One-Dimensional Zigzag Chain Structures with Intermolecular C–H··π and C–H···O Interactions Consisted of Phthalic Acid and Pyridine Derivatives

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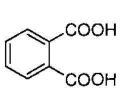
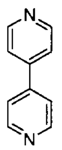
(Received February 16, 2001; CL-010137)

Crystal structures of co-crystals of phthalic acid with 4,4'-bipyridine or 4,4'-dipyridylacetylene contain one-dimensional zigzag chains connected by intermolecular O–H···N hydrogen bonds and edge-to-face packing of phthalic acid and pyridine rings stabilized by intermolecular C–H··π and C–H···O interactions.

Compounds containing a one-dimensional zigzag chain structure have attracted much attention for developing molecular based magnets[1–3] and non-linear optical materials.[4] Such a zigzag chain structure can be achieved by the reaction of a metal complex having two vacant or two substitutable coordination sites with a bridging ligand.[5] Bis(hexafluoroacetylacetonato)manganese(II) Mn(hfac)$_2$ and a bipyridine type ligand have been widely used for this purpose.[6] Zigzag chain structures composed of only organic molecules are also of interest from the viewpoint of crystal engineering as well as development of organic molecular materials. Such structures seem to be formed from phthalic acid and dipyridyl compounds because carboxyl moieties and nitrogen atoms of pyridyl groups form intermolecular hydrogen bondings with linear and robust structures,[7,8] and the angle of the direction of the two carboxyl groups of phthalic acid is 60°. On the other hand, edge-to-face packing with T-shaped geometry is important in crystal engineering.[9] Close packing of zigzag chains may produce such a T-shaped geometry of the two components by intermolecular C–H··π interactions.[10] From these viewpoints we have now carried out co-crystallization of phthalic acid with 4,4'-bipyridine or 4,4'-dipyridylacetylene[11] and have succeeded in constructing the expected crystal structures.



phthalic acid



4,4'-bipyridine

4,4'-dipyridylacetylene

The 1:1 co-crystals (**1**) and (**2**) were prepared from an acetone solution of phthalic acid with 4,4'-bipyridine and 4,4'-dipyridylacetylene, respectively. Single crystals suitable for X-ray crystallographic analysis[12] were grown at room temperature by slow evaporation. Both co-crystals form in the monoclinic crystal system with space group *C*2/*c*. The crystal structures of **1**[13] and **2**[14] consist of an infinite one-dimensional zigzag chain structure along the [1 0 –1] and the [2 0 1] directions, respectively (Figure 1). The zigzag chains are connected by strong intermolecular O–H···N hydrogen bonds (N···O distance 2.64 Å N···H distance 1.42 Å for both **1** and **2**). The two pyridine rings of 4,4'-bipyridine and 4,4'-dipyridylacetylene lie in a plane, and the angles between the least-squares planes of the pyridine rings and the benzene ring of phthalic acid are 89.4° and 61.9° for **1** and **2**, respectively. The angles between the zigzag chains (angles between the planes of the pyridine rings within the zigzag chains) are close to 60° (54.7° for **1**, 56.1° for **2**).

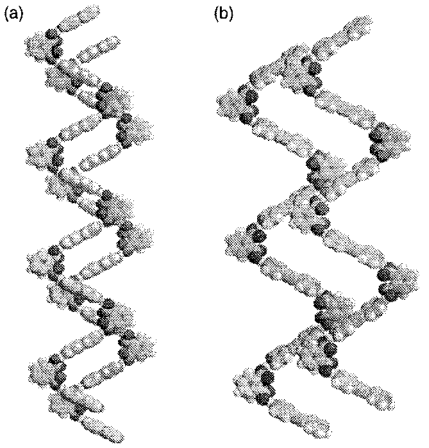


Figure 1. (a) Two one-dimensional zigzag chain structures in co-crystal **1** along the [1 0 1] direction, viewed along the [1 0 1] direction. (b) Two one-dimensional zigzag chain structures in co-crystal **2** along the [-1 0 1] direction, viewed along the [-1 0 1] direction.

Figure 2 shows the zigzag chain structures in the co-crystals **1** and **2** along a direction different from those in Figure 1. In both of **1** and **2**, edge-to-face packing with C–H··π intermolecular interactions between phthalic acid and pyridine rings was observed, and the zigzag chains form two-dimensional undulated sheet-like structures. The C–H··π distances (distances between the least-squares planes of the pyridine rings and the 3- and 4-position carbon and hydrogen atoms in phthalic acid) are 3.69, 3.64, 2.75, 2.84 Å for **1** and 3.45, 3.40, 2.70, 2.77 Å for **2**, respectively. The strong herringbone interactions with characteristic T-shaped geometry are similar to those found in crystals of benzene[15] and 2-aminophenol.[16] The unique structural patterns with the edge-to-face packing observed here are stabilized by various types of intermolecular hydrogen bonding interactions such as O–H···N, C–H··π and C–H··O. Thus, short C–H···O intermolecular interactions between the carbonyl oxygen atoms of phthalic acid and the aromatic hydrogen atoms at the 4-position carbon of the next phthalic acid exist in the crystals of **1** and **2** [2.54 Å (H···O), 3.42 Å (C···O) and 144.4° for **1**; 2.74 Å (H···O), 3.53 Å (C···O) and 139.5° for **2**]. These kinds of weak C–H···O interactions are also known to play an important role in determining the crystal packing in organic solids.[17] In the C–H···O interactions, typical values for H···O and C···O distances are 2.43.0 Å[17a] and 3.3–3.8 Å,[17b] respectively. The interchain distances between the planes of the pyridine derivatives in Figure 2 are 3.6 Å for **1** and 3.7 Å for **2**. Strong resemblance between the crystal structures of **1** and **2** suggests robustness and reproducing ability of the supramolecular synthon[18] formed with phthalic acid and pyridine rings. In this case a zigzag chain structure seems to be "programmed" to form in a crystal.

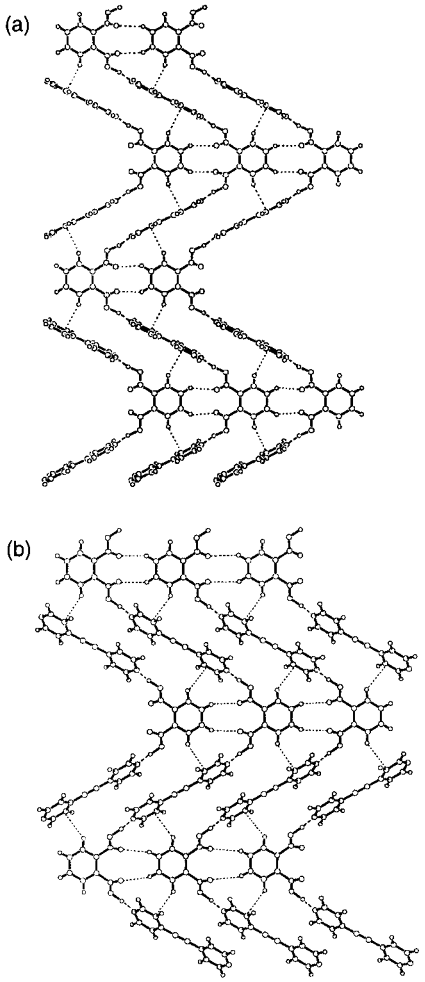


Figure 2. (a) Packing of the zigzag chain structures in co-crystal **1** along the b axis, viewed along the [1 0 1] direction. (b) Packing of the zigzag chain structures in co-crystal **2** along the b axis, viewed along the [-1 0 1] direction. Dotted lines show the intermolecular O–H···N hydrogen bonds, C–H···π and C–H···O interactions.

In conclusion the supramolecular synthons genetated by combination of simple compounds such as phthalic acid and bipyridine type derivatives were successfully used in the design of one-dimensional zigzag chain structures and could realize unique preserved crystal structures. Close packing of the zigzag chains produces edge-to-face packing with intermolecular C–H··π and C–H···O interactions. Studies on the construction of new one-dimensional zigzag chain structures containing functional molecules are now in progress.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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12 Reflection data for **1** and **2** were collected on a Rigaku R-AXIS IV imaging plate area detector with Mo Kα radiation (λ = 0.71070 Å) at 296(2) K. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with SHELX-97.[19] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were localized in the Fourier map and refined isotropically.
13 Crystal data for **1**: $C_{18}H_{14}N_2O_4$, M_x = 322.31, monoclinic, space group $C2/c$, a = 15.761(2), b = 7.821(2), c = 13.396(3) Å, β = 98.060(9)°, V = 1634.9(5) Å^3, Z = 4, D_c = 1.309 g cm^{-3}, $F(000)$ = 672, μ = 0.094 mm^{-1}, crystal dimensions 0.30 × 0.25 × 0.05 mm, 3304 reflections collected, 1212 independent (R_{int} = 0.0734), R_1 = 0.0570, wR_2 = 0.1505 for $I > 2\sigma(I)$, R_1 = 0.0902, wR_2 = 0.1881, S = 0.803 for all data. CCDC 152982.
14 Crystal data for **2**: $C_{20}H_{14}N_2O_4$, M_x = 346.33, monoclinic, space group $C2/c$, a = 11.936(6), b = 7.947(3), c = 20.077(6) Å, β = 107.76(3)°, V = 1814(1) Å^3, Z = 4, D_c = 1.268 g cm^{-3}, $F(000)$ = 720, μ = 0.090 mm^{-1}, crystal dimensions 0.20 × 0.20 × 0.10 mm, 2705 reflections collected, 1177 independent (R_{int} = 0.0850), R_1 = 0.0850, wR_2 = 0.1894 for $I > 2\sigma(I)$, R_1 = 0.1514, wR_2 = 0.2393, S = 1.117 for all data. CCDC 152983.
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