

Solvent Dependent Structures of Hydrogen-Bonded Organic Frameworks of 2,6-Diaminopurine

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(5) Supporting Information

ABSTRACT: Three solvent dependent structures of 2,6-diaminopurine in N,N'-dimethylforamide (DAP-1-DMF), water (DAP-2-H₂O), and methoxybenzene (DAP-3-CH₃OC₆H₅) have been structurally characterized. They exhibit different structures because of the different involvement of solvent molecules in the hydrogen bonded frameworks. The DAP molecules tend to be self-assembled with other DAP molecules through hydrogen bonding interactions. DAP has very similar hydrogen bonding interaction patterns to the established DAT group (2,4-diaminotriazinyl), underlying the potential of this new unit for the construction of porous hydrogen bonded organic frameworks.



INTRODUCTION

Hydrogen bonding is essential in biological systems to assemble complex supramolecules and direct their functionalities.^{1–3} Although the idea to make use of hydrogen bonding to construct porous hydrogen bonded organic frameworks (HOFs) has been proposed more than 20 years, little progress has been made to design and stabilize porous HOFs to establish their permanent porosities.^{4–12} Unlike traditional porous materials such as zeolites¹³ and metal–organic frameworks (MOFs),^{14–17} HOFs can be easily recovered through simple recrystallization. Furthermore, they have the advantages of solution process ability and characterization and easy purification, making them very promising functional materials for gas storage and separation. Recent discoveries on a few HOFs for hydrogen storage¹⁸ and carbon dioxide capture,^{19–23} acetylene storage²⁴ and separation of C_2H_2/C_2H_4 ,²⁵ enantioselective separation of alcohols,²⁶ and luminescent applications^{27–29} are really encouraging. These studies have established the feasibility to construct porous HOFs, although it is much more challenging than constructing porous zeolites and MOFs.

As revealed in Wuest's pioneering work and our recent discoveries, the 2,4-diaminotriazinyl (DAT) group is a very powerful building unit to assemble and stabilize porous HOFs because of their multiple sites for hydrogen bonding.^{25,26,30} The success of this DAT unit for the construction of porous HOFs has motivated us to explore new simple organic building units to develop HOF chemistry. We speculated that 2,6-diaminopurine (DAP) might have some similarity to DAT for involvement in hydrogen bonding. As shown in Scheme 1, DAP also has multiple sites for their potential hydrogen bonding interactions. Before we incorporate such a basic unit into organic backbones to synthesize a variety of organic linkers for the assembly of porous

Scheme 1. Chemical Structures of DAT Unit and DAP Molecule



HOFs, it is necessary to examine the basic hydrogen bonding motifs of the DAP molecule. Recrystallization of DAP molecules in N,N'-dimethylforamide (DMF), water (H2O), and methoxybenzene (anisole, CH₃OC₆H₅) readily led to crystals of DAP-1-DMF, DAP-2-H₂O, and DAP-3-CH₃OC₆H₅, respectively. Crystal structures of these different solvent included DAP hydrogen bonded organic frameworks do reveal some very basic hydrogen bonding motifs, which are similar to those discovered in DAT. It is also interesting that different solvents lead to the different framework structures of DAP molecules attributed to the different roles of solvent molecules in the self-assembly of HOFs. Because the methoxybenzene molecules are not involved in the hydrogen bonding with DAP molecules, self-assembly of DAP molecules in methoxybenzene solvent even forms a three-dimensional HOF DAP-3-CH₃OC₆H₅ with one-dimensional channels. Herein we report the X-ray crystal structures of these three solvent dependent hydrogen-bonded organic frameworks of 2,6-diaminopurine (DAP).

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EXPERIMENTAL SECTION

All reagents and solvents were used as received from commercial suppliers without further purification. FTIR spectra were performed on a Bruker Vector 22 spectrometer at room temperature. Thermogravimetric analyses (TGA) were measured using a Shimadzu TGA-50 analyzer under a nitrogen atmosphere with a heating rate of 5 °C min⁻¹. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku Ultima IV diffractometer operated at 40 kV and 44 mA with a scan rate of 1.0 deg min⁻¹. The crystallographic measurement of DAP-1-DMF, DAP-2-H₂O, and DAP-3-CH₃OC₆H₅ were collected at 298(2), 298(2), and 293(2) K respectively, on a Rigaku X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 3000 W power (50 kV, 40 mA) with Saturn 724 CCD detector. The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. The structure was solved by direct methods and refined by full matrix least-squares methods with the SHELX-97 program package. The solvent molecules in DAP-3-CH₃OC₆H₅ are highly disordered. The SQUEEZE subroutine of the PLATON software suit was used to remove the scattering from the highly disordered guest molecules in DAP-3-CH₃OC₆H₅. The resulting new files were used to further refine the structures. The H atoms on C atoms were generated geometrically. X-ray crystallographic data is summarized in Table 1.

Table 1. Crystallographic Data for the DAP-1-DMF, DAP-2- H_2O , and DAP-3-CH₃OC₆ H_5

identification	DAD 1 DME			
code	DAP-1-DMF	DAP-2-H ₂ O	DAP-3-CH ₃ OC ₆ H ₅	
empirical formula	$C_{11}H_{20}N_8O_2$	C ₅ H ₈ N ₆ O	$C_5H_6N_6$	
formula wt	296.35	168.17	150.16	
temp, K	298(2)	298(2)	293(2)	
cryst syst	monoclinic	triclinic	trigonal	
space group	$P2_1/n$	$P\overline{1}$	R3	
a, Å	13.978(4)	8.861(7)	18.711(3)	
b, Å	8.0838(19)	9.424(6)	18.711(3)	
<i>c,</i> Å	13.895(4)	9.490(6)	10.843(2)	
α , deg	90.00	69.25(6)	90.00	
β , deg	105.158(4)	73.03(6)	90.00	
γ, deg	90.00	73.75(6)	120.00	
vol, Å ³	1515.4(7)	694.9(8)	3287.3(9)	
Ζ	4	4	18	
$D_{\rm cal}~({\rm g~cm^{-3}})$	1.299	1.608	1.365	
$\mu \ (\mathrm{mm}^{-1})$	0.095	0.122	0.098	
F(000)	632.0	352.0	1404.0	
reflns collected	8040	3769	4517	
data/restraints/ params	2807/0/250	2701/0/265	1672/0/103	
GOF	0.992	0.999	1.015	
final R indexes $[I > 2\sigma(I)]$	$\begin{array}{l} R_1 = \ 0.0577, \\ wR_2 = \ 0.1309 \end{array}$	$\begin{array}{l} R_1 = \ 0.0503, \\ wR_2 = \ 0.1130 \end{array}$	$\begin{array}{l} R_1 = 0.0927, \\ wR_2 = 0.2186 \end{array}$	
Final <i>R</i> indexes [all data]	$\begin{array}{l} R_1 = 0.0630, \\ wR_2 = 0.1344 \end{array}$	$\begin{array}{l} R_1 = 0.0653, \\ wR_2 = 0.1241 \end{array}$	$\begin{array}{l} R_1 = \ 0.0997, \\ wR_2 = \ 0.2337 \end{array}$	
largest diff. peak/ hole. e Å ⁻³	0.54/-0.28	0.33/-0.28	0.53/-0.37	

Synthesis of DAP-1-DMF. 2,6-Diaminopurine (DAP) (50 mg) was dissolved in DMF (6 mL) under heating. The resulting solution was cooled to room temperature and filtered. The filtrate was allowed to evaporate at room temperature for 1 day. Large colorless block shaped crystals were obtained in 69% yield.

Synthesis of DAP-2-H₂O. 2,6-Diaminopurine (DAP) (50 mg) was dissolved in H₂O (6 mL) under heating. The resulting solution was cooled to room temperature and filtered. The filtrate was allowed to evaporate at room temperature for 1 day. Large yellow block shaped crystals were obtained in 91% yield.

Synthesis of DAP-3-CH₃OC₆H₅. 2,6-Diaminopurine (DAP) (50 mg) was dissolved in anisole (6 mL) under heating. The resulting

solution was cooled to room temperature and filtered. The filtrate was allowed to evaporate at room temperature for 1 day. Light blue block shaped crystals were obtained in 82% yield.

RESULTS AND DISCUSSION

Single crystals of DAP-1-DMF, DAP-2-H₂O, and DAP-3-CH₃OC₆H₅ were easily recrystallized from DMF, H₂O, and CH₃OC₆H₅, respectively. Their phase purities were confirmed by the powder X-ray diffraction patterns, which match well with their simulated ones from X-ray single crystal structures (Figure S1, Supporting Information). Thermogravimetric analysis (TGA) indicates that different amounts of solvent molecules exist within these frameworks, about 6.1% wt (from 60 to 150 °C), 10.5% wt (from 130 to 150 °C), and 6.7% wt (from 70 to 140 °C), respectively, in DAP-1-DMF, DAP-2-H₂O, and DAP-3-CH₃OC₆H₅ (Figure 1). NMR studies of the dissolved DAP-3-CH₃OC₆H₅



Figure 1. TGA curves of DAP-1-DMF (blue), DAP-2- H_2O (black), and DAP-3- $CH_3OC_6H_5$ (red).

Table 2. Summary of Hydrogen Bonding Motifs Revealed in These Three HOFs and Hydrogen Bonding Interaction Details and Geometries

motif type	donor—H…acceptor	D-Н (Å)	H…A (Å)	D−H…A (Å)	angle (deg)		
DAP-1-DMF ^a							
II	$N1-H1A\cdots N4^{i}$	0.89	2.11	3.14	143		
III	N5-H5A…N2 ⁱⁱ	0.96	2.08	3.12	170		
III	N5–H5B…N3 ⁱⁱⁱ	0.86	2.08	3.12	150		
$DAP-2-H_2O^b$							
Ι	N5-H5B…N7 ⁱ	0.90	2.13	3.03	175		
Ι	$N11-H11A\cdots N1^{ii}$	0.89	2.15	3.04	175		
II	N3-H3B…N8 ⁱⁱⁱ	0.89	1.98	2.86	170		
II	N9-H9A…N2 ^{iv}	0.85	2.08	2.92	169		
DAP-3-CH ₃ OC ₆ H ₅ ^c							
III	N6–H6A…N4 ^{iv}	0.86	2.19	3.02	161		
III	N6–H6B…N1 ^v	0.86	2.20	3.02	158		
IV	N5-H5A…N1 ⁱⁱ	0.86	2.37	3.08	140		
V	$N3-H3B\cdots N2^{i}$	0.86	2.15	2.90	145		
VI	N5-H5B…N4 ⁱⁱⁱ	0.86	2.29	3.12	162		

^aSymmetry codes: (i) 1 - x, -y, 1 - z; (ii) 3/2 - x, 1/2 + y, 1/2 - z; (iii) 3/2 - x, -1/2 + y, 1/2 - z. ^bsymmetry codes (i) x, y, 1 + z; (ii) x, y, -1 + z; (iii) 1 + x, y, z; (iv) -1 + x, y, z. ^csymmetry codes (i) y, -x + y, -z; (ii) 1/3 - x + y, 2/3 - x, -1/3 + z; (iii) 1/3 + y, 2/3 - x + y, 2/3 - z; (iv) x - y, x, 1 - z; (v) y, -x + y, 1 - z.

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Figure 2. X-ray crystal structure of **DAP-1-DMF** showing (a) the local hydrogen bonding environments of DAP molecules and DMF, (b) two-dimensional hydrogen bonded organic framework, and (c) packing of the framework in which the solvent DMF molecules reside between the 2D hydrogen bonded organic framework sheets.

show that the solvent molecules within this framework are only water molecules (Figure S3, Supporting Information).

X-ray Crystal Structure of DAP-1-DMF. As shown in Figure 2, DAP molecules are self-assembled together to form a two-dimensional HOF (Figure 2b). There exists one free $-NH_2$ site that is not involved in the hydrogen bonding within DAP molecules but interacts with DMF molecules through hydrogen bonding (Figure 2a). The packing diagram shows that the DMF molecules reside between the two-dimensional sheets of DAP molecules (Figure 2c).

X-ray Crystal Structure of DAP-2-H₂O. The stronger preference of H_2O molecules for their hydrogen bonding interactions with DAP leads to its different framework structure from DAP-1-DMF. As shown in Figure 3a, water molecules even bridge several DAP molecules together. In fact, without the considerations of water molecules, the framework of self-assembled DAP molecule is a zigzag chain. Once water molecules are



Figure 3. X-ray crystal structure of DAP-2-H₂O showing (a) a twodimensional water incorporated framework sheet and the local hydrogen bonding environments of DAP molecules and H₂O and (b) packing of the 3D framework.

considered as part of the framework, this HOF can be considered as a three-dimensional water incorporated framework in which the hydrogen bonding interactions between water molecules link the two-dimensional sheets (shown in Figure 3a) together (Figure 3b).

X-ray crystal structure of DAP-3-CH₃OC₆H₅. The X-ray crystal structure of DAP-3-CH₃OC₆H₅ is completely different from DAP-1-DMF and DAP-2-H₂O because of the hydrophobic nature of CH₃OC₆H₅ molecules, which excludes their hydrogen bonding interactions with DAP molecules. That enables DAP molecules to interact with nearby DAP molecules in as many hydrogen bonding interactions as possible. As shown in Figure 4a, each DAP molecule can link with eight DAP molecules through weak hydrogen bonding interactions to form a three-dimensional HOF without the involvement of solvent molecules (Figure 4b). More interestingly, one-dimensional channels even exist along the c axis (Figure 4c) of about 3.8 Å.

Basic Hydrogen Bonding Motifs. The detailed X-ray crystal structural studies of these three solvent dependent HOFs of DAP enable us to rationalize some basic hydrogen bonding motifs to connect DAP molecules. As summarized in Scheme 2, the hydrogen bonding motifs I, II, and III are very similar to those revealed in DAT based HOFs, underlying the

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Figure 4. X-ray crystal structure of **DAP-3-CH₃OC₆H₅** showing (a) the local hydrogen bonding environments of DAP molecules, (b) three-dimensional hydrogen bonded organic framework, and (c) packing of the framework showing one-dimensional channels of about of about 3.8 Å along the *c* axis.

feasibility of DAP unit for the synthesis of DAP containing organic linkers for the construction of porous HOFs. Some more structural features of the hydrogen bonding interactions are listed in Table 2 as well, once again confirming the richness of DAP molecules for their hydrogen bonding interactions.

In summary, X-ray crystal structural studies of 2,6-diaminopurine (DAP) in different solvents indicate that DAP molecules are indeed easily self-assembled with each other through hydrogen bonding interactions. As revealed in the detailed hydrogen bonding motifs in DAP HOFs, their intermolecular hydrogen bonding interaction patterns are quite similar to those discovered within DAT containing HOFs. That is really encouraging, because it shows the promise to make use of this DAP unit (Scheme 3) to synthesize a variety of DAP containing organic compounds to construct porous HOFs. DAP can be considered as an expanded DAT unit, so the porosities and pore surfaces of the resulting HOFs can be





Scheme 3. Potential New Building Unit for the Construction of Porous Hydrogen Bonded Organic Frameworks



systematically tuned in order to realize their specific recognition of small molecules and their applications.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic files (CIF), power X-ray diffraction analysis (PXRD) and IR spectra of **DAP-1-DMF**, **DAP-2-H**₂**O**, and **DAP-3-CH**₃**OC**₆**H**₅, and ¹H NMR spectra of **DAP-3-CH**₃**OC**₆**H**₅ and DAP without solvent digested in DMSO-*d*₆. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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