Neutron Diffraction Study of 1,2,3-Trichlorobenzene-d_3 *

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In order to explain the observed ^{35}Cl-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 $P2_1/c = C^5_{2h}$ 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, $\beta = 14.3(3)°$ at 295 K and $a = 1243(2)$ pm, $b = 815(1)$ pm, $c = 1494(2)$ pm, $\beta = 114.3(1)°$ 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 ^{35}Cl-NQR lines difference, Fourier syntheses were calculated. A reorientation or an order-disorder process as suggested by ^{35}Cl-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

^{35}Cl nuclear quadrupole resonance (NQR) studies of 1,2,3-trichlorobenzene-d_3 were made by Bray and Barnes [1, 2]. Six ^{35}Cl-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 ^{35}Cl-NQR frequencies at a temperature (T_B) of about 230 K. In addition, measurements of the ^{35}Cl-NQR linewidths, ^{1}H-NMR linewidths, and of the dielectric constant (ε') as functions of temperature were made. No variation of the ^{1}H-NMR linewidths was detected, whereas the ^{35}Cl-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 ^{35}Cl-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 ^{35}Cl-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 ^{35}Cl-Zeeman-NQR methods. The linewidths and the spin-lattice relaxation times (T_1) of the ^{35}Cl-NQR lines as functions of temperature were also studied. Increasing linewidths and decreasing T_1 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 ^{35}Cl-NQR lines. Investigations of the deuterated compound $C_6Cl_3D_3$ 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 EFGT 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_2O/DCl and D_2/DCl. 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 mm × 8 mm × 4 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 mm × 8 mm × 3 mm), used for the low temperature measurement, was treated in the same way.

The neutron diffraction experiments were carried out at the P 110 4-circle-diffractometer ("hot" source, 5C2) at the Orphée reactor, Laboratoire Léon Brillouin, C.E.A. – C.N.R.S., C.E.N. – Saclay. 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 ± 1 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 ψ 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.

Table 1. Experimental conditions and crystallographic parameters for 1,2,3-trichlorobenzene-d_3.

Neutron source	"Hot" source Orphée Reaktor, Laboratoire Léon Brillouin, C.E.A. – C.N.R.S., C.E.N. Saclay (France)	
Monochromator	vertical focussing Cu(220), Er filter (0.25 mm)	
Wavelengths/pm	83.07(10)	
Temperature/K	295, 158	
Compound	1,2,3-trichlorobenzene-d_3: $C_6D_3Cl_3$	
Formular mass/(g/mol)	184.47	
Space group	$P2_1/c = C^5_{2h}$	
Cell parameters	295 K	158 K
a/pm	1264(4)	1243(2)
b/pm	825(2)	815(1)
c/pm	1503(3)	1494(2)
β/°	114.3(3)	114.3(1)
Volume of the unit cell/(10^6 pm^3)	1428(4)	1379(4)
Molecules per unit cell	$Z = 8$	
Crystal faces	$(\bar{1}\bar{1}1)$, $(11\bar{1})$, (001), $(00\bar{1})$, (110), $(\bar{1}\bar{1}0)$, $(\bar{1}11)$, $(1\bar{1}\bar{1})$	
Measuring section	$\pm h$, $\pm k$, l	
Scan mode	ω-Scan	
Scan width (resolution adapted) $\Delta\omega^2 = A + B \tan\theta + C\, tan^2\,\theta$	$A = 10$, $B = -27$, $C = 40$	
Standard reflections	$(0\bar{6}0)$, (045)	
$(\sin\theta/\lambda)_{\max}$/pm^{-1}	$7.3 \cdot 10^{-3}$	
Linear absorption coefficient/cm^{-1}: μ	0.56	
Transmission factors	0.6016–0.7624	
Measured reflections	9409	6102
Unique reflections	4574	3407
R(intern)/%	3.65	2.81
Reflections used in final refinement ($I_0 > 2.5\,\sigma$): m	2363	2813
Number of parameters varied: n	219	219
R/%	5.08	3.23
R_w/%	3.59	2.89
"Goodness of Fit": S	1.651	1.535
Equivalent positions:	all atoms in 4e: x, y, z; $\bar{x}, \frac{1}{2}+x, \frac{1}{2}-z$; $\bar{x}, \bar{y}, \bar{z}$; $x, \frac{1}{2}-y, \frac{1}{2}+z$;	

$$R_w = \sqrt{\sum (w(F_0 - F_c)^2) / \sum (w F_c^2)}, \quad 1/w = \sqrt{\sigma^2 + (0.01\,F_0)^2}$$

$$S = \sqrt{(w(F_0 - F_c)^2)/(m - n)}$$

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 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

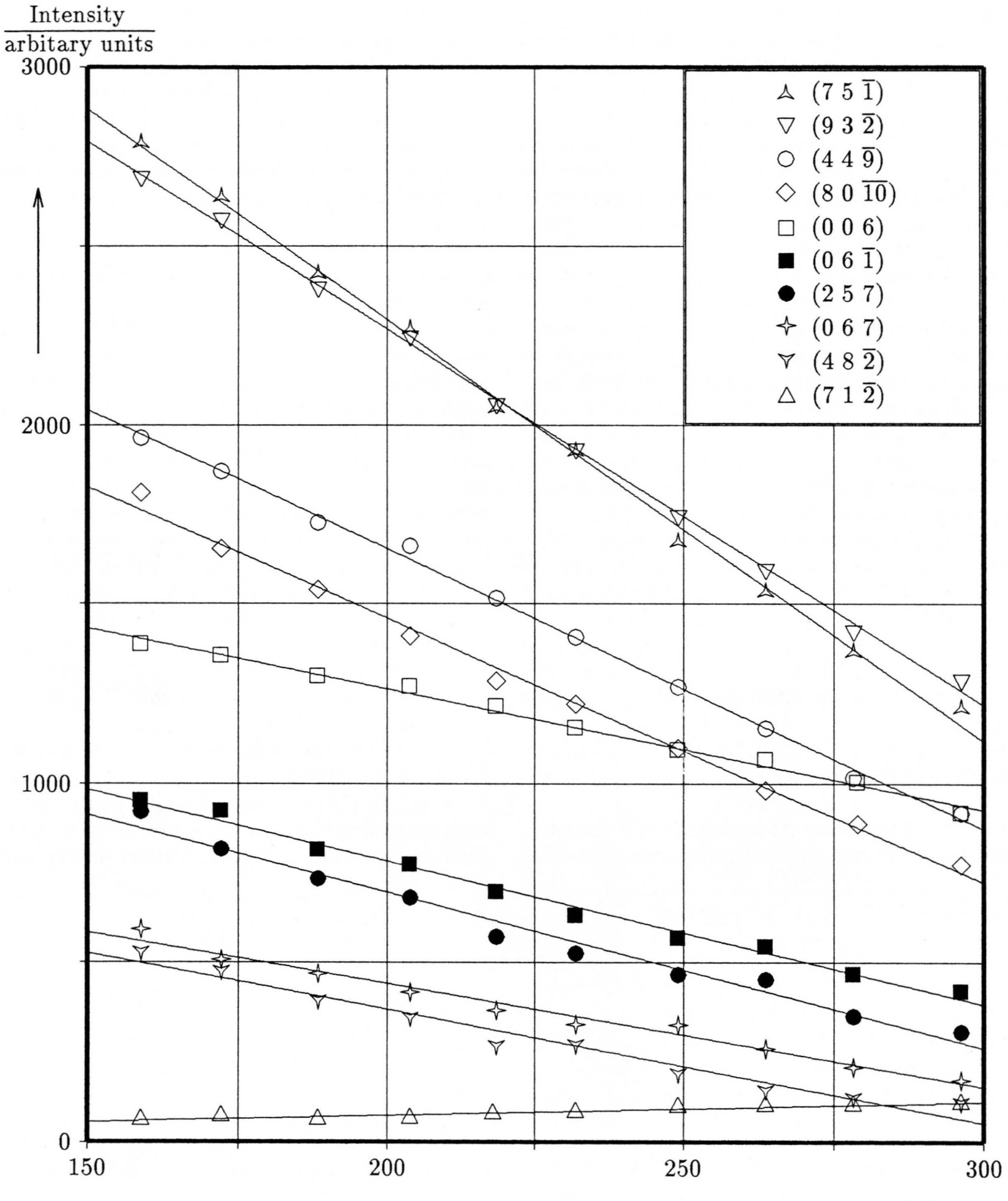


Fig. 1. Intensity of some reflections of 1,2,3-trichlorobenzene-d_3 vs. temperature.

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 ($\mu = 0.56\ \mathrm{cm}^{-1}$) 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: $b_D = 6.67$ fm, $b_{Cl} = 9.58$ fm, $b_C = 6.65$ 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 ellipsoides 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 ($7\ 1\ \bar{2}$) 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}Cl-NQR frequencies were observed.

The space group of the title compound was confirmed to be $P2_1/c = C_{2h}^5$ with 8 molecules per unit cell (2 inequivalent molecules). The cell parameters are $a = 1264(4)$ pm, $b = 825(2)$ pm, $c = 1503(3)$ pm, $\beta = 114.3(3)°$ at 295 K and $a = 1243(2)$ pm, $b = 815(1)$ pm, $c = 1494(2)$ 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_{equ}) for both experiments are listed in Table 2. Further information

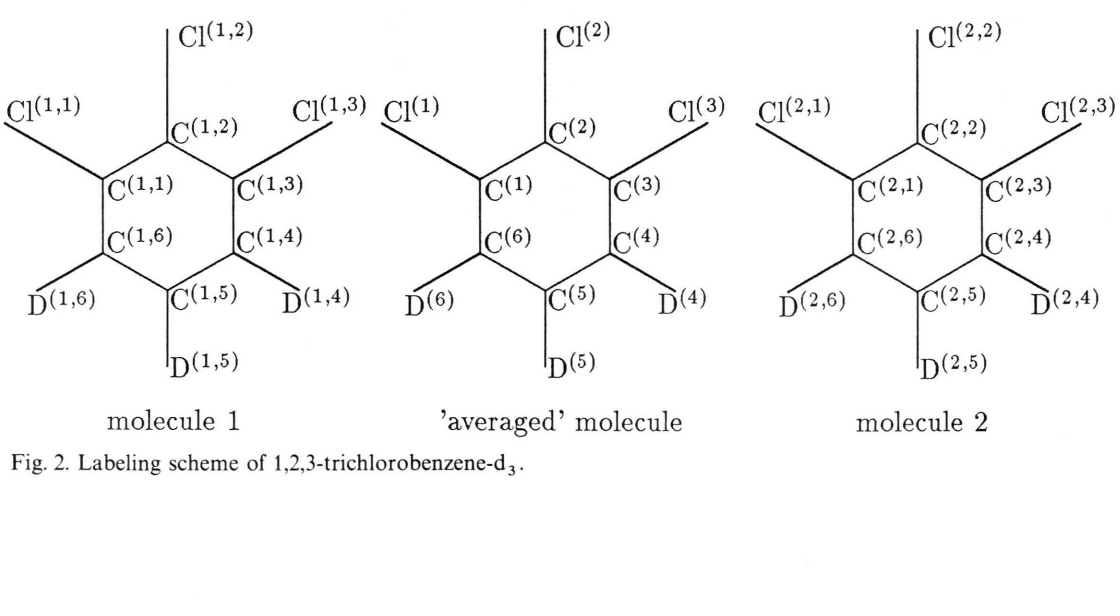


Fig. 2. Labeling scheme of 1,2,3-trichlorobenzene-d_3.

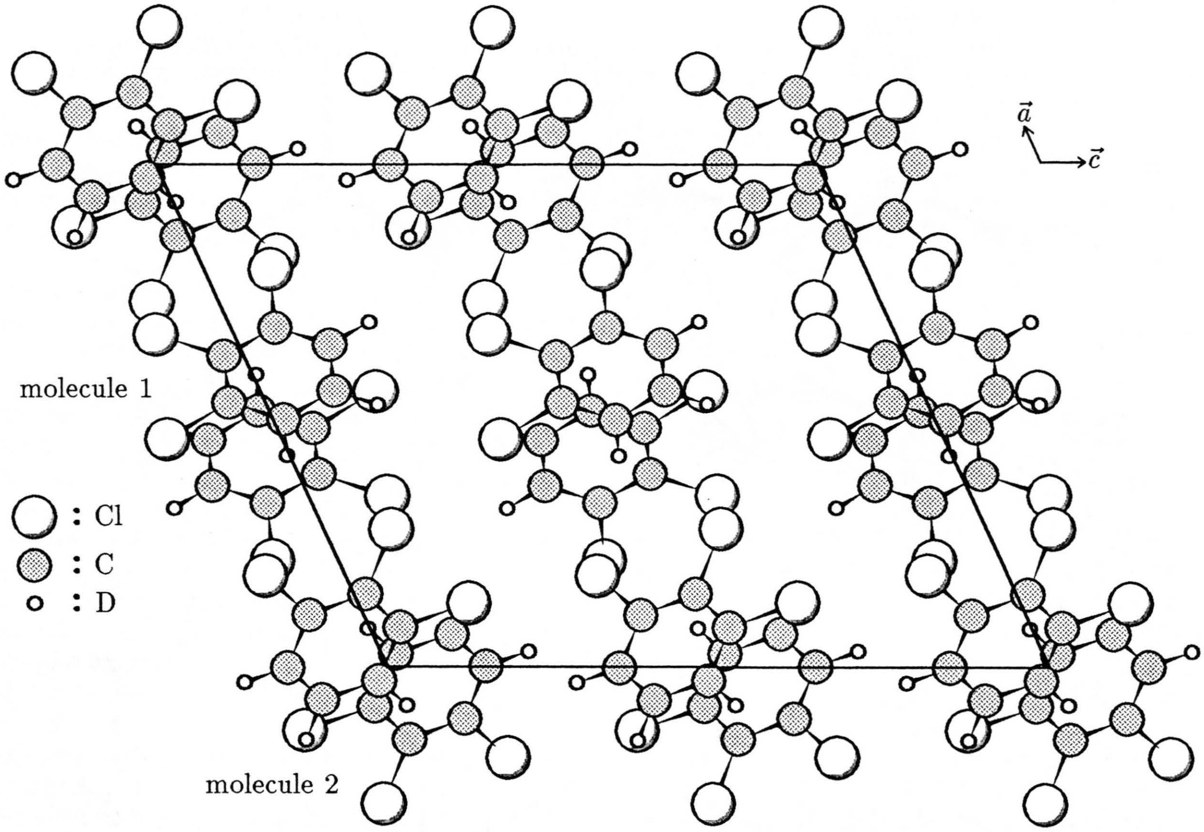


Fig. 3. Projection of the unit cell of 1,2,3-trichlorobenzene-d_3 (295 K) along the crystallographic ***b*** axis.

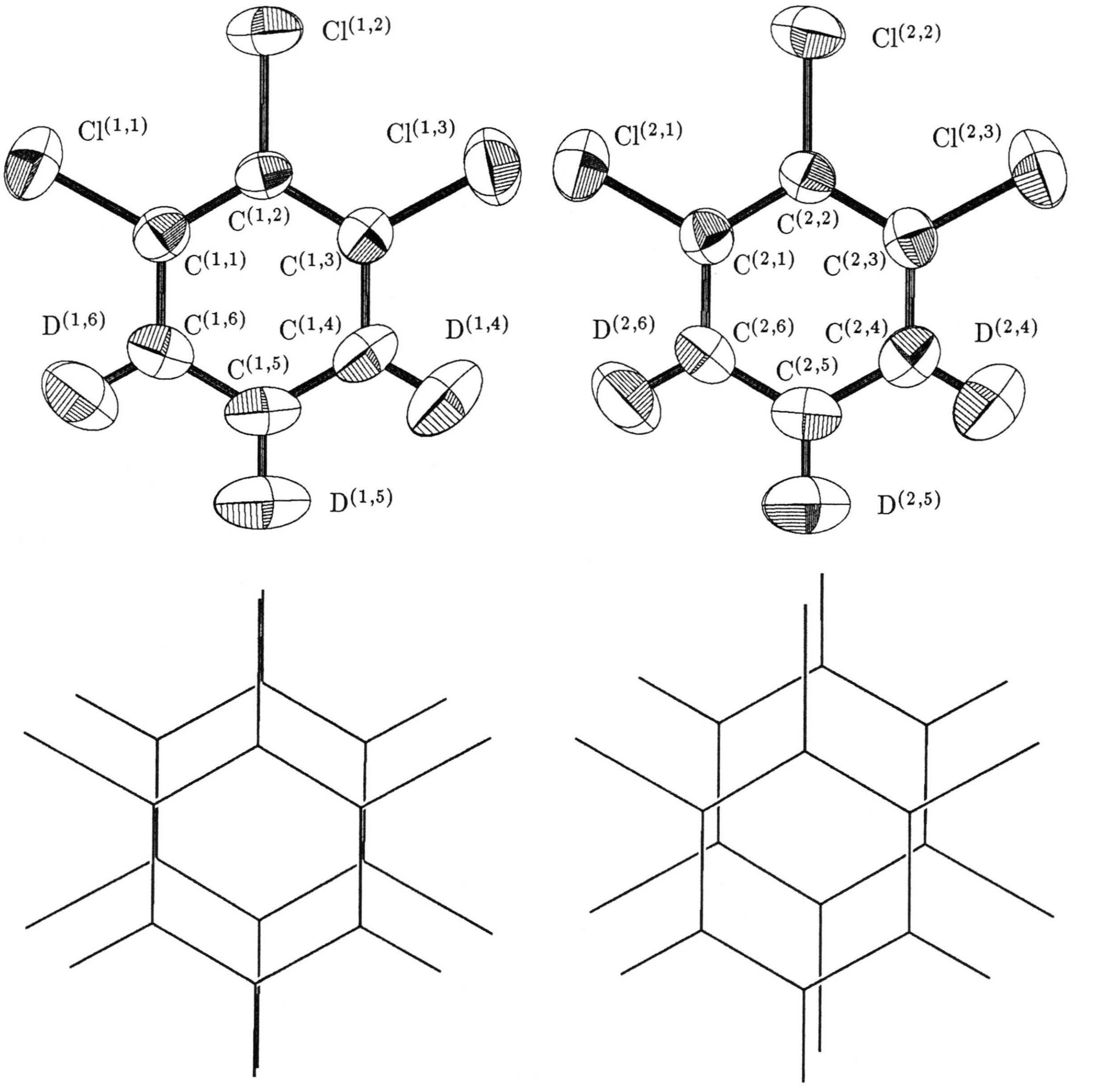
about the structure determination can be obtained from [13].

The molecules are slightly distorted from ideal geometry. Molecule 2 shows the stronger deviations. The averaged bond lengths are 139.8 pm for the $C^{(1)}-C^{(2)}$, $C^{(2)}-C^{(3)}$, 137.7 pm for the $C^{(3)}-C^{(4)}$, $C^{(1)}-C^{(6)}$, and 138.9 pm for the $C^{(4)}-C^{(5)}$, $C^{(5)}-C^{(6)}$ bonds. The C–Cl distances vary between 171.9 pm for the $C^{(1)}-Cl^{(1)}$, $C^{(3)}-Cl^{(3)}$, and 171.3 pm for the $C^{(2)}-Cl^{(2)}$ bond. The C–D bonds show an averaged bond length of 107.8 pm. These values are averaged over the two molecules in the unit cell for the 158 K study. $d(C^{(1)}-C^{(2)})$ and $d(C^{(2)}-C^{(3)})$ are elongated due to the repulsive interaction of the chlorine atoms (see Table 3).

The angles $C^{(6)}-C^{(1)}-Cl^{(1)}$, $C^{(4)}-C^{(3)}-Cl^{(3)}$, and $C^{(1)}-C^{(2)}-C^{(3)}$ 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 (≈ 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 1 molecule 2

Fig. 4. Projection of the molecules and molecule pairs perpendicular to the molecular planes of 1,2,3-trichlorobenzene-d_3 (295 K).

(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 2. Atom positions and B_{equ} for 1,2,3-trichlorobenzene-d_3 at 295 K and 158 K:

$$B_{\text{equ}} = \tfrac{4}{3} \cdot \{\beta_{11} a^2 + \ldots + 2\beta_{12}\, a\, b \cos\gamma + \ldots\}.$$

Temp./K	295	158	295	158	295	158	295	158
Atom	x/a		y/b		z/c		$B_{\text{equ}}/(10^2\ \text{pm}^2)$	
$C^{(1,1)}$	0.4744(1)	0.4760(1)	0.2658(1)	0.2648(1)	0.0543(1)	0.0543(1)	3.50(6)	1.53(3)
$C^{(1,2)}$	0.3814(1)	0.3817(1)	0.3723(2)	0.3746(1)	0.0302(1)	0.0299(1)	3.10(5)	1.39(3)
$C^{(1,3)}$	0.3243(1)	0.3236(1)	0.4220(2)	0.4245(1)	−0.0663(1)	−0.0677(1)	3.52(6)	1.52(3)
$C^{(1,4)}$	0.3584(2)	0.3579(1)	0.3665(2)	0.3670(1)	−0.1371(1)	−0.1392(1)	4.26(7)	1.86(3)
$C^{(1,5)}$	0.4508(2)	0.4518(1)	0.2600(2)	0.2576(1)	−0.1115(1)	−0.1133(1)	4.55(8)	1.95(3)
$C^{(1,6)}$	0.5090(2)	0.5111(1)	0.2096(2)	0.2066(1)	−0.0159(1)	−0.0166(1)	4.23(8)	1.83(3)
$Cl^{(1,1)}$	0.5480(1)	0.5509(1)	0.2011(2)	0.2006(1)	0.1724(1)	0.1736(1)	5.92(7)	2.59(3)
$Cl^{(1,2)}$	0.3385(1)	0.3383(1)	0.4419(2)	0.4468(1)	0.1174(1)	0.1175(1)	4.94(6)	2.12(2)
$Cl^{(1,3)}$	0.2089(1)	0.2068(1)	0.5530(2)	0.5590(1)	−0.0994(1)	−0.1013(1)	5.99(7)	2.55(3)
$D^{(1,4)}$	0.3130(3)	0.3121(1)	0.4086(4)	0.4093(2)	−0.2106(2)	−0.2134(1)	7.05(14)	3.35(6)
$D^{(1,5)}$	0.4781(3)	0.4792(2)	0.2173(4)	0.2124(2)	−0.1664(2)	−0.1686(1)	7.36(16)	3.52(6)
$D^{(1,6)}$	0.5815(2)	0.5849(1)	0.1280(4)	0.1231(2)	0.0048(2)	0.0048(1)	6.71(14)	3.29(6)
$C^{(2,1)}$	−0.1016(1)	−0.1002(1)	0.0756(1)	0.0739(1)	0.0809(1)	0.0813(1)	3.51(6)	1.54(3)
$C^{(2,2)}$	−0.1428(1)	−0.1425(1)	0.1178(2)	0.1170(1)	−0.0170(1)	−0.0178(1)	3.24(6)	1.42(3)
$C^{(2,3)}$	−0.0777(1)	−0.0761(1)	0.2245(2)	0.2264(1)	−0.0462(1)	−0.0468(1)	3.63(6)	1.57(3)
$C^{(2,4)}$	0.0263(2)	0.0294(1)	0.2873(2)	0.2905(1)	0.0216(1)	0.0211(1)	4.28(7)	1.88(3)
$C^{(2,5)}$	0.0649(2)	0.0689(1)	0.2445(3)	0.2473(1)	0.1187(1)	0.1194(1)	4.50(7)	1.93(3)
$C^{(2,6)}$	0.0014(2)	0.0047(1)	0.1386(2)	0.1388(1)	0.1491(1)	0.1499(1)	4.19(7)	1.80(3)
$Cl^{(2,1)}$	−0.1795(1)	−0.1795(1)	−0.0547(2)	−0.0592(1)	0.1198(1)	0.1203(1)	5.80(7)	2.51(3)
$Cl^{(2,2)}$	−0.2721(1)	−0.2738(1)	0.0428(2)	0.0400(1)	−0.1002(1)	−0.1012(1)	4.94(6)	2.11(2)
$Cl^{(2,3)}$	−0.1256(1)	−0.1251(1)	0.2826(2)	0.2848(1)	−0.1658(1)	−0.1675(1)	5.86(8)	2.52(3)
$D^{(2,4)}$	0.0755(2)	0.0792(1)	0.3691(4)	0.3740(2)	−0.0027(2)	−0.0033(1)	6.83(13)	3.25(6)
$D^{(2,5)}$	0.1449(2)	0.1503(1)	0.2941(4)	0.2986(2)	0.1711(2)	0.1722(1)	7.23(14)	3.46(6)
$D^{(2,6)}$	0.0310(2)	0.0347(1)	0.1040(4)	0.1041(2)	0.2241(2)	0.2259(1)	6.59(13)	3.26(5)

Table 3. Bond lengths in 1,2,3-trichlorobenzene-d_3 at $T = 295$ K and 158 K.

Molecule 1				Molecule 2			
atom 1	atom 2	d/pm (295 K)	d/pm (158 K)	atom 1	atom 2	d/pm (295 K)	d/pm (158 K)
$C^{(1,1)}$	$C^{(1,2)}$	139.0(4)	139.9(2)	$C^{(2,1)}$	$C^{(2,2)}$	138.8(4)	139.8(2)
$C^{(1,1)}$	$C^{(1,6)}$	137.8(4)	138.5(2)	$C^{(2,1)}$	$C^{(2,6)}$	138.4(4)	139.0(2)
$C^{(1,1)}$	$Cl^{(1,1)}$	171.5(5)	171.9(2)	$C^{(2,1)}$	$Cl^{(2,1)}$	171.5(3)	172.0(2)
$C^{(1,2)}$	$C^{(1,3)}$	138.9(4)	139.6(2)	$C^{(2,2)}$	$C^{(2,3)}$	139.4(3)	139.9(2)
$C^{(1,2)}$	$Cl^{(1,2)}$	171.1(4)	171.2(2)	$C^{(2,2)}$	$Cl^{(2,2)}$	171.2(5)	171.4(3)
$C^{(1,3)}$	$C^{(1,4)}$	138.1(4)	138.5(2)	$C^{(2,3)}$	$C^{(2,4)}$	138.9(4)	138.8(2)
$C^{(1,3)}$	$Cl^{(1,3)}$	171.6(4)	172.1(2)	$C^{(2,3)}$	$Cl^{(2,3)}$	171.2(5)	171.7(2)
$C^{(1,4)}$	$C^{(1,5)}$	138.3(4)	139.1(2)	$C^{(2,4)}$	$C^{(2,5)}$	138.0(4)	138.9(2)
$C^{(1,4)}$	$D^{(1,4)}$	107.1(4)	107.4(2)	$C^{(2,4)}$	$D^{(2,4)}$	107.8(4)	108.0(2)
$C^{(1,5)}$	$C^{(1,6)}$	138.2(4)	138.8(2)	$C^{(2,5)}$	$C^{(2,6)}$	138.5(3)	138.9(2)
$C^{(1,5)}$	$D^{(1,5)}$	107.6(4)	108.1(2)	$C^{(2,5)}$	$D^{(2,5)}$	107.4(5)	107.9(2)
$C^{(1,6)}$	$D^{(1,6)}$	107.4(4)	107.9(2)	$C^{(2,6)}$	$D^{(2,6)}$	107.1(4)	107.6(2)

good agreement with the sums of the van der Waals radii [17]. The intermolecular interaction is therefore dominated by van der Waals interactions. An averaged shortening of the intermolecular distances of 6.8 pm between 295 K and 158 K was observed. The same effect is found for the distances between the pairs of planes. This can be understood by the smaller influence of the thermal motion at lower temperatures. The larger thermal librational amplitudes will increase the intermolecular repulsion. This causes increasing distances between a pair of molecules with increasing temperature. The intramolecular chlorine distances vary between 312.1 pm and 313.6 pm (295 K) and 312.9 pm and 314.5 pm (158 K).

The intramolecular distances and bond angles (Tables 3 and 4) show no significant temperature dependence. Variations of distances and angles are within 1 e.s.d. for all atoms.

The temperature factors B_{equ} reveal an interesting behaviour. The values increase with increasing distance of the atom from the center of mass of the molecule (Table 2). This phenomenon can be explained by assuming thermal motions of the molecule as a whole. The molecular frame is the benzene ring which hinders uncorrelated motions of the atoms. Therefore, vibration of the molecule as a whole dominates the thermal motion. The variations of B_{equ} with the distance from the center of mass was also found for the low temperature experiment. To verify the rigid-body behaviour,

Table 4. Bond angles in 1,2,3-trichlorobenzene-d_3 at $T = 295$ K and 158 K.

Molecule 1			Molecule 2		
Atom 1–2–3	angle/° (295 K)	angle/° (158 K)	Atom 1–2–3	angle/° (295 K)	angle/° (158 K)
$C^{(1,2)}-C^{(1,1)}-C^{(1,6)}$	120.9(2)	120.9(1)	$C^{(2,2)}-C^{(2,1)}-C^{(2,6)}$	121.2(2)	121.0(1)
$C^{(1,2)}-C^{(1,1)}-Cl^{(1,1)}$	120.4(2)	120.2(1)	$C^{(2,2)}-C^{(2,1)}-Cl^{(2,1)}$	120.1(2)	120.0(1)
$C^{(1,6)}-C^{(1,1)}-Cl^{(1,1)}$	118.7(2)	118.9(1)	$C^{(2,6)}-C^{(2,1)}-Cl^{(2,1)}$	118.7(2)	119.0(1)
$C^{(1,1)}-C^{(1,2)}-C^{(1,3)}$	118.6(2)	118.5(1)	$C^{(2,1)}-C^{(2,2)}-C^{(2,3)}$	118.7(2)	118.4(1)
$C^{(1,1)}-C^{(1,2)}-Cl^{(1,2)}$	120.9(2)	121.0(1)	$C^{(2,1)}-C^{(2,2)}-Cl^{(2,2)}$	120.8(2)	120.6(1)
$C^{(1,3)}-C^{(1,2)}-Cl^{(1,2)}$	120.5(2)	120.5(1)	$C^{(2,3)}-C^{(2,2)}-Cl^{(2,2)}$	120.5(2)	121.0(1)
$C^{(1,2)}-C^{(1,3)}-C^{(1,4)}$	121.0(2)	121.1(1)	$C^{(2,2)}-C^{(2,3)}-C^{(2,4)}$	120.5(2)	121.0(1)
$C^{(1,2)}-C^{(1,3)}-Cl^{(1,3)}$	120.2(2)	120.1(1)	$C^{(2,2)}-C^{(2,3)}-Cl^{(2,3)}$	120.6(2)	120.1(1)
$C^{(1,4)}-C^{(1,3)}-Cl^{(1,3)}$	118.9(2)	118.8(1)	$C^{(2,4)}-C^{(2,3)}-Cl^{(2,3)}$	119.0(2)	118.9(1)
$C^{(1,3)}-C^{(1,4)}-C^{(1,5)}$	119.5(2)	119.4(1)	$C^{(2,3)}-C^{(2,4)}-C^{(2,5)}$	119.7(2)	119.6(1)
$C^{(1,3)}-C^{(1,4)}-D^{(1,4)}$	118.9(3)	119.1(2)	$C^{(2,3)}-C^{(2,4)}-D^{(2,4)}$	119.2(3)	119.5(2)
$C^{(1,5)}-C^{(1,4)}-D^{(1,4)}$	121.6(3)	121.5(2)	$C^{(2,5)}-C^{(2,4)}-D^{(2,4)}$	121.1(3)	120.9(2)
$C^{(1,4)}-C^{(1,5)}-C^{(1,6)}$	120.5(2)	120.6(1)	$C^{(2,4)}-C^{(2,5)}-C^{(2,6)}$	120.6(2)	120.5(1)
$C^{(1,4)}-C^{(1,5)}-D^{(1,5)}$	119.7(3)	119.8(2)	$C^{(2,4)}-C^{(2,5)}-D^{(2,5)}$	119.6(3)	119.5(2)
$C^{(1,6)}-C^{(1,5)}-D^{(1,5)}$	119.9(3)	119.7(2)	$C^{(2,6)}-C^{(2,5)}-D^{(2,5)}$	119.8(3)	120.0(2)
$C^{(1,1)}-C^{(1,6)}-C^{(1,5)}$	119.6(2)	119.6(1)	$C^{(2,1)}-C^{(2,6)}-C^{(2,5)}$	119.3(2)	119.5(1)
$C^{(1,1)}-C^{(1,6)}-D^{(1,6)}$	119.4(3)	119.1(2)	$C^{(2,1)}-C^{(2,6)}-D^{(2,6)}$	119.5(3)	119.4(2)
$C^{(1,5)}-C^{(1,6)}-D^{(1,6)}$	121.0(3)	121.4(1)	$C^{(2,5)}-C^{(2,6)}-D^{(2,6)}$	121.2(3)	121.1(2)

Table 5. Observed and calculated differences of the endocyclic angles from 120° in 1,2,3-trichlorobenzene-d_3; $\sum_{inc}$: sum of increments [16]; $\Delta(i)$, $i =$ I, II: angle difference from 120° (molecule i), Δ_{sym}: difference from 120° for symmetry averaged angles, labels of the atoms as shown in Fig. 2 for "averaged" molecule.

Angle	$\sum_{inc}/°$		$\Delta(I)/°$		$\Delta(II)/°$		$\Delta_{sym}/°$	
Temperature	295 K	158 K	295 K	158 K	295 K	158 K	295 K	158 K
$C^{(6)}$ $C^{(1)}$ $C^{(2)}$	1.1(4)	1.1(4)	0.9(2)	0.9(1)	1.2(2)	1.0(1)	0.9	1.0
$C^{(1)}$ $C^{(2)}$ $C^{(3)}$	−0.9(4)	−0.9(4)	−1.4(2)	−1.5(1)	−1.3(2)	−1.6(1)	−1.4	−1.6
$C^{(2)}$ $C^{(3)}$ $C^{(4)}$	1.1(4)	1.1(4)	1.0(2)	1.1(1)	0.5(2)	1.0(1)	0.9	1.0
$C^{(3)}$ $C^{(4)}$ $C^{(5)}$	−1.0(4)	−1.0(4)	−0.5(2)	−0.6(1)	−0.3(2)	−0.4(1)	−0.5	−0.5
$C^{(4)}$ $C^{(5)}$ $C^{(6)}$	1.0(4)	1.0(4)	0.5(2)	0.5(2)	0.6(2)	0.5(1)	0.6	0.6
$C^{(5)}$ $C^{(6)}$ $C^{(1)}$	−1.0(4)	−1.0(4)	−0.4(2)	−0.4(1)	−0.7(2)	−0.5(1)	−0.5	−0.5

Table 6. Comparison of C–D and C–H bond lengths in 1,2,3-trichlorobenzene-d_3 ($T = 295$ K) and 1,2,3-trichlorobenzene [4].

1,2,3-trichlorobenzene-d_3			1,2,3-trichlorobenzene		
atom 1	atom 2	d/pm	atom 1	atom 2	d/pm
$C^{(1,4)}$	$D^{(1,4)}$	107.1(4)	$C^{(1,4)}$	$H^{(1,4)}$	108.2
$C^{(1,5)}$	$D^{(1,5)}$	107.6(4)	$C^{(1,5)}$	$H^{(1,5)}$	108.7
$C^{(1,6)}$	$D^{(1,6)}$	107.4(4)	$C^{(1,6)}$	$H^{(1,6)}$	106.6
$C^{(2,4)}$	$D^{(2,4)}$	107.8(4)	$C^{(2,4)}$	$H^{(2,4)}$	107.1
$C^{(2,5)}$	$D^{(2,5)}$	107.4(5)	$C^{(2,5)}$	$H^{(2,5)}$	108.2
$C^{(2,6)}$	$D^{(2,6)}$	107.1(4)	$C^{(2,6)}$	$H^{(2,6)}$	108.4

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_{equ}) as functions of temperature leads to

Table 7. Distance to the best planes calculated for 1,2,3-trichlorobenzene-d_3.

295 K				158 K			
molecule 1		molecule 2		molecule 1		molecule 2	
atom	d/pm	atom	d/pm	atom	d/pm	atom	d/pm
$C^{(1,1)}$	−0.1	$C^{(2,1)}$	1.0	$C^{(1,1)}$	0.3	$C^{(2,1)}$	1.1
$C^{(1,2)}$	0.1	$C^{(2,2)}$	1.0	$C^{(1,2)}$	0.1	$C^{(2,2)}$	1.1
$C^{(1,3)}$	−0.1	$C^{(2,3)}$	0.9	$C^{(1,3)}$	0.0	$C^{(2,3)}$	0.7
$C^{(1,4)}$	0.2	$C^{(2,4)}$	0.8	$C^{(1,4)}$	0.2	$C^{(2,4)}$	0.9
$C^{(1,5)}$	0.7	$C^{(2,5)}$	−0.4	$C^{(1,5)}$	0.7	$C^{(2,5)}$	−0.4
$C^{(1,6)}$	0.4	$C^{(2,6)}$	−0.3	$C^{(1,6)}$	0.3	$C^{(2,6)}$	0.0
$Cl^{(1,7)}$	−0.1	$Cl^{(2,1)}$	0.4	$Cl^{(1,1)}$	−0.4	$Cl^{(2,1)}$	0.5
$Cl^{(1,2)}$	−0.3	$Cl^{(2,2)}$	−1.4	$Cl^{(1,2)}$	−0.1	$Cl^{(2,2)}$	−1.6
$Cl^{(1,3)}$	0.6	$Cl^{(2,3)}$	−1.4	$Cl^{(1,3)}$	0.3	$Cl^{(2,3)}$	−1.3
$D^{(1,4)}$	−1.1	$D^{(2,4)}$	1.3	$D^{(1,4)}$	−1.4	$D^{(2,4)}$	1.4
$D^{(1,5)}$	0.1	$D^{(2,5)}$	−1.6	$D^{(1,5)}$	0.5	$D^{(2,5)}$	−1.8
$D^{(1,6)}$	−0.4	$D^{(2,6)}$	−0.4	$D^{(1,6)}$	−0.7	$D^{(2,6)}$	−0.6

Equations of the best planes in triclinic coordinates.

Equation: $d = Ax + By + Cz + D$,

d: distance of the atom with coordinates x, y, z to the best plane, d_{pair}: distance between a pair of molecules.

Temp./K	molecule	A/pm	B/pm	C/pm	D/pm	d_{pair}/pm
295	1	−766.17	−638.39	126.84	526.22	352.1
295	2	774.67	−637.72	−600.69	176.55	353.1
158	1	−763.48	−626.88	135.42	522.38	345.6
158	2	768.17	−627.49	−598.68	173.25	346.5

Angle between the best planes of molecule 1 and 2:

Temperature/K	295	158
Angle/°	75.13	76.07

results which can be interpreted in terms of an anharmonicity of the molecular librational potential. If B_{equ} is fitted by a linear equation, as resulting for ideal harmonic behaviour, negative B_{equ} values at $T = 0$ K are obtained for all atoms. Taking the zero point energy into account, a small positive value should be observed. To verify this assumption it is necessary to determine the structure of 1,2,3-trichlorobenzene-d_3 at some more temperatures. Anharmonic effects can be understood by the small difference of room temperature and the melting point of 1,2,3-trichlorobenzene-d_3 ($T_m = 323$ K).

The deuteration of the samples was determined by refining the occupation factors of the deuterium sites. The deuteration can be calculated using $y = (x \cdot b_D - b_H)/(b_D - b_H)$ (b_H, b_D: scattering lengths, $b_H = -3.74$ fm [9]; x: occupation factor, y: degree of deuteration). In a first step, all occupation factors of the deuterium sites were refined independently. This leads to very similar results for the two molecules and for the 4- and 6-positions within each molecule. This result can be understood easily: the two crystallographically inequivalent molecules and the 4- and 6-positions of a molecule are chemically equivalent. Thus an identical degree of deuteration of these positions should result. Therefore in a second step, the occupation factors of the 4- and 6-positions and separately of both 5-positions were constrained. A degree of deuteration of 96.0(6)% (295 K) and 95.2(4)% (158 K) was calculated for the 4- and 6-position. A degree of the deuteration of 93.0(6)% (295 K) and

Table 8. Shortest intermolecular distances in 1,2,3-trichlorobenzene-d_3.

Distance	atom 1 ... atom 2	symmetry operation of atom 2	$d_{295\,K}$/pm	$d_{158\,K}$/pm	Δd/pm
C ··· C	$C^{(1,6)} \cdots C^{(1,6)}$	$1-x,\ \bar{y},\ \bar{z}$	350.9(7)	343.4(5)	7.5(12)
	$C^{(2,1)} \cdots C^{(2,3)}$	$\bar{x},\ \bar{y},\ \bar{z}$	353.6(6)	346.4(3)	7.2(9)
C ··· D	$D^{(1,6)} \cdots C^{(1,6)}$	$1-x,\ \bar{y},\ \bar{z}$	304.0(6)	297.6(4)	6.4(9)
	$D^{(2,4)} \cdots C^{(2,4)}$	$\bar{x},\ 1-y,\ \bar{z}$	307.6(6)	301.4(4)	6.3(10)
Cl ··· Cl	$Cl^{(1,1)} \cdots Cl^{(1,2)}$	$1-x,\ -\frac{1}{2}+y,\ \frac{1}{2}-z$	358.7(7)	352.0(3)	6.7(10)
	$Cl^{(2,3)} \cdots Cl^{(2,1)}$	$x,\ \frac{1}{2}-y,\ -\frac{1}{2}+z$	375.1(7)	370.9*(3)	4.1(10)
	$Cl^{(2,3)} \cdots Cl^{(1,3)}$	$\bar{x},\ -\frac{1}{2}+y,\ -\frac{1}{2}-z$	375.3*(8)	367.1(4)	8.2(11)
Cl ··· C	$Cl^{(1,3)} \cdots C^{(2,1)}$	$\bar{x},\ 1-y,\ \bar{z}$	340.6(6)	333.6(4)	7.0(9)
D ··· D	$D^{(1,4)} \cdots D^{(2,5)}$	$x,\ \frac{1}{2}-y,\ -\frac{1}{2}+z$	271.2(7)	264.8(4)	6.3(10)
D ··· Cl	$D^{(1,4)} \cdots Cl^{(2,2)}$	$\bar{x},\ \frac{1}{2}+y,\ -\frac{1}{2}-z$	289.2(7)	282.0(3)	7.2(10)

Distances marked with * are not the shortest Cl−Cl distances.

Table 9. Corrected bond lengths in 1,2,3-trichlorobenzene-d_3, d_{corr}: bond lengths corrected for rigid-body motion, Δ: difference between corrected and uncorrected bond lengths.

Molecule 1						Molecule 2					
Atom 1	atom 2	295 K		158 K		Atom 1	atom 2	295 K		158 K	
		d_{corr}/pm	Δ/pm	d_{corr}/pm	Δ/pm			d_{corr}/pm	Δ/pm	d_{corr}/pm	Δ/pm
$C^{(1,1)}$	$C^{(1,2)}$	140.0	1.0	140.4	0.5	$C^{(2,1)}$	$C^{(2,2)}$	139.7	0.9	140.3	0.5
$C^{(1,1)}$	$C^{(1,6)}$	138.7	0.9	138.8	0.4	$C^{(2,1)}$	$C^{(2,6)}$	139.3	0.9	139.4	0.4
$C^{(1,1)}$	$Cl^{(1,1)}$	172.7	1.3	172.5	0.6	$C^{(2,1)}$	$Cl^{(2,1)}$	172.6	1.2	172.6	0.6
$C^{(1,2)}$	$C^{(1,3)}$	139.9	1.0	140.1	0.5	$C^{(2,2)}$	$C^{(2,3)}$	140.3	0.9	140.3	0.5
$C^{(1,2)}$	$Cl^{(1,2)}$	172.3	1.2	171.8	0.6	$C^{(2,2)}$	$Cl^{(2,2)}$	172.4	1.1	172.0	0.5
$C^{(1,3)}$	$C^{(1,4)}$	139.0	0.9	139.0	0.4	$C^{(2,3)}$	$C^{(2,4)}$	139.8	0.9	139.3	0.4
$C^{(1,3)}$	$Cl^{(1,3)}$	172.8	1.2	172.6	0.6	$C^{(2,3)}$	$Cl^{(2,3)}$	172.3	1.1	172.2	0.6
$C^{(1,4)}$	$C^{(1,5)}$	139.3	1.0	139.5	0.5	$C^{(2,4)}$	$C^{(2,5)}$	138.9	0.9	139.3	0.5
$C^{(1,4)}$	$D^{(1,4)}$	107.9	0.8	107.8	0.4	$C^{(2,4)}$	$D^{(2,4)}$	108.6	0.7	108.3	0.3
$C^{(1,5)}$	$C^{(1,6)}$	139.2	1.0	139.3	0.5	$C^{(2,5)}$	$C^{(2,6)}$	139.4	0.9	139.4	0.4
$C^{(1,5)}$	$D^{(1,5)}$	108.3	0.7	108.4	0.3	$C^{(2,5)}$	$D^{(2,5)}$	108.1	0.7	108.2	0.3
$C^{(1,6)}$	$D^{(1,6)}$	108.2	0.8	108.3	0.4	$C^{(2,6)}$	$D^{(2,6)}$	107.8	0.7	108.0	0.4

Table 10. Rigid-body analysis of 1,2,3-trichlorobenzene-d_3 (295 K), x, $\parallel \boldsymbol{a}^*$, $y \parallel \boldsymbol{c} \times \boldsymbol{a}^*$, $z \parallel \boldsymbol{c}$.

Molecule 1				Molecule 2		
L tensor/rad²	0.0077(3)	−0.0003(3)	−0.0004(2)	0.0078(3)	0.0006(2)	−0.0001(2)
		0.0063(3)	0.0004(2)		0.0050(3)	−0.0001(2)
			0.0079(4)			0.0080(4)
T tensor/pm²	327(12)	−103(12)	− 3(10)	322(11)	75(11)	11(9)
		355(14)	−14(10)		381(13)	−69(10)
			279(10)			300(10)
S tensor/(pm rad)	−0.04(5)	−0.16(3)	0.06(4)	0.10(4)	0.07(3)	−0.03(4)
		0.06(4)	0.00(4)		−0.12(4)	−0.14(3)
			−0.02(5)			0.02(5)
Point for symmetric S tensor triclinic coord.	0.3877	0.3327	−0.0009	−0.1014	0.1509	0.0146
Center of mass triclinic coord.	0.3882	0.3617	0.0166	−0.1232	0.1312	−0.0039
R_g/%		5.53			5.31	

Table 11. Rigid-body analysis of 1,2,3-trichlorobenzene-d_3 (158 K), x, $\parallel \boldsymbol{a}^*$, $y \parallel \boldsymbol{c} \times \boldsymbol{a}^*$, $z \parallel \boldsymbol{c}$.

Molecule 1				Molecule 2		
L tensor/rad²	0.0037(2)	−0.0005(2)	−0.0002(2)	0.0040(3)	0.0005(2)	−0.0001(2)
		0.0029(2)	0.0003(2)		0.0024(2)	−0.0003(2)
		0.0040(3)	0.0040(3)			0.0039(3)
T tensor/pm²	141(9)	−52(9)	10(7)	138(8)	37(9)	22(7)
		150(11)	−5(8)		164(10)	−33(8)
			115(8)			114(8)
S tensor/(pm rad)	−0.01(4)	−0.07(2)	0.02(3)	0.04(3)	0.04(2)	−0.03(3)
		0.01(3)	0.00(3)		−0.07(3)	−0.07(3)
			0.00(4)			0.02(4)
Point of symmetric S tensor triclinic coord.	0.3851	0.3421	0.0009	−0.1060	0.1449	0.0091
Center of mass triclinic coord.	0.3890	0.3634	0.0159	−0.1224	0.1307	−0.0042
R_g/%		9.26			9.06	

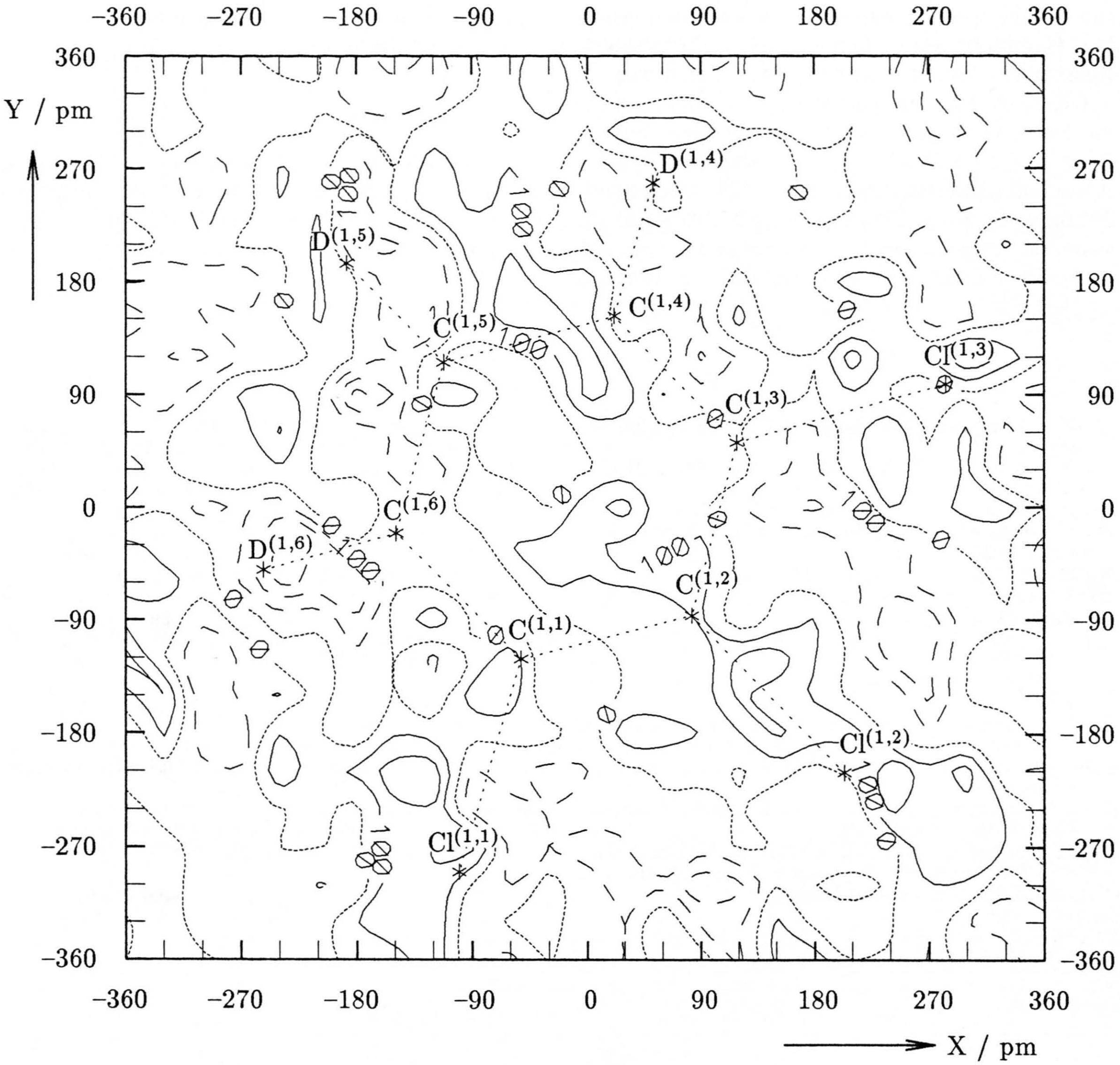


Fig. 5. Difference Fourier synthesis for the best plane of molecule 1 in 1,2,3-trichlorobenzene-d_3 at 295 K; scaling: arbitrary units; dashed lines: scattering density $\varrho < 0$; dotted lines: $\varrho = 0$; solid lines: $\varrho > 0$; difference between the topographic lines: 100 units.

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 an 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 significance of the decrease of the R_w value was confirmed by the "Hamilton" test ($\mathscr{R}$ 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.

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