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Layered Structures Formed by Dinitrobenzoic Acids

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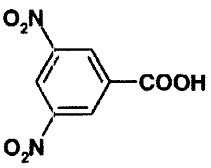
Abstract: 3,5-dinitrobenzoic acid, **1** and 3,5-dinitro-4-methylbenzoic acid, **2**, form co-crystals with 4,4'-bipyridyl but only the latter forms a layered structure, which can incorporate anthracene molecules. Furthermore, **2** forms a pillared type structure with thionicotinamide. © 1998 Elsevier Science Ltd. All rights reserved.

A variety of nanoporous inorganic structures are known.[1] Recently, there has been some effort to explore whether organic porous structures can be designed and synthesized by making use of supramolecular organization.[2] Thus, Yaghi et al.[3] have reported a microporous metal-organic framework based on a trimesic acid-pyridine-cobalt complex. Recently, novel layered and channel structures formed by trithiocyanuric acid (TTCA) were reported from this laboratory.[4] Crystallization of TTCA from acetone gave a layered structure, comparable to clays, pillared by acetone molecules while co-crystallization of TTCA from benzene solution gave a novel channel structure which could accommodate benzene. Encouraged by these findings, we wanted to examine other possible organic porous structures obtained by noncovalent synthesis.[5] In this context, it appeared to us that 3,5-dinitrobenzoic acid, **1** and 3,5-dinitro-4-methylbenzoic acid, **2** were well suited to form such structures. This is because, **1** is known to form a structure with cavities when crystallized from benzene solution, the cavities accommodating molecules such as anthracene.[6] In the absence of benzene, **1** does not form a layered structure. Crystallization of **2**, from most solvents, yields structures with cavities in a two-dimensional arrangement, which can accommodate anthracene.[6a] We have investigated whether the cavities formed by **1** and **2** could be modified by incorporating an azaaromatic donor molecule such as 4,4'-bipyridyl, **3**. In addition, we have examined the possibility of formation of layered structures by **1** and **2** by co-crystallization with other compounds.



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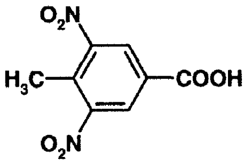

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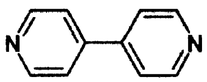

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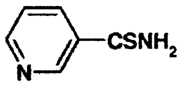

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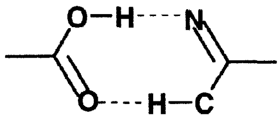
Crystallization of **1** and **2** in the presence of **3** gave complexes **1a** and **2a** respectively with 2:1 stoichiometry.[7] In both **1a** and **2a**, bipyridyl molecules break up the hydrogen bonds between the carboxyl groups as shown in Figure 1. Interestingly, interaction between the carboxylic acid and the bipyridyl molecule in these complexes occurs through the formation of a single O-H...N hydrogen bond[8] (see Figure 1) unlike the pair-wise hydrogen bond coupling, consisting of O-H...N and C-H...O bonds as shown below, observed in other related systems.[9] The H...N distances in **1a** and **2a** are 1.61 and 1.58-1.65Å respectively. Furthermore, molecules of **2a** are arranged in two dimensions to yield planar sheets (Figure 2) which in turn are stacked in the three-dimensional packing while molecules of **1a** adopts a herringbone packing pattern.



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Although both **1a** and **2a** do not possess cavities, the two-dimensional arrangement in **2a**, (Figure 1), which is similar to that of the structure of pure acid, 2[6b] encouraged us to investigate the co-crystallization of **1a** and **2a** in the presence of anthracene. **1a** did not yield any co-crystals with anthracene, but **2a** gave crystals of a quality suitable for single crystal X-ray diffraction studies.

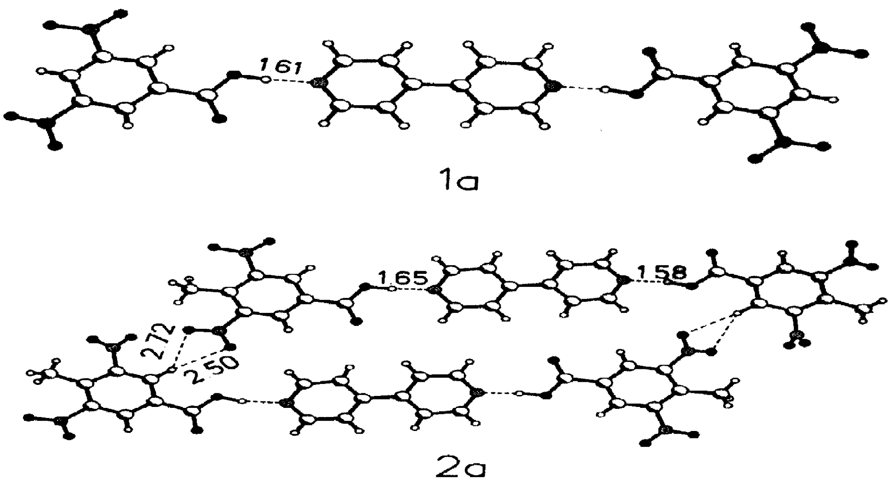


Figure 1: 1a) Recognition pattern between acid, **1** and 4,4'-bipyridyl in the molecular complex, **1a**. The dashed lines represent hydrogen bonds and unique H...O distance is quoted. 2a) Two-dimensional arrangement of supermolecules of acid, **2** and 4,4'-bipyridyl in **2a**. Notice the formation of a six membered ring formed through hydrogen bonds.

The complex of **2a** with anthracene (designated as **2b**[7]) is stabilized by the formation of O-H...N and C-H...O hydrogen bonds coupling[9] (Figure 2), not found either in **2a** or **1a**. The H...N and H...O distances between **2** and **3** in the anthracene adduct, **2b**, are 1.68 and 2.57Å respectively. Figure 2 shows that the supermolecules are arranged in two dimensions in a hexagonal mode through the formation of C-H...O hydrogen bonds between anthracene and the neighbouring molecules of carboxylic acid, **2** such that a cavity of dimension 10 x 12Å results. The anthracene molecules are accommodated in these cavities through the formation of C-H...O hydrogen bonds. The H...O distances are in the range of 2.76 – 2.93Å. A comparison of the structure of **2b** (Figure 2) with the anthracene adduct formed by the parent carboxylic acid, 2[6a] alone indicates that the recognition pattern between anthracene and the acid **2** is not perturbed with the presence of bipyridyl molecule in **2b**.

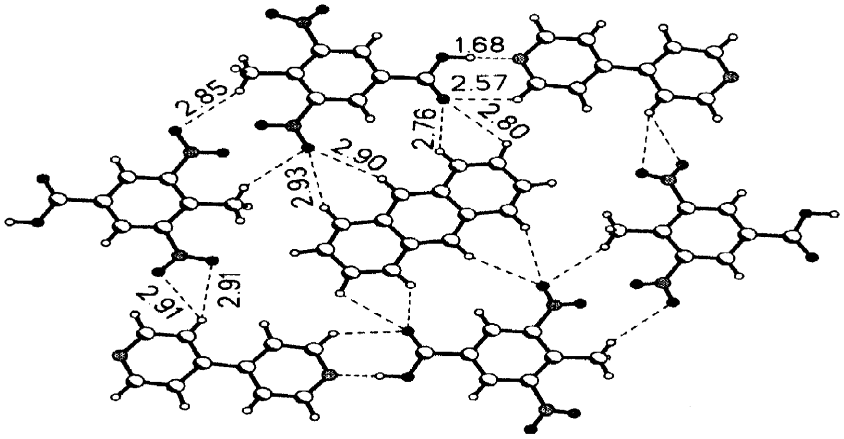


Figure 2: Two-dimensional arrangement of a cavity, formed by acid **2** and 4,4'-bipyridyl, which is filled by molecules of anthracene in the complex **2b**.

We have investigated the formation of pillared structures of **2** which forms layer structures even in the absence of guest molecules such as benzene. Crystallization of **2** from acetone gave a layered structure with no pillaring. We, therefore, crystallized **2** with compounds containing different types of hydrogen-bond donating and accepting sites. Crystallization of **2** with pyridine carboxylic acid or nicotinamide did not yield a molecular complex. We then examined the co-crystals of **2** with thionicotinamide, **4**, since the presence of sulfur could change the recognition pattern. It is known that sulfur-mediated hydrogen bonds such as N-H...S are indeed different from O-H...O, N-H...O and such hydrogen bonds.[4,10] Thus, **2** and **4** yield a complex **2c** upon co-crystallization from methanol.

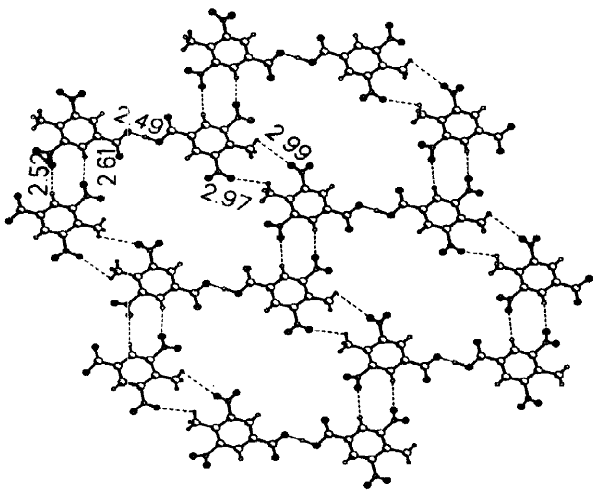


Figure 3: Two-dimensional arrangement of a layer of acid, **2** in the complex with thionicotinamide. The H...O bonds are shown in dashed lines and unique H...O distances are quoted for C-H...O hydrogen bond and O...O distance is quoted for O-H...O hydrogen bond.

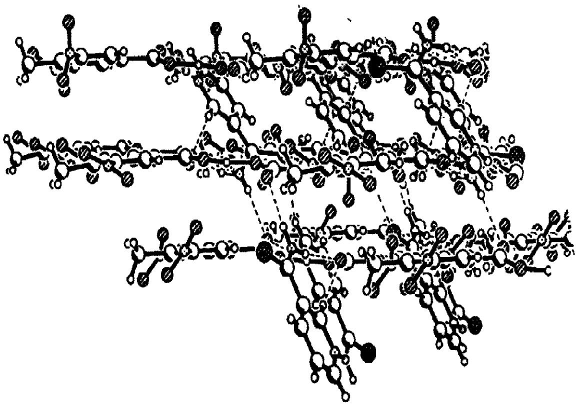
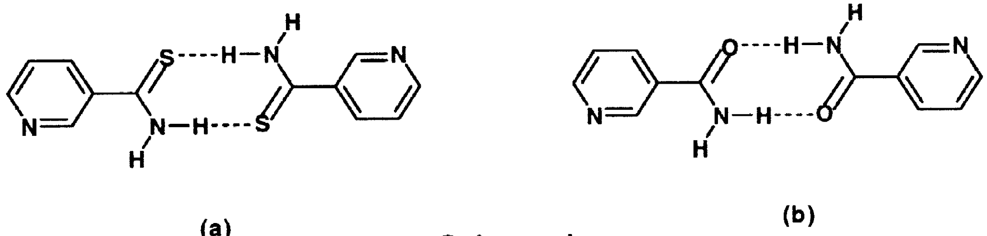


Figure 4: Stacking of layers in a three-dimensional arrangement in the complex, **2c**. Notice the pillaring of thionicotinamide molecules between the layers.

Crystal structure determination of the 2:1 adduct, **2c**[7], formed by **2** with thionicotinamide reveals that the asymmetric unit contains two symmetry independent molecules. Packing analysis shows that the co-crystals of **2** and **4** adopt a pillared type structure.[11] Each of the symmetry dependent molecules of **2** interacts with neighbouring molecules to form two-dimensional planar sheets (Figure 3) which in turn stack alternately in a three-dimensional arrangement through π-π interaction. It is clear from Figure 3 that in each sheet, molecules are held together through formation of O-H...O and C-H...O hydrogen bonds. The H...O distances are in the 2.55 - 3.00Å range. The -COOH groups of adjacent molecules form only a single O-H...O hydrogen bond rather than the well known cyclic hydrogen bonded system, as one of the acids is deprotonated. The mutual association of the molecules in each sheet, however, results in the formation of cavities of 7 x 12Å. The molecules of **4** are intercalated in between the sheets, to yield a pillared type structure, as shown in Figure 4. It is evident from Figure 4 that the molecules of **4** are inclined to the layers of acid, **2** unlike anthracene molecules which are coplanar with the sheets observed in the crystal structure of complex, **2b** (see Figure 2).



Scheme 1

It is rather surprising that thionicotinamide and nicotinamide show such different behaviour with respect to interaction with **2**. It appears that hydrogen bonding pattern shown in Scheme 1 plays a significant role. It is known that molecules with amide or thioamide groups exist as dimers rather than monomers. However, it is evident from Figure 4 that in the complex **2c**, the molecules of **4** intercalated in between the acid sheets are single. It is easier to obtain such single molecular units from **4** rather than nicotinamide as the dimers in the former are formed through weak N-H...S hydrogen bonds (Scheme 1a) whereas the dimers in nicotinamide result from the strong N-H...O hydrogen bonds (Scheme 1b).

Acknowledgements:

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7) Crystal structure determination procedure: Data were collected for all the crystals (**1a**, **2a** - **2c**) on Smart, CCD area detector using MoKα (λ=0.7107) at T=293 K. Structures were determined using SHELXTL-PLUS package (Sheldrick, G. M., SHELXTL, Users Manual, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, U. S. A., 1993). Crystal Data for **1a**: $2(C_7H_4N_2O_6):C_{10}H_8N_2$, M=580.43, monoclinic, $P2_1/n$, a=6.226(1), b=22.150(2), c=9.417(1)Å, β=99.17(1)°, Z=2, F(000)=596, R_1=0.065 and wR_2=0.087. Crystal Data for **2a**: $2(C_8H_6N_2O_6):C_{10}H_8N_2$, M=608.48, triclinic, $P\bar{1}$, a=9.852(1), b=11.297(1), c=14.827(1)Å, α=67.72(1), β=89.77(2), γ=64.85(1)°, Z=2, F(000)=628, R_1=0.049 and wR_2=0.098. Crystal Data for **2b**: $2(C_8H_6N_2O_6):(C_{14}H_{10}):(C_{10}H_8N_2)$, M=786.70, triclinic, P1, a=9.121(1), b=9.260(1), c=11.199(1)Å, α=73.83(1), β=89.58(1), γ=81.78(1)°, Z=1, F(000)=408, R_1=0.055 and wR_2=0.085. Crystal Data for **2c**: $2(C_8H_6N_2O_6):C_6H_6N_2S_1$, M=590.48, triclinic, $P\bar{1}$, a=12.840(1), b=14.270(1), c=15.506(1)Å, α=69.24(1), β=74.18(1), γ=82.07(1)°, Z=4, F(000)=1216, R_1=0.064 and wR2=0.124.
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