

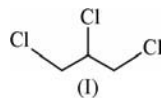
Pressure-frozen 1,2,3-trichloropropane

Marcin Podsiadło and Andrzej
Katrusiak*Faculty of Chemistry, Adam Mickiewicz
University, Grunwaldzka 6, 60-780 Poznań,
PolandCorrespondence e-mail: katran@amu.edu.plReceived 18 May 2006
Accepted 2 August 2006

The structure of 1,2,3-trichloropropane, $\text{ClCH}_2\text{CHClCH}_2\text{Cl}$, *in-situ* crystallized in a diamond–anvil cell, has been determined by single-crystal X-ray diffraction at 0.28 and 0.35 GPa. A melting point at 295 K and 0.22 GPa has been determined. The molecular conformation of aliphatic chain and terminal Cl atoms is approximately C_2 symmetric. Of the intermolecular contacts, the tightest are the $\text{Cl}\cdots\text{Cl}$ and then the $\text{Cl}\cdots\text{H}$ contacts, whereas the $\text{H}\cdots\text{H}$ distances are considerably longer than the sum of the van der Waals radii and leave narrow voids in the structure. The elevated pressure reduces the $\text{H}\cdots\text{H}$ separations but hardly affects the $\text{Cl}\cdots\text{Cl}$ distances. The crystal growth rates, compression and types of intermolecular interactions in the structures can be correlated with the directions of the $\text{Cl}\cdots\text{Cl}$ contacts, which can be considered the main motif responsible for the molecular arrangement in the structure.

1. Introduction

Propane and its derivatives are among the simplest flexible molecules and therefore are convenient for studying conformational transformations and intermolecular interactions at varied thermodynamical conditions (Thalladi & Boese, 2000). The conformation of molecules and their interactions can in turn affect the bulk properties of substances. When analysing weak $\text{Cl}\cdots\text{Cl}$ and $\text{Cl}\cdots\text{H}$ interactions, it is important to avoid other stronger interactions, which could dominate the molecular arrangement in the crystalline state. On the other hand, when no strong intermolecular forces are present, small-molecule substances are usually in the liquid or gaseous state under normal conditions. Thus, the structural studies of such simple compounds require that they be crystallized in low-temperature or high-pressure conditions.



In-situ high-pressure crystallization and determination of the high-pressure structure of 1,2,3-trichloropropane [see (I)] continue our studies on halogen \cdots halogen interactions in simple organic compounds. In 1,2-dichloro- and 1,1,2,2-tetrachloroethane, obtained by pressure freezing, disordered ethylene groups were observed, which suggested that the crystal packing is dominated by $\text{Cl}\cdots\text{Cl}$ contacts and leaves free space for the $-\text{CH}_2\text{CH}_2-$ dynamics (Bujak *et al.*, 2004; Bujak & Katrusiak, 2004), and Grineva & Zorky (1998, 2000) described chlorophobic properties. On the other hand,

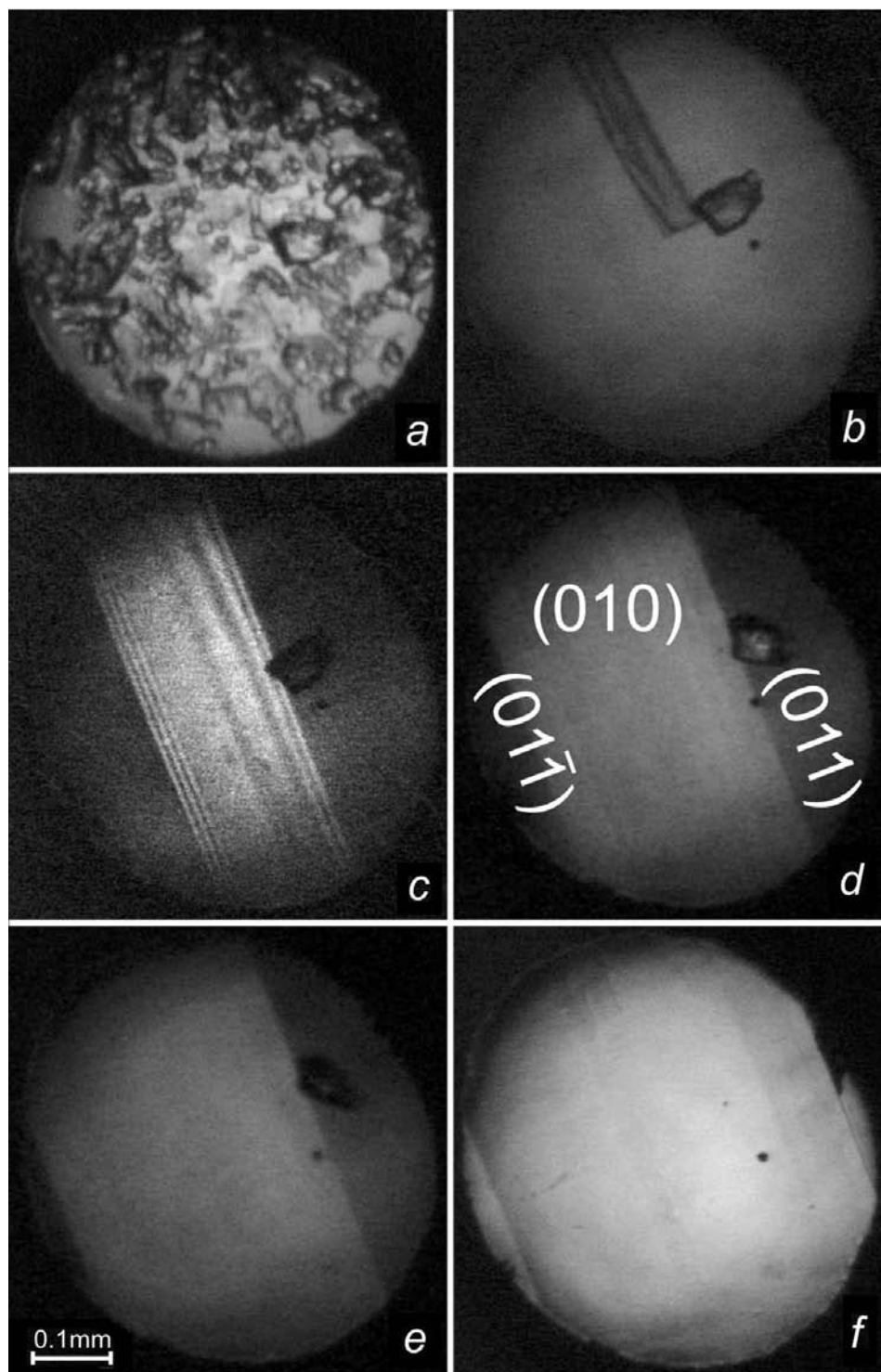


Figure 1

Stages of the 1,2,3-trichloropropane isochoric single-crystal growth inside the DAC chamber: (a) polycrystalline mass; (b) a single-crystal seed; (c) at 380 K the crystal immediately spreads across the chamber forming a very thin plate, producing the effect of clearly visible Newton fringes; (d) and (e) the crystal continues to grow across the culet surface and much more slowly toward the other culet; (f) the DAC chamber is nearly completely filled by the single crystal at 0.28 GPa. The small ruby chip for pressure calibration (at the central part of the right edge of the crystal) was pushed by the growing crystal from the middle part of the chamber to the gasket edge [(d)–(f)]. The Miller indices of the crystal faces are indicated in (d).

numerous halogenated compounds form crystal structures with no Cl···Cl contacts (Gajda *et al.*, 2006). Until now the crystal structure of 1,2,3-trichloropropane has not been determined experimentally, but its molecular conformation was extensively studied by theoretical computations (Thorbjørnsrud *et al.*, 1973).

The present study was aimed at determining the structure and molecular geometry of 1,2,3-trichloropropane, the hierarchy of the intermolecular contacts and their role as the crystal cohesion forces, and the melting curve of pressure and temperature for this substance. We also intended to investigate how the molecular dimensions and interactions relate to the crystal compressibility. Several methods can be applied to describe the changes in the molecular environment in the crystal at varied thermodynamic conditions or for assessing the differences between polymorphic or isostructural crystals (Dziubek & Katrusiak, 2004a). The strain in molecular structures was illustrated by distortions of Voronoi–Dirichlet polyhedra (Boldyreva *et al.*, 2000), the colour scale of distances on Hirshfeld surfaces (Dziubek & Katrusiak, 2004b; McKinnon *et al.*, 2004; Spackman & McKinnon, 2002) or plotted variations of the shortest distances (Boldyreva *et al.*, 1997; Dziubek & Katrusiak, 2004a). All these methods can be helpful in identifying the structural dimensions responsible for the specific phase stability, and in relating them to the crystal compression or thermal expansion. The analysis of compression of molecular structures inevitably pertains to the concepts of close packing (Kitaigorodskii, 1973) and van der Waals radii. It was our intention to employ the Hirshfeld surfaces and anisotropic van der Waals radii of

halogen atoms (Nyburg & Faerman, 1985) for obtaining a possibly accurate model of the molecule – its shape and interactions – in the crystal structure.

2. Experimental

1,2,3-Trichloropropane (m.p. 259 K at 0.1 MPa) of 99% purity from Sigma–Aldrich was used without further purification. This liquid was loaded into a four-pin diamond–anvil cell (DAC) and *in-situ* crystallized. The gasket was made of a 0.3 mm-thick steel foil, pre-indented to 0.28 mm, with a 0.5 mm spark-eroded hole. The freezing pressure of 1,2,3-trichloropropane at 295 K has been determined as 0.22 (5) GPa, when the crystal and liquid coexist in the DAC chamber. For calibrating pressure the ruby-fluorescence method (Piermarini *et al.*, 1975) and a BETSA PRL spectrometer were applied. The pressure was increased to 0.28 GPa, to ensure stable conditions for the process of single-crystal freezing in the whole volume of the chamber and stable conditions for the X-ray diffraction measurements. When the DAC was heated to *ca* 394 K, all but one grain of the polycrystalline mass inside the chamber melted. The DAC was then slowly cooled to room temperature, at which point the single crystal filled the whole volume of the chamber. The progress in growing the single crystal is shown in Fig. 1. The final dimensions of the chamber, and of the pressure-frozen crystal, were $0.46 \times 0.41 \times 0.26 \text{ mm}^3$. After verifying the pressure in the DAC and collecting the diffraction data, the DAC was heated again to *ca* 385 K, until the single crystal occupied about 5% of the chamber volume, and the pressure was increased. This time the single crystal filled the chamber completely ($0.45 \times 0.40 \times 0.18 \text{ mm}^3$) when the DAC was cooled to 325 K. At room temperature, the pressure measurement gave 0.35 GPa. This crystal was used for the next diffraction experiment. The process of obtaining single crystals from 1,2,3-trichloropropane proceeded smoothly and took about 1 h in each case. The main experimental problem was caused by a steep pressure dependence of melting temperature, which limited the pressure range of our study to 0.35 GPa. Higher pressures would require temperatures exceeding 500 K to melt the crystal. Temperatures over 500 K affect the strength of the beryllium discs – for this reason the Be discs are presently being replaced by steel backing plates in our DACs.

The single-crystal reflection data at both pressures and 295 K were collected using a KM-4 CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The DAC was centred by the gasket-shadow method (Budzianowski & Katrusiak, 2004). The reflections were collected with the ω -scan technique, with 0.9° frame width and 35 s exposures at 0.28 GPa, and 0.85° frame width and 40 s exposures at 0.35 GPa (Budzianowski & Katrusiak, 2004). For data collections, determination of the *UB* matrices, initial data reductions and *Lp* corrections, the *CrysAlis* program suite was used (Oxford Diffraction, 2004). The reflection intensities in both measurements have been corrected for the effects of absorption of X-rays by the DAC, shadowing of the beams by

Table 1

Crystal data and details of the refinements of 1,2,3-trichloropropane at 0.28 GPa and 0.35 GPa.

	0.28 (5) GPa	0.35 (5) GPa
Crystal data		
Chemical formula	C ₃ H ₅ Cl ₃	C ₃ H ₅ Cl ₃
M_r	147.42	147.42
Cell setting, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
Temperature (K)	295 (2)	295 (2)
a, b, c (Å)	5.1404 (10), 11.363 (2), 9.885 (2)	5.1285 (10), 11.377 (2), 9.859 (2)
β (°)	96.21 (3)	96.13 (3)
V (Å ³)	574.0 (2)	572.0 (2)
Z	4	4
D_x (Mg m ⁻³)	1.706	1.712
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm ⁻¹)	1.44	1.45
Crystal form, colour	Cylinder, colourless	Cylinder, colourless
Crystal size (mm)	0.46 × 0.41 × 0.26	0.45 × 0.40 × 0.18
Data collection		
Diffractometer	Kuma KM-4 CCD κ geometry	Kuma KM-4 CCD κ geometry
Data collection method	ω scans	ω scans
Absorption correction	Analytical	Analytical
T_{\min}	0.20	0.27
T_{\max}	0.61	0.69
No. of measured, independent and observed reflections	4431, 679, 520	4612, 538, 438
Criterion for observed reflections	$I > 4\sigma(I)$	$I > 4\sigma(I)$
R_{int}	0.082	0.112
θ_{max} (°)	30.1	29.7
Refinement		
Refinement on	F^2	F^2
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.063, 0.167, 1.03	0.061, 0.162, 1.02
No. of reflections	679	538
No. of parameters	77	77
H-atom treatment	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1174P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.123P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}}$	<0.0001	<0.0001
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.32, -0.34	0.28, -0.25
Absorption corrections	DAC, gasket and sample crystal	DAC, gasket and sample crystal
DAC transmission min/max	0.63/0.92	0.62/0.93
Gasket shadowing min/max	0.50/0.96	0.61/0.97
Sample transmission min/max	0.63/0.69	0.72/0.77

Computer programs used: *CrysAlis* (Oxford Diffraction, 2004), *SHELXS97* (Sheldrick, 1997), *SHELXL97* (Sheldrick, 1997), *XP* (Siemens, 1990).

the gasket edges and absorption of the sample crystal itself (Katrusiak, 2003, 2004). The structure was solved by direct methods using *SHELXS97* (Sheldrick, 1997), and refined with anisotropic displacement parameters for C and Cl atoms using *SHELXL97* (Sheldrick, 1997). The H atoms were located in a difference-Fourier map and refined with isotropic displace-

Table 2

Dimensions of the 1,2,3-trichloropropane molecule (Å, °) at 0.28 and 0.35 GPa.

Pressure/temperature	0.28 GPa/295 K	0.35 GPa/295 K
C1—C11	1.766 (7)	1.768 (9)
C2—C12	1.791 (7)	1.756 (9)
C3—C13	1.784 (7)	1.776 (9)
C1—C2	1.515 (7)	1.529 (9)
C2—C3	1.510 (10)	1.554 (14)
C11—C1—C2	112.6 (4)	112.3 (4)
C1—C2—C12	110.7 (4)	113.0 (4)
C1—C2—C3	114.9 (8)	111.6 (10)
C12—C2—C3	107.1 (3)	107.8 (3)
C2—C3—C13	110.7 (3)	111.8 (3)
C1—C2—C3—C13	63.2 (5)	62.0 (5)
C12—C2—C3—C13	-173.4 (3)	-173.4 (4)
C3—C2—C1—C11	59.2 (6)	62.3 (7)
C12—C2—C1—C11	-62.2 (8)	-59.4 (11)

ment parameters. Selected details of the crystal data and experiments are listed in Table 1.¹

3. Discussion

The space-group symmetry of 1,2,3-trichloropropane is identical to that of propane at 30 K (Boese *et al.*, 1999), and the unit-cell dimensions of these crystals are similar in that parameter *a* is the shortest and *b* is the longest. In both these structures the average planes of the molecules are approximately parallel to the crystallographic plane (100). In 1,2,3-trichloropropane and propane the molecules assume general positions. However, their orientation is considerably different; in 1,2,3-trichloropropane the bisector of the C—C—C angle is approximately parallel to the *b* axis, while in propane it is inclined by about 30° to the *c* axis (Thalladi & Boese, 2000). Different fragments of propane and 1,2,3-trichloropropane molecules form close intermolecular contacts in these structures, *i.e.* the mutual orientation of the interacting molecules is different in these two crystals. Thus, it appears that the identical space-group symmetry is accidental.

Except for the Cl2 atom, the molecule of 1,2,3-trichloropropane assumes a pseudo-*C*₂ symmetric conformation, with the Cl1—C1—C2—C3 and C1—C2—C3—Cl3 torsion angles differing by 4.0 (6)° at 0.28 GPa and by 0.3 (6)° at 0.35 GPa. The Cl2 atom is in the *gauche* position with respect to Cl1 and in the *s-trans* position with respect to Cl3 (see Table 2 and Fig. 2). According to the nomenclature applied to describe the molecular conformation of 1,2,3-trichloropropane (Thorbjørnsrud *et al.*, 1973) in the crystalline state, the molecules assume the conformation AG₋. It was found by electron diffraction (Stølevik, 1972) that an equilibrium exists in the gas phase, with the AG₋ conformation prevailing (68%) over AG₊ (28%) and G₊G₋ (4%). Dempster *et al.* (1969, 1971) studied 1,2,3-trichloropropane by IR and ¹H NMR spectro-

scopy, and concluded that the molecule assumes the AG₊ conformation in the crystalline state and that this conformation prevails in the liquid. The IR and Raman study reported by Thorbjørnsrud *et al.* (1973) did not allow them to distinguish between AG₋ and AG₊ conformations in the crystal.

A conformational analysis of the isolated 1,2,3-trichloropropane molecule has been performed with the *ab-initio*

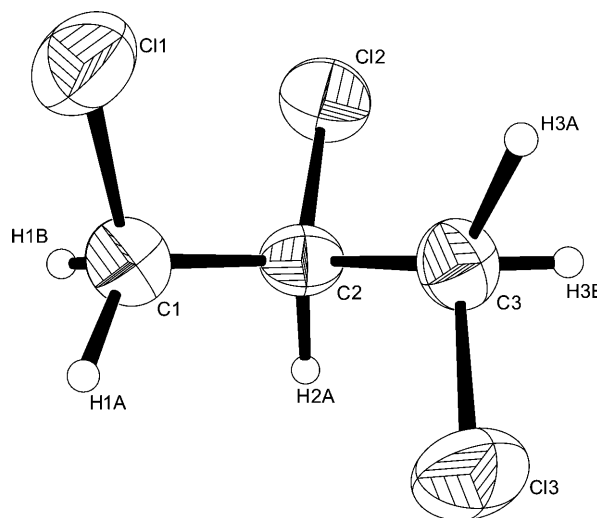


Figure 2
The 1,2,3-trichloropropane molecule viewed along its pseudo-symmetry *C*₂ axis. Atomic ellipsoids are shown at the 50% probability level.

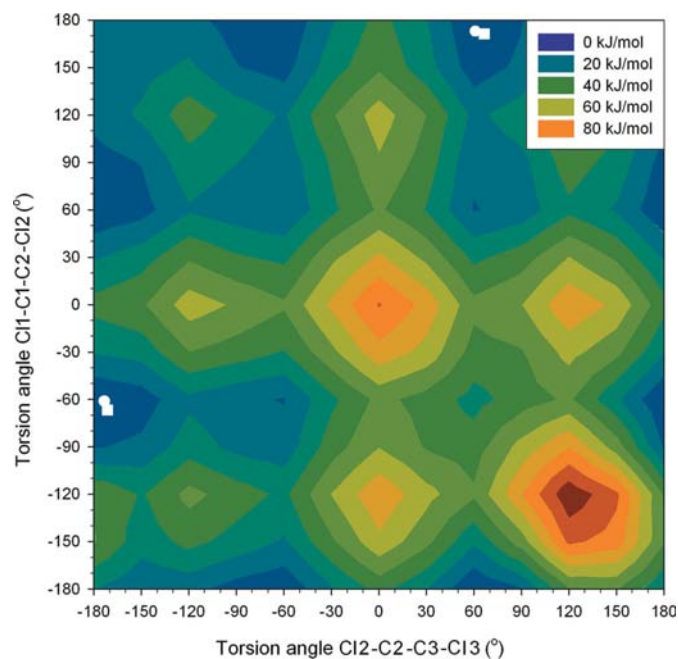


Figure 3
Potential energy map as a function of the C11—C1—C2—C12 and C12—C2—C3—C13 torsion angles of the isolated 1,2,3-trichloropropane molecule. The energy differences related to the minimum energy regions about the AG₋ conformation (at the torsion angles of 180 and -60°) have been plotted. The conformation fully optimized by *ab-initio* calculations for the isolated molecule (white square) and that observed in the crystalline state (white circle) are also shown.

¹ Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV5065). Services for accessing these data are described at the back of the journal.

approach at the Hartree–Fock level of theory, using the 6–31++g(*d,p*) basis set and carried out on a PC with *GAUSSIAN03* (Frisch *et al.*, 2003). The relaxed potential energy surface scan was obtained by varying the C1–C1–C2–C2 and C2–C2–C3–C3 torsion angles in 30° steps. The results indicate that the energetically favoured conformation is AG₁. As can be seen from the potential energy map (Fig. 3), the energy minimum corresponds to torsion angles of

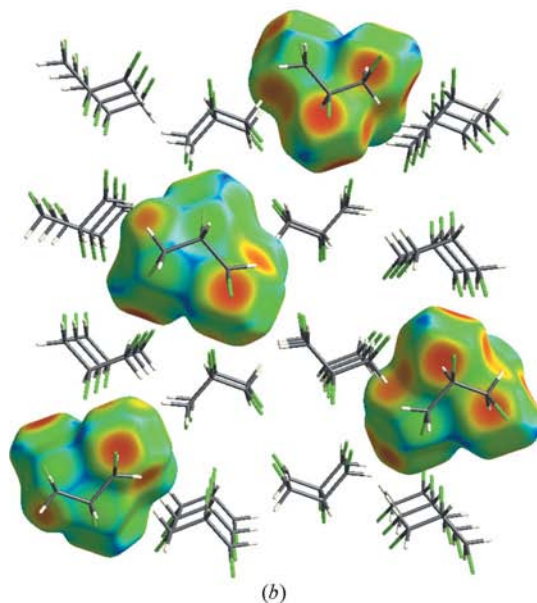
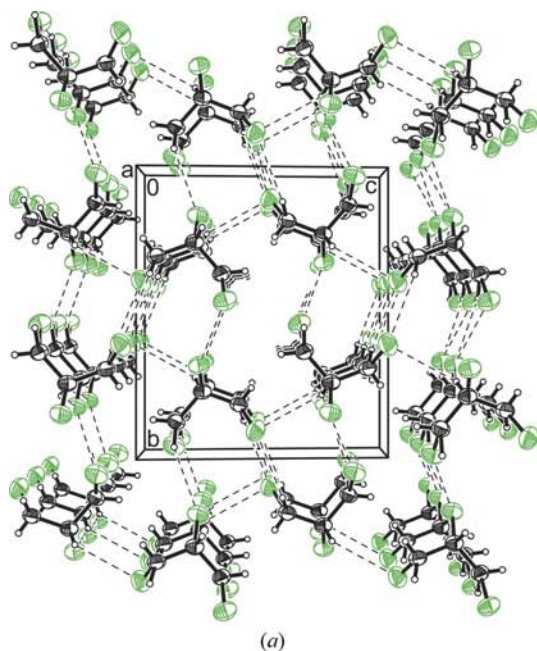


Figure 4

The molecular packing of pressure-frozen 1,2,3-trichloropropane viewed down the *a* axis at 0.35 GPa/295 K: (a) the shortest intermolecular Cl...Cl and Cl...H contacts are marked by dashed lines, and displacement ellipsoids are shown at the 50% probability level; (b) Hirshfeld surfaces for the 1,2,3-trichloropropane molecules in this structure with the colour scale illustrating the distance to the nearest atom centre exterior to the surface, mapped between 1.1 Å (red) and 2.5 Å (blue) (Wolff *et al.*, 2005).

Table 3

The shortest intermolecular distances (Å) and angles (°) in the crystal structure of 1,2,3-trichloropropane at 0.28 and 0.35 GPa.

Since the precision of H-atom positions refined from the X-ray diffraction data is lower than that of heavy atoms, the more reliable H atoms ideally located from the molecular geometry (C–H = 0.97 Å) have been used to calculate the intermolecular Cl...H contacts (see also Fig. 5). The assumption of elliptical shape of the van der Waals spheres has been applied, and the radii have been calculated according to the formula $r = (R_s^2 \cos^2 \varphi + R_l^2 \sin^2 \varphi)^{1/2}$, where φ is the C–Cl...Cl angle, and R_s and R_l are the minor and major Cl radii (Nyburg & Faerman, 1985).

Pressure/temperature	0.28 GPa/295 K	0.35 GPa/295 K	Calculated sum (Å) of anisotropic van der Waals radii†
Cl1...Cl1 ⁱ	3.462 (4)	3.454 (5)	3.191
Cl2...Cl3 ⁱⁱ	3.552 (3)	3.546 (4)	3.382
Cl1...Cl1 ⁱⁱⁱ	3.629 (4)	3.623 (5)	3.550
Cl1...H2A ^{iv}	2.900 (6)	2.889 (8)	2.977
Cl2...H3A ⁱⁱ	3.002 (9)	2.975 (13)	2.902
Cl2...H2A ^v	3.002 (4)	3.007 (5)	2.895
Cl3...H3A ^{vi}	3.022 (5)	3.021 (5)	2.889
Cl1...H1A ⁱⁱⁱ	3.067 (9)	3.053 (12)	2.935
Cl1...H1A ^v	3.089 (5)	3.081 (5)	2.911
H1B...H3B ^{vii}	2.646 (8)	2.620 (11)	–
H1B...H2A ^{iv}	3.125 (6)	3.145 (7)	–
H1A...H3B ^{vii}	3.187 (8)	3.242 (11)	–
C1–Cl1...Cl1 ⁱ	164.6 (3)	164.0 (4)	–
C2–Cl2...Cl3 ⁱⁱ	159.4 (2)	158.9 (2)	–
C3–Cl3...Cl2 ^{viii}	80.7 (3)	80.5 (3)	–
C1–Cl1...Cl1 ⁱⁱⁱ	80.9 (3)	80.2 (4)	–

Symmetry codes: (i) $-1 - x, -y, 1 - z$; (ii) $-\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (iii) $-x, -y, 1 - z$; (iv) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (v) $x - 1, y, z$; (vi) $1 + x, y, z$; (vii) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$; (viii) $-\frac{1}{2} - x, -\frac{1}{2} + y, \frac{3}{2} - z$. † According to Nyburg & Faerman (1985).

–171.3 and –67.2°. These torsion angles in the crystal structures at 0.28 and 0.35 GPa are very consistent; their averaged values are –173.4 and –60.8° and are thus very similar to those calculated for the isolated molecule. The calculations also confirmed the presence of an energetically favoured

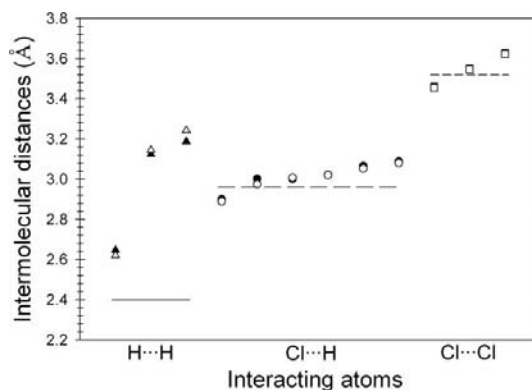


Figure 5

Shortest intermolecular distances (Å) grouped in ascending order for specific atomic types in the structure of 1,2,3-trichloropropane: H...H distances (triangles); Cl...H distances (circles); Cl...Cl distances (squares); full and open symbols for 0.28 and 0.35 GPa, respectively. Solid and dashed lines indicate the sums of spherical van der Waals radii of relevant atoms (Bondi, 1964, 1968). The distances for ideally located H atoms have been given. The error bars are smaller than the symbols used.

region about the AG₊ conformation, also observed in the gaseous phase.

The crystal compression is strongly anisotropic – the crystal contracts along the *a* and *c* axes, but expands along *b* (see Table 1). The linear compression coefficients calculated between 0.28 and 0.35 GPa are $\beta_a = 1/a(\delta a/\delta p) = -0.031 \text{ GPa}^{-1}$, $\beta_b = 1/b(\delta b/\delta p) = 0.018 \text{ GPa}^{-1}$ and $\beta_c = 1/c(\delta c/\delta p) = -0.038 \text{ GPa}^{-1}$.

The arrangement of the 1,2,3-trichloropropane molecules, illustrated in Fig. 4, is dominated by intermolecular Cl···Cl and Cl···H contacts, whereas no close H···H contacts are formed. The Cl···Cl distances are commensurate with the sum of spherical van der Waals radii of two Cl atoms, of 3.52 Å according to Bondi (1964, 1968). The shortest intermolecular Cl···Cl contacts are formed along the crystallographic [100] direction, while the contacts in other directions are mainly of the Cl···H type. The shortest of the intermolecular Cl···Cl distances is Cl1···Cl1ⁱ, and Cl2···Cl3ⁱⁱ is only 0.09 Å longer (see Table 3). Similarly consistent are the Cl···H contacts, the six shortest of which vary by up to 0.19 Å. The shortest of the Cl···H distances is *ca* 0.06 Å shorter than the sum of the spherical van der Waals radii of Cl and H (Bondi, 1964, 1968). The H···H contacts are the least consistent and the longest when related to the sum of the van der Waals radii. The shortest of the H···H distances is over 0.24 Å longer than the sum of the van der Waals radii of 2.4 Å (Bondi, 1964, 1968).

The observed distribution of intermolecular Cl···Cl distances is consistent with the anisotropic van der Waals radius of Cl described by Nyburg & Faerman (1985). According to that work, the shortest van der Waals radius of Cl is 1.58 Å along the C–Cl bond and the longest is 1.78 Å perpendicular to it. The sums of anisotropic van der Waals radii (Nyburg & Faerman, 1985) are given in Table 3. The shortest of the Cl···Cl contacts in 1,2,3-trichloropropane at 0.28 GPa, between Cl1 and Cl1ⁱ (see Table 3), is inclined by 164.6 (3)° to both C–Cl bonds [type I halogen···halogen interactions (Pedireddi *et al.*, 1994; Price *et al.*, 1994; Ramasubbu *et al.*, 1986)]; the inclinations of the next shortest contact, Cl2···Cl3ⁱⁱ, to the C–Cl bonds are 159.4 (2)° at Cl2 and 80.7 (3)° at Cl3ⁱⁱ, and can be classified as type II halogen···halogen interactions; the third shortest contact, Cl1···Cl1ⁱⁱⁱ, is inclined by 80.9(3)° to both the Cl–C bonds (type I). These angles change marginally between 0.28 and 0.35 GPa (the largest difference is of 0.7° for the longest of the contacts).

The shortest of the Cl···Cl and Cl···H contacts are shorter than the sums of the corresponding spherical van der Waals radii, as illustrated in Fig. 5. Therefore, the molecules interact mainly *via* the Cl···Cl and Cl···H contacts, while there is some ‘free’ space between the shortest H atoms of close molecules (Figs. 4 and 5). The compression of intermolecular contacts shows a similar regularity to the distributions of contacts. Thus, between 0.28 and 0.35 GPa the Cl···Cl contacts are compressed less than the Cl···H contacts. The shortest of the H···H contacts is compressed at increased pressure, whereas the second and third shortest H···H contacts become longer. These two longer H···H contacts are

much longer than the sum of the van der Waals radii, and their changes are likely to result from other interactions in the structure.

The shortest intermolecular contacts in 1,2,3-trichloropropane can be illustrated by using the Hirshfeld surface (Dziubek & Katrusiak, 2004b; McKinnon *et al.*, 1998; Spackman & McKinnon, 2002), as shown in Fig. 4. The colour scale on the Hirshfeld surface represents the distances from the surface points to the closest atom outside the surface; red corresponds to the closest contacts, blue to the longest. There are clearly visible contacting spots (red on the Hirshfeld surface) between the Cl atoms and gaps (blue) between the H atoms of the neighbouring molecules.

The compressions of the intermolecular contacts can be correlated with the compressibility of the crystal and the growth rates of the crystal along its crystal directions. The crystallographic [100] direction is most compressible, which may suggest that the main role in arranging the molecules in the crystal structure is played by the Cl···Cl interactions, formed mainly along this direction (see Fig. 4), while the Cl···H and H···H interactions are less important in the hierarchy of the crystal cohesion forces.

Several relations can be found between the lattice parameters, crystal morphology, intermolecular distances and compressibility of the 1,2,3-trichloropropane crystal. The shortest lattice parameter *a* corresponds to the fastest-growing direction for the crystal. As often observed, molecules arrange fastest into crystalline structures along the direction of their strongest interactions, and the corresponding translation-symmetry vector of the so-formed lattice is usually the shortest. It can be seen in Fig. 4 that the interactions in the [x] direction are dominated by Cl···Cl and Cl···H contacts – the warm colours on the Hirshfeld surfaces are along the [x] direction – which can be rationalized in terms of the high dispersion energy of the interactions involving these atoms.

It is a characteristic feature of 1,2,3-trichloropropane that its melting temperature in the DAC strongly depends on pressure. The heated DAC approximates isochoric conditions, and the temperature and pressure changes in the chamber are interdependent. The 1,2,3-trichloropropane crystal compressed at 0.28 GPa at room temperature (295 K) started to melt at *ca* 394 K. When compressed to 0.35 GPa at 295 K, the sample required temperatures as high as 433 K to start melting. Owing to this very strong rise of the melting point no structural studies of 1,2,3-trichloropropane have been carried out above 0.35 GPa.

4. Conclusions

The distribution of intermolecular distances in the 1,2,3-trichloropropane structure and their pressure dependence have shown that the closest (relative to the isotropic sums of the van der Waals radii) and least compressible are the Cl···Cl contacts, and that the H···H contacts are considerably longer than the sum of the van der Waals radii of two H atoms. This result suggests that it is the Cl···Cl interactions that are responsible for the molecular arrangement in this compound.

It still remains to be established if the absence of close H···H contacts is due to the steric hindrances around the Cl atoms preventing the mutual access of the CH groups or to the domination of considerably stronger Cl···Cl attraction over the weaker H···H interactions. It appears that the crystal-growth rates and compressibility are correlated with the strengths of intermolecular interactions in specific directions in the crystal structure.

This study was supported by the Polish Ministry of Scientific Research and Information Technology, Grant No. 3 T09A18127. We thank Dr Kamil Dziubek for expertise in *ab-initio* calculations.

References

- Boese, R., Weiss, H. C. & Bläser, D. (1999). *Angew. Chem. Int. Ed.* **38**, 988–992.
- Boldyreva, E., Kivikoski, J. & Howard, J. A. K. (1997). *Acta Cryst.* **B53**, 394–404.
- Boldyreva, E. V., Shakhtshneider, T. P., Vasilchenko, M. A., Ahsbahs, H. & Uchtmann, H. (2000). *Acta Cryst.* **B56**, 299–309.
- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- Bondi, A. (1968). *Physical Properties of Molecular Crystals, Liquids and Glasses*, pp. 450ff. New York: John Wiley.
- Budzianowski, A. & Katrusiak, A. (2004). *High-Pressure Crystallography*, edited by A. Katrusiak & P. F. McMillan, pp. 101–112. Dordrecht: Kluwer Academic Publishers.
- Bujak, M., Budzianowski, A. & Katrusiak, A. (2004). *Z. Kristallogr.* **219**, 573–579.
- Bujak, M. & Katrusiak, A. (2004). *Z. Kristallogr.* **219**, 669–674.
- Dempster, A. B., Price, K. & Sheppard, N. (1969). *Spectrochim. Acta Part A*, **25**, 1381–1392.
- Dempster, A. B., Price, K. & Sheppard, N. (1971). *Spectrochim. Acta Part A*, **27**, 1579–1595.
- Dziubek, K. & Katrusiak, A. (2004a). *Z. Kristallogr.* **219**, 1–11.
- Dziubek, K. & Katrusiak, A. (2004b). *J. Phys. Chem. B*, **108**, 19089–19092.
- Frisch, M. J. *et al.* (2003). *GAUSSIAN03*, Revision B.04. Gaussian Inc., Pittsburgh, PA, USA.
- Gajda, R., Dziubek, K. & Katrusiak, A. (2006). *Acta Cryst.* **B62**, 86–93.
- Grineva, O. V. & Zorky, P. M. (1998). *Zh. Fiz. Khim.* **72**, 714–720. (In Russian.)
- Grineva, O. V. & Zorky, P. M. (2000). *Kristallografiya*, **45**, 692–698. (In Russian.)
- Katrusiak, A. (2003). *REDSHABS*. Adam Mickiewicz University, Poznań, Poland.
- Katrusiak, A. (2004). *Z. Kristallogr.* **219**, 461–467.
- Kitaigorodskii, A. I. (1973). *Molecular Crystals and Molecules*. New York: Academic Press.
- McKinnon, J. J., Mitchel, A. S. & Spackman, M. A. (1998). *Chem. Eur. J.* **4**, 2136–2141.
- McKinnon, J. J., Spackman, M. A. & Mitchell A. S. (2004). *Acta Cryst.* **B60**, 627–668.
- Nyburg, S. C. & Faerman, C. H. (1985). *Acta Cryst.* **B41**, 274–279.
- Oxford Diffraction (2004). *CrysAlis Software System*, Version 1.171. Oxford Diffraction Ltd, Abingdon, UK.
- Pedireddi, V. R., Reddy, D. S., Goud, B. S., Craig, D. C., Rae, A. D. & Desiraju, G. R. (1994). *J. Chem. Soc. Perkin Trans. 2*, pp. 2353–2360.
- Piermarini, G. J., Block, S., Barnett, J. D. & Forman, R. A. (1975). *J. Appl. Phys.* **46**, 2774–2780.
- Price, S. L., Stone, A. J., Lucas, J., Rowland, R. S. & Thornley, A. E. (1994). *J. Am. Chem. Soc.* **116**, 4910–4918.
- Ramasubbu, N., Parthasarathy, R. & Murray-Rust, P. (1986). *J. Am. Chem. Soc.* **108**, 4308–4314.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Siemens (1990). *XP*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Spackman, M. A. & McKinnon, J. J. (2002). *Cryst. Eng. Commun.* **4**, 378–392.
- Stølevik, R. (1972). Personal communication.
- Thalladi, V. R. & Boese, R. (2000). *New J. Chem.* **24**, 579–581.
- Thorbjørnsrud, J., Ellestad, O. H., Klaboe, P. & Torggrimsen, T. (1973). *J. Mol. Struct.* **17**, 5–15.
- Wolff, S. K., Grimwood, D. J., McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2005). *Crystal Explorer*, Version 1.5.0. University of Western Australia, Perth, Australia.