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.

Acknowledgments. We thank J. K. Tyler for the 4-pyrone results prior to publication and I. M. Mills and R. A. Creswell for the tropone results prior to publication. The support of the National Science Foundation is gratefully acknowledged.

(24) P. Beak, J. Bonham, and J. T. Lee, Jr., *J. Amer. Chem. Soc.*, **90**, 1569 (1968); for an extension to tautomeric systems, see M. J. Cook, A. R. Katritzky, P. Linda, and R. D. Tack, *Chem. Commun.*, 510 (1971).

(25) A lack of correlation between magnetic and other criteria for 4-pyrones is implied by Smitherman and Ferguson, ref 7b.

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

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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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(1) (a) University of Illinois. (b) Columbia University.

(2) R. Breslow and G. Ryan, *J. Amer. Chem. Soc.*, **89**, 3073 (1967).

(3) (a) R. Breslow, G. Ryan, and J. T. Groves, *ibid.*, **92**, 988 (1970); (b) R. Breslow and M. Oda, *ibid.*, **94**, 4787 (1972).

Table I. Microwave Transitions (MHz) of Normal Cyclopropenone (see Figure 1) and Several Isotopic Species[a]

	Normal species		$^{13}C_1$		$^{13}C_2$		Dideuterio		^{18}O	
Transition	Obsd	Obsd − Calcd	Obsd	Obsd − Calcd	Obsd	Obsd − Calcd	Obsd	Obsd − Calcd	Obsd	Obsd − Calcd
$0_{00} \rightarrow 1_{01}$	14105.74	0.08					12846.79	0.19	13312.41	0.07
$1_{11} \rightarrow 2_{12}$	26667.02	−0.07	26642.18	−0.10	26227.44	−0.06	24030.23	0.13	25247.46	0.10
$1_{01} \rightarrow 2_{02}$	28139.89	0.08	28112.57	0.23	27691.34	0.04	25579.07	0.20	26568.68	+0.01
$1_{10} \rightarrow 2_{11}$	29755.51	−0.04	29724.88	0.06	29300.91	0.12	27356.49	0.19	28001.98	−0.01
$2_{12} \rightarrow 3_{13}$	39956.70	−0.07	39919.77	−0.13	39296.69	−0.07	35976.14	0.14	37836.63	−0.09
$2_{02} \rightarrow 3_{03}$							38086.26	0.23		
$2_{21} \rightarrow 3_{22}$							38539.43	−0.37		
$2_{20} \rightarrow 3_{21}$							38993.17	−0.40		
$3_{13} \rightarrow 3_{12}$	9263.49	0.19								
$4_{14} \rightarrow 4_{13}$	15427.90	0.10							13763.69	0.54
$5_{15} \rightarrow 5_{14}$	23105.58	−0.04					24809.73	0.13	20619.76	−0.13
$6_{16} \rightarrow 6_{15}$	32255.63	−0.43			32089.09	−0.32			28804.18	−0.39
$7_{26} \rightarrow 7_{25}$	8372.78	−0.18								
$8_{27} \rightarrow 8_{26}$	13394.57	0.82								
$9_{28} \rightarrow 9_{27}$	19994.89	0.66					27982.84	0.70		
$10_{29} \rightarrow 10_{28}$	28229.75	−0.05			28527.71	0.66	38289.25	−0.58	23028.86	0.82
$11_{2.10} \rightarrow 11_{2.9}$			37961.73	−0.03					31353.79	−0.22
$12_{3.10} \rightarrow 12_{3.9}$	9161.61	−0.10								
$13_{3.11} \rightarrow 13_{3.10}$	13980.48	−0.64								
$14_{3.12} \rightarrow 14_{3.11}$									14781.51	−0.38
$15_{3.13} \rightarrow 15_{3.12}$			28345.74	0.02	29302.16	−0.30				

[a] Experimental errors are estimated to be 0.05–0.1 MHz. The calculated frequencies were obtained from the rotational constants in Table II.

isolation and characterization[3b] of pure cyclopropenone as a distillable liquid, bp 30° at 0.45 Torr. This remarkably low vapor pressure for such a small molecule is still sufficient that microwave studies could be performed and we were able to observe and assign a strong rotational spectrum. The assignment of the rotational transitions in the various isotopic species has resulted in a complete substitutional structure in cyclopropenone. The structure obtained here will be compared with the ring substitutional structure of the similar cyclopropanone.[4] Also a limited comparison with cyclopropene is possible.[5,6]

The large electric dipole moment observed here in cyclopropenone indicates a much larger polarity in the CO bond than in other carbonyl compounds, except for the substituted cyclopropenones.

The molecular Zeeman effect leads to additional parameters of interest in the molecule. The molecular electric quadrupole moments lead to additional information on the static charge distribution in cyclopropenone and the results are compared to similar small ring compounds. The magnetic susceptibility anisotropies lead to information concerning the degree of delocalization of the ring electrons in cyclopropenone relative to other small ring compounds.

Microwave Spectrum

Cyclopropenone has C_{2v} symmetry with the dipole moment lying along the *a* principal inertial axis as shown in Figure 1. The *b* axis is also in the molecular plane. Preliminary structures were estimated from the information available on cyclopropene[6] and cyclopropanone.[4]

The microwave spectrum of the main isotopic species of cyclopropenone was observed with a standard microwave 5-kHz Stark modulated spectrograph[5] with the brass waveguide cooled to approximately −20 to −30°. A continuous flow of the pure cyclopropenone gas gave the best results. No impurities were observed. The rotational transitions were identified and assigned on the basis of their Stark effect and the observed transitions are listed in Table I.

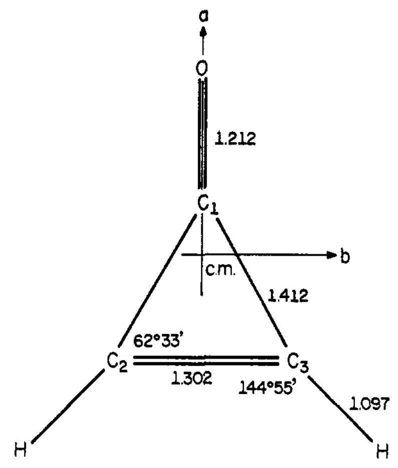

Figure 1. The molecular structure (see Table IV) and orientation of the principal inertial axes in cyclopropenone.

The two ^{13}C isotopically substituted species of cyclopropenone were assigned in their natural abundance of $^{13}C_1$ (1%) and $^{13}C_2$ (2%) by the characteristic Stark effect of the rotational transitions which are listed in Table I. The ^{18}O and dideuterio species were prepared in near 100% purity by the reactions reported earlier,[3a] modified in accord with our recent isolation procedures.[3b]

The microwave spectra of the ^{18}O and dideuterio compounds were easily assigned and the observed transitions are also listed in Table I.

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(4) J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *J. Amer. Chem. Soc.*, **91**, 1896 (1969).

(5) M. K. Kemp and W. H. Flygare, *ibid.*, **91**, 3163 (1969).

(6) P. H. Kasai, R. J. Myers, D. F. Eggers, and K. B. Wiberg, *J. Chem. Phys.*, **30**, 512 (1959).

Table II. Rotational Constants (MHz) and Moments of Inertia[a] (amu Å^2) for Cyclopropenone Isotopic Species

	Normal species	$^{13}C_1$	$^{13}C_2$	Dideuterio	^{18}O
A	32046.00 ± 0.5	32049.3 ± 5.0	31235.4 ± 5.0	24538.85 ± 0.9	32046.82 ± 0.6
B	7824.95 ± 0.06	7816.52 ± 0.05	7709.36 ± 0.05	7254.85 ± 0.03	7344.82 ± 0.04
C	6280.72 ± 0.06	6275.25 ± 0.05	6172.72 ± 0.05	5591.75 ± 0.03	5967.51 ± 0.04
I_A	15.7704 ± 0.0003	15.7687 ± 0.0025	16.1796 ± 0.0025	20.5950 ± 0.0008	15.7700 ± 0.0003
I_B	64.5853 ± 0.0005	64.6550 ± 0.0004	65.5537 ± 0.0004	69.6606 ± 0.0003	68.8073 ± 0.0004
I_C	80.4648 ± 0.0008	80.5350 ± 0.0006	81.8727 ± 0.0007	90.3790 ± 0.0005	84.6881 ± 0.0006
$I_A + I_B - I_C$	−0.1091 ± 0.0016	−0.1113 ± 0.0035	−0.1394 ± 0.0036	−0.1234 ± 0.0016	−0.1108 ± 0.0013

[a] Conversion factor = 505377 MHz amu Å^2.

The rotational constants for each isotopic species were obtained by a least-squares fit of all of the observed transitions for each molecule as listed in Table I. The resultant rotational constants are listed in Table II which also includes the moments of inertia and inertial defects. The inertial defects listed in Table II confirm the planarity of the molecule[7] ($I_a + I_b - I_c = \Sigma_i m_i c_i$,[3a] where m_i is the mass of the ith atom and c_i is the out-of-plane coordinate of the ith atom).

Molecular Structure

Table II lists the moments of inertia for the main as well as all possible isotopically substituted species. A proper analysis of these moments leads to a *substitutional* structure which minimizes the errors due to zero-point vibrations in the molecule.[8] The structural coordinates are all obtained from the moments of inertia in the center of mass (cm) coordinate system of the main isotopic species. For instance, the a and b coordinates of C_2 (or C_3, see Figure 1) are easily shown to be related to the moments of inertia by

$$\begin{aligned} a^2 &= \frac{1}{\mu}\Delta I_B\left(1 + \frac{\Delta I_A}{I_A{}^0 - I_B{}^0}\right) \\ b^2 &= \frac{1}{\mu}\Delta I_A\left(1 + \frac{\Delta I_B}{I_B{}^0 - I_A{}^0}\right) \\ \mu &= M\Delta m/(M + \Delta m) \\ \Delta I_B &= I_B{}' - I_B{}^0 \\ \Delta I_A &= I_A{}' - I_A{}^0 \end{aligned} \tag{1}$$

where the primes indicate the moments for the singly isotopically substituted molecule and the super zeros indicate the main isotopic species of mass M. Δm is the mass difference between the two different molecules. Substituting the moments in Table II for the main and $^{13}C_2$ isotopic species in cyclopropenone gives (see Figure 1) the C_2 (or C_3) coordinates

$$a = -0.9872 \pm 0.0005$$

$$b = -0.651 \pm 0.0022$$

where the uncertainties are due only to uncertainties in the moments of inertia arising from frequency measurements. The corresponding coordinates for the C_1 and O atoms in the main species cm system are obtained by identical methods where we have used $I_A{}' = I_A{}^0$ for both the $^{13}C_1$ and ^{18}O species relative to the main molecule. The substitutional coordinates of the protons were obtained from easily derived equations for the disubstituted species relative to the main species. The proton a and b coordinates are given by (Δm is the difference between the deuteron and proton masses)

$$\begin{aligned} a^2 &= \frac{M + 2\Delta m}{2M(\Delta m)}\Delta I_B \\ b^2 &= \frac{1}{2(\Delta m)}\Delta I_A \end{aligned} \tag{2}$$

The resulting substitutional coordinates are listed in Table III for all atoms and the structure of cyclopropenone was computed and listed in Table IV (see also Figure 1).

Table III. Center of Mass Coordinates for the Nuclei in Cyclopropenone[a]

Nucleus	a	b	c
C_1	0.2660 ± 0.0017	0	0
C_2	−0.9872 ± 0.0005	−0.651 ± 0.0022	0
C_3	−0.9872 ± 0.0005	+0.651 ± 0.0022	0
O	1.4778 ± 0.0004	0	0
H_1	−1.6171 ± 0.0002	−1.5481 ± 0.0004	0
H_2	−1.6171 ± 0.0002	+1.5481 ± 0.0004	0

[a] Distance in Å. The quoted errors are due to errors in frequency only; the actual errors in the coordinates are probably not better than ±0.002 Å (see text).

Table IV. Structure of Cyclopropenone[a]

C=O	1.212 ± 0.002
C—C	1.412 ± 0.003
C=C	1.302 ± 0.003
C—H	1.097 ± 0.003
$\angle HC_2C_3$	144° 55′ ± 20′
$\angle C_2C_3C_1$	62° 33′ ± 20′

[a] Distances are in Å.

Molecular Stark Effect

The molecular Stark effect was observed in the $1_{01} \rightarrow 2_{02}$ ($M = 0$ and $M = \pm 1$) and $1_{11} \rightarrow 2_{12}$ ($M = 0$) transitions at various electric fields. The electric field was calibrated using standard techniques with the $J = 0 \rightarrow J = 1$ transition of OCS.[5] The resulting Stark analysis gave the electric dipole moment of $|\mu| = (4.39 \pm 0.06) \times 10^{-18}$ esu cm along the a principal inertial axis. The results for each transition studied here are listed in Table V. This large dipole moment in the parent cyclopropenone molecule is similar to other cyclopropenone derivatives; by dielectric constant measurements in solution the dipole moment of dipropylcyclopropenone was found[9] to be 4.78 D, of diphenylcyclo-

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(7) See Table II in J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *J. Amer. Chem. Soc.*, **90**, 1072 (1968).

(8) C. C. Costain, *J. Chem. Phys.*, **29**, 684 (1958); J. Kraitchman, *Amer. J. Phys.*, **21**, 17 (1953).

(9) R. Breslow, T. Eicher, A. Krebs, R. Peterson, and J. Posner, *J. Amer. Chem. Soc.*, **87**, 1320 (1965).

Table V. Electric Dipole Moment of Cyclopropenone

Transition	M	$\lvert\mu\rvert$[a]
$1_{01} \rightarrow 2_{02}$	0	4.385 ± 0.05
$1_{01} \rightarrow 2_{02}$	1	4.326 ± 0.05
$1_{11} \rightarrow 2_{12}$	0	4.465 ± 0.07
		Av $\lvert\mu\rvert$ = 4.39 ± 0.06

[a] Units of 10^{-18} esu cm = D.

propenone 5.14 D, and of cycloheptenocyclopropenone 4.66 D.

Molecular Zeeman Effect

The molecular Zeeman effect is the observation of the effects of high magnetic fields on the rotational energy levels of the molecule. The energy of interaction with the magnetic field, H, is given by eq 3,[10]

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

where 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, 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 anisotropy parameters are linearly independent and 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.

Table VI. Molecular Zeeman Splittings Observed for Cyclopropenone[a]

Transition	$M_l \rightarrow M_\mu$	$\Delta\nu_{\text{exptl}}$, kHz	$\Delta\nu_{\text{calcd}}$, kHz[b]	$\Delta\nu_{\text{exptl}} - \Delta\nu_{\text{calcd}}$, kHz
$0_{00} \rightarrow 1_{01}$	$0 \rightarrow 0$	−130	−119	−11
H = 22,810 G				
$1_{11} \rightarrow 2_{12}$	$+1 \rightarrow +1$	−1560	−1573	+13
H = 22,810 G	$0 \rightarrow 0$	−10	−30	+20
	$-1 \rightarrow -1$	1170	1160	+10
$5_{15} \rightarrow 5_{14}$	$-5 \rightarrow -5$	−4080	−4095	+15
	$-4 \rightarrow -4$	−3080	−3087	+7
H = 22,700 G	$-3 \rightarrow -3$	−2120	−2141	+21
	$-2 \rightarrow -2$	−1270	−1259	−11
	$2 \rightarrow 2$	1710	1638	+72
	$3 \rightarrow 3$	2250	2204	+46
	$4 \rightarrow 4$	2780	2708	+72
	$5 \rightarrow 5$	3160	3148	+12
$0_{00} \rightarrow 1_{01}$	$0 \rightarrow -1$	−820	−822	+2
H = 21,120 G	$0 \rightarrow 1$	920	923	−3
$1_{11} \rightarrow 2_{12}$	$1 \rightarrow 0$	−2720	−2706	−14
	$0 \rightarrow -1$	−1080	−1098	+18
H = 21,140 G	$1 \rightarrow 2$	70	9	+61
	$-1 \rightarrow -2$	170	207	−37
	$0 \rightarrow 1$	1250	1236	+14
	$-1 \rightarrow 0$	2610	2161	−1
$1_{01} \rightarrow 2_{02}$	$0 \rightarrow -1$	−810	−794	−16
	$-1 \rightarrow -2$		−804	−6
H = 21,150 G	$1 \rightarrow 2$	860	867	−7
	$0 \rightarrow 1$		915	+55
$1_{10} \rightarrow 2_{11}$	$1 \rightarrow 0$	−2880	−2866	−14
	$0 \rightarrow -1$	−2080	−2057	−23
H = 21,170 G	$-1 \rightarrow -2$	−570	−565	−5
	$1 \rightarrow 2$	580	596	−16
	$0 \rightarrow 1$	1610	1641	−31
	$-1 \rightarrow 0$	3390	3368	+22

[a] The zero field frequencies are listed in Table I. [b] The calculated $\Delta\nu$ were obtained using eq 3 and the parameters in Table VII.

Table VII. Molecular Zeeman Parameters for Cyclopropenone[a]

g_{aa}	−0.2900 ± 0.0013
g_{bb}	−0.0963 ± 0.0004
g_{cc}	−0.0121 ± 0.0004
$2\chi_{aa} - \chi_{bb} - \chi_{cc}$	13.6 ± 1.1
$-\chi_{aa} + 2\chi_{bb} - \chi_{cc}$	22.0 ± 0.8
Q_{aa}	−3.0 ± 0.9
Q_{bb}	+4.0 ± 0.7
Q_{cc}	−1.0 ± 1.3
$\chi_{aa}{}^{\mathrm{p}}$	61.2 ± 0.3
$\chi_{bb}{}^{\mathrm{p}}$	173.9 ± 0.6
$\chi_{cc}{}^{\mathrm{p}}$	193.8 ± 0.6
$\langle a^2\rangle - \langle b^2\rangle$	25.9 ± 0.4
$\langle b^2\rangle - \langle c^2\rangle$	9.2 ± 0.3
$\langle c^2\rangle - \langle a^2\rangle$	−35.1 ± 0.4
$\langle c^2\rangle$	5.1[b]
$\langle b^2\rangle$	14.3[c]
$\langle a^2\rangle$	40.2[c]
$\chi_{aa}{}^{\mathrm{d}}$	−82.3[c]
$\chi_{bb}{}^{\mathrm{d}}$	−192.3[c]
$\chi_{cc}{}^{\mathrm{d}}$	−231.3[c]
χ_{aa}	−21.1[c]
χ_{bb}	−18.4[c]
χ_{cc}	−37.5[c]
χ	−25.7[c]

[a] The units of χ are 10^{-6} erg/(G^2 mol), the units of $Q_{\alpha\alpha}$ are 10^{-26} esu cm^2, and the units of $\langle\alpha^2\rangle$ are 10^{-16} cm^2. The a axis is the dipole axis and the c axis is perpendicular to the molecular plane. [b] Estimated using the additivity rules in ref 13. [c] Evaluated from $\langle c^2\rangle$.

The high-field Zeeman spectra relative to the zero-field frequencies are listed in Table VI. The experimental apparatus has been described previously.[11] The data in Table VI were analyzed by a least-squares method to the expression in eq 3 giving the g values and magnetic susceptibility anisotropies which are listed in Table VII. The molecular electric quadrupole moments are given by eq 4,[12] where $\lvert e\rvert$ is the electronic

$$Q_{xx} = \frac{1}{2}\lvert e\rvert\sum Z_n(3x_n{}^2 - r_n{}^2) - \frac{1}{2}\lvert e\rvert\left\langle 0\middle|\sum_i(3x_i{}^2 - r_i{}^2\middle|0\right\rangle = -\frac{\hbar\lvert e\rvert}{8\pi M}\left[\frac{2g_{xx}}{G_{xx}} - \frac{g_{yy}}{G_{yy}} - \frac{g_{zz}}{G_{zz}}\right] - \frac{2mc^2}{\lvert e\rvert N}(2\chi_{xx} - \chi_{yy} - \chi_{zz}) \quad (4)$$

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. Using eq 4, the rotational constants

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

(11) W. H. Flygare, W. Hüttner, R. L. Shoemaker, and P. D. Foster, *ibid.*, **50**, 1714 (1969).

(12) W. Hüttner, M. K. Lo, and W. H. Flygare, *ibid.*, **48**, 1206 (1968).

in Table II, and the Zeeman parameters in Table VII gives the molecular quadrupole moments also listed in Table VII.

Values of the paramagnetic susceptibility components as well as the anisotropies in the second moments of electronic charge are also available from the basic Zeeman parameters and the molecular structure (eq 5).[12]

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

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

$$\langle y^2\rangle = \left\langle 0\left|\sum_i y_i{}^2\right|0\right\rangle \qquad (5)$$

The values of the nuclear second moments, $\Sigma_n Z_n a_n{}^2$, $\Sigma_n Z_n b_n{}^2$, and $\Sigma_n Z_n c_n{}^2$ needed in these equations are obtained directly from the molecular structure in Table III giving

$$\sum_n Z_n a_n{}^2 = (34.81 \pm 0.11) \times 10^{-16}\ \mathrm{cm}^2$$
$$\sum_n Z_n b_n{}^2 = 9.88 \pm 0.05 \qquad (6)$$
$$\sum_n Z_n{}^2 c_n{}^2 = 0$$

The resultant values of $\chi_{xx}{}^{\mathrm{p}}$ and $\langle y^2\rangle - \langle x^2\rangle$ are listed in Table VII.

The diagonal elements in the total magnetic susceptibility tensor elements are written as a sum of diamagnetic, $\chi_{aa}{}^{\mathrm{d}}$, and paramagnetic, $\chi_{aa}{}^{\mathrm{p}}$, components.

$$\chi_{aa} = \chi_{aa}{}^{\mathrm{p}} + \chi_{aa}{}^{\mathrm{d}} = \chi_{aa}{}^{\mathrm{p}} - \frac{e^2N}{4mc^2}\left\langle 0\left|\sum_i(b_i{}^2 + c_i{}^2)\right|0\right\rangle \qquad (7)$$

In order to evaluate χ_{aa}, $\chi_{aa}{}^{\mathrm{d}}$, and $\langle a^2\rangle$ separately the bulk magnetic susceptibility $\chi = (^1/_3)(\chi_{aa} + \chi_{bb} + \chi_{cc})$ must be measured. χ is not known for cyclopropenone so an alternate method of estimating χ by evaluating $\langle c^2\rangle$ by a reliable method will be employed[13] to give $\langle c^2\rangle = 5.1 \times 10^{-16}$ cm². Using this number, the remaining results are calculated and listed in Table VII.

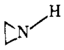
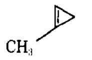
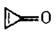
Conclusion and Discussion

The substitutional structure of cyclopropenone is shown in Figure 1. A limited comparison with cyclopropene is possible in spite of the fact that no ^{13}C isotopes were observed (in cyclopropene)[6] and therefore the cyclopropene ring structure may have larger uncertainties than the present work on cyclopropenone. It appears that the carbon double bond lengths (C_2–C_3) in cyclopropene and cyclopropenone are nearly identical, and the C_1–C_2(C_3) single bond is shorter in cyclopropenone. Just the opposite trends were observed in the cyclopropane–cyclopropanone molecules.[4] In cyclopropanone, both the C_1–C_2(C_3) single bond and the C_2–C_3 single bonds increased compared to the cyclopropane molecule.

The large molecular electric dipole and electric quadrupole moments in cyclopropenone compared to similar molecules[14,15] largely reflect the extremely large +CO− bond polarity in the molecule.

It is interesting to compare the ring magnetic susceptibility anisotropy in cyclopropenone with other three-membered ring molecules. The ring magnetic susceptibility anisotropy is the out-of-plane minus the average in-plane magnetic susceptibility ($\Delta\chi = \chi_{cc} - (^1/_2)(\chi_{aa} + \chi_{bb})$), which is independent of the orientation of the in-plane axes. In cyclopropenone (see Table VII) $\Delta\chi = -(17.8 \pm 1.0) \times 10^{-6}$ erg/(G² mol) compared to the nearly identical value of $\Delta\chi = -(17.0 \pm 0.5) \times 10^{-6}$ erg/(G² mol) in cyclopropene.[14] These results are listed in Table VIII along with $\Delta\chi$ for a number of other three-membered ring molecules.

Table VIII. The Magnetic Susceptibility Anisotropies $\Delta\chi = \chi_{cc} - (^1/_2)(\chi_{aa} + \chi_{bb})$ for a Number of Three-Membered Rings where *c* is the Out-of-Plane Axis

Molecule	$\Delta\chi$, 10^{-6} erg/(G² mol)	Ref
	−15.4 ± 0.4	*a*
	−9.5 ± 0.4	*b*
	−10.9 ± 0.7	*c*
	−10.0	*d*
	−16.6 ± 0.6	*e*
	−17.0 ± 0.5	*f*
	−15.2 ± 0.5	*g*
	−17.8 ± 1.0	This work

[a] D. H. Sutter and W. H. Flygare, *Mol. Phys.*, **16**, 153 (1969). [b] D. H. Sutter, W. Huttner, and W. H. Flygare, *J. Chem. Phys.*, **50**, 2869 (1969). [c] D. H. Sutter and W. H. Flygare, *J. Amer. Chem. Soc.*, **91**, 6895 (1969). [d] Estimated in ref 15. [e] R. C. Benson and W. H. Flygare, *J. Chem. Phys.*, **53**, 4470 (1970). [f] Reference 15. [g] R. C. Benson and W. H. Flygare, *ibid.*, in press.

The use of $\Delta\chi$ for a criterion of the extent of ring electronic delocalization has been discussed and there is substantial evidence to indicate that ring molecules with more negative values of $\Delta\chi$ than predicted on the basis of a local group set of $\Delta\chi$ values possess ring delocalization and a degree of aromaticity.[16] It also appears that the presence of a carbonyl group in a potentially aromatic ring dramatically suppresses nonlocal contributions to the out-of-plane molecular magnetic susceptibilities.[17]

In the case of cyclopropene it appears that a diamagnetic ring current exists (compare cyclopropene $\Delta\chi = -17.0 \pm 0.5$ with the open ring analog propene $\Delta\chi = -6.4 \pm 0.8$).[18] The expected effect of adding the C=O group in place of the CH_2 group in cyclopropene is to draw electrons out of the ring into the polar

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(13) T. D. Gierke, H. L. Tigelaar, and W. H. Flygare, *J. Amer. Chem. Soc.*, **94**, 330 (1972).

(14) W. H. Flygare and R. C. Benson, *Mol. Phys.*, **20**, 225 (1971).

(15) R. C. Benson and W. H. Flygare, *J. Chem. Phys.*, **51**, 3087 (1969).

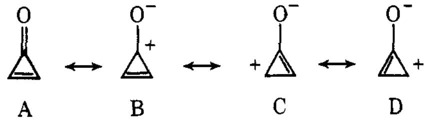
(16) R. C. Benson, C. L. Norris, W. H. Flygare, and P. A. Beak, *J. Amer. Chem. Soc.*, **93**, 5592 (1971).

(17) C. L. Norris, R. C. Benson, P. Beak, and W. H. Flygare, *ibid.*, **95**, 2766 (1973).

(18) R. C. Benson and W. H. Flygare, *Chem. Phys. Lett.*, **4**, 141 (1969).

$+C{=}O$ bond leaving the ring with the diamagnetic $4n + 2$ configuration of electrons. Thus, on first analysis, cyclopropenone should have a more negative $\Delta\chi$ (increased diamagnetism) than cyclopropene, a prediction which is in contrast with the observation. Two factors may be contributing to the lack of large diamagnetism in cyclopropenone. First of all, even in the completely delocalized cyclopropenyl cation, to which cyclopropenone is related, the diamagnetic ring current effects are small. As has been pointed out[19] in connection with the nmr spectra of cyclopropenyl cations, the delocalization of only two π electrons over such a small ring leads to ring-current deshielding effects only 25% of those in benzene.

The second factor is that cyclopropenone is not completely "delocalized;" *i.e.*, it is a hybrid of structures A–D which differ in energy and it is not simply a hybrid



of B, C, and D mixed with equal weight. This is apparent from the geometry determined in the present study and from ^{13}C nmr signals (in $CDCl_3$) at −155.1 ppm (C_1) and −158.3 ppm (C_2 and C_3) relative to tetramethylsilane; cyclopropenyl cation has its ^{13}C nmr signal at −174 ppm *vs.* tetramethylsilane.[20] Thus, cyclopropenone cannot be considered to be a cyclopropenyl cation almost unperturbed by the oxide substituent. In fact, our earlier work would suggest that the carbonyl group would act to suppress the diamagnetic anisotropy which could be present in the noncarbonyl substituted parent molecule. Discussion of the delocalization in terms of the above unequal contributions due to the presence of the carbonyl is a situation which has apparently not been treated in detail theoretically, although it is clear that if structure B is lower in energy than structures C and D, the result will be a decreased ring current compared with that in unperturbed cyclopropenyl cation.

It is interesting that by the magnetic criterion "aromaticity" cannot be detected, although aromaticity in cyclopropenone is suggested by its other chemical and physical properties. This again raises the question of the correlation between the different criteria of aromatic character and issues a caution that statements about "aromaticity" should be made only with respect to well-defined criteria and models.

Acknowledgment. We wish to thank J. Pochan, H. Andrist, and G. Ryan for help in the early stages of this work. The support of the National Science Foundation is gratefully acknowledged.

[19] R. Breslow, H. Hover, and H. W. Chang, *J. Amer. Chem. Soc.*, **84**, 3168 (1962).

[20] G. A. Olah and G. D. Mateescu, *ibid.*, **92**, 1430 (1970), report +17.8 ppm relative to CS_2; we have corrected this to the TMS scale.

Microwave Spectrum and Conformation of Formimide

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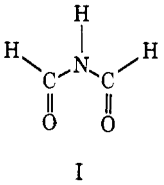
Abstract: The microwave spectrum of formimide and *N*-deuterioformimide has been investigated. Vibrational satellite structure and rotational constants strongly support an asymmetric cis–trans planar structure in the gas phase. An approximate treatment of the observed quadrupole coupling constants gives a C–N double bond character of 66%. A reinterpretation of the infrared spectrum of molten formimide shows that the cis–trans conformer is also preferred in the liquid phase. A cis–trans conformation is consistent with a bond dipole model and with the structures of similar compounds.

Formimide (diformamide, $HN(CHO)_2$) is one of the simplest molecules with an amide bond, a key determinant of protein conformation. The microwave spectrum of formimide was investigated to determine the gas phase conformational properties of this bond. All detailed structural studies to date on amides have shown the bond to be planar (solid state studies)[1–3] or very nearly planar (gas phase studies)[4–6] so formimide can be expected to be approximately planar. Three planar conformers (I–III) are possible in the keto form.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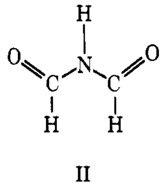
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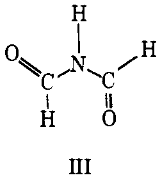
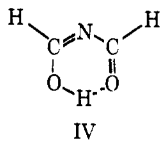

III


IV

Six rotameric forms of the enol tautomer are possible. Based on published studies of keto–enol isomerism,[7]

[1] J. E. Worsham, Jr., H. A. Levy, and S. W. Peterson, *Acta Crystallogr.*, **10**, 319 (1957).

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[3] M. Hospital and J. Housty, *Acta Crystallogr.*, **20**, 368 (1966); **21**, 413 (1966); D. R. Davies and R. A. Pasternak, *ibid.*, **9**, 334 (1956).

[4] D. J. Millen, G. Topping, and D. R. Lide, Jr., *J. Mol. Spectrosc.*, **8**, 153 (1962).

[5] J. K. Tyler, *ibid.*, **11**, 39 (1963).

[6] C. C. Costain and J. M. Dowling, *J. Chem. Phys.*, **32**, 158 (1960).

[7] J. Zabicky, Ed., "The Chemistry of the Carbonyl Group," Interscience, New York, N. Y., 1970, p 157.