670.88 MHz. The rotational constants for thiophene are[4b] A = 8041.77, B = 5418.12, and C = 3235.77 MHz. Several rotational transitions in both furan and thiophene were observed at zero field and at high fields in both the ΔM = 0 and ΔM = ±1 absorption cells. The observed transitions, frequencies, and magnetic fields in furan are listed in Table I. The thiophene results are listed in Table II. Only the strongest and well-resolved spectra were used to extract the three g values and the two magnetic susceptibility anisotropy parameters. The data in the first four transitions in both Tables I and II were used to obtain a least-squares fit for the five Zeeman parameters, and the results are listed in Table III. Only the relative signs of the g values are obtained experimentally. However, we will show conclusively below that the signs must be assigned to the values given in Table III. Several additional transitions are listed in Tables I and II. These additional data are fit very well with the assigned parameters in Table III.

Table I. The Observed Zeeman Spectra in Furan[a]

Transition ν_0, MHz H, G	M_l	M_u	$\Delta\nu_{\text{exptl}}$	$\Delta\nu_{\text{calcd}}$	$\Delta\nu_{\text{exptl}} - \Delta\nu_{\text{calcd}}$
0_{00}–1_{01}*	0 →	1	0.621	0.620	0.001
ν_0 = 13,917.512	0 →	−1	−0.160	−0.157	−0.003
H = 25,388					
1_{11}–2_{12}*	−1 →	0	−0.395	−0.397	+0.002
ν_0 = 23,259.195	0 →	1	−0.008	+0.002	−0.006
	1 →	2	−0.120	−0.118	−0.002
H = 25,470	−1 →	−2	0.943	0.944	−0.001
	0 →	−1	0.138	0.144	−0.006
	1 →	0	−1.155	−1.174	+0.019
1_{01}–2_{02}*	−1 →	0	−0.429	−0.432	+0.003
	0 →	1	+0.092	+0.093	−0.001
ν_0 = 23,453.144	1 →	2	−0.164	−0.166	+0.002
H = 25,246	−1 →	−2	+0.891	+0.887	+0.004
	0 →	−1	+0.228	+0.233	−0.005
	1 →	0	−1.204	−1.206	+0.002
3_{22}–3_{21}*	−3 →	−3	−3.055	−3.056	+0.001
	−2 →	−2	−1.601	−1.602	+0.001
ν_0 = 13,431.144	−1 →	−1	...	−0.410	...
H = 29,512	1 →	1	...	+1.192	...
	2 →	2	1.610	+1.602	+0.008
	3 →	3	1.744	+1.752	−0.008
1_{01}–2_{02}	−1 →	−1	−0.14[b]	−0.125	−0.015
ν_0 = 23,453.144	0 →	0	−0.14[b]	−0.156	+0.016
H = 27,512	1 →	1	−1.120	−1.120	+0.000
2_{12}–3_{13}	−2 →	−1	...	−0.982	...
ν_0 = 32,697.055	−1 →	0	−0.465[b]	−0.478	+0.013
H = 25,678	0 →	1	−0.255	−0.228	+0.003
	1 →	2	−0.225	−0.231	+0.006
	2 →	3	−0.465[b]	−0.488	+0.023
	−2 →	−3	+1.025	+1.047	−0.022
	−1 →	−2	+0.825	+0.840	−0.015
	0 →	−1	+0.385	+0.379	+0.006
	1 →	0	...	−0.335	...
	2 →	1	...	−1.302	...
2_{02}–2_{21}	−2 →	−1	−1.850	−1.890	+0.040
ν_0 = 14,335.25	−1 →	0	+0.65[b]	+0.566	+0.084
H = 25,533	0 →	1	2.09	2.083	+0.013
	1 →	2	2.68	2.663	+0.017
	−1 →	−2	−2.67	−2.729	+0.059
	0 →	−1	−0.50	−0.542	+0.042
	1 →	0	+0.65[b]	+0.707	−0.057
	2 →	1	...	+1.018	...
2_{12}–2_{11}	−2 →	−1	−1.930	−1.927	−0.003
ν_0 = 13,727.689	−1 →	0	+0.510	+0.498	+0.012
H = 25,549	0 →	1	+2.030	+2.052	−0.022
	1 →	2	+2.690	+2.736	−0.046
	−1 →	−2	−2.610	−2.668	+0.058
	0 →	−1	−0.570	−0.578	+0.008
	1 →	0	+0.640	+0.641	−0.001
	2 →	1	+0.990	+0.989	+0.001
	−2 →	−2	−4.41	−4.425	+0.015
	−1 →	−1	−1.00	−1.025	+0.025
	1 →	1	Unresolved shoulder	+2.212	(−0.152)
	2 →	2	2.06	+2.050	+0.010
1_{11}–2_{12}	−1 →	−1	−0.09	−0.075	−0.015
ν_0 = 23,259.195	0 →	0	−0.25	−0.268	+0.018
H = 27,694	1 →	1	−1.06	−1.074	+0.014

[a] The starred data in the first four transitions are used in the least-squares analysis to give the first five parameters in Table III. The calculated entries in this table are from the data in Table III. All frequencies are listed in MHz and the differences (Δ) are with respect to ν_0. [b] Unresolved.

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

Table II. The Observed Zeeman Spectra in Thiophene[a]

Transition ν_0, MHz H, G	M_l	M_u	$\Delta\nu_{\text{exptl}}$	$\Delta\nu_{\text{calcd}}$	$\Delta\nu_{\text{exptl}} - \Delta\nu_{\text{calcd}}$
1_{11}–2_{12}*	−1 →	0	...	−0.703	...
ν_0 = 15,125.603	0 →	1	−0.002	+0.005	−0.007
H = 25,534	1 →	2	−0.153	−0.159	+0.006
	−1 →	−2	+1.173	+1.167	+0.006
	0 →	−1	+0.317	+0.327	−0.010
	1 →	0	...	−1.406	...
2_{20}–3_{21}*	−2 →	−1	...	+2.630	...
ν_0 = 28,879.89	−1 →	0	+1.54	+1.523	+0.017
H = 25,044	0 →	1	+0.817	+0.79	+0.027
	1 →	2	0.511[b]		−0.069
	2 →	3	0.605	0.580	+0.025
	−2 →	−3	−0.48	−0.483	+0.003
	−1 →	−2	−1.18	−1.137	−0.043
	0 →	1	−1.40	−1.391	−0.009
	1 →	0[b]		−1.246	...
	2 →	1		−0.700	...
0_{00}–1_{01}*	0 →	1	0.429	0.430	−0.001
ν_0 = 8654.05	0 →	−1	0.123	0.117	+0.006
H = 25,688					
4_{23}–4_{22}*	−4 →	−4	−3.78	−3.791	+0.011
ν_0 = 9061.30	−3 →	−3	−2.30	−2.311	+0.011
H = 29,117	−2 →	−2	...	−1.069	...
	−1 →	−1	...	−0.036	...
	1 →	1	...	0.760	...
	2 →	2		1.667	+0.033
	3 →	3[b]	1.70	1.780	−0.080
	4 →	4		1.664	+0.036
2_{11}–3_{12}	−2	−1	...	1.684	...
ν_0 = 28,488.88	−1	0	...	0.923	...
H = 25,028	0	1		0.461	−0.021
	1	2[b]	0.44	0.300	+0.140
	2	3		0.440	+0.00
	−2	−3	−0.07	−0.072	+0.002
	−1	−2	−0.69	−0.678	−0.012
	1	−1[b]	−1.0	−0.984	−0.016
	1	0		−0.990	−0.010
	2	1	...	−0.694	...
2_{12}–3_{13}	−2	−1	...	−1.393	...
ν_0 = 22,202.32	−1	0	...	−0.642	...
H = 25,412	0	1[b]		−0.226	...
	1	2		−0.145	...
	2	3	−0.40	−0.401	0.001
2_{02}–3_{03}	−2	−1	...	1.141	...
ν_0 = 23,044.21	−1	0	−0.63	−0.591	−0.039
H = 25,581	0	1		−0.278	−0.122
	1	2[b]	−0.32	−0.201	−0.199
	2	3		−0.362	−0.038
	−2	−3	1.14	1.137	+0.003
	−1	−2	0.84	0.855	−0.015
	0	−1	0.32	0.356	−0.036
1_{10}–2_{11}	−1	0	...	+2.453	...
ν_0 = 19,490.52	0	1	+0.080	+0.075	+0.015
H = 25,773	1	2	+0.62	+0.628	−0.008
	−1	−2	−0.30	−0.319	+0.019
	0	−1	...	−1.896	...
	1	0	...	−0.540	...

[a] The starred data in the first four transitions are used in the least-squares analysis to give the first five parameters in Table III. The calculated entries in this table are from the data in Table III. All frequencies are listed in MHz and the differences (Δ) are with respect to ν_0. [b] Unresolved.

Table III. Zeeman Parameters, Molecular Quadrupole Moments, and Second Moment of the Charge Distributions in Furan and Thiophene[a]

	Furan	Thiophene
g_{aa}	−0.0911 ± 0.0007	−0.0862 ± 0.0023
g_{bb}	−0.0913 ± 0.0002	−0.0662 ± 0.0006
g_{cc}	+0.0511 ± 0.0001	+0.0501 ± 0.0005
$2\chi_{aa} - \chi_{bb} - \chi_{cc}$	43.04 ± 0.24	49.6 ± 1.1
$2\chi_{bb} - \chi_{cc} - \chi_{aa}$	34.39 ± 0.20	50.6 ± 1.3
Q_{aa}	0.2 ± 0.4	1.7 ± 1.6
Q_{bb}	5.9 ± 0.3	6.6 ± 1.5
Q_{cc}	−6.1 ± 0.4	−8.3 ± 2.2
$\chi_{aa}{}^{\text{p}}$	159.0 ± 0.4	184.8 ± 2.0
$\chi_{bb}{}^{\text{p}}$	149.2 ± 0.2	244.3 ± 1.5
$\chi_{cc}{}^{\text{p}}$	243.3 ± 0.2	347.3 ± 1.6
$\langle a^2\rangle - \langle b^2\rangle$	−1.6 ± 0.2	13.9 ± 1.0
$\langle b^2\rangle - \langle a^2\rangle$	31.0 ± 0.1	36.1 ± 0.7
$\langle c^2\rangle - \langle a^2\rangle$	−29.4 ± 0.1	−50.0 ± 0.8
$\chi = {}^1/_3(\chi_{aa} + \chi_{bb} + \chi_{cc})$	−44.80 ± 1.5	−57.40 ± 0.86
χ_{aa}	−30.5 ± 1.6	−40.9 ± 1.2
χ_{bb}	−33.3 ± 1.6	−40.5 ± 1.3
χ_{cc}	−70.6 ± 1.6	−90.8 ± 1.7
$\chi_{aa}{}^{\text{d}}$	−189.5 ± 1.8	−225.7 ± 3.0
$\chi_{bb}{}^{\text{d}}$	−182.5 ± 1.8	−284.8 ± 3.0
$\chi_{cc}{}^{\text{d}}$	−313.9 ± 1.8	−438.1 ± 3.0
$\langle a^2\rangle$	36.2 ± 0.7	58.6 ± 1.3
$\langle b^2\rangle$	37.8 ± 0.7	44.6 ± 1.2
$\langle c^2\rangle$	6.8 ± 0.7	8.5 ± 1.2

[a] The a and b axes are in the plane and the a axis bisects the COC or CSC angle. The magnetic susceptibilities are listed in units of 10^{-6} erg/(G^2 mole). The quadrupole moments are in units of 10^{-26} esu cm^2, and the values of $\langle a^2\rangle$ are in units of 10^{-16} cm^2.

Molecular Quadrupole Moments

Hüttner, Lo, and Flygare[6] have given a general expression relating the molecular quadrupole moments to the measured Zeeman parameters in Table III. This equation is

$$Q_{zz} = \frac{|e|}{2}\sum_n Z_n(3z_n^2 - r_n^2) - \frac{|e|}{2}\left\langle 0\left|\sum_i(3z_i^2 - r_i^2)\right|0\right\rangle$$

$$= -\frac{\hbar|e|}{8\pi M}\left[\frac{2g_{zz}}{G_{zz}} - \frac{g_{xx}}{G_{xx}} - \frac{g_{yy}}{G_{yy}}\right] - \frac{2mc^2}{|e|N} \times$$

$$(2\chi_{zz} - \chi_{xx} - \chi_{yy}) \quad (3)$$

$|e|$ is the electronic charge, Z_n is the charge on the nth nucleus, and 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, $\hbar$ is Planck's constant divided by 2π, G_{zz} is the rotational constant along the zth principal inertial axis, c is the speed of light, m is the electron mass, and N is Avogadro's number. Direct substitution from Table III into eq 3 gives two sets of Q for either choice of the signs of the g values. The a axis bisects the COC and CSC angles and the b axis is also in the molecular plane. Referring to Table III we can now compute the molecular quadrupole moments for both molecules (in units of 10^{-26} esu cm^2).

Furan

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

$$Q_{aa} = 0.2 \pm 0.4$$
$$Q_{bb} = 5.9 \pm 0.3 \quad (4)$$
$$Q_{cc} = -6.1 \pm 0.4$$

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

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

$$\begin{aligned} Q_{aa} &= -48.9 \pm 0.4 \\ Q_{bb} &= -44.8 \pm 0.3 \\ Q_{cc} &= 93.7 \pm 0.4 \end{aligned} \tag{5}$$

Thiophene

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

$$\begin{aligned} Q_{aa} &= 1.7 \pm 1.6 \\ Q_{bb} &= 6.6 \pm 1.5 \\ Q_{cc} &= -8.3 \pm 2.2 \end{aligned} \tag{6}$$

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

$$\begin{aligned} Q_{aa} &= -57.8 \pm 1.6 \\ Q_{bb} &= -63.8 \pm 1.5 \\ Q_{cc} &= 121.6 \pm 2.2 \end{aligned} \tag{7}$$

The signs, magnitudes, and trends for the molecular quadrupole moments in furan and thiophene are similar for either choice for the signs of the molecular g values. We will compare the above quadrupole moments with other molecules in the last section. However, we will note here two reasons for choosing eq 4 and 6 for the correct molecular quadrupole moments. The first reason is that the results in eq 5 and 7 give moments which are an order of magnitude larger than expected when compared to similar molecules such as ethylene oxide, ethylene sulfide, and fluorobenzene (see last section). Furthermore, we expect the b-axis quadrupole moment to be positive due to the protons, and we also expect the quadrupole moment perpendicular to the planar ring to be negative due to the electron density above and below the ring. We will demonstrate more conclusively in a later section that the signs for the g values given in Table III are correct. We have listed the preferred quadrupole moments for both molecules in Table III.

The 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 III and the known molecular structure of both molecules.[4]

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

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

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

$$\begin{aligned} \langle x^2\rangle &= \left\langle 0\middle|\sum_i x_i^2\middle|0\right\rangle \\ \langle y^2\rangle &= \left\langle 0\middle|\sum_i y_i^2\middle|0\right\rangle \\ \langle z^2\rangle &= \left\langle 0\middle|\sum_i z_i^2\middle|0\right\rangle \end{aligned} \tag{9}$$

Returning to eq 9, we can relate the anisotropies of the second moments in eq 9 to the observables in Table III and the known molecular structures.[4] The appropriate equation is

$$\begin{aligned} \langle y^2\rangle - \langle x^2\rangle = \sum_n Z_n(y_n^2 - x_n^2) + {}& \\ \frac{\hbar}{4\pi M}\left(\frac{g_{yy}}{G_{yy}} - \frac{g_{xx}}{G_{xx}}\right) + \frac{4mc^2}{3e^2N}[(2\chi_{yy} - \chi_{xx} - \chi_{zz}) - {}& \\ (2\chi_{xx} - \chi_{yy} - \chi_{zz})]& \end{aligned} \tag{10}$$

The values of $\Sigma_n Z_n x_n^2$, $\Sigma_n Z_n y_n^2$, and $\Sigma_n Z_n z_n^2$ for the nuclei in furan[4a] and thiophene[4b] are given below (in units of 10^{-16} cm^2)

Furan

$$\begin{aligned} \sum_n Z_n a_n^2 &= 30.20 \pm 0.04 \\ \sum_n Z_n b_n^2 &= 32.62 \pm 0.06 \\ \sum_n Z_n c_n^2 &= 0.00 \end{aligned} \tag{11}$$

Thiophene

$$\begin{aligned} \sum_n Z_n a_n^2 &= 51.43 \pm 0.30 \\ \sum_n Z_n b_n^2 &= 38.16 \pm 0.34 \\ \sum_n Z_n c_n^2 &= 0.00 \end{aligned} \tag{12}$$

The experimental uncertainties are from the structures given in ref 4a and 4b.

Substituting the experimental g values and magnetic susceptibility anisotropies into eq 10 along with the nuclear squared coordinates in eq 11 and 12 gives the anisotropies in the second moment of the electronic charge distributions which are listed in Table III.

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 both liquid furan and thiophene have been measured by several groups and the results have been summarized.[7] We choose here the best values as (the uncertainties are our estimates)

Furan

$$\chi = \frac{1}{3}(\chi_{aa} + \chi_{bb} + \chi_{cc}) = -(44.80 \pm 1.5) \times 10^{-6}\ \mathrm{erg/(G^2\ mole)} \tag{13}$$

Thiophene

$$\chi = \frac{1}{3}(\chi_{aa} + \chi_{bb} + \chi_{cc}) = -(57.40 \pm 0.86) \times 10^{-6}\ \mathrm{erg/(G^2\ mole)} \tag{14}$$

The above bulk values can be combined with the experimental anisotropies in Table III to yield the individual components. The results are listed in Table

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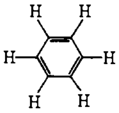
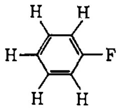
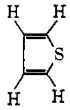
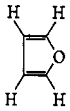
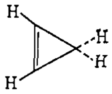
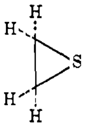
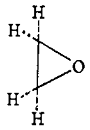
[7] Landolt-Börnstein, "Physikalisch-Chemische Tabellen," Vol. 2, Part 10, Springer-Verlag, Berlin, 1951.

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

Molecule y x	$(\chi_{xx} - \chi_{yy})^a$	$\chi_{zz} - \frac{1}{2}(\chi_{xx} + \chi_{yy})^a$	Q_{xx} Q_{yy} Q_{zz} [b]	$\langle z^2 \rangle \times 10^{16}$ cm	Ref
	0	−59.7	2.8 ± 1.6 2.8 ± 1.6 −5.6 ± 2.8	7.8 ± 1.6	*c*
	−3.6 ± 0.6	−58.3 ± 0.8	−1.9 ± 0.8 5.1 ± 1.0 −3.2 ± 1.0	8.4 ± 0.6	*d*
	−0.1 ± 0.6	−50.1 ± 1.1	1.7 ± 1.6 6.6 ± 1.5 −8.3 ± 2.2	8.5 ± 1.2	*e*
	2.8 ± 0.4	−38.7 ± 0.5	0.2 ± 0.4 5.9 ± 0.3 −6.1 ± 0.4	6.8 ± 0.7	*e*
	−6.6 ± 0.5	−17.0 ± 0.5	−0.4 ± 0.4 2.4 ± 0.3 −2.0 ± 0.6	. . .	
	−2.2 ± 0.4	−15.4 ± 0.4	−0.5 ± 0.7 1.2 ± 0.8 −0.7 ± 0.7	8.0 (estd)	*g,f*
	−5.8 ± 0.4	−9.4 ± 0.4	−4.3 ± 0.5 2.5 ± 0.4 1.8 ± 0.8	6.8 ± 0.4	*h*

[a] In units of 10^{-6} erg/(G^2 mol). [b] In units of 10^{-26} esu cm^2. [c] R. L. Shoemaker and W. H. Flygare, unpublished results. [d] W. Hüttner and W. H. Flygare, *ibid.*, **50**, 2863 (1969). [e] This work. [f] R. C. Benson and W. H. Flygare, unpublished results. [g] D. Sutter and W. H. Flygare, *Mol. Phys.*, **16**, 153 (1969). [h] D. Sutter, W. Hüttner, and W. H. Flygare, *J. Chem. Phys.*, **50**, 2869 (1969).

III. Also listed in Table III are the diagonal elements in the diamagnetic susceptibility tensor.

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

$$\left\langle 0 \left| \sum_i x_i^2 \right| 0 \right\rangle = \langle x^2 \rangle = -\frac{2mc^2}{e^2N}[\chi_{yy}^{\mathrm{d}} + \chi_{zz}^{\mathrm{d}} - \chi_{xx}^{\mathrm{d}}] = -\frac{2mc^2}{e^2N}[(\chi_{yy} + \chi_{zz} - \chi_{xx}) - (\chi_{yy}^{\mathrm{p}} + \chi_{zz}^{\mathrm{p}} - \chi_{xx}^{\mathrm{p}})] \tag{15}$$

Rewriting eq 15 in terms of the molecular *g* values and molecular structure (see eq 8) gives

$$\langle x^2 \rangle = -\frac{2mc^2}{e^2N}[(\chi_{yy} + \chi_{zz} - \chi_{xx}) + \sum_n Z_n x_n^2] - \frac{\hbar}{8\pi M}\left(\frac{g_{yy}}{G_{yy}} + \frac{g_{zz}}{G_{zz}} - \frac{g_{xx}}{G_{xx}}\right) \tag{16}$$

It is interesting now to compute the square of the out-of-plane coordinate in both molecules for both signs of the molecular *g* values. Using eq 16, the χ elements in Table III, the structural coordinates in eq 11 and 12, and both signs for the *g* values gives the results listed below for $\langle c^2 \rangle$ (in units of 10^{-16} cm^2).

Furan

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

$$\langle c^2 \rangle = 6.8 \pm 0.7 \tag{17}$$

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

$$\langle c^2 \rangle = -8.4 \pm 0.7 \tag{18}$$

Thiophene

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

$$\langle c^2 \rangle = 8.5 \pm 1.2 \tag{19}$$

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

$$\langle c^2 \rangle = -10.7 \pm 1.2 \tag{20}$$

The results in eq 18 and 20 are clearly unreasonable. Thus, the *g*-value signs in both molecules are conclusively assigned leading to the results in eq 4 and 17 for furan and eq 6 and 19 for thiophene. The remaining components of the second moment of the charge distribution are listed in Table III for both molecules.

Discussion

It is interesting to compare several of the parameters in Table III with the similar and recently available results for other molecules. Several results of interest are listed in Table IV. The experimentally determined anisotropies of the magnetic susceptibility in the molecular plane ($\chi_{xx} - \chi_{yy}$) show that the sulfur-containing rings present less asymmetry in their response to the magnetic field than the corresponding oxygen-containing rings. It is also evident that the values of $\chi_{zz} - {}^1/_2(\chi_{xx} + \chi_{yy})$ decrease in magnitude progressively from benzene to ethylene oxide in Table IV. The values of $\chi_{zz} - {}^1/_2(\chi_{xx} + \chi_{yy})$ may be considered a criterion for aromaticity or delocalization of the perpendicular π electrons in these ring systems. In other words,[8] ring currents can be excited by magnetic fields perpendicular to the ring with increasing ease in the series from ethylene oxide to benzene in Table IV.

It is also interesting to compare the molecular quadrupole moments in these ring compounds. The out-of-plane (x) molecular quadrupole moments are negative in all molecules in Table IV except ethylene oxide. This indicates the presence of the electrons above and below the molecular plane. Furthermore, the in-plane moments perpendicular to the symmetry axes (y) are all positive. These positive moments are due to the partially shielded protons in the outer regions of the molecule along the y axes. These simple correlations may be of help in estimating molecular quadrupole moments along the principal inertial axes in other molecules.

The out-of-plane values for the second moment of the charge distribution in these molecules are also listed in Table IV. These values seem to correlate as expected with the number and type of heavy atoms in the plane and the number of out-of-plane protons.

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The Reduction of Benzene by Hydrated Electrons in γ-Ray Irradiated Alkaline Solutions[1]

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Abstract: Hydrated electrons convert benzene into 1,4-cyclohexadiene (1,4-C_6H_8) which is further reduced to cyclohexene (C_6H_{10}) and cyclohexane (C_6H_{12}). In addition dimeric products progress from $C_{12}H_{14}$ to $C_{12}H_{22}$ as reduction proceeds. The hydrated electrons were produced by the γ-ray irradiation of pH 13 solutions saturated with H_2 at 1500 psi pressure.

Since the hydrated electron (e_{aq}^-) was identified in 1962 its rate of reaction with some 400 organic compounds has been measured. However, only in comparatively few cases were the products identified. The hydrated electrons, H atoms, and OH radicals formed by ionizing radiations in aqueous solutions react with benzene to form complex combinations of partially reduced and oxidized compounds including biphenyl and phenol.[2–6] In a recent pulse radiolysis study of aqueous benzene at pH 3 with methanol as the OH radical scavenger, the cyclohexadienyl radical, resulting from H-atom addition, was identified. This radical disappears in a second-order diffusion-controlled reaction.[7] Product analysis of the aqueous solutions was not attempted. In the radiolytic reduction of gaseous benzene in hydrogen and argon mixtures the H atom produces the cyclohexadienyl radical intermediate and 1,4-C_6H_8 and 1,3-C_6H_8 as the final products. When the hydroxyl radical reacts with aqueous C_6H_6 it too adds to the ring and forms the hydroxycyclohexadienyl radical, C_6H_8OH.[8] In the present work, complications introduced by the H atoms and OH radicals were avoided by irradiating C_6H_6 solutions at 100 atm of H_2 pressure at pH 13. Under these conditions H and OH change into e_{aq}^- by the reactions

$$OH + H_2 = H_2O + H$$

$$H + OH^- = e_{aq}^- + H_2O$$

At pH 13 the equilibrium ratio $[(e_{aq}^-)/(H)]_{equil} = 2300$ [calculated from $k(e_{aq}^- + H_2O) = 16\ M^{-1}\ sec^{-1}$ and $k(H + OH) = 2 \times 10^7\ M^{-1}\ sec^{-1}$]. Because the rate constant ratio $k(e_{aq}^- + C_6H_6)/k(H + C_6H_6) = 0.01$, the e_{aq}^- reaction dominates H-atom addition to benzene by a factor of 23.[9] Consequently with less than 40

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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