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A supramolecular ladder motif in 2-(2,2,6,6-tetramethylpiperidin-1-yloxy)propane-1,3-diol

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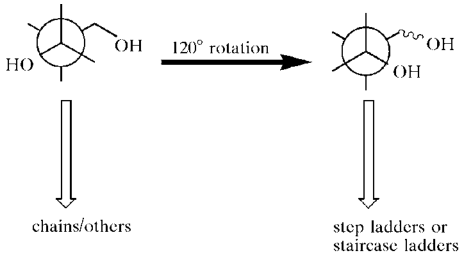
An O—H···O hydrogen-bonded step-ladder motif was observed in the crystal structure of the title compound, $C_{12}H_{25}NO_3$. The ladder arrangement is typical of 1,2- and 1,3-diols with a synclinal orientation of the diol functionality.

Comment

Hydrogen-bonding motifs play an important role in the interaction, recognition and conformation of both small and large molecules [*e.g.* in biologically active molecules (Watson & Crick, 1953; Zeng *et al.*, 2000)]. These motifs have frequently been used as supramolecular synthons to direct solid-state structures (crystal engineering; Steiner, 2002; Aakeröy & Seddon, 1993) and for the synthesis of complex supramolecules. The predictability of such interactions (N—H···N, N—H···O, O—H···N and O—H···O bonds) depends on the robustness and reproducibility of such interactions.



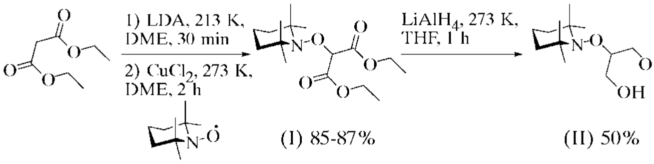
Simple diols are becoming increasingly important synthons for the preparation of unidirectional architectures, such as ladders, in the solid state (Nguyen *et al.*, 2001; Schmittel *et al.*, 2003). Depending on the arrangement of the rung region, ladders usually adopt two distinct shapes, with a clear distinction between the ‘staircase’ or the ‘step-ladder’ types. In staircase ladders, the rung region is made up of chains of $(OH)_n$ groups, while in step ladders, it contains discrete $(OH)_4$ rings.

Unfortunately, there is no general trend in the substitution pattern that would enable us to exploit hydrogen-bonding interactions for building ladder structures, except that 1,3-diols tend to form ladder-like structures more easily than 1,2-diols; furthermore, racemic, achiral or 2-substituted 1,3-propanediols form step ladders.

From a Newman projection analysis of 1,3-diols known to form ladders (Nguyen *et al.*, 2001), it appears that the antiperiplanar conformation leads to chain structures, whereas in the synclinal conformation, ladder-like structures are preferred (see scheme above).

Our long-standing interest in building highly ordered and predictable supramolecular aggregates based on metal complexation (Schmittel, Ammon *et al.*, 2002; Schmittel, Ganz & Fenske, 2002; Schmittel *et al.*, 2001) and more recently on hydrogen-bonded motifs (Schmittel *et al.*, 2003) encouraged us to synthesize the achiral 1,3-diol (II) [2-(2,2,6,6-tetramethylpiperidin-1-yloxy)propane-1,3-diol] and to investigate its structural properties.

Compound (II) was prepared in reasonable yields starting from diethyl malonate *via* a method involving an initial trapping of a carbon-centred radical by the 2,2,6,6-tetramethylpiperidin-1-yloxy radical (Jahn *et al.*, 2002), followed by lithium aluminium hydride reduction of diethyl 2-(2,2,6,6-tetramethylpiperidin-1-yloxy)malonate, (I).



The crystal structure contains one molecule in the asymmetric unit. The piperidinoxy ring adopts the usual chair conformation. Atom O1 is antiperiplanar with atom O2 [−178.12 (7)°] and synclinal with atom O3 [−58.52 (9)°; Fig. 1]. Intramolecular C—H···O interactions (H···O = 2.44 Å) were observed between the axial methyl groups of the piperidinyloxy group (C10 and C12) and atom O1.

Intermolecular O—H···O hydrogen-bonding interactions predominate in the extended structure of (II); the primary O atoms act as both acceptor and donor (Table 1). The net effect

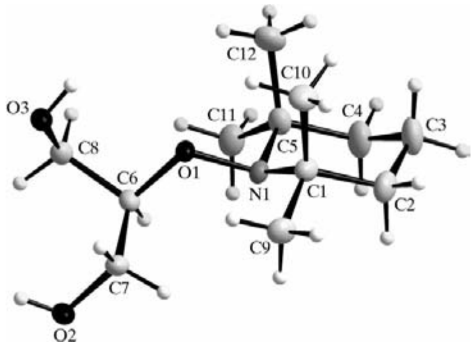


Figure 1
The molecular structure of (II), with 50% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary size.

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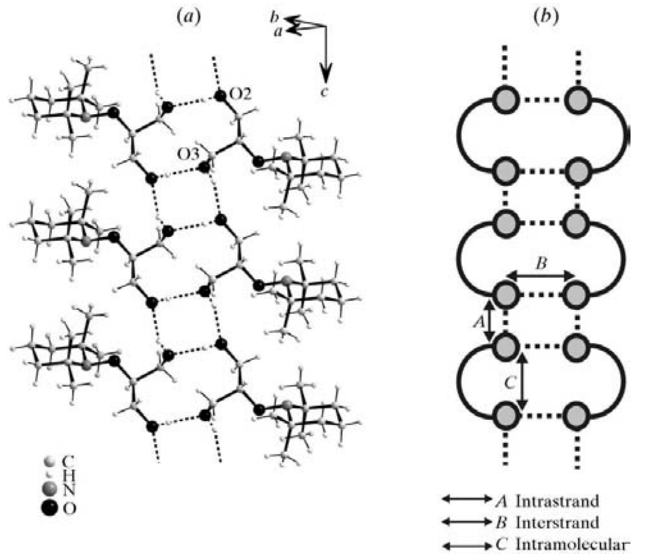

Figure 2
The hydrogen-bonded secondary structure of (II), showing a step-ladder arrangement in different presentations, *viz*. (*a*) a ball-and-stick model and (*b*) a schematic representation.

is to connect the molecules into a chain structure parallel to [001], with a $C_1^1(6)$ graph-set designator; two such chains are linked to form a two-dimensional hydrogen-bonding network with a supramolecular ladder-like arrangement (Fig. 2), as expected for a symmetrically substituted achiral 1,3-diol, with $(OH)_4$ rings in the rung region. The intrastrand O···O distance [*A* = 2.7494 (10) Å; Fig. 2 and Table 1] is slightly greater than the interstrand O···O distance [*B* = 2.7133 (10) Å; Fig. 2 and Table 1], and the same is necessarily true of the H···O distances; the interstrand hydrogen bonding is thus presumably slightly stronger. The intramolecular O···O distance (*C*) is 3.6371 (10) Å (Fig. 2 and Table 1), which is in the usual range for step-ladder motifs (Nguyen *et al.*, 2001).

Experimental

For the preparation of (I), diethyl malonate (240 mg, 1.50 mmol) was added to a solution of butyllithium (780 µl, 1.95 mmol) and diisopropylamine (197 mg, 1.95 mmol) in dry dimethoxyethane (30 ml) cooled to 195 K. After 30 min, 2,2,6,6-tetramethylpiperidin-1-oxyl (328 mg, 2.10 mmol) was added. The reaction mixture was warmed slowly to 273 K and dry copper (II) chloride was added portionwise (large excess, until a green colour persisted) over a period of 10 min. The reaction mixture was stirred at 273 K for 2 h, quenched with saturated ammonium chloride solution (10 ml) and extracted with ether (3 × 25 ml). The combined organic layer was washed with water (5 × 100 ml), dried over Na_2SO_4 (anhydrous) and concentrated under reduced pressure. The crude product was purified by flash column chromatography with 2% ethyl acetate in hexane as eluant, yielding a colourless low-melting-point solid (m.p. 301–303 K). IR (cm^{-1}, KBr): 2977, 2935, 1767, 1746, 1468, 1367, 1213, 1183, 1097, 1028, 960; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.08, 1.20 (2*s*, 12H, CH_3), 1.29 (*t*, *J* = 7.1 Hz, 6H, CH_3), 1.46 (*bs*, 6H, CH_2), 4.20–4.27 (*m*, 4H, CH_2), 4.92 (*s*, 1H, CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ 15.1, 18.0, 21.1, 33.6, 41.1, 61.3, 62.6, 87.7, 168.3. Analysis calculated for $C_{16}H_{29}NO_5$: C 60.93, H 9.27, N 4.44%; found: C 61.04, H 9.38, N 4.57%. For the preparation of (II), lithium aluminium hydride (133 mg, 3.50 mmol) was added to a solution of (I) (420 mg, 1.30 mmol) in 20 ml of dry tetrahydrofuran at 273 K. After 1 h, ethyl acetate (15 ml) was added to the reaction mixture at 273 K. After 30 min, the reaction mixture was poured into water and extracted with dichloromethane (3 × 25 ml). The combined organic layer was dried over Na_2SO_4 (anhydrous) and concentrated under reduced pressure. The crude product was purified by flash column chromatography with 50% ethyl acetate in hexane as eluant, yielding a colourless solid (m.p. 354 K). IR (cm^{-1}, KBr): 3310, 2920, 1360, 1244, 1133, 1112, 1094, 1039, 975, 959; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.15, 1.33 (2*s*, 12H, CH_3), 1.52 (*bs*, 6H, CH_2), 3.61 (*bs*, 4H, CH_2 and OH), 3.83 (*t*, *J* = 7.1 Hz, 2H, CH_2), 4.38 (*t*, *J* = 7.1 Hz, 1H, CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ 18.0, 21.3, 34.5, 41.2, 61.9, 65.1, 82.0. Analysis calculated for $C_{12}H_{25}NO_3$: C 62.30, H 10.89, N 6.05%; found C 61.70, H 11.17, N 5.99%. Single crystals of (II) suitable for X-ray analysis were obtained upon evaporation of the solvent (hexane/ethyl acetate, 50%) under reduced pressure (313 K).

Crystal data

$C_{12}H_{25}NO_3$
M_r = 231.33
Monoclinic, $P2_1/n$
a = 14.6525 (13) Å
b = 14.6357 (8) Å
c = 6.1793 (5) Å
β = 93.801 (10)°
V = 1322.23 (17) Å^3
Z = 4
D_x = 1.162 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8000 reflections
θ = 2.8–30.4°
μ = 0.08 mm^{-1}
T = 173 (2) K
Needle, colourless
0.20 × 0.10 × 0.08 mm

Data collection

Stoe IPDS diffractometer
φ scans
15 527 measured reflections
3992 independent reflections
2635 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.043
$\theta_{\rm max}$ = 30.5°
$h = -20 \rightarrow 20$
$k = -20 \rightarrow 19$
$l = -8 \rightarrow 8$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.093
S = 0.93
3992 reflections
158 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0619P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.25 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.19 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.019 (2)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O3	0.873 (15)	3.287 (15)	3.6371 (10)	106.8 (11)
C10—H10*C*···O1	0.98	2.44	2.8524 (12)	105
C12—H12*A*···O1	0.98	2.44	2.8645 (13)	106
O2—H2···O3$^{\rm i}$	0.873 (15)	1.844 (15)	2.7133 (10)	173.3 (14)
O3—H3···O2$^{\rm ii}$	0.855 (15)	1.952 (15)	2.7494 (10)	154.8 (13)

Symmetry codes: (i) $2 - x, 1 - y, -z$; (ii) $x, y, 1 + z$.

C-bound H atoms were placed in geometrically idealized positions, with C—H distances of 0.99 (CH_2) or 0.98 Å (CH_3), and treated as riding atoms, with $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$ of the parent C atoms. The positions of the hydroxy H atoms were found from difference Fourier maps and refined, with $U_{\rm iso}$(H) values fixed at $1.5U_{\rm eq}$ of the parent O atoms.

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Data collection: *EXPOSE* in *IPDS Software* (Stoe & Cie, 1999); cell refinement: *CELL* and *SELECT* in *IPDS Software*; data reduction: *X-RED* (Stoe & Cie, 1999); structure solution: *SHELXS*97 (Sheldrick, 1997); structure refinement: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Crystal Impact, 1999); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1616). Services for accessing these data are described at the back of the journal.

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