

Interplay of hydrogen bonding and aromatic ring interactions in supramolecular complexes of phenazine with *N,N'*-bis(2-pyridyl)aryldiamines



Paper

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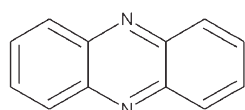
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Five crystalline molecular complexes of phenazine (**phz**) with *N,N*-bis(2-pyridyl)aryldiamines and *N,N*-diphenyl-1,4-diaminobenzene of different stoichiometries were prepared and their structures were studied by X-ray crystallography. The observed crystal packing results from concerted action of the N–H⋯N hydrogen bonds, π – π stacking of the **phz** units and edge-to-face interactions between the aromatic rings of the component molecules. The planar *Z* conformation adopted by the *N*-aryl-2-aminopyridine moieties facilitates their interaction with the **phz** system.

Introduction

Strong hydrogen bonds O–H⋯Y and N–H⋯Y (Y = O, N) play a major role in molecular recognition and self-organization in supramolecular chemistry and biology.¹ On the other hand, much weaker interactions like C–H⋯Y (Y = O, N) hydrogen bonds and interactions between aromatic units have been recently recognized as equally important factors determining packing of molecules in crystals and have found a broad application in crystal engineering for the design of new functional materials.^{2,3} Phenazine (**phz**) has potential for all these types of interaction; it contains two equivalent strong proton acceptors (sp² nitrogen atoms) and several potential weak C–H donors, whereas the aromatic system can act as a good π -donor. Therefore **phz** attracts increasing interest as a useful substrate for the creation of ordered and predictable solid state architectures.^{4–8}

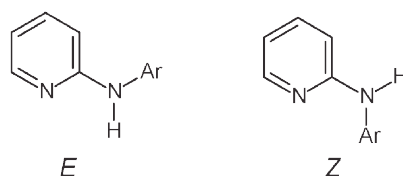


phz

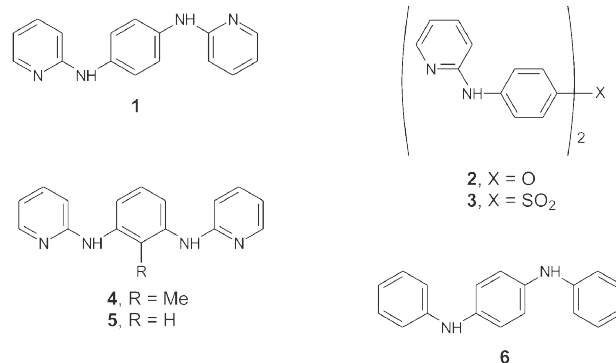
It has been found that **phz** readily forms co-ordination polymers with transition metals⁴ and hydrogen-bonded assemblies with dicarboxylic acids,⁵ diphenols⁶ and dihydroxybenzoquinones⁷ with structures stabilized by the O–H⋯N hydrogen bonds and/or aromatic ring interactions. In contrast, the construction of crystal networks *via* N–H⋯N hydrogen bonds with **phz** as a supramolecular substrate is much less advanced.⁸

Recently, we have shown that *N*-aryl-2-aminopyridine systems are good N–H proton donors as well as proton acceptors able to self-assemble *via* R₂²(8) or C(4) hydrogen-bond motifs⁹ into homomeric aggregates¹⁰ and to form heterodimeric R₂²(8) or R₂²(9) motifs with carboxylic acids¹¹ and α -hydroxy carbonyl compounds, respectively.^{11,12} Moreover, we have noticed that the *N*-aryl-2-aminopyridine system should be able to switch off its proton-acceptor function and

act solely as a N–H proton donor in intermolecular hydrogen bonds by adopting a planar *Z* conformation stabilised by the intramolecular C–H⋯N interaction.^{10b} We also expected that co-planarity of its constituent aryl rings should make this system more susceptible to π – π stacking interactions with other aromatic units that makes *N,N'*-bis(2-pyridyl)aryldiamines good candidates for the creation of supramolecular aggregates with **phz**.



Here, we report examples of supramolecular arrays created by complexation of **phz** with the compounds **1–4**. Their structures were determined by X-ray diffraction studies. For comparison we also prepared the **phz** complex with *N,N'*-diphenyl-1,4-diaminobenzene (**6**), being a structural analogue of **1**, and examined its crystal structure.



Results and discussion

Co-crystallization of the 1,4-diaminobenzene derivative **1** and **phz** by cooling of the ethanolic solution yielded large red