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ORIGINAL PAPER

Crystal and Molecular Structure of Two Organic Acid–Base Salts from Nicotinamide and Aromatic Acids

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Abstract Two crystalline organic acid–base salts (nicotinamide):(3,5-dinitrosalicylic acid) [$(HL^+)\cdots(3,5\text{-dns}^-)$, $3,5\text{-dns}^- = 3,5$-dinitrosalicylate] **(1)**, and (nicotinamide):(4-nitro-phthalic acid) [$(HL^+)\cdots(Hnpa^-)$, $Hnpa^- = 4$-nitro-hydrogenphthalate] **(2)** derived from nicotinamide and aromatic carboxylic acids (3,5-dinitrosalicylic acid, and 4-nitro-phthalic acid) were prepared and characterized by X-ray diffraction analysis, IR, mp, and elemental analysis. Compound **1** crystallizes in the monoclinic, space group P2(1)/c, with a = 4.7950(3) Å, b = 22.290(2) Å, c = 14.3901(13) Å, $\beta = 104.861(2)^\circ$, V = 1486.6(2) $Å^3$, Z = 4. Compound **2** crystallizes in the monoclinic, space group P2(1)/c, with a = 15.0173(14) Å, b = 12.9849(13) Å, c = 7.7281(6) Å, $\beta = 111.6040(10)^\circ$, V = 1401.1(2) $Å^3$, Z = 4. Both supramolecular architectures of the compounds **1**–**2** involve O–H···O/N–H···O hydrogen bonds as well as other noncovalent association. The role of these noncovalent interactions in the crystal packing is ascertained. For the presence of these weak noncovalent interactions, both compounds displayed 3D framework structure.

Keywords Crystal structure · Hydrogen bonding · Noncovalent interactions · Organic salts · Nicotinamide · Aromatic acids

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Introduction

Intermolecular interactions are responsible for crystal packing and gaining an understanding of them allows us to comprehend collective properties and permits the design of new crystals with specific physical and chemical properties [1]. Intermolecular forces, such as hydrogen bonding, π–π stacking, CH–π/CH_2–π/CH_3–π interactions, CH–O/CH_2–O/CH_3–O interactions, ion pairing, and donor–acceptor interactions are well-known for making aggregates of molecules and linking discrete molecular building blocks or low-dimensional structures into high-dimensional supramolecular frameworks [2–7]. Hydrogen bonding is one of the most important noncovalent interactions that determines and controls the assembly of molecules and ions [8–11].

In recent years, efforts have been made to explore the synthesis of multicomponent supermolecules or supramolecular arrays utilizing noncovalent bonding. Thus, the supramolecular synthesis successfully exploits hydrogen-bonding and other types of non-covalent interactions, in building supramolecular systems [12]. In this regard, there are many interesting topological structures such as one-dimensional (1D) tapes, two-dimensional (2D) sheets, and three-dimensional (3D) networks which have been constructed through hydrogen bonding interactions [13, 14]. The carboxylic acids are capable of functioning as hydrogen bond donors and/or acceptors resulting in supramolecular frameworks by intermolecular hydrogen bond interactions and have been widely utilized in crystal engineering [15]. Carboxylic acids aggregate in the solid state as dimer, catemer, and bridged motifs [16–23]. It is interesting to exploit the robust and directional recognition of carboxylic acids with *N*-containing heterocyclic compounds [24–28].

Nicotinamide is one of the widely used cocrystal formers, as it is not only classified as a GRAS substance

but also contains two well-known hydrogen-bonding groups (pyridine N and amide) in the structure [29]. Some adducts have been successfully prepared from nicotinamide and carboxylic acids [30–32]. However, although both pyridine N and amide of nicotinamide are able to generate reliable synthons with carboxylic group, only few organic salts of nicotinamide have been documented [33–35]. The organic salts from isonicotinamide are also very rare in the literature [36].

Therefore, it is important to investigate supramolecular interactions between nicotinamide and carboxylic acids by cocrystallization, herein we report the preparation and structures of two organic acid–base salts assembled from nicotinamide (L) and the corresponding carboxylic compounds (Scheme 1), respectively. The two organic salts are (nicotinamide):(3,5-dinitrosalicylic acid) [$(HL^+)\cdots(3,5\text{-}dns^-)$, 3,5-$dns^-$ = 3,5-dinitrosalicylate] **(1)**, and (nicotinamide):(4-nitro-phthalic acid) [$(HL^+)\cdots(Hnpa^-)$, $Hnpa^-$ = 4-nitro-hydrogenphthalate] **(2)** (Scheme 2).

Experimental Section

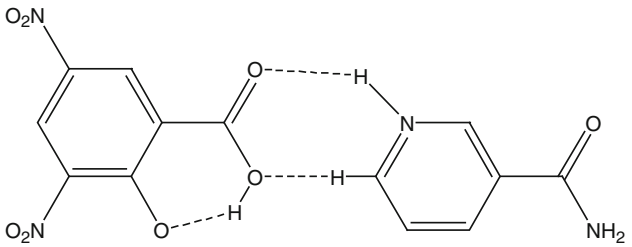
Materials and Physical Measurements

The chemicals and solvents used in this work are of analytical grade and available commercially and were used without further purification. The FT-IR spectra were recorded from KBr pellets in range 4,000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Microanalytical (C, H, and N) data were obtained with a Perkin–Elmer Model 2400II elemental analyzer. Melting points of new compounds were recorded on an XT-4 thermal apparatus without correction.

Preparation of the Organic Acid–Base Salts **1–2**

*(Nicotinamide):(3,5-Dinitrosalicylic Acid) [$(HL^+)\cdots(3,5\text{-}dns^-)$] (**1**)*

A solution of 3,5-dinitrosalicylic acid (22.8 mg, 0.1 mmol) in methanol (10 ml) was added dropwise to a vigorously stirred solution of nicotinamide (12.2 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 [$(HL^+)\cdots(3,5\text{-}dns^-)$] (**1**). (yield: 28 mg, 79.94 %). mp 154–155 °C. Elemental analysis: Calc. for $C_{13}H_{10}N_4O_8$ (350.25): C, 44.54; H, 2.86; N, 15.99. Found: C, 44.48; H, 2.83; N, 15.95. Infrared spectrum (cm^{-1}): 3,698s(ν(OH), 3,463s(ν_{as}(NH)), 3,359s(ν_s(NH)), 3246m, 3198m, 2971m, 2866m, 1695s(ν_{as}(C=O)), 1634s, 1603m, 1572m, 1528s($\nu_{as}(NO_2)$), 1426m, 1401s, 1354m, 1317s(νs(NO_2)), 1286s(νs(C–O)), 1217m, 1169s, 1094m, 1038w, 956w, 856m, 789w, 697m, 651w, 608m.



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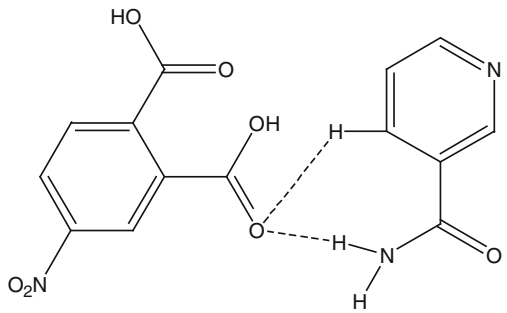

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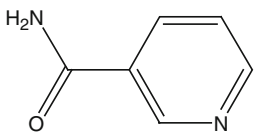
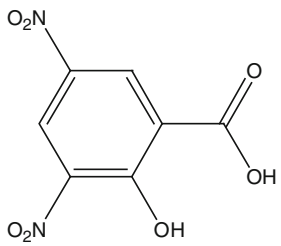
Scheme 2 The two organic acid–base salts described in this paper, **1–2**

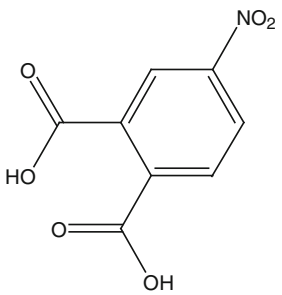
Scheme 1 Hydrogen bond tectons discussed in this paper



nicotinamide



3,5-dinitrosalicylic acid



4-nitro-phthalic acid

*(Nicotinamide):(4-Nitro-Phthalic Acid) [(HL^+)···($Hnpa^-$)] (**2**)*

A solution of 4-nitro-phthalic acid (21.1 mg, 0.1 mmol) in methanol (8 ml) was added dropwise to a vigorously stirred solution of nicotinamide (12.2 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 [(HL^+)···($Hnpa^-$)] (**2**). (yield: 26 mg, 78.02 %). mp 142–144 °C. Elemental analysis: Calc. for $C_{14}H_{11}N_3O_7$ (333.26): C, 50.41; H, 3.30; N, 12.60. Found: C, 50.33; H, 3.28; N, 12.54. Infrared spectrum (cm^{-1}): 3,679s(ν(OH)), 3,482s(multiple, ν_{as}(NH)), 3,348s(ν_s(NH)), 3268m, 3138m, 3047m, 2989m, 2927m, 2847m, 1728s(ν(C=O)), 1638m, 1596s($\nu_{as}(COO^-)$), 1558m, 1522s($\nu_{as}(NO_2)$), 1474s, 1423s, 1377s($\nu_s(COO^-)$), 1,324s(νs(NO_2)), 1,291s(ν(C–O)), 1241m, 1193m, 1145m, 1091m, 1053m, 999m, 928m, 863m, 804m, 743m, 679m, 614m.

X-Ray Crystallography and Data Collection

Suitable crystals were mounted on a glass fiber on a Bruker SMART 1000 CCD diffractometer operating at 50 kV and 40 mA using Mo Kα radiation (0.71073 Å). Data collection and reduction were performed using the SMART and SAINT software [37]. 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 [38].

Hydrogen atoms for the two structures were placed in calculated positions using riding models. Further details of the structural analysis are summarized in Table 1. Selected bond lengths and angles for the compounds **1**–**2** are listed in Table 2, the relevant hydrogen bond parameters are provided in Table 3.

Results and Discussion

Preparation and General Characterization

The preparation of compounds **1**–**2** were carried out with nicotinamide and the corresponding carboxylic acids in 1:1 ratio in the methanolic solution, which was allowed to evaporate at ambient conditions to give the final crystalline products. In both structures of **1** and **2** the heteroaromatic Lewis base molecules are protonated, therefore these structures can be classified as organic salts. The two compounds are not hygroscopic. The molecular structures and their atom labelling schemes for the two structures are illustrated in Figs. 1 and 3, respectively. The elemental analysis data for the two crystalline compounds are in good agreement with their compositions. The infrared spectra of the two compounds are consistent with their chemical formulas determined by elemental analysis and further confirmed by X-ray diffraction analysis. In **1**, only the phenol group has ionized. In **2**, only one proton of the carboxyl units has transferred to the ring N atom of nicotinamide molecule to form the corresponding hydrogen carboxylate salt. Thus the acids in both **1** and **2** present the valence number of −1.

The bands at approximately 3,700–3,100 cm^{-1} in the IR spectra of the two compounds arise from O–H or N–H stretching frequencies. Pyridinic ring stretching and bending are attributed to the medium intensity bands in the regions of 1,500–1,630 and 600–750 cm^{-1}, respectively. Compound **1** bears characteristic bands for COOH groups only, while the salt **2** exhibits the characteristic bands for both COO^- and COOH groups. IR spectroscopy has also proven to be useful for the recognition of proton transfer compounds [39, 40]. The most distinct feature in the IR spectrum of proton transfer compounds are the presence of strong asymmetrical and symmetrical carboxylate stretching frequencies at 1,550–1,610 and 1,300–1,420 cm^{-1} respectively in the compound **2**.

Structural Descriptions

*X-Ray Structure of (Nicotinamide):(3,5-Dinitrosalicylic Acid) [(HL^+)···(3,5-dns^-)] (**1**)*

Crystallization of nicotinamide and 3,5-dinitrosalicylic acid in a 1:1 ratio from the methanol gave single crystals suitable for X-ray diffraction. Structure determination (Table 1) revealed that nicotinamide and 3,5-dinitrosalicylic acid are present in a 1:1 ratio in the molecular complex **1**. The crystal structure of **1** consists of one monoprotonated L, and one monoanion of 3,5-dinitrosalicylic acid in the asymmetric unit (Fig. 1). Compound **1** crystallizes in the Monoclinic space group P2(1)/c. Different from the salt of isonicotinamide and 3,5-dinitrosalicylic acid [36], in **1** the OH groups of 3,5-dinitrosalicylic acids are ionized by proton transfer to the ring nitrogen atoms of the nicotinamide moieties, and the COOH group remains protonized. The O atom of the phenolate are disordered over two positions with equal occupancies of 0.5, respectively. There are some differences between **1** and the documented data [35]. One different is that the volume of the unit cell in **1** was somewhat larger that the reported structure. The other difference lies in the fact in **1** all oxygen atoms were not refined isotropically, while in the

Table 1 Summary of X-ray crystallographic data for complexes **1**, and **2**

	1	**2**
Formula	$C_{13}H_{10}N_4O_8$	$C_{14}H_{11}N_3O_7$
Fw	350.25	333.26
T, K	298(2)	298(2)
Wavelength, (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/c
a, (Å)	4.7950(3)	15.0173(14)
b, (Å)	22.290(2)	12.9849(13)
c, (Å)	14.3901(13)	7.7281(6)
α, deg.	90	90
β, deg.	104.861(2)	111.6040(10)
γ, deg.	90	90
V, Å^3	1486.6(2)	1401.1(2)
Z	4	4
D_{calcd}, (mg/m^3)	1.565	1.580
Absorption coefficient, (mm^{-1})	0.133	0.130
F(000)	720	688
Crystal size, (mm^3)	0.46 × 0.17 × 0.126	0.42 × 0.39 × 0.13
θ range, deg	2.93–25.01	2.92–28.59
	$-5 \le h \le 5$	$-19 \le h \le 12$
Limiting indices	$-25 \le k \le 26$	$-17 \le k \le 15$
	$-17 \le l \le 9$	$-10 \le l \le 10$
Reflections collected	6,688	8,748
Reflections independent (R_{int})	2,599(0.1196)	3,497(0.0526)
Goodness-of-fit on F^2	1.073	0.961
R indices [$I > 2\sigma I$]	0.1204, 0.2797	0.0541, 0.1239
R indices (all data)	0.1994, 0.3298	0.1065, 0.1465
Largest diff. peak and hole, e.Å^{-3}	0.352, −0.474	0.288, −0.268

documented structure some O atoms were refined isotropically [35].

The C–O distances 1.328(10) Å (O(4)–C(9)), and 1.34(2) Å (O(4′)–C(13)) concerning the phenolate are longer than the proton transfer compound bearing the 3,5-dns$^-$ in which only the phenol group has been deprotonated [35, 41]. In the COOH group, two C–O bond lengths are obviously different between O(2)–C(7) (1.240(8) Å), and O(3)–C(7) (1.287(9) Å) with the Δ value of 0.047 Å. The relatively larger Δ value which is expected for neutral C=O and C–O bond distances [42] are also confirming the reliability of adding H atoms experimentally by different electron density onto O atoms (Table 3).

Protonation of the nicotinamide base on N2 site is reflected in a change in bond angle. The angle at unprotonated ring N atom is 118.56(13)° [43], while for protonated N the angle (C(6)–N(2)–C(2)) is 123.5(7)°. The torsion angles O6–N3–C10–C9, and O8–N4–C12–C11 are 174.40°, and 170.97°, respectively. In this regard, both nitro groups are nearly in the same plane as the benzene ring of the anion, yet the 3-nitro (O8–N4–O7, 8.7°) deviates somewhat more from the plane than the 5-nitro (O6–N3–O5, 5.1°) group, which is similar with the published results [44]. The rms deviation of the pyridine ring in the cation is 0.0034 Å, the amide group deviates by 27.5° from the pyridine ring plane. The rms deviation of the phenyl ring in the anion is 0.0102 Å, the interplane angle between the aromatic rings of the anion and the cation is 9.5 Å.

Since the potentially hydrogen bonding carboxyl group is present in the *ortho* position to the phenolate group in the anion, it forms the more facile intramolecular hydrogen bonding. Thus the usual intramolecular hydrogen bond is found between the phenolate group and a carboxyl OH (O3–H3···O(4), 2.451 Å, 155.05°) which is similar to the corresponding value (2.409 Å) in proton-transfer compound of [(hmt)$^+$ [(dnsa)$^-$] [45, 46]. Yet the value is as expected generally smaller than the distance found for the parent dnsa acid monohydrate [2.566(3) Å] [47], and in the neutral species found in the adduct compound. For the presence of the intramolecular hydrogen bond, there also

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

1			
N(1)–C(1)	1.327(9)	N(2)–C(2)	1.339(9)
N(2)–C(6)	1.364(10)	N(3)–O(5)	1.210(9)
N(3)–O(6)	1.225(9)	N(3)–C(10)	1.433(10)
N(4)–O(8)	1.205(9)	N(4)–O(7)	1.252(9)
N(4)–C(12)	1.491(9)	O(1)–C(1)	1.253(8)
O(2)–C(7)	1.240(8)	O(3)–C(7)	1.287(9)
O(4)–C(9)	1.328(10)	O(4′)–C(13)	1.34(2)
C(2)–N(2)–C(6)	123.5(7)	O(5)–N(3)–O(6)	121.2(8)
O(1)–C(1)–N(1)	123.6(7)	O(2)–C(7)–O(3)	122.8(7)
2			
N(1)–C(6)	1.331(3)	N(1)–C(2)	1.334(3)
N(2)–C(1)	1.323(3)	N(3)–O(6)	1.213(3)
N(3)–O(7)	1.217(3)	N(3)–C(12)	1.474(3)
O(1)–C(1)	1.218(3)	O(2)–C(7)	1.257(3)
O(3)–C(7)	1.240(3)	O(4)–C(8)	1.206(3)
O(5)–C(8)	1.304(3)	C(6)–N(1)–C(2)	122.0(2)
O(6)–N(3)–O(7)	124.0(2)	O(1)–C(1)–N(2)	122.4(2)
O(3)–C(7)–O(2)	125.5(2)	O(4)–C(8)–O(5)	124.8(2)

exists hydrogen bonded motif with graphical descriptor of $S_1^1(6)$. The cation adopted the E conformation according to Borba et al. [48], in which the torsion angle of C2–C3–C1–O1 (151.39°) is comparable to the corresponding angle (150.58°) in the reported salt [35].

One anion and one cation formed a heteroadduct via the N–H···O hydrogen bond between the NH^+ cation and the carbonyl unit with N···O distance of 2.650(8) Å, and CH···O association between the 6-CH of the cation and the OH moiety in the COOH of the anion with C–O distance of 3.251 Å. Two neighboring heteroadducts were joined together via the N–H···O hydrogen bond between the amide group and the 5-nitro group of the anion with N···O separation of 3.074(9) Å, and CH···O interaction between the 2-CH of the cation and the same O atom at the 5-nitro group that is hydrogen-bonded with the amide group with C···O distance of 3.576 Å to form a tetracomponent aggregate. In the tetracomponent aggregate, the corresponding anions and the cations were inversionally related. The tetracomponent aggregates were linked together by the N–H···O hydrogen bond between the amide group and the 3-nitro group of the anion with N···O separation of 3.032(8) Å to form 1D wave chain running along the c axis direction. The 1D wave chains were joined together by the interchain CH···O association between the 6-CH of the cation and the carbonyl unit of the cation with C···O distance of 3.306 Å, and O···π interaction between the phenolate and the aromatic ring of the cation with O···Cg distance of 3.101 Å to form 2D corrugated sheet (Fig. 2). Herein the plane defined by the two neighboring chains were almost perpendicular with each other, while the first chain was parallel to the third chain, so did the second chain and the fourth chain. The sheets were further stacked along the a axis direction via the intersheet O···π interaction (between the 5-nitro group of the anion and the phenyl ring of the anion with O···Cg distance of 3.192 Å, and between the carbonyl group of the cation and the aromatic ring of the cation with O···Cg distance of 3.090 Å), C(carbonyl)···π association between the C atom at COOH group of the anion and the phenyl ring of the anion with C···Cg distance of 3.394 Å, and N–H···O hydrogen bond between the amide group and the carbonyl group of the cations belonging to two adjacent sheets with N···O distance of 3.028(8) Å to form 3D network structure. In this regard, the neighboring sheets were slipped some distance from its extending direction.

Table 3 Hydrogen bond distances and angles in studied structures **1–2**

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
1				
N(2)–H(2)···O(2)#1	0.86	1.79	2.650(8)	176.0
N(1)–H(1B)···O(7)#2	0.86	2.39	3.074(9)	136.7
N(1)–H(1B)···O(1)#3	0.86	2.34	3.028(8)	137.7
N(1)–H(1A)···O(5)#4	0.86	2.19	3.032(8)	165.5
O3–H3···O(4)	0.82	1.683	2.451	155.05
2				
O(5)–H(5)···O(2)#1	0.82	1.74	2.526(2)	160.9
N(2)–H(2B)···O(4)	0.86	2.21	3.051(3)	166.7
N(2)–H(2A)···O(2)#2	0.86	2.25	3.087(3)	163.2
N(1)–H(1)···O(3)#3	0.86	1.79	2.624(2)	162.7

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

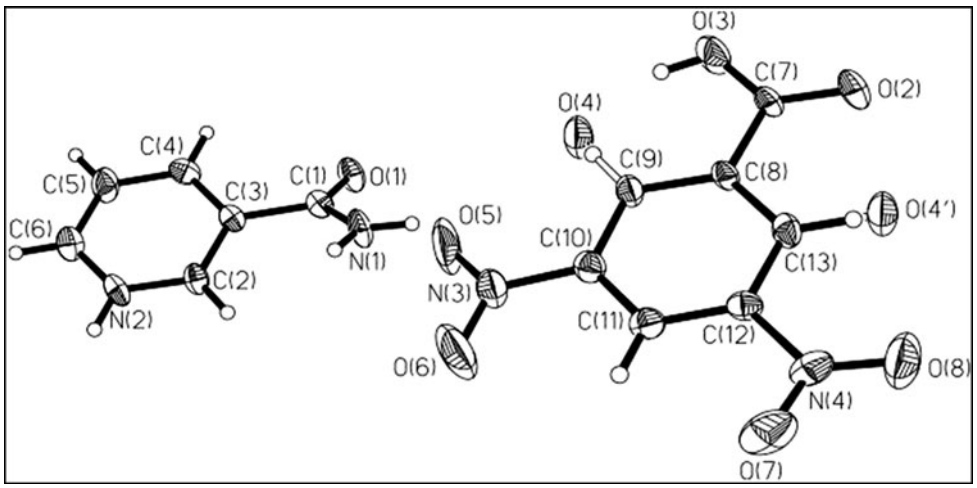


Fig. 1 Molecular structure of **1** showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30 % probability level

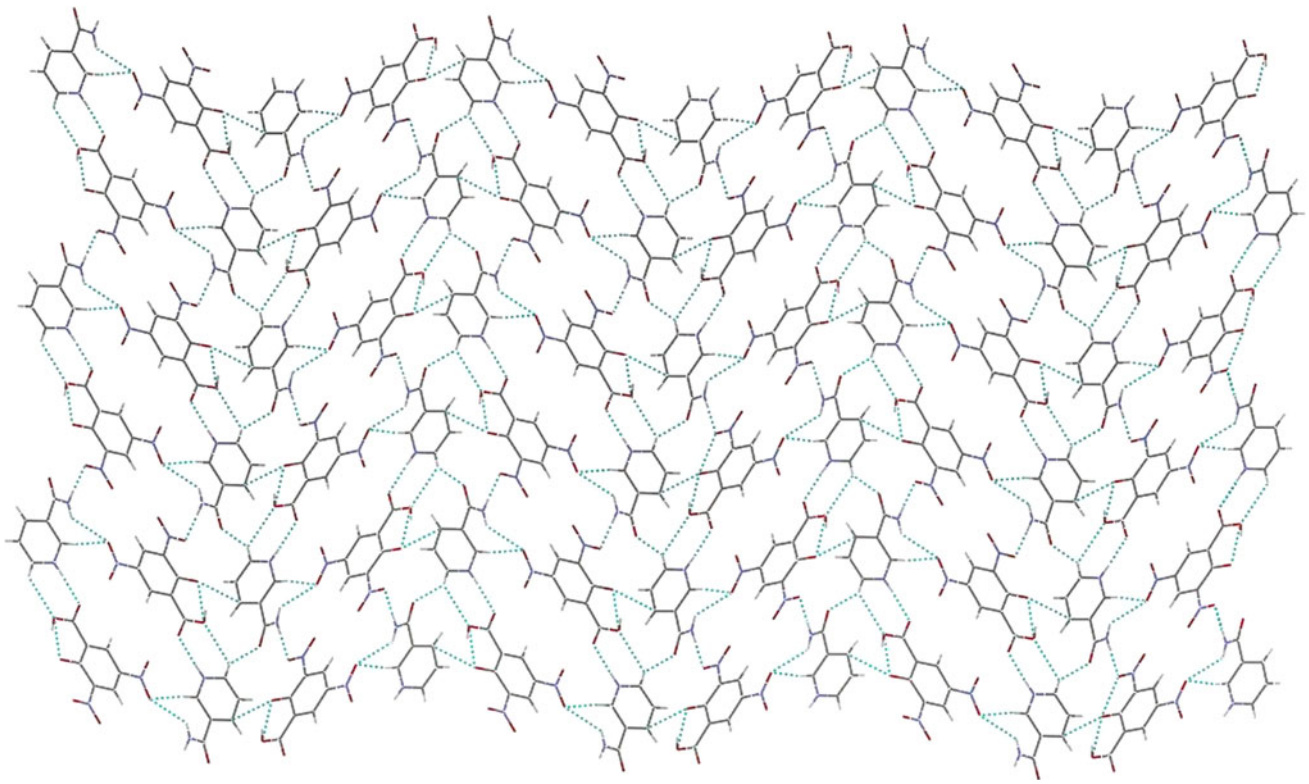


Fig. 2 2D corrugated sheet structure of **1**

*X-Ray Structure of (Nicotinamide):(4-Nitro-Phthalic Acid) [$(HL^{+})\cdots(Hnpa^{-})$] (**2**)*

Similar to **1**, the compound **2** of the composition [$(HL^{+})\cdots(Hnpa^{-})$] was prepared by reaction equal mol of nicotinamide and 4-nitro-phthalic acid. The crystal structure of **2** comprises one monocation of nicotinamide, and one monoanion of 4-nitro-phthalic acid in the asymmetric unit (Fig. 3). The compound is also a salt, in which only one proton of the two carboxyl groups in the 4-nitro-phthalic acid was ionized. Compound **2** crystallizes in the Monoclinic space group P2(1)/c. Its single crystal structure shows the expected proton transfer from the acid to the pyridyl nitrogen atom. Protonation of the nicotinamide base on N1 site is reflected in a change in bond angle. The angle at unprotonated ring N atom is 118.56(13)° [43],

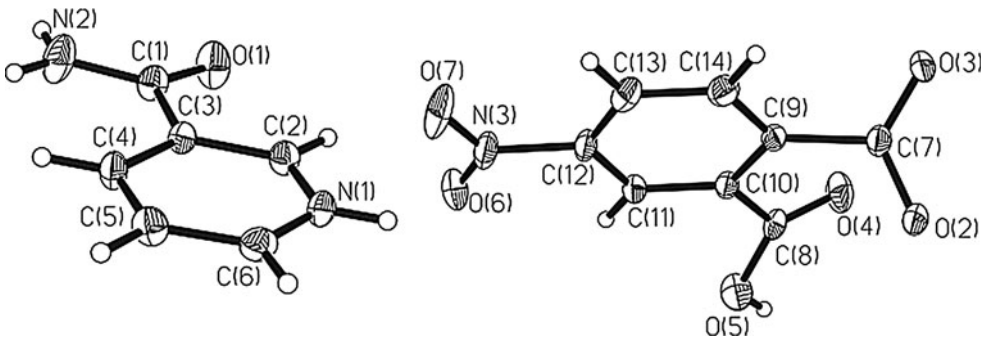


Fig. 3 Molecular structure of **2** showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30 % probability level

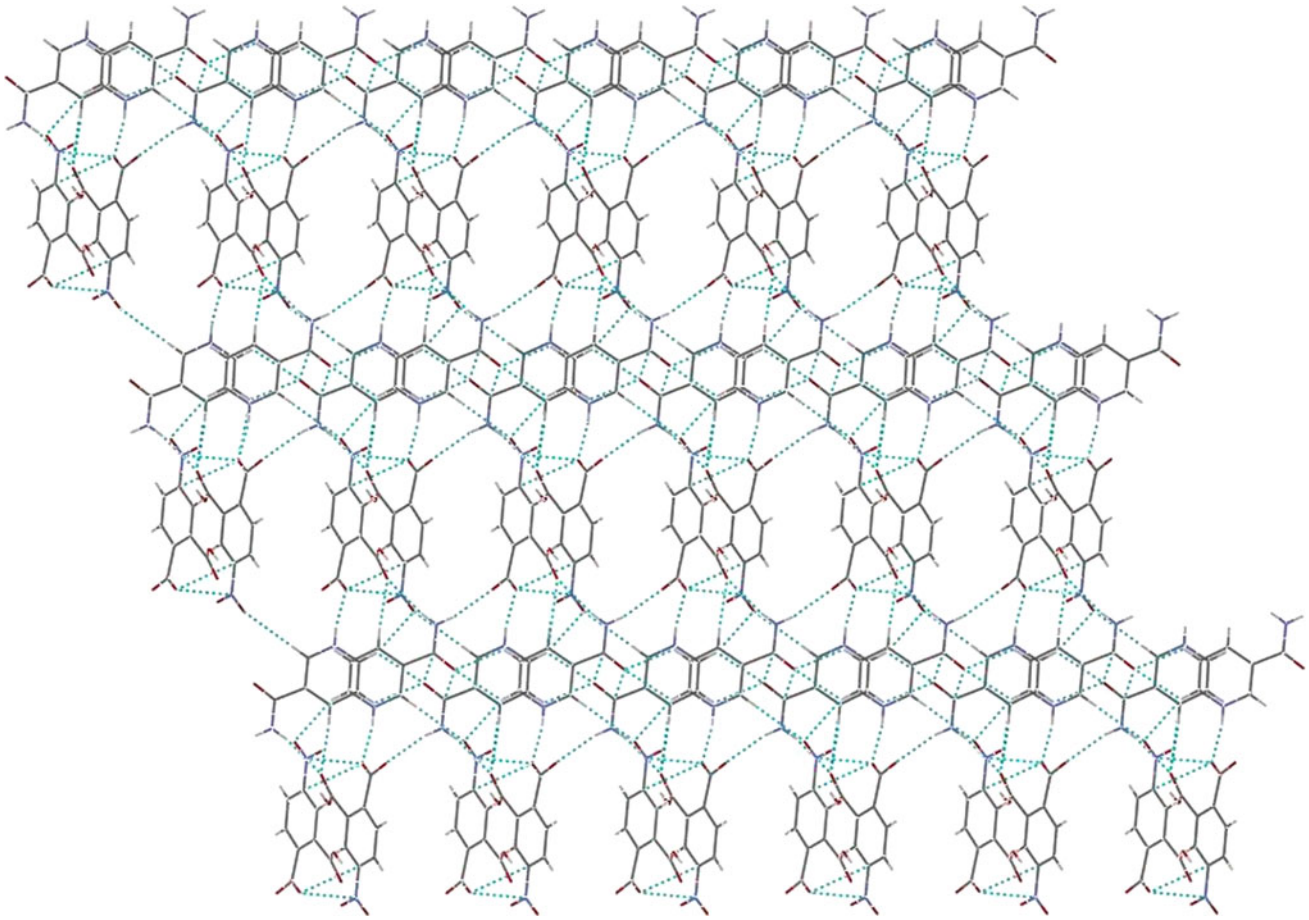


Fig. 4 2D sheet extending on the ac plane

while for protonated N the angle (C(6)–N(1)–C(2)) is 122.0(2)°. And this angle was also smaller than that found in compound **1**.

Different from **1**, the cation adopted the Z conformation according to Borba et al. [48], in which the C2–C3–C1–O1 torsion angle is −2.3°. The rms deviation of the phenyl ring of the anion is 0.0062 Å, the carboxyl groups with O2–O3–C7, and O4–O5–C8 are rotated from the plane by 33.3°, and 65.2°, respectively. The groups O2–O3–C7, and O4–O5–C8 intersected at an angle of 65°. The group O1–C1–N2 rotated by 4.0° from the pyridine ring plane. The dihedral angle between the phenyl ring of C9–C14 and the ring of N1–C2–C3–C4–C5–C6 was 117.0°.

The cations were connected together by the CH···O associations between the 5-, and 6-CH of the cation and the carbonyl group of the cation with C···O distances of 3.038–3.095 Å to form 1D chain running along the c axis direction. The discrete chains extending in the same plane were joined together by the anions through the N–H···O, and CH···O associations to form 2D grid structure. In the 2D

grid the OH groups of the COOH were protruded from the plane of the sheet, so did one O atom of the nitro group and one O atom of the COO^- group. Two neighboring 2D grid sheets were held together by the same face of the sheet via the N–H···O hydrogen bond between the NH^+ cation and the carboxylate with N···O separation of 2.624(2) Å, O···π interaction between the carboxylate of the anion and the phenyl ring of the anion with O···Cg distance of 3.145 Å, O···N contact between the carboxylate and the nitro group with O···N distance of 2.912 Å, O···C(carbonyl) contact between the carbonyl unit of the cations with O···C distance of 3.129 Å to form double sheet structure (Fig. 4). The double sheets were further stacked along the b axis direction by the O–H···O hydrogen bond between the COOH and COO^- group with O···O distance of 2.526(2) Å, O···π association between the OH of the carboxyl and the phenyl ring of the anion with O···Cg distance of 3.084 Å, and C···π association between the C(carbonyl) of the cation and the pyridine ring of the cation with C···Cg distance of 3.247 Å to form 3D network structure.

Supporting Information Available

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 908429 for **1**, and 897098 for **2**. 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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References

1. Lam CK, Mak TCW (2000) Tetrahedron 56:6657
2. Tanase S, Bouwman E, Long GJ, Shahin AM, Mills AM, Jan Reedijk ALS (2004) Eur J Inorg Chem 4572
3. Janiak C (2000) J Chem Soc Dalton Trans 3885
4. Takahashi O, Kohno Y, Nishio M (2010) Chem Rev 110:6049
5. Berkovitch-Yellin Z, Leiserowitz L (1984) Acta Cryst B40:159
6. Cho KH, No KT, Scheraga HA (2000) J Phys Chem A 104:6505
7. Koch W, Frenking G, Gauss J, Cremer D (1986) J Am Chem Soc 108:5808
8. Desiraju GR (2002) Acc Chem Res 35:565
9. Braga D, Maini L, Paganelli F, Tagliavini E, Casolari S, Grepioni F (2001) J Organomet Chem 637–639:609
10. Liu JQ, Wang YY, Ma LF, Zhang WH, Zeng XR, Zhong F, Shi QZ, Peng SM (2008) Inorg Chim Acta 361:173
11. Biswas C, Drew MGB, Escudero D, Frontera A, Ghosh A (2009) Eur J Inorg Chem 2238
12. Maamen M, Gordon DM (1995) Acc Chem Res 28:37 and references therein
13. Weyna DR, Shattock T, Vishweshwar P, Zaworotko MJ (2009) Cryst Growth Des 9:1106
14. Du M, Zhang ZH, Zhao XJ (2005) Cryst Growth Des 5:1247
15. Desiraju GR (1989) Crystal engineering, the design of organic solids. Elsevier, Amsterdam
16. Leiserowitz L (1976) Acta Crystallogr B32:775
17. Kolotuchin SV, Fenlon EE, Wilson SR, Loweth CJ, Zimmerman SC (1995) Angew Chem Int Ed Engl 34:2654
18. Kuduva SS, Craig DC, Nangia A, Desiraju GR (1999) J Am Chem Soc 121:1936
19. Bernstein J, Etter MC, Leiserowitz L (1994) Struct Correl 2:431
20. Moulton B, Zaworotko MJ (2001) Chem Rev 101:1629
21. Reddy LS, Bethune SJ, Kampf JW, Rodríguez-Hornedo N (2009) Cryst Growth Des 9:378
22. Lee IS, Shin DM, Chung YK (2003) Cryst Growth Des 3:521
23. Bhogala BR, Nangia A (2003) Cryst Growth Des 3:547
24. MacDonald JC, Dorrestein PC, Pilley MM (2001) Cryst Growth Des 1:29
25. Highfill ML, Chandrasekaran A, Lynch DE, Hamilton DG (2002) Cryst Growth Des 2:15
26. Vishweshwar P, Nangia A, Lynch VM (2002) J Org Chem 67:556
27. Nichol GS, Clegg W (2009) Cryst Growth Des 9:1844
28. Men YB, Sun JL, Huang ZT, Zheng QY (2009) CrystEngComm 11:978
29. Báthori NB, Lemmerer A, Venter GA, Bourne SA, Caira MR (2011) Cryst Growth Des 11:75
30. Nicoli S, Bilzi S, Santi P, Caira MR, Li J, Bettini R (2008) J Pharm Sci 97:4830
31. Cheney ML, Shan N, Healey ER, Hanna M, Wojtas L, Zaworotko MJ, Sava V, Song S, Sanchez-Ramos JR (2010) Cryst Growth Des 10:394
32. Arenas-García JI, Herrera-Ruiz D, Mondragón-Vásquez K, Morales-Rojas H, Höpfl H (2010) Cryst Growth Des 10:3732
33. Athimoolam S, Natarajan S (2007) Acta Cryst E63:o1811
34. Athimoolam S, Natarajan S (2007) Acta Cryst E63:o2430
35. Koman M, Martiska L, Valigura D, Glowiak T (2003) Acta Cryst E59:o441
36. Zulfiya A, Zhao FH, Che YX (2010) Chin J Struct Chem 29:1185
37. Bruker (2004) SMART and SAINT. Bruker AXS, Madison, WI
38. Sheldrick GM (2000) SHELXTL, Structure Determination Software Suite, version 6.14. Bruker AXS, Madison, WI
39. Lynch DE, Thomas LC, Smith G, Byriel KA, Kennard CHL (1998) Aust J Chem 51:867
40. Smith G, White JM (2001) Aust J Chem 54:97
41. Smith G, Wermuth UD, Healy PC, White JM (2011) J Chem Crystallogr 41:1649
42. Aakeröy CB, Fasulo ME, Desper J (2007) Mol Pharm 4:317
43. Orola L, Veidis MV (2009) CrystEngComm 11:415
44. González FV, Jain A, Rodríguez S, Sáez JA, Vicent C, Peris G (2010) J Org Chem 75:5888
45. Ng SW, Naumov P, Drew MGB, Wojciechowski G, Brzezinski B (2001) J Mol Struct 595:29
46. Smith G, Wermuth UD, Bott RC, Healy PC, White JM (2002) Aust J Chem 55:349
47. Smith G, Lynch DE, Byriel KA, Kennard CHL (1995) Aust J Chem 48:1133
48. Borba A, Albrecht M, Gómez-Zavaglia A, Lapinski L, Nowak MJ, Suhm MA, Fausto R (2008) Phys Chem Chem Phys 10:7010