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Structure and Phase Transition of 1,3-Cyclohexanedione Crystals as a Function of Temperature

By Andrzej Katrusiak

Department of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 *Poznań, Poland*

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Abstract

$C_6H_8O_2$, $M_r = 112{\cdot}13$, monoclinic, $P2_1/c$, $a = 6{\cdot}1549\,(6)$, $b = 11{\cdot}731\,(1)$, $c = 8{\cdot}194\,(1)$ Å, $\beta = 99{\cdot}386\,(8)^\circ$, $V = 583{\cdot}7\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}276$ g cm^{-1}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu(\mathrm{Cu}\ K\alpha) = 7{\cdot}05$ cm^{-1}, $F(000) = 240$, $T = 303$ K, $R = 0{\cdot}084$ for 558 reflections with $I \geq 1{\cdot}96\sigma_I$. 1,3-Cyclohexanedione (enol form) is known to undergo a strong pressure-induced phase transition involving proton transfer in the hydrogen bond; it also forms inclusion compounds with benzene. In this paper we report the temperature dependence of the 1,3-cyclohexanedione structure. The unit-cell dimensions have been measured between 213 and 323 K and the structure has been determined at 213, 273 and 303 K. At $T_c = 287\,(1)$ K, the crystals undergo a strong structural transformation in which the crystal shape is markedly deformed; the transition is similar to that observed at high pressures. At the transition point the disordered methylene $C(5)H_2$ becomes ordered, molecules significantly change their positions in the crystal lattice and the enolic proton changes its donor and acceptor sites. This offers a unique opportunity for an analysis of the factors destabilizing the position of the proton forming a hydrogen bond. Despite a large change of the unit-cell dimensions [at 273 K $a = 5{\cdot}683\,(1)$, $b = 11{\cdot}623\,(2)$, $c = 8{\cdot}724\,(2)$ Å, $\beta = 95{\cdot}40\,(2)^\circ$] the crystal preserves its high-temperature space group $P2_1/c$, owing to the disappearance of the non-crystallographic mirror plane along $(10\bar{2})$ when the crystal is cooled below 287 K.

Introduction

The crystal structure of 1,3-cyclohexanedione (hereinafter referred to as CHD) was reported by Etter, Urbańczyk-Lipkowska, Jahn & Frye (1986); the same authors also reported the inclusion compound of CHD with benzene. Most recently the unit-cell dimensions and the structure of the CHD crystals were studied at high hydrostatic pressures by X-ray diffraction (Katrusiak, 1990*a*). When subjected to pressures of about 100 MPa the CHD crystals undergo a strong structural transformation which significantly changes the arrangement of the molecules and the shape of the crystals, but their space group ($P2_1/c$) remains unchanged. The pressure-induced transformation involves the ordering of the methylene group $C(5)H_2$ (which is disordered at room temperature and ambient pressure), and a transfer of the enolic proton between the donor and acceptor sites of the hydrogen bond.

In this contribution, we report the temperature dependence of the CHD structure. The crystals undergo a structural transformation at 287 (1) K, similar to that observed at high pressures. Two low-temperature structural determinations of CHD have been performed, at 213 and 273 K, and the low-temperature and the high-pressure structures have been compared. The main aim of this study was to determine the differences between the temperature- and pressure-induced changes in these crystals and to compare the changes in the low- and high-temperature phases. However, we were also interested in the geometry of the hydrogen bond in the low-temperature (high-pressure) phase which, due to the experimental limitations of the high-pressure X-ray experiments, could not be obtained under high-pressure conditions. The CHD structure has also been determined at 303 K, to show the temperature dependence of the high-temperature (ambient-pressure) phase. Since the high-pressure and low-temperature structures of CHD are similar, they will both be referred to as CHD2, and the high-temperature (ambient-pressure) phase will be referred to as CHD1.

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Experimental

The crystals of CHD1 were obtained by slow evaporation from acetone solution. They were colourless trapezoidal plates with well-developed faces. The CHD1/CHD2 ambient-pressure transformation temperature was determined visually by observing the shape of the crystal, which changed markedly at 287 (1) K (see Fig. 1). To avoid strains in the sample during the transformation, face $(10\bar{2})$ of the sample was glued to a glass fibre. The crystal was cooled or heated with a stream of gaseous nitrogen. A Syntex $P2_1$ diffractometer and 2θ–θ scan mode were used. The unit-cell dimensions (Table 1) were obtained from the least-squares fit of 15 automatically centred reflections ($10 < \theta < 22°$). The intensity data collection was carried out at 213 (1), 273 (1) and 303 (2) K Two control reflections monitored every 200 reflections showed no systematic change in their intensity at low temperatures. However, at 303 K their intensity steadily decreased to 0·91 due to the slow sublimation of the sample (Katrusiak, 1990*a*). The intensities were corrected for Lp effects and the 303 K data were also corrected for crystal decay. The room-temperature structure (Etter, Urbańczyk-Lipkowska, Jahn & Frye, 1986) was used as a starting model in refining the 303 K structure; the high-pressure CHD2 structure served as a starting model for the 213 and 273 K refinements. After the anisotropic refinement of the C and O atoms at 213 and 273 K, all the H atoms were located from the ΔF maps and included in the refinements with isotropic temperature factors. Above 287 K, the positions of the H atoms at C(4), C(5) and C(6) are disordered because of the disorder of C(5), which occupies two sites on both sides of the molecular ring: the two C(5) sites are denoted C(5*A*) and C(5*B*). The refinements of the site-occupation factors for C(5*A*) and C(5*B*) gave 0·5 for each of these positions which agrees with the results obtained by Etter, Urbańczyk-Lipkowska, Jahn & Frye (1986) at room temperature. Therefore, in the stucture model at 303 K, two sets of H positions at C(4), C(5) and C(6) were calculated with 0·5 occupancy for the molecular geometry depending on the position of C(5); the positions of these H atoms were recalculated after each cycle of refinement based on the shifts of the corresponding C atoms. H(1) and H(2) were found from a ΔF map and refined with isotropic thermal parameters. Details of data collection and the refinements are listed in Table 2, final atomic parameters of the CHD structure at 213, 273 and 303 K are listed in Table 3.* Most of the calculations were performed with *SHELX*76 (Sheldrick, 1976) using an IBM XT computer. Atomic scattering factors were those incorporated in *SHELX*76.

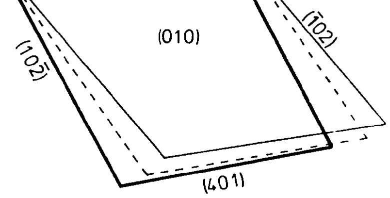

Fig. 1. Shape of the 1,3-cyclohexanedione crystal (CHD1) viewed along [010] at room temperature (thick solid line), the same sample at 273 K (structure CHD2 – dashed line), and at 291 K and 1·5 MPa (thin solid line). Compare with Fig. 4 of Katrusiak (1990*a*).

Table 1. *Temperature dependence of the unit-cell dimensions of* 1,3-*cyclohexanedione* (*CHD*1 *and CHD*2)

T (K)	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)
333	6·164 (2)	11·745 (4)	8·429 (4)	99·66 (4)	588·7 (4)
323	6·163 (1)	11·745 (2)	8·233 (2)	99·53 (2)	588·2 (2)
303	6·1549 (6)	11·731 (1)	8·194 (1)	99·386 (8)	583·7 (1)
293	6·145 (2)	11·711 (2)	8·196 (1)	99·43 (1)	581·9 (3)
273	5·683 (1)	11·623 (2)	8·724 (2)	95·40 (2)	573·8 (2)
243	5·618 (2)	11·586 (5)	8·773 (6)	94·81 (5)	569·1 (6)
228	5·581 (1)	11·566 (2)	8·800 (3)	94·92 (2)	565·9 (3)
213	5·5363 (6)	11·518 (2)	8·826 (2)	94·00 (1)	562·6 (2)

Results and discussion

Fig. 2 shows the temperature dependence of the relative changes in the unit-cell dimensions of the CHD crystals. At 287 (1) K, a strong anomalous change of these parameters takes place: **a** becomes shorter by about −8% of its room-temperature (and ambient-pressure) length, **c** lengthens by almost 7% and the monoclinic angle β changes by about 4°; smaller changes are observed for **b** which shortens by *ca* −0·5% and for the unit-cell volume (−0·5%). As the temperature decreases below 287 K, **c** lengthens at the rate $\mathrm{d}c/\mathrm{d}T = -1{\cdot}7 \times 10^{-3}$ Å K^{-1}. Similar changes in the unit-cell dimensions were observed when the transformation of the CHD crystals was induced by elevated pressures [compare Fig. 2 with Fig. 3 of Katrusiak (1990*a*)]. It is characteristic that after the initial lengthening of **c** by about 7% at 110 MPa, **c** continues to increase in length to about 300 MPa. However, this lengthening of **c** is 'compressed' at pressures above 400 MPa.

The strongly anisotropic changes of the unit-cell dimensions reflect the anisotropic structure of these crystals: the enolic molecules are linked into chains

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* Lists of structure factors for the measurements at 213, 273 and 303 K, anisotropic thermal parameters, and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53784 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Details of data collection and refinements for 1,3-cyclohexanedione at* 303, 213 *and* 273 K

	CHD1	CHD2	CHD2
Temperature (K)	303 (2)	213 (1)	273 (1)
D_x (g cm^{-3})	1·276	1·324	1·298
λ(Cu $K\alpha$) (Å)		1·54178	
μ(Cu $K\alpha$) (cm^{-1})	7·05	7·31	7·15
Crystal size (mm)		0·3 × 0·3 × 0·4	
$\theta_{\max}$ (°)	57·5	57·5	57·5
Range of h	0/6	0/6	0/6
k	0/12	0/12	0/12
l	−8/8	−9/9	−9/9
Number of reflections			
Total	830	791	802
Unique with $I \geq 1{\cdot}96\sigma_I$	558	673	681
$R_{\rm int}$	0·021	0·012	0·014
Check-reflection			
fluctuations (%) (061)	−9·1	±0·4	±0·8
(311)	−9·8	±0·5	±1·0
Final least-squares refinement			
R	0·084	0·043	0·058
wR, $w = \sigma(F_o)^{-2}$	0·083	0·046	0·065
S	1·8	1·42	2·1
$\Delta/\sigma_{\max}$	0·010	0·022	0·07
Final ΔF map (e Å^{-3})			
Highest peak	0·19	0·12	0·11
Lowest peak	−0·21	−0·13	−0·10

Table 3. *Fractional coordinates and equivalent thermal parameters of non-*H *atoms for* 1,3-*cyclohexanedione at* 303, 273 *and* 213 K

Occupancy of C(5*A*) and C(5*B*) is 0·5 at 303 K. The position of the enolic H atom H(1) (not refined at 303 K) and $U_{\rm iso}$ are also given. $U_{\rm eq} = (U_{11} + U_{22} + U_{33})/3$.

	x	y	z	$U_{\rm eq}$(Å^2)
303 K				
O(1)	0·3931 (6)	0·2950 (3)	0·5832 (4)	0·102
O(2)	1·0712 (6)	0·3178 (3)	0·9205 (4)	0·099
C(1)	0·5537 (9)	0·2463 (4)	0·6651 (5)	0·080
C(2)	0·7333 (8)	0·3067 (3)	0·7526 (5)	0·082
C(3)	0·9107 (8)	0·2557 (4)	0·8390 (5)	0·076
C(4)	0·9341 (8)	0·1287 (3)	0·8511 (6)	0·083
C(5*A*)	0·7833 (25)	0·0675 (13)	0·7192 (16)	0·091
C(5*B*)	0·7079 (24)	0·0688 (12)	0·8081 (15)	0·084
C(6)	0·5586 (9)	0·1181 (4)	0·6744 (6)	0·095
H(1)	1·191	0·273	0·970	0·15 (2)
273 K				
O(1)	0·4134 (4)	0·3282 (2)	0·5853 (2)	0·066
O(2)	1·0910 (4)	0·2842 (2)	0·9184 (2)	0·069
C(1)	0·5705 (5)	0·2600 (2)	0·6622 (3)	0·049
C(2)	0·7533 (5)	0·3072 (3)	0·7505 (3)	0·054
C(3)	0·9244 (5)	0·2394 (2)	0·8375 (3)	0·051
C(4)	0·8968 (6)	0·1111 (3)	0·8340 (4)	0·061
C(5)	0·7621 (7)	0·0663 (3)	0·6921 (5)	0·081
C(6)	0·5372 (6)	0·1330 (3)	0·6484 (4)	0·059
H(1)	0·290 (6)	0·280 (3)	0·523 (4)	0·11 (1)
213 K				
O(1)	0·4101 (3)	0·3311 (1)	0·5897 (2)	0·046
O(2)	1·0897 (3)	0·2807 (1)	0·9218 (2)	0·048
C(1)	0·5660 (4)	0·2616 (2)	0·6660 (2)	0·036
C(2)	0·7512 (4)	0·3073 (2)	0·7544 (2)	0·038
C(3)	0·9191 (4)	0·2371 (2)	0·8417 (2)	0·036
C(4)	0·8828 (5)	0·1075 (2)	0·8389 (3)	0·041
C(5)	0·7612 (5)	0·0657 (2)	0·6899 (3)	0·046
C(6)	0·5292 (5)	0·1333 (2)	0·6500 (3)	0·042
H(1)	0·287 (5)	0·288 (3)	0·524 (3)	0·098 (9)

by short hydrogen bonds, and the planar chains lie along [201] and parallel to the crystallographic plane $(10\bar{2})$. The chains are arranged such that each has one neighbouring chain on both sides and forms sheets of chains perpendicular to [010] (Fig. 3). The intermolecular interactions between the molecules within one sheet are dominated by electrostatic forces between the HO—C═C—C═O moieties, while the interactions between the sheets are mainly of van der Waals type [see Figs. 1 and 2 of Katrusiak (1990*a*)]. This arrangement of the CHD molecules is preserved in both the ambient- and high-pressure phases. The low-temperature structure of CHD clearly corresponds to the high-pressure structure of these crystals (Katrusiak, 1990*a*).

The position of molecules in the structures CHD1 and CHD2 can be conveniently described by two parameters: the angle ρ between the line drawn through atoms O(1) and O(2) and the central line of the chain [the central line of the chain is the intersection of the plane of the chain, $(10\bar{2})$, and the glide plane c at $y = 0{\cdot}25$ or $0{\cdot}75$, see Fig. 4], and the displacement δ of the molecules in adjacent chains related by glide plane c (the parameters δ and ρ are shown in Figs. 3 and 4). The main differences between CHD1 and CHD2 are:

(*a*) Atom C(5), which at ambient pressure is disordered in two sites [C(5*A*) and C(5*B*)] on both sides of the molecular plane, becomes ordered [into position C(5*A*)] in CHD2 (see Fig. 5).

(*b*) The molecules rearrange such that δ increases from 1·86 Å (at 293 K) to 2·45 Å at 273 K and 2·60 Å at 213 K; at the same time ρ changes from

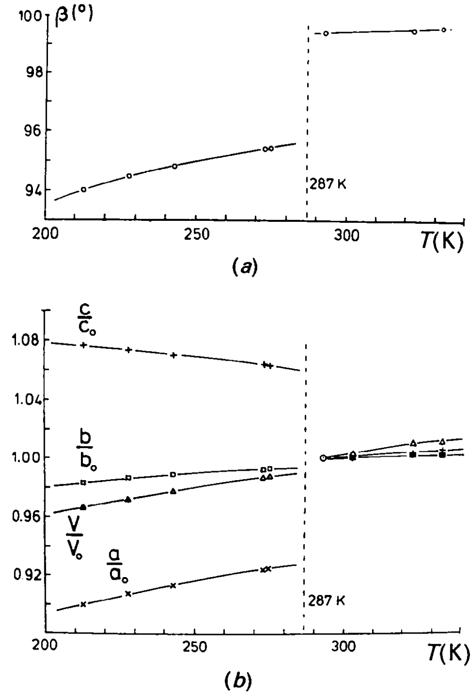

Fig. 2. Temperature dependence of the unit-cell dimensions of 1,3-cyclohexanedione: (*a*) changes in monoclinic angle β and (*b*) relative changes in **a**, **b** and **c**. The vertical dashed line marks the transformation temperature 287 K.

3·38° (293 K) to −6·32 (1) and −7·20 (1)° at 273 and 213 K, respectively.

(*c*) The enolic proton interchanges its donor and acceptor sites, and simultaneously the sequence of double and single bonds in the conjugated-bond fragment is changed [O(1)=C(1)—C(2)=C(3)—O(2)H becomes HO(1)—C(1)=C(2)—C(3)=O(2)].

Structure and unit-cell dimensions

The parameter δ, describing the relative positions of molecules in neighbouring chains, is connected with the unit-cell dimensions (Katrusiak, 1990*a*):

$$\delta = (c^2/4 - s^2)^{1/2} \qquad (1)$$

where s is the separation between neighbouring chains within one sheet (see Fig. 3):

$$s = ac\sin\beta/2l \qquad (2)$$

and l is the period of the chain for one molecule:

$$l = (c^2/4 + a^2 + ac\cos\beta)^{1/2}. \qquad (3)$$

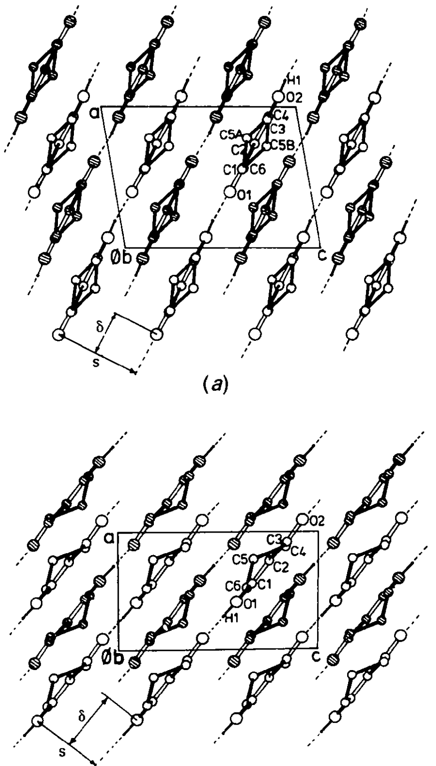

Fig. 3. Projection of the 1,3-cyclohexanedione structure down **b**: (*a*) CHD1 structure at 303 K and 0·1 MPa, two positions of disordered atom C(5) are indicated, and (*b*) CHD2 structure at 291 K and 1·9 GPa. Open circles represent atoms of molecules in one sheet of chains at $y = 0{\cdot}25$ and shaded circles show the molecules in the sheet at $y = 0{\cdot}75$. Hydrogen bonds are indicated by broken lines. For clarity all H atoms, except H(1) and H(2), are omitted.

Consequently, the unit-cell dimensions a, c and β can be calculated from the parameters described above:

$$a = [s^2 + (l - \delta)^2]^{1/2} \qquad (4)$$

$$c = 2(s^2 + \delta^2)^{1/2} \qquad (5)$$

$$\beta = 180° - \sin^{-1}(l\sin\zeta/a) \qquad (6)$$

where ζ is the angle of inclination between plane $(10\bar{2})$ and $\mathbf{z}$:

$$\zeta = \tan^{-1}(s/\delta). \qquad (7)$$

The relative changes in l and s are shown in Fig. 6. The separation, s, changes abruptly at 287 K [s is 3·651 (1) at 291 K and 3·614 (1) Å at 275 K], below and above this temperature s changes at a similar rate: ds/dT is $7{\cdot}9 \times 10^{-4}$ and $6{\cdot}1 \times 10^{-4}$ Å K^{-1} below and above 287 K, respectively. A small anomalous change of l can also be noted at 287 K. Below this temperature, l becomes shorter with increasing temperature: $dl/dT = -6{\cdot}2 \times 10^{-5}$ Å K^{-1}; a small lengthening of l was also observed from 110 to 260 MPa for CHD2. Similarly,

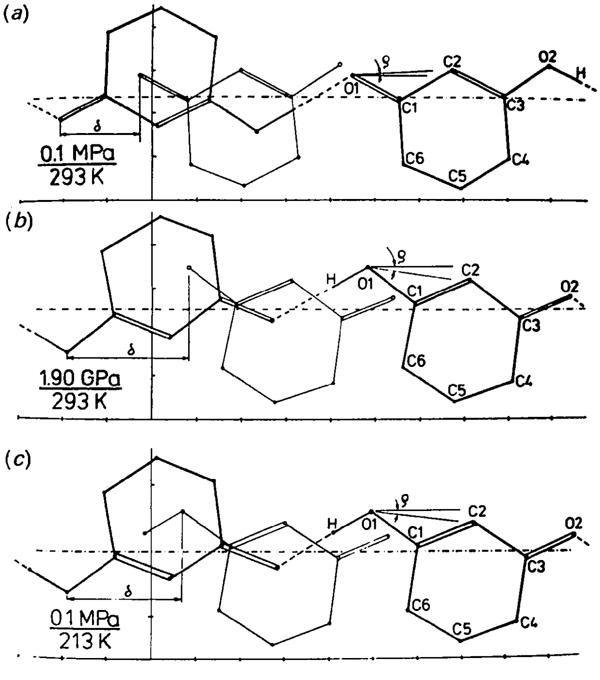

Fig. 4. Projection on plane $(10\bar{2})$ of two 1,3-cyclohexanedione molecules from one chain (thick solid lines) and of one molecule of the neighbouring chain (thin solid lines) down the direction perpendicular to the $(10\bar{2})$ plane (the two superimposing molecules are symmetry-related by a glide plane c): (*a*) CHD1 structure at 303 K, (*b*) CHD2 structure at 291 K and 1·9 GPa, and (*c*) at 213 K and 0·1 MPa. The dashed lines represent hydrogen bonds, the dash–dot line is the central line of the chain (see text). Angle ρ is between the central line of the chain and the line through O(1) and O(2), and δ is the displacement measured along [201] between two molecules of neighouring chains (related by glide plane c, see Fig. 3).

as observed for the pressure-induced CHD1/CHD2 transformation, changes of s and l are much smaller than the changes in displacement δ (see Fig. 7), and changes in δ give the main contribution to the abrupt changes in the unit-cell dimensions **a**, c and β [see (4), (5) and (6) above].

Molecular geometry

The bond lengths and valency angles of the CHD molecule at 213, 273 K, room temperature and 303 K are listed in Table 4. The lengths of the bonds in HO—C=C—C=O clearly demonstrate that the sequence of double and single bonds changes between CHD1 and CHD2; this is connected with the transfer of the enolic proton in the O(1)---O(2^{i}) hydrogen bond (the symmetry codes are given in Table 5). The transformation is also observed in the valency angles of the C(sp^3) atoms, particularly by comparing angle O(1)—C(1)—C(6) with O(2)—C(3)—C(4), O(1)—C(1)—C(2) with O(2)—C(3)—C(2), C(2)—C(1)—C(6) with C(2)—C(3)—C(4), and the valency angles involving H(2) at C(2).

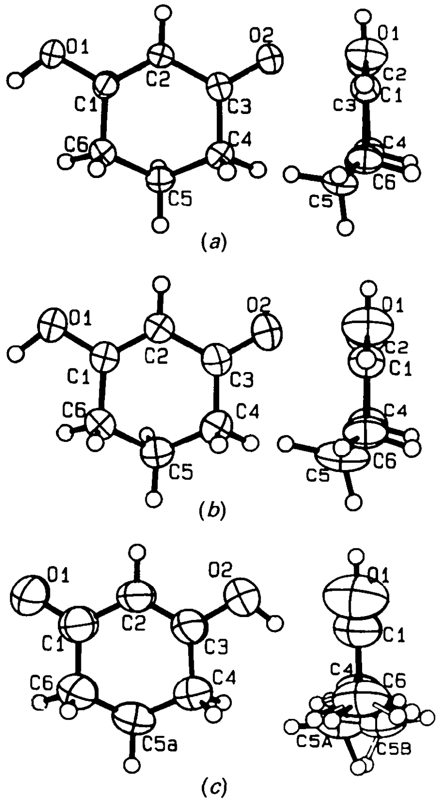

Fig. 5. *ORTEP* (Johnson, 1965) drawing of the 1,3-cyclohexanedione molecule viewed perpendicular to its plane and along C(1)···C(3): (*a*) in the CHD2 structure at 213 K and (*b*) at 273 K, and (*c*) in the CHD1 structure at 303 K. The vibrational ellipsoids correspond to 50% probability contours of mean atomic displacements and the H atoms are presented as small circles. For clarity, the planar view of the molecule at 303 K (*c*) includes only one position of disordered atom C(5) and the view along C(1)···C(3) contains both C(5*A*) and C(5*B*); the full bonds of H atoms at C(4), C(5*A*) and C(6) correspond to C(5) in position C(5*A*) and open bonds to C(5) in position C(5*B*).

The shortest intermolecular distances are listed in Table 5. A small, but significant lengthening of the hydrogen bond is observed at the transition from structure CHD1 to CHD2. This change of 0·022 (5) Å [from the value of 2·651 (4) Å reported for CHD1 at room temperature by Etter, Urbańczyk-Lipkowska, Jahn & Frye (1986) to CHD2 at 273 K] may be due to significant changes in the packing and crystallographic environment of the molecules. However, strong vibrations of the molecules in CHD1 may cause some systematic errors in bond lengths. The other short intermolecular distances listed in Table 5 illustrate the strong changes in van der Waals contacts which take place at the CHD1/CHD2 transformation. The distance O(1)···C(5B^{iv}), if atom C(5) still occupied this site below 287 K, would be reduced to below 3·0 Å, which is less than the sum of the van der Waals radii of O and C. The intermolecular distances still change considerably in the CHD2 structure between 273 and 213 K. This is also observed in the changes of the unit-cell

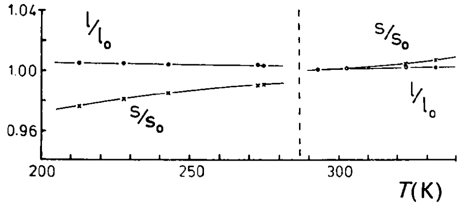

Fig. 6. Temperature dependence of the relative changes in l and s (see Fig. 3). The vertical dashed line marks the transformation temperature 287 K.

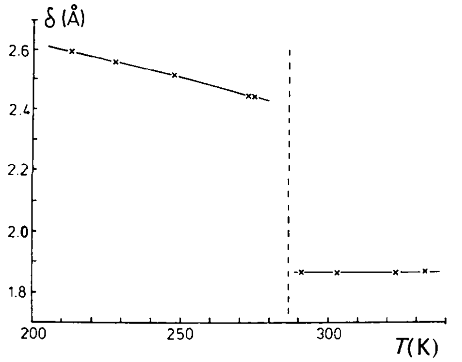

Fig. 7. Changes with temperature of δ, the displacement measured along [201] between the molecules of neighbouring chains (related by glide plane c), see Figs. 3 and 4. The vertical dashed line marks the transformation temperature 287 K.

Table 4. *Bond lengths* (Å) *and valency angles* (°) *for* 1,3-*cyclohexanedione at* 213, 273 K, *room temperature and* 303 K

The values for this study were calculated from unrounded coordinates and a variance–covariance matrix; the values at room temperature, RT, are from Etter, Urbańczyk-Lipkowska, Jahn & Frye (1986). Dimensions of the hydrogen bonds are also given in this table (in square brackets).

	213 K	273 K	RT	303 K
O(1)—C(1)	1·327 (2)	1·327 (3)	1·243 (2)	1·238 (5)
O(2)—C(3)	1·245 (2)	1·241 (3)	1·323 (4)	1·317 (5)
C(1)—C(2)	1·351 (3)	1·350 (3)	1·409 (5)	1·404 (5)
C(1)—C(6)	1·496 (3)	1·491 (4)	1·490 (6)	1·504 (6)
C(2)—C(3)	1·417 (3)	1·416 (3)	1·345 (5)	1·339 (5)
C(3)—C(4)	1·508 (3)	1·500 (4)	1·483 (5)	1·495 (6)
C(4)—C(5*A*)	1·514 (3)	1·487 (4)	1·49 (1)	1·49 (1)
C(4)—C(5*B*)	—	—	1·49 (1)	1·55 (2)
C(5*A*)—C(6)	1·522 (3)	1·513 (5)	1·43 (1)	1·49 (1)
C(5*B*)—C(6)	—	–	1·48 (1)	1·43 (1)
H(1)—O(1)	1·00 (3)	1·02 (4)	[1·63 (5)]	[1·63]
H(1)—O(2)	[1·58 (3)]	[1·57 (3)]	0·94 (5)	0·95 (3)
H(2)—C(2)	0·97 (2)	0·95 (3)	0·94 (5)	0·97 (4)
C(1)—O(1)—H(1)	113 (1)	110 (2)	—	—
C(3)—O(2)—H(1)	--	—	111 (3)	111 (2)
C(1)—C(2)—H(2)	122 (1)	122 (2)	118 (2)	117 (2)
C(3)—C(2)—H(2)	116 (1)	116 (2)	120 (2)	120 (3)
C(2)—C(1)—O(1)	119·9 (2)	119·4 (3)	121·1 (2)	122·4 (4)
C(6)—C(1)—O(1)	118·0 (2)	118·4 (2)	120·5 (4)	119·6 (5)
C(6)—C(1)—C(2)	122·1 (2)	122·2 (3)	118·4 (4)	118·0 (4)
C(3)—C(2)—C(1)	122·3 (2)	122·2 (3)	122·0 (3)	123·3 (4)
C(2)—C(3)—O(2)	121·5 (2)	121·4 (3)	118·9 (3)	119·9 (4)
C(4)—C(3)—O(2)	120·2 (2)	120·2 (2)	118·6 (3)	117·4 (4)
C(4)—C(3)—C(2)	118·3 (2)	118·5 (2)	122·5 (4)	122·7 (4)
C(5*A*)—C(4)—C(3)	112·3 (2)	114·1 (3)	113·4 (5)	112·9 (7)
C(5*B*)—C(4)—C(3)	-	—	113·9 (5)	111·3 (7)
C(6)—C(5*A*)—C(4)	110·8 (2)	112·8 (3)	116·1 (8)	115·3 (9)
C(6)—C(5*B*)—C(4)		—	113·8 (3)	115·6 (9)
C(5*A*)—C(6)—C(1)	112·1 (2)	112·9 (3)	116·5 (6)	114·7 (7)
C(5*B*)—C(6)—C(1)	-	—	116·5 (5)	116·5 (7)
O(1)—H(1)—O(2′)	[179 (2)]	[174 (3)]	[170 (5)]	[170]

Table 5. *Intermolecular distances* (Å) *for* 1,3-*cyclohexanedione at* 303, 273, 213 K/0·1 MPa *and* 291 K/1·9 GPa

The values for this study were calculated from unrounded coordinates and a variance–covariance matrix; distances at 291 K/1·9 GPa (Katrusiak, 1990*a*) are also included for comparison. The last column gives the symmetry operations relating the molecules in contact.

	303 K	273 K	213 K	291 K/ 1·9GPa	Symmetry code
O(1)---O(2′)	2·563 (5)	2·583 (2)	2·575 (2)	2·496 (12)	$x-1, 0{\cdot}5-y, z-0{\cdot}5$
O(1)···O(2″)	3·662 (5)	3·615 (3)	3·577 (3)	3·301 (15)	$x-1, y, z$
O(1)···C(4‴)	4·189 (6)	3·740 (4)	3·614 (3)	3·324 (17)	$x, 0{\cdot}5-y, z-0{\cdot}5$
O(1)···C(4^{iv})	4·468 (5)	3·827 (4)	3·646 (3)	3·268 (11)	$1-x, 0{\cdot}5+y, 1{\cdot}5-z$
O(1)···C(4′)	3·259 (6)	3·565 (4)	3·609 (3)	3·596 (16)	$x-1, 0{\cdot}5-y, z-0{\cdot}5$
O(1)···C(5*A*^{iv})	3·816 (16)	3·577 (5)	3·498 (3)	3·259 (15)	$1-x, 0{\cdot}5+y, 1{\cdot}5-z$
O(1)···C(5*B*^{iv})	3·412 (15)		—	–	$1-x, 0{\cdot}5+y, 1{\cdot}5-z$
O(1)···C(5*B*‴)	3·579 (15)	-	—	—	$x, 0{\cdot}5-y, z-0{\cdot}5$
O(2)···C(1^{v})	3·988 (7)	3·694 (4)	3·595 (3)	3·224 (15)	$x+1, y, z$
O(2)···C(1^{vi})	3·381 (6)	3·334 (3)	3·322 (3)	3·233 (15)	$x+1, 0{\cdot}5-y, 0{\cdot}5+z$
O(2)···C(5*A*^{vii})	3·514 (16)	3·614 (5)	3·556 (3)	3·325 (16)	$x, 0{\cdot}5-y, 0{\cdot}5+z$
O(2)···C(5*B*^{vii})	4·378 (16)	—	—	—	$x, 0{\cdot}5-y, 0{\cdot}5+z$
O(2)···C(6^{vi})	3·438 (6)	3·228 (4)	3·206 (3)	3·116 (15)	$x+1, 0{\cdot}5-y, 0{\cdot}5+z$
C(1)···C(3‴)	3·725 (7)	3·626 (4)	3·357 (3)	3·30 (2)	$x, 0{\cdot}5-y, z-0{\cdot}5$

dimensions (Fig. 2) and of parameter δ (Fig. 7). In the high-pressure study, the strong non-linear changes in δ, ρ and unit-cell dimensions were observed to about 1·3 GPa, which corresponds to the pressure range in which the strongest compression in the mean-square displacements of atoms takes place for this type of molecular crystal (Katrusiak, 1991).

Transformation mechanism

The present study indicates the significant role of the movements of $C(5)H_2$, the only group possessing much conformational freedom (the rest of the molecule is relatively rigid), in the structural transformation of the CHD crystals. It turns out that above 287 (1) K, the $C(5)H_2$ methylene group moves between two positions, which can be characterized by a double-well potential. The depth of these two wells is equal for the isolated CHD molecule due to its mirror-plane symmetry (see Fig. 8). However, in the crystal structure the molecule lies in a general position and the depths of the wells may differ owing to differences in the crystallographic environments of C(5*A*) and C(5*B*). It must be stressed that these vibrations most probably are not a simple flipping motion of C(5) with the rest of the molecule rigid, but that the motion of C(5) may also involve complex movements of C(4) and C(6) within and outside the plane of the molecule. Since the molecule is relatively small, it is difficult to discriminate between the contributions of the internal and external molecular vibrations to the observed temperature factors of the atoms [other than C(5)] (see Fig. 5). Below 287 K, it is most probably the onset of ordering of C(5) in position C(5*A*) which leads to the transformation of CHD1 to the CHD2 structure. At 273 K, however, atom C(5) still has a strongly elongated ellipsoid of thermal vibration (see Fig. 5). At 213 K, atom C(5) has similar thermal parameters to the other atoms in the molecule. It appears that the large changes observed in the CHD2 structure, which follow the transformation taking place with reduction of temperature, can be associated with these movements of C(5) (*e.g.* see changes in δ plotted in Fig. 7).

After the transition, when C(5) is ordered, the CHD2 structure retains the symmetry of CHD1,

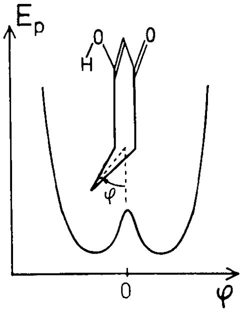

Fig. 8. Double-well potential energy suggested for the 1,3-cyclohexanedione molecule as a function of the position of the $C(5)H_2$ group flipping between two energy minima on both sides of the molecular plane. As described in the text, the flipping motion may also involve movements of C(4) and C(6). H atoms, except H(1), are omitted for clarity.

space group $P2_1/c$. This is evidently because the CHD molecule, which possesses mirror symmetry when atom C(5) is disordered, does not lie on a mirror plane in the CHD1 structure. Consequently, when C(5) becomes ordered, no crystallographic symmetry element is destroyed. Also, as the two sites C(5*A*) and C(5*B*) are not crystallographically equivalent, the transformation proceeds in one direction and the crystal is neither twinned nor cracked.

The transfer of the enolic proton appears not to be directly connected with the ordering of C(5), but is one of the consequences which follows the ordering of C(5) in the CHD1 structure. It was suggested (Katrusiak, 1990*a*) that the transfer of H(1) can be caused by electrostatic interactions between the molecules of neighbouring chains. The shift of the chains proceeds in the direction which in the CHD1 structure would significantly decrease the distance between O(1) and O(2^{ii}) (see Fig. 4 and Table 5), the two atoms with the largest negative atomic charges in the molecule (Katrusiak, 1990*a*). A larger distance between O(1) and O(2^{ii}) can be retained if the molecule is rotated and the values of angle ρ changed from positive to negative (see Fig. 4). This rotation, however, causes strains in the hydrogen bond, which can be released by the observed change in the H-atom position. In CHD1 the carbonyl group is closer to the central line of the chain than the hydroxyl group: such a small inclination of the molecules depends on the hydrogen-bond geometry and was also observed in the crystal structure of 1,3-cyclopentanedione (Katrusiak, 1990*b*). After the rotation, the previous inclination of the CHD molecule to the central line of the chain can be restored as a consequence of the transfer of the enolic H atom to O(1) from O(2^{i}) (Table 5) in the hydrogen bond.

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Automated Conformational Analysis from Crystallographic Data. 5.* Recognition of Special Positions in Conformational Space in Symmetry-Modified Clustering Algorithms

By Frank H. Allen

Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

and Robin Taylor

ICI Agrochemicals, Jealott's Hill Research Station, Bracknell, Berkshire RG12 6EY, England

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Abstract

This paper reports an extension to algorithms for the conformational classification of symmetrical chemical fragments on the basis of torsion-angle descriptors [Allen, Doyle & Taylor (1991). *Acta Cryst.* B47, 29–40, 41–49, 50–61]. The algorithms take account of 2D topological symmetry and bring all cluster centroids into a single asymmetric unit of conformational space. In some cases, however, mean conformational geometries show marginal distortions from ideal symmetric forms, *i.e.* the centroid lies close to a special symmetry position in conformational space. Here we examine a number of methods by which this proximity can be recognized. A simple, general solution is adopted based on the torsional dissimilarities, $D(C_c,C_{c'})$, between a given cluster centroid (C_c) and each of its symmetry equivalents ($C_{c'}$). Symmetry-related clusters, c', are coalesced with the original cluster, c, if $D(C_c,C_{c'}) \leq \mathrm{MULT} \times (D_c)_{\max}$, where $(D_c)_{\max}$ is the maximum dissimilarity between any

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* Part 4: Allen & Johnson (1991).

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