

while in peptide I and molecule *B* of peptide V only one of the N...O distances falls within this range. In peptide II, both N...O distances are longer than normally accepted for hydrogen-bonding interactions (Table 4). Yet for all these molecules, the description of the conformation of the Schwyzer model is applicable. The absence or presence of N—H...O hydrogen bonds can in most cases be related to solvent interactions, which suggests that in general cross-ring N—H...O interactions are weak and that they do not make the backbone conformation more rigid but are instead a consequence of the conformation. The conformational similarity between the structures of peptides IV and V supports the prediction that in a cyclic peptide with a given series of amino-acid residues, the relative positions of the residues would have less effect on the backbone conformation than would the absolute configurations of the residues. It also appears that the packing and solvent interactions of cyclic hexapeptides are largely influenced by the backbone symmetry, which in turn is determined by the absolute configuration (L or D) of the residues composing the corners of the β -turns.

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High-Pressure X-ray Diffraction Study on the Structure and Phase Transition of 1,3-Cyclohexanedione Crystals

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Abstract

1,3-Cyclohexanedione (enol form), C₆H₈O₂, monoclinic, was studied at high pressures using a Merrill-Bassett diamond-anvil high-pressure cell and X-ray diffraction. The unit-cell parameters were measured to over 2.8 GPa and the structure was determined at

0.52, 1.14 and 1.90 (5) GPa. The crystals undergo a phase transition between 0.1 MPa and 0.3 GPa. In this pressure range a strong anomalous change in the unit-cell dimensions takes place with *a* being compressed by over 7% and *c* lengthening by more than 6% in comparison with the ambient-pressure lengths. Much smaller effects of anomalous compressibility

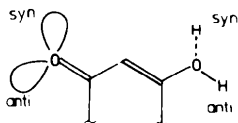
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are also observed for other unit-cell dimensions; the determination of the structure revealed that the protons in the hydrogen bonds that link the enolic molecules into chains change their sites thus interchanging the positions of the hydroxyl and carbonyl groups in the molecules and reversing the polarization of the chains. Atom C(5), which at 0.1 MPa is disordered over two sites on either side of the ring, becomes ordered, but this process, proceeding in two stages, requires higher pressures than the observed phase transition and C(5) is still partly disordered at 0.52 GPa. The phase transition is associated with a strong, visually observable change of the crystal shape, but the crystal preserves its ambient-pressure space group, $P2_1/c$. The MNDO method was used to calculate the net atomic charges in the molecule. A microscopic mechanism is suggested for the phase transition. Crystal data for the structure at 1.14 GPa: $a = 5.317(3)$, $b = 11.183(7)$, $c = 8.645(5)$ Å, $\beta = 91.40(5)^\circ$, $V = 513.8(8)$ Å³, $D_x = 1.405$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.66$ cm⁻¹, $T = 293$ K, $R = 0.094$ for 174 independent reflections.

Introduction

Cyclic β -diketoalkanes in their enol form possess interesting properties resulting from their alternating π -electron bond system HO—C=C—C=O. In this polar fragment the hydroxyl group can (potentially) lose its H atom and the carbonyl O atom can accept another H atom from a neighbouring molecule. Such an exchange produces an alternate sequence of single and double bonds in the conjugated bond system and changes the polarization of the molecule. In the crystalline state, cyclic β -diketoalkanes form aggregates (chains or helices) of molecules linked together by strong (shorter than 2.6 Å) hydrogen bonds between the carbonyl and hydroxyl O atoms. The H atom can assume one of two favourable positions in the hydroxyl group — *syn* or *anti* — both in the plane or close to the plane of the O=C—C=C—O fragment:



Similarly, two acceptor sites can be defined for the carbonyl group. The 1,3-cyclohexanedione (CHD) molecules in the crystal are linked into chains by *anti-anti* hydrogen bonds (the hydroxyl configuration is specified first and the carbonyl hydrogen-bond orientation second); CHD also forms an inclusion complex in which six molecules are hydrogen bonded (*syn-anti*) into a cyclomer hosting one benzene molecule (Etter, Urbańczyk-Lipkowska, Jahn & Frye,

1986). In crystals of 1,3-cyclopentanedione (CPD) the molecules are also linked into chains by *anti-anti* hydrogen bonds (Katrusiak, 1990a). A different *anti-syn* configuration of the hydrogen bond has been observed in 2-methyl-1,3-cyclopentanedione (Katrusiak, 1989). Hydrogen bonds with *syn-syn* configuration, linking the molecules into helices, have been observed in crystals of dimedone (*i.e.* 5,5-dimethyl-1,3-cyclohexanedione) (Semmingsen, 1974; Singh & Calvo, 1975). In all these structures the geometry of the hydrogen bonds and the conjugation of the bonds in the HO—C=C—C=O fragments are similar and it seems that they are little affected by the configuration of the hydrogen bonds, which, however can play an important role in the possible collective motion of the H atoms. Such a collective exchange of the donor and acceptor sites (simultaneous with reversing the sequence of double and single bonds) would not change the configuration of the *anti-anti* hydrogen bonds, and the position of the H atom would also be almost unchanged. The two sites can, however, have significantly different environments in the crystal lattice. It has already been reported that CPD crystals undergo a transformation at a pressure of about 0.3 GPa which damages the sample and makes the determination of the high-pressure structure impossible by single-crystal methods (Katrusiak, 1990a). The structure of CHD is similar to that of CPD in this respect; in both structures the molecules are connected by *anti-anti* hydrogen bonds into chains and are approximately coplanar. However, the space groups and some features of the arrangement of the chains are different. Also, CHD crystals undergo a pressure-induced phase transition between 0.1 MPa and 0.3 GPa, but, unlike CPD, are not damaged and could be brought through the phase transition many times without deterioration.

The main aim of this study was to determine the high-pressure structure of CHD and the pressure dependence of the unit-cell parameters and the structural changes. It was hoped that the explanation of the mechanism of the structural transformation in CHD would afford an interpretation of the phase transition in CPD and would also provide information on the order-disorder phase transitions from (anti)ferroelectric to paraelectric structures, specifically the structural factors destabilizing the low-temperature/low-pressure structure approaching its T_c point. The CHD crystal provides a convenient model for analysing these factors because it retains its ambient-pressure symmetry and because during the phase transition the increase of hydrostatic pressure forces the H atom to interchange its donor and acceptor sites, but does not stabilize a paraelectric phase with collective motion of the H atoms. We were also interested in molecular deformations in the

high-pressure structure, in particular in the pressure modifications of the sp^2 -atom fragment and of the conformation of the ring.

Structure of CHD at atmospheric pressure

The structure of CHD at room temperature and ambient pressure has been determined by X-ray diffraction by Etter, Urbańczyk-Lipkowska, Jahn & Frye (1986). The crystal is monoclinic, space group $P2_1/c$, $Z=4$; the unit-cell dimensions are given in Table 1. A projection of the structure down b is shown in Fig. 1. The CHD molecules, linked by *anti-anti* hydrogen bonds, form chains along the crystallographic direction $[201]$, two hydrogen-bonded molecules in one chain being related by the symmetry operation $(x \pm 1, 0.5 - y, z \pm 0.5)$. In further discussion the central lines of the chains will be defined as lines along $[201]$ lying at the intersection of the planes of the chains, $(10\bar{2})$, and the glide plane c at $y=0.25$ or 0.75 (as indicated in Fig. 6). The CHD molecule, except for C(5), is planar and the molecules of one chain lie approximately in a plane parallel to the crystallographic plane $(10\bar{2})$. The line drawn through atoms O(1) and O(2) is inclined at an angle $\rho = 3.45(1)^\circ$ to the central line of the chain (and to plane xz); the carbonyl O atom is closer to this line (see Fig. 2; ρ is defined in Fig. 6). Chains are related by glide planes c ; thus, the polarization of neighbouring chains along $[201]$ is the same. The CHD structure can be considered as consisting of sheets of chains perpendicular to y . The contacts between the sheets can be classified mainly as van der Waals interactions, while the interactions between the neighbouring chains within one sheet – as indicated by their arrangement (see Fig. 2) – are dominated by electrostatic forces between atomic net charges in the $O=C-C=C-OH$ fragments (see the scheme in *MNDO calculations*). The electrostatic interactions between the sheets, although present and manifested in antiparallel stacking of the sheets, are much weaker than those between close chains within one sheet – the distances between sp^2 atoms of neighbouring sheets are on average twice those between close chains within one sheet.

The CHD ring has a sofa conformation with atoms $C(6)-C(1)-C(2)=C(3)-C(4)$ in a plane; at ambient pressure the ring is partly disordered with atom C(5) exhibiting equal occupation of two symmetry-independent positions on either side of the ring plane. The positions of C(5), determined in the X-ray diffraction experiment, approximate the average positions of strongly vibrating C(5A) and C(5B) atoms, explaining the discrepancies between observed and expected bond lengths and angles involving C(5) (see Table 4). The positions of the H atoms at C(4), C(5) and C(6) all depend on the

Table 1. Variation of the unit-cell dimensions with pressure for 1,3-cyclohexanedione at 293 K

The room-temperature (RT) measurement by Etter, Urbańczyk-Lipkowska, Jahn & Frye (1986) is also included. The high pressures were calibrated with an accuracy of about 0.05 GPa.

Pressure	a (Å)	b (Å)	c (Å)	β ($^\circ$)	V (Å ³)
0.1 MPa	6.145 (2)	11.711 (2)	8.196 (1)	99.43 (1)	581.9 (1)
0.1 MPa/RT	6.128 (3)	11.712 (3)	8.191 (5)	99.44 (4)	580.1 (2)
0.11 GPa	5.6670 (7)	11.562 (1)	8.693 (2)	95.25 (2)	567.2 (1)
0.26	5.5865 (5)	11.514 (5)	8.7190 (9)	94.378 (8)	559.2 (2)
0.52	5.476 (4)	11.395 (7)	8.721 (5)	93.09 (7)	543.3 (7)
0.73	5.406 (1)	11.313 (8)	8.700 (2)	92.35 (2)	531.6 (4)
1.03	5.3289 (8)	11.213 (3)	8.6605 (9)	91.33 (1)	517.35 (9)
1.14	5.317 (3)	11.183 (7)	8.645 (5)	91.40 (5)	513.8 (8)
1.35	5.2866 (8)	11.137 (4)	8.636 (2)	90.91 (1)	508.4 (4)
1.68	5.226 (1)	11.064 (4)	8.570 (1)	90.39 (2)	495.5 (2)
1.90	5.197 (2)	11.017 (1)	8.528 (2)	89.60 (2)	488.3 (1)
2.04	5.198 (9)	11.01 (1)	8.519 (7)	89.9 (1)	487.5 (9)
2.40	5.1625 (9)	10.965 (3)	8.477 (2)	89.37 (1)	479.8 (3)
2.83	5.143 (2)	10.919 (1)	8.4271 (4)	88.75 (3)	473.1 (2)

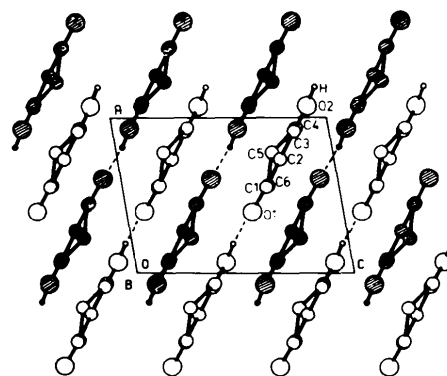


Fig. 1. Projection of the 1,3-cyclohexanedione ambient-pressure structure down b . For clarity all H atoms, except H(1) of O(2), have been omitted and only one position of the disordered C(5) atom has been included. Open circles represent atoms of molecules in one sheet; shaded circles show molecules in the other sheet. Hydrogen bonds are indicated by broken lines.

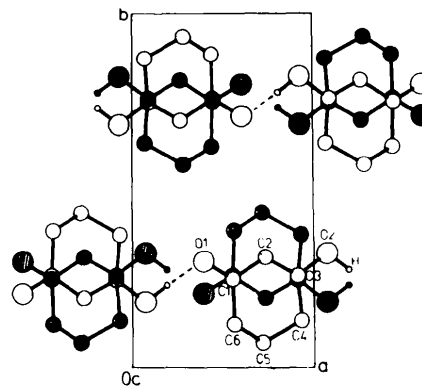


Fig. 2. Projection of the 1,3-cyclohexanedione ambient-pressure structure down c . The unshaded molecules are hydrogen bonded into chains along $[201]$, shaded molecules are the nearest neighbouring molecules on each side of the chain.

position of C(5) and will be denoted below by the letters *A* or *B*, respectively.

The bond orders in conjugated system O(1)=C(1)—C(2)=C(3)—O(2)H, as estimated from the bond lengths (Allmann, 1977), are 1.8, 1.4, 1.95 and 1.3, respectively. These well defined bonds are a good indication of the position of the enolic proton, which could not be detected in the high-pressure X-ray diffraction experiment.

Experimental

CHD forms colourless trapezoidal crystal plates with well developed faces. In most cases they are plates elongated along *c* with *b* being the shortest dimension. Good cleavage directions are along planes parallel to [201], which reflects the arrangement of the molecules; this direction is also indicated by the relief on the (010) face (see Fig. 4*a*). The crystals, which sublime slowly, were obtained from acetone by slow evaporation and resublimation above the solution. A Merrill–Bassett diamond-anvil high-pressure cell (Merrill & Bassett, 1974) and a CAD-4 diffractometer (graphite-monochromated Mo *K* α radiation) were used. To minimize the background-to-signal ratio, large crystal samples (about 0.25 \times 0.25 \times 0.12 mm) were mounted in the cell and the smallest possible gasket-hole diameters (large enough to avoid shadowing of the sample) were employed (Katrusiak, 1990*b*). Inconel gaskets 0.2 mm thick with an initial hole diameter of 0.40–0.45 mm were used with glycerin as the hydrostatic fluid. The crystals were fixed to the diamond culet with a dab of insoluble vacuum grease. CHD crystals dissolve slightly in glycerin; therefore, to allow for dissolution, samples with dimensions somewhat larger than the sample dimensions planned for the experiment were mounted in the cell. The pressure inside the diamond-anvil cell was calibrated to an accuracy of about 0.05 GPa before and after each diffraction measurement using the pressure dependence of the *R*₁ ruby fluorescence line (Piermarini, Block, Barnett & Forman, 1975). Unit-cell dimensions were measured at 293 K at several pressures from 0.1 MPa up to 2.83 (5) GPa; the ambient-pressure unit-cell parameters were remeasured using 16–25 reflections in the least-squares fit. Unit-cell dimensions are listed in Table 1. To perform these measurements several crystals had to be mounted in the high-pressure cell since CHD crystals are fragile and were easily damaged during pressure generation. Inspection of systematic absences showed that the crystal preserves its ambient-pressure space group *P*2₁/*c* in the high-pressure phase; this result was confirmed by rotation photographs about all three axes of the crystal.

The Merrill–Bassett high-pressure cell significantly limits the accessible volume of reciprocal space; only about 50% of the reflections with $\theta_{\max} = 22^\circ$ could be measured (Merrill & Bassett, 1974). The limits depend on the crystal orientation such that only the reflections with small Miller indices are available in the direction parallel to the cylindrical axis of the Merrill–Bassett cell while there are no limits of access (up to $\theta = 40^\circ$) to the high-angle reflections lying along the reciprocal directions perpendicular to this axis. Consequently, the best resolution of the final results is obtained for crystal directions perpendicular to the axis of the cell. As the CHD crystal undergoes a phase transition between 0.1 MPa and 0.3 GPa the sample crystal was oriented in two different ways to facilitate the solution of the high-pressure structure: at 0.52 and 1.90 GPa the (10 $\bar{2}$) crystal plane was arranged perpendicular to the cylindrical axis of the high-pressure cell, and at 1.14 GPa the (010) plane was made perpendicular to this axis. The ω -scan method was employed, with the scan speed dependent on reflection intensity and stationary background measurements. The setting angles of reflections were calculated according to the $\varphi = 0^\circ$ method described by Finger & King (1978) and incorporated in the CAD-4 data-collection program (King, 1981). Reflections for which either the primary or reflected beam lay beyond 40° from the diamond-cell axis were excluded from calculations. The intensities were corrected for absorption by the diamond-anvil cell and for *L*_p effects, but not for crystal absorption effects. The structure was solved by a trial-and-error method in which the CHD molecule was displaced slightly from its ambient-pressure position. Only one C(5) position was found and the difference Fourier maps for the measurements at 0.52, 1.14 and 1.90 GPa revealed no peaks corresponding to a disordered position of this atom. The C and O atoms were refined isotropically; the positions of the H atoms were calculated from the molecular geometry after each cycle of refinement ($d_{\text{C-H}} = 1.07 \text{ \AA}$) and were assigned a common $U = 0.05 \text{ \AA}^2$. The hydroxyl H atom was excluded from the refinement. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = \sigma(F_o)^{-2}$. Crystal data and the data-collection and structure-refinement parameters are given in Table 2; the final atomic parameters are listed in Table 3.* Data reduction was performed with an *ad hoc* computer program. The structures were solved and refined with *SHELX76* (Sheldrick, 1976) on an IBM XT

* Lists of structure factors for the measurements at 0.52, 1.14 and 1.90 (5) GPa have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52451 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Crystal data, and data-collection and refinement parameters for 1,3-cyclohexanedione at 0.52, 1.14 and 1.90 GPa

	0.52 GPa	1.14 GPa	1.90 GPa
D_x (g cm ⁻³)	1.333	1.405	1.484
μ (Mo $K\alpha$) (cm ⁻¹)	0.62	0.66	0.69
θ_{max} (°)	22	23	22
Scan speed (° min ⁻¹)			
Max.	20.0	20.0	20.0
Min.	0.6	0.4	0.4
Max. h, k, l	6, 11, 5	5, 4, 9	5, 10, 5
Crystal plane perpendicular to the axis of the high-pressure cell	(10 $\bar{2}$)	(010)	(10 $\bar{2}$)
No. of reflections			
Measured	348	772	687
Independent	141	174	228
R	0.105	0.094	0.082
wR	0.102	0.089	0.087
$(\Delta/\sigma)_{max}$	0.001	0.001	0.001
ΔF_{max} (e Å ⁻³)	0.28	0.28	0.50
ΔF_{min} (e Å ⁻³)	-0.25	-0.36	-0.64

Table 3. Fractional atomic coordinates and isotropic thermal parameters (Å²) for 1,3-cyclohexanedione at 0.52, 1.14 and 1.90 (5) GPa

Ambient-pressure coordinates and equivalent temperature factors (Etter, Urbańczyk-Lipkowska, Jahn & Frye, 1986) are given for comparison. The unit-cell dimensions are those listed in Table 1.

	x	y	z	U_{iso}
0.52 GPa				
O(1)	0.3998 (22)	0.331 (1)	0.595 (3)	0.044 (8)
O(2)	1.0917 (22)	0.2803 (8)	0.9174 (22)	0.033 (7)
C(1)	0.564 (3)	0.260 (2)	0.667 (4)	0.032 (9)
C(2)	0.754 (3)	0.308 (2)	0.746 (4)	0.021 (9)
C(3)	0.916 (4)	0.234 (2)	0.837 (4)	0.041 (10)
C(4)	0.886 (3)	0.107 (2)	0.826 (4)	0.026 (10)
C(5)	0.747 (3)	0.063 (2)	0.699 (4)	0.056 (11)
C(6)	0.530 (3)	0.129 (2)	0.648 (4)	0.033 (9)
1.14 GPa				
O(1)	0.409 (1)	0.336 (1)	0.5908 (8)	0.032 (3)
O(2)	1.092 (1)	0.278 (1)	0.9224 (8)	0.039 (3)
C(1)	0.565 (2)	0.265 (3)	0.666 (1)	0.018 (4)
C(2)	0.750 (2)	0.308 (3)	0.755 (1)	0.028 (3)
C(3)	0.912 (2)	0.234 (3)	0.840 (1)	0.024 (4)
C(4)	0.880 (2)	0.096 (3)	0.839 (1)	0.029 (4)
C(5)	0.761 (1)	0.058 (2)	0.684 (1)	0.037 (4)
C(6)	0.522 (2)	0.125 (3)	0.645 (1)	0.028 (4)
1.90 GPa				
O(1)	0.408 (2)	0.3376 (5)	0.591 (1)	0.026 (2)
O(2)	1.100 (2)	0.2749 (5)	0.921 (1)	0.025 (2)
C(1)	0.563 (2)	0.2619 (8)	0.668 (2)	0.020 (3)
C(2)	0.754 (2)	0.3098 (8)	0.755 (2)	0.018 (3)
C(3)	0.913 (2)	0.2297 (8)	0.844 (2)	0.020 (3)
C(4)	0.876 (2)	0.0965 (7)	0.837 (2)	0.018 (3)
C(5)	0.769 (2)	0.0567 (7)	0.675 (2)	0.026 (3)
C(6)	0.528 (2)	0.1287 (7)	0.642 (2)	0.014 (3)
0.1 MPa				
O(1)	0.3928 (2)	0.2951 (1)	0.5834 (3)	0.080 (4)
O(2)	1.0722 (2)	0.3183 (1)	0.9197 (2)	0.075 (4)
C(1)	0.5533 (3)	0.2454 (2)	0.6658 (3)	0.057 (4)
C(2)	0.7328 (3)	0.3073 (2)	0.7526 (3)	0.057 (4)
C(3)	0.9103 (3)	0.2551 (2)	0.8395 (2)	0.053 (4)
C(4)	0.9308 (3)	0.1290 (2)	0.8498 (3)	0.066 (5)
C(5A)	0.7751 (8)	0.0679 (3)	0.7194 (6)	0.067 (11)
C(5B)	0.7163 (7)	0.0677 (3)	0.8113 (6)	0.066 (11)
C(6)	0.5613 (4)	0.1184 (2)	0.6734 (3)	0.079 (6)
H(O2)	1.191 (4)	0.272 (2)	0.969 (3)	0.114 (9)

computer. Scattering factors incorporated in SHELX76 were applied. The crystal structures in Figs. 1 and 2 were drawn using PLUTO (Motherwell, 1976).

Results

The relative changes of the unit-cell dimensions with pressure are shown in Fig. 3; they were the first evidence of a structural transformation in the CHD crystal. A strong compressibility of a and c is observed at pressures between 0.1 MPa and 0.3 GPa: a pressure increase of 0.1 GPa shortens a by 0.478 (2) Å (*i.e.* by almost 8%) while c lengthens by 0.498 (2) Å (over 6%). This pressure increase is also associated with an anomalous change in β of 4.17 (2)°. Much smaller, but clearly indicated by the measurements, are the anomalies in the compressibility of b or of the unit-cell volume. The anomalous compressibility of the crystal between 0.1 MPa and 0.3 GPa is so substantial that this transformation

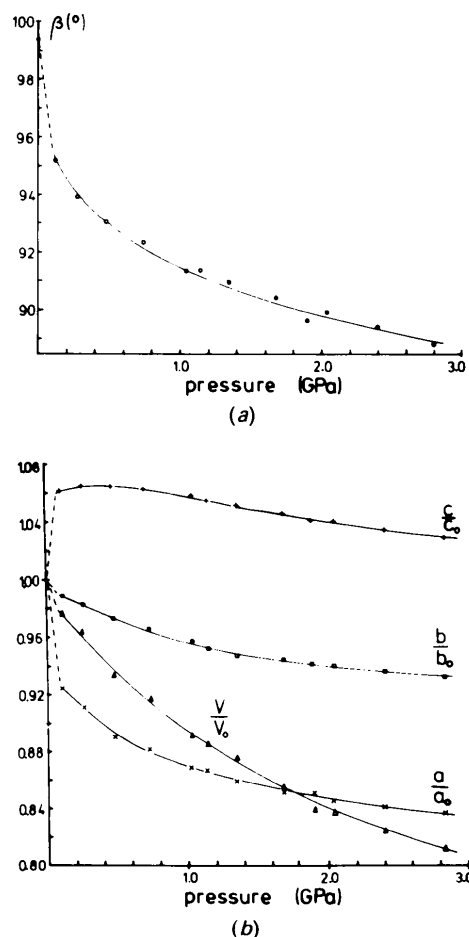


Fig. 3. (a) Changes in β and (b) relative changes in the lengths of a , b and c with pressure.

can be clearly observed by eye. Fig. 4 shows a CHD crystal mounted inside the diamond-anvil cell with **b** perpendicular to the diamond culets (and to the photographs) at 0.1 MPa and at 1.5 GPa; the deformation of the crystal is directly connected with the changes of the unit-cell dimensions (Table 1). At pressures above 0.3 GPa a continuous change of the unit-cell dimensions is observed, but the compressibility of all the dimensions and the changes in β are significantly nonlinear. In this pressure range the compressibility of **b** is larger than those of **a** or **c**, which reflects weak van der Waals interactions between the sheets perpendicular to **y** (see Fig. 2). No strong anomalous effects – as found for **a**, **c** or β – were observed for the length of one CHD molecule measured along chain direction [201], l [as two neighbouring molecules in one chain are symmetry-related, this interval can be calculated from the unit-cell dimensions: $l = (c^2/4 + a^2)^{1/2}$], or for the separation between the neighbouring chains within one sheet, s [also obtainable from the unit-cell dimensions: $s = (ac \sin \beta)/(2l)$]. As can be seen from Fig. 5, l initially does not change or only slightly increases by about 0.2% [from 6.805 (3) Å at ambient pressure to 6.819 (3) Å at 0.11 GPa, 6.819 (2) Å at 0.26 GPa and 6.813 (5) Å at 0.52 GPa]; above 1.0 GPa l steadily decreases and at 2.83 GPa is shortened to 6.719 (4) Å. Two other parameters which can be used to describe the arrangement of the chains and the orientation of the molecules in the chain are δ and ρ (Fig. 6). δ is the displacement of the corresponding atoms of two overlapping molecules when two neighbouring chains are projected onto the plane (102), and ρ is

the angle between the central line of the chain [*i.e.* glide plane c projected onto (102)] and the straight line through O(1) and O(2). As can be seen from Fig. 7, the displacement δ changes abruptly between 0.1 MPa and 0.2 GPa and then slowly saturates to assume an approximately constant value of 2.70 Å at about 2.0 GPa. A similar sudden change can be observed for the angle ρ at the pressures at which the phase transition takes place and, as was observed for δ , ρ saturates smoothly at the higher pressures to about -8.0° at 2.0 GPa (see Fig. 8).

Several significant changes have been found in the molecular dimensions of the CHD molecule in the high-pressure phase (Table 4). Atom C(5) becomes ordered at higher pressures, but the characteristic shortening of bonds C(4)–C(5) and C(5)–C(6) as well as the widening of valency angles C(3)–C(4)–C(5), C(4)–C(5)–C(6) and C(1)–C(6)–C(5) (also observed at ambient pressure) may suggest, in spite of the large standard deviations, that C(5) still has large vibrations at 0.52 GPa. It appears that the vibrational freedom of C(5) is substantially confined at still higher pressures as these effects were not observed in the structure at 1.14 or 1.90 GPa. Other bond lengths and valency angles in these high-pressure structures are consistent within three e.s.d.'s.

It is evident (compare O=C–C=C–OH bonds in Table 3) that the sequence of double and single bonds in the ambient-pressure conjugated system is reversed at high pressures, indicating that the H atom has changed its donor and acceptor sites in the hydrogen bond. Some systematic changes can be noted in the lengths of the bonds between the sp^2

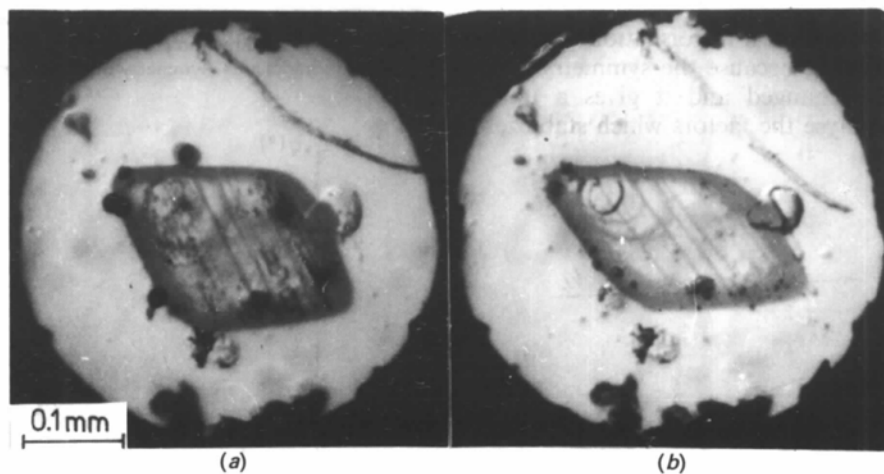


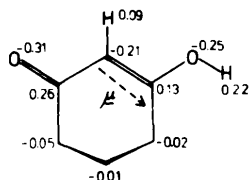
Fig. 4. The ambient- and high-pressure shape of a 1,3-cyclohexanedione crystal. (a) An inside view of the high-pressure chamber with a CHD sample at ambient pressure. The specimen has its **b** axis perpendicular to the photograph and its **c** axis horizontal; the relief grooves on its (010) face are along direction [201] and the edges of the sample are rounded since it partly dissolved in glycerin. Vacuum grease dabs are clearly visible in the photographs – one of the dabs covers a fragment of the (102) face and protects it from dissolving in glycerin; ruby crystal fragments are visible at the bottom. The small round dark objects are air bubbles. (b) The same sample crystal of CHD at about 1.5 GPa.

atoms, which are particularly sensitive to the effects of pressure (Nicol & Yin, 1984; Dremin & Babare, 1984). For example, a bond elongation can be observed for the carbonyl group of CHD at high pressures (see Table 4). However, the uncertainty of the atomic positions in our experiment does not allow any definite conclusions to be drawn.

Table 5 lists some of the shortest intermolecular distances describing the pressure dependence of the intermolecular interactions in the CHD crystal.

MNDO calculations

The MNDO method (Dewar & Thiel, 1977) was used to calculate an approximate charge distribution in the (enolized) CHD molecule. Net atomic charges are given in the scheme below [H atoms at C(4), C(5) and C(6) have positive charges smaller than 0.04 e].



The orientation of the dipole-moment vector, μ [$= 5.15$ debye (1.72×10^{-29} C m)], is also shown in this drawing. The above calculations were based on the geometry of the CHD molecule determined at 0.1 MPa, but recalculating the position of C(5) and of the H atoms bonded to C(4), C(5) and C(6) under standard geometrical assumptions.

The structural transformation

The very strong structural transformation of CHD is particularly interesting because the symmetry of the crystal remains unchanged and it gives a unique opportunity to analyse the factors which stabilize or

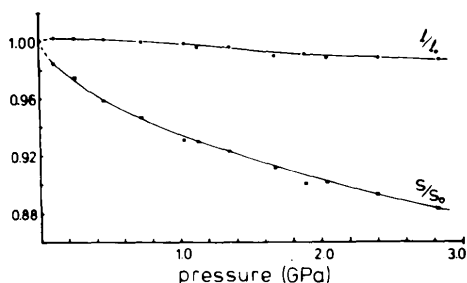


Fig. 5. Relative changes with pressure of the length of one 1,3-cyclohexanedione molecule measured along chain direction [201], l , and of the separation of the neighbouring chains within one sheet, s .

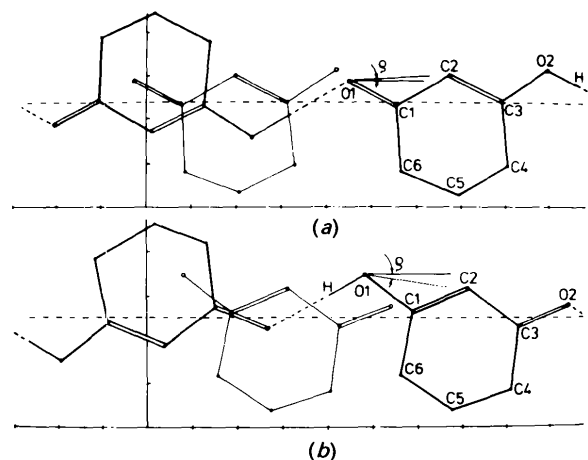


Fig. 6. Projection onto plane $(10\bar{2})$ of two 1,3-cyclohexanedione molecules from one chain (thick solid lines) and of one molecule of its closest neighbouring chain along c (thin solid lines) at 0.1 MPa (a) and 1.90 GPa (b). The dashed lines represent hydrogen bonds, the dash-dotted line is the central line of the chain (see text). Angle ρ is between the central line of the chain and the straight line through O(1) and O(2).

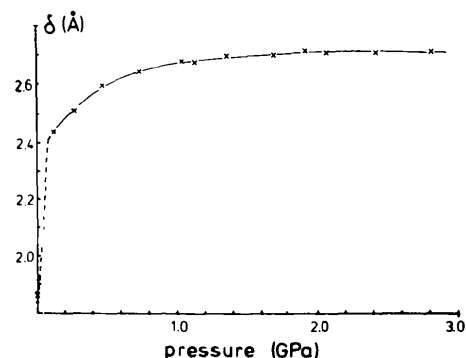


Fig. 7. Pressure dependence of the changes in δ – the displacement measured along direction [201] of two overlapping molecules of neighbouring chains (symmetry operation: $x, 0.5 - y, 0.5 + z$).

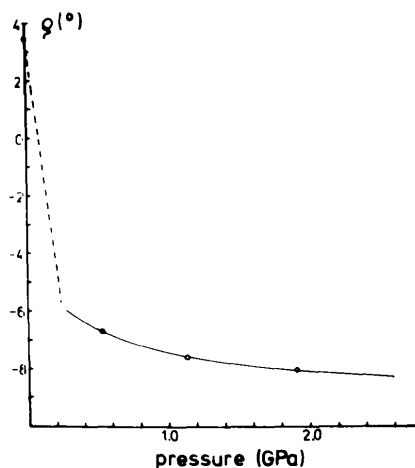


Fig. 8. Variation of ρ (Fig. 6) with pressure.

Table 4. Bond lengths (Å) and valency angles (°) in 1,3-cyclohexanedione at 0.52, 1.14 and 1.90 GPa

The ambient-pressure values (Etter, Urbańczyk-Lipkowska, Jahn & Frye, 1986) are given for comparison.

	0.1 MPa	0.52 GPa	1.14 GPa	1.90 GPa
O(1)—C(1)	1.243 (2)	1.34 (2)	1.31 (2)	1.33 (1)
O(2)—C(3)	1.323 (4)	1.27 (2)	1.28 (2)	1.275 (9)
C(1)—C(2)	1.409 (3)	1.33 (2)	1.33 (2)	1.35 (1)
C(1)—C(6)	1.490 (6)	1.50 (3)	1.59 (4)	1.49 (1)
C(2)—C(3)	1.345 (5)	1.43 (2)	1.39 (3)	1.43 (1)
C(3)—C(4)	1.483 (5)	1.46 (2)	1.56 (5)	1.48 (1)
C(4)—C(5)	1.49 (1), 1.49 (1)	1.41 (3)	1.52 (2)	1.55 (2)
C(5)—C(6)	1.43 (1), 1.48 (1)	1.46 (2)	1.50 (2)	1.51 (1)
O(1)—C(1)—C(2)	121.1 (2)	118 (2)	122 (3)	118.3 (8)
O(1)—C(1)—C(6)	120.5 (4)	118 (2)	117 (1)	117.9 (8)
C(2)—C(1)—C(6)	118.4 (4)	124 (2)	122 (2)	123.6 (8)
C(1)—C(2)—C(3)	122.0 (3)	119 (2)	122 (3)	118.7 (8)
C(2)—C(3)—C(4)	122.5 (4)	121 (2)	122 (2)	120.8 (8)
C(2)—C(3)—O(2)	118.9 (3)	120 (2)	121 (3)	118.5 (8)
O(2)—C(3)—C(4)	118.6 (3)	119 (2)	118 (2)	120.5 (8)
C(3)—C(4)—C(5)	113.4 (5), 113.9 (5)	117 (2)	108 (2)	111 (1)
C(4)—C(5)—C(6)	116.1 (8), 113.8 (3)	117 (2)	113 (2)	109 (1)
C(1)—C(6)—C(5)	116.5 (6), 116.5 (5)	113 (1)	110 (2)	112.8 (7)

Table 5. Intermolecular distances (Å) for 1,3-cyclohexanedione at 0.52, 1.14 and 1.90 GPa

The 0.1 MPa values (Etter, Urbańczyk-Lipkowska, Jahn & Frye, 1986) are also given.

	0.1 MPa	0.52 GPa	1.14 GPa	1.90 GPa	Symmetry operation (i)
O(1)—O(2)	2.561 (4)	2.56 (2)	2.54 (2)	2.49 (1)	$x - 1, 0.5 - y, z - 0.5$
O(1)—O(2)	3.647 (3)	3.40 (3)	3.42 (1)	3.30 (2)	$x - 1, y, z$
O(1)—C(4)	4.170 (3)	3.71 (3)	3.44 (2)	3.32 (2)	$x, 0.5 - y, z - 0.5$
O(1)—C(4)	4.459 (3)	3.60 (2)	3.35 (4)	3.27 (1)	$1 - x, 0.5 + y, 1.5 - z$
O(1)—C(4)	3.270 (3)	3.63 (3)	3.60 (2)	3.59 (2)	$x - 1, 0.5 - y, z - 0.5$
O(1)—C(5A')	3.798 (4)	3.32 (3)	3.30 (3)	3.26 (2)	$1 - x, 0.5 + y, 1.5 - z$
O(1)—C(5B')	3.402 (4)	—	—	—	$1 - x, 0.5 + y, 1.5 - z$
O(1)—C(5B')	3.596 (4)	—	—	—	$x, 0.5 - y, z - 0.5$
O(1)—C(5A')	4.387 (5)	4.21 (4)	4.19 (2)	4.17 (2)	$x, 0.5 - y, z - 0.5$
O(2)—C(1)	3.970 (3)	3.40 (3)	3.39 (1)	3.22 (2)	$x - 1, y, z$
O(2)—C(1)	3.371 (3)	3.32 (3)	3.27 (1)	3.23 (2)	$x + 1, 0.5 - y, 0.5 + z$
O(2)—C(5A')	3.548 (6)	3.64 (3)	3.43 (2)	3.32 (2)	$x, 0.5 - y, 0.5 + z$
O(2)—C(5B')	4.374 (6)	—	—	—	$x, 0.5 - y, 0.5 + z$
O(2)—C(6)	3.437 (3)	3.22 (3)	3.15 (2)	3.12 (2)	$x + 1, 0.5 - y, 0.5 + z$
C(1)—C(3)	3.778 (4)	3.55 (5)	3.41 (2)	3.30 (2)	$x, 0.5 - y, z - 0.5$

destabilize the low- and high-pressure structures. Moreover, the structural changes of CHD are coupled with the position assumed by the enolic H atoms in the hydrogen bonds, a phenomenon of interest to chemists concerned with hydrogen bonds, physicists working on ferroelectric crystals with phase transitions driven by H-atom ordering, and biologists considering hydrogen-bonded molecular systems and their transformations in living organisms.

Therefore, we attempted to combine the structural changes observed in CHD into a model that would help in understanding the mechanism of this transformation. The data on pressure-dependence of CPD (Katrusiak, 1990a) and MCPD (Katrusiak, 1989, 1990c) also provide a helpful reference in this analysis. The suggested mechanism of the structural

transformation is based on the following considerations:

(a) Electrostatic forces between the molecules of neighbouring chains are one of the factors which can produce internal strains leading to the structural transformation of CHD. These forces can be roughly approximated by the dipole-dipole interactions. In Fig. 9, the CHD molecules in one sheet perpendicular to y are represented schematically to show the arrangement of their dipole moments μ . All molecules within one chain and within one sheet have the same component of μ along the [201] chain direction (the direction and sense of μ are indicated by small arrows in Fig. 9). Thus, when the structure is compressed and the separation between chains, s , is reduced, the dipole-dipole interactions between chains increase and shear strains between the chains within each sheet can lead to shifts of the chains along [201] (*i.e.* to changes of δ) tending to reduce

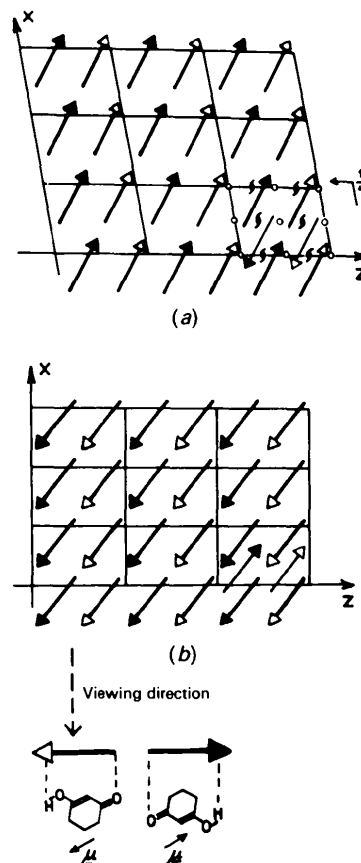


Fig. 9. Arrangement of the 1,3-cyclohexanedione dipoles in the crystal at (a) 0.1 MPa and (b) 1.5 GPa. Arrowheads indicate the position of the hydroxyl group in the molecule: open arrowheads, negative y components of μ ; closed arrowheads, positive y components of μ . The position of the molecules of the neighbouring sheet is shown in one unit cell in the bottom right-hand corner.

the overlap of neighbouring molecules (see Fig. 6) and hence decrease the interactions of their dipole moments. The hypothesis of an electrostatic origin for this transformation seems to be strongly supported by the high-pressure studies on CPD and MCPD. In CPD crystals (as in CHD), the molecules have the same polarization along the chain direction within one sheet (Katrusiak, 1990a); in contrast, MCPD, which has an antiparallel arrangement of the chains within one sheet, is very stable at high pressures (Katrusiak, 1990c). A high-pressure study of dimedone (Katrusiak, 1990d) also indicates the importance of electrostatic interactions for pressure-induced structural changes. Nevertheless, other forces must be considered in this transformation. For instance, the disorder of C(5) is eliminated at high pressures and changes in δ could just be a shift of the chains leading to the tighter packing of the structure (although no disorder was observed in the five-membered ring of CPD).

(b) In the CHD molecules, the carbonyl O(1) atom has the highest negative net charge and, in the 0.1 MPa structure, it is situated closely to hydroxyl O(2ⁱ) atom ($x - 1, y, z$) of the molecule in the close neighbouring chain (see Fig. 6 and Table 5), with the next largest negative net charge. Compression of s makes the contacts between charges even closer and would significantly increase the repulsion counteracting the shear strains that tends to reduce the overlap of the molecules.

(c) To reduce interactions between O(1) and O(2ⁱ), the molecule can change its angle of inclination to the central line of the chain (see Fig. 6). As can be seen from the ρ values plotted *versus* pressure in Fig. 8, the molecule swings through $\rho = 0^\circ$ at pressures smaller than 0.3 GPa, reducing the obstacle associated with the repulsive forces between O(1) and O(2ⁱ), and triggering the shift of the chains, which reduces the overlapping of neighbouring molecules (see Figs. 6 and 7).

(d) The rotation of the CHD molecule significantly changes the orientation of μ with respect to the central line of the chain: the angle between μ and the [201] direction becomes larger and the component of μ along y increases while the component along [201] becomes smaller. In the ambient-pressure structures of both CPD and CHD the carbonyl O atoms are closer to the central line of the chain than to the hydroxyl O atoms, which indicates that in both these structures the angle between μ and chain direction is reduced. In the high-pressure structure the small angle can be restored by a change of sites of all enolic protons in the hydrogen bonds, as actually takes place.

The probable mechanism of the structural transformation of CHD suggested above implies a significant role of electrostatic interactions in the

transformation and in the jump of enolic protons. The influence of crystal environment forces on the site of protonation can also be observed in crystals with several symmetry-independent molecules in the asymmetric unit (Dupont, Lamotte, Campsteyn & Vermeire, 1978).

The structure of CHD resembles in several respects the (anti)ferroelectric or ferroelastic crystals with hydrogen bonds. The transitions from paraelectric to (anti)ferroelectric phases principally involve ordering of the H atoms from a symmetric distribution in hydrogen bonds above T_c to off-centre sites below T_c , and occur in crystals whose (anti)ferroelectric phase structure approximates their paraelectric structure. Usually, the symmetry is broken mainly by the positions of H atoms in hydrogen bonds and also by small displacements of other constituent atoms. The high-symmetry (high-temperature) phases are often referred to as prototype structures and there are at least two possible orientational states – identical or enantiomorphous low-symmetry (low-temperature) structures, but different in their spontaneous polarization and/or strain (Sapriel, 1975). When a ferroelectric crystal approaches T_c , the departures from its prototype symmetry become smaller. The usual examples of such structures are KH_2PO_4 (KDP), squaric acid (*i.e.* 3,4-dihydroxy-3-cyclobutene-1,2-dione) and $PbHPO_4$ (in which the HPO_4^{2-} anions are linked into chains). Above T_c the protons in these structures move collectively in a symmetric double-well potential of the $O \cdots HO$ bonds, the structures become disordered, and new symmetry elements, like a centre of symmetry between two sites of the disordered H atom, appear. For all these structures T_c is strongly pressure dependent, which is explained by the reduction of the potential barrier between two H-atom sites in the compressed hydrogen bond.

The structure of CHD resembles such (anti)ferroelectric crystals in that the H atom in the hydrogen bond can interchange between donor and acceptor sites and that the non-H atoms in the ambient pressure structure approximate the space group $C2/c$. The additional elements of symmetry (absent in CHD) would be: a centre of symmetry between O(1) and O(2ⁱ) (symmetry code: $x - 1, 0.5 - y, z + 0.5$) at $x = 0.25, y = 0.25, z = 0.5$, a twofold axis passing through C(2) at $x = 0.25$ and $z = 0.25$, and a glide plane n at $y = 0$. However, the departures from $C2/c$ symmetry are substantial: for example, angle ρ in space group $C2/c$ would have to be 0° . Also, the departures are much larger than those from the prototype structures usually observed in (anti)ferroelectric crystals. It is possible that the CHD crystals have a domain structure and that on increasing temperature the departures from prototype $C2/c$ become smaller. The relief on faces (010) and (0 $\bar{1}$ 0)

may be an indication of the domain structure of these crystals (see Fig. 4); such an assumption seems to be supported by the observation that on changing temperature the crystals break along $(10\bar{2})$ which may be due to internal strains along possible domain walls.

The transformation of CHD observed at high pressures takes a different course than would be expected for an (anti)ferroelectric structure. In the high-pressure structure of CHD the enolic proton changes its site in the hydrogen bond, but it remains ordered and no new symmetry elements appear. At high pressures (from the transformation to almost 3.0 GPa), the departures of the CHD structure from its prototype symmetry $C2/c$ become much larger than at ambient pressure. The hydrogen bond in CHD at about 1.5 GPa becomes shorter than the hydrogen bond in squaric acid at $P(T_c = 293 \text{ K}) = 0.75 \text{ GPa}$ (Katrusiak & Nelmés, 1986; Samara & Semmingsen, 1979; Tun, Nelmés & McIntyre, 1987).

The anomalous changes in the unit-cell dimensions and, connected with them, changes in δ and ρ allow the pressure at which the transition takes place to be assessed. The changes indicate (see Figs. 3, 7 and 8) that the main structural transformation and the collective jump of the protons in the hydrogen bonds occur between 0.1 MPa and 0.11 (5) GPa. Yet as some of these parameters still show anomalous compression above this pressure range (to about 0.3 GPa; see the pressure dependence of c and l in Figs. 3 and 4), a wider pressure range has been used for a complete description of all the anomalous changes in the CHD structure. According to the observed pressure dependence of the structural parameters and to the microscopic mechanism of the transformation presented above, the phase transition is first order. Pressures higher than about 0.3 GPa cause monotonous changes in the CHD structure.

The interchain distance, s , shows no significant anomalous points at the transition pressure. Similarly, only an initial small increase in the length of the CHD molecule in the chain measured along $[201]$ l is observed, and at still higher pressures a slow, steady compression of l takes place as expected for this 'hardest' direction in the CHD crystal. Thus, the pressure dependence of these two parameters, as well as of the separation of the sheets of chains along y and the volume of the unit cell, seems to be little affected by the transformation suddenly adjusting the CHD molecules in the neighbouring chains. This adjustment has a strong effect only on the parameters describing the position of the CHD molecule in the chain (ρ) and the relative displacement of the molecules in neighbouring chains (δ). As the symmetry of the crystal is preserved, the only way of accomplishing the shifts of the chains with respect to their neighbours is to change the inclination angle

between z and planes $(10\bar{2})$ comprising the chains of CHD molecules. This, in turn, is combined with the changes in the unit-cell parameters a , c and β . Simple trigonometric formula allow a , c and β to be calculated from s , l and the inclination angle between the $(10\bar{2})$ plane and z , ζ :

$$\begin{aligned} a &= [(s^2/\sin^2\zeta) + l^2 - 2sl\tan\zeta]^{1/2} \\ &= [s^2 + (l - \delta)^2]^{1/2} \\ c &= 2s/\sin\zeta = 2(s^2 + \delta^2)^{1/2} \\ \beta &= 180^\circ - \sin^{-1}(l\sin\zeta/a), \end{aligned}$$

where $\zeta = \tan^{-1}(s/\delta)$. Providing that the interchain separation, s , and interval l change slowly and smoothly with pressure – as a monotonous function of the applied force (see Fig. 5) – the rapid change of δ and ζ must result in the rapid shortening of a , the elongation of c and the change in β .

Ordering of atom C(5) with pressure

Ordering of C(5) in the CHD ring presumably results from the transformation of the structure, the compression of the unit cell and tighter packing of the molecules at higher pressures. The two disordered positions of atom C(5) (at ambient pressure) are denoted C(5A) and C(5B). These two sites of C(5) have close intermolecular contacts with several carbonyl and hydroxyl O atoms of the molecules lying in the same and neighbouring sheets of chains (see Table 5). The shortest of these distances is between C(5B) and atom O(1') (symmetry code: $1 - x, 0.5 + y, 1.5 - z$) of the molecule in the neighbouring sheet. This distance is significantly shortened at higher pressures, mainly owing to the compression of b and to the change in the tilt of the molecules, described by ρ . At 1.0 GPa, if C(5B) were to retain its position, distance C(5B)⋯O(1') would be reduced to under 2.7 Å, which is much less than the sum of the van der Waals radii of C and O. An important role in the conformational and structural changes of CHD can be attributed to H⋯H intermolecular contacts; for instance H(61A)⋯H(61A') ($1 - x, \bar{y}, 1 - z$) distances of two neighbouring sheets are 2.20, 2.64, 2.42 and 2.55 Å, and H(41A)⋯H(62A') ($1 + x, y, z$) distances of two close chains within one sheet are 2.41, 2.06, 2.15 and 2.08 Å at 0.0001, 0.52, 1.15 and 1.90 GPa, respectively. A likely mechanism implies that atom C(5) is forced to one side of the molecule, the site previously labelled C(5A), but still vibrates strongly at 0.52 GPa, as denoted by the large temperature factor of C(5) and strong distortions of molecular dimensions involving this atom (see Tables 3 and 4). At higher pressures even the vibrations are suppressed by tightening intermolecular interactions (see Table 5).

Concluding remarks

The pressure-induced structural transformation of CHD involves, apart from other effects, the interchange of donor and acceptor sites by the enolic H atoms in the hydrogen bonds. The structure, despite its close similarities with antiferroelectric crystals, is ordered in the high-pressure phase, also retaining its low-pressure symmetry. It is possible that the crystals have a domain structure in both low- and high-pressure phases. The proposed mechanism of the transformation strongly suggests an important role of electrostatic interactions in the transformation and in the jump of the enolic H atom to its other site in the OH...O bond. This mechanism also affords an explanation of the phase transition observed in CPD and of the exceptional stability of MCPD at high pressures; however, several points still need to be confirmed and further studies are being carried out on the CHD crystals.

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Graph-Set Analysis of Hydrogen-Bond Patterns in Organic Crystals

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Abstract

A method is presented based on graph theory for categorizing hydrogen-bond motifs in such a way that complex hydrogen-bond patterns can be disentangled, or decoded, systematically and consistently.

This method is based on viewing hydrogen-bond patterns topologically as if they were intertwined nets with molecules as the nodes and hydrogen bonds as the lines. Surprisingly, very few parameters are needed to define the hydrogen-bond motifs comprising these networks. The methods for making these assignments, and examples of their chemical utility are given.

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