

**(4a*R*,8a*S*,9a*R*,10a*S*)-8a,9a-Difluoro-1,4,4a,5,8,8a,9,9a,10,10a-decahydroanthracene-4a,10a-diol hemihydrate**

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Received 13 June 2011

Accepted 21 June 2011

Online 5 July 2011

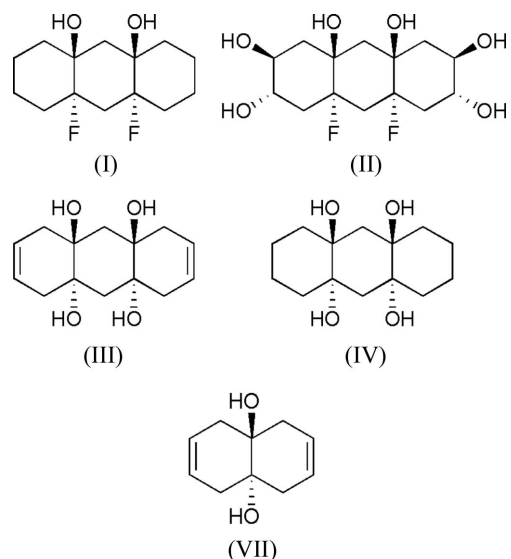
The title compound,  $C_{14}H_{18}F_2O_2 \cdot 0.5H_2O$ , a hemihydrate of a  $C_s$ -symmetric unsaturated difluorodiol, crystallizes in the centrosymmetric space group  $P2/m$  ( $Z = 4$ ). The asymmetric unit contains two crystallographically independent difluorodiol half-molecules, occupying the mirror planes at  $(x, 0, z)$  and  $(x, \frac{1}{2}, z)$ , and half a molecule of water, lying on the twofold axis at  $(0, y, 0)$ . Four difluorodiol molecules self-assemble around each solvent water molecule *via*  $O-H \cdots O$  hydrogen bonds in a near tetrahedral symmetry to generate a cylindrical column-like architecture.

**Comment**

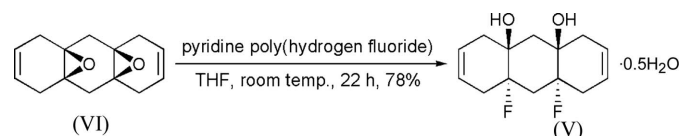
As part of our ongoing research, we have been actively involved in unravelling the interplay of various noncovalent interactions involved in the crystal structure of functionalized *trans*-decalins (Mehta *et al.*, 2007; Mehta & Sen, 2009*a,b*, 2010). The primary focus of this investigation has been the  $O-H \cdots O$  hydrogen-bonding networks in cyclitols (Posternak, 1962; Hudlicky & Cebulak, 1993) and their designer variants (polycyclitols) fashioned from a prototypical rigid 4a,8a-dihydroxy-*trans*-decalin backbone (Mehta & Ramesh, 2000, 2001; Nangia, 2010). In a recent endeavour along these lines, we reported the synthesis of the fluorinated polycyclitols (I) and (II), the solid-state self-assemblies of which were probed to elucidate the role of organic fluorine in crystal structures laden with  $O-H \cdots O$  hydrogen bonds (Mehta & Sen, 2010).

The motivation for undertaking this study came from one of the well known scientific debates of the recent past – does organic fluorine engage in hydrogen bonding? (Howard *et al.*, 1996; Dunitz & Taylor, 1997; Dunitz, 2004; Reichenbaeher *et al.*, 2005; Dunitz & Schweizer, 2006; Cozzi *et al.*, 2007). Being the most electronegative element and nearly isosteric with a hydroxy group (Bondi, 1964), covalently bonded fluorine might appear capable of mimicking an OH functionality as a potential hydrogen-bond acceptor. While a large body of scientific evidence points towards organic fluorine being a

weak hydrogen-bond acceptor, capable of engaging in  $C-F \cdots H-X$  ( $X$  is O, N or C) interactions (Madhavi *et al.*, 2000; Nangia, 2000; Vangala *et al.*, 2002; Desiraju, 2002; Mountford *et al.*, 2003; Li *et al.*, 2005; Bernet & Vasella, 2007; Borho & Xu, 2008; Chopra & Guru Row, 2011), other studies conclude that fluorine may not be involved in hydrogen bonding at all (Dunitz & Taylor, 1997; Dunitz, 2004; Dunitz & Schweizer, 2006; Cozzi *et al.*, 2007).

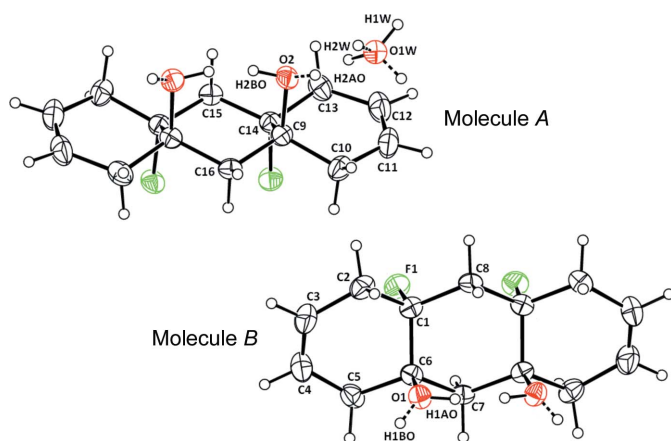


Interestingly, weak  $Csp^3-F \cdots H-Csp^3$  interactions were observed and supramolecular recognition units, involving such interactions, were found to be conserved in the crystal structures of (I) and (II). As a comparative study, inspired by a similar analysis carried out on the solid-state self-assemblies of (III) and (IV) (Mehta, Sen & Venkatesan, 2005), we report here the molecular packing of the title fluorinated polycyclitol (V), the common synthetic precursor to both (I) and (II), obtained as a single diastereomer in a one-pot regio- and stereoselective epoxide ring opening of the *syn*-diepoxide (VI) (Mehta *et al.*, 2007) with pyridine poly(hydrogen fluoride) (see reaction scheme).



The unsaturated difluorodiol (V) crystallizes as a hemihydrate in the centrosymmetric monoclinic space group  $P2/m$  ( $Z = 4$ ). The asymmetric unit contains two  $C_s$ -symmetric half-molecules (Fig. 1), occupying the mirror planes at  $(x, 0, z)$  and  $(x, \frac{1}{2}, z)$ , and half a molecule of water, lying on the twofold axis at  $(0, y, 0)$ . The symmetry constraints thus imposed on the molecules of water by their occupancy at the special positions introduce a disorder in the positions of atoms H1W and H2W bonded to them. In addition, the hydroxy H atoms on O1 and O2 in the asymmetric unit were also found to be disordered over two sites, *viz.* *A* and *B* (Fig. 1).

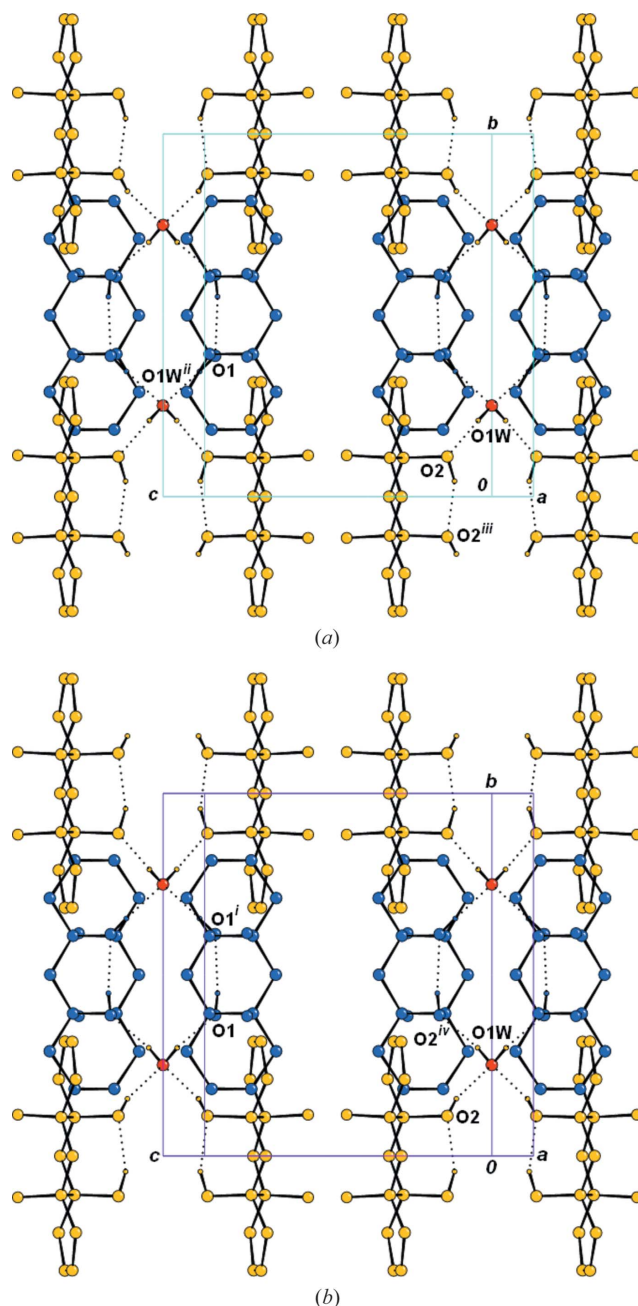
Physically, this disorder in the H-atom positions can be viewed as a statistical average of the two possible modes in

**Figure 1**

The molecular structure of the difluorodiol hemihydrate, (V), showing the atom-numbering scheme of the asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level. For the sake of clarity, the two crystallographically independent difluorodiol molecules have been labelled *A* and *B*. Unlabelled atoms are related to labelled atoms by the symmetry operators  $(x, -y + 1, z)$  and  $(x, -y, z)$  for molecules *A* and *B*, respectively. The disordered H atoms have been labelled in order to lend clarity to the discussion of O—H...O hydrogen bonding in (V).

which the 1,3-syndiaxial hydroxy groups in (V) can participate in intramolecular O—H...O hydrogen bonding while being linked to the water molecules through intermolecular O—H...O hydrogen bonds (Fig. 2). Thus, each water molecule exhibits a near tetrahedral coordination around the O atom and is hydrogen bonded to four molecules of (V) in a cylindrical column-like architecture, consisting of a hydrophilic interior and a hydrophobic exterior. The translationally related channels are held together primarily *via* van der Waals interactions, though soft C—H...F contacts ( $C2-H2B...F2 = 2.55 \text{ \AA}$  and  $131^\circ$ ) can also be discerned between them.

While understandably bearing very little resemblance to the molecular packing in anhydrous (I), the water-directed solid-state self-assembly of (V) displays an uncanny similarity to that observed for the crystalline monohydrate of the  $C_{2h}$ -symmetric diol (VII) (Mehta, Sen & Ramesh, 2005). Crystallizing in the centrosymmetric tetragonal space group  $P4_2/m$  ( $Z = 2$ ), the  $C_{2h}$ -symmetric diol molecules of (VII) occupy centres of symmetry at  $(\frac{1}{2}, 0, 0)$  and  $(0, \frac{1}{2}, \frac{1}{2})$  (site symmetry  $2/m$ ), while the water molecules are located on the  $4_2$  axis at special positions  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{4})$  and  $(\frac{1}{2}, \frac{1}{2}, \frac{3}{4})$  (site symmetry  $\bar{4}$ ). Consequently, a disorder in the positions of the O-bound H atoms – nearly identical to that observed in (V) – and a highly symmetric tetrahedral arrangement of the diol molecules around each molecule of water are also noted in the crystal structure of (VII). A possible rationale for the observed similarities in the water-directed self-assemblies of (V) and (VII) might lie in (a) a compatible match between the hydroxy group and water as being able to function as both hydrogen-bond donors and acceptors, and (b) the maximization of the hydrogen bonding and the formation of extended hydrogen-bonding chains by allowing water molecules to act as bridges between the less accessible axially locked tertiary hydroxy groups.

**Figure 2**

The molecular packing of (V), showing the tetrahedral coordination of the difluorodiol molecules around the solvent water molecules. The disorder in the positions of the water H atoms and the hydroxy groups can be modelled as the statistical average of O—H...O hydrogen-bonding modes (a) and (b). Non-interacting H atoms have been removed for clarity. Dotted lines indicate O—H...O hydrogen bonds. (In the electronic version of the paper, difluorodiol molecules *A* and *B* are shown in blue and orange, respectively.) (Symmetry codes as in Table 1.)

## Experimental

Details pertaining to the synthesis and spectroscopic characterization of (V) have already been reported (Mehta & Sen, 2010). Single crystals of (V) suitable for X-ray diffraction studies were grown by slow solvent evaporation from a solution in dichloromethane under ambient temperature and pressure.

**Table 1**

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1A O...O1 <sup>i</sup>	0.81 (4)	1.93 (4)	2.664 (2)	150 (3)
O1—H1B O...O1W <sup>ii</sup>	0.76 (4)	2.00 (4)	2.762 (2)	174 (4)
O2—H2A O...O1W	0.77 (3)	2.02 (3)	2.769 (2)	165 (3)
O2—H2B O...O2 <sup>iii</sup>	0.85 (4)	1.85 (4)	2.641 (2)	155 (3)
O1W—H1W...O1 <sup>iv</sup>	0.85 (4)	1.92 (4)	2.762 (2)	172 (4)
O1W—H2W...O2	0.85 (3)	1.92 (3)	2.769 (2)	179 (4)

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

*Crystal data*

C<sub>14</sub>H<sub>18</sub>F<sub>2</sub>O<sub>2</sub>·0.5H<sub>2</sub>O

*M<sub>r</sub>* = 265.29

Monoclinic, *P2*/*m*

*a* = 10.812 (2) Å

*b* = 11.942 (2) Å

*c* = 10.868 (2) Å

β = 102.274 (3)°

*V* = 1371.2 (4) Å<sup>3</sup>

*Z* = 4

Mo *K*α radiation

μ = 0.10 mm<sup>-1</sup>

*T* = 291 K

0.12 × 0.09 × 0.08 mm

*Data collection*

Bruker SMART APEX CCD area-detector diffractometer

Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)

*T<sub>min</sub>* = 0.988, *T<sub>max</sub>* = 0.992

10273 measured reflections

2677 independent reflections

1857 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.024

*Refinement*

*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.042

*wR* (*F*<sup>2</sup>) = 0.124

*S* = 1.02

2677 reflections

198 parameters

2 restraints

H atoms treated by a mixture of independent and constrained refinement

Δρ<sub>max</sub> = 0.26 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.14 e Å<sup>-3</sup>

The methine (CH) and methylene (CH<sub>2</sub>) H atoms were placed in geometrically idealized positions and allowed to ride on their parent atoms, with C—H = 0.93 and 0.97 Å respectively, and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C). All O-bound H atoms were located in a difference Fourier map. Their positions were refined freely, along with an isotropic displacement parameter. However, a DFIX restraint (*SHELXL97*; Sheldrick, 2008) was applied to the O—H distances [target value 0.84 (2) Å] for each of the two H atoms of the water molecule while refining their positions.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 1998); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *PLATON* (Spek, 2009).

The authors thank the Department of Science and Technology (DST), India, for the SMART APEX CCD facility at the Indian Institute of Science (IISc), Bangalore. GM thanks the Council for Scientific and Industrial Research (CSIR), India, for research support and the award of a Bhatnagar Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: EG3073). Services for accessing these data are described at the back of the journal.

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