

Howard A. Shallard-Brown,*
David J. Watkin and
Andrew R. CowleyChemical Crystallography Laboratory, Chemistry
Research Laboratory, Mansfield Road, Oxford
University, Oxford OX1 3TA, EnglandCorrespondence e-mail:
howard.shallard-brown@lmh.ox.ac.uk

Key indicators

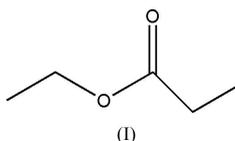
Single-crystal X-ray study
 $T = 185\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.011\text{ \AA}$
Disorder in main residue
 R factor = 0.062
 wR factor = 0.100
Data-to-parameter ratio = 8.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

Ethyl propionate at 185 K

The title compound, $\text{C}_5\text{H}_{10}\text{O}_2$, was prepared by a modified zone-refining technique, and has a layered structure with a high degree of disorder within the layers.Received 9 February 2005
Accepted 16 February 2005
Online 25 March 2005

Comment

Many of the esters and ketones used in the flavours and fragrances industry are liquid at room temperature; thus, in the past, crystalline derivatives have had to be prepared for X-ray analysis. The examination of this substance is part of a programme to simplify and systematize the study of substances which are liquid at room temperature.



The diffraction pattern could be indexed as tetragonal with $a = 9.52\text{ \AA}$ and $c = 6.89\text{ \AA}$. If some weak and diffuse reflections in layers perpendicular to c were included in the indexing, this doubled the c axis. The diffraction data were processed on the basis of both cells. In both cases, the space group assignment was uncertain. A clear molecular motif could be obtained by direct methods for a range of space groups, though those for the larger cell could not be refined. Eventually, it was decided to discard the weak layers, and work only with the smaller cell. For this cell, space groups $P4_2bc$ (No. 106) and $P4_2/mbc$ (No. 135) gave plausible but disordered solutions. In both cases, the molecules lie at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, with their molecular mirror plane more or less perpendicular to c . This leads to the molecules lying in sheets perpendicular to c , with an intersheet spacing of 3.45 \AA . In space group No. 106, the molecule lies on a twofold rotation axis only, whereas in space group No. 135 it lies on the centre of symmetry at the intersection of a twofold axis and a mirror plane. The structure was refined in both space groups.

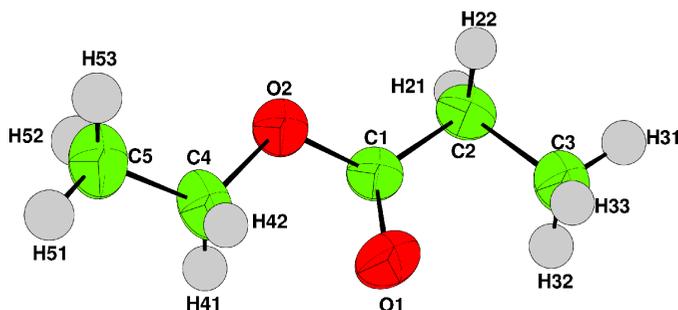


Figure 1

The title molecular structure, with displacement ellipsoids drawn at the 50% probability level. H atoms are of arbitrary radii. The disorder is not shown.

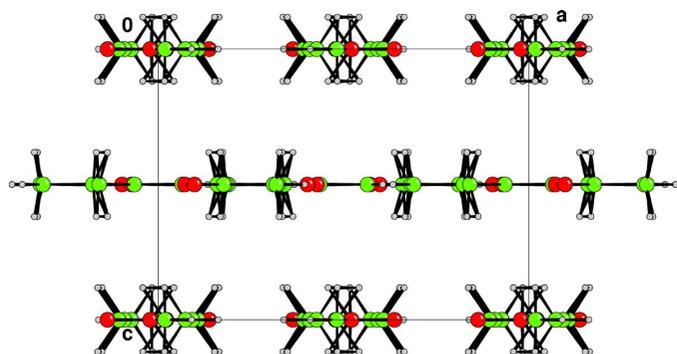


Figure 2
Packing diagram, showing the overall layered structure, viewed along the *b* axis, with disorder included.

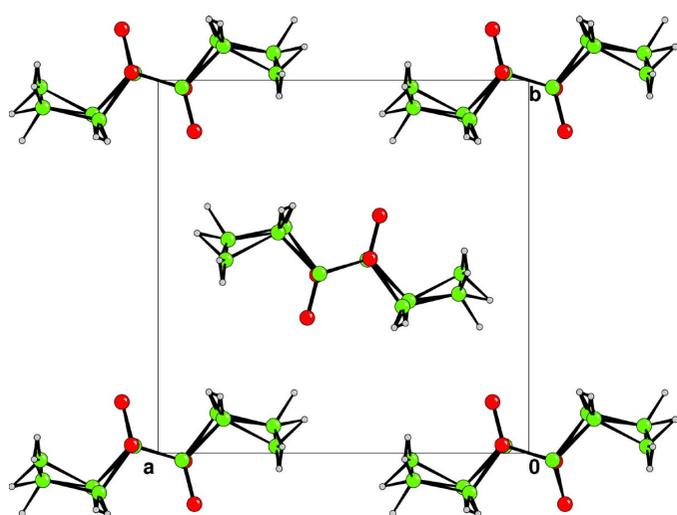


Figure 3
Diagram showing the twofold disordered molecules within one layer, viewed along the *c* axis.

Because both types of disorder lead to interpenetration of the molecule with its image, unrestrained geometric parameters were slightly abnormal. Target values for bond lengths and inter-bond angles were taken from the *MOGUL* database (Bruno *et al.*, 2004), together with standard uncertainties. These were used as restraints for refinement in both space groups.

In space group No. 106, the twofold rotation does not require the molecule to be planar, and the deviations of the non-H atoms from their mean plane are C3 0.08 (2), C2 -0.04 (2), C1 -0.15 (2), O1 -0.04 (2), O2 0.08 (2), C4 0.12 (2), C5 -0.07 (2) Å. The relatively large anisotropic displacement parameters were restrained to satisfy the Hirshfeld (1976) condition for rigid bonds. This refinement concluded satisfactorily with a conventional *R* value of 0.053 for 64 parameters and 383 observations. However, we could see no reason why the disordered molecule should not lie on a centre of symmetry, so the refinement was repeated in space group No. 135. The molecule is not required to be planar, even in this space group, but the atoms lie so close to the mirror that disordered displacements from it could not be modelled. In

this space group, the anisotropic displacement parameters are less eccentric than in No. 106, and provide no evidence for believing that the non-H atoms do not actually lie on the mirror plane. It is this refinement which is presented for publication, though we suspect that, in reality, the crystal may suffer from stacking faults and possibly twinning.

Experimental

A 3 mm column of the title material, which is a liquid at room temperature, was sealed in a 0.2 mm Lindemann tube. A single crystal was grown by keeping the compound under a cold nitrogen gas stream at 185 K (not far below its melting point of 198 K) and slowly moving a small liquid zone, created by a micro-heating coil, up and down the sample. Once a suitable approximately single crystal had been obtained, the main data collection was undertaken at this temperature.

Crystal data

$C_5H_{10}O_2$
 $M_r = 102.14$
Tetragonal, $P4_2/mbc$
 $a = 9.5153$ (3) Å
 $c = 6.8933$ (2) Å
 $V = 624.13$ (3) Å³
 $Z = 4$
 $D_x = 1.087$ Mg m⁻³

Mo $K\alpha$ radiation
Cell parameters from 458 reflections
 $\theta = 5\text{--}27^\circ$
 $\mu = 0.08$ mm⁻¹
 $T = 185$ K
Cylinder, colourless
0.50 × 0.1 mm (radius)

Data collection

Nonius KappaCCD diffractometer
 ω scans
Absorption correction: multi-scan
DENZO/SCALEPACK
(Otwinowski & Minor, 1997)
 $T_{\min} = 0.98$, $T_{\max} = 0.98$
719 measured reflections

384 independent reflections
383 reflections with $I > -3\sigma(I)$
 $R_{\text{int}} = 0.013$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -12 \rightarrow 12$
 $k = -12 \rightarrow 12$
 $l = -8 \rightarrow 8$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.062$
 $wR(F^2) = 0.100$
 $S = 0.90$
383 reflections
43 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F^2) + 0.04 + 0.17P]$
where $P = [\max(F_o^2, 0) + 2F_c^2]/3$
 $(\Delta/\sigma)_{\text{max}} = 0.013$
 $\Delta\rho_{\text{max}} = 0.14$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.17$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

O1—C1	1.168 (16)	C1—C2	1.497 (14)
O2—C1	1.351 (6)	C2—C3	1.519 (10)
O2—C4	1.483 (13)	C4—C5	1.481 (10)
C1—O2—C4	107.6 (6)	O1—C1—C2	119.0 (12)
O2—C1—O1	122.4 (10)	C1—C2—C3	107.8 (9)
O2—C1—C2	118.7 (8)	O2—C4—C5	111.6 (10)

H atoms were positioned geometrically after each cycle, with C—H = 1.0 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. All atoms are disordered, with occupancy factor 0.5.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics:

CAMERON (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

References

- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
- Bruno, I. J., Cole, J. C., Kessler, M., Luo, J., Motherwell, W. D. S., Purkis, L. H., Smith, B. R., Taylor, R., Cooper, R. I., Harris, S. E. & Orpen, A. G. (2004). *J. Chem. Inf. Comput. Sci.* **44**, 2133–2144.
- Hirshfeld, F. L. (1976). *Acta Cryst.* **A32**, 239–244.
- Nonius (2001). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.
- Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, Oxford, England.

supporting information

Acta Cryst. (2005). E61, o1118–o1120 [https://doi.org/10.1107/S1600536805005271]

Ethyl propionate at 185 K

Howard A. Shallard-Brown, David J. Watkin and Andrew R. Cowley

(I)

Crystal data

$C_5H_{10}O_2$

$M_r = 102.14$

Tetragonal, $P4_2/mbc$

$a = 9.5153$ (3) Å

$c = 6.8933$ (2) Å

$V = 624.13$ (3) Å³

$Z = 4$

$F(000) = 224$

$D_x = 1.087$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 458 reflections

$\theta = 5$ – 27°

$\mu = 0.08$ mm⁻¹

$T = 185$ K

Cylinder, colourless

$0.50 \times 0.20 \times 0.20 \times 0.1$ (radius) mm

Data collection

Nonius KappaCCD

diffractometer

Graphite monochromator

ω scans

Absorption correction: multi-scan

DENZO/SCALEPACK (Otwinowski & Minor, 1997)

$T_{\min} = 0.98$, $T_{\max} = 0.98$

719 measured reflections

384 independent reflections

383 reflections with $I > -3\sigma(I)$

$R_{\text{int}} = 0.013$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 5.2^\circ$

$h = -12 \rightarrow 12$

$k = -12 \rightarrow 12$

$l = -8 \rightarrow 8$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.062$

$wR(F^2) = 0.100$

$S = 0.90$

383 reflections

43 parameters

42 restraints

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F^2) + 0.04 + 0.17P]$

where $P = [\max(F_o^2, 0) + 2F_c^2]/3$

$(\Delta/\sigma)_{\max} = 0.013$

$\Delta\rho_{\max} = 0.14$ e Å⁻³

$\Delta\rho_{\min} = -0.17$ e Å⁻³

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O1	0.5978 (3)	0.3630 (3)	0.5000	0.0785	0.5000
O2	0.4285 (12)	0.5218 (12)	0.5000	0.0569	0.5000
C1	0.5646 (18)	0.4812 (16)	0.5000	0.0535	0.5000
C2	0.6764 (16)	0.5919 (14)	0.5000	0.0597	0.5000
C3	0.8180 (13)	0.5182 (8)	0.5000	0.0677	0.5000

C4	0.3407 (17)	0.3930 (15)	0.5000	0.0687	0.5000
C5	0.1889 (14)	0.4272 (9)	0.5000	0.0860	0.5000
H21	0.6673	0.6519	0.6184	0.0717*	0.5000
H31	0.8948	0.5900	0.5000	0.0813*	0.5000
H32	0.8262	0.4581	0.6185	0.0813*	0.5000
H41	0.3630	0.3366	0.6184	0.0824*	0.5000
H51	0.1329	0.3382	0.5000	0.1032*	0.5000
H52	0.1656	0.4832	0.6185	0.1032*	0.5000

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.070 (2)	0.0585 (18)	0.107 (2)	0.0162 (15)	0.0000	0.0000
O2	0.054 (2)	0.059 (3)	0.058 (5)	-0.001 (3)	0.0000	0.0000
C1	0.057 (2)	0.050 (3)	0.054 (7)	0.000 (3)	0.0000	0.0000
C2	0.065 (5)	0.050 (3)	0.065 (5)	-0.004 (3)	0.0000	0.0000
C3	0.056 (3)	0.064 (4)	0.084 (3)	-0.007 (3)	0.0000	0.0000
C4	0.059 (4)	0.082 (7)	0.066 (5)	-0.019 (4)	0.0000	0.0000
C5	0.062 (4)	0.097 (7)	0.098 (5)	-0.007 (5)	0.0000	0.0000

Geometric parameters (Å, °)

O1—C1	1.168 (16)	C3—H31	1.000
O2—C1	1.351 (6)	C3—H32	1.000
O2—C4	1.483 (13)	C4—C5	1.481 (10)
C1—C2	1.497 (14)	C4—H41	1.000
C2—C3	1.519 (10)	C5—H51	1.000
C2—H21	1.000	C5—H52	1.000
C1—O2—C4	107.6 (6)	C2—C3—H32	109.5
O2—C1—O1	122.4 (10)	H31—C3—H32	109.5
O2—C1—C2	118.7 (8)	O2—C4—C5	111.6 (10)
O1—C1—C2	119.0 (12)	O2—C4—H41	108.9
C1—C2—C3	107.8 (9)	C5—C4—H41	108.9
C1—C2—H21	109.9	C4—C5—H51	109.5
C3—C2—H21	109.9	C4—C5—H52	109.5
C2—C3—H31	109.5	H51—C5—H52	109.5