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The complex packing pattern of *cis*-1,2-dimethylcyclobutane-1,2-diol

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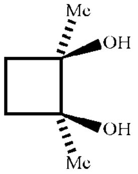
cis-1,2-Dimethylcyclobutane-1,2-diol, $C_6H_{12}O_2$, crystallizes with five molecules in the asymmetric unit. Of these, two molecules are the building blocks of columns with a complex hydrogen-bonding pattern in their hydrophilic core. The walls of the columns are formed by the lipophilic parts of the molecules. The remaining three molecules of the asymmetric unit build columns with a less complex hydrogen-bonding system. In terms of co-operativity, the most significant feature is the formation of homodromic rings of six hydroxy functions.

Comment

On crystallization, the polar (hydrophilic) and apolar (lipophilic) parts of amphiphilic molecules usually segregate into polar and apolar building blocks of the crystal structure, respectively. If the polar and apolar parts occupy volume fractions of different sizes, only the larger part normally establishes intermolecular contacts in all three dimensions, whereas the smaller part may be restricted to intermolecular contacts in zero (pairs of molecules, clusters) or one dimension (chains, columns).

The diols are a particularly widespread class of compounds which illustrate this principle since, owing to the variety of residues that may be attached to the diol function, the size ratios between the polar and apolar parts may span an extended range. Moreover, the diols have attracted our interest as they are the parent acids of potentially chelating ligands. Examples of structurally characterized diols which are representative examples in terms of the size ratio between the polar and apolar molecular parts include 1,2-dicyclopentylethane-1,2-diol (Betz *et al.*, 2007) and bi-1,1′-cycloheptyl-1,1′-diol (Betz & Klüfers, 2007), in both of which the diol functions are assembled in hydrogen-bonded chains, and *cis*- and *rac*-*trans*-cyclohexane-1,2-diol (Sillanpää *et al.*, 1984) which exhibit hydrogen-bonded layers. Finite hydrogen-bonding patterns have been found with pinacol, for example, namely eight-membered homodromic rings in tetramers of the diol (Jeffrey & Robbins, 1978).

In the title compound, (I), the apolar part fills, to a similar extent as in pinacol, the major part of the volume of the crystal and restricts the polar part to the core of columns with an apolar shell. What makes (I) remarkable is the complexity with which the molecules assemble into the crystal structure; no less than five molecules are found in the asymmetric unit, one of them exhibiting disorder in the apolar part. Fig. 1 shows two of the five independent molecules, while Fig. 2 shows the remaining three molecules. A common feature of all the molecules is the slightly twisted cyclobutane ring, which, together with the methyl substituents, imparts a certain degree of rigidity to the molecules such that the diol torsion angles of all five molecules are within 4° of 30°. One molecule exhibits disorder of the ethylene unit of the cyclobutane ring and of the



(I)

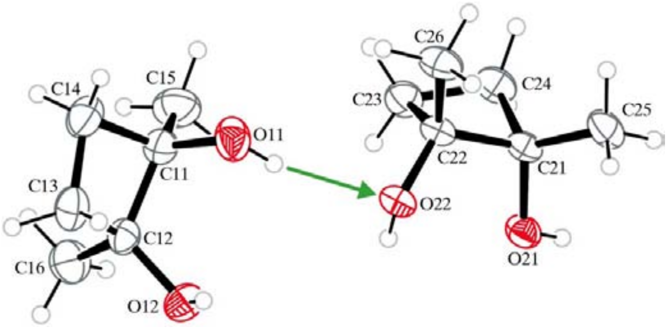


Figure 1
Two of the five symmetry-independent molecules of (I). Displacement ellipsoids are drawn at the 40% probability level.

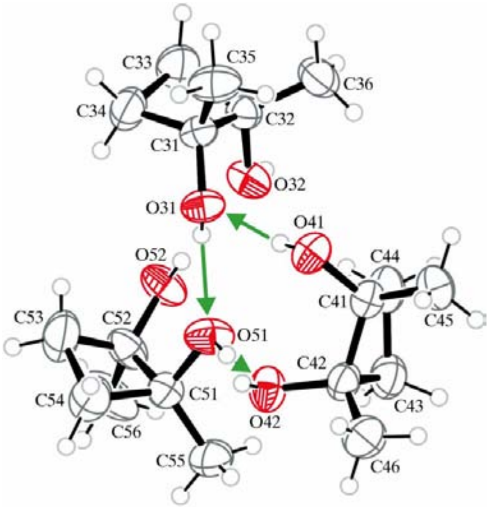


Figure 2
The three remaining independent molecules of (I). Displacement ellipsoids are drawn at the 40% probability level. Only the major component of disordered molecule 4 (atomic labels *X*4*n*) is shown.

two methyl substituents (Fig. 3). It should be noted that the two disordered forms are connected by a 180° rotation, which leaves the orientation of the diol function unaltered, so that both disordered forms are compatible with the hydrogen-bonding pattern.

The dimer and the trimer of diols depicted in Figs. 1 and 2, respectively, are the building blocks of two different kinds of hydrogen-bonded columns, termed d_2 and d_3, respectively. Although built by the more complex asymmetric building block, the core of the d_3 column has a simpler construction principle in terms of co-operativity; isolated homodromic rings made up of six symmetry-independent hydroxy functions are linked by a diol dimer (Fig. 4). Hence, although the core of a column provides an infinite stack of approximately equidistant hydroxy groups, their O—H vectors do not combine to form an infinite co-operative hydrogen-bonded system. Specifically, infinite co-operativity *via* intra-diol hydrogen bonding, as found in the related bicycloheptyldiol structure (Betz & Klüfers, 2007), is only weakly, if at all, exhibited both in the d_3 and in the d_2 strands (*cf.* the last three entries in Table 1).

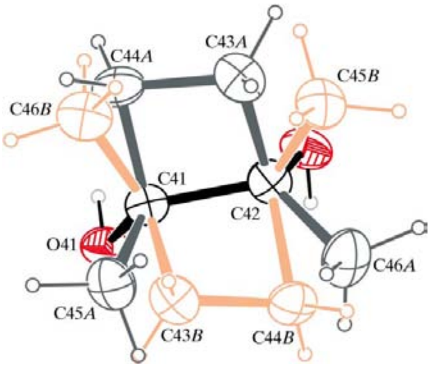


Figure 3
Disordered molecule 4 (30% ellipsoid probability), with the diol function fully occupied; the major disordered component (dark grey part) has an occupancy of 0.639 (5) and the minor part is drawn in buff (light grey).

The core of the d_2 columns shows a closely related, but more complex, hydrogen-bonding pattern (Fig. 5). Similar homodromic rings of another six hydroxy functions are again aligned by diol links, but two more hydroxy donors, which bind to two acceptor sites at opposite ring positions, complete the pattern.

For the hydrogen bonds observed in the two different columns, graph-set analysis (Etter *et al.*, 1990; Bernstein *et al.*, 1995) was applied. Each column was analyzed separately because the d_2 and d_3 columns have no linking hydrogen bonds.

The hydrogen bonds in the more basic d_3 column are not crystallographically equivalent, so on the unitary graph level the pattern should be assigned a *DDDDDD* descriptor. As depicted in Fig. 4, on the binary graph level the descriptor converts to two $C_2^2(7)$ chains connected by an $R_2^2(10)$ ring. Finally, an $R_6^6(12)[R_3^3(9)R_3^3(9)]$ six-level graph set (N_6) [on the ternary level two $R_3^3(9)$ rings are found] fits the homodromic rings mentioned above made up of six hydroxy functions. In conclusion, the most important description seems to be that of the second-level graph set, as the unitary graph set provides only finite motifs and the higher levels can be assembled by the patterns of the second level.

The graph-set analysis of the d_2 column results in an $R_2^2(10)DDD$ descriptor on the unitary graph level. On the binary graph level the pattern can be depicted by two $C_2^2(7)$ chains with opposite co-operativity connected by an $R_4^2(14)$ ring (Fig. 5). Finally, on the ternary graph level the homodromic rings mentioned above are found, to which the $R_6^6(12)$ descriptor can be assigned.

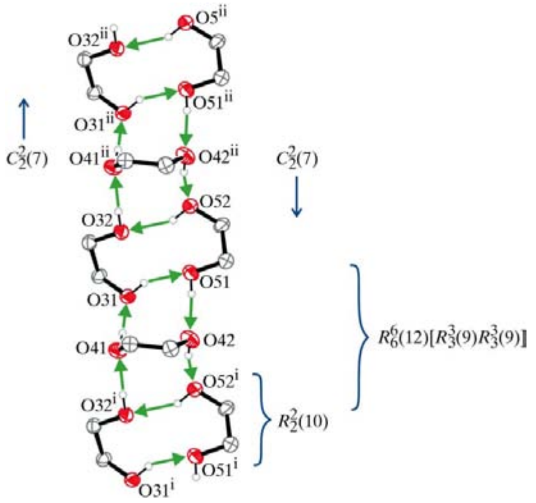


Figure 4
Hydrogen bonding in the d_3 columns (vertical axis [100]); atoms that are not part of a diol function have been omitted. Note the homodromic rings made up of six symmetry-independent hydroxy functions. For graph-set notation, see *Comment*. [Symmetry codes: (i) $x - 1, y, z$; (ii) $x + 1, y, z$.]

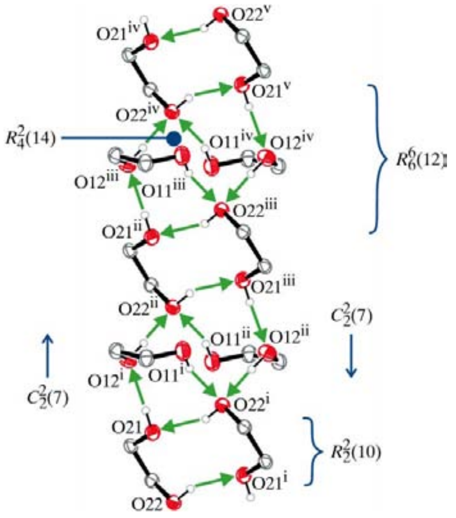


Figure 5
Hydrogen bonding in the d_2 columns (vertical axis [100]); atoms that are not part of a diol function have been omitted. Centrosymmetric homodromic rings made up of three symmetry-independent hydroxy functions are supplemented by O11-hydroxy functions. For graph-set notation, see *Comment*. [Symmetry codes: (ii) $x + 1, y, z$; (iii) $-x + 2, -y, -z + 1$; (iv) $x + 2, y, z$; (v) $-x + 3, -y, -z + 1$; (vi) $-x + 1, -y, -z + 1$.]

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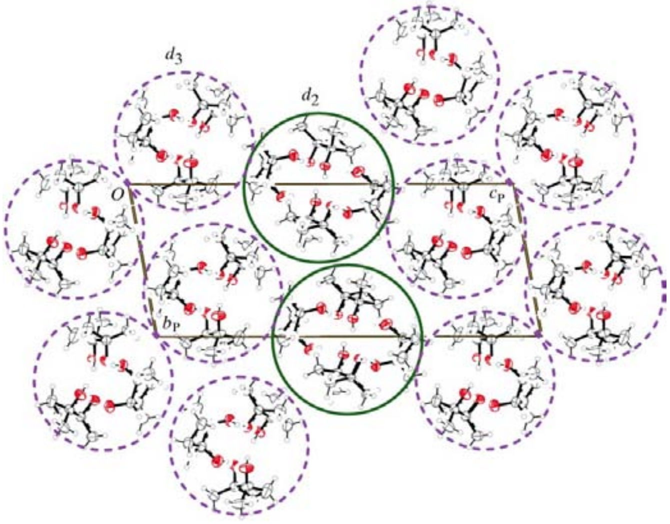

Figure 6
The pseudo-hexagonal packing of d_2- and d_3-type columns viewed along [$\bar{1}$00].

The entire crystal structure is assembled by a pseudo-hexagonal stacking of both d_2- and d_3-type [100] columns in the *bc* plane (Fig. 6).

Experimental

The title compound was prepared according to a published procedure (Corey *et al.*, 1976) upon pinacolic coupling of hexane-2,5-dione by means of amalgamated magnesium filings and titanium tetrachloride in tetrahydrofuran. After an aqueous alkaline work-up, extraction with diethyl ether and subsequent distillation yielded the desired product, which had already crystallized in the cooler of the distillation head (m.p. 290 K). Crystals suitable for X-ray analysis were obtained directly from the crystallized reaction product.

Crystal data

$C_6H_{12}O_2$
$M_r = 116.16$
Triclinic, $P\bar{1}$
$a = 6.9715$ (2) Å
$b = 10.5549$ (3) Å
$c = 24.8914$ (8) Å
$\alpha = 79.614$ (2)°
$\beta = 88.741$ (2)°
$\gamma = 72.225$ (2)°
$V = 1714.63$ (9) Å^3
$Z = 10$
Mo $K\alpha$ radiation
$\mu = 0.08$ mm^{-1}
$T = 200$ (2) K
0.24 × 0.07 × 0.06 mm

Data collection

Nonius KappaCCD diffractometer
12129 measured reflections
6647 independent reflections
4077 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.039$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.139$
$S = 1.03$
6647 reflections
420 parameters
5 restraints
H-atom parameters constrained
$\Delta\rho_{\rm max} = 0.21$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.20$ e Å^{-3}

The C-bonded H atoms were refined as riding on their parent atoms, with C—H distances of 0.98 (methyl) or 0.99 Å (methylene) and with $U_{\rm iso}$(H) values of $1.5U_{\rm eq}$(C) for the methyl groups and $1.2U_{\rm eq}$(C) for the methylene groups. The O-bonded H atoms were located in a difference map, and their positions were optimized geometrically and refined as riding on their parent atoms using the electron-density-related AFIX 147 instruction of *SHELXL97* (Sheldrick, 2008) [O—H = 0.84 Å and $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm O})$]. The population parameter of the major disordered component in one of the five molecules refined to 0.639 (5), where the sum of the population parameters of the major and minor disordered components was constrained to unity. The C—C distances of the minor disordered component were tied to the corresponding values of the major form by a similarity restraint (the SADI instruction of *SHELXL97* with $\sigma = 0.01$).

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

D—H···A	D—H	H···A	D···A	D—H···A
O11—H11···O22	0.84	2.11	2.924 (2)	162
O12—H12···O22$^{\rm vii}$	0.84	2.03	2.845 (2)	162
O21—H21···O12$^{\rm vi}$	0.84	1.97	2.808 (2)	177
O22—H22···O21$^{\rm vi}$	0.84	2.01	2.795 (2)	154
O31—H31···O51	0.84	2.05	2.826 (2)	153
O32—H32···O41$^{\rm ii}$	0.84	1.89	2.729 (2)	177
O41—H41···O31	0.84	1.94	2.774 (2)	170
O42—H42···O52$^{\rm i}$	0.84	1.93	2.758 (2)	168
O51—H51···O42	0.84	1.85	2.687 (2)	176
O52—H52···O32	0.84	2.06	2.832 (2)	152
O22—H22···O21	0.84	2.46	2.715 (2)	99
O31—H31···O32	0.84	2.24	2.658 (2)	111
O52—H52···O51	0.84	2.23	2.644 (2)	110

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

Data collection: *COLLECT* (Nonius, 2004); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3079). Services for accessing these data are described at the back of the journal.

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