Neutron Diffraction Study of 1,2,3-Trichlorobenzene-d₃ *

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In order to explain the observed ³⁵Cl-NQR anomaly of the title compound, a neutron diffraction study on single crystals was carried out at 295 K and 158 K. No significant structural changes concerning phase transitions or molecular disorder between the two experiments were observed. The space group is P₃₁/c (C₃h) with 8 molecules per unit cell. The asymmetric unit contains 2 molecules. The cell parameters were determined to a = 1264(4) pm, b = 825(2) pm, c = 1503(3) pm, β = 143(3)° at 295 K and a = 1243(2) pm, b = 815(1) pm, c = 1494(2) pm, β = 114.3(1)° at 158 K. The molecules show rigid-body behaviour. No significant changes of the molecular geometry were observed. A strong variation of the temperature factors as function of the temperature was detected. An anharmonicity of the librational potential of the molecules was found by evaluation of the thermal parameters as function of temperature. For verifying the existence of dynamic processes which lead to a bleaching out of the ³⁵Cl-NQR lines difference, Fourier syntheses were calculated. A reorientation or an order-disorder process as suggested by ³⁵Cl-NQR spectroscopy above 230 K could not be confirmed within the error of the experiments. The degree of deuteration of the samples was determined by refinement of the occupation factors of the deuterium sites.

Introduction

³⁵Cl nuclear quadrupole resonance (NQR) studies of 1,2,3-trichlorobenzene-d₃ were made by Bray and Barnes [1, 2]. Six ³⁵Cl-NQR lines were detected at 77 K, corresponding to 2 crystallographic inequivalent molecules per unit cell. However at room temperature no signals were found. Further investigations of the compound have been reported by Tatsuzaki [3]. He found a bleaching out of the ³⁵Cl-NQR frequencies at a temperature (T°) of about 230 K. In addition, measurements of the ³⁵Cl-NQR linewidths, ¹H-NMR linewidths, and of the dielectric constant (ε') as functions of temperature were made. No variation of the ¹H-NMR linewidths was detected, whereas the ³⁵Cl-NQR lines show broadening near the bleaching out temperature. The dielectric constant increases from the low temperature value (2.19) to the high temperature value (2.59) at a temperature of 255 K. The bleaching out of the ³⁵Cl-NQR lines was explained by a reorientation of the molecules around an axis perpendicular to the molecular plane. A determination of the crystal structure of the protonated compound by means of neutron diffraction is due to Hazell et al. [4]. The structure contains two inequivalent molecules per unit cell, as predicted by ³⁵Cl-NQR-spectroscopy. The structure was refined using a rigid-body constraint [5]. Sharma et al. [6] determined the orientation of the electric field gradient tensors (EFGT) by means of ³⁵Cl-Zeeman-NQR methods. The linewidths and the spin-lattice relaxation times (T₁) of the ³⁵Cl-NQR lines as functions of temperature were also studied. Increasing linewidths and decreasing T₁ above 230 K were observed, and activation energies for the bleaching out process were determined. Both molecules show slightly different activation energies (molecule 1: 30.6 kJ/mole, molecule 2: 35.6 kJ/mole). An order-disorder phenomenon was proposed as the reason for the bleaching out of the ³⁵Cl-NQR lines. Investigations of the deuterated compound C₆Cl₃D₃ were performed by Wigand et al. [7, 8]. The quadrupole coupling constants of the deuterium nuclei were measured as functions of temperature; they show no change with temperature. Furthermore principal axes, magnitude and

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orientation of the EFG of the $^2$H nuclei were determined. A reorientation of the molecules was discussed in order to explain the bleaching out of $^{35}$Cl-NQR lines.

**Experimental**

The compound was prepared by catalytic deuteration of commercial 1,2,3-trichlorobenzene with $D_2$O/DCI and $D_2$/DCI. After several cycles a degree of deuteration of about 90%, determined by $^1$H-NMR, was obtained. The substance was then purified by zone refining. Single crystals were grown from ethanol solution by slow evaporation of the solvent [7]. A crystal with dimensions $8 \text{ mm} \times 8 \text{ mm} \times 4 \text{ mm}$ was used for the room temperature neutron diffraction study (295 K). The material shows high vapour pressure at room temperature; it was necessary to enclose the sample in an aluminium container. In order to reduce extinction effects, the highly perfect crystal was quenched in liquid nitrogen. Some strong reflections, e.g. (0 0 2), show an increase of intensity by a factor of 6 after quenching. A second crystal ($8 \text{ mm} \times 8 \text{ mm} \times 3 \text{ mm}$), used for the low temperature measurement, was treated in the same way.

The neutron diffraction experiments were carried out at the P110 4-circle-diffractometer (“hot” source, 5C2) at the Orphée reactor, Laboratoire Léon Brillouin, C.E.A. – C.N.R.S., C.E.N. – Saclay (France). The cell parameters at room temperature were determined from a set of centered angles of 20 reflections. The low temperature cell parameters were determined using 19 reflections. A temperature $T = 158$ K was obtained by means of a single-stage DISPLEX cryorefrigerator. The temperature was stabilized within $\pm 1 \text{ K}$ during the time of the experiment. For measuring as many reflection intensities as possible the normal bisecting mode of measurement was accomplished by the $\psi$ scan technique. Two standard reflections were repeated every 180 min to control the stability of the experiments. During the room temperature measurement the standard reflections show a slight decrease of intensity of about 2% within 13 days, probably due to some evaporation of the sample.

To get reliable information about the thermal parameters it is necessary to collect intensity data up to rather high $\sin \theta / \lambda$ values. In order to optimize the measuring time with respect to the quality of the data and the number of significant reflections, the reflections at higher $\sin \theta / \lambda$ were collected, sorted by the 

![Table 1. Experimental conditions and crystallographic parameters for 1,2,3-trichlorobenzene-$d_3$.](image)

values of their calculated structure factors. The model used for the calculation of structure factors was based on the results of Hazell et al. [4] accomplished by the already measured lower angle reflections. We have developed this measuring procedure and used it for the low temperature experiment. The diffractometer software was modified in order to sort the reflections according to their calculated structure factors. Thus
Fig. 1. Intensity of some reflections of 1,2,3-trichlorobenzene-d$_3$ vs. temperature.
the ratio between measured and observed reflections can be considerably increased, and about 50% of the measuring time can be saved. The saved time was used to improve the I/σ ratio of weaker reflections.

The intensities of both experiments were collected with the step scan technique (35 steps, variable range, profile measurement, background correction) with counting times between 0.7 and 4 seconds per step. In order to get more reliable intensity data, the reflections were measured twice symmetrically equivalent. The integration of peak intensities was made with 6 points for the left and the right background. Absorption correction using the crystal shape was applied. The absorption coefficient (μ = 0.56 cm⁻¹) was determined by minimizing the internal R value of the data. Extinction corrections lead to no significant changes in the atomic parameters or R values. Extinction effects seem to become rather small by quenching the crystal in liquid nitrogen. The scattering lengths used were: \( b_D = 6.67 \text{ fm}, b_{Ci} = 9.58 \text{ fm}, b_C = 6.65 \text{ fm} \) [9].

The experimental conditions are summarized in Table 1. The refinement was carried out with the program chain of Lundgren [10] (UPALS, etc.) at C.I.R.C.E. center (France) on an IBM 3090 computer. Structural drawings including thermal ellipsoids were made using ORTEP [11], further figures with a home made program HANDLE 3 [12].

Results and Discussion

While cooling down the crystal to 158 K the intensities of several reflections were measured every 10 K. The temperature variation of these reflections show an increase of intensity of about a factor 2 (Figure 1). The reflection (7 1 2) shows a decrease of intensity with decreasing temperature. This behaviour is probably caused by the special phase relation for this reflection. The temperature variations show no discontinuity or change in slope. No effects which correspond to the bleaching out of the \(^{35}\text{Cl}-\text{NQR}\) frequencies were observed.

The space group of the title compound was confirmed to be \( P2_1/c = C_{2h}^2 \) with 8 molecules per unit cell (2 inequivalent molecules). The cell parameters are \( a = 1264(4) \text{ pm}, b = 825(2) \text{ pm}, c = 1503(3) \text{ pm}, \beta = 114.3(3)° \) at 295 K and \( a = 1243(2) \text{ pm}, b = 815(1) \text{ pm}, c = 1494(2) \text{ pm}, \beta = 114.3(1)° \) at 158 K. As pointed out by Hazell et al. [4] the structure contains pairs of molecules in antiparallel arrangement, related by a center of symmetry. The two inequivalent molecules lead to two different types of pairs. The pairs of molecules of type 1 are centered at \( \frac{1}{2}, \frac{1}{2}, 0 \) and \( \frac{1}{2}, 0, \frac{1}{2} \) (point position: 2d). The centers of the molecule type 2 are situated at 0, 0, 0 and 0, \( \frac{1}{2}, \frac{1}{2} \) (point position: 2a). A labeling scheme of the molecules is shown in Figure 2. An “averaged” molecule was added for the discussion of the molecular geometry. The arrangement of the molecules in the unit cell is shown in Fig. 3; projections of the molecules and the pairs are given in Figure 4.

The structure was refined to \( R(F) = 5.1\% \) (295 K), \( R_w(F) = 3.6\% \) (295 K) and \( R(F) = 3.2\% \) (158 K), \( R_w(F) = 2.9\% \) (158 K). The final positional and equivalent isotropic thermal parameters (\( B_{eq} \)) for both experiments are listed in Table 2. Further information
Fig. 3. Projection of the unit cell of 1,2,3-trichlorobenzene-d₃ (295 K) along the crystallographic b axis.

The angles $\angle C(6)-C(1)-C(1)$, $\angle C(4)-C(3)-C(3)$, and $\angle C(1)-C(2)-C(2)$ are smaller than 120° (Table 4). Deviations of the endocyclic angles from 120° can be explained by applying the valance-shell electron-pair repulsion theory (VSEPR) [14, 15]. Increment tables for certain substituents of the phenyl system are published in [16]. The values calculated from the increments are in good agreement with the experiment (Table 5).

The positions of the non-hydrogen atoms do not differ significantly ($\approx 1$ e.s.d.) from the values determined for the protonated compound [4]. The bond lengths of the C–D bonds are by about 1 pm shorter than the C–H bonds. Assuming an anharmonic interatomic potential, C–D bonds are shorter than the C–H bonds due to a smaller zero point energy of the C–D system. The bonds C(1,6)$^-$H(1,6) and C(2,4)$^-$H(2,4) show a different behaviour (Table 6), being shorter than the corresponding C–D bonds. We cannot explain this difference, which was not visible in our structure analyses on the deuterated compound. Perhaps there might be some experimental difficulties in the study of protonated 1,2,3-trichlorobenzene, due to the strong incoherent scattering.

The distances between the planes of a pair of molecules are 352.1 pm (molecule 1: 295 K), 353.1 pm
(molecule 2: 295 K), and 345.6 pm (molecule 1: 158 K), 346.4 pm (molecule 2: 158 K). The angles between the molecular planes of the inequivalent molecules were determined to 75.1° (295 K) and 76.1° (158 K). Both molecules show almost planar conformations. Equations and distances of the atoms to the calculated best planes are given in Table 7. Largest deviations are found for the chlorine atoms, up to 1.6 pm, and the deuterium atoms, up to 1.8 pm. The "non-planarity" of the molecules is slightly increasing with decreasing temperature.

The shortest intermolecular distances were calculated for all combinations of carbon, chlorine, and deuterium atoms (Table 8). These distances are in
Table 4. Bond angles in 1,2,3-trichlorobenzene-d₃ at T = 295 K and 158 K.

Molecule 1  Molecule 2

<table>
<thead>
<tr>
<th>Atom 1</th>
<th>Atom 2</th>
<th>Atom 3</th>
<th>Angle/° (295 K)</th>
<th>Angle/° (158 K)</th>
</tr>
</thead>
<tbody>
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<td>C(1,2)</td>
<td>C(1,1)</td>
<td>C(1,6)</td>
<td>120.9(2)</td>
<td>120.9(1)</td>
</tr>
<tr>
<td>C(1,2)</td>
<td>C(1,1)</td>
<td>C(1,1)</td>
<td>120.4(2)</td>
<td>120.2(1)</td>
</tr>
<tr>
<td>C(1,6)</td>
<td>C(1,1)</td>
<td>C(1,1)</td>
<td>118.7(2)</td>
<td>118.9(1)</td>
</tr>
<tr>
<td>C(1,1)</td>
<td>C(1,2)</td>
<td>C(1,3)</td>
<td>118.6(2)</td>
<td>118.5(1)</td>
</tr>
<tr>
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<td>C(1,2)</td>
<td>C(1,2)</td>
<td>120.9(2)</td>
<td>121.0(1)</td>
</tr>
<tr>
<td>C(1,3)</td>
<td>C(1,2)</td>
<td>C(1,3)</td>
<td>120.5(2)</td>
<td>120.5(1)</td>
</tr>
<tr>
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<td>C(1,3)</td>
<td>C(1,4)</td>
<td>121.0(2)</td>
<td>121.1(1)</td>
</tr>
<tr>
<td>C(1,3)</td>
<td>C(1,3)</td>
<td>C(1,3)</td>
<td>118.9(2)</td>
<td>118.8(1)</td>
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<td>C(1,4)</td>
<td>C(1,5)</td>
<td>119.5(2)</td>
<td>119.4(1)</td>
</tr>
<tr>
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<td>C(1,4)</td>
<td>D(1,4)</td>
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<td>119.1(2)</td>
</tr>
<tr>
<td>C(1,5)</td>
<td>C(1,4)</td>
<td>D(1,4)</td>
<td>121.6(3)</td>
<td>121.5(2)</td>
</tr>
<tr>
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<td>C(1,5)</td>
<td>C(1,6)</td>
<td>120.5(2)</td>
<td>120.6(1)</td>
</tr>
<tr>
<td>C(1,4)</td>
<td>C(1,5)</td>
<td>D(1,5)</td>
<td>119.7(3)</td>
<td>119.8(2)</td>
</tr>
<tr>
<td>C(1,6)</td>
<td>C(1,5)</td>
<td>D(1,5)</td>
<td>119.9(3)</td>
<td>119.7(2)</td>
</tr>
<tr>
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<td>C(1,6)</td>
<td>C(1,5)</td>
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<td>119.6(1)</td>
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<tr>
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<td>C(1,6)</td>
<td>D(1,6)</td>
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<td>C(1,6)</td>
<td>D(1,6)</td>
<td>121.0(3)</td>
<td>121.4(1)</td>
</tr>
</tbody>
</table>

Table 5. Observed and calculated differences of the endocyclic angles from 120° in 1,2,3-trichlorobenzene-d₃; \( \sum_{\text{inc}} \) : sum of increments [16]; \( \Delta(i)_i \): angle difference from 120° (molecule i), \( \Delta_{\text{sym}} \): difference from 120° for symmetry averaged angles.

<table>
<thead>
<tr>
<th>Angle</th>
<th>( \sum_{\text{inc}}/° )</th>
<th>( \Delta(I)/° )</th>
<th>( \Delta(II)/° )</th>
<th>( \Delta_{\text{sym}}/° )</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>295 K</td>
<td>158 K</td>
<td>295 K</td>
<td>158 K</td>
</tr>
<tr>
<td>C(6)</td>
<td>C(1)</td>
<td>C(2)</td>
<td>1.1(4)</td>
<td>1.1(4)</td>
</tr>
<tr>
<td>C(1)</td>
<td>C(2)</td>
<td>C(3)</td>
<td>-0.9(4)</td>
<td>-0.9(4)</td>
</tr>
<tr>
<td>C(2)</td>
<td>C(3)</td>
<td>C(4)</td>
<td>1.1(4)</td>
<td>1.1(4)</td>
</tr>
<tr>
<td>C(3)</td>
<td>C(4)</td>
<td>C(5)</td>
<td>-1.0(4)</td>
<td>-1.0(4)</td>
</tr>
<tr>
<td>C(4)</td>
<td>C(5)</td>
<td>C(6)</td>
<td>1.0(4)</td>
<td>1.0(4)</td>
</tr>
<tr>
<td>C(5)</td>
<td>C(6)</td>
<td></td>
<td>-1.0(4)</td>
<td>-1.0(4)</td>
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</tbody>
</table>

Table 6. Comparison of C–D and C–H bond lengths in 1,2,3-trichlorobenzene-d₃, (T = 295 K) and 1,2,3-trichlorobenzene [4].

<table>
<thead>
<tr>
<th>Atom 1</th>
<th>Atom 2</th>
<th>1,2,3-trichlorobenzene</th>
<th>1,2,3-trichlorobenzene-d₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>atom 1</td>
<td>atom 2</td>
<td>d/pm</td>
</tr>
<tr>
<td>C(1,4)</td>
<td>D(1,4)</td>
<td></td>
<td>107.1(4)</td>
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<tr>
<td>C(1,5)</td>
<td>D(1,5)</td>
<td></td>
<td>107.6(4)</td>
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<tr>
<td>C(1,6)</td>
<td>D(1,6)</td>
<td></td>
<td>107.4(4)</td>
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<tr>
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<td>D(2,4)</td>
<td></td>
<td>107.8(4)</td>
</tr>
<tr>
<td>C(2,5)</td>
<td>D(2,5)</td>
<td></td>
<td>107.4(5)</td>
</tr>
<tr>
<td>C(2,6)</td>
<td>D(2,6)</td>
<td></td>
<td>107.1(4)</td>
</tr>
</tbody>
</table>

Calculations of T-, L-, S-tensors were carried out with the program XANADU by Roberts and Sheldrick [18]. The formalism corresponds to that given by Schomaker and Trueblood [19]. By calculation, good agreement for the room and low temperature data is found. The quality of the calculation is expressed by the \( R_g \) value. \( R_g \) describes the agreement of observed and calculated orthogonalized anisotropic temperature parameters. We obtained \( R_g = 5.53% \) (molecule 1) and \( R_g = 5.31% \) (molecule 2) at room temperature and \( R_g = 9.26% \) (molecule 1) and \( R_g = 9.06% \) (molecule 2) for the low temperature experiment. The lower \( R_g \) value of the room temperature study is caused by the more important contribution of the molecular librations at higher temperatures. The corrections of the bond lengths due to the rigid-body motion are referred in Table 9. The maximum change of the bond lengths is 1.2 pm. The T-, L-, S-tensors are given in Tables 10 and 11. The positions which give symmetric S-tensors have an averaged distance of 30 pm to the center of mass of the molecule.

The evaluation of the equivalent isotropic temperature factors (\( B_{eq} \)) as functions of temperature leads to...
Table 7. Distance to the best planes calculated for 1,2,3-trichlorobenzene-d₃.

<table>
<thead>
<tr>
<th>Distance</th>
<th>atom 1</th>
<th>atom 2</th>
<th>symmetry operation of atom 2</th>
<th>d₂₉₅K/pm</th>
<th>d₁₅₈K/pm</th>
<th>Δd/pm</th>
</tr>
</thead>
<tbody>
<tr>
<td>C ••• C</td>
<td>C(1,6) • C(1,6)</td>
<td>1 - x,  y,  z</td>
<td>350.9(7)</td>
<td>343.4(5)</td>
<td>7.5(12)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C(2,1) • C(2,3)</td>
<td></td>
<td>353.6(6)</td>
<td>346.4(3)</td>
<td>7.2(9)</td>
<td></td>
</tr>
<tr>
<td>C ••• D</td>
<td>D(1,6) • C(1,6)</td>
<td>1 - x,  y,  z</td>
<td>304.0(6)</td>
<td>297.6(4)</td>
<td>6.4(9)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>D(2,4) • C(2,4)</td>
<td>x,  1 - y,  z</td>
<td>307.6(6)</td>
<td>301.4(4)</td>
<td>6.3(10)</td>
<td></td>
</tr>
<tr>
<td>Cl ••• Cl</td>
<td>Cl(1,1) • Cl(1,2)</td>
<td>1 - x,  -1/2 + y,  1/2 - z</td>
<td>358.7(7)</td>
<td>352.0(3)</td>
<td>6.7(10)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cl(2,3) • Cl(2,1)</td>
<td>x,  1/2 - y,  1/2 + z</td>
<td>375.1(7)</td>
<td>370.9(3)</td>
<td>4.1(10)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cl(2,3) • Cl(1,3)</td>
<td>x,  -1/2 + y,  -1/2 - z</td>
<td>375.3(8)</td>
<td>367.1(4)</td>
<td>8.2(11)</td>
<td></td>
</tr>
<tr>
<td>Cl ••• C</td>
<td>Cl(1,3) • C(2,1)</td>
<td>x,  1 - y,  z</td>
<td>340.6(6)</td>
<td>333.6(4)</td>
<td>7.0(9)</td>
<td></td>
</tr>
<tr>
<td>D ••• D</td>
<td>D(1,4) • D(2,5)</td>
<td>x,  1/2 - y,  1/2 + z</td>
<td>271.2(7)</td>
<td>264.8(4)</td>
<td>6.3(10)</td>
<td></td>
</tr>
<tr>
<td>D ••• Cl</td>
<td>D(1,4) • Cl(2,2)</td>
<td>x,  1/2 + y,  -1/2 - z</td>
<td>289.2(7)</td>
<td>282.0(3)</td>
<td>7.2(10)</td>
<td></td>
</tr>
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</table>

Distances marked with * are not the shortest Cl–Cl distances.
Table 9. Corrected bond lengths in 1,2,3-trichlorobenzene-d₃, $d_{\text{corr}}$: bond lengths corrected for rigid-body motion, $\Delta$: difference between corrected and uncorrected bond lengths.

<table>
<thead>
<tr>
<th>Molecule 1</th>
<th>Molecule 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom 1</td>
<td>Atom 2</td>
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<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>C(1,1)</td>
<td>C(1,2)</td>
</tr>
<tr>
<td>C(1,1)</td>
<td>C(1,6)</td>
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</tbody>
</table>

Table 10. Rigid-body analysis of 1,2,3-trichlorobenzene-d₃ (295 K), $x$, $y$, $z$, $c$.

<table>
<thead>
<tr>
<th>Molecule 1</th>
<th>Molecule 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>L tensor/rad²</td>
<td>L tensor/rad²</td>
</tr>
<tr>
<td>0.0077(3)</td>
<td>0.0037(2)</td>
</tr>
<tr>
<td>T tensor/pm²</td>
<td>T tensor/pm²</td>
</tr>
<tr>
<td>327(12)</td>
<td>141(9)</td>
</tr>
<tr>
<td>S tensor/(pm rad)</td>
<td>S tensor/(pm rad)</td>
</tr>
<tr>
<td>-0.04(5)</td>
<td>-0.01(4)</td>
</tr>
<tr>
<td>Point for symmetric S tensor triclinic coord.</td>
<td>Point for symmetric S tensor triclinic coord.</td>
</tr>
<tr>
<td>0.3877</td>
<td>0.3882</td>
</tr>
<tr>
<td>Center of mass triclinic coord.</td>
<td>Center of mass triclinic coord.</td>
</tr>
<tr>
<td>0.3882</td>
<td>0.3882</td>
</tr>
</tbody>
</table>

| Rₖ/% | Rₖ/% |
| 5.53 | 5.31 |

Table 11. Rigid-body analysis of 1,2,3-trichlorobenzene-d₃ (158 K), $x$, $y$, $z$, $c$.

<table>
<thead>
<tr>
<th>Molecule 1</th>
<th>Molecule 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>L tensor/rad²</td>
<td>L tensor/rad²</td>
</tr>
<tr>
<td>0.0037(2)</td>
<td>0.00037(2)</td>
</tr>
<tr>
<td>T tensor/pm²</td>
<td>T tensor/pm²</td>
</tr>
<tr>
<td>141(9)</td>
<td>141(9)</td>
</tr>
<tr>
<td>S tensor/(pm rad)</td>
<td>S tensor/(pm rad)</td>
</tr>
<tr>
<td>-0.01(4)</td>
<td>-0.01(4)</td>
</tr>
<tr>
<td>Point of symmetric S tensor triclinic coord.</td>
<td>Point of symmetric S tensor triclinic coord.</td>
</tr>
<tr>
<td>0.3881</td>
<td>0.3881</td>
</tr>
<tr>
<td>Center of mass triclinic coord.</td>
<td>Center of mass triclinic coord.</td>
</tr>
<tr>
<td>0.3881</td>
<td>0.3881</td>
</tr>
</tbody>
</table>

| Rₖ/% | Rₖ/% |
| 9.26 | 9.26 |
92.5(4)% (158 K) results for the 5-position. The results for the two crystals used for the experiment show good agreement. The total degree of deuteration results in 95.0(6)% and 94.3(4)% for the first and the second crystal, respectively.

The reason for the lower deuteration of the 5-position is the lower reactivity of this position. The ortho and para positions (4-, 6-position) have a higher reactivity than the meta position (for electrophile aromatic substitution). Summing up the number of neighbours with respect to ortho, para and meta positions, a number of 1 ortho, 1 para, and 1 meta position results for the 4- and 6-position. For the 5-position a number of 1 para and 2 meta neighbours is found. The higher deuteration of the 4- and 6-positions can be understood using this simple picture. The \( R_w(F) \) value decreases by 0.5% if a refinement of the occupation factors of the deuterium sites is allowed. The signifi-
cance of the decrease of the $R_w$ value was confirmed by the "Hamilton" test ($\mathcal{F}$ factor test) [20, 21]. A significance level of better than 99.5% was determined.

Difference Fourier syntheses for the planes of the molecules show no structures. A difference Fourier synthesis for a molecule of type 1 is shown in Figure 5. A residual scattering density up to 2.2% (molecule 1: 295 K) and up to 2.3% (molecule 2: 295 K) of the strongest Fourier peak (chlorine) was observed. Therefore no indications for molecular disorder as discussed by Sharma et al. [6] were found in the difference Fourier syntheses.

Acknowledgements

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