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Key indicators

Single-crystal X-ray study
 T = 173 K
 Mean $\sigma(C-C)$ = 0.002 Å
 R factor = 0.049
 wR factor = 0.136
 Data-to-parameter ratio = 18.5

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

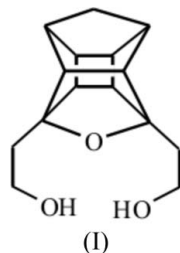
3,5-Bis(2-hydroxyethyl)-4-oxahexacyclo-
 [5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]dodecane

The title molecule, C₁₅H₂₀O₃, exhibits C—C bond lengths that deviate from normal values. A number of long and short C—C bonds are observed. Neighbouring molecules interact *via* strong O—H...O hydrogen bonds, forming two-dimensional hydrogen-bonded sheets.

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Comment

The present study is part of an ongoing investigation of the chemical reactivity and solid-state structures of substituted pentacycloundecane cage compounds. The title compound, (I), has been utilized in various macrocycles (Levistskaia *et al.*, 2001; Boyle *et al.*, 2004), and the fact that the pentacycloundecane (PCU) cage forms part of the macrocycle backbone results in enhanced selectivity and lipophilicity in the macrocycle.



The molecular geometries of PCU cage derivatives have been reported in a number of studies, and are of interest because certain bonds tend to be longer or shorter than the value of 1.54 Å expected for a C—C single bond (see, for

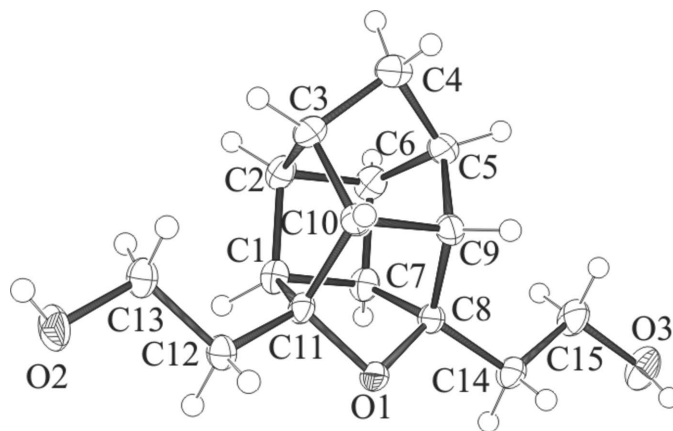


Figure 1
 The molecular structure of (I) (ORTEP3; Farrugia, 1997), showing the atomic numbering scheme and displacement ellipsoids drawn at the 50% probability level

example, Flippen-Anderson *et al.*, 1991; Linden *et al.*, 2005). In particular, the C9–C10 bond has been found to be abnormally long, whereas the bonds connecting atoms C8 and C11 to the cage, as well as the bonds involving atom C4, are often shorter than normal.

To our knowledge, the structures of eight compounds related to (I), in which the mouth of a simple PCU cage is linked by an oxo bridge, and with various substituents at atoms C8 and C11, have been reported in the literature. Of these, six are symmetrically substituted at atoms C8 and C11, with substituents including benzoylcarbonyl, (II) (Pinkerton *et al.*, 2001), pyrrolidinyl, (III), morpholino, (IV), 4-acetylpiperziny, (V) (Bott *et al.*, 1995), and ethynyl, (VI) (Bott *et al.*, 1999), groups. The structures of two unsymmetrically substituted simple cages have been reported, *viz.* (VII) which is substituted only at atom C8 by a benzylamino group (van der Schyf *et al.*, 1989), and (VIII), in which atom C8 is bonded to a trifluoromethyl group, and atom C11 is connected to an alcohol function. It should also be noted that, of the related compounds listed above, only (VIII) forms classical hydrogen bonds involving the alcohol substituent and the oxo-bridge O atom.

In the title molecule, (I) (Fig. 1), the shortening or elongation of specific C–C bonds, as reported previously for related compounds, is also observed. The C9–C10 bond is long with a value of 1.568 (2) Å, which is shorter than values reported for cage compounds in which atoms C8 and C11 are not linked by the oxo bridge; for example, values of 1.579 (4), 1.600 (7) and 1.585 (4) Å have been reported (Flippen-Anderson *et al.*, 1991). The C2–C6 and C1–C7 bonds, which form part of the cyclobutyl group, are also long, with values of 1.567 (2) and 1.553 (2) Å, respectively. These values agree with corresponding bond lengths in related compounds; for example, in (VIII), the C2–C6 bond length is 1.561 Å and the C1–C7 bond length is 1.557 Å.

The bonds involving atoms C4, C12 and C14 are shorter than expected; C3–C4, C4–C5, C11–C12, C8–C14, C12–C13 and C14–C15 have lengths of 1.531 (2), 1.532 (2), 1.5090 (19), 1.5104 (19), 1.513 (2) and 1.519 (2) Å, respectively. The short bonds involving C4, as well as the small C3–C4–C5 bond angle [95.26 (12)°] observed in (I), have also been reported for related compounds. The ethyl alcohol chains are in the energetically favourable all-*trans* conformation, with atoms O3, C15, C14, C8, O1, C11, C12 and C13 coplanar [r.m.s. deviation = 0.0373 (4) Å]. It is interesting that the C12–C13 and C14–C15 bonds are also short, despite not forming part of the cage.

In (I), the molecules pack in hydrogen-bonded layers. Both alcohol functional groups on a molecule participate in hydrogen bonding, with each acting as both a hydrogen-bond donor and acceptor (Table 1). Atom O2 interacts with atom O3 at $(x - 1, y, z + 1)$ via H2, and atom O3 interacts with atom O2 at $(x + 1, \frac{1}{2} - y, z - \frac{1}{2})$ through H3. A hydrogen-bonded linear chain is formed, which can be classified by the graph-set motif *C*(3) (Etter & MacDonald, 1990). Because both ends of a molecule are involved in hydrogen bonding, molecules are connected to form corrugated two-dimensional sheets (Fig. 2).

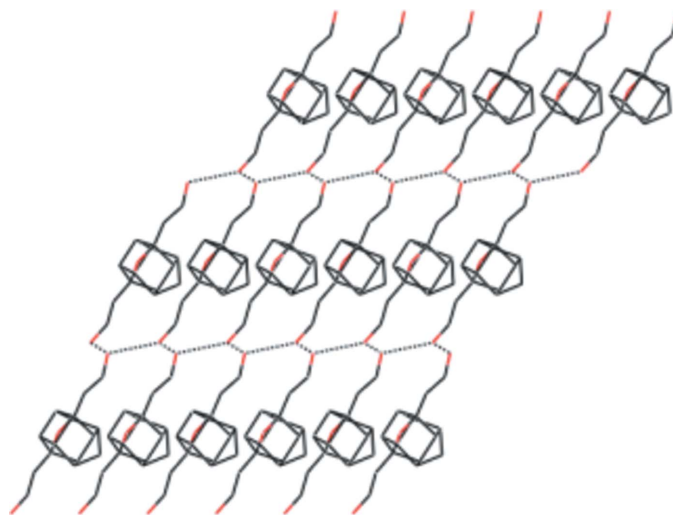


Figure 2
Packing diagram of (I) (MERCURY; Bruno *et al.*, 2002), illustrating the layered structure and interactions. H atoms have been omitted.

It should be noted that the oxo atom, which is a potential hydrogen-bond acceptor and participates in hydrogen-bond formation to form a hydrogen-bonded dimer in (VIII), does not interact with any of the hydrogen-bond donors in (I).

Experimental

A solution of 3,5-diallyl-4-oxahexacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]-dodecane (Boyle *et al.*, 2004) (14.5 g, 20.3 mmol) in dry methanol (150 ml) was cooled to 195 K *via* application of an external dry ice–acetone bath and was then purged with argon for 20 min. Ozone was bubbled into the mixture until a blue–purple colour persisted, thereby indicating the presence of excess ozone and completion of the reaction. Excess ozone was flushed from the reaction vessel with a stream of argon, and the reaction mixture was transferred to a 2 l flask. Sodium borohydride (3 g, 81.0 mmol) was added over 1 h to a stirred ice-bath-cooled mixture of the ozonide. The resulting mixture was stirred at ambient temperature for 12 h. The reaction mixture was concentrated *in vacuo*, excess sodium borohydride was quenched with 10% HCl (200 ml), and the mixture was extracted with ethyl acetate to give pure (I) (4.4 g, 89%) obtained as a colourless microcrystalline solid (m.p. 426.0–426.5 K). IR (KBr): max 3320 (*m*), 2980 (*s*) cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 1.52 (*d*, *J* = 10.3 Hz, ¹H), 1.70–2.05 (*m*, 4H), 2.28–2.69 (*m*, 9H), 3.50–3.86 (*m*, 6H); ¹³C NMR (CDCl₃, 75 MHz): δ C 34.3 (*t*), 41.4 (*d*), 43.5 (*t*), 44.1 (*d*), 47.7 (*d*), 58.2 (*d*), 60.0 (*t*), 92.4 (*s*).

Crystal data

C₁₅H₂₀O₃
M_r = 248.31
 Monoclinic, *P*2₁/*c*
a = 8.8011 (2) Å
b = 19.8310 (4) Å
c = 7.0073 (1) Å
 β = 93.783 (1)°
V = 1220.35 (4) Å³
Z = 4

D_x = 1.352 Mg m⁻³
 Mo K α radiation
 Cell parameters from 4355 reflections
 θ = 2.3–29.7°
 μ = 0.09 mm⁻¹
T = 173 (2) K
 Plate, colourless
 0.25 × 0.24 × 0.11 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: none
 12806 measured reflections
 2942 independent reflections

2321 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$
 $\theta_{\text{max}} = 28.0^\circ$
 $h = -11 \rightarrow 11$
 $k = -26 \rightarrow 26$
 $l = -9 \rightarrow 9$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.136$
 $S = 1.05$
 2942 reflections
 159 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0731P)^2 + 0.4354P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.006$
 $\Delta\rho_{\text{max}} = 0.43 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.23 \text{ e } \text{Å}^{-3}$

Table 1

Hydrogen-bond geometry ($\text{Å}, ^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O2-H2A \cdots O3^i$	0.84	1.85	2.6811 (16)	171
$O3-H3A \cdots O2^{ii}$	0.84	1.90	2.7367 (17)	174

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

All H atoms were placed in calculated positions, with C—H distances of 1.00 Å and O—H distances of 0.84 Å, and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$.

Data collection: SMART-NT (Bruker, 1998); cell refinement: SAINT-Plus (Bruker, 1999); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXTL (Bruker, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics:

ORTEP3 (Farrugia, 1997) and MERCURY (Bruno *et al.*, 2002); software used to prepare material for publication: SHELXTL.

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