Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2-Ethyl-2-(hydroxymethyl)-1,3-propanediol at 120 K: three hydrogen bonds generate a three-dimensional structure

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.036
wR factor = 0.100
Data-to-parameter ratio = 19.2

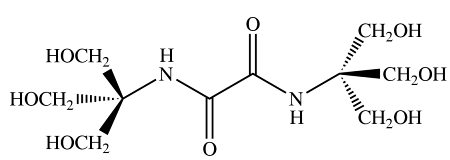
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 8 October 2001
Accepted 12 October 2001
Online 20 October 2001

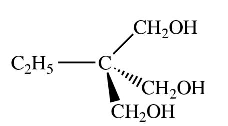
Molecules of the title compound, $C_2H_5C(CH_2OH)_3$, are linked by three O—H···O hydrogen bonds [H···O, 1.87–1.90 Å; O···O 2.704 (2)–2.719 (2) Å; O—H···O, 164–174°] into a single three-dimensional framework. This framework is readily analysed in terms of parallel molecular ladders, generated by two of the hydrogen bonds, linked together by the third hydrogen bond.

Comment

We recently reported the structure of *N,N*′-bis[tris(hydroxymethyl)methyl]ethanediamide, $(HOCH_2)_3CNHCOCONHC(CH_2OH)_3$, (I), where, despite the presence of six independent O—H···O hydrogen bonds, the supramolecular structure is only two-dimensional (Ross *et al.*, 2001). A simpler analogue of (I) is the title compound, $C_2H_5C(CH_2OH)_3$, (II), whose phase relationships were studied a number of years ago (Gowda *et al.*, 1982). When a melt of (II) was cooled to below the melting temperature (333 K) a disordered cubic phase, having space group *Fm*3*m* and *Z* = 4, was first obtained: when this phase was cooled to 273 K or allowed to stand at ambient temperature it was transformed into an ordered monoclinic phase with space group $P2_1/n$ and *Z* = 4. Here we report a low temperature, 120 (2) K, study of the monoclinic phase of (II), as grown directly from solution rather than obtained indirectly from the melt, and we give a detailed analysis of the hydrogen bonding. Although there are only three independent O—H···O hydrogen bonds in (II) (Table 2), the supramolecular structure is three-dimensional, in contrast to that of (I).



(I)



(II)

Polyhydroxy compounds such as (I) and (II) have very limited solubility in non-hydrogen-bonding solvents: this, in combination with the very hygroscopic nature of (II) makes

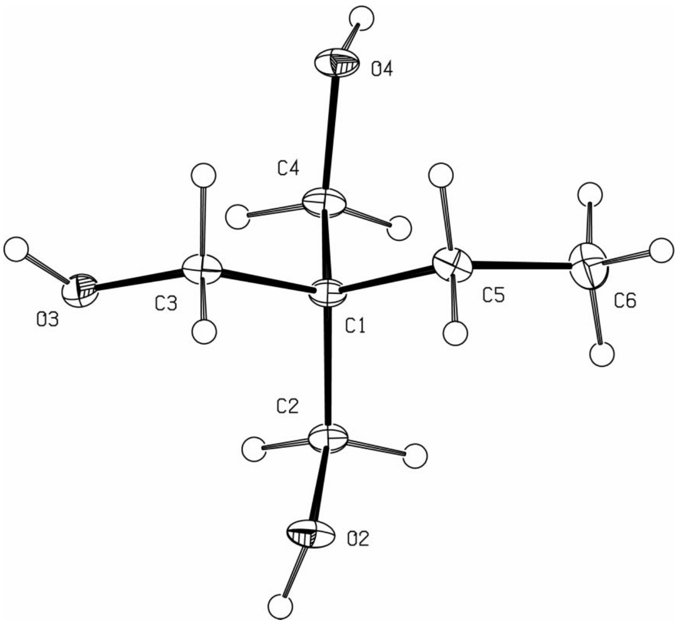


Figure 1
The molecule of (II) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

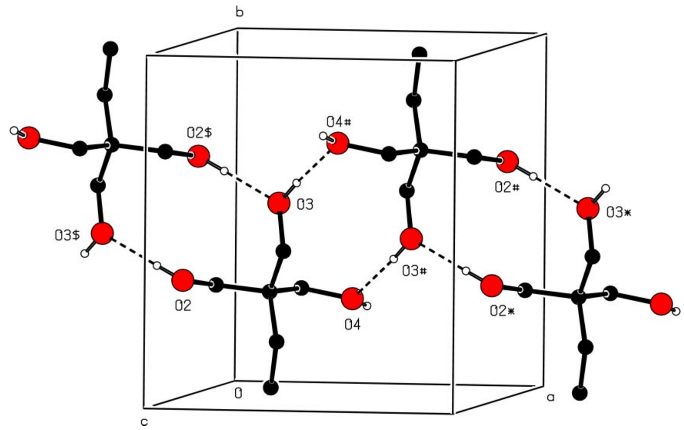


Figure 2
Part of the crystal structure of (II) showing formation of a molecular ladder along [100]. For the sake of clarity, H atoms bonded to C are omitted. The atoms marked with a star (*), hash (#) or dollar sign ($) are at the symmetry positions (1+*x, y, z*), (1−*x*, 1−*y*, 1−*z*) and (−*x*, 1−*y*, 1−*z*), respectively.

the growth from solution of solvent-free crystals of (II) a troublesome matter. After many unsuccessful attempts using a wide range of solvents, we were able to grow satisfactory solvent-free crystals from a solution in ethyl benzoylacetate, $PhCOCH_2COOEt$; the molecules of this compound contain sufficient hydrogen-bond-acceptor sites to render it an effective solvent for (II), while the molecular size and the irregular molecular shape effectively preclude the inclusion of solvent molecules in the resulting crystals of (II). When crystallized in this way, (II) forms the same monoclinic phase as was obtained earlier from the metastable cubic phase.

The supramolecular structure of (II) is most readily analysed using the sub-structure approach (Gregson *et al.*, 2000); a simple combination of two of the hydrogen bonds generates a molecular ladder, and all of the molecular ladders are linked into a single three-dimensional framework by the action of the third hydrogen bond. Hydroxyl O2 (Fig. 1) at (*x, y, z*) acts as hydrogen-bond donor to O3 at (−*x*, 1−*y*, 1−*z*), while O2 at (−*x*, 1−*y*, 1−*z*) acts as donor to O3 at (*x, y, z*) so generating a centrosymmetric $R_2^2(12)$ motif (Fig. 2). Similarly, O3 at (*x, y, z*) acts as hydrogen-bond donor to O4 at (1−*x*, 1−*y*, 1−*z*), so generating a second centrosymmetric $R_2^2(12)$ ring (Fig. 2). The combination and propagation of these two hydrogen bonds generates a molecular ladder running parallel to the [100] direction (Fig. 2). The uprights of the ladder are an antiparallel pair of $C_2^2(8)$ chains, and the C1—C3—O3 portion of the molecule acts as the rungs of the ladder. Between the rungs are the $R_2^2(12)$ rings, with the rings containing O2 centred at (*n*, 0.5, 0.5) (*n* = zero or integer) and those containing O4 centred at (*n*+0.5, 0.5, 0.5) (*n* = zero or integer).

This ladder lies along the line (*x*, 0.5, 0.5) and there are symmetry-related ladders running along the cell edges, on the lines (*x*, 0, 0), (*x*, 0, 1) and so on: hence two ladders pass through each unit cell, and the ladders are linked by the third hydrogen bond. Hydroxyl O4 at (*x, y, z*) acts as hydrogen-bond donor to O2 at (0.5+*x*, 0.5−*y*, −0.5+*z*), while O4 at (0.5+*x*, 0.5−*y*, −0.5+*z*) in turn acts as donor to O2 at (1+*x, y*, −1+*z*), so producing a *C*(6) chain running parallel to the $[10\overline{1}]$ direction, and generated by the *n*-glide plane at *y* = 0.25 (Fig. 3).

The hydroxyl atoms O4 at (*x, y, z*) and (1−*x*, 1−*y*, 1−*z*) are both part of the ladder which runs along the line (*x*, 0, 0); these O atoms act as hydrogen-bond donors to atoms O2 at (0.5+*x*, 0.5−*y*, −0.5+*z*) and (0.5−*x*, 0.5+*y*, 1.5−*z*) respectively, which lie in the ladders along (*x*, 0, 0) and (*x*, 1, 1) respectively. The atoms O2 at (*x, y, z*) and (1−*x*, 1−*y*, 1−*z*) in the (*x*, 0.5, 0.5) ladder act as hydrogen-bond acceptors from atoms O4 at (−0.5+*x*, 0.5−*y*, 0.5+*z*) and (1.5−*x*, 0.5+*y*, 0.5−*z*) respectively, which themselves lie in the ladders along (*x*, 0, 1) and (*x*, 1, 0) respectively. Hence, the ladder along (*x*, 0.5, 0.5) is linked directly to the four ladders along the unit cell edges (Fig. 3), and hence all the ladders in the structure are linked into a single three-dimensional framework.

While the bond lengths and angles in (II) present no unusual features, the molecular conformation (Table 1) is of interest. There is almost perfect staggering about all of the C—C bonds, but the $-C(CH_2OH)_3$ fragment does not exhibit the idealized threefold local symmetry; instead the molecule as a whole has a conformation close to C_s (*m*) molecular symmetry (Fig. 1, and Table 1)

Experimental

A sample of (II) was purchased from Aldrich. Solvent-free crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in ethyl benzoylacetate with rigorous exclusion of moisture.

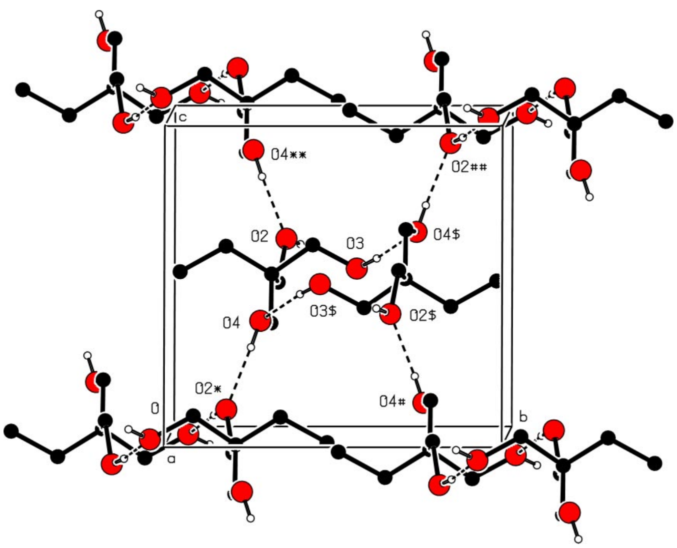


Figure 3
Part of the crystal structure of (II) showing the linking of the [100] molecular ladders into a three-dimensional framework. For the sake of clarity, H atoms bonded to C are omitted. The atoms marked with a dollar sign ($), single or double stars (*), or single or double hashes (#) are at the symmetry positions (1−*x*, 1−*y*, 1−*z*), (0.5+*x*, 0.5−*y*, −0.5+*z*), (−0.5+ *x*, 0.5−*y*, 0.5+*z*), (1.5−*x*, 0.5+*y*, 0.5−*z*) and (0.5−*x*, 0.5+*y*, 1.5−*z*) respectively.

Crystal data

$C_6H_{14}O_3$
M_r = 134.17
Monoclinic, $P2_1/n$
a = 8.3806 (2) Å
b = 9.5768 (3) Å
c = 9.1466 (3) Å
β = 99.4790 (13)°
V = 724.08 (4) Å^3
Z = 4
D_x = 1.231 Mg m^{-3}
Mo K*α* radiation
Cell parameters from 1647 reflections
θ = 3.1–27.5°
μ = 0.10 mm^{-1}
T = 120 (2) K
Lath, colourless
0.22 × 0.14 × 0.10 mm

Data collection

KappaCCD diffractometer
φ s, and *ω* scans with *κ* offset scans
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
T_{min} = 0.979, T_{max} = 0.990
6745 measured reflections
1647 independent reflections
1348 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 27.5°
h = −10 → 10
k = −12 → 12
l = −11 → 11

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.100
S = 1.06
1647 reflections
86 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 0.1161P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C6—C5—C1—C2	66.4 (2)	C5—C1—C2—O2	66.9 (2)
C6—C5—C1—C3	−172.93 (9)	C5—C1—C3—O3	178.88 (8)
C6—C5—C1—C4	−51.4 (2)	C5—C1—C4—O4	−52.8 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O3^{i}	0.84	1.87	2.704 (2)	174
O3—H3···O4^{ii}	0.84	1.87	2.711 (2)	174
O4—H4···O2^{iii}	0.84	1.90	2.719 (2)	164

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

Compound (II) crystallized in the monoclinic system; space group $P2_1/n$ was uniquely assigned from the systematic absences. H atoms were treated as riding atoms with C—H distances of 0.98 (CH_3) or 0.99 Å (CH_2) and an O—H distance of 0.84 Å. Two data sets were collected at 120 (2) K from crystals obtained in two separate crystallizations; the results reported here are based on the dataset which gave marginally the lower *R* value (0.0355 *versus* 0.0366).

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2001); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, UK, using an Enraf–Nonius KappaCCD diffractometer. The authors thank the staff for all their help and advice. CMZ thanks the Association of Commonwealth Universities for the award of a Commonwealth Fellowship 2000–2001.

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