THE SELF-ASSEMBLED STRUCTURES OF 2,6-DIACYLAMINO)PYRIDINES

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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(amiino)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
solution and boiling of the confined water in the peptide columns. The good agreement
between the crystal structures of their ammonium diperchloride salt was solved by single crystal X-ray
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 C_{66}H_{68}O_{6}; 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 tetrahomodioxap-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 tetrahomodioxa p-
phenylcalix[4]arene tetrahexyl ether other has own center of symmetry, and the
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Keywords: SELF-ASSEMBLY, 2,6-DIACYLAMINO)PYRIDINES,
COMPLEXES

SYNTHESIS AND STRUCTURES OF TWO HOMOOXACALIX[4]ARENES

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Calixarenes are synthetic macrocycle available in a variety of ring sizes and are
of interest both as complexion 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
tetrahomodioxap-p-phenylcalix[4]arene by refluxing the bishydroxymethylated
p-phenol in toluene. There have been only limited studies for the
solution conformation and crystal structure of homooxacalix[4]arene
derivatives. In this study, reaction of tetrahomodioxap-p-phenylcalix[4]arene
with allyl bromide and hexyl iodide in the presence of NaH produced tetra-
allyloxy 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(C_{78}H_{92}O_{6}); 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(C_{46}H_{46}O_{6}); 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 tetrahomodioxap-
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 tetrahomodioxa 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
TETRAHOMODIOXAP-P-PHENYLCALIX[4]ARENE
TETRAALKYLEETHER

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

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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-diazahexane and
characterized the structure of its perchlorate salt. 1,6-bis(3-pyridyl)-2,5-
diazahexane ligand was prepared by the modified procedures reported for the
synthesis of 2,6-di(acylamino)pyridines. The bipyridyl ligand can exist in a
number of conformations, such as cisoid and transoid forms.

We have also carried out an extensive molecular dynamics
study 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


STRUCTURE AND DYNAMICS OF WATER CHANNELS INSIDE
SELF-ASSEMBLING Dipeptide NANOTUBES

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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 as model systems for ion channels
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 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


Reference:

Keywords: HYDROGEN BOND BIPYRIDYL LIGNET NETWORK


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