

A zwitterion of 1,5-bis(2-hydroxybenzamido)-3-azapentane: a two-dimensional hydrogen-bonding network involving dimers

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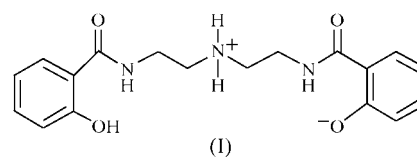
The title compound, 2-*N*-[2-(2-hydroxybenzamido)ethylammonioethyl]aminocarbonylphenolate, $C_{18}H_{21}N_3O_4$, crystallizes in a zwitterionic form as a result of intermolecular proton transfer and possesses a negatively charged phenolate group and a protonated amino group. The 2-hydroxybenzamide and 2-(aminocarbonyl)phenolate moieties attached to the two ends of the C—C—N—C—C backbone adopt a *cis* conformation in relation to this backbone. All N- and O-bound H atoms are involved in hydrogen-bond formation; the zwitterions are first linked into head-to-tail dimers, which are further organized into a two-dimensional network parallel to the crystallographic *bc* plane.

Comment

There is considerable interest in complexes that are capable of mimicking the active sites of metalloproteins (Cao *et al.*, 2004; Tolman & Spencer, 2001; Xing & DeRose, 2001). Generally, these model complexes are obtained from bulky multidentate ligands in order to construct an environment similar to that found in the proteins. 1,5-Bis(2-hydroxybenzamido)-3-azapentane, bhap, is a potentially pentadentate coordinating ligand containing N- and O-donor atoms, and has been synthesized in order to study its coordination behavior with several transition metal ions (*e.g.* Zn^{2+} , Cu^{2+} and Co^{2+} , which are the most abundant and important metals in biology; Lipscomb & Sträter, 1996). In previous reports, this compound exhibited different chelating modes in the formation of mononuclear or binuclear complexes with copper(II) (Sureshan & Bhattacharya, 1999) and iron(III) ions (Dash & Rath, 2004; Rath *et al.*, 2002). However, to the best of our knowledge, there are no published data related to the crystal structure of either bhap or its complexes mentioned above.

It is commonly accepted that the aliphatic amino group acts as a comparatively strong base, whereas the phenol group, as

an acid, can be deprotonated in a polar medium. Recently, it was reported that some 5,5'-derivatives of 3-diethylamino-methyl-2,2'-biphenol exist as zwitterions in the crystalline state (Ng *et al.*, 2002; Bartoszak-Adamska *et al.*, 2000; Brzezinski *et al.*, 1998, 1995). The reason for the formation of the zwitterions, confirmed by experimental and theoretical methods, is that the $-CH_2N(C_2H_5)_2$ group, as a relatively strong base, causes deprotonation of the nearby phenol group and thereby builds a short intramolecular hydrogen bond involving a six-membered ring. Other zwitterionic species, such as the salicylideneimine Schiff bases (Mondal *et al.*, 2002; Hazell *et al.*, 1997), are also formed as the result of an intramolecular proton transfer. These results prompted us to look into the structure of the bhap molecule, which also bears both aliphatic amine and phenol groups. We present here the crystal structure of the title compound, (I), which is the zwitterion of bhap obtained by recrystallization from methanol/water.



The structure of compound (I) (Fig. 1) is composed of a 2-hydroxybenzamide group and a 2-(aminocarbonyl)phenolate moiety linked by a protonated 3-azapentanediy chain. The zwitterionic nature is confirmed by the location and free refinement of the relevant H atoms. The two pendant moieties attached to the ends of the C—C—N—C—C backbone adopt a *cis* conformation, as shown by the N1—C8—C9—N2 [65.1 (2)°] and N2—C10—C11—N3 [78.6 (2)°]. Similar to the previously studied 5,5'-derivatives of 3-diethylaminomethyl-2,2'-biphenol, (I) exists as a zwitterion, a H atom from one phenol hydroxy group having been transferred to the 3-azapentanediy N atom. The C8—C9—

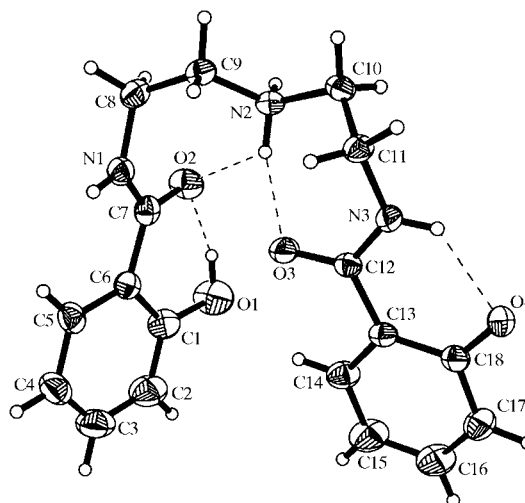


Figure 1

A view of the structure of (I), showing the atom-numbering scheme and displacement ellipsoids at the 30% probability level. The dashed lines represent intramolecular hydrogen bonds.

N2—C10—C11 backbone does not adopt a normal *anti* staggered conformation as is the case for some polymethylene carbon chains (Wang *et al.*, 2004, 2005); the C10—N2—C9—C8 and C9—N2—C10—C11 torsion angles are -176.63 (14) and 86.81 (19) $^\circ$, and atom C11 deviates from the C10/N2/C9/C8 plane by 1.4242 (9) Å. The protonated N2 atom exhibits tetrahedral sp^3 hybridization, whereas the two amide N atoms display planar sp^2 hybridization. As can be seen from Table 1, the N1—C8 and N3—C11 bond distances are shorter than the N2—C9 and N2—C10 bonds as a result of the p - π conjugation. The planarity of the benzamide group is well documented (Halfpenny & Small, 1980; Palmer *et al.*, 1995). In our case, the 2-hydroxybenzamide moiety is also planar, with atoms O2 and N1 deviating by 0.2131 (6) and -0.2611 (6) Å from the C1—C7/O1 plane. The 2-(aminocarbonyl)phenolate moiety is also planar, with a mean deviation of 0.0267 (5) Å. The two benzene rings subtend a dihedral angle of 73.4 (6) $^\circ$. The O1—C1—C6 [121.7 (2) $^\circ$] and O4—C18—C13 [122.92 (15) $^\circ$] angles are slightly larger than the ideal angle of 120° for sp^2 hybridization. The bond lengths in the two benzene groups show significant differences at the oxygen substitution sites. The negative charge of atom O4 is partly transferred to the benzene ring, lengthening the C13—C18 and C18—C17 bonds to 1.414 (3) and 1.409 (3) Å, respectively. The extensive delocalization of the negative charge also causes C18—O4 [1.320 (2) Å] to be slightly shorter than C1—O1 [1.359 (3) Å].

All H atoms bonded to O or N atoms are involved in hydrogen bonds. Within the intramolecular hydrogen-bonding system (Fig. 1 and Table 2), atom O2 atom acts as a double (bifurcated) hydrogen-bond acceptor towards the N2⁺—H2B

group and the O1—H1 hydroxy group, forming seven- and six-membered rings, respectively. The former hydrogen bond is comparatively weak because it forms the longer branch of an asymmetric three-centre system (see below). Whereas atom O2 lies in a position close to the hydroxy group, carbonyl atom O3 of the 2-(aminocarbonyl)phenolate moiety is located opposite the negatively charged O4 atom, with C1—C6—C7—O2 and O3—C12—C13—C18 torsion angles of 12.4 (3) and -175.45 (16) $^\circ$, respectively. Such an arrangement allows carbonyl atom O3, like atom O2, to act as a hydrogen-bond acceptor towards the same N2⁺—H2B H atom, thus forming a three-centre hydrogen-bond system and a second seven-membered ring. The final intramolecular hydrogen bond involves the phenolate O4 atom, which acts as acceptor towards the N3—H3 group, forming a six-membered ring.

The crystal packing is characterized by two intermolecular hydrogen bonds, which lead to a supramolecular network pattern. As shown in Fig. 2, the zwitterions are dimerized head-to-tail through three pairs of N1—H1A...O4, C5—H5...O4 and C11—H11B...O3 hydrogen-bond interactions. These centrosymmetric dimers are joined by N2⁺—H2A...O4 interactions into a two-dimensional network parallel to the crystallographic *bc* plane.

Experimental

The title compound was synthesized according to the method reported by Sureshan & Bhattacharya (1999). A mixture of methyl salicylate (12.20 g, 0.1 mol) and diethylenetriamine (5.16 g, 0.05 mol) were stirred at 322 K for 12 h. The product was crystallized from methanol to afford a colorless solid (m.p. 424–425 K, yield 77%). Crystals of (I) suitable for single-crystal X-ray diffraction were grown by slow evaporation of a methanol–water (1:1) solution.

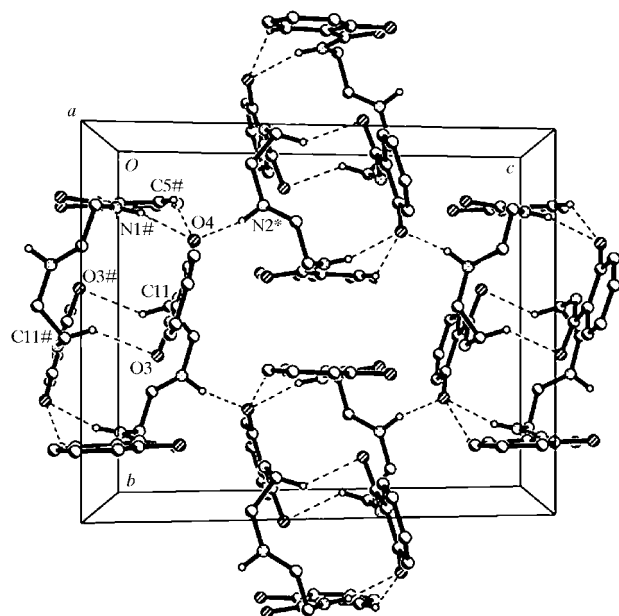


Figure 2

A packing diagram for (I), showing the two-dimensional supramolecular network involving the dimers. For the sake of clarity, H atoms not involved in the intermolecular hydrogen bonds have been omitted. Atoms marked with a hash sign (#) or an asterisk (*) are at the symmetry positions $(-x, 1-y, -z)$ and $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$, respectively.

Crystal data

C₁₈H₂₁N₃O₄
M_r = 343.38
 Monoclinic, *P*₂₁/*c*
a = 10.775 (2) Å
b = 11.668 (2) Å
c = 14.290 (3) Å
 β = 100.572 (3) $^\circ$
V = 1766.1 (6) Å³
Z = 4

D_x = 1.291 Mg m⁻³
 Mo K α radiation
 Cell parameters from 2404 reflections
 θ = 2.6–24.3 $^\circ$
 μ = 0.09 mm⁻¹
T = 294 (2) K
 Block, colorless
 0.30 × 0.28 × 0.12 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.972, *T_{max}* = 0.992
 9668 measured reflections

3616 independent reflections
 2100 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
 θ_{\max} = 26.4 $^\circ$
h = $-13 \rightarrow 13$
k = $-14 \rightarrow 13$
l = $-12 \rightarrow 17$

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.041
wR(*F*²) = 0.118
S = 1.00
 3616 reflections
 246 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0557P)^2 + 0.2173P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.14 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.16 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

O2—C7	1.251 (2)	N2—C9	1.479 (2)
O3—C12	1.244 (2)	N2—C10	1.490 (2)
N1—C8	1.448 (2)	N3—C11	1.452 (2)
C7—N1—C8	121.96 (17)	C12—N3—C11	123.58 (16)
C9—N2—C10	114.78 (14)		

Table 2

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>
N1—H1A...O4 ⁱ	0.88 (2)	2.01 (2)	2.865 (2)	165.7 (18)
N2—H2A...O4 ⁱⁱ	1.04 (2)	1.61 (2)	2.6342 (19)	167.0 (19)
N2—H2B...O3	0.97 (2)	1.75 (2)	2.6933 (19)	163.7 (17)
N2—H2B...O2	0.97 (2)	2.689 (19)	3.109 (2)	106.5 (13)
N3—H3...O4	0.890 (19)	1.87 (2)	2.6475 (19)	145.4 (18)
O1—H1...O2	1.05 (3)	1.51 (3)	2.518 (2)	158 (2)
C5—H5...O4 ⁱ	0.93	2.60	3.380 (3)	141
C11—H11B...O3 ⁱ	0.97	2.71	3.413 (2)	130

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

All C-bound H atoms were positioned geometrically and refined as riding [with C—H = 0.93–0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$]. The H atoms attached to the hydroxy O atom and to the N atoms were located in a difference map and refined freely.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 1997); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1772). Services for accessing these data are described at the back of the journal.

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