N,N'-Bis(2-hydroxybenzylidene)-pentane-1,5-diamine

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In the title potential O,N,N',O'-tetradentate Schiff base ligand {systematic name: 2,2'-[pentane-1,5-diylbis(nitrilomethylidyne)]diphenol}, $C_{19}H_{22}N_2O_2$, the mutual orientation of the three planar fragments determines the conformation of the molecule. The dihedral angles between the planes of the two salicylidene groups and the plane of the central extended pentane chain are 78.4 (2) and 62.0 (3)°, and the angle between the terminal ring planes is 55.4 (1)°. Strong intramolecular O—H···N hydrogen bonds close almost-planar six-membered rings, and the O—H bonds are elongated as a result of hydrogen-bond formation.

Comment

Much effort has been devoted in recent years to the design and synthesis of salicylaldimines and their metal complexes displaying binding properties toward deoxyribonucleic acid (DNA), with the aim of developing novel therapeutic agents which prevent the growth and replication of cancerous cells (Silvestri *et al.*, 2007). Among the chemical moieties which have been used as part of chemotherapeutic agents are biogenic polyamines (Karigiannis & Papaioannou, 2000). The incorporation of biogenic polyamine fragments with flexibility and strong affinity for nucleic acids can prompt the emergence of new architectures with novel physicochemical properties and potential applications in technology and pharmaceutics. It seemed, therefore, to be of interest for us to synthesize the new salicylaldimine system derived from cadaverine, a biogenic amine.
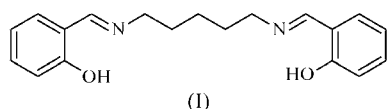
The conformation of the title compound, (I), and its analogues can be described by the mutual orientation of three approximately planar fragments, *A*, *B* and *C* (Fig. 1): two salicylidene groups, for which the maximum deviations from the least-squares plane through nine atoms are 0.018 (3) Å for

fragment *A* and 0.067 (3) Å for fragment *B*, and the central pentane chain (*C*), which adopts the exended conformation and is planar to within 0.044 (2) Å. The corresponding dihedral angles are: *A/C* = 78.4 (2)°, *B/C* = 62.0 (3)° and *A/B* = 55.4 (1)°. It should be noted that the conformation is not symmetrical. For fragment *A*, atom N8 is almost coplanar with the plane of the pentane chain [N8—C9—C10—C11 torsion angle 177.1 (3)°], while atom N14 is displaced by almost 1.5 Å [N14—C13—C12—C11 = 68.0 (4)°] from this plane.

In the analogues of (I) with different aliphatic chain lengths, two conformations are observed, depending on the presence of an even or odd number of atoms in the chain. This is related to the symmetry of the molecule, which is also a function of
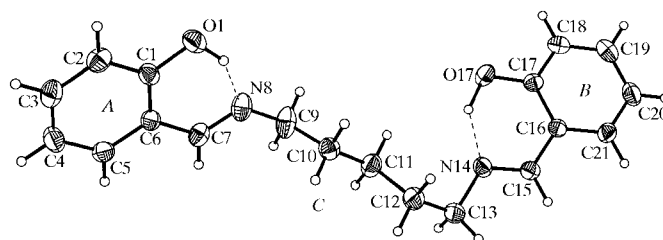
Figure 1
The molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The three fragments are denoted *A*, *B* and *C*.
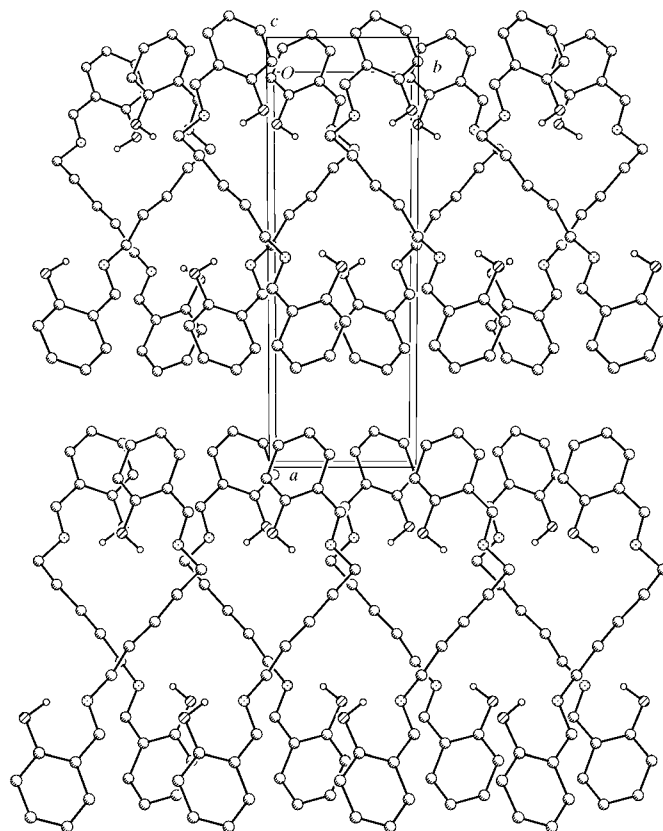
Figure 2
The crystal packing of (I), as seen approximately along the *c* direction.

the number of atoms in the aliphatic chain. For aliphatic chains with an even number of C atoms, the molecule can be centrosymmetric, with the centre of symmetry situated at the middle of the central C—C bond. In this case, due to the symmetry, the terminal ring planes have to be exactly parallel. This symmetry is realised in the analogues of (I) with $n = 2$ (Bresciani Pahor *et al.*, 1978; in this case the symmetry is only approximate), $n = 4$ (Kennedy & Reglinski, 2001), $n = 6$ (Sheikhshoaie & Sharif, 2006) and $n = 10$ (Yu, 2006). The same symmetry is also observed for a dioxo derivative of the $n = 8$ compound, *viz.* 2,2-[3,6-dioxa-1,8-octanediylbis(nitrilomethylidene)]bisphenol (Etemadi *et al.*, 2004).

When the number of C atoms in the chain is odd, the molecule cannot be centrosymmetric, and this is the case for (I), as well as for the molecules with $n = 1$, which lies on a twofold axis (Novitchi *et al.*, 2002), and $n = 3$ (Elderman *et al.*, 1991), with the molecule on a general position.

Interestingly, despite the different conformations, in three 'intermediate-length' cases ($n = 4$, 5 and 6), the shape of the unit cell is similar. In particular, the *b* axes, which are parallel to the twofold screw axes for $n = 4$ and $n = 6$, are almost equal (*ca* 5.7 Å). In the case of (I), a pseudo-2_1 axis can be found along *b* (Fig. 2).

Short intramolecular O—H···N hydrogen bonds serve to close the almost planar six-membered rings [maximum deviations of 0.03 (3) and 0.06 (3) Å for fragments *A* and *B*, respectively]. The H atoms involved in these bonds (H1 and H17) are significantly displaced towards acceptor N atoms; the refined O—H distances are long in comparison with typical values. The reliability of these results is demonstrated by the difference Fourier maps (Fig. 3) calculated for a model without these H atoms.
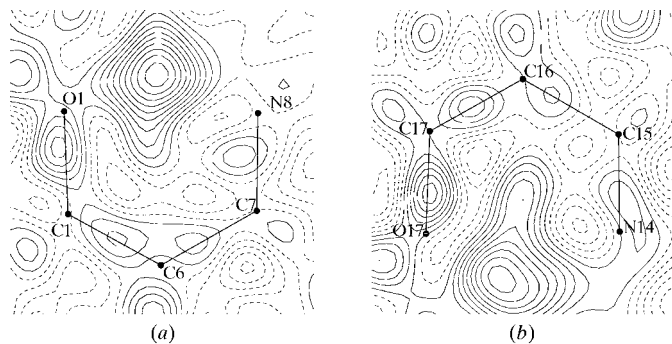

Figure 3
The difference Fourier maps calculated for a model without H atoms involved in intramolecular hydrogen bonds: (*a*) H1 and (*b*) H17. Solid lines indicate positive values and dashed lines indicate negative values. Contour level = 0.04 e Å^{-3}.

Experimental

To a solution of salicylaldehyde (0.4 mmol) in ethanol (30 ml), a solution of cadaverine (0.1 mmol) in methanol (30 ml) was added dropwise over a period of 30 min with stirring. The reaction was carried out for 72 h under an argon atmosphere. The solution volume was then reduced to 5 ml by rotary evaporation and the remaining solution was left to stand in a freezer. After 7 d, yellow crystals of (I) suitable for X-ray diffraction analysis were isolated.

Crystal data

$C_{19}H_{22}N_2O_2$	$V = 825.88 (14)$ Å^3
$M_r = 310.39$	$Z = 2$
Monoclinic, Pc	Mo $K\alpha$ radiation
$a = 16.3631 (18)$ Å	$\mu = 0.08$ mm^{-1}
$b = 5.6428 (5)$ Å	$T = 100 (1)$ K
$c = 9.1251 (8)$ Å	$0.45 \times 0.3 \times 0.2$ mm
$\beta = 101.418 (10)°$	

Data collection

Kuma KM-4 CCD four-circle diffractometer	1868 independent reflections
	1484 reflections with $I > 2\sigma(I)$
8735 measured reflections	$R_{int} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.063$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.113$	
$S = 1.15$	
1868 reflections	$\Delta\rho_{max} = 0.36$ e Å^{-3}
216 parameters	$\Delta\rho_{min} = -0.25$ e Å^{-3}
2 restraints	

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N8	1.00 (7)	1.64 (7)	2.552 (5)	148 (6)
O17—H17···N14	1.20 (6)	1.55 (6)	2.555 (5)	136 (5)
C13—H13A···O17^i	0.99	2.60	3.533 (6)	156

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

The H atoms of the hydroxy groups were found in a difference Fourier map (*cf.* Fig. 3) and their positional and isotropic displacement parameters were refined (see Table 1). The other H atoms were placed in idealized positions and refined as riding, with C—H = 0.95–0.99 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. Since the molecule is not chiral and lacks any heavy atoms, Friedel pairs were merged before the final refinement.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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