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Conformational changes in C_{methyl} -resorcinarene pyridine *N*-oxide inclusion complexes in the solid state†

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Aromatic *N*-oxides interact with C_{methyl} -resorcinarene resulting in marked changes in the conformation of the host resorcinarene. In the solid state, 2- and 3-methylpyridine *N*-oxides form pseudo-capsular 2:2 *endo* host-guest complexes with C_{methyl} -resorcinarene stabilized by C-H \cdots π interactions. The C_{methyl} -resorcinarene-2-methylpyridine *N*-oxide complex has a C_{4v} crown conformation, while the C_{methyl} -resorcinarene-3-methylpyridine *N*-oxide complex has a slightly open C_{2v} boat conformation. On the contrary, other *para*-substituted and benzo-fused pyridine *N*-oxides form only *exo* complexes with C_{methyl} -resorcinarene. In the *exo* complexes, the asymmetry of the guest, conformational flexibility and preferred inter-host hydrogen bonding of C_{methyl} -resorcinarenes exclude *endo* complexation. All the *exo* complexes form robust 1-D hydrogen bonded chains between the host hydroxyl groups assisted by the guest N-O groups, resulting in a C_{2v} boat conformation.

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Introduction

With flexible host molecules, several factors such as substituents, size and electronic properties of the guest, solvents, temperature or even reaction conditions can induce conformational changes in the host.¹ The understanding of the interplay of host-guest interactions, both in the solid state and in solution, is a very important research area in supramolecular chemistry due to its major impact on the potential applications of host-guest systems as functional materials.² Many host and receptor molecules adopt specific geometries and conformations. Amongst these compounds are resorcinarenes and pyrogallarenes which natively occur in the crown C_{4v} conformation, and this favourable conformation allows them to act as hosts for a variety of guest molecules.² The versatility of these host systems originates from the synthetically easy modifications either at the upper or lower rim of these macrocycles.² However, it is known that core (unsubstituted) resorcinarene conformations are quite easily modulated by the reaction conditions when the host is synthesized. The most common resorcinarene and pyrogallarene conformations are crown, boat, chair, diamond and saddle.³

Other unusual conformations such as the rarely observed *rcct*-diamond C_{methyl} -resorcinarene,³ the *rcct*-boat C_{methyl} -2-nitroresorcinarene⁴ and the *rcct*-crown C_{4t} -pyrogallarene ($4t =$ *tert*-butyl)⁵ have been reported. In the C_{4v} conformation, intramolecular circular hydrogen bonds (HB) between adjacent phenolic hydroxyl groups preserve the crown structure.⁵ In this conformation, the π -rich cavity is suitable for inclusion of spherical and planar guests such as ammonium and phosphonium cations, the main complexation force being the cation \cdots π interactions.⁶ With resorcinarenes, these cationic guests play a key role in numerous solid-state architectures such as open inclusion complexes,⁷ dimers,⁸ hexamers,⁹ and tubular assemblies.¹⁰ Though inclusion complexes of resorcinarenes with cationic compounds are prevalent, there are several reports of complexes with neutral N-heteroaromatic five- and six-membered planar guests as well.¹¹ N-Aromatic compounds such as 2,2'- and 4,4'-bipyridines, due to their size and strong hydrogen bond acceptor properties, have been particularly effective in inducing conformational changes in resorcinarene complexes.¹² A Cambridge Structural Database (CSD)¹³ search using C_{methyl} -resorcinarene **1** as the host revealed 34 crystal structures with 4,4'-bipyridine as the guest molecule.^{14,12a-c}

Aromatic *N*-oxides are well-known synthetic intermediates for functionalization of the pyridine ring in organic synthesis,¹⁵ and as ligands in supramolecular chemistry.¹⁶ The oxygen in the *N*-oxide group can exhibit hyper-dentate coordination behaviour with metal cations, resulting in interesting supramolecular architectures.¹⁶ Most recently, pyridine *N*-oxides (PyNOs) have been shown to be excellent halogen bond acceptors and thus form very strong halogen bonds.¹⁷ The

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N-oxide, *viz.* $^+N-O^-$, group makes the aromatic ring electron deficient but the electron deficiency can be modulated by the substituents on the aromatic ring, and due to this, aromatic *N*-oxides can act as guest molecules with calixarenes and cavitands.¹⁸ Recently, we have reported dimeric pseudo-capsular assemblies with aromatic *N*-oxides using C_{ethyl} -2-methylresorcinarene as the host.¹⁹ The C-H $\cdots\pi$ and $\pi\cdots\pi$ interactions²⁰ have proven to be the governing factors in the recognition of electron-deficient *N*-oxides by π -rich host systems.

In addition, halogen bond breaking using C_{ethyl} -2-methylresorcinarene in halo-substituted pyridine *N*-oxide systems was an unexpected result of the conformational change in the host.²¹ While our previous work has focused on C_{ethyl} -2-methylresorcinarene,^{19,21} there exists one study with 4,4'-bipyridine *N,N'*-dioxide and C_{methyl} -resorcinarene as the host.²² In this work, we report solid-state complexes with C_{methyl} -resorcinarene **1** as the host and seven PyNOs (Fig. 1) as the guests, and the conformational behaviour of the host upon complexation.

Results and discussion

X-ray crystallography

Single crystals of the complexes were obtained from slow evaporation of the methanolic solution of a 1:1 mixture of the host and guest molecules. Attempts to crystallize PyNO,

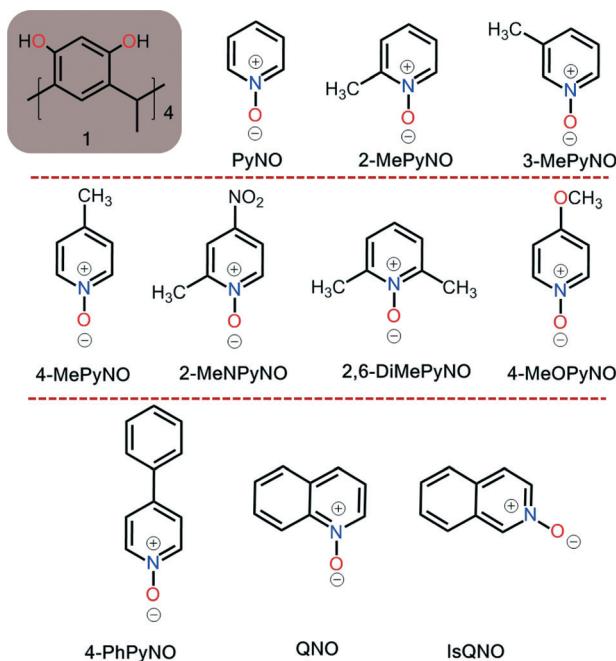


Fig. 1 The chemical structures of C_{methyl} -resorcinarene (**1**), pyridine *N*-oxide (PyNO), 2-methylpyridine *N*-oxide (2-MePyNO), 3-methylpyridine *N*-oxide (3-MePyNO), 4-methylpyridine *N*-oxide (4-MePyNO), 2-methyl-4-nitropyridine *N*-oxide (2-MeNPyNO), 2,6-dimethylpyridine *N*-oxide (2,6-DiMePyNO), 4-methoxypyridine *N*-oxide (4-MeOPyNO), 4-phenylpyridine *N*-oxide (4-PhPyNO), quinoline *N*-oxide (QNO), and isoquinoline *N*-oxide (IsQNO).

2,6-DiMePyNO and **QNO** with **1** were unsuccessful. In the *endo* complexes, the *N*-oxide oxygen atoms point away from the cavity (Fig. 2). Complexes of 2-MePyNO and 3-MePyNO with host **1** resulted in mixed *endo/exo* complexes, 2-MePyNO-**1** and 3-MePyNO-**1** (Fig. 2), which are remarkably similar to our previous results with C_{ethyl} -2-methylresorcinarene.²¹ Complex 2-MePyNO-**1** [formally $1:(2\text{-MePyNO})_{endo}:3(2\text{-MePyNO})_{exo}$] can be described as a discrete dimeric pseudo-capsular 2:2 complex which is then hydrogen bonded to six *exo*-cavity 2-MePyNO molecules, as shown in Fig. 2b. In complex 2-MePyNO-**1**, host **1** retains the crown conformation (centroid-to-centroid distances being nearly equal, *ca.* 6.8/7.0 Å, Fig. 3), encapsulating one 2-MePyNO molecule. The guest, 2-MePyNO, resides 3.2 Å from the centroid of the lower rim carbon atoms (calculated from the PyNO benzene ring carbon deepest in the cavity). The hydrogen atoms *para* to the N-O and $-CH_3$ groups of 2-MePyNO manifest C-H $\cdots\pi$ interactions with the aromatic rings of host **1** with distances ranging between 2.7 Å and 3.1 Å (Fig. 3a). Complex 3-MePyNO-**1** [formally $1:(3\text{-MePyNO})_{endo}:3(3\text{-MePyNO})_{exo}$] forms a similar dimeric pseudo-capsular 2:2 complex to 2-MePyNO (Fig. 2c). These dimers are hydrogen-bonded to each other by bridging *exo* 3-MePyNO molecules as shown in Fig. 2d. In complex 3-MePyNO-**1**, the cavity of host **1** is elongated so that the centroid-to-centroid distances

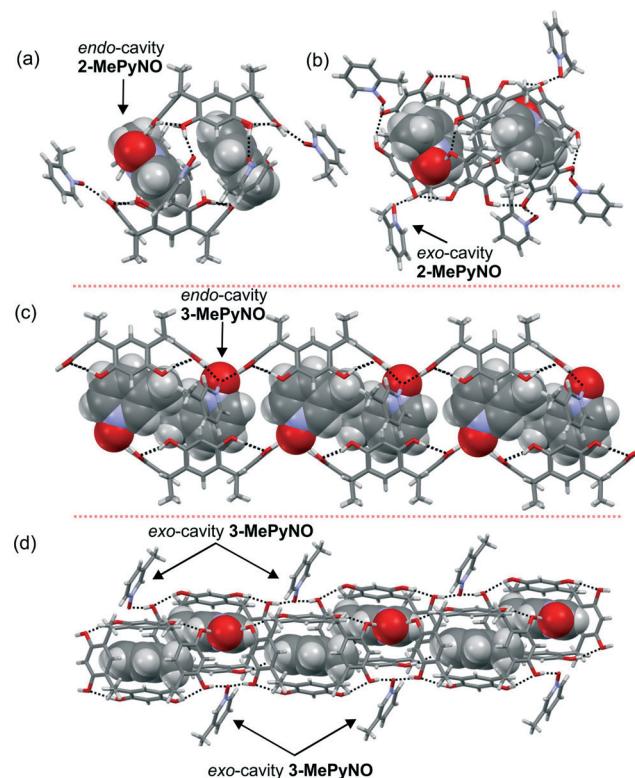


Fig. 2 (a) Side view of the discrete dimeric structure of 2-MePyNO-**1**, and (b) top view showing *exo*-cavity HB monodentate decorated 2-MePyNO with host **1**. (c) Section of the 1-D polymeric crystal packing in 3-MePyNO-**1** showing *endo* 3-MePyNO as a bidentate HB acceptor, and the respective (d) side view showing the *exo*-cavity HB bidentate 3-MePyNO molecules.



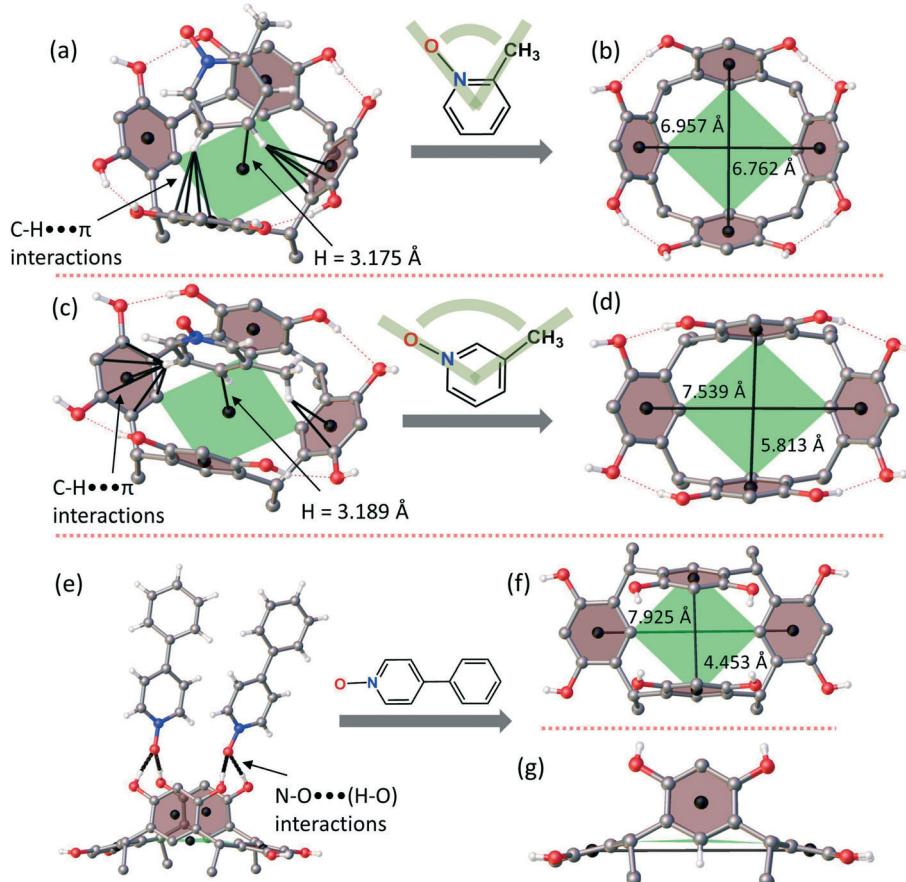


Fig. 3 (a) C-H \cdots π interactions in 2-MePyNO-1. (b) The cavity of host 1 in 2-MePyNO-1 highlighting the flexibility. (c) C-H \cdots π interactions in 3-MePyNO-1. (d) The cavity of host 1 in 3-MePyNO-1 highlighting the flexibility. (e) Complex 4-PhPyNO-1 displaying bidentate bridging 4-PhPyNO molecules through (N-O) \cdots (H-O) interactions. (f) Top view of the C_{2v} boat conformer in complex 4-PhPyNO-1. (g) Side view of the C_{2v} boat conformer in complex 4-PhPyNO-1. Black broken lines in Fig. 3e represent (N-O) \cdots (H-O) interactions.

are 5.8 and 7.5 Å to accommodate the slightly bigger 3-MePyNO molecule, as shown in Fig. 3d. The *endo* guest in 3-MePyNO-1 is situated 3.2 Å from the centroid of the lower rim carbon atoms, exactly the same distance as that in 2-MePyNO-1 and previously studied 3-MePyNO-C_{ethyl}-2-methylresorcinarene.²¹ In 3-MePyNO-1, the guest is situated near the center of the cavity between the benzene rings with no apparent aromatic $\pi\cdots\pi$ interaction, but manifesting a weak methyl C-H \cdots O hydrogen bond to the host O-H group (C-H \cdots O distance of 2.51 Å) and C-H \cdots π interactions from the hydrogen atoms *meta* to the N-O group (Fig. 3c). These C-H \cdots π distances range from 2.8 Å to 2.9 Å. The increased conformational flexibility of host 1 and the larger guest size in the *endo* complexation *via* the C-H \cdots π interactions between the host and the guest distort the parent C_{4v} crown conformation to a nearly ideal C_{2v} boat conformation (Fig. 3d). With our previous work on resorcinarene *endo* PyNO complexes,²¹ the PyNOs located deep in the cavity, *viz.* <2.9 Å from the centroid of the lower rim carbon atoms, usually show short C-H \cdots π (centroid) contacts. However in 3-MePyNO-1, where the 3-MePyNO guest is situated higher in the cavity (3.2 Å), the shortest C-H \cdots π (centroid) distance of

ca. 2.5 Å was observed. Comparing the host-guest chemistry of 2-MePyNO-1 and 3-MePyNO-1 with that of C_{ethyl}-2-methylresorcinarene,²¹ both host systems show a similar encapsulation profile to 2-MePyNO and 3-MePyNO. In general, the formation of *endo* complexes with host 1 is considerably more difficult than that with conformationally more rigid host molecules due to the stronger influence of the intermolecular hydrogen bonding between the hosts, which can lead to the conformational change and subsequent formation of host-to-host 1-D, 2-D or 3-D networks.

The conformational flexibility of resorcinarenes is due to their lower rim R chains. The methyl chain is smaller, thus allowing more different conformations for the resorcinarene skeleton. The ethyl chain is sterically more bulky and thus results in conformationally less flexible resorcinarenes.^{2,5} Sterically suitable PyNOs like 2-MePyNO and 3-MePyNO which do form *endo* complexes with conformationally flexible host systems are also proven to form *endo* complexes with more rigid systems; this we have recently shown with C_{ethyl}-2-methylresorcinarene.²¹ The question arises if the larger PyNOs²¹ would also behave similarly to the more flexible host 1. As such, larger PyNOs were utilized to probe their behaviour.

Complexes **4-MePyNO·1** [formally $1:2(4\text{-MePyNO})_{\text{exo}}:\text{CH}_3\text{OH}$], **4-MeOPyNO·1** [formally $1:2(4\text{-MeOPyNO})_{\text{exo}}$], **2-MeNPyNO·1** [formally $1:2(2\text{-MeNPyNO})_{\text{exo}}:4\text{CH}_3\text{OH}:\text{H}_2\text{O}$], **4-PhPyNO·1** [formally $1:2(4\text{-PhPyNO})_{\text{exo}}$], and **IsQNO·1** [formally $1:2(\text{IsQNO})_{\text{exo}}:4\text{CH}_3\text{OH}:4\text{H}_2\text{O}$] manifest only *exo* complexes with a prominent feature being the formation of 1-D tubular hydrogen-bonded chains with a C_{2v} boat conformation of the host (Fig. 3f and g). The asymmetric structure and larger size of these PyNOs prevent the formation of *endo* complexes and the ease of intermolecular hydrogen bond formation leads to the formation of host-to-host 1-D tubular chains in all complexes, as shown in Fig. 4. During crystallization, the host interactions with themselves, the guest and the solvent molecules (methanol and water) change the conformation from the C_{4v} crown to C_{2v} boat and provide possibilities for better intermolecular hydrogen bonding between the hydroxyl groups of the hosts. Two types of 1-D chains were observed, only PyNOs (type 1) and a combination of PyNOs and solvent molecules (type 2). The type 1 situation appears in complexes **4-MeOPyNO·1** and **4-PhPyNO·1**, while type 2 is observed in complexes **2-MeNPyNO·1** and **IsQNO·1** (Fig. 5 and ESI,[†] Fig. S6).

In complex **4-MePyNO·1**, the **4-MePyNO** molecules bridge the hosts *via* the *N*-oxide oxygen atom ($\text{O}-\text{H}_{\text{host}}\cdots(\text{O}-\text{N})\cdots(\text{O}-\text{H})_{\text{host}}$ with distances of 2.60 and 2.67 Å, generating a zigzag 1-D tubular chain (Fig. 5a). A closer look at the 3-D crystal packing reveals that the **4-MePyNO** molecules of the 1-D polymeric chain are additionally stabilised by $\pi\cdots\pi$ interactions at centroid-to-centroid distances of *ca.* 3.9 Å (ESI,[†] Fig. S1b). Both **4-MeOPyNO·1** and **4-PhPyNO·1** manifest a regular 1-D chain joined by the bidentate *N*-oxide oxygen atom with ($\text{O}-\text{H}_{\text{host}}\cdots(\text{O}-\text{N})\cdots(\text{O}-\text{H})_{\text{host}}$ distances of 2.64 Å (**4-MeOPyNO·1**), and *ca.* 2.66–2.72 Å (**4-PhPyNO·1**) as shown in Fig. 5b and c.

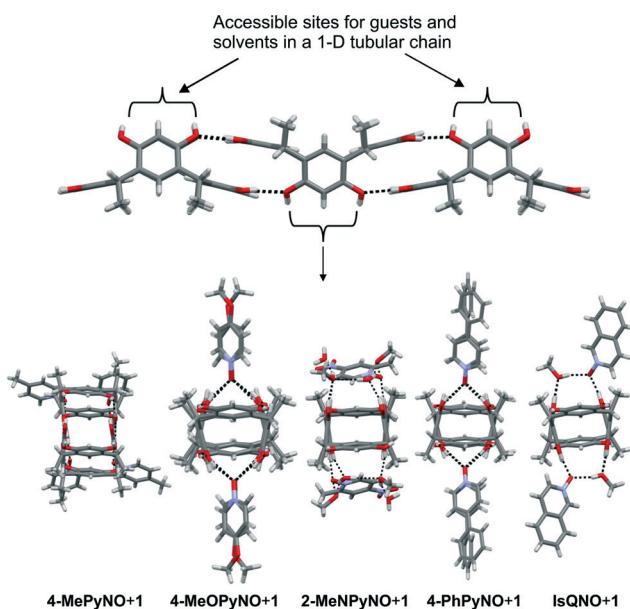


Fig. 4 Repeating units of the crystal packing viewed along the 1-D chains of complexes in **4-MePyNO·1**, **4-MeOPyNO·1**, **2-MeNPyNO·1**, **4-PhPyNO·1**, and **IsQNO·1** (left to right).

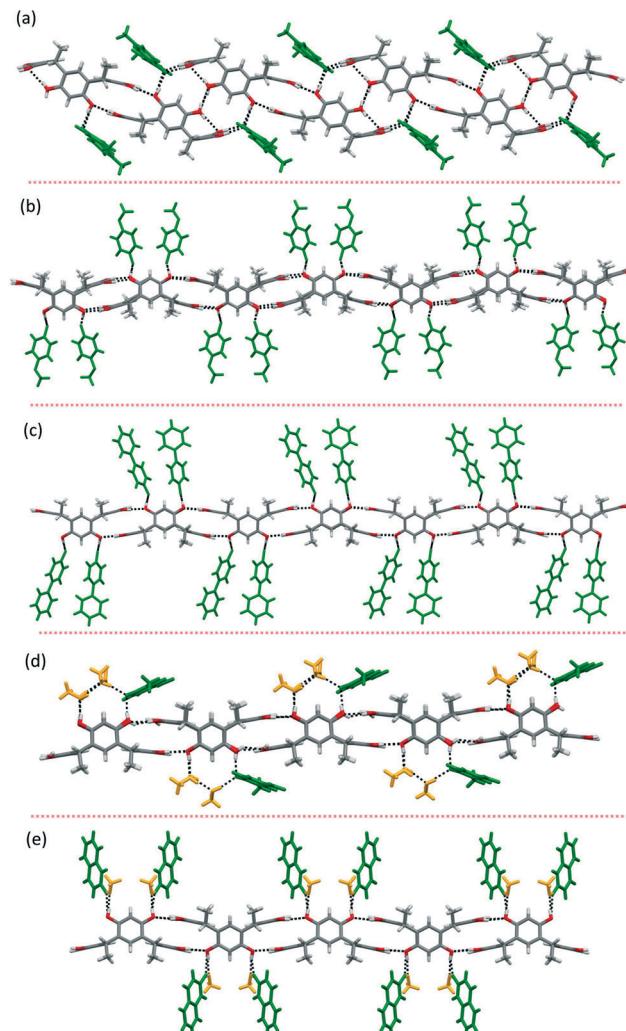


Fig. 5 Side view of the 1-D HB chains of host 1. (a) **4-MePyNO·1**, (b) **4-MeOPyNO·1**, (c) **4-PhPyNO·1**, (d) **2-MeNPyNO·1** and (e) **IsQNO·1**. The PyNO molecules are shown in green. The solvent molecules are shown in orange in figures (d) and (e).

Further analysis of the crystal packing shows that the 1-D chains in **4-MeOPyNO·1** and **4-PhPyNO·1** interdigitate to form 2-D supramolecular sheets (see the ESI,[†] Fig. S2). These interdigitated 1-D chains are stabilized by $\text{C}-\text{H}\cdots\pi$ and $\pi\cdots\pi$ interactions. During interdigititation, the aromatic rings of host 1, and the hydrogen atoms of the methoxy group in **4-MeOPyNO**, and the *para* hydrogen atoms of **4-PhPyNO** have short $\text{C}-\text{H}\cdots\pi$ contacts with distances of *ca.* 2.8 Å and 2.7 Å, respectively (see the ESI,[†] Fig. S2 and S3).

The host molecules in complex **2-MeNPyNO·1** also form a 1-D hydrogen bonded chain as shown in Fig. 5d. However, the hydrogen bonding *via* the hydroxyl groups of the host and the crystal packing differ due to interactions with solvent molecules and a second **2-MeNPyNO** molecule in the asymmetric unit. Two methanol molecules, a water molecule and a **2-MeNPyNO** molecule hydrogen bond to three host hydroxyl groups of the 1-D tubular chain in a continuous fashion ($\text{O}-\text{H}_{\text{host}}\cdots(\text{O}-\text{H})_{\text{CH}_3\text{OH}}\cdots(\text{O}-\text{H})_{\text{H}_2\text{O}}\cdots(\text{O}-\text{H})_{\text{CH}_3\text{OH}}\cdots(\text{O}-\text{N})_{\text{PyNO}}$



(see the ESI,† Fig. S4a). Also, the second **2-MePyNO** molecule hydrogen bonds to water and resides close to the host aromatic ring at centroid-to-centroid distances of *ca.* 3.7 Å. The crystal packing of **2-MePyNO-1** shows that the 1-D chains are connected by two methanol molecules to give a 2-D sheet motif (see the ESI,† Fig. S4c).

The mode of action of the host **1** hydroxyl groups in the 1-D polymeric chain of complex **IsQNO-1** (Fig. 5e) is different from other complexes. The host hydroxyl groups are connected by methanol and **IsQNO** molecules through hydrogen bonds, $(\text{O}-\text{H})_{\text{host}} \cdots (\text{O}-\text{H})_{\text{CH}_3\text{OH}} \cdots (\text{O}-\text{N})_{\text{IsQNO}} \cdots (\text{O}-\text{H})_{\text{host}}$ with distances of *ca.* 2.61, 2.64 and 2.63 Å, respectively. Once again, the 1-D chains interdigitate by extensive $\text{C}-\text{H} \cdots \pi$ and $\pi \cdots \pi$ interactions between **IsQNO** molecules to give a 2-D sheet (see the ESI,† Fig. S5) motif. During interdigititation, the aromatic rings of **IsQNO** molecules have centroid-to-centroid distances of *ca.* 3.9 Å, and $\text{C}-\text{H} \cdots \pi$ contacts with the host aromatic rings at distances of *ca.* 2.8 Å.

Solution studies

Solution studies between host **1** and PyNO, 2-MePyNO, 3-MePyNO, 4-MePyNO, 2-MeNPyNO, 2,6-DiMePyNO, 4-MeOPyNO, 4-PhPyNO, QNO and **IsQNO** as guests were conducted *via* ^1H NMR experiments in CD_3OD at 293 K. In these experiments, the host and guests were mixed in a 1:1 (6.6 mM on both molecules) ratio in CD_3OD ; the ^1H NMR spectra were measured and the results were compared with the free host (6.6 mM) and free guests (6.6 mM).

Complexation-induced shielding of the guest proton resonances was observed in all cases except with **4-PhPyNO**. The shielding effects of the aromatic rings of the bowl-shaped host cavity upon addition of the guest are responsible for this upfield shift and indicate that guest exchange is fast on the NMR time scale. Taking the 1:1 mixture between **1** and 3-MePyNO as an example (Fig. 6, I), the aromatic protons (g, f) are the most shielded (0.16 ppm and 0.17 ppm). These shift changes confirm the orientation of the guest deep in the host cavity, supporting the X-ray crystal structure (Fig. 3). Analysis of the 1:1 mixture between **1** and QNO (Fig. 6, II) reveals the aromatic protons (f, g) to be the most shielded (0.14–0.15 ppm), once again suggesting the localization of QNO within the host cavity. The analyses of the ^1H NMR results between the host and the other guests (PyNO, 2-MePyNO, 4-MePyNO, 2-MeNPyNO, 2,6-DiMePyNO, 4-MeOPyNO, and **IsQNO**) also indicate the localization of the guest in the host cavity (Fig. S7–S16†). No shift changes were observed with **4-PhPyNO**, implying that in solution no host–guest complex is formed (Fig. S14†).

Variable temperature (233–333 K) ^1H NMR experiments were done to probe the conformational changes of host **1** in the presence of the different guests (Fig. S17–S18†). No obvious changes in the host **1** signals were observed, implying that the conformational changes observed in the solid state with the *N*-oxide guests are caused by multiple intermolecular interactions existing only in the solid state.

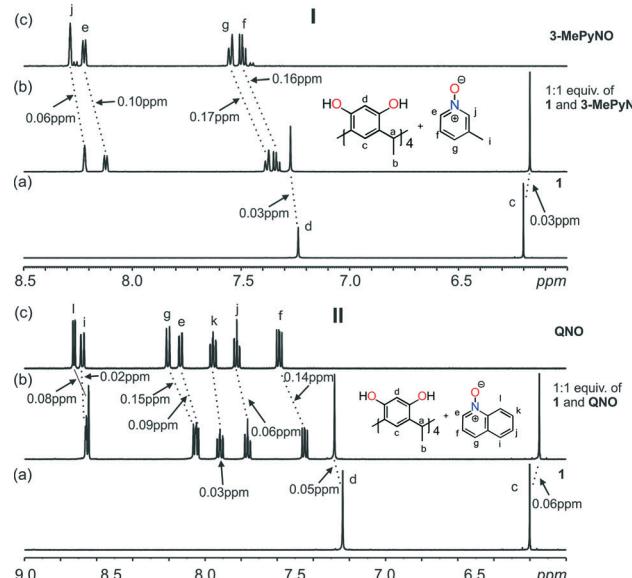


Fig. 6 Selected region of the ^1H NMR (CD_3OD , 293 K) of: (I) a mixture of 3-MePyNO and **1**, (a) **1** (6.6 mM), (b) **1**+3-MePyNO (1:1), (c) 3-MePyNO (6.6 mM) and (II) a mixture of QNO and **1**, (a) **1** (6.6 mM), (b) **1**+QNO (1:1), (c) QNO (6.6 mM). The shift changes in the guest and host signals of the complexes in ppm are highlighted.

Conclusions

The X-ray structures of seven PyNO complexes led to the conclusion that there is either *endo* complexation *via* $\text{C}-\text{H} \cdots \pi$ interactions or *exo* complexation *via* $(\text{N}-\text{O}) \cdots (\text{H}-\text{O})_{\text{host}}$ hydrogen bonds between the aromatic *N*-oxides and C_{methyl} -resorcinarene. Due to the rarity of C_{methyl} -resorcinarene-pyridine *N*-oxide complexes, the *endo* host–guest complexes **2-MePyNO-1** and **3-MePyNO-1** were compared with our previous results with C_{ethyl} -2-methylresorcinarene,²¹ which allowed us to probe factors such as the conformational flexibility of the cavity, the strength of $\text{C}-\text{H} \cdots \pi$ interactions and the localization of the guest molecule in the cavity. Despite the enhanced conformational flexibility, C_{methyl} -resorcinarene forms a pseudo-capsular 2:2 *endo* complex with 2-MePyNO and 3-MePyNO stabilized by $\text{C}-\text{H} \cdots \pi$ interactions in the solid state. The larger overall size of 3-MePyNO forces the C_{4v} crown conformation to open, very close to the ideal C_{2v} boat conformation, but still having the guest inside the cavity. Additionally, the strong $\text{C}-\text{H} \cdots \pi$ interactions found in the *endo* complex **3-MePyNO-1** hint that the guest similar to 3-MePyNO with C_{methyl} -resorcinarene could show interesting host–guest interactions. The larger guests 4-MePyNO, 2-MeNPyNO, 4-MeOPyNO, 4-PhPyNO and **IsQNO** do not form *endo* complexes, as the *exo* complexes are preferred due to the strong intermolecular hydrogen bonding between the host **1** molecules leading to 1-D chains. All *exo* complexes show very similar overall crystal packings. The complementary solution studies show that host–guest complexes between host **1** and all the *N*-oxide molecules, except **4-PhPyNO**, are formed in solution. Furthermore, the variable temperature ^1H NMR



measurements proved that the conformational changes in host **1**, observed in the solid state upon complexation, were not observed in solution.

Acknowledgements

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