either. This is indeed an unfortunate circumstance. However, the protonation red shifts of the ^1L_a absorption bands (but not of the ^1L_b bands) of quinoline and its 2-, 4-, and 6-methyl derivatives are comparable in magnitude to the protonation red shift observed for the fluorescence spectra of these compounds. It is tempting to speculate that the ^1L_a state of the neutral species of the latter quinoline derivatives is the fluorescing state. This would mean that either fluorescence arises from the second excited singlet state in these compounds or that the thermally relaxed ^1L_a state lies below the thermally relaxed ^1L_b state. However, in the absence of corroborative data this must remain only a speculation.

Microwave Spectrum of 2-Pyrone and the Molecular Zeeman Effect in Tropone, 2-Pyrone, and 4-Pyrone. Suppression of Nonlocal Contributions to the Out-of-Plane Molecular Magnetic Susceptibilities by the Insertion of a Carbonyl Group into an Aromatic Ring

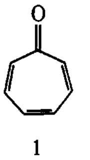
C. L. Norris, R. C. Benson, P. Beak,* and W. H. Flygare*

Contribution from the Roger Adams and W. A. Noyes Chemical Laboratories, University of Illinois, Urbana, Illinois 61801. *Received September 20, 1972*

Abstract: The microwave spectrum of 2-pyrone is assigned and gives rotational constants of $A = 5677.64 \pm 0.02$ MHz, $B = 2882.24 \pm 0.01$ MHz, and $C = 1912.13 \pm 0.01$ MHz. The high-field (20,000 G) molecular Zeeman effect is observed and analyzed in 2-pyrone, 4-pyrone, and tropone. The molecular g values, magnetic susceptibility anisotropies, diagonal elements in the paramagnetic and diamagnetic susceptibility tensors, and the molecular quadrupole moments are listed for 2- and 4-pyrone, and the magnetic susceptibility anisotropy for tropone is given. Magnetic susceptibility anisotropies are analyzed in terms of local and nonlocal contributions, and it is shown that 2-pyrone, 4-pyrone, and tropone have negligibly small nonlocal contributions and should be considered nonaromatic by the magnetic criterion. The observation that formal insertion of a carbonyl group into an aromatic ring leads to almost complete suppression of nonlocal contributions to the out-of-plane molecular magnetic susceptibility is noted for the present cases.

Molecular Zeeman studies in our laboratory have resulted in the direct measurement of magnetic susceptibility anisotropies of a large number of isolated and unperturbed molecules. We have established a set of rules to determine the magnitude of local contributions to this anisotropy,[1] and these rules have been used to demonstrate a large nonlocal negative contribution to the anisotropies of molecules known to be aromatic, attributable to $4n + 2$ π-electron delocalization in the cyclic conjugated system leading to a "ring current." [1-5] From this work it appears that use of microwave determined magnetic susceptibility anisotropies offers at present the most reliable method for investigation of the relationship between magnetic properties and aromatic character. Although many observations have been reported which relate ring currents to aromatic character, these measurements often have involved indirect measurements or estimates of the out-of-plane molecular magnetic susceptibility anisotropies.

The perturbation of aromatic character introduced by insertion of a carbonyl group into the ring of an aromatic compound has been a matter of interest for some time. Tropone (**1**), which can be viewed formally as a benzene ring with a carbonyl group incorporated, 2-pyrone (**2**), and 4-pyrone (**3**), which can be considered carbonyl insertion derivatives of furan, have been considered both aromatic and nonaromatic at different times and by different criteria.[1,6,7] Tropone especially has been discussed by many investigators and most recently has been assessed as nonaromatic.[6] The 2-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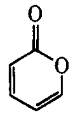
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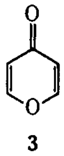
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(1) R. C. Benson, C. L, Norris, W. H. Flygare, and P. A. Beak, *J. Amer. Chem. Soc.*, 93, 5591 (1971), and references cited therein.

(2) R. C. Benson and W. H. Flygare, *ibid.*, **92**, 7523 (1970).

(3) R. C. Benson and W. H. Flygare, *J. Chem. Phys.*, **53**, 4470 (1970).

(4) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York, N. Y., 1966, Chapter 4, provides an excellent review.

(5) A. J. Jones, *Rev. Pure Appl. Chem.*, **18**, 253 (1968).

(6) Tropone: D. J. Bertelli and T. G. Andrews, Jr., *J. Amer. Chem. Soc.*, **91**, 5280 (1969); D. J. Bertelli, T. G. Andrews, Jr., and P. O. Crews, *ibid.*, **91**, 5286 (1969); W. Jackson, T. S. Hurg, and H. P. Hopkins, Jr., *J. Chem. Thermodyn.*, 3, 347 (1971); D. J. Watkin and T. A. Hamor, *J. Chem. Soc. B*, 2167 (1971); D. W. S. Cruickshank, G. Filippini, and O. S. Mills, *Chem. Commun.*, 101 (1972); M. J. S. Dewar and N. Trinajstic, *Croat. Chem. Acta*, 42, 1 (1970).

(7) Pyrones: (a) P. Beak, *Tetrahedron*, 20, 831 (1964); (b) H. C. Smitherman and L. H. Ferguson, *ibid.*, **24**, 923 (1968); (c) C. T. Mathis and J. H. Goldstein, *Spectrochem. Acta*, 20, 871 (1964); (d) A. R. Katritzky and J. M. Lagowski, "The Principles of Heterocyclic Chemistry," Methuen, London, 1967, pp 14, 30–32, 34, 50, 64, 167; (e) A. Albert, "Heterocyclic Chemistry," The Athlone Press, London, 1968, pp 336–342; (f) F. M. Dean, "Naturally Occurring Oxygen Ring Compounds," Butterworths, London, 1963, pp 82–84; (g) J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, New York, N. Y., 1965, p 1024.

and 4-pyrones have been discussed less frequently but most recent authors do not claim appreciable aromatic character for **2** and **3**.[7]

In order to assess the effect of formal introduction of a carbonyl group into a carbocyclic and a heterocyclic aromatic ring by using experimentally accurate magnetic susceptibility anisotropies, we undertook molecular Zeeman studies of **1**, **2**, and **3** and have concluded that 2-pyrone, 4-pyrone, and tropone are all essentially nonaromatic by the magnetic criterion. Insertion of a carbonyl group into an aromatic ring appears to dramatically suppress nonlocal contributions to the out-of-plane molecular magnetic susceptibility anisotropies.

Experimental Section

Purified samples of both 2-pyrone and 4-pyrone were obtained by standard techniques and a pure sample of tropone was obtained from Koch-Light Laboratories Ltd., England.

The zero-field microwave spectrum of 4-pyrone has been studied elsewhere[8] and the results of that study are given in Table I, Table II, and Figure 1.

Table I. Rotational Constants and Moments of Inertia in 4-Pyrone[8]

Rotational constants, MHz		Moments of inertia, amu Å^2
Exptl	Calcd[a]	Exptl
A = 5859.17	5867.73	I_{aa} = 86.2803
B = 2715.09	2751.60	I_{bb} = 186.1930
C = 1855.55	1873.19	I_{cc} = 272.4426
		$I_{aa} + I_{bb} - I_{cc}$ = 0.0313

[a] Calculated from the structure given in Table II and shown in Figure 1.

Table II. Bond Distances (Å) and Angles of 4-Pyrone[a]

$O_1—C_1$; $O_1—C_5$	1.355	$\angle C_5O_1C_1$	117° 6′
$C_1—C_2$; $C_4—C_5$	1.356	$\angle O_1C_1C_2$	123° 55′
$C_2—C_3$; $C_3—C_4$	1.440	$\angle C_1C_2C_3$	119° 58′
$C_3{=}O_2$	1.248	$\angle C_2C_3C_4$	115° 7′
$C_2—H_2$, $C_4—H_4$	1.083	$\angle C_3C_4H_4$	120° 51′
$C_1—H_1$, $C_5—H_5$	1.083	$\angle C_4C_5H_5$	125° 5′

[a] See Figure 1 and ref 8.

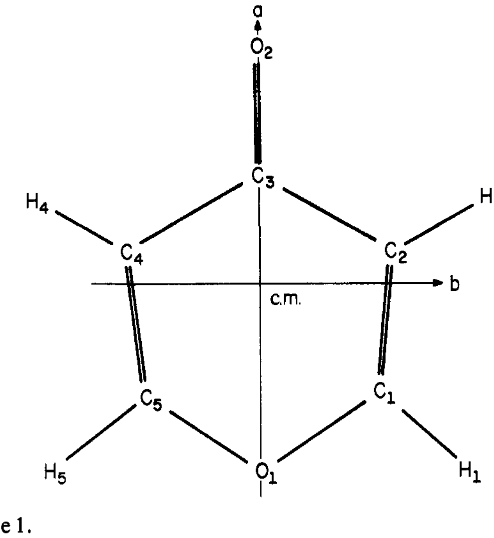

Figure 1.

Table III. Assigned Rotational Transitions in 2-Pyrone[a]

Transition	Obsd freq, MHz	Obsd − calcd
	a-Dipole	
$1_{11} \rightarrow 2_{12}$[b]	8618.66 ± 0.02	+0.02
$1_{01} \rightarrow 2_{02}$[b]	9377.01 ± 0.02	+0.01
$1_{10} \rightarrow 2_{11}$[b]	10558.87 ± 0.02	+0.02
$2_{12} \rightarrow 3_{13}$[b]	12807.42 ± 0.02	+0.02
$2_{02} \rightarrow 3_{03}$[b]	13595.21 ± 0.02	+0.01
$2_{21} \rightarrow 3_{22}$	14383.14 ± 0.03	+0.02
$2_{20} \rightarrow 3_{21}$	15171.03 ± 0.03	+0.01
$2_{11} \rightarrow 3_{12}$[b]	15687.99 ± 0.02	−0.01
$3_{13} \rightarrow 4_{14}$	16888.30 ± 0.10	+0.07
$3_{03} \rightarrow 4_{04}$	17479.70 ± 0.02	+0.01
$4_{14} \rightarrow 4_{13}$	9498.95 ± 0.04	+0.05
$6_{24} \rightarrow 6_{25}$	−9110.26 ± 0.04	−0.04
$9_{37} \rightarrow 9_{36}$	12259.10 ± 0.03	−0.25
$11_{47} \rightarrow 11_{48}$	−10187.21 ± 0.03	−0.54
	b-Dipole	
$1_{01} \rightarrow 2_{12}$[b]	11414.02 ± 0.05	−0.02
$2_{12} \rightarrow 3_{03}$[b]	11558.14 ± 0.05	−0.03
$4_{04} \rightarrow 4_{13}$	10156.68 ± 0.05	+0.00
$4_{22} \rightarrow 4_{13}$	−8189.97 ± 0.05	+0.00
$5_{23} \rightarrow 5_{14}$	−9256.13 ± 0.05	−0.06
$6_{24} \rightarrow 6_{15}$	−11485.00 ± 0.04	−0.08
$7_{25} \rightarrow 7_{34}$	12244.83 ± 0.04	−0.11

[a] The calculated frequencies are obtained by using the experimental rotational constants given in Table IV. [b] Used in a least-squares fit to obtain the rotational constants in Table IV.

Table IV. Rotational Constants and Moments of Inertia in 2-Pyrone

Rotational constants, MHz		Moments of inertia, amu Å^2
Exptl	Calcd[a]	Exptl
A = 5677.643 ± 0.020	5679.59	I_{aa} = 89.03
B = 2882.240 ± 0.005	2882.42	I_{bb} = 175.39
C = 1912.133 ± 0.003	1912.04	I_{cc} = 264.38
		$I_{aa} + I_{bb} - I_{cc}$ = +0.04

[a] Calculated from the structure in Table V.

Since no microwave spectrum has been reported for 2-pyrone, it was necessary for us to assign the zero-field microwave spectrum before the Zeeman work could be undertaken. The microwave spectrograph used in this work has been described previously.[9] A preliminary estimate of the 2-pyrone structure indicated that *a*-dipole transitions would be substantially stronger than the *b*-dipole transitions, so *a* lines were the ones first searched for. The microwave spectrum of 2-pyrone consists of many strong lines which are due not only to ground-state transitions but also to excited vibrational states. Assignment of the ground-state spectrum was made with the help of the characteristic Stark patterns and a preliminary structure. The experimental and calculated rigid rotor frequencies of the measured transitions are given in Table III, and the resultant rotational constants and moments of inertia are given in Table IV. After the ground-state spectrum had been assigned from *a*-dipole transitions, several *b*-dipole transitions were determined. These *b*-dipole transitions were indeed much weaker than the *a*-type transitions, indicating that the total dipole moment lies close to the *a* principal inertial axis. A structure for 2-pyrone is given in Table V (see Figure 2). This structure is modeled after the result in 4-pyrone and similar molecules and yields the rotational constants given in Table IV.

The zero-field microwave spectrum of tropone has been assigned elsewhere,[10] and the rotational constants are listed in Table VI.

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[8] J. K. Tyler, Department of Chemistry, The University of Glasgow. The assignment and complete substitutional structure have been obtained. We are indebted to Dr. Tyler for providing us with this valuable information prior to publication.

[9] W. H. Flygare, *J. Chem. Phys.*, **41**, 206 (1964).

[10] R. A. Creswell and I. M. Mills, University of Reading, Berkshire, England. We are indebted to Drs. Creswell and Mills for providing us with their data prior to publication.

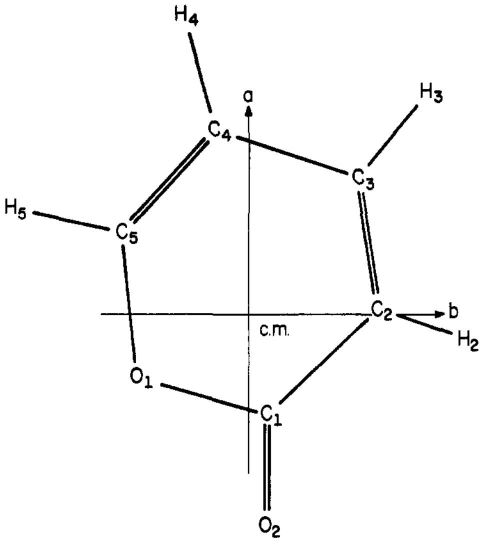

Figure 2.

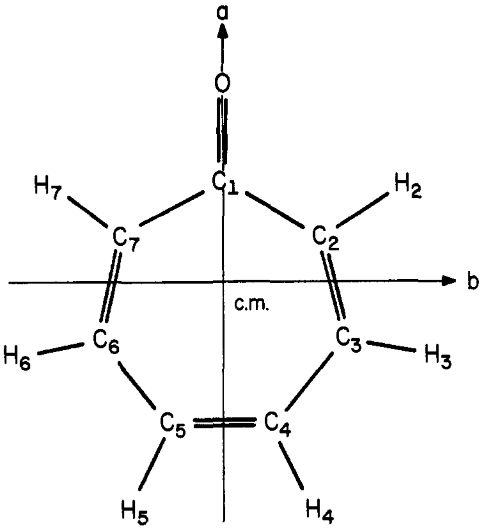

Figure 3.

Table V. Bond Distances (Å) and Angles Estimated for 2-Pyrone as Shown in Figure 2

$O_1—C_1$	1.390	$\angle C_5O_1C_1$	112° 50′
$C_1═O_2$	1.239	$\angle O_1C_1C_2$	119° 30′
$C_1—C_2$	1.478	$\angle C_1C_2C_3$	123° 30′
$C_2═C_3$	1.333	$\angle C_2C_3C_4$	116° 30′
$C_3—C_4$	1.470	$\angle C_3C_4C_5$	115° 30′
$C_4—C_5$	1.344	$\angle C_4C_5O_1$	132° 10′
$C_5—O_1$	1.350	$\angle O_1C_1O_2$	104°
C—H	1.080	$\angle C_1C_2H_2$	116°
		$\angle C_2C_3H_3$	121° 45′
		$\angle H_4C_4C_5$	121° 30′
		$\angle H_5C_5O_1$	106°

Table VI. Rotational Constants and Moments of Inertia in Tropone[10]

Rotational constants, MHz		Moments of inertia, amu Å^2
Exptl	Calcd[a]	Exptl
$A = 3712.35$	3704.31	$I_{aa} = 136.174$
$B = 2027.64$	2029.02	$I_{bb} = 249.320$
$C = 1313.14$	1310.95	$I_{cc} = 384.980$
		$I_{aa} + I_{bb} - I_{cc} = +0.515$

[a] Calculated from the structure given in Table VII and Figure 3.

Table VII. Bond Distances (Å) and Angles (deg) Estimated for Tropone as Shown in Figure 3

$O═C_1$	1.240	$\angle C_7C_1C_2$	120.8
$C_1—C_2 = C_7—C_1$	1.470	$\angle C_1C_2C_3 = \angle C_6C_7C_1$	133.1
$C_2═C_3 = C_6═C_7$	1.330	$\angle C_2C_3C_4 = \angle C_5C_6C_7$	128
$C_3—C_4 = C_5—C_6$	1.475	$\angle C_3C_4C_5 = \angle C_4C_5C_6$	128.5
$C_4═C_5$	1.340		
C—H	1.080		

The structure given in Table VII and Figure 3 was obtained by varying the molecular parameters for similar molecules until a reasonable fit of the experimental rotational constants was achieved. The rotational constants corresponding to this structure are given in Table VI.

The microwave spectrometer and high-field electromagnet used in the Zeeman studies reported here have been described.[11] For the present work the 12 × 72 in. flat poles were used, and measurements were made in both C-band and S-band waveguides. The spectra of both pyrones were taken at −20°; however, a flow system had to be used with 4-pyrone. The spectrum of tropone was taken at −10 to −15° and here too a flow system had to be used.

The theory of the rotational Zeeman effect in diamagnetic molecules has been given by Hüttner and Flygare.[12] In the absence of nuclear spin the energy levels for an asymmetric rotor in the presence of a static external magnetic field are described by eq 1.

$$E(J,M_J) = -{}^1/_2\chi H_2 - \left[\frac{\mu_0 M_J}{J(J+1)}\right]H\sum_g g_{gg}\langle J_g{}^2\rangle - \frac{H^2[3M_J{}^2 - J(J+1)]}{[J(J+1)(2J-1)(2J+3)]}\sum_g(\chi_{gg} - \chi)\langle J_g{}^2\rangle \quad (1)$$

In this expression, J and M_J are the rotational quantum numbers in units of $\hbar$; $\chi = {}^1/_3(\chi_{aa} + \chi_{bb} + \chi_{cc})$ is the average magnetic susceptibility and χ_{gg} is the element of the magnetic susceptibility tensor along the gth principal inertial axis of the molecule; H is the static magnetic field; μ_0 is the nuclear magneton; g_{gg} is the molecular g value along the gth principal inertial axis; and $\langle J_g{}^2\rangle$ is the average of the squared rotational angular momentum along the gth principal inertial axis. Since only energy differences are observed, the $-{}^1/_2\chi H^2$ term cancels out. Only two of the three magnetic anistotropy parameters are linearly independent. These are 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 can be measured directly.

The values of $\langle J_g{}^2\rangle$ were calculated[13,14] by use of the ground-state rotational constants given in Table I for 4-pyrone, Table IV for 2-pyrone, and Table VI for tropone.

Results

A. Molecular g Values and Magnetic Susceptibility Anisotropies. The rotational Zeeman splittings were measured for several $\Delta J = \pm 1$, $\Delta M = 0, \pm 1$ transitions in 4-pyrone, 2-pyrone, and tropone. The results of these measurements are available upon request.[13] The data consist of from 20–50 Zeeman transitions in each molecule. These measurements were least-squares fit to eq 1[14] to give the five Zeeman parameters (three g values and two magnetic susceptibility anisotropies) for

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

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

[13] See C. L. Norris, Ph.D. Thesis, University of Illinois, 1973.

[14] W. Hüttner, M. K. Lo, and W. H. Flygare, *J. Chem. Phys.*, 48, 1206 (1968). See also W. Hüttner and W. H. Flygare, *ibid.*, 50, 2863 (1969), for the data analysis.

Table VIII. Molecular g Values for 2-Pyrone and 4-Pyrone and Magnetic Susceptibility Anisotropies for 4-Pyrone, 2-Pyrone, and Tropone[a]

	4-Pyrone	2-Pyrone	Tropone
g_{aa}	$\pm 0.0771 \pm 0.0021$	$\pm 0.0753 \pm 0.0016$	
g_{bb}	$\pm 0.0542 \pm 0.0010$	$\pm 0.0488 \pm 0.0011$	
g_{cc}	$\pm 0.0093 \pm 0.0009$	$\pm 0.0059 \pm 0.0009$	
$2\chi_{aa} - \chi_{bb} - \chi_{cc}$	23.9 ± 1.4	22.1 ± 1.2	32.1 ± 5.0
$-\chi_{aa} + 2\chi_{bb} - \chi_{cc}$	21.9 ± 2.0	27.4 ± 1.4	39.8 ± 7.0

[a] The a and b axes are in the molecular plane. The magnetic susceptibilities are in units of 10^{-6} erg/(G^2 mol) and negative g values are favored (see text).

Table IX. Molecular Quadrupole Moments, Anisotropies in the Second Moment of Charge Distribution, and Individual Elements in the Paramagnetic Susceptibility Tensor[a]

	4-Pyrone		2-Pyrone	
Quality	$+g$ values	$-g$ values	$+g$ values	$-g$ values
Q_{aa}	-15.2 ± 2.7	-11.9 ± 2.7	-20.4 ± 2.7	-4.7 ± 2.7
Q_{bb}	-38.6 ± 3.0	$+13.8 \pm 3.0$	-36.6 ± 2.6	$+5.6 \pm 2.6$
Q_{cc}	$+53.8 \pm 4.0$	-1.9 ± 4.0	$+57.0 \pm 3.4$	-0.9 ± 3.4
$\langle 0 \lvert a^2 - b^2 \rvert 0 \rangle$	40.7 ± 2.1	47.5 ± 2.1	40.5 ± 3.7	44.2 ± 3.7
$\langle 0 \lvert b^2 - c^2 \rvert 0 \rangle$	64.4 ± 1.4	49.4 ± 1.4	64.7 ± 2.1	50.8 ± 2.1
$\langle 0 \lvert c^2 - a^2 \rvert 0 \rangle$	-105.1 ± 1.6	-97.0 ± 1.6	-105.2 ± 2.5	-95.0 ± 2.5
χ_{aa}^{p}	191.1 ± 3.3	247.1 ± 3.3	191.4 ± 6.3	247.8 ± 6.3
χ_{bb}^{p}	363.0 ± 4.3	448.1 ± 4.3	365.0 ± 8.6	437.1 ± 8.6
χ_{cc}^{p}	614.0 ± 4.6	635.4 ± 4.6	614.1 ± 8.7	627.2 ± 8.7

[a] The results are independent of the bulk susceptibility, χ. The quadrupole moments, anisotropies in second moments, and paramagnetic susceptibilities are in units of 10^{-26} esu cm^2, 10^{-16} cm^2, and 10^{-6} erg/(G^2 mol), respectively.

2-pyrone and 4-pyrone. These parameters are listed in Table VIII. Only the relative signs of the g values can be determined experimentally because we cannot determine experimentally the signs of M_J in eq 1,[14] but arguments will be given which indicate that the negative g values are the correct ones for 2-pyrone and 4-pyrone.

In tropone, the magnetic susceptibility anisotropies were determined by least-squares fitting the measured Zeeman shifts to the quadratic field dependent term of of eq 1. The resultant magnetic susceptibility anisotropies are listed in Table VIII. A reasonable set of g values was also obtained by fitting the measured Zeeman splittings to the linear field term of eq 1. However, the splittings were small and the various $\Delta M = 0$ and ± 1 transitions were not resolvable; thus, the resulting g values had large uncertainties and the values were not necessarily unique. Therefore, we will not carry the Zeeman analysis in tropone any further here. It should be emphasized that tropone has quite weak transition absorptions and we were unable to observe even the shifts with our conventional spectrograph.[11] Instead, for tropone we used a computer driven digital sweep system which allowed a longer effective integration time and a higher signal to noise ratio.

B. Molecular Quadrupole Moments. A general expression relating the five Zeeman parameters to the molecular quadrupole moments has been given by Hüttner, Lo, and Flygare[14] (eq 2). In this expression

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

$|e|$ is the electronic charge; Z_n is the charge on the nth nucleus; x_n and x_i are the nuclear and electronic center of mass coordinates, respectively, and are 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_{xx} is the rotational constant along the xth principal inertial axis; c is the speed of light; m is the electron mass; and N is Avogadro's number.

Substituting the five Zeeman parameters from Table VIII into eq 2 gives two sets of quadrupole moments for the 2-pyrone and 4-pyrone—one for each choice of the signs of the g value. These resultant sets of molecular quadrupole moments are given in Table IX for 2-pyrone and 4-pyrone. It will be shown that the negative g values are correct in both molecules.

C. Second Moments of the Electronic Charge Distribution and Magnetic Susceptibilities. The average value of the second moment of the electronic charge distribution along any axis, x, is defined as

$$\langle x^2 \rangle = \langle 0|\sum_i x_i^2|0\rangle \quad (3)$$

The anisotropies in the second moments are related to the molecular structure and the Zeeman parameters by eq 4. The values for the nuclear second moments

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

($\Sigma_n Z_n x_n^2$, $\Sigma_n Z_n y_n^2$, $\Sigma_n Z_n z_n^2$) needed in eq 4 may be calculated from the molecular structure. The known structure for 4-pyrone (Table II) gives eq 5 in units of

$$\begin{aligned} \sum_n Z_n a_n^2 &= 96.37 \pm 0.57 \\ \sum_n Z_n b_n^2 &= 51.39 \pm 0.37 \\ \sum_n Z_n c_n^2 &= 0.00 \pm 0.00 \end{aligned} \quad (5)$$

10^{-16} cm^2. The uncertainties are based on our estimates of the uncertainties in the structure. The structure for 2-pyrone is not accurately known, but since the nuclear second moments are relatively unchanged by small variations in structure, our estimated structure is adequate to give the needed values, which are in units of 10^{-16} cm^2 (eq 6).

$$\begin{aligned}\sum_n Z_n a_n^2 &= 94.50 \pm 1.82\\ \sum_n Z_n b_n^2 &= 51.74 \pm 1.35\\ \sum_n Z_n c_n^2 &= 0.00 \pm 0.00\end{aligned} \tag{6}$$

Substituting the above values, the measured g values, and the measured magnetic susceptibility anisotropies into eq 4 gives the anisotropies in the second moment of of the electronic charge distribution. These values are listed in Table IX for 4-pyrone and 2-pyrone.

The total magnetic susceptibility tensor element χ_{xx} along any axis, x, may be written as the sum of a diamagnetic component, $\chi_{xx}{}^{\mathrm{d}}$, and a paramagnetic component, $\chi_{xx}{}^{\mathrm{p}}$ defined by[12,14] eq 7. Therefore, the paramagnetic

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

susceptibility tensor elements, $\chi_{xx}{}^{\mathrm{p}}$, can be obtained from the molecular structure and the measured Zeeman parameters by using eq 7. These values are also given in Table IX.

Finally, if the bulk magnetic susceptibility is known, it may be combined with the measured magnetic susceptibility anisotropies to yield the individual elements of the total magnetic (and thus also diamagnetic) susceptibility tensor. It is then possible to calculate the individual second moments of electronic charge distribution from eq 8.

$$\begin{aligned}\langle x^2\rangle &= -\frac{2mc^2}{e^2}[\chi_{yy}{}^{\mathrm{d}} + \chi_{zz}{}^{\mathrm{d}} - \chi_{xx}{}^{\mathrm{d}}] =\\ &-\frac{2mc^2}{e^2}[(\chi_{yy} + \chi_{zz} - \chi_{xx}) - (\chi_{yy}{}^{\mathrm{p}} + \chi_{zz}{}^{\mathrm{p}} - \chi_{xx}{}^{\mathrm{p}})]\end{aligned} \tag{8}$$

The bulk magnetic susceptibility of tropone has been measured to be $\chi = -53.0 \times 10^{-6}$.[15] Although the bulk susceptibility has not been measured for either 4-pyrone or 2-pyrone, it is possible to use an empirical method for estimating χ.[16] This method gives $\chi = {}^1/_3 \cdot (\chi_{aa} + \chi_{bb} + \chi_{cc}) = -42.2 \times 10^{-6}$ for 4-pyrone and $\chi = -45.0 \times 10^{-6}$ for 2-pyrone. These numbers are combined with eq 7 and 8 to give the remaining pertinent results listed in Table X for 4-pyrone, 2-pyrone, and tropone. To obtain these results it was assumed that the negative g values were the correct ones for 2-pyrone and 4-pyrone. Results similar to those shown in Table X are obtained by use of a model recently proposed by Gierke, Tigelaar, and Flygare to predict bulk susceptibilities[17] or by use of additivity rules to determine $\langle c^2\rangle$.[18]

Table X. Estimates of the Second Moments of Electronic Charge Distribution and Magnetic Susceptibility Tensor Elements for 4-Pyrone and 2-Pyrone from the Estimated Values of χ (see text)[a]

	4-Pyrone	2-Pyrone	Tropone
$\langle a^2\rangle$	105.4 ± 3.8	103.2 ± 5.4	
$\langle b^2\rangle$	57.9 ± 3.8	59.1 ± 5.4	
$\langle c^2\rangle$	8.4 ± 3.8	8.2 ± 5.4	
$\chi_{aa}{}^{\mathrm{d}}$	−281.4 ± 8.8	−285.5 ± 11.7	
$\chi_{bb}{}^{\mathrm{d}}$	−483.0 ± 10.0	−473.0 ± 14.0	
$\chi_{cc}{}^{\mathrm{d}}$	−692.8 ± 10.7	−688.8 ± 14.6	
χ_{aa}	−34.2 ± 5.5	−37.6 ± 5.4	−42.3 ± 5.5
χ_{bb}	−34.9 ± 5.6	−35.9 ± 5.5	−39.7 ± 5.5
χ_{cc}	−57.5 ± 6.1	−61.5 ± 5.8	−77.0 ± 7.0
χ	−42.2[b]	−45.0[b]	−53.0

[a] The second moments are in units of 10^{-16} cm^2 and the magnetic susceptibilities are in units of 10^{-6} erg/(G^2 mol). The negative g values are used in this calculation. The results for tropone are from an experimental evaluation of χ. [b] Estimated from ref 16.

D. Assignment of the Negative Values for the Signs of the *g* Values. The choice of the negative signs for the g values in 4-pyrone and 2-pyrone is based on two arguments. The first argument involves the quadrupole moments calculated using both choices of g-value signs (Table IX). The positive molecular g values give unreasonably large quadrupole moments for both molecules when compared with the results for a large number of similar molecules.[19] Furthermore Q_{bb} would be expected to be positive in both molecules, since protons dominate the charge distribution at both large positive and large negative values of the b coordinate. Since one would also expect Q_{cc} to be very small or somewhat negative because of the π electron distributions at positive and negative c coordinates, the negative g values are favored as the correct ones.

The second point in favor of negative signs of the g values arises from a comparison of the values of $\langle c^2\rangle$ obtained experimentally with those estimated from a reliable set of additivity rules (Table XI).[18] It is evident that the positive g values are excluded in the molecules by this comparison. In summary, there is little doubt that the negative g values in 2-pyrone and 4-pyrone are correct.

Table XI. Out-of-Plane Second Moments of Electronic Charge Distribution, $\langle c^2\rangle$, for 4-Pyrone and 2-Pyrone[a]

	$\langle c^2\rangle$ using all positive g values	$\langle c^2\rangle$ using all negative g values	$\langle c^2\rangle$ from additivity rules
3	−5.7 ± 3.8	8.4 ± 3.8	9.0
2	−5.4 ± 5.4	8.2 ± 5.4	9.0

[a] Units are 10^{-16} cm^2. The values of $\langle c^2\rangle$ for g all positive are clearly excluded.

Discussion

Of the many indications of aromatic character, magnetic criteria have proved particularly popular in recent

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(17) T. D. Gierke, H. L. Tigelaar, and W. H. Flygare, *ibid.*, in press.

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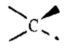
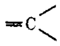
years, principally because the "ring current effect" is considered to make a major contribution to the readily measured nmr chemical shifts of aromatic protons.[5,20] Accordingly, chemical shifts have been used extensively to estimate aromatic character although the difficulty of accounting for other contributions to these shifts is well recognized and has been discussed.[5] The fundamental relationship of electron delocalization and magnetic susceptibility anisotropies and the separation of the latter into local ($\Delta\chi_{\text{local}}$) and nonlocal ($\Delta\chi_{\text{nonlocal}}$) effects also has been well discussed.[4] In essence, large nonlocal diamagnetic effects are associated with electron delocalization and aromatic compounds have large nonlocal contributions to their molecular susceptibility anisotropies while nonaromatic compounds do not. Of the methods used for the semiquantitative evaluation of aromatic character based on magnetic properties,[21,22] only the microwave method gives a direct experimental measurement of the magnetic susceptibility anisotropies.[1]

Although the molecules tropone, 2-pyrone, and 4-pyrone do not strictly possess $4n + 2$ π electrons in a cyclic conjugated system, **1**, **2**, and **3** were at one time considered to be aromatic, on the basis of the usual representations of the carbonyl group. At present these compounds are considered to be nonaromatic by most criteria.[6,7] Molecules which have the structural relationship of the isomeric pyrones **2** and **3**, if aromatic, could be particularly appropriate compounds for comparing and evaluating criteria of aromaticity since the property under consideration could be compared directly between the isomers as well as indirectly with the estimated property of the hypothetical model. Relative thermodynamic stabilities favor a derivative of 2-pyrone over a derivative of 4-pyrone, but evaluation of this result in terms of π bond energies is made uncertain by the unknown equilibrium constant, by differences in σ bond energies of the isomers, and by possible association effects.[7a] An appreciable delocalization energy is predicted for **2** and **3** by the simple Hückel method[7a] using both local and noncyclic models for the hypothetical nonaromatic molecule, but CNDO calculations give conflicting results, as far as relative energies of the occupied π orbitals are concerned, when molecular parameters are changed slightly. In any case, the extent to which the carbonyl group perturbs the aromatic character of a parent aromatic system is a central question for many "nonbenzenoid aromatic" compounds,[23] and the formal carbonyl insertion relationship between **1** and benzene and **2** and **3** and furan is noted above.

From microwave data we have developed a set of empirical rules which allow determination of the magnitude of the local contributions to the anisotropy[1,3] and these can be used to extract the nonlocal contributions to $\Delta\chi$ for **1**, **2**, and **3**. The local contributions previously estimated from the magnetic susceptibility anisotropies of a series of open-chain molecules and ring molecules possessing no cyclic delocalization[1] have been refined through the use of more data, including planar, five-membered or larger rings, and by excluding nonplanar and strained rings to give local group anisotropy values as shown in Table XII. In Table XIII experimental anisotropies are compared with those local anisotropies predicted by the rules for **1**, **2**, **3**, benzene, furan, and the compounds used to obtain the local values. The calculated local and experimental values for the anisotropies are in good agreement for all molecules except benzene and furan, which clearly show large nonlocal contributions to the anisotropies. This is, of course, the expected result for benzene and furan, which have been judged aromatic by many criteria.

Table XII. Local Group Anisotropy Values (in units of 10^{-6} erg/(G^2 mol))

Group[a]	$\chi_{cc} - {}^1/_2(\chi_{aa} + \chi_{bb})$
sp^3 carbon 	$+1.6 \pm 0.8$
sp^2 carbon 	-4.4 ± 0.4
Carbonyl oxygen =O	-6.5 ± 0.7
Ether oxygen —O	$+2.0 \pm 1.5$

[a] The open valences can be assigned to other groups or the hydrogen which is assigned a $\Delta\chi$ of 0.

Table XIII. Experimental and Predicted Values of Magnetic Susceptibility Anisotropies[a]

Molecule	$\chi_{cc} - {}^1/_2(\chi_{aa} + \chi_{bb})$ Exptl	Local[b]	Ref
	Open-Chain Molecules[c]		
Propene	-6.3 ± 0.4	-7.2 ± 1.6	19
Isoprene	-18.0 ± 1.1	-16.0 ± 2.4	2
Acrolein	-20.6 ± 1.2	-19.7 ± 1.9	19
Formaldehyde	-10.8 ± 0.4	-10.9 ± 1.1	19
Acetaldehyde	-8.9 ± 2.0	-9.3 ± 1.9	19
Dimethyl ether	$+4.6 \pm 0.5$	$+5.2 \pm 3.1$	19
Methyl formate	-7.0 ± 1.0	-7.3 ± 3.4	19
	Ring Molecules		
Vinylene carbonate[c]	-14.5 ± 1.3	-15.7 ± 4.9	19
Maleic anhydride[c]	-26.6 ± 1.8	-28.6 ± 4.5	19
Cyclopent-2-en-1-one[c]	-19.0 ± 1.5	-16.5 ± 3.5	*d*
Cyclopent-3-en-1-one[c]	-16.8 ± 1.0	-16.5 ± 3.5	*d*
Furan	-38.7 ± 0.5	-15.6 ± 3.1	19
Benzene	-59.7	-26.4 ± 2.4	19
4-Pyrone	-22.9 ± 1.7	-26.5 ± 4.2	*e*
2-Pyrone	-24.8 ± 1.3	-26.5 ± 4.2	*e*
Tropone	-36.6 ± 4.5	-37.3 ± 3.5	*e*

[a] Units are of 10^{-6} erg/(G^2 mol) and the c axis is perpendicular to the heavy atom plane. [b] Predicted from local group anisotropy rules (Table XII). [c] Used to obtain local group anisotropy rules. [d] C. L. Norris, R. C. Benson, and W. H. Flygare, *Chem. Phys. Lett.*, **10**, 75 (1971). [e] This work.

For 4-pyrone, 2-pyrone, and tropone the experimental magnetic susceptibility anisotropies are within experimental error of those predicted by local effects, suggesting that **1**, **2**, and **3** should all be considered essentially nonaromatic by magnetic criteria. It should be stressed that while it is possible to use the nonlocal contributions to magnetic susceptibility anisotropies to establish "degrees" of aromaticity, the experimental errors in most criteria, the lack of a clear relationship between different criteria, and the primarily qualitative utility

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of the concept of aromaticity, which is itself somewhat an artifact of inadequate structural description, suggest that such designations are not presently justifiable.

Consideration of tropone as formally related to benzene by carbonyl insertion of 2- and 4-pyrone as similarly related to furan shows that insertion of a carbonyl group into these aromatic rings drastically suppresses the contribution of nonlocal effects to the molecular magnetic susceptibility.

Extrapolation of these results beyond the present studies raises the questions of whether formal carbonyl insertion into other aromatic compounds will lead to a large suppression of aromatic character as judged by magnetic criteria and whether this suppression will be manifest in other criteria of aromatic character. Qualitative correlation between the magnetic, thermodynamic, spectroscopic, and calculational criteria of aromatic character is usually observed, but the interrelationships are sufficiently vague that it is not clear to what extent the present demonstration of a low degree of aromatic character for **1**, **2**, and **3** by magnetic criteria should be reflected in other criteria. For example, in considering the relationship between a suggested nmr-based quantitative criterion for aromaticity and the thermodynamic criterion for aromaticity, it was shown that in a thermodynamic comparison of the stabilization energy of *N*-methyl-2-pyridone with 2-methoxypyridine the latter was found to be favored by only about 6 kcal/mol, while the nmr criterion suggested a much greater difference.[24,25] This lack of agreement could reflect failure of the nmr method to correctly estimate the "ring current" effect in *N*-methyl-2-pyridone, difficulties in presumed cancellations of energies between similar functionalities in the thermodynamic criteria, or a lack of correlation between criteria. It seems clear that at present predictions and investigations of aromatic character should be made with respect to specific criteria and that of the present magnetic criteria, microwave based molecular magnetic susceptibilities give the most reliable results.

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Microwave Spectrum, Substitutional Structure, and Stark and Zeeman Effects in Cyclopropenone

R. C. Benson,[1a] W. H. Flygare,*[1a] M. Oda,[1b] and R. Breslow[1b]

Contribution from the Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801, and the Department of Chemistry, Columbia University, New York, New York 10027. *Received October 7, 1972*

Abstract: The microwave spectra of the normal and four other isotopic species of cyclopropenone have been assigned leading to a complete substitutional structure. The structural parameters are $d_{C=O} = 1.212 \pm 0.002$, $d_{C-C} = 1.412 \pm 0.003$, $d_{C=C} = 1.302 \pm 0.003$, $d_{C-H} = 1.097 \pm 0.003$ in units of 10^{-8} cm and the angles are $\angle HC_2C_3 = 144° 55' \pm 20'$ and $\angle C_2C_3C_1 = 62° 33' \pm 20'$. The molecular Stark effect has been observed giving an electric dipole moment of $|\mu| = (4.39 \pm 0.06) \times 10^{-18}$ esu cm. The molecular Zeeman effect has been observed giving the molecular *g* values of $g_{aa} = -0.2900 \pm 0.0013$, $g_{bb} = -0.0963 \pm 0.0004$, and $g_{cc} = -0.0121 \pm 0.0004$ and the magnetic susceptibility anisotropies of $2\chi_{aa} - \chi_{bb} - \chi_{cc} = 13.6 \pm 1.1$ and $2\chi_{bb} - \chi_{aa} - \chi_{cc} = 22.0 \pm 0.8$ in units of 10^{-6} erg/(G^2 mol). The *a* axis is the electric dipole axis and the *b* axis is also in the molecular plane. The corresponding molecular electric quadrupole moments are $Q_{aa} = -3.0 \pm 0.9$, $Q_{bb} = 4.0 \pm 0.7$, and $Q_{cc} = -1.0 \pm 1.3$ in units of 10^{-26} esu cm^2. The molecular structure and electronic structure of cyclopropenone are discussed and compared with those of similar molecules.

In this paper we report the assignment of the microwave spectrum of cyclopropenone (Figure 1) including the main isotopic species and all substituted species including the $^{13}C_1$, $^{13}C_2$, ^{18}O, and the dideuterio compounds. These data allow a determination of the complete substitutional structure of the molecule. The molecular Stark effect was observed on several rotational transitions in the main isotopic species to give the molecular electric dipole moment. The molecular Zeeman effect was observed on several rotational transitions in the main isotopic species to yield the molecular magnetic *g* values, the molecular magnetic susceptibility anisotropies, molecular electric quadrupole moments, and other magnetic parameters of interest in this molecule.

Cyclopropenone was first reported in 1967[2] and we attempted at that time to observe the microwave spectrum of the gas from dilute solutions in both water and acetonitrile. Although cyclopropenone was clearly in the solution (as determined from the nmr spectrum) we were only able to observe the propynal rearrangement product in the gas phase.

Subsequent preparative studies[3a] culminated in the

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