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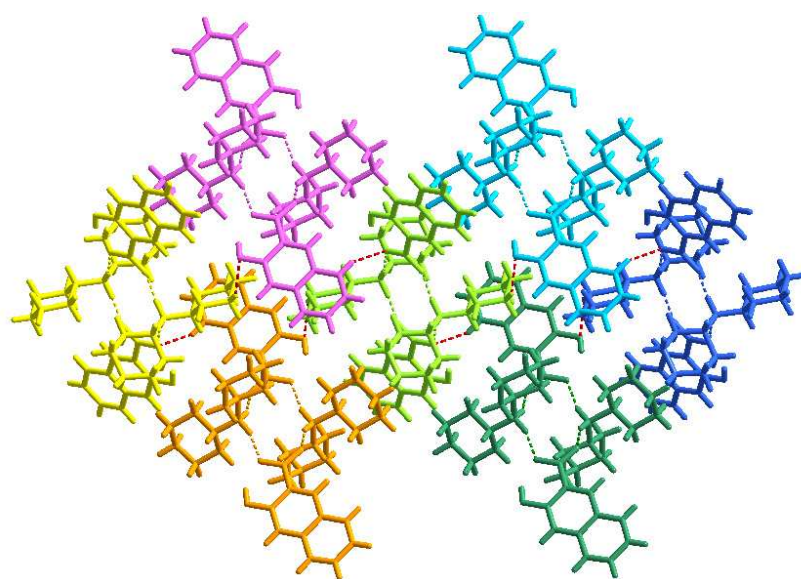
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### **Supramolecular Assemblies of 2-hydroxy-3-naphthoic Acid and N-Heterocycles via Various Strong Hydrogen Bonds and Weak $X\cdots\pi$ ( $X= C-H, \pi$ ) Interactions**

Yanyan Pang, Peiqi Xing, Xiujuan Geng, Yu Yang,\* Faqian Liu, and Lei Wang,\*



Hydrogen bonds and weak  $X\cdots\pi$  ( $X= C-H, \pi$ ) Interactions in a series of multi-component molecular constructed by 2-hydroxy-3-naphthoic acid with N-heterocycles were discussed in the context.

## ARTICLE

# Supramolecular Assemblies of 2-hydroxy-3-naphthoic Acid and N-Heterocycles via Various Strong Hydrogen Bonds and Weak $X\cdots\pi$ ( $X = C-H, \pi$ ) Interactions

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The analysis of weak interactions, including hydrogen bonds and aromatic stacking interactions, and primary hydrogen-bonded synthons in the crystals of 2-hydroxy-3-naphthoic acid with various N-containing cocrystal formers (coformers) is presented. Molecular complexes of 2-hydroxy-3-naphthoic acid with 3-hydroxy pyridine **1**, 2-amino-4,6-dimethoxy pyrimidine **2**, 2-amino-4,6-dimethyl pyrimidine **3**, 1-phenyl piperazine **4**, cyclohexylamine **5**, dicyclohexylamine **6**, 1,10-phenanthroline **7** have been obtained as single crystals in slow solvent evaporation approach, and investigated utilizing X-ray diffraction techniques. Single crystal X-ray diffraction studies show total proton transfer from 2-hydroxy-3-naphthoic acid to coformer in crystals **1–6** and partial proton transfer in **7**. Crystals **1, 2, 3, 5** and **7** exhibit 3-D supramolecular networks extended by various hydrogen bonds,  $C-H\cdots\pi$  and  $\pi\cdots\pi$  stacking; while crystals **4** and **6** exhibit 2-D supramolecular structures *via* hydrogen bonds. In every crystal structure, hydrogen bonds ( $N-H\cdots O$ ,  $O-H\cdots N$ ,  $C-H\cdots O$ , etc) and aromatic stacking interactions ( $C-H\cdots\pi$ ,  $\pi\cdots\pi$  stacking, etc) direct the packing modes of molecular crystals together. Some classical supramolecular synthons, such as  $R^2_2(8)$  and  $R^4_4(12)$ , usually observed in organic solids of carboxylic acids with other N-heterocycles, are again shown to be involved in constructing most of these hydrogen-bonding networks. Moreover, these multicomponent samples are characterized by infrared and thermogravimetric analysis. Thermogravimetric analysis of mass loss for seven compounds has been shown to correlate with the strength of hydrogen bonds in the packing fraction.

## Introduction

Stable organic solid with potentially tailor-made properties based on weak non-covalent intermolecular interactions is one of the main research directions of crystal engineering. That how to obtain desired product with predetermined connectivities and stoichiometries is still a great challenge, due to the comparatively weak and reversible nature of weak non-covalent intermolecular.<sup>1</sup> From the point of view of crystal engineering,

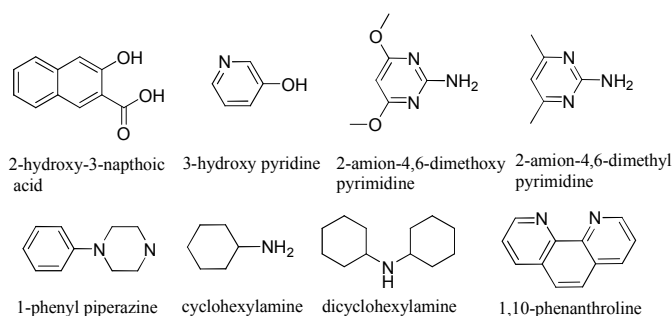
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† Electronic Supplementary Information (ESI) available: IR data and synthons. CCDC reference numbers 1032721-1032727. For ESI and crystallographic data in CIF or other electronic format see DOI: XXXXXXXX. A complete understanding of the supramolecular chemistry of functional groups in a compound is precondition for the rational design of cocrystals and salts with desired structure features.<sup>2</sup> As one kind of numerous organic supramolecular building blocks, aromatic carboxylic acid has aroused high degree of attention on account of its capability for the creation of extended architectures through directional noncovalent forces, mainly hydrogen bonding.<sup>3</sup> It is generally known that carboxylic acid ligands could facilitate self-association with supramolecular homosynthons that are made up of selfsame complementary functional groups.<sup>4</sup> Furthermore, aromatic carboxylic acids also could form persistent supramolecular heterosynthons with different but complementary functional groups (aromatic nitrogen, amide, etc). Indeed, in the literature,

supramolecular heterosynthons containing carboxylic acids such as carboxylic acid...amide, carboxylic acid...pyridine are used generally as robust yet versatile supramolecular synthetic tools for the design and synthesis of cocrystals.<sup>5</sup>

In the past few decades, hydroxybenzoic acids have been selected widely as building blocks for study in crystal engineering since they represent one of the most ubiquitous aromatic carboxylic acids.<sup>6</sup> For example, as far as salicylic acid is concerned, an analysis of the Cambridge Structural Database (CSD) data shows that, from 1971 H. S. Kim and G. A. Jeffrey synthesized the salt  $[(C_{10}H_{15}N^{2+})_{1.5} \cdot (C_7H_5O_3^-)]$ <sup>7</sup> to H. C. Stephen Chan, G. R. Woollam, T. Wagner, M. U. Schmidt and R. A. Lewis composed the cocrystal  $[(C_7H_6O_3) \cdot (C_6H_6N_2O_2)]$  in 2014<sup>8</sup>, approximate 460 compounds which used salicylic acid as the linker ligand have been reported. On the other hand, up to the present only twelve multicomponent molecular solids of 2-hydroxy-3-naphthoic acid which is salicylic acid derivative have been reported in the structural database, although some related metal complexes have been reported recently.<sup>9</sup>

In this context, we chose 2-hydroxy-3-naphthoic acid as major organic building block mainly considering its advantages compared with the usual and shorter hydroxybenzoic acids (e.g., the ubiquitous salicylic acid): (i) Like salicylic acid, 2-hydroxy-3-naphthoic acid also has many position isomers and each of them has two main potential hydrogen bonding donors: strong carboxyl and weak hydroxyl. Besides, they have more weak hydrogen bonding donors (C–H) and thus are anticipated to form new supramolecular networks with aza compounds *via* weak C–H...N/C–H...O. Weaker interactions like the C–H...O play a key role in directing the packing modes of molecular crystals in chemical systems, in spite of their comparatively weak and reversible nature.<sup>10</sup> In addition, the co-existence of various non-covalent interactions between the synthons makes the self-assembly process more stable.<sup>11</sup> (ii) The structural geometry of this building block adds another benzene ring upon salicylic acid and makes the aromatic stacking interactions more obvious. Aromatic stacking interactions which are regarded as weak hydrogen bonds occurring between soft acids and soft bases also have a vital role in directing supramolecular assembly, especially in crystal packing of aromatic compounds.<sup>12</sup> They are usually considered in two main prototypical systems of the benzene dimer: face-to-face ( $\pi \cdots \pi$  interactions) and edge-to-face (C–H... $\pi$  interactions).<sup>13</sup> As with other weak interactions, these two modes are nowadays widely studied and aimed at gaining an insight into the interaction patterns and generating a variety of crystal structures.<sup>14</sup>



**Scheme 1** Structural formulas of the organic crystals components in this work

To further understand the role of C–H...O/ C–H...N/ C–H... $\pi$ /  $\pi \cdots \pi$  stacking interactions and the effect of co-existence of various noncovalent interactions between synthons on supramolecular self-assembly process, we will report herein the preparations, structures, and thermal stabilities of seven new organic crystals consisting of 2-hydroxy-3-naphthoic acid and some typical N-containing cofomers, including 3-hydroxy pyridine, 2-amino-4,6-dimethoxy pyrimidine, 2-amino-4,6-dimethyl pyrimidine, 1-phenyl piperazine, cyclohexylamine, dicyclohexylamine, 1,10-phenanthroline (structural formulas given in Scheme 1).

## Experimental

### Materials and General Procedures

All reagents and solvents for synthesis were purchased commercially and used without further purification. Single crystals of these novel supramolecular compounds were prepared *via* slow solvent evaporation method of suitable stoichiometric amounts of various cofomers in an appropriate solvent or solvent mixture and isolated from their mother liquor several days later. Respective compositions were confirmed by a Perkin-Elmer 2400 elemental analyzer. Fourier transform infrared (FT-IR) spectra were performed with a Nicolet Impact 410 FTIR spectrometer, and the samples were made as KBr pellets in range 4000–400  $\text{cm}^{-1}$ . Absorptions were signified as follows: strong (s), medium (m), and weak (w) in the synthesis section. All products were air stable and their thermal stability was investigated by thermogravimetric analysis (TGA) experiment which was carried out on a Perkin-Elmer TGA 7 thermogravimetric analyzer in the temperature range of 0–900  $^{\circ}\text{C}$  under  $\text{N}_2$  atmosphere at a heating rate of 10  $^{\circ}\text{C}/\text{min}$ . The crystals were prepared as follows.

### Preparation of complexes 1–7

**2-hydroxy-3-naphthoic acid:3-hydroxy pyridine 1:1 salt (1)** 3-hydroxy pyridine (0.0190g, 0.2mmol) and 2-hydroxy-3-naphthoic acid (0.0376g, 0.2mmol) were weighed out in a beaker containing an ethanol-distilled water mixture (5:5mL), the mixture was stirred for 10–15 min until a homogeneous solution was obtained. The solution was filtered through a qualitative filter paper and allowed to slowly evaporate at room temperature. Large, clubbed, yellow crystals appeared concomitantly two weeks later. Single crystals suitable for X-ray diffraction were separated from the mother liquor by filtration, and dried under vacuum. Yield: 72%. Anal. calcd for  $\text{C}_{16}\text{H}_{13}\text{NO}_4$ : C,

67.78; H, 4.59; N, 4.94%. Found: C, 68.21; H, 4.93; N, 4.50%. Infrared spectrum (KBr disc,  $\text{cm}^{-1}$ ): 3439w, 3053w, 2749m, 2601m, 2132w, 1838w, 1638m, 1575m, 1505s, 1453s, 1397s, 1328s, 1286s, 1246s, 1207m, 1153m, 1111m, 1005w, 914w, 845m, 812m, 781m, 678m, 617m, 478m.

**2-hydroxy-3-naphthoic acid:2-amino-4,6-dimethoxy pyrimidine 1:2 salt (2)** A methanol solution (7mL) of 2-hydroxy-3-naphthoic acid (0.0188g, 0.1mmol) was added to a stirred distilled water solution (3mL) of 2-amino-4,6-dimethoxy pyrimidine (0.0310g, 0.2mmol) and the reaction mixture stirred for 30 min. The resulting light yellow solution was filtered through a qualitative filter paper and allowed to stand in air at room temperature for 15 days yielding yellow, diamond crystals in about 84% yield. Single crystals suitable for X-ray diffraction were separated from the mother liquor by filtration, and dried under vacuum. Anal. calcd for  $\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_5$ : C, 59.42; H, 4.95; N, 12.23%. Found: C, 59.77; H, 5.38; N, 11.97%. Infrared spectrum (KBr disc,  $\text{cm}^{-1}$ ): 3325m, 2950m, 2809w, 1694s, 1628s, 1579m, 1553m, 1519m, 1455s, 1368s, 1313m, 1245m, 1218s, 1167m, 1070m, 882m, 842m, 782m, 746m, 597m.

**2-hydroxy-3-naphthoic acid:2-amino-4,6-dimethyl pyrimidine 1:1 salt (3)** 2-hydroxy-3-naphthoic acid (0.0188g, 0.1mmol) was dissolved in methanol (5mL), to which a distilled water solution of 2-amino-4,6-dimethyl pyrimidine (5mL, 0.2mmol/mL) was added with stirring for 10-15 min. The mixture was then filtered to a beaker, and allowed to slowly evaporate at room temperature, upon which yellow, irregular, clubbed single crystals fitted for X-ray diffraction were culled from the mother solution by filtration several days later. The crystals were dried under vacuum. Yield: 79%. Anal. calcd for  $\text{C}_{34}\text{H}_{34}\text{N}_6\text{O}_6$ : C, 65.52; H, 5.46; N, 13.49%. Found: C, 65.09; H, 5.80; N, 13.31%. Infrared spectrum (KBr disc,  $\text{cm}^{-1}$ ): 3411w, 3185w, 2992w, 2791w, 1948w, 1707m, 1629m, 1514m,

1469m, 1449m, 1397m, 1372m, 1357m, 1315m, 1246m, 1209w, 1148w, 984w, 940w, 919w, 887w, 843m, 781m, 746w, 595m, 519m.

**2-hydroxy-3-naphthoic acid:1-phenyl piperazine 1:1 salt (4)** A 1:1 stoichiometric amount of 2-hydroxy-3-naphthoic acid (0.0188g, 0.1mmol) and 1-phenyl piperazine (15 $\mu$ L, 0.1mmol) was dissolved in 5mL methanol. Another five milliliter of distilled water was added to the above solution with stirring for 15 min until gained a light yellow homogeneous solution. The resulting solution was left to stand at ambient temperature. Yellow, irregular, sheet crystals of compound 4 were harvested after one week in a yield of 85%. Single crystals suitable for X-ray analysis were picked up from their mother liquor by filtration and dried under vacuum. Anal. calcd for  $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_3$ : C, 71.92; H, 6.28; N, 7.99%. Found: C, 72.32; H, 6.87; N, 8.36%. Infrared spectrum (KBr disc,  $\text{cm}^{-1}$ ): 3443w, 3025m, 2977m, 2842m, 2642m, 2520m, 1925w, 1648s, 1617s, 1599m, 1578s, 1509s, 1456s, 1398m, 1331m, 1308s, 1258m, 1210w, 1033w, 921m, 873m, 842m, 747m, 689m, 525m.

**2-hydroxy-3-naphthoic acid:cyclohexylamine 1:2 salt (5)** Cyclohexylamine (24 $\mu$ L, 0.2mmol) and 2-hydroxy-3-naphthoic acid (0.0188g, 0.1mmol) were mixed in acetone/distilled water solution (v/v=4:1, 10mL) with stirring for 30min. Upon slow evaporation of the dark yellow, homogeneous solution, yellow, irregular, block crystals were produced over ten days. Single crystals suitable for X-ray diffraction were culled from the mother liquor by filtration, and dried under vacuum. Yield: 73%. Anal. calcd for  $\text{C}_{17}\text{H}_{21}\text{NO}_3$ : C, 70.99; H, 7.31; N, 4.87%. Found: C, 70.75; H, 7.58; N, 4.53%. Infrared spectrum (KBr disc,  $\text{cm}^{-1}$ ): 3446m, 3055m, 2932s, 2857s, 2602m, 1662s, 1623m, 1577s, 1515s, 1450s, 1397s, 1373s, 1327s, 1237m, 1205w, 1066w, 924w, 868m, 783m, 742m, 596m.

**2-hydroxy-3-naphthoic acid:dicyclohexylamine 2:1 salt (6)** A solution of 2-hydroxy-3-naphthoic acid (0.0188g, 0.1mmol) in

Table 1 Crystallographic Parameters of structures 1–7

	1	2	3	4	5	6	7
Empirical formula	$\text{C}_{16}\text{H}_{13}\text{NO}_4$	$\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_5$	$\text{C}_{34}\text{H}_{34}\text{N}_6\text{O}_6$	$\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_3$	$\text{C}_{17}\text{H}_{21}\text{NO}_3$	$\text{C}_{46}\text{H}_{62}\text{N}_2\text{O}_6$	$\text{C}_{34}\text{H}_{24}\text{N}_2\text{O}_6$
<i>M</i>	283.27	343.33	622.67	350.40	287.35	738.98	556.55
Crystal system	monoclinic	triclinic	triclinic	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_12_1$	$P2_1/n$	$P2_1/c$	$P2_1/c$
<i>a</i> /Å	6.970(4)	7.8075(6)	7.6965(5)	6.2836(6)	7.0998(11)	13.1744(4)	16.409(1)
<i>b</i> /Å	16.371(8)	9.3259(5)	9.3446(6)	8.1666(10)	16.265(3)	14.8970(4)	11.6515(4)
<i>c</i> /Å	11.719(6)	12.6323(10)	11.9676(9)	34.870(3)	14.012(3)	21.1083(7)	15.1195(10)
$\alpha$ /deg	90	97.038(6)	76.523(6)	90	90	90	90
$\beta$ /deg	100.000(8)	107.168(7)	86.187(6)	90	97.333(18)	90.01	114.910(7)
$\gamma$ /deg	90	109.563(6)	67.033(7)	90	90	90	90
<i>V</i> /Å <sup>3</sup>	1316.8(11)	802.65(11)	770.38(10)	1789.4(3)	1604.9(5)	4142.7(2)	2621.8(3)
<i>Z</i>	4	2	1	4	4	4	4
$\rho_{\text{calcd}}$ (g/cm <sup>3</sup> )	1.429	1.421	1.342	1.301	1.189	1.185	1.410
$\mu$ (mm <sup>-1</sup> )	0.104	0.106	0.094	0.088	0.081	0.077	0.098
<i>F</i> (000)	592.0	360.0	328.0	744.0	616.0	1600.0	1160.0
Total/Independent reflections	7994/2994	5318/2817	4770/2716	5111/2979	6499/2832	27764/7316	14293/6182

ARTICLE							Journal Name
Data/Restraints/ Parameters	2994/0/242	2817/1/241	2716/0/208	2979/0/236	2832/0/192	7316/0/487	6182/1/475
$R_{\text{int}}$	0.1166	0.0216	0.0153	0.0298	0.0290	0.0345	0.0292
$R_w^a, R_w^b$	0.0484, 0.1240	0.0644, 0.1119	0.0663, 0.1467	0.0710, 0.1138	0.1102, 0.1966	0.0734, 0.1141	0.0882, 0.1151
GOF on $F^2$	1.047	0.959	1.046	1.049	1.018	1.031	1.042

methanol (7mL) was carefully layered onto a distilled water (3mL) solution of dicyclohexylamine (0.0090g, 0.05mmol) in a beaker. The resulting solution was stirred for 30 min and allowed to stand at room temperature. Two weeks later, dark yellow, irregular, block crystals which was fit for X-ray determination were collected from the mother liquor by filtration and dried under vacuum. Yield: 70%. Anal. calcd for  $C_{46}H_{62}N_2O_6$ : C, 74.70; H, 8.39; N, 3.79%. Found: C, 75.35; H, 8.83; N, 3.35%. Infrared spectrum (KBr disc,  $\text{cm}^{-1}$ ): 3439w, 3016w, 2934m, 2861m, 2750w, 2563w, 1651m, 1620m, 1594w, 1576w, 1513m, 1449m, 1401m, 1368m, 1346s, 1312m, 1243w, 1206w, 1147w, 1062w, 867w, 840m, 778w, 739m, 594w.

### 2-hydroxy-3-naphthoic acid:1,10-phenanthroline 1:2 cocrystal

(7) A methanol (7mL) solution of 2-hydroxy-3-naphthoic acid (0.0188g, 0.1mmol) was added to a distilled water (3mL) solution of 1,10-phenanthroline (0.0396g, 0.2mmol) with constant stirring for 10-15 min until a homogeneous solution was obtained. Light yellow, rodlike crystals suitable for X-ray analysis were facilely obtained after a period of one week upon slow evaporation of the solvents. Good quality single crystals, suitable for diffraction, were gathered from their mother solution by filtration and dried under vacuum. Yield: 88%. Anal. calcd for  $C_{34}H_{24}N_2O_6$ : C, 73.31; H, 4.31; N, 5.03%. Found: C, 73.90; H, 4.67; N, 5.52%. Infrared spectrum (KBr disc,  $\text{cm}^{-1}$ ): 3425m, 3056w, 2921w, 2852w, 1651m, 1617m, 1595w, 1510m, 1450m, 1420m, 1368w, 1327w, 1217w, 1141w 880w, 841m, 765m, 716m, 618w, 591w, 482m.

### X-Ray crystallography

The samples for X-ray single-crystal diffraction of compounds 1–7 were synthesised through the procedure described above and selected under a microscope. Then the suitable crystals were mounted on a goniometer by gluing to a glass fiber with cyanoacrylate adhesive, and crystal data for 1–7 were collected on a Siemens Smart CCD diffractometer equipped with a normal-focus, 2.4 kW sealed-tube X-ray source (graphite-monochromatic MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ )) operating at 50 kV and 40 mA. The structures were solved by direct methods with Shelxs97<sup>15</sup> and refined against  $F^2$  by full-matrix least-squares techniques using the Shelxs97 software package and Olex2<sup>16</sup>. All the non-hydrogen atoms were refined with anisotropic displacement parameters. The Hydrogen atoms attached to 2–6 were placed in geometrically idealized positions and refined using a riding models. The Hydrogen atoms residing on the atoms of 1 and 7 were located by Fourier maps. Crystallographic parameters for 1–7 are summarized in Table 1.

### Results and discussion

Seven novel multicomponent organic crystals of 2-hydroxy-3-naphthoic acid with common N-containing heterocycles, including 3-hydroxy pyridine, 2-amino-4,6-dimethoxy pyrimidine, 2-amino-4,6-dimethyl pyrimidine, 1-phenyl piperazine, cyclohexylamine, dicyclohexylamine, 1,10-phenanthroline, were discovered by common solvent evaporation method (Table 1). These new organic solids were characterized by single crystal X-ray diffraction, IR and TGA. The outcome of single crystal X-ray diffraction reveals the formation of one new cocrystal and six salts. The crystal structures of compounds 1–7 contain extensive hydrogen bond networks in which the 2-hydroxy-3-naphthoic acid and base components form a range of possible synthons shown in Scheme 2 and supporting information. Details of lengths and angles of selected hydrogen bonds for 1–7 are listed in Table 2. In these structures, various weak forces, i.e. hydrogen bonds, C–H $\cdots\pi$  and  $\pi\cdots\pi$  stacking interactions, play an important role as anticipated in stabilizing the supramolecular self-assembly process observed for all organic solids. We now detailedly discuss the structural aspects and thermal stabilities of these new multicomponent molecular complexes.

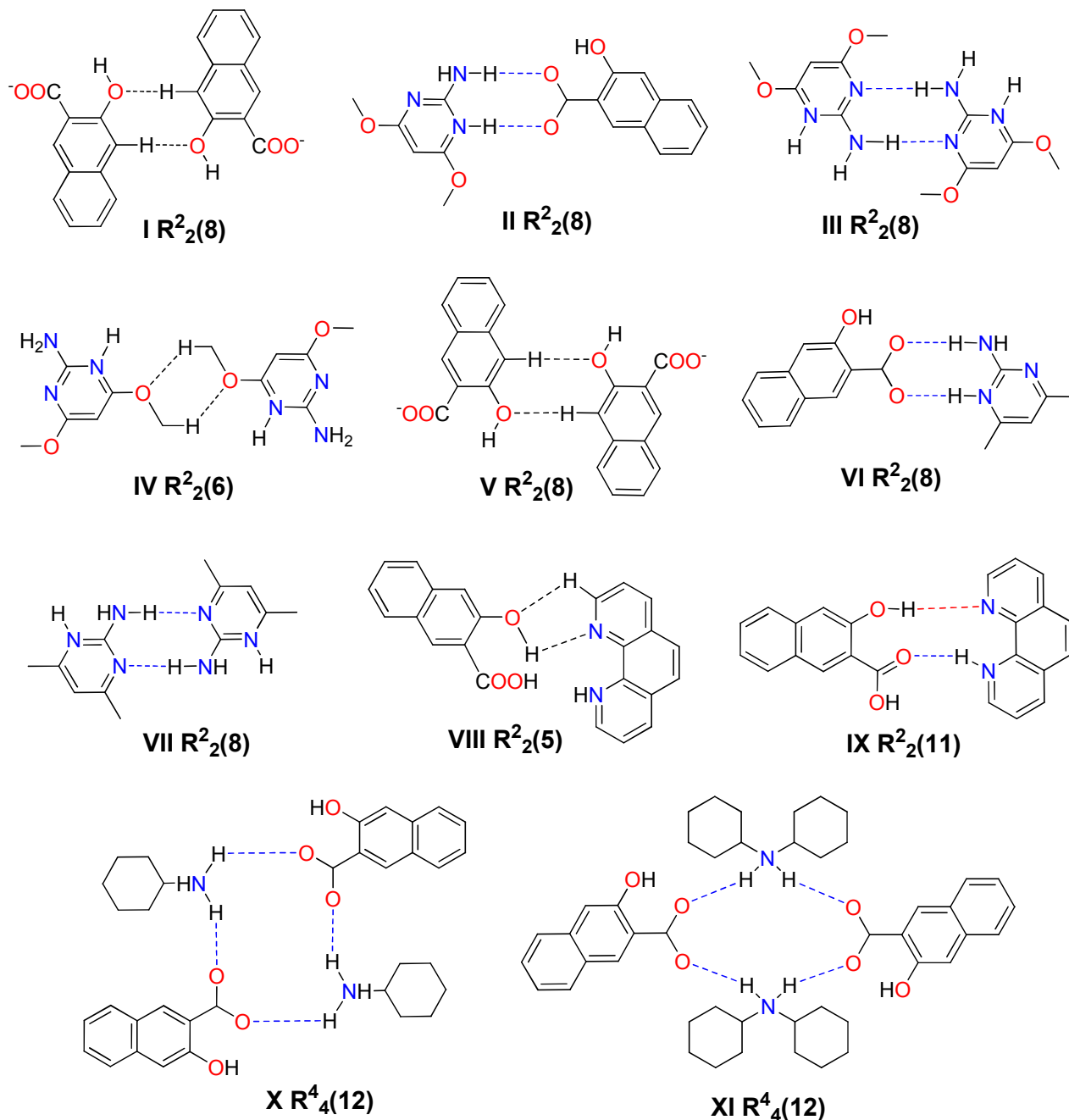
**Crystal Structure of 2-hydroxy-3-naphthoic acid:3-hydroxy pyridine 1:1 salt (1).** As depicted in Figure 1a, the molecular structure of 1 which belongs to the monoclinic  $P2_1/n$  space group, crystallizes with one molecule of 2-hydroxy-3-naphthoic acid which is absolutely deprotonated and one molecule of protonated 3-hydroxy pyridine. Within each 2-hydroxy-3-naphthoic acid anion, the carboxyl makes dihedral angle of  $6.328(1)^\circ$  with the naphthalene ring, and the dihedral angle between the naphthalene

Table 2 Hydrogen Bond Metrics for Complexes 1–7

	D-H $\cdots$ A( $\text{\AA}$ )	D-H( $\text{\AA}$ )	H $\cdots$ A( $\text{\AA}$ )	D $\cdots$ A( $\text{\AA}$ )	D-H $\cdots$ A (deg)
1	N1–H1A $\cdots$ O2 <sup>a</sup>	0.97	1.69	2.612(3)	149
	O1–H1 $\cdots$ O3 <sup>b</sup>	1.01	1.51	2.519(1)	172
	C15–H15 $\cdots$ O4 <sup>a</sup>	0.95	2.81	3.769(1)	178
2	N1–H1B $\cdots$ N3 <sup>c</sup>	0.98	2.15	3.124(2)	173
	C24–H24B $\cdots$ O4 <sup>c</sup>	0.96	2.73	3.555(2)	144
	N2–H2 $\cdots$ O3 <sup>d</sup>	0.86	1.74	2.604(2)	179
	N1–H1A $\cdots$ O2 <sup>d</sup>	0.83	1.97	2.804(2)	177
	C21–H21 $\cdots$ O1 <sup>d</sup>	0.93	2.54	3.440(2)	162
3	C20–H20A $\cdots$ O1 <sup>e</sup>	0.96	2.78	3.438(3)	127
	C10–H10 $\cdots$ O1 <sup>d</sup>	0.93	2.49	3.375(2)	160
	N15–H15B $\cdots$ O2 <sup>d</sup>	0.86	1.89	2.745(2)	177
	N15–H15A $\cdots$ N7 <sup>f</sup>	0.86	2.12	2.983(2)	177
	C21–H21C $\cdots$ O3 <sup>d</sup>	0.96	2.88	3.637(2)	137
	C22–H22B $\cdots$ O2 <sup>d</sup>	0.96	2.81	3.713(3)	156
4	C9–H9B $\cdots$ O3 <sup>e</sup>	0.97	2.69	3.409(2)	131
	N2–H2A $\cdots$ O1 <sup>h</sup>	0.97	1.86	2.749(2)	152
	N2–H2B $\cdots$ O2 <sup>h</sup>	0.97	1.79	2.743(3)	168
5	N1–H1C $\cdots$ O3 <sup>i</sup>	0.89	2.04	2.888(5)	159

N1–H1B...O2 <sup>i</sup>	0.89	1.90	2.786(5)	174	O4–H4...O1 <sup>d</sup>	0.88	1.62	2.491(3)	168
C15–H15...O3 <sup>i</sup>	0.93	2.81	3.644(5)	150	C28–H28...O1 <sup>d</sup>	0.98	2.39	3.295(1)	151
N1–H1A...O1 <sup>j</sup>	0.89	1.88	2.746(4)	163	C29–H29...O1 <sup>d</sup>	0.96	2.64	3.602(1)	172
6 N1–H1A...O17 <sup>k</sup>	0.97	1.83	2.724(1)	157	C24–H24...O2 <sup>d</sup>	0.99	2.52	3.185(3)	123
N1–H1B...O27 <sup>k</sup>	0.97	1.82	2.758(1)	161	C18–H18...O2 <sup>d</sup>	0.94	2.52	3.301(1)	141
C47–H47A...O11 <sup>l</sup>	0.97	2.54	3.384(1)	145					
C22–H22...O27 <sup>m</sup>	0.93	2.88	3.592(1)	134					
7 N1–H1...O5 <sup>d</sup>	0.92	1.87	2.738(2)	157					
O6–H6...N2 <sup>k</sup>	0.95	2.62	3.182(2)	117					
C24–H24...O6 <sup>d</sup>	0.99	2.58	3.234(1)	123					

<sup>a</sup>  $-x, -l-y, -z^b -l-x, -l-y, -z^c -x, -y, -l-z^d x, -l+y, z^e x, y, z^f x, y, -l+z^g -l+x, 2+y, z^h x, -2+y, z^i -x, -l-y, -l-z^j -x, -y, -z^k -x, -0.5+y, 0.5-z^l -x, 0.5+y, 0.5-z$   
<sup>m</sup>  $l+x, l+y, z$



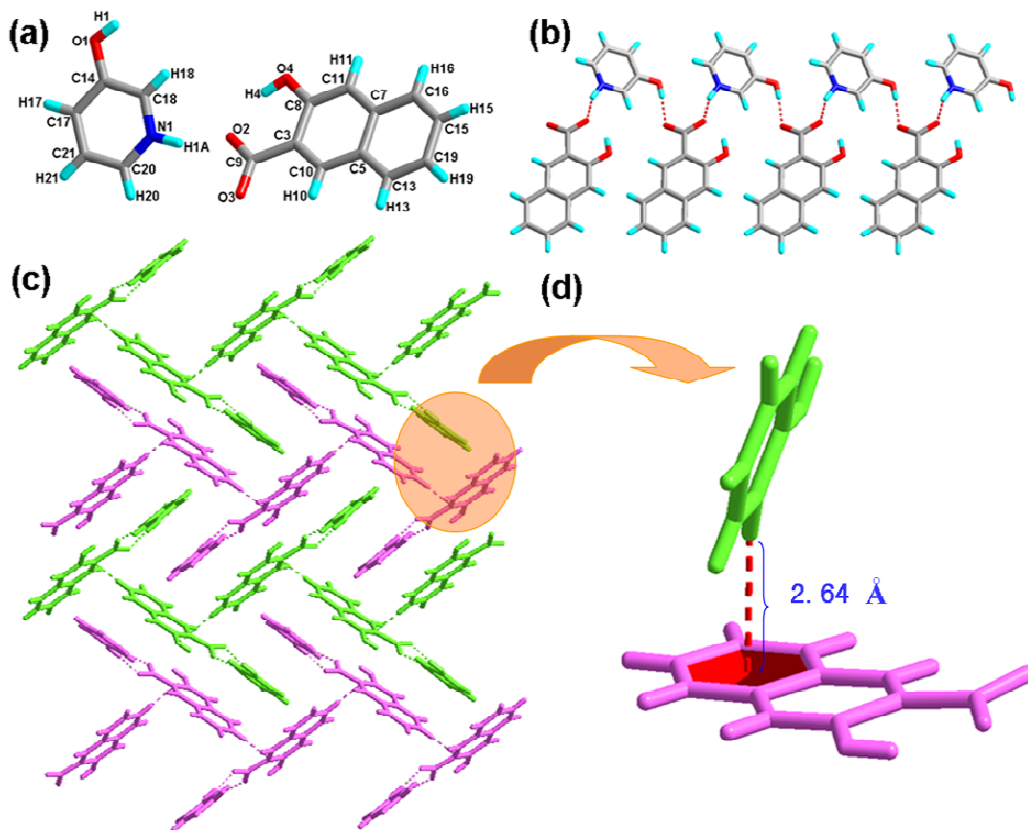
**Scheme 2.** Main Synthons Anticipated and/or Observed in the Crystal Structures of 2-hydroxy-3-naphthoic acid Solid Forms

ring and the pyridine ring of 3-hydroxy pyridine is 23.697(7)°.

As illustrated in Figure 1b, each 3-hydroxy pyridine cation connects neighboring 2-hydroxy-3-naphthoic acid anions *via* hydrogen bond N1–H1A···O2 (2.612(3) Å) and hydrogen bond O1–H1···O3 (2.519(1) Å) forming 1D chain along the crystallographic [001] direction. Furthermore, Hydrogen-bondings C15–H15···O4 (3.769(1) Å) and weak interactions C–H··· $\pi$  connect 1D chains to form 3D networks along the crystallographic [001] direction (Figure 1c). The distance of C17–H17··· $\pi$  stacking between C17 and the centroid C<sub>g</sub> of the aromatic group C15, C16, C7, C5, C13 and C19 is 3.472(2) Å, as shown in Figure 1d. The angle of C17–H17···C<sub>g</sub> is approximately 146°. Besides, weak hydrogen-bonding interactions C–H···O further consolidating this

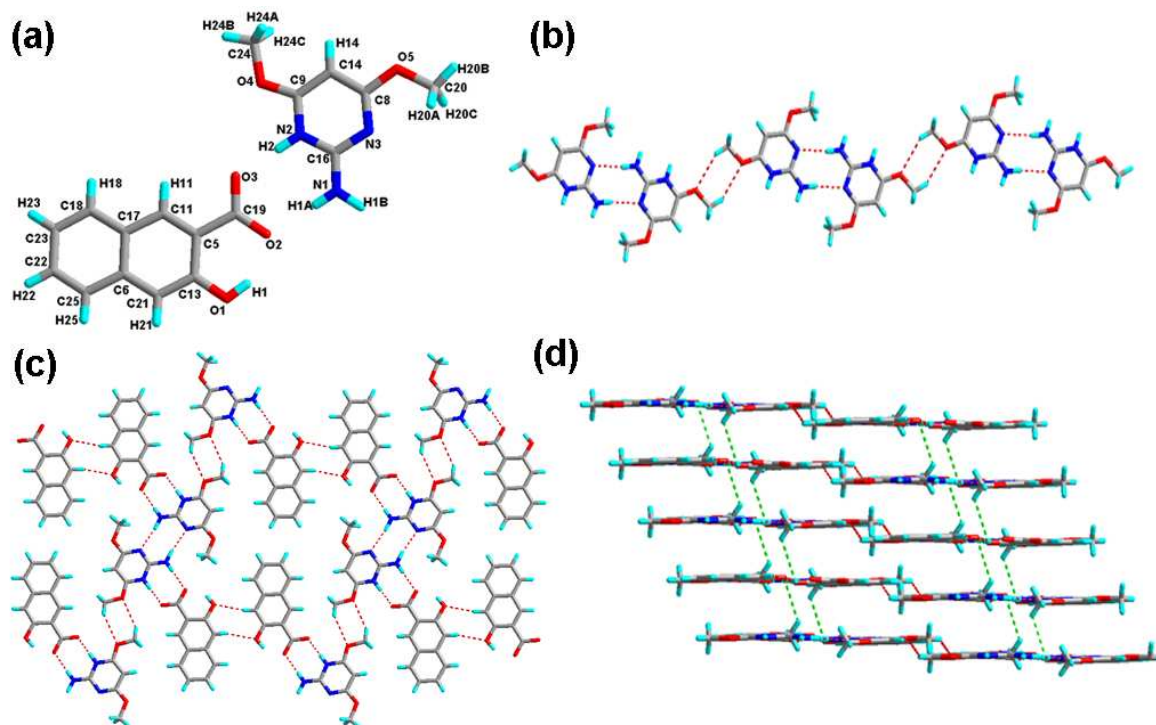
3D structure along the crystallographic [001] direction, containing synthon XII R<sup>3</sup><sub>4</sub>(20), which is shown in supporting information.

**Crystal Structure of 2-hydroxy-3-naphthoic acid:2-amino-4,6-dimethoxy pyrimidine 1:2 salt (2).** In the local structure of salt 2 as shown in Figure 2a, the molecular structure of 2 contains one 2-amino-4,6-dimethoxy pyrimidine monocation and one 2-hydroxy-3-naphthoic acid monoanion in the triclinic *P* $\bar{1}$  space group. The mean plane of 2-hydroxy-3-naphthoic acid anion makes a dihedral angle of 2.645° with the 2-amino-4,6-dimethoxy pyrimidine cation. The carboxylic group in each acid anion makes the dihedral angle of 4.233° with the naphthalene ring.



**Figure 1.** (a) Molecular structure of 1 with atom labeling of the asymmetric unit; (b) 1D chain via O–H···O and N–H···O hydrogen bonds; (c) 3-D supramolecular network extended by C–H···O hydrogen bonds and weak C–H··· $\pi$  interaction; (d) the weak C–H··· $\pi$  interaction (O, red; N, blue; C, gray; H, turquoise in this and the subsequent figures)





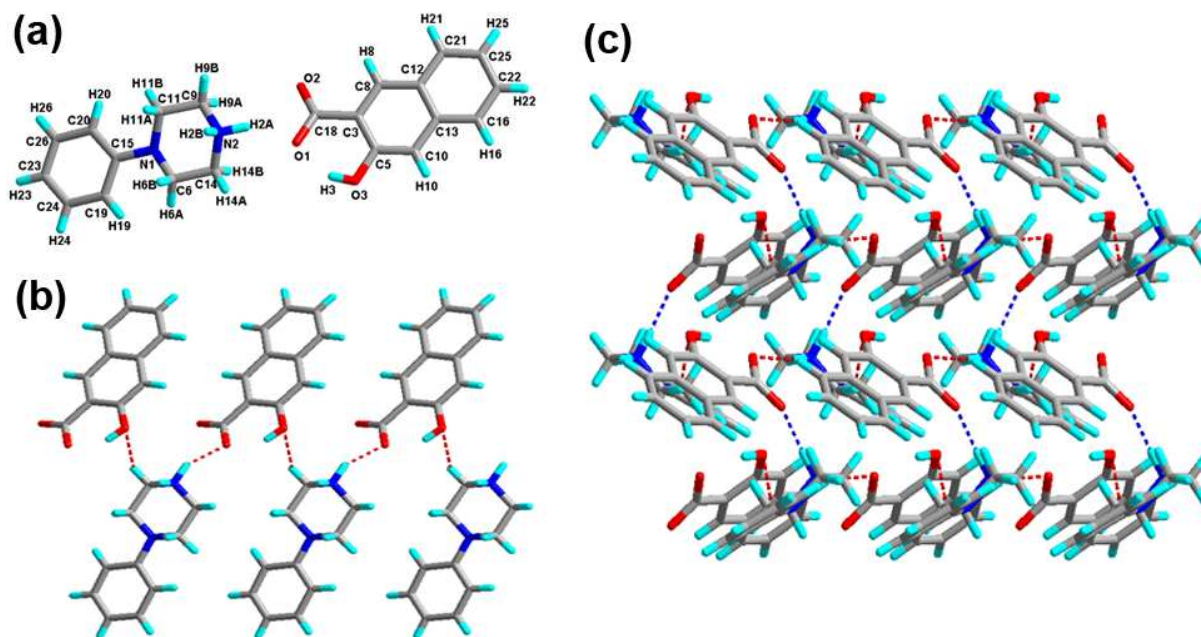
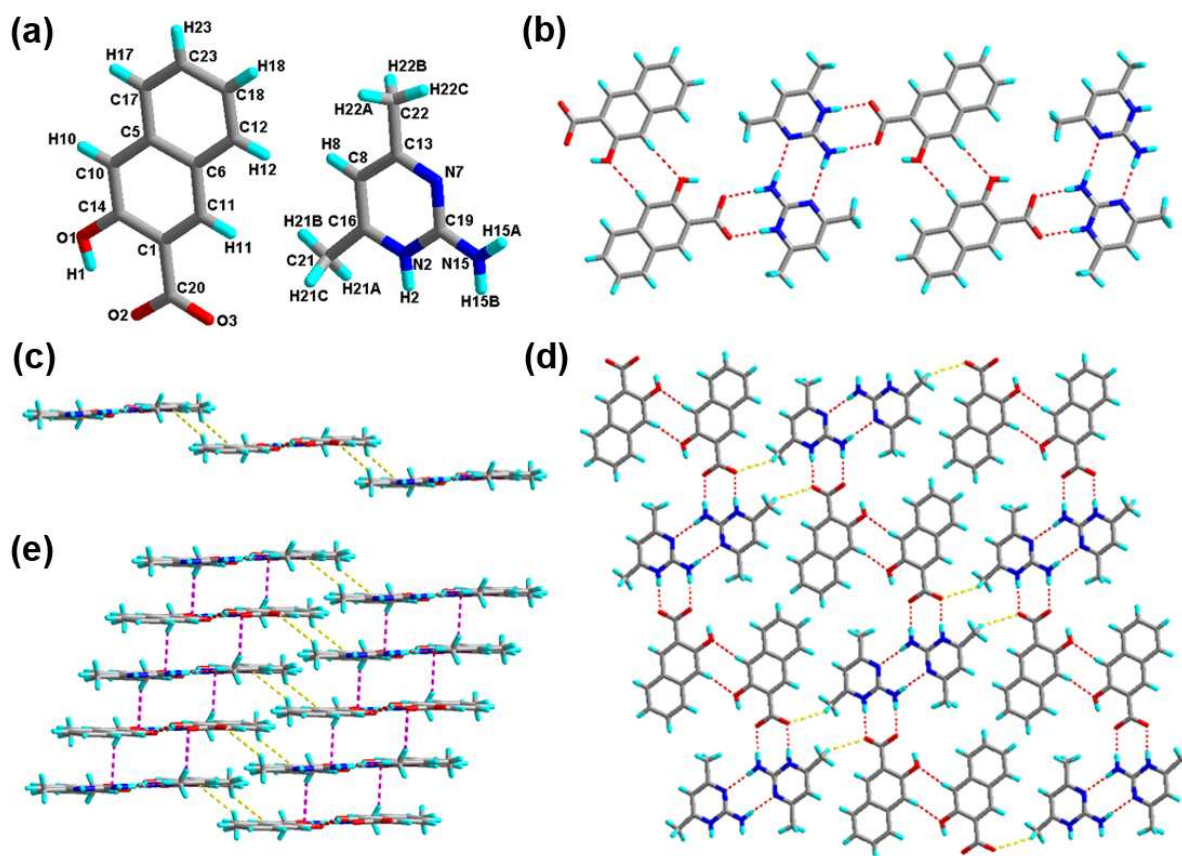
**Figure 2.** (a) Molecular structure of **2** with atom labeling of the asymmetric unit; (b) 1D wavelike chain via synthons III  $R^2_2(8)$  and IV  $R^2_2(6)$ ; (c) 2D layer structure extended by hydrogen bonding interactions (d) the resultant 3D network connected by C–H $\cdots$ O hydrogen bonds (green broken lines)

As shown in Figure 2b, adjacent 2-amino-4,6-dimethoxy pyrimidine cations are linked each other into 1D chains by pyrimidine-pyrimidine homosynthons III  $R^2_2(8)$  (N1–H1B $\cdots$ N3, 3.124(2) Å) and IV  $R^2_2(6)$  (C24–H24B $\cdots$ O4, 3.555(2) Å). These 1D pyrimidine chains are connected by the 2-hydroxy-3-naphthoic acid anion via pyrimidine-carboxylic acid heterosynthons II  $R^2_2(8)$  (N1–H1A $\cdots$ O2, 2.804(2) Å and N2–H2 $\cdots$ O3, 2.604(2) Å) and homosynthons I  $R^2_2(8)$  (C21–H21 $\cdots$ O1, 3.440(2) Å) (Figure 2c), thus, 2D planar layered structure are formed. Meanwhile, there exist interlayer C20–H20A $\cdots$ O1 hydrogen-bonding interactions between C20–H20A donors of acid anions and O1 acceptors of base cations, which connect the adjoining 2D layers to general a 3-D supramolecular network along the crystallographic [001] direction (see Figure 2d). It is to be noted, in previous work, the pyridine-carboxylic acid heterosynthon  $R^2_2(7)$  for its stable and reliable as the best combination of hydrogen-bonding donor/acceptor, has been proved to be an effective tool in synthesizing the predictable hydrogen-bonding networks.<sup>17</sup> Compared to synthon  $R^2_2(7)$ , pyrimidine-carboxylic acid heterosynthon II  $R^2_2(8)$ , and pyrimidine-pyrimidine homosynthon III  $R^2_2(8)$  have been found in a large number of cocrystals and salts,<sup>18</sup> also may be used as effective tools to construct the desired supramolecular architectures. Here, as expected, these two different synthons  $R^2_2(8)$  are also observed in the structure of **2**. In addition, three types of large synthons, notated as XIII  $R^6_6(26)$ , XIV  $R^4_6(30)$

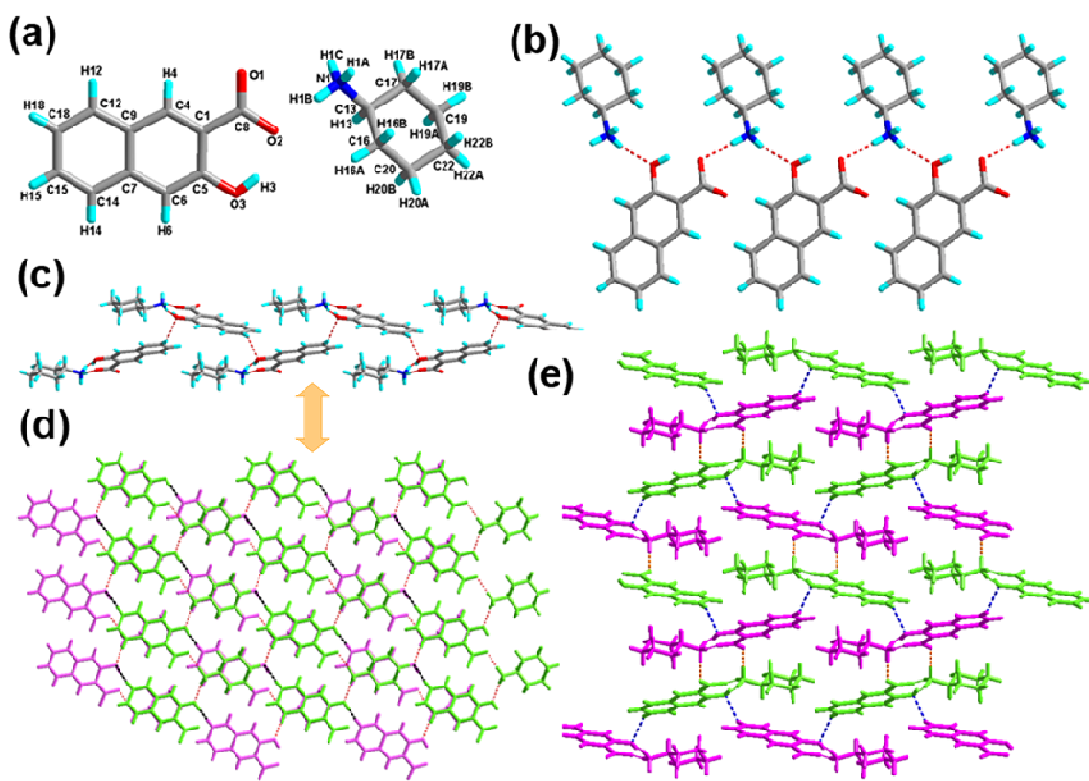
and XV  $R^{10}_{10}(50)$  are observed in this 3D array and described in supporting information.

**Crystal Structure of 2-hydroxy-3-naphthoic acid:2-amino-4,6-dimethyl pyrimidine 1:1 salt (3).** In regard to compound **3**, it is a monosalt as the same with crystal of **2**. In the structure of **3**, crystallizing in the triclinic space group  $P\bar{1}$ , the asymmetric unit is consisted of one 2-hydroxy-3-naphthoic acid monoanion and one 2-amino-4,6-dimethyl pyrimidine monocation (shown in Fig.3a). Within each 2-hydroxy-3-naphthoic acid subunit, the dihedral angle between the carboxylic group and the naphthalene nucleus is 6.911(101)°, and the dihedral angle between acid and base components is 7.301(49)°.

In this study, for compound **3**, the classical pyridine-carboxylic acid heterosynthons  $R^2_2(8)$  and pyridine-pyridine homosynthons  $R^2_2(8)$  are furnished as well as **2**. Similar to the one-dimensional chains of the compound **2**, in crystal of **3**, the 2-amino-4,6-dimethyl pyrimidine cations are self-assembled into an infinite waved chain (shown in Fig.3b) *via* synthons V  $R^2_2(8)$  (based on two weak C–H $\cdots$ O interactions), VI  $R^2_2(8)$  (based on two strong N–H $\cdots$ O interactions) and VII  $R^2_2(8)$  (based on two N–H $\cdots$ N interactions). Then these 1D chains are linked into a ladder-shaped two-dimensional layer through secondary C–H $\cdots$ O hydrogen bonds (C21 $\cdots$ O3, 3.637(2) Å) (shown in Fig. 3c). Further analysis of the crystal packing of **3** indicates that the additional interlayered C22–H22B $\cdots$ O2 hydrogen-bonding interactions between the acid anions



**Figure 3** (a) Molecular structure of **3** with atom labeling of the asymmetric unit; (b) 1D supramolecular tape via synthons V  $R^2_2(8)$ , VI  $R^2_2(8)$  and XII  $R^2_2(8)$ ; (c) Perspective view of the 2D hydrogen-bonded layer connected by C–H $\cdots$ O hydrogen bonds (yellow broken lines); (d) The resultant 2D layer in the other direction; (e) 3D network via C–H $\cdots$ O hydrogen bond



**Figure 5** (a) Molecular structure of **5** with atom labeling of the asymmetric unit; (b) 1D chain via N–H···O hydrogen bonds; (c) 2D wave overlapped layer connected by C–H···O hydrogen bonds; (d) The overlapped 2D layer in the other direction in two colors; (e) 3D network via N–H···O hydrogen bonds

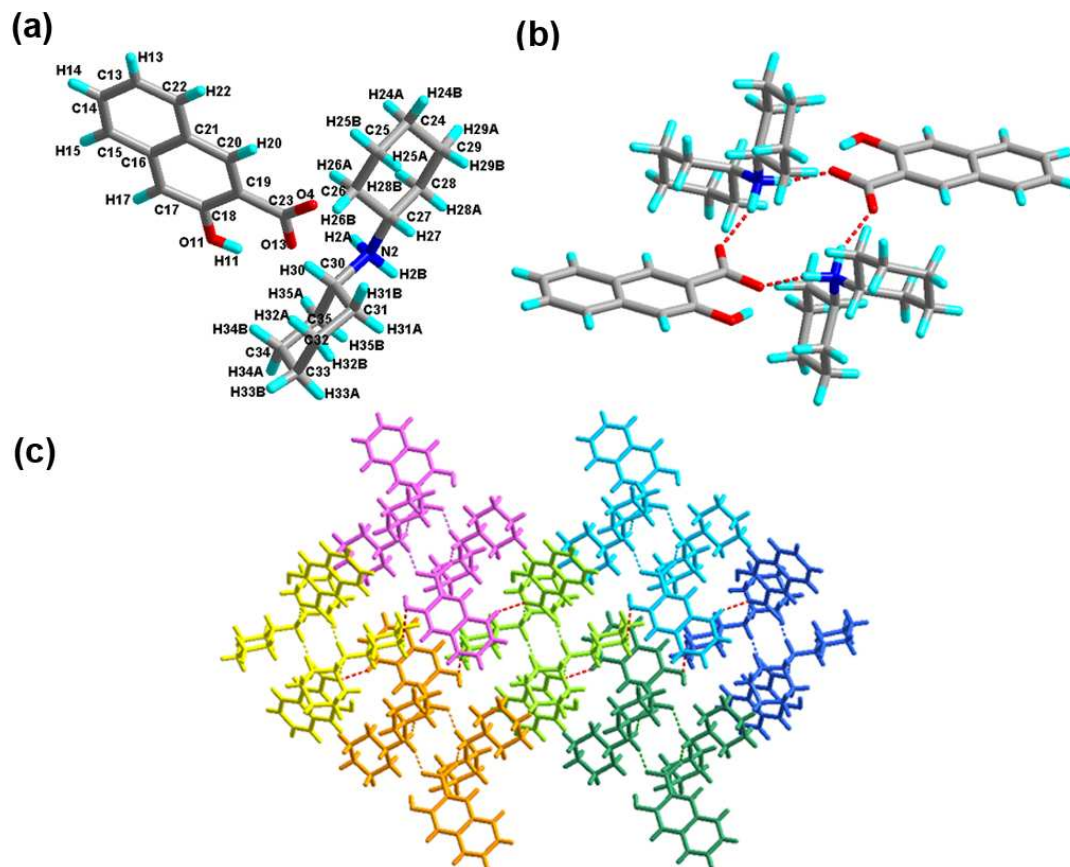
and base cations link two adjoining 2D ladder-shaped layers to give a 3D network motif (shown in Fig. 3d). Additionally, related heterodimers are connected to each other through weak C–H···O to form some large ring motifs, such as XVI  $R^8_8(40)$ , XVII  $R^4_6(16)$  and XVIII  $R^4_4(20)$  (shown in supporting information).

**Crystal Structure of 2-hydroxy-3-naphthoic acid:1-phenyl piperazine 1:1 salt (4).** Structure determination of **4** reveals that acid and base are present in a 1:1 ratio in the compound **4**, and the asymmetric unit is shown in Fig. 4a. The crystal structure of **4** reveals a salt compound with one monoanion of 2-hydroxy-3-naphthoic acid and one monocation of 1-phenyl piperazine in the asymmetric unit in orthorhombic space group  $P2_12_12_1$ . Within each 2-hydroxy-3-naphthoic acid anion, the carboxyl makes dihedral angle of  $11.340^\circ$  with the naphthalene ring, and the dihedral angle between the naphthalene ring and the aromatic ring of 1-phenyl piperazine is  $20.728^\circ$ .

The crystal packing of **4** can be envisaged as an interesting 2D network resulted from the packing of infinite 1D undulated chains by strong hydrogen bonds N2–H2B···O2 ( $2.743(3)$  Å) (shown in Fig. 4c). The 1D wavelike chains are further composed of acid monocations alternating with base monoanions, connecting via strong N2–H2A···O1 ( $2.749(2)$  Å) and auxiliary weak C9–H9B···O3 ( $3.409(2)$  Å) interactions (shown in Fig. 4b), meanwhile, synthon XIX  $R^6_6(24)$  (supporting information) is observed in this structure.

**Crystal Structure of 2-hydroxy-3-naphthoic acid:cyclohexylamine 1:2 salt (5).** Crystal structure of compound **5** crystallizes in the monoclinic space group  $P2_1/n$  ( $Z=4$ ) with one of the host molecule of 2-hydroxy-3-naphthoic acid which is absolutely deprotonated and one molecule of protonated cyclohexylamine in the asymmetric unit which is displayed in Figure 5a. The protonated cyclohexylamine molecule keeps the chair conformation. Within each acid subunit, two benzene rings of 2-hydroxy-3-naphthoic acid form the dihedral angles of  $2.390^\circ$  and the carboxylic group is nearly coplanar with the naphthalene ring.

The molecular packing analysis shows that each amino group of cyclohexylamine cations can form two hydrogen bonds with neighbouring acid anions, i.e. N1–H1C···O3 ( $2.888(5)$  Å), N1–H1B···O2 ( $2.786(5)$  Å). These hydrogen bonds connect the cofomers into a 1D linear chain (see Fig. 5b). Then neighbouring 1D chains are linked together and continued into a 2D wavelike supramolecular layer via auxiliary weak hydrogen bonds C15–H15···O3 ( $3.644(5)$  Å) (see Fig. 5c). The adjacent layers are bridged by hydrogen bonds N1–H1A···O1 ( $2.746(4)$  Å) and extended to a 3D supramolecular network (see Fig. 5d), forming three types of synthons, notated as X  $R^4_4(12)$  (Scheme 2), XX  $R^4_4(16)$  and XXI  $R^5_6(28)$  (supporting information), respectively.



**Figure 6** (a) Molecular structure of **6** with atom labeling of the asymmetric unit; (b) Synthon  $R_4^4(12)$  between 2-hydroxy-3-naphthoic acid and dicyclohexylamine; (c) Two-dimensional layer *via* synthon  $R_4^4(12)$  (each synthon is expressed as a different color)

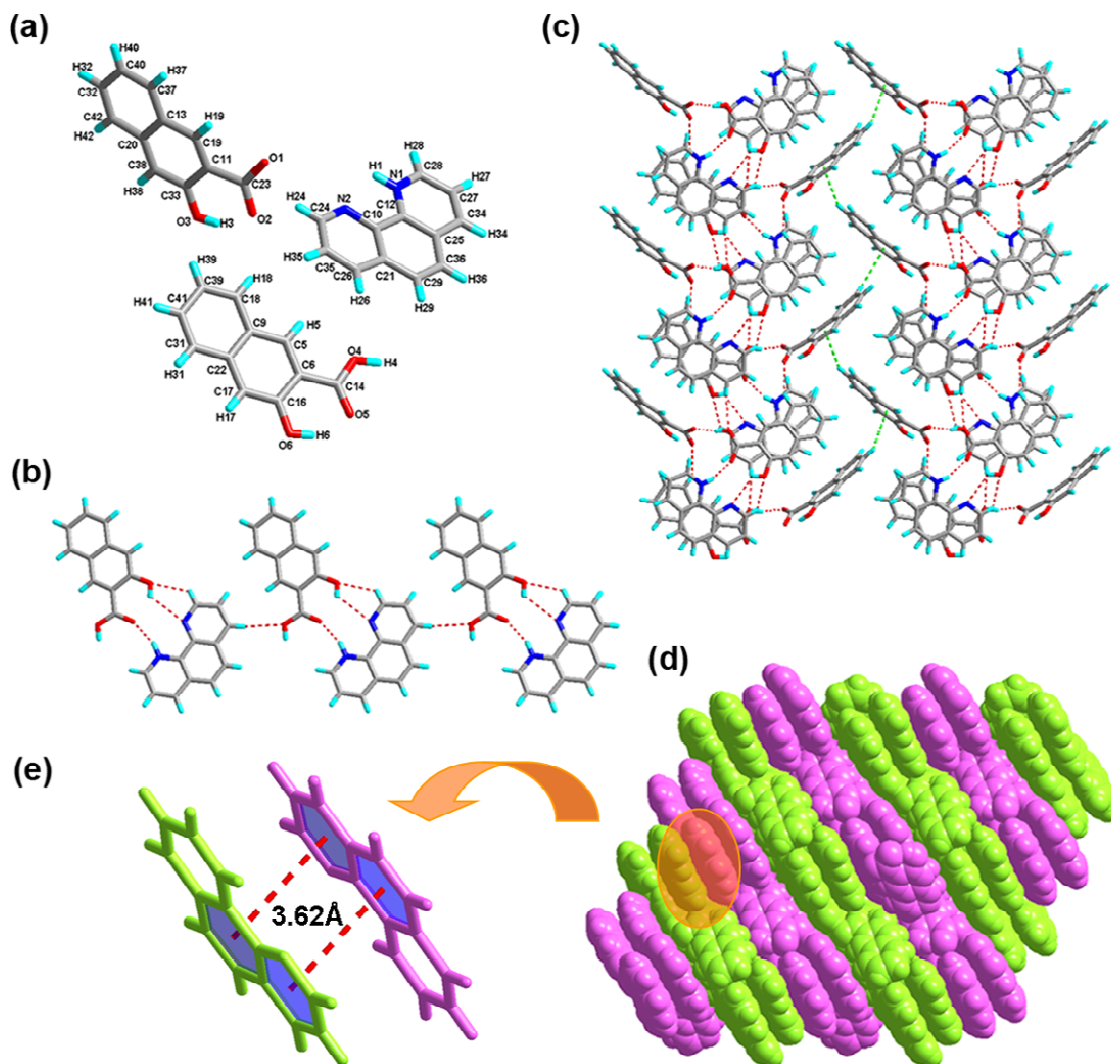
**Crystal Structure of 2-hydroxy-3-naphthoic acid:dicyclohexylamine 2:1 salt (6).** As shown in Fig. 6a, the crystal structure of **6** reveals a salt compound with one monoanion of 2-hydroxy-3-naphthoic acid and one monocation of dicyclohexylamine in the asymmetric unit in monoclinic space group  $P2_1/c$ . Within each 2-hydroxy-3-naphthoic acid anion, the carboxyl makes dihedral angle of  $8.203^\circ$  with the naphthalene ring.

Firstly, two dicyclohexylamine monocations and two 2-hydroxy-3-naphthoic acid monoanions are self-assembled to form a stable tetramer by two pairs of hydrogen bonds  $N1-H1A \cdots O17$  ( $2.724(1)$  Å) and  $N1-H1B \cdots O27$  ( $2.758(1)$  Å) with an  $R_4^4(12)$  motif (see Fig. 6b). Then the acid anions in each tetramer can form two hydrogen bonds with neighbouring tetramers ( $C47-H47A \cdots O11 = 3.384(1)$  Å,  $C22-H22 \cdots O27 = 3.592(1)$  Å), connecting the tetramers to form a 2D supramolecular layer along  $c$  axis (see Fig. 6c). The supramolecular synthon  $X R_4^4(12)$  or  $XI R_4^4(12)$  is made up of two classical  $N-H \cdots O$  hydrogen bonds, usually observed in

organic solids of carboxylic acids with other heterocyclic bases, is again shown to be involved in constructing of hydrogen-bonding networks **5** and **6**.<sup>19</sup> Moreover, two different  $S(6)$  synthons (XXII and XXIII, described in supporting information) have been found in this structure.

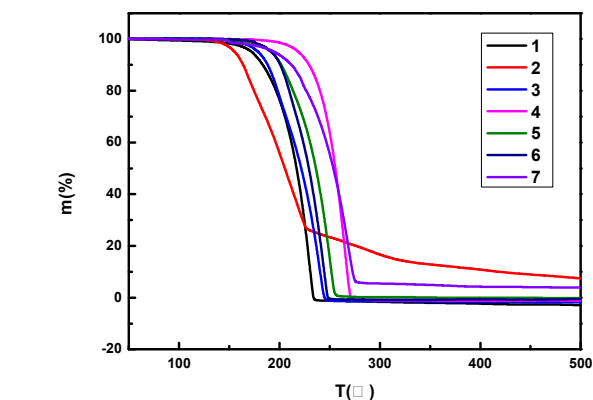
**Crystal Structure of 2-hydroxy-3-naphthoic acid:1,10-phenanthroline cocrystal 1:2 (7).** Different from salts **1–6**, the molecular structure of cocrystal **7** crystallizes in space group  $P2_1/c$  and contains one crystallographically independent 1,10-phenanthroline monocation, one 2-hydroxy-3-naphthoic acid monoanion and one 2-hydroxy-3-naphthoic acid neutral molecule (Figure 7a). In this structure, the dihedral angles between the aryl ring plane of 2-hydroxy-3-naphthoic acids and the 1,10-phenanthroline ring are  $17.977^\circ$  and  $88.806^\circ$ , respectively. And the dihedral angle between two naphthalene rings is  $75.241^\circ$ .

As shown in Fig. 7b, the two coformers are connected through three hydrogen bonds,  $N1-H1 \cdots O5$ ,  $O6-H6 \cdots N2$  and  $C24-H24 \cdots O6$ , together creating synthons VIII  $R_2^2(5)$  and IX  $R_2^2(11)$ ,



**Figure 7** (a) Molecular structure of **7** with atom labeling of the asymmetric unit; (b) 1D banded chain extended by hydrogen bonds; (c) 2D bilayer connected by C–H $\cdots$  $\pi$  interactions (C–H $\cdots$  $\pi$  interactions were denoted as green dashed lines); (d) Space filling representation of the stacking of 3D network *via*  $\pi$  $\cdots$  $\pi$  interactions; (e) The  $\pi$  $\cdots$  $\pi$  interaction between 1,10-phenanthroline monocations (centroid-to-centroid distance of 3.62Å) resulting in a dimer motif. These dimer motifs are linked through weak hydrogen bonds C26–H26 $\cdots$ O4 to form a 1D banded chain along *a* axis. Then deprotonated 2-hydroxy-3-naphthoic acid molecules connect adjacent 1D chains into a stable 1D double chain *via* hydrogen bonds O4–H4 $\cdots$ O1 and C18–H18 $\cdots$ O2. Furthermore, weak interaction C–H $\cdots$  $\pi$  connect 1D double chains to form 2D double-deck sheet (see Fig. 7c). As a consequence, hydrogen-bonded pattern marked as synthons XXIV R<sup>2</sup><sub>3</sub>(9), XXV R<sup>2</sup><sub>3</sub>(8), XXVI R<sup>2</sup><sub>3</sub>(13) (illustrated in supporting information) come into being. As illustrated in Figure 7d, the 1,10-phenanthroline rings of the adjacent layers come very close to each other and result in strong  $\pi$  $\cdots$  $\pi$  stacking (centroid-to-centroid distance of 3.617(2)Å) and lead to final 3D tessellate-type supramolecular architecture. In this 3D array, two large types of synthons, notated as XXVII R<sup>4</sup><sub>4</sub>(21), and XXVIII R<sup>4</sup><sub>4</sub>(22) are observed and expressed in supporting informatin.

### Thermal Stability



**Figure 8** The thermogravimetric analysis for compounds **1–7**. All compounds **1–7** are stable in air and can retain their structural integrity at ambient conditions for a considerable length of time. The thermogravimetric analysis (TGA) was

implemented to confirm the thermal stability of these crystalline materials between 0 and 900°C in nitrogen atmosphere, and the TGA curves are shown in Fig. 8. The TGA curve of compound **2** shows two consecutive weight losses of all crystalline samples from 100°C to 500°C (peaking at 169°C and 218°C, respectively). Both the two weight losses are 99.8%, which is in accord with the losses of the base and acid molecules (calcd: 100%). For **7**, the TGA result indicates that it remains intact until 158°C, and then there is a sharp weight loss ending at 280°C (peak: 253°C for crystal **7**), corresponding to the explosion of all base and acid components. The TGA curve of compounds **3**, **5** and **6** indicate that they have a similar trend of decomposition. They are stable up to about 130°C at which temperature they start to melt and decompose. The curves show single weight losses of the three crystalline samples from 130 to 260 °C (peaking at 222°C for **3**, 237°C for **5**, and 240°C for **6**, respectively). The TGA curves of **1** and **4** indicate that there are single weight losses of the two samples. Compound **4** decomposes from 160°C to 280°C (peaking at 256°C), while **1** is less stable than compound **4** and decomposition of the framework begins at 134 °C (peaking at 219°C).

## Conclusions

Seven new solid forms of 2-hydroxy-3-naphthoic acid were obtained in the form of six salts and one cocrystal. Their crystal structures were determined by single crystal X-ray diffraction. 2-hydroxy-3-naphthoic acid is shown to form cocrystal with 1,10-phenanthroline and salts with 3-hydroxy pyridine, 2-amino-4,6-dimethoxy pyrimidine, 2-amino-4,6-dimethyl pyrimidine, 1-phenyl piperazine, cyclohexylamine, and dicyclohexylamine. From Crystal structures **1–7**, we can observed that the strong intermolecular hydrogen bondings (N–H···O, O–H···N, O–H···O) are still the main force that self-assemble to form 1D-chains structure. However, as expected, further crystal packing managed by weaker interactions (C–H···O, C–H···N, C–H··· $\pi$  and  $\pi$ ··· $\pi$  stacking interactions) leads to the final formation of distinct 2D and/or 3D networks, which makes the overall arrangement more diversiform and stable. This systematic study also reveals that hydroxynaphthoic acids are excellent candidates for constructing supramolecular architectures with amides. In this study, several small and large sized ring motifs are observed, such as R<sup>2</sup><sub>2</sub>(6), R<sup>2</sup><sub>2</sub>(8), R<sup>3</sup><sub>3</sub>(9), R<sup>2</sup><sub>4</sub>(12), R<sup>4</sup><sub>4</sub>(12), R<sup>4</sup><sub>4</sub>(20), and R<sup>6</sup><sub>6</sub>(24). But not all of them occur repeatedly, as most of them arise only in specific cases. Nevertheless R<sup>2</sup><sub>2</sub>(8) and R<sup>4</sup><sub>4</sub>(12) motifs have been the most recurrently occurring ones in the present study and previous reports. By using Cambridge Structural Database (CSD), we can see that among the two robust and popular synthons, the former one frequently occur between a carboxylic acid and an aminopyrimidine, while the later one frequently occur between a carboxylic acid and an aminoheterocycle. Moreover, these multicomponent organic solids are characterized by infrared and thermogravimetric analysis.

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