

# A structural comparison of salt forms of dopamine with the structures of other phenylethylamines

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Received 28 June 2023

Accepted 4 September 2023

Edited by R. I. Cooper, University of Oxford, United Kingdom

**Keywords:** crystal structure; active pharmaceutical ingredient; API; salt selection; form selection; dopamine; phenylethylamine.

**CCDC references:** 2292822; 2043930; 2292821; 2043931

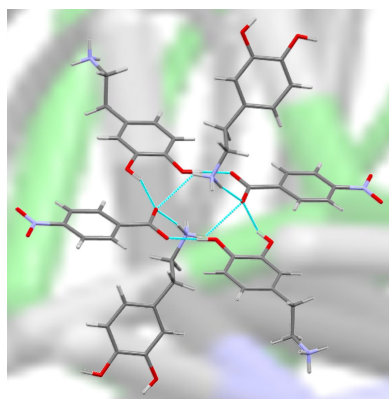
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The structures of four salt forms of dopamine are reported. These are dopamine [2-(3,4-dihydroxyphenyl)ethan-1-aminium] benzoate,  $C_8H_{12}NO_2^+ \cdot C_7H_5O_2^-$ , **I**, dopamine 4-nitrobenzoate,  $C_8H_{12}NO_2^+ \cdot C_7H_4NO_4^-$ , **II**, dopamine ethanedisulfonate,  $2C_8H_{12}NO_2^+ \cdot C_2H_4O_6S_2^{2-}$ , **III**, and dopamine 4-hydroxybenzenesulfonate monohydrate,  $C_8H_{12}NO_2^+ \cdot C_6H_5O_4S^- \cdot H_2O$ , **IV**. In all four structures, the dopamine cation adopts an extended conformation. Intermolecular interaction motifs that are common in the salt forms of tyramine can be found in related dopamine structures, but hydrogen bonding in the dopamine structures appear to be more variable and less predictable than for tyramine. Packing analysis discovered three dopamine-containing groups of structures that can be described as isostructural with regards to the cation positions. Two of these groups contain both dopamine and tyramine species, and one of these is also highly variable in other ways too, containing anhydrous and hydrated forms, different anion types and ionized and neutral phenylethylamine species. As such, the group illustrates that packing behaviour can be robust and similar even where intermolecular interactions such as hydrogen bonds are very different.

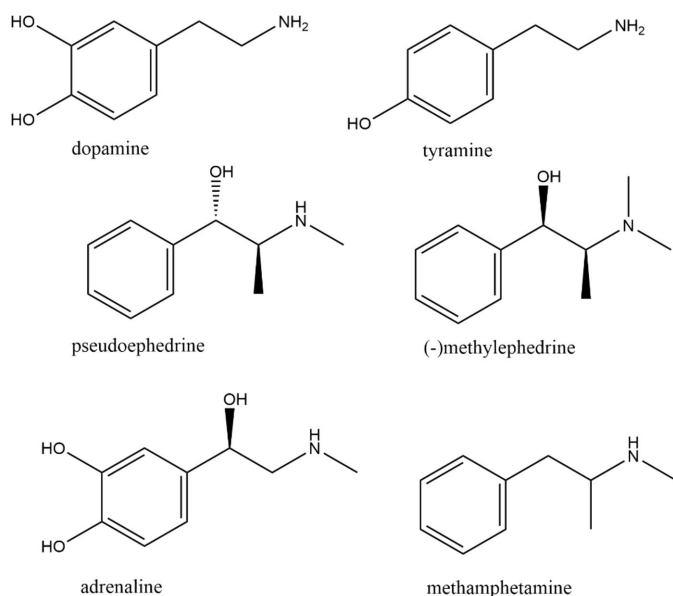
## 1. Introduction

The generation of salt forms of an active pharmaceutical ingredient (API) is a well-known process used by the pharmaceutical industry to change important material properties of the API. Idealizing properties such as solubility, stability or hygroscopicity is important to the development of an effective and commercially successful API (Stahl & Wermuth, 2008). It is generally accepted that there are links between the solid-state structure and the material properties of interest, and that a greater understanding of such structure-to-property correlations should help to rationalize salt screening and other form-choice processes.

Phenylethylamine (PEA) compounds (Scheme 1) have long been known to have a large variety of pharmaceutical and biological roles (*e.g.* Brown *et al.*, 1979; Drew *et al.*, 1978; Broadley, 2010; Dennany *et al.*, 2015). Due to their favourable handling characteristics, several have been used in studies where relatively large numbers of salt forms of a given API have been crystallographically characterized and the structures then used to systematically investigate material properties. The earliest examples of this are the studies by Davey investigating the structures and crystal properties of pseudoephedrine salts forms and their relationships to solubility (Black *et al.*, 2007; Collier *et al.*, 2006). A problem with similar studies using large numbers of crystal structures is how to simply compare and contrast multiple structures. One solution to this are the packing similarity tools available within *Mercury* (Taylor & Wood, 2019; Childs *et al.*, 2009; Macrae *et al.*, 2020). In the area of PEA salt forms, these tools have been



used to investigate hydrate formation in tyramine salt forms (Briggs *et al.*, 2012), and density and melting point in pairs of enantiopure and racemic methylephedrine salt forms (Kennedy *et al.*, 2011). An intriguing result using this approach was that groups of methylephedrine salt forms that showed isostructural cation packing also showed tighter correlation between aqueous solubility and melting point than did similar salt forms that were not part of isostructural packing groups (de Moraes *et al.*, 2017).



Scheme 1

Dopamine is a biologically significant member of the PEA family and arguably the most well known. In the brain it is a neurotransmitter and it is known to play a role in a wide range of human bodily functions, including motor control, motivation, gastrointestinal tract function and operation of the immune system. It is well known that loss of the ability to secrete dopamine leads to Parkinson's disease (*e.g.* Wenzel *et al.*, 2015; Schultz, 2007). Perhaps less well known is that dopamine in the form of its HCl salt is used as an API, for instance, in the treatment of neonatal shock (Noori *et al.*, 2003). Some crystallographic work has been undertaken on forms of dopamine. Dopamine itself has been shown to exist in the solid as a zwitterionic form, with deprotonation of the OH group *meta* to the ethylamine substituent (Cruikshank *et al.*, 2013). The structures of some simple salt forms of dopamine are also known. These include forms with inorganic anions [the halides DOPAMN01, QQQAEJ02 and ATOLUR04 (Giesecke, 1980; Pike & Dziura, 2013; Ivanova & Spitteller, 2017); the nitrate CIZYAN (Gatfaoui *et al.*, 2014); and the perchlorate OGE-GAJ (Boghaei *et al.*, 2008)] and four forms with small to medium sized organic anions (ATOLIF, ATOMAY, RAWDEB and MIYLOV; Ivanova & Spitteller, 2010; Feng *et al.*, 2017; Ohba & Ito, 2002). This gives a total of ten relevant literature structures available from the Cambridge Structural Database (CSD, Version 5.43, update of November 2022, Groom *et al.*, 2016). To this data set we herein add the structures of the benzoate,

4-nitrobenzoate, ethanedisulfonate and 4-hydroxybenzenesulfonate salt forms of dopamine. The new structures are described and a comparative analysis of the packing of dopamine and its salt forms, and those of the closely related PEA species tyramine is presented.

## 2. Experimental

### 2.1. Synthesis and crystallization

Dopamine hydrochloride was purchased from Sigma-Aldrich. Because of the well-known rapid oxidation of dopamine under basic conditions (Richter & Waddell, 1983), the HCl salt was converted to neutral dopamine under an N<sub>2</sub> atmosphere and in a Schlenk tube. This was done by addition of NaOH to ice-cooled aqueous solutions of dopamine HCl. Dopamine free base precipitated in 51–59% yield after 2 h. The white solid was separated by filtration and stored under N<sub>2</sub> before use. Salt forms **I** to **IV** were prepared by adding dopamine (0.2 g) and an equimolar amount of the appropriate acid to degassed water (5 ml). The mixtures were stirred and heated under N<sub>2</sub> to 313 K before being filtered to leave clear solutions. These solutions were left to evaporate slowly. Crystals suitable for single-crystal diffraction were obtained directly from these solutions within one week. For both **I** and **II**, crystals of the salt form grew alongside a small number of crystals of the parent benzoic acid.

### 2.2. Refinement

The anion of **IV** was found to be disordered, with the benzene ring rotated by approximately 52° around an axis that runs through atoms S1, C9, C12 and O6. Thus, four aromatic C–H groups were each modelled as split over two sites with occupancies refined to a 50:50 ratio. No further restraints or constraints were required to satisfactorily model these disordered atoms. For **I**, **II** and **III**, all H atoms bonded to O or N atoms were positioned as found by difference synthesis and refined freely and isotropically. For **IV**, restraints on the O–H bond lengths were required and they were set to 0.88 (1) Å. For **I** to **IV**, H atoms bound to C atoms were placed in idealized positions and refined in riding modes. C–H bond lengths of 0.95 and 0.99 Å were used for CH and CH<sub>2</sub> groups, respectively, and *U*<sub>iso</sub>(H) values were set at 1.2*U*<sub>eq</sub>(C) of the parent atom. Further crystallographic details and refinement parameters are given in Table 1.

## 3. Results and discussion

The structures of **I–IV** are shown in Figs. 1–4, with crystallographic parameters detailed in Table 1 and hydrogen-bonding parameters detailed in Tables 2–5. The asymmetric units of both **I** and **II** consist of a dopamine cation and a (substituted) benzoate anion. The asymmetric unit of **III** consists of a dopamine cation and half of an ethanedisulfonate dianion. Here the dianion has a crystallographic centre of symmetry in the middle of its C–C bond. Finally, **IV** is a monohydrate and so the asymmetric unit consists of a dopa-

**Table 1**

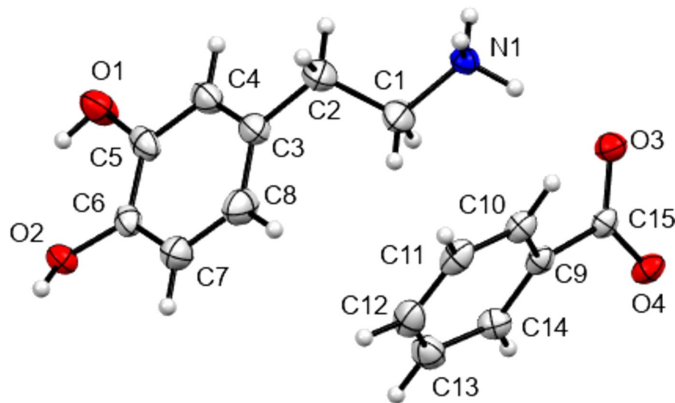
Experimental details.

For all structures:  $Z = 4$ . Experiments were carried out at 123 K. Absorption was corrected for by multi-scan methods (*CrysAlis PRO*; Rigaku OD, 2019). H atoms were treated by a mixture of independent and constrained refinement.

	I	II	III	IV
Crystal data				
Chemical formula	$C_8H_{12}NO_2^+ \cdot C_7H_5O_2^-$	$C_8H_{12}NO_2^+ \cdot C_7H_4NO_4^-$	$2C_8H_{12}NO_2^+ \cdot C_2H_4O_6S_2^{2-}$	$C_8H_{12}NO_2^+ \cdot C_6H_5O_4S^- \cdot H_2O$
$M_r$	275.29	320.30	496.54	345.36
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$	Orthorhombic, $Pbca$	Monoclinic, $P2_1/c$
$a, b, c$ (Å)	11.7637 (6), 11.7460 (5), 10.3316 (5)	7.4993 (2), 18.5051 (5), 10.7610 (3)	10.6328 (5), 8.5651 (5), 23.8669 (13)	17.4085 (8), 11.9234 (5), 7.6779 (3)
$\alpha, \beta, \gamma$ (°)	90, 111.384 (6), 90	90, 99.628 (3), 90	90, 90, 90	90, 95.273 (4), 90
$V$ (Å <sup>3</sup> )	1329.30 (12)	1472.33 (7)	2173.6 (2)	1586.95 (12)
Radiation type	Cu $K\alpha$	Mo $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.83	0.11	2.75	2.15
Crystal size (mm)	$0.35 \times 0.10 \times 0.02$	$0.35 \times 0.25 \times 0.05$	$0.30 \times 0.15 \times 0.05$	$0.5 \times 0.15 \times 0.07$
Data collection				
Diffractometer	Oxford Diffraction Gemini S	Oxford Diffraction Xcalibur E	Oxford Diffraction Gemini S	Oxford Diffraction Gemini S
$T_{min}, T_{max}$	0.761, 1.000	0.928, 1.000	0.500, 1.000	0.653, 1.000
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	5127, 2614, 2033	7174, 3573, 2620	7583, 2172, 1924	6603, 3113, 2474
$R_{int}$	0.026	0.026	0.032	0.040
$(\sin \theta/\lambda)_{max}$ (Å <sup>-1</sup> )	0.619	0.682	0.626	0.621
Refinement				
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.060, 0.171, 1.02	0.048, 0.112, 1.03	0.041, 0.134, 1.14	0.057, 0.169, 1.04
No. of reflections	2614	3573	2172	3113
No. of parameters	201	228	165	277
No. of restraints	0	0	0	5
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.63, -0.27	0.34, -0.23	0.62, -0.57	0.81, -0.41

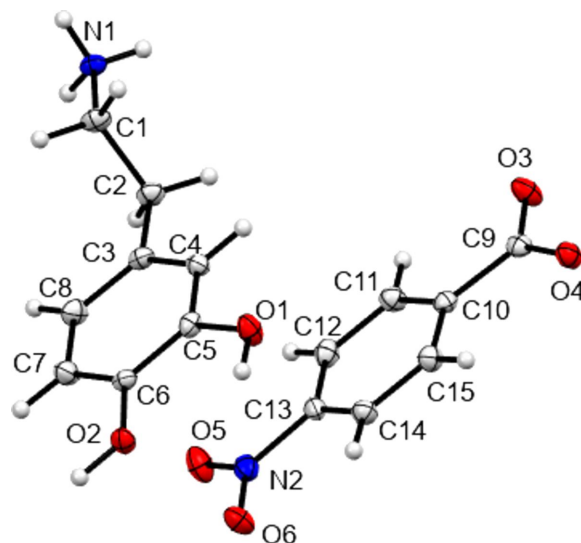
Computer programs: *CrysAlis PRO* (Rigaku OD, 2019), *SIR92* (Altomare *et al.*, 1994), *SHELXS* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2020) and *SHELXL* in *WinGX* (Farrugia, 2012).

mine cation, a disordered hydroxybenzenesulfonate anion and a water molecule. In all four cases, the dopamine moiety has been protonated at the amine group and the H atom of the *meta*-hydroxy substituent is orientated towards the O atom of the *para*-hydroxy group to form an intramolecular hydrogen bond. All of the ethylammonium chains adopt extended conformations, with the N1–C1–C2–C3 torsion angles ranging from  $-168.89$  (14) to  $176.39$  (16)°. This corresponds to an *anti* arrangement of the large aromatic and NH<sub>3</sub> substituents on the C1–C2 fragment. The relevant literature

**Figure 1**

View of the asymmetric unit contents of **I**, with non-H atoms shown as 50% probability displacement ellipsoids. Here and in Figs. 2–4, H atoms are drawn as spheres of arbitrary size.

salt forms as listed in Table 6 also adopt extended conformations, with the exception of the dinitrobenzoate salt MIYLOV. This is the only form to have a folded conformation, displaying an N–C–C–C torsion angle of 60.5° (Ohba & Ito, 2002). This distribution of conformations resembles that found for the salt forms of the closely related tyramine cation. Of 42 tyramine salt forms, the majority displayed extended confor-

**Figure 2**

View of the asymmetric unit contents of **II**, with non-H atoms shown as 50% probability displacement ellipsoids.

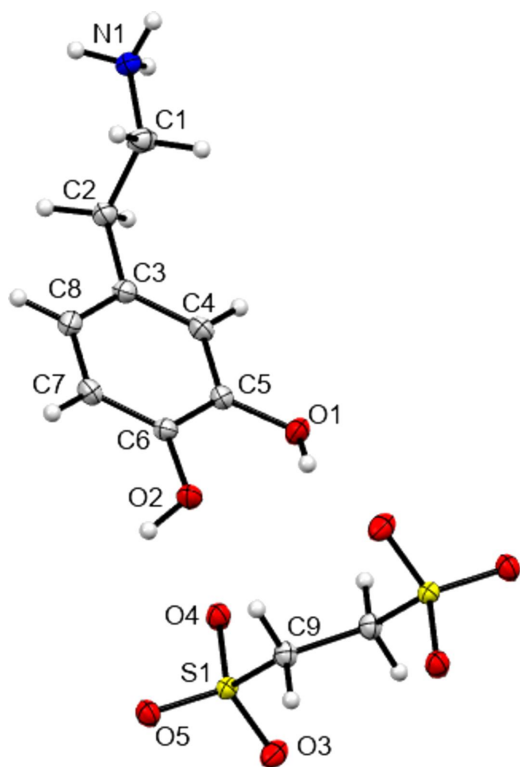
**Table 2**  
Hydrogen-bond geometry (Å, °) for **I**.

<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>
O1—H1H···O2	0.84 (4)	2.29 (4)	2.736 (3)	113 (3)
O1—H1H···O3 <sup>i</sup>	0.84 (4)	2.17 (4)	2.872 (3)	141 (3)
O2—H2H···O4 <sup>ii</sup>	0.85 (4)	1.83 (4)	2.666 (2)	171 (3)
N1—H1N···O4 <sup>iii</sup>	0.98 (3)	1.87 (4)	2.834 (3)	167 (3)
N1—H2N···O3	0.95 (3)	1.93 (3)	2.867 (3)	171 (3)
N1—H3N···O3 <sup>iv</sup>	0.87 (4)	2.04 (4)	2.866 (3)	156 (3)

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

mations and only four displayed a folded conformation (Briggs *et al.*, 2012).

The dopamine cations of **I–IV** utilize all three NH groups and both OH groups as hydrogen-bond donors, but apart from that, there is little similarity between them and in detail each acts in a different manner. As shown in Table 7, in benzoate **I** all potential donors make a single hydrogen bond to an O atom of a benzoate COO group. Here, none of the atoms of the cation acts as an acceptor and hydrogen bonds exist only between cations and anions. In **II**, the number of potential hydrogen-bond acceptors is increased by the inclusion of an NO<sub>2</sub> group on the anion. This leads to the cation making extra donor interactions, with one NH group and the *para*-OH group both acting as bifurcated donors to two hydrogen bonds. Again, no atom of the cation acts as an acceptor and all hydrogen bonds are formed between cations and anions. In **III**, all five cation donor groups make single hydrogen bonds,



**Figure 3**  
View of the asymmetric unit contents of **III**, extended to show the complete dianion generated by the inversion centre in the C–C bond. Non-H atoms are shown as 50% probability displacement ellipsoids.

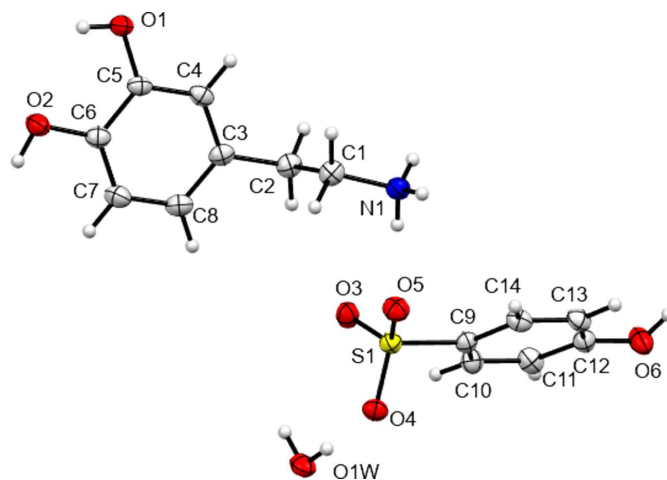
**Table 3**  
Hydrogen-bond geometry (Å, °) for **II**.

<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>
O1—H1H···O2	0.87 (2)	2.31 (2)	2.7384 (17)	110.4 (19)
O1—H1H···O4 <sup>i</sup>	0.87 (2)	1.99 (2)	2.8030 (17)	156 (2)
O2—H2H···O3 <sup>ii</sup>	0.94 (2)	1.64 (2)	2.5780 (16)	178 (2)
N1—H1N···O4 <sup>iii</sup>	0.97 (2)	1.80 (3)	2.763 (2)	170 (2)
N1—H2N···O2 <sup>iv</sup>	0.90 (2)	2.44 (2)	2.9890 (18)	119.7 (16)
N1—H2N···O6 <sup>iv</sup>	0.90 (2)	2.41 (2)	3.095 (2)	133.8 (17)
N1—H3N···O2 <sup>v</sup>	0.88 (2)	2.50 (2)	2.9956 (19)	116.6 (15)
N1—H3N···O4 <sup>vi</sup>	0.88 (2)	2.50 (2)	3.1125 (18)	127.5 (16)
N1—H3N···O5 <sup>vii</sup>	0.88 (2)	2.48 (2)	3.181 (2)	137.3 (16)

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

but in contrast to **I** and **II**, the *para*-OH group also acts as an acceptor, accepting a hydrogen-bond contact from a neighbouring RNH<sub>3</sub> group. Thus, in **III**, there are hydrogen bonds both between cations and anions, and between pairs of cations. In the hydrate **IV**, one of the NH groups makes a bifurcated donor interaction with two neighbouring SO<sub>3</sub> groups and all other cation donor atoms make single hydrogen bonds. That from the *para*-OH group donates to a water molecule, but all others are to anions. The *para*-OH group also accepts a hydrogen bond from a water molecule. In **IV**, hydrogen bonds link cations to anions, and both cations and anions to water. However, unlike **III**, there are no cation-to-cation hydrogen-bond contacts.

A large-scale structural study on tyramine salt forms identified two common hydrogen-bonding motifs that co-existed in 19 of 24 benzoate and sulfonate salts of that compound (Briggs *et al.*, 2012). These motifs were both one-dimensional (1D) chain structures, one of graph set C<sub>2</sub><sup>2</sup>(6) corresponding to an (···OXO···HNH···)<sub>n</sub> (X = C or S) linkage and one of graph set C<sub>2</sub><sup>2</sup>(13) corresponding to COO or SO<sub>3</sub> groups bonding to both the NH<sub>3</sub> head and the *para*-OH tail of the cation. Here only structures **I** and **III** show both motifs. They also have an additional C<sub>2</sub><sup>2</sup>(12) motif. This latter is equivalent



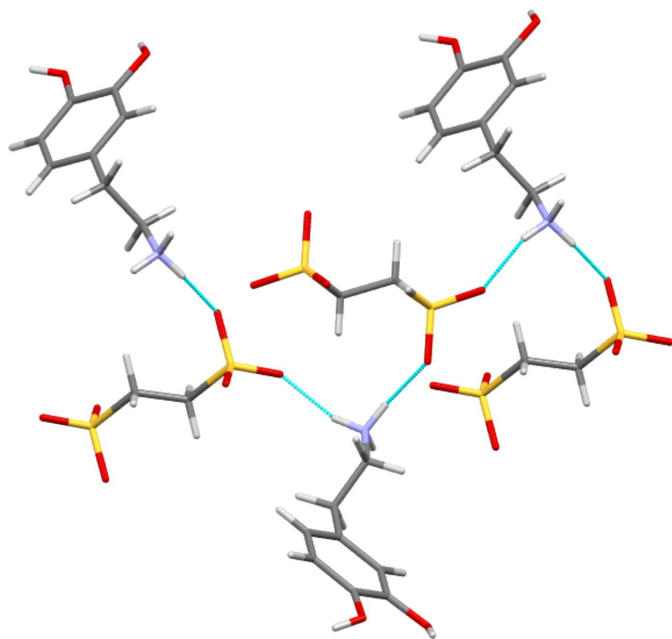
**Figure 4**  
View of the asymmetric unit contents of **IV**, with disorder of atoms C10, C11, C13 and C14 hidden for clarity. Non-H atoms are shown as 50% probability displacement ellipsoids.

**Table 4**  
Hydrogen-bond geometry (Å, °) for **III**.

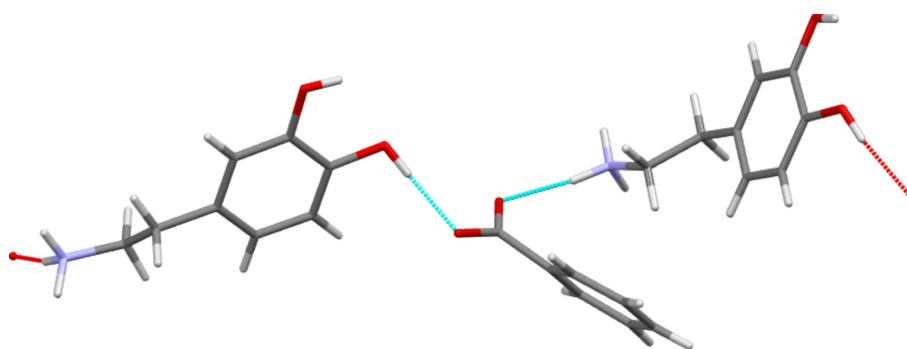
$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1–H1H $\cdots$ O2	0.85 (3)	2.32 (3)	2.746 (2)	112 (2)
O1–H1H $\cdots$ O3 <sup>i</sup>	0.85 (3)	2.02 (3)	2.807 (2)	154 (3)
O2–H2H $\cdots$ O4 <sup>ii</sup>	0.89 (3)	1.85 (3)	2.727 (2)	167 (3)
N1–H1N $\cdots$ O5 <sup>iii</sup>	0.90 (3)	1.89 (3)	2.762 (2)	163 (2)
N1–H2N $\cdots$ O2 <sup>iv</sup>	0.85 (3)	2.11 (3)	2.890 (2)	152 (2)
N1–H2N $\cdots$ O3 <sup>v</sup>	0.85 (3)	2.49 (3)	2.974 (2)	117 (2)
N1–H3N $\cdots$ O4 <sup>vi</sup>	0.89 (3)	2.00 (3)	2.776 (2)	146 (3)
N1–H3N $\cdots$ O5 <sup>vii</sup>	0.89 (3)	2.61 (3)	3.112 (2)	117 (2)

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

to the  $C_2^2(13)$  motif, but utilizes the extra *meta*-OH group of dopamine rather than the *para*-OH group which is common to both dopamine and tyramine. Figs. 5 and 6 illustrate these hydrogen-bonded-chain features. Structure **IV** contains both



**Figure 5**  
Part of the 1D  $C_2^2(6)$  motif found in **III**. The hydrogen-bonded chain propagates parallel to the  $a$  direction.



**Figure 6**  
An illustration showing the repeating core of the  $C_2^2(13)$  motif, utilizing the *para*-OH group, of structure **I**. A similar  $C_2^2(12)$  motif, using the same functional groups but utilizing the *meta*-OH group rather than the *para*-OH group, also exists here.

**Table 5**  
Hydrogen-bond geometry (Å, °) for **IV**.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1–H1H $\cdots$ O2	0.87 (1)	2.28 (3)	2.749 (3)	114 (3)
O1–H1H $\cdots$ O3 <sup>i</sup>	0.87 (1)	1.95 (2)	2.754 (3)	152 (3)
O2–H2H $\cdots$ O1W <sup>ii</sup>	0.88 (1)	1.84 (2)	2.693 (3)	164 (4)
N1–H1N $\cdots$ O4 <sup>iii</sup>	0.86 (4)	1.99 (4)	2.850 (3)	178 (4)
N1–H2N $\cdots$ O5	0.86 (4)	1.91 (4)	2.766 (3)	172 (3)
N1–H3N $\cdots$ O3 <sup>iv</sup>	0.86 (4)	2.27 (4)	2.927 (3)	133 (3)
N1–H3N $\cdots$ O6 <sup>v</sup>	0.86 (4)	2.46 (4)	3.005 (3)	122 (3)
O6–H3H $\cdots$ O1W <sup>v</sup>	0.88 (1)	1.83 (2)	2.686 (3)	164 (4)
O1W–H1W $\cdots$ O2 <sup>vi</sup>	0.88 (1)	1.88 (1)	2.752 (3)	175 (4)
O1W–H2W $\cdots$ O4	0.88 (1)	1.82 (1)	2.698 (3)	177 (4)

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

the  $C_2^2(6)$  and the  $C_2^2(12)$  motifs, but the *para*-OH group of this hydrate only hydrogen bonds to water molecules and thus the  $C_2^2(13)$  motif does not occur here. In contrast, of the three motifs described above, the nitrobenzoate salt **II** only displays the  $C_2^2(13)$  chain. In the hydrogen bonding of structure **II**, ring motifs become prevalent, including that formed by a tetramer consisting of two cations and two anions. These are linked by hydrogen bonding between the catechol moieties and the carboxylate groups in an  $R_4^4(18)$  motif. This coplanar tetramer is then capped on each side of the plane through hydrogen bonds to the  $RNH_3$  groups of two further cations, as shown in Fig. 7.

On attempting to compare the hydrogen-bonding behaviour of dopamine cations in structures **I–IV** with that in the literature salt forms, a problem was observed. The H-atom positions recovered for the structures of ATOLIF, ATOMAY and, to a certain extent, ATOLUR04 appeared unusual (Fig. 8) (Ivanova & Spiteller, 2010, 2017). As well as unusual out-of-plane conformations, those groups which would be expected to be strong hydrogen-bond donors did not connect with geometrically reasonable acceptor atoms, in contradiction to Etter's rules (Etter, 1990). In all three cases, alternative H-atom positions that did give typical hydrogen-bond interactions were available. Thus, for these structures, before hydrogen-bonding motifs were analysed, the H atoms were removed and manually replaced with the H atoms situated so as to give typical hydrogen-bonding geometries. For the hydrate ATOLUR04, H atoms were missing from the water

**Table 6**  
Available crystal structures of dopamine forms.

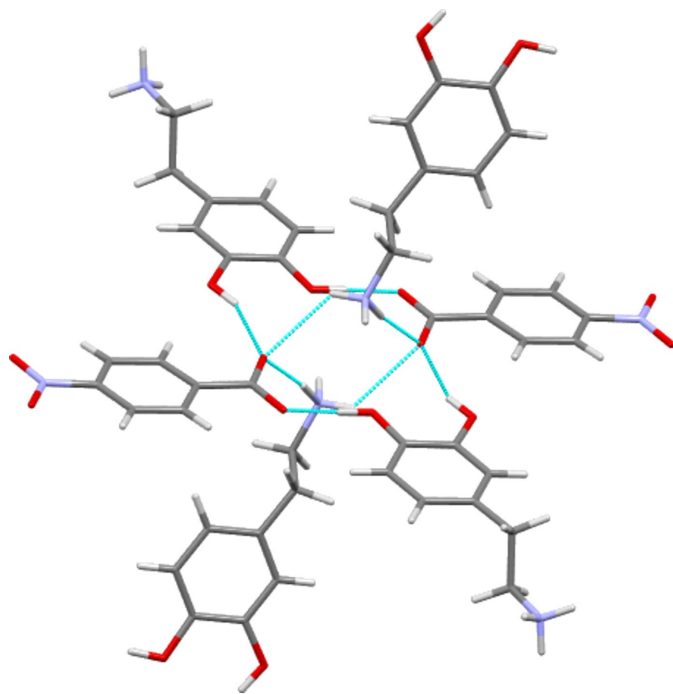
CSD refcode	Anion	Solvent	Comment	Reference
TIRZAX	None – free base structure	none	Zwitterion	Cruickshank <i>et al.</i> (2013)
DOPAMN01	Chloride	none		Giesecke (1980)
QQQAEJ02	Bromide	none		Pike & Dziura (2013)
ATOLUR04	Iodide	none	H-atom positions changed	Ivanova & Spittler (2017)
CIZYAN	Nitrate	none	$Z' = 2$	Gatfaoui <i>et al.</i> (2014)
OEGEJAJ	Perchlorate	none		Boghaei <i>et al.</i> (2008)
ATOLIF	3-Carboxy-4-hydroxybenzenesulfonate	1.5 H <sub>2</sub> O	H-atom positions changed	Ivanova & Spittler (2010)
ATOMAY	Hydrogen squarate	none	H-atom positions changed	Ivanova & Spittler (2010)
RAWDEB	Pyrenetetrasulfonate	5 H <sub>2</sub> O	Contains 1 dopamine and 3 guanidinium cations	Feng <i>et al.</i> (2017)
MIYLOV	3,5-Dinitrobenzoate	none		Ohba & Ito (2002)
<b>I</b>	Benzoate	none		This work
<b>II</b>	4-Nitrobenzoate	none		This work
<b>III</b>	Ethanedisulfonate	none		This work
<b>IV</b>	4-Hydroxybenzenesulfonate	1 H <sub>2</sub> O	Disordered anion	This work

molecule sites. Thus, before analysis, these H atoms were also added in geometrically reasonable expected positions. All further discussion of the hydrogen bonding of these three compounds thus refers to the edited structures. Atomic structures for these edited structures are given in CIF format in the supporting information.

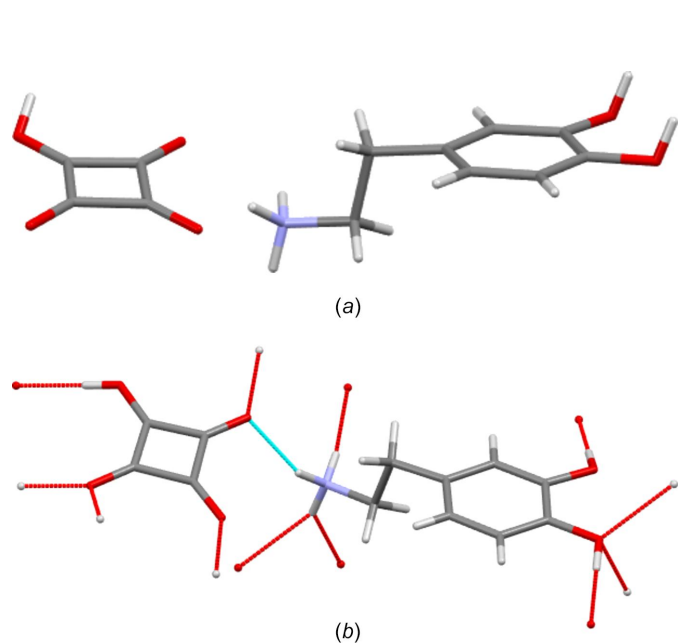
When examining all 13 available salt forms of dopamine in Table 7, it becomes apparent that the hydrogen-bonding behaviour of the cation is very variable. Of 14 crystallographically independent dopamine fragments, only two, those of the chloride DOPAMN01 and the bromide QQQAEJ01, have the same set of interactions originating from the dopamine cation. Furthermore, none of the literature carboxylate

or sulfonate structures feature the combination of  $C_2^2(6)$  and  $C_2^2(13)$  chains that is found to be prevalent in tyramine salt forms (Briggs *et al.*, 2012). The halide salt forms of dopamine (Cl, Br and I) do though present the  $C_2^1(4)$ ,  $C_2^1(11)$  and  $C_2^1(10)$  chains that are the monoatomic ion equivalent of the three motifs discussed above for COO<sup>-</sup> and SO<sub>3</sub><sup>-</sup>-based ions. Finally, it is noted that the ladder-like structures commonly seen for other carboxylate salt forms of RNH<sub>3</sub><sup>+</sup> species (Kinbara *et al.*, 1996) are found for neither dopamine salt forms nor for tyramine salt forms.

In an attempt to find further comparable features across the structural group, use was made of the ‘crystal packing similarity’ module within *Mercury* (Macrae *et al.*, 2020; Childs *et al.*, 2009). This was used to investigate similarity in the cation packing across the available dopamine forms by investigating



**Figure 7**  
A central hydrogen-bonding motif in **II** consisting of four coplanar groups linked *via* the catechol and carboxylate groups. This unit is capped top and bottom by hydrogen bonds to the RNH<sub>3</sub> group of the cation.



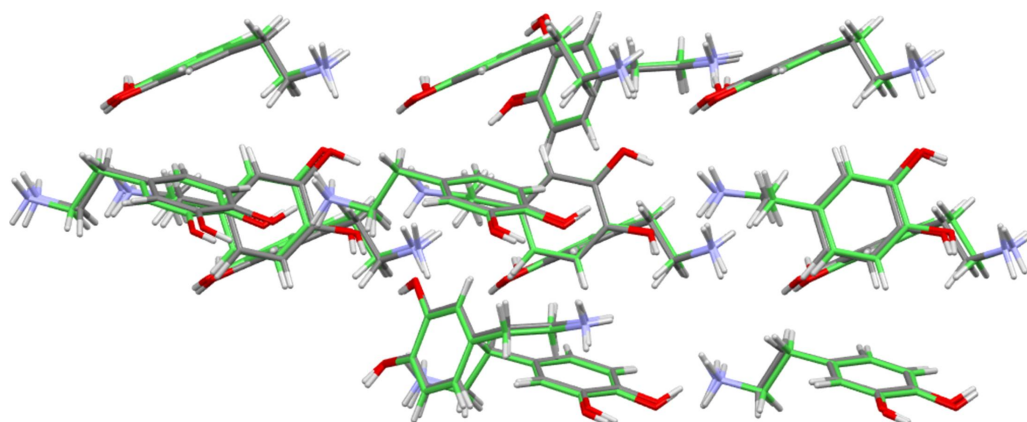
**Figure 8**  
(a) The structure of ATOMAY as recovered from the CSD. Note the unusual out-of-plane geometry of the H atoms of the OH substituents. These out-of-plane H atoms do not form hydrogen bonds with neighbouring ions. (b) The structure of ATOMAY edited so as to place H atoms in-plane and in geometries that maximize hydrogen bonding.

**Table 7**

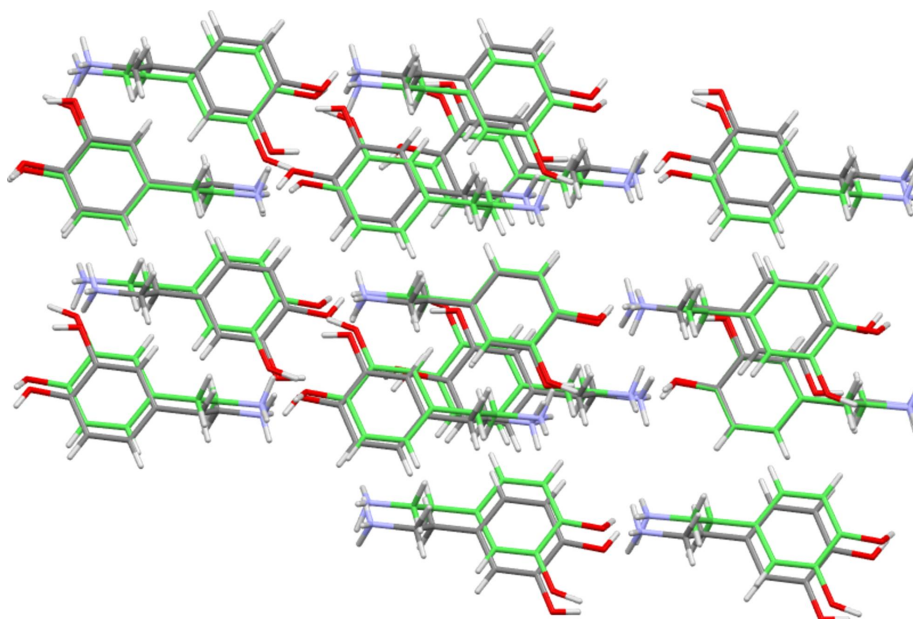
Selected hydrogen-bonding features in the structures of salt forms of dopamine.

 The table shows the various potential acceptor (*A*) and donor (*D*) groups of the dopamine cation (first row) and details the types of fragment that form hydrogen bonds with these groups (body of table).

CSD refcode	Anion	<i>para</i> -OH <i>D</i>	<i>para</i> -OH <i>A</i>	<i>meta</i> -OH <i>D</i>	<i>meta</i> -OH <i>A</i>	1st NH <i>D</i>	2nd NH <i>D</i>	3rd NH <i>D</i>
DOPAMN01	Cl	anion	NH	anion		anion and OH	anion	anion
QQQARJ02	Br	anion	NH	anion		anion and OH	anion	anion
ATOLUR04	I	anion	NH	anion	NH	anion and OH	anion and OH	anion
CIZYAN Fragment 1	NO <sub>3</sub>	2 O of anion		anion	NH	anion and OH	2 O of anion	2 × anions
CIZYAN Fragment 2	NO <sub>3</sub>	anion	NH	anion	NH	OH	2 O of anion	2 × anions and OH
OGEGAJ	ClO <sub>4</sub>	anion	NH	anion	NH	anion and OH	anion	OH
ATOLIF	carboxyhydroxybenzenesulfonate	anion	H <sub>2</sub> O	H <sub>2</sub> O		anion	anion	H <sub>2</sub> O
ATOMAY	squarate	anion	2 × NH	anion		anion	anion	2 × OH
RAWDEB	pyrenetetrasulfonate	H <sub>2</sub> O		anion	2 × NH (quad)	H <sub>2</sub> O	H <sub>2</sub> O	H <sub>2</sub> O
MIYLOV	dinitrobenzoate	anion		anion (nitro)		anion	anion (nitro)	2 O of anion
<b>I</b>	benzoate	anion		anion		anion	anion	anion
<b>II</b>	nitrobenzoate	2 O of anion		anion		anion	anion (nitro)	2 × anion (COO and nitro)
<b>III</b>	ethanedisulfonate	anion	NH	anion		anion	anion	OH
<b>IV</b>	hydroxybenzenesulfonate	H <sub>2</sub> O	H <sub>2</sub> O	anion		anion and OH	anion	anion


**Figure 9**

Overlay diagram showing the packing of 15 dopamine cations of the chloride structure (multicoloured) and 15 dopamine cations of the bromide structure (green). The r.m.s. value is 0.210 Å. Anions have been omitted for clarity.


**Figure 10**

Overlay diagram showing the packing of 15 dopamine cations of the perchlorate structure (multicoloured) and 15 dopamine cations of the iodide structure (green). The r.m.s. value is 0.451 Å. Anions have been omitted for clarity.

**Table 8**  
Groups identified as having isostructural packing of cations.

	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6
Cations	Dop only	Dop and Tyr	Dop and Tyr	Tyr only	Tyr only	Tyr only
Structure	ATOLUR04 [dop][I] OGEGAJ [dop][ClO <sub>4</sub> ]	<b>I</b> [dop][benzoate] MEDDEG [tyr][4-aminobenzoate] MEDFEI [tyr][4-methylbenzoate]	DOPAMN01 [dop][Cl] QQQAEJ02 [dop][Br]  <b>III</b> [dop][ethanedisulfonate]  TIRZEB Tyramine hemihydrate TYRAMC11 [tyr][Cl] MECYAW [tyr][Br] MECYIE [tyr][BF <sub>4</sub> ]-H <sub>2</sub> O MECYUQ [tyr][PO <sub>4</sub> H <sub>2</sub> ]-2H <sub>2</sub> O MECYOK [tyr][ClO <sub>4</sub> ]-H <sub>2</sub> O	MEDGEJ MEDGUZ  MEDHEK	MEDBAA MEDBII	MEDBOO MEDBUU  MEDCEF MEDDOQ
Comments		Mixed cations with benzoate or <i>para</i> -substituted benzoate anions	Mixed cations and neutral tryamine; mixed anhydrate and hydrate; simple inorganic anions	All dicarboxylate anions	Benzoate and halobenzoate anions	All halo or methyl-substituted benzoate anions

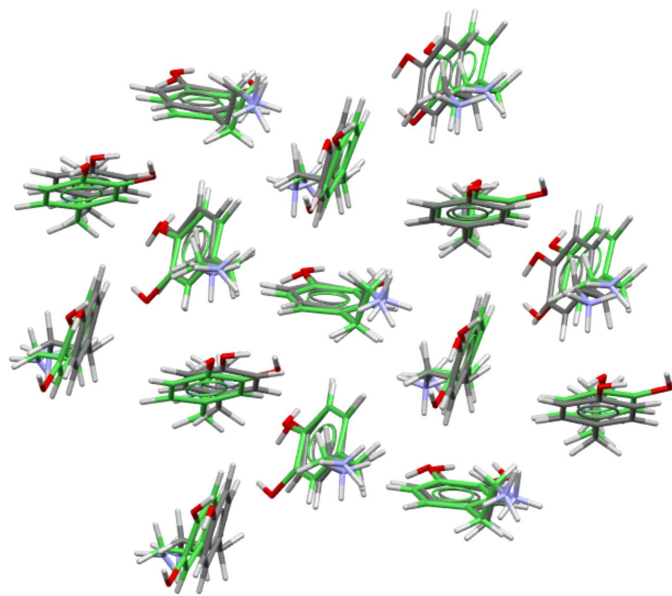
Note: Dop is the dopamine cation and Tyr is the tyramine cation.

geometrical similarity between small clusters of dopamine cations. In doing so other species present, such as anions and solvent molecules, were ignored. An initial calculation using only the dopamine structures identified that the chloride and bromide salts of dopamine were isostructural at a cluster size of 15 cations, and that the iodide and perchlorate salt forms were similarly isostructural (Figs. 9 and 10). For the Cl/Br pair, the reported unit cells and space groups clearly indicate that the complete structures are both isostructural and isomorphous (Giesecke, 1980; Pike & Dziura, 2013). However, there is no such similarity in the unit cells of the I/ClO<sub>4</sub> pair (Ivanova & Spitteller, 2017; Boghaei *et al.*, 2008).

More interesting results were obtained when the packing similarity module was applied to a data set that included both the available dopamine forms and those of tyramine. This time

six groups of structures with similar cation packing arrays at the level of a 15 from 15 match were identified (Table 8). Group 1 contains only the dopamine I/ClO<sub>4</sub> pair as already seen, and groups 4, 5 and 6 contain only tyramine structures. However, groups 2 and 3 are interesting as they contain both dopamine and tyramine structures. Group 2 contains **I**, the benzoate salt of dopamine, and both the 4-amino- and 4-methylbenzoate salt forms of tyramine. Group 3 is an expanded version of the dopamine Cl/Br grouping that now also contains **III**, the ethanedisulfonate salt of dopamine, and six forms of tyramine. These are the chloride, bromide, perchlorate, BF<sub>4</sub> and dihydrogen phosphate salts of tyramine, and also the neutral hemihydrate of tyramine. (Note: when assessing dopamine structures alone, the ethanedisulfonate structure **III** was found to be related to the Cl/Br group, but only at a level with 7 from 15 matches. However, the larger and more varied dopamine/tyramine group appears to allow a fuller match.) Each group of Table 8 is composed of structures with broadly similar anion types. Thus, for example, group 2 contains only structures with benzoate or *para*-benzoate anions, and group 3 is composed of species with simple inorganic anions or cofomers. Beyond this basic similarity though lies a great deal of variation. For example, group 3 encompasses structures with different cations, with different anions, with and without solvent present, and with neutral PEA species rather than charged ones, see Fig. 11 as an example.

This, of course, leads to very different hydrogen bonding throughout the structures of these compounds. From a chemical identity point of view, the two most different structures of group 3 are the ethanedisulfonate salt of dopamine, **III**, and the hemihydrate of tyramine, TIRZEB (Cruickshank *et al.*, 2013). The ethanedisulfonate dianion does not fit well with the descriptor used above of a 'simple inorganic anion' being as it is both larger than the other anions in this group and doubly charged. This is reconciled simply. The ethanedisulfonate ion lies upon a crystallographic centre of symmetry, thus making the unique repeating structural part the much smaller 'O<sub>3</sub>SCH<sub>2</sub>' fragment which is a reasonable match to a 'simple inorganic anion'. The ethanedisulfonate anion takes the structural place of two anions in other group



**Figure 11**  
Overlay diagram showing the packing of 15 dopamine cations of the chloride structure (green) and 15 tyramine units of the hemihydrate structure. The r.m.s. value is 0.566 Å. Anions and water molecules have been omitted for clarity.



member structures, such as that of dopamine chloride, DOPAMN01. The intramolecular S··S separation of 4.338 Å in **III** compares well with the intermolecular Cl··Cl distance of 4.303 Å in the chloride. Tyramine hemihydrate, TIRZEB, is an interesting structure. Disorder of the phenol H-atom positions in this structure means that the tyramine fragments present are best thought of as a mix of neutral, cationic and zwitterionic forms of tyramine (Cruickshank *et al.*, 2013). This presents some difference to the cationic PEA forms that make up the rest of group 3. Water is obviously a neutral cofomer rather than the small anions found in the rest of group 3, but a further difference is stoichiometry. There is only one water molecule per two tyramine fragments in TIRZEB, as opposed to one monoanionic fragment per organic cation in all the other structures of group 3. Despite all this variation in chemical identity and in the type and number of the strong hydrogen-bonding intermolecular interactions, the cations of these groups still adopt similar packing arrangements. Conversely, similarities in hydrogen bonding do not necessarily seem to lead to similarity in cation packing. One of the few patterns in the hydrogen-bonding behaviour of the dopamine salts is that all three halides have structures based around the same chain-type interactions (see above). Despite this hydrogen-bonding similarity, only the Cl and Br salt forms are found in group 3, with the iodide salt grouping with the perchlorate in group 1. A similar observation that PEA cation packing was not governed by hydrogen-bond formation, though one from a data set that did not feature different cations, was made in a study on methylephedrine salt forms (Kennedy *et al.*, 2011). In a related point, Collier *et al.* (2006) noted that it was simply the gross amphiphilic nature of the ephedrine cation that dominated packing in structures of its salt forms, rather than the detail of the functional groups or individual interaction types.

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## supporting information

*Acta Cryst.* (2023). C79 [https://doi.org/10.1107/S2053229623007696]

## A structural comparison of salt forms of dopamine with the structures of other phenylethylamines

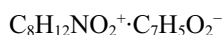
**Alan R. Kennedy, Laura Cruickshank, Pamela Maher and Zoe McKinnon**

### Computing details

For all structures, data collection: *CrysAlis PRO* (Rigaku OD, 2019); cell refinement: *CrysAlis PRO* (Rigaku OD, 2019); data reduction: *CrysAlis PRO* (Rigaku OD, 2019). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994) for (I); *SHELXS* (Sheldrick, 2015a) for (II), (III), (IV). For all structures, program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2020). Software used to prepare material for publication: *SHELXL2018* in *WinGX* (Farrugia, 2012) for (I), (II); *SHELXL* in *WinGX* (Farrugia, 2012) for (III), (IV).

### 2-(3,4-Dihydroxyphenyl)ethan-1-aminium benzoate (I)

#### Crystal data



$M_r = 275.29$

Monoclinic,  $P2_1/c$

$a = 11.7637$  (6) Å

$b = 11.7460$  (5) Å

$c = 10.3316$  (5) Å

$\beta = 111.384$  (6)°

$V = 1329.30$  (12) Å<sup>3</sup>

$Z = 4$

$F(000) = 584$

$D_x = 1.376$  Mg m<sup>-3</sup>

Cu  $K\alpha$  radiation,  $\lambda = 1.5418$  Å

Cell parameters from 1775 reflections

$\theta = 5.5\text{--}72.6^\circ$

$\mu = 0.83$  mm<sup>-1</sup>

$T = 123$  K

Blade, colourless

$0.35 \times 0.10 \times 0.02$  mm

#### Data collection

Oxford Diffraction Gemini S  
diffractometer

Radiation source: sealed tube

$\omega$  scans

Absorption correction: multi-scan  
(*CrysAlis PRO*; Rigaku OD, 2019)

$T_{\min} = 0.761$ ,  $T_{\max} = 1.000$

5127 measured reflections

2614 independent reflections

2033 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 72.8^\circ$ ,  $\theta_{\min} = 8.1^\circ$

$h = -14 \rightarrow 14$

$k = -14 \rightarrow 14$

$l = -9 \rightarrow 12$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.060$

$wR(F^2) = 0.171$

$S = 1.02$

2614 reflections

201 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0888P)^2 + 0.9631P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.63$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.26$  e Å<sup>-3</sup>

*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.

**Refinement.** All measurements were made with Oxford Diffraction instruments using *Crysalis PRO* software for data collection and reduction (Rigaku OD, 2019). Solution was by direct methods, *SIR92* or *SHELXS* (Altomare *et al.*, 1994; Sheldrick, 2015a). All structures were refined to convergence against  $F^2$  using all unique reflections and the program *SHELXL2018* as implemented within *WinGX* (Sheldrick, 2015b; Farrugia, 2012).

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	1.20255 (19)	0.04346 (18)	0.6282 (2)	0.0421 (5)
O2	1.28979 (15)	0.19051 (14)	0.84779 (19)	0.0276 (4)
O3	0.43021 (15)	0.11232 (14)	0.60916 (17)	0.0292 (4)
O4	0.40997 (15)	0.30029 (14)	0.62181 (17)	0.0281 (4)
N1	0.62199 (17)	−0.05339 (17)	0.6759 (2)	0.0244 (4)
C1	0.7372 (2)	0.0150 (2)	0.7240 (4)	0.0409 (7)
H1A	0.728184	0.079754	0.659696	0.049*
H1B	0.750566	0.046542	0.817302	0.049*
C2	0.8451 (2)	−0.0529 (2)	0.7309 (3)	0.0413 (7)
H2A	0.827626	−0.092126	0.640880	0.050*
H2B	0.860028	−0.111904	0.803610	0.050*
C3	0.9600 (2)	0.0188 (2)	0.7628 (3)	0.0358 (6)
C4	1.0295 (2)	0.0041 (2)	0.6822 (3)	0.0345 (6)
H4	1.003729	−0.048194	0.606940	0.041*
C5	1.1370 (2)	0.0650 (2)	0.7098 (3)	0.0319 (6)
C6	1.1783 (2)	0.14003 (19)	0.8221 (3)	0.0275 (5)
C7	1.1075 (2)	0.1579 (2)	0.9009 (3)	0.0368 (6)
H7	1.132590	0.210908	0.975447	0.044*
C8	0.9974 (3)	0.0971 (2)	0.8703 (3)	0.0426 (7)
H8	0.948218	0.110046	0.924125	0.051*
C9	0.5586 (2)	0.20615 (19)	0.8119 (2)	0.0235 (5)
C10	0.5704 (2)	0.1143 (2)	0.9017 (2)	0.0271 (5)
H10	0.511138	0.055248	0.877067	0.033*
C11	0.6686 (2)	0.1094 (2)	1.0268 (3)	0.0322 (6)
H11	0.674677	0.048533	1.089462	0.039*
C12	0.7579 (2)	0.1925 (2)	1.0610 (3)	0.0362 (6)
H12	0.826813	0.186991	1.145034	0.043*
C13	0.7464 (2)	0.2843 (2)	0.9716 (3)	0.0353 (6)
H13	0.807283	0.341913	0.994916	0.042*
C14	0.6458 (2)	0.2915 (2)	0.8487 (2)	0.0279 (5)
H14	0.636740	0.355359	0.789335	0.033*
C15	0.4585 (2)	0.20679 (19)	0.6709 (2)	0.0230 (5)
H1N	0.618 (3)	−0.112 (3)	0.741 (3)	0.044 (9)*
H2N	0.555 (3)	−0.003 (3)	0.660 (3)	0.044 (9)*
H3N	0.607 (3)	−0.091 (3)	0.599 (4)	0.040 (8)*

H1H	1.266 (3)	0.084 (3)	0.654 (4)	0.049 (10)*
H2H	1.324 (3)	0.200 (3)	0.935 (4)	0.045 (10)*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0401 (11)	0.0485 (12)	0.0364 (11)	-0.0140 (9)	0.0126 (9)	-0.0125 (9)
O2	0.0259 (8)	0.0289 (9)	0.0274 (10)	-0.0054 (6)	0.0090 (7)	-0.0019 (7)
O3	0.0327 (9)	0.0249 (8)	0.0276 (9)	0.0030 (7)	0.0081 (7)	-0.0012 (7)
O4	0.0351 (9)	0.0250 (8)	0.0244 (9)	0.0084 (7)	0.0109 (7)	0.0030 (6)
N1	0.0249 (10)	0.0216 (9)	0.0253 (11)	-0.0021 (7)	0.0077 (8)	0.0006 (8)
C1	0.0309 (13)	0.0294 (13)	0.065 (2)	-0.0063 (10)	0.0201 (13)	-0.0031 (12)
C2	0.0335 (13)	0.0304 (13)	0.0571 (19)	-0.0042 (11)	0.0131 (12)	-0.0056 (12)
C3	0.0291 (12)	0.0287 (12)	0.0435 (16)	-0.0006 (10)	0.0062 (11)	-0.0022 (11)
C4	0.0309 (12)	0.0319 (13)	0.0327 (14)	-0.0026 (10)	0.0020 (10)	-0.0012 (10)
C5	0.0276 (11)	0.0297 (12)	0.0286 (13)	-0.0016 (10)	-0.0013 (10)	0.0061 (10)
C6	0.0226 (11)	0.0239 (11)	0.0325 (13)	0.0006 (8)	0.0058 (9)	0.0057 (9)
C7	0.0336 (13)	0.0344 (13)	0.0438 (16)	-0.0015 (11)	0.0161 (12)	-0.0047 (11)
C8	0.0388 (14)	0.0368 (14)	0.0608 (19)	-0.0016 (11)	0.0285 (14)	-0.0039 (13)
C9	0.0270 (11)	0.0253 (11)	0.0197 (11)	0.0052 (8)	0.0102 (9)	-0.0004 (8)
C10	0.0313 (11)	0.0261 (11)	0.0267 (12)	0.0052 (9)	0.0139 (10)	0.0031 (9)
C11	0.0410 (13)	0.0326 (12)	0.0250 (13)	0.0120 (10)	0.0145 (11)	0.0069 (10)
C12	0.0352 (13)	0.0461 (15)	0.0233 (13)	0.0096 (11)	0.0058 (10)	-0.0002 (11)
C13	0.0337 (13)	0.0400 (14)	0.0302 (13)	-0.0035 (11)	0.0094 (11)	-0.0059 (11)
C14	0.0340 (12)	0.0274 (11)	0.0235 (12)	0.0007 (9)	0.0120 (10)	0.0013 (9)
C15	0.0243 (10)	0.0254 (11)	0.0228 (11)	0.0037 (8)	0.0129 (9)	0.0018 (8)

*Geometric parameters (Å, °)*

O1—C5	1.358 (3)	C4—H4	0.9500
O1—H1H	0.84 (4)	C5—C6	1.396 (4)
O2—C6	1.374 (3)	C6—C7	1.377 (4)
O2—H2H	0.85 (4)	C7—C8	1.410 (4)
O3—C15	1.263 (3)	C7—H7	0.9500
O4—C15	1.256 (3)	C8—H8	0.9500
N1—C1	1.496 (3)	C9—C14	1.385 (3)
N1—H1N	0.98 (3)	C9—C10	1.396 (3)
N1—H2N	0.95 (3)	C9—C15	1.503 (3)
N1—H3N	0.87 (4)	C10—C11	1.386 (4)
C1—C2	1.478 (4)	C10—H10	0.9500
C1—H1A	0.9900	C11—C12	1.381 (4)
C1—H1B	0.9900	C11—H11	0.9500
C2—C3	1.523 (3)	C12—C13	1.394 (4)
C2—H2A	0.9900	C12—H12	0.9500
C2—H2B	0.9900	C13—C14	1.387 (4)
C3—C4	1.373 (4)	C13—H13	0.9500
C3—C8	1.384 (4)	C14—H14	0.9500
C4—C5	1.389 (4)		

C5—O1—H1H	110 (2)	O2—C6—C5	116.8 (2)
C6—O2—H2H	108 (2)	C7—C6—C5	119.0 (2)
C1—N1—H1N	114.8 (19)	C6—C7—C8	119.6 (3)
C1—N1—H2N	108 (2)	C6—C7—H7	120.2
H1N—N1—H2N	108 (3)	C8—C7—H7	120.2
C1—N1—H3N	116 (2)	C3—C8—C7	120.9 (3)
H1N—N1—H3N	103 (3)	C3—C8—H8	119.5
H2N—N1—H3N	106 (3)	C7—C8—H8	119.5
C2—C1—N1	112.6 (2)	C14—C9—C10	119.5 (2)
C2—C1—H1A	109.1	C14—C9—C15	120.2 (2)
N1—C1—H1A	109.1	C10—C9—C15	120.0 (2)
C2—C1—H1B	109.1	C11—C10—C9	119.9 (2)
N1—C1—H1B	109.1	C11—C10—H10	120.0
H1A—C1—H1B	107.8	C9—C10—H10	120.0
C1—C2—C3	113.0 (2)	C12—C11—C10	120.5 (2)
C1—C2—H2A	109.0	C12—C11—H11	119.8
C3—C2—H2A	109.0	C10—C11—H11	119.8
C1—C2—H2B	109.0	C11—C12—C13	119.7 (2)
C3—C2—H2B	109.0	C11—C12—H12	120.1
H2A—C2—H2B	107.8	C13—C12—H12	120.1
C4—C3—C8	119.0 (2)	C14—C13—C12	119.8 (2)
C4—C3—C2	118.5 (2)	C14—C13—H13	120.1
C8—C3—C2	122.6 (3)	C12—C13—H13	120.1
C3—C4—C5	120.6 (3)	C9—C14—C13	120.4 (2)
C3—C4—H4	119.7	C9—C14—H14	119.8
C5—C4—H4	119.7	C13—C14—H14	119.8
O1—C5—C4	117.3 (2)	O4—C15—O3	124.5 (2)
O1—C5—C6	122.0 (2)	O4—C15—C9	118.4 (2)
C4—C5—C6	120.7 (3)	O3—C15—C9	117.03 (19)
O2—C6—C7	124.1 (2)		
N1—C1—C2—C3	173.1 (2)	C2—C3—C8—C7	176.9 (3)
C1—C2—C3—C4	-132.1 (3)	C6—C7—C8—C3	0.6 (4)
C1—C2—C3—C8	48.5 (4)	C14—C9—C10—C11	0.3 (3)
C8—C3—C4—C5	1.4 (4)	C15—C9—C10—C11	174.7 (2)
C2—C3—C4—C5	-178.1 (2)	C9—C10—C11—C12	-2.6 (4)
C3—C4—C5—O1	178.1 (2)	C10—C11—C12—C13	2.7 (4)
C3—C4—C5—C6	1.7 (4)	C11—C12—C13—C14	-0.3 (4)
O1—C5—C6—O2	-0.7 (3)	C10—C9—C14—C13	2.1 (3)
C4—C5—C6—O2	175.4 (2)	C15—C9—C14—C13	-172.3 (2)
O1—C5—C6—C7	-179.9 (2)	C12—C13—C14—C9	-2.0 (4)
C4—C5—C6—C7	-3.7 (4)	C14—C9—C15—O4	-40.3 (3)
O2—C6—C7—C8	-176.6 (2)	C10—C9—C15—O4	145.3 (2)
C5—C6—C7—C8	2.5 (4)	C14—C9—C15—O3	138.7 (2)
C4—C3—C8—C7	-2.6 (4)	C10—C9—C15—O3	-35.7 (3)

## 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>
O1—H1H...O2	0.84 (4)	2.29 (4)	2.736 (3)	113 (3)
O1—H1H...O3 <sup>i</sup>	0.84 (4)	2.17 (4)	2.872 (3)	141 (3)
O2—H2H...O4 <sup>ii</sup>	0.85 (4)	1.83 (4)	2.666 (2)	171 (3)
N1—H1N...O4 <sup>iii</sup>	0.98 (3)	1.87 (4)	2.834 (3)	167 (3)
N1—H2N...O3	0.95 (3)	1.93 (3)	2.867 (3)	171 (3)
N1—H3N...O3 <sup>iv</sup>	0.87 (4)	2.04 (4)	2.866 (3)	156 (3)

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

## 2-(3,4-Dihydroxyphenyl)ethan-1-aminium 4-nitrobenzoate (II)

## Crystal data

$C_8H_{12}NO_2^+ \cdot C_7H_4NO_4^-$

$M_r = 320.30$

Monoclinic,  $P2_1/n$

$a = 7.4993$  (2) Å

$b = 18.5051$  (5) Å

$c = 10.7610$  (3) Å

$\beta = 99.628$  (3)°

$V = 1472.33$  (7) Å<sup>3</sup>

$Z = 4$

$F(000) = 672$

$D_x = 1.445$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 2686 reflections

$\theta = 3.3$ – $29.5$ °

$\mu = 0.11$  mm<sup>-1</sup>

$T = 123$  K

Fragment from sheet, light orange

$0.35 \times 0.25 \times 0.05$  mm

## Data collection

Oxford Diffraction Xcalibur E  
diffractometer

Radiation source: fine-focus sealed tube

$\omega$  scans

Absorption correction: multi-scan

(CrysAlis PRO; Rigaku OD, 2019)

$T_{\min} = 0.928$ ,  $T_{\max} = 1.000$

7174 measured reflections

3573 independent reflections

2620 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 29.0$ °,  $\theta_{\min} = 3.3$ °

$h = -9 \rightarrow 10$

$k = -23 \rightarrow 22$

$l = -14 \rightarrow 14$

## Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.048$

$wR(F^2) = 0.112$

$S = 1.03$

3573 reflections

228 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0434P)^2 + 0.3527P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.34$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.23$  e Å<sup>-3</sup>

## 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.

**Refinement.** All measurements were made with Oxford Diffraction instruments using *CrysAlis PRO* software for data collection and reduction (Rigaku OD, 2019). Solution was by direct methods, *SIR92* or *SHELXS* (Altomare *et al.*, 1994; Sheldrick, 2015a). All structures were refined to convergence against  $F^2$  using all unique reflections and the program *SHELXL2018* as implemented within *WinGX* (Sheldrick, 2015b; Farrugia, 2012).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	−0.02468 (17)	0.39442 (7)	0.68207 (11)	0.0229 (3)
O2	0.10642 (16)	0.39286 (6)	0.93533 (11)	0.0184 (3)
O3	0.27783 (16)	0.38212 (6)	0.16312 (11)	0.0238 (3)
O4	0.12298 (16)	0.48019 (6)	0.19981 (11)	0.0211 (3)
O5	0.63600 (17)	0.36449 (7)	0.79848 (11)	0.0290 (3)
O6	0.47314 (17)	0.45641 (7)	0.83201 (11)	0.0255 (3)
N1	0.2961 (2)	0.04959 (8)	0.54829 (14)	0.0169 (3)
N2	0.52353 (19)	0.41058 (8)	0.76138 (13)	0.0205 (3)
C1	0.2126 (2)	0.10833 (8)	0.61416 (16)	0.0196 (4)
H1A	0.210221	0.093736	0.702380	0.023*
H1B	0.086304	0.116090	0.571975	0.023*
C2	0.3181 (2)	0.17811 (8)	0.61303 (15)	0.0188 (4)
H2A	0.448645	0.168180	0.639465	0.023*
H2B	0.300404	0.197705	0.526225	0.023*
C3	0.2576 (2)	0.23360 (8)	0.70057 (15)	0.0166 (3)
C4	0.1396 (2)	0.28844 (9)	0.65451 (15)	0.0162 (3)
H4	0.093867	0.290570	0.566768	0.019*
C5	0.0869 (2)	0.34033 (8)	0.73371 (15)	0.0157 (3)
C6	0.1551 (2)	0.33782 (8)	0.86302 (15)	0.0151 (3)
C7	0.2698 (2)	0.28231 (9)	0.91013 (15)	0.0193 (4)
H7	0.313978	0.279609	0.998056	0.023*
C8	0.3211 (2)	0.23034 (9)	0.82974 (16)	0.0198 (4)
H8	0.400042	0.192336	0.863103	0.024*
C9	0.2296 (2)	0.42853 (9)	0.23546 (15)	0.0164 (3)
C10	0.3042 (2)	0.42168 (9)	0.37466 (15)	0.0157 (3)
C11	0.4354 (2)	0.36997 (9)	0.41723 (15)	0.0190 (4)
H11	0.475185	0.337692	0.358919	0.023*
C12	0.5082 (2)	0.36536 (9)	0.54460 (16)	0.0196 (4)
H12	0.598230	0.330520	0.574636	0.023*
C13	0.4454 (2)	0.41318 (9)	0.62609 (15)	0.0171 (3)
C14	0.3140 (2)	0.46390 (9)	0.58735 (15)	0.0187 (4)
H14	0.272637	0.495226	0.646414	0.022*
C15	0.2434 (2)	0.46829 (9)	0.46006 (15)	0.0185 (4)
H15	0.153088	0.503198	0.431017	0.022*
H1H	−0.044 (3)	0.4259 (13)	0.738 (2)	0.053 (7)*
H2H	0.170 (3)	0.3879 (12)	1.018 (2)	0.050 (7)*
H1N	0.416 (3)	0.0382 (11)	0.593 (2)	0.047 (7)*
H2N	0.233 (3)	0.0082 (12)	0.5439 (19)	0.033 (6)*
H3N	0.306 (3)	0.0615 (10)	0.470 (2)	0.031 (6)*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0292 (7)	0.0225 (7)	0.0167 (6)	0.0109 (5)	0.0025 (5)	0.0010 (5)
O2	0.0255 (6)	0.0160 (6)	0.0142 (6)	0.0048 (5)	0.0047 (5)	−0.0013 (5)

O3	0.0249 (7)	0.0277 (7)	0.0175 (6)	0.0075 (6)	0.0001 (5)	-0.0057 (5)
O4	0.0248 (6)	0.0190 (6)	0.0178 (6)	0.0053 (5)	-0.0015 (5)	-0.0009 (5)
O5	0.0284 (7)	0.0360 (8)	0.0210 (6)	0.0088 (6)	-0.0004 (5)	0.0066 (6)
O6	0.0296 (7)	0.0300 (7)	0.0166 (6)	0.0003 (6)	0.0031 (5)	-0.0052 (5)
N1	0.0180 (7)	0.0145 (7)	0.0185 (7)	-0.0010 (6)	0.0039 (6)	-0.0038 (6)
N2	0.0188 (7)	0.0241 (8)	0.0183 (7)	-0.0037 (6)	0.0021 (6)	0.0031 (6)
C1	0.0209 (8)	0.0166 (8)	0.0228 (8)	-0.0001 (7)	0.0084 (7)	-0.0063 (7)
C2	0.0214 (9)	0.0161 (8)	0.0201 (8)	-0.0002 (7)	0.0067 (7)	-0.0038 (7)
C3	0.0170 (8)	0.0136 (8)	0.0197 (8)	-0.0024 (7)	0.0047 (7)	-0.0029 (7)
C4	0.0166 (8)	0.0177 (8)	0.0143 (7)	-0.0020 (7)	0.0027 (6)	-0.0014 (7)
C5	0.0136 (8)	0.0145 (8)	0.0191 (8)	0.0008 (6)	0.0030 (6)	0.0019 (7)
C6	0.0163 (8)	0.0126 (7)	0.0171 (8)	-0.0022 (6)	0.0044 (6)	-0.0031 (7)
C7	0.0217 (9)	0.0188 (8)	0.0165 (8)	0.0014 (7)	0.0007 (7)	-0.0018 (7)
C8	0.0199 (9)	0.0154 (8)	0.0228 (9)	0.0043 (7)	0.0001 (7)	-0.0003 (7)
C9	0.0136 (8)	0.0181 (8)	0.0173 (8)	-0.0014 (7)	0.0024 (6)	-0.0007 (7)
C10	0.0150 (8)	0.0153 (8)	0.0167 (8)	-0.0025 (7)	0.0023 (6)	-0.0006 (7)
C11	0.0197 (8)	0.0185 (8)	0.0188 (8)	0.0014 (7)	0.0035 (7)	-0.0020 (7)
C12	0.0176 (8)	0.0189 (8)	0.0217 (8)	0.0024 (7)	0.0021 (7)	0.0036 (7)
C13	0.0176 (8)	0.0196 (8)	0.0137 (8)	-0.0043 (7)	0.0009 (6)	0.0019 (7)
C14	0.0213 (9)	0.0181 (8)	0.0173 (8)	-0.0013 (7)	0.0045 (7)	-0.0021 (7)
C15	0.0178 (8)	0.0180 (8)	0.0192 (8)	0.0015 (7)	0.0017 (7)	-0.0003 (7)

*Geometric parameters (Å, °)*

O1—C5	1.3619 (19)	C3—C8	1.393 (2)
O1—H1H	0.87 (2)	C4—C5	1.385 (2)
O2—C6	1.3681 (18)	C4—H4	0.9500
O2—H2H	0.94 (2)	C5—C6	1.401 (2)
O3—C9	1.2524 (19)	C6—C7	1.381 (2)
O4—C9	1.2641 (19)	C7—C8	1.390 (2)
O5—N2	1.2188 (18)	C7—H7	0.9500
O6—N2	1.2392 (18)	C8—H8	0.9500
N1—C1	1.491 (2)	C9—C10	1.514 (2)
N1—H1N	0.97 (2)	C10—C15	1.392 (2)
N1—H2N	0.90 (2)	C10—C11	1.393 (2)
N1—H3N	0.88 (2)	C11—C12	1.391 (2)
N2—C13	1.477 (2)	C11—H11	0.9500
C1—C2	1.515 (2)	C12—C13	1.383 (2)
C1—H1A	0.9900	C12—H12	0.9500
C1—H1B	0.9900	C13—C14	1.374 (2)
C2—C3	1.513 (2)	C14—C15	1.386 (2)
C2—H2A	0.9900	C14—H14	0.9500
C2—H2B	0.9900	C15—H15	0.9500
C3—C4	1.383 (2)		
C5—O1—H1H	111.8 (16)	C4—C5—C6	119.58 (15)
C6—O2—H2H	108.8 (14)	O2—C6—C7	123.66 (14)
C1—N1—H1N	110.5 (13)	O2—C6—C5	116.89 (14)



C1—N1—H2N	112.9 (13)	C7—C6—C5	119.42 (14)
H1N—N1—H2N	106.0 (18)	C6—C7—C8	120.43 (15)
C1—N1—H3N	112.2 (13)	C6—C7—H7	119.8
H1N—N1—H3N	108.0 (18)	C8—C7—H7	119.8
H2N—N1—H3N	106.9 (18)	C7—C8—C3	120.45 (15)
O5—N2—O6	122.91 (14)	C7—C8—H8	119.8
O5—N2—C13	118.99 (14)	C3—C8—H8	119.8
O6—N2—C13	118.09 (14)	O3—C9—O4	124.31 (15)
N1—C1—C2	110.85 (13)	O3—C9—C10	117.40 (14)
N1—C1—H1A	109.5	O4—C9—C10	118.29 (14)
C2—C1—H1A	109.5	C15—C10—C11	119.99 (15)
N1—C1—H1B	109.5	C15—C10—C9	119.58 (14)
C2—C1—H1B	109.5	C11—C10—C9	120.42 (14)
H1A—C1—H1B	108.1	C12—C11—C10	120.37 (15)
C3—C2—C1	111.22 (13)	C12—C11—H11	119.8
C3—C2—H2A	109.4	C10—C11—H11	119.8
C1—C2—H2A	109.4	C13—C12—C11	117.78 (15)
C3—C2—H2B	109.4	C13—C12—H12	121.1
C1—C2—H2B	109.4	C11—C12—H12	121.1
H2A—C2—H2B	108.0	C14—C13—C12	123.22 (15)
C4—C3—C8	118.75 (15)	C14—C13—N2	117.89 (14)
C4—C3—C2	121.02 (14)	C12—C13—N2	118.89 (15)
C8—C3—C2	120.23 (15)	C13—C14—C15	118.44 (15)
C3—C4—C5	121.33 (15)	C13—C14—H14	120.8
C3—C4—H4	119.3	C15—C14—H14	120.8
C5—C4—H4	119.3	C14—C15—C10	120.18 (15)
O1—C5—C4	118.54 (14)	C14—C15—H15	119.9
O1—C5—C6	121.82 (14)	C10—C15—H15	119.9
N1—C1—C2—C3	-168.89 (14)	O4—C9—C10—C15	5.0 (2)
C1—C2—C3—C4	-99.97 (18)	O3—C9—C10—C11	6.4 (2)
C1—C2—C3—C8	80.32 (19)	O4—C9—C10—C11	-173.84 (15)
C8—C3—C4—C5	1.2 (2)	C15—C10—C11—C12	-1.1 (2)
C2—C3—C4—C5	-178.55 (15)	C9—C10—C11—C12	177.81 (15)
C3—C4—C5—O1	177.74 (14)	C10—C11—C12—C13	0.4 (2)
C3—C4—C5—C6	0.5 (2)	C11—C12—C13—C14	0.8 (2)
O1—C5—C6—O2	-0.8 (2)	C11—C12—C13—N2	-178.59 (14)
C4—C5—C6—O2	176.30 (14)	O5—N2—C13—C14	177.64 (14)
O1—C5—C6—C7	-179.07 (15)	O6—N2—C13—C14	-3.4 (2)
C4—C5—C6—C7	-2.0 (2)	O5—N2—C13—C12	-2.9 (2)
O2—C6—C7—C8	-176.47 (15)	O6—N2—C13—C12	176.00 (14)
C5—C6—C7—C8	1.7 (2)	C12—C13—C14—C15	-1.2 (2)
C6—C7—C8—C3	0.0 (3)	N2—C13—C14—C15	178.16 (14)
C4—C3—C8—C7	-1.5 (2)	C13—C14—C15—C10	0.5 (2)
C2—C3—C8—C7	178.26 (15)	C11—C10—C15—C14	0.6 (2)
O3—C9—C10—C15	-174.74 (15)	C9—C10—C15—C14	-178.26 (15)

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>
O1—H1H...O2	0.87 (2)	2.31 (2)	2.7384 (17)	110.4 (19)
O1—H1H...O4 <sup>i</sup>	0.87 (2)	1.99 (2)	2.8030 (17)	156 (2)
O2—H2H...O3 <sup>ii</sup>	0.94 (2)	1.64 (2)	2.5780 (16)	178 (2)
N1—H1N...O4 <sup>iii</sup>	0.97 (2)	1.80 (3)	2.763 (2)	170 (2)
N1—H2N...O2 <sup>iv</sup>	0.90 (2)	2.44 (2)	2.9890 (18)	119.7 (16)
N1—H2N...O6 <sup>iv</sup>	0.90 (2)	2.41 (2)	3.095 (2)	133.8 (17)
N1—H3N...O2 <sup>v</sup>	0.88 (2)	2.50 (2)	2.9956 (19)	116.6 (15)
N1—H3N...O4 <sup>vi</sup>	0.88 (2)	2.50 (2)	3.1125 (18)	127.5 (16)
N1—H3N...O5 <sup>vii</sup>	0.88 (2)	2.48 (2)	3.181 (2)	137.3 (16)

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

2-(3,4-Dihydroxyphenyl)ethan-1-aminium ethane-1,2-disulfonate (III)

Crystal data

$2\text{C}_8\text{H}_{12}\text{NO}_2^+ \cdot \text{C}_2\text{H}_4\text{O}_6\text{S}_2^{2-}$

$M_r = 496.54$

Orthorhombic, *Pbca*

$a = 10.6328$  (5) Å

$b = 8.5651$  (5) Å

$c = 23.8669$  (13) Å

$V = 2173.6$  (2) Å<sup>3</sup>

$Z = 4$

$F(000) = 1048$

$D_x = 1.517$  Mg m<sup>-3</sup>

Cu  $K\alpha$  radiation,  $\lambda = 1.5418$  Å

Cell parameters from 3597 reflections

$\theta = 3.7\text{--}74.7^\circ$

$\mu = 2.75$  mm<sup>-1</sup>

$T = 123$  K

Slab, yellow

$0.30 \times 0.15 \times 0.05$  mm

Data collection

Oxford Diffraction Gemini S  
diffractometer

Radiation source: fine-focus sealed tube

$\omega$  scans

Absorption correction: multi-scan

(CrysAlis PRO; Rigaku OD, 2019)

$T_{\min} = 0.500$ ,  $T_{\max} = 1.000$

7583 measured reflections

2172 independent reflections

1924 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\max} = 74.9^\circ$ ,  $\theta_{\min} = 3.7^\circ$

$h = -12 \rightarrow 12$

$k = -8 \rightarrow 10$

$l = -29 \rightarrow 26$

Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.134$

$S = 1.14$

2172 reflections

165 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0781P)^2 + 1.1139P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.62$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.57$  e Å<sup>-3</sup>

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.

**Refinement.** All measurements were made with Oxford Diffraction instruments using *Crysalis PRO* software for data collection and reduction (Rigaku OD, 2019). Solution was by direct methods, *SIR92* or *SHELXS* (Altomare *et al.*, 1994; Sheldrick, 2015a). All structures were refined to convergence against  $F^2$  using all unique reflections and the program *SHELXL2018* as implemented within *WinGX* (Sheldrick, 2015b; Farrugia, 2012).

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.67052 (4)	0.63900 (5)	1.00071 (2)	0.0157 (2)
O1	0.44177 (14)	0.44564 (19)	0.85879 (6)	0.0250 (4)
O2	0.63054 (14)	0.24475 (17)	0.88987 (6)	0.0219 (3)
O3	0.63463 (14)	0.73346 (17)	1.04876 (6)	0.0236 (4)
O4	0.64846 (13)	0.71856 (17)	0.94706 (6)	0.0212 (3)
O5	0.79810 (15)	0.57875 (18)	1.00334 (5)	0.0211 (4)
N1	0.50796 (17)	0.4682 (2)	0.57846 (7)	0.0195 (4)
C1	0.5254 (2)	0.4025 (3)	0.63567 (8)	0.0231 (4)
H1A	0.558048	0.294597	0.632664	0.028*
H1B	0.442950	0.398005	0.654908	0.028*
C2	0.61585 (19)	0.4999 (2)	0.67027 (8)	0.0206 (4)
H2A	0.700116	0.498691	0.652638	0.025*
H2B	0.586209	0.609429	0.671606	0.025*
C3	0.62440 (18)	0.4351 (2)	0.72921 (8)	0.0190 (4)
C4	0.53191 (19)	0.4718 (2)	0.76855 (8)	0.0199 (4)
H4	0.466013	0.541546	0.758704	0.024*
C5	0.53525 (17)	0.4074 (2)	0.82203 (8)	0.0188 (4)
C6	0.63283 (18)	0.3064 (2)	0.83667 (8)	0.0186 (4)
C7	0.72407 (18)	0.2677 (2)	0.79749 (8)	0.0214 (4)
H7	0.789426	0.196986	0.807165	0.026*
C8	0.71985 (18)	0.3322 (2)	0.74412 (8)	0.0212 (4)
H8	0.782847	0.305750	0.717539	0.025*
C9	0.5686 (2)	0.4744 (2)	1.00146 (7)	0.0191 (5)
H9A	0.587986	0.406096	0.969125	0.023*
H9B	0.582627	0.413584	1.036173	0.023*
H1H	0.443 (3)	0.383 (3)	0.8861 (12)	0.034 (7)*
H1N	0.578 (3)	0.470 (3)	0.5576 (11)	0.033 (7)*
H2H	0.707 (3)	0.228 (3)	0.9040 (12)	0.041 (8)*
H2N	0.482 (2)	0.563 (3)	0.5787 (9)	0.020 (6)*
H3N	0.451 (3)	0.415 (4)	0.5588 (12)	0.038 (7)*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0138 (3)	0.0198 (3)	0.0135 (3)	−0.00014 (16)	0.00111 (14)	0.00113 (15)
O1	0.0206 (7)	0.0374 (9)	0.0168 (7)	0.0070 (6)	0.0034 (5)	0.0027 (6)
O2	0.0174 (7)	0.0321 (8)	0.0163 (7)	0.0005 (6)	−0.0013 (5)	0.0045 (5)
O3	0.0260 (8)	0.0247 (7)	0.0201 (7)	−0.0046 (6)	0.0057 (6)	−0.0040 (5)
O4	0.0168 (7)	0.0278 (8)	0.0191 (7)	0.0002 (6)	0.0013 (5)	0.0064 (6)
O5	0.0154 (7)	0.0264 (8)	0.0216 (7)	0.0025 (6)	−0.0010 (5)	0.0032 (5)

N1	0.0197 (9)	0.0246 (9)	0.0143 (8)	-0.0012 (7)	0.0001 (6)	0.0004 (7)
C1	0.0262 (11)	0.0274 (10)	0.0158 (9)	-0.0067 (9)	-0.0005 (7)	0.0030 (8)
C2	0.0178 (10)	0.0271 (10)	0.0170 (9)	-0.0021 (8)	-0.0004 (7)	0.0028 (7)
C3	0.0173 (9)	0.0240 (9)	0.0156 (9)	-0.0026 (8)	-0.0017 (7)	-0.0001 (7)
C4	0.0155 (9)	0.0246 (9)	0.0195 (9)	0.0021 (7)	-0.0033 (7)	0.0011 (7)
C5	0.0137 (9)	0.0260 (10)	0.0167 (9)	-0.0009 (8)	-0.0004 (7)	-0.0015 (7)
C6	0.0168 (9)	0.0248 (10)	0.0143 (9)	-0.0022 (8)	-0.0021 (7)	0.0006 (7)
C7	0.0150 (9)	0.0281 (10)	0.0212 (9)	0.0019 (8)	-0.0025 (7)	-0.0010 (8)
C8	0.0166 (9)	0.0286 (10)	0.0184 (9)	-0.0013 (8)	0.0020 (7)	-0.0041 (8)
C9	0.0170 (12)	0.0219 (10)	0.0185 (10)	0.0031 (8)	0.0007 (6)	-0.0005 (7)

*Geometric parameters (Å, °)*

S1—O5	1.4527 (16)	C2—C3	1.515 (2)
S1—O3	1.4544 (14)	C2—H2A	0.9900
S1—O4	1.4693 (14)	C2—H2B	0.9900
S1—C9	1.778 (2)	C3—C8	1.390 (3)
O1—C5	1.366 (2)	C3—C4	1.396 (3)
O1—H1H	0.85 (3)	C4—C5	1.391 (3)
O2—C6	1.375 (2)	C4—H4	0.9500
O2—H2H	0.89 (3)	C5—C6	1.396 (3)
N1—C1	1.488 (2)	C6—C7	1.388 (3)
N1—H1N	0.90 (3)	C7—C8	1.389 (3)
N1—H2N	0.85 (3)	C7—H7	0.9500
N1—H3N	0.89 (3)	C8—H8	0.9500
C1—C2	1.518 (3)	C9—C9 <sup>i</sup>	1.525 (4)
C1—H1A	0.9900	C9—H9A	0.9900
C1—H1B	0.9900	C9—H9B	0.9900
O5—S1—O3	114.11 (9)	H2A—C2—H2B	108.2
O5—S1—O4	110.58 (8)	C8—C3—C4	119.03 (18)
O3—S1—O4	112.78 (9)	C8—C3—C2	120.91 (17)
O5—S1—C9	106.68 (10)	C4—C3—C2	119.97 (17)
O3—S1—C9	105.85 (9)	C5—C4—C3	120.65 (18)
O4—S1—C9	106.21 (9)	C5—C4—H4	119.7
C5—O1—H1H	109.1 (19)	C3—C4—H4	119.7
C6—O2—H2H	113.2 (18)	O1—C5—C4	118.42 (17)
C1—N1—H1N	114.3 (17)	O1—C5—C6	121.93 (17)
C1—N1—H2N	113.1 (15)	C4—C5—C6	119.64 (17)
H1N—N1—H2N	105 (2)	O2—C6—C7	122.86 (17)
C1—N1—H3N	112.1 (18)	O2—C6—C5	117.13 (17)
H1N—N1—H3N	106 (2)	C7—C6—C5	119.96 (18)
H2N—N1—H3N	106 (2)	C6—C7—C8	120.00 (18)
N1—C1—C2	111.72 (16)	C6—C7—H7	120.0
N1—C1—H1A	109.3	C8—C7—H7	120.0
C2—C1—H1A	109.3	C7—C8—C3	120.69 (18)
N1—C1—H1B	109.3	C7—C8—H8	119.7
C2—C1—H1B	109.3	C3—C8—H8	119.7

H1A—C1—H1B	107.9	C9 <sup>i</sup> —C9—S1	110.76 (19)
C3—C2—C1	109.98 (16)	C9 <sup>i</sup> —C9—H9A	109.5
C3—C2—H2A	109.7	S1—C9—H9A	109.5
C1—C2—H2A	109.7	C9 <sup>i</sup> —C9—H9B	109.5
C3—C2—H2B	109.7	S1—C9—H9B	109.5
C1—C2—H2B	109.7	H9A—C9—H9B	108.1
N1—C1—C2—C3	176.39 (16)	C4—C5—C6—C7	-1.6 (3)
C1—C2—C3—C8	95.6 (2)	O2—C6—C7—C8	178.95 (17)
C1—C2—C3—C4	-81.0 (2)	C5—C6—C7—C8	1.5 (3)
C8—C3—C4—C5	0.4 (3)	C6—C7—C8—C3	-0.4 (3)
C2—C3—C4—C5	176.98 (17)	C4—C3—C8—C7	-0.5 (3)
C3—C4—C5—O1	-179.24 (18)	C2—C3—C8—C7	-177.11 (18)
C3—C4—C5—C6	0.7 (3)	O5—S1—C9—C9 <sup>i</sup>	-179.75 (15)
O1—C5—C6—O2	0.7 (3)	O3—S1—C9—C9 <sup>i</sup>	58.36 (18)
C4—C5—C6—O2	-179.24 (17)	O4—S1—C9—C9 <sup>i</sup>	-61.76 (18)
O1—C5—C6—C7	178.33 (18)		

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

#### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

<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>
O1—H1H $\cdots$ O2	0.85 (3)	2.32 (3)	2.746 (2)	112 (2)
O1—H1H $\cdots$ O3 <sup>i</sup>	0.85 (3)	2.02 (3)	2.807 (2)	154 (3)
O2—H2H $\cdots$ O4 <sup>ii</sup>	0.89 (3)	1.85 (3)	2.727 (2)	167 (3)
N1—H1N $\cdots$ O5 <sup>iii</sup>	0.90 (3)	1.89 (3)	2.762 (2)	163 (2)
N1—H2N $\cdots$ O2 <sup>iv</sup>	0.85 (3)	2.11 (3)	2.890 (2)	152 (2)
N1—H2N $\cdots$ O3 <sup>v</sup>	0.85 (3)	2.49 (3)	2.974 (2)	117 (2)
N1—H3N $\cdots$ O4 <sup>vi</sup>	0.89 (3)	2.00 (3)	2.776 (2)	146 (3)
N1—H3N $\cdots$ O5 <sup>vii</sup>	0.89 (3)	2.61 (3)	3.112 (2)	117 (2)

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

#### 2-(3,4-Dihydroxyphenyl)ethan-1-aminium 4-hydroxybenzenesulfonate monohydrate (IV)

##### Crystal data

$\text{C}_8\text{H}_{12}\text{NO}_2^+ \cdot \text{C}_6\text{H}_5\text{O}_4\text{S}^- \cdot \text{H}_2\text{O}$

$M_r = 345.36$

Monoclinic,  $P2_1/c$

$a = 17.4085$  (8)  $\text{\AA}$

$b = 11.9234$  (5)  $\text{\AA}$

$c = 7.6779$  (3)  $\text{\AA}$

$\beta = 95.273$  (4) $^\circ$

$V = 1586.95$  (12)  $\text{\AA}^3$

$Z = 4$

$F(000) = 728$

$D_x = 1.446$   $\text{Mg m}^{-3}$

Cu  $K\alpha$  radiation,  $\lambda = 1.5418$   $\text{\AA}$

Cell parameters from 2384 reflections

$\theta = 4.5\text{--}73.0^\circ$

$\mu = 2.15$   $\text{mm}^{-1}$

$T = 123$  K

Cut lath, colourless

$0.5 \times 0.15 \times 0.07$  mm

Data collection

Oxford Diffraction Gemini S  
diffractometer  
Radiation source: fine-focus sealed tube  
 $\omega$  scans  
Absorption correction: multi-scan  
(CrysAlis PRO; Rigaku OD, 2019)  
 $T_{\min} = 0.653$ ,  $T_{\max} = 1.000$   
6603 measured reflections

3113 independent reflections  
2474 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.040$   
 $\theta_{\max} = 73.1^\circ$ ,  $\theta_{\min} = 4.5^\circ$   
 $h = -20 \rightarrow 21$   
 $k = -9 \rightarrow 14$   
 $l = -6 \rightarrow 9$

Refinement

Refinement on  $F^2$   
Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.057$   
 $wR(F^2) = 0.169$   
 $S = 1.04$   
3113 reflections  
277 parameters  
5 restraints

Hydrogen site location: mixed  
H atoms treated by a mixture of independent  
and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.107P)^2 + 0.1388P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.81 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.41 \text{ e } \text{\AA}^{-3}$

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.

**Refinement.** All measurements were made with Oxford Diffraction instruments using *CrysAlis PRO* software for data collection and reduction (Rigaku OD, 2019). Solution was by direct methods, *SIR92* or *SHELXS* (Altomare *et al.*, 1994; Sheldrick, 2015a). All structures were refined to convergence against  $F^2$  using all unique reflections and the program *SHELXL2018* as implemented within *WinGX* (Sheldrick, 2015b; Farrugia, 2012).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
S1	0.31573 (4)	0.39989 (5)	0.60904 (7)	0.0224 (2)	
O1	-0.11995 (11)	-0.01838 (17)	0.8196 (3)	0.0286 (4)	
O2	-0.19486 (11)	0.15240 (17)	0.6330 (3)	0.0299 (5)	
O3	0.27420 (11)	0.43408 (18)	0.7561 (3)	0.0308 (5)	
O4	0.31045 (11)	0.48640 (17)	0.4714 (2)	0.0266 (4)	
O5	0.29390 (12)	0.29108 (17)	0.5367 (3)	0.0308 (5)	
O6	0.64350 (13)	0.37956 (18)	0.8833 (3)	0.0360 (5)	
O1W	0.27025 (12)	0.69308 (17)	0.5738 (3)	0.0315 (5)	
N1	0.25024 (14)	0.0775 (2)	0.6281 (3)	0.0255 (5)	
C9	0.41447 (15)	0.3914 (2)	0.6877 (3)	0.0222 (5)	
C6	-0.11546 (16)	0.1565 (2)	0.6607 (3)	0.0259 (6)	
C1	0.16405 (16)	0.0764 (2)	0.6140 (3)	0.0266 (6)	
H1A	0.145838	-0.001595	0.626794	0.032*	
H1B	0.144028	0.103494	0.496643	0.032*	
C2	0.13242 (16)	0.1494 (2)	0.7523 (3)	0.0267 (6)	
H2A	0.153259	0.226421	0.745624	0.032*	
H2B	0.148574	0.119018	0.870012	0.032*	
C4	0.00070 (16)	0.0649 (2)	0.7806 (3)	0.0244 (5)	

H4	0.025452	0.002839	0.839654	0.029*	
C12	0.56822 (16)	0.3803 (2)	0.8163 (4)	0.0263 (6)	
C5	-0.07927 (16)	0.0670 (2)	0.7523 (3)	0.0229 (5)	
C7	-0.07172 (17)	0.2442 (2)	0.6040 (4)	0.0295 (6)	
H7	-0.096434	0.305605	0.543098	0.035*	
C8	0.00801 (17)	0.2426 (2)	0.6361 (4)	0.0285 (6)	
H8	0.037566	0.303407	0.598122	0.034*	
C3	0.04508 (16)	0.1524 (2)	0.7237 (3)	0.0238 (5)	
C11	0.5229 (3)	0.4732 (5)	0.8581 (7)	0.0282 (13)	0.503 (5)
H11	0.544809	0.531986	0.929891	0.034*	0.503 (5)
C13	0.5367 (3)	0.2934 (5)	0.7181 (8)	0.0263 (13)	0.503 (5)
H13	0.567283	0.230072	0.695150	0.032*	0.503 (5)
C14	0.4587 (3)	0.2980 (4)	0.6512 (7)	0.0260 (13)	0.503 (5)
H14	0.436354	0.238259	0.581989	0.031*	0.503 (5)
C10	0.4459 (3)	0.4773 (5)	0.7929 (7)	0.0278 (13)	0.503 (5)
H10	0.414731	0.539082	0.820398	0.033*	0.503 (5)
C10A	0.4634 (3)	0.4819 (5)	0.6575 (7)	0.0242 (12)	0.497 (5)
H10A	0.444006	0.546019	0.594667	0.029*	0.497 (5)
C11A	0.5408 (3)	0.4758 (5)	0.7211 (7)	0.0281 (13)	0.497 (5)
H11A	0.574896	0.535508	0.700573	0.034*	0.497 (5)
C14A	0.4415 (3)	0.2978 (5)	0.7743 (7)	0.0240 (12)	0.497 (5)
H14A	0.407490	0.237325	0.791765	0.029*	0.497 (5)
C13A	0.5190 (3)	0.2905 (4)	0.8374 (7)	0.0247 (12)	0.497 (5)
H13A	0.538135	0.224221	0.894819	0.030*	0.497 (5)
H1H	-0.1688 (8)	-0.009 (3)	0.785 (5)	0.032 (9)*	
H2H	-0.211 (2)	0.206 (2)	0.559 (4)	0.039 (10)*	
H1N	0.268 (2)	0.056 (3)	0.731 (5)	0.032 (9)*	
H2N	0.2645 (19)	0.146 (3)	0.610 (4)	0.025 (8)*	
H3N	0.268 (2)	0.037 (3)	0.547 (5)	0.041 (10)*	
H3H	0.663 (2)	0.3119 (16)	0.891 (5)	0.047 (11)*	
H1W	0.247 (2)	0.676 (4)	0.666 (4)	0.057 (13)*	
H2W	0.284 (2)	0.6270 (18)	0.537 (5)	0.050 (12)*	

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0243 (3)	0.0241 (4)	0.0189 (3)	0.0011 (2)	0.0023 (2)	0.0001 (2)
O1	0.0270 (9)	0.0270 (10)	0.0316 (10)	-0.0015 (8)	0.0015 (8)	0.0091 (8)
O2	0.0281 (10)	0.0271 (10)	0.0337 (10)	-0.0001 (8)	-0.0020 (8)	0.0072 (8)
O3	0.0278 (10)	0.0403 (12)	0.0245 (9)	0.0075 (9)	0.0040 (7)	0.0025 (8)
O4	0.0310 (9)	0.0279 (10)	0.0206 (9)	0.0000 (8)	0.0007 (7)	0.0022 (7)
O5	0.0324 (10)	0.0273 (10)	0.0321 (10)	-0.0012 (8)	0.0000 (8)	-0.0007 (8)
O6	0.0280 (10)	0.0269 (11)	0.0513 (13)	0.0008 (9)	-0.0060 (9)	0.0027 (9)
O1W	0.0322 (10)	0.0221 (10)	0.0394 (11)	-0.0005 (9)	-0.0012 (9)	0.0049 (8)
N1	0.0301 (12)	0.0272 (13)	0.0198 (11)	0.0030 (10)	0.0046 (9)	0.0004 (9)
C9	0.0236 (12)	0.0252 (13)	0.0181 (11)	0.0014 (10)	0.0038 (9)	-0.0008 (10)
C6	0.0303 (13)	0.0245 (13)	0.0228 (12)	-0.0020 (11)	0.0019 (10)	0.0002 (10)
C1	0.0281 (14)	0.0291 (14)	0.0225 (12)	-0.0028 (11)	0.0016 (10)	-0.0045 (10)

C2	0.0303 (14)	0.0280 (14)	0.0219 (12)	-0.0012 (11)	0.0031 (10)	-0.0031 (10)
C4	0.0306 (13)	0.0233 (13)	0.0188 (11)	0.0017 (11)	-0.0005 (10)	0.0003 (10)
C12	0.0257 (13)	0.0284 (14)	0.0249 (12)	0.0029 (11)	0.0023 (10)	0.0005 (11)
C5	0.0300 (13)	0.0200 (12)	0.0190 (11)	-0.0018 (10)	0.0041 (10)	0.0003 (9)
C7	0.0341 (14)	0.0259 (14)	0.0279 (13)	-0.0001 (12)	-0.0015 (10)	0.0048 (11)
C8	0.0349 (14)	0.0259 (14)	0.0249 (12)	-0.0046 (12)	0.0037 (10)	0.0022 (11)
C3	0.0294 (13)	0.0263 (13)	0.0161 (11)	-0.0030 (11)	0.0036 (9)	-0.0024 (10)
C11	0.033 (3)	0.028 (3)	0.023 (3)	0.004 (2)	0.000 (2)	-0.003 (2)
C13	0.032 (3)	0.020 (3)	0.027 (3)	0.004 (2)	0.003 (2)	0.000 (2)
C14	0.032 (3)	0.022 (3)	0.023 (3)	-0.001 (2)	0.000 (2)	-0.001 (2)
C10	0.030 (3)	0.025 (3)	0.030 (3)	0.004 (2)	0.007 (2)	-0.002 (2)
C10A	0.029 (3)	0.024 (3)	0.020 (2)	0.004 (2)	0.0033 (19)	0.001 (2)
C11A	0.031 (3)	0.025 (3)	0.029 (3)	-0.005 (2)	0.004 (2)	0.003 (2)
C14A	0.026 (3)	0.024 (3)	0.022 (3)	-0.006 (2)	0.006 (2)	0.000 (2)
C13A	0.031 (3)	0.021 (3)	0.022 (3)	0.002 (2)	0.004 (2)	-0.001 (2)

*Geometric parameters (Å, °)*

S1—O5	1.448 (2)	C2—H2A	0.9900
S1—O3	1.454 (2)	C2—H2B	0.9900
S1—O4	1.4734 (19)	C4—C5	1.389 (4)
S1—C9	1.772 (3)	C4—C3	1.393 (4)
O1—C5	1.369 (3)	C4—H4	0.9500
O1—H1H	0.874 (10)	C12—C13	1.366 (6)
O2—C6	1.380 (3)	C12—C13A	1.391 (6)
O2—H2H	0.880 (10)	C12—C11A	1.412 (6)
O6—C12	1.363 (3)	C12—C11	1.414 (6)
O6—H3H	0.876 (10)	C7—C8	1.387 (4)
O1W—H1W	0.876 (10)	C7—H7	0.9500
O1W—H2W	0.878 (10)	C8—C3	1.395 (4)
N1—C1	1.495 (3)	C8—H8	0.9500
N1—H1N	0.86 (4)	C11—C10	1.387 (8)
N1—H2N	0.86 (4)	C11—H11	0.9500
N1—H3N	0.86 (4)	C13—C14	1.408 (8)
C9—C14A	1.361 (6)	C13—H13	0.9500
C9—C10	1.385 (6)	C14—H14	0.9500
C9—C14	1.397 (6)	C10—H10	0.9500
C9—C10A	1.407 (6)	C10A—C11A	1.391 (8)
C6—C7	1.387 (4)	C10A—H10A	0.9500
C6—C5	1.396 (4)	C11A—H11A	0.9500
C1—C2	1.516 (4)	C14A—C13A	1.393 (7)
C1—H1A	0.9900	C14A—H14A	0.9500
C1—H1B	0.9900	C13A—H13A	0.9500
C2—C3	1.517 (4)		
O5—S1—O3	114.67 (13)	O6—C12—C13A	122.2 (3)
O5—S1—O4	110.80 (11)	O6—C12—C11A	117.9 (3)
O3—S1—O4	110.98 (12)	C13A—C12—C11A	119.9 (4)



O5—S1—C9	106.98 (12)	O6—C12—C11	117.2 (3)
O3—S1—C9	106.68 (12)	C13—C12—C11	121.0 (4)
O4—S1—C9	106.20 (12)	O1—C5—C4	118.2 (2)
C5—O1—H1H	108 (2)	O1—C5—C6	122.3 (2)
C6—O2—H2H	109 (2)	C4—C5—C6	119.5 (2)
C12—O6—H3H	113 (3)	C6—C7—C8	120.2 (3)
H1W—O1W—H2W	102 (4)	C6—C7—H7	119.9
C1—N1—H1N	110 (2)	C8—C7—H7	119.9
C1—N1—H2N	107 (2)	C7—C8—C3	120.5 (3)
H1N—N1—H2N	110 (3)	C7—C8—H8	119.8
C1—N1—H3N	111 (3)	C3—C8—H8	119.8
H1N—N1—H3N	112 (3)	C4—C3—C8	118.9 (3)
H2N—N1—H3N	106 (3)	C4—C3—C2	121.0 (2)
C10—C9—C14	120.8 (4)	C8—C3—C2	120.1 (2)
C14A—C9—C10A	121.5 (4)	C10—C11—C12	119.1 (5)
C14A—C9—S1	119.6 (3)	C10—C11—H11	120.4
C10—C9—S1	118.4 (3)	C12—C11—H11	120.4
C14—C9—S1	120.8 (3)	C12—C13—C14	119.8 (5)
C10A—C9—S1	118.9 (3)	C12—C13—H13	120.1
O2—C6—C7	123.3 (2)	C14—C13—H13	120.1
O2—C6—C5	116.7 (2)	C9—C14—C13	119.2 (5)
C7—C6—C5	119.9 (3)	C9—C14—H14	120.4
N1—C1—C2	111.8 (2)	C13—C14—H14	120.4
N1—C1—H1A	109.3	C9—C10—C11	120.1 (5)
C2—C1—H1A	109.3	C9—C10—H10	120.0
N1—C1—H1B	109.3	C11—C10—H10	120.0
C2—C1—H1B	109.3	C11A—C10A—C9	118.9 (5)
H1A—C1—H1B	107.9	C11A—C10A—H10A	120.5
C1—C2—C3	109.6 (2)	C9—C10A—H10A	120.5
C1—C2—H2A	109.8	C10A—C11A—C12	119.6 (5)
C3—C2—H2A	109.8	C10A—C11A—H11A	120.2
C1—C2—H2B	109.8	C12—C11A—H11A	120.2
C3—C2—H2B	109.8	C9—C14A—C13A	120.1 (4)
H2A—C2—H2B	108.2	C9—C14A—H14A	120.0
C5—C4—C3	120.9 (3)	C13A—C14A—H14A	120.0
C5—C4—H4	119.5	C12—C13A—C14A	119.9 (5)
C3—C4—H4	119.5	C12—C13A—H13A	120.0
O6—C12—C13	121.8 (3)	C14A—C13A—H13A	120.0
O5—S1—C9—C14A	-41.3 (3)	C7—C8—C3—C4	-0.9 (4)
O3—S1—C9—C14A	81.9 (3)	C7—C8—C3—C2	177.8 (2)
O4—S1—C9—C14A	-159.6 (3)	C1—C2—C3—C4	80.3 (3)
O5—S1—C9—C10	-167.9 (3)	C1—C2—C3—C8	-98.4 (3)
O3—S1—C9—C10	-44.7 (3)	O6—C12—C11—C10	-179.9 (4)
O4—S1—C9—C10	73.7 (3)	C13—C12—C11—C10	-2.3 (7)
O5—S1—C9—C14	9.2 (3)	O6—C12—C13—C14	-179.8 (4)
O3—S1—C9—C14	132.4 (3)	C11—C12—C13—C14	2.7 (7)
O4—S1—C9—C14	-109.2 (3)	C10—C9—C14—C13	-2.0 (7)

O5—S1—C9—C10A	138.1 (3)	S1—C9—C14—C13	-179.0 (4)
O3—S1—C9—C10A	-98.7 (3)	C12—C13—C14—C9	-0.5 (8)
O4—S1—C9—C10A	19.8 (3)	C14—C9—C10—C11	2.4 (7)
N1—C1—C2—C3	175.7 (2)	S1—C9—C10—C11	179.5 (4)
C3—C4—C5—O1	-176.5 (2)	C12—C11—C10—C9	-0.3 (8)
C3—C4—C5—C6	2.0 (4)	C14A—C9—C10A—C11A	-1.4 (7)
O2—C6—C5—O1	-3.1 (4)	S1—C9—C10A—C11A	179.3 (4)
C7—C6—C5—O1	176.2 (2)	C9—C10A—C11A—C12	-0.9 (7)
O2—C6—C5—C4	178.4 (2)	O6—C12—C11A—C10A	-177.1 (4)
C7—C6—C5—C4	-2.2 (4)	C13A—C12—C11A—C10A	3.6 (7)
O2—C6—C7—C8	-179.8 (2)	C10A—C9—C14A—C13A	0.9 (7)
C5—C6—C7—C8	0.9 (4)	S1—C9—C14A—C13A	-179.7 (4)
C6—C7—C8—C3	0.7 (4)	O6—C12—C13A—C14A	176.6 (4)
C5—C4—C3—C8	-0.4 (4)	C11A—C12—C13A—C14A	-4.1 (7)
C5—C4—C3—C2	-179.2 (2)	C9—C14A—C13A—C12	1.8 (7)

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>
O1—H1H...O2	0.87 (1)	2.28 (3)	2.749 (3)	114 (3)
O1—H1H...O3 <sup>i</sup>	0.87 (1)	1.95 (2)	2.754 (3)	152 (3)
O2—H2H...O1W <sup>ii</sup>	0.88 (1)	1.84 (2)	2.693 (3)	164 (4)
N1—H1N...O4 <sup>iii</sup>	0.86 (4)	1.99 (4)	2.850 (3)	178 (4)
N1—H2N...O5	0.86 (4)	1.91 (4)	2.766 (3)	172 (3)
N1—H3N...O3 <sup>iv</sup>	0.86 (4)	2.27 (4)	2.927 (3)	133 (3)
N1—H3N...O6 <sup>v</sup>	0.86 (4)	2.46 (4)	3.005 (3)	122 (3)
O6—H3H...O1W <sup>v</sup>	0.88 (1)	1.83 (2)	2.686 (3)	164 (4)
O1W—H1W...O2 <sup>vi</sup>	0.88 (1)	1.88 (1)	2.752 (3)	175 (4)
O1W—H2W...O4	0.88 (1)	1.82 (1)	2.698 (3)	177 (4)

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