**11B-Quadrupole Hyperfine Structure in the Rotational Spectrum of Phenyldifluoroborane**

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We present an investigation and interpretation of the 11B-quadrupole hyperfine structure (hfs) in the rotational spectrum of phenyldifluoroborane in the torsional ground state of the BF2 group. The measurements were made with a microwave Fourier transform (MWFT) spectrometer in the frequency range between 5 and 8 GHz.

**Experimental and Analysis**

Both isotopic species (11B, 10B) of phenyldifluoroborane, F2B(C6H5), were first investigated and assigned by Christen, Lister and Sheridan [1]. They determined the rotational constants of the torsional ground and some excited states of the BF2 group and the torsional potential height.

The preparation of phenyldifluoroborane was carried out in two steps. First we prepared phenylchlorodichloroborane C12B(C6H5)2 by the reaction between boron trichloride and tetraphenyltin [2]. The second step was the fluorination of phenylchlorodichloroborane with antimony trifluoride [3].

The spectra were recorded at temperatures between −20° and −30°C and pressures between 0.4 and 1 mTorr (0.052–0.13 Pa). The measured transitions are listed in Table 1. All frequencies were determined by a least squares fit of the multiplet signals in the time domain to minimize overlapping effects [4, 5]. The assignment of our transitions has been checked by a centrifugal distortion analysis including the transitions reported by Christen, Lister and Sheridan. We used the Watson A reduction of 4th order [6]. The centrifugal distortion constants AJK and δj had to be fixed to zero. Because our measurements and those of [1] were of different accuracy, the deviations δ0 of the fit were relatively high. The hfs splittings were analyzed by first order approximation [7]. The rotational and centrifugal distortion constants are given in Table 2, the quadrupole coupling constants in Table 3.

**Boron Coupling Discussion**

We use a hybridisation analogue to pyridine, given by Gordy and Cook [8], to interpret the boron quadrupole coupling. The three valence orbitals in the molecular plane are sp2 hybrids, the fourth orbital, perpendicular to the plane, is a pure p orbital.

\[
\psi_1 = (1 - 2 a_2) \frac{1}{2} \psi_s + (2 a_2) \frac{1}{2} \psi_p, \quad \text{BC bonding orbital,}
\]

\[
\psi_{2,3} = a_4 \psi_s - [(1 - 2 a_2) \frac{1}{2} \psi_p \pm (1/2) \psi_z], \quad \text{BF bonding orbitals,}
\]

\[
\psi_a = \psi_{p_z}, \quad \text{p orbital.}
\]

\[
a_2^2 \text{ represents the amount of s character in each boron bonding orbital [9].}
\]

\[
a_2^2 = \cos \theta (\cos \theta - 1) = 0.311
\]

with θ the FBF angle given in [1] as θ = 116.0°.

The molecular principal axes can be identified with the principal quadrupole coupling tensor axes in the following way: z → a, x → b and y → c. The experimental data provide two independent coupling parameters. Therefore we are able to determine two parameters: i, the ionic character of the BF bond and i, the occupation of the pure p orbital. With the assumption of a polarized BC bond the population numbers of the molecular orbitals are

\[
n(\psi_1) = 1 - [(\text{ENphenyl} - \text{ENB})/2]
\]

\[
= 1 - [(2.3 - 2.0)/2] = 1 - 0.15,
\]

\[
\text{ENphenyl}: \text{group electronegativity of the phenyl ring [10]},
\]

\[
\text{ENB}: \text{electronegativity of boron [11].}
\]

\[
n(\psi_4) = 1 - i_p,
\]

\[
n(\psi_2) = 1 - i_c,
\]

\[
n(\psi_3) = 1 - i_c,
\]

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Table 1. Measured transition frequencies [MHz] of phenyldifluoroborane with hfs-splittings. \( v \): measured frequency, \( \Delta v_{\text{hfs}} \): hfs-splitting referred to the strongest component, \( \delta_{v_0} \): deviation of the experimental and the calculated splitting, \( v_0 \): hypothetical unsplit line frequency calculated with the hfs-splittings added to the frequencies of the components, \( \delta_{\text{calc}} \): deviation of the calculated and the experimental centre frequency.

<table>
<thead>
<tr>
<th>( J )</th>
<th>( K )</th>
<th>( K_+ )</th>
<th>( F )</th>
<th>( F' )</th>
<th>( v ) [MHz]</th>
<th>( \Delta v_{\text{hfs}} ) [MHz]</th>
<th>( \delta_{v_0} ) [MHz]</th>
<th>( v_0 ) [MHz]</th>
<th>( \delta_{\text{calc}} ) [kHz]</th>
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<tbody>
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<td>3</td>
<td>2</td>
<td>1</td>
<td>2</td>
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<td>2</td>
<td>9/2-7/2</td>
<td>5770.316</td>
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<td>11</td>
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<td>3</td>
<td>12</td>
<td>31/2-31/2</td>
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<td>19</td>
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<td>7054.816</td>
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</tbody>
</table>

The coupling constants \( \chi_{xx} \) and \( \chi_{yy} \) may be expressed as

\[
\chi_{xx} = [n(\psi_{p_+}) - n(\psi_{p_+}) + n(\psi_{p_+})]/2
\]

\[
eQ q_{210}(1 + c^+ \epsilon),
\]

\[
\chi_{yy} = [n(\psi_{p_+}) - n(\psi_{p_+}) + n(\psi_{p_+})]/2
\]

\[
eQ q_{210}(1 + c^+ \epsilon),
\]

\[
c^+ = 0.15 + 2i_\sigma - i_\pi,
\]

\[
eQ q_{210} = -5.39 \text{ MHz}[12].
\]

Table 2. Rotational and centrifugal distortion constants of phenyldifluoroborane, \( A_{JK} \) and \( \delta_{\epsilon} \) fixed to zero. The standard deviation of the fit is 58 kHz, highest correlation coefficient \(|(A_{K}, \delta_{\epsilon})| = 0.923.

<table>
<thead>
<tr>
<th>( A )</th>
<th>3686.278 (47) MHz</th>
<th>( [A_{JK}] 0.0 ) kHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>( B )</td>
<td>1099.4297 (16) MHz</td>
<td>( [\delta_{\epsilon}] 0.0 ) kHz</td>
</tr>
<tr>
<td>( C )</td>
<td>847.1989 (13) MHz</td>
<td>( \delta_{\epsilon} 1.21 (35) ) kHz</td>
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<tr>
<td>( A_{JK} )</td>
<td>0.0392 (85) kHz</td>
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<tr>
<td>( A_{K} )</td>
<td>14.7 (58) kHz</td>
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</tbody>
</table>

Table 3. Quadrupole coupling constants [MHz] of phenyldifluoroborane, \( F_1^+ \)B(C_6H_5)_2. \( \{\chi^+, \chi^-\} \) correlation coefficient. The standard deviation of the hfs analysis of 17 splittings is 4 kHz, the mean splitting is 232 kHz.

<table>
<thead>
<tr>
<th>( \chi^+ )</th>
<th>2.589 (12) MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \chi^- )</td>
<td>-3.788 (17) MHz</td>
</tr>
<tr>
<td>( \beta )</td>
<td>0.143</td>
</tr>
<tr>
<td>( \epsilon )</td>
<td>3.189 (15) MHz</td>
</tr>
</tbody>
</table>

We get from (1) with the orthonormality of the orbitals for the occupation of the orbitals of boron

\[
n(\psi_{p_+}) = 1 - i_\sigma,
\]

\[
n(\psi_{p_-}) = i_\pi,
\]

\[
n(\psi_{p_0}) = (1 - 0.15)(2a_\pi^2) + 2(1 - i_\sigma)(1 - 2a_\pi^2)/2,
\]

\[
n(\psi_{p_0}) = 1 - 0.15 + 2a_\pi^2(0.15) - i_\sigma.
\]
The result is

\[ i_a = 43.5\%, \quad i_K = 20.4\% . \]

The values of \( i_a \) are nearly equal, as expected. We assume that the errors, caused by the model, are minimized by comparison of the two similar molecules. Therefore we believe that the difference of the \( i_a \) values is significant although it is small. The larger \( i_a \) for phenyldifluoroborane may be caused by interactions with the \( \pi \) system of the phenyl ring. In our opinion the main part of the occupation of the \( p_x \) orbital is produced by back donation of electrons by the fluorine atoms.

We thank members of our group for help and discussion, the Deutsche Forschungsgemeinschaft, the Land Schleswig-Holstein and the Fonds der Chemie for funds. The calculations were made at the computer center of the University of Kiel.

[11] l.c. [7], Appendix G.
[12] l.c. [7], Chapt. XIV, Table 14.2.
[13] l.c. [7], Chapt. XIV, Table 14.3.