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Zwitterionic 4-bromo-6-methoxy-2-[[tris(hydroxymethyl)methyl]iminiumylmethyl]phenolate: crystal structure and Hirshfeld surface analysis

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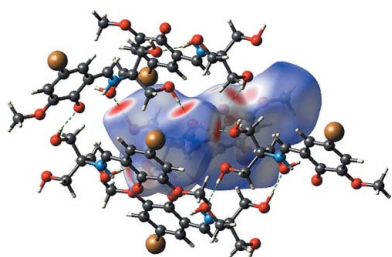
In the solid state, the title compound, $C_{12}H_{16}BrNO_5$ [systematic name: 4-bromo-2-((1*E*)-[[1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl]iminiumyl)methyl]-6-methoxybenzen-1-olate], $C_{12}H_{16}BrNO_5$, is found in the keto–amine tautomeric form, with an intramolecular iminium-N–H···O(phenolate) hydrogen bond and an *E* conformation about the C=N bond. Both *gauche* (two) and *anti* relationships are found for the methylhydroxy groups. In the crystal, a supramolecular layer in the *bc* plane is formed *via* hydroxy-O–H···O(hydroxy) and charge-assisted hydroxy-O–H···O(phenolate) hydrogen-bonding interactions; various C–H···O interactions provide additional cohesion to the layers, which stack along the *a* axis with no directional interactions between them. A Hirshfeld surface analysis confirms the lack of specific interactions in the inter-layer region.

1. Chemical context

Interest in molecules related to the title Schiff base compound derived from tris(hydroxymethyl)aminomethane (see Scheme) rests largely with the biological activity exhibited by their metal complexes. Thus, various species have been studied for their anticancer potential, *e.g.* vanadium (Back *et al.*, 2012) and tin (Lee *et al.*, 2015). The insulin-mimetic behaviour of vanadium complexes have been explored (Rehder *et al.*, 2002), as has the catecolase activity of binuclear cobalt complexes (Dey & Mukherjee, 2014). More recently, the adipogenic (cell differentiation) capacity of vanadium (Halevas *et al.*, 2015) and zinc complexes has been described (Tsave *et al.*, 2015). Over and above these considerations, magnetochemistry motivates on-going investigations, especially single-molecule (Wu *et al.*, 2007; Chandrasekhar *et al.*, 2013; Dey *et al.*, 2015) and lanthanide-containing species (Zou *et al.*, 2015; Das *et al.*, 2015). It was during on-going biological assays (Lee *et al.*, 2015) that the title compound, (I), became available. Herein, the crystal and molecular structures of (I) are described, as well as a Hirshfeld surface analysis.

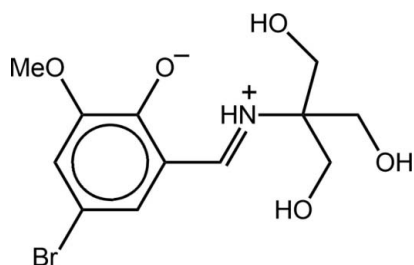
2. Structural commentary

The molecular structure of (I) (Fig. 1) exists as a zwitterion in the solid state, with the iminium N atom being protonated and the phenolate O atom being deprotonated. The observed keto–amine tautomeric form for (I) is the common form for molecules of this type, see *Database survey*. The conformation about the iminium bond [1.295 (4) Å] is *E* and this residue is almost coplanar with the benzene ring, forming a C2–C1–



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C7—N1 torsion angle of 1.9 (4)°. This arrangement allows for the formation of a tight charge-assisted iminium-N—H···O(phenolate) hydrogen bond (Table 1). The conformations of the methylhydroxy groups are variable, with *gauche* relationships about the C8—C9 and C8—C11 bonds [N1—C8—C9—O2 is 45.9 (3)°, *i.e.* +synclinal, and N1—C8—C11—O4 is −80.2 (3)°, *i.e.* −synclinal], and an *anti* relationship about the C8—C10 bond [N1—C8—C10—O3 is 178.8 (2)°, *i.e.* +antiperiplanar]. The methoxy group is almost coplanar with the ring it is connected to, as seen in the value of the C12—O5—C3—C2 torsion angle of 177.7 (2)°.



3. Supramolecular features

As anticipated from the chemical composition of (I), there are considerable hydrogen-bonding interactions operating in the crystal; geometric characteristics of these are listed in Table 1. Each of the hydroxy O2 and O3 atoms participates in hydroxy-O—H···O(hydroxy) hydrogen-bonding interactions, while the hydroxy O4 atom forms a donor interaction with the phenolate O1 atom. The result is the formation of a supramolecular layer parallel to (100) (Fig. 2*a*). Within this framework are a number of C—H···O interactions, *i.e.* imine-C7—H···O(phenolate), methylene-C11—H···O(phenolate) and methylene-C9—H···O(hydroxy) (Fig. 2*b*). In accord with the distance criteria in *PLATON* (Spek, 2009), layers stack along the *a* axis with no directional interactions between them. In

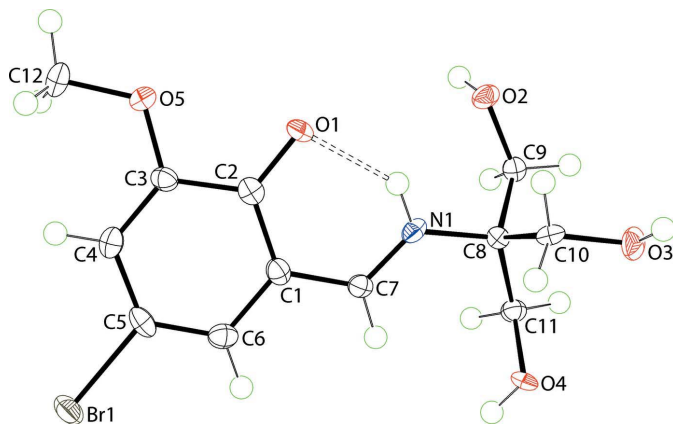


Figure 1

The molecular structure of (I), showing the atom-labelling scheme and displacement ellipsoids at the 70% probability level. The intramolecular N—H···O hydrogen bond is shown as a double-dashed line (see Table 1)

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> |
|-----------------------------|-------------|---------------|-----------------------|-------------------------|
| N1—H1N···O1 | 0.85 (2) | 1.90 (2) | 2.608 (3) | 140 (3) |
| O2—H2O···O4 ⁱ | 0.82 (2) | 1.93 (2) | 2.741 (3) | 170 (3) |
| O3—H3O···O2 ⁱⁱ | 0.81 (2) | 1.91 (2) | 2.704 (3) | 167 (4) |
| O4—H4O···O1 ⁱⁱⁱ | 0.82 (3) | 1.98 (3) | 2.760 (3) | 158 (3) |
| C7—H7···O1 ⁱⁱⁱ | 0.93 | 2.55 | 3.429 (4) | 158 |
| C9—H9B···O3 ⁱ | 0.97 | 2.51 | 3.242 (4) | 132 |
| C11—H11B···O1 ^{iv} | 0.97 | 2.39 | 3.353 (3) | 171 |

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

order to gain more insight into the molecular packing of (I), a Hirshfeld surface analysis was conducted.

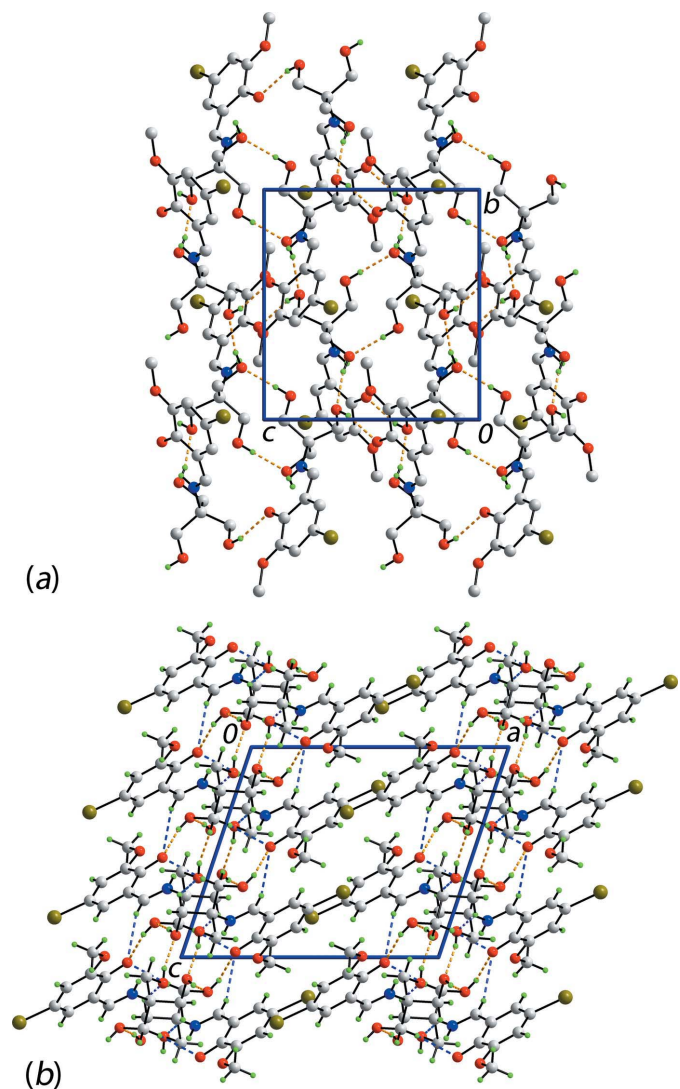


Figure 2

The molecular packing in (I), showing (a) a view of the supramolecular layer sustained by O—H···O hydrogen bonding, shown as orange dashed lines, and (b) a view of the unit-cell contents shown in projection down the *b* axis, highlighting the stacking of layers along the *a* axis. In (a), only acidic H atoms are shown.

4. Analysis of the Hirshfeld surfaces

The Hirshfeld surface of (I) was mapped over the d_{norm} contact distance within the range of -0.67 to 1.31 Å through calculation of the internal (d_i) and external (d_e) Hirshfeld surface distances to the nearest nucleus (McKinnon *et al.*, 2007; Spackman & Jayatilaka, 2009). Two-dimensional fingerprint plots associated with relevant close contacts were obtained through the plot of d_e versus d_i (Spackman & McKinnon, 2002). The electrostatic potential (ESP) of the crystal structure was mapped onto the Hirshfeld surface by an *ab initio* quantum modelling approach at the Hartree–Fock level of theory with the STO-3G basis set (HF/STO-3G) over the range of -0.122 to 0.189 au. All Hirshfeld surface and fingerprints plots were generated using *Crystal Explorer*

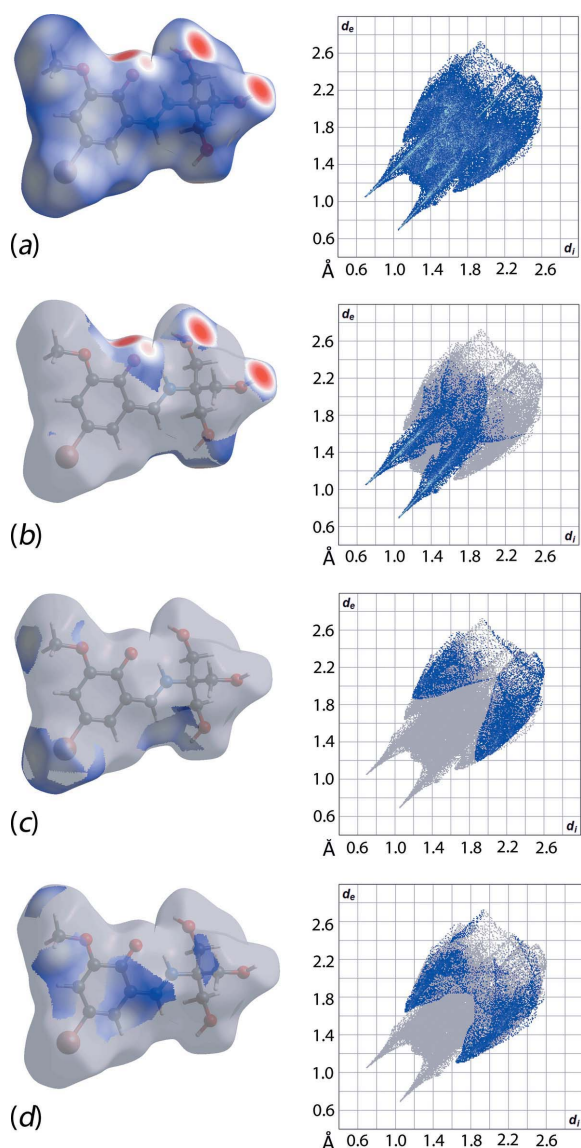


Figure 3
(a) Overall Hirshfeld surface and the two-dimensional fingerprint plot for (I), and d_{norm} surfaces and two-dimensional plots associated with (b) $O \cdots H/H \cdots O$, (c) $Br \cdots H/H \cdots Br$ and (d) $C \cdots H/H \cdots C$ interactions.

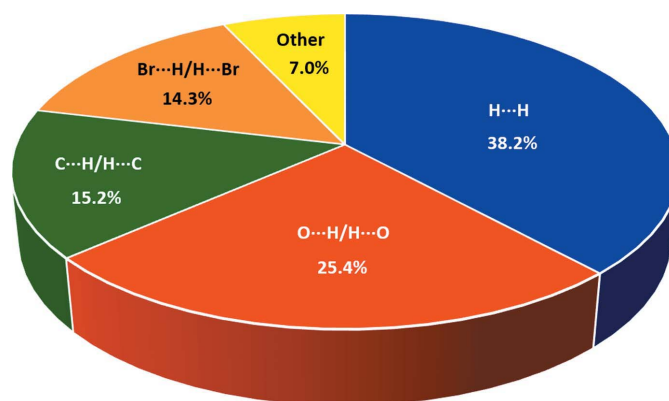


Figure 4
Percentage distribution of the corresponding close contacts to the Hirshfeld surface of (I).

(Wolff *et al.*, 2012), while the ESP was calculated by *TONTO* (Spackman *et al.*, 2008) as implemented in *Crystal Explorer*. Distances involving H atoms were normalized to the standard neutron diffraction bond lengths.

The Hirshfeld surface map provides a visual summary of any close contacts (shown as red) in contrast to relatively long contacts (shown as white and blue). As displayed in Fig. 3(a), there are several red spots observed on the Hirshfeld surface of (I), particularly around the O atoms, indicating close interactions at distances shorter than the sum of the van der Waals radii. A quantitative analysis of the decomposed two-dimensional fingerprint plot of the relevant $O \cdots H/H \cdots O$ interactions reveals a distinctive reciprocal spike in the plot of d_e versus d_i (Fig. 3b), with the sum of contact distances being approximately 1.74 Å, signifying a strong intermolecular interaction. Such strong interactions constitute the second major contribution to the Hirshfeld surface, *i.e.* 25.4%, between the most prominent $H \cdots H$ (38.2%) and other major contacts, like $C \cdots H/H \cdots C$ (15.2%) and $Br \cdots H/H \cdots Br$ (14.3%) (Fig. 4). Their contributions to the overall Hirshfeld

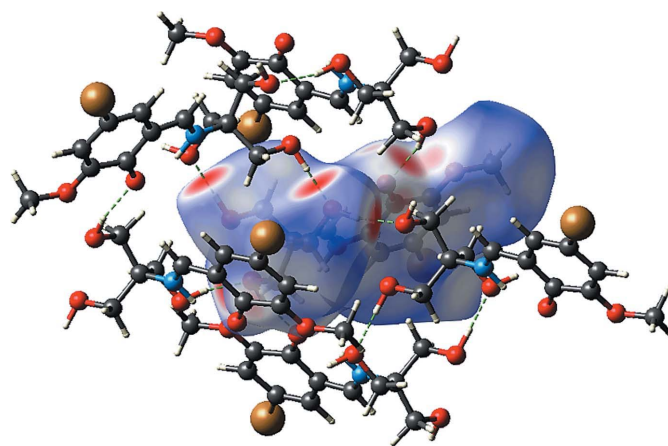


Figure 5
The d_{norm} surface for (I), highlighting the $O \cdots H$ hydrogen-bonding interactions which connect molecules in the molecular packing.

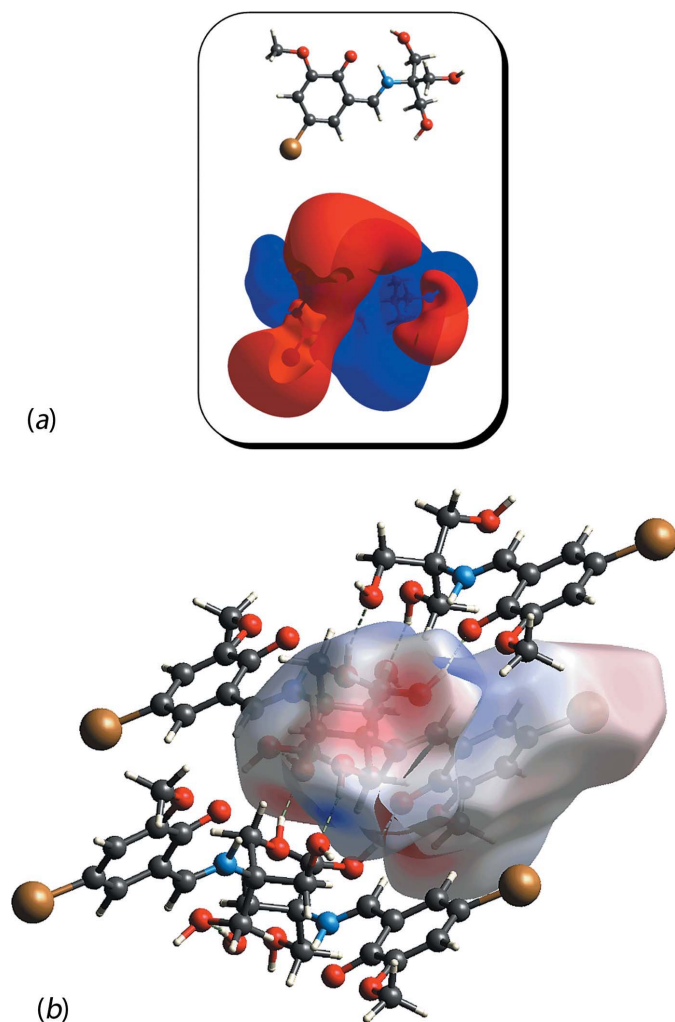


Figure 6
 (a) The electrostatic potential map of (I) within the range of -0.008 to 0.008 au and (b) the ESP mapped over the Hirshfeld surface, showing the attraction between the electronegative (red) and electropositive (blue) sites in (I).

surface notwithstanding, as seen from Figs. 3(c) and 3(d), $C \cdots H$ and $Br \cdots H$ contacts are at distances greater than their respective van der Waals radii. Fig. 5 shows the $O-H \cdots O$ interactions formed between a reference molecule and symmetry-related molecules.

In order to gain a qualitative insight into the electrostatic interaction and rationalize the packing motif of the structure, the ESP was mapped over the Hirshfeld surface. The result illustrated in Fig. 6(a), shows that the electronegative sites are predominantly converged on O atoms and that, upon crystallization, the electronegative and electropositive sites are connected (Fig. 6b). It is noteworthy that despite bromine being an electrophilic element, it did not form a significant non-covalent interaction with neighbouring molecules in the inter-layer region where these atoms are directed. The closest contact in this region occurs with methyl- $C \cdots H12C^i$, at 3.12 \AA , *i.e.* beyond the sum of the respective van der Waals radii (Spek, 2009) [symmetry code: (i) $x, -\frac{1}{2} - y, \frac{1}{2} + z$].

5. Database survey

There are several closely related structures to (I) in the crystallographic literature (Groom *et al.*, 2016). What might be termed the parent compound, *i.e.* with no substitution at the phenolate ring other than the imino group in the 2-position, (II), exists in the keto–amine tautomeric form and has been the subject of several investigations (Asgedom *et al.*, 1996; Tatar *et al.*, 2005). Similar zwitterionic structures are found in the 4-bromo, (III) (Martinez *et al.*, 2011), and 6-methoxy, (IV) (Odabaşoğlu *et al.*, 2003), derivatives, both closely related to (I), suggesting this is the most stable form for these molecules, at least in the solid state. Despite the similar electronic structures, conformational differences exist about the ring between (I) and (IV) as seen in the relative dispositions of the methoxy groups, *i.e.* $C12-O5-C3-C2$ is $177.7 (2)^\circ$ in (I) but $-165.75 (14)^\circ$ in (IV) (Fig. 7). Differences in conformation of the methylhydroxy groups are also apparent, no doubt due to the different hydrogen-bonding patterns in the respective crystal structures.

6. Synthesis and crystallization

A solution of tris(hydroxymethyl)aminomethane (1.21 g, 0.01 mol) was added to an ethanolic solution of 5-bromo-3-methoxy-2-hydroxybenzaldehyde (2.31 g, 0.01 mol) and refluxed for 2 h. The solution was allowed to stand at room temperature, during which an orange solid formed. This was recrystallized by slow evaporation of its ethanol solution. Yield: 2.67 (80%). Yellow crystals. M.p. 465–466 K. Analysis calculated for $C_{12}H_{16}BrNO_5$: C 44.48, H 3.70, N 1.99%; found: C 44.81, H 3.42, N 1.64%. IR (cm^{-1}): 3330 (*b*) $\nu(N-H, O-$

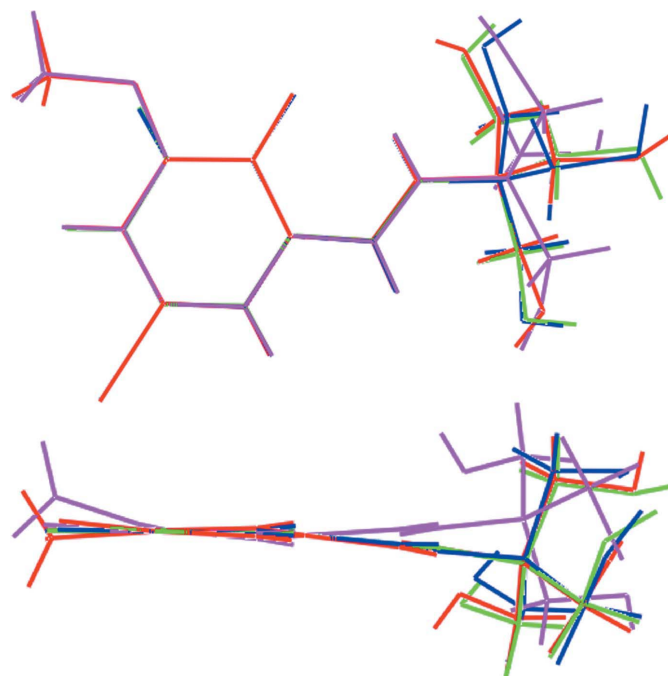


Figure 7
 Overlay diagrams for (I) (red image), (II) (green), (III) (blue) and (IV) (pink). Images have been drawn so the benzene rings overlap.

Table 2
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | C ₁₂ H ₁₆ BrNO ₅ |
| <i>M_r</i> | 334.17 |
| Crystal system, space group | Monoclinic, <i>P</i> ₂ / <i>c</i> |
| Temperature (K) | 293 |
| <i>a</i> , <i>b</i> , <i>c</i> (Å) | 12.2872 (9), 10.7186 (8), 10.5830 (8) |
| β (°) | 108.462 (1) |
| <i>V</i> (Å ³) | 1322.06 (17) |
| <i>Z</i> | 4 |
| Radiation type | Mo <i>K</i> α |
| μ (mm ⁻¹) | 3.13 |
| Crystal size (mm) | 0.26 × 0.10 × 0.08 |
| Data collection | |
| Diffraction | Bruker SMART APEX |
| Absorption correction | Multi-scan (<i>SADABS</i> ; Sheldrick, 1996) |
| <i>T_{min}</i> , <i>T_{max}</i> | 0.497, 0.788 |
| No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections | 5095, 2257, 1923 |
| <i>R_{int}</i> | 0.032 |
| (<i>sin</i> θ / λ) _{max} (Å ⁻¹) | 0.595 |
| Refinement | |
| <i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i> | 0.030, 0.068, 1.04 |
| No. of reflections | 2257 |
| No. of parameters | 185 |
| No. of restraints | 4 |
| $\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³) | 0.41, -0.54 |

Computer programs: *SMART* and *SAINT* (Bruker, 2008), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *QMol* (Gans & Shalloway, 2001), *DIAMOND* (Brandenburg, 2006) and *pubCIF* (Westrip, 2010).

H), 1640 (*s*) ν (C=N), 1528 (*m*) ν (-O-C=C-), 1066 (*m*) ν (C-O-C). ¹H NMR (400 MHz, CDCl₃): δ 8.35 [*s*, 1H, -N=C(H)], 7.01–7.10 (*m*, 1H, aryl H), 6.83–6.89 (*m*, 1H, aryl H), 5.06 (*s*, 3H, OH), 3.95 (*s*, 3H, OCH₃), 3.37–3.75 (*m*, 6H, aliphatic H).

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The carbon-bound H atoms were placed in calculated positions (C–H = 0.93–0.97 Å) and were included in the refinement in the riding-model approximation, with *U*_{iso}(H) set at 1.2–1.5*U*_{eq}(C). The O- and N-bound H atoms were located from difference Fourier maps and refined with distance restraints O–H = 0.82 ± 0.01 Å and N–H = 0.86 ± 0.01 Å, and with *U*_{iso}(H) set at 1.5*U*_{eq}(O) and *U*_{iso}(H) set at 1.2*U*_{eq}(N), respectively. Owing to poor agreement, several reflections, *i.e.* (–9 7 7), (–12 4 6), (–10 5 6) and (–3 3 2), were omitted from the final cycles of refinement.

Acknowledgements

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Zwitterionic 4-bromo-6-methoxy-2-[[tris(hydroxymethyl)methyl]iminiumyl-methyl]phenolate: crystal structure and Hirshfeld surface analysis

See Mun Lee, Kong Mun Lo, Sang Loon Tan and Edward R. T. Tiekink

Computing details

Data collection: *SMART* (Bruker, 2008); cell refinement: *SMART* (Bruker, 2008); data reduction: *SAINTE* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012), *QMol* (Gans & Shalloway, 2001), *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

4-Bromo-2-((1*E*)-[[1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl]iminiumyl)methyl-6-methoxybenzen-1-olate

Crystal data

C₁₂H₁₆BrNO₅

M_r = 334.17

Monoclinic, *P*2₁/*c*

a = 12.2872 (9) Å

b = 10.7186 (8) Å

c = 10.5830 (8) Å

β = 108.462 (1)°

V = 1322.06 (17) Å³

Z = 4

F(000) = 680

D_x = 1.679 Mg m⁻³

Mo *Kα* radiation, λ = 0.71073 Å

Cell parameters from 1493 reflections

θ = 2.6–27.9°

μ = 3.13 mm⁻¹

T = 293 K

Prism, yellow

0.26 × 0.10 × 0.08 mm

Data collection

Bruker SMART APEX
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)

T_{min} = 0.497, *T_{max}* = 0.788

5095 measured reflections

2257 independent reflections

1923 reflections with *I* > 2σ(*I*)

R_{int} = 0.032

θ_{max} = 25.0°, θ_{min} = 1.8°

h = -10→14

k = -12→12

l = -9→12

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.030

wR(*F*²) = 0.068

S = 1.04

2257 reflections

185 parameters

4 restraints

Hydrogen site location: mixed

w = 1/[σ²(*F_o*²) + (0.0206*P*)² + 0.8903*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.41 e Å⁻³

Δρ_{min} = -0.54 e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|---------------|--------------|----------------------------------|
| Br1 | 0.45516 (2) | -0.01276 (3) | 0.80991 (3) | 0.01835 (11) |
| O1 | 0.79706 (16) | 0.09687 (18) | 0.52558 (18) | 0.0134 (4) |
| O2 | 1.05037 (18) | 0.27428 (18) | 0.60436 (19) | 0.0141 (5) |
| H2O | 1.083 (2) | 0.2087 (17) | 0.632 (3) | 0.021* |
| O3 | 0.96322 (18) | 0.60240 (19) | 0.62300 (19) | 0.0174 (5) |
| H3O | 0.948 (3) | 0.641 (3) | 0.5535 (19) | 0.026* |
| O4 | 0.85256 (17) | 0.54263 (18) | 0.83553 (19) | 0.0132 (4) |
| H4O | 0.824 (3) | 0.517 (3) | 0.891 (2) | 0.020* |
| O5 | 0.70096 (17) | -0.12504 (18) | 0.49502 (19) | 0.0153 (5) |
| N1 | 0.8572 (2) | 0.2954 (2) | 0.6738 (2) | 0.0118 (5) |
| H1N | 0.865 (3) | 0.245 (2) | 0.615 (2) | 0.014* |
| C1 | 0.7122 (2) | 0.1554 (3) | 0.6915 (3) | 0.0125 (6) |
| C2 | 0.7298 (2) | 0.0719 (3) | 0.5940 (3) | 0.0110 (6) |
| C3 | 0.6701 (2) | -0.0452 (3) | 0.5783 (3) | 0.0122 (6) |
| C4 | 0.5921 (2) | -0.0711 (3) | 0.6427 (3) | 0.0133 (6) |
| H4 | 0.5531 | -0.1467 | 0.6289 | 0.016* |
| C5 | 0.5715 (2) | 0.0190 (3) | 0.7308 (3) | 0.0146 (6) |
| C6 | 0.6309 (2) | 0.1276 (3) | 0.7580 (3) | 0.0140 (6) |
| H6 | 0.6186 | 0.1835 | 0.8193 | 0.017* |
| C7 | 0.7801 (2) | 0.2645 (3) | 0.7279 (3) | 0.0109 (6) |
| H7 | 0.7689 | 0.3161 | 0.7933 | 0.013* |
| C8 | 0.9361 (2) | 0.4026 (3) | 0.7066 (3) | 0.0110 (6) |
| C9 | 1.0558 (2) | 0.3539 (3) | 0.7151 (3) | 0.0129 (6) |
| H9A | 1.1060 | 0.4239 | 0.7159 | 0.016* |
| H9B | 1.0878 | 0.3079 | 0.7975 | 0.016* |
| C10 | 0.8904 (2) | 0.4963 (2) | 0.5932 (3) | 0.0120 (6) |
| H10A | 0.8904 | 0.4597 | 0.5094 | 0.014* |
| H10B | 0.8124 | 0.5201 | 0.5856 | 0.014* |
| C11 | 0.9462 (2) | 0.4610 (3) | 0.8413 (3) | 0.0121 (6) |
| H11A | 0.9492 | 0.3952 | 0.9052 | 0.014* |
| H11B | 1.0175 | 0.5076 | 0.8725 | 0.014* |
| C12 | 0.6500 (3) | -0.2459 (3) | 0.4763 (3) | 0.0216 (7) |
| H12A | 0.6684 | -0.2879 | 0.5606 | 0.032* |
| H12B | 0.6791 | -0.2933 | 0.4170 | 0.032* |
| H12C | 0.5683 | -0.2380 | 0.4388 | 0.032* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|---------------|--------------|--------------|
| Br1 | 0.01640 (17) | 0.01891 (18) | 0.02421 (18) | -0.00122 (13) | 0.01279 (13) | 0.00285 (13) |
| O1 | 0.0139 (11) | 0.0159 (11) | 0.0136 (10) | -0.0018 (8) | 0.0089 (9) | -0.0016 (8) |
| O2 | 0.0205 (12) | 0.0093 (10) | 0.0139 (11) | 0.0039 (9) | 0.0075 (9) | 0.0016 (8) |
| O3 | 0.0284 (13) | 0.0112 (11) | 0.0141 (11) | -0.0034 (9) | 0.0091 (10) | 0.0029 (8) |
| O4 | 0.0141 (11) | 0.0153 (11) | 0.0145 (11) | 0.0004 (8) | 0.0108 (9) | -0.0009 (9) |
| O5 | 0.0192 (12) | 0.0123 (10) | 0.0173 (11) | -0.0026 (9) | 0.0099 (9) | -0.0049 (9) |
| N1 | 0.0151 (13) | 0.0091 (12) | 0.0109 (13) | -0.0001 (10) | 0.0034 (11) | -0.0023 (10) |
| C1 | 0.0106 (15) | 0.0127 (15) | 0.0145 (15) | -0.0002 (12) | 0.0043 (12) | 0.0015 (12) |
| C2 | 0.0079 (14) | 0.0123 (15) | 0.0110 (14) | 0.0025 (11) | 0.0008 (12) | 0.0037 (12) |
| C3 | 0.0094 (15) | 0.0149 (15) | 0.0126 (15) | 0.0007 (12) | 0.0038 (12) | -0.0008 (12) |
| C4 | 0.0132 (16) | 0.0104 (14) | 0.0142 (15) | -0.0009 (12) | 0.0013 (12) | 0.0009 (12) |
| C5 | 0.0122 (15) | 0.0180 (16) | 0.0147 (15) | -0.0013 (12) | 0.0060 (12) | 0.0054 (12) |
| C6 | 0.0140 (15) | 0.0140 (15) | 0.0145 (15) | 0.0035 (12) | 0.0052 (12) | 0.0007 (12) |
| C7 | 0.0121 (15) | 0.0098 (14) | 0.0115 (14) | 0.0028 (11) | 0.0049 (12) | 0.0025 (11) |
| C8 | 0.0124 (15) | 0.0105 (14) | 0.0114 (14) | -0.0008 (11) | 0.0055 (12) | -0.0004 (11) |
| C9 | 0.0137 (16) | 0.0124 (15) | 0.0137 (15) | -0.0019 (12) | 0.0056 (12) | -0.0010 (11) |
| C10 | 0.0132 (14) | 0.0117 (14) | 0.0118 (14) | 0.0021 (12) | 0.0052 (11) | -0.0028 (12) |
| C11 | 0.0123 (15) | 0.0117 (14) | 0.0128 (15) | 0.0016 (12) | 0.0048 (12) | -0.0002 (11) |
| C12 | 0.0263 (19) | 0.0138 (16) | 0.0267 (18) | -0.0091 (13) | 0.0112 (15) | -0.0070 (13) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|------------|------------|------------|-----------|
| Br1—C5 | 1.902 (3) | C4—C5 | 1.420 (4) |
| O1—C2 | 1.287 (3) | C4—H4 | 0.9300 |
| O2—C9 | 1.434 (3) | C5—C6 | 1.355 (4) |
| O2—H2O | 0.818 (10) | C6—H6 | 0.9300 |
| O3—C10 | 1.419 (3) | C7—H7 | 0.9300 |
| O3—H3O | 0.815 (10) | C8—C11 | 1.525 (4) |
| O4—C11 | 1.432 (3) | C8—C10 | 1.529 (4) |
| O4—H4O | 0.819 (10) | C8—C9 | 1.536 (4) |
| O5—C3 | 1.365 (3) | C9—H9A | 0.9700 |
| O5—C12 | 1.425 (3) | C9—H9B | 0.9700 |
| N1—C7 | 1.295 (4) | C10—H10A | 0.9700 |
| N1—C8 | 1.473 (4) | C10—H10B | 0.9700 |
| N1—H1N | 0.856 (10) | C11—H11A | 0.9700 |
| C1—C7 | 1.417 (4) | C11—H11B | 0.9700 |
| C1—C6 | 1.424 (4) | C12—H12A | 0.9600 |
| C1—C2 | 1.432 (4) | C12—H12B | 0.9600 |
| C2—C3 | 1.438 (4) | C12—H12C | 0.9600 |
| C3—C4 | 1.369 (4) | | |
| C9—O2—H2O | 109 (2) | N1—C8—C10 | 106.1 (2) |
| C10—O3—H3O | 105 (2) | C11—C8—C10 | 111.4 (2) |
| C11—O4—H4O | 107 (2) | N1—C8—C9 | 107.2 (2) |
| C3—O5—C12 | 117.3 (2) | C11—C8—C9 | 107.0 (2) |

| | | | |
|--------------|------------|---------------|------------|
| C7—N1—C8 | 127.9 (2) | C10—C8—C9 | 112.1 (2) |
| C7—N1—H1N | 115 (2) | O2—C9—C8 | 111.0 (2) |
| C8—N1—H1N | 117 (2) | O2—C9—H9A | 109.4 |
| C7—C1—C6 | 118.9 (3) | C8—C9—H9A | 109.4 |
| C7—C1—C2 | 120.1 (3) | O2—C9—H9B | 109.4 |
| C6—C1—C2 | 121.0 (3) | C8—C9—H9B | 109.4 |
| O1—C2—C1 | 123.0 (3) | H9A—C9—H9B | 108.0 |
| O1—C2—C3 | 120.8 (3) | O3—C10—C8 | 107.6 (2) |
| C1—C2—C3 | 116.2 (3) | O3—C10—H10A | 110.2 |
| O5—C3—C4 | 125.2 (3) | C8—C10—H10A | 110.2 |
| O5—C3—C2 | 112.7 (2) | O3—C10—H10B | 110.2 |
| C4—C3—C2 | 122.1 (3) | C8—C10—H10B | 110.2 |
| C3—C4—C5 | 119.2 (3) | H10A—C10—H10B | 108.5 |
| C3—C4—H4 | 120.4 | O4—C11—C8 | 112.6 (2) |
| C5—C4—H4 | 120.4 | O4—C11—H11A | 109.1 |
| C6—C5—C4 | 121.8 (3) | C8—C11—H11A | 109.1 |
| C6—C5—Br1 | 119.3 (2) | O4—C11—H11B | 109.1 |
| C4—C5—Br1 | 118.8 (2) | C8—C11—H11B | 109.1 |
| C5—C6—C1 | 119.3 (3) | H11A—C11—H11B | 107.8 |
| C5—C6—H6 | 120.3 | O5—C12—H12A | 109.5 |
| C1—C6—H6 | 120.3 | O5—C12—H12B | 109.5 |
| N1—C7—C1 | 122.7 (3) | H12A—C12—H12B | 109.5 |
| N1—C7—H7 | 118.6 | O5—C12—H12C | 109.5 |
| C1—C7—H7 | 118.6 | H12A—C12—H12C | 109.5 |
| N1—C8—C11 | 113.2 (2) | H12B—C12—H12C | 109.5 |
| | | | |
| C7—C1—C2—O1 | -7.6 (4) | C2—C1—C6—C5 | 1.7 (4) |
| C6—C1—C2—O1 | 175.5 (2) | C8—N1—C7—C1 | -177.2 (3) |
| C7—C1—C2—C3 | 170.7 (2) | C6—C1—C7—N1 | 178.9 (3) |
| C6—C1—C2—C3 | -6.2 (4) | C2—C1—C7—N1 | 1.9 (4) |
| C12—O5—C3—C4 | -1.6 (4) | C7—N1—C8—C11 | 16.6 (4) |
| C12—O5—C3—C2 | 177.7 (2) | C7—N1—C8—C10 | -105.8 (3) |
| O1—C2—C3—O5 | 5.3 (4) | C7—N1—C8—C9 | 134.3 (3) |
| C1—C2—C3—O5 | -173.1 (2) | N1—C8—C9—O2 | 45.9 (3) |
| O1—C2—C3—C4 | -175.4 (3) | C11—C8—C9—O2 | 167.6 (2) |
| C1—C2—C3—C4 | 6.2 (4) | C10—C8—C9—O2 | -70.0 (3) |
| O5—C3—C4—C5 | 177.5 (3) | N1—C8—C10—O3 | 178.8 (2) |
| C2—C3—C4—C5 | -1.8 (4) | C11—C8—C10—O3 | 55.2 (3) |
| C3—C4—C5—C6 | -3.2 (4) | C9—C8—C10—O3 | -64.6 (3) |
| C3—C4—C5—Br1 | 175.5 (2) | N1—C8—C11—O4 | -80.2 (3) |
| C4—C5—C6—C1 | 3.2 (4) | C10—C8—C11—O4 | 39.2 (3) |
| Br1—C5—C6—C1 | -175.5 (2) | C9—C8—C11—O4 | 162.0 (2) |
| C7—C1—C6—C5 | -175.2 (3) | | |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|-------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N1—H1N \cdots O1 | 0.85 (2) | 1.90 (2) | 2.608 (3) | 140 (3) |

| | | | | |
|-----------------------------|----------|----------|-----------|---------|
| O2—H2O···O4 ⁱ | 0.82 (2) | 1.93 (2) | 2.741 (3) | 170 (3) |
| O3—H3O···O2 ⁱⁱ | 0.81 (2) | 1.91 (2) | 2.704 (3) | 167 (4) |
| O4—H4O···O1 ⁱⁱⁱ | 0.82 (3) | 1.98 (3) | 2.760 (3) | 158 (3) |
| C7—H7···O1 ⁱⁱⁱ | 0.93 | 2.55 | 3.429 (4) | 158 |
| C9—H9B···O3 ⁱ | 0.97 | 2.51 | 3.242 (4) | 132 |
| C11—H11B···O1 ^{iv} | 0.97 | 2.39 | 3.353 (3) | 171 |

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