The Molecular Zeeman-Effect in 1,3-Difluorobenzene and 3-Methylfurane*

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The rotational Zeeman effect of 1,3-difluorobenzene and 3-methylfurane has been studied at magnetic fields close to 25 kG. From the splittings of the rotational transitions the diagonal elements of the molecular g-tensors and the anisotropies of the diagonal elements of the magnetic susceptibility tensors have been determined as:

$$g_{aa} = -0.0486 \pm 0.0002, \quad g_{bb} = -0.0315 \pm 0.0003, \quad g_{cc} = +0.0116 \pm 0.0003,$$
$$(2\,\chi_{aa} - \chi_{bb} - \chi_{cc})\,N_{\text{L}} = (46.6 \pm 0.4) \cdot 10^{-6}\ \text{erg}/(\text{G}^2\ \text{mole}),$$
$$(2\,\chi_{bb} - \chi_{cc} - \chi_{aa})\,N_{\text{L}} = (55.7 \pm 0.4) \cdot 10^{-6}\ \text{erg}/(\text{G}^2\ \text{mole})$$

for 1,3-difluorobenzene and as

$$g_{aa} = -0.0716 \pm 0.0006, \quad g_{bb} = -0.0370 \pm 0.0003, \quad g_{cc} = 0.0222 \pm 0.0003,$$
$$(2\,\chi_{aa} - \chi_{bb} - \chi_{cc})\,N_{\text{L}} = (25.7 \pm 0.6) \cdot 10^{-6}\ \text{erg}/(\text{G}^2\ \text{mole}),$$
$$(2\,\chi_{bb} - \chi_{cc} - \chi_{aa})\,N_{\text{L}} = (43.1 \pm 0.5) \cdot 10^{-6}\ \text{erg}/(\text{G}^2\ \text{mole})$$

for 3-methylfurane. From comparison with related compounds position dependent substitution effects on the susceptibility anisotropies become appearent. The scheme of local atom susceptibilities is extended to fluorine containing molecules.

The rotational spectra of 1,3-difluorobenzene and of 3-methylfurane are well known from earlier microwave spectroscopical investigations[1, 2]. In the following we report the results of a rotational Zeeman-effect investigation carried out in order to get more information on substitution effects on the magnetic susceptibility anisotropies of small aromatic molecules[3–5].

Experimental

The 1,3-difluorobenzene sample has been obtained from EGA-Chemie and was used after a vacuum destillation without further purification. 3-Methylfurane has been prepared from 4,4-dimethoxy-2-butane and methylchloracetate by a method described by Burness[6, 7]. The spectra were recorded with a conventional Stark-effect modulated microwave spectrometer equipped with an electromagnet of 2.5 m gap length. The effective cell length was reduced to 1.8 m in order to avoid the inhomogenious regions at both ends of the gap. A frequency of 33 kHz was used for the square wave Stark-effect modulation field. Details of the design of the Zeeman-microwave-spectrometer may be found in References[8, 9]. All spectra were taken at sample pressures close to 10 mTorr and at temperatures close to −60 °C. Observed linewidths which are essentially due to collision broadening were on the order of 100 to 150 kHz. The measured zero field frequencies and shifts of the Zeeman satellites with respect to the zero field frequencies are listed in Tables 1 and 2.

Analysis of the Zeeman-splittings

The standard effective Hamiltonian of a rigid rotor molecular rotating in an exterior magnetic field given by Eq. (1)[10] was used for the analysis of the Zeeman splittings.

$$\mathcal{H}_{\text{eff}} = \underbrace{h\,\{A\,\mathbf{J}_a^2 + B\,\mathbf{J}_b^2 + C\,\mathbf{J}_c^2\}}_{\mathcal{H}_{\text{rot}}} \underbrace{- \frac{\mu_{\text{N}}}{2}\{\mathbf{J}^{\text{t}} \cdot g^{\dagger} \cdot \mathbf{H} + \mathbf{H}^{\text{t}} \cdot g \cdot \mathbf{J}\}}_{\mathcal{H}_g} \underbrace{- \tfrac{1}{2}\,\mathbf{H}^{\text{t}} \cdot \chi \cdot \mathbf{H}}_{\mathcal{H}_\chi} \tag{1}$$

$\mathbf{J}^{\text{t}} = (\mathbf{J}_a, \mathbf{J}_b\ \mathbf{J}_c)$ = one row matrix corresponding to the rotational angular momentum vector measured in units of $\hbar$ and referred to the molecular principal inertia axes system $(a,\ b,\ c)$. Super t denotes the transposed matrix.

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Table 1. Measured and calculated frequencies of Zeeman satellites of some rotational transitions of 1,3-difluorobenzene used for the calculation of the Zeeman parameters g_{aa}, g_{bb}, g_{cc}, $2\chi_{aa}-\chi_{bb}-\chi_{cc}$ and $2\chi_{bb}-\chi_{cc}-\chi_{aa}$ by a least squares fit. Given fieldstrengths are the arithmetic mean over the absorption volume. For some satellites a lineshape analysis was necessary. Lorentzians with 100 kHz full widths at half height were used in these calculations. $\Delta\nu_{\mathrm{corr}}$ gives the overlap-correction, while $\Delta\nu_{\mathrm{cal}}$ are Zeeman shifts calculated for zero linewidths (bar spectrum). The observed shifts should be compared to $\Delta\nu_{\mathrm{cal}}+\Delta\nu_{\mathrm{corr}}$.

rotational transition frequency magnetic fieldstrength	$M \rightarrow M'$	$\Delta\nu_{\mathrm{exp}}$ [kHz]	$\Delta\nu_{\mathrm{cal}}$ [kHz]	$\Delta\nu_{\mathrm{corr}}$ [kHz]
$3_{13} \rightarrow 3_{22}$	−3 → −3	−2318	−2316	
8545.330 MHz	−2 → −2	−823	−822	
25.565 kG	3 → 3	150	149	
	2 → 2	823	822	
$2_{02} \rightarrow 3_{13}$	2 → 2	−733	−734	
9493.392 MHz	1 → 1	−505	−512	
25.565 kG	0 → 0	−351	−361	7
	−1 → −1	−294	−283	−4
$3_{21} \rightarrow 3_{30}$	−3 → −3	−884	−885	
10900.827 MHz	−2 → −2	−442	−450	
25.565 kG	3 → 3	459	466	−4
$3_{22} \rightarrow 3_{31}$	−3 → −3	−1556	−1556	
11386.346 MHz	−2 → −2	−646	−653	
25.565 kG	3 → 3	400	403	
	2 → 2	650	653	−4
$1_{10} \rightarrow 2_{21}$	0 → 0	−748	−754	
12430.111 MHz	1 → 1	653	656	
25.565 kG	−1 → −1	826	825	
$1_{10} \rightarrow 2_{21}$	0 → −1	−1295	−1286	
12430.111 MHz	−1 → −2	−381	−381	
21.940 kG	1 → 2	672	668	
$1_{10} \rightarrow 2_{21}$	0 → −1	−1494	−1492	
12430.111 MHz	1 → 2	738	751	
24.153 kG				
$1_{11} \rightarrow 2_{20}$	−1 → −1	−432	−432	
13097.117 MHz	1 → 1	339	330	
25.560 kG	0 → 0	1109	1113	
$1_{11} \rightarrow 2_{20}$	−1 → −2	−1793	−1784	
13097.117 MHz	1 → 0	−158	−161	
24.165 kG	0 → −1	78	69	
	1 → 2	353	337	
	−1 → 0	511	521	
	0 → 1	1476	1470	
$2_{11} \rightarrow 3_{22}$	0 → 0	−412	−434	6
14824.813 MHz	1 → 1	−310	−302	−3
25.560 kG	−1 → −1	−151	−133	−4
	2 → 2	273	265	
	−2 → −2	608	603	
$2_{11} \rightarrow 3_{22}$	2 → 3	650	648	
14824.813 MHz				
24.153 kG				
$2_{12} \rightarrow 3_{21}$	−2 → −2	−1669	−1679	
17012.104 MHz	0 → 0	1078	1103	−15
25.560 kG	1 → 1	1078	1068	17
$2_{12} \rightarrow 3_{21}$	−2 → −3	−2396	−2407	
17012.104 MHz	1 → 2	1280	1293	
24.170 kG				
$2_{12} \rightarrow 3_{21}$	−2 → −3	−2425	−2405	
17012.104 MHz	−1 → −2	−565	−580	
24.153 kG	1 → 0	527	525	
	1 → 2	1300	1292	
	0 → 1	1440	1436	

Table 2. Measured and calculated frequencies of Zeeman-satellites of some rotational transitions of 3-methylfurane, used for the calculation of the Zeeman parameters g_{aa}, g_{bb}, g_{cc}, $2\chi_{aa}-\chi_{bb}-\chi_{cc}$ and $2\chi_{bb}-\chi_{cc}-\chi_{aa}$ by a least squares fit. Only the A-species satellites have been used for the fit. In bracketts some E-species frequencies are given for comparison. Within the present approximation the calculated Zeeman splittings for both species are the same. Given fieldstrengths are the arithmetic mean over the absorption volume. These values were used for the least squares fit.

rotational transition frequency magnetic fieldstrength	$M \rightarrow M'$	$\Delta\nu_{\mathrm{exp}}$ [kHz]	$\Delta\nu_{\mathrm{cal}}$ [kHz]
$3_{03} \rightarrow 3_{12}$			
9052.450 MHz	−3 → −3	−1975	−1981
24.10 kG			
$1_{11} \rightarrow 2_{12}$	−1 → −1	−64 (−65)	−54
10804.900 MHz	0 → 0	−64 (−65)	−59
(10805.825 MHz)	1 → 1	−838	−841
24.10 kG			
$1_{11} \rightarrow 2_{12}$			
10804.900 MHz	1 → 2	−47 (−87)	−65
(10805.825 MHz)	−1 → −2	608	600
24.09 kG			
$0_{00} \rightarrow 1_{11}$			
11372.523 MHz	0 → 1	580 (555)	584
(11367.618 MHz)	0 → −1	−251 (−225)	−240
21.88 kG			
$0_{00} \rightarrow 1_{11}$			
11372.523 MHz	0 → 0	−415 (−417)	−418
(11367.618 MHz)			
24.10 kG			
$1_{01} \rightarrow 2_{02}$			
11593.904 MHz	0 → 0	25 (25)	17
(11593.904 MHz)			
25.57 kG			
$1_{10} \rightarrow 2_{11}$			
12580.079 MHz	0 → 0	−378 (−376)	−369
(12579.161 MHz)			
24.10 kG			
$1_{10} \rightarrow 2_{11}$			
12580.079 MHz	−1 → −2	−168 (−178)	−176
(12579.161 MHz)			
24.09 kG			
$1_{01} \rightarrow 2_{12}$	−1 → −1	−287 (−302)	−329
16331.170 MHz	0 → 0	−287 (−302)	−256
(16327.180 MHz)	1 → 1	−491 (−487)	−489
25.57 kG			
$2_{21} \rightarrow 3_{22}$	−2 → −2	1055	1033
17538.701 MHz	−1 → −1	317	317
25.54 kG	0 → 0	−202	−200
$2_{11} \rightarrow 3_{12}$	−1 → −1	124 (142)	135
18804.702 MHz	0 → 0	−112 (−113)	−89
(18804.443 MHz)	1 → 1	−112 (−113)	−101
25.57 kG	2 → 2	124 (142)	101
$2_{11} \rightarrow 3_{12}$	−1 → 0	661	674
18804.702 MHz	−2 → −3	−251 (−277)	−247
(18804.443 MHz)	−1 → −2	−536 (−545)	−532
24.09 kG	1 → 0	−536 (−545)	−534
	2 → 1	−251 (−277)	−252
$4_{14} \rightarrow 4_{23}$	−4 → −4	−2491	−2491
22507.820 MHz	−3 → −3	−1539	−1554
24.10 kG	3 → 3	1240	1240
	4 → 4	1240	1235
$4_{14} \rightarrow 4_{23}$			
22507.820 MHz	−2 → −1	−398	−396
21.88 kG			

$\mathbf{H}^t = H_Z(\cos a\,Z,\ \cos b\,Z,\ \cos c\,Z)$ = one row matrix corresponding to the vector of the exterior magnetic field if referred to the principal inertia axes system. The exterior field is assumed to point into the direction of the space fixed Z-axis. $\cos a\,Z$, $\cos b\,Z$, $\cos c\,Z$ are the instantaneous direction cosines between the space fixed Z-axis and the a-, b-, and c-principal inertia axis of the rotating molecule.

$\mu_N = |e|\,\hbar/2\,M_p\,c$ = nuclear magneton.

g = 3 by 3 matrix corresponding to the molecular g-tensor. $g^\dagger$ denotes the complex conjugate of the transposed g-matrix (g is not hermitian).

χ = 3 by 3 matrix corresponding to the molecular magnetic susceptibility tensor.

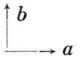
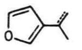
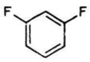
Equation (1) results from a second order perturbation treatment within the electronic states[11] which also leads to the theoretical expressions for the rotational constants and the g- and χ-tensor elements. Since at fields close to 25 kG $\mathcal{H}_g$ and $\mathcal{H}_\chi$ lead to matrix elements which are on the order of 10^{-3} smaller than those of $\mathcal{H}_{\text{rot}}$, a first order perturbation treatment within the asymmetric top basis $|J, \tau, M\rangle$ (in which $\mathcal{H}_{\text{rot}}$ is diagonal) is sufficient to reproduce the Zeeman splittings within the experimental uncertainties. This leads to a first order Zeeman contribution to the rotational energy levels as given in Equation (2)[12].

$$\Delta E_{J\tau M} = -\mu_N H_z \frac{M}{J(J+1)} \sum_{\gamma=a,b,c} g_{\gamma\gamma} \langle J, \tau \| \mathbf{J}_\gamma^2 \| J, \tau \rangle - \tfrac{1}{2}\overline{\chi} H_z^2 - H_z^2 \frac{3M^2 - J(J+1)}{(2J-1)(2J+3)J(J+1)} \cdot \sum_{\gamma=a,b,c} (\chi_{\gamma\gamma} - \overline{\chi}) \langle J, \tau \| J_\gamma^2 \| J, \tau \rangle\,. \tag{2}$$

M and J are rotational quantum numbers; $\chi_{\gamma\gamma}$ are the diagonal elements of the susceptibility tensor ($\gamma = a, b, c$); $\overline{\chi} = (\chi_{aa} + \chi_{bb} + \chi_{cc})/3$ is the bulk susceptibility; $g_{\gamma\gamma}$ are the diagonal elements of the molecular g-tensor ($\gamma = a, b, c$); $\langle \| J_\gamma^2 \| \rangle$ are the asymmetric top expectation values for the squares of the angular momentum operators.

Equation (2) may be used not only for difluorobenzene but also for 3-methylfurane even though internal methyl top rotation is present in this molecule and causes a splitting of the rotational absorption lines into A,E-doublets[13, 14] of equal intensity with a spacing typically on the order of 1 MHz. The E-type components stem from molecules in which the methyl top may be regarded to "tunnel" clock-

Table 3. g-values, magnetic susceptibility anisotropies and rigid rotor rotational constants of 3-methylfurane and m-difluorobenzene fitted to the splittings and zero field frequencies resp. given in Tables 1 and 2. The rotational constants agree within 20 kHz with those published by[1, 2]. Quoted uncertainties are standard deviations from the least squares fit. (With the present experimental setup only the relative signs of the g-values can be determined. The choice in bracketts would lead to a negative value of the electronic ground state expectation value for the sum of the squares of the c-coordinates of the electrons and may be discarded.)

			
Molecular g-values	g_{aa}	($\mp$) 0.0716(6)	($\mp$) 0.0486(2)
	g_{bb}	($\mp$) 0.0370(3)	($\mp$) 0.0315(3)
	g_{cc}	($\pm$) 0.0222(3)	($\pm$) 0.0116(3)
Molar magnetic susceptibility anisotropies	$N_L(2\chi_{aa} - \chi_{bb} - \chi_{cc})$ [10^{-6} erg/(G^2 mole)]	25.7(6)	46.6(4)
	$N_L(2\chi_{bb} - \chi_{cc} - \chi_{aa})$ [10^{-6} erg/(G^2 mole)]	43.1(5)	55.7(4)
Rotational constants	A [MHz]	8893.176(15) *	3744.249(1)
	B [MHz]	3366.905(05) *	1760.545(1)
	C [MHz]	2479.321(05) *	1197.355(1)
Liquid-phase bulk magnetic susceptibilities in units of 10^{-6} erg/(G^2 mole) $\chi_{\text{bulk,mole}} = N_L(\chi_{aa} + \chi_{bb} + \chi_{cc})/3$		-53.2 ± 5.0 **	-62.9 ± 2.0 ***

* A-species rotational constants.

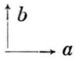
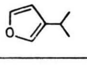
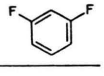
** This value was determined by an NMR method[24–26].

*** Determined by the Faraday method [experimental uncertainty: $0.5 \cdot 10^{-6}$ erg/(G^2 mole)]. Given uncertainties for the bulk susceptibilities are estimated and believed to embrace also possible differences between gas- and liquid-phase values.

wise or counter-clockwise through the potential barrier, while the A-type components stem from molecules in which the tops may be regarded "at rest" with respect to the potential wells. In molecules with extremely low barriers such as CH_3NO_2 and CH_3BF_2 internal methyl top rotation indeed becomes evident also in the Zeeman spectra [15, 16]. In 3-methylfurane however with $V_3 = 1.19$ kcal/mole [17] the barrier is sufficiently high so that internal rotation may be neglected as far as the Zeeman fine structure is concerned [18]. Thus, within the experimental uncertainties of a microwave experiment, the Zeeman satellite patterns consist of two superimposed identical multiplets with splittings governed by Eq. (2), one multiplet originating from the A- and the other from the E-zero field frequency.

Through Eq. (2) each measured Zeeman satellite leads to a linear equation with g_{aa}, g_{bb}, g_{cc}, $2\chi_{aa} - \chi_{bb} - \chi_{cc}$ and $2\chi_{bb} - \chi_{cc} - \chi_{aa}$ as unknowns. A least squares fit of these molecular parameters to

Table 4. Molecular quantities derived from the experimental data given in Table 3 the geometries of the nuclear frames and the bulk magnetic susceptibilities. Quoted uncertainties follow from standard error propagation.

			
Molecular quadrupole moments in units of 10^{-26} esu cm²	Q_{aa}	2.4±0.8	−5.0±0.9
$Q_{aa} = \frac{\lvert e \rvert}{2} \{ \sum_n^{\text{nuclei}} (2a_n^2 - b_n^2 - c_n^2) - \langle 0 \mid \sum_\varepsilon^{\text{electrons}} (2a_\varepsilon^2 - b_\varepsilon^2 - c_\varepsilon^2) \mid 0 \rangle \}$	Q_{bb}	3.1±0.7	7.6±1.0
$= - \frac{h \lvert e \rvert}{16\pi^2 M_p} \left\{ \frac{2g_{aa}}{A} - \frac{g_{bb}}{B} - \frac{g_{cc}}{C} \right\} - \frac{2mc^2}{\lvert e \rvert} \{ 2\chi_{aa} - \chi_{bb} - \chi_{cc} \}$	Q_{cc}	−5.5±1.1	−2.6±1.3
Second moments of the nuclear charge distribution calculated	$\sum_n Z_n a_n^2$	87.2±0.8 **	143.3±2.0
from the geometry of the nuclear frame. The units are Å².	$\sum_n Z_n b_n^2$	34.8±0.3 **	71.3±2.0
See Figure 1.	$\sum_n Z_n c_n^2$	1.6±0.02 **	0.0±0.0
Paramagnetic susceptibilities in units of 10^{-6} erg/(G² mole).	$\chi^{p}_{aa,\,\text{mole}}$	171.6±1.5	330.3±8.6
$\chi^{p}_{aa,\,\text{mole}} = - \frac{N_L e^2}{2m^2c^2} \sum_\nu^{\text{excited states}} \frac{\lvert \langle 0 \mid L_a \mid \nu \rangle \rvert^2 *}{E_0 - E_\nu}$	$\chi^{p}_{bb,\,\text{mole}}$	400.3±3.7	646.4±8.9
$= - \frac{e^2}{4mc^2} \left\{ \frac{h}{8\pi^2 M_p} \frac{g_{aa}}{A} - \sum_n^{\text{nuclei}} Z_n (b_n^2 - c_n^2) \right\} N_L$	$\chi^{p}_{cc,\,\text{mole}}$	498.8±3.7	890.3±9.0
Diamagnetic susceptibilities in units of 10^{-6} erg/(G² mole).	$\chi^{d}_{aa,\,\text{mole}}$	−216.3±6.7	−377.6±10.7
$\chi^{d}_{aa,\,\text{mole}} = - \frac{N_L e^2}{4mc^2} \langle 0 \mid \sum_\varepsilon^{\text{electrons}} b_\varepsilon^2 + c_\varepsilon^2 \mid 0 \rangle$	$\chi^{d}_{bb,\,\text{mole}}$	−439.1±8.8	−690.7±11.0
$= \chi_{aa,\,\text{mole}} - \chi^{p}_{aa,\,\text{mole}}$	$\chi^{d}_{cc,\,\text{mole}}$	−574.9±9.1	−987.4±11.3
Second moments of the electronic charge distribution in Å²	$\langle 0 \mid \sum_\varepsilon a_\varepsilon^2 \mid 0 \rangle$	94.0±3.0	153.2± 4.9
$\langle 0 \mid \sum_\varepsilon^{\text{electrons}} a_\varepsilon^2 \mid 0 \rangle = - \frac{2mc^2}{e^2} (\chi_{bb} + \chi_{cc} - \chi_{aa})$	$\langle 0 \mid \sum_\varepsilon b_\varepsilon^2 \mid 0 \rangle$	41.5±3.0	79.4± 4.9
$- \frac{h}{16\pi^2 M_p} \left(\frac{g_{bb}}{B} + \frac{g_{cc}}{C} - \frac{g_{aa}}{A} \right) + \sum_n^{\text{nuclei}} Z_n a_n^2$	$\langle 0 \mid \sum_\varepsilon c_\varepsilon^2 \mid 0 \rangle$	9.5±3.0	9.5± 4.9
Molecular quadrupole moments calculated from INDO wavefunctions [19]. The units are 10^{-26} esu cm²	Q_{aa}^{INDO}	0.0	−6.3
	Q_{bb}^{INDO}	4.0	7.7
	Q_{cc}^{INDO}	−4.0	−1.4
Second moments of the electronic charge distribution calculated from INDO wavefunctions [19]. The units are Å²	$\langle 0 \mid \sum_\varepsilon a_\varepsilon^2 \mid 0 \rangle^{\text{INDO}}$	93.8	152.5
	$\langle 0 \mid \sum_\varepsilon b_\varepsilon^2 \mid 0 \rangle^{\text{INDO}}$	40.4	82.9
	$\langle 0 \mid \sum_\varepsilon c_\varepsilon^2 \mid 0 \rangle^{\text{INDO}}$	8.9	8.8

* $L_a = \frac{\hbar}{i} \sum_\varepsilon^{\text{electrons}} \left(b_\varepsilon \frac{\partial}{\partial c_\varepsilon} - c_\varepsilon \frac{\partial}{\partial b_\varepsilon} \right)$ corresponds to the operator for the *a*-component of the electronic angular momentum.

** Quoted uncertainties are based on an estimated upper limit of 0.02 Å for the uncertainties of the bond lengths.

the observed frequency shifts gives the results presented in Table 3; in addition the measured bulk magnetic susceptibilities and the experimental rigid rotor rotational constants which enter into the subsequent analysis of the Zeeman data are listed in this Table. Table 4 gives a list of derived quantities which follow from the experimental values listed in Table 3 and the rigid rotor theoretical expressions for the rotational constants and the g- and χ-tensor elements. Also listed for comparison are values calculated from INDO-wavefunctions using certain approximations as discussed in Reference [19].

Discussion

In the following we will discuss briefly the effects of F- and CH_3-substitutions on the magnetic susceptibilities. As was pointed out first by Flygare and coworkers [20] it is possible within certain limits to break up the measured susceptibilities into a sum of local (atomic) contributions plus a nonlocal (molecular) contribution. In their paper Flygare et al. also proposed the out of plane molecular susceptibility, in our case $\chi_{cc,\,\text{nonlocal}}$, as a measure of electron delocalization over the ring. For the present investigation the original list [21] of local susceptibility tensors was extended to fluorine [22]. A detailed description of the procedure has been given in Refs. [22] and [23] and will not be repeated here. In Table 5 a list of presently available atomic susceptibility tensors is reproduced from which the local contribution to the molecular susceptibility tensor may be calculated according to Eq. (3)

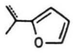
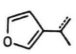
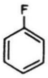
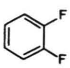
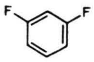
$$\chi_{aa,\,\text{nonlocal}} = \sum_{A}^{\text{atoms}} \{\cos^2(a\,x^{(A)})\,\chi_{xx}^{(A)} + \cos^2(a\,y^{(A)})\,\chi_{yy}^{(A)} + \cos^2(a\,z^{(A)})\,\chi_{zz}^{(A)}\} \text{ and cyclic permutations}. \quad (3)$$

In this Equation $\chi_{aa}^{(A)}$, $\chi_{yy}^{(A)}$, $\chi_{zz}^{(A)}$ are the diagonal elements of the atomic susceptibility tensor in its principal axes system, which is assumed to be oriented with respect to the bonds as illustrated in the first column of Table 5. $\cos(a\,x^{(A)})$ etc. is the direction cosine between the atomic x-axis and the a-principal inertia axis of the molecule etc. In Table 6 the local and nonlocal contributions are given for χ_{aa}, χ_{bb} and χ_{cc} for 3-methylfurane, 1,3-difluorbenzene and some related molecules. As is seen from the $\chi_{cc,\,\text{nonlocal}}$ data (c-axis perpendicular to the molecular plane), meta-substitution of the second fluorine atom is clearly more effective than ortho-substitution in quenching $\chi_{cc,\,\text{nonlocal}}$, i. e. the field induced molecular ring current. It should be noted that the difference of the nonlocal contributions to χ_{cc} is

Table 5. Table of atom susceptibilities in units of 10^{-6} erg/(G^2 mole) which were used to calculate the local contributions to the molecular susceptibility tensors (see Ref. [5], p. 106).

$\uparrow y$ $\longrightarrow x$	χ_{xx}	χ_{yy}	χ_{zz}
H−	−1.17 (53)	−2.08 (38)	−2.08 (38)
F−	−8.22 (116)	−6.87 (111)	−5.42 (52)
$C_{sp_3}(H_3C-)$	−9.92 (181)	−8.27 (149)	−8.27 (149)
$C_{sp_3}(H_2C\langle)$	−7.45 (118)	−7.19 (125)	−8.26 (107)
$C_{sp_2}(\rangle C=)$	−3.64 (51)	−3.75 (60)	−7.33 (55)
$O_{\text{ether}}(O\langle)$	−8.73 (101)	−10.35 (104)	−8.23 (95)
$O_{\text{carbonyl}}(O=)$	1.90 (120)	−1.29 (120)	−5.70 (107)

Table 6. Local and nonlocal molecular susceptibilities of some fluorobenzenes and furanes. The local susceptibilities have been calculated from the increments in Table 5 ($\chi_{\gamma\gamma}^{\text{nl}} = \chi_{\gamma\gamma}^{\text{exp}} - \chi_{\gamma\gamma}^{\text{l}}$ $\gamma = a, b, c$). The values are given in units of 10^{-6} erg/(G^2 mole).

$\uparrow b$ $\longrightarrow a$ molecule	local susceptibilities $\chi_{aa,\,\text{mole}}^{\text{l}}$ $\chi_{bb,\,\text{mole}}^{\text{l}}$ $\chi_{cc,\,\text{mole}}^{\text{l}}$	nonlocal susceptibilities $\chi_{aa,\,\text{mole}}^{\text{nl}}$ $\chi_{bb,\,\text{mole}}^{\text{nl}}$ $\chi_{cc,\,\text{mole}}^{\text{nl}}$
	−31.5 −30.1 −45.9	1.1 −3.2 −24.7
	−45.9 −41.6 −57.1	2.8 5.5 −16.4
	−45.3 −42.3 −57.1	0.7 3.5 −19.1
	−39.0 −36.7 −59.8	−1.6 −0.4 −37.4
	−44.9 −42.6 −63.1	−2.7 −2.6 −37.6
	−44.9 −42.6 −63.1	−2.5 −1.7 −33.9
	−31.9 −31.9 −56.5	−3.0 −3.0 −38.1

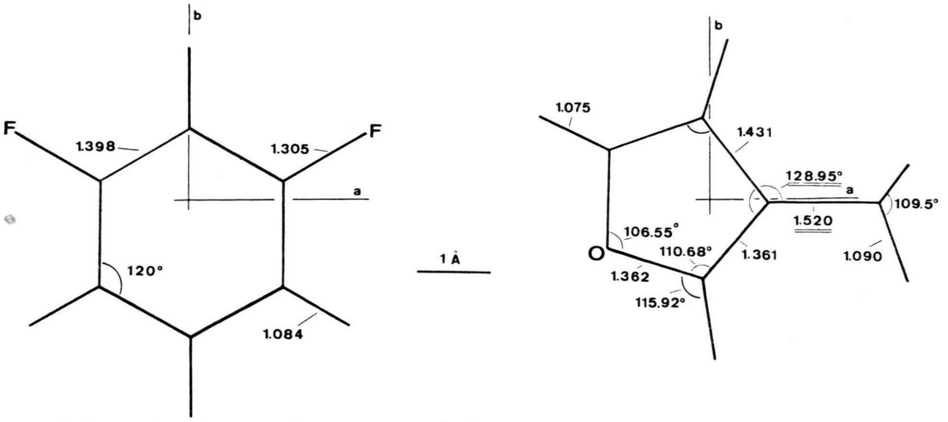


Fig. 1. Geometry of the nuclear frame and orientations of the principal inertia axes systems of 1,3-difluorobenzene and 3-methylfurane used for computing the second moments of the nuclear charge distribution given in Table 4 (see Ref. [1] and [2]). (In Ref. [1] a hexagonal geometry was assumed for the ring. In Ref. [2] an undistorted furane ring and methyl group were assumed and only the underlined parameters were optimized to give the best least squares agreement between calculated and observed rotational constants.) The distances are given in Å.

equal to the difference of the experimental χ_{cc}-values since the local contributions are the same for both difluorobenzenes and cancel in the difference.

For a plot of the experimental out of plane minus average in plane susceptibilities of a greater number of aromatic molecules, which also indicates that the susceptibility anisotropy of isolated benzene molecules is greater than was assumed from molecular crystal measurements see Ref. [5], page 113.

In Fig. 2 relative changes of $\chi_{cc,\,\text{nonlocal}}$ of 2-methylfurane and 3-methylfurane with respect to furane itself are plotted together with relative changes in proton chemical shifts. The latter are defined as

$$\Delta\delta^*_{\text{rel}}=\sum_{i=1}^{3}(\delta^*_{i\text{F}}-\delta^*_{i\text{MF}})\Big/\sum_{i=1}^{3}\delta^*_{i\text{F}} \qquad (4)$$

where $\delta^*_{i\text{F}}$ and $\delta^*_{i\text{MP}}$ are the chemical shifts of the three not substituted protons in furane and the methylfurane respectively. The asterisk indicates that the δ^* values are referred to ethene as standard, $\delta^*=\sigma_{=}-\sigma_{\text{sample}}$; σ are the shielding constants defined by $H=H_0(1-\sigma)$ (H is the magnetic field at the position of the nucleus and H_0 is the external magnetic field).

To compare relative chemical shifts with nonlocal contributions to the susceptibilities the shielding has been devided in a local contribution σ_{l} and a contribution from ringcurrents σ_{ring}; $\sigma=\sigma_{\text{l}}+\sigma_{\text{ring}}$. Taking the sum over the ring protons and choosing ethene as standard was to compensate as far as possible for the local contribution σ_{l} by $\sigma_{=}$. In this rather simplified picture the relative chemical shifts

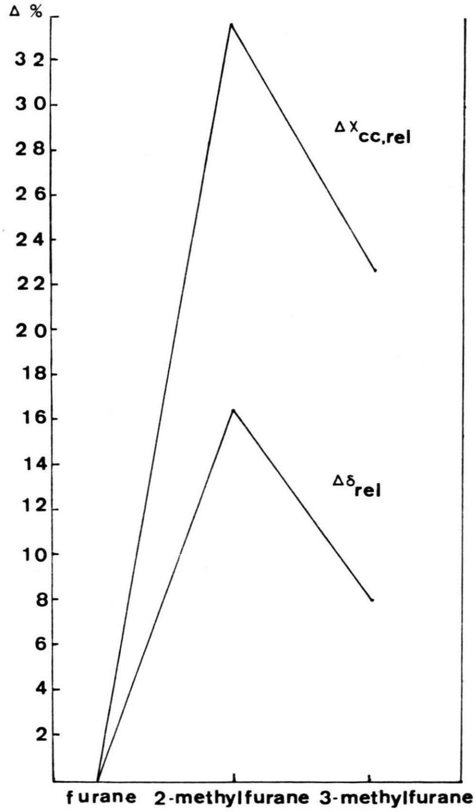


Fig. 2. Relative nonlocal contributions to the susceptibilities $\Delta\chi_{cc,\,\text{rel}}$ and relative changes in proton chemical shifts $\Delta\delta^*_{\text{rel}}$ of 2-methylfurane and 3-methylfurane [see Eq. (4) and (6)]. The relative changes are referred to the corresponding value for furane: $N_{\text{L}}\cdot\chi_{cc,\,\text{nonlocal}}$ (Furane) $= -24.7\cdot10^{-6}$ erg/(G^2 mole). The chemical shifts, used for the calculation of $\Delta\delta^*_{\text{rel}}$, are referred to ethene as standard [27–29].

defined in Eq. (4) should come close to the relative ringcurrent contributions to the shielding.

$$\Delta\delta^*_{\mathrm{rel}} \approx \frac{\sigma_{\mathrm{ring,\,methylfurane}} - \sigma_{\mathrm{ring,\,furane}}}{\sigma_{\mathrm{ring,\,furane}}} = \frac{I_{\mathrm{ring,\,methylfurane}} - I_{\mathrm{ring,\,furane}}}{I_{\mathrm{ring,\,furane}}} . \tag{5}$$

Within such a rough picture the same values should be expected from the relative nonlocal contributions to the susceptibilities:

$$\Delta\chi_{cc,\,\mathrm{rel}} = \frac{\chi^{\mathrm{nonlocal}}_{cc,\,\mathrm{methylfurane}} - \chi^{\mathrm{nonlocal}}_{cc,\,\mathrm{furane}}}{\chi^{\mathrm{nonlocal}}_{cc,\,\mathrm{furane}}} = \frac{I_{\mathrm{ring,\,methylfurane}} - I_{\mathrm{ring,\,furane}}}{I_{\mathrm{ring,\,furane}}} . \tag{6}$$

Taking into account that the underlying model is extremetly crude, Fig. 2 shows parallel trends for $\Delta\chi_{cc,\,\mathrm{rel}}$ and $\Delta\delta^*_{\mathrm{rel}}$.

This finding indicates that there might be some hope for future attempts to link up Zeeman data for the molecular susceptibilities which NMR-shielding data.

Acknowledgement

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[1] L. Nygaard, E. R. Hansen, R. L. Hansen, J. Rastrup-Andersen, and G. O. Sørensen, Spectrochim. Acta **23 A**, 2813 [1967].

[2] T. Ogata and K. Kozima, Bull. Chem. Soc. Japan **44**, 2344 [1971].

[3] C. L. Norris, R. C. Benson, P. Beak, and W. H. Flygare, J. Amer. Chem. Soc. **95**, 2766 [1973].

[4] D. H. Sutter, Z. Naturforsch. **29 a**, 786 [1974].

[5] For a review on recent rotational Zeeman effect studies see D. H. Sutter and W. H. Flygare, The Molecular Zeeman Effect, Topics in Current Chemistry, Vol. 63, 89–196, Springer-Verlag, Heidelberg 1976.

[6] D. M. Burness, J. Org. Chem. **21**, 102 [1956].

[7] D. M. Burness, Org. Synth. Coll. Vol. IV, 628 [1963].

[8] D. H. Sutter, Z. Naturforsch. **26 a**, 1644 [1971].

[9] see Ref. [5], Chap. III.A.

[10] W. Hüttner and W. H. Flygare, J. Chem. Phys. **47**, 4137 [1967].

[11] see Ref. [5], Chap. IV and references cited therein.

[12] see Ref. [10], Equation (28).

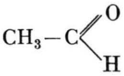
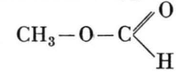
[13] C. C. Lin and J. D. Swalen, Rev. Mod. Phys. **31**, 841 [1959].

[14] H. Dreizler, Mikrowellenspektroskopische Bestimmung von Rotationsbarrieren freier Moleküle, Fortschritte der Chemischen Forschung **10**, 59–155 [1968].

[15] D. Sutter and A. Guarnieri, Z. Naturforsch. **25 a**, 1036 [1970].

[16] L. Engelbrecht, D. Sutter, and H. Dreizler, Z. Naturforsch. **28 a**, 709 [1973]; L. Engelbrecht, Ph.D. Thesis, Kiel 1975; L. Engelbrecht and D. H. Sutter, Z. Naturforsch. **30 a**, 1265 [1975].

[17] T. Ogata and K. Kozima, Bull. Chem. Soc. Japan **44**, 2344 [1971].

[18] Other examples for molecules with intermediate barriers were internal rotation does not yet show up in the rotational Zeeman splittings are for instance:  $CH_3-C(=O)H$ ($V_3 = 1.17$ kcal/mole) see W. Hüttner and W. H. Flygare, Trans. Faraday Soc. **65**, 1953 [1969];  $CH_3-O-C(=O)H$ ($V_3 = 1.19$ kcal/mole) see J. H. S. Wang and W. H. Flygare, J. Chem. Phys. **53**, 4479 [1970]; J. Chem. Phys. **55**, 3616 [1971]; $H_3C-S-CH_3$ ($V_3 = 2.18$ kcal/mol); R. C. Benson and W. H. Flygare, J. Chem. Phys. **52**, 5291 [1970]; E. Hamer, D. H. Sutter, and H. Dreizler, Z. Naturforsch. **27 a**, 1159 [1972].

[19] E. Hamer, L. Engelbrecht, and D. H. Sutter, Z. Naturforsch. **29 a**, 924 [1974], The original parametrization of Pople and Beveridge, was used for the numerical calculations.

[20] T. D. Gierke, H. L. Tigelaar, and W. H. Flygare, J. Amer. Chem. Soc. **94**, 330 [1972].

[21] T. G. Schmalz, C. L. Norris, and W. H. Flygare, J. Amer. Chem. Soc. **95**, 7961 [1973].

[22] J. Wiese, Diplomarbeit, Kiel 1975.

[23] see Ref. [20, 21, 5], Chap. II.

[24] R. A. Flath, N. Henderson, and R. E. Lundi, Applied Spectroscopy **21**, 183 [1967].

[25] K. Hatada, Y. Terawaki, and H. Okuda, Bull. Chem. Soc. Japan **42**, 1781 [1969].

[26] W. Czieslik, Thesis, Kiel 1976.

[27] G. S. Reddy and J. H. Goldstein, J. Amer. Chem. Soc. **83**, 2045 [1961].

[28] S. Rodmar, S. Forsen, B. Gestblom, S. Gronowitz, and R. A. Hoffman, Acta Chem. Scan. **19**, 485 [1965].

[29] J. M. Read, C. T. Mathis, and J. H. Goldstein, Spectrochim. Acta **21**, 85 [1965].