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2,4,6-Tris{[(*S*)-1-hydroxy-3-methylbutan-2-ylamino]methylene}cyclohexane-1,3,5-trione

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.010 Å
Disorder in main residue
R factor = 0.066
wR factor = 0.202
Data-to-parameter ratio = 9.3

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

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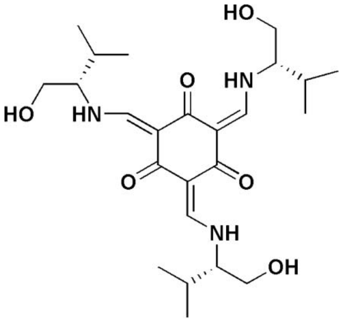
The title compound, $C_{24}H_{39}N_3O_6$, also known as tris[(*S*)-*N*-salicylidenevalinol], crystallizes with two molecules in the asymmetric unit. These two molecules form a disc-shaped dimeric box and are linked to each other through 11 O—H···O hydrogen bonds. These self-assembled dimers are connected by a 12th hydrogen bond to form a one-dimensional hydrogen-bonded network along the *b*-axis direction.

Comment

Hydrogen-bonded dimeric aggregates in capsules, cages and boxes have been well studied in systems like substituted glycoluril (Wyler *et al.*, 1993), calixarenes (Conn & Rebek, 1997) and resorcinarenes (MacGillivray & Atwood, 1997). Recently, hydrogen-bonded dimers have also been reported in urea derivatives of C_3-symmetric tripodal tribenzylamines (Alajarin *et al.*, 2004) and triphenylmethanes (Rudzevich *et al.*, 2005). In the present investigation we report a new type of self-assembled one-dimensional hydrogen-bonded dimer, (I), in a zigzag network derived from C_3-symmetric tripodal tris[(*S*)-*N*-salicylidenevalinol] (TSV).



(I)

Fig. 1 shows the two monomers of the asymmetric unit. Fig. 2 shows two dimers with their intra- and inter-dimer hydrogen-bonding arrangements. Compound (I) is in the keto–enamine form in the solid state. The central cyclohexanetrione unit is similar to that of tris(*N*-salicylideneaniline) (Chong *et al.*, 2003). Even though the aromaticity of the central benzene ring is lost as a result of the tautomerism, the central ring is planar. The cyclohexanetrione ring $Csp^2—Csp^2$ single bonds average a distance of 1.445 Å, typical of conjugation. The six consecutive double bonds connected to the ring C atoms make the ring planar. The cyclohexanetrione C═O bond lengths observed in the structure are characteristic of ketones rather than phenols, and the C—N bond is elongated relative to that

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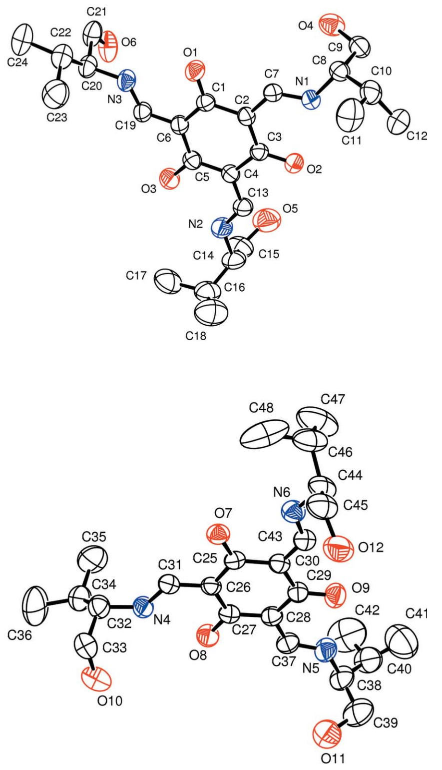

Figure 1
The structures of the two molecules in the asymmetric unit, with 40% probability displacement parameters. H atoms have been omitted for the sake of clarity.

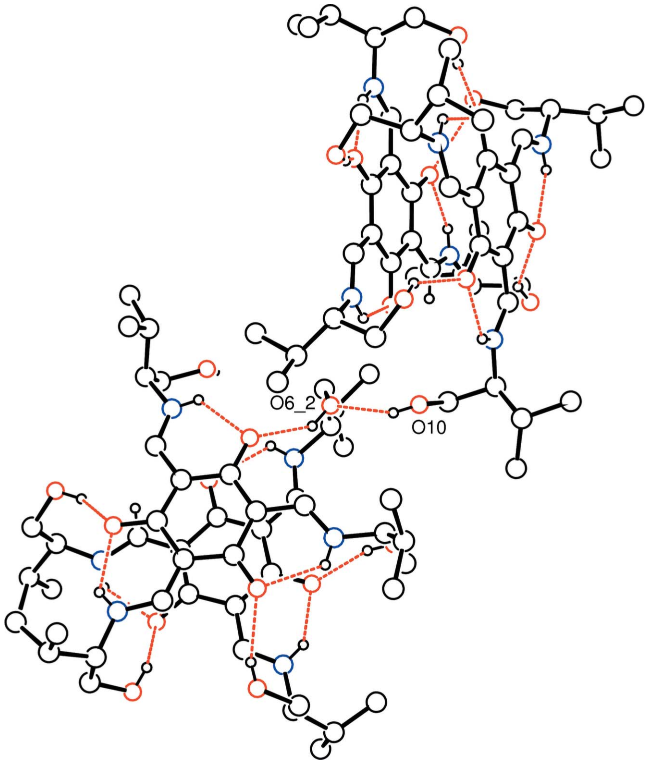

Figure 2
Two dimers with intra- and inter-dimer hydrogen-bonding arrangements. Hydrogen bonds are shown as dashed lines and H atoms not involved in these interactions have been omitted. [Symmetry code: (_2) $-x + 2, y - \frac{1}{2}, -z + 1$.]

of a typical imine. The two molecules of the asymmetric unit that form the dimer are nearly identical and are held together by hydrogen bonding and π–π interactions. The dihedral angle between the ring planes of the dimer is 1.0 (4)°, and the distance between the ring centroids is 3.411 Å. The molecules of the dimer are staggered by about 30°. The CH_2OH groups of the three amino alcohols are arranged nearly at right angles to the cyclohexatrione plane. The conformation of one of the six amino alcohol chains of the dimer differs from the others in that the terminal hydroxyl group (O10/H10*A*) is positioned to form an O—H⋯O hydrogen bond with the neighbouring dimer. The other five amino alcohol groups have nearly the same conformation, and their hydroxyl groups form intra-dimer O—H⋯O hydrogen bonds with keto O atoms. Details of the hydrogen-bond geometry are reported in Table 1. The hydrogen-bonded pairs of dimers propagate along the *b* axis. The packing of the molecules in the unit cell shows a large irregular-shaped void about the middle of the *ac* face which runs as a cavity parallel to the *b* axis. The cavity is mostly surrounded by hydrophobic isopropyl groups. The presence of this cavity must be responsible for the low density (1.026 Mg m^{-3}) of the substance.

Experimental

1,3,5-Triformylphloroglucinol was synthesized by Duff formylation of phloroglucinol (Duff & Bills, 1941). To a solution of 1,3,5-triformylphloroglucinol (1 mmol) in 1 ml of ethanol was added a solution of (*S*)-2-aminovalinol (3.2 mmol) in 1 ml of ethanol. This homogeneous mixture was irradiated in an unmodified domestic microwave oven at low power setting for 5 min. The reaction mixture was cooled to room temperature and ethanol was removed under reduced pressure. The crude product was purified by column chromatography over silica gel using 5% MeOH/EtOAc to afford pure yellow solid tris[(*S*)-*N*-salicylidenevalinol] (96% yield). The crystals were grown by slow diffusion of hexane into dichloromethane solution.

Crystal data

$C_{24}H_{39}N_3O_6$
$M_r = 465.58$
Monoclinic, $P2_1$
$a = 16.7989$ (12) Å
$b = 11.2993$ (14) Å
$c = 16.9258$ (12) Å
$\beta = 110.190$ (5)°
$V = 3015.4$ (5) Å^3

$Z = 4$
$D_x = 1.026$ Mg m^{-3}
Cu $K\alpha$ radiation
$\mu = 0.60$ mm^{-1}
$T = 293$ (2) K
Rectangular block, dark yellow
0.4 × 0.3 × 0.3 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.964$, $T_{\max} = 0.998$ (expected range = 0.807–0.835)
5998 measured reflections

5791 independent reflections
3817 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.053$
$\theta_{\max} = 68.0$°
2 standard reflections every 1 hour intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.066$
$wR(F^2) = 0.202$
$S = 1.04$
5791 reflections
621 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1452P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00035 (15)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4···O7	0.82	2.09	2.726 (5)	135
O5—H5···O9	0.82	2.14	2.822 (6)	141
O6—H6···O8	0.82	1.96	2.652 (5)	142
O10—H10*A*···O6^{i}	0.82	2.03	2.793 (7)	156
O11—H11···O3	0.82	2.01	2.806 (10)	163
O12—H12···O2	0.82	2.05	2.716 (5)	138
N1—H1N···O2	0.834 (10)	2.03 (5)	2.658 (5)	132 (6)
N2—H2N···O3	0.827 (11)	1.89 (4)	2.591 (5)	142 (6)
N3—H3N···O1	0.823 (10)	2.12 (4)	2.656 (5)	122 (3)
N4—H4N···O8	0.83 (5)	2.06 (5)	2.625 (6)	125 (5)
N5—H5N···O9	0.831 (10)	2.04 (5)	2.622 (6)	127 (5)
N6—H6N···O7	0.830 (10)	2.04 (4)	2.636 (5)	128 (4)

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

In the absence of significant anomalous scattering effects, Friedel pairs were merged; the absolute configuration is known from the synthesis. All the H atoms could be located in a difference Fourier map. However, the C- and O-bound H atoms were positioned geometrically and refined using a riding model, with U_{iso}(H) = $1.2U_{eq}$(C,O). The aromatic C—H distances were fixed at 0.93 Å while the tertiary CH, secondary CH_2 and primary CH_3 were assigned distances of 0.98, 0.97 and 0.96 Å, respectively. The hydroxyl H atoms were fixed at 0.82 Å. The amine H atoms were restrained to a distance of 0.830 (1) Å from N atoms. This was done to avoid abnormal bond distances. Atom O11 showed a positional disorder due to thermal motion; site occupancy factors for O11 and O11′ refined to 0.70 (2) and 0.30 (2), respectively. The positions of O11 and O11′ were restrained with C—O distances of 1.410 (1) Å. No anisotropic displacement parameters were assigned for O11 and O11′ as that would lead to further meaningless splitting of positions. The bond distance C40—C42 in a terminal isopropyl group was restrained to 1.530 (1) Å.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-32* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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