

## Compressed hydrogen-bond effects in the pressure-frozen chloroacetic acid

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The competing effects of squeezed OH $\cdots$ O bonds, destabilizing the H-atom position, and of displaced hydrogen donor and acceptor groups, favouring the ordered H-atom sites, have been tuned by pressure in the pressure-frozen dichloroacetic acid. Its structure has been determined at 0.1, 0.7, 0.9 and 1.4 GPa: in this pressure range the crystals are stable in the monoclinic space group  $P2_1/n$ . The molecules are O—H $\cdots$ O hydrogen bonded into dimers, which in turn interact *via* a unique pattern of halogen $\cdots$ halogen contacts. Between 0.1 and 1.4 GPa the OH $\cdots$ O bond is squeezed from 2.674 (13) to 2.632 (9) Å. Within the pressure range investigated the hydrogen bonds are squeezed and the shear displacement of the molecules compensate, and the H atoms remain ordered.

## 1. Introduction

The formation of dimers linked by a pair of strong O—H $\cdots$ O hydrogen bonds is a well known feature observed in most carboxylic acid structures (Hendricks, 1935; Ewald & Hermann, 1931); an alternative association into catameric chains is much less frequent (Leiserowitz, 1976; Derissen & Smit, 1977). One of the most intriguing aspects of the structure of carboxylic acid dimers is the behaviour of the H atoms in the O—H $\cdots$ O hydrogen bonds. Under normal conditions the H atoms can either be ordered (with the C=O bonds well defined and clearly shorter than the C—OH bonds) or disordered (when the C—O bonds have approximately equal average lengths). It was postulated that H-atom disordering in the carboxylic acid dimers depends on the 'hydrogen-bond strain' depending on the mutual orientation of the molecules forming the dimer (Katrusiak, 1993, 1996). Thus, in a 'relaxed' dimer, where the C—O1 $\cdots$ O2' angle is much larger than the C—O2 $\cdots$ O1' angle (primes denote the O atoms of the second molecule in the dimer, most often related by a centre of inversion to the first one), the H atoms are ordered in a pair of hydrogen bonds. In the 'strained' dimer, where these angles are approximately equal, the H-atom sites are not favoured by the molecular shifts and the H atoms are disordered. The origin of the 'relaxed' or 'strained' hydrogen bonds depends upon the crystal environments of the dimers, which either favour the opposite positions of the COOH groups (the C—O $\cdots$ O angles nearly equal and the two C—COOH bonds nearly collinear), or the groups shifted from the opposite sites in this way so that the C—O $\cdots$ O angles are different.

The effect of disordered H atoms in carboxylic acid dimers has been studied for decades (*e.g.* see Manojlovič & Speakman, 1967). The H atoms jumping or static disorder was considered to be caused by a mixture of carboxylic acid groups in opposite orientations. H-atom behaviour was correlated with the carboxylic acid group dimensions: C—OH ( $r_1$ ), C=O

( $r_2$ ),  $X-C-OH$  angle ( $\varphi_1$ ),  $X-C=O$  ( $\varphi_2$ ). For the disordered H atoms  $\Delta r = r_1 - r_2$  and  $\Delta\varphi = \varphi_1 - \varphi_2$  are close to zero, and for all the carboxylic acid dimers (both disordered and ordered) the  $\Delta r$  and  $\Delta\varphi$  values are linearly correlated (Dieterich *et al.*, 1974). The dynamical character of the H-atoms disorder was confirmed by variable-temperature studies on fluoromalonic (Kanters *et al.*, 1975; Roelofsen *et al.*, 1971), benzoic (Hayashi & Umemura, 1974) and formic (Hayashi *et al.*, 1984) acids.

To investigate the role of the crystal environment in these changes (the geometry of hydrogen bonds and their role in the formation of dimers), we have chosen to study the structure of dichloroacetic acid (DCAA) using a high-pressure diffraction technique. The crystal structure of DCAA is mainly governed by the hydrogen bonds binding the molecules into dimers and by halogen...halogen interactions. The molecular structure of DCAA determined in this high-pressure study at 0.7 GPa is shown in Fig. 1.

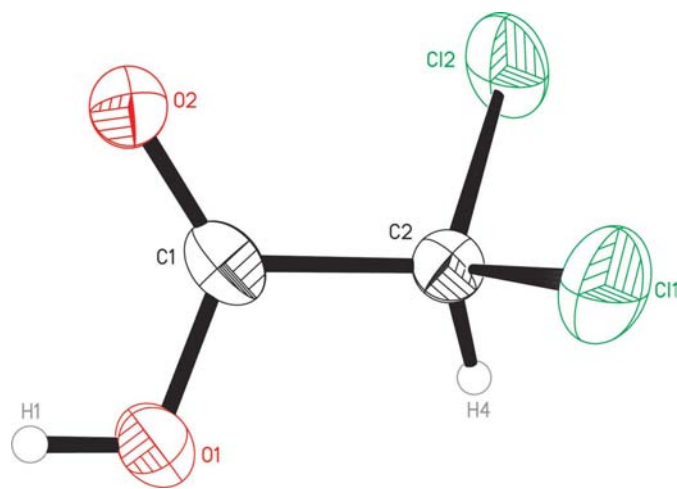
Two main structural changes generated by elevated pressure can be anticipated in the DCAA crystal (Katrusiak, 1996):

(i) the increased skewness of the mutual positions of the molecules within the dimer, owing to their asymmetric shape and intensified intermolecular interactions with the crystal environment; and

(ii) the lowered potential-energy barrier separating the lowered H-atom sites in the squeezed  $O-H\cdots O$  hydrogen bonds.

The increased skewness of the hydrogen-bonded carboxylic groups favours H-atom ordering, while the lower energy barrier facilitates the H-atom disordering. The main purpose of this study was to establish which of these factors would prevail, and how elevated pressure would modify the crystal structure of dichloroacetic acid.

In DCAA, owing to the asymmetrically positioned Cl atoms at C2, the van der Waals interactions of the molecules in the crystal should favour the skew positions of the carboxyl



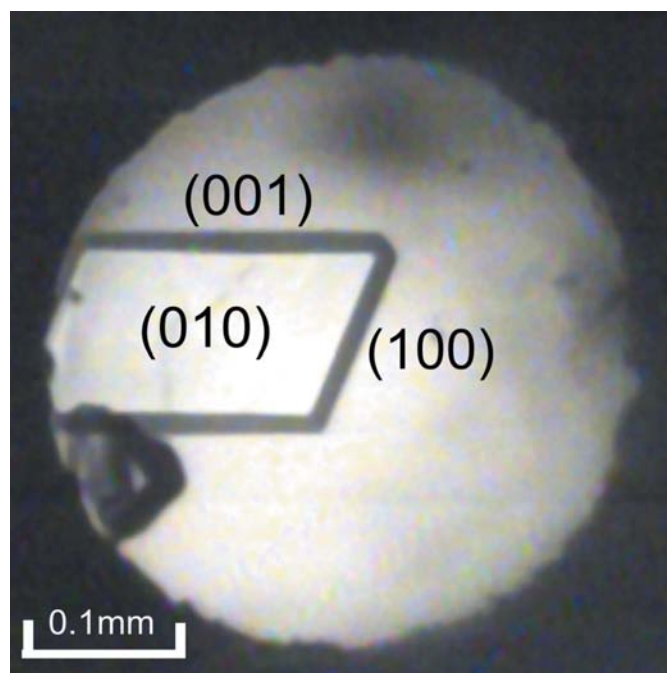
**Figure 1**  
Molecular structure of DCAA at 0.7 GPa, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

groups, which in turn should promote H-atom ordering in the hydrogen bonds. This effect competes with the squeezing of the  $O-H\cdots O$  hydrogen bonds, promoting H-atom disordering.

The high-pressure technique is convenient for studying intermolecular interactions and arrangements, because pressure can considerably squeeze the crystal volume and reduce the intermolecular distances. In certain cases it is possible to separate the contribution of different types of interactions to the crystal cohesion forces (Katrusiak, 2001a). In the strongly modified environment, the molecules adjust their interactions and these changes can be helpful in understanding the nature of crystal-structure formation. It is also important that by using pressure and temperature optimum conditions for growing single crystals can be found, other than by just varying the temperature. Pressure was already applied to study simple carboxylic acids: in formic acid at 0.8 GPa and acetic acid at 0.2 GPa the molecules are arranged in infinite hydrogen-bonded chains (Allan & Clark, 1999a,b). It was also established that relatively small substitution changes in the molecules of carboxylic acids  $CClF_2COOH$  and  $CCl_2FCOOH$  can lead to significant changes in the molecular association into dimers and tetramers, respectively (Schilling & Mootz, 1995).

## 2. Experimental

Dichloroacetic acid (analytical grade without further purification),  $C_2H_2O_2Cl_2$ , was pressure frozen *in situ* in a diamond-anvil cell (DAC), and its structure determined by X-rays at 0.1, 0.7, 0.9 and 1.4 GPa. A DAC of modified Merrill & Bassett



**Figure 2**  
View of the DAC high-pressure chamber with a pressure-frozen single crystal of DCAA obtained under isochoric conditions at the initial stage of its growth. The ruby chip for pressure calibration is in the bottom-left edge of the pressure chamber.

**Table 1**

Selected experimental and crystal data for the high-pressure structure of dichloroacetic acid at 0.1, 0.7, 0.9 and 1.4 GPa.

	0.1 GPa	0.7 GPa	0.9 GPa	1.4 GPa
Crystal data				
Chemical formula	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub> Cl <sub>2</sub>	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub> Cl <sub>2</sub>	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub> Cl <sub>2</sub>	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub> Cl <sub>2</sub>
<i>M<sub>r</sub></i>	128.94	128.94	128.94	128.94
Cell setting, space group	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>n</i>	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>n</i>	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>n</i>	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>n</i>
Temperature (K)	293 (2)	293 (2)	293 (2)	293 (2)
<i>a</i> , <i>b</i> , <i>c</i> (Å)	4.914 (2), 11.384 (7), 8.418 (5)	4.6404 (18), 11.134 (7), 8.299 (5)	4.6589 (9), 11.174 (2), 8.2013 (16)	4.563 (2), 10.978 (8), 8.087 (6)
β (°)	93.45 (6)	92.89 (5)	92.88 (3)	92.60 (6)
<i>V</i> (Å <sup>3</sup> )	470.1 (5)	428.2 (4)	426.42 (14)	404.7 (4)
<i>Z</i>	4	4	4	4
<i>D<sub>x</sub></i> (Mg m <sup>-3</sup> )	1.822	2.000	2.008	2.116
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm <sup>-1</sup> )	1.23	1.35	1.36	1.43
Crystal form, colour	Disc, colourless	Disc, colourless	Disc, colourless	Disc, colourless
Crystal size (mm)	0.44 × 0.40 × 0.18	0.36 × 0.34 × 0.18	0.46 × 0.44 × 0.18	0.44 × 0.42 × 0.18
Data collection				
Diffractometer	KUMA KM4-CCD	KUMA KM4-CCD	KUMA KM4-CCD	KUMA KM4-CCD
Data collection method	ω scans	ω scans	ω scans	ω scans
Absorption correction	Analytical	Analytical	Analytical	Analytical
<i>T<sub>min</sub></i>	0.43	0.45	0.71	0.73
<i>T<sub>max</sub></i>	0.89	0.88	0.97	0.97
No. of measured, independent and observed reflections	3383, 508, 413	2443, 468, 409	1184, 176, 166	936, 146, 141
Criterion for observed reflections	<i>I</i> > 2σ( <i>I</i> )	<i>I</i> > 2σ( <i>I</i> )	<i>I</i> > 2σ( <i>I</i> )	<i>I</i> > 2σ( <i>I</i> )
<i>R<sub>int</sub></i>	0.080	0.051	0.041	0.038
θ <sub>max</sub> (°)	29.3	29.8	25.1	24.0
Refinement				
Refinement on	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.117, 0.191, 1.37	0.053, 0.091, 1.30	0.025, 0.057, 1.10	0.030, 0.073, 1.22
No. of reflections	508	468	176	146
No. of parameters	59	63	58	57
H-atom treatment	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0327P)^2 + 1.9238P]$ , where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0244P)^2 + 0.4612P]$ , where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0232P)^2 + 0.6301P]$ , where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.046P)^2 + 0.3851P]$ , where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ) <sub>max</sub>	< 0.0001	< 0.0001	< 0.0001	< 0.0001
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.24, -0.31	0.19, -0.16	0.10, -0.11	0.16, -0.15

Computer programs used: *CrysAlis* (Oxford Diffraction, 2003), *SHELXS97* (Sheldrick, 1997a), *SHELXL97* (Sheldrick, 1997b), *XP* (Siemens, 1990).

(1974) design made in our departmental workshop was used. Since DCAA is a relatively strong acid, a gasket made of an iron–rhenium–molybdenum alloy was used. The pressure was calibrated with a BETSA PRL spectrometer by the ruby-fluorescence method with a precision of 0.05 GPa (Piermarini *et al.*, 1975).

After placing a ruby chip for pressure calibration and filling the chamber with DCAA, the pressure was gradually increased up to 0.1 GPa when a small crystal of DCAA appeared. At this pressure the solid and liquid phases coexisted (Fig. 2). The DAC screws were then tightened until the crystal almost filled all of the pressure chamber. The recalibration of pressure gave 0.103 GPa, and at this pressure the diffraction data was collected for this isothermally grown single crystal. Measurements at higher pressure were performed for new DCAA crystals grown at isochoric conditions: the sample was pressure frozen in the polycrystalline form, after which the DAC was heated until all the crystallites but one melted, and then temperature was slowly lowered

until the single crystal grew to entirely fill the pressure chamber.

A single crystal of DCAA was centred on a KUMA KM4 CCD diffractometer by the gasket-shadow method, and the X-ray reflection intensities were collected in the ω-scan mode (Budzianowski & Katrusiak, 2004). Mo *K*α radiation was graphite-monochromated. The *CrysAlis* programs (Oxford Diffraction, 2003) were used for data collection, unit-cell refinement and initial data reduction. The data were corrected for the DAC absorption, gasket shadowing and absorption of the sample itself (Katrusiak, 2003, 2004). The structure was solved by direct methods using the program *SHELXS97* (Sheldrick, 1997a) and refined using *SHELXL97* (Sheldrick, 1997b). The crystallographic data are summarized in Table 1.<sup>1</sup>

<sup>1</sup> Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV5090). Services for accessing these data are described at the back of the journal.

**Table 2**

 Selected bond lengths, valency angles and torsion angles ( $\text{\AA}$ ,  $^\circ$ ) in dichloroacetic acid.

Pressure	0.1 GPa	0.7 GPa	0.9 GPa	1.4 GPa
C1—C2	1.750 (15)	1.767 (7)	1.779 (9)	1.764 (16)
C12—C2	1.753 (12)	1.748 (6)	1.754 (7)	1.746 (14)
O1—C1	1.290 (12)	1.288 (6)	1.301 (7)	1.327 (14)
O2—C1	1.197 (17)	1.210 (7)	1.196 (9)	1.189 (14)
C1—C2	1.55 (2)	1.524 (8)	1.513 (11)	1.518 (15)
O2—C1—O1	127.2 (13)	126.3 (5)	126.2 (7)	128.0 (9)
O2—C1—C2	123.1 (9)	123.0 (5)	123.0 (6)	122.9 (10)
O1—C1—C2	109.5 (13)	110.5 (6)	110.8 (8)	108.9 (14)
C1—C2—Cl2	109.4 (12)	110.8 (6)	111.8 (8)	110.8 (15)
C1—C2—Cl1	108.2 (8)	108.0 (4)	106.6 (5)	107.0 (11)
C1—C2—Cl2	110.9 (6)	110.5 (3)	109.8 (3)	109.9 (4)
O2—C1—C2—Cl1	86.8 (15)	89.2 (7)	89.1 (9)	88 (2)
O1—C1—C2—Cl1	−88.5 (9)	−87.8 (4)	−89.2 (5)	−87.9 (8)
O2—C1—C2—Cl2	−34.1 (16)	−31.9 (7)	−30.9 (10)	−31 (2)
O1—C1—C2—Cl2	150.6 (8)	151.0 (4)	150.8 (5)	152.4 (7)

**Table 3**

 Hydrogen bond O1—H1...O2 dimensions ( $\text{\AA}$ ,  $^\circ$ ) at various pressures.

Pressure	0.1 GPa	0.7 GPa	0.9 GPa	1.4 GPa
D—H	0.82	0.80 (6)	0.83 (9)	1.10 (15)
H...A	1.86	1.88 (7)	1.94 (16)	1.66 (12)
D...A	2.674 (13)	2.662 (5)	2.651 (8)	2.632 (9)
D—H...A	174	163 (10)	144 (18)	144 (14)

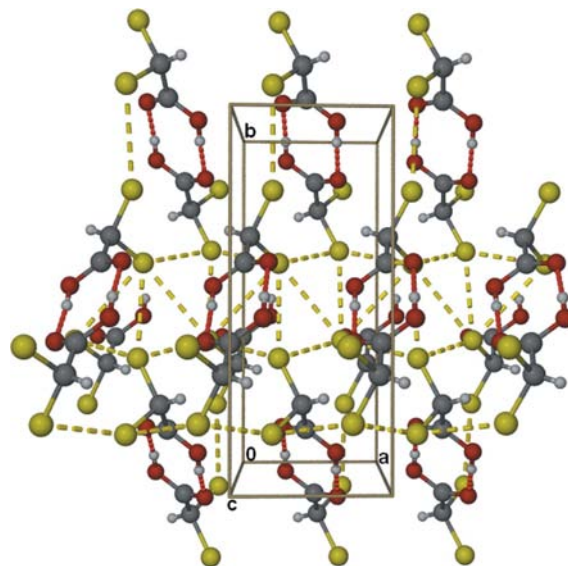
 Symmetry code: (i)  $1 - x, -y, -z$ .

The Cl, C and O atoms were refined with anisotropic displacement parameters, except for the C atoms which were refined isotropically at 0.1. As expected, the accuracy of structural data at 0.1 GPa and 293 K is lower than those of subsequent measurements at higher pressures. The reason for this is that the structure at 0.1 GPa is very close to the melting conditions of DCAA. For example, the larger temperature factors of atoms, lower intensities of high-angle reflections, fewer observed reflections *etc.* A somewhat lower accuracy of the data at 1.4 GPa is due to the lower quality of the sample crystal (strains in the sample cooled in the confined volume of the DAC chamber). The H atoms were located from the difference-Fourier maps, and their positions and isotropic temperature factors were refined.

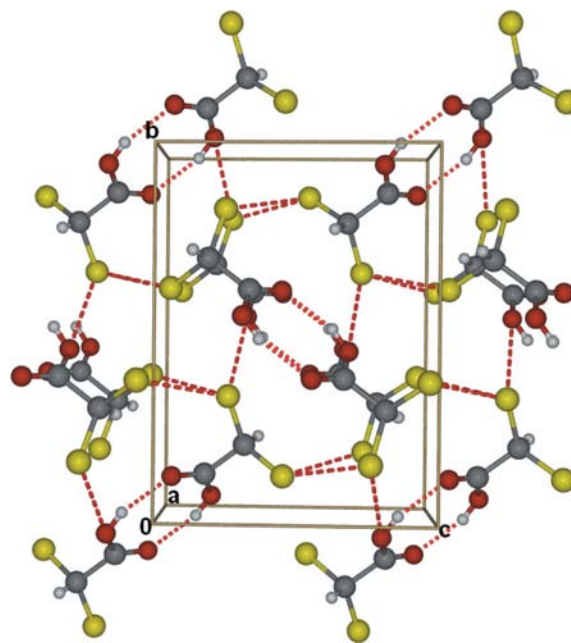
### 3. Crystal and molecular structure of compressed DCAA

In the pressure-frozen crystals the DCAA molecules form hydrogen-bonded dimers (Fig. 3), characteristic of carboxylic acids. Two polymorphs of monochloroacetic acid were described: form  $\alpha$  consists of centrosymmetric tetramers formed by hydrogen bonds between carboxyl groups, whereas form  $\beta$  is built of cyclic centrosymmetric hydrogen-bonded dimers (Kanters & Roelofsen, 1976; Kanters *et al.*, 1976), in an analogous manner to trichloroacetic acid (Rajagopal *et al.*, 2003). It appears from this comparison that hydrogen-bonded dimers are preferentially formed for acetic acids substituted with bulky Cl atoms, while only unsubstituted acetic acid forms catameric aggregates.

In the high-pressure structures of DCAA the C=O bonds are clearly shorter than the C—OH bonds, confirming that the H atoms are ordered (Table 2) and consistent with the average bond. The average bond lengths and angles in carboxylic acids are C=O 1.21, C—O(H) 1.31  $\text{\AA}$ , O=C—O 123 $^\circ$  and C—O—H between 110–114.5 $^\circ$  (Leiserowitz, 1976). The torsion angles change only slightly between the pressures investigated.


**Figure 3**

Autostereographic projection (Katrusiak, 2001b) of the dichloroacetic acid structure at 0.7 GPa with the hydrogen bonds (red dotted lines) and short chlorine...chlorine contacts (yellow dashed lines) indicated.


**Figure 4**

Intermolecular contacts (hydrogen bonds, halogen...halogen contacts and halogen...oxygen interactions) in the high-pressure crystal structure of DCAA. For clarity only the two shortest chlorine...chlorine contacts are presented.

**Table 4**

Parameters  $\Delta r$  (Å) and  $\Delta\varphi$  (°) describing the coupling of the H-atom sites with molecular dimensions and the arrangement of molecules in carboxylic acid dimers.

$\Delta r = r_1 - r_2$ , where  $r_1$  and  $r_2$  are the lengths of the C—O and C=O bonds;  $\Delta\varphi$  is the difference between angles O1—C1—C2 ( $\varphi_1$ ) and O2—C1—C2 ( $\varphi_2$ ).

Pressure	0.1 GPa	0.7 GPa	0.9 GPa	1.4 GPa
$\Delta r = r_1 - r_2$ (Å)	0.093 (21)	0.078 (9)	0.105 (11)	0.138 (20)
$\Delta\varphi = \varphi_1 - \varphi_2$ (°)	13.6 (16)	12.5 (8)	12.2 (10)	14.0 (17)

#### 4. Intermolecular interactions

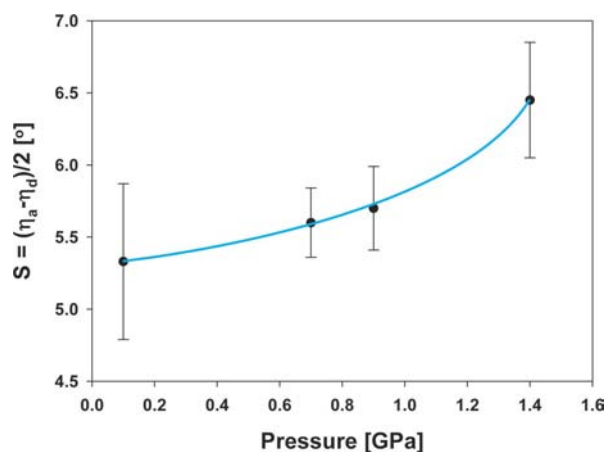
There are three types of short intermolecular contacts in the high-pressure crystal structure of DCAA: O—H...O hydrogen bonds, chlorine...chlorine interactions and chlorine...oxygen interactions, all of them indicated in Fig. 4.

##### 4.1. Hydrogen bonds

Strong hydrogen bonds between carboxyl groups bind two molecules of DCAA into a dimer (Figs. 3 and 4). The two carboxyl groups and the pair of hydrogen bonds are related by a centre of symmetry. The dimensions of the hydrogen bonds in the function of pressure are listed in Table 3.

The ordered position of H1 is confirmed by the skew position of the carboxyl groups in addition to the differences in the C—O1 and C=O2 bond lengths. The skewness parameter  $S$  is defined as the difference between two angles C—O2...O1' ( $\eta_a$ ) and C—O1...O2' ( $\eta_d$ ) divided by two. So, the defined skewness parameter  $S$  is equal to 5.3 (5)° at 0.1 GPa. As anticipated from the asymmetric shape of the molecule, it increases to 6.5 (4)° at 1.4 GPa (Fig. 5).

Also, the values of parameters  $\Delta r$  and  $\Delta\varphi$  described in §1 are consistent with the ordered H-atom sites (Table 4). The values of both parameters  $\Delta\varphi$  and  $\Delta r$  initially decrease slightly and then rise with pressure (Fig. 6). This behaviour of  $\Delta r$  and  $\Delta\varphi$  can result from the increased interactions between the H atom and its acceptor in the hydrogen bond (Katrusiak, 1991) and from the modified crystal structure. The dimensions



**Figure 5**  
Skewness parameter  $S$  as a function of pressure.

**Table 5**

Halogen...oxygen interaction geometry O1...Cl2 (Å) at various pressures.

Pressure	0.1 GPa	0.7 GPa	0.9 GPa	1.4 GPa
O1...Cl2	3.424 (8)	3.249 (5)	3.259 (5)	3.157 (9)

Symmetry code:  $(i) \frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$ .

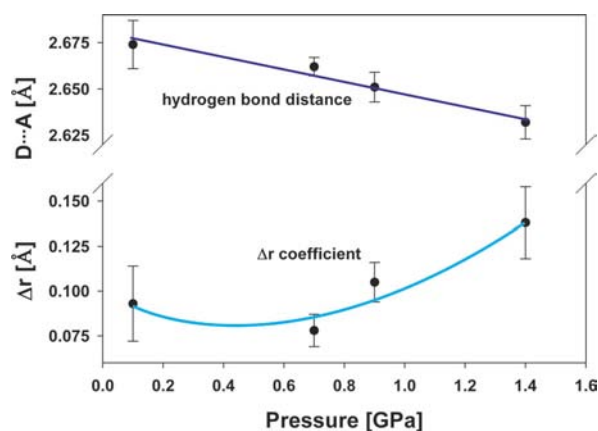
of the hydrogen bonds at variable temperature and pressure were also discussed by Boldyreva *et al.* (1998, 2000).

##### 4.2. The halogen...oxygen interaction

Chlorine...oxygen interactions involve hydroxyl O atoms (see Fig. 4). In terms of charge-transfer exchange, the oxygen is the electron-pair donor and the Cl atom the electron-pair acceptor in this interaction (Hassel & Rømming, 1962). The Cl...O interaction is weak and therefore this contact is not always formed in compounds containing halogen and O atoms. The dimensions of the halogen...oxygen contacts in DCAA are listed in Table 5. The sum of the van der Waals radii of O (1.52 Å) and Cl (1.75 Å) is 3.27 Å, according to Bondi (1964). Thus, it can be estimated that the Cl...O contacts in DCAA become shorter than this sum above 0.6 GPa.

##### 4.3. The halogen...halogen contacts

The nature of the halogen...halogen interactions, and particularly the Cl...Cl contacts, has been extensively studied (Desiraju & Parthasarathy, 1989; Price *et al.*, 1994; Grineva & Zorky, 1998, 2000, 2001, 2002; Bujak *et al.*, 2004, 2007). The limiting distance between two nonbonded Cl atoms was assessed by Bondi (1964) as 3.52 Å, and was 3.60 Å according to Rowland & Taylor (1996). Nyburg & Faerman (1985) postulated that the strength of the intermolecular halogen...halogen interactions depends not only on bond distances, but also on bond angles, because the van der Waals radii (hereinafter *vdW*) are anisotropic. They showed that covalently bonded halogen atoms are ellipsoidal because of the anisotropic distribution of electron density around the halogen nucleus. Consequently, the effective atomic radius of



**Figure 6**  
Changes of hydrogen-bond distance O...O and  $\Delta r = r_1 - r_2$  (Å) as a function of pressure.

a halogen atom  $X$  along the direction of the extended C— $X$  bond is shorter than in the perpendicular directions:  $d_m = 3.16 \text{ \AA}$  versus  $d_M = 3.56 \text{ \AA}$  (minor and major axes), respectively. Hence, the so-called ‘polar flattening’ has been described for the halogen atoms (Lommerse *et al.*, 1996). Generally, because of their terminal location in molecules, halogen atoms are prone to participate in short intermolecular contacts. Two preferred geometries of these contacts can be distinguished:

(i) of type 1 when  $\theta_1 = \theta_2$ ; and

(ii) of type 2 when  $\theta_1 \simeq 180^\circ$  and  $\theta_2 \simeq 90^\circ$ ; where  $\theta_1$  is the C—Cl $\cdots$ Cl' angle, and  $\theta_2$  is Cl $\cdots$ Cl'—C'.

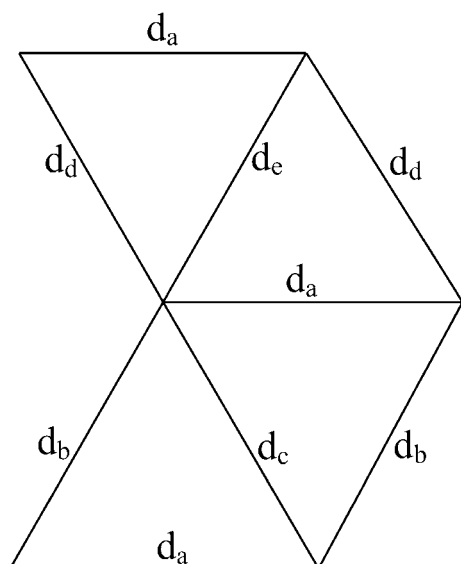
Thus, the halogen $\cdots$ halogen nonbonding contacts have to be characterized by halogen $\cdots$ halogen distances,  $d_x$ , and angles,  $\theta_1$  and  $\theta_2$ .

Two shortest chlorine $\cdots$ chlorine contacts connect the DCAA dimers into infinite chains along [100] (Fig. 4). There are two such contacts of each type per one molecule, which are perpendicular to each other.

There are also weaker intermolecular halogen $\cdots$ halogen interactions (Table 6), which contribute to the formation of specific triangular Cl $_3$  patterns (Broder *et al.*, 2000; Bosch & Barnes, 2002; Saha *et al.*, 2005). Each of these triangles has a common edge with two neighbouring triangles (Fig. 7). Two of them are nearly coplanar and the third is nearly perpendicular to them. The triangles are arranged in a supramolecular structure resembling the  $\beta$ -sheet (Fig. 3).

## 5. Conclusions

The pressure of 1.4 GPa has no effect on the H-atom ordering in DCAA. All the parameters related to the H-atom positions



**Figure 7**

Schematic illustration of chlorine $\cdots$ chlorine intermolecular interactions in DCAA:  $d_a$  denotes the Cl1 $\cdots$ Cl2' distance, with the Cl2' atom transformed according to the transformation code  $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$ ;  $d_b$ : Cl1 $\cdots$ Cl2 at  $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ ;  $d_c$ : Cl1 $\cdots$ Cl1 at  $-x, -y, 1 - z$ ;  $d_d$ : Cl1 $\cdots$ Cl2 at  $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ ;  $d_e$ : Cl1 $\cdots$ Cl1 at  $1 - x, -y, 1 - z$ .

**Table 6**

Chlorine $\cdots$ chlorine distances ( $d_i$ ) and carbon–chlorine $\cdots$ chlorine angles ( $\theta_1, \theta_2$ ) in DCAA compared with the sums of anisotropic vdW radii at variable pressures.

Distances  $d_{NF}$  have been calculated of elliptical vdW radii according to Nyburg & Faerman (1985). The codes for the Cl $\cdots$ Cl contacts are given in Fig. 7.

$d_x$	$d$	$\theta_1$	$\theta_2$	Sum of vdW radii $d_{NF}$	Length vdW
Pressure 0.1 GPa					
$d_a$	3.709 (5)	155.79 (45)	98.89 (41)	3.390	+0.319
$d_b$	3.531 (6)	142.66 (36)	94.46 (49)	3.435	+0.096
$d_c$	3.813 (6)	152.45 (51)	152.45 (51)	3.250	+0.563
$d_d$	3.638 (6)	128.70 (46)	88.01 (49)	3.485	+0.153
$d_e$	3.861 (7)	96.64 (39)	96.64 (39)	3.554	+0.307
Pressure 0.7 GPa					
$d_a$	3.647 (3)	151.59 (20)	95.71 (17)	3.405	+0.242
$d_b$	3.426 (3)	141.91 (16)	92.60 (22)	3.439	−0.013
$d_c$	3.555 (3)	149.37 (21)	149.37 (21)	3.268	+0.228
$d_d$	3.482 (3)	128.17 (20)	91.04 (21)	3.486	−0.004
$d_e$	3.669 (3)	96.67 (18)	96.67 (18)	3.554	+0.115
Pressure 0.9 GPa					
$d_a$	3.653 (3)	151.01 (25)	95.98 (22)	3.407	+0.246
$d_b$	3.404 (3)	141.73 (19)	91.81 (29)	3.439	−0.035
$d_c$	3.555 (3)	149.19 (28)	149.19 (28)	3.270	+0.285
$d_d$	3.467 (3)	128.17 (27)	90.12 (27)	3.486	−0.019
$d_e$	3.679 (3)	96.05 (22)	96.05 (21)	3.556	+0.123
Pressure 1.4 GPa					
$d_a$	3.598 (4)	149.51 (41)	94.95 (30)	3.413	+0.185
$d_b$	3.345 (4)	141.49 (32)	91.21 (43)	3.440	−0.095
$d_c$	3.442 (4)	148.30 (35)	148.30 (35)	3.276	+0.166
$d_d$	3.399 (4)	128.15 (35)	90.54 (39)	3.486	−0.087
$d_e$	3.599 (4)	95.47 (39)	95.47 (39)	3.556	+0.043

in the OH $\cdots$ O bonds in the carboxylic acid dimers ( $S$ ,  $\Delta r$  and  $\Delta\varphi$ ) indicate that the H atoms remain ordered at this pressure. These parameters also increase their magnitudes with increasing pressure, suggesting that pressure in this range further stabilizes the ordered H-atom sites. Thus, the effect of shear displacements of the molecules overcomes the effect of lowering the potential energy barrier separating the H-atom sites in this compound. The effect of pressure on other carboxylic acids still requires investigation.

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