For publication in Journal of Chemical Crystallography.

(a) ***Cover Page***

Structural Systematics of the Anhydrous 1:1 Proton-Transfer Compounds of 3,5-Dinitrosalicylic Acid with Aniline and Monosubstituted Anilines

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(b) ***Index Abstract***

Structural Systematics of the Anhydrous 1:1 Proton-Transfer Compounds of 3,5-Dinitrosalicylic Acid with Aniline and Monosubstituted Anilines

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The crystal structure determinations of the anhydrous 1:1 proton-transfer compounds of 3,5-dinitrosalicylic acid with aniline and a set of six monosubstituted anilines (2-hydroxy-, 2-methoxy-, 3-methoxy-, 4-fluoro-, 4-chloro- and 2-aminoaniline) have allowed the hydrogen-bonding systematics to be examined.

Figure for insertion in Index Abstract: (use DNSA4ABS.TIF)

Abstract The crystal structures of the proton-transfer compounds of 3,5-dinitrosalicylic acid (DNSA) with a series of aniline-type Lewis bases [aniline, 2-hydroxyaniline, 2-methoxyaniline, 3-methoxyaniline, 4-fluoroaniline, 4-chloroaniline and 2-aminoaniline] have been determined and their hydrogen-bonding systems analysed. All are anhydrous 1:1 salts: $[(C_6H_8N)^+(C_7H_3N_2O_7)^-]$, (**1**), $[(C_6H_8NO)^+(C_7H_3N_2O_7)^-]$, (**2**), $[(C_7H_{10}NO)^+(C_7H_3N_2O_7)^-]$, (**3**), $[(C_7H_{10}NO)^+(C_7H_3N_2O_7)^-]$, (**4**), $[(C_6H_7FN)^+(C_7H_3N_2O_7)^-]$, (**5**), $[(C_6H_7ClN)^+(C_7H_3N_2O_7)^-]$, (**6**), and $[(C_6H_9N_2)^+(C_7H_3N_2O_7)^-]$, (**7**) respectively. Crystals of **1** and **6** are triclinic, space group *P*-1 while the remainder are monoclinic with space group either $P2_1/n$ (**2, 4, 5** and **7**) or $P2_1$ (**3**). Unit cell dimensions and contents are: for **1**, a = 7.2027(17), b = 7.5699(17), c = 12.9615(16) Å, α = 84.464(14), β = 86.387(15), γ = 75.580(14)°, Z = 2; for **2**, a = 7.407(3), b = 6.987(3), c = 27.653(11) Å, β = 94.906(7)°, Z = 4; for **3**, a = 8.2816(18), b = 23.151(6), c = 3.9338(10), β = 95.255(19)°, Z = 2; for **4**, a = 11.209(2), b = 8.7858(19), c = 15.171(3) Å, β = 93.717(4)°, Z = 4; for **5**, a = 26.377(3), b = 10.1602(12), c = 5.1384(10) Å, β = 91.996(13)°, Z = 4; for **6**, a = 11.217(3), b = 14.156(5), c = 4.860(3) Å, α = 99.10(4), β = 96.99(4), γ = 76.35(2)°, Z = 2; for **7**, a = 12.830(4), b = 8.145(3), c = 14.302(4) Å, β = 102.631(6)°, Z = 4. In all compounds at least one primary linear intermolecular N^+-H…O(carboxyl) hydrogen-bonding interaction is present which, together with secondary hydrogen bonding results in the formation of mostly two-dimensional network structures, exceptions being with compounds **4** and **5** (one-dimensional) and compound **6** (three-dimensional). In only two cases [compounds **1** and **4**], are weak cation-anion or cation-cation π-π interactions found while weak aromatic C-H…O interactions are insignificant. The study shows that all compounds fit the previously formulated classification scheme for primary and secondary interactive modes for proton-transfer compounds of 3,5-dinitrosalicylic acid but there are some unusual variants.

Key Words: Hydrogen bonding; proton-transfer compounds; 3,5-dinitrosalicylic acid; anilines.

Running Title: Anilinium salts of 3,5-dinitrosalicylic acid

Introduction

Because of its acid strength (pK_a = 2.2), 3,5-dinitrosalicylic acid (DNSA) is capable of protonating most nitrogen Lewis bases giving compounds with significantly enhanced crystallinity through hydrogen bonding involving the aminium group and the oxygen acceptors of the substituent groups (carboxyl, phenol, nitro). We have previously crystallographically characterized and reported the structures of *ca*. 40 of these proton-transfer compounds [including series with aliphatic amines [1], monocyclic aromatic and heteroaromatic amines [2] and polycyclic aromatic and heteroaromatic amines [3]. Only one example of a non-transfer Lewis base-DNSA complex has been described, that with the very weak base phenazine [4], although the 1:1 adducts with urea [5], 1,1-diethylurea [6], phenylurea [7], *trans*-1,4-dithiane-1,4-dioxide [8] and the pseudopolymorphic DNSA solvate compounds, which may be also be loosely considered as adducts of this acid. These solvates are the two monohydrate polymorphs [9, 10], four 1,4-dioxane solvates and a *t*-butyl alcohol solvate [10]. However, solvates are uncommon among the DNSA proton-transfer compounds with only seven known examples: five hydrates and two ethanol solvates. The five hydrates are ethylenediaminium 3,5-dinitrosalicylate monohydrate [1], salicylaldoximium 3,5-dinitrosalicylate dihydrate [11], brucinium 3,5-dinitrosalicylate monohydrate [12], 1-ammonio-5-hydroxynaphthalene monohydrate [13] and the unusual mixed piperidine DNSA-picrate (a monohydrate) [14]. The two ethanol solvates are considered more novel, but possible because crystals of most of these DNSA compounds are obtained from ethanol-water solvent. They are a partial ethanolate, 2-aminopyridinium-3,5-dinitrosalicylate-ethanol (4/4/1) [2] and benzidinium^{1+}-benzidinium^{2+}-3,5-dinitrosalicylate-ethanol (3/1/4/2) [15]. The stoichiometry for these DNSA compounds is predominantly 1:1, usually formed as a preferred product irrespective of reactant ratios, which is consistent with observations for carboxylic acid-2-aminopyrimidine compounds [16]. Only two DNSA examples are known in which adduct formation is found, one with 4-aminobenzoic acid [4-carboxyanilinium 3,5-dinitrosalicylate-4-aminobenzoic acid (1:1:1) [17] and one with pyridine [pyridinium 3,5-dinitrosalicylate-3,5-dinitrosalicylic acid (1:1:1) [2], the latter differing from the former in having the DNSA proton-donor molecule rather than the base-acceptor molecule as the adduct molecule. With the bifunctional examples, the utility of the protonated amino group in enhancing secondary associative effects, through the formation of hydrogen-bonding networks, is well recognized [1].

A number of compounds of DNSA with a series of substituted primary anilines [18], *N*-substituted anilines [19] and phenylenediamines [20] have been synthesized and characterized spectroscopically to ascertain the presence of proton transfer and/or electron transfer. It was found, as expected on the grounds of pK_a differences between the Lewis base and DNSA, that proton-transfer compounds predominate, with electron transfer restricted to compounds not only considered possible on pK_a grounds but those prepared from aprotic solvents rather than ethanol or aqueous ethanol. We have also observed that among the crystallographically characterized proton-transfer DNSA compounds (all prepared using ethanol or aqueous ethanol as solvent), there is a low

incidence of what can be considered secondary π-π interactive effects involving the aromatic cations and the DNSA anions [e.g. almost exclusively those with the polycyclic Lewis bases, e.g. quinoline, quinaldic acid and 1,10-phenanthroline [3], 1-amino-5-hydroxynaphthalene [13] and benzidene [15]. Furthermore, with the same set of aromatic bases, there is an increased incidence of weaker aromatic ring C-H…O hydrogen bonding, e.g. in the structure of the 1:1 DNSA compound with 2,2'-bipyridine [3] where there is only one formal inter-species N^+-H…O hydrogen bond, there are seven C-H…O associations.

1.1 Associative modes in the DNSA proton-transfer compounds

From a consideration of the structural features of the large number of examples of DNSA-Lewis base proton-transfer compounds characterized crystallographically, we have previously systematized the modes of hydrogen-bonding association on the basis of primary and secondary intermolecular interactions [3]. With all orders of both aliphatic, aromatic and heteroaromatic amines, protonation is usually followed by primary N^+-H (aminium)….O (carboxylate) cation-anion association. Secondary structure-building hydrogen-bonding associations then occur through other available donor and acceptor sites to expand the basic cation-anion units into one-dimensional chains, two-dimensional networks or three-dimensional framework structures. There is, not surprisingly a decrease in the associative efficacy of the protonated functional group of the Lewis base proceeding from primary to secondary to tertiary amines. There are only four examples in which the carboxyl-O is not involved in the primary cation-anion interaction but instead usually participates in only weaker secondary O…H-C interactions. They are the compounds of DNSA with hexamethylenetetramine [1, 21], 4-cyanopyridine [2] and strychnine [22] [in both of these examples there is a primary cyclic bidentate N^+-H….O, O' (phenol, nitro) interaction [graph set $R^2_1(6)$ [23], but with 1-amino-5-hydroxynaphthalene, a carboxyl-O acts as an acceptor in a strong hydrogen bond with the hydroxyl group of the cation [13]. This $R^2_1(6)$ interaction is common in

secondary structure extensions among proton-transfer compounds of DNSA [3].

INSERT 1: Scheme 1. DNSA4.1.eps: Proximal $R^2_1(6)$ interaction

The primary N^+-H…O associative modes for the DNSA proton-transfer compounds [3] are as follows:

Type 1: **Single linear interaction.** This set of structures involves a single primary aminium N^+-H ….O(carboxyl) interaction [graph set D], with secondary propagating interactions giving one-, two- and three-dimensional extension. Examples of one- and two-dimensional extension are mostly confined to the tertiary aliphatic examples, e. g. with triethylamine [1], although aromatic examples are known e.g. with 8-aminoquinoline [24] and 8-hydroxyquinoline [25]. Three-dimensional extension is common among the primary amines where strong secondary interactions are present, e.g. in the isomeric monoaminobenzoic acid compounds [16] but compounds with the polycyclic heteroaromatics such as 1,10-phenanthroline [3] and 2,2'-bipyridine [3, 26], where significant aromatic C-H…O interactions are present together with a minor incidence of cation-anion π-π association.

Type 2: **Cyclic $R^2_1(4)$ interaction.** This category involves the aminium N^+-H group in a cyclic three-centred bidentate interaction with both carboxylate oxygens [graph set $R^2_1(4)$] and is quite common, e.g. the compounds with 3-amino-1,2,4-triazole [27] and benzylamine [28].

Type 3: Cyclic $R^2_2(N)$ interaction. This category involves two proton donors of the cation including one aminium proton and both carboxylate-O acceptors in a cyclic $R^2_2(N)$ association, where *N* is usually 8 , e.g. the compounds with 2-aminopyrimidine [2], cytosine [29], guanidine [30], 2-aminothiazole [31] and trimethoprim [32], but *N* may also be 7 {the compounds with benzimidazole [3] and salicylaldoxime [11]}. Another $R^2_2(8)$ variant involves the aminium proton and an adjacent aromatic ring H atom donor in an asymmetric cyclic association, such as is found in

the structure of quinolinium 3,5-dinitrosalicylate [3].

INSERT 2: Scheme 2. DNSA4.2.eps: Type 1-3 interactions

The object of the current work was to prepare and structurally characterize a series of compounds of DNSA with a number of primary anilines which, although relatively weak bases, have pK_a values which would result in formation of proton-transfer compounds. The structures of these could then be used to test the assembly mode types on the basis of the previously described classifications [3] and possibly allow a systematization of the structural aspects of the DNSA compounds with the primary anilines. The anilines chosen were the parent aniline (AN) and the monosubstituted analogs, 2-hydroxyaniline (*o*-aminophenol = OAP), 2-methoxyaniline (*o*-anisidine = OAN), 3-methoxyaniline (*m*-anisidine = MAN), 4-chloroaniline (FLAN), 4-chloroaniline (CLAN) and 2-aminoaniline (*o*-phenylenediamine = OPDA) (pK_a range for the set: 4.00-4.74). We have previously described the compounds with the monocarboxy-substituted aniline compounds (the isomeric monoaminobenzoic acids), 2-aminobenzoic acid and 3-aminobenzoic acid (both 1:1), and the previously mentioned 1:1:1 adduct example with 4-aminobenzoic acid [9]. In all of these (as with primary amines generally), protonation of the amine group results in a Type 1 linear hydrogen-bonding interaction with the carboxyl group of DNSA, together with secondary extension through strong N^+-H…O hydrogen bonds involving the other aminium protons. These interactions, which may number up to six per aminium group are largely responsible for the formation of stable two- and three-dimensional network or framework structures, usually giving crystals with relatively high melting points and good morphology. The DNSA compounds reported here are all anhydrous 1:1 salts, as follows: with aniline $[(C_6H_8N)^+(C_7H_3N_2O_7)^-]$, (**1**); with 2-hydroxyaniline, $[(C_6H_8NO)^+(C_7H_3N_2O_7)^-]$ (**2**); with 2-methoxyaniline, $[(C_7H_{10}NO)^+(C_7H_3N_2O_7)^-]$ (**3**); with 3-

methoxyaniline, $[(C_7H_{10}NO)^+(C_7H_3N_2O_7)^-]$ (**4**); with 4-fluoroaniline, $[(C_6H_7FN)^+(C_7H_3N_2O_7)^-]$ (**5**); with 4-chloroaniline, $[(C_6H_7ClN)^+(C_7H_3N_2O_7)^-]$ (**6**), and with 2-aminoaniline, $[(C_6H_9N_2)^+(C_7H_3N_2O_7)^-]$ (**7**). With the exception of **5**, the 1:1 compounds of DNSA with the set of anilines used in this work have previously been reported {the anilines in **1-4** and **6** [18] and *o*-phenylenediamine **7** [20] } but only two of them [**2** and **4**] appear not to be the same as the compounds reported in this work.

INSERT 3: DNSA4.3.eps. Scheme 3. The interacting compounds for 1-7

2. Experimental

2.1 *Preparation of compounds*.

Compounds **1-7** were prepared using equimolar quantities (0.10 mmol) of 3,5-dinitrosalicylic acid with the appropriate Lewis base. All preparations involved heating 50 cm^3 of a solution of the two reactants in 80:20% ethanol-water under reflux for *ca*. 10 min. Volume reduction to *ca*. 40 cm^3 followed by partial or complete room temperature evaporation of the hot-filtered solutions gave in all cases, crystals with good morphology. However, the melting points for these compounds indicate that **2** and **4** are probably different from the Issa *et al.* [18, 20] (1980, 1981) compounds [melting points (K) with comparative Issa values given in parentheses: (**1**) 451.6-454.9 (453); (**2**) 480.4-481.1 (433); (**3**) 452.0-453.3 (446); (**4**) 426.8-427.5 (463); (**5**) 453.8-458.0 (not reported); (**6**) 466.7-468.0 (468); (**7**) 479.8-480.2 (483)]. The differences in the products obtained with **2** and **4** are probably due the use of benzene-ethanol solvent in the original preparations rather than aqueous ethanol.

2.2 *Data collection, structure solution and refinement*

X-ray diffraction data were collected at ambient temperature on either a Bruker SMART CCD-

detector diffractometer [compounds **2**, **4** and **7**] or a Rigaku AFC 7R diffractometer [compounds **1**, **3**, **5** and **7**]. Graphite crystal monochromatized Mo *Kα* X-radiation (λ = 0.71073Å) was used in all cases, with the Rigaku instrument from a 12 kW rotating anode source. With all compounds no significant crystal decay was in evidence [maximum 2.1% for **3**]. Data were corrected for Lorentz and polarization effects but not for extinction and only in the case of compound **6**, for absorption. The structures were solved by direct methods and refined using full-matrix least-squares (on F^2) using *SHELX97* [33], [in the case of compounds **1**, **3**, **4** and **5** using the *TeXsan* system [34]. Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atoms potentially involved in hydrogen-bonding interactions were located by difference methods and both positional and thermal parameters were refined while others were included at calculated positions and treated as riding models. A complete listing of cell and structural refinement data is given in Table 1. In the case of compound **2**, crystal twinning was found to be a problem but an adequate specimen was found and used for data collection. Nevertheless a problem was evident in the refinement, resulting in a high refinement residual, considered to be partially the result of the presence of rotational disorder about the C7-C1…C4 ring diagonal in the DNSA anion, which generates two partial sites for the C2 phenolic substituent group and the attached H (O2A, H2A) (see Fig. 1b), giving site occupancies of 0.833(10) (O2) and 0.177(10) (O2A). This creates larger than normal displacement parameters for the oxygen atoms in the conformationally dissimilar nitro groups at C3 and C5.

3. Results and discussion

3.1 *The comparative structures* **1-7**.

In all of the structures reported here **1-7** the presence of anhydrous 1:1 proton-transfer compounds of DNSA has been confirmed. The protonated nitrogen of the amine substituent group of the anilinium cation subsequently gives hydrogen-bonding interactions with the oxygen

acceptors (carboxylate, phenol or nitro) on the DNSA anion, giving in all cases either two- or three-dimensional framework structures. A full listing of hydrogen-bonding interactions is given in Table 2, and comparative structural parameters in Table 3. The individual structures are considered below. All structures fit the previously described general structural motif categories for primary DNSA-protonated Lewis base interactions. Although the Type 3 motif has a high probability of occurrence in general molecular interactions [35], its incidence is relatively small because of its functional group specificity. It would therefore be reasonable to assume that among the anilinium compounds of DNSA, Type 3 interactions would be excluded and that Type 1 and Type 2 structural motifs would be found. This is the case, with the compounds **1-4** being Type 1 while **5-7** are Type 2. Of the other analogous aniline-type compounds of DNSA, with the isomeric monoaminobenzoic acids [16] (Smith *et al*., 1995), two have Type 1 interactions while the third is Type 2. These three, together with the compounds from this series (**1-7**) have the commonly-occurring cyclic $R^2_1(6)$ N^+-H…O,O'(phenol, nitro) proximal group interactions among the secondary hydrogen-bonding extensions.

With the DNSA anion, the intramolecular O(phenol)….O(carboxyl) hydrogen bond [graph set S(6)] with the acid proton *anti*-related on the carboxyl group is found in three of the present examples [**3, 4** and **7** { O…O, 2.495(2), 2.482(3) and 2.447(4) Å respectively}] and has a 73% incidence among the 39 previously reported examples of proton-transfer compounds of DNSA [3] (Smith *et al*., 2007). With the DNSA anion, it has been determined that the phenate species has greater thermodynamic stability *cf.* the salicylate species [21] so this observed statistic is not unexpected. However, the occurrence of the salicylate anion form is certainly influenced by crystal environment, particularly with respect to the disposition of the cation donor groups relative to the facially located proximal acceptor groups of the DNSA anion (carboxyl, phenolic and nitro). The intramolecular hydrogen bond in the DNSA salicylate-type anion species [as found in compounds

1,2, 5 and **6** {O…O, 2.447(2), 2.469(6), 2.465(3) and 2.435(3) Å respectively}], in which the proton is located on the phenolic-O, is similar to those found in salicylic acid [36], in the DNSA acid solvates [9 10] and its adducts [4-8].

With all compounds reported here the atom numbering scheme for the DNSA anion and the anilinium cations in **1-7** is as shown in Figs. 1a-1g. For DNSA, this scheme is consistent with that used in previous reports on proton-transfer compounds of DNSA completed in our laboratories [1-3].

INSERT 4: FIGURES 1a-1g: DNSA41a.tif- DNSA41f.tif; Atom numbering schemes for 1-7

3.2 *The individual structures*

[$(C_6H_8N)^+(C_7H_3N_2O_7)^-$] (1)

With the product from the reaction of aniline (AN) with DNSA in 80% ethanol-water, [$(AN)^+$(DNSA)$^-$], **1** (Fig. 1a), the anilinium group gives not one but two primary linear Type 1 hydrogen-bonding interactions with carboxyl oxygen acceptor groups of separate DNSA anions [N11-H….O71^{i}, 2.861(3)Å; N11-H….O72^{ii}, 2.797(3)Å; symmetry codes: (i) $x + 1$, y, $z + 1$; (ii) $–x + 1$, $-y + 1$, $- z$] (Fig. 2). This type of duplex interaction is unusual among proton-transfer compounds of DNSA. In addition, a symmetric cyclic $R^2_1(6)$ proximal group extension is present, as well as an R22(4) association across an inversion centre (Table 2a) result in a two-dimensional framework structure, which extends down the *a* cell direction in the unit cell. In addition there significant cation-anion π-π aromatic ring interactions with inter-ring separation [$Cg_{(C1-C6)}\ldots Cg_{(C11-C61)}$] and inter-ring dihedral angle ($\alpha_{1,2}$) of 3.53(1) Å and 2.1(5)^o respectively.

INSERT 4: FIGURE 2: DNSA4_2.tif; Hydrogen bonding in 1

$[(C_6H_8NO)^+(C_7H_3N_2O_7)^-]$ (2)

The structure of the compound of 2-hydroxyaniline with DNSA, $[(OAP)^+(DNSA)^-]$, **2** (Fig. 1b) suffers from both a minor twinning problem as well as rotational disorder about the C7-C1…C4 ring diagonal of the DNSA anion. This disorder phenomenon results in the C2 phenolic group rotating into two partial sites [O2 (SOF = 0.823(10) and O2A (S.O.F. = 0.177(10)] and is not unknown in DNSA species, being found in its compounds with nicotinamide (S.O.F. 0.76 : 0.24) [35] (Koman *et al*., 2003), 2,6-diaminopyridine (0.90:0.10) [2] and quinaldic acid (0.59:0.41) [3] as well as in the adduct with urea (0.80:0.20) [5].

However the structure of **2** is quite well defined as proton-transfer having extensive hydrogen bonding (Fig. 3). The aminium group of the OAP cation molecule forms a primary Type 1 hydrogen-bonding association with a DNSA carboxylate-O [N11-H…O72, 2.777(5) Å], while the other two protons give three further associations, two to proximal phenolic (O2) and nitro (O31) oxygen acceptors [$R^2_1(6)$] and the third to an OAP phenolic-O (O21). The OAP phenolic group is also strongly linked to the second DNSA carboxylate-O extending the structure in the *b*-cell direction [O21-H…O71^i, 2.593(4) Å; symmetry code: (i) $x,\ y+1,\ z$] (Fig. 3). This gives a two-dimensional hydrogen-bonded network structure which does not involve the second nitro group nor is there any evidence of any π-π stacking effects. Also present in the OAP cation is an intramolecular hydrogen bond between the aminium group and the phenolic-O [2.689(5) Å].

INSERT 5: FIGURE 3: DNSA43.tif; Hydrogen bonding in 2

$[(C_7H_{10}NO)^+(C_7H_3N_2O_7)^-]$ (3)

The structure of the DNSA compound with 2-methoxyaniline, [$(OAN)^+(DNSA)^-$], **3** (Fig. 1c) is based on a primary Type 1, N^+-H…O(carboxyl) interaction [N11-H….$O71^{ii}$, 2.750(3)Å; symmetry code: (ii) $x + 1, y + 1, z$]. This, together with secondary linkages, including an asymmetric $R^2_1(6)$ association with DNSA phenolate- and nitro-O acceptors (Table 2c) link the cation-anion pairs into sheets perpendicular to the *b* axis of the cell, giving a two-dimensional network structure which involves no cation-anion π-π associations (Fig. 4). No interactions involving the oxygen of the substituent methoxy group are found and this group is close to co-planar with the parent ring [torsion angle C31-C21-O21-C211, -2.4(3)°].

INSERT 6: FIGURE 4: DNSA44.tif; Hydrogen bonding in 3

[$(C_7H_{10}NO)^+(C_7H_3N_2O_7)^-$] (4)

The proton-transfer compound from the reaction of *m*-anisidine (MAN) with DNSA, [$(MAN)^+(DNSA)^-$], **4** (Fig. 1d) shows the primary Type 1 N^+-H…O (carboxyl) interaction [N11-H…$O71^i$, 2.770(3) Å: symmetry code: (i) x , $y - 1$, z]. Three other interactions (Table 2d) involving the MAN aminium protons and oxygen acceptors of the DNSA anions (including a symmetric three-centre $R^2_1(6)$ proximal extension] link the cations and anions into centrosymmetric heterotetramer units about an $R^4_4(12)$ ring system, which is extended into one-dimensional ribbons along the *b* axial direction (Fig. 5). The alternating stacks of DNSA anions forming down the approximate *c* axial direction are separated by distances which suggest anion-anion π-π interactions [ring centroid separation *Cg* …*Cg* (C1-C6), 3.480(2) Å]. The cation-anion separations are larger [3.892(2) Å] but these associations result in the structure being layered. As with the OAN cations in **3** the methoxy groups are not involved in hydrogen bonding and the methoxy-O is essentially coplanar with the benzene ring.

INSERT 7: FIGURE 5: DNSA45.tif; Hydrogen bonding in 4

$[(C_6H_7FN)^+(C_7H_3N_2O_7)^-]$ (5)

The compound of 4-fluoroaniline with DNSA, $[(FLAN)^+(DNSA)^-]$, **5** (Fig. 1e) has a primary symmetric Type 2 anilinium N^+-H…O,O' (carboxyl) association [N11-H….O71^{ii}, 2.965(5) Å; ….O72^{ii}, 3.091(5) Å: symmetry code: (ii) $-x + 1$, $-y + 1$, $-z + 1$] and is propagated through a number of secondary interactions (Table 2e), including a symmetric $R^2_1(6)$ proximal association with O(phenol) and O(nitro) acceptors, giving a one-dimensional hydrogen-bonded chain structure which extends down the *c* cell direction (Fig. 6). No cation-anion π-π interactions are present.

INSERT 8: FIGURE 6: DNSA4_6.tif; Hydrogen bonding in 5

$[(C_6H_7ClN)^+(C_7H_3N_2O_7)^-]$ (6)

The compound of 4-chloroaniline with DNSA, $[(CLAN)^+(DNSA)^-]$, **6** (Fig. 1f) gives a three-dimensional hydrogen-bonded framework structure (Fig. 7). The primary anilinium N^+-H…O (carboxyl) association is asymmetric Type 2 [N11-H….O71^{iii}, 2.814(4) Å; ….O72^{iii}, 3.208(4) Å: symmetry code: (ii) x, y, $z - 1$]. This unit is propagated through five secondary N^+-H…O,O' hydrogen-bonding interactions to carboxyl, phenolic and nitro oxygen acceptors (Table 2f), including an asymmetric $R^2_1(6)$ association with O(phenol) and O(nitro) acceptors as well as other minor C-H…O interactions. No cation-anion π-π interactions are present

INSERT 9: FIGURE 7: DNSA46.tif; Hydrogen bonding in 6

[$(C_6H_9N_2)^+(C_7H_3N_2O_7)^-$] (7)

The 1:1 compound of 2-aminoaniline with DNSA, [$(OPDA)^+(DNSA)^-$], **7** (Fig. 1g) appears to be the same compound as that reported by Issa *et al*. [20], on the basis of its melting point. This would confirm the observation that unlike benzidene which forms both 1:1 and 1:2 compounds with DNSA, 2-aminoaniline favours a 1:1 stoichiometry. With **7**, only one of the substituent amine nitrogens (N11) is protonated and this and the second amine group are involved in a total of seven hydrogen-bonding associations. Five of these are with protons from N11 and two with those of the second group (N21), and all but one of these are with DNSA oxygen acceptors. The exception is an intermolecular N^+-H…N(amine) association [N11-H….$N21^i$, 2.909(3) Å: symmetry code: (i) $-x + 1, -y, -z + 2$]. The primary aminium-carboxylate interaction is symmetric Type 2 [N11-H….$O71^i$, 2.914(3) Å; …$O72^i$, 3.050(3) Å] while the unprotonated amine group involves a single direct interaction to the same carboxylate group. These, together with peripheral extensions (Table 2g), including a symmetric cyclic $R^2_1(6)$ N^+-H…O,O' association, give a two-dimensional sheet structure (Fig. 8) which shows no π-π interactions.

INSERT 10: FIGURE 8: DNSA48.tif; Hydrogen bonding in 7

3.3 *Structural systematics of the DNSA-aniline compounds*

Considering the overall structural features of the compounds **1**-**7** and the previously reported DNSA structures with the analogous isomeric monoamino-substituted benzoic acids, in the light of the general systematics previously derived for the general series of proton-transfer compounds, it may be predicted that all anilinium salts of DNSA should fall into the standard Type 1 and Type 2 modes of primary heteromeric cation-anion interaction. An unusual Type 1 variant is found with **1** where the duplex N^+-H…O interaction involving two different anilinium protons to two separate

carboxyl groups [found only in the analogous compound with 2-aminobenzoic acid [9]. (Smith *et al*., 1996)]. Due to the nature and disposition of the substituent functional groups on the DNSA anion species, particularly the proximal carboxyl, phenol and nitro groups, the secondary propagation in the molecular assembly process will most commonly involve either symmetric or asymmetric three-centre cyclic N^{+}-H…O,O' (phenolic, nitro) [$R^{2}_{1}(6)$] interactions. This is present in the six compounds of this series, as well as the three compounds with the isomeric monoaminobenzoic acids [9]. (Smith *et al*., 1996). There is also a strong tendency for the generation of two- rather than three-dimensional hydrogen-bonded structures, such as those usually found with the aliphatic primary amine salts, while only a minor incidence of aromatic C-H…O and π-π interactions contribute to molecular assembly. However, the presence of the aromatic ring does affect the dimensionality of the structural extension in which layering is common.

3.4 *Structural systematics of the DNSA anions*.

The stereochemical features of the of the DNSA anion molecules in both proton-transfer compounds and co-crystalline adducts contribute significantly to the particular efficacy of this molecule in structural assembly. This is because of the presence of the proximally located carboxylic acid/carboxyl group, the phenolic/phenate group and the N3 nitro group. All are commonly involved in heteromolecular hydrogen-bonding interactions. The N5 nitro group is potentially available for hydrogen bonding but participates to a much lesser extent in molecular assembly, in the present series only in one structure (**7**). These important structural parameters are seen in Tables 2 and 3.

3.4.1 The carboxylate and phenolic groups are, with two exceptions {the DNSA dianions in [$2(EN)^{2+}$ $2(DNSA)^{2-}.(H_2O)$] [1] and the mixed piperidinium DNSA-picrate compound [$3(PIP)^{+}$ $(DNSA)^{2-}$ $0.79(DNSA)^{-}.$ $0.21(PA)^{-}.$ H_2O] [14] }, involved in an intramolecular hydrogen bond {the range for the 48 members of the overall series, including **1**-**7** is 2.409(3) Å {the compound with

hexamethylenetetramine [1]} to 2.540(3) Å {the compound with 8-aminoquinoline [24]} (Smith *et al*., 2001)]}. The mean for the same series (2.463 Å) is very similar to the values for the current set (**1**-**7**) [range: 2.435(3)-2.495(2) Å]. It is subsequently expected that the carboxylate group should be essentially coplanar with the benzene ring and this is reflected in the C2-C1-C7-O71 torsion angle {Table 3 for the **1**-**7** set and refs. [1-3] for the other reported structures}, where the maximum deviation from coplanarity (compound **5,** *ca*. 9°) is typical.

3.4.2 The proximal C3 nitro group is commonly involved in cyclic $R^2_1(6)$ extension interactions and is consequently found to be rotated out of the plane of the benzene ring with a higher incidence and generally to a greater extent than the less interactive C5 nitro group. This is reflected in the C2-C3-N3-O32 torsion angle which within the overall series is commonly 20° from planarity [maximum *ca*. 37° in **5** in this series], compared to the C4-C5-N5-O52 torsion angle where the maximum deviation for this series is *ca*. 16° [compound **2**], but is commonly *ca*. 10°.

Supplementary material

CCDC depositions 752776-752782 contains supplementary crystallographic data for compounds **1**-**7** respectively for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data request/cif by e-mailing datarequest@ccdc.cam.ac.uk, or contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ.

Acknowledgements

The authors acknowledge financial support from the Faculty of Science and Technology, Queensland University of Technology, the School of Biomolecular and Physical Sciences, Griffith University and the School of Chemistry, University of Melbourne.

References

[1]. Smith G, Wermuth UD, Bott RC, Healy PC, White JM (2002) Aust. J. Chem 55:349

[2]. Smith G, Wermuth UD, Healy PC, White JM (2002) Aust. J. Chem 56:, 707

[3]. Smith G, Wermuth UD, Healy PC, White JM (2007) Aust. J. Chem 60:264

[4]. Kumar VSS, Kuduva SS, Desiraju GR (2002) Acta Crystallogr E58:o865

[5]. Smith G, Baldry KE, Byriel KA, Kennard CHL (1997) Aust J Chem 50:727

[6]. Smith G, Coyne MG, White JM (2000) Aust J Chem 53:203

[7]. Bott RC, Smith G, Wermuth UD, Dwyer NC (2000) Aust J Chem 53:767

[8]. Kumar VSS, Nangia A, Katz AK, Carrell HL (2002) Cryst Growth Design 2:313

[9]. Smith G, Lynch DE, Byriel KA, Kennard CHL (1995) Aust J Chem 48:1133

[10]. Kumar VSS, Kuduva SS, Desiraju GR (1999) J Chem Soc Perkin Trans 2:1069

[11]. Smith G, Wermuth UD, White JM (2002) Acta Crystallogr E58:o1315.

[12]. Smith G, Wermuth UD, Healy PC, White JM (2006) Aust J Chem 59:320

[13]. Smith G, Wermuth UD, Young DJ, Healy PC (2007) Acta Crystallogr E63:o2517

[14]. Smith G, Wermuth UD, Healy PC (2006) Acta Crystallogr E62:o610

[15]. Smith G, Wermuth UD, White JM (2006) Acta Crystallogr C62:o402

[16]. Etter MC, Adsmond D (1990) J Chem Soc Chem Commun:589

[17]. Etter MC, Frankenbach GM (1989) Materials 1:10

[18]. Issa YM, Hindawey AM, Issa RM, Nassar AMG (1980) Rev Roum Chim 25:1535

[19]. Hindawey AM, Nassar AMG, Issa RM, Issa YM (1980) Ind J Chem A19 61:5619

[20]. Issa YM, Hindawey AM, El-Kholy AE, Issa RM (1981) Gazz Chim Ital 111:27

[21]. Ng SW, Naumov P, Drew MGB, Wojciechowski G, Brzezinski B (2001) J Mol Struct 595:29

[22]. Smith G, Wermuth UD, White JM (2005) Acta Crystallogr C61:o464

[23]. Etter MC, MacDonald JC, Bernstein J, (1990) Acta Crystallogr B46:256.

[24]. Smith G, Wermuth UD, Bott RC, White JM, Willis AC (2001) Aust. J. Chem 54:165

[25]. Smith G, Wermuth UD, White JM (2001) Aust J Chem 54:171

[26]. Song W-D, Guo X-X, Yu L (2007) Acta Crystallogr E63:o1890

[27]. Smith G, Lynch DE, Byriel KA, Kennard CHL (1996) Acta Crystallogr C52: 231

[28]. Smith G, Wermuth UD, Healy PC (2002) Acta Crystallogr E58:o845

[29]. Smith G, Wermuth UD, White JM (2005) Acta Crystallogr E62:o746

[30]. Smith G, Bott RC, Wermuth UD (2001) Acta Crystallogr E57:o640

[31]. Mohamed HA, El-Medani SM, Ramadan RM (2005) J Ind Chem Soc 82:799

[32]. Subashini A, Samuel E, Muthiah PT, Bocelli G, Cantoni A (2007) Acta Crystallogr E63:o4049

[33]. Sheldrick GM (2008) Acta Crystallogr A64:112. SHELX97, Program for Crystal Structure Determination, University of Göttingen,

[34]. Molecular Structure Corporation: TeXsan for Windows. Version 1.06. MSC, 9009 New Plains

Drive, The Woodlands, TX 77381, USA, 1999.

[35]. Allen FH, Raithby PR, Shields GP, Taylor R (1998). J Chem Soc Chem Commun:1034.

[36]. Sundaralingam M, Jensen LH (1965) Acta Crystallogr 18:1053

[37]. Koman M, Martiska L, Valigura D, Glowiak T (2003) Acta Crystallogr E59:o441

[38]. Spek AL (2003) J Appl Cryst 36:7. PLATON: A crystallographic computing suite

Figures

Figure 1. Atom numbering scheme for the individual anilinium cation and DNSA anion species in compounds **1-7** (Figs. 1a-1g). In **2**, atoms O2 and O2A [S.O.F. 0.823(10) and 0.177(10) respectively] represent rotationally disordered sites for the phenolic

group. In all figures, atoms are shown as 30% probability displacement ellipsoids [38]. Inter-species hydrogen-bonding interactions are shown as dashed lines.

Figure 2. A perspective view of the packing of **1** in the unit cell viewed down *a*. Hydrogen-bonding associations are shown as dashed lines. For symmetry codes in this figure and in Figs. 3-8, see Table 2.

Figure 3. A view of the packing of **2** in the unit cell viewed down *b*. The minor disordered phenolic group is not shown.

Figure 4. A perspective view of the packing of **3** in the unit cell viewed down *c*.

Figure 5. A perspective view of the packing of **4** in the unit cell viewed down *a*.showing partial anion ring superimposition.

Figure 6. A view of the packing of **5** in the unit cell viewed down the approximate *c* cell direction.

Figure 7. A perspective view of the packing of **6** in the unit cell viewed down *c*.

Figure 8. A view of the packing of **7** in the unit cell viewed down *b*.

Table 1. Crystallographic data for compounds **1**-**7**.

Identification code	**1**	**2**	**3**	**4**	**5**	**6**	**7**
CCDC reference	752776	752777	752778	752779	752780	752781	752782
Melting point (K)	451.6-454.9 (dec)	480.4-481.1 (dec)	452.0-453.3 (dec)	426.8-427.5 (dec)	453.8-458.0 (dec)	466.7-468.0 (dec)	479.8-480.2
Colour	yellow	black	yellow	pale brown	yellow-brown	yellow	brown
Molecular formula	$C_{13}H_{11}N_3O_7$	$C_{13}H_{11}N_3O_8$	$C_{14}H_{13}N_3O_8$	$C_{14}H_{13}N_3O_8$	$C_{13}H_{10}FN_3O_7$	$C_{13}H_{10}ClN_3O_7$	$C_{13}H_{12}N_4O_7$
M_r	321.25	337.25	351.27	351.27	339.24	355.69	336.27
Temperature (K)	298(2)	295(2)	298(2)	295(2)	298(2)	298(2)	295(2)
Wavelength (λ)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	*P*-1	$P2_1/n$	$P2_1$	$P2_1/n$	$P2_1/n$	*P*-1	$P2_1/n$
a (Å)	7.2027(17)	7.407(3)	8.2816(18)	11.209(2)	26.377(3)	11.217(3)	12.830(4)
b (Å)	7.5699(17)	6.987(3)	23.151(6)	8.7858(19)	10.1602(12)	14.156(5)	8.145(3)
c (Å)	12.9615(16)	27.653(11)	3.9338(10)	15.171(3)	5.1384(10)	4.860(3)	14.302(4)
α (°)	84.464(14)	90	90	90	90	99.10(4)	90
β (°)	86.387(15)	94.906(7)	95.255(19)	93.717(4)	91.996(13)	96.99(4)	102.631(6)
γ (°)	75.580(14)	90	90	90	90	76.35(2)	90
V (Å^3)	680.7(2)	1426.0(9)	751.0(3)	1490.9(6)	1376.2(3)	737.7(6)	1458.4(8)
Z	2	4	2	4	4	2	4
D_c (Mg m^{-3})	1.567	1.566	1.553	1.565	1.637	1.601	1.531
μ (mm^{-1})	0.130	0.130	0.130	0.131	0.143	0.304	0.127
F(000)	332	692	364	728	696	364	696
Instrument	Rigaku AFC 7R	Bruker CCD	Rigaku AFC 7R	Bruker CCD	Rigaku AFC 7R	Rigaku AFC 7R	Bruker CCD
Crystal Size (mm)	0.50 x 0.34 x 0.15	0.40 x 0.35 x 0.12	0.40 x 0.40 x 0.30	0.45 x 0.30 x 0.15	0.35 x 0.20 x 0.05	0.55 x 0.30 x 0.15	0.30 x 0.25 x 0.15
Reflections: Total; (θ_{max})	3505 27.5	9516 25.0	2031 27.5	7586 25.0	2895 25.0	3965 27.5	8291 27.5
Collection range *h* *k* *l*	-3 to 9 -9 to 9 -16 to 16	-8 to 8 -8 to 8 -32 to 32	-5 to 10 0 to 30 -5 to 5	-13 to 9 -10 to 10 -18 to 17	-31 to 31 0 to 12 -6 to 3	-14 to 14 -18 to 18 -2 to 6	-11 to 15 -9 to 9 -17 to 13
Reflections Independent	3135	2499	1765	2624	2407	3400	2567
Reflections [$I>2\sigma(I)$]	2093	2322	1558	1554	1346	2148	2150
R_{int}	0.029	0.088	0.010	0.070	0.027	0.056	0.021
$R1$[a] [$I.>2\sigma I$)]	0.052	0.082	0.033	0.051	0.043	0.058	0.045
$wR2$[a] (all data)	0.165	0.178	0.104	0.120	0.170	0.159	0.125
S[a]	0.916	1.08	0.89	0.91	0.85	1.04	1.04
n_p	224	248	242	244	233	233	242
A,B [b]	0.100, 0.3968	0.0398, 2.881	0.100, 0.0754	0.0476, 0.0	0.100, 6.597	0.0880, 0.3797	0.0642, 0.5887
Residuals (Δρ) Min/max(e Å^{-3})	-0.296, 0.311	-0.246, 0.263	-0.180, 0.211	-0.233, 0.250	-0.219, 0.182	-0.443, 0.611	-0.379, 0.554

[a] $R1 = (\Sigma\ |F_o| - |F_c|\ )/\Sigma|F_o|)$; $wR2 = \{\Sigma w[(F_o^2 - F_c^2)]^2 / \Sigma\ [w(F_o^2)^2]\}^{½}$; $S = \{\Sigma\ [w(F_o^2 - F_c^2)^2] / (n\text{-}p)\}^{½}$;

[b] $w = [\sigma^2\ (F_o^2) + (AP)^2 + BP]^{-1})$ {where $P = [(\max.\ F_o^2, 0) + 2(F_c^2)]/3$}

Table 2 Hydrogen-bonding associations (Å/^{o}) for compounds **1-7**

(a) (**1**) $[(AN)^{+}(DNSA)^{-}]$

D	H	A	D - H	H...A	D...A	D - H..A
O2	H2	O72	0.96(4)	1.49(4)	2.448(2)	174(4)
N11	H11A	O71^{i}	0.94(3)	1.93(3)	2.861(3)	170(2)
N11	H11B	O72^{ii}	0.98(3)	1.82(4)	2.797(3)	173(3)
N11	H11C	O2	0.91(3)	2.39(3)	3.123(3)	138(2)
N11	H11C	O31	0.91(3)	2.55(3)	3.198(3)	129(2)
N11	H11C	O31^{iii}	0.91(3)	2.47(3)	3.074(3)	125(2)

Symmetry codes: (i) = $x + 1, y - 1, z$; (ii) = $-x, -y + 1, -z + 1$;
(iii) = $-x + 1, -y + 1, -z + 1$.

(b) (**2**) $[(OAP)^{+}(DNSA)^{-}]$

D	H	A	D - H	H...A	D...A	D - H..A
O2	H2	O72	0.96(6)	1.52(6)	2.469(6)	169(5)
O2A	H2A	O71	0.93	1.60	2.53	175
O21	H21	O71^{i}	0.90(6)	1.70(6)	2.593(4)	175(4)
N11	H11A	O21	0.86(6)	2.39(6)	2.689(5)	101(4)
N11	H11A	O21^{ii}	0.86(6)	2.14(6)	2.940(5)	154(5)
N11	H11B	O72^{iii}	0.90(7)	1.88(7)	2.777(5)	180(9)
N11	H11C	O2^{iv}	1.00(7)	2.46(7)	3.270(7)	138(4)
N11	H11C	O2^{i}	1.00(7)	2.36(6)	2.979(6)	120(4)
N11	H11C	O31^{i}	1.00(7)	2.26(6)	2.997(5)	130(4)

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

(c) (**3**) $[(OAN)^{+}(DNSA)^{-}]$

D	H	A	D - H	H...A	D...A	D - H..A

O72	H72	O2	0.86(5)	1.66(5)	2.495(2)	161(5)
N11	H11A	O2^{i}	0.89(4)	1.90(4)	2.735(3)	156(3)
N11	H11A	O31^{i}	0.89(4)	2.35(4)	2.966(4)	126(3)
N11	H11B	O2	0.96(3)	2.11(3)	2.965(3)	148(3)
N11	H11C	O71^{ii}	0.83(4)	1.92(4)	2.750(3)	171(4)

Symmetry codes: (i) = *x*, *y*, *z* - 1; (ii) = *x* + 1, *y* + 1, *z*.

(d) (**4**) [$(MAN)^{+}(DNSA)^{-}$]

D	H	A	D - H	H...A	D...A	D - H..A
O72	H72	O2	0.99(3)	1.53(3)	2.482(3)	160(3)
N11	H11A	O2	0.88(3)	1.93(3)	2.802(3)	170(2)
N11	H11A	O31	0.88(3)	2.58(3)	2.893(4)	102(2)
N11	H11B	O71^{i}	0.99(3)	1.80(3)	2.770(3)	168(3)
N11	H11C	O32^{ii}	0.81(3)	2.13(3)	2.939(3)	176(4)

Symmetry codes: (i) = *x*, *y* - 1, *z*; (ii) = -*x*, -*y* + 1, -*z* + 1.

(e) (**5**) [$(FLAN)^{+}(DNSA)^{-}$]

D	H	A	D - H	H...A	D...A	D - H..A
O2	H2	O72	0.98(5)	1.53(5)	2.465(4)	157(5)
O2	H2	O72^{i}	0.98(5)	2.47(5)	2.929(4)	108(4)
N11	H11A	O71^{i}	0.93(5)	2.04(5)	2.965(5)	175(5)
N11	H11A	O72^{i}	0.93(5)	2.47(5)	3.091(5)	124(4)
N11	H11B	O2	0.94(5)	2.26(5)	3.107(5)	125(4)
N11	H11B	O31	0.94(5)	2.26(5)	3.041(5)	140(4)
N11	H11B	O32^{ii}	0.94(5)	2.31(5)	3.003(5)	130(4)
N11	H11C	O71^{iii}	0.91(6)	1.93(6)	2.839(5)	179(5)

Symmetry codes: (i) = -*x* + 1, -*y* + 2, -*z* + 1; (ii) = -*x* + 1, -*y* + 1, -*z* + 1;
(iii) = -*x* + 1, -*y* + 2, -*z*.

(f) (**6**) [$(CLAN)^{+}(DNSA)^{-}$]

D	H	A	D - H	H...A	D...A	D - H..A

O2	H2	O72	0.81(5)	1.66(6)	2.435(3)	161(6)
O2	H2	O72 [i]	0.81(5)	2.53(5)	2.950(3)	114(4)
N11	H11A	O2 [ii]	0.87(5)	2.38(4)	3.140(4)	147(4)
N11	H11A	O31 [ii]	0.87(5)	2.32(4)	2.960(4)	130(4)
N11	H11B	O71 [iii]	0.98(4)	1.84(4)	2.814(4)	173(4)
N11	H11B	O72 [iii]	0.98(4)	2.53(4)	3.208(4)	126(3)
N11	H11C	O71	0.90(4)	2.09(4)	2.988(4)	180(4) .

Symmetry codes: (i) = -*x* + 2, -*y* + 1, -*z* + 3; (ii) = -*x* + 2, -*y* + 1, -z + 2;
(iii) = *x*, *y*, z – 1.

(g) (**7**) [$(OPDA)^+ (DNSA)^-$]

D	H	A	D - H	H...A	D...A	D - H..A	symm
O72	H72	O2	0.97(3)	1.49(4)	2.447(2)	165(3)	
N11	H11A	N21 [i]	0.98(2)	1.93(2)	2.909(3)	175(2)	
N11	H11B	O71 [i]	0.89(3)	2.13(3)	2.914(3)	146(2)	
N11	H11B	O72 [i]	0.89(3)	2.56(3)	3.050(3)	116(2)	
N11	H11C	O2 [ii]	0.95(2)	1.86(2)	2.800(2)	170(2)	
N11	H11C	O31 [ii]	0.95(2)	2.33(3)	2.822(3)	112(2)	
N21	H21A	O51 [iii]	0.84(3)	2.41(3)	3.245(3)	175(2)	
N21	H21B	O71 [i]	0.91(3)	2.08(3)	2.973(3)	167(2)	

Symmetry codes: (i) = -*x* + 1, -*y*, -*z* + 2; (ii) = *x* + ½ , -*y* + ½, *z* + ½ ;
(iii) = *x* + ½ , -*y* + ½, *z* - ½ .

TABLE 3 Comparative structural features (Å/ ^{o}) for the DNSA moiety in the compounds **1-7**.

Compound	-O_p…H-O_c	-O_p-H…O_c	C2-C1-C7-O71	C2-C3-N3-O32	C4-C5-N5-O52	Reference
$[(AN)^+(DNSA)^-]$ (**1**)	-	2.447(2)	-178.2(2)	-174.8(2)	-172.2(2)	This work
$[(OAP)^+(DNSA)^-]$ (**2**)	-	2.469(6)	-179.8(4)	-177.5(4)	-163.8(4)	This work
$[(OAN)^+(DNSA)^-]$ (**3**)	2.495(2)	-	-178.0(2)	-168.9(2)	174.6(3)	This work
$[(MAN)^+(DNSA)^-]$ (**4**)	2.482(3)	-	-172.9(2)	175.0(2)	-179.3(2)	This work
$[(FLAN)^+(DNSA)^-]$ (**5**)	-	2.465(4)	-171.0(3)	142.8(3)	-179.3(4)	This work
$[(CLAN)^+(DNSA)^-]$ (**6**)	-	2.435(3)	-171.5(2)	148.7(3)	-179.1(2)	This work
$[(OPDA)^+(DNSA)^-]$ (**7**)	2.447(4)		-173.8(2)	179.7(2)	177.6(2)	This work
α-(DNSA).H_2O	-	2.566(3)	178.3(4)	170.8(3)	177.9(3)	[9]
β-(DNSA).H_2O	-	2.549(4)	178.3(4)	160.0(3)	176.6(4)	[10]

AN = aniline; OAP = 2-hydroxyaniline; OAN = 2-methoxyaniline; MAN = 3-methoxyaniline; FLAN = 4-fluoroaniline; CLAN = 4-chloroaniline; OPDA = 2-aminoaniline.

$ O_p = phenolic-O; O_c = carboxyl-O

α- and β- represent the two polymorphs of DNSA monohydrate