

**THE SELF-ASSEMBLED STRUCTURES OF
2,6-DI(ACYLAMINO)PYRIDINES**

E. Marfo-Owusu T. Kato

The University of Tokyo Department of Chemistry and Biotechnology
Graduate School of Engineering, Dept. of Chem. & Biotech The Univ. of
Tokyo, Hongo Campus, Tokyo BUNKYO-KU, TOKYO TOKYO 113-8656
JAPAN

Recently, Kato and co-workers [1] prepared supramolecular liquid crystals. For example, doubly hydrogen-bonded supramolecular liquid-crystalline complexes (low molecular weight and polymeric complexes) derived from 2,6-bis(amino)pyridines and carboxylic acids were shown to exhibit smectic phases. These molecular materials show a variety of mesomorphic properties and assembled structures with potential usefulness for generation of novel materials. However, there is not yet any crystallographic evidence supporting the findings on these assembled structures. As an initial approach, we were prompted to investigate the molecular structures of low molecular weight complexes between 2,6-di(acylamino)pyridines (nAPy, n = number of carbon atoms in the alkyl chain) and alkoxybenzoic acids (guests). It is of relevance, therefore, in the context of crystal engineering and supramolecular architecture and as part of our preliminary work to investigate the hydrogen bonding network and crystal packing of nAPy (hosts) molecules. Presently, we have determined series of crystal structures of nAPy (n = 1,2,3,4 and 5) using X-ray diffraction techniques. The crystals were grown from hexane/ethylacetate mixed solvents by slow evaporation method. The crystal structures analyses revealed that the driving force that controls the molecular aggregation of 2,6-di(acylamino)pyridines is mainly by N-H...O hydrogen bonding. Both NH groups in nAPy are intermolecularly hydrogen-bonded to the amide carbonyl groups in an intriguing ribbon-like pattern. The crystal packing and molecular aggregation modes are dependent on the length of alkyl chain. Research studies on complexes of nAPy with alkoxybenzoic acids is now in progress.

[1] T. Kato, Y. Kubota, T. Uryu, and S. Ujiie, *Angew. Chem.Int.Ed.Engl.*, 36,1617(1997)

Keywords: SELF-ASSEMBLY, 2,6-DI(ACYLAMINO)PYRIDINES, COMPLEXES

**STRUCTURE AND DYNAMICS OF WATER CHANNELS INSIDE
SELF-ASSEMBLING DIPEPTIDE NANOTUBES**

P. Pattison^{1,2} Y. Pan¹ G. Chapuis¹ H. Birkedal³

Swiss-Norwegian Beamline SNBL / ESRF GRENOBLE F-38043 FRANCE

¹Institute of Crystallography, University of Lausanne, BSP Dorigny, 1015

Lausanne, Switzerland ²Swiss-Norwegian Beam Line, SNBL/ESRF, PO Box 220, F-38043 Grenoble, France ³Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106, USA

The supramolecular self-assembly of certain dipeptides can lead to the formation of nanotubes in crystals. This behavior has attracted interest both because of their unusual topology and also as model systems for ion channels and membrane pores [G. H. Goerbitz, *Chem. Eur. J.* (2001) 7, 5153-5159]. The structures consist of helical columns of peptide molecules with hydrophobic external surfaces that make them water-repellent, and yet the columns have a hydrophilic interior that can fill with water. The confinement of material on the nanometer scale can induce behavior not seen in bulk systems, as illustrated recently for the case of water-filled carbon nanotubes [G. Hummer, J. C. Rasaiah and J. P. Noworyta, *Nature* (2001) 414, 188-190]. We have previously used synchrotron radiation to investigate the dipeptide tryptophylglycine monohydrate [H. Birkedal, D. Schwarzenbach and P. Pattison, *Angew. Chem. Int. Ed* (2002) in press], in which we have observed unusual one-dimensional negative thermal expansion along the nanotube direction below room temperature. We tentatively ascribed this behavior to a water condensation mechanism, in which the increased localization of water at low temperature leads to an enhanced correlation along the tube, which in turn requires more space and hence results in negative thermal expansion. In order to elucidate further this mechanism, we have undertaken a series of synchrotron powder and single crystal measurements of tryptophylglycine monohydrate above room temperature. We have also carried out an extensive molecular dynamics study both on the monohydrate and the dehydrated form, at temperatures between 100 K and 450 K. The experimental data reveal three different temperature domains characterized by changes in the temperature dependence of the lattice constants. These domains can be labeled as condensation, melting and boiling of the confined water in the peptide columns. The good agreement between experiment and the molecular dynamics simulation greatly facilitates the interpretation of the various mechanisms at play in this system.

Keywords: PEPTIDE NANOTUBE MOLECULAR DYNAMICS

**SYNTHESIS AND STRUCTURES OF TWO
HOMOOXACALIX[4]ARENES**

Y. Park K. No

Sook Myung Womens University Dept. of Chemistry Chungpa-Dong,
Yongsan-Ku SEOUL 140-742 SOUTH KOREA

Calixarenes are synthetic macrocycle available in a variety of ring sizes and are of interest both as complexation hosts for ions and molecules and as frameworks for elaborating more complex structures and have received a great deal of attention in recent years. In contrast to the calix[4]arenes, homooxacalix[4]arenes, containing extra oxygen in the macrocyclic ring, have received little attention mainly because they can only be synthesized in relatively small yield. Recently we reported the facile synthesis of tetrahomodioxo p-phenylcalix[4]arene by refluxing the bishydroxymethylated p-phenyl phenol in toluene. There have only been limited studies for the solution conformation and crystal structure of homooxacalix[4]arene derivatives. In this study, reaction of tetrahomodioxo p-phenylcalix[4]arene with allyl bromide and hexyl iodide in the presence of NaH produced tetraallyloxy and tetra-hexyloxy derivatives, respectively. Conformations of these derivatives were determined by NMR spectra and X-ray crystallography as C-1,2-alternate conformations having two pairs of opposite phenyl rings which are approximately parallel to each other. The crystal data are for tetrahexylether(C₇₈H₉₂O₆); triclinic, P-1, a=10.787(1), b=11.759(4), c=13.409(3) Å α=81.00(2), β=84.78(1), γ=80.99(2)° and Z=1, for tetraallylether(C₆₆H₆₈O₆); triclinic, P-1, a=13.354(7), b=14.163(5), c=15.026(3) Å, α=76.21(3), β=70.32(2), γ=76.76(5)° and Z=2. The tetrahomodioxo p-phenylcalix[4]arene tetrahexyl ether has own its center of symmetry, and the crystal structure is remarkable in forming layer structure in which the central region of the layers, composed largely of tetrahomodioxo p-phenylcalix[4]arenes is closely packed and the packing of the flexible hexyl ether chains form the interface region between layers.

Keywords: CALIXARENE HOMOOXACALIX[4]ARENE
TETRAHOMODIOXA P-PHENYLCALIX[4]ARENE
TETRAALKYLETHER

**3-D HYDROGEN BONDING NETWORK OF 1,2-BIS((PYRIDINE-3-
YLMETHYL)AMMONIUM)ETHANE DIPERCHLORIDE**

R. Zou L. Weng X. Leng X. Zeng

Fudan University Department of Chemistry 220 Handan Road SHANGHAI
200433 CHINA

The ligands based on bipyridyl with different space group are particularly attractive building blocks for the preparation of supramolecular structures. In the sense, we synthesize bipyridyl ligand 1,6-bis(3-pyridyl)-2,5-diazahehexane and characterized the structure of its perchloride salt. 1,6-bis(3-pyridyl)-2,5-diazahehexane ligand was prepared by the modified procedures reported for the synthesis of 1,3-bis(2-pyridylmethyleneamino)propane [1]. The crystal structure of its ammonium diperchloride salt was solved by single crystal X-ray diffraction. The crystal data for C₄₀₁ Mr = 443.24, monoclinic space group P2₁/c, a = 9.7570(17), b = 8.7604(15), c = 11.176(2) Å, β = 107.364(3)°, V = 911.7(3) Å³ Z = 3, R 0.0347, wR = 0.0942. The cation has a crystallographically imposed Ci-symmetry on the center of C(7)-C(7A). The conformation of structure of the cation consists of two pyridyl rings spaced by a diaminohehexane chain. Two pyridyl rings do not share a common plane, but offset about 4.10 Å Six atoms of diaminohehexane chain are planar and form a dihedral angle of 74.59(12)° with the pyridyl ring. Each primary amino (-NH group acts as a double hydrogen-bond donor to form hydrogen bonds with one N atom from pyridyl ring and one O atom from perchloride. There also exist weak C-H...O interactions. These interactions result in an infinite 3D network (Figure 1). In the interactions, the distances of N_i-N and N O are 2.797 (2) and 2.928 (2) Å, respectively. The N-H_i-N and N-H-O angles of 173 (2)° and 147 (2)°, respectively.

Reference:

[1] A. Jantti, K. Rissanen and J. Valkonen, *Acta Chem. Scand.*, 1998, 52, 1010.

Keywords: HYDROGEN BOND BIPYRIDYL LIGAND NETWORK