Journal of Molecular Structure 1004 (2011) 227–236

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Five organic salts assembled from carboxylic acids and bis-imidazole derivatives through collective noncovalent interactions

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ARTICLE INFO

Article history:
Received 4 May 2011
Received in revised form 3 August 2011
Accepted 3 August 2011
Available online 26 August 2011

Keywords:
Crystal structure
3D framework
Hydrogen bonds
Noncovalent interactions
Bis-imidazoles
Carboxylic acids

ABSTRACT

Five multicomponent crystals of bis(imidazole) derivatives have been prepared with 5-nitrosalicylic acid, 5-sulfosalicylic acid, and phthalic acid. The five crystalline forms reported are organic salts of which the crystal structures have all been determined by X-ray diffraction. The results presented herein indicate that the strength and directionality of the N—H···O, O—H···O, and N—H···N hydrogen bonds (ionic or neutral) between carboxylic acids and ditopic imidazoles are sufficient to bring about the formation of binary organic salts.

All supramolecular architectures of the organic salts **1**–**5** involve extensive O—H···O, and N—H···O hydrogen bonds as well as other noncovalent interactions. The role of weak and strong noncovalent interactions in the crystal packing is ascertained. These noncovalent interactions combined, all the complexes displayed 3D framework structure.

1. Introduction

Noncovalent interactions between molecules are weak intermolecular contacts that govern the physicochemical properties of molecular systems in the condensed phase [1]. Noncovalent binding interactions are nowadays commonly used for the self-assembly of large supramolecular aggregates in solution [2]. Supramolecular interactions have attracted considerable attention during the past few years [3] because the utilization of intermolecular noncovalent interactions is relied upon for the design and development of functional materials. Noncovalent interactions form the backbone of supramolecular chemistry and include classical/nonclassical hydrogen bond, stacking, electro-static, hydrophobic and charge-transfer interactions [4]. Of these interactions hydrogen bond interactions are well-established supramolecular interactions and numerous crystallographic examples are regularly reported [5,6].

Because of the predictable supramolecular properties and the ability to form strong and directional hydrogen bonds, carboxylic acids were frequently chosen as building blocks for crystal engineering [7–9]. Numerous heterodimers composed of carboxylic acids and a variety of N-containing basic building blocks have been documented recently [10–14]. The hydrogen bonding between hydroxyl group of carboxylic acid and heterocyclic nitrogen atom has been proved to be a useful and powerful organizing force for the formation of supramolecules. Imidazole and its derivatives are ubiquitous in biological and biochemical structure and function, and great efforts have been devoted to the development of organic molecular crystals containing a variety of imidazole architectures [15–17]. Among these supramolecular architectures, however, only a very few reports described the crystals composed of bis(imidazole) derivatives [18–22] (e.g., 1,4-bis[(imidazol-1-yl)methyl]-benzene [18,22], (bis(1-methyl-imidazol-2-yl)methyl)-4-nitroimidazol-2-yl)methyl)amine [20], etc.).

Following our previous works of acid–base adducts based on bis(imidazole) and dicarboxylic acid [23–25], herein we report the synthesis and crystal structure of five supramolecular complexes assembled through noncovalent interactions between carboxylic acids and bis(imidazole). In this study, we got five organic complexes composed of carboxylic acids and symmetric ditopic bis-imidazol-1-yl compounds (Scheme 1), namely 1-(3-(1H-benzimidazol-1-yl)propyl)-1H-benzimidazole:(5-nitrosalicylic acid)$_2$:2MeOH (**1**) [$(H_2L1)^{2+}\cdot(5\text{-nsa}^-)_2\cdot$2MeOH, L1 = 1-(3-(1H-benzimidazol-1-yl)propyl)-1H-benzimidazole, 5-nsa$^-$ = 5-nitrosalicylate], 1,5-bis(1-benzimidazolyl)-3-oxapentane:(5-nitrosalicylic acid)$_2$ (**2**) [$(H_2L2)^{2+}\cdot(5\text{-nsa}^-)_2$, L2 = 1,5-bis(1-benzimidazolyl)-3-oxapentane], bis(*N*-imidazolyl)methane:(5-sulfosalicylic acid) (**3**) [$(H_2L3)^{2+}\cdot(5\text{-ssa}^{2-})$, L3 = bis(*N*-imidazolyl)methane, 5-ssa^{2-} = 5-sulfosalicylate], 1,4-bis(*N*-imidazolyl)butane:(5-sulfosalicylic acid) (**4**) [$(H_2L4)^{2+}\cdot(5\text{-ssa}^{2-})$, L4 = 1,4-bis(*N*-imidazolyl)butane], and 1,4-bis(*N*-imidazolyl)butane:(phthalic acid) (**5**) [$(HL4)^+\cdot$(Hpta$^-$), Hpta$^-$ = hydrogen phthalate].

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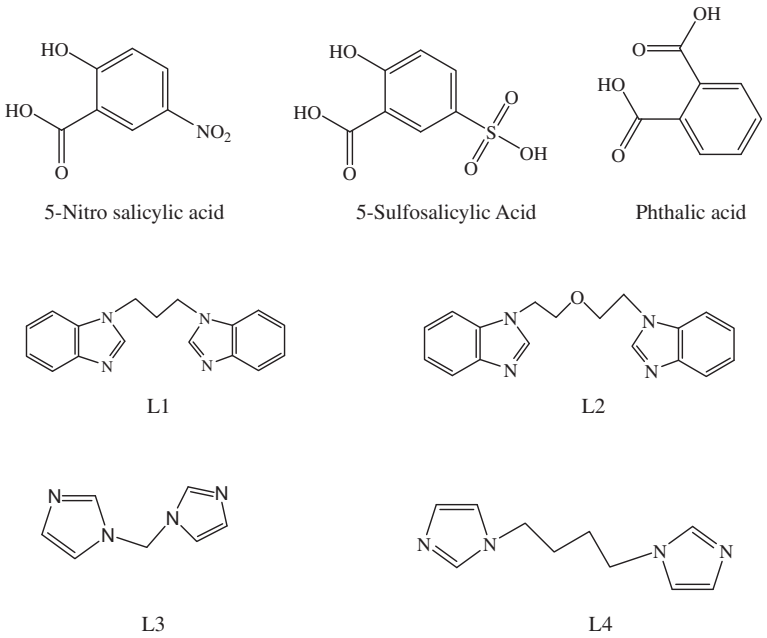
doi:10.1016/j.molstruc.2011.08.010



Scheme 1. Hydrogen bond synthons discussed in this paper.

2. Experimental

2.1. Materials and methods

All reagents were commercially available and used as received. L1–L4 were prepared according to modified procedures of the literatures [26–27]. The C, H, and N micro-analysis were carried out with a Carlo Erba 1106 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in range 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Melting points of new compounds were recorded on an XT-4 thermal apparatus without correction.

2.2. Preparation of supramolecular complexes

2.2.1. 1-(3-(1H-benzimidazol-1-yl)propyl)-1H-benzimidazole:(5-nitrosalicylic acid)$_2$:2MeOH [$(H_2L1)^{2+}\cdot(5\text{-}nsa^-)_2\cdot 2MeOH$, 5-nsa$^-$ = 5-nitrosalicylate], (**1**)

1-(3-(1H-benzimidazol-1-yl)propyl)-1H-benzimidazole L1 (28 mg, 0.10 mmol) was dissolved in 3 mL methanol. To this solution was added 5-nitrosalicylic acid (18.3 mg, 0.1 mmol) in 4 mL methanol. Colorless block crystals were afforded after several days by slow evaporation of the solvent. yield: 35 mg, 49.53% (based on L1). mp 196–198 °C. Elemental analysis: Calc. for $C_{33}H_{34}N_6O_{12}$ (706.66): C, 56.04; H, 4.81; N, 11.89. Found: C, 55.96; H, 4.78; N, 11.85. Infrared spectrum (KBr disk, cm^{-1}): 3558s(ν(OH)), 3506s(multiple, ν_{as}(NH)), 3362s(ν_s(NH)), 3290s, 3118m, 3046m, 2960m, 2842m, 2718m, 2448w, 2374m, 2213m, 1976w, 1836w, 1764w, 1586s($\nu_{as}(COO^-)$), 1552m, 1526s($\nu_{as}(NO_2)$), 1486w, 1394s($\nu_s(COO^-)$), 1366m, 1321s($\nu_s(NO_2)$), 1270m, 1195m, 1131m, 1079m, 952m, 903m, 853m, 806m, 760m, 716m, 680m, 637m, 582m.

2.2.2. 1,5-bis(1-benzimidazolyl)-3-oxapentane:(5-nitrosalicylic acid)$_2$ [$(H_2L2)^{2+}\cdot(5\text{-}nsa^-)_2$, 5-nsa$^-$ = 5-nitrosalicylate], (**2**)

1-(4-(1H-benzimidazol-1-yl)butyl)-1H-benzimidazole L2 (29 mg, 0.10 mmol) dissolved in 1 mL ethanol. To this solution was added 5-nitrosalicylic acid (18.3 mg, 0.1 mmol) in 4 mL methanol. Colorless prisms were afforded after several days of slow evaporation of the solvent, yield: 42 mg, 62.44% (based on L2). mp 206–209 °C. Elemental analysis: Calc. for $C_{32}H_{28}N_6O_{11}$ (672.60): C, 57.09; H, 4.16; N, 12.49. Found: C, 56.98; H, 4.09; N, 12.44. Infrared spectrum (KBr disk, cm^{-1}): 3574s (ν(OH)), 3486s(multiple, ν_{as}(NH)), 3338s(ν_s(NH)), 3115m, 3054m, 2972m, 2846m, 2724m, 2432w, 2386m, 2231m, 1996w, 1868w, 1783w, 1614m, 1592s($\nu_{as}(COO^-)$), 1540s($\nu_{as}(NO_2)$), 1474w, 1406s($\nu_s(COO^-)$), 1358m, 1314s($\nu_s(NO_2)$), 1240m, 1120m, 1013m, 946m, 868m, 806m, 757m, 680m, 637m, 558m.

2.2.3. Bis(N-imidazolyl)methane:(5-sulfosalicylic acid) [$(H_2L3)^{2+}\cdot(5\text{-}ssa^{2-})$, 5-ssa^{2-} = 5-sulfosalicylate], (**3**)

Bis(*N*-imidazolyl)methane L3 (30 mg, 0.2 mmol) dissolved in 2 mL of methanol. To this solution was added 5-sulfosalicylic acid (43.6 mg, 0.2 mmol) in 8 mL ethanol. Colorless prisms were afforded after several days of slow evaporation of the solvent, yield: 56 mg, 76.43% (based on L3). mp 112–114 °C. Elemental analysis: Calc. for $C_{14}H_{14}N_4O_6S$ (366.35): C, 45.86; H, 3.82; N, 15.29; S, 8.73. Found: C, 45.82; H, 3.78; N, 15.22; S, 8.66. Infrared spectrum (KBr disk, cm^{-1}): 3582s(ν(OH)), 3448s(multiple, ν_{as}(NH)), 3353s(ν_s(NH)), 3213s, 3115w, 3064m, 2960m, 2842m, 2718m, 2468w, 2374m, 2242w, 1996w, 1662w, 1551s($\nu_{as}(COO^-)$), 1510m, 1478w, 1395m, 1368s($\nu_s(COO^-)$), 1234s, 1195m, 1131m, 1087m, 1032w, 936m, 842m, 766m, 714m, 658m, 611w.

2.2.4. 1,4-Bis(N-imidazolyl)butane:(5-sulfosalicylic acid) [$(H_2L4)^{2+}\cdot(5\text{-}ssa^{2-})$] (**4**)

1,4-Bis(*N*-imidazolyl)butane L4 (19.9 mg, 0.1 mmol) dissolved in 2 mL of ethanol. To this solution was added 5-sulfosalicylic acid (21.8 mg, 0.1 mmol) in 5 mL methanol. Colorless prisms were afforded after several days of slow evaporation of the solvent, yield: 32 mg, 78.35% (based on L4). mp 106–108 °C. Elemental analysis: Calc. for $C_{17}H_{20}N_4O_6S$ (408.43): C, 49.95; H, 4.90; N, 13.71; S, 7.83. Found: C, 49.92; H, 4.84; N, 13.67; S, 7.78. Infrared spectrum (KBr disk, cm^{-1}): 3586s (ν(OH)), 3472s(multiple, ν_{as}(NH)), 3373s(ν_s(NH)), 3109m, 3064m, 2972m, 2844m, 2726m, 2428w, 2362m, 2213m, 1976w, 1836w, 1783w, 1626m, 1564s($\nu_{as}(COO^-)$), 1513m, 1483w, 1388s($\nu_s(COO^-)$), 1195m, 1109m, 1045m, 925m, 835m, 757m, 710m, 680m, 626m, 546m.

*2.2.5. 1,4-Bis(N-imidazolyl)butane:(phthalic acid) [(HL4)$^{+}$·(Hpta^{-})] (**5**)*

1,4-Bis(*N*-imidazolyl)butane L4 (19.9 mg, 0.1 mmol) dissolved in 2 mL of ethanol. To this solution was added phthalic acid (17 mg, 0.1 mmol) in 5 mL ethanol. Colorless prisms were afforded after several days of slow evaporation of the solvent, yield: 29 mg, 81.37% (based on L4). mp 166–168 °C. Elemental analysis: Calc. for $C_{18}H_{20}N_4O_4$ (356.38): C, 60.61; H, 5.61; N, 15.71. Found: C, 60.56; H, 5.54; N, 15.68. Infrared spectrum (KBr disk, cm^{-1}): 3560s(ν(OH)), 3454s(multiple, ν_{as}(NH)), 3332s(ν_s(NH)), 3140m, 3032m, 2979m, 2926m, 2842m, 2724m, 2610w, 2356m, 2179m, 1998w, 1812w, 1769w, 1713s(ν_{as}(C═O)), 1676w, 1638m, 1586m, 1558s(ν_{as}(COO^{-})), 1470m, 1426m, 1376s(ν_s(COO^{-})), 1304m, 1286s(ν_s(C—O)), 1232m, 1196m, 1126m, 1073m, 1020m, 930m, 888m, 802m, 716m, 656m, 614m, 574m, 510m, 464m.

2.3. X-ray crystallography

Suitable crystals were performed on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). Data collections and reductions were performed using the SMART and SAINT software [28–29]. The structures were solved by direct methods, and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using SHELXTL package [30]. Hydrogen atom positions for the two structures were generated geometrically. Further details of the structural analysis are summarized in Table 1. Selected bond lengths and angles for complexes **1–5** are listed in Table 2, the relevant hydrogen bond parameters are provided in Table 3.

3. Results and discussion

3.1. Syntheses and general characterization

L1–L4 have good solubility in common organic solvents, such as CH_3OH, C_2H_5OH, CH_3CN, $CHCl_3$, and CH_2Cl_2. For the preparation of **1–5**, the acids were mixed directly with the bases L1–L4 in 1:1 ratio in methanol and/or ethanol solvents, which was allowed to evaporate at ambient conditions to give the final crystalline products. The molecular structures and their atom labeling schemes for the four structures are shown in Figs. 1, 3, 5, 7 and 9, respectively.

The elemental analyses for all the compounds are in good agreement with their compositions. The infrared spectra of **1–5** are consistent with their chemical formulas determined by elemental analysis and further confirmed by X-ray diffraction analysis. The very strong and broad features at 3600–3300 cm^{-1} arise from O—H or N—H stretching frequencies. Aromatic and imidazol ring stretching and bending are in the regions of 1500–1630 cm^{-1} and 600–750 cm^{-1}, respectively. The intense peak at ca. 1713 cm^{-1} was derived from the existence of the C═O stretches, and the band at ca. 1286 cm^{-1} exhibited the presence of the C—O stretches of the carboxylate for salt **5**. The absence of two broad bands at ca. 2500 cm^{-1} and 1900 cm^{-1} which is characteristic of a neutral O—H···N hydrogen-bond interaction was interpreted as a lack of co-crystal formation in compounds **1–5** [31]. The most distinct feature in the IR spectrum of proton transfer compounds are the presence of strong asymmetrical and symmetrical carboxylate stretching frequencies at 1550–1610 cm^{-1} and 1300–1420 cm^{-1} in **1**, **2**, **3**, **4**, and **5**, respectively [32].

3.2. X-ray structure of 1-(3-(1H-benzimidazol-1-yl)propyl)-1H-benzimidazole:(5-nitrosalicylic acid)$_2$:2MeOH [$(H_2L1)^{2+}$·(5-nsa^{-})$_2$·2MeOH, 5-nsa^{-} = 5-nitrosalicylate], (**1**)

Salt **1** was prepared by reacting of a methanol solution of 1-(3-(1H-benzimidazol-1-yl)propyl)-1H-benzimidazole and 5-nitrosalicylic acid in 1: 1 ratio, which crystallizes as monoclinic pale yellow crystals in the centrosymmetric space group C2/c. The asymmetric unit of **1** consists of half a dication of L1, one anion of 5-nitrosalicylate, and one methanol molecule as shown in Fig. 1. This is a salt where the COOH groups of 5-nitrosalicylic acids are ionized by proton transfer to the nitrogen atoms of the 1-(3-(1H-benzimidazol-1-yl)propyl)-1H-benzimidazole moieties, which is also confirmed by the bond distances of O(1)—C(10) (1.257(5) Å) and O(2)—C(10)

Table 1
Summary of X-ray crystallographic data for complexes **1–5**.

	1	**2**	**3**	**4**	**5**
Formula	$C_{33}H_{34}N_6O_{12}$	$C_{32}H_{28}N_6O_{11}$	$C_{14}H_{14}N_4O_6S$	$C_{17}H_{20}N_4O_6S$	$C_{18}H_{20}N_4O_4$
Fw	706.66	672.60	366.35	408.43	356.38
T, 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	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	C2/c	C2/c	P2(1)2(1)2(1)	Pna2(1)	Pna2(1)
a, Å	29.596(3)	29.602(3)	9.2099(11)	18.5227(16)	13.0059(12)
b, Å	7.4337(7)	6.3885(7)	10.0436(13)	9.6884(8)	7.9942(6)
c, Å	18.3375(17)	7.8276(7)	16.7967(16)	10.0139(11)	16.7147(16)
α, deg	90	90	90	90	90
β, deg	125.864(2)	90.8320(10)	90	90	90
γ, deg	90	90	90	90	90
V, Å^3	3269.5(5)	1480.1(3)	1553.7(3)	1797.0(3)	1737.9(3)
Z	4	2	4	4	4
D_{calcd}, Mg/m^3	1.436	1.509	1.566	1.510	1.362
Absorption coefficient, mm^{-1}	0.111	0.116	0.251	0.226	0.098
F(000)	1480	700	760	856	752
Crystal size, mm^3	0.24 × 0.22 × 0.20	0.40 × 0.37 × 0.14	0.34 × 0.20 × 0.14	0.20 × 0.09 × 0.07	0.40 × 0.38 × 0.28
θ range, deg	2.22–25.02	2.60–25.02	2.36–25.02	2.37–25.01	2.82–25.02
Limiting indices	$-34 \leqslant h \leqslant 34$ $-8 \leqslant k \leqslant 4$ $-21 \leqslant l \leqslant 21$	$-34 \leqslant h \leqslant 33$ $-7 \leqslant k \leqslant 4$ $-9 \leqslant l \leqslant 9$	$-9 \leqslant h \leqslant 10$ $-11 \leqslant k \leqslant 11$ $-16 \leqslant l \leqslant 19$	$-14 \leqslant h \leqslant 21$ $-11 \leqslant k \leqslant 11$ $-11 \leqslant l \leqslant 11$	$-15 \leqslant h \leqslant 15$ $-6 \leqslant k \leqslant 9$ $-19 \leqslant l \leqslant 19$
Reflections collected	7899	3850	6475	9086	8210
Reflections independent (R_{int})	2876 (0.0914)	1868 (0.0425)	2717 (0.0418)	3062 (0.0555)	1592 (0.0357)
Goodness-of-fit on F^2	0.884	1.036	0.919	0.971	1.099
R indices [$I > 2\sigma I$]	0.0635, 0.1576	0.0698, 0.1794	0.0396, 0.0724	0.0407, 0.0825	0.0345, 0.0809
R indices (all data)	0.1306, 0.1916	0.1106, 0.2106	0.0584, 0.0780	0.0560, 0.0886	0.0494, 0.0908
Largest diff. peak and hole, e Å^{-3}	0.207, −0.322	0.657, −0.251	0.246, −0.279	0.251, −0.152	0.177, −0.160

Table 2
Selected bond lengths (Å) and angles (°) for **1**–**5**.

1			
N(1)—C(3)	1.344(4)	N(1)—C(5)	1.395(4)
N(1)—C(1)	1.477(4)	N(2)—C(3)	1.321(4)
N(2)—C(4)	1.390(4)	N(3)—C(15)	1.455(5)
O(1)—C(10)	1.257(5)	O(2)—C(10)	1.266(5)
O(3)—C(12)	1.339(4)	O(6)—C(17)	1.387(6)
C(3)—N(1)—C(5)	107.8(3)	C(3)—N(1)—C(1)	125.8(3)
C(5)—N(1)—C(1)	126.3(2)	C(3)—N(2)—C(4)	109.0(3)
O(1)—C(10)—O(2)	123.9(4)		
2			
N(1)—C(3)	1.313(9)	N(1)—C(5)	1.399(8)
N(1)—C(1)	1.458(9)	N(2)—C(3)	1.280(8)
N(2)—C(4)	1.330(8)	O(1)—C(2)	1.406(8)
O(2)—C(10)	1.256(7)	O(3)—C(10)	1.257(7)
O(4)—C(12)	1.344(7)	C(3)—N(1)—C(5)	111.1(6)
C(3)—N(1)—C(1)	121.0(6)	C(5)—N(1)—C(1)	127.7(6)
C(3)—N(2)—C(4)	113.4(6)	N(2)—C(3)—N(1)	108.3(7)
O(2)—C(10)—O(3)	124.2(6)		
3			
N(1)—C(2)	1.327(4)	N(1)—C(4)	1.374(4)
N(1)—C(1)	1.437(3)	N(2)—C(2)	1.310(4)
N(2)—C(3)	1.354(4)	N(3)—C(5)	1.316(4)
N(3)—C(7)	1.374(4)	N(3)—C(1)	1.455(3)
N(4)—C(5)	1.306(4)	N(4)—C(6)	1.349(4)
O(1)—C(8)	1.269(4)	O(2)—C(8)	1.257(4)
O(3)—C(10)	1.339(3)	O(4)—S(1)	1.443(2)
O(5)—S(1)	1.443(2)	O(6)—S(1)	1.4387(19)
C(2)—N(1)—C(4)	108.4(2)	C(2)—N(1)—C(1)	125.9(3)
C(4)—N(1)—C(1)	125.4(3)	C(2)—N(2)—C(3)	109.5(3)
C(5)—N(3)—C(7)	108.6(3)	C(5)—N(3)—C(1)	123.1(3)
C(7)—N(3)—C(1)	128.1(3)	C(5)—N(4)—C(6)	109.5(3)
N(1)—C(1)—N(3)	111.5(2)	N(2)—C(2)—N(1)	108.0(3)
N(4)—C(5)—N(3)	108.4(3)	O(2)—C(8)—O(1)	123.1(3)
4			
N(1)—C(5)	1.317(4)	N(1)—C(7)	1.369(4)
N(1)—C(1)	1.463(4)	N(2)—C(5)	1.307(4)
N(2)—C(6)	1.361(4)	N(3)—C(8)	1.314(4)
N(3)—C(10)	1.359(4)	N(3)—C(4)	1.468(4)
N(4)—C(8)	1.309(4)	N(4)—C(9)	1.343(4)
O(1)—C(11)	1.229(4)	O(2)—C(11)	1.282(4)
O(3)—C(13)	1.355(3)	O(4)—S(1)	1.442(3)
O(5)—S(1)	1.415(2)	O(6)—S(1)	1.446(2)
C(5)—N(1)—C(7)	108.6(3)	C(5)—N(1)—C(1)	126.6(3)
C(7)—N(1)—C(1)	124.8(3)	C(5)—N(2)—C(6)	109.4(3)
C(8)—N(3)—C(10)	107.7(3)	C(8)—N(3)—C(4)	126.7(3)
C(10)—N(3)—C(4)	125.6(3)	C(8)—N(4)—C(9)	109.0(3)
N(2)—C(5)—N(1)	108.5(3)	N(4)—C(8)—N(3)	109.0(3)
O(1)—C(11)—O(2)	124.4(3)		
5			
N(1)—C(5)	1.337(4)	N(1)—C(7)	1.367(5)
N(1)—C(1)	1.472(4)	N(2)—C(5)	1.315(4)
N(2)—C(6)	1.363(5)	N(3)—C(8)	1.321(4)
N(3)—C(10)	1.376(4)	N(3)—C(4)	1.466(4)
N(4)—C(9)	1.368(4)	N(4)—C(8)	1.322(4)
O(1)—C(11)	1.289(4)	O(2)—C(11)	1.214(4)
O(3)—C(12)	1.229(4)	O(4)—C(12)	1.274(4)
C(5)—N(1)—C(7)	107.1(3)	C(5)—N(1)—C(1)	125.9(3)
C(7)—N(1)—C(1)	127.0(3)	C(5)-N(2)—C(6)	105.1(3)
C(8)—N(3)—C(10)	107.9(3)	C(8)—N(3)—C(4)	126.8(3)
C(10)—N(3)—C(4)	125.3(3)	C(8)—N(4)—C(9)	108.4(3)
N(2)—C(5)-N(1)	111.4(3)	N(3)—C(8)—N(4)	109.3(3)
O(2)—C(11)—O(1)	125.1(3)	O(3)—C(12)—O(4)	125.2(3)

(1.266(5) Å) for the carboxylate. L1 is doubly protonated and the cation with the NH^+ groups on the benzimidazole rings in **1** resembles 4,4′-H_2bipy cation [33]. The protonated L1 cation displays trans configuration in which the inversion center is located at C(2).

In the compound, there are two pairs of ion pair with two methanol molecules accompanied, which is well agreement with the micro-analysis results. In the solid state, there is consistently hydrogen bonds formed between the NH^+ group, and the 5-nitrosalicylate ions, which is to be expected [34]. There also exist strong electrostatic interactions between charged cation units of NH^+ and the 5-nitrosalicylate anions.

Because of the presence of the intramolecular hydrogen bond between the carboxylate group and the phenol group (O(3)—H(3)···O(2), 2.507(4) Å), it is generally expected and found that the carboxylate group is essentially coplanar with the benzene ring [torsion angle C12—C11—C10—O1, 177.85°]. This feature is similar to that found in salicylic acid [35], and in the previously reported structure of proton-transfer compound based on 5-nsa$^-$ [36]. As expected the O—O separation is essentially in the range of the documented data [2.489–2.509 Å] [36], but it is slightly contracted compared with the nonproton transfer examples (2.547–2.604 Å, mean: 2.588 Å), as a result of deprotonation. The 5-nitro group also varies little conformationally [torsion angle C14—C15—N3—O5, 178.68°] compared with the reported data within this set of compounds (175.4–180°) [36].

Two anions were bounded to the cations through the N—H···O hydrogen bond between the NH^+ cation and the carboxylate group with N—O distance of ca. 2.664(4) Å to form a heteroadduct. At every carboxylate there was bonded a methanol molecule through the O—H···O (O—O separation is 2.629(5) Å) hydrogen bond produced by the same O atom that is involved in the N—H···O hydrogen bond. The adjacent heteroadducts were connected together via two CH—O and one CH_2—O associations between the cation and the NO_2 group to form a 1D chain running along the *a* axis direction. One CH—O interaction is existed between 2-CH of one benzimidazole moiety and one O atom of the nitro group with C—O distance of 3.463 Å, the other CH—O interaction is between CH of the benzene ring of another benzimidazole moiety in the same cation and the remaining O atom of the NO_2 group with C—O distance of 3.369 Å, this O atom also made a CH_2—O contact with the propane spacer of the cation with C—O distance of 3.483 Å. For the presence of such three interactions there are close joint $R_2^2(8)$ and $R_2^2(9)$ ring motifs. There are also chains that are antiparallel to the above chains. These two kinds of chains were combined together along the *b* axis direction via the CH—O interaction between aromatic CH of the anion and the methanol molecule with C—O distance of 3.266 Å to form a double chain running along the *a* axis direction also. Here the two chains were slipped some distance from each other along the *a*, and *c* axis directions, respectively. Such double chains were further joined together by the CH_2—O interaction between the propane spacer and the carboxylate with C—O distance of 3.420 Å to form a sheet extending on the *ac* plane (Fig. 2). The sheets were further stacked along the *b* axis direction by the intersheet CH_2—O associations between the propane spacer and the carboxylate with C—O distance of 3.420 Å to form a 3D network structure.

*3.3. X-ray structure of 1,5-bis(1-benzimidazolyl)-3-oxapentane:(5-nitrosalicylic acid)$_2$ [$(H_2L2)^{2+}$·(5-nsa$^-$)$_2$, 5-nsa$^-$ = 5-nitrosalicylate], (**2**)*

Crystallization of 1,5-bis(1-benzimidazolyl)-3-oxapentane and 5-nitrosalicylic acid in a 1:1 ratio from the mixed solvent of methanol and ethanol gave single crystals suitable for X-ray diffraction. Structure determination (Table 1) revealed that 1,5-bis(1-benzimidazolyl)-3-oxapentane and 5-nitrosalicylic acid are present in a 1:2 ratio in the molecular complex **2**. The crystal structure of **2** consists of half a diprotonated L2, and one monoanion of 5-nitrosalicylate in the asymmetric unit (Fig. 3). The C—O distances in the carboxylate are almost equal with each other within the experimental error, indicating that the negative charge was distributed equally on both O atoms.

The H_2L2 adopts a cis configuration with the planes of the two benzimidazole rings in the same cation inclined by 54.4°. The two benzimidazole rings formed dihedral angles of 73.7° with the plane

Table 3
Hydrogen bond distances and angles in studied structures **1** – **5**.

D—H···A	d(D—H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠(DHA)[°]
		1		
N(2)—H(2)···O(1)#2	0.86	1.81	2.664(4)	176.1
O(3)—H(3)···O(2)	0.82	1.78	2.507(4)	147.4
O(6)—H(6)···O(1)	0.82	1.81	2.629(5)	173.3
		2		
O(4)—H(4)···O(3)	0.82	1.76	2.498(7)	148.9
N(2)—H(2)···O(2)#2	0.86	1.83	2.674(8)	165.9
		3		
O(3)—H(3)···O(2)	0.82	1.74	2.473(3)	148.5
N(4)—H(4)···O(1)#1	0.86	1.97	2.802(4)	162.8
N(2)—H(2)···O(2)	0.86	2.50	2.957(4)	114.0
N(2)—H(2)···O(1)	0.86	1.94	2.763(3)	161.0
		4		
O(3)—H(3)···O(2)	0.82	1.76	2.493(3)	147.1
N(4)—H(4)···O(6)#1	0.86	1.91	2.707(3)	153.3
N(2)—H(2C)···O(2)#2	0.86	1.77	2.630(4)	173.0
		5		
N(4)—H(4)···N(2)#1	0.86	1.85	2.709(4)	176.7
O(1)—H(1)···O(4)#2	0.82	1.95	2.506(3)	124.3

Symmetry transformations used to generate equivalent atoms for **1**: #1 $-x+1, y, -z+3/2$; #2 $x+1/2, y+1/2, z$. Symmetry transformations used to generate equivalent atoms for **2**: #2 $x, y-1, z+1$. Symmetry transformations used to generate equivalent atoms for **3**: #1 $x, y-1, z$. Symmetry transformations used to generate equivalent atoms for **4**: #1 $x, y-1, z-1$; #2 $x, y+1, z$. Symmetry transformations used to generate equivalent atoms for **5**: #1 $x-1, y, z$; #2 $x-1/2, -y+5/2, z$.

defined by the oxapentane spacer, and the benzene ring of the anion made a dihedral angle of 78° with the plane defined by the oxapentane spacer.

At each imidazolium moiety there was bonded an anion by the hydrogen bond (N(2)—H(2)···O(2)#2, 2.674(8) Å) between the NH^+ cation and one O atom of the carboxylate and CH—O interaction between the benzene CH of the cation and another O atom of the carboxylate with C—O distance of 3.464 Å. Due to these two non-bonding interactions the carboxylate and the imidazole form a $R_2^2(8)$ ring according to Bernstein et al. [37]. For the presence of such interactions two anions and one dication form a heteroadduct. The heteroadducts were connected together via the CH—O interactions generated between the NO_2 group and the benzene CH of the cation with C—O distance of 3.488 Å, and CH_2—O interactions between the oxapentane spacer and the NO_2 group with C—O distance of 3.460 Å to form a 1D chain running along the *b* axis direction. Here one O atom of the NO_2 group functioned as bifurcate hydrogen bond acceptor to form a $R_2^2(7)$ graph set with the cation. Such chains were linked together by the interchain O—π interactions (between the carboxylate O that bears a CH—O interaction with the cation and the benzene ring of the anion with O—Cg distance of ca. 3.195 Å) to form a 2D sheet with the thickness of ca. 11.970 Å that is extending on the *bc* plane (Fig. 4). Such sheets were joined together along the *a* axis direction via the inter-sheet CH—O interaction (between the OH group and 3-CH of the anionic benzene ring with C—O distance of 3.515 Å, and between the CH of the benzimidazole cation and the carboxylate with C—O distance of 3.420 Å) to form a 3D network structure.

*3.4. X-ray structure of bis(N-imidazolyl)methane:(5-sulfosalicylic acid) [$(H_2L3)^{2+}$·(5-ssa^{2-}), 5-ssa^{2-} = 5-sulfosalicylate], (**3**)*

Different from compounds **1**, and **2**, in **3** the asymmetric unit is occupied by one dianion of 5-sulfosalicylic acid and one dication of bis(*N*-imidazol-1-ium)methane $(H_2L3)^+$ (Fig. 5). Different from other reported organic salts containing 5-ssa$^-$ monoanion [38,39], here both protons at the SO_3H and COOH groups have ionized, and the phenol OH remains protonized. It is further verified by the C—O distances of the carboxylate group [O(1)—C(8), 1.269(4) Å; and O(2)—C(8), 1.257(4) Å with the Δ value of 0.012 Å]. The C—O bond distance (O(3)—C(10), 1.339(3) Å) concerning the phenol group indicates that there does not exist phenolate ion. The S—O distances in SO_3^- are ranging from 1.4387(19) to 1.443(2) Å which is in the range of the deprotonated SO_3H group (1.435 (2)–1.4599 (17) Å) [40]. The carboxylate deviated by 8° from the benzene plane of the anion.

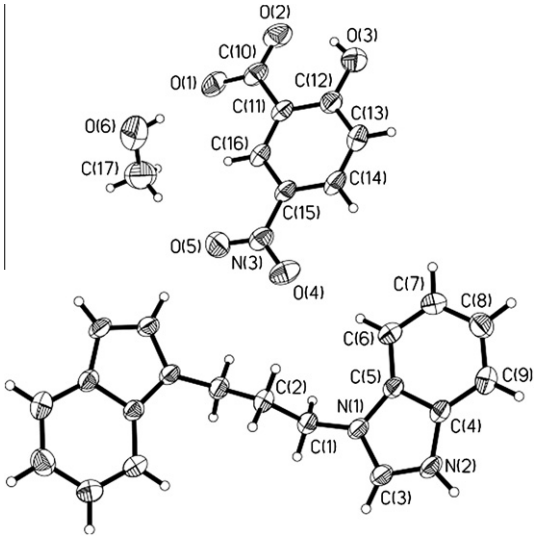


Fig. 1. The structure of **1**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

The cation displayed cis conformation. One anion is bounded to the cation through one ionic hydrogen bond (N(4)—H(4)···O(1)#1, 2.802(4) Å), two CH—O associations, and two CH—π interactions to form a heteroadduct. One O atom of the sulfonyl group forms two CH—O associations with both of the N—CH—N at the same H_2L3 cation in bifurcate fashion with C—O distances of 3.225–3.259 Å. The CH—π interactions exist between the N—CH—N of the cation and the benzene ring of the anion and between 6-CH of the anion and the imidazole ring with C—Cg distance of 3.499 Å. Like **1**, and **2**, the usual intramolecular hydrogen bond is found between the phenol group and a carboxylate O atom [O(3)—H(3)···O(2);

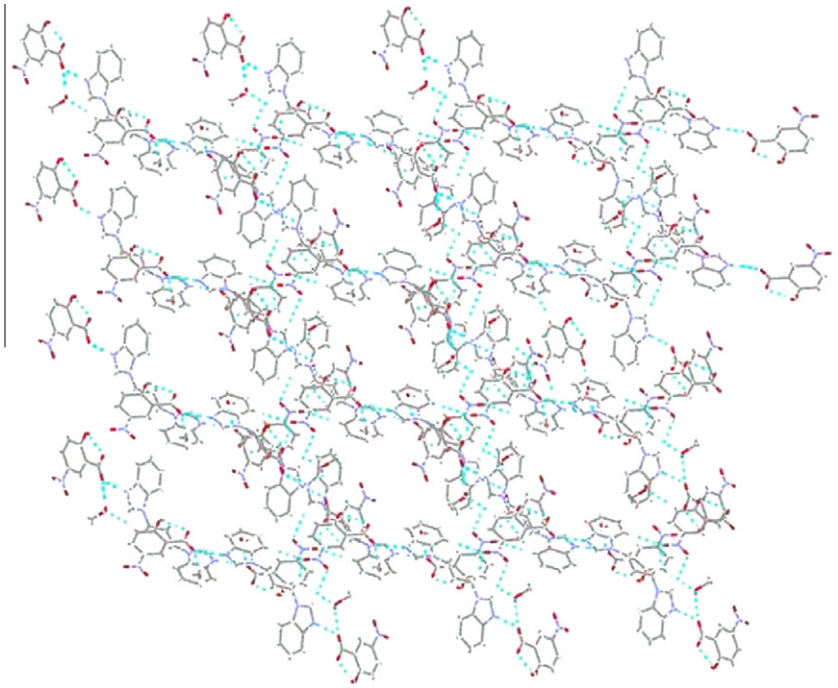


Fig. 2. 2D sheet structure of **1** extending on the *ac* plane.

O—O = 2.473(3) Å], essentially giving coplanarity of the carboxylate group and the benzene ring [torsion angle O(1)—C(8)—C(9)—C(10); −174.85(2)°]. This hydrogen bond geometries were similar to the documented data [40]. For the presence of this hydrogen bond, compound **3** bears the $S_1^1(6)$ loop motif.

The heteroadducts were linked together by the N—H···O, and CH—O interactions along the *b* axis direction to form a 1D chain. The chains were joined together by the interchain CH_2—O and CH—O interactions to form a 2D sheet extending on the *ab* plane (Fig. 6). Here the CH_2—O interaction is formed between the CH_2 bridge of the cation and the sulfonyl group with C—O distance of 3.354 Å. One 5-CH of the bis-imidazole cation formed two CH—O interactions in bifurcate mode, i.e. one is with the sulfonyl group with C—O distance of 3.136 Å, the other CH—O interaction involves the phenol group with the C—O distance of 3.291 Å. While the other 5-CH of the same cation is involved in only one CH—O interaction with the sulfonyl group with C—O distance of 3.461 Å. For the presence of such hydrogen bonding interactions the close joint $R_2^2(8)$ and $R_2^2(6)$ motifs were produced. Such sheets were further stacked along the *c* axis direction via CH_2—O, and O—π interactions to form a 3D network structure. Here the CH_2 bridge of the cation formed two CH_2—O associations in bifurcate fashion, one is arised from the sulfonyl group with C—O distance of 2.961 Å, the other is arised from the phenol group with C—O distance of 3.197 Å. The O—π interaction is formed between the phenol group and the imidazole ring with the O—Cg distance of 3.158 Å. The O—Cg distance is comparable to the documented data (3.12 Å) [41]. In the 3D network structure, the adjacent sheets were slipped some distance from each other along the *a*, and *b* axis directions, respectively.

3.5. X-ray structure of 1,4-bis(N-imidazolyl)butane:(5-sulfosalicylic acid) [$(H_2L4)^{2+}\cdot(5\text{-ssa}^{2-})$] (**4**)

Similar to the salt **3**, the asymmetric unit of **4** consists of one dication of N,N′-butylenebis(imidazole) and one dianion of 5-ssa^{2-}, as shown in Fig. 7. The C—O distances of the COO^- of 5-sulfosalicylate are ranging from 1.229(4) (O(1)—C(11)) to 1.282(4) (O(2)—C(11)) Å with the Δ value of 0.053 Å, which suggests that the carboxyl group is deprotonated, while the N atom of N,N′-butylenebis(imidazole) is protonated. The significant difference in bond distances between O(1)—C(11) and O(2)—C(11) in the carboxylate group is contributed to O(2) is involved in forming more hydrogen bonds than that of O1 (Table 3). The S—O bond lengths and the O—S—O bond angles in the SO_3^- are not perfectly equivalent, but vary with the environment around the O atoms. Their values reported in Table 2, indicate relatively little distortion from a regular pyramid.

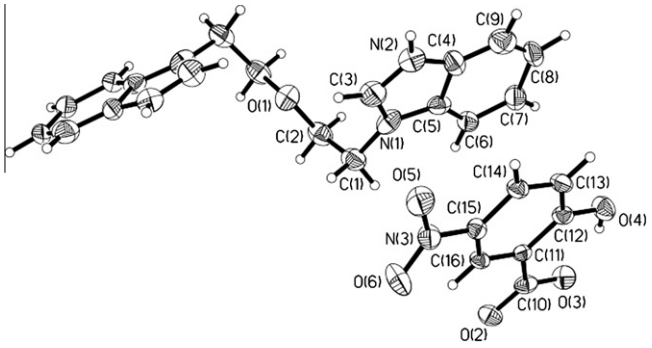


Fig. 3. The structure of **2**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

In the cation, protonation at atoms N2, and N4 leads to an increase in the C5—N2—C6 [109.42°] and C(8)—N(4)—C(9) [109.06°] angles compared to that observed in the neutral L4 (104.15(4)°), and this angle is almost equal to the corresponding angle on its hydrochloride salt (109.08(3)°) [42]. It was found that protonation of the imidazole ring nitrogen atoms causes no significant change in conformation of the $(H_2L4)^{2+}$ dication in **4** in comparison to the corresponding neutral molecule 1-(4-(1H-imidazol-1-yl)butyl)-1H-imidazole (L4) [42]. The imidazole rings in **4** have trans-(ap) position in respect to C2—C3 bond (angle C1—C2—C3—C4,

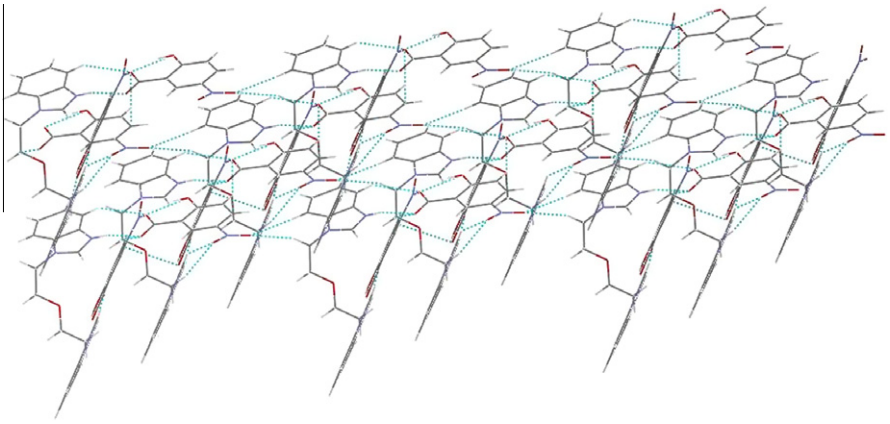


Fig. 4. 2D sheet structure of **2** that is extending on the *bc* plane.

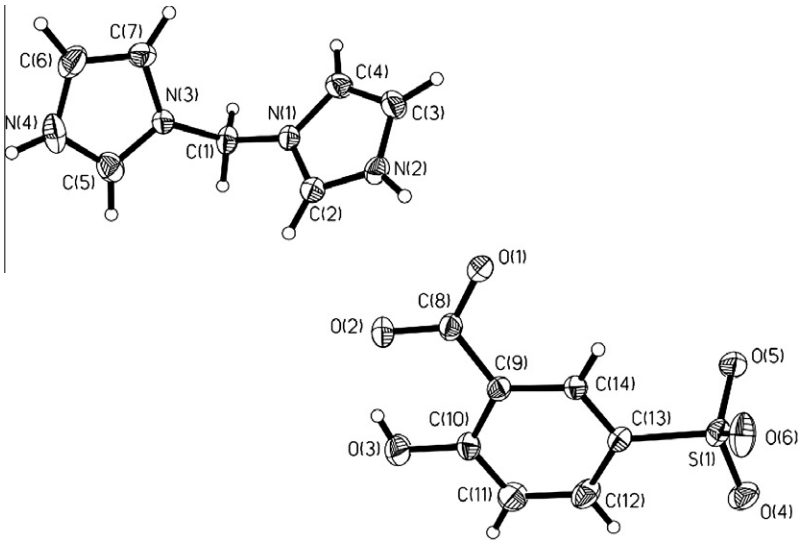


Fig. 5. The structure of **3**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

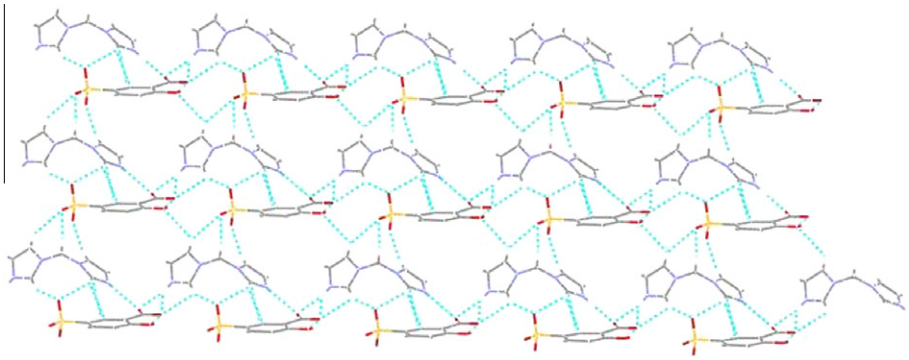


Fig. 6. 2D sheet structure of **3** extending on the *ab* plane.

178.3°), which is different from the corresponding 1,1′-(1,4-butanediyl)bis(imidazolium) dihydrochloride [42]. The two imidazole rings in the same cation make a dihedral angle of 167.6° with each other. The imidazolium rings (N1, N2, C5, C6, C7, and N3, N4, C8, C9, C10) form dihedral angles of 90.1° and 101.4° with the plane defined by the C atoms of the —$(CH_2)_4$— aliphatic linker in the $(H_2L4)^{2+}$ cation. Compared with **3**, the carboxylate deviated by only 1.3° from the phenyl ring plane of the 5-sulfosalicylate.

The anions and the cations were connected together by the N—H···O hydrogen bonds to form a 1D chain running along the *b* axis direction. The N—H···O hydrogen bonds are formed between the imidazolium and the carboxylate group (N(2)—H(2C)···O(2)#2, 2.630(4) Å, 173.0°, #2 x, $y+1$, z) and the sulfonyl moiety (N(4)—H(4)···O(6)#1, 2.707(3) Å, 153.3°, #1 x, $y-1$, $z-1$). Adjacent chains were held together by the interchain CH—O (between the N—CH—N of the cation and the sulfonyl group with C—O

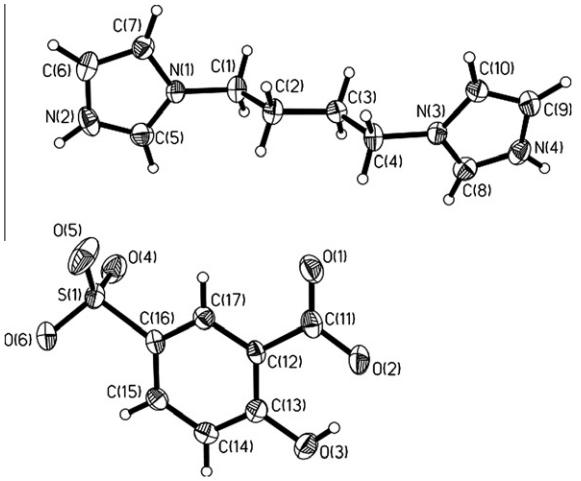


Fig. 7. The structure of **4**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

distance of 3.250 Å), CH_2—O (between the butane spacer and the carboxylate group with C—O distance of 3.544 Å), O—π (between the phenol group of the anion and the imidazole ring with O—Cg distance of 2.967 Å), and π—π interactions (between two imidazole rings with Cg—Cg separation of 3.373 Å). Here the O—Cg distance is significantly shorter than the O—Cg distance in **3**. Under these interactions the chains were combined together to form a 2D sheet extending along the *bc* plane (Fig. 8). The two adjacent sheets were joined together along the *a* axis direction via the intersheet CH—O interaction between 5-CH of the imidazole and the carboxylate with C—O distance of 3.229 Å, and CH_2—O interaction between the butane spacer and the sulfonyl group with C—O distance of 3.235 Å to form a double sheet structure. The double sheets were connected together by the CH—O (between the N—CH—N of the cation and the sulfonyl group with C—O distance of 3.093 Å), N—H···O (between the NH^+ cation and the SO_3^- group with N—O distance of 3.162 Å), CH_2—O (between the butane spacer and the phenol group with C—O distance of 3.305 Å), and CH—π interactions (between the N—CH—N of the cation and the benzene ring of the anion with C—Cg distance of 3.661 Å) to form a 3D ABAB layer network structure. Here the adjacent double sheets were extended along different directions and made an angle of ca. 30° with each other, yet the third double sheet has the same project on the *bc* plane as the first double sheet, so did the second double sheet and the fourth double sheet.

3.6. X-ray structure of 1,4-bis(N-imidazolyl)butane:(phthalic acid) [$(HL4)^+ \cdot (Hpta^-)$] (**5**)

he asymmetric unit of **5** consists of one monocation of N,N′-butylenebis(imidazole), and one monoanion of phthalic acid, which is shown in Fig. 9. Different from the above adducts, here only one N atom of the 1-(4-(1H-imidazol-1-yl)-butyl)-1H-imidazole is protonated by the phthalic acid. Thus only one proton of the phthalic acid is deprotonated to maintain the charge neutrality. In the compound, there is one pair of ion pair with no included solvent molecules. In the cation, protonation at the atom N4 leads to an increase in the C(8)—N(4)—C(9) [108.38°] angle compared to that observed in the neutral L4 (104.15(4)°), and this angle is slightly smaller than the corresponding angle in **4** and its hydrochloride salt (109.08(3)°) [42].

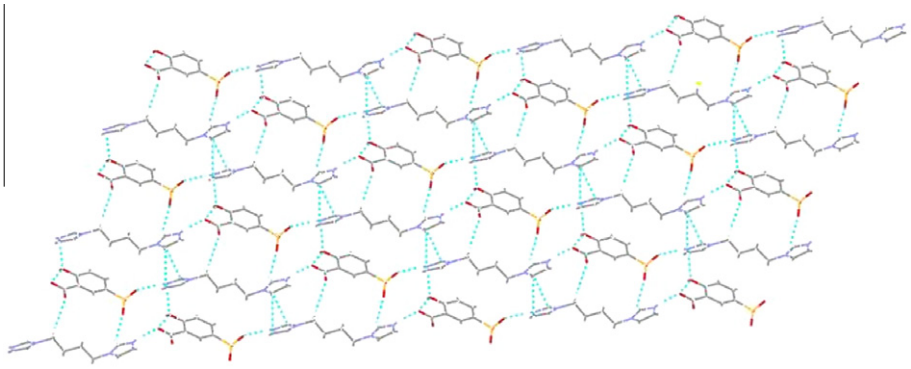


Fig. 8. 2D sheet structure of the salt **4** which is viewed along the *a* axis direction.

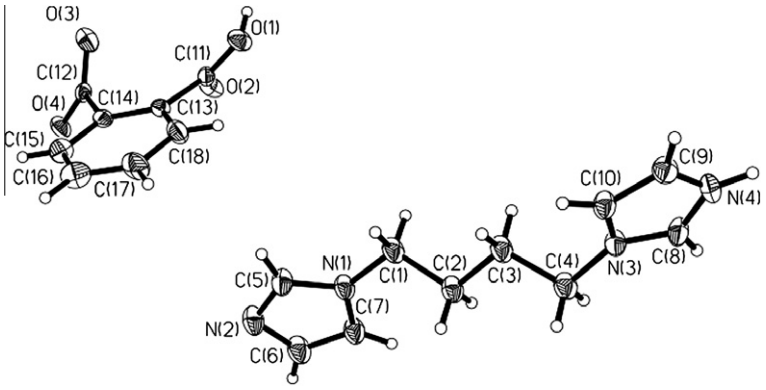


Fig. 9. The structure of **5**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

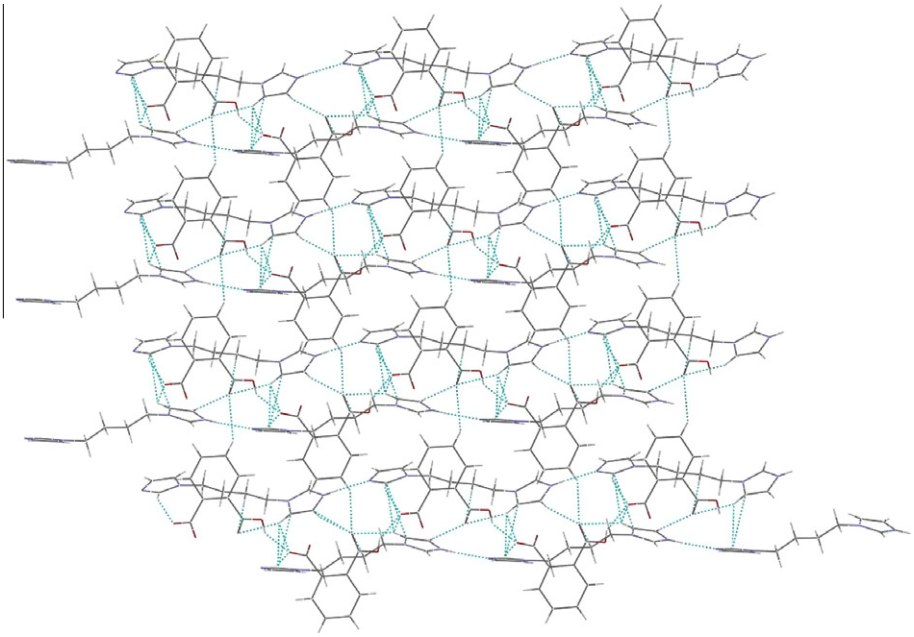


Fig. 10. 3D ABAB layer structure of the salt **5**.

Similar to **4,** protonation of the imidazole ring N atoms causes no significant change in conformation of $(HL4)^+$ in **5** in comparison to the corresponding neutral molecule L4 [42]. Different from the salt of 1,1′-(1,4-butanediyl)bis(imidazolium) dihydrochloride [42], the imidazole rings in **5** have trans-(ap) position in respect to C2—C3 bond (angle C1—C2—C3—C4, 179.46°).

The two imidazole rings have a dihedral angle of 15.3°. The two imidazolium rings (N1, N2, C5, C6, C7; and N3, N4, C8, C9, C10) make dihedral angles of 36.6°, and 51.9 (3)° with the plane defined by the C atoms of the $-(CH_2)_4-$ aliphatic linker in the HL4 cation, respectively. The dihedral angles are significantly smaller than those in **4**, which may be attributed to the different hydrogen bonding strength existed in the two compounds. The carboxylates deviated by 43° (O(1)—C(11)—O(2)), and 125.4° (O3—C12—O4) from the phenyl ring plane of the phthalate, respectively, which is different from the reported adduct of phthalate in which the carboxylates are almost coplanar with the phenyl ring [43].

It is clear that the difference in bond lengths of C—O within the carboxyl group (0.075 Å) is much greater than the one found in the phthalate anions (0.045 Å). Also the average distance for C—O (1.251 Å) in the phthalate is less than the single bond C—O (1.289(4) Å) and greater than the double bond C=O (1.214(4) Å) in the carboxyl group of the phthalic acid. This supports our correct assignment of the phthalate anions. So the negative charge in CO_2^- group is localized on O(4) atom. Whereas the corresponding distances for $CO_2^-\cdots$HOOC (O(1)—C(11), 1.289(4) Å) support the existence of non-ionic acid moieties indicating co-crystal formation.

The anions formed a 1D chain along the *b* axis direction via the CH—O interactions between the benzene CH of one anion and the carbonyl group of its neighboring anion with C—O distance of 3.493 Å. In the chain the anions were arranged in head to tail fashion. The COOH groups on the adjacent chains were directed toward opposite directions, i.e. at one chain the carboxyl is directed to the $+b$ axis direction, while the carboxyl on its neighboring chain is directed to the $-b$ axis direction. So did the COO^- groups. The chains arranged in such a fashion on the *ab* plane alternatively and they are joined together by the interchain O—H···O hydrogen bond between the COOH group and the carboxylate group with O—O separation of 2.506(3) Å to form a 2D sheet extending on the *ab* plane. The cations also formed a 1D chain running along the *a* axis direction through the N—H···N hydrogen bond between the NH^+ group and the unprotonated imidazole N atom with N—N separation of 2.709(4) Å. Two adjacent chains were combined together by the CH—π, and π—π interactions between the protonated imidazole moieties and the unprotonated imidazole moieties to form a cationic double chain. There are no N—H···O, and O—H···N hydrogen bonds between the cations and the anions.

The cationic double chains were intercalated between the anion sheets through the CH—O, CH_2—O, and CH—π interactions to form a 3D ABAB layer network structure (Fig. 10). The double chains were linked with the first sheet layer through CH—O interactions that include the CH—O interaction between 2-CH of the unprotonated imidazole unit and the carboxylate with C—O distance of 3.536 Å, the CH—O interaction between 4-CH of the protonated imidazole unit and the C=O of the COOH with C—O distance of 3.201 Å, and the CH—O interaction between 5-CH of the protonated imidazole and the COO^- with C—O distance of 3.226 Å. There are also CH_2—O associations generated between the butane CH_2 of the cation and the C=O of the first anionic sheet with C—O distance of 3.498 Å.

The cationic double chains were connected with the second anionic sheet layer through CH—O interactions that include the CH—O interaction between 2-CH of the protonated imidazole unit and the carboxylate with C—O distance of 3.181 Å, the CH—O interaction between 4-CH of the unprotonated imidazole unit and the COO^- with C—O distance of 3.522 Å, and the CH—O interaction between 5-CH of the unprotonated imidazole unit and the COO^- group with C—O distance of 3.211 Å. There are CH_2—O associations generated between the butane spacer of the cation and the carboxylate of the second anionic sheet with C—O distance of 3.463 Å. There are also CH_2—O associations produced between the butane bridge of the cation and the phenol group of the second anionic sheet with C—O distance of 3.557 Å. There also exist CH—π interactions between 2-CH of the protonated imidazole and the anionic benzene ring of the second sheet layer with C—Cg distance of 3.618 Å. Obviously these interactions contribute to the formation and stabilization of the final 3D structure.

4. Conclusion

Five organic salts with different topologies have been prepared and structurally characterized. All five examples involve proton transfer from the carboxylic acids to the N atom of the bis(imidazole) molecules, with subsequent hydrogen bonding linking the cation and the anion to give 3D framework structures (3D network structure, 3D layer structure, and 3D ABAB layer structure) in all cases. The most common hydrogen-bonded $R_2^2(8)$ graph set has been observed in salts **1**–**3**.

This study has demonstrated that the N—H···O hydrogen bond is the primary intermolecular force in a family of structures containing the COOH···im synthons, except the salt **5**. Since the potentially hydrogen bonding phenol group is present in the ortho position to the carboxylate group in **1**–**4**, it forms the more facile intramolecular O—H···O hydrogen bond. Except the classical hydrogen bonding interactions, the secondary propagating interactions also play an important role in structure extension. All salts possess C—H···O, and CH_2···O associations. Two types of secondary C—H···O, and CH_2···O hydrogen bonds were observed based upon their geometric preferences, intra- and interchain interactions. Based upon an analysis of the metrics displayed by each set of interactions, it seems that intra- and interchain C—H···O/CH_2—O interactions are of equal structural importance. There are CH—π interactions in compounds **3**, **4,** and **5**. Organic salts **4**, and **5** possess π—π interactions. There also exist strong intermolecular O—π interactions in **2**, **3**, and **4** with the O—Cg distances in the range of 2.967–3.158 Å.

In conclusion, we have shown that higher-dimensional structures (3D) can be constructed from discrete ions by the collective noncovalent interactions such as strong directional hydrogen bond, O—π, CH—O/CH_2—O, CH—π, and π—π interactions.

Supporting information

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic data center, CCDC Nos. 809891 for **1**, 809889 for **2**, 809894 for **3**, 809678 for **4**, and 809890 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.

Acknowledgements

We gratefully acknowledge the financial support of the Education Office Foundation of Zhejiang Province (Project No. Y201017321) and the financial support of the Zhejiang A & F University Science Foundation (Project No. 2009FK63).

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