The Rotational Zeeman Effect of Thiazole and Isothiazole

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The rotational Zeeman effect of low J rotational transitions (J \leq 3) has been investigated for Thiazole and Isothiazole. The measured susceptibilities are compared to those calculated within the model of localized (atomic) susceptibilities, and nonlocal contributions to the susceptibility component perpendicular to the ring are obtained. These nonlocal susceptibilities, if compared to those of a set of related compounds appear to correlate to the "aromatic character" as determined by chemical reactivity. Five or six membered rings with \( \chi_{\text{nonlocal}} < -3 \times 10^{-6} \text{erg/G}^2 \text{mol} \) show "aromatic reactions" while molecules with \( -20 \cdot 10^{-6} \text{erg/G}^2 < \chi_{\text{nonlocal}} < -6 \times 10^{-6} \text{erg/G}^2 \) show "olefinic reactions".

Introduction

In general aromatic molecules are assumed to be characterized by a ringsystem containing \( 4n + 2 \) more or less delocalized \( \pi \)-electrons [1]. Despite this apparently well defined basic property of aromatic molecules, it is not easy to define aromaticity in a unique way in terms of measurable physical or chemical quantities [2]. One method proposed to "measure" aromaticity is to investigate the diamagnetic susceptibility perpendicular to the ring whose nonlocal contribution is related to the nonlocal (molecular) diamagnetic ring current and thus — at least intuitively — to the delocalisation of the \( \pi \)-system [3]. In principle the nonlocal susceptibility should be extractable from NMR-shielding/deshielding data, but strong local contributions may considerably complicate the analysis [4]. In the case of rotational Zeeman spectroscopy, where the molecular susceptibility anisotropies of free molecules are measured directly, such complications do not arise. In the following we report the results of a rotational Zeeman effect study for Thiazole and Isothiazole which closes a gap in the system of five membered rings studied so far [5]. This enables us to give a better judgement of the use of the nonlocal susceptibility perpendicular to the ring [6] as a measure for "aromaticity".

Experimental

P.a. grade Thiazole and Isothiazole from Merck, Germany, were used after a bulb to bulb distillation without further purification. The spectra were recorded with a conventional Stark-effect modulated microwave spectrometer using 33 kHz square wave modulation. For the Zeeman measurements the spectrometer is equipped with an electromagnet capable to deliver a field of about 25 kG (2.5 Tesla) over a gap of 3.5 cm height and 2.5 m length. Details of the spectrometer may be found in Ref. [5 b] and [7]. Under typical recording conditions sample pressures were about 5 m Torr (7 \( \cdot \) 10\(^{-6} \) Pascal) and cell temperatures were about —50 °C. At these conditions zero field linewidths (half width at half height) of 80 to 100 kHz were obtained and the \(^{14}N\) quadrupole hyperfine structure was generally well resolved. With the magnetic field set to about 25 kG the absorption lines further split with overall splittings on the order of 1 to 6 MHz depending on the rotational transition under investigation. Since the presence of the \(^{14}N\) quadrupole nucleus with spin \( I = 1 \) triples the number of Zeeman satellites as compared to the standard rigid rotor case, overlapping of lines frequently occurs in the Zeeman patterns. It was however possible to arrive at a unique assignment of the recorded Zeeman satellites and to determine accurate molecular g-values and susceptibility anisotropies for both molecules.

Analysis of the Spectra

The molecular parameters for the Thiazoles were determined in a two step procedure. In the first step the rotational constants and \(^{14}N\) nuclear quadrupole coupling constants were fitted to the zero field spectra (Tables 1 and 2). Since only rotational transitions with \( J \leq 3 \) were used, centrifugal distortions proved negligible and the spectra could be
Table 1. Observed and deviations to calculated frequencies of rotational transitions of Thiazole and Isothiazole. The calculated frequencies were determined by using the model of the rigid rotor. The observed frequencies are averages of the measured hyperfine transition frequencies corrected by the calculated hyperfine splitting (using the constants of Table 4).

<table>
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<tr>
<th>Transition</th>
<th>Thiazole</th>
<th>Isothiazole</th>
</tr>
</thead>
<tbody>
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<td>$\Delta v_{e-c}$/kHz</td>
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<tr>
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</tr>
<tr>
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Table 2a. Observed and calculated frequencies of hyperfine transitions of Thiazole used for fitting the nuclear quadrupole coupling constants (s. Table 4). If overlapping of lines occurs the intensity weighted averages of the calculated frequencies are given.

<table>
<thead>
<tr>
<th>$J_K$ $\to$ $J'_K$</th>
<th>$F$ $\to$ $F'$</th>
<th>$v_{exp}$/MHz</th>
<th>$\Delta v_{exp}$/kHz</th>
<th>$\Delta v_{calc}$/kHz</th>
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* In Tables 2 and 3 the two zeros trailing the decimal point have no meaning. Experimental satellite frequency uncertainties are ± 5 kHz for well resolved lines and ± 10 kHz to ± 20 kHz for peak frequencies originating from overlapping lines. The calculated frequencies have been rounded to the next full kHz value.
fitted to the standard rigid rotor energy expression [8]. Only the quadrupole coupling matrix elements diagonal in $J$ (and $\ell$) are included in this energy expression. This approximation holds very good in the case of the weakly coupled $^{14}$N nucleus. It is however insufficient to reproduce the microwave spectra of molecules containing strongly coupled nuclei such as for instance $^{81}$Br.

<table>
<thead>
<tr>
<th>$J-K$ - $J'-K'$</th>
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<th>$v_{exp}/\text{MHz}$</th>
<th>$\Delta v_{exp}/\text{kHz}$</th>
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Table 2a. (continued 1).

Table 2b. Observed and calculated frequencies of some hyperfine transitions of Isothiazole used for fitting the nuclear quadrupole coupling constants (s. Table 4). If overlapping of lines occurs the intensity weighted averages of the calculated frequencies are given.
In the second step the molecular g-values and susceptibility anisotropies were fitted to the high-field Zeeman hyperfine patterns (Tables 3a and 3b). For this fit the rotational constants and quadrupole coupling constants were kept fixed to their values derived from the zero field spectra (Table 4). Again hyperfine- (and Zeeman-) matrix elements off diagonal in the rotational quantum numbers $J$ and $K_+ K_-$ were neglected. For each rotational state the corresponding $M_J M_I$ submatrix was set up in the uncoupled basis $|J, K_+ K_- , M_J > |I, M_I >$ [9] and sufficiently accurate sublevel energies were calculated by second order perturbation theory. This considerably simplifies the least squares procedure. A posteriori the validity of this second order perturbation treatment was checked by diagonalizing the submatrices for each rotational state numerically. The Zeeman-hyperfine-splittings

<table>
<thead>
<tr>
<th>Transition $J K_+ K_- \rightarrow J' K'<em>+ K'</em>-$, $M_J \rightarrow M_J$, $M_I$</th>
<th>$\Delta v_{\text{exp}}/\text{kHz}$</th>
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</tbody>
</table>

Table 3a. Observed and calculated frequency splittings of some Zeeman-hyperfine-satellites of Thiazole with respect to the corresponding hypothetical rigid rotor frequencies. The given splittings were used to fit the Zeeman parameters (see Table 5). Since the magnetic field effectively uncouples overall and spin angular momentum, $M_J$ and $M_I$ rather than $M_F$ and $F$ are the appropriate quantum numbers to label the rotational states with $\Delta M_J = 0$ as selection rule for the $^{14}$N spin. If overlapping of lines occurs, the calculated splittings are intensity averaged splittings (see text).
Table 3a (continued 1).

<table>
<thead>
<tr>
<th>Transition</th>
<th>( J_{K_{1},K_{-1}} \rightarrow J'<em>{K'</em>{1},K'_{-1}} )</th>
<th>( M_{J} \rightarrow M_{J'} )</th>
<th>( M_{J} )</th>
<th>( \Delta v_{\text{exp/kHz}} )</th>
<th>( \Delta v_{\text{calc/kHz}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^2_{02} \rightarrow ^2_{11} )</td>
<td>(-2)</td>
<td>(-2)</td>
<td>(-1)</td>
<td>(-3490.00)</td>
<td>(-3486.00)</td>
</tr>
<tr>
<td>25.62 kGauss</td>
<td>(-2)</td>
<td>(-2)</td>
<td>(1)</td>
<td>(-2850.00)</td>
<td>(-2851.00)</td>
</tr>
<tr>
<td>(-2)</td>
<td>(-2)</td>
<td>(0)</td>
<td>(946.00)</td>
<td>(972.00)</td>
<td></td>
</tr>
<tr>
<td>(-2)</td>
<td>(-2)</td>
<td>(1)</td>
<td>(1051.00)</td>
<td>(1058.00)</td>
<td></td>
</tr>
<tr>
<td>(2)</td>
<td>(2)</td>
<td>(-1)</td>
<td>(-312.00)</td>
<td>(-319.00)</td>
<td></td>
</tr>
<tr>
<td>(2)</td>
<td>(2)</td>
<td>(1)</td>
<td>(-303.00)</td>
<td>(-297.00)</td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>(-2)</td>
<td>(-1)</td>
<td>(-1811.00)</td>
<td>(-1805.00)</td>
<td></td>
</tr>
<tr>
<td>(-2)</td>
<td>(-1)</td>
<td>(-1)</td>
<td>(-127.00)</td>
<td>(-1077.00)</td>
<td></td>
</tr>
<tr>
<td>(-0)</td>
<td>(-1)</td>
<td>(0)</td>
<td>(-303.00)</td>
<td>(-297.00)</td>
<td></td>
</tr>
<tr>
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<td>(-1)</td>
<td>(1)</td>
<td>(-303.00)</td>
<td>(-297.00)</td>
<td></td>
</tr>
<tr>
<td>(-1)</td>
<td>(0)</td>
<td>(-1)</td>
<td>(-332.00)</td>
<td>(-343.00)</td>
<td></td>
</tr>
<tr>
<td>(2)</td>
<td>(1)</td>
<td>(1)</td>
<td>(-303.00)</td>
<td>(-297.00)</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>(1)</td>
<td>(-1)</td>
<td>(-303.00)</td>
<td>(-297.00)</td>
<td></td>
</tr>
<tr>
<td>(1)</td>
<td>(2)</td>
<td>(-1)</td>
<td>(-346.00)</td>
<td>(-339.00)</td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>(2)</td>
<td>(1)</td>
<td>(-346.00)</td>
<td>(-339.00)</td>
<td></td>
</tr>
<tr>
<td>(1)</td>
<td>(2)</td>
<td>(-1)</td>
<td>(-346.00)</td>
<td>(-339.00)</td>
<td></td>
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<tr>
<td>(0)</td>
<td>(2)</td>
<td>(1)</td>
<td>(-346.00)</td>
<td>(-339.00)</td>
<td></td>
</tr>
</tbody>
</table>

calculated by the two methods differ by 5 kHz at most, which is still within the experimental uncertainty of the frequency determinations and thus justifies the use of the second order perturbation treatment. If — as was frequently the case — two or even more Zeeman hyperfine satellites overlapped within one zero-field halfwidth, the observed peak frequency was assumed to be sufficiently well reproduced by the intensity-weighted average frequency of the constituent satellites (compare Ref. [10] for a detailed discussion of the analysis of unresolved lines). The diagonal elements of the molecular g-tensor and the anisotropies of the magnetic susceptibility tensor obtained by the least squares fit to the splittings are given in Table 5. Also listed in Table 5 are the molecular electric quadrupole moments, the individual components of the diagonal elements of the susceptibility tensor, and the ground state expectation values for the sums of the squares of the electron coordinates, all referred to the principal axis systems of the moment of inertia tensor (center of mass system). To
Table 3b. Observed and calculated frequency splittings of some Zeeman-hyperfine-satellites of Isothiazole.

<table>
<thead>
<tr>
<th>Transition</th>
<th>$J_{K, K'} \rightarrow J_{K', K''}$</th>
<th>$M_J \rightarrow M_{J'}$</th>
<th>$M_I$</th>
<th>$\Delta v_{exp}$/kHz</th>
<th>$\Delta v_{calc}$/kHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,0 $\rightarrow$ 1,01</td>
<td>19.75 kGauss</td>
<td>0 $\rightarrow$ -1</td>
<td>-1</td>
<td>-142.00</td>
<td>-142.00</td>
</tr>
<tr>
<td>0,0 $\rightarrow$ 1,1</td>
<td>25.62 kGauss</td>
<td>0 $\rightarrow$ 0</td>
<td>0</td>
<td>-766.00</td>
<td>-799.00</td>
</tr>
<tr>
<td>0,0 $\rightarrow$ 1,1</td>
<td>19.75 kGauss</td>
<td>0 $\rightarrow$ -1</td>
<td>0</td>
<td>-404.00</td>
<td>-386.00</td>
</tr>
<tr>
<td>0,0 $\rightarrow$ 1,01</td>
<td>25.62 kGauss</td>
<td>0 $\rightarrow$ 0</td>
<td>0</td>
<td>942.00</td>
<td>959.00</td>
</tr>
<tr>
<td>1,1 $\rightarrow$ 2,0</td>
<td>25.63 kGauss</td>
<td>-1 $\rightarrow$ -1</td>
<td>-1</td>
<td>-1187.00</td>
<td>-1208.00</td>
</tr>
<tr>
<td>1,1 $\rightarrow$ 2,0</td>
<td>24.21 kGauss</td>
<td>-1 $\rightarrow$ -2</td>
<td>-1</td>
<td>-4036.00</td>
<td>-4074.00</td>
</tr>
<tr>
<td>1,1 $\rightarrow$ 2,1</td>
<td>25.63 kGauss</td>
<td>0 $\rightarrow$ 0</td>
<td>0</td>
<td>-875.00</td>
<td>-872.00</td>
</tr>
<tr>
<td>1,1 $\rightarrow$ 2,1</td>
<td>24.21 kGauss</td>
<td>0 $\rightarrow$ 0</td>
<td>0</td>
<td>1171.00</td>
<td>1153.00</td>
</tr>
<tr>
<td>1,1 $\rightarrow$ 2,1</td>
<td>24.21 kGauss</td>
<td>0 $\rightarrow$ 0</td>
<td>0</td>
<td>1526.00</td>
<td>1534.00</td>
</tr>
<tr>
<td>1,1 $\rightarrow$ 2,1</td>
<td>24.21 kGauss</td>
<td>0 $\rightarrow$ 0</td>
<td>0</td>
<td>-1187.00</td>
<td>-1208.00</td>
</tr>
<tr>
<td>1,1 $\rightarrow$ 2,1</td>
<td>24.21 kGauss</td>
<td>0 $\rightarrow$ 0</td>
<td>0</td>
<td>-3680.00</td>
<td>-3680.00</td>
</tr>
<tr>
<td>1,1 $\rightarrow$ 2,1</td>
<td>24.21 kGauss</td>
<td>0 $\rightarrow$ 0</td>
<td>0</td>
<td>-1568.00</td>
<td>-1594.00</td>
</tr>
<tr>
<td>1,1 $\rightarrow$ 2,1</td>
<td>24.21 kGauss</td>
<td>0 $\rightarrow$ 0</td>
<td>0</td>
<td>835.00</td>
<td>852.00</td>
</tr>
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<td>1,1 $\rightarrow$ 2,1</td>
<td>24.21 kGauss</td>
<td>0 $\rightarrow$ 0</td>
<td>0</td>
<td>-1568.00</td>
<td>-1594.00</td>
</tr>
<tr>
<td>1,1 $\rightarrow$ 2,1</td>
<td>24.21 kGauss</td>
<td>0 $\rightarrow$ 0</td>
<td>0</td>
<td>835.00</td>
<td>852.00</td>
</tr>
<tr>
<td>1,1 $\rightarrow$ 2,1</td>
<td>24.21 kGauss</td>
<td>0 $\rightarrow$ 0</td>
<td>0</td>
<td>-1568.00</td>
<td>-1594.00</td>
</tr>
<tr>
<td>1,1 $\rightarrow$ 2,1</td>
<td>24.21 kGauss</td>
<td>0 $\rightarrow$ 0</td>
<td>0</td>
<td>835.00</td>
<td>852.00</td>
</tr>
<tr>
<td>1,1 $\rightarrow$ 2,1</td>
<td>24.21 kGauss</td>
<td>0 $\rightarrow$ 0</td>
<td>0</td>
<td>-1568.00</td>
<td>-1594.00</td>
</tr>
<tr>
<td>1,1 $\rightarrow$ 2,1</td>
<td>24.21 kGauss</td>
<td>0 $\rightarrow$ 0</td>
<td>0</td>
<td>835.00</td>
<td>852.00</td>
</tr>
<tr>
<td>1,1 $\rightarrow$ 2,1</td>
<td>24.21 kGauss</td>
<td>0 $\rightarrow$ 0</td>
<td>0</td>
<td>-1568.00</td>
<td>-1594.00</td>
</tr>
<tr>
<td>1,1 $\rightarrow$ 2,1</td>
<td>24.21 kGauss</td>
<td>0 $\rightarrow$ 0</td>
<td>0</td>
<td>835.00</td>
<td>852.00</td>
</tr>
<tr>
<td>Transition</td>
<td>$J_{K,K'} \rightarrow J'_{K',K''}$</td>
<td>$M_J \rightarrow M_{J'}$</td>
<td>$M_I$</td>
<td>$\Delta v_{exp}$/kHz</td>
<td>$\Delta v_{calc}$/kHz</td>
</tr>
<tr>
<td>------------</td>
<td>-----------------------------------</td>
<td>--------------------------</td>
<td>--------</td>
<td>-----------------------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>$2_{02} \rightarrow 2_{21}$</td>
<td>[11] $-1 -2$</td>
<td>$-1$</td>
<td>$-2098.00$</td>
<td>$-2128.00$</td>
<td></td>
</tr>
<tr>
<td>19.75 kGauss</td>
<td>$-2 -1$</td>
<td>$-1$</td>
<td>$-1063.00$</td>
<td>$-1098.00$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$0 -1$</td>
<td>$-1$</td>
<td>$-325.00$</td>
<td>$-351.00$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$0 1$</td>
<td>$-1$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$1 2$</td>
<td>$-1$</td>
<td>$1717.00$</td>
<td>$1699.00$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$0 1$</td>
<td>$1$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| $2_{12} \rightarrow 2_{21}$ | $-2 -2$ | $0$ | $-4617.00$ | $-4627.00$ |
| 25.63 kGauss | $-1 -1$ | $-1$ | $-1047.00$ | $-1047.00$ |
| | $1 2$ | $-1$ | $2124.00$ | $2089.00$ |
| | $2 2$ | $1$ | | |

| $2_{11} \rightarrow 2_{20}$ | $-2 -2$ | $-1$ | $-1611.00$ | $-1636.00$ |
| 25.62 kGauss | $-1 -1$ | $-1$ | $-621.00$ | $-648.00$ |
| | $1 1$ | $1$ | $877.00$ | $813.00$ |
| | $2 2$ | $0$ | $1234.00$ | $1286.00$ |
| | $2 2$ | $1$ | | |

| $2_{11} \rightarrow 2_{20}$ | $0 -1$ | $-1$ | $-1750.00$ | $-1753.00$ |
| 19.75 kGauss | $0 0$ | $-1$ | $-784.00$ | $-760.00$ |
| | $1 0$ | $1$ | $205.00$ | $182.00$ |
| | $-2 -1$ | $0$ | $543.00$ | $533.00$ |

| $2_{20} \rightarrow 3_{21}$ | $1 1$ | $-1$ | $-308.00$ | $-366.00$ |
| 25.63 kGauss | $0 0$ | $0$ | $334.00$ | $325.00$ |
| | $1 1$ | $1$ | $610.00$ | $617.00$ |
| | $-1 -1$ | $0$ | $1730.00$ | $1739.00$ |
| | $-2 -2$ | $1$ | | |

Calculate the quadrupole moments the structures given in Fig. 1 were used. To calculate the individual components of the susceptibilities the liquid phase bulk susceptibility of Thiazole [11] was used as additional information. Since liquid phase and gasphase susceptibilities may differ, we increased the uncertainty limits of the bulk value to ±2·10\(^{-6}\) erg/G\(^2\) mol for Thiazole and to ±3·10\(^{-6}\) erg/G\(^2\) mol for Isothiazole as compared to ±0.5·10\(^{-6}\) erg/G\(^2\) mol which to our experience is a typical experimental uncertainty for a liquid phase bulk susceptibility determination using the Faraday method [12] or an NMR technique [13]. For a discussion of the implicit neglect of molecular vibra-
Table 4. Rotational constants and nuclear quadrupole coupling constants, $\chi^{N14}$, of Thiazole and Isothiazole (see Table 1 and 2). Our values agree within two standard deviations with those of the earlier determinations\textsuperscript{18,19}. However, our values for Isothiazole could be determined with experimental uncertainties reduced by a factor of 20 as compared to the earlier investigation\textsuperscript{18}.

<table>
<thead>
<tr>
<th></th>
<th>Thiazole</th>
<th>Isothiazole</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$/MHz</td>
<td>8529.425 (4)</td>
<td>8275.575 (5)</td>
</tr>
<tr>
<td>$B$/MHz</td>
<td>5505.755 (3)</td>
<td>5846.228 (3)</td>
</tr>
<tr>
<td>$C$/MHz</td>
<td>3344.298 (3)</td>
<td>3424.193 (3)</td>
</tr>
<tr>
<td>$\chi^{N14}$/MHz</td>
<td>$-2.708$ (22)</td>
<td>$1.037$ (23)</td>
</tr>
<tr>
<td>$\chi^{N14}$/MHz</td>
<td>$0.113$ (34)</td>
<td>$-2.494$ (27)</td>
</tr>
<tr>
<td>$\chi^{N14}$/MHz</td>
<td>$2.595$ (34)</td>
<td>$1.367$ (27)</td>
</tr>
</tbody>
</table>

Local and Nonlocal Susceptibilities

Pascal\textsuperscript{[14]} was the first to introduce the concept of local susceptibilities to calculate bulk susceptibilities from atomic increments. When more detailed information obtained from rotational Zeeman effect measurements on free molecules became available, Benson and Flygare\textsuperscript{[15]} developed a scheme to calculate the individual components of the molecular susceptibility tensors from atomic tensors as building blocks\textsuperscript{[16]}. The orientation of the atomic susceptibility tensors with respect to the molecular frame is determined by the orientation of the bond directions and a rough allowance for the special bonding situation of the atom under consideration is made by assigning different atomic susceptibility tensors to say sp\textsuperscript{2} and sp\textsuperscript{3}-hybridized carbon atoms etc. Since the first table of local

Table 5. Molecular quantities derived from the experimental data given in Tables 3, the geometries of the nuclear frames and the bulk magnetic susceptibilities. Quoted uncertainties are standard errors of the least squares fit.

<table>
<thead>
<tr>
<th></th>
<th>Thiazol</th>
<th>Isothiazol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular $g$-values</td>
<td>$g_{aa}$</td>
<td>$-0.1057$ (3)</td>
</tr>
<tr>
<td></td>
<td>$g_{bb}$</td>
<td>$-0.0847$ (3)</td>
</tr>
<tr>
<td></td>
<td>$g_{cc}$</td>
<td>$0.0404$ (3)</td>
</tr>
<tr>
<td>Molar magnetic susceptibility anisotropies</td>
<td>$N_L(2\chi_{aa}-\chi_{bb}-\chi_{cc})$</td>
<td>$51.3$ (5)</td>
</tr>
<tr>
<td></td>
<td>$[10^{-6}$ erg/(G\textsuperscript{2} mole)]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$N_L(2\chi_{bb}-\chi_{cc}-\chi_{aa})$</td>
<td>$50.7$ (5)</td>
</tr>
<tr>
<td></td>
<td>$[10^{-6}$ erg/(G\textsuperscript{2} mole)]</td>
<td></td>
</tr>
<tr>
<td>Liquid phase bulk magnetic susceptibilities in units of $10^{-6}$ erg/(G\textsuperscript{2} mole)</td>
<td>$\chi_{bulk}$</td>
<td>$-50.6$ (20)</td>
</tr>
<tr>
<td>Molecular quadrupole moments in units of $10^{-26}$ esu cm\textsuperscript{2}</td>
<td>$Q_{aa}$</td>
<td>$-3.2$ (5)</td>
</tr>
<tr>
<td></td>
<td>$Q_{bb}$</td>
<td>$0.9$ (6)</td>
</tr>
<tr>
<td></td>
<td>$Q_{cc}$</td>
<td>$-4.8$ (9)</td>
</tr>
<tr>
<td>Magnetic susceptibilities in units of $10^{-6}$ erg/(G\textsuperscript{2} mole)</td>
<td>(\chi_{aa})</td>
<td>$-33.5$ (22)</td>
</tr>
<tr>
<td></td>
<td>(\chi_{bb})</td>
<td>$-33.7$ (22)</td>
</tr>
<tr>
<td></td>
<td>(\chi_{cc})</td>
<td>$-84.6$ (23)</td>
</tr>
<tr>
<td>Second moments of the nuclear charge distribution calculated from the geometry of the nuclear frame given in Å\textsuperscript{2}</td>
<td>$\sum Z_n a_n^2$</td>
<td>$48.2$ (1)</td>
</tr>
<tr>
<td></td>
<td>$\sum Z_n b_n^2$</td>
<td>$35.4$ (1)</td>
</tr>
<tr>
<td></td>
<td>$\sum Z_n c_n^2$</td>
<td>$0$ (0)</td>
</tr>
<tr>
<td>Second moments of the electronic charge distribution in Å\textsuperscript{2}</td>
<td>$\langle 0</td>
<td>\sum \xi a_\xi^2</td>
</tr>
<tr>
<td></td>
<td>$\langle 0</td>
<td>\sum \xi b_\xi^2</td>
</tr>
<tr>
<td></td>
<td>$\langle 0</td>
<td>\sum \xi c_\xi^2</td>
</tr>
</tbody>
</table>
Fig. 1. Structures and orientation of the principal inertia axes system of Thiazole and Isothiazole used to calculate the molecular electric quadrupole moments etc. from the Zeeman data. While the given structure of Thiazole is a reconstructed, determined by the substitution method from the rotational constants of an extensive set of isotopes [19], the given structure for Isothiazole is only an estimated structure, based on the discussion given in Ref. [20] and in accordance with the observed rotational constants (Table 4).

susceptibilities was presented by Schmalz, Norris and Flygare [17], the available data has increased considerably and a revised and extended table of local susceptibilities was published in 1976 [5 b]. In Table 6 we give that part of our present list of local susceptibilities which was used for the subsequent discussion. As already shown in the earlier publications, the model of local susceptibilities described above appears indeed well suited to predict the molecular susceptibility tensor in molecules with localized bonds. It is also well suited to predict the average in-plane susceptibility in aromatic rings. It fails however completely to reproduce the susceptibility component perpendicular to the plane of the aromatic rings which generally turns out to be more negative than predicted within the local model. Intuitively this excess “nonlocal” susceptibility may be attributed to an aromatic field induced ring current, a concept commonly used in NMR spectroscopy.

To demonstrate the presence of the nonlocal (ring current) contribution in aromatic molecules, we list the experimental and calculated susceptibilities for a number of five- and six membered rings in Table 7. Isoprene, included at the top of the table, is intended as an example of a nonaromatic molecule in which quite generally both, the average in plane and the out of plane susceptibility are reasonably well reproduced by the local model.

As is seen from the table, the closely related molecules Thiazole, Isothiazole and Thiophene as well as Oxazole, Isoxazole and Furane show almost identical values for \( \chi_{\text{nonlocal}} \). The same holds for the group of benzene derivatives and Pyridine.

In such a group the molecules show great similarities in their chemical reactions and it appears that a correlation exists between \( \chi_{\text{nonlocal}} \) and chemical behaviour. Molecules with \( \chi_{\text{nonlocal}} < -30 \cdot 10^{-6} \text{erg/G}^2 \text{mol} \) show typical aromatic reactions but no olefinic reactions. Molecules with \( \chi_{\text{nonlocal}} > -20 \cdot 10^{-6} \text{erg/G}^2 \text{mol} \) only show olefinic reactions and molecules with \( \chi_{\text{nonlocal}} > -25 \cdot 10^{-6} \text{erg/G}^2 \text{mol} \) show both types of reactions. In this context substitution reactions are considered typical for an aromatic molecule and addition reactions and Diels Alder reactions are considered as typical olefine

<table>
<thead>
<tr>
<th>Atom ( \chi )</th>
<th>( \chi_{\text{nonlocal}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>-1.70</td>
</tr>
<tr>
<td>C</td>
<td>-3.54</td>
</tr>
<tr>
<td>O</td>
<td>0.15</td>
</tr>
<tr>
<td>O&lt;</td>
<td>-9.43</td>
</tr>
<tr>
<td>S&lt;</td>
<td>-17.0</td>
</tr>
<tr>
<td>N&lt; (planar)</td>
<td>-11.9</td>
</tr>
<tr>
<td>N=</td>
<td>0.0</td>
</tr>
<tr>
<td>F&lt;</td>
<td>-7.6</td>
</tr>
</tbody>
</table>

Table 6. Increments of the local atomic magnetic susceptibility components used for the calculations of \( \chi_{\text{local}} \) (see Table 7). The increments are given in units of \( 10^{-6} \text{erg/G}^2 \text{mol} \).
Table 7. Comparison of experimental susceptibilities and susceptibilities calculated within the local model from the atomic increments listed in Table 6. \( Z_i = (Z_{aa} + Z_{bb})/2 \), \( Z_\perp \) = Zcc, c-axis perpendicular to the plane of the ring. Isoprene at the top of the list was included as an example of an open chain molecule where generally \( Z_\parallel \) and \( Z_\perp \) are reproduced well within the local model. The values of the susceptibilities are given in units of 10^{-6} erg/Gauss^2/mole.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Experimental susceptibilities</th>
<th>Nonlocal susceptibilities</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( Z_\parallel )</td>
<td>( Z_\perp )</td>
</tr>
<tr>
<td>![Molecule Image]</td>
<td>![Experimental Susceptibility]</td>
<td>![Nonlocal Susceptibility]</td>
</tr>
<tr>
<td>![Molecule Image]</td>
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In an attempt to get a deeper understanding of \( Z_\perp \) nonlocal we have also carried out CNDO calculations. Although the quality of the CNDO-approach may be questionable for molecules with highly delocalized orbitals it may be interesting to note that in each of the closely related pairs Thiazole/Isothiazole; Oxazole/Isoxazole and 1,2-Defluorobenzene/1,3-Defluorobenzene the partner with the less negative \( Z_\perp \) nonlocal also turns out to be the one which shows the higher “CNDO-polarity” in the ring. By “CNDO-polarity” we mean the sum of the absolute values of the excess CNDO atomic charges of the ring atoms. In other words, the more the CNDO-calculations indicates that certain atoms tend to attract, others to give off electrons, the smaller is the value of the negative nonlocal susceptibility.

Acknowledgements


[1] E. Hückel, Z. Physik 70, 204 (1931); 72, 310 (1931); 76, 628 (1932).

[16] A detailed description of the procedure is also given in Ref. [5b], Chapter II.C.