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Hydrogen bonding in proton-transfer compounds of 5-sulfosalicylic acid with *ortho*-substituted monocyclic heteroaromatic Lewis bases

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Abstract: The crystal structures of the 1:1 proton-transfer compounds of 5-sulfosalicylic acid with the *ortho*-substituted monocyclic heteroaromatic Lewis bases, 2-aminopyridine, 2-hydroxypyridine and 2-aminopyrimidine, viz. 2-aminopyridinium 5-sulfosalicylate (**1**), 2-hydroxypyridinium 5-sulfosalicylate monohydrate (**2**) and 2-aminopyrimidinium 5-sulfosalicylate monohydrate (**3**) have been determined and their hydrogen-bonding patterns described. All compounds are monoclinic, space group $P2_1/c$, with Z=4 in cells with dimensions a=7.898(5), b=11.159(11), c=14.912(7) Å, β=96.849(11)° (**1**);=7.260(2), b=15.292(3), c=12.615(2) Å, β=102.45(5)° (**2**) and a=7.0430(7), b=12.1871(16), c=16.2825(12) Å, β=101.364(7)° (**3**). All three compounds show some molecular disorder, in **1** within the cation species and with both **2** and **3**, a similar rotational disorder in the anion sulfonate group. Hydrogen bonding in all three compounds together with significant cation-anion or cation-cation inter-ring π–π interactions generate three-dimensional layered polymer structures.

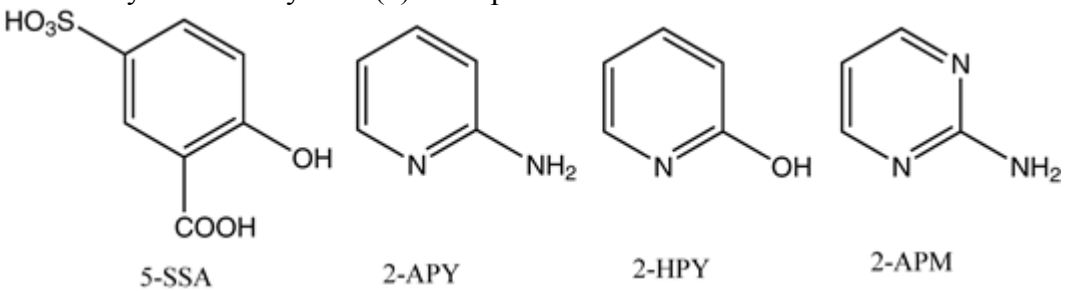
KEY WORDS: 5-Sulfosalicylic acid - proton-transfer compounds - heteroaromatic lewis bases - hydrogen bonding

Introduction, results and discussion

The substituted salicylic acid 3-carboxy-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid, 5-SSA) is a particularly strong acid which is capable of protonating water and several hydrated structures of the acid are known, e.g. the dihydrate and dideuterate,[1] [−] [3] the trihydrate,[4] and the pentahydrate,[5] in which various protonated poly-aqua oxonium species e.g. $H_7O_3^+$ have been identified.[4] This property is also considered to be the reason for the unusual conductivity properties of the acid and many of its compounds. The acid strength also means that Lewis bases are readily protonated by 5-SSA and because of the presence of the additional interactive carboxylic acid and phenolic substituent groups the acid has potential for structure extension through hydrogen bonding, making it a useful synthon for crystal engineering purposes.

The crystal structures of the 1:1 proton-transfer compounds with aniline[6], the 4-X-substituted anilines (X=F, Cl, Br [7], CO_2H[8]), 3-aminobenzoic acid,[9] benzylamine,[10] the aromatic polyamines,[11,12] and the bicyclic heteroaromatic amines[13,14] have been reported, together with the compounds with theophylline,[15] trimethoprim[16] and pyrimethamine.[17] The greater ability to generate stable crystal networks with aromatic Lewis bases is reflected in the very few examples of 5-SSA compounds with aliphatic amines: guanidinium 5-sulfosalicylate,[18] ethylenediaminium 5-sulfosalicylate tetrahydrate,[19] and bis(guanidi-nium) 5-sulfosalicylate monohydrate[21] (the last two and benzylamine[10] representing uncommon organic compounds in which the 5-SSA species are dianionic). Because of the presence of the sulfonate group in these compounds, water molecules of solvation are found in the majority of the structures, acting as proton donors and acceptors in hydrogen-bonding associations.

To further test the theory that aromatic ring systems contributed to structure stabilization through some π–π interactions in proton-transfer compounds of 5-SSA with aromatic Lewis bases,[11,13] we attempted the preparation and characterization of a series of compounds with the monocyclic heteroaromatic amines, using pyridine and a number of substituted pyridines and pyrimidines. The most rewarding results among these occurred with the *ortho*-substituted analogues and the crystal structures of the compounds with 2-aminopyridine (2-APY), 2-hydroxypyridine (2-HPY) and 2-aminopyrimidine (2-APM), viz. 2-aminopyridinium 5-sulfosalicylate (**1**), 2-hydroxypyridinium 5-sulfosalicylate monohydrate (**2**) and 2-aminopyrimidinium 5-sulfosalicylate monohydrate (**3**) are reported here.



5-SSA 2-APY 2-HPY 2-APM

Of the three Lewis bases used in this work, 2-aminopyrimidine has been the most studied[21–25] because of its ability to extend the basic cyclic homomolecular 2-APM-2-APM (P-P) motif into polymeric structures mostly through heteromolecular acid-2-APM (A-P) hydrogen-bonding associations. These various modes of polymeric extension e.g. $[A\text{-}(P\text{-}P)]_n$ and $[A\text{-}(P\text{-}P)\text{-}A]_n$ have also been classified.[25] By comparison, 2-aminopyridine shows much less structure-extending potential compared to 2-APM and this is reflected in significantly fewer reported structures e.g. the 1:1 proton-transfer compounds with 2,6-dihydroxybenzoic acid,[22] and Kemp's triacid,[26] and the adduct 2-aminopyridinium-fumarate-fumaric acid (2/1/1).[27]

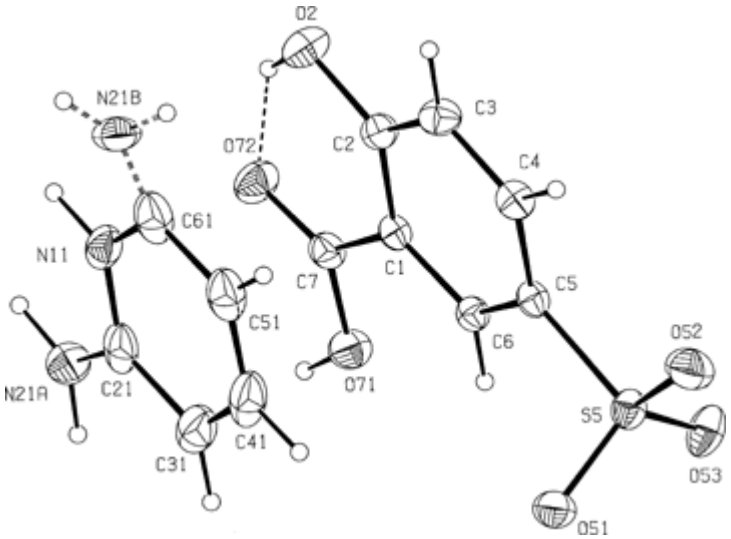


Fig. 1. Molecular configuration and atom numbering scheme for the individual 5-SSA anion and the disordered 2-aminopyridinium cation species in **1**. The rotational disorder occurs about the N11···C41 ring axis giving amine sites N21A (78%) and N2B (22%). Non−hydrogen atoms are shown as 30% probability displacement ellipsoids.[33]

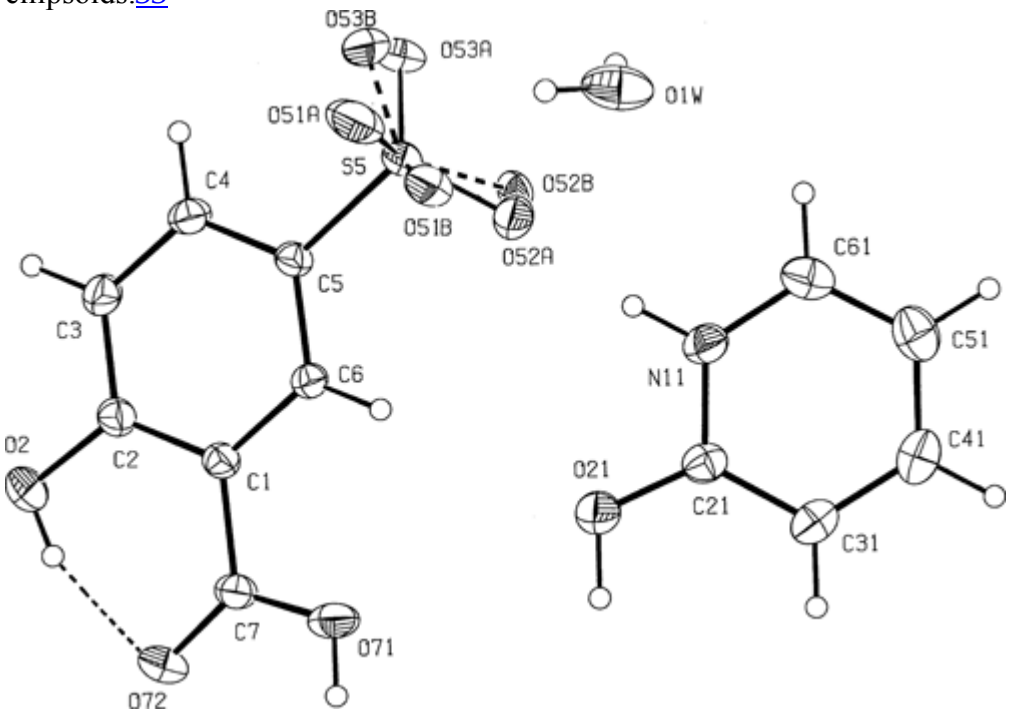


Fig. 2. Molecular configuration and atom numbering scheme for the disordered 5-SSA anion and the 2-hydroxypyridinium cation species in **2**. Anion disorder rotates sulfonate oxygen atoms O51A, O52A, O53A (80%) into alternative sites O51B, O52B, O53B (20%). A similar disorder occurs in **3** [(A, 75%, B (25%)]. Non−hydrogen atoms are shown as 30% probability displacement ellipsoids.

General structure comparison

The structure determinations of compounds **1-3** all show three-dimensional layered hydrogen-bonded polymer structures in which significant cation-anion π–π ring interactions are present. General structural details for compounds 1–3 are given in Table 1 while Table 2 lists hydrogen-bonding interactions. Figures 1 and 2 show the molecular configuration and atom naming schemes used for the individual 5-SSA

anion species and the protonated cation species in **1** and **2**, together with the disorder in the 2-APM species in **1** and the 5-SSA sulfonate group in **2**. The same sulfonate disorder is found in **3** where the atom numbering is consistent with that used in **2**. Figure 3 shows the atom numbering scheme used for the 2-APM cation in **3**.

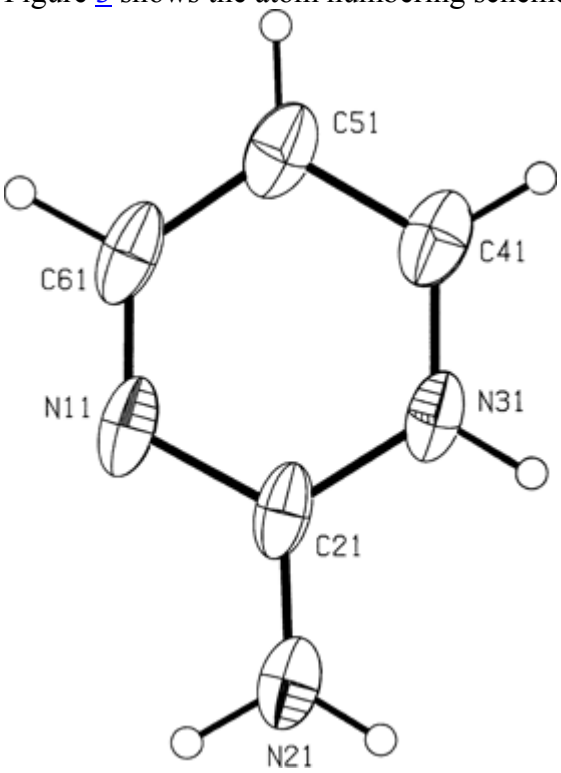


Fig. 3. Atom numbering scheme for the 2-aminoprimidinium cation in **3** (30% probability). In this compound the 5-SSA anion employs the same numbering scheme as for **1** and **2**.

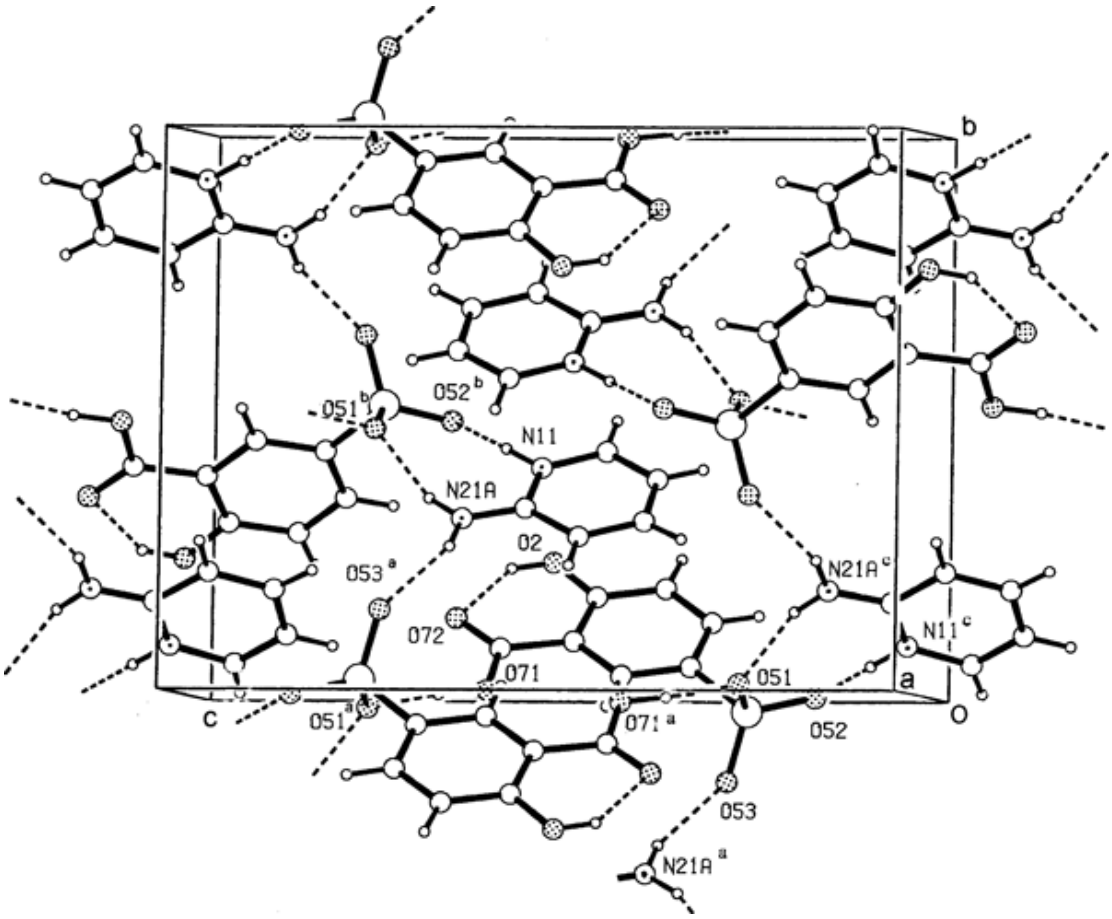


Fig. 4. Perspective view of the packing of **1** in the unit cell viewed down the approximate *a* cell direction. [symmetry code [c]: *x*, 1/2 −*y*, 1/2 ± *z*; for other codes, see Table 2a]. Hydrogen−bonding associations are shown as broken lines. Disordered atoms are omitted in this figure as well as in Figs. 5 and 6.

In all three compounds, single protonation by the sulfonate group of 5-SSA of the pyridine nitrogen of the Lewis base occurs, with a subsequent strong primary hydrogen-bonding interaction between this group and an oxygen acceptor from the 5-SSA sulfonate group. One of the generalizations[28] from a study of 594 structures of aminium sulfonates in the CSD, that with the presence of water in such structures, there is a high tendency for that to form a hydrogen bond with a sulfonate oxygen acceptor. This is consistent with the observation for **2** and **3** where a water···sulfonate interaction is present. A further observation with these compounds is that where it is feasible for a cyclic bidentate $R^2_2(8)$ interaction to form between the aminium species and the sulfonate group, it does so with *ca*. 75% incidence. Such is the case in both **1** and **3**. In **2** it might be considered feasible for a similar bidentate cyclic interaction to occur between the pyridinium and *ortho*-related hydroxyl groups of the 2-HPY cation and two oxygen acceptors of a sulfonate group but this is not found. Instead, this group provides an O−H···O(sulfonate) polymer linkage. In all three structures, a strong 5-SSA carboxylic acid···O interaction is present, again with water when present [2.614(2) Å (**2**); 2.619(4) Å (**3**)] or with a sulfonate-O [2.622(4) Å] in anhydrous **1**. In addition, significant inter-ring cation-anion or cation-cation interactions are present and all compounds give three-dimensional layered polymer structures.

Table 1. Crystal data for compounds **1-3**

Compound	**1**	**2**	**3**
Colour	Colourless	Colourless	Colourless
Melting point (°C)	240—241	198—203	204–206
Molecular formula	$C_{12}H_{12}N_2O_6S$	$C_{12}H_{13}NO_8S$	$C_{11}H_{13}N_3O_7S$
M_r	312.87	331.30	331.31
Temperature (K)	297(2)	297(2)	297(2)
Wavelength (λ) (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	7.898(5)	7.260(2)	7.0430(7)
b (Å)	11.159(11)	15.292(3)	12.1871(16)
c (Å)	14.912(7)	12.615(2)	16.2825(12)
β (°)	96.849(11)	102.45(5)	101.364(7)
V (Å3)	1304.9(17)	1367.6(6	1370.2(2)
Z	4	4	4
D_c (g cm^{-} 3)	1.593	1.609	1.606
μ (mm^{-} 1)	0.280	0.280	0.278
F(000)	648	688	688
Instrument	Rigaku AFC 7R	Rigaku AFC 7R	Rigaku AFC 7R
Reflections total, θ_{max} (°)	2622, 25.0	3599, 27.5	3492, 27.5
Crystal size (mm)	0.30× 0.25×0.25	0.30×0.15×0.10	0.50×0.45×0.40
Collection range:			
h	−9 to 9	−9 to 4	−9 to 8
k	−13 to 0	−19 to 0	−15 to 0
l	−8 to 17	−16 to 16	−9 to 21
Reflections (independent)	2292	3140	3143
Reflections [$F^2 > 2\sigma(F^2)$]	1501	2048	2617
R_{int}	0.029	0.030	0.040
Crystal decay (%)	0.0	0.7	1.7
Trans. Factors (max/min)	0.933/0.921	0.973/0.923	0.895/0.870
$R1$ [a] [$F^2 > 2\sigma(F^2)$]	0.044	0.043	0.043
$wR2$ [a] (all data)	0.145	0.156	0.134
S [a]	1.05	0.88	0.80
n_p	216	241	254
Residuals: $\Delta_{max./min}$ (eÅ^{-} 3)	0.240/−0.297	0.287/−0.278	0.472/−0.424

a

$$R1 = (\sum ||F_o| - |F_c||) / \sum |F_o|); \quad wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}; \quad S = \{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$$

.

Table 2. Hydrogen-bonding interactions (Å/°) for **1-3**

D—H···A	**D—H**	**H···A**	**D···A**	**DH···A**
(a) Compound **1**				
O2—H2···O72	0.87(4)	1.87(4)	2.637(5)	145(4)
O71—H71···O51 [a]	0.96(5)	1.68(5)	2.621(4)	166(4)
N11—H11···O52 [b]	0.95(4)	1.94(4)	2.856(5)	161(4)
N21—H21A···O51 [b]	0.95(5)	1.95(5)	2.861(6)	160(5)
N21—H21B···O53 [a]	0.95(4)	1.99(4)	2.850(6)	150(4)
(b) Compound **2**				
O2—H2···O72	0.82(5)	1.83(5)	2.606(4)	156(5)
O21—H21···O53A [c]	0.95(6)	1.70(6)	2.647(4)	176(5)
O71—H71···O1W [c]	0.85(6)	1.79(6)	2.619(4)	165(5)
N11—H11···O52A	0.92(4)	1.89(4)	2.757(4)	156(4)
O1W—H1W···O51A [d]	0.92(5)	1.95(5)	2.855(5)	165(5)
O1W—H2W···O53A	0.90(4)	2.16(4)	3.064(7)	179(4)
(c) Compound **3**				
O2—H2···O72	0.85(3)	1.79(4)	2.609(2)	160(3)
O71—H71···O1W [e]	0.91(3)	1.72(3)	2.614(2)	172(4)
N21—H21A···O52A	0.82(4)	2.23(3)	3.025(3)	163(3)
N21—H21B···N11 [f]	0.92(5)	2.13(5)	3.047(4)	176(5)
N31—H31···O53A	0.87(4)	1.90(2)	2.759(3)	169(3)
O1W—H1W···O53A	0.88(2)	1.78(2)	2.623(3)	161(2)
O1W—H2W···O52A [g]	0.90(2)	1.75(2)	2.644(3)	180(3)

Note. Symmetry codes: [a] 1−*x*, −*y*, 1−*z*, [b] *x*, 1/2 −*y*, 1/2 +*z*, [c] 1−*x*, −1/2 + *y*, 1/2 −*z*, [d] *x*−1, *y*, *z*, [e] 1−*x*, 1−*y*, −*z*, [f] 2−*x*, 1−*y*, −*z*, [g] *x*−1, *y*−1, *z*.

The individual structures

[(2-APY) $^{+}$ **(5-SSA)** $^{-}$**]** (**1**). The structure of anhydrous **1** shows a direct bidentate $R^2_2(8)$ interaction between the sulfonate group and the protonated *ortho*-substituted pyridinium cation species. This interaction is symmetric [N11···O52[b], 2.856(5); N21A···O51[b], 2.861(6) Å; symmetry code ([b]) *x*, 1/2 −*y*, 1/2 ± *z*] but is somewhat twisted (Fig. 4). Structure extension occurs through the second amine proton donor with a sulfonate-O (Table 2a) and in the absence of any water molecules of solvation, through a 5-SSA carboxylic acid···sulfonate-O interaction [O71···O51[a], 2.621(4) Å: symmetry code ([a]) 1−*x*, −*y*, 1−*z*]. This is classified as a Type 7 cation-sulfonate interaction which has a 55% probability[28] among these types of structures and in **1** results in a three-dimensional layered polymer structure. Partial cation-anion ring superimposition is present giving molecular stacking down the approximate *b* axial direction [ring centroid separation (C_g–C_g)=3.568(6) Å; inter-plane dihedral angle (α)=3.70(1)°], indicating the presence of significant π–π interactions. The disorder in the 2-APY cation is the result of rotation about the N11···C41 ring diagonal giving a

statistical amine group population of 78% (N21A) to 22% (N21B). However, the interactions relating to N21B were not considered in the solid-state packing for **1**.

[(2-HPY)$^{+}$ (5-SSA)$^{-}$. H$_2$O] (2). The structure of the monohydrate 2 shows a direct N^{+}−H···O(sulfonate) hydrogen-bonding interaction [N11···O52A, 2.757(4) Å] linking the 2-HPY cation and 5-SSA anion species (Fig. 5). However, the ortho-related hydroxy group does not complete a cyclic interaction with a second sulfonate oxygen acceptor, forming instead an O−H···O(sulfonate) polymer link [O21···O53a, 2.647(4) Å; symmetry code: (^{a}) 1−*x*, −1/2 +*y*, 1/2 −*z*]. The sulfonate group also acts as a proton acceptor in associations with two water molecules (Table 2b) which extend the structure in the *a* and *c* axial directions. The 5-SSA carboxylic acid group gives the common strong interaction with the water molecule [O71−H71···O1W^{a}, 2.619(4) Å]. Cation-cation ring stacking is also present [C_g−C_g=3.525(5) Å; α=0.0(1)°]

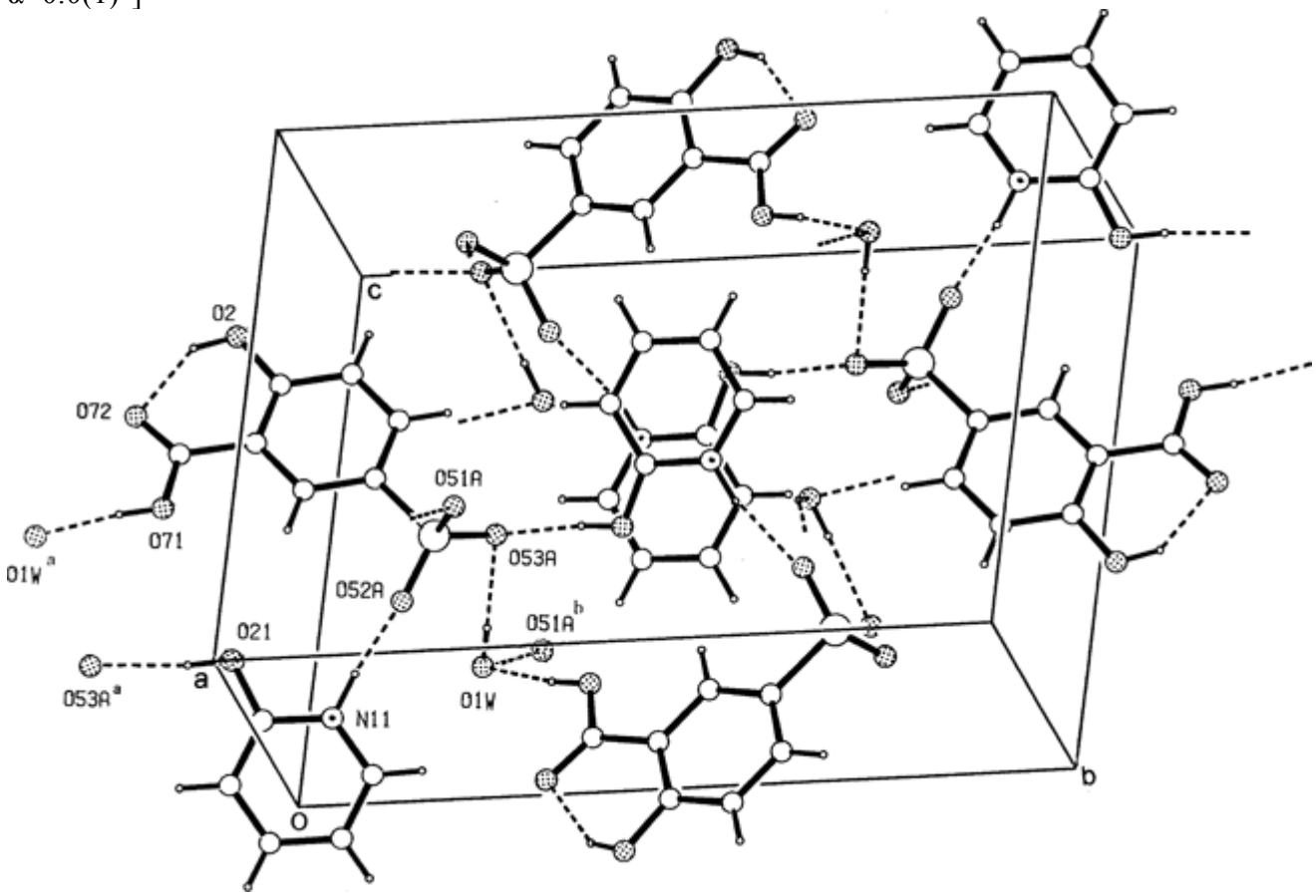


Fig. 5. Perspective view of the packing of **2** in the unit cell viewed down the approximate *a* cell direction. [for symmetry codes, see Table 2b].

[(2-APM)$^{+}$ (5-SSA)$^{-}$. H$_2$O] (3). The structure of the monohydrate 3 is based upon the previously described*21*, *25* P-P hydrogen-bonded cyclic homodimers formed in **3** through a centrosymmetric $R^2_2(8)$ association between the aminium and adjacent amine donor groups of the 2-aminopyrimidine cations [N21−H21B···N11^{b}, 3.047(4) Å; symmetry code (^{b}) 2−*x*, 1−*y*, −*z*] (Fig. 5). The dimers are extended into a $[(A)\text{-}(P\text{-}P)\text{-}(A)]_n$ *24* convoluted chain structure also through cyclic but twisted and asymmetric $R^2_2(8)$ interactions with two sulfonate oxygen acceptors of the 5-SSA anions [N21−H21A···O52A, 3.025(3) Å; N31−H31···O53A, 2.759(3) Å]. The chains

extend along the *b* axial direction and are linked into a three-dimensional polymer structure by hydrogen bonding (Table 2c) (Fig. 6) through the water molecule which associates with two sulfonate-O acceptors (along *a*) and the 5-SSA carboxylic acid donor group (along *c*). Cation-cation ring stacking is also present [C_g–C_g=3.503(3) Å; α=0.03(6)°].

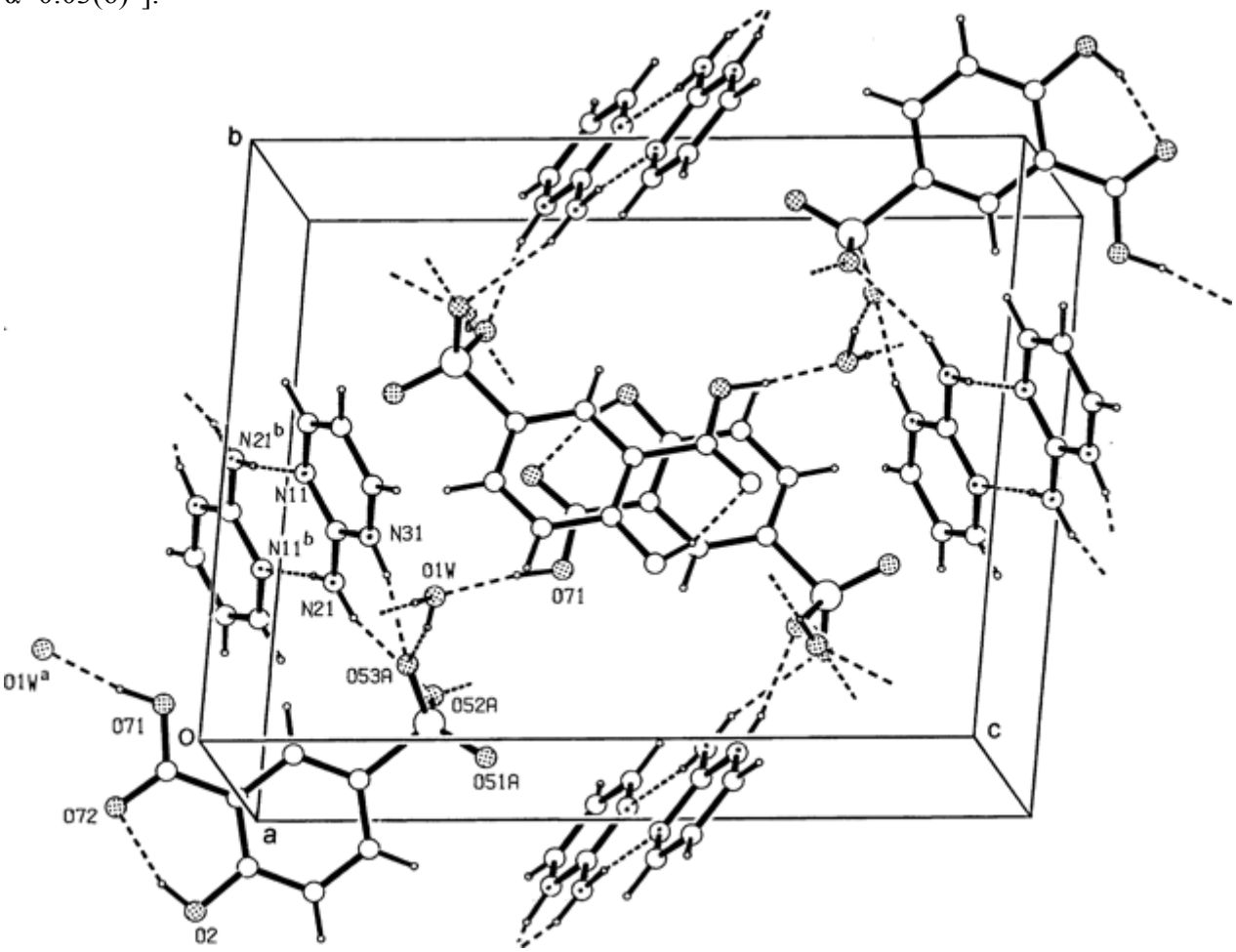


Fig. 6. Perspective view of the packing of **3** in the unit cell viewed down the approximate *a* cell direction. [for symmetry codes, see Table 2c].

Conclusion

The presence of *ortho*- (interactive group) substitution in pyridine-like heteroaromatic Lewis bases effectively promotes structure extension in proton-transfer compounds of aromatic sulfonates, in particular with the multi-functionally substituted analogue, 5-sulfosalicylic acid. This is largely achieved through the particularly robust cyclic $R^2_2(8)$ hydrogen-bonding association which occurs with high probability among examples such as these reported here. Furthermore, aromatic Lewis bases play an important role in structure building through cation-anion π–π ring stacking interactions, resulting commonly in three-dimensional layered polymer structures.

Experimental

Preparation

The title compounds **1-3** was synthesized by heating 1 mmol quantities of 5-sulfosalicylic acid (3-carboxy-5-hydroxybenzenesulfonic acid) and the appropriate

Lewis base [2-aminopyridine (**1**), 2-hydroxypyridine (2-aminophenol) (**2**) and 2-aminopyrimidine (**3**)] in 50 mL of 50% ethanol/water under reflux for 10 min. After concentration to *ca*. 30 mL, partial room temperature evaporation of the hot-filtered solutions gave in all cases colourless crystal prisms of compounds **1-3**. It is noteworthy that no crystalline product was obtained in an attempted preparation of pyridinium 5-sulfosalicylate.

Crystallography

X-ray diffraction data for **1-3** were obtained at ambient temperature on a Rigaku AFC 7R four-circle diffractometer using crystal monochromatised Mo-Kα X-radiation (λ=0.71073 Å) from a 12 kW rotating anode source. Data were corrected for extinction and for absorption. The structures were solved by direct methods using SIR-92*30* and refined with anisotropic thermal parameters for all non-hydrogen atoms using SHELXL 97*31* operating within the TeXsan system.*32* Hydrogen atoms potentially involved in hydrogen-bonding interactions were located by difference methods and their positional and isotropic thermal displacement parameters were refined. Others were included in the refinement at calculated positions and treated as riding models. In all three structures, disorder was found. With **1**, the 2-aminopyridinium cation was rotationally disordered over two sites related by a twofold rotational axis passing through the N1···C4 ring atoms. This places the 2-amino substituent group in two sites [N2A (78%) and N2B (22%)]. In both **2** and **3**, the disorder is found in the sulfonate anion where the primary set of three oxygen atoms [O51A-O53A] rotate into a minor occupancy set [O51B-O53B] [SOF, 0.75/0.25 (**2**) and 0.80/0.20 (**3**)]. General structural details are given in Table 1. The atom numbering scheme employed for the 5-SSA anion species in **1** and **2** is shown in Figs. 1 and 2 and is the same as used in **3**. This follows the convention used in previous structural studies by this group.*7* ¯ *11* , *13* , *20*

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Supplementary material

CCDC 286383, 286384 and 286385 contain supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/datarequest/cif by e-mailing datarequest@ccdc.cam.ac.uk, or contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ.