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Creation of hydrogen bonded 1D networks by co-crystallization of *N*,*N*′-bis(2-pyridyl)aryldiamines with dicarboxylic acids †

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Received 26th November 2002, Accepted 26th February 2003
First published as an Advance Article on the web 18th March 2003

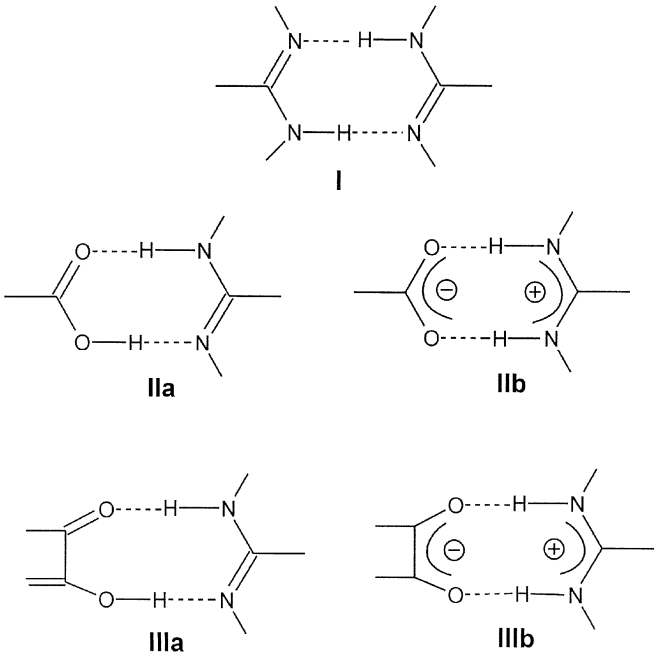
The preparation and crystal structures of fourteen complexes of *N*,*N*′-bis(2-pyridyl)aryldiamines with dicarboxylic acids and two complexes with squaric acid are reported. The recognition between the carboxylic acids and the 2-aminopyridine units occurs through the formation of the cyclic R^2_2 (8) hydrogen bond motif, whereas squaric acid creates the analogous R^2_2 (9) motif. In the 1 : 1 complexes the cyclic motifs generate infinite hydrogen-bonded 1D networks with the alternating component molecules. These networks are further organised into densely packed layers assembled through weaker C–H ··· O interactions. Analysis of the intermolecular interactions in these complexes led us to the synthesis of *N*,*N*′-bis(2-pyridyl)-2,2′-oxybis(aminobenzene) (**5**) which acts as a tritopic receptor of the carboxylic group and forms exclusively 2 : 1 complexes with dicarboxylic acids.

Introduction

The design and preparation of ordered solid-state structures by means of specific intermolecular interactions is an area of crystal engineering.[1] This rapidly expanding branch of supramolecular chemistry offers a possibility for rational development of new materials with potentially useful physical and chemical properties.[2] A considerable progress has been made in recent years in controlling the assembly of individual molecules into extended arrays of various dimensionalities in a pre-determined fashion. Particularly hydrogen bonds as directional and strong intermolecular interactions offer a powerful tool to control solid-state structures.[1,3] Thus far, many hydrogen bonding patterns that can be used for a manipulation of the spatial arrangement of molecules in the solid-state have been identified and reported.[4]

Recently, we have shown that hydrogen bonded *N*,*N*′-bis-(2-pyridyl)aryldiamines are able to form 1D networks by the cyclic R^2_2(8) motif **I**.[5,6] However, due to a low energy barrier to C–N rotation, the 2-arylaminopyridine system can adopt either (*Z*) or (*E*) conformations giving rise to the formation of conformational polymorphs. Indeed, in several cases, besides the aforementioned motif **I**, we were able to isolate the second crystalline form, polymorph or solvate, where the 2-arylaminopyridine monomeric units assumed the (*Z*) conformation and the molecules were assembled *via* a catemeric C(4) motif into 1D, 2D or even 3D networks.[5] Since the conformational polymorphism significantly reduces the level of predictability of the supramolecular structures it would be desirable to restrict the conformational space available to molecules in crystals by choosing specific, strong non-covalent interactions which would significantly limit the number of possible conformers. The solid-state molecule-based architectures can be constructed by self-assembly not only of one but also two or more components and the co-crystallization of selected molecules bearing complementary functional groups may generate well defined extended supramolecular frameworks.[7] It is well known that the 2-aminopyridine function is capable of forming cyclic R^2_2 (8) hydrogen bond motifs **IIa,b** with the carboxyl group[8] and furthermore, in the solid state it prefers to bind to the carboxyl group rather than to itself.[4a,9] Therefore the robust motif **IIa** formed by *N*-acyl-2-aminopyridines or 2-aminopyrimidines and carboxylic acids have been frequently utilized for crystal engineering.[9] We expected that this kind of cyclic complexation should force the 2-aminopyridine units in the title compounds to adopt the (*E*) conformation and hence direct the aggregation process towards the desired 1D networks shown in Scheme 1. In the present study, we report the preparation and crystal structure determination of the hydrogen bonded heteromeric systems formed by *N*,*N*′-bis(2-pyridyl)aryldiamines **1**–**5** with several aliphatic and aromatic dicarboxylic acids, which include oxalic (**oxa**), malonic (**mal**), succinic (**suc**), sebacic (**seb**), fumaric (**fum**), isophthalic (**iso**), terephthalic (**tere**), diphenic (**diph**) and 4,4′-oxybisbenzoic (**obe**) acids.

In addition we tested the utility of squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione) (**sq**) for complexation of *N*,*N*′-bis(2-pyridyl)aryldiamines. Interaction of this strong



† Supramolecular structures formed by 2-aminopyridine derivatives. Part II.[5]

DOI: 10.1039/b211675h