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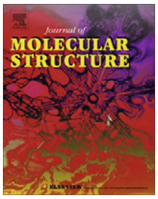

Six hydrogen bond directed supramolecular adducts formed between racemic-bis-β-naphthol and N-containing aromatic bases

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ABSTRACT

Studies concentrating on hydrogen bonding between the base of exobidentate bis(imidazole) derivatives, and 2-aminoheterocyclic compounds, and (±)-1,10-binaphthalene-2,2′-diol have led to an increased understanding of the role the aromatic N-containing compounds have in binding with (±)-1,10-binaphthalene-2,2′-diol. Here anhydrous multicomponent adducts of N-containing aromatic bases such as 1,4-bis(N-imidazolyl)butane (L1), 1,3-bis(N-benzimidazolyl)propane (L2), 1,4-bis(N-benzimidazolyl)butane (L3), 1,5-bis(N-benzimidazolyl)-3-oxapentane (L4), 2-amino-4-phenylthiazole (L5), and 2-amino-5,7-dimethyl-1,8-naphthyridine (L6) have been prepared with (±)-1,10-binaphthalene-2,2′-diol (binol). The six crystalline forms reported are cocrystals of which the crystals and complexes were characterized by X-ray diffraction analysis, IR, mp, and elemental analysis. The inter-ring angles (naphthol/naphthol) in the same binol of the six cocrystals ranged from 70.71° to 104.2° as the organic bases varied. In the six cocrystals, the binols exist either as both of the enantiomers of *rac*-binol or as only of its single enantiomer. All supramolecular architectures of cocrystals **1**–**6** are stabilized by O–H···N hydrogen bonds. In addition other non-conventional interactions (CH–π, CH_3–π, NH–π, S–π, and π–π interactions) play an important role in the solid-state packing of co-crystallization as well. These weak interactions combined, all of the six complexes displayed 3D network structure.

1. Introduction

Currently, H-bonding interactions have been widely developed in the area of crystal engineering, supramolecular chemistry, material science, and biological recognition [1–9]. The application of intermolecular hydrogen bonds is a well known and efficient tool in the field of organic crystal design because of its strength and directional properties [9]. As is known, the strong and directional O–H···N and O–H···O hydrogen bonds are frequently used to construct various co-crystals [10].

There are many interesting hydrogen bonded topological structures which ranged from infinite 1-D chain to 3-D supramolecular frameworks [11,12]. Phenols and pyridine moieties are known to form a variety of supramolecular aggregates via O–H···N hydrogen bonds. Phenol–aza/amine interactions also provide a predictable and robust organizing force to generate a variety of supramolecular aggregates via O–H···N hydrogen bonds [13].

However, comparing with various phenol molecules such as resorcinol, (±)-1,10-binaphthalene-2,2′-diol (binol) is a more flexible molecule with a scissor-shaped backbone, and also has functional hydroxy groups for effective hydrogen binding. These structural features of binol suggest that the binol can be utilized as a structure-directing component in the co-crystal preparation and adopts various conformations suitable for self-assembly architectures. Documented literatures show that the binol can form co-crystals with a wide range of aromatic diimines derivatives [14]. Also, great efforts have been devoted to the development of organic molecular crystals containing a variety of imidazole architectures [15–17]. Among these supramolecular architectures, however, only a very few reports described the crystals composed of bridged imidazoles [18–22] (e.g., 1,4-bis[(imidazol-1-yl)methyl]-benzene [18,22], (bis(1-methyl-imidazol-2-yl)methyl)-4-nitroimidazol-2-yl)methyl)amine [20], etc.). As the bridged imidazoles with different flexibility resulting different spacer length, when they interact with the binol, they can adopt various conformation and generate different structures.

Recently 2-aminoheterocyclic compounds have been reported to form supramolecular compounds with the carboxylic acid derivatives under the multiple hydrogen bonding action [23–24]. In addition to being planar rigid molecules (the planarity of the molecules favors aromatic stacking interactions), the 2-aminoheterocyclic compounds 2-amino-4-phenylthiazole, and 2-amino-5,7-dimethyl-1,8-naphthyridine may act as potentially tridentate ligands (NNN and NSN). The binary adduct of the binol and 2-aminoheterocyclic compounds may display the different hydrogen-bonding patterns from the three different donor atoms. However to the best of our

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knowledge there are no reports based on binol and bridged imidazole and 2-aminoheterocyclic compounds.

It is interesting to exploit the robust and directional recognition of OH group with N-heterocyclic moieties [25]. As an extension of our study of weak interactions (hydrogen bonding, π–π interaction, and halogen bonding) concerning aromatic N-containing derivatives [26], herein we report the preparation and structures of six heteroadducts assembled from 1,4-bis(N-imidazolyl)butane (L1), 1,3-bis(N-benzimidazolyl)propane (L2), 1,4-bis(N-benzimidazolyl)butane (L3), 1,5-bis(N-benzimidazolyl)-3-oxapentane (L4), 2-amino-4-phenylthiazole (L5), and 2-amino-5,7-dimethyl-1,8-naphthyridine (L6) and racemic-bis-*β*-naphthol (binol) (Scheme 1), respectively. The six cocrystals are (1,4-bis(N-imidazolyl)butane): (Binol) [(L1). (Binol)] (**1**), (1,3-bis(N-benzimidazolyl)propane): (Binol) [(L2). (Binol)] (**2**), (1,4-bis(N-benzimidazolyl) butane): $(\text{Binol})_2$ [(L3). $(\text{Binol})_2$] **(3)**, 1,5-bis(N-benzimidazolyl)-3-oxapentane: $(\text{Binol})_2$ [(L4). $(\text{Binol})_2$] **(4)**, (2-amino-4-phenylthiazole): (Binol) **(5)** [(L5). (Binol)], and $(\text{2-amino-5,7-dimethyl-1,8-naphthyridine})_2$: (Binol) [$(\text{L6})_2$. (Binol)] **(6)**.

2. Experimental section

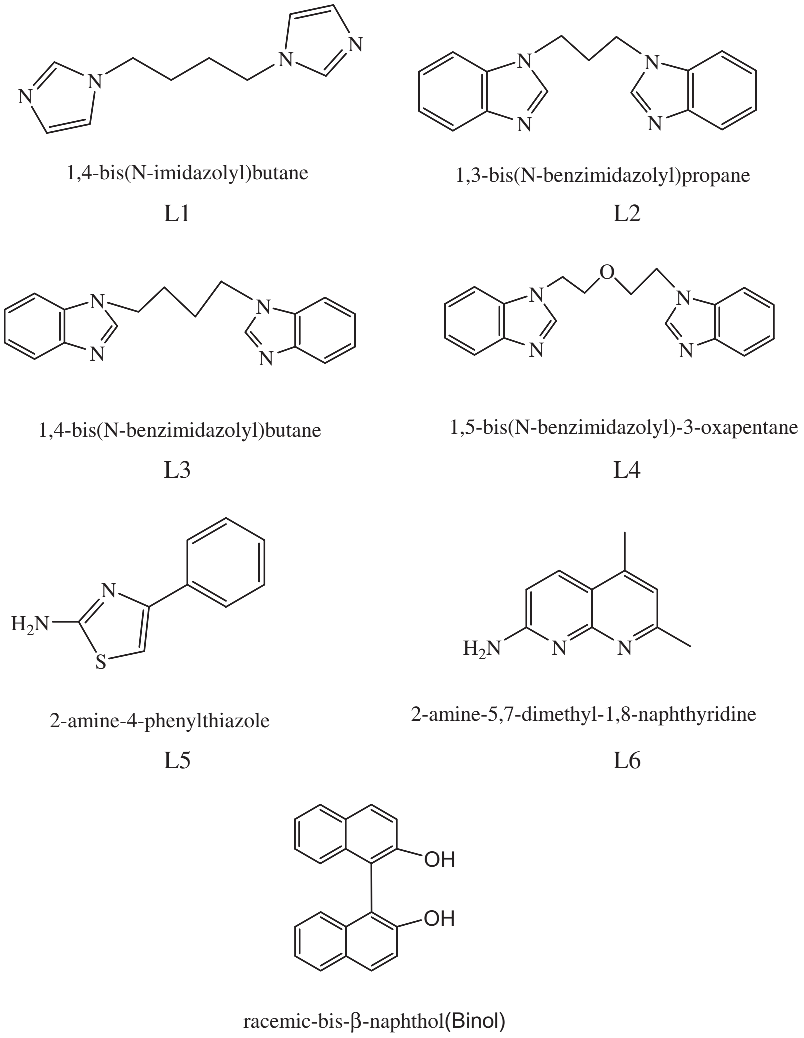
2.1. Materials and physical measurements

The bis(imidazole) derivatives [27], 2-amino-4-phenylthiazole, and 2-amino-5,7-dimethyl-1,8-naphthyridine were prepared by the method described in the literature [28–29]. The other 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 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Microanalytical (C, H, N, S) 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.

2.2. Preparation of the cocrystals **1–6**

2.2.1. (1,4-bis(N-imidazolyl)butane): (Binol) [(L1)·(Binol)] (**1**)

To a methanol solution (2 ml) of 1,4-bis(N-imidazolyl)butane (L1) (38 mg, 0.2 mmol) was added Binol (57.3 mg, 0.2 mmol) dissolved in acetonitrile (8 ml). The solution was stirred for half an hour, 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 collected and dried in air to give the title compound [(L1). (Binol)] (**1**). Yield: 78 mg, 81.84%. M.p. 199–201 °C. Anal. Calcd for $C_{30}H_{28}N_4O_2$ (476.56): C, 75.54; H, 5.88; N, 11.75. Found: C, 75.48; H, 5.79; N, 11.72. Infrared spectrum (KBr disc, cm^{-1}): 3632s, 3446w, 3135w, 2943w, 1612m, 1591m, 1515m, 1488m, 1448m, 1370w, 1342s, 1238w, 1196m, 1098m, 952w, 877w, 831m, 797w, 724m, 654w, 618w.



Scheme 1. Hydrogen bond synthons discussed in this paper.

2.2.2. (1,3-bis(N-benzimidazolyl)propane): (Binol) [(L2)·(Binol)] (2)

To an acetonitrile solution (4 ml) of 1,3-bis(N-benzimidazolyl)propane (L2) (56 mg, 0.20 mmol) was added Binol (57.3 mg, 0.2 mmol) dissolved in acetonitrile (8 ml). The solution was stirred for half an hour, 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 collected and dried in air to give the title compound [(L2)·(Binol)] (**2**). Yield: 92 mg, 81.76%. M.p. 212–213 °C. Anal. Calcd for $C_{37}H_{30}N_4O_2$ (562.65): C, 78.91; H, 5.33; N, 9.95. Found: C, 78.86; H, 5.28; N, 9.91. Infrared spectrum (KBr disc, cm^{-1}): 3646s, 3500s, 3360s, 3290s, 3120s, 3040s, 1760s, 1605s, 1580s, 1560s, 1500s, 1440s, 1380s, 1260m, 1240m, 1180m, 1140m, 1060m, 1010m, 970m, 930m, 870m, 760m, 716m, 682m, 620m.

2.2.3. (1,4-bis(N-benzimidazolyl)butane): $(Binol)_2$ $[(L3)\cdot(Binol)_2]$ (3)

To a methanol solution (5 ml) of 1,4-bis(N-benzimidazolyl)butane (L3) (58 mg, 0.20 mmol) was added Binol (57.3 mg, 0.2 mmol) dissolved in acetonitrile (8 ml). The solution was stirred for half an hour, 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 collected and dried in air to give the title compound $[(L3)\cdot(Binol)_2]$ (**3**). Yield: 85 mg, 49.24% (based on L3). M.p. 224–226 °C. Anal. Calcd for $C_{58}H_{46}N_4O_4$ (862.99): C, 80.65; H, 5.33; N, 6.49. Found: C, 80.62; H, 5.31; N, 6.43. Infrared spectrum (KBr disc, cm^{-1}): 3463s, 3442s, 3289m, 3118s, 3047s, 2862s, 2366m, 1759m, 1621m, 1565m, 1458m, 1382m, 1328m, 1243m, 1124m, 1009m, 938m, 862m, 784m, 707m, 663m, 615w.

2.2.4. (1,5-bis(N-benzimidazolyl)-3-oxapentane): $(Binol)_2$ $[(L4)\cdot(Binol)_2]$ (4)

To an ethanol solution (8 ml) of 1,5-bis(N-benzimidazolyl)-3-oxapentane (L4) (62 mg, 0.20 mmol) was added Binol (57.3 mg, 0.2 mmol) dissolved in acetonitrile (8 ml). The solution was stirred for half an hour, 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 collected and dried in air to give the title compound $[(L4)\cdot(Binol)_2]$ (**4**). Yield: 85 mg, 48.35% (based on L4). M.p. 236–238 °C. Anal. Calcd for $C_{58}H_{46}N_4O_5$ (878.99): C, 79.18; H, 5.23; N, 6.37. Found: C, 79.12; H, 5.18; N, 6.32. Infrared spectrum (KBr disc, cm^{-1}): 3474s, 3440s, 3296m, 3120s, 3080s, 2940m, 2860m, 1960m, 1720m, 1680m, 1604m, 1551m, 1512m, 1456m, 1382m, 1344m, 1292m, 1215m, 1174m, 1106m, 1042m, 878m, 821m, 764m, 723m, 654w, 618w.

2.2.5. (2-Amino-4-phenylthiazole): (Binol) [(L5)·(Binol)] (5)

To a methanol solution (5 ml) of 2-amino-4-phenylthiazole (L5) (35.2 mg, 0.2 mmol) was added Binol (57.3 mg, 0.2 mmol) dissolved in acetonitrile (8 ml). The solution was stirred for half an hour, then the solution was filtered into a test tube. The solution was left standing at room temperature for several days, colorless crystals were isolated after slow evaporation of the mixed solution in air. The crystals were collected and dried in air to give the title compound [(L5)·(Binol)]. Yield: 80 mg, 86.48%. M.p. 243–244 °C. Elemental analysis performed on crystals exposed to the atmosphere: Calcd for $C_{29}H_{22}N_2O_2S$ (462.55): C, 75.24; H, 4.75; N, 6.05; S, 6.92. Found: C, 75.22; H, 4.71; N, 5.97; S, 6.86. Infrared spectrum (KBr disc, cm^{-1}): 3560s, 3458s, 3319s, 3114m, 3062m, 2963m, 2841m, 2717m, 2466w, 2372m, 2209m, 1976w, 1837w, 1783w, 1662w, 1592m, 1533m, 1487w, 1331m, 1251m, 1199m, 1133m, 1074m, 956m, 905m, 848m, 802m, 755m, 727m, 682m, 636m.

2.2.6. (2-Amino-5,7-dimethyl-1,8-naphthyridine)$_2$: (Binol) $[(L6)_2\cdot(Binol)]$ (6)

To an ethanol solution (8 ml) of 2-amino-5,7-dimethyl-1,8-naphthyridine (L6) (34.8 mg, 0.2 mmol) was added Binol (57.3 mg, 0.2 mmol) dissolved in 8 ml acetonitrile. The solution was stirred for half an hour, 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 collected and dried in air to give the title compound $[(L6)_2\cdot(Binol)]$ (**6**). Yield: 75 mg, 59.26% (based on L6). M.p. 256–258 °C. Anal. Calcd for $C_{40}H_{36}N_6O_2$ (632.75): C, 75.86; H, 5.68; N, 13.28. Found: C, 75.78; H, 5.62; N, 13.24. Infrared spectrum (KBr disc, cm^{-1}): 3638s, 3362s, 3306s, 3148s, 3074s, 2980s, 2926s, 2378m, 2318m, 2086w, 1760w, 1672s, 1624s, 1602m, 1540s, 1500m, 1487m, 1448m, 1400m, 1295m, 1240m, 1202m, 1158m, 1088m, 1002m, 928m, 846m, 742s, 706m, 646s, 610m.

2.3. 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 [30]. 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 [31]. Hydrogen atoms were introduced at fixed distances from carbon atoms and assigned fixed thermal parameters. The hydrogen atoms attached to the oxygen and the nitrogen atoms were refined isotropically. Further details of the structural analysis are summarized in Table 1. Selected bond lengths and angles for **1**–**6** are listed in Table 2, the relevant hydrogen bond parameters are provided in Table 3.

3. Results and discussion

3.1. Preparation and general characterization

The bis(imidazole) derivatives (L1–L4), 2-amino-4-phenylthiazole, and 2-amino-5,7-dimethyl-1,8-naphthyridine all have good solubility in common organic solvents, such as methanol, ethanol, dichloromethane, chloroform, and acetonitrile.

In the preparation of the organic cocrystals **1**–**6**, the racemic-bis-β-naphthols were mixed directly with the bases in the corresponding solution in 1:1 ratio, which was allowed to evaporate at ambient conditions to give the final crystalline products. In all of the structures the base molecules are not protonated therefore the structure can be classified as cocrystals, not ionic compounds. The six cocrystals are not hygroscopic, and they all crystallized without solvent molecules accompanied. The elemental analysis data for the six compounds are in good agreement with their compositions. The infrared spectra of the six compounds are fully consistent with their chemical formulas determined by elemental analysis and further confirmed by X-ray diffraction analysis. H atoms connected to O or N atoms were well found from the difference electron density map, which also indirectly confirms the cocrystal formation.

The very strong and broad features at approximately 3700–3100 cm^{-1} in the IR spectra of the six compounds arise from O–H or N–H stretching frequencies. Aromatic, imidazolyl, phenylthiazolic, and naphthyridinic ring stretching and bending are attributed to the medium intensity bands in the regions of 1500–1630 cm^{-1} and 600–750 cm^{-1}, respectively.

Table 1
Summary of X-ray crystallographic data for complexes **1**–**6**.

	1	**2**	**3**	**4**	**5**	**6**
Formula	$C_{30}H_{28}N_4O_2$	$C_{37}H_{30}N_4O_2$	$C_{58}H_{46}N_4O_4$	$C_{58}H_{46}N_4O_5$	$C_{29}H_{22}N_2O_2S$	$C_{40}H_{36}N_6O_2$
Fw	476.56	562.65	862.99	878.99	462.55	632.75
T (K)	298(2)	298(2)	298(2)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	C2/c	P2(1)/c	P-1	P-1	P-1	C2/c
a (Å)	14.9212(13)	12.0744(15)	10.7325(9)	10.5603(12)	9.4798(8)	20.062(2)
b (Å)	9.8700(8)	9.6562(13)	10.9564(10)	11.1141(13)	11.0126(11)	15.8357(15)
c (Å)	17.9897(15)	26.593(3)	11.9692(15)	11.7869(14)	13.0166(16)	10.5822(9)
α (°)	90	90	115.088(2)	114.2390(10)	68.2120(10)	90
β (°)	109.2730(10)	100.473(2)	99.5660(10)	101.0700(10)	87.980(2)	109.3160(10)
γ (°)	90	90	108.6580(10)	106.296(2)	64.8140(10)	90
V (Å^3)	2500.9(4)	3048.9(7)	1130.5(2)	1133.7(2)	1129.6(2)	3172.7(5)
Z	4	4	1	1	2	4
D_{calcd} (Mg/m^3)	1.266	1.226	1.268	1.287	1.360	1.325
Absorption coefficient (mm^{-1})	0.081	0.077	0.080	0.083	0.174	0.084
F(000)	1008	1184	454	462	484	1336
Crystal size (mm^3)	0.49 × 0.48 × 0.45	0.39 × 0.38 × 0.26	0.13 × 0.12 × 0.06	0.48 × 0.38 × 0.29	0.45 × 0.34 × 0.25	0.45 × 0.42 × 0.16
θ range (°)	2.40–25.02	2.62–25.02	2.28–25.01	2.38–25.02	1.70–25.01	2.57–25.02
Limiting indices	$-17 \leqslant h \leqslant 16$	$-14 \leqslant h \leqslant 11$	$-11 \leqslant h \leqslant 12$	$-11 \leqslant h \leqslant 12$	$-10 \leqslant h \leqslant 11$	$-23 \leqslant h \leqslant 22$
	$-11 \leqslant k \leqslant 6$	$-11 \leqslant k \leqslant 11$	$-13 \leqslant k \leqslant 10$	$-8 \leqslant k \leqslant 13$	$-13 \leqslant k \leqslant 13$	$-17 \leqslant k \leqslant 18$
	$-21 \leqslant l \leqslant 20$	$-23 \leqslant l \leqslant 31$	$-12 \leqslant l \leqslant 14$	$-13 \leqslant l \leqslant 14$	$-15 \leqslant l \leqslant 12$	$-12 \leqslant l \leqslant 12$
Reflections collected	6111	15169	5985	5999	5865	7778
Reflections independent (R_{int})	2213 (0.0307)	5390 (0.0983)	3926 (0.0264)	3963 (0.0309)	3921 (0.0222)	2792 (0.0438)
Goodness-of-fit on F^2	1.087	0.855	0.876	0.811	1.007	1.071
R indices [$I > 2\sigma I$]	0.0415, 0.0906	0.0655, 0.1555	0.0445, 0.0926	0.0515, 0.1119	0.0496, 0.1137	0.0412, 0.0966
R indices (all data)	0.0695, 0.1122	0.1610, 0.2055	0.0978, 0.1097	0.1267, 0.1352	0.0927, 0.1414	0.0868, 0.1275
Largest diff. peak and hole (e Å^{-3})	0.119, −0.186	0.187, −0.206	0.127, −0.147	0.155, −0.171	0.279, −0.228	0.198, −0.227

3.2. Structural descriptions

*3.2.1. X-ray structure of (1,4-bis(N-imidazolyl)butane): (Binol) [(L1)·(Binol)] (**1**)*

The compound **1** of the composition [(L1)·(Binol)] was prepared by crystallizing equal mol of 1,4-bis(N-imidazolyl)butane and binol in a mixed solvent of methanol and acetonitrile, in which both protons of the binol were remained with the O atoms. This structure is not a solvate. In the asymmetric unit of **1** there existed half a molecule of 1,4-bis(N-imidazolyl)butane, and half a molecule of binol, respectively, as shown in Fig. 1(i). Compound **1** crystallizes as monoclinic block crystals in the space group C2/c.

The C–O (O(1)–C(2)) distance concerning the OH group of the binol is 1.357(2) Å which is similar to the C–O distance in other binary aromatic aza adduct of binol (1.356(2)–1.364(2)) [14b,14e], which confirms the reliability of adding H atoms experimentally by different electron density onto O atoms, and also clearly indicates that the binol is not ionized. The H-atoms of both hydroxyl groups are approximately in plane with the aromatic systems that they are attached. Intracyclic C–C–C angles span a range of 117.78(16)–121.59(19)° with the biggest angle found on the C(9)–C(10)–C(5).

It was found that although the N atom of L1 is involved in hydrogen bonding interaction with the binol molecule the conformation of 1,4-bis(N-imidazolyl)butane in **1** has not experienced significant change in comparison to the corresponding neutral molecule L1 [32]. The imidazole rings in **1** have trans-(ap) position in respect to C15–C15a bond (angle C14–C15–C15a–C14a, 180°), which is different from the corresponding angle in the ionic compound 1,1′-(1,4-butanediyl)bis(imidazolium) dihydrochloride [32]. The imidazole ring forms a dihedral angle of 80.4 (2)° with the plane defined by the C atoms of the $-(CH_2)_4-$ aliphatic linker in 1,4-bis(N-imidazolyl)butane, which is larger than the corresponding value in its nitrate salt (62.7 (3)°) [33].

The two naphthalene rings in the same binol are almost planar with the r.m.s deviations of 0.0262 Å, and 0.0218 Å, respectively. The imidazole ring is also planar with r.m.s deviation of 0.0013 Å. The dihedral angle between the two naphthalene rings in the same binol is 72.7°, the dihedral angle between the imidazole ring and the two naphthalene rings are 105.5°, and 77° respectively. In this arrangement, two naphthalene rings rotate for more close array along the C–C bond than those reported by Ji (for the dihedral angle (72.7°) of the two naphthalene rings in **1** is smaller than the reported values of 74.9°, and 75.1° by Ji) [14b].

The adjacent binol molecules are parallel to each other, and they are held together through C–H⋯O association (between the C(9)–H(9) of one naphthyl group and the OH group of another binol molecule with C–O distance of 3.341 Å) and edge-to-face C–H⋯π interaction (between C(10)–H(10) of one binol and the aromatic ring of the other adjacent binol with C–Cg (Cg is the gravity center of the naphthalene ring of the binol) distance of ca. 3.475 Å) (Fig. 1(ii)).

Under the above intermolecular interactions the binol molecules formed a 1D chain running along the *c* axis direction. The chains were further connected together through C–H⋯O and CH–π interactions along the [1 0 0] axis direction to form 2D grid extending along the *ac* plane.

The grids formed by binols stacked along the *b* axis direction in which the binol molecules at adjacent grids were antiparallely arranged. And the third grid has the same projection at the *ac* plane as the first grid. The L1 molecules were sandwiched between two adjacent grids through CH–π (between C(13)–H(13) of one imidazole ring of L1 and the naphthyl group of binol of one grid with C–Cg distance of 3.717 Å) and O–H⋯N interactions (between the naphthol OH group of another grid and the terminal N atom of another imidazole ring of the same L1, O(1)–H(1)⋯N(2)#3, 2.704(2) Å).

In this case the L1 molecules were located almost at the center of the cavities of the grid formed by binols. The L1 molecules sandwiched between the same two adjacent grids are parallel to each other, but the L1 molecules sandwiched between the second grid and the third grid is almost perpendicular to those sandwiched between the first grid and the second grid. Such an arrangement repeated the final structure of the compound displays 3D layer network structure without channels (Fig. 1(iii)).

Table 2
Selected bond lengths (Å) and angles (°) for compounds **1–6**.

1			
N(1)–C(11)	N(1)–C(11)	N(1)–C(11)	N(1)–C(11)
N(1)–C(14)	N(1)–C(14)	N(1)–C(14)	N(1)–C(14)
N(2)–C(12)	N(2)–C(12)	N(2)–C(12)	N(2)–C(12)
C(1)–C(2)	C(1)–C(2)	C(1)–C(2)	C(1)–C(2)
C(11)–N(1)–C(13)	C(11)–N(1)–C(13)	C(11)–N(1)–C(13)	C(11)–N(1)–C(13)
C(13)–N(1)–C(14)	C(13)–N(1)–C(14)	C(13)–N(1)–C(14)	C(13)–N(1)–C(14)
N(2)–C(11)–N(1)	N(2)–C(11)–N(1)	N(2)–C(11)–N(1)	N(2)–C(11)–N(1)
2			
N(1)–C(21)	N(1)–C(21)	N(1)–C(21)	N(1)–C(21)
N(1)–C(35)	N(1)–C(35)	N(1)–C(35)	N(1)–C(35)
N(2)–C(22)	N(2)–C(22)	N(2)–C(22)	N(2)–C(22)
N(3)–C(30)	N(3)–C(30)	N(3)–C(30)	N(3)–C(30)
N(4)–C(28)	N(4)–C(28)	N(4)–C(28)	N(4)–C(28)
O(1)–C(2)	O(1)–C(2)	O(1)–C(2)	O(1)–C(2)
C(21)–N(1)–C(23)	C(21)–N(1)–C(23)	C(21)–N(1)–C(23)	C(21)–N(1)–C(23)
C(23)–N(1)–C(35)	C(23)–N(1)–C(35)	C(23)–N(1)–C(35)	C(23)–N(1)–C(35)
C(28)–N(3)–C(30)	C(28)–N(3)–C(30)	C(28)–N(3)–C(30)	C(28)–N(3)–C(30)
C(30)–N(3)–C(37)	C(30)–N(3)–C(37)	C(30)–N(3)–C(37)	C(30)–N(3)–C(37)
N(2)–C(21)–N(1)	N(2)–C(21)–N(1)	N(2)–C(21)–N(1)	N(2)–C(21)–N(1)
3			
N(1)–C(1)	N(1)–C(1)	N(1)–C(1)	N(1)–C(1)
N(1)–C(8)	N(1)–C(8)	N(1)–C(8)	N(1)–C(8)
N(2)–C(2)	N(2)–C(2)	N(2)–C(2)	N(2)–C(2)
O(2)–C(21)	O(2)–C(21)	O(2)–C(21)	O(2)–C(21)
C(1)–N(1)–C(8)	C(1)–N(1)–C(8)	C(1)–N(1)–C(8)	C(1)–N(1)–C(8)
C(1)–N(2)–C(2)	C(1)–N(2)–C(2)	C(1)–N(2)–C(2)	C(1)–N(2)–C(2)
4			
N(1)–C(1)	N(1)–C(1)	N(1)–C(1)	N(1)–C(1)
N(1)–C(8)	N(1)–C(8)	N(1)–C(8)	N(1)–C(8)
N(2)–C(2)	N(2)–C(2)	N(2)–C(2)	N(2)–C(2)
O(1)–C(9)	O(1)–C(9)	O(1)–C(9)	O(1)–C(9)
O(3)–C(21)	O(3)–C(21)	O(3)–C(21)	O(3)–C(21)
C(1)–N(1)–C(8)	C(1)–N(1)–C(8)	C(1)–N(1)–C(8)	C(1)–N(1)–C(8)
C(1)–N(2)–C(2)	C(1)–N(2)–C(2)	C(1)–N(2)–C(2)	C(1)–N(2)–C(2)
N(2)–C(1)–N(1)	N(2)–C(1)–N(1)	N(2)–C(1)–N(1)	N(2)–C(1)–N(1)
5			
N(1)–C(1)	N(1)–C(1)	N(1)–C(1)	N(1)–C(1)
N(2)–C(1)	N(2)–C(1)	N(2)–C(1)	N(2)–C(1)
O(2)–C(21)	O(2)–C(21)	O(2)–C(21)	O(2)–C(21)
S(1)–C(1)	S(1)–C(1)	S(1)–C(1)	S(1)–C(1)
C(2)–C(4)	C(2)–C(4)	C(2)–C(4)	C(2)–C(4)
C(3)–S(1)–C(1)	C(3)–S(1)–C(1)	C(3)–S(1)–C(1)	C(3)–S(1)–C(1)
N(1)–C(1)–S(1)	N(1)–C(1)–S(1)	N(1)–C(1)–S(1)	N(1)–C(1)–S(1)
6			
N(1)–C(1)	N(1)–C(1)	N(1)–C(1)	N(1)–C(1)
N(2)–C(6)	N(2)–C(6)	N(2)–C(6)	N(2)–C(6)
N(3)–C(1)	N(3)–C(1)	N(3)–C(1)	N(3)–C(1)
C(1)–N(1)–C(5)	C(1)–N(1)–C(5)	C(1)–N(1)–C(5)	C(1)–N(1)–C(5)
N(1)–C(1)–N(3)	N(1)–C(1)–N(3)	N(1)–C(1)–N(3)	N(1)–C(1)–N(3)

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

Table 3
Hydrogen bond distances and angles in studied structures of **1–6**.

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	<(DHA) (°)
1				
O(1)–H(1)···N(2)#3	0.82	1.95	2.704(2)	153.4
2				
O(2)–H(2)···N(4)#1	0.82	1.91	2.718(3)	169.7
O(1)–H(1)···N(2)#2	0.82	1.91	2.679(4)	155.7
3				
O(2)–H(2)···N(2)	0.82	1.88	2.655(2)	157.9
O(1)–H(1)···O(2)#2	0.82	1.96	2.7509(19)	162.4
4				
O(3)–H(3)···O(2)#2	0.82	1.96	2.754(2)	162.9
O(2)–H(2)···N(2)	0.82	1.87	2.640(3)	156.5
5				
O(2)–H(2)···O(2)#1	0.82	2.62	3.018(4)	111.4
O(1)–H(1)···N(1)#2	0.82	2.21	2.861(3)	137.2
N(2)–H(2B)···O(1)	0.86	2.35	3.047(3)	138.8
N(2)–H(2A)···O(2)#2	0.86	2.27	3.123(3)	170.2
6				
O(1)–H(1)···N(2)#2	0.82	1.94	2.718(2)	158.2
N(3)–H(3B)···O(1)#3	0.86	2.28	2.893(3)	128.7
N(3)–H(3A)···N(1)#4	0.86	2.26	3.104(3)	167.3

Symmetry transformations used to generate equivalent atoms for **1**: #3 x, $y-1$, z. Symmetry transformations used to generate equivalent atoms for **2**: #1 x, $y-1$, z; #2 x, $-y+3/2$, $z+1/2$. Symmetry transformations used to generate equivalent atoms for **3**: #2 $-x+1$, $-y$, $-z+1$. Symmetry transformations used to generate equivalent atoms for **4**: #2 $-x+1$, $-y$, $-z+1$. Symmetry transformations used to generate equivalent atoms for **5**: #1 $-x+1$, $-y+1$, $-z+1$, #2 $-x$, $-y+1$, $-z+1$. Symmetry transformations used to generate equivalent atoms for **6**: #2 $-x+1/2$, $-y+1/2$, $-z+1$; #3 $x+1/2$, $y-1/2$, z; #4 $-x+1$, $-y$, $-z+1$.

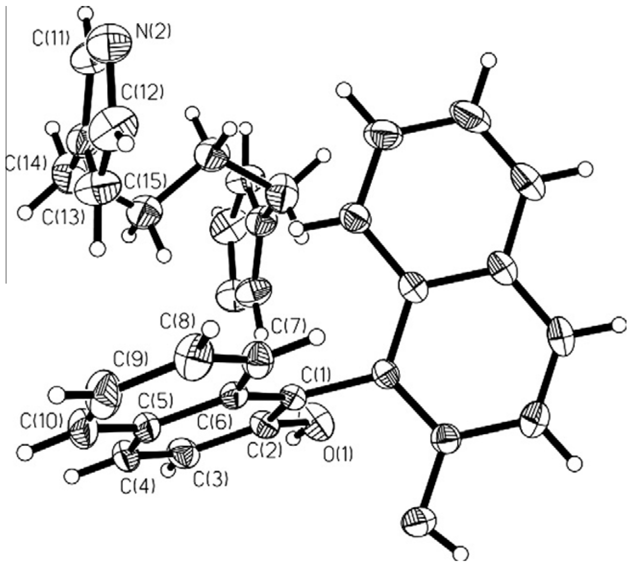


Fig. 1(i). Molecular structure of **1** showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

*3.2.2. X-ray structure of (1,3-bis(N-benzimidazolyl)propane): (Binol) [(L2)·(Binol)] (**2**)*

Cocrystallization of L2 with binol from acetonitrile occurred in a 1:1 ratio to give cocrystal **2**. The asymmetric unit of **2** consists of one molecule of each starting material in the unit cell as shown in Fig. 2(i). There exist two O–H···N hydrogen bonds between the OH group of binol and the N atom of L2 (O(2)–N(4)#1, 2.718(3) Å, and O(1)–N(2)#2, 2.679(4) Å). The L2 forms 1D zigzag chain running along the *b* axis direction under the edge to face CH–π interaction with C–Cg distance of 3.688 Å between the benzene CH of one L2 and the benzene ring of its adjacent L2. Two such adjacent chains were joined together through the interchain CH–π interaction between the N–CH–N of the benzimidazole moiety and the benzene ring of L2 with C–Cg distance of 3.491 Å to form a double chain extending in the *bc* plane (Fig. 2(ii)).

The r.m.s deviations of the naphthalene ring atoms in **2** from the mean planes of the rings containing atoms C1–C10 and C11–C20 are 0.0031 Å and 0.0192 Å, respectively. The dihedral angle between the two rings is 72.7° which is almost the same as the corresponding value in **1**. As expected, the benzimidazole rings are

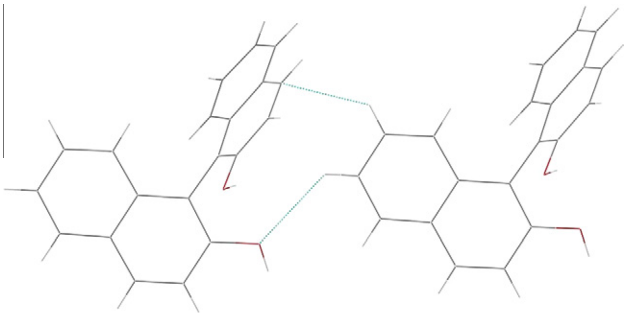


Fig. 1(ii). C–H···π and C–H···O interactions between binol.

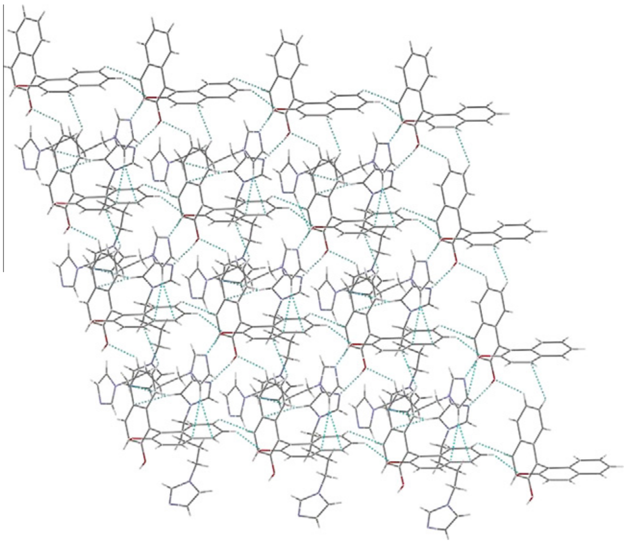


Fig. 1(iii). 3D layer structure of the compound **1** which is viewed along the c axis.

planar in which the mean deviations of the benzimidazole rings containing N3, N4, and N1, N2 atoms from the mean planes are 0.0083 Å and 0.0164, respectively. The dihedral angle between the two benzimidazole rings in the same L2 is 74.4°. The benzimidazole plane containing N3, and N4 atoms makes dihedral angles of 75°, and 93.7° respectively with the above two naphthalene rings. The benzimidazole ring containing N1, and N2 atoms forms dihedral angle of 0.7° with the naphthalene plane defined by the atoms C1–C10, indicating the coplanarity of both rings.

One binol molecule is bonded to two adjacent L2 molecules in the chain with the same half part of the binol, i.e. the OH group forms one O–H···N hydrogen bond with the terminal N of one L2 with N–O distance of 2.718 Å, and the CH coming from the same naphthalene ring as the OH group associates with the benzimidazole ring of another adjacent L2 in the chain through CH–π interaction (with C–Cg distance of 3.660 Å). In this case the binol molecules bonded to the same chain formed by L2 are parallel and those binol molecules bonded to different chains of the double chain are antiparallely arranged. Under these two kinds of interactions the compound displays 2D sheet structure (Fig. 2(iii)). Adjacent sheets were stacked along the *a* axis direction through O–H···N (between OH group of the first sheet and the imidazole N atom of the adjacent sheet with N–O distance of 2.679 Å), and CH–π (between N–CH–N of the benzimidazole of the second sheet and the naphthalene moiety of the first sheet with C–Cg distance of 3.78 Å) interactions to form double sheet structure. There are also CH_2–O interaction between the propane spacer of the first sheet and the O atom of the binol of the second sheet with C–O distance of 3.554 Å. In the double sheet the two adjacent sheets were slipped some distance from each other. Adjacent double sheets were further connected together by π–π interaction between the naphthalene ring and the benzimidazole ring with Cg–Cg distance of 3.283 Å along the *a* axis direction to form 3D layer structure. In the 3D structure the third sheet has the same projection on the *bc* plane as the first sheet.

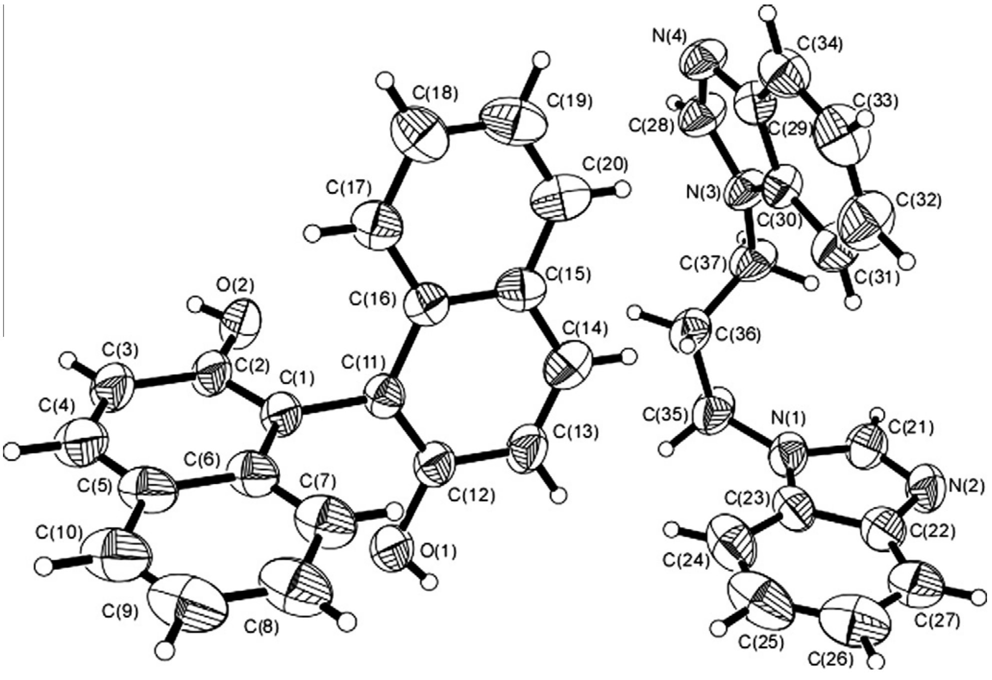


Fig. 2(i). The structure of **2**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

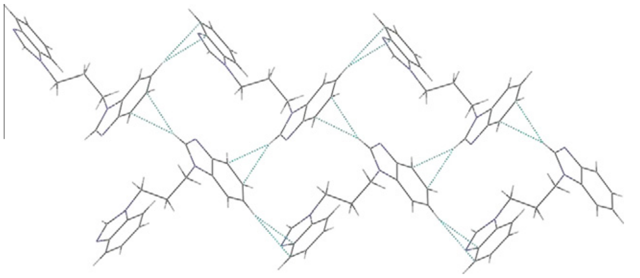


Fig. 2(ii). The double chain formed via intrachain and interchain CH–π interactions.

*3.2.3. X-ray structure of (1,4-bis(N-benzimidazolyl)butane): (Binol)$_2$ [(L3)·(Binol)$_2$] (**3**)*

Although the compound **3** was prepared in the same way as the compound **1**, the composition of the compound **3** is different from **1**. Compound **3** of the formula [(L3)·(Binol)$_2$] (L3 = 1,4-bis(N-benzimidazolyl)butane) crystallizes in the triclinic P-1 space group, and there are 1 formula unit in its cell content. In **3** the asymmetric unit is occupied by one binol and a half L3 molecules (Fig. 3(i)).

Similar with {[Zn(FcCOO)$_2$(L3)]·2H$_2$O}$_n$ [34], the two benzimidazole rings in the same L3 molecule of compound **3** were antiparallel to each other also, but it is different from the reported compound of [(H$_2$L3)CdCl$_4$] in which the two benzimidazole rings are perpendicular to each other (the dihedral angle between the two benzimidazole rings is 91.1°) [35]. The L3 in **3** is twisted with the torsion angles of 61.08° and −61.08° for N1–C8–C9–C9a and C9–C9a–C8a–N1a, respectively, which is different from our previously reported results (−172.6°, and 175.52°) [35], yet it is similar to the documented value of ±58.70° [36].

As expected, the benzimidazole rings are planar (the r.m.s deviation from the mean plane is 0.0035 Å) within the L3 molecule. The r.m.s deviation of the naphthalene ring bearing C10–C19 atoms from the mean plane is 0.0167 Å, which forms dihedral angle of 110.7° with the benzimidazole ring. The r.m.s deviation of the naphthalene ring containing atoms C20–C29 from the mean plane of the ring is 0.0101 Å, which makes dihedral angle of 60.7° with the benzimidazole rings. The dihedral angle between two naphthalene rings in the same binol is 97.6° which is greatly larger than those found in **1**, and **2**.

Two binols form homodimers through two pairs of O–H···O hydrogen bonding interactions between the OH groups with O–O distance of 2.7509(19) Å to display a $R_2^2(14)$ ring motif. In this

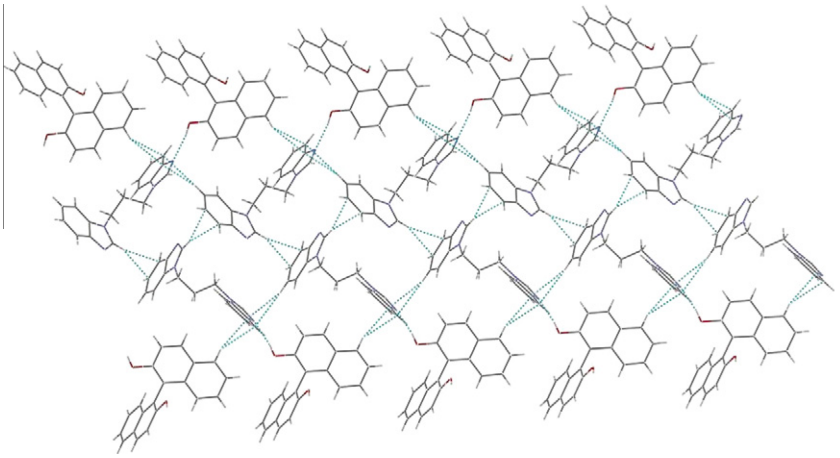


Fig. 2(iii). 2D sheet structure of the compound **2** viewed along the *a* axis direction.

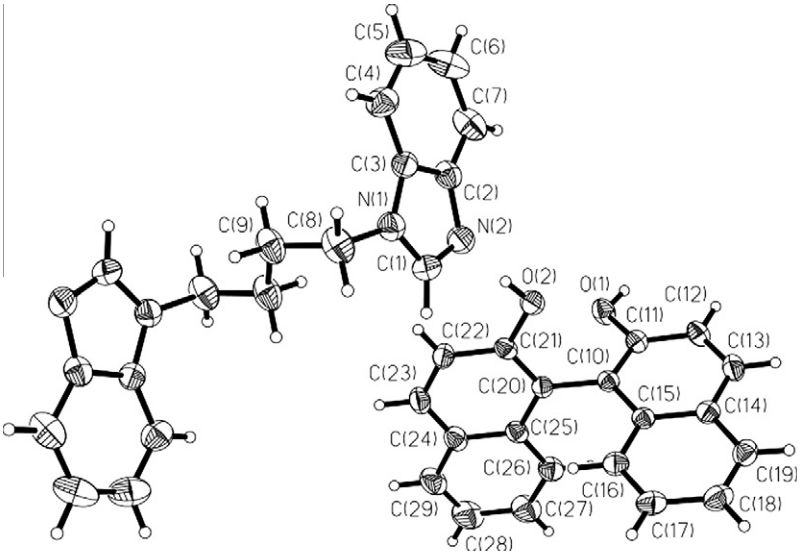


Fig. 3(i). Molecular structure of **3** showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

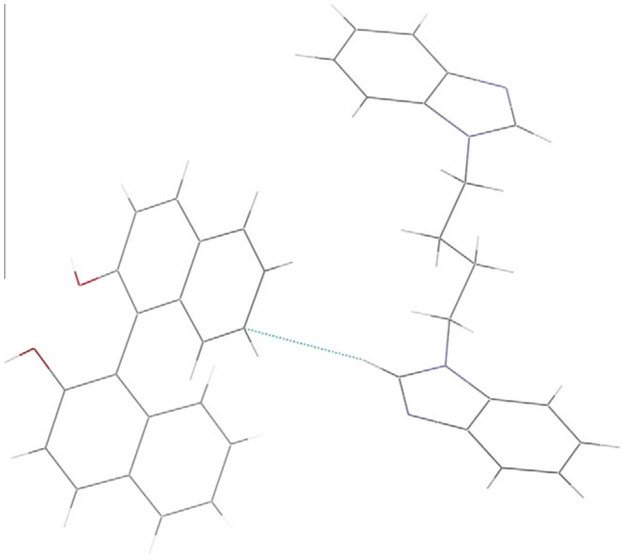


Fig. 3(ii). CH–π interaction between the N–CH–N of L3 and the naphthalene ring.

regard, the intermolecular O–O distance is slightly smaller than the corresponding value in (R)-(+)-Binol, (R,S)-(±)-Binol, and (S)-(−)-Binol in which the O–O distances ranged from 2.86 to 2.96 Å [37]. In the homodimers the two binol molecules are inversionally related, and thus the homodimer is constituted by both the enantiomers of *rac*-binol.

The binol dimers and the L3 were arranged alternatively along the *b* axis direction to form a 1D chain. Adjacent chains were connected together by CH–π interaction (Fig. 3(ii)) between the N–CH–N of L3 and the naphthalene ring with C–Cg distance of 3.749 Å to form a 2D grid (Fig. 3(iii)). The grids were further stacked along the *a* axis direction through the CH_2–O interaction (between CH_2 of the butane spacer and the OH group of the naphthalene unit with C–O distance of 3.394 Å), CH_2–π interaction (between CH_2 of the butane spacer and the naphthalene ring with C–Cg distance of 3.640 Å), and CH–π interaction (between two naphthalene rings at two neighboring grids with C–Cg distance of 3.400 Å) to form 3D layer network structure. In this case the adjacent grids were also slipped some distance from each other.

*3.2.4. X-ray structure of 1,5-bis(N-benzimidazolyl)-3-oxapentane: $(Binol)_2$ [(L4)·$(Binol)_2$] (**4**)*

Similar to **3**, the crystal structure of **4** also consists of half a molecule of L4, and one molecule of binol in the asymmetric unit (Fig. 4(i)). The compound crystallizes in a triclinic space group P-1 with unit content of one formula unit also. The L4 ligand adopts a trans configuration with the planes of the two benzimidazole rings in the same L4 molecule antiparallely arranged. The bridged O atom of the spacer in L4 is disordered over two positions with occupancies of 0.5 respectively.

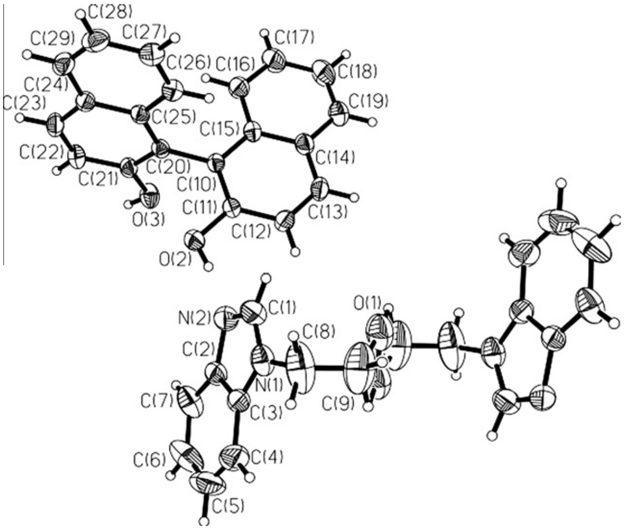


Fig. 4(i). Molecular structure of **4** showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

The r.m.s deviation of the benzimidazole ring atoms from the mean plane of the ring containing atoms C1–C7, N1, and N2 is 0.0040 Å. The r.m.s deviations of the naphthalene rings bearing C10–C19 and C20–C29 atoms from the mean planes are 0.0152 Å, and 0.0136 Å, respectively. The dihedral angle between the two naphthalene planes is 95.5° which is slightly smaller than the corresponding value in **3**, yet it is still greatly larger than that in **1**, and **2**. The benzimidazole ring forms dihedral angles of 65.3°, and 106.4° respectively with the two naphthalene rings in the same binol molecule.

The binols also form homodimers through two pairs of intermolecular O–H···O hydrogen bond between two binols with O–O distance of 2.754 Å, which is similar to that in **3**. The L4 connected the dimer through O–H···N hydrogen bond to form a 1D chain running along the *b* axis direction, in the chain the binol dimer and the L4 were arranged alternately. Adjacent chains were connected together through CH–π interaction (Fig. 4(ii)) between the naphthalene rings at the two chains with C–Cg distance of 3.586 Å to form 2D sheet extending on the *ab* plane (Fig. 4(iii)). The sheets were further stacked along the *c* axis direction such that the chains of the second sheet were just located above the center of two

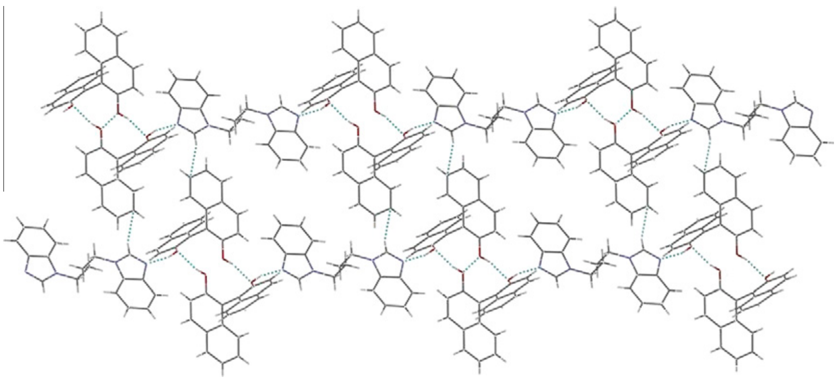


Fig. 3(iii). 2D grid structure of **3** running along the *b* axis direction.

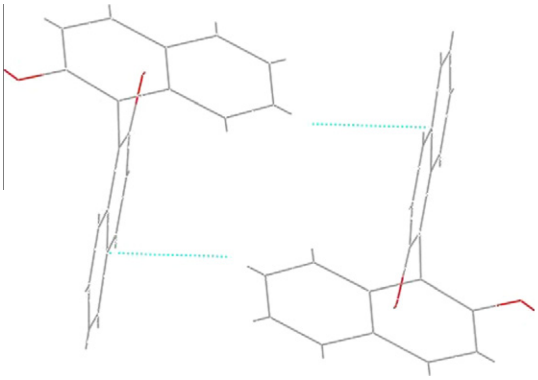


Fig. 4(ii). CH–π interaction between the naphthalene rings at the two adjacent chains.

adjacent chains in the first sheet. Such stacks repeated that the final structure of the title compound displayed 3D network structure without channels when viewed along the *c* axis direction. Like cocrystal **3** there are also CH_2–π and CH_2-O interactions between adjacent sheets.

3.2.5. X-ray structure of (2-amino-4-phenylthiazole): (Binol) [(L5)·(Binol)] (5)

The compound **5** was also prepared by crystallizing of 2-amino-4-phenylthiazole with binol in 1:1 ratio, which crystallizes as triclinic block crystals in the centrosymmetric space group P-1. The compound consists of one molecule of each reactant in the unit cell (Fig. 5(i)).

The compound is also a cocrystal. As shown in table 2, all the bond angles and bond distances are in the normal range. The O–C bond distance concerning the naphthol group was 1.370(3) Å, which is also expected for neutral C–O bond distance. But it is somewhat longer than that (1.357(2) Å) in compound **1**. The difference between the two C–O bonds is 0.013 Å which is due to the fact that in **5** the O atom is involved in forming more hydrogen bonds than the O atom in **1**, as shown in table 3. The angle C3–S1–C1 (88.5 (2)°) is similar to the corresponding angle in the neutral molecule (88.7 (2)°) [38], yet it is smaller than that in the salt

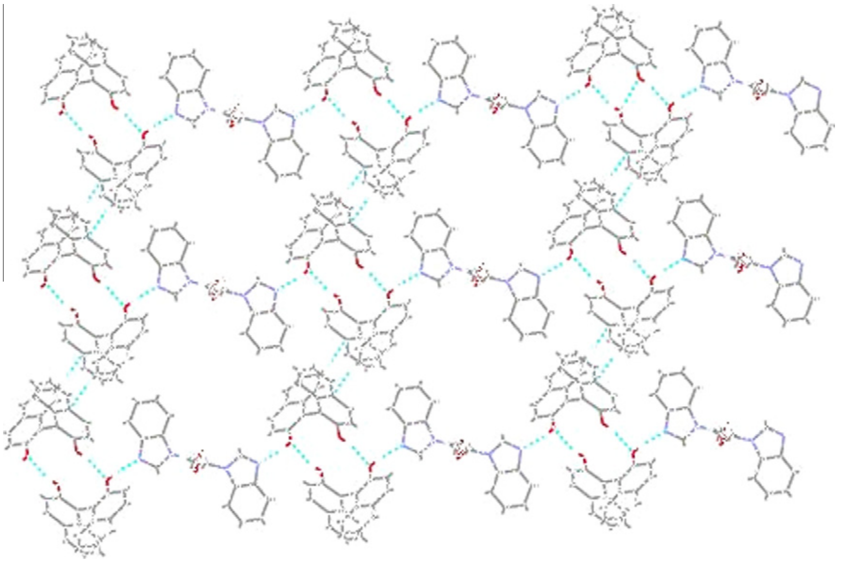


Fig. 4(iii). 2D sheet structure of **4** extending on the *ab* plane.

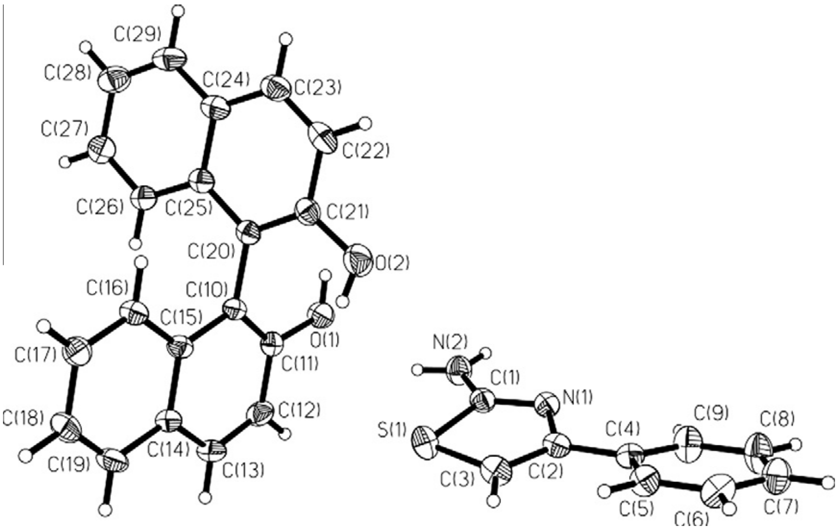


Fig. 5(i). Molecular structure of **5** showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

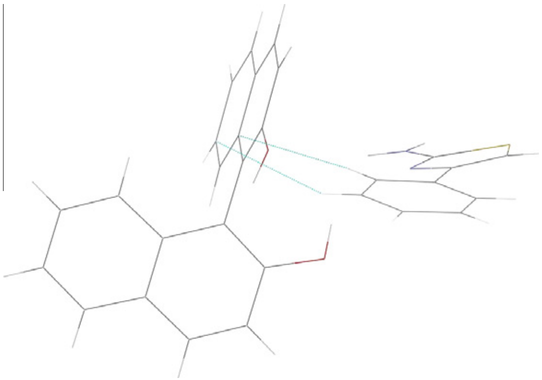


Fig. 5(ii). Edge to face CH–π interactions between L5 and binol.

2-amino-4-phenylthiazole hydrobromide monohydrate (90.17°) [39]. This may be due to the difference of the hydrogen bonding strength in the corresponding compound. The dihedral angle between the planes of the phenyl and thiazole rings in the same L5 molecule is 17.7 (3)°, which is also smaller than the value (19.23°) in 2-amino-4-phenylthiazole hydrobromine monohydrate. But the 2-amino-4-phenylthiazole in compound **5** is less planar than the neutral L5 in which the dihedral angle between the phenyl ring and the thiazole ring is (6.2(3)°) [38]. The planarity of **5** is further verified by the shorter C(2)–C(4) bond distance [1.466(4) Å] in **5** compared with the value of 1.506 Å found in 2-amino-4-phenylthiazole hydrobromine monohydrate [39].

The two naphthalene rings in the same binol are almost planar with the r.m.s deviations of 0.0047 Å, and 0.0037 Å respectively. The dihedral angle between the two naphthalene rings in the same binol is 104.2°, the dihedral angles between L5 and the two naphthalene rings in the same binol are 88.7°, and 76.3° respectively, indicating that L5 is almost perpendicular with one half part of the binol moiety.

The 2-amino-4-phenylthiazole molecule was bonded to the binol molecule through one N–H···O hydrogen bond between the amine group of L5 and one OH group of binol, one O–H···N hydrogen bond between another OH group of the binol and the ring N atom of L5. There are edge to face CH–π interactions with C–Cg distance of 3.553 Å between L5 and binol (Fig. 5(ii)). And there are also NH–π interactions between the amine group of L5 and the binol ring with N–Cg distance of 3.532 Å. The 2-amino-4-phenylthiazole molecule and the binol molecule formed heterodimers through the above mentioned weak interactions. Such adjacent heterodimers were connected together by CH–π interaction between the CH_{binol} and the benzene ring of L5 with C–Cg distance of 3.639 Å to form a 1D chain running along the *a* axis direction. Such chains were connected together through O–H···O hydrogen bonds between two OH groups of two adjacent chains with O–O distance of 3.018 (4) Å, which is similar to the published data in (R)-(+)-binol, and (S)-(−)-binol (2.96 Å) [37]. Here the intermolecular O–H···O hydrogen bond is slightly weaker than that in **3**, and **4**. There exist N–H···O hydrogen bonds between the amine group of L5 in one chain and the OH group of the adjacent chain with N–O distance of 3.048 Å, which is in the upper limit of the sum of the van der Waals radii for N and O (3.07 Å) [40]. There are also S–π interactions between the S atom of the thiazole ring in one chain and the naphthalene ring of the adjacent chain with the S–C contact of 3.452 Å which is similar to the previously published literature data [41]. But the S–C contact is in the lower limit of the recently reported S–C contact values [3.390–3.888 Å] [42]. In the adjacent chains the corresponding naphthalene and the thiazole moieties were antiparallely arranged. The adjacent chains were joined together through the above mentioned collective weak interactions to form a double chain structure. Such double chains were further connected together by CH–O interaction between CH of the benzene ring of L5 and O atom from the OH group of binol with C–O distance of 3.581 Å to form a 2D corrugated sheet extending on the *ac* plane (Fig. 5(iii)). Adjacent sheets were further stacked along the *b* axis direction through CH–π interactions

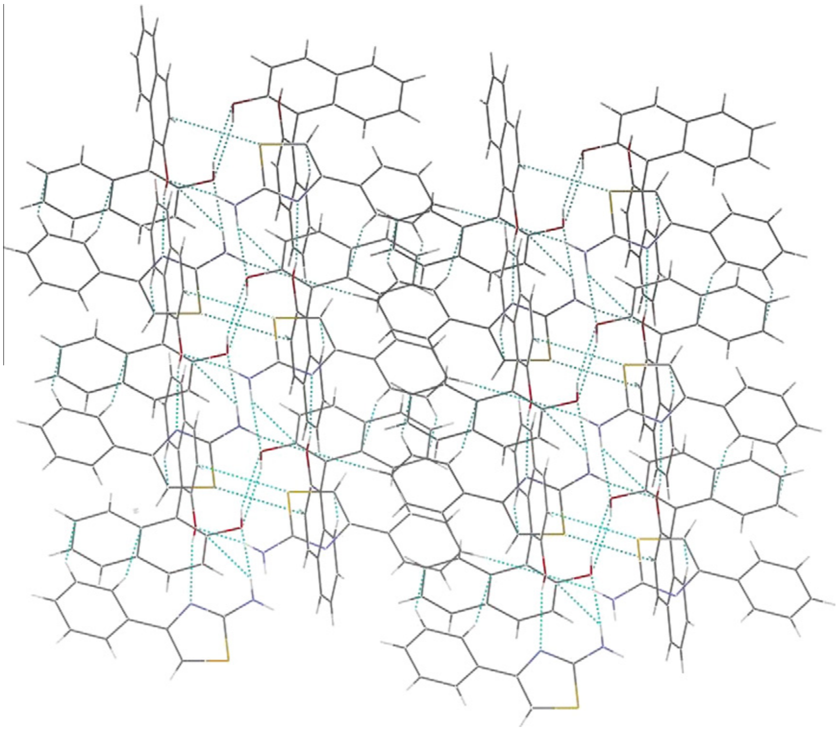


Fig. 5(iii). 2D corrugated sheet of **5** extending on the ac plane.

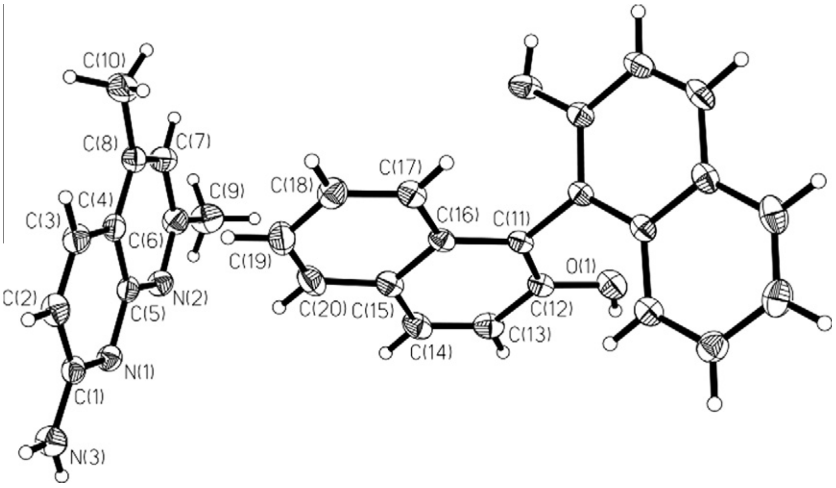


Fig. 6(i). Molecular structure of **6** showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

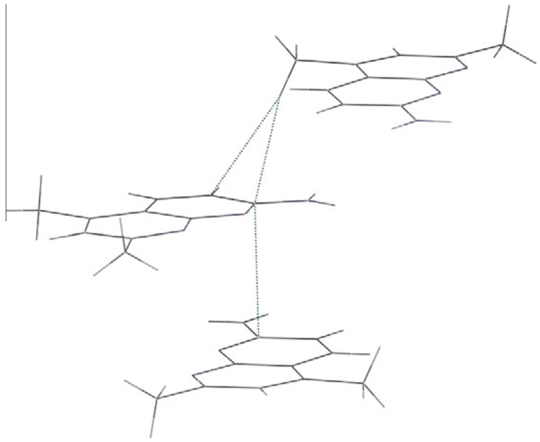


Fig. 6(ii). The head to tail π–π interaction and the head to head CH_3–π interaction between L6.

between CH of the naphthyl group of one sheet and the benzene ring of L5 at the adjacent sheet with C–Cg distance of 3.737 Å to form 3D network structure.

*3.2.6. X-ray structure of (2-amino-5,7-dimethyl-1,8-naphthyridine)$_2$: (Binol) [(L6)$_2$·(Binol)] (**6**)*

The compound **6** of the composition [(L6)$_2$·(Binol)] was prepared by crystallizing equal mol of 2-amino-5,7-dimethyl-1,8-naphthyridine and binol, in which the proton of binol was not transferred to any N atoms of the naphthyridine moiety. This structure is also an anhydrous cocrystal. In the asymmetric unit of **6** there existed one molecule of 2-amino-5,7-dimethyl-1,8-naphthyridine, and a half molecule of binol, as shown in Fig. 6(i).

The C–O distances involving the OH group of the binol are 1.358(3) Å which is similar to the above corresponding data and the documented results as well. The N–H···O hydrogen bond is formed between the amine group of L6 and the OH group of binol (N(3)–H(3B)···O(1)#3, 2.893(3) Å), there does not exist ionic N^+–

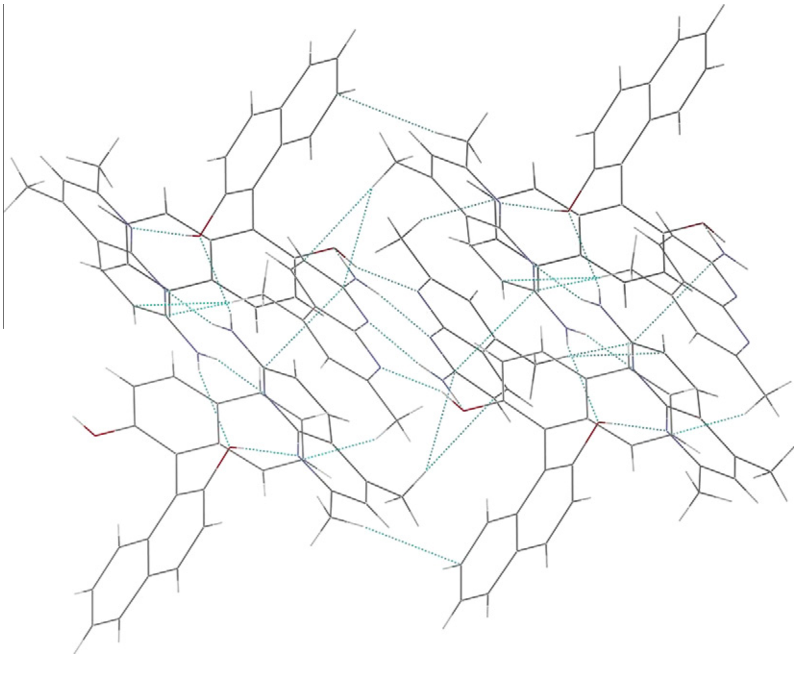


Fig. 6(iii). 3D ladder structure of **6**.

H$\cdots$O$^-$ hydrogen bond. There was also an O–H$\cdots$N (O(1)–H(1)$\cdots$N(2)#2, 2.718(2) Å) hydrogen bond between the OH group of the binol and the ring N atom of the pyridine bearing the CH$_3$ group. As expected, the naphthyridine ring is planar (the mean deviation from plane is 0.0207 Å within the L6 molecule). The r.m.s deviation of the naphthalene ring containing atoms C11–C20 in **6** from the mean plane of the ring is 0.0072 Å. The dihedral angle between the plane formed by C11–C20 atoms and the naphthyridine ring is 67°. The torsion angle between the two naphthalene rings in the same binol is ca. 70.71°, which is agreement with the value in **1**, and **2**.

Two L6 formed dimers through intermolecular hydrogen bonding (N–H$\cdots$N) interactions of the type DA–AD between two pyridine rings containing the amine group. Two binol molecules were each bonded to the L6 dimer through one N–H$\cdots$O and one O–H$\cdots$N hydrogen bonding interactions arising from the same OH group (Table 3). In this case the two binol molecules were inversionally located, and therefore the binol is not constituted by only a single enantiomer but constituted by both the enantiomers of *rac*-binol. In the L6 dimers the two L6 molecules are also inversionally located.

Of the binol molecule one OH group is hydrogen bonded to the L6 dimers through one N–H$\cdots$O and one O–H$\cdots$N hydrogen bonding interactions. The other OH group is also hydrogen bonded to the adjacent parallel L6 dimer through one N–H$\cdots$O and one O–H$\cdots$N hydrogen bonding interactions.

The adjacent naphthyridine dimers were joined together through the π–π interactions (between two naphthyridine rings with the Cg–Cg distance of 3.288 Å) and CH$_3$–π interactions (between the 5-CH$_3$ of L6 and the naphthyridine ring with C–Cg distance of 3.742 Å) along the *a* axis direction to form a ladder structure. Here the two adjacent dimers were slipped some distance from each other, thus the π–π interaction can be regarded as head to tail interaction, while the CH$_3$–π interaction can be viewed as head to head interaction (Fig. 6(ii)). There also exist 7-CH$_3$–π interactions between the L6 dimers of the third step of the ladder and the naphthalene ring whose OH group is bonded to the L6 dimer of the first step of the ladder in which the C–Cg distance is 3.778 Å. These interactions combined, the compound **6** exhibited 3D ladder structure as shown in Fig. 6(iii).

4. Conclusions

Single crystal X-ray diffraction has enabled the elucidation of six examples of N-containing aromatic bases-binol cocrystals, novel contributions to the extensive research into the occurrence of phenol-aza motifs in cocrystals. In their place are a series of motifs in which extensive strong classical hydrogen bonds (neutral) combine with weaker interactions (CH–π, CH$_3$–π, NH–π, S–π, and π–π interactions). This variety, coupled with the varying molecular flexibility/rigidity, molecular conformation, molecular shape, and number of N groups of the aromatic bases employed, has led to the creation of a range of supramolecular arrays, from 3D sandwiched layer network structure, 3D layer network structure, to 3D ladder structure. This study has demonstrated that the O–H$\cdots$N hydrogen bond is the primary intermolecular force in a family of structures containing the binol$\cdots$aza (aza is bis-imidazole or 2-aminoheterocyclic derivatives) synthons. Furthermore, hydrogen bonds can introduce distortion in molecular shape to a varying degree in order to optimize hydrogen-bonding interactions, such as the dihedral angles formed by the two naphthalene rings in the same binol ranged from 70.71° to 104.2° as the organic bases varied. In the six cocrystals the binols exist either as both of the enantiomers of *rac*-binol or as only of its single enantiomer.

5. Supporting information available

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic data center, CCDC Nos. 791894 for **1**, 799292 for **2**, 799891 for **3**, 800023 for **4**, 791893 for **5**, and 800874 for **6**. 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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