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Influence of Solvents in Assembling Tris(4-halophenyl)benzene-1,3,5-tricarboxamides: Interplay of N−H···O and Halogen···Halogen Interactions

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Ⓢ Supporting Information

ABSTRACT: The influence of solvents in the crystallization of tris(*p*-halogen-phenyl) substituted benzene-1,3,5-tricarboxamides, **1**, was studied by using the solvents capable of forming hydrogen bonds with amide N−H groups. All four halogen (I, Br, Cl and F) derivatives have shown a tendency to form triple helices *via* amide-to-amide hydrogen bonds in the presence of THF molecules. The crystallization of the fluoro derivative was found to have no solvent influence as the same material was obtained repeatedly from various solvents. The bromo analogue affords two solvates from THF and DMF, respectively, while seven solvated crystals were obtained in the case of the iodo derivative when it was crystallized from acetone, acetaldehyde-THF, pyridine, *γ*-picoline cyclohexanone, DMF or THF solvents. The solvates exhibited different molecular as well as supramolecular geometries to adjust with the solvent inclusion in the crystal lattices. The I_3 trimer synthon was accomplished in the cyclohexanone solvate of the iodo derivative where cyclohexanone was able to block all the three amide groups. The Cambridge Structural Database (CSD) analysis was performed on the X_3 synthon (X = Cl, Br and I) in order to understand their formation. Sorption studies on the THF included materials show that they are mesoporous and have a greater tendency to adsorb nitrogen over hydrogen.

R: *p*-halo-phenyl
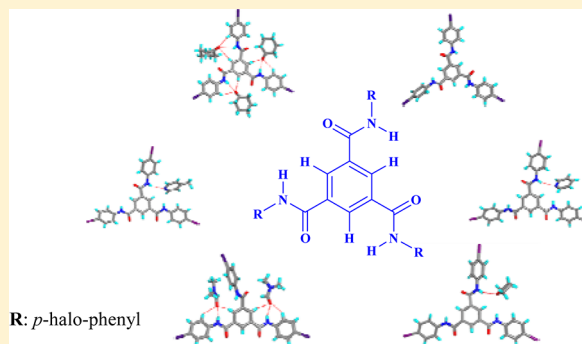
■ INTRODUCTION

Crystal engineering deals with the identification of useful supramolecular synthons and exploring robustness of the synthons with various substrates containing interfering functionalities. Organic supramolecular solids are of importance due to their potential applications in gas storage, catalysis, separation, optical, electronic and mechanical properties.[1−5] Hydrogen bonding is one of the major cohesive interactions in crystal engineering for the construction of supramolecular assemblies with predefined architectures. In recent years, the interactions involving halogens such as halogen bonds and halogen···halogen interactions have been demonstrated as important tools for assembling molecules in crystal lattices. Several tailor-made organic compounds containing functional groups capable of forming robust supramolecular synthons have been demonstrated to form solids with predicted architectures.[6] For example, using amide recognition motifs several novel supramolecular networks in the form of sheets,[7] helices,[8] tubes,[9] and ribbons[10] have been constructed. On the other hand, the utilization of molecules containing more than one functional group, which have the capability of playing a significant role in the assembling process, coupled with conformational flexibility increases number of possible modes of assembling and thereby increases the complexity in structure prediction. In such cases the solvent of crystallization, the presence of guest molecules and the reaction conditions have a profound influence on assembling process similar to their metal−organic counter parts.

One of the easiest ways to build the predictable supramolecular architectures is to use molecules that have symmetric substitution of functional groups with the anticipation of transfer of molecular symmetry to supramolecular symmetry. The molecules with 3-fold symmetry such as 1,3,5-benzenetricarboxylic acid and its derivatives are popular targets for obtaining aesthetically appealing networks as well as novel properties.[11] For example, 1,3,5-benzenetricarboxamides (**1**) (Scheme 1) are at the center of attraction because of their wide range of applications as nanostructured materials,[12] nucleating agents,[13] organogelators,[14] and liquid crystals.[15] The pyridine containing derivatives are used for the construction of metal−organic frameworks (MOFs).[16] The presence of three amide functionalities for self-recognition, central aromatic ring for the stacking interactions and the R-group which can be fine-tuned according to the targeted properties makes the molecule **1** an attractive choice for self-assembly study. Further certain derivatives of **1** were shown to exhibit triple helices *via* amide-to-amide hydrogen bonds.[8]
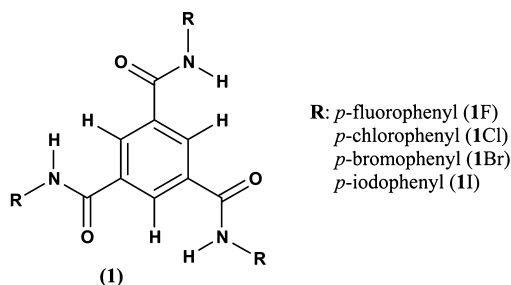
Scheme 1

R: *p*-fluorophenyl (**1F**)
p-chlorophenyl (**1Cl**)
*p*-bromophenyl (**1Br**)
p-iodophenyl (**1I**)

(**1**)

Recently, we have communicated our preliminary results on the porous nature of crystalline solids of 4-iodo/bromo/chlorophenyl derivatives of **1** that are crystallized from THF. In these solids, the halogen···halogen interactions assembles N−H···O hydrogen bonded triple helices to form 3D networks having continuous channels.[17] The halogen···halogen interactions observed in the structures exhibit type-I geometry (Scheme 2).[18] Previously, it was also shown by us that halogen···halogen

Scheme 2. Geometrical Classification of Halogen···Halogen Interactions: (a) Type-I, (b) Type-II, X₃ Synthons (c) with Type-I, and (d) Type-II Interactions
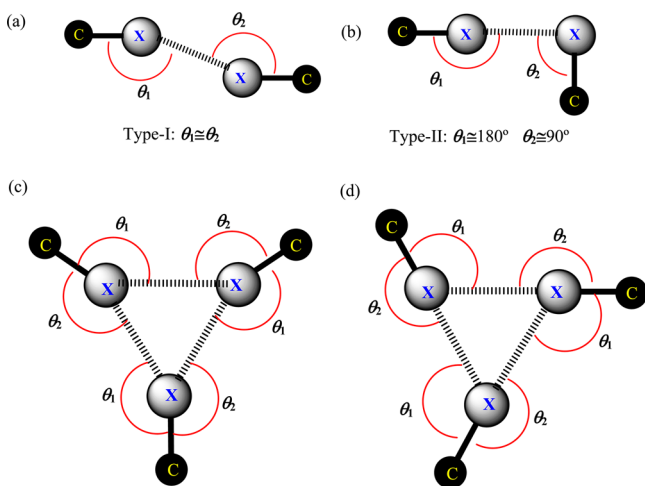
interactions predictably assemble β-sheets of bis-amide into two-dimensional layers.[19] Further, our previous studies with 3- and 4-pyridyl derivatives of **1** reveal that the crystallization outcome of these derivatives severely depends on reaction conditions and solvent of crystallization.[20] Furthermore, C₃-symmetric 2,4,6-tris(4-iodo/bromo/chlorophenoxy)-1,3,5-triazine molecules were shown to exhibit X₃ supramolecular synthon and included several solvent molecules.[21] However, the related triester derivatives do not form such X₃ synthons; they rather form halogen bonding interactions with C=O or halogen···pi interactions.[22] Therefore, in the current study we intend to explore the solvent dependency on the crystallization outcome and resultant interactions of *p*-haloaryl derivatives of **1**. The gas sorption properties of obtained porous materials were also explored. As solvents of crystallization, the polar solvents with the ability to form hydrogen bonding with amide functionalities were considered. In this article, crystal structures and analyses of 11 crystalline forms of halogen derivatives of **1** and gas sorption properties of THF solvates will be presented.

■ RESULTS AND DISCUSSION

All the halogen derivatives of **1** were prepared by treating trimesyl chloride with corresponding 4-halophenylamines. Previously, the compounds **1F** and **1Br** were synthesized and explored as nucleating agents for polymeric materials,[23] whereas compounds **1Cl** and **1I** are the newly synthesized compounds by us. The single crystals without any solvent inclusion in the crystal lattice were obtained only in the case of **1F**. The crystallization of **1I** in THF resulted in the single crystals of **1I·2THF** (**2**), while crystallizations of **1Br** and **1Cl** from THF resulted in **1Br·2THF** (**3**) and **1Cl·THF** (**4**) whose structures were determined by X-ray powder diffraction analysis. The crystal structures of **1F** and **2−4** were previously published by us.[17] Crystallizations of **1I** and **1Br** from DMF produced single crystals of **1I·2DMF** (**5**) and **1Br·2DMF** (**6**), respectively. Further, the crystallization of **1I** in acetone (ACT), acetaldehyde-THF, pyridine (PY), γ-picoline (PIC) and cylohexanone (CYH) resulted in the single crystals of **1I·ACT** (**7**), **1I·H₂O·THF** (**8**), **1I·PY** (**9**), **1I·PIC** (**10**), and **1I·3CYH** (**11**), respectively. Pertinent crystallographic details of **2−11**, hydrogen bonding and halogen···halogen interaction

Table 1. Crystallographic Parameters for 5−11

	5	6	7	8	9	10	11
formula	$C_{33}H_{32}N_5O_5I_3$	$C_{33}H_{32}N_5O_5Br_3$	$C_{30}H_{24}N_3O_4I_3$	$C_{31}H_{26}I_3N_3O_4$	$C_{32}H_{23}I_3N_4O_3$	$C_{33}H_{25}I_3N_4O_3$	$C_{45}H_{48}N_3O_6I_3$
MW	959.35	818.37	813.14	904.27	892.24	906.27	1107.56
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
system	triclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$C2/c$	$P2_1/c$	$P2_1/c$	Cc
a (Å)	8.0723(3)	7.0659(1)	4.7382(1)	39.960(11)	17.8538(15)	18.81(20)	17.760(3)
b (Å)	13.5230(6)	14.211(3)	24.239(6)	10.876(3)	11.1100(9)	10.847(17)	21.165(3)
c (Å)	17.3911(7)	18.081(3)	24.486(6)	15.680(4)	15.7183(13)	15.820(19)	14.066(2)
α (°)	76.1950(1)	100.885(6)	90	90	90	90	90
β (°)	81.2250(1)	98.237(6)	93.295(7)	110..393(8)	97.874(2)	101.48(5)	120.104(4)
γ (°)	82.9370(1)	94.120(6)	90	90	90	90	90
vol (Å³)	1814.6(1)	1755.4(6)	2807.6(1)	6388(3)	3088.4(4)	3163.21	4574.1(1)
Z	2	2	4	8	4	4	4
D_{calc} (Mg/m³)	1.756	1.548	1.924	1.881	1.919	1.903	1.608
R_1 ($I > 2\sigma(I)$)	0.0519	0.0620	0.0582	0.0723	0.0480	0.0496	0.0562
wR_2 (on F_2, all data)	0.1629	0.1858	0.1602	0.2087	0.1691	0.1522	0.1741

parameters for all the compounds are given in Tables 1, 2, and 3, respectively.

One-Dimensional Columns with Triple Helicity. The compound **1F** crystallizes in orthorhombic space group *Pbca* and the asymmetric unit is constituted by only one moiety of

Table 2. Geometrical Parameters of Amide-to-Amide Hydrogen Bonds in the Crystal Structures of 5−11

compound	type	H⋯A (Å)	D⋯A (Å)	D−H⋯A (deg)
5	N(21)−H(21)⋯O(1)	2.02	2.873(7)	172
	N(11)−H(11)⋯O(201)	2.09	2.919(8)	161
	N(31)−H(31)⋯O(100)	2.07	2.887(9)	157
	C(4)−H(4)⋯O(100)	2.58	3.154(8)	121
	C(2)−H(2)⋯O(201)	2.41	3.293(9)	160
	C(12)−H(12)⋯O(201)	2.49	3.246(1)	138
	C(32)−H(32)⋯O(100)	2.57	3.308(1)	137
6	N(31)−H(31)⋯O(1)	2.07	2.912(6)	165
	N(11)−H(11)⋯O(100)	2.11	2.946(6)	164
	N(31)−H(31)⋯O(1)	2.29	3.125(9)	166
	C(4)−H(4)⋯O(200)	2.42	3.281(9)	155
	C(6)−H(6)⋯O(100)	2.42	3.247(7)	147
	C(16)−H(16)⋯O(100)	2.44	3.237(7)	144
	C(26)−H(26)⋯O(200)	2.59	3.400(1)	146
7	N(40)−H(40)⋯O(40)	2.15	2.901(6)	146
	N(30)−H(30)⋯O(20)	2.43	3.126(7)	138
8	N(11)−H(11)⋯O(100)	2.20	3.008(15)	156
	N(31)−H(31)⋯O(21)	2.23	3.045(11)	158
	C(2)−H(2)⋯O(100)	2.55	3.438(18)	160
	C(32)−H(32)⋯O(21)	2.44	3.258(15)	147
	C(33)−H(33)⋯O(31)	2.57	3.437(15)	156
9	N(11)−H(11)⋯O(2)	2.19	3.001(5)	157
	N(31)−H(31)⋯N(100)	2.45	3.268(7)	159
	C(4)−H(4)⋯N(100)	2.55	3.467(9)	167
	C(15)−H(15)⋯O(1)	2.52	3.399(6)	158
	C(16)−H(16)⋯O(2)	2.38	3.185(6)	144
10	N(21)−H(21)⋯O(11)	2.17	2.978(9)	156
	N(31)−H(31)⋯N(100)	2.40	3.198(10)	156
	C(6)−H(6)⋯N(100)	2.53	3.440(11)	165
	C(25)−H(25)⋯O(21)	2.51	3.391(10)	157
	C(26)−H(26)⋯O(11)	2.39	3.174(10)	143
11	N(21)−H(21)⋯O(31)	2.04	2.836(1)	154
	N(11)−H(11)⋯O(101)	2.21	3.023(1)	159
	N(31)−H(31)⋯O(201)	2.13	2.971(1)	167
	C(4)−H(4)⋯O(201)	2.51	3.170(1)	128
	C(6)−H(6)⋯O(101)	2.55	3.388(1)	150

Table 3. Halogen⋯Halogen Interaction Parameters for 2−11

compd	dist (X⋯X int) (Å)	angle (C−X⋯X) (deg)
2	3.684	147.95, 147.95
3	3.590	144.45, 148.78
4	3.541	142.18, 146.3
5	4.077	82.23, 170.25
	4.186	88.55, 161.84
6	3.642	85.78, 167.58
7	3.914	86.32, 155.44
8	3.937	154.18, 94.70
9	4.155	79.29, 107.83
	4.277	89.90, 159.20
10	4.228	79.23, 79.23
	4.324	84.90, 129.31

1F. The molecules are assembled into a one-dimensional column via three helical N−H⋯O hydrogen bonds (Figure 1a).
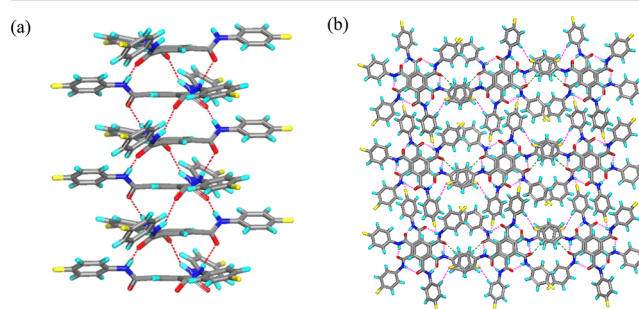

Figure 1. Illustrations for the crystal structure of **1F**: (a) triple helical amide-to-amide hydrogen bonded column; (b) 3D packing via C−H⋯O, C−H⋯F hydrogen bonds and F⋯C=O dipole interaction.

Notably, all the three hydrogen bonds have approximately equal geometrical parameters (Table 2). Apart from N−H⋯O hydrogen bonds, one of the C−H groups of halophenyl is also involved in C−H⋯O hydrogen bond with carbonyl O-atom (Figure 1b). The central phenyl rings stack on each other in a staggered manner with a very short distance of 3.58 Å along the *a*-axis. The aromatic stacks are generated using a crystallographic screw axis. The packing of the triple helices occurs through several weak interactions, notably two supramolecular synthons: one contains C−H⋯O and C−H⋯F hydrogen bonds and the other contains dipolar interactions between F and C-atom of C=O and aromatic π−π interactions. It is important to note here that no F⋯F contacts were observed in the structure which is in agreement with our previous observations on fluorine related compounds.[19] The packing of the columns is very compact and the fluorophenyl rings of neighboring columns are interdigitated. Solvates or polymorphs of **1F** were not obtained despite several trials of crystallization from several other solvents.

Aggregation of 3-Fold Helices into Porous Solids via Halogen⋯Halogen Interactions (2−4). The crystal structures of compounds **2−4** significantly differ from that of the fluoro derivative. The crystallization of **1I** from THF resulted in single crystals of **2** (**1I·2THF**) that are suitable for single crystal analysis, while compounds **1Br** and **1Cl** resulted in the materials of **3** (**1Br·2THF**) and **4** (**1Cl·THF**), respectively, which were not suitable for single crystal analysis. Nevertheless, the crystal structures of **3** and **4** were obtained from powder diffraction patterns. The crystal structures of **2−4** exhibit

isostructurality with some minor differences. In **2**, the central C_6-ring and carbonyl groups of **1I** are found to exhibit disorder, while the I−C_6H_4−N moieties are ordered. No such disorder was encountered in case of **3** and **4** which are solved and refined from XRPD patterns (Figure 2). They all contain an
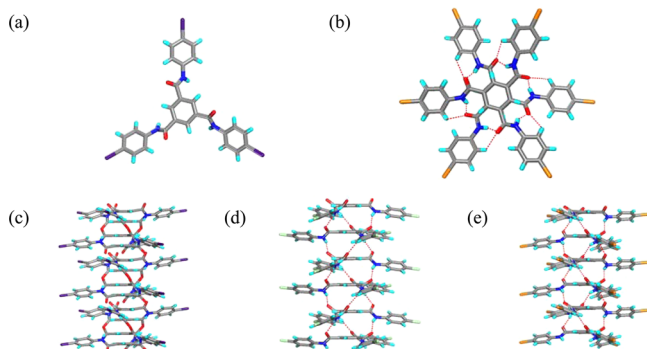

Figure 2. Illustrations for the triple helices in the crystal structures of **2**−**4**: (a) the geometry of **1I** in **2**; (b) top view of triple helical column of **1Br** in **3**; side views of the triple helical columns in (c) **2**, (d) **3** and (e) **4**.

amide-to-amide hydrogen bonded triple helix similar to the one observed in **1**. The assembling of the helices significantly differ from that of **1**; in these structures halogen···halogen interactions play a significant role in assembling the helices. The triple helices run along the *c*-axis with a repeat distance of 7.3−7.5 Å (7.519 Å in **2**, 7.347 Å in **3**, and 7.301 Å in **4**). These molecules (**1I**/**1Br**/**1Cl**) are assembled in the *ab*-plane, via halogen···halogen (type-I) interactions to form a honeycomb layer (Figure 3a,b). Three of such hexagonal layers inter-
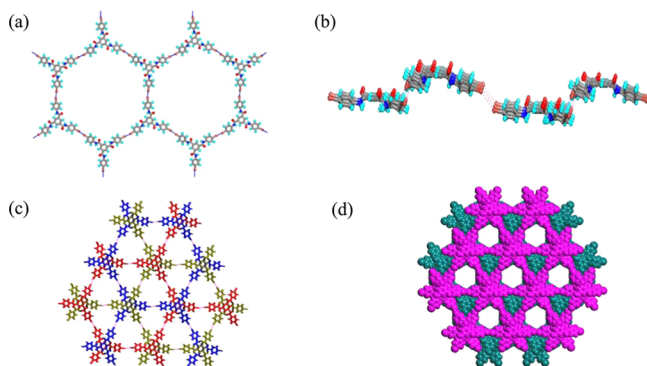

Figure 3. Illustrations for the crystal structures **2**−**4**: honeycomb network of **1Br** via Br···Br interactions in **3** (a) top view and (b) side view; triply interpenetrated honeycomb network (parallel mode) (c) top view, (d) 2-fold interpenetration of 3D-networks in space-fill mode (shown in two different colors).

penetrate in parallel mode such that the above-described hexagonal cavity subdivides into six triangular channels (Figure 3c). These triple interpenetrated layers are connected along the *z*-axis via amide-to-amide hydrogen bonds such that the channels of the layers are unaltered. On a whole this can be described as a three-dimensional network, in which the triple helices are joined via halogen···halogen interactions, containing triangular channels. In the crystal lattice two of these 3D networks interpenetrate such that three of the six channels were filled by the triple helices. This type of interpenetration also alters the shape of remaining three channels into a hexagonal

shape (Figure 3d). Notably, the geometries of halogen···halogen contacts in the case of all three compounds found to be of type-I (θ_1 and θ_2: 147.95 and 147.95 in **2**, 144.45 and 148.78 in **3** and 144.45 and 148.78 in **4**.

The Solvent Interference in Amide-to-Amide Hydrogen Bonds: DMF Solvates (5 and 6). The crystallization of compounds **1I** and **1Br** from DMF form single crystals of **1I·2DMF** (**5**) and **1Br·2DMF** (**6**). However, the crystallization of **1Cl** in DMF failed to produce suitable crystals for single crystal X-ray analysis. The crystal structures of **5** and **6** exhibit isostructurality and crystallized in $P\bar{1}$ space group. The asymmetric unit is constituted by one unit of **1I** and two units of DMF molecules. The molecular geometry significantly differs from those of **1F** and **2-4**; two of the amides are nearly coplanar with the central C_6-ring (14° and 20°) while one is out of the plane (44°) (Figure 4a,b). The molecular geometry
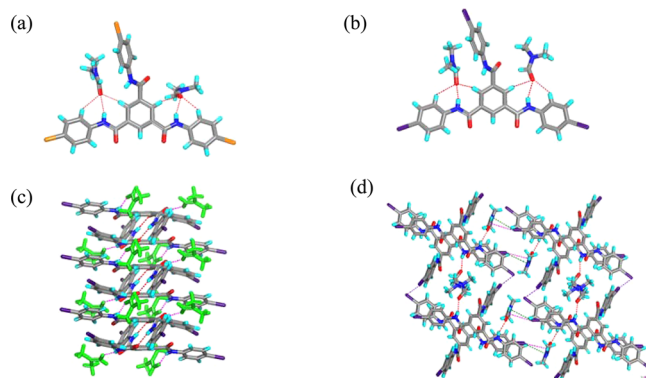

Figure 4. Illustrations for the crystal structures **5** and **6**: molecular geometry of (a) **1Br** in **5** and (b) **1I** in **6**; (c) stacking of amide-to-amide hydrogen bonded dimers of **1I** in **6** (DMF molecules are shown in green color), and (d) lateral packing of stacked columns via halogen···halogen and dipolar interactions in **6**.

can be best described as T-shape geometry. The two in-plane amide N−H groups are hydrogen bonded to DMF while the out of plane amide forms N−H···O dimer of **1I**/**1Br** of two molecules (Figure 4c). The carbonyl of DMF also binds to the C−H groups of aromatic rings *via* C−H···O hydrogen bonds. These dimers pack on each other with edge-to-face aromatic interactions between central C_6-ring and halo-phenyl rings. As a result the centroid-to-centroid distance between central C_6-rings of two dimers is as high as 6.913 Å in **5** and 4.896 Å in **6**. In **6**, two of the bromine atoms involved in Br···Br interactions (type-II) in joining the dimers as a one-dimensional chain in lateral directions (Figure 4d). Further, the third bromine atom is involved in dipolar interactions with carbonyl carbon of DMF (I···C═O distance: 3.742 Å). The DMF molecules in **5** and **6** occupy the crystal volume of 32% and 35%, respectively.

Acetone Solvate (7). The crystallization of **1I** from acetone (ACT) resulted in the crystals of **1I·ACT**, **7**. X-ray structural analysis revealed that **7** crystallizes in monoclinic $P2_1/c$ space group and the asymmetric unit contains one unit of **1I**. In the crystal structure of **7**, the molecule **1I** deviates from 3-fold symmetry, one of the amide plane is nearly coplanar with the central C_6-ring (inter planar angles: 14°), while the other two are non-coplanar with the central C_6-ring (31° and 37°) (Figure 5a). The **1I** units form a column using translational symmetry along *c*-axis with the repeat distance of 4.75 Å (length of *c*-axis). In this column, among the three amide
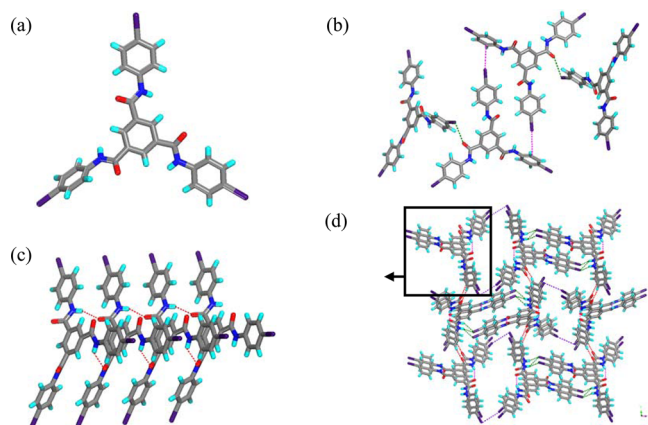

Figure 5. Illustrations for the crystal structure of **7**: (a) the geometry of **1I**; (b) side view of offset stacks via two strands (one helical and one linear) of amide-to-amide hydrogen bonds; the packing of offset stacks via (c) I···π and I···O=C interactions, and (d) I···I (type-II) interactions.

Figure 6. Illustrations for the crystal structures of **8**, **9** and **10**: (a) **1I** in **8**; (b) **1I** in **9**; (c) **1I** in **10**; (d) 1D-chain constituted of amide-to-amide hydrogen bonds and C=O···I contacts in **9**; (e) top view of 2D-layer formed by the 1D-chain through I···I (type-II) interactions in **9**; (f) side view of the 2D-layer in **9**.

groups, one forms a linear amide-to-amide N−H···O hydrogen bond and the second one forms a helical type of N−H···O hydrogen bond (Figure 5b). The third N−H group forms a bifurcated N−H···I hydrogen bond with adjacent columns. As a result, columns are laterally joined in the *bc*-plane via N−H···I, C−H···O hydrogen bonds and iodo-carbonyl (I···O=C distance: 3.690 Å), I···π (I···C distance: 3.548 Å) and I···I (3.914 Å) interactions (Figure 5c). The I···I contacts observed here are of type-II (86.32° and 155.44°). The iodo-phenyl rings from adjacent columns interact with each other via offset stacking (C···C distance: 4.036 Å). As a result of lateral interactions, each column is surrounded by six of its neighboring columns (Figure 5d). Similar type of packing was observed in the case of the phenyl derivative of **1**.[24] The included acetone molecules could not be located in the structure, but the crystal lattice contains cavities of 126 Å³ indicating the presence of acetone.

Water-THF (8), Pyridine (9) and γ-Picoline (10) Solvates. Crystallization of **1I** from THF-acetaldehyde, THF-pyridine and THF-picoline solvent mixture afforded crystals of **1I·H₂O·THF (8)**, **1I·PY (9)** and **1I·PIC (10)**, respectively. The compound **8** crystallizes in *C2/c* space group and the asymmetric unit contains one unit each of THF and **1I**. While compounds **9** and **10** crystallizes in *P2₁/c* space group and the asymmetric units contain one unit each of **1I** and pyridine or picoline moieties. The **1I** molecules do not exhibit 3-fold symmetry in none of these three structures (Figure 6a–c). Interestingly, in all the structures the THF/PY/PIC units block two of the amide N−H groups via N−H···O/N hydrogen bonds (1:1 adduct). Further, these 1:1 adducts joined into one-dimensional chains via amide-to-amide hydrogen bonds.

Within the 1D chain the molecules of **1I** have slipped packing via π−π interactions between iodo-phenyl and central C₆-ring. In all three structures, two of the three I-atoms of **1I** are involved in I···I interactions and the third I-atom forms halogen bond with the amide C=O of the adjacent molecule. In summary, the 1D chain contain N−H···O, π−π and halogen bonds (Figure 6d). In the crystal lattice, these 1D-chains interact with each other via I···I interactions (type-II). The packing of the 1D-chains in **8** differ from that of **9** and **10** given the differences in space group and cell parameters (Figure 6e,f).
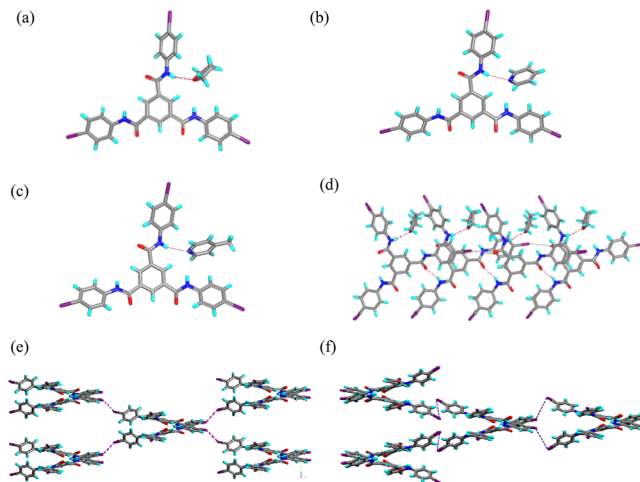
We note here that although crystals of **8** were obtained from acetaldehyde-THF mixture, acetaldehyde was not included in the crystal lattice. It includes one water molecule per **1I** which could not be located. However, the presence of water molecule was identified by void calculations using PLATON which shows the voids of ~40 Å³. THF molecules were located and refined, they occupy 18.8% volume of the crystal lattice, while pyridine and γ-picoline molecules in **9** and **10** occupy volume of 18.9% and 23.1%, respectively.

I₃ Synthon: Cyclohexanone Solvate of 1I (11). The crystallization of **1I** from THF-cyclohexanone (CYH) solvent mixture resulted in the crystals of **1I·3CYH**, **11**. It crystallizes in monoclinic *Cc* space group and the asymmetric unit is constituted by one unit of **1I** and three units of cyclohexanone molecules. In the crystal structure of **11**, **1I** significantly deviates from trigonal geometry (Figure 7a). However, all the three amide N−H groups are blocked by CYH moieties via N−H···O

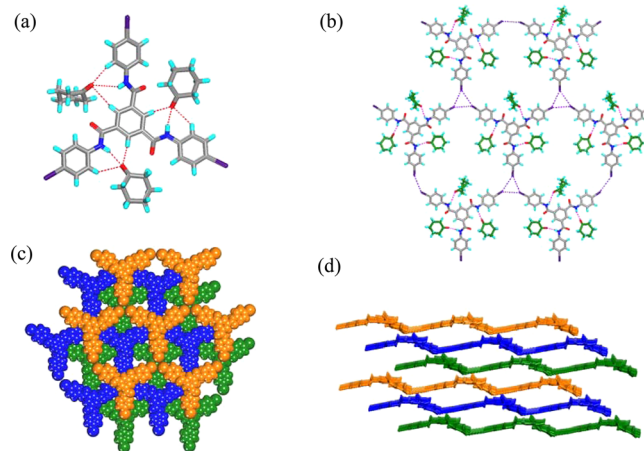**Figure 7.** Illustrations for the crystal structure of **11**: (a) 1:3 hydrogen bonding aggregate of **1I** and cyclohexanones; (b) (3,6)-network between **1I** molecules *via* I₃ synthons, note the presence cyclohexanone in the cavities; the offset packing of adjacent layers (c) top view (space-fill mode) and (d) side view, note the repeat of the layer for every three layers.
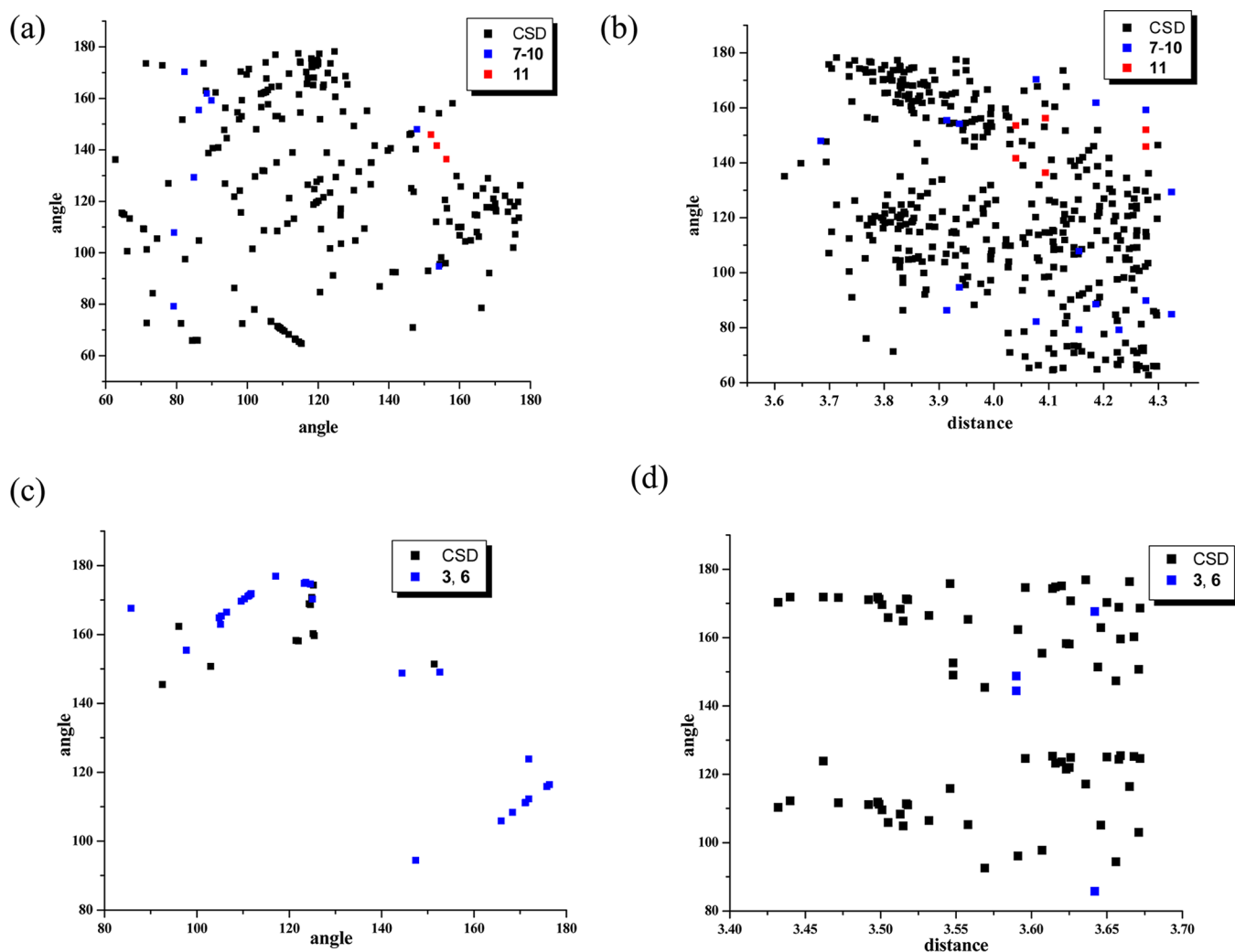
Figure 8. Scattergrams of C−X···X (θ_1) vs C−X···X (θ_2) for (a) iodo; (c) bromo; and C−X···X (θ_1) vs X···X distance for (b) iodo; (d) bromo.

hydrogen bonds, leading to a discrete self-assembly of four components (one **1I** and three CYH units) (Figure 7b). The CO of the cyclohexanones is also involved in weak C−H···O hydrogen bonds with aromatic C−H groups of iodophenyl and central C_6-ring. These discrete assemblies further aggregate into an interesting trigonal network via I···I interactions. The I-atoms of **1I** exhibit trimeric I_3 synthon to aggregate these assemblies. Notably, the I_3 synthon in this structure exhibits type-I geometry.

The 2D layers pack on each other in an offset fashion such that the I_3 synthon overlap on the C_6-ring of I−C_6H_4- of **1I** from the neighboring layers; the distance between centroid of I_3 and C_6 ring is 3.744 Å. The cavities and channels formed in the lattices were filled by cyclohexanones which interact with the adjacent layers via C−H···π interactions. The cyclohexanone molecules occupy 50.2% (2294.1 Å^3) volume of unit cell. Further, one of the amide N−H forms bifurcated hydrogen bonds to extend the amide-to-amide N−H···O hydrogen bonds between the layers. As a result this N−H forms somewhat longer N−H···O (2.925 Å, 113.66°, 3.364 Å) hydrogen bond with cyclohexanone compared to those of other two N−H groups. Overall, the packing of the layers can be described as ABCABC type as shown in Figure 7c,d. We note here that the similar crystallization reaction of **1F**, **1Br** or **1Cl** in THF-

cyclohexanone solvent mixture resulted in the formation powders which do not contain cyclohexanone.

CSD Analysis on X_3 Synthons. The Cambridge Structural Database (CSD)[25] analysis was performed on X_3 synthon (X = Cl, Br and I) to understand the following features: (1) the frequency of its occurrence; (2) molecular symmetry vs X_3 synthon; (3) crystallographic symmetry vs X_3 synthon; (4) nature of halogen···halogen interactions involved in X_3 synthon. For this purpose only X_3 synthons formed by halogen substituted aryl groups were considered. The contact distances for Cl···Cl, Br···Br and I···I were considered up to sum of the van der Walls radii 3.50, 3.70 and 3.96 Å, respectively.

Only seven hits were found containing Cl_3 synthon, and interestingly all these contain Cl···Cl interactions with type II character. Out of seven, in one entry, MEQBOA, the molecule does not contain 3-fold symmetry yet crystallizes in symmetric space group (R3), while the other six structures consist of 2,4,6-trisubstituted-1,3,5-triazine derivatives and crystallize in $P6_3/m$ or $P6_3$.[26,27]

The Br_3 synthon was found in 23 structures. Out of these 23, 19 structures correspond to 2,4,6-trisubstituted-1,3,5-triazine derivatives exhibiting trigonal or hexagonal space groups (R-3, $P6_3/m$, $P\overline{3}1/c$, R3c, $P6_3$).[28] The remaining four molecules do not possess 3-fold symmetry and, only one of these, 4-bromo-N-(3-oxo-1-phenyl-1-(trifluoromethyl)butyl)benzamide (COC-
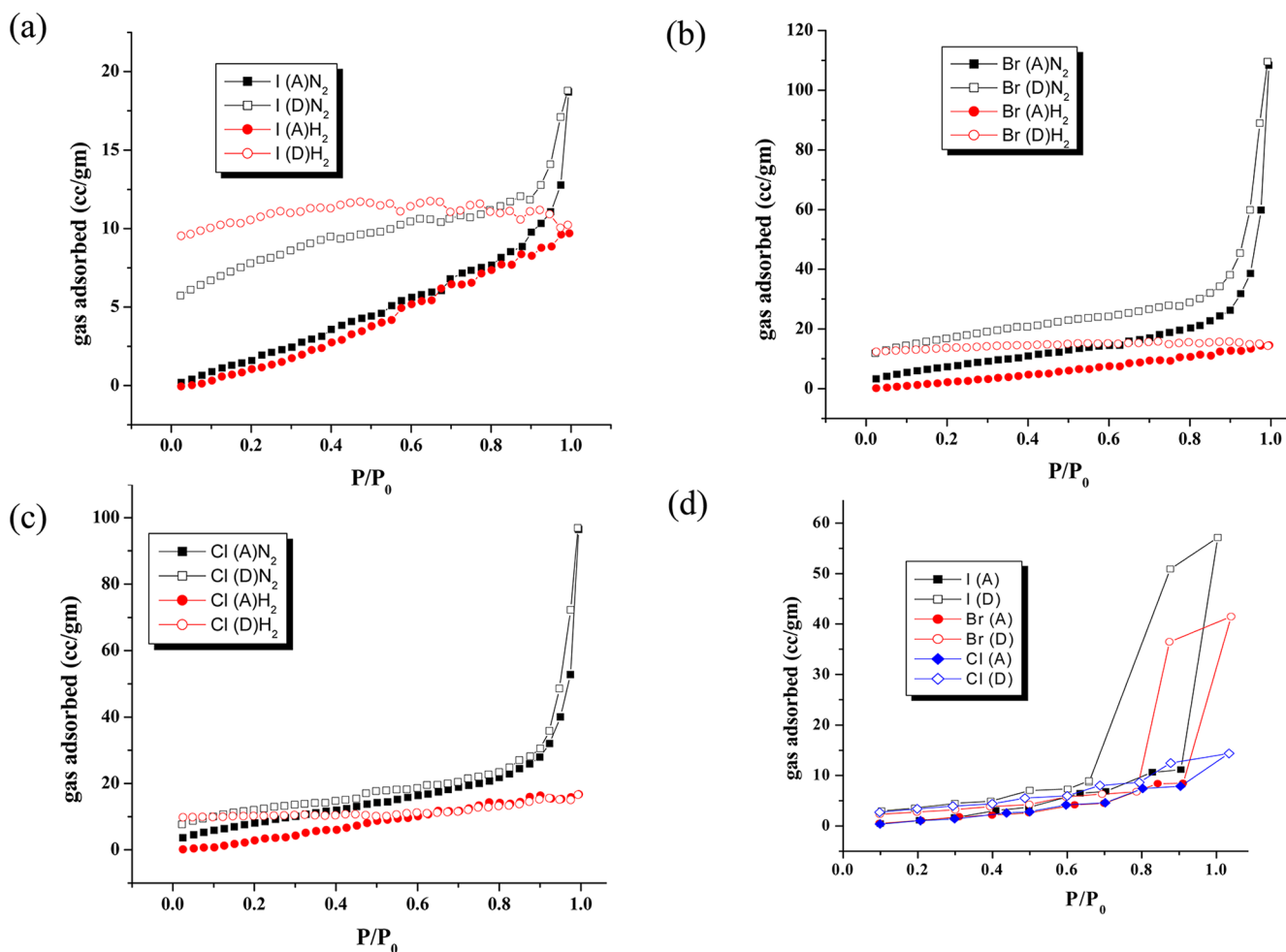
Figure 9. Nitrogen and hydrogen sorption isotherms at 77 K for compounds (a) **2**; (b) **3** and (c) **4**. (d) Water vapor sorption isotherms for **2**, **3** and **4** at room temperature.

GEH) crystallized in $P6_3$ space group, while other three are crystallized in $P\bar{1}$ space group.[29−32] Interestingly, all exhibit type-II contacts with the exception of one, PAXREM. In this compound, out of three Br···Br interactions, two are of type-I and one is of type-II [Br···Br, θ_1 and θ_2: 3.644 Å 151°, 151°; 3.548 Å, 152°, 149°; 3.569 Å, 92°, 145°].

In the case of iodo-aryl, a total of 18 molecules found to exhibit I_3 synthon. Out of 18, 10 entries involve a family of clathrates of 2,4,6-tris(4-iodophenoxy)-1,3,5-triazine.[21] All these 10 molecules crystallized in $R\bar{3}$ space group and exhibit θ values around 103° and 161°, respectively, which indicates that halogen···halogen contacts observed here involve type-II interaction. Six entries contain di, tri, or hexa halo substituted benzene and crystallize in either $P2_1/n$ or $P\bar{1}$ space groups.[33] Out of the remaining two hits, QODRUW is 2,2′,4,4′,6,6′-hexaiodo-1,1′-biphenyl-3,3′,5,5′-tetraol and crystallizes in $P2_1/a$ space group; and XOGVOF01 represents 2-nitrophenylthio-2-iodophenylamine molecule.[34,35] Interestingly, although the molecule XOGVOF01 lacks 3-fold symmetry, it crystallizes in $R\bar{3}$ space group. Notably, type-II interactions are exhibited in all the entries.

The CSD study indicates that halogen···halogen interactions involved in X_3 synthon generally are of type-II in nature. It was also observed that the X_3 synthons are formed mostly by the molecules having no strong hydrogen bonding functional groups. We note here that in the current study, **1I** exhibits I_3

synthon only when all the three hydrogen bonding groups (amide) are blocked by cyclohexanone (**11**).

In order to understand the nature of interactions and geometrical parameters involved in X_3 synthon, the scatter-grams between angles (θ_1 and θ_2) and distances were plotted (Figure 8).[36] For this purpose, the I···I distances were considered up to 4.3 Å as the I_3 synthon observed in the present study contains somewhat longer distances due to the presence of cyclohexanone moiety. These plots reveal that the θ values of the molecules exhibiting tri-iodo synthon are clustered in the range of 100−120° and 160−180° up to X···X < 4.05 Å; and above this distance the θ values are scattered uniformly between 60 and 130°. We note here that the θ values observed in case of **11** (153.54°, 141.64°; 156.25°, 136.32°; 151.94°, 145.88°) does not fall in the region of 60−130° indicating that these interactions are of significant in nature although they exhibit longer I···I distances. On the other hand, the θ values observed in case of **7−10** distributed from 79 to 130°. Similarly, the scattergram of θ values versus Br···Br distances of tribromo synthon reveals that the segregation between θ becomes indistinct after 3.65 Å.

Gas (N$_2$, H$_2$ and H$_2$O) Sorption Study. Porous organic compounds are classified into two types as intrinsic and extrinsic porous compounds. Intrinsic porosity is the inherent property of the molecule however extrinsic porosity occurs by self-assembling of molecules *via* noncovalent interactions

especially hydrogen bonding. The porosity of the later materials is less explored compared to that of former variety. The materials of **2−4** belong to the class of extrinsic porous materials.

In **2−4**, the solvent THF contributes to ~25% of the crystal volume and exist in the channels. Sorption analyses were conducted on activated samples of **2**(I), **3**(Br) and **4**(Cl) under identical conditions to explore the gas sorption behavior. All the three materials are mesoporous in nature. The BET surface areas of **2**, **3** and **4** are 14, 34, and 31 m^2 g^{-1}, respectively, as estimated from the N_2-sorption isotherms (Figure 9a−c). The materials of **2**, **3** and **4** were found to adsorb ~19, ~110 and ~97 mL g^{-1} of N_2, respectively. The uptake values and surface areas of **3** and **4** are found to be significantly higher than those of **2**. Further, the values of **3** and **4** are on par with those of other related organic materials. For example, tris-(phenylenedioxy)cyclophasphazene (TPP),[1h] cucurbit[6]uril[1k] and 1,2-dimethoxy-*p*-*t*-butylcalix[4]dihydroquinone[1i] were shown to exhibit N_2 uptake values of ~55, ~85 and ~90 mL g^{-1}, respectively. However, the highest uptake up to 754 mL g^{-1} is reported by Mastalerz et al. on triptycene trisbenzimidazolone (TTBI).[1l]

The H_2 and H_2O vapor sorptions of these materials were also explored. The H_2 sorption values (at 77 K) of **2**, **3** and **4** were found to be ~12, ~16 and ~16 mL g^{-1}, respectively (Figure 9a−c), whereas for H_2O these values are ~57, ~41 and ~14 mL g^{-1}, respectively (Figure 9d). It is interesting to note here that the sorption values of N_2 and H_2 for **2** are much lower than those of **3** and **4**. Further, **3** and **4** show more propensities to adsorb N_2 than H_2. In contrast, the material of **2** shows a better tendency to adsorb water vapor than those of **3** and **4**. The better water sorption of material **2** indicates that the material containing I is more hydrophilic in nature than those containing Cl and Br. Further, higher uptake of water observed at higher P/P_0 is probably due to the high vaporization energy of water.

CONCLUSION

It was shown that the adoption of a particular structure type in the crystallization reaction of tris(4-halophenyl)benzene-1,3,5-tricarboxamide, in particular with **1I**, depends on the solvent of crystallization. The moiety of **1** was found to adopt a variety of geometries depending on the varying degree of interference in the formation of N−H···O hydrogen bonds between amide functional groups. The triple helical structures (**2−4**) were found to form only in the presence of THF as it does not disturb the amide-to-amide hydrogen bonds, while the blocking of amide groups by solvents to varying extents resulted in the crystal structures of **5−11**. In the cyclohexanone (CYH) solvate of **1I** (**11**), CYH molecules were able to block all the three amide groups and propagate the packing exclusively *via* I_3 synthons in two dimensions. It is interesting to note here that the ester analogues of **1I** were shown to form metastable clathrates in the presence of several solvent molecules.[22b] These metastable crystals finally convert into nonsolvated variety by keeping the crystals in touch with mother liquor for prolonged periods. However, the structures obtained here are very stable and no such transformations were observed. The CSD analysis on X_3 synthons shows that in the majority of such cases the molecules contain 3-fold symmetry and do not contain strong hydrogen bonding groups. The X_3 synthon observed in **11** exhibits type-I interactions unlike the ones in the CSD, which exhibit type-II interactions. The gas sorption studies indicate

that the materials **2−4** can exhibit a better tendency to adsorb N_2 gas over H_2. The material containing iodo substitution showed a lesser tendency to adsorb N_2 and H_2 but a better tendency to adsorb water.

ASSOCIATED CONTENT

Ⓢ Supporting Information
Experimental details, IR-spectra, elemental analysis. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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