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Structure of four molecular salts assembled from noncovalent associations between carboxylic acids and aromatic bases containing benzimidazole moiety

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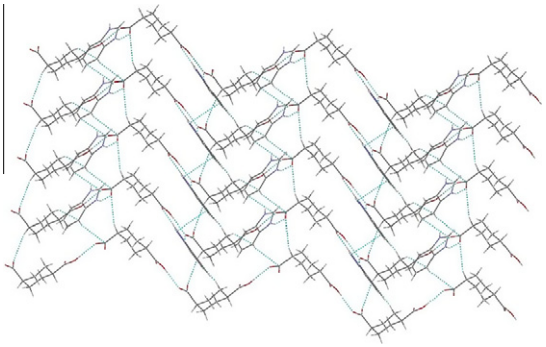
HIGHLIGHTS

- Four supramolecular compounds with 3D structure have been prepared and characterized.
- The noncovalent interaction between benzimidazole moiety and carboxylic acids have been analyzed.
- The N—H···O/O—H···O hydrogen bond is the primary force in a family of structures containing the OH···im synthons.
- The CH—O associations have also been discussed.

GRAPHICAL ABSTRACT

Due to the weak noncovalent interactions, the compounds displayed 3D framework structure.



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ABSTRACT

Single crystal X-ray diffraction has enabled the elucidation of four examples of benzimidazole-acid salts, novel contributions to the extensive research into the occurrence of benzimidazole-acid compound motifs in organic salts. In their place are a series of motifs in which extensive strong classical N—H···O/O—H···O hydrogen bonds (ionic or neutral) combine with other nonconventional weaker interactions. This variety, coupled with the varying geometries and number of acidic groups of the acids employed, has led to the creation of four supramolecular arrays with 3D network structure.

All salts were formed in solution and obtained by the slow evaporation technique. The role of weak and strong noncovalent interactions in the crystal packing is analyzed. The results presented herein indicate that the strength and directionality of the N—H···O, and O—H···O hydrogen bonds (ionic or neutral) between acids and benzimidazole derivatives are sufficient to bring about the formation of organic salts.

1. Introduction

Multicomponent crystals and organic acid_base complexes have received considerable attention over the past few years [1,2] not only because of their intriguing structural motifs [3,4] but also for their useful properties and promising applications as functional materials [5,6]. The design and construction of multi-component supermolecules or supramolecular arrays utilizing noncovalent bonding is a rapidly developing area in supramolecular synthesis. Thus, the supramolecular synthesis successfully exploits hydrogen-bonding and other types of noncovalent interactions, in building supramolecular systems [7]. Of these interactions hydrogen bond interactions are the most powerful organizing force for the formation of supermolecules [8–11].

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

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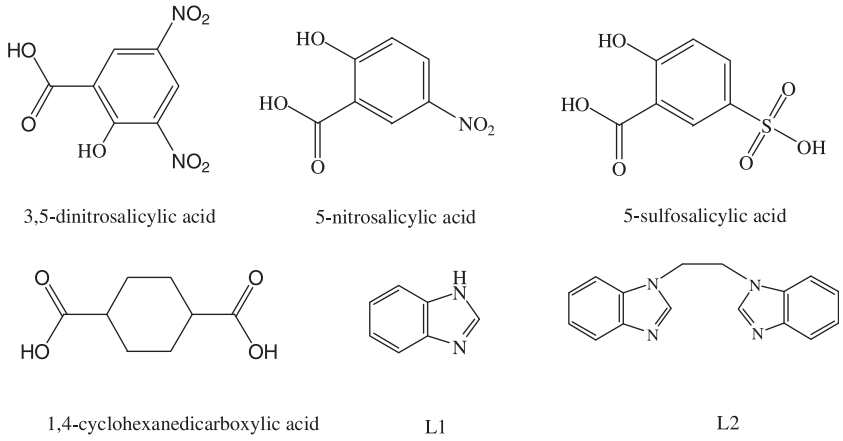


Scheme 1. The building blocks discussed in this paper.

engineering [12–14]. Numerous organic acid_base compounds from carboxylic acids and a variety of N-containing basic building blocks have been documented recently [15–19].

Imidazole and its derivatives are ubiquitous in biological and biochemical structure and function, which attracted special attention in the construction of some interesting metal–organic frameworks in recent years [20–25]. And also, great efforts have been devoted to the development of organic molecular crystals containing a variety of imidazole architectures [26–28]. Among these supramolecular architectures, however, only a very few reports described the crystals composed of imidazoles [29–33] (e.g., 1,4-bis[(imidazol-1-yl)methyl]-benzene [29,33], (bis(1-methyl-imidazol-2-yl)methyl)-4-nitroimidazol-2-yl)methyl)amine [31], etc.).

Following our previous works of acid–base adducts based on bis(imidazole) and dicarboxylic acid [34,35], herein we report the synthesis and crystal structure of four supramolecular compounds assembled via hydrogen bonding interactions between carboxylic acids and benzimidazole or its derivative. In this study, we got four organic compounds composed of carboxylic acids and benzimidazolyl compounds (Scheme 1), namely (benzimidazole):(3,5-dinitrosalicylic acid) [$(HL1^+)\cdot(3,5\text{-}dns^-)$, L1 = benzimidazole, $3,5\text{-}dns^-$ = 3,5-dinitrosalicylate] **(1)**, $(benzimidazole)_2$:(5-nitrosalicylic acid) $[(HL1)^+(L1)\cdot(5\text{-}nsa^-)$, $5\text{-}nsa^-$ = 5-nitrosalicylate] (**2**), (benzimidazole):1-(2-(1H-benzimidazol-1-yl)ethyl)-1H-benzimidazole:(5-sulfosalicylic acid):$4H_2O$ $[(HL1^+)_2\cdot(H_2L2)^{2+}\cdot(5\text{-}ssa^{2-})_2\cdot 4H_2O$, L2 = 1-(2-(1H-benzimidazol-1-yl)ethyl)-1H-benzimidazole, $5\text{-}ssa^{2-}$ = 5-sulfosalicylate] **(3)**, and (benzimidazole):(1,4-cyclohexanedicarboxylic acid) $[(HL1^+)\cdot(HChda^-)$, $HChda^-$ = hydrogen 1,4-cyclohexanedicarboxylate], **(4)** (Scheme 2).

2. Experimental section

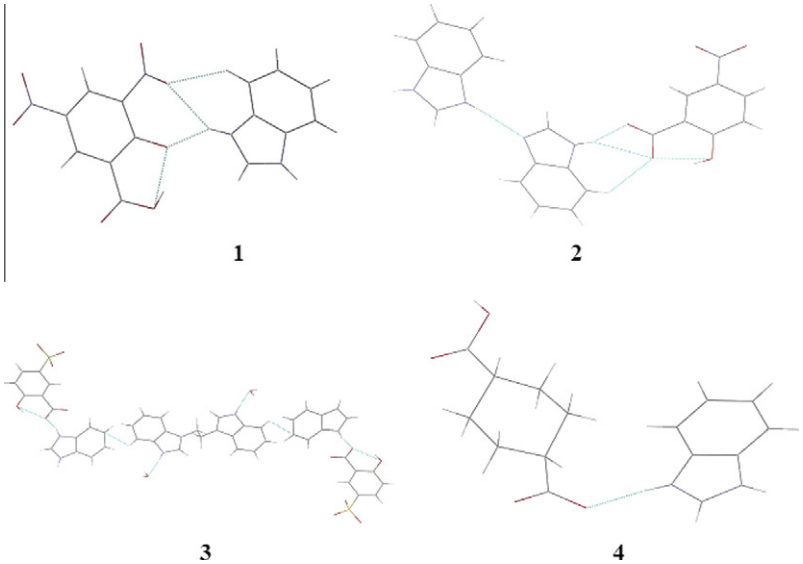
2.1. Materials and methods

L2 was prepared as described previously [36]. All other reagents were commercially available and used as received. The C, H, N, and S microanalysis 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 the salts

2.2.1. (Benzimidazole):(3,5-dinitrosalicylic acid) $[(HL1^+)\cdot(3,5\text{-}dns^-)]$ (*1*)

Benzimidazole L1 (11.8 mg, 0.1 mmol) was dissolved in 3 mL of methanol. To this solution was added 3,5-dinitrosalicylic acid



Scheme 2. The four compounds described in this paper, **1**–**4**.

(22.8 mg, 0.1 mmol) in 6 mL methanol. 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 several days, colorless block crystals were isolated after slow evaporation of the solution in air. The crystals were dried in air to give the title compound [(HL1$^+$)·(3,5-dns$^-$)] (**1**), yield 28 mg, 80.86% (Based on L1). m. p. 182–184 °C. Elemental analysis performed on crystals exposed to the atmosphere: Calc. for $C_{14}H_{10}N_4O_7$ (346.26): C, 48.52; H, 2.88; N, 16.17. Found: C, 48.49; H, 2.83; N, 16.14. Infrared spectrum (KBr disk, cm^{-1}): 3614s (ν(OH)), 3473s(multiple, ν_{as}(NH)), 3352s(ν_s(NH)), 3128m, 3042m, 2989m, 1994w, 1870w, 1781w, 1642s(ν(C═O)), 1599m, 1532s(ν_{as}(NO_2)), 1472w, 1416m, 1358m, 1314s(ν_s(NO_2)), 1284s(ν(C—O)), 1243m, 1126m, 1016m, 944m, 876m, 809m, 754m, 696m, 634m.

*2.2.2. (Benzimidazole)$_2$:(5-nitrosalicylic acid) [(HL1)$^+$·(L1)·(5-nsa$^-$), 5-nsa$^-$ = 5-nitrosalicylate], (**2**)*

Benzimidazole L1 (11.8 mg, 0.1 mmol) was dissolved in 3 mL of methanol. To this solution was added 5-nitrosalicylic acid (18.3 mg, 0.1 mmol) in 9 mL 95% ethanol. Colorless block crystals were afforded after several days by slow evaporation of the solvent (yield: 16.0 mg, 76.30%, based on L1). mp 199–201 °C. Elemental analysis: Calc. for $C_{21}H_{17}N_5O_5$ (419.40): C, 60.08; H, 4.05; N, 16.69. Found: C, 60.02; H, 3.97; N, 16.62. Infrared spectrum (KBr disk, cm^{-1}): 3664s(ν(OH)), 3492s(multiple, ν_{as}(NH)), 3374s(ν_s(NH)), 3138m, 3054m, 2996m, 1981w, 1835w, 1766w, 1598s(ν_{as}(COO$^-$)), 1556m, 1524s(ν_{as}(NO_2)), 1485w, 1393s(ν_s(COO$^-$)), 1358m, 1319s(ν_s(NO_2)), 1246m, 1196m, 1137m, 1086m, 1032m, 956m, 865m, 779m, 716m, 682m, 635m, 602m.

*2.2.3. (Benzimidazole):1-(2-(1H-benzimidazol-1-yl)ethyl)-1H-benzimidazole:(5-sulfosalicylic acid):4H_2O [(HL1$^+$)$_2$·(H_2L2)$^{2+}$·(5-ssa^{2-})$_2$·4H_2O, 5-ssa^{2-} = 5-sulfosalicylate], (**3**)*

1-(2-(1H-benzimidazol-1-yl)ethyl)-1H-benzimidazole L2 (28 mg, 0.10 mmol), and benzimidazole L1 (11.8 mg, 0.1 mmol) were dissolved in 7 mL of methanol. To this solution was added 5-sulfosalicylic acid (21.8 mg, 0.1 mmol) in 5 mL ethanol. Colorless prisms were afforded after several days of slow evaporation of the solvent, yield: 52 mg, 51.64% (based on L2). mp 152–154 °C. Elemental analysis: Calc. for $C_{44}H_{46}N_8O_{16}S_2$ (1007.01): C, 52.43; H, 4.56; N, 11.12; S, 6.35. Found: C, 52.41; H, 4.49; N, 11.05; S, 6.29. Infrared spectrum (KBr disk, cm^{-1}): 3682s(ν(OH)), 3468s(multiple, ν_{as}(NH)), 3359s(ν_s(NH)), 3118m, 3068m, 2986m, 2842m, 2718m, 1997w, 1663w, 1552s(ν_{as}(COO$^-$)), 1508m, 1474w, 1399m, 1368s(ν_s(COO$^-$)), 1233s, 1191m, 1139m, 1082m, 1038w, 956m, 844m, 769m, 714m, 666m, 612w.

*2.2.4. (Benzimidazole):(1,4-cyclohexanedicarboxylic acid) [(HL1$^+$)·(HChda$^-$)], (**4**)*

A solution of 1,4-cyclohexanedicarboxylic acid (17.2 mg, 0.1 mmol) in methanol (2 mL) was added dropwise to a vigorously stirred solution of benzimidazole L1 (11.8 mg, 0.1 mmol) in methanol (3 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 several 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 the title compound [(HL1$^+$)·(HChda$^-$)] (**4**). (yield: 22 mg, 75.78%). mp 167–168 °C. Elemental analysis: Calc. for $C_{15}H_{18}N_2O_4$ (290.31): C, 62.00; H, 6.20; N, 9.64. Found: C, 61.93; H, 6.16; N, 9.57. Infrared spectrum (cm^{-1}): 3684s(ν(OH), 3426s(ν_{as}(NH)), 3342s(ν_s(NH)), 3184m, 3112s, 2974m, 2878m, 1713s(ν_{as}(C═O)), 1629m, 1591s(ν_{as}(COO$^-$)), 1552m, 1476m, 1441m, 1400m, 1380s(ν_s(COO$^-$)), 1342m, 1274s(ν_s(C—O)), 1228m, 1156m, 1102w, 1085m, 1032m, 978m, 869m, 808m, 771m, 722m, 676m, 645m, 602m.

2.3. X-ray crystallography

Suitable crystals were performed on a Bruker SMART 1000 CCD diffractometer using MoKα radiation (λ = 0.71073 Å). Data collections and reductions were performed using the SMART and SAINT software [37,38]. 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 [39]. Hydrogen atoms for the four structures were set in calculated positions. Further details of the structural analysis are summarized in Table 1. Selected bond lengths and angles for compounds **1**–**4** 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

1-(2-(1H-benzimidazol-1-yl)ethyl)-1H-benzimidazole, and benzimidazole both 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**–**4**, the acids were mixed directly with the base in methanol and/or ethanol solvents in 1:1 ratio, 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 and 7, respectively.

The elemental analyses for the four compounds are in good agreement with their compositions. The infrared spectra of **1**–**4** 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 3684–3342 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. Compounds **2**–**4** show the characteristic bands for COO$^-$ group. Compounds **1**, and **4** display additional strong IR peaks for COOH groups. The bands at ca. 1525 and 1315 cm^{-1} were attributed to the ν_{as}(NO_2) and ν_s(NO_2), respectively [40].

*3.2. X-ray structure of (benzimidazole):(3,5-dinitrobenzoic acid) [(HL1$^+$)·(dna$^-$)] (**1**)*

Salt **1** was prepared by reacting of a methanol solution of benzimidazole and 3,5-dinitrobenzoic acid in 1:1 ratio, which crystallizes as triclinic colorless crystals in the centrosymmetric space group P-1. The asymmetric unit of **1** consists of a cation of HL1$^+$, and one anion of 3,5-dinitrosalicylate, as shown in Fig. 1.

However in this case it is the phenol H that has been deprotonated and the COOH group remains protonated. The C—O distance 1.294(7) Å (O(3)—C(10)) concerning the phenolate is similar to the proton transfer compound bearing the 3,5-dns$^-$ in which only the phenol group has been deprotonated [41]. The C—O distances 1.221(8) Å (O(1)—C(8)), and 1.305(7) Å (O(2)—C(8)) in the COOH show characteristic C═O, and C—O distances which are also confirming the reliability of adding H atoms experimentally by different electron density onto O atoms as mentioned above.

The torsion angles O5—N3—C11—C10, and O6—N4—C13—C14 are 149.33°, and 177.42°, respectively. Similar to the published results [42], herein the 5-nitro (O6—N4—O7) group is essentially coplanar with the phenyl ring of the anion, while the 3-nitro (O5—N3—O4) group is rotated out of the plane.

Since the potentially hydrogen bonding hydroxyl group is present in the ortho position to the carboxyl group in the anion, it forms the more facile intramolecular hydrogen bonding. Thus the

Table 1
Summary of X-ray crystallographic data for complexes **1**–**4**.

	1	**2**	**3**	**4**
Formula	$C_{14}H_{10}N_4O_7$	$C_{21}H_{17}N_5O_5$	$C_{44}H_{46}N_8O_{16}S_2$	$C_{15}H_{18}N_2O_4$
Fw	346.26	419.40	1007.01	290.31
T (K)	298(2)	298(2)	298(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Orthorhombic
Space group	P-1	P-1	P-1	P2(1)2(1)2(1)
a (Å)	7.3380(7)	8.9060(8)	7.2760(7)	5.3285(2)
b (Å)	9.6799(11)	9.2819(9)	10.2287(12)	15.8581(5)
c (Å)	10.5201(12)	12.3591(11)	16.7003(19)	16.3215(6)
α (°)	78.1500(10)	93.7100(10)	73.3520(10)	90
β (°)	83.2490(10)	101.480(2)	86.249(2)	90
γ (°)	88.941(2)	90.4000(10)	70.9100(10)	90
V (Å^3)	726.25(14)	998.92(16)	1124.8(2)	1379.16(8)
Z	**2**	**2**	**1**	**4**
D_{calcd} (Mg/m^3)	1.583	1.394	1.487	1.398
Absorption coefficient (mm^{-1})	0.130	0.103	0.202	0.102
F(000)	356	436	526	616
Crystal size (mm^3)	0.33 × 0.30 × 0.18	0.43 × 0.33 × 0.19	0.40 × 0.22 × 0.15	0.33 × 0.19 × 0.16
θ Range (°)	2.61–25.02	2.68–25.02	2.55–25.02	2.57–25.02
	$-8 \leqslant h \leqslant 8$	$-10 \leqslant h \leqslant 10$	$-8 \leqslant h \leqslant 8$	$-6 \leqslant h \leqslant 4$
Limiting indices	$-11 \leqslant k \leqslant 7$	$-11 \leqslant k \leqslant 9$	$-11 \leqslant k \leqslant 12$	$-18 \leqslant k \leqslant 18$
	$-12 \leqslant l \leqslant 12$	$-14 \leqslant l \leqslant 11$	$-19 \leqslant l \leqslant 19$	$-19 \leqslant l \leqslant 15$
Reflections collected	3459	4926	5735	4978
Reflections independent (R_{int})	2402(0.1014)	3441(0.0351)	3913(0.0312)	2393(0.0196)
Goodness-of-fit on F^2	0.803	1.519	0.888	1.055
R indices [$I > 2\sigma I$]	0.0887, 0.1866	0.1399, 0.4094	0.0524, 0.1158	0.0313, 0.0751
R indices (all data)	0.2242, 0.2396	0.2038, 0.4523	0.0909, 0.1296	0.0358, 0.0780
Largest diff. peak and hole (eÅ^{-3})	0.351, −0.368	2.669, −0.397	0.352, −0.265	0.104, −0.118

Table 2
Selected bond lengths (Å) and angles (°) for **1**–**4**.

1			
N(1)—C(1)	1.338(8)	N(1)—C(3)	1.374(8)
N(2)—C(1)	1.317(8)	N(2)—C(2)	1.391(8)
N(3)—C(11)	1.472(8)	N(4)—C(13)	1.451(8)
O(1)—C(8)	1.221(8)	O(2)—C(8)	1.305(7)
O(3)—C(10)	1.294(7)	C(1)—N(1)—C(3)	109.6(6)
C(1)—N(2)—C(2)	109.5(6)	N(2)—C(1)—N(1)	108.5(7)
O(1)—C(8)—O(2)	122.0(7)		
2			
N(1)—C(1)	1.376(11)	N(1)—C(3)	1.385(10)
N(2)—C(1)	1.299(10)	N(2)—C(2)	1.376(9)
N(3)—C(8)	1.314(10)	N(3)—C(10)	1.409(9)
N(4)—C(8)	1.313(10)	N(4)—C(9)	1.397(10)
N(5)—C(20)	1.434(9)	O(1)—C(15)	1.260(11)
O(2)—C(15)	1.273(10)	O(3)—C(17)	1.310(9)
C(1)—N(1)—C(3)	106.8(7)	C(1)—N(2)—C(2)	105.5(7)
C(8)—N(3)—C(10)	107.5(7)	C(8)—N(4)—C(9)	108.7(7)
N(2)—C(1)—N(1)	112.3(7)	N(4)—C(8)—N(3)	111.8(7)
O(1)—C(15)—O(2)	125.1(8)		
3			
N(1)—C(1)	1.320(4)	N(1)—C(3)	1.387(4)
N(1)—C(8)	1.458(4)	N(2)—C(1)	1.324(4)
N(2)—C(2)	1.384(4)	N(3)—C(9)	1.304(4)
N(3)—C(11)	1.370(4)	N(4)—C(9)	1.310(4)
N(4)—C(10)	1.382(4)	O(1)—C(16)	1.246(3)
O(2)—C(16)	1.266(4)	O(3)—C(18)	1.349(3)
O(4)—S(1)	1.437(2)	O(5)—S(1)	1.460(2)
O(6)—S(1)	1.453(2)	S(1)—C(21)	1.762(3)
C(1)—N(1)—C(3)	108.3(2)	C(1)—N(1)—C(8)	125.9(3)
C(3)—N(1)—C(8)	125.7(3)	C(1)—N(2)—C(2)	108.1(3)
C(9)—N(3)—C(11)	108.6(3)	C(9)—N(4)—C(10)	107.9(3)
N(1)—C(1)—N(2)	110.5(3)	N(3)—C(9)—N(4)	110.8(3)
O(1)—C(16)—O(2)	123.9(3)		
4			
N(1)—C(9)	1.320(2)	N(1)—C(11)	1.392(2)
N(2)—C(9)	1.320(2)	N(2)—C(10)	1.386(2)
O(1)—C(1)	1.318(2)	O(2)—C(1)	1.202(2)
O(3)—C(2)	1.2721(19)	O(4)—C(2)	1.243(2)
C(9)—N(1)—C(11)	108.10(14)	C(9)—N(2)—C(10)	108.53(14)
O(2)—C(1)—O(1)	123.02(16)	O(4)—C(2)—O(3)	123.35(16)
N(1)—C(9)—N(2)	110.87(16)		

Table 3
Hydrogen bond distances and angles in studied structures **1**–**4**.

D—H···A	d(D—H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
1				
O(2)—H(2A)···O(3)	0.82	1.68	2.453(6)	155.3
N(2)—H(2)···O(1)#1	0.86	1.99	2.832(7)	165.5
N(1)—H(1)···O(4)#2	0.86	2.32	3.052(8)	143.3
N(1)—H(1)···O(3)#2	0.86	2.04	2.750(7)	139.2
2				
O(3)—H(3A)···O(2)	0.82	1.72	2.462(10)	149.4
N(4)—H(4)···O(2)#1	0.86	2.60	3.281(11)	136.5
N(4)—H(4)···O(1)#1	0.86	1.87	2.704(8)	163.4
N(2)—H(2)···N(3)	0.86	1.98	2.825(9)	168.0
3				
O(8)—H(8F)···O(1)#2	0.85	1.96	2.810(3)	179.1
O(8)—H(8E)···O(1)	0.85	1.96	2.810(4)	179.0
O(7)—H(7D)···S(1)#3	0.85	2.82	3.527(2)	142.1
O(7)—H(7D)···O(6)#3	0.85	2.01	2.854(3)	171.2
O(7)—H(7C)···O(5)#4	0.85	1.96	2.805(3)	171.1
O(3)—H(3A)···O(2)	0.82	1.81	2.535(3)	146.2
N(4)—H(4)···O(8)#3	0.86	1.79	2.646(4)	175.5
N(3)—H(3)···O(2)	0.86	1.82	2.638(3)	159.0
N(2)—H(2)···O(7)#5	0.86	1.90	2.756(3)	174.8
4				
O(1)—H(1)···O(3)#1	0.82	1.81	2.6195(18)	169.6
N(2)—H(2)···O(4)#2	0.86	1.82	2.6207(18)	154.5
N(1)—H(1A)···O(3)#3	0.86	1.89	2.7152(18)	159.9

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

usual intramolecular hydrogen bond is found between the phenol OH group and a carboxylate O atom (O(2)—H(2A)···O(3), 2.453(6) Å, 155.3°) which is similar to the corresponding value (2.409 Å) in proton-transfer compound of [(hmt)$^+$ [(dnsa)$^-$] [43,44]. Yet the value is as expected generally smaller than the

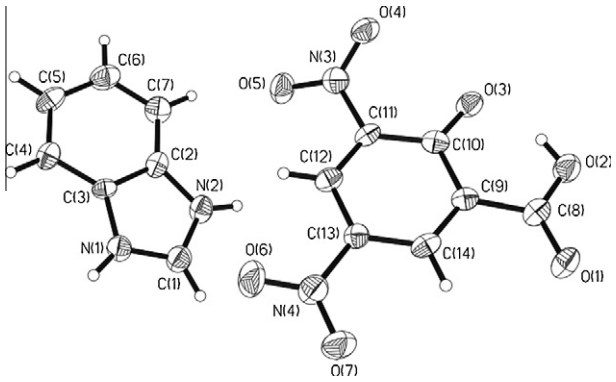


Fig. 1. The structure of **1**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

distance found for the parent dnsa acid monohydrate [2.566(3) Å] [45], and in the neutral species found in the adduct compound. For the presence of the intramolecular hydrogen bond, there also exists hydrogen bonded motif with graphical descriptor of $S_1^1(6)$.

One anion is bonded to one cation via the bifurcate N—H···O hydrogen bonds arising from the NH group, the phenolate and the 3-nitro group with N—O distances of 2.750(7)–3.052(8) Å, and CH—O contact between the phenyl CH of the benzimidazole and the same O atom of the 3-nitro group that has a N—H···O association with C—O distance of 3.389 Å to form a heteroadduct. Two adjacent heteroadducts were combined together by N—H···O hydrogen bond between the NH moiety and the carbonyl group of the anion with N—O distance of 2.832(7) Å, and CH—O contact between the N—CH—N of the cation and the OH group of the carboxyl unit with C—O distance of 3.066 Å to form a tetracomponent aggregate. In the tetracomponent aggregate the two cations and the two anions are symmetrily related. The tetracomponent aggregates were linked together by the CH—O association between the phenyl CH of the cation and the 5-nitro group of the anion with C—O distance of 3.256 Å, and O—O association between the 3-nitro groups with O—O separation of 3.017 Å to form a 1D chain. The 1D chains were further joined together by the interchain CH—O interaction between the phenyl CH of the cation and the 5-NO_2 group of the dnsa$^-$ with C—O distance of 3.419 Å to form 2D sheet extending along the direction that made an angle of 45° with the bc plane (Fig. 2). The 2D sheets were further stacked along the direction that is perpendicular with its extending direction through the O–π association between the 3-nitro group of the anion and the aromatic ring of the cation with O—Cg distance of 3.186 Å to form 3D ABAB layer network structure. Herein the neighboring sheets were slipped some distance along its extending direction, while the third sheet has the same projection as the first sheet on its extending plane, so does the second sheet and the fourth sheet.

3.3. X-ray structure of (benzimidazole)$_2$:(5-nitrosalicylic acid) [(HL1)$^+$·(L1)·(5-nsa$^-$), 5-nsa$^-$ = 5-nitrosalicylate], (**2**)

Similar to **1**, compound **2** was also prepared by reacting of a methanol solution of benzimidazole and 5-nitrosalicylic acid in 1:1 ratio, which crystallizes as triclinic pale yellow crystals in the centrosymmetric space group P-1. The asymmetric unit of **2** consists of one protonated L1, one neutral L1, and one 5-nitrosalicylate anion, as shown in Fig. 3. Compound **2** is also a salt where the COOH group of one 5-nitrosalicylic acid is deprotonated, which is confirmed by the pairs of bond distances of O(1)—C(15) (1.260(11) Å), and O(2)—C(15) (1.273(10) Å) for the carboxylate.

In the solid state, there is consistently hydrogen bond formed between the NH group, and the 5-nitrosalicylate ion, which is to be expected [46]. There also exist strong coulombic 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), 2.462(10) Å,), it is generally expected and found that the carboxylate group is nearly coplanar with the benzene ring [torsion angle C17—C16—C15—O1, 175.42°]. There exists a hydrogen bonded $S_1^1(6)$ ring in the anion. This feature is similar to that found in salicylic acid [47], and in the previously reported structure of proton-transfer compound based on 5-nsa$^-$ [48]. As expected the O—O separation is in the lower limit of the documented data [2.489–2.509 Å] [48], but it is somewhat 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 C19—C20—N5—O5, 178.41°] compared with the reported torsion angle (175.4–180°) within this set of compounds [48].

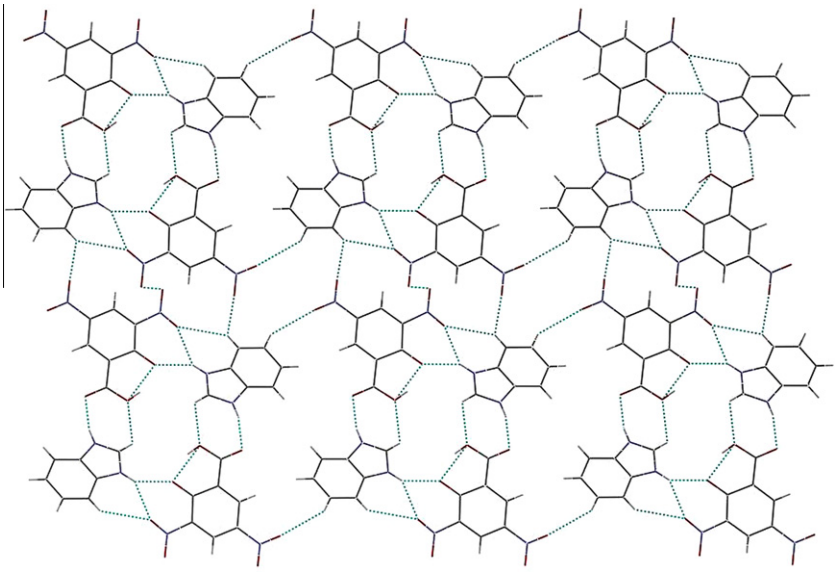


Fig. 2. 2D sheet structure of **1** extending along the direction that made an angle of 45° with the bc plane.

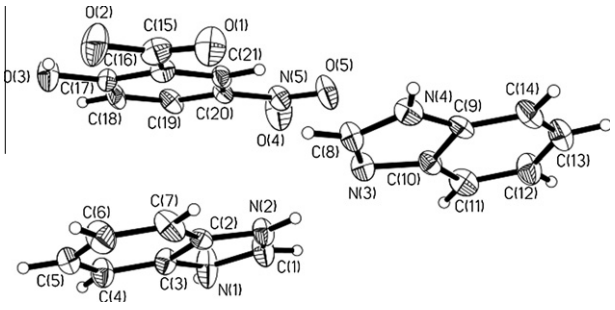


Fig. 3. The structure of **2**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

The anion was bonded to the neutral L1 via the bifurcated N—H···O association between the uncharged NH moiety of L1 and both O atoms of the carboxylate with N—O distances of 2.704(8)–3.281(11) Å, and CH—O contact between the phenyl CH of L1 and one O atom of the carboxylate with C—O distance of 3.417 Å to form a bicomponent adduct. At the adduct there was bonded a cation by the N—H···N hydrogen bond with N—N separation of 2.825(9) Å to produce a tricomponent aggregate. The tricomponent aggregates were linked together by the CH—O associations to form 1D grid structure. The grids were stacked along the direction that is perpendicular to its extending direction via the π–π interactions between the aromatic rings of the cation and the anion with Cg—Cg distance of 3.363 Å to form 3D network structure (Fig. 4). In this regard the adjacent grids were slipped about half the width of the grid from each other.

*3.4. X-ray structure of (benzimidazole):1-(2-(1H-benzimidazol-1-yl)ethyl)-1H-benzimidazole:(5-sulfosalicylic acid):4H_2O [$(HL1^+)_2\cdot(H_2L2)^{2+}\cdot(5\text{-}ssa^{2-})_2\cdot 4H_2O$, 5-$ssa^{2-}$ = 5-sulfosalicylate], (**3**)*

The asymmetric unit of **3** consists of one monocation of benzimidazole, half a dication of 1-(2-(1H-benzimidazol-1-yl)ethyl)-1H-benzimidazole, one dianion of 5-ssa^{2-}, and two water molecules as shown in Fig. 5. The C—O distances of the COO^- of 5-sulfosalicylate are ranging from 1.246(3) (O(1)═C(16)) to 1.266(4) Å (O(2)—C(16)) Å with the Δ value of 0.020 Å, which suggests that the carboxylate group is deprotonated. 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. The S-O distances in SO_3^- are ranging from 1.437(2) Å to 1.460(2) Å (Δ is 0.023 Å) with the average value of 1.448 Å which is in the range of the deprotonated SO_3H moiety

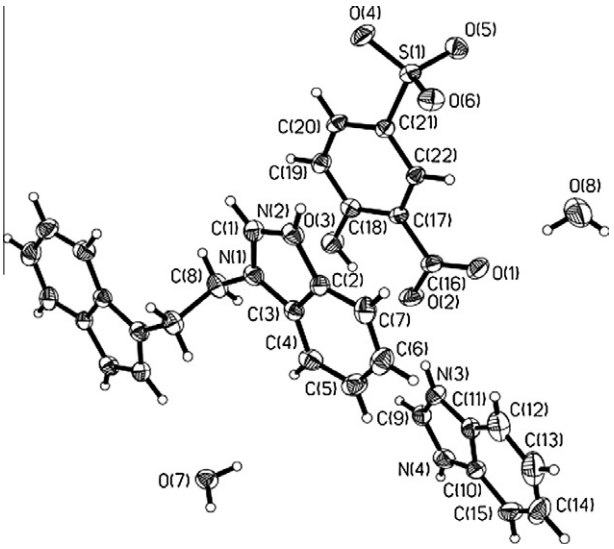


Fig. 5. The structure of **3**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

(1.435(2)–1.4599(17) Å) [49]. The O—S—O angles in SO_3^- are ranging from 111.74(13)°–113.10(13)° with the average value of 112.42° which is in the range of the deprotonated SO_3H moiety also [49]. The phenol group remains unionized which is evidenced by the C18—O3 bond distance of 1.349(3) Å. The H_2L2 cations display trans conformation.

At the L2 cation there were bonded two water molecules via the N—H···O hydrogen bond. The 5-sulfosalicylates were bonded with the L1 cation through the N—H···O association arising from the carboxylate with N—O distance of 2.638(3) Å. Two L1 cations were attached to one L2 cation by the CH–π interaction between the phenyl CH of the L2 cation and the aromatic ring of the L1 cation with C—Cg distance of 3.430 Å to form a seven-component adduct. In the seven-component adduct there existed an inversion center located at the middle point of the ethane bridge of the L2 cation. The seven-component adducts were joined together by the O—H···O hydrogen bond between the water molecule and the carboxylate with O—O separation of 2.810(3) Å, CH—O interaction between the N—CH—N of L1 and the sulfonate with C—O distance of 3.084 Å, CH—O interaction between the N—CH—N of L2 and the water molecule with C—O distance of 3.329 Å, and O–π association between the sulfonate and the aromatic moiety of the L1 with O—Cg distance of 3.203 Å to form 2D sheet extending along the bc plane (Fig. 6). The width of the sheet is ca. two times the length of the c axis. There are no contacts between the sheets extending at

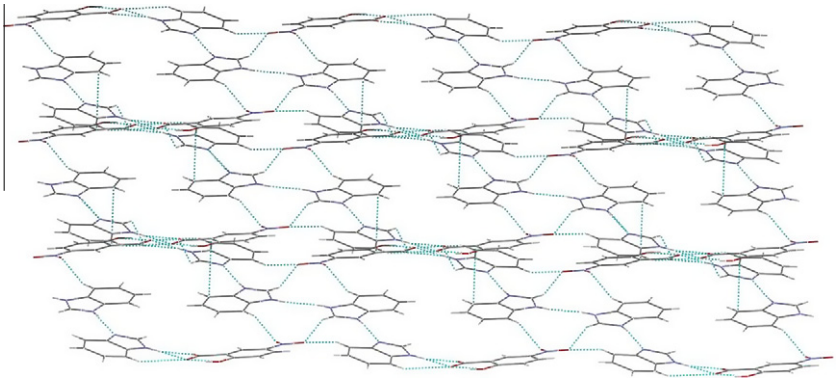


Fig. 4. 3D network structure of **2** formed by the grids via the π–π interactions.

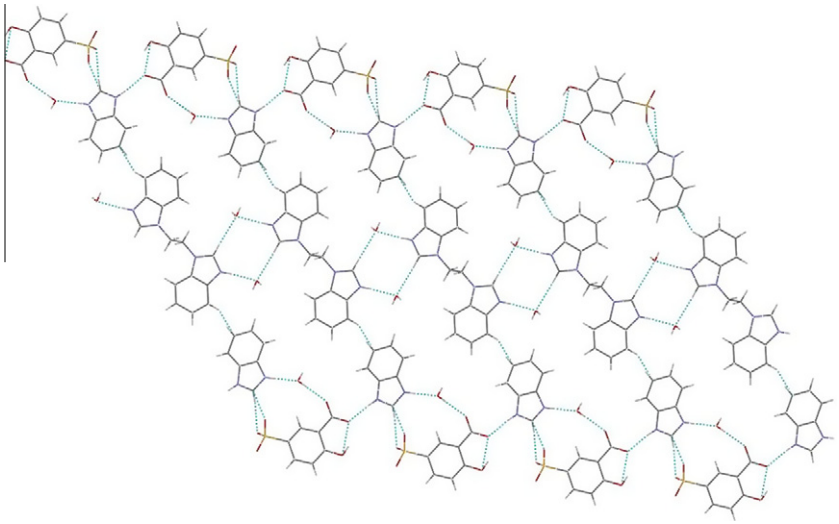


Fig. 6. 2D sheet structure of **3** which is extending in the direction that made an angle of ca 45° with the bc plane.

the same plane. The sheets were further stacked along the a axis direction via the O—H···O hydrogen bonds (between the water molecules attached to the L2 cation and the sulfonate with O—O distances of 2.805(3)–2.854(3) Å), O—H···S hydrogen bond (between the water molecule and the S atom of the sulfonate with O-S distance of 3.527(2) Å), CH—O associations (between the phenyl CH of the cation, the sulfonate, and the carboxylate unit with C—O distances of 3.359–3.451 Å), CH_2—O interaction (between the CH_2 of the ethane spacer and the sulfonate with C—O distance of 3.481 Å), O–π association (between the sulfonate and the aromatic ring of L2 with O—Cg distance of 2.903 Å), and π–π interaction with Cg—Cg distances of 3.183–3.397 Å to form 3D network structure.

3.5. X-ray structure of (benzimidazole):(1,4-cyclohexanedicarboxylic acid) [($HL1^+$)·($HChda^-$)], (4)

Crystallization of benzimidazole and 1,4-cyclohexanedicarboxylic acid in a 1:1 ratio from the mixed solvent of methanol and ethanol gave single crystals suitable for X-ray diffraction. In the compound **4** only one proton of the 1,4-cyclohexanedicarboxylic acid was transferred to the ring N atom of the L1. Thus **4** is also an organic salt. In the asymmetric unit of **4** there existed one cation of L1, and one monoanion of 1,4-cyclohexanedicarboxylic acid, as shown in Fig. 7.

The C—O distances of COO^- (C(2)—O(3)—O(4)) group of the 1,4-cyclohexanedicarboxylic acid are ranging from 1.243(2) (O(4)—C(2)) to 1.2721(19) Å (O(3)—C(2)) with the Δ value of 0.0291 Å. The C—O distances of the other COOH (O(1)—C(1)—O(2)) group of the 1,4-cyclohexanedicarboxylic acid are ranging from 1.202(2) (O(2)—C(1)) to 1.318(2) Å (O(1)—C(1)) with the Δ value of 0.116 Å. The differences in bond distances between the two pairs of C—O bond distances in the carboxyl group further confirm our correct assignment of the H atom attached to the carboxyl unit. Herein the 1,4-cyclohexanedicarboxylic acid molecules adopt chair conformation with the two carboxyl units in e, e positions, respectively.

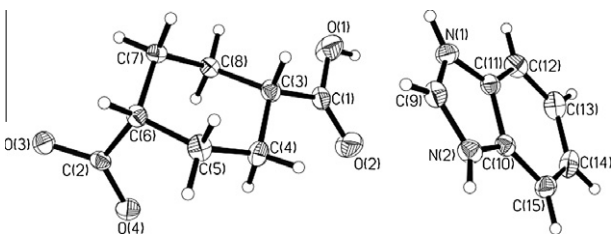


Fig. 7. The structure of **4**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

The anions form a 1D wave chain extending along the *c* axis direction via the intermolecular COOH···$^-$OOC contacts with O—O distance of 2.6195(18) Å. In the same chain the cyclohexane rings of adjacent anions are almost perpendicular to each other, while the cyclohexane ring of the third anion is parallel to the cyclohexane ring of the first anion, so does the cyclohexane ring of the second anion and the cyclohexane ring of the fourth anion. The chains were combined together by the CH—O association between the CH of the anion and the O atom of the carboxylate that is not involved in O—H···O hydrogen bond with C—O distance of 3.548 Å to form 2D corrugated sheet extending parallel to the ac plane. The cations also generated 1D chain running along the a axis direction via the offset π–π association with Cg—Cg distance of 3.376 Å. The cationic chains were connected to the anionic sheet by the N—H···O hydrogen bond between the NH unit of the cation and the carboxylate with N—O distance of 2.6207(18) Å, CH_2–π interaction between the CH_2 moiety of the anion and the benzimidazole ring of the cation with C—Cg distance of 3.552 Å (Fig. 8). In this case the cations in the same chain were parallel to each other, while the cations at different chains were almost perpendicular to each other. An alternative reading of this structure is possible when we emphasize the relative arrangement of the cations and the anions, i.e., the cations were intercalated between the anionic sheets to produce 3D ABAB layer network structure.

4. Conclusion

Four organic salts have been prepared and structurally characterized. All four examples involve proton transfer from the carboxylic acids to the N atom of benzimidazole moiety, with subsequent hydrogen bonding linking the cation and the anion to give 3D framework structures (3D network structure, and 3D ABAB layer structure) in all cases. It is worthy to note that both the sulfonic proton and the carboxyl H are deprotonated for the salt based on 5-sulfosalicylic acid. While for the salt **1**, only phenol group has ionized.

This study has demonstrated that the N—H···O hydrogen bond is the primary intermolecular force in a family of structures

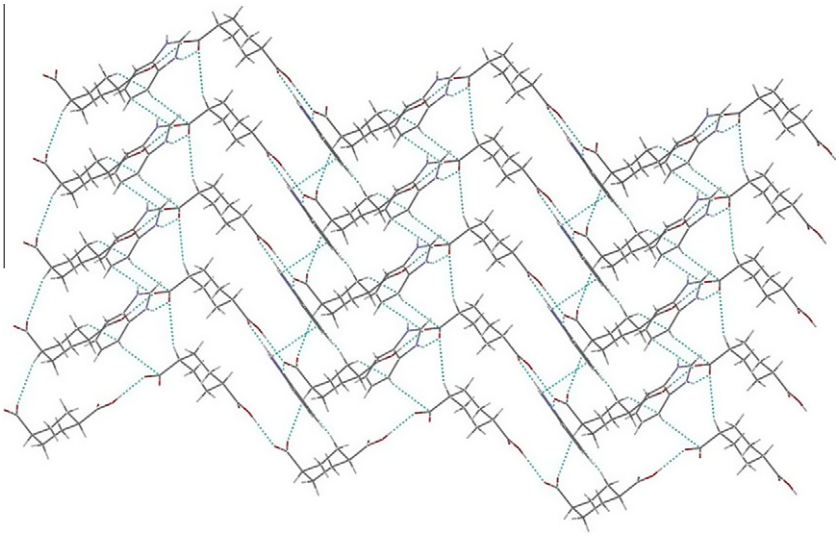


Fig. 8. The arrangement of the cations and the anions in **4**.

containing the COOH···im synthons. Since the potentially hydrogen bonding phenol hydroxyl group is present in the ortho position to the carboxylate group in **1**–**3**, it forms the more facile intramolecular O—H···O hydrogen bond. Except the classical hydrogen bonding interactions, the secondary propagating interactions also play important role in structure extension. All products possess weak C—H···O associations. Two C—H···O hydrogen bond type interactions were observed based upon their geometric preferences, intra- and interchain interactions. From an analysis of the metrics displayed by each set of interactions, it seems that intra- and interchain C—H···O interactions are of equal structural importance. There are π–π interactions in compounds **2**, **3**, and **4**. Organic salts **1**, and **3** possess O–π interactions with the O—Cg distances in the range of 2.903–3.203 Å. These interactions are responsible for the supramolecular assembly of benzimidazole group and carboxylic acids into salts, with desired connectivities.

In conclusion, we have shown that 3D structures containing strong hydrogen bond interactions or mixture of strong and weak hydrogen bond interactions can be constructed and the structure may be modulated to have nonplanar structure by functional groups on planar system.

Supporting information available

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic data center, CCDC Nos. 874224 for **1**, 851646 for **2**, 851938 for **3**, and 867638 for **4**. 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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