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In-situ high-pressure study of the ordered phase of ethyl propionate

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Ethyl propionate, $C_5H_{10}O_2$ (m.p. 199 K), has been *in-situ* pressure-frozen and its structure determined at 1.34, 1.98 and 2.45 GPa. The crystal structure of the new high-pressure phase (denoted β) is different from phase α obtained by lowering the temperature. The freezing pressure of ethyl propionate at 296 K is 1.03 GPa. The molecule assumes an extended chain *s-trans–trans–trans* conformation, only slightly distorted from planarity. The closest intermolecular contacts in both phases are formed between carbonyl O and methyl H atoms; however, the ethyl-group H atoms in phase β form no contacts shorter than 2.58 Å. A considerable molecular volume difference of 24.2 Å^3 between phases α and β can be rationalized in terms of degrees of freedom of molecules arranged into closely packed structures: the three degrees of freedom allowed for rearrangements of molecules confined to planar sheets in phase α, but are not sufficient for obtaining a densely packed pattern.

1. Introduction

Molecular disorder is not uncommon among the structures of molecular crystals. It can occur in various forms, involving separate molecules (*e.g.* guest molecules in inclusion compounds), molecular fragments (rotating methyl groups, hopping protons, H tautomers, ring puckering) or molecular orientation. Moreover, the disorder can be static or dynamic, and the freezing conditions may differently affect the crystallization. Thus, it is possible that essentially the same structures with or without disorder, or completely different polymorphic structures, one of which is disordered while the other is not, can be obtained under various conditions. In certain cases, different phases of the same compound, so-called concomitant polymorphs, can be obtained from one crystallization vessel (Bernstein, 2002). The crystallization process of molecular organic compounds and their solvates is of particular interest for technological applications, *e.g.* in the pharmaceutical industry, where strict control over polymorphic forms of the product is required (Bernstein, 2002). On the other hand, the occurrence of disorder is interesting by itself, because it reveals possible types of molecular association that are energetically very similar. In certain cases this property may lead to phase transitions, which change the properties of the crystal and can also be of practical interest.

Most recently we observed disorder in the pressure-frozen crystals of dichloroethane and tetrachloroethane (Bujak *et al.*, 2004; Bujak & Katrusiak, 2004), the molecules of which are flexible, but in which the molecular interactions are dominated by halogen···halogen contacts. The temperature-freezing of dichloroethane yielded an ordered phase of this compound. We have now studied the structure of ethyl propionate,

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$C_5H_{10}O_2$ (denoted EP). It is liquid at normal conditions, and below 199 K it crystallizes in the tetragonal space group $P4_2/mbc$, with the molecules disordered orientationally in two positions (Shallard-Brown *et al.*, 2005). Ethyl propionate is an intriguing compound used in the flavours and fragrances industry. Many ketones and esters are liquids at room temperature, and ethyl propionate was chosen by Shallard-Brown *et al.* (2005) as a representative of these compounds for structural analysis of the crystal *in-situ* frozen at 185 K. The EP molecule consists of five rotor fragments; however, its conformation is extended and planar in the low-temperature structure, denoted phase α. The symmetry of the EP molecule is lower than the C_{2h}-symmetric special site it occupies in the α phase at 185 K, the most distinct element of this molecular-shape asymmetry being the carbonyl O atom (Fig. 1). Hence the molecule is disordered in two orientations, if a planar molecular conformation is assumed. The disorder appears to be static, because a dynamic disorder would require that the long molecules (of about 9.4 Å) rotate about the [001] axis, while the cavities containing the molecules are too narrow (*ca* 4.2 Å) to allow this type of motion. Hence the α phase transition to an ordered structure at still lower temperatures is highly unlikely. Generally, phase transitions eliminating dynamical disorder and breaking crystal symmetry are likely to crack the sample. Thus, at still lower temperatures either the static disorder will persist or the structure ordering may result in twinning or breaking of the sample, which would hamper single-crystal diffraction studies.

We have crystallized EP by pressure freezing. It was hoped that by changing the conditions of freezing the disorder could be eliminated, particularly in this case of EP, where the carbonyl-atom disordering requires two cavities, one of which is occupied and the other remains empty for each molecule in the crystal (on average each of the cavities is half-occupied). Elevated pressure naturally eliminates empty voids. Thus, pressure freezing could be an efficient alternative for investigating disordered structures. On the other hand, we were particularly interested in the pressure-induced ordering. If effective, it could lead to a group–subgroup relation between the phases or to a completely symmetry-independent new phase. The molecular structure of EP determined in the high-pressure phase in this study is shown in Fig. 1.

2. Experimental

Ethyl propionate (from Aldrich, analytical grade without further purification) was pressure-frozen in a modified Merrill & Bassett (1974) diamond–anvil cell (DAC) made in our departmental workshop. The gasket was made of 0.3 mm steel foil and the initial diameter of the spark-eroded hole was 0.5 mm. 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 EP, the pressure was gradually increased, but the liquid did not crystallize despite pressure of over 2.0 GPa. It became apparent that the sample formed a glassy phase. When several attempts to grow crystals directly by increasing pressure failed, the method of applying an ultrasound generator for crystallizing at low temperature was applied. When the ultra-sound method did not give positive results, yet another method, similar to that described by Budzianowski *et al.* (2006), was applied. The pressure was decreased to 0.57 GPa and the DAC was placed in a Dewar flask with dry ice at 195 K. This method was successful, and instead of the glassy phase the sample froze in the polycrystalline form. When the DAC was warmed to 296 K and polycrystalline EP melted, the pressure was increased by a small fraction of a GPa and the freezing by cooling was repeated in the elevated pressure conditions. Eventually, when the pressure of the liquid was increased to 1.98 GPa at room temperature, the crystals frozen in this way at 195 K did not melt when the DAC was warmed to 297 K. The DAC was then heated until all the crystallites but one melted, after which the temperature was slowly lowered until the single crystal grew to

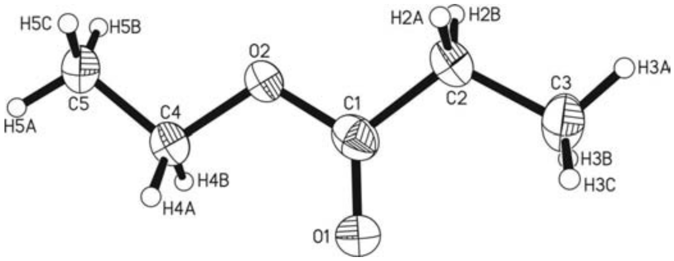

Figure 1
A molecule of ethyl propionate as determined in the crystal structure of phase β at 2.45 GPa. Displacement ellipsoids have been drawn at the 50% probability level.

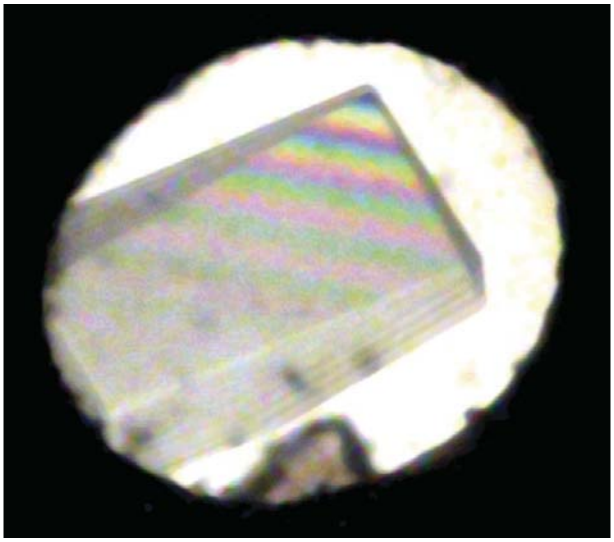

Figure 2
A view of the DAC high-pressure chamber with the pressure-frozen single crystal of EP, obtained under isochoric conditions at the initial stage of its growth. The ruby chip for pressure calibration is located at the bottom edge of the chamber. Newton fringes are formed between the thin crystal faces.

Table 1
Selected experimental and crystal data for $C_5H_{10}O_2$ in the high-pressure β phase (this work), compared with the low-temperature α phase after Shallard-Brown *et al.* (2005).

	Phase α	Phase β		
Pressure	0.1 MPa	1.34 GPa	1.98 GPa	2.45 GPa
Crystal data				
Chemical formula	$C_5H_{10}O_2$	$C_5H_{10}O_2$	$C_5H_{10}O_2$	$C_5H_{10}O_2$
M_r	102.13	102.13	102.13	102.13
Cell setting, space group	Tetragonal, $P4_2/mbc$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Temperature (K)	185	293 (2)	293 (2)	293 (2)
a, b, c (Å)	9.5153 (3), 9.5153 (3), 6.8933 (2)	4.9347 (10), 9.4163 (19), 11.321 (2)	4.8917 (10), 9.3649 (19), 11.318 (2)	4.8455 (10), 9.3249 (19), 11.251 (2)
β (°)	90	97.39 (3)	97.24 (3)	97.52 (3)
V (Å^3)	624.13 (3)	521.70 (18)	514.35 (18)	504.00 (18)
Z	4	4	4	4
D_x (Mg m^{-3})	1.087	1.300	1.319	1.346
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.08	0.10	0.10	0.10
Crystal form, colour	Cylinder, colourless	Cylinder, colourless	Cylinder, colourless	Cylinder, colourless
Crystal size (mm)	0.5 × 0.1 (radius)	0.36 × 0.28 × 0.15	0.36 × 0.28 × 0.14	0.36 × 0.28 × 0.13
Data collection				
Diffractometer	Nonius KappaCCD diffractometer	Kuma KM-4 CCD κ geometry	Kuma KM-4 CCD κ geometry	Kuma KM-4 CCD κ geometry
Data collection method	ω scans	ω scans	ω scans	ω scans
Absorption correction	Multi-scan	Analytical	Analytical	Analytical
$T_{\min}$	0.98	0.68	0.67	0.68
$T_{\max}$	0.98	0.96	0.97	0.97
No. of measured, independent and observed reflections	719, 384, 383	1838, 316, 259	2054, 283, 264	2119, 299, 268
Criterion for observed reflections	$I > 3\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	0.013	0.142	0.059	0.047
$\theta_{\max}$ (°)	27.5	27.3	24.8	25.0
Refinement				
Refinement on	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.062, 0.100, 0.90	0.099, 0.270, 1.25	0.054, 0.107, 1.20	0.048, 0.119, 1.14
No. of reflections	383	316	283	299
No. of parameters	43	60	71	71
H-atom treatment	Constrained to parent site	Constrained to parent site	Constrained to parent site	Constrained to parent site
Weighting scheme	$w = 1/[\sigma^2(F^2) + 0.04 + 0.17P]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$	$w = 1/[\sigma^2(F_o^2) + (0.1734P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.048P)^2 + 0.3823P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0645P)^2 + 0.3573P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.013	<0.0001	<0.0001	<0.0001
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.14, −0.17	0.15, −0.16	0.12, −0.10	0.13, −0.13
Extinction method	None	*SHELXL*97	*SHELXL*97	*SHELXL*97
Extinction coefficient	–	0.22 (11)	0.02 (2)	0.04 (3)

Computer programs used: *CrysAlis* (Oxford Diffraction, 2003), *SHELXS*97 (Sheldrick, 1997), *SHELXL*97 (Sheldrick, 1997), *XP* (Siemens, 1990).

entirely fill the pressure chamber at room temperature (Fig. 2). The freezing pressure at 296 K has been determined as 1.03 GPa where the solid and liquid phases coexisted.

A single crystal of ethyl propionate was centred on a Kuma KM-4 CCD diffractometer by the gasket-shadow method (Budzianowski & Katrusiak, 2004). The X-ray reflection intensities were collected in the ω-scan mode (Budzianowski & Katrusiak, 2004). The Mo $K\alpha$ 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*b*); the unit-cell dimensions were corrected for the reflection shifts due to the gasket shadowing (Katrusiak, 2004*a*). The structure was solved by direct methods using the program *SHELXS*97 and refined using *SHELXL*97 (Sheldrick, 1997). The crystallographic data are summarized in Table 1.[1] The C and O atoms were refined with anisotropic displacement parameters. The H atoms were located from the molecular geometry [in the methyl groups C—H = 0.96 Å and $U_{\rm iso}(\rm H) = 1.5U_{\rm eq}(\rm C)$; in the methylene groups C—H = 0.97 Å and $U_{\rm iso}(\rm H) = 1.2U_{\rm eq}(\rm C)$]. In the final cycles of the refinement the idealized methyl groups were allowed to rotate about the C—C bonds.

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV5069). Services for accessing these data are described at the back of the journal.

Table 2
Torsion angles in the molecule of ethyl propionate in phase β at 1.34, 1.98 and 2.45 GPa at 296 K.

	Phase α†	Phase β		
P/*T*	0.1 MPa/ 185 K	1.3 GPa/ 293 K	1.9 GPa/ 293 K	2.45 GPa/ 293 K
C4—O2—C1—O1	0.0	−0.1 (12)	2.6 (6)	2.1 (6)
C4—O2—C1—C2	180.0	−177.7 (6)	−178.4 (3)	−178.2 (3)
C3—C2—C1—O1	0.0	6.9 (13)	2.7 (7)	3.1 (7)
C3—C2—C1—O2	180.0	−175.6 (8)	−176.2 (4)	−176.6 (4)
C1—O2—C4—C5	180.0	176.2 (7)	175.1 (4)	175.3 (4)

† Average values of disordered molecule after Shallard-Brown *et al.* (2005).

Table 3
Selected molecular dimensions (Å, °) of ethyl propionate in phase α at 0.1 MPa and 185 K (Shallard-Brown *et al.*, 2005), and in phase β (this work).

	Phase α	Phase β		
P/*T*	0.1 MPa/ 185 K	1.3 GPa/ 293 K	1.9 GPa/ 293 K	2.45 GPa/ 293 K
O1—C1	1.168 (16)	1.197 (9)	1.202 (6)	1.204 (6)
O2—C1	1.351 (6)	1.320 (11)	1.341 (6)	1.337 (6)
O2—C4	1.483 (13)	1.431 (6)	1.449 (4)	1.445 (4)
C1—C2	1.497 (14)	1.479 (8)	1.486 (6)	1.489 (6)
C2—C3	1.519 (10)	1.468 (12)	1.497 (7)	1.498 (7)
C4—C5	1.481 (10)	1.457 (12)	1.479 (7)	1.479 (7)
C1—O2—C4	107.6 (6)	118.8 (5)	116.5 (3)	116.3 (3)
O2—C1—O1	122.4 (10)	121.0 (6)	122.1 (4)	122.3 (4)
O2—C1—C2	118.7 (8)	113.5 (6)	111.6 (4)	111.8 (4)
O1—C1—C2	119.0 (12)	125.4 (9)	126.3 (6)	125.9 (5)
C1—C2—C3	107.8 (9)	115.8 (6)	114.2 (4)	114.4 (4)
O2—C4—C5	111.6 (10)	109.7 (5)	107.7 (3)	107.7 (3)

3. Discussion

3.1. The crystal structure of the high-pressure ethyl propionate (phase β)

The low-temperature phase α (Shallard-Brown *et al.*, 2005) and the high-pressure phase β (determined at 1.34, 1.98 and 2.45 GPa) have different symmetries; phase α is tetragonal, space group $P4_2/mbc$, and phase β is monoclinic, space group $P2_1/c$ (the structures are compared in Fig. 3).

In both phases the number of molecules in the unit cell (Z) is the same, but in phase β molecules lie at general positions and are ordered. Despite the potentially flexible chain, the molecule assumes a very similar conformation in phases α and β, which can be described as *s-trans–trans–trans* with respect to the main-chain atoms. The torsion angles of the C3—C2—C1—O2—C4—C5 chain and those involving the =O1 atom (Table 2) deviate by up to 4.4 (8)° from the 180 and 0° angles, respectively, corresponding to the ideally planar conformation. Thus, the molecule is nearly flat, but the distortions from planarity are statistically significant and consistent for the structure at three different pressures. The deviations of the C and O atoms from the plane fitted to all non-H atoms do not exceed 0.042 (3) Å in any of the high-pressure structures.

Despite the pressure change of over 1.1 GPa no systematic differences in the molecular conformation have been observed in phase β. Moreover, no significant changes have been observed in other molecular dimensions of EP in the α and β phases, compared in Table 3. However, a small monotonic lengthening of the O1=C1 bond with pressure, by 0.029 (16) Å between 0.1 MPa and 1.34 GPa, and by 0.008 (9) Å over the next 1.1 GPa, is consistent with the decreased order of this bond accompanying the intensified intermolecular interactions of the O atom (Katrusiak, 1991; Allmann, 1977); on the other hand, the lengthening of the O1=C1 bond between 0.1 MPa and 1.43 GPa may be an artefact caused by a superposition of two non-planar molecules not considered for phase α.

3.2. EP compression

It can be observed from Fig. 4 that the molecular volumes (V_m) of liquid EP at 296 K and of phase α at 185 K are considerably higher than that of phase β. The molecular volume of ethyl propionate in the liquid phase, equal to

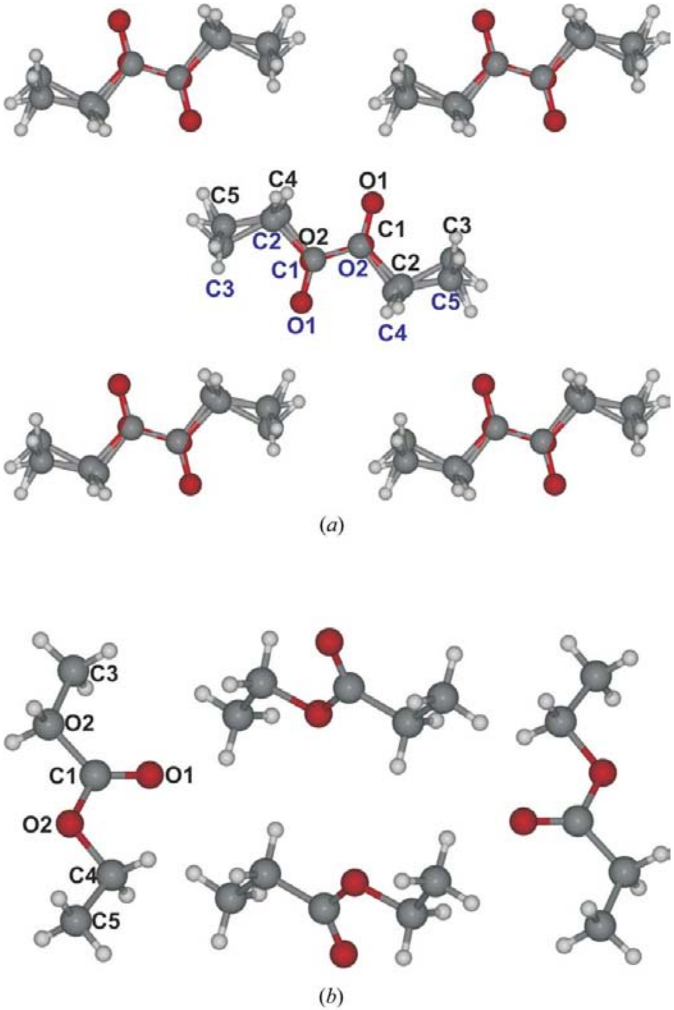

Figure 3
Schematic illustration of structures of EP: (*a*) low-temperature phase α (the black symbols above the molecule denote atoms in one of two possible orientations and the purple symbols under the molecule denote atoms in the second possible orientation of the molecule); (*b*) high-pressure phase β. This figure is in colour in the electronic version of this paper.

189.1 Å^3 at 298 K, reduces to 156.0 Å^3 as the result of isobaric temperature contraction of the liquid, volume contraction on freezing and solid phase α contraction to 185 K. The isothermal compression of the liquid, the volume change at pressure freezing and the compression of the solid EP in phase β decreases the molecular volume to 130.4, 128.6 and 126.1 Å^3 at 1.34, 1.98 and 2.45 GPa, respectively. This large difference of 24.2 Å^3 between phase α at 185 K and phase β estimated to the freezing pressure at 1.03 GPa is due to the different molecular arrangement.

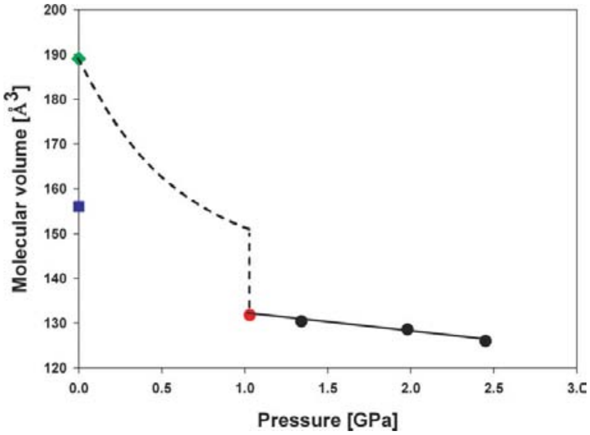

Figure 4
The pressure dependence of molecular volume (V_m) of ethyl propionate in phase β (black circles), as well as in the liquid at 296 K (green diamond) and in phase α at 185 K (blue square). The dashed line, representing an idealized compression of liquid and transition volume change (Bridgman, 1931), has been drawn only as a guide to the eye; the molecular volume at the freezing pressure of 1.03 GPa (red circle) has been estimated from the compression of phase β. This figure is in colour in the electronic version of this paper.

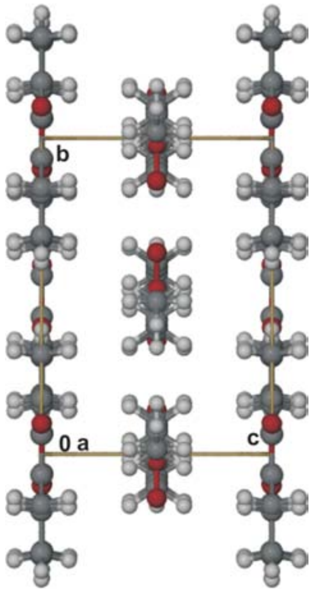

Figure 5
The layered structure of ethyl propionate low-temperature phase α at 185 K, viewed down **x**.

These differences can be clearly seen in Figs. 5 and 6. In the low-temperature phase α the molecules of EP form a layered structure. Within one layer the disordered molecules are located at centres of inversion and oriented antiparallel to each other.

In the high-pressure phase β the molecular arrangement is completely altered. The molecules do not form such layers but form pairs of close molecules antiparallel and nearly perpendicular to other close near neighbours. The pairs of antiparallel molecules are related by centres of inversion located between them. The molecular packing in phase β is much more tight than in disordered phase α. It appears that the EP

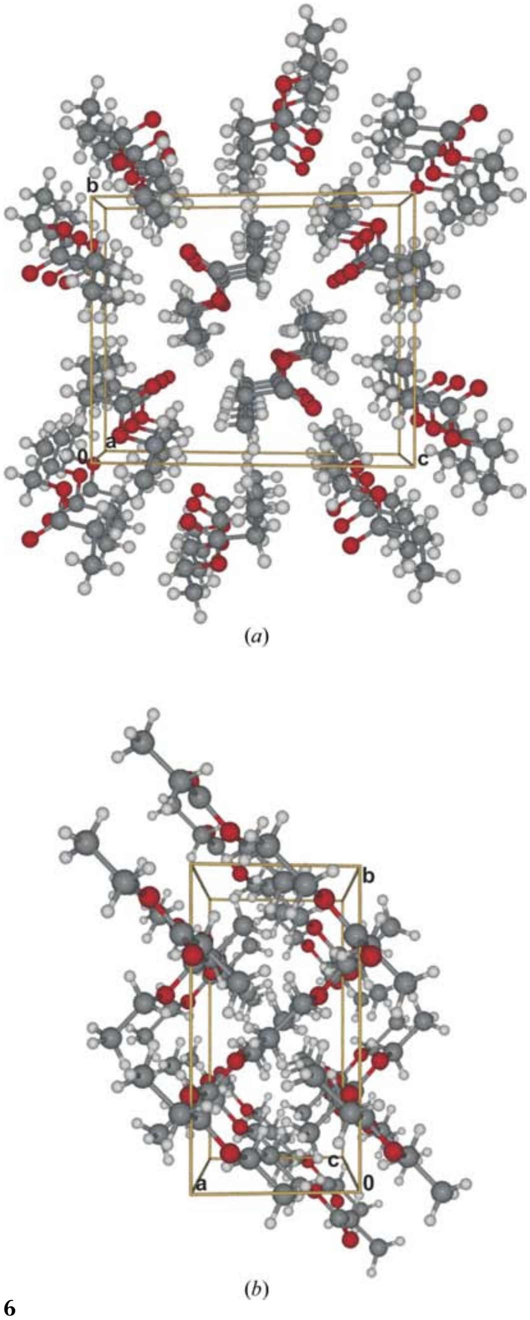

Figure 6
The molecular arrangement of ethyl propionate in high-pressure phase β at 2.45 GPa, (*a*) viewed down **x** and (*b*) viewed down **z**.

Table 4
Intermolecular contacts shorter than 2.7 Å in ethyl propionate high-pressure phase β (Å) at 1.34, 1.98 and 2.45 GPa.

Pressure	1.34 GPa		1.98 GPa		2.45 GPa	
$D-\text{H}\cdots A$	$\text{H}\cdots A$	$D\cdots A$	$\text{H}\cdots A$	$D\cdots A$	$\text{H}\cdots A$	$D\cdots A$
$\text{C3}-\text{H3}B\cdots\text{O2}^{\text{i}}$	2.667	3.523	2.631	3.501	2.636	3.469
$\text{C4}-\text{H4}B\cdots\text{O1}^{\text{ii}}$	2.628	3.288	2.609	3.264	2.586	3.234
$\text{C5}-\text{H5}B\cdots\text{O1}^{\text{ii}}$	2.690	3.205	2.627	3.195	2.600	3.160
$\text{C5}-\text{H5}A\cdots\text{O1}^{\text{iii}}$	2.707	3.435	2.652	3.393	2.603	3.356
$\text{C2}-\text{H2}B\cdots\text{O2}^{\text{iv}}$	–	–	2.654	3.605	2.639	3.588
$\text{C5}-\text{H5}C\cdots\text{O2}^{\text{v}}$	–	–	2.700	3.385	2.686	3.355
$\text{C2}-\text{H2}A\cdots\text{O2}^{\text{iv}}$	2.714	3.668	–	–	–	–

Symmetry codes: (i) $x-1, y, z$; (ii) $-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iii) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $-x, 1-y, 1-z$; (v) $1-x, 1-y, 1-z$.

molecules cannot be packed efficiently when only three degrees of freedom (shifts along **x** and **y** and rotations about **z**) are applied to arrange the molecules within the planar sheet (two possible orientations about the longest axis of the molecule have been neglected, because they do not occur in phase α).

3.3. Intermolecular interactions

The considerably denser molecular packing of phase β compared with phase α is consistent with intermolecular interactions in these phases. The closest contacts in phase β are presented in Table 4. They are formed between carbonyl O and methyl H atoms; however, no contacts in the β phase are shorter than 2.58 Å.

The closest intermolecular contacts between non-H atoms in the two phases are compared in Fig. 7. It can be observed that the β phase is monotonically compressed with pressure. The low-temperature phase α is over 18% less dense than phase β at 1.30 GPa. This fact shows that the structure of phase α obtained by temperature freezing is loosely packed.

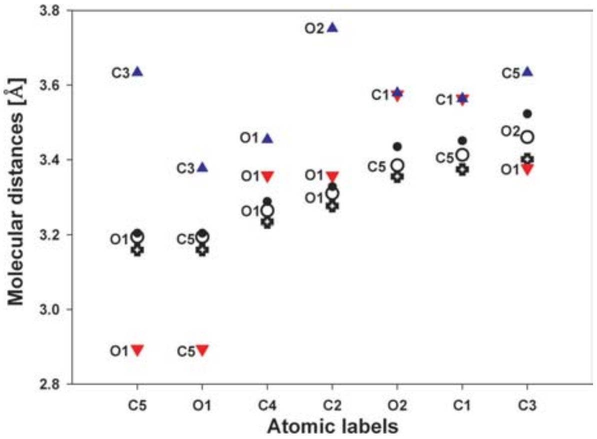

Figure 7
The closest intermolecular distances in phase β (black points for 1.34 GPa, black open circles for 1.98 GPa and black crosses for 2.45 GPa) and in phase α [red triangles for the closest contacts involving both sites of the disordered molecules (as shown in Fig. 6*a*), and blue triangles for the distances between these close molecular sites, which have no contacts shorter than the sums of van der Waals radii (this is equivalent to eliminating the closest neighbouring molecular sites, as shown in Fig. 6*b*; in this way only one of the disordered sites is analyzed)].

It can be seen in Fig. 8(*a*) that, although the disordered molecules densely fill the space in phase α, elimination of one of the disordered sites leaves empty spaces. The reconstruction of one sheet with the overlapping disordered sites eliminated is presented in Fig. 8(*b*). The size of these voids can be evaluated from the plot in Fig. 7. It can be seen that the molecules in phase α could be arranged in an ordered structure such that, on average, each atom's contact to its closest neighbour would be about 0.2 Å longer than in phase α.

The intermolecular contacts of the EP molecule in the β phase are illustrated in Fig. 9 using the Hirshfeld surface method (McKinnon *et al.*, 2004; Dziubek & Katrusiak, 2004). Fig. 9 shows that the most asymmetric part of the molecule is around the O atoms, and that in the β form both O1 and O2 have close contacts with the crystal environment – hence the ordered β structure. In the α form (Fig. 8) the molecules have free space in the vicinity of this molecular fragment, and therefore they can assume different orientations.

4. Conclusions

The high-pressure structural determination of EP, which is liquid at normal conditions, afforded structural information

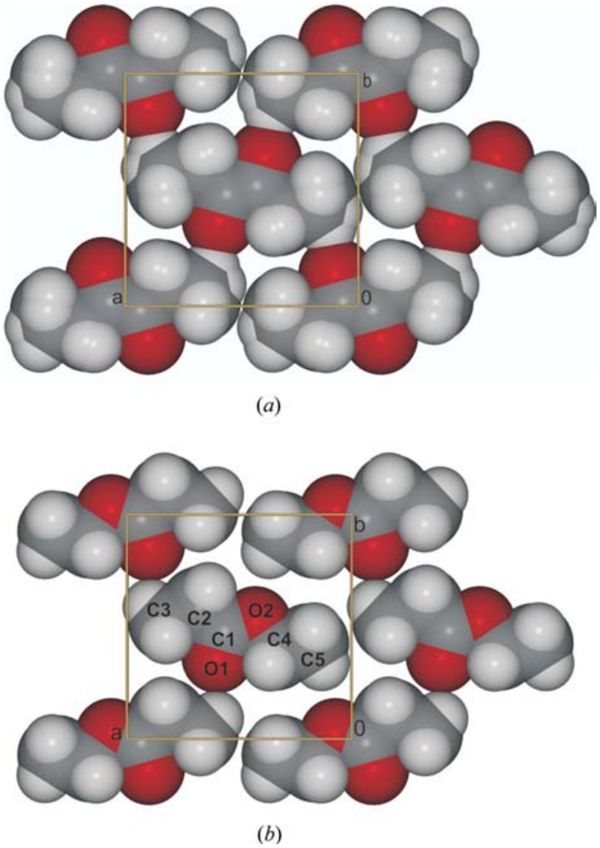

Figure 8
(*a*) A space-filling model of one sheet of disordered ethyl propionate molecules in phase α at 185 K; (*b*) the same sheet after eliminating the disorder (only one of the disordered sites has been included).

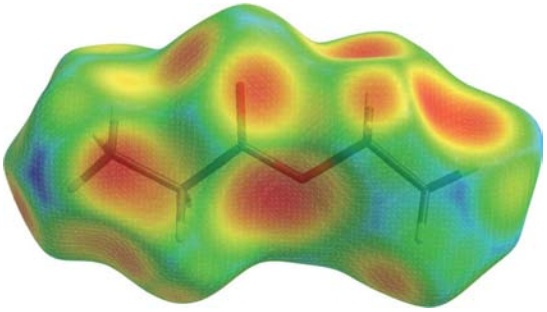

Figure 9
Hirshfeld surface for the EP molecule embedded in the crystal structure at 2.45 GPa. The colour scale on the surface represents distances from the surface elements to the closest atoms outside the surface (red colour corresponds to the shortest contacts, blue to the longest). The Hirshfeld surface was plotted with the program *CrystalExplorer* (Grimwood *et al.*, 2005).

that is more precise and accurate than could be obtained from the low-temperature measurement. Full structural information about the molecule of ethyl propionate has been obtained in this way. High-pressure phase β of ethyl propionate is ordered, whereas the disorder of phase α hampered the structural study by temperature freezing and only approximate molecular dimensions were obtained. The disordered phase α is a layered structure with the molecules arranged in sheets parallel to the molecular plane. The molecules arranged in these sheets have three degrees of freedom with which to optimize the crystal packing. It appears that these three degrees of freedom are not sufficient to eliminate voids within the sheets, leaving space for the molecules to assume alternative orientations (rotations about **z** and possibly very close sites related by the mirror-plane symmetry – the resolution of the diffraction data is too low to resolve such positions, but the molecule is clearly nonplanar in the β phase). When the molecules arrange in three dimensions in phase β, the additional degrees of freedom allow the molecules to pack more tightly and the orientational disorder is eliminated. The difference in the degrees of freedom for molecular packing in phases α and β results in a considerable volume change approaching 18% between the temperature-freezing and pressure-freezing points. Such a rearrangement is possible owing to the absence of strong directional forces between the ethyl propionate molecules. Thus, the occurrence of dense phase β is favoured at elevated pressure because the disordered asymmetric molecule in phase α requires considerably more volume than the ordered molecules in phase β. Generally, molecules are packed more tightly and empty voids are eliminated at elevated pressures, as is the orientational or conformational disorder (Gallois *et al.*, 1986; Molchanov *et al.*, 1986; Katrusiak, 1990). Thus, the pressure-freezing technique can be efficiently used not only for obtaining new polymorphs different from those frozen at low temperatures (Brodalla, 1983), but also for obtaining precise molecular dimensions in the structures where pressure eliminates the molecular disorder.

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