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Supramolecular pseudopolymorphs: double helix and planar structures with channels

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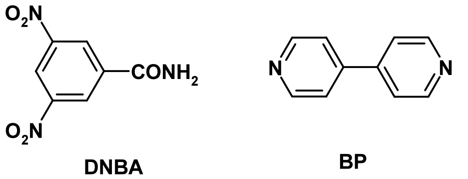
Abstract—3,5-Dinitrobenzamide (**DNBA**) and 4,4′-bipyridyl (**BP**) co-crystallize to yield different types of channel structure from methanol and water, constituting supramolecular pseudopolymorphs. While, in the methanol adduct, **DNBA** and methanol molecules form a double helix network, in the water adduct, **DNBA** and water molecules yield a planar layer structure. However, in both the adducts, **BP** molecules sit in the channels created in the three-dimensional packing of the double helix or layers.

Polymorphism,[1] a phenomenon which laid the foundations for studies in solid-state organic chemistry,[2] has emerged as a frontier area of research, with the realization of different properties for the polymorphs of a compound.[3] Since polymorphs are prepared by crystallization of compounds from different solvent(s), at times solvent molecules are incorporated into the crystal lattice, yielding different types of crystal structures that are technically referred to as pseudopolymorphs.[1,4] In fact, several bio-active compounds (drugs, inhibitors, etc.) crystallize as psuedopolymorphs.[5]

In supramolecular synthesis[6,7] (the creation of network structures by co-crystallization of different components through molecular recognition), studies on polymorphism are not well advanced; perhaps, due to the directed synthesis of targeted assemblies. Since solvent molecules are often incorporated within cavities or channels formed by the supramolecular organization in numerous supramolecular assemblies, it should be possible to obtain pseudopolymorphs with ease through supramolecular synthesis. Herein, we report pseudopolymorphs obtained during the supramolecular synthesis of the molecular complex between 3,5-dinitrobenzamide (**DNBA**) and 4,4′-bipyridyl (**BP**). The pseudopolymorphs are formed with different types of channel structures and varying conformations of the guest molecule, depending upon the solvent(s) employed for the co-crystallization.



Adduct 1) 2(DNBA) : BP : 2(H_2O)
Adduct 2) 2(DNBA) : BP : 2(MeOH)

In our continuing interest on studies on the ability of the amide functionality for the creation of novel supramolecular assemblies,[8] we have carried out co-crystallization of **DNBA** and **BP** from various solvents, such as methanol, ethanol, chloroform, water, etc. X-ray diffraction studies on single crystals, thus, obtained from methanol and water, revealed[9] that **DNBA** forms 2:1 adducts with **BP** along with two molecules of either methanol or water. The water and methanol adducts are labeled as **1** and **2**, respectively. While adduct **1** crystallizes in triclinic,[10] adduct **2** crystallizes in a monoclinic[11] space group. The three-dimensional arrangement of the constituent molecules in the crystal structures of both adducts is shown in Figure 1.

Interestingly, both adducts **1** and **2** form channel structures as shown in Figure 1, with the channels being occupied by **BP** molecules. In fact, these are the first examples wherein **BP** acts as a guest, rather than a rigid spacer of the host system as found from the CSD analysis.[12] Apart from this global similarity, adducts **1** and **2** differ, distinctly, in the way the channels are established.

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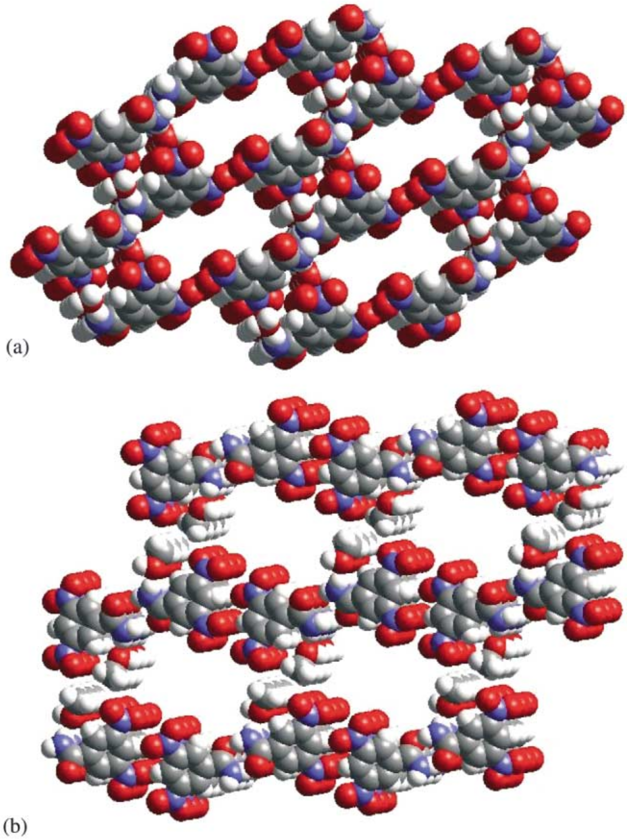

Figure 1. Illustration of channels observed in the crystal structures of the adducts (a) **1** and (b) **2**. Guest molecules (4,4′-bipyridine) are not shown for the clear vision of channels.

In adduct **1**, the channels are created by the stacking of planar layers, possessing cavities, as shown in Figure 2(a). The arrangement of molecules in a typical layer is shown in Figure 2(b). In each layer, **DNBA** molecules and water molecules together form a host lattice, constituting an hexagonal arrangement by connecting each of six molecules of **DNBA** through centrosymmetric cyclic N–H···O (H···O, 2.10 Å), and C–H···O (H···O, 2.94 Å) hydrogen bonds formed using amide and –NO_2 groups, respectively. The H_2O molecules are attached to **DNBA** molecules through N–H···O (H···O, 2.02 Å) hydrogen bonds involving the *anti*-hydrogen atom of the amide functional group. In addition, there is also a $NO_2 \cdots NO_2$ close contact with O···O distance of 3.19 Å.[13] The characteristics of all noncovalent bonds are in agreement with reported data in the literature.[14] Such an arrangement forms an elliptical cavity of 7×11 Å in dimension, which is occupied by planar **BP** molecules.

The guest molecules (**BP**) interact with **DNBA** through H_2O molecules by forming O–H···N (H···N, 1.99 Å) hydrogen bonds. A close observation of Figure 2 further reveals that binding between the host and guest molecules is further strengthened with the formation of C–H···O hydrogen bonds, with the H···O distances in the range 2.34–2.66 Å, and involving all the hydrogen atoms of the **BP** molecule.

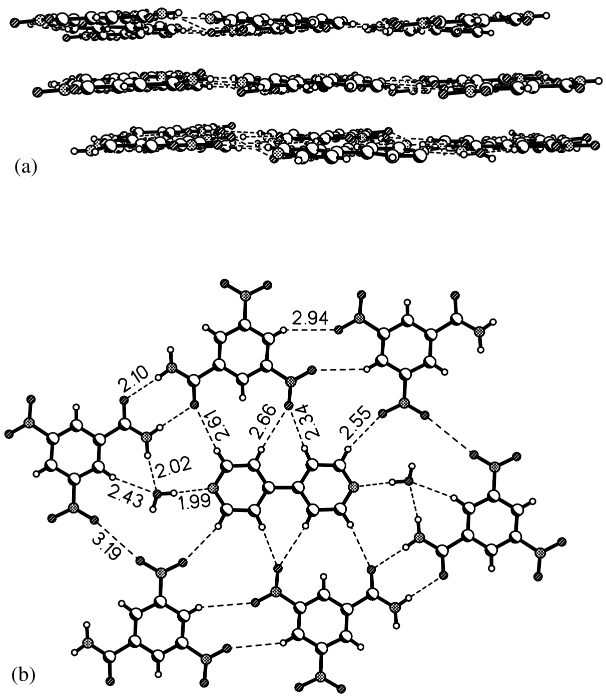

Figure 2. (a) The stacking of layers in the crystal structure of adduct, **1**, in a direction perpendicular to the channels in Figure 1(a). (b) Arrangement of molecules in a two-dimensional layer in the crystal structure of adduct **1**.

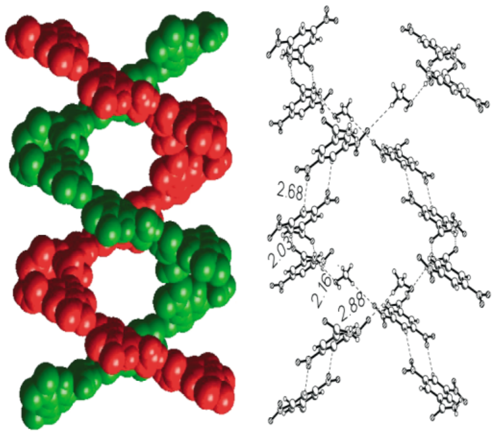

Figure 3. Arrangement of **DNBA** and methanol molecules in the crystal structure of adduct, **2** forming a double helix network. (Left) A typical double helix. (Right) Annotation of interactions between the molecules in the helices.

In adduct **2**, however, the channels are obtained by the stacking of helical chains rather than planar sheets as observed in **1**. A fascinating feature is that the helices, running in an *anti*-parallel manner, constitute a double helix. A typical double helix, viewed perpendicular to the channels axis, is shown in Figure 3 (left). In each helix, the constituent molecules interact in a manner similar to those of adduct **1** forming centrosymmetric cyclic N–H···O (H···O, 2.03 Å) and C–H···O (H···O, 2.68 Å) hydrogen bonds through the amide and –NO_2 groups, respectively (see Fig. 3 (right)). However, instead of water, methanol molecules interact with **DNBA** by forming N–H···O (H···O, 2.16 Å) and C–H···O (H···O, 2.88 Å) hydrogen bonds, through –CH_3 and –OH groups to create the host network. In addition, methanol molecules, lying in the helices of each double helix, are connected to **BP** molecules through O–H···N (H···N, 1.85 Å) hydrogen bonds. An interesting feature about the **BP** molecules is that the two aromatic rings are twisted with a dihedral angle of 35° unlike those in adduct **1**. The conformational variations in **BP** molecules, as a spacer, is well known in the literature, but, the differences in the conformations of **BP** molecules observed in the adducts **1** and **2**, commensurate with the host arrangement, perhaps a coincidence, nevertheless, is unique.

Thus, adducts **1** and **2** are quite different from other supramolecular systems[15] that crystallize with solvent molecules in the crystal lattice, wherein the host network remains constant with the incorporation of the solvent of crystallization. However, in adducts **1** and **2**, the arrangement of the host lattice is dependent on the solvent of crystallization forming a different type of channel structure mediated by either a planar or a double helix arrangement of the host molecules. Hence, adducts **1** and **2** qualify to be considered as pseudopolymorphs of a supramolecular assembly.

In conclusion, two pseudopolymorphs of a supramolecular complex of **DNBA** and **BP** have been reported. We believe that, these are the first examples of supramolecular pseudopolymorphs and also show a new role for **BP** as a guest molecule. Further experiments are in progress looking at the interconversion of **1** and **2** by a solvent exchange process, and also for obtaining pseudopolymorphs by varying the solvent as well as the guest molecule.

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10. Crystal data for adduct, **1**: $2(C_7H_5N_3O_5):C_{10}H_8N_2:2(H_2O)$, $M=307.25$, triclinic, $P\bar{1}$ (No. 2), $a=5.788(3)$ Å, $b=8.899(5)$ Å, $c=13.410(7)$ Å, $\alpha=98.84(1)°$, $\beta=96.93(1)°$, $\gamma=90.19(1)°$, $V=677.4(6)$ Å^3, $Z=1$, $D_{\text{cacld}}=1.506$ g cm^{-3}, $F(000)=318$, λ(Mo-Kα)$=0.71073$, $T=293$ K, reflections collected/unique 2846/1937, Final $GooF=1.061$, $R_1=0.057$, $wR_2=0.140$, R indices based on 1492 reflections with $I>2\sigma(I)$, CCDC 202779.
11. Crystal data for adduct, **2**: $2(C_7H_5N_3O_5):C_{10}H_8N_2:2(CH_4O)$, $M=642.55$, monoclinic, $P2/n$ (No. 13), $a=15.722(3)$ Å, $b=3.789(1)$ Å, $c=24.405(5)$ Å, $\beta=91.85(1)°$, $V=1452.9(5)$ Å^3, $Z=2$, $D_{\text{cacld}}=1.469$ g cm^{-3}, $F(000)=668$, λ(Mo-Kα)$=0.71073$, $T=293$ K, reflections collected/unique 5684/2095, Final $GooF=1.029$, $R_1=0.040$, $wR_2=0.100$, R indices based on 1638 reflections with $I>2\sigma(I)$, CCDC 183249.
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