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LETTERS

New helical hydrogen-bonded assemblies forming channel-inclusion complexes

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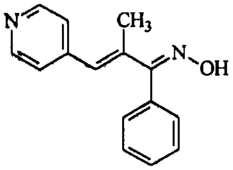
Abstract

Helical hydrogen-bonded assemblies of 2-methyl-1-phenyl-3-pyridin-4′-yl-2-propen-1-on-oxime create three-dimensional networks containing large channels with hydrophobic environments, which are able to trap suitable guest molecules. © 1999 Elsevier Science Ltd. All rights reserved.

The rational design and synthesis of molecular solids with specific and useful chemical, mechanical, electronic, or optical properties is an important goal of supramolecular chemistry.[1] The required solid-state properties are influenced by solid-state structure, therefore the design of new materials must be concerned with controlling both molecular and supramolecular structure. Chemists take particular advantage of the characteristic strength and directionality of hydrogen bonds to control the creation of new assemblies.[2] Within this context both formation of helical structures[3] and the creation of channel-inclusion complexes[4] are of particular interest. Additionally, the canal topology and helicity play important roles in the function of certain biological systems.[4a]

Here the formation of an interesting new channel-type host lattice through helical hydrogen-bonding assemblies of a simple molecule, namely 2-methyl-1-phenyl-3-pyridin-4′-yl-2-propen-1-on-oxime **1** is described.



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Compound **1** was prepared in 80% overall yield by condensation reaction of pyridine-4-carbaldehyde with 1-phenyl-1-propanone ($CHCl_3$, HCl, 25°C, 48 h), followed by oximation ($NH_2OH{\cdot}HCl$, NaOH, ethanol, 4 h) of the resulting 2-methyl-1-phenyl-3-pyridin-4′-yl-2-propen-1-one.

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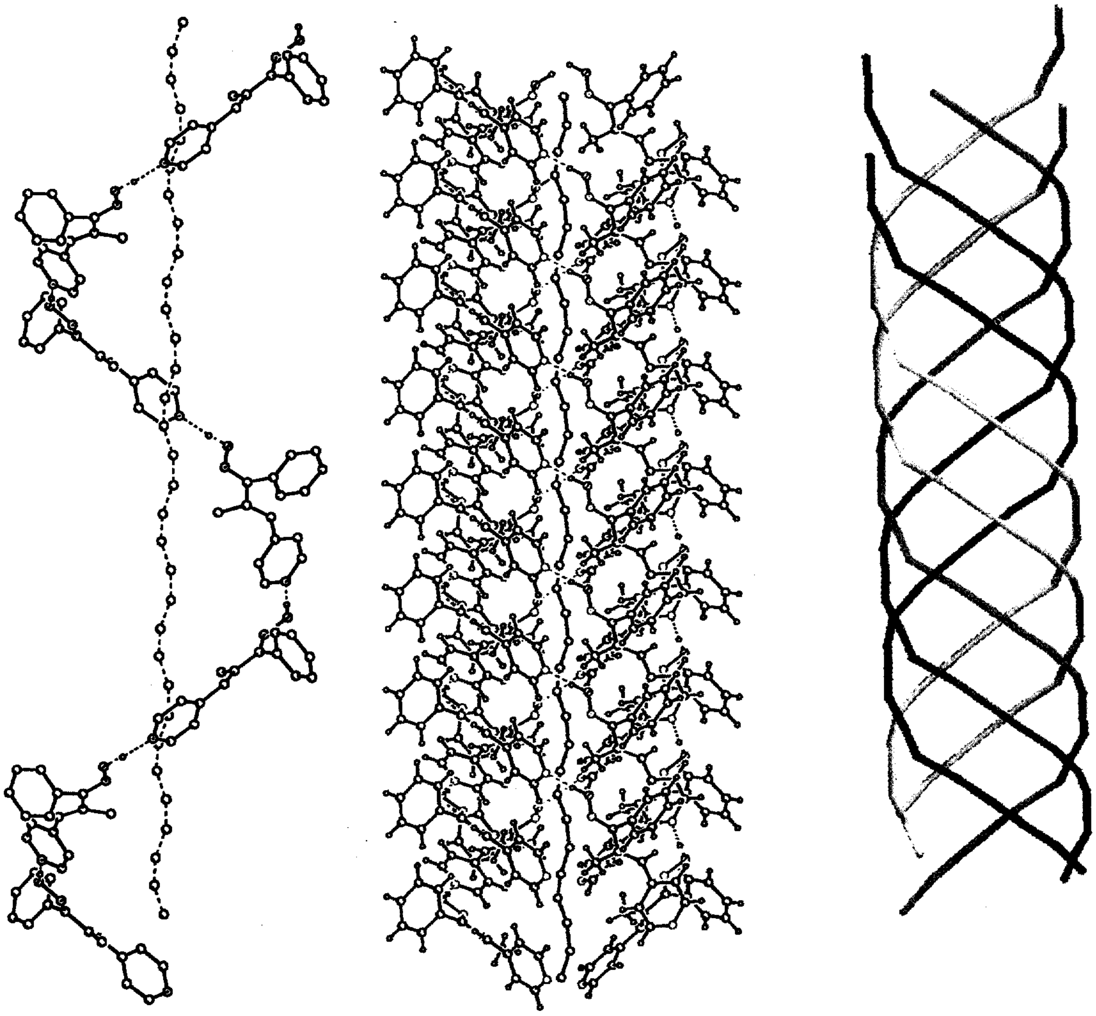

Figure 1. The helical motif of **1** in the crystal and the X-ray and schematic structure of one channel

Crystals of **1** were obtained by slow evaporation of the solvent from ethanol or ethanol/diethyl ether solutions. 2-Methyl-1-phenyl-3-pyridin-4′-yl-2-propen-1-on-oxime crystallized in space group $I4_1a$. X-Ray crystallography[5] estabilished that the molecules of **1** interact via strong OH· · ·N hydrogen bonds, forming a helically grown structure as a basic motif (Fig. 1).

Each molecule of **1** forms two hydrogen bonds with two neighbouring residues. The intermolecular OH· · ·N contacts between the hydroxyl hydrogen and the pyridine nitrogen have a distance of 1.74 Å (O· · ·N distance, 2.69 Å; OH· · ·N angle, 175.7°). Five helical chains of **1** create the walls of well-defined channels with an inner diameter of about 14 Å in which solvent molecules are incorporated (Fig. 1). Noteworthy, the open channels of crystalline **1** possess hydrophobic environments through the inside orientation of the methyl groups, which define voids that are ca. 7 Å in diameter (Fig. 2). The phenyl rings located on the outside, are nearly vertically oriented to the walls of the channels. The phenyl groups prevent the host from packing closely, hence creating substantial voids between parallel channels in the crystal. The walls of the adjacent channels are constructed alternatingly by right- and

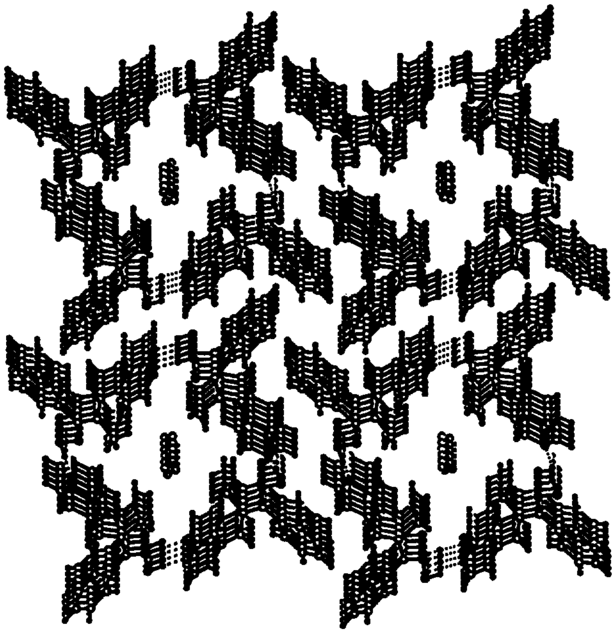

Figure 2. Packing of the channels of **1** in the crystal

left-handed helixes (as four-fold screw axis). The solvent molecules are accommodated as linear chains in the individual channels, with all channels (and guests) aligned parallel.

The guest species are disordered, therefore it was not possible to determine unambiguously the identity of the guest by X-ray analysis. The residual electron density was assigned as a carbon atom with an occupancy factor of 0.5, which produced chains with interatomic distances at 1.46 Å. The inclusion of ethanol and diethyl ether in the channels of **1** could be unequivocally determined by ^{1}H NMR analysis of dissolved crystals. Included guest molecules were also identified by mass spectrometry. The host:guest ratios in the resulting crystals were determined by NMR integration. The channels in crystals of **1** obtained from ethanol/diethyl ether solutions are occupied by both types of solvent molecules, the mole ratio of oxime:guest is about 5:1. Similar to the present case, the guest molecules in the well-known urea inclusion complexes are also generally disordered, as shown by Forst, Jagodzinski, Boysen and Frey.[6] The synthesis of the above self-assembled architecture is directed by the intrinsic information stored in the structure of the precursor. Fig. 3 shows the monomeric unit of **1** in the crystal.

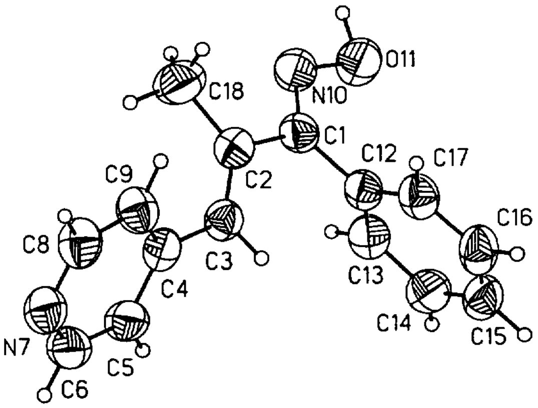

Figure 3. ORTEP drawing of **1** showing the monomeric unit (torsion angle N10–C1–C2–C3, 163°)

The fact that helical assemblies of **1** form three-dimensional networks containing large channels with hydrophobic environments, which are able to trap suitable guest molecules, may offer new interesting applications. Presently the formation of inclusion complexes with a variety of guests, including chiral compounds, are investigated. The most obvious property of a synthetic helical structure, chirality, has been barely studied. Little is also known about the relationship between the structure of the parent molecules and the formation of chiral aggregates.

Acknowledgements

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5. Crystal data for **1**: $C_{15}H_{14}N_2O \cdot C_{0.5}$, M=244.29, crystal dimensions 0.28×0.13×0.03 Å^3, crystal system tetragonal, space group *I*4$_1$*a*, a=31.5612(3), b=31.5612(3), c=5.53120(10) Å, $\alpha=\beta=\gamma=90°$, V=5509.68(12) Å^3, *Z*=16, ρ_{calcd}=1.178 gcm^{-3}, wavelength 0.71073 Å, 7838 reflections collected (full sphere, θ-range 3.74–22.50°), 1746 independent reflections (R_{int}=0.0394, empirical absorption correction), 1462 observed [F_o>=4s(F_o)], 172 parameters, R1=0.0480, wR2=0.1316, residual electron density 0.193 eÅ^{-3}, μ=0.075 mm^{-1}, max/min transmission 1.00/0.71. The structure was solved using Direct Methods and refined on F^2 using SHELXTL (Vers.5.03). The data was obtained with a Siemens SMART-CCD three circle diffractometer (MoK_α-radiation, graphite-monochromator) at 293 K. All non-H atoms were anisotropically refined and aromatic and methyl H atoms were treated as riding groups with the 1.2 fold U-value (1.5 for methyl hydrogens) of the corresponding C-atoms, hydroxy hydrogen atoms were located in a difference Fourier map and then treated as riding atoms. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-104955.
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