The Molecular Zeeman Effect in 2-Methylfuran

W. Czieslik, U. Andresen, and H. Dreizler

Abteilung Chemische Physik im Institut für Physikalische Chemie der Universität Kiel

(Z. Naturforsch. **28 a**, 1906–1910 [1973]; received 3 October 1973)

The rotational Zeeman effect in 2-methylfuran has been measured and the results are compared with those of furan. The Zeeman parameters for the torsional A-species are $g_{aa} = -0.0704 \pm 0.0005$, $g_{bb} = -0.0335 \pm 0.0004$, $g_{cc} = +0.0253 \pm 0.0005$, $2\chi_{aa} - \chi_{bb} - \chi_{cc} = (23.6 \pm 0.9) \cdot 10^{-6}$ erg/(G^2 mole), $2\chi_{bb} - \chi_{aa} - \chi_{cc} = (44.2 \pm 0.7) \cdot 10^{-6}$ erg/(G^{2}mole). The corresponding values of the torsional E-species agree with those of the A-species within twice the standard deviation.

The out-of-plane minus the average in-plane components of the magnetic susceptibility, $\Delta\chi = \chi_{cc} - 1/2\,(\chi_{aa} + \chi_{bb})$, for 2-methylfuran and furan are compared. The substitution of a methyl group for a proton in the 2-position of furan changes $\Delta\chi$ by $+ (4.8 \pm 1.0) \cdot 10^{-6}$ erg/(G^{2}mole).

This communication is part of our investigations of substituted aromatic compounds. The analysis of the Zeeman-effect in 2-methylfuran extends the studies on heteroatomic five membered rings[1,2] to methyl substituted compounds. The special purpose of this work is to investigate the influence of a methyl group on the electronic structure of the ring.

The Zeeman microwave spectrometer used in this work is a conventional Stark-effect modulated microwave spectrometer combined with an electromagnet. The effective cell length is 2.10 m and the modulation frequency is 33 KHz. A detailed description of the spectrometer is given in Reference[3].

The microwave spectrum of 2-methylfuran had been assigned previously[4,5] and the zero field transitions were found without difficulty. Tables 1 and 2 show the observed and calculated Zeeman splittings for the torsional A- and E-species.

The analysis of the splittings follows a first order perturbation treatment given by Hüttner and Flygare[6]. The effect of the magnetic field on the rotational spectrum of a diamagnetic molecule with no nuclear quadrupole moment is given by

$$E(J,\tau,M) = -\tfrac{1}{2}\chi H_Z^2 - \mu_0 \frac{M H_Z}{J(J+1)} \sum_g g_{gg}\langle J_g^2\rangle - H_Z^2 \frac{3M^2 - J(J+1)}{(2J-1)(2J+3)(J+1)J} \cdot \sum_g (\chi_{gg} - \chi)\langle J_g^2\rangle . \quad (1)$$

J, τ and M are the rotational quantum numbers, $\chi = 1/3\,(\chi_{aa} + \chi_{bb} + \chi_{cc})$ is the bulk magnetic susceptibility; χ_{gg} are the diagonal elements of the susceptibility tensor; $g = a, b, c$ are the principal inertial axes; H_Z is the magnetic field in the space-fixed Z-direction, g_{gg} are the diagonal elements of the molecular g-tensor, $\langle J_g^2\rangle$ is the expectation value of the squared angular momentum component along the g-axis.

The magnitude and the relative signs of the g-values and two independent magnetic susceptibility anisotropies, which are chosen to be

$$2\chi_{aa} - \chi_{bb} - \chi_{cc} \quad \text{and} \quad 2\chi_{bb} - \chi_{aa} - \chi_{cc},$$

were calculated from Equation (1). The absolute signs of the g-values could be determined by the fact that the sum $\langle 0 | \sum c_i^2 | 0\rangle$ is a positive definite value; the other choice of the signs as given in Table 3 and 4 would lead to a negative value of $\langle 0 | \sum c_i^2 | 0\rangle$.

For a critical evaluation of the resulting constants, which were calculated by a least squares fit of the measured satellites, two main sources of systematic error should be considered:

1) The selection of the rotational transitions and their satellites for the calculation of the Zeeman parameters, as Eq. (1) neglects second and higher order perturbations.
2) The inhomogeneity of the magnetic field along the absorption cell.

To get an idea of the uncertainties arising from source 1, we calculated the Zeeman parameters for the torsional A- and E-species with different selections of satellites. First all resolved satellites were included. Then we repeated this calculation excluding those lines arising from near degenerate energy levels (energy differences less than 200 MHz). In the special case of 2-methylfuran these levels are

Reprint requests to W. Czieslik, Institut für Physikalische Chemie der Universität Kiel, Abteilung Chemische Physik, *D-2300 Kiel*, Olshausenstraße 40–60.

Table 1. Observed and calculated Zeeman splittings for the torsional A-species of 2-methylfuran (For explanation of the asterisks see Table 3).

J	K_-	K_+	—	J'	K'_-	K'_+	Frequency (MHz)		Fieldstrength (K Gauss)	
				M_l	M_u		Int.	Exp (KHz)	Cal (KHz)	Exp-Cal (KHz)
2	0	2	—	2	1	1	7329.499		$H = 24.16$	
				−2		−1	10	+ 482.0	494.5	−12.5
3	0	3	—	3	1	2	9197.065		$H = 21.84$	
				−2		−3	6	−1429.0	−1453.0	24.0
				−1		−2	10	− 620.0	− 623.9	3.9*
				−2		−1	10	− 284.0	− 294.7	10.7*
				0		−1	12	− 32.0	− 9.5	−22.5*
				0		1	12	754.0	775.2	−21.2*
3	0	3	—	3	1	2	9197.065		$H = 24.15$	
				−3		−3	9	−2043.0	−2028.9	−14.1*
				−2		−2	4	− 948.0	− 914.8	−33.2*
				3		3	9	724.0	715.5	8.5*
				2		2	4	904.0	914.8	−10.8*
1	1	1	—	2	1	2	11240.128		$H = 24.15$	
				1		1	3	− 871.0	− 859.2	−11.8
0	0	0	—	1	1	1	11358.717		$H = 21.84$	
				0		−1	2	− 231.0	− 199.6	−31.4*
				0		1	2	582.0	552.3	29.7*
0	0	0	—	1	1	1	11358.717		$H = 24.15$	
				0		0	1	− 428.0	− 431.4	3.4*
1	1	0	—	2	1	1	13195.541		$H = 24.15$	
				−1		−1	3	908.0	892.1	15.9*
2	1	1	—	2	2	0	15873.616		$H = 21.84$	
				−1		−2	4	−1496.0	−1499.6	3.6
				0		−1	6	− 972.0	−1000.6	28.6
				1		0	6	− 424.0	− 436.5	12.5
				2		1	4	195.0	192.8	2.2
2	1	1	—	2	2	0	15873.616		$H = 24.15$	
				−2		−2	4	− 672.0	− 683.0	11.0
				2		2	4	844.0	842.3	1.7
2	0	2	—	3	1	3	21183.211		$H = 22.07$	
				−2		−3	30	678.0	678.6	− 0.6*
2	0	2	—	3	1	3	21183.211		$H = 25.53$	
				2		2	5	− 538.0	− 550.2	12.2*
				1		1	8	− 442.0	− 435.9	− 6.1*
				0		0	9	− 286.0	− 299.5	13.5*
				−1		−1	8	− 141.0	− 141.0	− 0.0*
				−2		−2	5	48.0	39.7	8.3*
3	2	2	—	4	2	3	24338.569		$H = 25.53$	
				2		2	12	− 409.0	− 397.6	−11.4*
				0		0	16	− 85.0	− 82.1	− 2.9
				−1		−1	15	107.0	112.6	− 5.6*
2	1	1	—	3	2	2	34076.038		$H = 24.19$	
				−2		−3	30	− 41.0	− 40.1	− 0.9*
2	1	1	—	3	2	2	34076.038		$H = 25.53$	
				0		0	9	− 333.0	− 344.2	11.2
				1		1	8	− 197.0	− 243.0	46.0
				−1		−1	8	− 66.0	− 101.2	35.2*
				2		2	5	228.0	202.3	25.7*
				−2		−2	5	537.0	486.0	51.0*

Table 2. Observed and calculated Zeeman splittings for the torsional E-species of 2-methylfuran (For explanation of the asterisks see Table 4).

J	K_-	K_+	—	J'	K'_-	K'_+	Frequency (MHz) Int.	Exp (KHz)	Fieldstrength (K Gauss) Cal (KHz)	Exp-Cal (KHz)
				M_l		M_u				
2	0	2	—	2	1	1	7327.351		$H = 22.07$	
				−1		−2	4	−1145.0	−1148.5	3.5
				−2		−1	4	− 486.0	− 492.6	6.6
				−0		−1	6	− 189.0	− 191.9	2.9
2	0	2	—	2	1	1	7327.351		$H = 24.16$	
				−2		−2	4	−1593.0	−1577.1	−15.9
3	0	3	—	3	1	2	9194.981		$H = 21.84$	
				−1		−2	10	− 651.0	− 637.0	−14.0*
				−2		−1	10	− 270.0	− 281.8	11.8*
				0		−1	12	− 29.0	− 20.2	− 8.8*
				0		1	12	759.0	798.4	−39.4*
3	0	3	—	3	1	2	9194.981		$H = 24.15$	
				−3		−3	9	−2057.0	−2043.3	−13.7*
				−2		−2	4	− 911.0	− 918.3	7.3*
				3		3	9	724.0	711.6	12.4*
				2		2	4	912.0	918.3	− 6.3*
0	0	0	—	1	1	1	11355.765		$H = 21.84$	
				0		−1	2	− 213.0	− 206.7	− 6.3 *
				0		1	2	561.0	560.1	0.9*
0	0	0	—	1	1	1	11355.765		$H = 24.15$	
				0		0	1	− 419.0	− 432.2	13.2*
1	1	0	—	2	1	1	13195.193		$H = 24.15$	
				0		0	4	− 394.0	− 364.7	−29.3
				−1		−1	3	880.0	893.2	−13.2*
2	0	2	—	3	1	3	21180.791		$H = 22.07$	
				−2		−3	30	659.0	674.2	−15.2*
2	0	2	—	3	1	3	21180.791		$H = 25.53$	
				2		2	5	− 572.0	− 566.3	− 5.7*
				1		1	8	− 440.0	− 442.7	2.7*
				0		0	9	− 293.0	− 301.0	8.0*
				−1		−1	8	− 134.0	− 141.2	7.2*
				−2		−2	5	42.0	36.9	5.1*
3	2	2	—	4	2	3	24340.883		$H = 25.53$	
				3		3	7	− 479.0	− 511.2	32.2
				2		2	12	− 413.0	− 394.9	−18.1*
				−1		−1	15	108.0	107.7	0.3*
2	1	1	—	3	2	2	34065.211		$H = 24.19$	
				−2		−3	30	− 27.0	− 43.1	16.1*
2	1	1	—	3	2	2	34065.211		$H = 25.53$	
				−1		−1	8	− 96.0	− 96.5	0.5*
				2		2	5	236.0	193.0	43.0*
				−2		−2	5	501.0	496.6	4.4*

Table 3. Zeeman parameters for the torsional A-species of 2-methylfuran.

α: Fit of all resolved satellites (36 equations).

β: Fit excluding transitions to or from the levels 2_{21}, 2_{20} and 3_{22} (21 equations).

γ: Fit of those satellites marked with an asterisk in table 1 for comparison with the corresponding values for the E-species in Table 4 (24 equations).

δ: Fit taking into account the magnetic field inhomogeneity. All resolved satellites are used (36 equations).

quantity	α	β	γ	δ	unit
g_{aa}	-0.0704 ± 0.0005	-0.0724 ± 0.0009	-0.0716 ± 0.0009	-0.0705 ± 0.0005	—
g_{bb}	-0.0335 ± 0.0004	-0.0333 ± 0.0006	-0.0341 ± 0.0006	-0.0335 ± 0.0004	—
g_{cc}	0.0253 ± 0.0005	0.0252 ± 0.0005	0.0242 ± 0.0006	0.0253 ± 0.0005	—
$2\chi_{aa} - \chi_{bb} - \chi_{cc}$	23.6 ± 0.9	23.6 ± 1.2	22.2 ± 1.3	23.6 ± 0.9	10^{-6} erg/(G^{2}mole)
$2\chi_{bb} - \chi_{aa} - \chi_{cc}$	44.2 ± 0.7	44.1 ± 0.9	45.3 ± 0.9	44.2 ± 0.7	10^{-6} erg/(G^{2}mole)

Table 4. Zeeman parameters for the torsional E-species of 2-methylfuran.
α: Fit of all resolved satellites (30 equations).
β: Fit excluding transitions to or from the levels 2_{21}, 2_{20} and 3_{22} (23 equations).
γ: Fit of those satellites marked with an asterisk in table 2 for comparison with the corresponding values of the A-species in Table 3 (24 equations).
δ: Fit taking into account the magnetic field inhomogeneity. All resolved satellites are used (30 equations).

quantity	α	β	γ	δ	unit
g_{aa}	-0.0706 ± 0.0007	-0.0708 ± 0.0008	-0.0710 ± 0.0007	-0.0707 ± 0.0007	—
g_{bb}	-0.0347 ± 0.0005	-0.0350 ± 0.0004	-0.0344 ± 0.0005	-0.0347 ± 0.0005	—
g_{cc}	0.0246 ± 0.0004	0.0244 ± 0.0004	0.0248 ± 0.0004	0.0246 ± 0.0004	—
$2\chi_{aa} - \chi_{bb} - \chi_{cc}$	24.7 ± 0.9	25.5 ± 0.8	23.2 ± 1.1	24.7 ± 0.9	10^{-6} erg/(G^{2}mole)
$2\chi_{bb} - \chi_{aa} - \chi_{cc}$	44.3 ± 0.7	43.3 ± 0.7	44.7 ± 0.7	44.3 ± 0.7	10^{-6} erg/(G^{2}mole)

2_{21}, 2_{20}, 3_{22}, 3_{31}, 3_{30} and 4_{04}. For comparison the results are given in Table 3 and 4 column 1 and 2. It may be seen from the data that all Zeeman parameters agree within twice the standard deviation; the approximation used in Eq. (1) seems to be sufficient.

It was shown that a constant "effective" field can be found in a way that the calculated Zeeman parameters agree within the standard deviation with those considering the inhomogenious field. These results are given in Table 3 and 4 column 4.

To compare the Zeeman parameters for the torsional A- and E-species the procedure described is repeated for the same set of satellites from both species. The results of these calculations are given in Table 3 and 4, column 3. As may be seen from the data there are no differences between the Zeeman parameters of the torsional A- and E-species within twice the standard deviation. The influence of the torsion on the magnetic constants is not evident for this molecule.

From the above Zeeman parameters, together with the rotational constants, the geometry of the molecule and the bulk magnetic susceptibility the following quantities could be derived and are given in Table 5:

a) The diagonal elements Q_{gg} of the molecular quadrupole moment [Eq. (3) of Reference 1].
b) The diagonal elements $\chi_{gg}{}^p$ of the paramagnetic susceptibility tensor [Eq. (8) of Reference 1].
c) The anisotropies of the second moments of the electric charge distribution [Eq. (10) of Reference 1].
d) The diagonal elements χ_{gg} of the susceptibility tensor.
e) The diagonal elements $\chi_{gg}{}^d$ of the diamagnetic susceptibility tensor.
f) The second moments $\langle 0 | \sum g_i{}^2 | 0 \rangle$ of the electric charge distribution [Eq. (15) of Reference 1].

Since the r_s-structure of 2-methylfuran is not yet known we assumed the same structure as that given in Reference [5]. The sums $\sum Z_n g_n{}^2$ over all nuclei are included in Table 5 (Z_n = atomic number, $g_n = a$, b and c coordinate of the n-th atom respectively). The bulk magnetic susceptibility

$$\chi = 1/3\,(\chi_{aa} + \chi_{bb} + \chi_{cc})$$

was available only from liquid state measurements as $\chi = (-50.9 \pm 1.6) \cdot 10^{-6}$ erg/(G^2 mole)[7]. To account for the probable difference between the liquid and gas state values the above experimental error of χ was replaced by $\pm 5.0 \cdot 10^{-6}$ erg/(G^2 mole).

Table 5. Molecular constants of 2-methylfuran. The values are calculated with the Zeeman parameters of Table 3, column 1.

quantity	value	unit
Q_{aa}	6.4 ± 1.0	10^{-26} esu cm^2
Q_{bb}	0.0 ± 1.0	10^{-26} esu cm^2
Q_{cc}	-6.4 ± 1.6	10^{-26} esu cm^2
$\chi_{aa}{}^p$	164.3 ± 2.2	10^{-6} erg/(G^{2}mole)
$\chi_{bb}{}^p$	387.9 ± 4.9	10^{-6} erg/(Gmole)^2
$\chi_{cc}{}^p$	480.5 ± 5.1	10^{-6} erg/(G^{2}mole)
$\langle 0 \vert \sum (a_i{}^2 - b_i{}^2) \vert 0 \rangle$	51.1 ± 1.4	10^{-16} cm^2
$\langle 0 \vert \sum (b_i{}^2 - c_i{}^2) \vert 0 \rangle$	30.6 ± 0.8	10^{-16} cm^2
$\langle 0 \vert \sum (c_i{}^2 - a_i{}^2) \vert 0 \rangle$	-81.7 ± 1.4	10^{-16} cm^2
$\sum Z_n a_n{}^2$	85.6 ± 0.9	10^{-16} cm^2
$\sum Z_n b_n{}^2$	33.1 ± 0.3	10^{-16} cm^2
$\sum Z_n c_n{}^2$	1.6 ± 0.2	10^{-16} cm^2
$1/3\,(\chi_{aa} + \chi_{bb} + \chi_{cc})$	-50.9 ± 1.6	10^{-6} erg/(G^{2}mole)
χ_{aa}	-43.0 ± 5.3	10^{-6} erg/(G^{2}mole)
χ_{bb}	-36.2 ± 5.2	10^{-6} erg/(G^{2}mole)
χ_{cc}	-73.5 ± 5.5	10^{-6} erg/(G^{2}mole)
$\langle 0 \vert \sum a_i{}^2 \vert 0 \rangle$	90.8 ± 3.4	10^{-16} cm^2
$\langle 0 \vert \sum b_i{}^2 \vert 0 \rangle$	39.7 ± 3.4	10^{-15} cm^2
$\langle 0 \vert \sum c_i{}^2 \vert 0 \rangle$	9.1 ± 3.4	10^{-16} cm^2
$\chi_{aa}{}^d$	-207.3 ± 7.6	10^{-6} erg/(G^{2}mole)
$\chi_{bb}{}^d$	-424.0 ± 10.2	10^{-6} erg/(G^{2}mole)
$\chi_{cc}{}^d$	-554.1 ± 10.6	10^{-6} erg/(G^{2}mole)

Discussion

It is interesting to compare the out-of-plane minus the average in-plane component of the magnetic susceptibility $\Delta\chi = \chi_{cc} - 1/2\,(\chi_{aa} + \chi_{bb})$ of 2-methylfuran (for the A-species)

$$\Delta\chi = -\,(33.92 \pm 0.80) \cdot 10^{-6}\,\mathrm{erg/(G^2\,mole)}$$

with the corresponding value for furan

$$\Delta\chi = -\,(38.70 \pm 0.22) \cdot 10^{-6}\,\mathrm{erg/(G^2\,mole)}.$$

We find that the substitution of a proton in the 2-position of furan by a methyl group changes $\Delta\chi$ by $+\,(4.8 \pm 1.0) \cdot 10^{-6}\,\mathrm{erg/(G^2\,mole)}$.

According to Benson[8] it is possible to split the magnetic susceptibility anisotropy into a local and a nonlocal part. The latter is related to the molecular ring current, which may be taken as a measure of the aromaticity of the molecule. The local part of the susceptibility anisotropy can be calculated from the atomic susceptibility anisotropies given in Table 6. The results for 2-methylfuran and furan are

$$\Delta\chi_{'local'} = -\,(14.0 \pm 3.9) \cdot 10^{-6}\,\mathrm{erg/(G^2\,mole)}$$

and $\Delta\chi_{'local'} = -\,(15.6 \pm 3.1) \cdot 10^{-6}\,\mathrm{erg/(G^2\,mole)}$,

respectively. These values combined with the observed anisotropies $\Delta\chi$ lead to a nonlocal part

$$\Delta\chi_{'nonlocal'} = -\,(19.9 \pm 4.7) \cdot 10^{-}\,\mathrm{erg/(G^2\,mole)}$$

and $\Delta\chi_{'nonlocal'} = -\,(23.1 \pm 3.3) \cdot 10^{-6}\,\mathrm{erg/(G^2\,mole)}$

for 2-methylfuran and furan, respectively. The results show no significant difference between the nonlocal parts of the susceptibility anisotropies of 2-methylfuran and furan. Therefore, we cannot conclude that the ring currents and the associated aromaticities of furan and 2-methylfuran are different.

A detailed discussion of these results will be given when analogous data for more methyl substituted compounds are available.

Table 6. Susceptibility anisotropy $\Delta\chi_{atomic}$ of some groups of bonded atoms. Values taken from Reference 8, 9).

quantity		value	unit
sp^3-carbon,	$-C-$	$+\,1.6 \pm 0.8$	$10^{-6}\,\mathrm{erg/(G^2mole)}$
sp^2-carbon,	$=C-$	$-\,4.4 \pm 0.4$	$10^{-6}\,\mathrm{erg/(G^2mole)}$
carbonyl oxygen	$=O$	$-\,6.5 \pm 0.7$	$10^{-6}\,\mathrm{erg/(G^2mole)}$
ether oxygen	$-O-$	$+\,2.0 \pm 1.5$	$10^{-6}\,\mathrm{erg/(G^2mole)}$
sulfur	$-S-$	0.0 ± 2.0	$10^{-6}\,\mathrm{erg/(G^2mole)}$
hydrogen	$-H-$	≈ 0	$10^{-6}\,\mathrm{erg/(G^2mole)}$

Acknowledgement

We wish to thank Dr. D. Sutter who stimulated this investigation and Dr. H. Frieske who measured the liquid state bulk magnetic susceptibility. The calculations were done on the PDP 10 computer of the "Rechenzentrum der Universität Kiel". The financial support of the "Deutsche Forschungsgemeinschaft" and the "Fonds der Chemie" are gratefully acknowledged.

1 D. H. Sutter and W. H. Flygare, J. Amer. Chem. Soc. **91**, 4063 [1969].
2 W. Czieslik, D. Sutter, H. Dreizler, L. Norris, S. L. Rock, and W. H. Flygare, Z. Naturforsch. **27a**, 1691 [1972].
3 D. Sutter, Z. Naturforsch. **26a**, 1644 [1971].
4 W. G. Norris and L. C. Krisher, J. Chem. Phys. **51**, 403 [1969].
5 U. Andresen and H. Dreizler, Z. Naturforsch. **25a**, 570 [1970].
6 W. Hüttner and W. H. Flygare, J. Chem. Phys. **47**, 4137 [1967].
7 H. Frieske, private communication.
8 R. C. Benson, Ph. D. Thesis, University of Illinois, Urbana, Illinois 1972.
9 R. C. Benson, C. L. Norris, W. H. Flygare and P. Beak, J. Amer. Chem. Soc. **93**, 5591 [1971].