#### **ORIGINAL PAPER**



# Crystal and Molecular Structures of Five 3D Organic Salts from 2,6-Dimethylaniline and Organic Acids

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#### Abstract

Five crystalline organic acid-base salts [(HL)·(dnsa<sup>-</sup>), L=2,6-dimethylaniline, dnsa<sup>-</sup> = 3,5-dinitrosalicylate] (1), [(HL<sup>+</sup>)·(4-Hnpta<sup>-</sup>), 4-Hnpta<sup>-</sup> = 4-nitrophthalate] (2), [(HL)<sub>2</sub>·(nds)·(H<sub>2</sub>O)<sub>2</sub>, nds = 1,5-naphthalenedisulfonate] (3), [(HL)·(dnb)·(Hdnb), dnb = 3,5-dinitrobenzoate, Hdnb = 3,5-dinitrobenzoic acid] (4) and [(HL)·(dca), dca = dichloroacetate] (5) from 2,6-dimethylaniline and organic acids were prepared and characterized by XRD analysis, IR, mp and elemental analysis. Compound 1 adopts the triclinic, space group Pī, with a = 7.6261(6) Å, b = 8.3429(8) Å, c = 13.1147(12) Å,  $\alpha$  = 91.3610(10)°,  $\beta$ =102.755(2)°,  $\gamma$  = 102.597(2)°, V = 791.96(12) Å<sup>3</sup>, Z=2. Compound 2 belongs to the monoclinic, space group P2(1)/c, with a = 14.2552(15) Å, b = 8.1436(8) Å, c = 14.5708(13) Å,  $\alpha$  = 90°,  $\beta$  = 113.795(2)°,  $\gamma$  = 90°, V = 1547.7(3) Å<sup>3</sup>, Z=4. Compound 3 crystallizes in the monoclinic, space group P2(1)/c, with a = 8.4784(7) Å, b = 17.4798(15) Å, c = 9.1119(8) Å,  $\alpha$  = 90°,  $\beta$ =99.742(2)°,  $\gamma$  = 90°, V = 1330.9(2) Å<sup>3</sup>, Z=2. Compound 4 has orthorhombic, space group Pna2(1), with a = 24.5029(19) Å, b = 7.5322(9) Å, c = 26.665(2) Å,  $\alpha$ =90°,  $\beta$ =90°,  $\gamma$ =90°, V = 4921.3(8) Å<sup>3</sup>, Z=8. Compound 5 crystallizes in the monoclinic, space group C2/c, with a = 19.8970(17) Å, b = 11.1850(11) Å, c = 13.1590(12) Å,  $\alpha$ =90°,  $\beta$ =123.408(3)°,  $\gamma$ =90°, V = 2444.6(4) Å<sup>3</sup>, Z=8. For 1 it was the relatively weak phenol that has ionized, different from 2 to 5. All supramolecular architectures of 1–5 involve N–H···O H-bonds as well as CH<sub>3</sub>···O interactions. The other noncovalent interactions (CH···O, CH···CI, O···N, O···O, Cl···CI, C···π, O···π, CH<sub>3</sub>···π and π···π) in the crystal packing were also ascertained. These weak interactions combined, all compounds displayed 3D framework structures.

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#### **Graphical Abstract**

In the five prepared supramolecular assemblies there are plenty of weak bonding interactions such as directional H-bonds of N–H···O, O–H···O, O–H···S, O–H···N and noncovalent bonds of CH···O, CH<sub>3</sub>···O, CH···Cl, O···C, O···N, O···O, Cl–Cl, C··· $\pi$ , O··· $\pi$ , CH<sub>3</sub>··· $\pi$ , and aryl···aryl interactions. All compounds displayed the 3D framework structures



Keywords Crystal structures · H-bonding · Noncovalent interactions · 2,6-Dimethylaniline · Organic acids

# Introduction

Noncovalent interactions of electrostatic forces, H-bonding, CH··· $\pi$ ,  $\pi$ ··· $\pi$  stacking, cation··· $\pi$ , anion··· $\pi$  and lone pair··· $\pi$  associations, as well as other weak forces play significant roles in numerous fields from molecular recognition, host–guest chemistry, crystal engineering, supramolecular chemistry, biochemistry, pharmaceutical chemistry, to materials science [1–16]. In the past few years, great efforts have been made to elucidate these interactions and their relationship to the final supramolecular structures [17–21].

In the case of pharmaceutical ingredients, solid salts with such biopharmaceutical properties as solubility, stability and hygroscopicity have been studied systematically, and these properties are related to the noncovalent interactions [22–33]. The organic acids carry the nice donor–acceptor units for the supramolecular crystal engineering [34–36], and they aggregate in the solid as dimer, catemer and bridged modes [37–44]. Except the acidic units, the phenol, NO<sub>2</sub>, X and the aryl kernel are all good at numerous noncovalent associations, thus the acids with the above units were selected. It is very critical to study the powerful and directional recognition from the organic acids and the basic components of organic amine and pyridyl derivatives [45–51]. It is interesting to exploit the robust and directional recognition of acids with N-containing compounds [47, 48, 50, 52, 53].

Recently aromatic amine derivatives have been reported to form supramolecular compounds with the acid derivatives under the H-bonding action [54–57]. As a benzene amine derivative, the organic acid–base adducts based on 2,6-dimethylaniline have also been studied [58, 59].

In continuation of our study on organic acid-base adducts concerning aryl *N*-containing derivatives [60–65], herein we report the preparation and structures of five organic acid-base salts from 2,6-dimethylaniline (L) and the corresponding organic acids (Scheme 1), respectively. The five salts are [(HL)·(dnsa<sup>-</sup>), L=2,6-dimethylaniline, dnsa<sup>-</sup> = 3,5-dinitrosalicylate] (1), [(HL<sup>+</sup>)·(4-Hnpta<sup>-</sup>), 4-Hnpta<sup>-</sup> = 4-nitrophthalate] (2), [(HL)<sub>2</sub>·(nds)·(H<sub>2</sub>O)<sub>2</sub>, nds=1,5-naphthalenedisulfonate] (3), [(HL)·(dnb)·(Hdnb), dnb = 3,5-dinitrobenzoate, Hdnb = 3,5-dinitrobenzoic acid] (4), and [(HL)·(dca), dca = dichloroacetate] (5) (Scheme 2).

# **Experimental Section**

#### **Materials and Physical Measurements**

The chemicals and solvents in this work are analytical grade and available commercially and used without further purification. FT-IR spectra were recorded from KBr pellets in 4000–400 cm<sup>-1</sup> on a Mattson Alpha-Centauri spectrometer. Microanalytical (C, H, N, S) data were taken by a Perkin-Elmer Model 2400II elemental analyzer. Melting points of the salts were recorded on an XT-4 thermal apparatus without correction.



### Preparation of the Organic Salts 1–5

#### (2,6-Dimethylaniline):(3,5-Dinitrosalicylic acid) [(HL)·(dnsa<sup>-</sup>)] (1)

A solution of 3,5-dinitrosalicylic acid (45.6 mg, 2.0 mmol) in methanol (16 ml) was added dropwise to a vigorously stirred solution of 2,6-dimethylaniline (24.2 mg, 2.0 mmol) in methanol (5 ml) over a period of 5 min. The solution was stirred for a few minutes, then the solution was filtered into a test tube. The solution was left standing at room temperature for 15 days, colorless block crystals were isolated after slow evaporation of the methanol solution in air. The crystals were collected and dried in air to give  $[(HL)\cdot(dnsa^{-})](1)$ . (yield: 48 mg, 68.71%). mp 140-142 °C. Elemental analysis: Calc. for C<sub>15</sub>H<sub>15</sub>N<sub>3</sub>O<sub>7</sub> (349.30): C, 51.53; H, 4.29; N, 12.02. Found: C, 51.42; H, 4.21; N, 11.94. Infrared spectrum  $(cm^{-1})$ : 3666s ( $\nu$ (OH)), 3442s (multiple,  $\nu_{as}$ (NH)), 3333s (v<sub>s</sub>(NH)), 3160w, 3048m, 2978m, 1828w, 1708s (v<sub>as</sub>(C=O)), 1618m, 1530s ( $\nu_{as}(NO_2)$ ), 1484w, 1440m, 1399m, 1358m, 1320s ( $\nu_s(NO_2)$ ), 1280s ( $\nu_s(C-O)$ ), 1238m, 1196m, 1154m, 1112m, 1066m, 1025m, 982m, 940m, 896m, 852m, 808m, 765m, 722m, 678m, 636m, 602m.

# (2,6-Dimethylaniline):(4-Nitrophthalic acid) [(HL<sup>+</sup>) $\cdot$ (4-Hnpta<sup>-</sup>)] (2)

A solution of 4-nitrophthalic acid (42.2 mg, 2.0 mmol) in methanol (10 ml) was added dropwise to a vigorously stirred solution of 2,6-dimethylaniline (24.2 mg, 2.0 mmol) in methanol (5 ml) over a period of 5 min. The solution was

stirred for a few minutes, then the solution was filtered into a test tube. The solution was left standing at room temperature for 10 days, colorless block crystals were isolated after slow evaporation of the methanol solution in air. The crystals were collected and dried in air to give  $[(HL^+) \cdot (4-Hnpta^-)]$  (2). (yield: 54 mg, 81.25%). mp 117–118 °C. Elemental analysis: Calc. for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>6</sub> (332.31): C, 57.78; H, 4.81; N, 8.42. Found: C, 57.69; H, 4.75; N, 8.33. Infrared spectrum (cm<sup>-1</sup>): 3590s ( $\nu$ (OH)), 3432s ( $\nu$ <sub>as</sub>(NH)), 3326s ( $\nu$ <sub>s</sub>(NH)), 3175m, 3123m, 3084m, 2912m, 2828m, 1680s ( $\nu$ (C=O)), 1618s ( $\nu$ <sub>as</sub>(CO<sub>2</sub><sup>-</sup>)), 1572m, 1528s ( $\nu$ <sub>as</sub>(NO<sub>2</sub>)), 1487m, 1445m, 1406s ( $\nu$ <sub>s</sub>(CO<sub>2</sub><sup>-</sup>)), 1365m, 1324s ( $\nu$ <sub>s</sub>(NO<sub>2</sub>)), 1282s ( $\nu$ (C–O)), 1236m, 1193m, 1152m, 1109m, 966m, 924m, 882m, 836m, 792m, 749m, 705m, 664m, 621m, 600m.

# $(2,6-Dimethylaniline)_2:(1, 5-Naphthalenedisulfonic acid):(H_2O)_2 [(HL)_2·(nds)·(H_2O)_2] (3)$

A solution of 1,5-naphthalenedisulfonic acid tetrahydrate (72 mg, 2.0 mmol) in methanol (30 ml) was added dropwise to a vigorously stirred solution of 2,6-dimethylaniline (24.2 mg, 2.0 mmol) in methanol (5 ml) over a period of 5 min. The solution was stirred for a few minutes, then the solution was filtered into a test tube. The solution was left standing at room temperature for 24 days, colorless block crystals were isolated after slow evaporation of the methanol solution in air. The crystals were collected and dried in air to give  $[(HL)_2 \cdot (nds) \cdot (H_2O)_2]$  (3). (yield: 70 mg, 61.76%, based on 1,5-naphthalenedisulfonic acid tetrahydrate). mp 183–185 °C. Elemental analysis: Calc. for  $C_{26}H_{34}N_2O_8S_2$  (566.67): C, 55.06; H, 6.00; N, 4.94; S,











Scheme 2 The five organic acid–base salts 1-5 described in this paper

11.29. Found: C, 55.01; H, 5.92; N, 4.88; S, 11.18. Infrared spectrum (cm<sup>-1</sup>):  $3628w(\nu(OH))$ ,  $3473s(\nu_{as}(NH))$ ,  $3350s(\nu_{s}(NH))$ , 3262w, 3144m, 3090m, 1668m, 1620m, 1560m, 1516m, 1470m, 1428m, 1386m, 1344m, 1303mm, 1260m, 1217m, 1175m, 1133m, 1090m, 1049m, 1003m, 960m, 917m, 876m, 835m, 794m, 748m, 706m, 665m, 627m, 608m.

#### (2,6-Dimethylaniline):(3,5-Dinitrobenzoic acid)<sub>2</sub> [(HL)·(dnb)·(Hdnb)] (4)

A solution of 3,5-dinitrobenzoic acid (42.4 mg, 2.0 mmol) in methanol (12 ml) was added dropwise to a vigorously stirred solution of 2,6-dimethylaniline (24.2 mg, 2.0 mmol) in methanol (5 ml) over a period of 5 min. The solution was stirred for a few minutes, then the solution was filtered into a test tube. The solution was left standing at room temperature for 12 days, colorless block crystals were isolated after slow evaporation of the methanol solution in air. The crystals were collected and dried in air to give  $[(HL)\cdot(dnb)\cdot(Hdnb)]$  (4). (yield: 42 mg, 77.00%, based on 3,5-dinitrobenzoic acid). mp 173-175 °C. Elemental analysis: Calc. for C<sub>22</sub>H<sub>19</sub>N<sub>5</sub>O<sub>12</sub> (545.42): C, 48.40; H, 3.48; N, 12.83. Found: C, 48.31; H, 3.42; N, 12.76. Infrared spectrum (cm<sup>-1</sup>): 3470s (multiple,  $\nu_{as}$ (NH)), 3354s (v<sub>s</sub>(NH)), 3248w, 3162w, 3080m, 2998m, 1694s  $(\nu(C=O)), 1606s (\nu_{as}(CO_2^{-})), 1564m, 1522s (\nu_{as}(NO_2))),$ 1452w, 1408s (v<sub>s</sub>(CO<sub>2</sub><sup>-</sup>)), 1367m, 1325s (v<sub>s</sub> (NO<sub>2</sub>)), 1284s (v(C–O)), 1240m, 1199m, 1158m, 1115m, 1073m, 1031m, 988m, 955m, 914m, 868m, 824m, 780m, 736m, 694m, 652m. 618m.

#### (2,6-Dimethylaniline):(Dichloroacetic acid) [(HL)·(dca)] (5)

A solution of dichloroacetic acid (25.8 mg, 2.0 mmol) in methanol (8 ml) was added dropwise to a vigorously stirred solution of 2,6-dimethylaniline (24.2 mg, 2.0 mmol) in methanol (5 ml) over a period of 5 min. The solution was stirred for a few minutes, then the solution was filtered into a test tube. The solution was left standing at room temperature for 8 days, colorless block crystals were isolated after slow evaporation of the methanol solution in air. The crystals were collected and dried in air to give  $[(HL)\cdot(dca)]$  (5). (yield: 42 mg, 83.96%). mp 147–149 °C. Elemental analysis: Calc. for C<sub>10</sub>H<sub>13</sub>Cl<sub>2</sub>NO<sub>2</sub> (250.11): C, 47.98; H, 5.20; N, 5.60. Found: C, 47.92; H, 5.11; N, 5.54. Infrared spectrum (cm<sup>-1</sup>): 3448s ( $\nu_{as}$ (NH)), 3360s ( $\nu_{s}$ (NH)), 3242m, 3160m, 3080m, 2990m, 2920m, 2832m, 1598s (v<sub>as</sub>(CO<sub>2</sub><sup>-</sup>)), 1555m, 1513m, 1470m, 1426m, 1384s ( $\nu_s(CO_2^{-})$ ), 1340m, 1298m, 1257m, 1215m, 1174m, 1133m, 1088m, 1046m, 1004m, 962w, 922m, 878w, 836m, 792w, 748m, 706, 660w, 628w, 604w.

#### X-ray Crystallography and Data Collection

Suitable crystals were mounted on a glass fiber at a Bruker SMART 1000 CCD diffractometer operating at 50 kV and 40 mA using Mo K $\alpha$  radiation (0.71073 Å). Data collection and reduction were taken by the SMART and SAINT software [66]. The structures were solved by direct methods, and the non-Hs were subjected to anisotropic refinement by full-matrix least squares on  $F^2$  by SHELXTL package [67]. H-atom positions for the five structures were located in a difference map and refined independently. Further details of the structural analysis are summarized in Table 1. Selected bond lengths and angles for 1–5 are listed in Table 2, the relevant H-bond parameters in Table 3.

### **Results and Discussion**

#### **Preparation and General Characterization**

The preparation of 1-5 were carried out with 2,6-dimethylaniline and the corresponding acids at 1:1 in the methanolic solution, which was allowed to evaporate at ambient conditions to give the final crystalline products. In all the structure, the 2,6-dimethylaniline molecule is protonated therefore these structure can be classified as organic salts. The five compounds are not hygroscopic. The molecular structures and their atom labelling schemes for the five structures are shown in Fig. 1, Fig. 3, Fig. 5, Fig. 7, and Fig. 9, respectively. The elemental analysis data for the five crystalline compounds are in accordance with their compositions. The infrared spectra of the five compounds fit well with their chemical formulas determined by elemental analysis and further confirmed by XRD analysis. Hs connected to O/N atoms were well found from the difference electron density map. In 2, only one proton of the carboxyl units has transferred to the N of 2,6-dimethylaniline molecule to get the corresponding hydrogen carboxylate salt, thus the acid in 2 presents a valence number of -1.

The very strong and broad features at  $3666-3326 \text{ cm}^{-1}$  in the IR spectra of the five compounds arise from O–H/N–H stretching frequencies. Aryl ring stretching and bending are attributed to the medium intensity bands in 1500-1630 and  $600-750 \text{ cm}^{-1}$ , respectively. Compound **1** bears characteristic bands for CO<sub>2</sub>H only, while the salts **2** and **4** show the typical bands for both CO<sub>2</sub><sup>-</sup> and CO<sub>2</sub>H. IR spectroscopy is also useful for recognizing proton transfer compounds [68, 69]. The most salient feature in the IR spectrum of proton transfer compounds are the presence of strong asymmetrical/ symmetrical CO<sub>2</sub><sup>-</sup> stretching frequencies at 1598–1618 and 1384–1408 cm<sup>-1</sup> respectively except **3**.

	1	2	3	4	5
Formula	C <sub>15</sub> H <sub>15</sub> N <sub>3</sub> O <sub>7</sub>	C <sub>16</sub> H <sub>16</sub> N <sub>2</sub> O <sub>6</sub>	C <sub>26</sub> H <sub>34</sub> N <sub>2</sub> O <sub>8</sub> S <sub>2</sub>	C <sub>22</sub> H <sub>19</sub> N <sub>5</sub> O <sub>12</sub>	C <sub>10</sub> H <sub>13</sub> Cl <sub>2</sub> NO <sub>2</sub>
Fw	349.30	332.31	566.67	545.42	250.11
<i>T</i> (K)	298 (2)	298 (2)	298 (2)	298 (2)	298 (2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
space group	P-1	P2(1)/c	P2(1)/c	Pna2(1)	C2/c
<i>a</i> (Å)	7.6261(6)	14.2552(15)	8.4784(7)	24.5029(19)	19.8970(17)
<i>b</i> (Å)	8.3429(8)	8.1436(8)	17.4798(15)	7.5322(9)	11.1850(11)
c (Å)	13.1147(12)	14.5708(13)	9.1119(8)	26.665(2)	13.1590(12)
α (°)	91.3610(10)	90	90	90	90
β (°)	102.755(2)	113.795(2)	99.742(2)	90	123.408(3)
γ (°)	102.597(2)	90	90	90	90
$V, Å^3$	791.96(12)	1547.7(3)	1330.9(2)	4921.3(8)	2444.6(4)
Z	2	4	2	8	8
$D_{\text{calcd}}, \text{Mg/m}^3$	1.465	1.426	1.414	1.472	1.359
Absorption coefficient, mm <sup>-1</sup>	0.118	0.111	0.253	0.122	0.512
<i>F</i> (000)	364	696	600	2256	1040
Crystal size (mm <sup>3</sup> )	$0.45 \times 0.23 \times 0.12$	$0.45 \times 0.26 \times 0.11$	$0.21 \times 0.18 \times 0.16$	$0.49 \times 0.30 \times 0.17$	0.49×0.45×0.43
$\theta$ range (°)	2.51-25.02	2.93-25.02	2.44-25.01	2.81-25.02	2.40-25.02
	$-9 \le h \le 5$	$-16 \le h \le 8$	$-9 \le h \le 10$	$-29 \le h \le 29$	$-21 \le h \le 23$
Limiting indices	$-9 \le k \le 9$	$-9 \le k \le 9$	$-19 \le k \le 20$	$-7 \le k \le 8$	$-13 \le k \le 13$
	$-15 \le l \le 15$	$-16 \le 1 \le 17$	$-10 \le 1 \le 10$	$-31 \le 1 \le 31$	$-15 \le l \le 15$
Reflections collected	3976	7641	6464	23,166	6022
Reflections independent $(R_{int})$	2722 (0.0271)	2716 (0.0873)	2328 (0.0806)	8578 (0.0976)	2141 (0.0552)
Goodness-of-fit on $F^2$	1.057	0.828	0.939	0.922	1.090
<i>R</i> indices $[I > 2\sigma I]$	0.0527, 0.1213	0.0571, 0.1244	0.0503, 0.1106	0.0838, 0.1807	0.0673, 0.2031
R indices (all data)	0.1040, 0.1425	0.1202, 0.1453	0.1147, 0.1366	0.1693, 0.2124	0.1021, 0.2294
Largest diff. peak and hole, $e.Å^{-3}$	0.268, - 0.189	0.246, - 0.184	0.282, - 0.246	0.518, - 0.250	0.754, - 0.368

#### Table 1 X-ray crystallographic data for 1–5

### **Structural Descriptions**

#### X-ray Structure of (2,6-Dimethylaniline):(3,5-Dinitrosalicylic Acid) [(HL)·(dnsa<sup>-</sup>)] (1)

The compound **1** of the composition  $[(HL) \cdot (dnsa^{-})]$  was prepared by reacting equal mol of 2,6-dimethylaniline and 3,5-dinitrosalicylic acid, in which the phenol H of the 3,5-dinitrosalicylic acid was transferred to the NH<sub>2</sub> of the 2,6-dimethylaniline. Thus **1** can be classified as an organic salt. In the asymmetric unit of **1** there existed one HL, and one dnsa<sup>-</sup> (Fig. 1). In this case it is the phenol not the CO<sub>2</sub>H that has been ionized which differs from the 3,5-dinitrosalicylate salts based on bis(1-benzimidazolyl)-3-oxapentane [70] and cytosine [71], but it resembles the filed ones [72–74]. This phenomenon may be attributed to the steric effect of this combination, although the Pka of the phenol is larger than the Pka of the CO<sub>2</sub>H.

The C-O distance 1.280(3) Å (O(3)–C(11)) was close to the one in the filed proton transfer compound bearing the

dnsa<sup>-</sup> where only the phenol has been deprotonated also [72–74]. The C–O bond distances O(1)–C(9) (1.220(3) Å) and O(2)–C(9) (1.299(3) Å) in the CO<sub>2</sub>H show characteristic C–O and C=O bond distances which are also confirming the reliability of adding Hs experimentally by Fourier different electron density onto O atoms as mentioned above (Table 3). The C–N bond concerning the protonated N was 1.480(3) Å (N(1)–C(1)), similar to the corresponding values at 2,6-dimethylanilinium chloride monohydrate [58] and 2,6-dimethylanilinium nitrate [75].

The nitro groups N2–O4–O5 and N3–O6–O7 deviate by 28.3(2) and 7.2(2)° from the mean plane of the phenyl ring of the anion. The two NO<sub>2</sub> intersected at 34.9(2)° to each other. The CO<sub>2</sub>H deviated by only 1.6(2)° from the phenyl ring plane of the 3,5-dinitrosalicylate. The rings C1–C6 and C10–C15 made dihedral angle of 127.1(2)° to each other. There exists intramolecular O–H···O H-bond with graph set of S<sub>1</sub><sup>-1</sup>(6) from the CO<sub>2</sub>H and the phenolate with O···O separation of 2.498(3) Å, and the O···O contact between the phenolate and the 3-NO<sub>2</sub> with O···O separation of 2.695(2)

Journal of Chemical Crystallography

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Table 2	Selected bor	nd lengths	[A] an	d angles [	for <b>1–5</b>

1	l			
	N(1)–C(1)	1.480(3)	N(2)–C(12)	1.462(3)
	N(3)-C(14)	1.457(3)	O(1)–C(9)	1.220(3)
	O(2)–C(9)	1.299(3)	O(3)–C(11)	1.280(3)
	O(1)-C(9)-O(2)	120.0(3)		
2	2			
	N(1)–C(1)	1.473(4)	N(2)–C(14)	1.468(4)
	O(1)–C(9)	1.203(4)	O(2)–C(9)	1.307(4)
	O(3)–C(10)	1.241(4)	O(4)–C(10)	1.266(3)
	O(1)–C(9)–O(2)	125.8(3)	O(3)–C(10)–O(4)	125.4(3)
2	3			
	N(1)–C(1)	1.484(4)	O(1)–S(1)	1.449(2)
	O(2)–S(1)	1.455(3)	O(3)–S(1)	1.455(3)
	S(1)–C(11)	1.795(3)	O(1)–S(1)–O(2)	112.96(16)
	O(1)-S(1)-O(3)	111.08(16)	O(2)–S(1)–O(3)	112.69(16)
4	ł			
	N(1)-C(1)	1.497(8)	N(2)-C(9)	1.466(8)
	N(3)-C(20)	1.464(11)	N(4)-C(22)	1.471(9)
	N(5)-C(27)	1.496(13)	N(6)–C(29)	1.443(12)
	N(7)-C(34)	1.466(9)	N(8)–C(36)	1.535(10)
	N(9)-C(41)	1.476(12)	N(10)-C(43)	1.464(13)
	O(1)–C(17)	1.238(9)	O(2)–C(17)	1.244(9)
	O(7)–C(24)	1.212(9)	O(8)–C(24)	1.275(10)
	O(13)-C(31)	1.198(12)	O(14)–C(31)	1.216(11)
	O(19)-C(38)	1.195(9)	O(20)–C(38)	1.326(10)
	O(1)-C(17)-O(2)	124.8(7)	O(7)–C(24)–O(8)	125.5(7)
	O(13)–C(31)– O(14)	126.6(9)	O(19)-C(38)-O(20)	124.9(7)
5	5			
	Cl(1)-C(10)	1.727(5)	Cl(2)–C(10)	1.699(5)
	Cl(1')-C(10)	1.470(9)	Cl(2')-C(10)	1.791(9)
	N(1)-C(1)	1.462(4)	O(1)–C(9)	1.209(4)
	O(2)–C(9)	1.209(4)	O(1)-C(9)-O(2)	125.8(3)

Å. The O···O separation at the intramolecular O–H···O H-bond resembled that at 3,5-dimethylpyrazolium 3,5-dinitrosalicylate and  $(s)-(\pm)$ -1-phenylethylaminium 3,5-dinitrosalicylate [76, 77].

One HL was bonded to one dnsa<sup>-</sup> by the bifurcated N–H···O H-bonds between one H of the NH<sub>3</sub><sup>+</sup>, the 3-NO<sub>2</sub>, and the phenolate with N···O distances of 2.971(3) and 2.816(3) Å, CH<sub>3</sub>···O association from the CH<sub>3</sub> and the phenolate with C···O distance of 3.478(2) Å, and O···π association between the 3-NO<sub>2</sub> and the phenyl ring of the cation with O···Cg separation of 3.178(2) Å to give a bicomponent adduct. The bicomponent adducts were joined together by the N–H···O H-bond from the second H of the NH<sub>3</sub><sup>+</sup> and the carbonyl unit with N···O distance of 2.841(3) Å, CH<sub>3</sub>···O association between the CH<sub>3</sub> and the same carbonyl unit as in the N–H···O H-bond with C···O distance of 3.391(2) Å, and O···O contact between the O at the OH in the CO<sub>2</sub>H

with O…O distance of 2.925(2) Å to form a tetracomponent aggregate. The tetracomponent aggregates were linked together by the CH…O association from the phenyl CH of the cation and the carbonyl unit with C…O distance of 3.273(2) Å to get 1D chain running along the c axis. The 1D chains were combined together by the CH<sub>3</sub>...O association from the CH<sub>3</sub> at HL and the 3-NO<sub>2</sub> with C···O distance of 3.375(2) Å, and C··· $\pi$  contact between the  $\pi$ -C of the CO<sub>2</sub>H and the phenyl ring of the anion with C…Cg separation of 3.299(3) Å to form 2D sheet extending parallel to the acplane (Fig. 2). The 2D sheets were further piled along the baxis by the N–H···O H-bond from the third H of the  $NH_3^+$ and the 5-NO<sub>2</sub> with N···O distance of 3.148(3) Å, O···O contact between the 5-NO<sub>2</sub> and the OH of the CO<sub>2</sub>H with O···O distance of 2.995(1) Å, and O···O contact from the 5-NO<sub>2</sub> groups with O···O distance of 3.022(2) Å to make 3D network. In this case the O…O separations were in the filed data [78], but the intermolecular O…O separations were longer than the above mentioned intramolecular one.

# X-ray Structure of (2,6-Dimethylaniline):(4-Nitrophthalic acid) [(HL<sup>+</sup>)·(4-Hnpta<sup>-</sup>)] (2)

The analysis of the XRD data indicated the compound **2** crystallized as monoclinic colorless block crystals in the space group P2(1)/c with Z=4. The compound **2** is a salt with only one CO<sub>2</sub>H of the 4-nitro-phthalic acid fully donated its H to the N of the L, which resembled the known salts [79]. Figure 3 shows the asymmetric unit of the compound **2** that contains one HL and one 4-nitro-hydrogenphthalate. In **2**, there is an ion pair without solvent molecules, which agrees well with the micro-analysis results, and thus there exist strong electrostatic interactions from the NH<sub>3</sub><sup>+</sup> and the 4-Hnpta<sup>-</sup>.

It is clear that the difference in bond lengths of the C–O at CO<sub>2</sub>H (0.104 Å) is much greater than the one in  $CO_2^-$  (0.025 Å). Also the average distance for C–O (1.254(4) Å) in the  $CO_2^-$  is less than the C–O single bond (1.307(4) Å) and greater than the C=O double bond (1.203(4) Å) in the CO<sub>2</sub>H of the 4-Hnpta<sup>-</sup>. This verifies the right assignment of the 4-nitro-hydrogenphthalate monoanion. The N(1)–C(1) (1.473(4)) was similar to that at **1**. The phenyl rings with C1–C6 and C11–C16 intersected at 8.4(1)° to each other. The carboxylates O1–C9–O2 and O3–C10–O4 rotated out of the phenyl plane by 111.8(2) and 139.1(2)°, respectively, and the two carboxyl moieties intersected at 61.4(2)° with each other, which is different from the reported adduct of phthalate [79, 80].

One cation was bonded to one anion by the N–H···O H-bond from one H of the  $NH_3^+$  and the  $CO_2^-$  with N···O distance of 2.860(3) Å to form a bicomponent adduct. The bicomponent adducts were linked together by the N–H···O hydrogen bond from the second H of the  $NH_3^+$  and the

Table 3The hydrogen bondinggeometry (Å, °) in 1–5

D–H···A	d(D–H) [Å]	d(H…A) <b>[Å]</b>	d(D…A) [Å]	<(DHA)[°]
1				
O(2)-H(2)···O(3)	0.82	1.74	2.498(3)	154.0
N(1)-H(1C)···O(4)	0.89	2.45	2.971(3)	117.8
N(1)-H(1C)···O(3)	0.89	1.94	2.816(3)	166.9
N(1)-H(1B)····O(1)#1	0.89	1.95	2.841(3)	177.7
N(1)-H(1A)····O(7)#2	0.89	2.43	3.148(3)	138.5
2				
O(2)-H(2)···O(4)#1	0.82	1.71	2.495(3)	158.3
N(1)-H(1C)···O(3)#2	0.89	1.89	2.775(4)	176.2
N(1)-H(1B)····O(4)	0.89	2.56	3.077(4)	117.6
N(1)-H(1B)····O(1)#3	0.89	2.09	2.869(3)	145.4
N(1)-H(1A)····O(3)#1	0.89	2.11	2.860(3)	141.8
3				
O(4)-H(4D)S(1)#2	0.85	2.94	3.766(3)	163.1
O(4)-H(4D)···O(3)#2	0.85	2.20	3.034(4)	168.4
O(4)-H(4C)···O(3)	0.85	2.00	2.837(3)	168.3
N(1)-H(1C)···O(1)#3	0.89	2.04	2.840(4)	148.9
N(1)-H(1B)····O(2)	0.89	1.93	2.793(4)	163.5
N(1)-H(1A)···O(4)#4	0.89	1.89	2.758(4)	165.5
4				
O(20)-H(20)···O(1)#1	0.82	1.70	2.505(8)	165.3
O(8)-H(8)····N(8)#2	0.82	2.66	3.409(10)	152.1
O(8)-H(8)···O(18)#2	0.82	1.68	2.491(8)	171.7
N(2)-H(2C)···O(2)#3	0.89	1.97	2.855(8)	176.4
N(2)-H(2B)O(17)	0.89	2.06	2.827(7)	144.1
N(2)-H(2A)···O(19)#4	0.89	2.06	2.893(7)	155.1
N(1)-H(1C)····O(2)	0.89	2.06	2.833(7)	144.4
N(1)-H(1B)····O(7)	0.89	2.05	2.885(7)	156.5
N(1)-H(1A)····O(17)	0.89	1.94	2.829(8)	175.8
5				
N(1)-H(1C)····O(1)#1	0.89	1.86	2.729(4)	164.6
N(1)-H(1B)····O(1)#2	0.89	2.56	3.204(4)	130.0
N(1)-H(1B)····O(2)#2	0.89	2.27	2.978(4)	136.7
N(1)-H(1A)···O(2)#3	0.89	1.88	2.715(4)	155.4

Symmetry codes for 1: #1 - x, - y, - z; #2 - x + 1, - y + 1, - z. Symmetry codes for 2: #1 - x + 2, y + 1/2, - z + 1/2; #2 x, - y + 3/2, z + 1/2; #3 - x + 2, y - 1/2, - z + 1/2. Symmetry codes for 3: #2 x, - y + 3/2, z + 1/2; #3 - x + 1, - y + 1, - z; #4 - x + 1, - y + 1, - z + 1. Symmetry codes for 4: #1 x + 1/2, - y + 1/2, z; #2 x, y + 1, z; #3 x, y - 1, z; #4 x - 1/2, - y + 1/2, z. Symmetry codes for 5: #1 - x + 1/2, y - 1/2, - z; #2 x - 1/2, y + 1/2, z; #3 - x + 1/2, y + 1/2, - z + 1/2

carbonyl of the CO<sub>2</sub>H with N···O distance of 2.869(3) Å, and CH<sub>3</sub>···O association from the CH<sub>3</sub> of HL and the C=O of the CO<sub>2</sub>H with C···O distance of 3.232(2) Å to get 1D chain. Two 1D chains were combined together by the N–H···O H-bond of 3.077(4) Å from the second H of the NH<sub>3</sub><sup>+</sup> and the CO<sub>2</sub><sup>-</sup>, O–H···O hydrogen bond of the CO<sub>2</sub>H···CO<sub>2</sub><sup>-</sup> with O···O distance of 2.495(3) Å, CH<sub>3</sub>···O association from the CH<sub>3</sub> and the CO<sub>2</sub><sup>-</sup> with C···O distance of 3.557(2) Å, and CH<sub>3</sub>···O contact from the CH<sub>3</sub> and the OH of the CO<sub>2</sub>H with C···O distance of 3.241(2) Å to build a double chain. The double chains were connected together by the N–H···O H-bond from the third H of the NH<sub>3</sub><sup>+</sup> and the CO<sub>2</sub><sup>-</sup> with N–O distance of 2.775(4) Å, aromatic···aromatic association between the phenyl ring of the cation and the aryl ring of the anion with Cg···Cg distance of 3.384(2) Å, and O··· $\pi$  contact from the NO<sub>2</sub> and the phenyl ring of the cation with O···Cg distance of 3.152(2) Å to form 2D sheet extending parallel to the *bc* plane (Fig. 4). The 2D sheets were further packed along the *a* axis by the CH···O contact from the phenyl CH of the cation and the NO<sub>2</sub> with C···O separation of 3.500(2) Å to get 3D network.



Fig.1 Molecular structure of 1 showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level

#### X-ray Structure of (2,6-Dimethylaniline)<sub>2</sub>:(1,5-Naphthalenedisulfonic acid):(H<sub>2</sub>O)<sub>2</sub> [(HL)<sub>2</sub>.(nds).(H<sub>2</sub>O)<sub>2</sub>] (**3**)

Cocrystallization of 2,6-dimethylaniline and naphthalene-1,5-disulfonic acid in 1:1 gave single crystals suitable for X-ray diffraction, but the crystal structure determination (Table 1) revealed that 2,6-dimethylaniline and naphthalene-1,5-disulfonic acid are in a 2:1 ratio. The crystal structure of **3** consists of one HL, half a dianion of naphthalene-1,5-disulfonate, and one water molecule in the asymmetric unit (Fig. 5). Salt **3** crystallizes in the monoclinic space group P2(1)/c. The 2,6-dimethylaniline is protonated at the NH<sub>2</sub> also. The C–N bond length concerning the NH<sub>3</sub><sup>+</sup> in HL was 1.484(4) Å for N(1)–C(1), which is like the corresponding bond lengths at **1** and **2**. The S–O bond lengths in the SO<sub>3</sub><sup>-</sup> range from 1.449(2) Å to 1.455(3) Å ( $\Delta$ =0.006 Å), which are close to the corresponding S–O bonds at the SO<sub>3</sub><sup>-</sup> [81].

Two cations, two water molecules and one dianion produce a five-component adduct exhibiting the  $R_1^2(3)$  and  $R_2^{-1}(7)$  rings denoted by Bernstein [82], at the five-component adduct there found an inversion centre that is situated at the centre of the C10–C10A bond. Herein the cation associated with the anion by the N–H···O hydrogen bond from one H of the NH<sub>3</sub><sup>+</sup> and one O of the SO<sub>3</sub><sup>-</sup> with N···O distance of 2.793(4) Å, and CH<sub>3</sub>···O association between the CH<sub>3</sub> and the same O of the SO<sub>3</sub><sup>-</sup> with C···O distance of 3.483(2) Å. The water molecule associated with the SO<sub>3</sub><sup>-</sup> by the O–H···O H-bond from the second O of the SO<sub>3</sub><sup>-</sup> with O···O distance of 3.034(4) Å, and O–H···S H-bond from the S of the SO<sub>3</sub><sup>-</sup> with O···S distance of 3.766(3) Å. The fivecomponent adducts were linked together by the N–H···O H-bond between the second H of the NH<sub>3</sub><sup>+</sup> and one O of the SO<sub>3</sub><sup>-</sup> with N···O distance of 2.840(4) Å, CH···O association from the naphthalene CH and the SO<sub>3</sub><sup>-</sup> with C···O distance



Fig.3 Molecular structure of 2 showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level



**Fig. 2** 2D sheet structure of **1** extending at the *ac* plane

**Fig. 4** 2D sheet structure of **2** extending parallel to the *bc* plane



of 3.468(4) Å, and  $CH_3$ ...O association between the  $CH_3$ and the O of the  $SO_3^-$  with C···O distance of 3.405(2) Å to give 1D chain running along the a axis. The 1D chains were connected together by the N-H···O H-bond from the third H of the  $NH_3^+$  and the H<sub>2</sub>O with N···O distance of 2.758(4) Å, O–H···O H-bond between the water and the  $SO_3^-$  with O···O distance of 2.837(3) Å, and  $CH_3 \cdots \pi$  contact from the  $CH_3$  and the phenyl ring of the cation with C···Cg distance of 3.666(3) Å to get 2D sheet (Fig. 6) extending at the direction that made  $ca. 60^{\circ}$  with the ab plane. The five-component adducts at the neighboring chains were rotated ca. 90° from each other. Along the direction that was perpendicular with its extending direction the 2D sheets were further piled by the N–H···O H-bond between the  $NH_3^+$  and the H<sub>2</sub>O with N–O distance of 2.758(4) Å, and O–H…O H-bond of 2.837(3) Å from the H<sub>2</sub>O and the SO<sub>3</sub><sup>-</sup> to get 3D network. There also found intersheet  $CH_3 \cdots \pi$  contact from the  $CH_3$ and the phenyl ring of the cation with C…Cg distance of 3.666(3) Å.



Fig.5 Molecular structure of 3 showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level

X-ray Structure of (2,6-Dimethylaniline):(3,5-Dinitrobenzoic Acid) [(HL)·(dnb)·(Hdnb)] (4)

Salt 4 crystallizes as orthorhombic pale yellow crystals in the space group Pna2(1). The asymmetric unit of 4 consists of two cations of 2,6-dimethylaniline, two 3,5-dinitrobenzoate anions, and two 3,5-dinitrobenzoic acids, as depicted in Fig. 7. This is a salt where the CO<sub>2</sub>H of one 3.5-dinitrobenzoic acids is ionized by H transfer to the N of the 2,6-dimethylaniline, which is also confirmed by the bond distances of O(1)-C(17) (1.238(9) Å), O(2)-C(17) (1.244(9) Å), O(13)-C(31) (1.198(12) Å) and O(14)-C(31) (1.216(11) Å) for the CO<sub>2</sub><sup>-</sup> (Table 2). The differences ( $\Delta = 0.006$  and 0.018 Å) in bond distances between the pair of bonds in the  $CO_2^-$  agreed well with the deprotonated  $CO_2H$ . The O(7)-C(24) (1.212(9) Å), O(8)-C(24) (1.275(10) Å), O(19)–C(38) (1.195(9) Å) and O(20)–C(38) (1.326(10) Å) distances are for CO<sub>2</sub>H. The N(1)–C(1) (1.497(8) Å) and N(2)-C(9) (1.466(8) Å) ones were comparable to the corresponding bonds at 1-3.

One cation was bonded to an anion by a N-H-O H-bond between one H of the NH<sub>3</sub><sup>+</sup> and the CO<sub>2</sub><sup>-</sup> with N···O distance of 2.833(7) Å, and a 3,5-dinitrobenzoic acid by the N-H···O H-bond from the second H of  $NH_3^+$  and the C=O of the CO<sub>2</sub>H with N···O distance of 2.885(7) Å to get a tricomponent adduct (A) In the tricomponent adduct A there existed the O<sup> $\dots$ </sup>  $\pi$  association from the NO<sub>2</sub> of the anion and the phenyl ring of the 3,5-dinitrobenzoic acid with O…Cg distance of 2.966(2) Å and O···N contact from the  $NO_2$ groups with O…N distance of 3.024(2) Å. An anion was bonded to the other cation by a N-H···O H-bond from one H of the  $NH_3^+$  and the NO<sub>2</sub> with N···O distance of 2.827(7) Å, and a 3,5-dinitrobenzoic acid by the N-H···O hydrogen bond from the second H of  $NH_3^+$  and the C=O of the  $CO_2H$ with N…O distance of 2.893(7) Å to form a tricomponent adduct (B) In the tricomponent adduct B there was an  $O^{\dots}\pi$ contact from the NO<sub>2</sub> of the anion and the phenyl ring of the 3,5-dinitrobenzoic acid with O…Cg distance of 2.926(2) Å and O···N contact between the nitro groups with O···N

Fig. 6 2D sheet structure of **3** extending at the direction that made an angle of ca.  $60^{\circ}$  with the *ab* plane





Fig. 7 Molecular structure of 4 (for the crowdedness of the structure the atom-numbering was not labeled). Displacement ellipsoids are drawn at the 30% probability level

distance of 3.052(2) Å. The tricomponent adducts A and B were linked together by the N-H…O H-bond from the second H of  $NH_3^+$  at the tricomponent adduct A and the NO<sub>2</sub> of the anion at the tricomponent adduct B with N···O distance of 2.893(7) Å, N-H···O H-bond between the third H of  $NH_3^+$  at the tricomponent adduct B and the  $CO_2^-$  at the tricomponent adduct A with N···O distance of 2.855(8) Å, CH<sub>3</sub>...O contact between the CH<sub>3</sub> and the OH of the 3,5-dinitrobenzoic acid with C···O separation of 3.362(1) Å, O<sup> $\dots$ </sup>  $\pi$  association from the NO<sub>2</sub> and the phenyl ring of the cation with O…Cg distance of 3.103(1) Å, and aryl…aryl association between the phenyl ring of the cation and the phenyl ring of the anion with Cg…Cg distance of 3.336(2) Å to get a six-component aggregate. The six-component aggregates were linked together by the N-H…O H-bond from the second H of NH<sub>3</sub><sup>+</sup> at the tricomponent adduct B and the CO<sub>2</sub><sup>-</sup> at the tricomponent adduct A with N···O distance of 3.007(2) Å, N-H…O hydrogen bond from the third H of

 $NH_3^+$  at the tricomponent adduct A and the NO<sub>2</sub> of the anion at the tricomponent adduct B with N···O distance of 2.827(7) Å, O–H···O H-bond of the  $CO_2H$ ··· $CO_2^-$  with O···O distance of 2.505(8) Å, CH<sub>3</sub>...O association from CH<sub>3</sub> and the OH of the CO<sub>2</sub>H with C···O distance of 3.343(1) Å, N···O contact between the nitro groups with N···O distance of 3.034(2)Å, aryl---aryl association from the phenyl ring of the cation and the phenyl ring of the anion with Cg…Cg distance of 3.382(2) Å, and O··· $\pi$  contact from the CO<sub>2</sub><sup>-</sup> and the phenyl core of the cation with O…Cg distance of 3.113(2) Å to get 1D chain running along the b axis. The 1D chains were combined together by the CH···O association from the phenyl CH of the 3,5-dinitrobenzoic acid at the tricomponent adduct B and the nitro unit of the 3,5-dinitrobenzoic acid at the tricomponent adduct A with C···O distance of 3.578(2) Å to give 2D sheet extending parallel to the *ab* plane (Fig. 8). In the *c*-axis the 2D sheets were further packed by the CH…O contact from the 4-CH of the cation and the nitro group with C···O distance of 3.380(3) Å, CH<sub>3</sub>···O contact of 3.511(2) Å from CH<sub>3</sub> of the cation and the nitro group, O…O contacts between the nitro groups with O…O distances of 2.873(2)–2.927(2) Å, and O···C association from the NO<sub>2</sub> and the C of the  $CO_2^-$  with O···C separation of 2.994(2) Å to get 3D ABAB layer network. Herein the corresponding components at the adjacent sheets made ca.  $60^{\circ}$  to each other. The corresponding components at the first sheet were parallel to the corresponding components at the third sheet, so did the corresponding ones at the second and the fourth sheet.

# X-ray Structure of (2,6-Dimethylaniline):(Dichloroacetic acid) [(HL)·(dca)] (5)

Compound **5** with the composition  $[(HL) \cdot (dca)]$  prepared by reacting equal mol of 2,6-dimethylaniline and dichloroacetic acid crystallizes as monoclinic colorless crystals in the space group C2/c. The asymmetric unit of **5** consists of one HL and one dca (Fig. 9). The H and Cl atoms at the Cl<sub>2</sub>CH were all disordered over two sites with equal occupancy for each atom. The molecular composition of **5** was the same as the crystal structure of diisopropylaminium dichloroacetate [83] with the HL substituted of diisopropylaminium.

Compound **5** is classified as a salt in which  $CO_2H$  of the dichloroacetic acid is absolutely ionized by H transfer to the NH<sub>2</sub> of the 2,6-dimethylaniline, which is also supported by the equal C–O bond lengths (1.209(4) Å) at C9–O1–O2. Here the two C–O bonds were the same indicating the equal



Fig. 8 2D sheet structure of 4 extending parallel to the *ab* plane



Fig.9 Molecular structure of 5 showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level

distribution of the negative charge on both O. The C–N bond (N(1)-C(1), 1.462(4) Å) is similar to the corresponding C–N bonds at 1–4.

One cation was bonded to one anion by the bifurcated N–H···O H-bonds from one H of the NH<sub>3</sub><sup>+</sup> and both O of the CO<sub>2</sub><sup>-</sup> with N···O distances of 2.978(4)–3.204(4) Å, and the CH<sub>3</sub>···O association between the CH<sub>3</sub> of HL and the CO<sub>2</sub><sup>-</sup> with C···O distance of 3.434(2) Å to get a bicomponent adduct. Two bicomponent adducts were held together by the N–H···O H-bonds from the second H of the NH<sub>3</sub><sup>+</sup> and the CO<sub>2</sub><sup>-</sup> with N···O distance of 2.729(4) Å to get a tetracomponent aggregate with R<sub>1</sub><sup>2</sup>(4), R<sub>2</sub><sup>-1</sup>(7) and R<sub>4</sub><sup>2</sup>(8) rings. The tetracomponent aggregates were linked together by the N–H···O H-bonds from the third H of the NH<sub>3</sub><sup>+</sup> and the CO<sub>2</sub><sup>-</sup> with N–O distance of 2.715(4) Å, and CH<sub>3</sub>–O association from the CH<sub>3</sub> and the CO<sub>2</sub><sup>-</sup> with C···O distance

**Fig. 10** 2D sheet structure of **5** extending parallel to the *bc* plane

of 3.416(2) Å to get 1D chain running along the *c* axis. The 1D chains were combined together by the CH···Cl contact from the phenyl CH of the cation and the Cl at the anion with C···Cl distance of 3.781(3) Å to form 2D sheet extending parallel to the *bc* plane (Fig. 10). At the *a* axis the 2D sheets were further piled by the Cl···Cl bonds with Cl···Cl separation of 3.206(2) Å to get 3D network.

### Conclusion

Five organic acid–base crystals have been prepared and their crystal structures determined. The different H-bond interaction modes of the acids and the 2,6-dimethylaniline lead to different structures of 3D network and 3D ABAB layer structure.

All of the organic acid-base adducts involve H-transfer from the acidic units to the NH<sub>2</sub> of the 2,6-dimethylaniline except the remarkable phenolate case to form a monocation. This study has demonstrated that the N-H...O H-bonds are the primary intermolecular forces in a set of structures containing the OH-2,6-dimethylaniline synthons. Except the classical H-bonds, the secondary propagating interactions also made critical contribution to the structure extension. The five salts all possess  $CH_3$ ...O associations, 1, 2 and 3 have the CH…O association. O…O contacts were found at 1 and 4. Salt 1 has the C<sup> $\cdots$ </sup>  $\pi$  contact, 4 has the O<sup> $\cdots$ </sup>C and O<sup> $\cdots$ </sup>N associations. There are also aromatic ... aromatic contacts in 2 and 4. The O<sup> $\dots$ </sup> $\pi$  interactions were found in 1, 2 and 4, 3 possesses additional  $CH_3 \cdots \pi$  interaction. Salt 5 bears the CH…Cl and Cl…Cl non-covalent bonds. In conclusion, we have shown that 3D structures can be made by the synergic



effects of classical H-bonds and other noncovalent contacts from discrete components.

# **Supporting Information Available**

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic data center, CCDC Nos. 1056246 for **1**, 1055981 for **2**, 1055982 for **3**, 1450208 for **4** and 1447998 for **5**. Copies of this information may be obtained free of charge from the +44(1223)336-033 or Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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