N,N'-Bis[tris(hydroxymethyl)methyl]-ethanediamide: six O—H···O hydrogen bonds generate only a two-dimensional structure

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Molecules of the title compound, $C_{10}H_{20}N_2O_8$, adopt a conformation which is almost centrosymmetric. The molecules are disordered over two sets of sites with an occupancy ratio of 0.94:0.06. In the major form, there are two intramolecular O—H···O hydrogen bonds [O···O 2.756 (4) and 2.765 (4) Å; O—H···O 144 and 146°], in which the two amidic O atoms act as acceptors. In addition, there are four intermolecular O—H···O hydrogen bonds [O···O 2.650 (3)–2.666 (3) Å; O—H···O 158–171°]; these link each molecule to six others in a continuous sheet structure which contains five distinct ring motifs, two of the $S(7)$ type, two of the $R_3^3(10)$ type and one of the $R_2^2(22)$ type.

Comment

Molecules of pentaerythritol, $C(CH_2OH)_4$, have crystallographically imposed $\bar{4}$ (S_4) symmetry in the solid state and the hydroxyl groups act as both hydrogen-bond donors and hydrogen-bond acceptors; the molecules are linked by O—H···O hydrogen bonds into sheets built from $R_4^4(8)$ and $R_2^2(12)$ rings arranged in a checkerboard fashion (Ladd, 1979; Eilerman & Rudman, 1979a; Hope & Nichols, 1981; Semmingsen, 1988; Katrusiak, 1995). Although each molecule participates in eight hydrogen bonds, and is thereby linked to four other molecules in a (4,4)-net (Batten & Robson, 1998), the elegant simplicity of the supramolecular structure owes much to the symmetry equivalence of all the hydrogen bonds.

In the ordered orthorhombic phase of the related aminotriol $H_2NC(CH_2OH)_3$ (Eilerman & Rudman, 1980; Castellari & Ottani, 1997), the amino group and the three hydroxyl groups all act as both donors and acceptors of hydrogen bonds. However, since the molecules lie in general positions, there are four distinct hydrogen bonds in the structure, two of the O—H···O type and one each of the O—H···N and

N—H···O types; the hydrogen bonding is thus of considerable complexity although the supramolecular aggregation is still two-dimensional, as in pentaerythritol. There is also a cubic plastic phase of this material, with $Z = 2$ in space group $Im3m$ (Eilerman & Rudman, 1980), but the orientational disorder of the molecules in this phase precludes detailed discussion of the hydrogen bonding. By contrast, in tris(hydroxymethyl)-acetic acid, $HOOCC(CH_2OH)_3$ (Eilerman & Rudman, 1979b), the hydrogen bonding generates a three-dimensional supramolecular structure, although the $R_2^2(8)$ motif so characteristic of carboxylic acids is absent; this material also exhibits a disordered cubic phase, with $Z = 4$ in space group $Fm3m$ (Doshi et al., 1973).
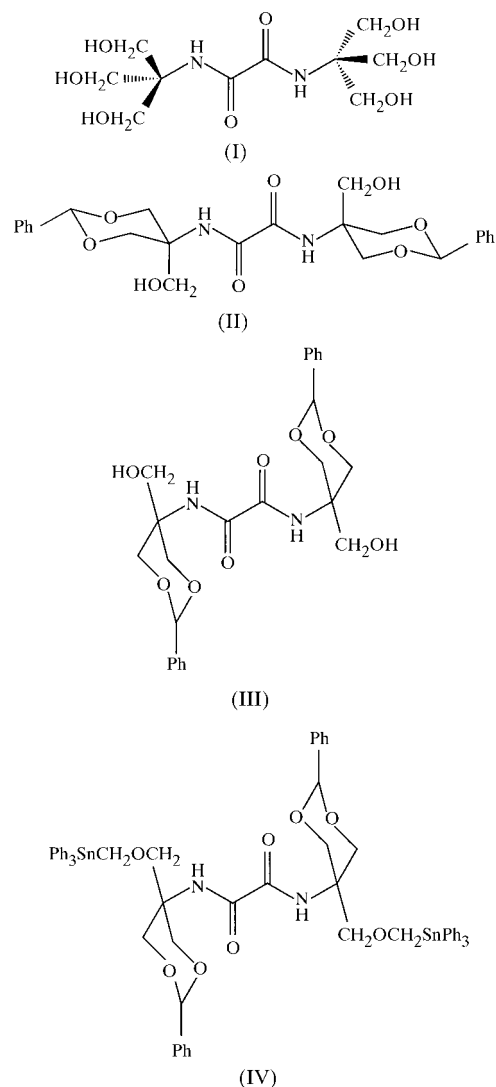
In view of the two-dimensional aggregation in both $C(CH_2OH)_4$ and ordered $H_2NC(CH_2OH)_3$, and the three-dimensional aggregation in ordered $HOOCC(CH_2OH)_3$, it is of interest to investigate the structure of the related hexahydroxy analogue N,N'-bis[tris(hydroxymethyl)methyl]-ethanediamide, $(HOCH_2)_3CNHCOCONHC(CH_2OH)_3$, (I), originally synthesized (DuBois et al., 1992) as one of the more recent examples in a long series of adventitious sweetening agents (Exodus, undated pp. xvi, vv, 13–15, 31; Grami, 1998).

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organic compounds

Molecules of (I) (Fig. 1) lie in general positions in space group $Pna2_1$; they are disordered over two sets of sites with occupancies of 0.94 and 0.06, and the two sets of sites are approximately related to one another by reflection across the plane $y = 0.75$. Because of the constraints applied to the minor component, only the major component will be discussed. For the major form, the overall dimensions and the conformation indicate that the molecules are close to being centrosymmetric; in particular, corresponding pairs of torsion angles have closely similar magnitudes with opposite signs. However, a search for possible additional symmetry showed that none was present; this is so even if all the H atoms are ignored. The non-centrosymmetric nature of the molecules in (I) may be contrasted with the behaviour of derivatives (II)–(IV), in all of which the molecules lie across centres of inversion (Ross *et al.*, 1996*a,b*). The central portion of the molecule is essentially planar, with neighbouring N—H and C=O units mutually *trans*; the central C—C bond is long, as typically found in oxalic acid derivatives (de With & Harkema, 1977; Allen *et al.*, 1987; Ross *et al.*, 1996*a,b*).
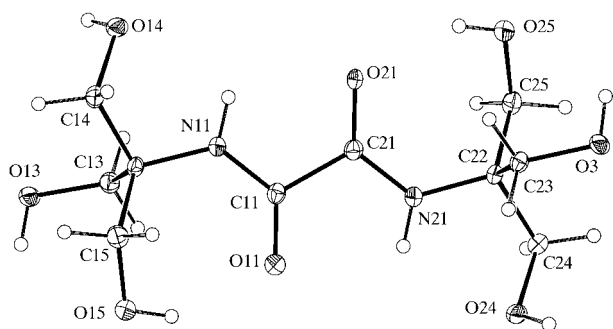

Figure 1
The major form of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Each of the hydroxyl groups in (I) acts both as a hydrogen-bond donor and as a hydrogen-bond acceptor, but the N—H units play no role in the supramolecular aggregation (Table 2). There are two intramolecular O—H$\cdots$O hydrogen bonds, each of which generates an $S(7)$ motif (Fig. 2). Each molecule therefore acts as a fourfold donor and acceptor in intermolecular hydrogen bonds, and each molecule is thereby linked to six others in the resulting two-dimensional structure, but by adoption of the substructure approach (Gregson *et al.*, 2000), the rather complex supramolecular aggregation can readily be analysed in terms of three simple motifs.

Atoms O13 and O23 in the molecule at (x, y, z) act as donors to O14 at $(x, -1 + y, z)$ and to O24 at $(x, 1 + y, z)$, respectively. Propagation of these two hydrogen bonds generates a molecular ladder running parallel to the [010] direction; the two rungs of the ladder consist of independent $C(6)$ chains, while the molecular backbone from O13 to O23 provides the rungs of the ladder (Fig. 2). Between the rungs there are $R_2^2(22)$ rings, in the interior of which are the $S(7)$ rings.

The [010] ladders are linked by two independent spiral-chain motifs. Atom O14 in the molecule at (x, y, z) acts as donor to O23 at $(-\frac{1}{2} + x, \frac{3}{2} - y, z)$, while O14 at $(-\frac{1}{2} + x, \frac{3}{2} - y, z)$ in turn acts as donor to O23 at $(-1 + x, y, z)$; in this manner is generated a $C(11)$ spiral around the 2_1 screw axis along $(x, \frac{3}{4}, 0)$. Similarly, O24 at (x, y, z) acts as donor to O13 at $(\frac{1}{2} + x,$
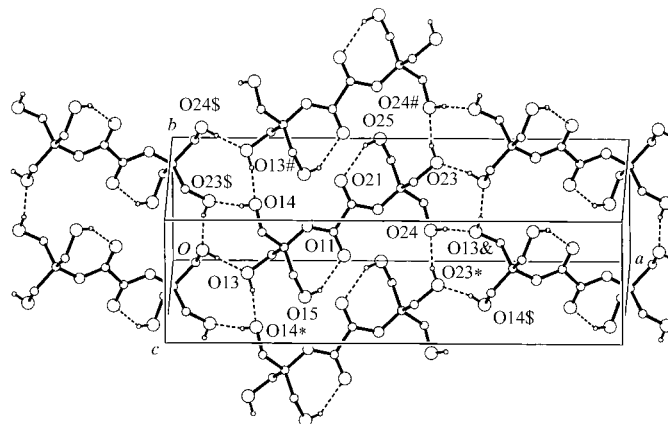

Figure 2
Part of the crystal structure of (I) showing the formation of a (001) sheet. For the sake of clarity, only the major form is shown, and H atoms bonded to C or N atoms have been omitted. Atoms marked with an asterisk (*), hash (#), dollar sign ($) or ampersand (&) are at the symmetry positions $(x, -1 + y, z)$, $(x, 1 + y, z)$, $(-\frac{1}{2} + x, \frac{3}{2} - y, z)$ and $(\frac{1}{2} + x, \frac{1}{2} - y, z)$, respectively.

$\frac{1}{2} - y, z)$ and propagation of this interaction generates a second $C(11)$ spiral around the 2_1 screw axis along $(x, \frac{1}{2}, 0)$. The combined effect of these two independent $C(11)$ chains along [100] is to link the [010] ladders into a sheet parallel to (001). This sheet is built from two types of $R_3^3(10)$ ring, in addition to the $R_2^2(22)$ ring and the two types of $S(7)$ ring noted earlier (Fig. 2). The reference (001) sheet lies in the domain $-0.09 < z < 0.47$, and a second sheet runs through the unit cell in the domain $0.41 < z < 0.97$. There are no hydrogen bonds between adjacent sheets, so that the supramolecular aggregation is two-dimensional.

Experimental

A sample of (I) was prepared according to the published procedure of DuBois *et al.* (1992). Crystals suitable for single-crystal X-ray diffraction were obtained from a solution in ethanol.

Crystal data

$C_{10}H_{20}N_2O_8$	Mo $K\alpha$ radiation
$M_r = 296.28$	Cell parameters from 9375
Orthorhombic, $Pna2_1$	reflections
$a = 21.4097 (3)$ Å	$\theta = 2.9$–$27.5°$
$b = 6.1559 (6)$ Å	$\mu = 0.13$ mm^{-1}
$c = 10.0605 (13)$ Å	$T = 150 (2)$ K
$V = 1325.9 (2)$ Å^3	Needle, colourless
$Z = 4$	$0.30 \times 0.10 \times 0.10$ mm
$D_x = 1.484$ Mg m^{-3}	

Data collection

KappaCCD diffractometer	1573 independent reflections
φ and ω scans with κ offsets	1282 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{int} = 0.101$
(*DENZO–SMN*; Otwinowski &	$\theta_{max} = 27.5°$
Minor, 1997)	$h = -25 \rightarrow 27$
$T_{min} = 0.962$, $T_{max} = 0.987$	$k = -6 \rightarrow 7$
7853 measured reflections	$l = -9 \rightarrow 12$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.047$	$w = 1/[\sigma^2(F_o^2) + (0.0800P)^2]$
$wR(F^2) = 0.120$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
1573 reflections	$\Delta\rho_{max} = 0.26$ e Å^{-3}
235 parameters	$\Delta\rho_{min} = -0.28$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C11—O11	1.242 (4)	C21—O21	1.229 (3)
C11—N11	1.323 (4)	C21—N21	1.332 (4)
N11—C12	1.470 (4)	N21—C22	1.467 (4)
C11—C21	1.535 (4)		
O11—C11—N11	127.1 (3)	O21—C21—N21	126.9 (3)
O11—C11—C21	120.4 (3)	O21—C21—C11	120.3 (3)
N11—C11—C21	112.5 (2)	N21—C21—C11	112.8 (2)
C11—N11—C12	127.8 (3)	C21—N21—C22	126.7 (2)
C12—N11—C11—C21	176.3 (3)	C22—N21—C21—C11	−175.8 (3)
C12—N11—C11—O11	−5.3 (6)	C22—N21—C21—O21	4.2 (6)
O11—C11—C21—O21	−179.8 (5)	N11—C11—C21—N21	178.8 (4)
C11—N11—C12—C13	−75.8 (4)	C21—N21—C22—C23	78.7 (4)
C11—N11—C12—C14	165.4 (3)	C21—N21—C22—C24	−163.8 (3)
C11—N11—C12—C15	47.3 (5)	C21—N21—C22—C25	−45.0 (4)
N11—C12—C13—O13	−175.4 (2)	N21—C22—C23—O23	176.5 (2)
N11—C12—C14—O14	50.6 (4)	N21—C22—C24—O24	−50.7 (3)
N11—C12—C15—O15	−86.3 (3)	N21—C22—C25—O25	87.9 (3)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O13—H13$\cdots$O14^i	0.84	1.85	2.652 (3)	158
O14—H14$\cdots$O23^{ii}	0.84	1.82	2.650 (3)	167
O15—H15$\cdots$O11	0.84	2.03	2.765 (4)	146
O23—H23$\cdots$O24^{iii}	0.84	1.84	2.658 (3)	163
O24—H24$\cdots$O13^{iv}	0.84	1.84	2.666 (3)	171
O25—H25$\cdots$O21	0.84	2.03	2.756 (4)	144

Symmetry codes: (i) $x, y - 1, z$; (ii) $x - \frac{1}{2}, \frac{3}{2} - y, z$; (iii) $x, 1 + y, z$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, z$.

Compound (I) is orthorhombic. The systematic absences permitted $Pna2_1$ and $Pnam$ as possible space groups, and since the unit-cell volume indicated $Z = 4$, $Pna2_1$ was selected and confirmed by the subsequent structure analysis; no additional symmetry could be detected in the refined structure. H atoms were treated as riding with C—H = 0.99 Å, N—H = 0.88 Å and O—H = 0.84 Å. The quality of the diffraction data was poor, even at 150 (2) K, with an R_{int} value of 0.101. It was apparent from the residual electron densities that the diffraction data could not be completely satisfied by just one molecular orientation, and it became clear that there was a small contribution from a second orientation of the molecule, whose occupancy derived from various refinements ranged from 0.058 (3) to 0.066 (3),

and whose coordinates were approximately related to those of the major form by reflection across the plane $y = 0.75$. Free refinement of this component led to highly unrealistic interatomic distances and so it was handled *via* an extensive series of *DFIX* commands constraining all of the distances and some of the angles. O21*B* lay at the centre of a rather broad region of residual electron density, and attempts to refine its coordinates were unsuccessful; accordingly, its coordinates were fixed. To ensure the stability of the final refinements, the minor component was assigned a common isotropic displacement parameter and the occupancy was fixed at 0.06. In the absence of any significant anomalous scatterers, the refined Flack parameter (Flack, 1983) of −1.3 (18) was inconclusive (Flack & Bernardinelli, 2000); hence the Friedel equivalents were merged before the final refinements.

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 (Sheldrick, 1997) and *PRPKAPPA* (Ferguson, 1999).

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