Molecular g-Values, Magnetic Susceptibility Anisotropies and Molecular Electric Quadrupole Moment of Methylenecyclobutenone

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The rotational Zeeman-effect of methylenecyclobutenone has been investigated giving the molecular g-values: $g_{aa} = -0.0925 \pm 0.0003$, $g_{bb} = -0.0729 \pm 0.0003$, $g_{cc} = -0.0086 \pm 0.0003$ and the magnetic susceptibility anisotropies:

$$2\,\chi_{aa} - \chi_{bb} - \chi_{cc} = (23.0 \pm 0.5) \cdot 10^{-6}\ \mathrm{erg}/G^2\ \text{mole and}$$
$$2\,\chi_{bb} - \chi_{cc} - \chi_{aa} = (25.5 \pm 0.5) \cdot 10^{-6}\ \mathrm{erg}/G^2\ \text{mole.}$$

These values correspond to the following molecular electric quadrupole moments given in units of 10^{-26} esu cm^2: $Q_{aa} = 1.0 \pm 0.6$, $Q_{bb} = 2.8 \pm 0.6$ and $Q_{cc} = 3.8 \pm 1.0$. The experimental data of methylenecyclobutenone and similar strained ring molecules are compared with the results of INDO-calculations and values obtained from additivity rules for bond contributions.

The microwave spectrum of methylenecyclobutenone, its rotational constants, a tentative structure and the components of the electric dipole moment have been reported in a previous paper[1]. In the present note we report the results of a rotational Zeeman effect study at magnetic fieldstrengths close to 25 kG giving the diagonal elements of the molecular g-tensor, the magnetic susceptibility anisotropies and the diagonal elements of the molecular electric quadrupole moment tensor.

The sample was prepared by gas phase pyrolysis of furfuryl benzoate as described in Ref. [2]. The Zeeman spectrometer is a conventional 33 kHz Stark modulated microwave spectrograph combined with a high field electromagnet; experimental details may be found in Ref. [3].

Because of the presence of impurities comparatively high total pressures (5 to 10 mTorr) had to be used in order to get a good signal to noise ratio. Thus, pressure broadening determined the experimental line widths, which ranged from 150 to 250 kHz (full width at half height).

Only Zeeman splittings of rotational transitions with $J \leqq 3$, which are listed in Table 1, were used for the least squares fit of the magnetic constants. Because of sufficient spacing between the rotational levels first order perturbation theory within the basis of the asymmetric top eigenfunctions could be used[4] during the fitting procedure. The slight inhomogenity of the magnetic field was accounted for numerically as described in Ref. [5, 6].

The results are given in Table 2. Since $\Delta M = +1$ and $\Delta M = -1$ transitions could not be distinguished with the present setup, two sets of g-values, which differ only in sign, are suited to reproduce the Zeeman splittings. Additionally listed are the diagonal elements of the tensor of the molecular electric quadrupole moment as calculated from the g-values, the rotational constants and the susceptibility anisotropies according to Equation (1)[7].

$$\begin{aligned} Q_{aa} &= \frac{|e|}{2} \sum_{n}^{\text{nuclei}} Z_n \,(2\,a_n^2 - b_n^2 - c_n^2) - \frac{|e|}{2} \langle 0 | \sum_{\varepsilon}^{\text{electrons}} (2\,a_\varepsilon^2 - b_\varepsilon^2 - c_\varepsilon^2) | 0 \rangle \\ &= -\frac{|e|\,h}{16\,\pi^2 M_{\mathrm{p}}} \left(\frac{2\,g_{aa}}{G_{aa}} - \frac{g_{bb}}{G_{bb}} - \frac{g_{cc}}{G_{cc}} \right) - \frac{2\,m\,c^2}{|e|} (2\,\chi_{aa} - \chi_{bb} - \chi_{cc}) \qquad \text{and cyclic permutations.} \qquad (1) \end{aligned}$$

With the exception of $G_{aa} = 5775.664 \pm 0.009$ MHz, $G_{bb} = 4312.314 \pm 0.007$ MHz and $G_{cc} = 2467.814 \pm 0.008$ MHz, which stand for the rotational constants and are taken from Ref. [1], all symbols have their standard meanings. Since methylenecyclobutenone has an electric dipole moment, the quadrupole moments depend on the origin of the reference system. The values given in Table 2 are referred to the prin-

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Table 1. Zero field frequencies ν_0 and Zeeman splittings, $\Delta\nu=\nu-\nu_0$ for some low J rotational transitions of methylene-cyclobutenone. Listed fieldstrengths are values averaged over the effective volume of the absorption cell. Firs order perturbation theory within the asymmetric top eigenfunctions was used to calculate $\Delta\nu_{\mathrm{cal}}$ from the optimized g-values and susceptibilitiy anisotropies given in Table 2.

$J\,K_-\,K_+$	$-J'\,K'_-\,K'_+$		Frequency ν_0 [MHz]		Fieldstrength H [k Gauss]
	M	M'	$\Delta\nu_{\mathrm{exp}}$ [kHz]	$\Delta\nu_{\mathrm{cal}}$ [kHz]	$\Delta\nu_{\mathrm{exp}}-\Delta\nu_{\mathrm{cal}}$ [kHz]
1_{01}	-2_{02}		12589.413		$H=24.44$
	1	0	−1178.0	−1180.0	2.0
	1	2	698.0	674.0	24.0
	0	1	698.0	698.0	0.0
1_{10}	-2_{11}		15404.754		$H=25.54$
	0	0	−337.0	−330.0	−7.0
	1	1	24.0	28.0	−4.0
	−1	−1	693.0	699.0	−6.0
1_{10}	-2_{11}		15404.754		$H=24.44$
	0	−1	−1618.0	−1613.0	−5.0
	−1	0	1964.0	1965.0	−1.0
1_{11}	-2_{12}		11715.752		$H=25.54$
	1	1	−650.0	−663.0	13.0
1_{01}	-2_{12}		13179.140		$H=24.44$
	1	0	−1197.0	−1220.0	23.0
1_{11}	-2_{02}		11126.034		$H=25.54$
	1	1	−614.0	−641.0	27.0
1_{11}	-2_{20}		22610.256		H=25.54
	−1	−1	−572.0	−597.0	25.0
1_{11}	-2_{20}		22610.256		$H=24.44$
	−1	−2	−2586.0	−2571.0	−15.0
	0	−1	−1128.0	−1133.0	5.0
	−1	0	1129.0	1120.0	9.0
1_{10}	-2_{21}		19794.873		$H=25.54$
	0	0	−373.0	−350.0	23.0
	1	1	205.0	209.0	−4.0
	−1	−1	479.0	499.0	−20.0
1_{10}	-2_{21}		19794.873		$H=24.44$
	0	−1	−1812.0	−1804.0	−8.0
	0	1	976.0	1000.0	−24.0
	1	2	1313.0	1341.0	−28.0
	−1	0	1931.0	1947.0	−16.0
2_{20}	-3_{21}		23188.784		$H=24.44$
	0	−1	−1466.0	−1464.0	−2.0
	1	0	−1466.0	−1463.0	−3.0
	−2	−3	−912.0	−895.0	−17.0
	−1	0	1593.0	1618.0	−25.0
2_{11}	-3_{12}		22223.193		H=25.54
	−1	−1	101.0	108.0	−7.0
	−2	−2	508.0	513.0	−5.0
3_{13}	-3_{22}		13198.220		H=25.54
	−3	−3	−2346.0	−2343.0	−3.0
	−2	−2	−1206.0	−1203.0	−3.0
	−1	−1	−265.0	−279.0	14.0
3_{13}	-3_{22}		13198.220		$H=24.44$
	−1	0	800.0	801.0	−1.0
3_{22}	-3_{31}		12435.760		H=25.54
	−3	−3	−1685.0	−1676.0	−9.0
	−2	−2	−925.0	−913.0	−12.0
	−1	−1	−291.0	−272.0	−19.0
3_{22}	-3_{31}		12435.760		$H=24.44$
	−1	−2	−1977.0	−1954.0	−23.0
	0	−1	−1359.0	−1349.0	−10.0
3_{03}	-3_{12}		10854.581		H=25.54
	−3	−3	−2362.0	−2360.0	−2.0
	−2	−2	−1169.0	−1169.0	0.0
3_{03}	-3_{12}		10854.581		$H=24.44$
	−1	0	865.0	858.0	7.0

Table 2. Diagonal elements of the molecular *g*-tensor, magnetic susceptibility anisotropies and diagonal elements of the electric quadrupole tensor calculated according to Equation (1). The two sets of *g*-values can not be distinguished by the experiment. However set II, leading to unreasonably large *Q*-values, can be discarded. All experimental uncertainties are single standard deviations following from a least squares fit of the magnetic constants to the Zeeman splitting given in Table 1.

	I	II
g_{aa}	-0.0925 ± 0.0003	0.0925 ± 0.0003
g_{bb}	-0.0729 ± 0.0003	0.0729 ± 0.0003
g_{cc}	-0.0086 ± 0.0003	0.0086 ± 0.0003
$2\chi_{aa}-\chi_{bb}-\chi_{cc}$	$(23.0 \pm 0.5) \cdot 10^{-6}$ erg/G^2 mole	
$2\chi_{bb}-\chi_{cc}-\chi_{aa}$	$(25.5 \pm 0.5) \cdot 10^{-6}$ erg/G^2 mole	
$\Delta\chi = 2\chi_{cc}-\chi_{aa}-\chi_{bb}$	$-(48.5 \pm 1.0) \cdot 10^{-6}$ erg/G^2 mole	
Q_{aa}	$1.0 \pm 0.6 \cdot 10^{-26}$ esu cm^2	$-27.0 \pm 0.6 \cdot 10^{-26}$ esu cm^2
Q_{bb}	$2.8 \pm 0.6 \cdot 10^{-26}$ esu cm^2	$-31.7 \pm 0.6 \cdot 10^{-26}$ esu cm^2
Q_{cc}	$-3.8 \pm 1.0 \cdot 10^{-26}$ esu cm^2	$58.7 \pm 1.0 \cdot 10^{-26}$ esu cm^2

cipal axis system of the molecular moment of inertia tensor of the most abundant species (center of mass system).

With the quadrupole moments calculated from the two sets of *g*-values it is possible to make an unambigous choice for the signs of the *g*-values. Since the set with the positive values would lead to unreasonably large *Q*-values as compared to other molecules, it may be discarded.

Furthermore a short comment on vibrational averaging may be in place. Since experimental values, which are averaged over the zero point vibrations are used for the *g*-, *G*- and χ-values, the *Q*-values calculated from Eq. (1) do not correspond to the equilibrium configuration of the nuclear frame. Instead they will come quite close to the vibrationally averaged quadrupole moments, although the *g*- and *G*-values entering in Eq. (1) are averaged individually. A rough estimate based on the assumption, that all instantaneous values will not differ by more than 1% from the corresponding equilibrium values[8], leads to a discrepancy between quadrupole moments calculated from Eq. (1) and true zero point expectation values, which should not exceed 0.1×10^{-26} esu cm^2; this value is well below the experimental uncertainties.

For all further discussions of the data a knowledge of the structure of the nuclear frame is necessary. Since no complete structure informations are available for methylenecyclobutenone, we used the tentative structure derived in Ref.[1], which we feel to be sufficiently accurate to make the discussions meaningfull. With the sums $\sum_n Z_n a_n^2 = 66.0$ Å and $\sum_n Z_n b_n^2 = 50.3$ Å derived from the structure, we calculated the anisotropies of the second moments of the electronic charge distribution and the diagonal elements of the paramagnetic susceptibility tensor according to Eqs. (2) and (3) (an uncertainty of 1% for the above sums was assumed for the error propagation analysis). These values are given in Table 3.

Table 3. Anisotropies of the second moments of the electronic charge distribution calculated with Eq. (2) and for comparison the anisotropies calculated with INDO wavefunctions[9]. Diagonal elements of the paramagnetic susceptibility tensor calculated with Equation (3). The tentative structure presented in Ref.[1] was used for these calculations.

$\langle 0 \mid \sum_\varepsilon (a_\varepsilon^2 - b_\varepsilon) \mid 0 \rangle^{\mathrm{Exp}}$	$16.0 \pm 1.2 \cdot 10^{-16}$ cm^2
$\langle 0 \mid \sum_\varepsilon (b_\varepsilon^2 - c_\varepsilon^2) \mid 0 \rangle^{\mathrm{Exp}}$	$49.4 \pm 0.7 \cdot 10^{-16}$ cm^2
$\langle 0 \mid \sum_\varepsilon (c_\varepsilon^2 - a_\varepsilon^2) \mid 0 \rangle^{\mathrm{Exp}}$	$-65.4 \pm 0.8 \cdot 10^{-16}$ cm^2
$\langle 0 \mid \sum_\varepsilon (a_\varepsilon^2 - b_\varepsilon^2) \mid 0 \rangle^{\mathrm{INDO}}$	$16.1 \quad \cdot 10^{-16}$ cm^2
$\langle 0 \mid \sum_\varepsilon (b_\varepsilon^2 - c_\varepsilon^2) \mid 0 \rangle^{\mathrm{INDO}}$	$49.8 \quad \cdot 10^{-16}$ cm^2
$\langle 0 \mid \sum_\varepsilon (c_\varepsilon^2 - a_\varepsilon^2) \mid 0 \rangle^{\mathrm{INDO}}$	$-65.9 \quad \cdot 10^{-16}$ cm^2
χ_{aa}^{p}	$247.7 \pm 2.2 \cdot 10^{-6}$ erg/G^2 mole
χ_{bb}^{p}	$316.3 \pm 2.7 \cdot 10^{-6}$ erg/G^2 mole
χ_{cc}^{p}	$501.4 \pm 2.8 \cdot 10^{-6}$ erg/G^2 mole

$$\langle 0 \mid \sum_\varepsilon (a_\varepsilon^2 - b_\varepsilon^2) \mid 0 \rangle = \sum_n Z_n (a_n^2 - b_n^2) + \frac{h}{8\pi^2 M_{\mathrm{p}}} \left(\frac{g_{aa}}{G_{aa}} - \frac{g_{bb}}{G_{bb}} \right) + \frac{4 m c^2}{3 e^2} \left[(2\chi_{aa} - \chi_{bb} - \chi_{cc}) - (2\chi_{bb} - \chi_{cc} - \chi_{aa}) \right] \tag{2}$$

$$\chi_{aa}^{(\mathrm{p})} = -\frac{e^2}{2 m^2 c^2} \sum_\nu \frac{|\langle 0 \mid L_a \mid \nu \rangle|^2}{E_0 - E_\nu} = -\frac{e^2}{4 m c^2} \left(\frac{h}{8\pi^2 M_{\mathrm{p}}} \frac{g_{aa}}{G_{aa}} - \sum_n Z_n (b_n^2 + c_n^2) \right) \text{ and cyclic permutations .} \tag{3}$$

Eqs. (2) and (3) follow from the theoretical expressions for the effective G-, g- and χ-values, given in Eqs. (4), (5) and (6), if the small corrections $\frac{2}{I_{aa}^{(n)}}\left(\frac{L_a L_a}{\Delta}\right) \ll 1$ are neglected.

$$G_{aa} = \frac{h}{8\pi^2 I_{aa}^{(n)}}\left(1 + \frac{2}{I_{aa}^{(n)}}\left(\frac{L_a L_a}{\Delta}\right)\right) \tag{4}$$

$$g_{aa} = \frac{M_\mathrm{p}}{I_{aa}^{(n)}}\left(1 + \frac{2}{I_{aa}^{(n)}}\left(\frac{L_a L_a}{\Delta}\right)\right) \sum_n Z_n (b_n{}^2 + c_n{}^2) + \frac{2 M_\mathrm{p}}{m\, I_{aa}^{(n)}}\left(\frac{L_a L_a}{\Delta}\right) \tag{5}$$

$$\chi_{aa} = -\frac{e^2}{4 m c^2} \langle 0 | \sum_\varepsilon (b_\varepsilon{}^2 + c_\varepsilon{}^2) | 0 \rangle - \frac{e^2}{2 m^2 c^2}\left(\frac{L_a L_a}{\Delta}\right) = \chi_{aa}^\mathrm{d} + \chi_{aa}^\mathrm{p} \quad \text{and cyclic permutations.} \tag{6}$$

Equations (4) through (6) result from a second order perturbation treatment within the electronic functions under the neglect of vibration (see for instance Ref. [3]).

For comparison with the experimental values we have calculated the anisotropies $\langle 0 | \sum_\varepsilon a_\varepsilon{}^2 - b_\varepsilon{}^2 | 0 \rangle$ etc. from INDO wavefunctions as described in Ref. [9]. In Table 3 these calculated values are given additionally. They are in surprisingly close agreement with the values derived from the Zeeman data and the tentative structure. However, such a good agreement between calculated and experimental anisotropies $\langle 0 | \sum_\varepsilon a_\varepsilon{}^2 - b_\varepsilon{}^2 | 0 \rangle$ etc. appears to be quite normal as is demonstrated in Table 4. Actually the approximations used in the semiempirical approach and the neglect of vibrational averaging lead to INDO-values for $\langle 0 | \sum_\varepsilon a_\varepsilon{}^2 | 0 \rangle$ etc., which are generally slightly smaller than the experimental values derived from the magnetic data and rotational constants (compare too Table 4 in Ref. [9]). In the anisotropies, $\langle 0 | \sum_\varepsilon a_\varepsilon{}^2 - b_\varepsilon{}^2 | 0 \rangle$ etc., these systematic discrepancies do largely cancel and this leads to the good agreement between experimental and semiempirical values observed in Table 4.

For a complete evaluation of the Zeeman data leading to the individual components of the magnetic susceptibility tensor and of the second moments of the electronic charge distribution a knowledge of the bulk susceptibility, $\chi = (\chi_{aa} + \chi_{bb} + \chi_{cc})/3$ would be necessary. Because of experimental difficulties this value could not yet be determined. However, using the theoretical expressions for the g- and χ-values [Eqs. (4), (5) and (6)] together with the g-values, susceptibility anisotropies and rotational constants from the experiment and second moments for the electronic charge distribution as calculated from INDO-wavefunctions, it is possible to predict reasonable values for the missing data according to Equation (7).

$$\chi_{aa\,(\mathrm{predicted})} = -\frac{e^2}{4 m c^2}\left(\langle 0 | \sum_\varepsilon (b_\varepsilon{}^2 + c_\varepsilon{}^2) | 0 \rangle^\mathrm{INDO} + \frac{h}{8\pi^2 M_\mathrm{p}} \frac{g_{aa}}{G_{aa}} - \sum_n Z_n (b_n{}^2 + c_n{}^2)\right) \quad \text{and cyclic permutations.} \tag{7}$$

In view of the slight discrepancies between experimental and "INDO-values" for $\langle 0 | \Sigma a_\varepsilon{}^2 | 0 \rangle$ etc. mentioned above, we would expect that after a successful determination of the bulk susceptibility of methylenecyclobutenone, the experimental χ-values will turn out about 1.5 units more negative than the corresponding values given in Table 5.

In the last section we will briefly discuss the "nonlocal" contribution to the susceptibility anisotropy $2\chi_{cc} - (\chi_{aa} + \chi_{bb})$, which has been brought into connection with cyclic delocalization of π electrons and molecular currents in ring molecules [10, 11]. For this purpose the experimental susceptibilities are broken down into a sum over bond susceptibilities and a remaining rest called "nonlocal" or "molecular" susceptibility contribution. Flygare and coworkers [12] have derived a set of bond susceptibilities from a list of 14 nonstrained molecules, which in the traditional sense contain localized bonds only. For this purpose the authors fitted the bond susceptibilities $\chi_{(xx}^{\mathrm{b})}$, $\chi_{yy}^{(\mathrm{b})}$ and $\chi_{zz}^{(\mathrm{b})}$ by a least squares procedure to the experimental data $\chi_{aa}^{\mathrm{m})}$, $\chi_{bb}^{(\mathrm{m})}$, $\chi_{cc}^{(\mathrm{m})}$ of the different molecules according to Equation (8).

$$\chi_{aa}^{(m)} = \sum_{b}^{\text{bonds}} \left[\cos^2(a, x^{(b)})\,\chi_{xx}^{(b)} + \cos^2(a, y^{(b)})\,\chi_{yy}^{(b)} + \cos^2(a, z^{(b)})\,\chi_{jz}^{(b)}\right] \text{ and cyclic permutations} \qquad (8)$$

($\cos(a\,x^{(b)})$ = direction cosine between the molecular a-axis and the direction of the νth bond. For the definition of the xyz-system used for the bonds compare Table 6, where these bond susceptibilities which are of interest here are listed).

It should be mentioned that the standard deviations of the so obtained bond susceptibilities are relatively large (in the order of units). We feel that this does not merely reflect the experimental uncertainties, but also the fact that localized orbitals [13], which form the theoretical basis for all ad-

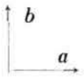
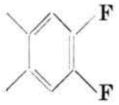
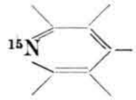
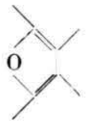
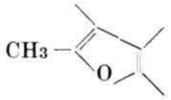
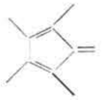
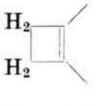
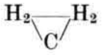
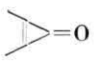
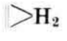
	$\langle 0 \mid \sum_\varepsilon a_\varepsilon^2 - b_\varepsilon^2 \mid 0\rangle^{\text{INDO}}$ $\langle 0 \mid \sum_\varepsilon b_\varepsilon^2 - c_\varepsilon^2 \mid 0\rangle^{\text{INDO}}$ $\langle 0 \mid \sum_\varepsilon c_\varepsilon^2 - a_\varepsilon^2 \mid 0\rangle^{\text{INDO}}$	$\langle 0 \mid \sum_\varepsilon a_\varepsilon^2 - b_\varepsilon^2 \mid 0\rangle^{\text{Exp}}$ $\langle 0 \mid \sum_\varepsilon b_\varepsilon^2 - c_\varepsilon^2 \mid 0\rangle^{\text{Exp}}$ $\langle 0 \mid \sum_\varepsilon c_\varepsilon^2 - a_\varepsilon^2 \mid 0\rangle^{\text{Exp}}$	Ref. for the experimental values
	37.1 82.3 −119.4	37.8 ± 1.6 81.8 ± 1.2 −119.5 ± 1.3	5
	0.4 49.0 −49.4	0.6 ± 0.2 48.6 ± 0.2 −49.2 ± 0.2	20
	−0.5 31.3 −30.7	−0.5 ± 0.2 31.0 ± 0.1 −31.4 ± 0.1	21
	51.4 30.9 −82.2	51.1 ± 1.4 30.6 ± 0.8 −81.7 ± 1.4	6
	40.2 37.0 −77.2	40.2 ± 1.0 36.6 ± 1.0 −76.8 ± 1.0	14
	16.2 54.2 −70.4	13.7 ± 1.6 * 55.9 ± 1.0 * −69.6 ± 1.2 *	14
	1.3 19.4 −20.7	1.6 ± 0.4 19.3 ± 0.4 −20.9 ± 0.3	15
	3.0 6.4 −9.4	3.0 ± 0.2 6.3 ± 0.1 −9.3 ± 0.1	20
	26.1 9.5 −35.6	25.9 ± 0.4 9.2 ± 0.3 −35.1 ± 0.4	16
	3.4 8.3 −11.6	4.2 ± 0.2 7.8 ± 0.4 −12.0 ± 0.2	17

Table 4. Experimental and calculated anisotropies of the second moment of the electronic charge distribution for some molecules. The experimental values have been evaluated with Eq. (2) and the INDO-values have been calculated with INDO wave functions [9]. The values are given in units of 10^{-16} cm^2.

* The experimental anisotropies of the second moments of the electronic charge distribution for 3,4-dimethylenecyclobutene have been recalculated according to Eq. (3) with data given in Ref [14], because the value for $\langle 0 \mid \sum_\varepsilon a_\varepsilon^2 - b_\varepsilon^2 \mid 0\rangle$ given in Ref. [14] is obviously a printing error.

Table 5. Second moments of the electronic charge distribution, diagonal elements of the diamagnetic susceptibility tensor and of the susceptibility tensor and bulk susceptibility. INDO-values [9] for the second moments of the electronic charge distribution lead to INDO-values for the diamagnetic part of the susceptibilities,

$$\chi_{aa}^{\mathrm{d}} = -(e^2/4\,m\,c^2)\,\langle 0 \mid \sum b_\varepsilon^2 + c_\varepsilon^2 \mid 0 \rangle^{\mathrm{INDO}} \text{ etc.}$$

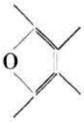
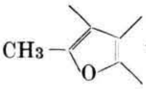
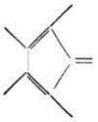
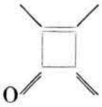
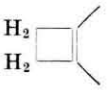
These values combined with the experimental g-values and rotational constants were used to predict the diagonal elements of the susceptibility tensor according to Equation (7).

$\langle 0 \mid \sum_\varepsilon a_\varepsilon^2 \mid 0 \rangle^{\mathrm{INDO}}$	$72.8 \cdot 10^{-16}\ \mathrm{cm}^2$
$\langle 0 \mid \sum_\varepsilon b_\varepsilon^2 \mid 0 \rangle^{\mathrm{INDO}}$	$56.7 \cdot 10^{-16}\ \mathrm{cm}^2$
$\langle 0 \mid \sum_\varepsilon c_\varepsilon^2 \mid 0 \rangle^{\mathrm{INDO}}$	$6.9 \cdot 10^{-16}\ \mathrm{cm}^2$
$\chi_{aa}^{\mathrm{d\ INDO}}$	$-269.9 \cdot 10^{-6}\ \mathrm{erg}/G^2$ mole
$\chi_{bb}^{\mathrm{d\ INDO}}$	$-338.1 \cdot 10^{-6}\ \mathrm{erg}/G^2$ mole
$\chi_{cc}^{\mathrm{d\ INDO}}$	$-549.5 \cdot 10^{-6}\ \mathrm{erg}/G^2$ mole
$\chi_{aa}^{\mathrm{predicted}}$	$-22.2 \cdot 10^{-6}\ \mathrm{erg}/G^2$ mole
$\chi_{bb}^{\mathrm{predicted}}$	$-21.8 \cdot 10^{-6}\ \mathrm{erg}/G^2$ mole
$\chi_{cc}^{\mathrm{predicted}}$	$-48.1 \cdot 10^{-6}\ \mathrm{erg}/G^2$ mole
$\overset{\mathrm{predicted}}{\chi} = (\chi_{aa} + \chi_{bb} + \chi_{cc})/3$	$-30.7 \cdot 10^{-6}\ \mathrm{erg}/G^2$ mole

Table 6. Some bond susceptibilities, used for the calculation of $\Delta\chi_{\mathrm{local}}$ in Table 7. These values are taken from Ref. [12] and given in units of $10^{-6}\ \mathrm{erg}/G^2$ mole. a) The $x\,y$-plane is assumed to the nodal plane of the π orbitals. b) The $x\,y$-plane is assumed to be spanned by the two single bonds of the oxygen atom.

bond ↑ y → x ↘ z (out of plane)	x	y	z
C−H	−5.6	−3.1	−3.1
C−C	−7.9	−0.2	−0.2
>C=C [a]	−0.8	4.0	−13.8
>C=O [a]	−1.3	2.2	−13.0
C−O [b]	−7.2	−6.7	−3.8

Table 7. Out-of-plane minus average in plane component of the magnetic susceptibility $\Delta\chi = 2\,\chi_{cc} - \chi_{aa} - \chi_{bb}$ for some molecules. The out of plane axis is c. Thevalues are given in units of $10^{-6}\ \mathrm{erg}/G^2$ mole.

↑ b a →	$\Delta\chi_{\mathrm{exp}}$	$\Delta\chi_{\mathrm{local}}$	$\Delta\chi_{\mathrm{nonlocal}} = \Delta\chi_{\mathrm{exp}} - \Delta\chi_{\mathrm{local}}$	Ref. for the experimental values
	−77.4 ± 0.5	−31.3	−46.1	6
	−67.8 ± 1.6	−28.5	−39.3	5
	−74.0 ± 1.8	−54.0	−19.8	12
	−48.5 ± 1.0	−55.4	6.9	this work
	−43.5 ± 1.3	−54.3	11.0	12
	−4.1 ± 1.2	−12.6	8.5	13

ditivity rules are never completely localized. We would there fore expect small "nonlocal" contributions to the $\chi_{aa}^{(\mathrm{m})}$ etc. even in the case of molecules with so called localized bonds only.

From the bond susceptibilities given in Table 6 the local contribution to the susceptibility anisotropy $2\,\chi_{cc} - (\chi_{aa} + \chi_{bb})$, c being the axis perpendicular to the molecular plane, has been calculated for methylenecyclobutenone and several other molecules. These values are given in Table 7. Even in view of the uncertainties of the bond susceptibility values a general trend is obvious from this table: Molecules which are aromatic in the formal sense (i.e. contain $[(4\,n+2)$ π-electrons$]$ show big negative or diamagnetic nonlocal contributions to the susceptibility anisotropy. On the other hand the three four-membered rings measured so far show positive (paramagnetic) nonlocal contributions.

Thus, similar to the situation in 3,4-dimethylenecyclobutene, the rather strong deshielding of the ring protons observed in the NMR-spectrum [2, 18] should probably not be explained as due to the molecular ring current induced in the π-system of the four membered ring.

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