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Inclusion Complexes of C_{ethyl}-2-Methylresorcinarene and Pyridine *N*-oxides: Breaking C-I···$^{-}$O-N^{+} Halogen Bond by Host-Guest Complexation

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The C_{ethyl}-2-Methylresorcinarene forms host–guest complexes with aromatic *N*-oxides through multiple intra- and intermolecular hydrogen bonds and C–H···π interactions. The host shows conformational flexibility to accommodate 3-methylpyridine *N*-oxide, while retaining a crown conformation for 2-methyl- and 4-methoxy-pyridine *N*-oxides highlighting the susbsitutent effect of the guest. The *N*-methylmorpholine *N*-oxide, a 6-membered ring aliphatic *N*-oxide with a methyl at the N-oxide nitrogen is bound with the equatorial –N–CH_3 group located deep in the cavity. The 2-iodopyridine *N*-oxide is the only guest that manifests intermolecular N–O···I–C halogen bond interactions, which are broken down by the host resulting in a 2:2 pseudocapsular complex stabilized by additional C–I···π interactions between the two 2-iodopyridine *N*-oxides located in two adjacent hosts. These host-guest complexes were analyzed in the solid-state by single crystal X-ray crystallography and in solution by ^{1}H NMR spectroscopy.

Introduction

Resorcinarenes represent a unique family of host compounds, which are extensively studied in host-guest chemistry due to their π-rich electron cavity in the C_{4v} conformation.[1] In the C_{4v} conformation the bowl shaped cavity of resorcinarenes accommodates a wide range of guest molecules via non-covalent interactions such as cation···π, C-H···π and π···π interactions depending upon the size and charge distribution of the guest molecules.[2] Besides lattice stabilization, the phenolic groups participate in hydrogen bonds (HBs) with appropriate guest molecules during complexation.[2] As a result, the construction of hydrogen bonded supramolecular networks utilizing resorcinarenes as the key components has been studied with alcohols,[3] sugars,[4] steroids,[5] heterocyclic five- and six-membered ring compounds[6] as guest molecules.

Pyridine *N*-oxides (PyNOs) are widely recognized as synthetic intermediates for functionalization of pyridine rings in organic synthesis.[7] This is due to the specific electronic nature the $^{+}$N–O^{-} group which makes the aromatic ring electron deficient and thus a very interesting guest molecules with electron-rich host systems.[8] Alternatively, the structural and electronic properties of these *N*-oxide compounds with the polar $^{+}$N–O^{-} group makes them excellent hydrogen bond acceptors.[9] In spite of increasing number of reports of PyNOs complexes with calixarenes[8a,10] and cavitands,[8b,11] the reports on host-guest chemistry of *N*-oxides and resorcinarenes are very rare.[8c,12] The report of host-guest complexes between C_{ethyl}-2-methylresorcinarene and aromatic *N*-oxides highlighted the importance of π···π, C–H···π interactions with the PyNOs located inside the C_{ethyl}-2-methylresorcinarene cavity.[8c] These observations prompted us to further probe the C_{ethyl}-2-methylresorcinarene as a reaction vessel to control the coordination sphere of copper(II) in the multicomponent reactions of PyNO copper(II) complexes.[12] The π···π, C–H···π and HB interactions held the PyNOs in the C_{ethyl}-2-methylresorcinarene cavity thus controlling the geometry around the copper(II).[12] The π-rich C_{ethyl}-2-methylresorcinarene and the π-deficient PyNO guests with multiple HB interaction sites makes them a perfect pair for host-guest complexation. Thus, exploring a range of structurally and electronically different aromatic *N*-oxides with subtle changes in their structure and their ability to template supramolecular host-guest complexes with π-rich host compounds will give a crystal engineering tool to study the intermolecular interactions involved. Despite the numerous literature reports on resorcinarenes, only a handful of crystal structures[13] containing the C_{ethyl}-2-methylresorcin-arene **1** can be found from the Cambridge Crystallographic Database (CSD). Furthermore, there has been no systematic study on host-guest complexes between PyNOs as guests and any member of the resorcinarene family as the hosts.

In the present study, we explore five different host-guest systems utilizing the C_{ethyl}-2-methylresorcinarene (**1**) as the host and five structurally and electronically different PyNOs as guests (Fig. 1). The C_{ethyl}-2-methylresorcinarene (**1**) adopts the C_{4v} crown conformation in the solid-state.[3a,8c,12] Initially, we used

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2-methylpyridine *N*-oxide (**2MePyNO**) and 3-methylpyridine *N*-oxide (**3MePyNO**) to get insight of the substituent effect on the structure of the host-guest complexes. The 4-methoxypyridine *N*-oxide (**4MeOPyNO**) was utilized to study the electronic influence of oxygen atom as a *para*-substituent. The *N*-methylmorpholine *N*-oxide (**NMO**) was also used as a guest to study the influence of the methyl group at the $^{+}$N–O^{-} group within an alicylic ring system.

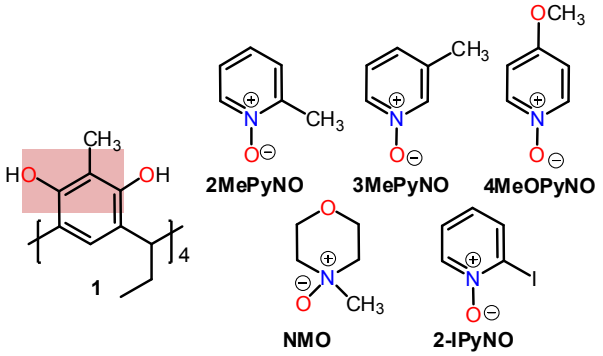

Fig. 1. The chemical structures of C_{ethyl}-2-Methylresorcinarene (**1**), 2-methylpyridine *N*-oxide (**2MePyNO**), 3-methylpyridine *N*-oxide (**3MePyNO**), 4-methoxypyridine *N*-oxide (**4MeOPyNO**), N-methylmorpholine *N*-oxide (**NMO**) and 2-iodopyridine *N*-oxide (**2-IPyNO**).

As the electron-deficient aromatic ring system in PyNO's will polarize the iodine atom in *ortho*-iodopyridine *N*-oxide (**2-IPyNO**) and thus induce possible halogen bonding,[14] it was selected as the fifth and multifunctional guest. Based on the previous reports, the halogen bond (XB) between donor part (the iodine atom) and the XB acceptor part (the *N*-oxide oxygen) of the **2-IPyNO** was envisaged.[15] Based on the earlier studies on halo-PyNO's,[15] the self-complementary XB between the XB donor part (the iodine atom) and the XB acceptor part (the *N*-oxide oxygen) of the **2-IPyNO** was envisaged. The hypothesis was to probe if in the complex between **2-IPyNO and** C_{ethyl}-2-methylresorcinarene the resorcinarene host would be able to break the moderately strong dimeric C-I···$^{-}$O-N^{+} XB by forming a stronger 1:1 **2-IPyNO:1** complex. The obtained host-guest complexes were analysed in the solid state by single crystal X-ray diffraction and in solution by ^{1}H NMR spectroscopy.

Results and Discussion

X-ray Crystallography

Complexes **2MePyNO@1** and **3MePyNO@1** crystallized (See SI for experimental procedures) in monoclinic space group $P2_1/n$ and triclinic space group *P*-1, respectively. In both cases, there are two molecules of *N*-oxides in the asymmetric unit; one sitting inside the cavity and the other outside the cavity. In complex **2MePyNO@1**, one **2MePyNO** sits inside the cavity with the N–O group pointing up, and is a bifurcated HB acceptor for two host –OH groups [*d*(O–H···O), 2.679(3) Å and 2.674(3) Å; ∠O–H···O, 159° and 166°] as shown in Fig. 2b. The exo-cavity **2MePyNO** directly interacts with the –OH group of host **1** [*d*(O–H···O), 2.551(3) Å; ∠O–H···O, 160°] *via* a monodentate hydrogen bond (Fig. 2a). All the O···O distances are below the sum of the van der Waals radii of oxygen atoms, and clearly the monodentate HB interaction is stronger than the bidentate HB. Along the *a*-directions, the -OH groups of host **1** forms HB by $(O\text{-}H)_{host}$···$(O\text{-}H)_{host}$ interactions to give a 2-D polymeric sheet like structure with the exo-cavity **2MePyNO** being a passive spectator as shown in Fig. 2a. **3MePyNO@1** forms complex 2-D HB network with the in-cavity **3MePyNO** being monodentate and directly hydrogen bonded to the host –OH group [*d*(O–H···O) 2.659(7) Å; ∠O–H···O, 171°]. The exo-cavity**3MePyNO** together with methanol molecule connects **3MePyNO@1** units by $(O–H)_{host}$···$(O–H)_{CH3OH}$···O_{py}···$(H–O)_{host}$ interactions, as shown in Fig. 2c.

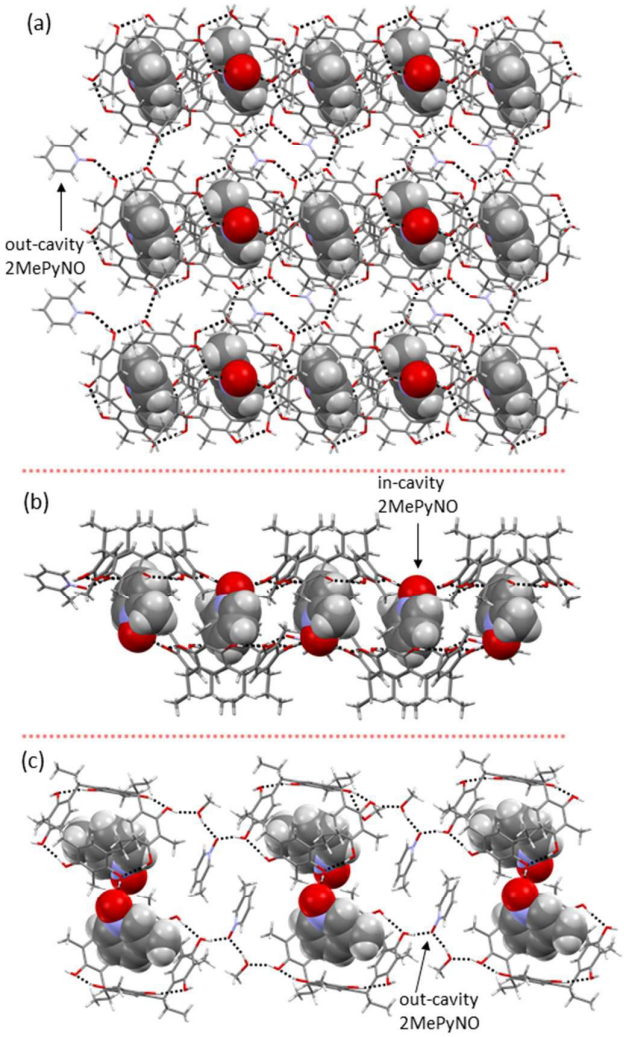

Fig. 2. (a) 2–D Polymeric structure of **2MePyNO@1**, and (b) side-view to show in-cavity **2MePyNO** bridging two host molecules by O–H···O interactions as bidentate HB acceptor. (c) Section of crystal packing in **3MePyNO@1** to show the exo-cavity **3MePyNO** as bidentate HB acceptor.

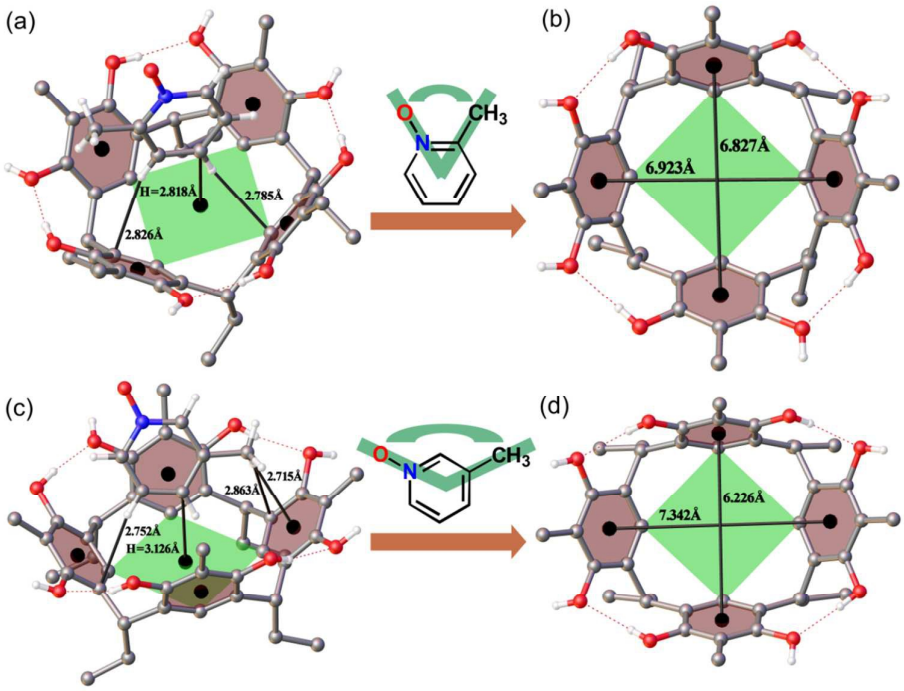

Fig. 3. (a) C–H···π interactions in **2MePyNO@1**. (b) The cavity of host **1** in **2MePyNO@1** to highlight the flexibility. (c) C–H···π Interactions in **3MePyNO@1**. (d) The cavity of host **1** in **3MePyNO@1** to highlight the flexibility.

C_{ethyl}-2-Methylresorcinarene **1** exhibits remarkable conformational flexibility due to the positioning of the methyl substituents in **2MePyNO** and **3MePyNO**, thus resulting in varied C–H···π interactions.[14] The *para*- and *meta*- protons of the **2MePyNO** (Fig. 3a) show C–H···π interactions at distances of *ca.* 2.785 Å [∠C–H···C, 149°] and 2.826 Å [∠C–H···C, 163°], respectively. On the other hand, in complex **3MePyNO@1**, the *meta*- and $-CH_3$ hydrogens of **3MePyNO** show C–H···π interactions at distances of *ca.* 2.752 Å [∠C–H···C, 160°] and 2.863 Å [∠C–H···C, 162°], respectively. As shown in Fig. 3c, hydrogen of $-CH_3$ group to the centroid of the aromatic ring has the shortest contact at distances of *ca.* 2.715 Å [∠C–H···π(centroid), 147°]. Guests with substituents close to N-O group sits deep in the cavity. As a result, **2MePyNO** sits at a height of 2.818 Å while **3MePyNO** at distances of 3.126 Å from the centroids of the lower rim carbon atoms of the host **1**. Furthermore, **2MePyNO** with approximately 60° angle between the N–O and methyl groups sits inside the host cavity without deformation resulting in near similar centroid-to-centroid [6.923 Å and 6.827 Å] distances between opposite aromatic rings (Fig. 3c). However, **3MePyNO** with approximately 120° angle caused significant changes in host centroid-to-centroid distances between opposite aromatic rings [7.342 Å and 6.226 Å] as shown in Fig. 3d.

Complex **4MeOPyNO@1** forms a 2-D polymeric sheet structure with 1:1 host-guest ratio. In **4MeOPyNO@1**, the N-O group of **4MeOPyNO** is pointing up and is bidentate with N–O···$(O–H)_{host}$ and N–O···$(O–H)_{CH3OH}$ interactions at distances of 2.650(3) Å [∠O–H···O, 158°]and 2.580(3) Å [∠O–H···O, 175°], respectively (Fig. 4a). The extent of the HB interaction of **4MeOPyNO** and **2MePyNO** with the host -OH groups are very similar. Unlike **2MePyNO@1** and **3MePyNO@1**, no C–H···$\pi_{(host)}$ interactions between the aromatic ring protons of **4MeOPyNO** and the C_{ethyl}-2-methylresorcinarene **1** are observed. Moreover, the in-cavity -OCH_3 group also assists the 3D crystal packing by weak O···H–C interactions with the adjacent C_{ethyl} chain of the host.

Complex **NMO@1** contains an in-cavity and exo-cavity **NMO** molecules. The in-cavity N–O group and the host –OH group are connected by two methanol molecules while the exo-cavity **NMO** directly HB to the –OH group of host **1** (Fig. 4b). The difference in host cavity distortions depends on the guest height situated in the cavity, *viz*. 3.077 Å for **4MeOPyNO** and 2.920 Å for **NMO**. In both the cases, the guest molecules are situated to the corner of the host, stabilized *via* C–H···π interactions. In **4MeOPyNO@1**, -OCH_3 group and host aromatic ring are stabilized by C–H···π interactions at distances ranging between 2.919 Å and 3.129 Å, of which C–H···centroid observed to have the shortest contact with a distance of 2.681 Å (Fig. S4a). In **NMO@1**, the in-cavity **NMO** interacts with the host aromatic ring through C–H···π at distances of 2.937 Å and 3.221 Å (Fig. S4b). The N-O group appears to be the reason for the presence of the in-cavity –N–CH_3 group, which makes **NMO** unique guest molecule from other *N*-oxides.

The complex **2-IPyNO@1** reveals pseudo-capsular arrangement as shown in Figure 5. The asymmetric unit contains two C_{ethyl}-2-methylresorcinarenes each accommodating **2-IPyNO** molecules together with six exo-cavitywater molecules. The N–O groups of in-cavity **2-IPyNO** acts as bidentate and tridentate (Fig. S5) HB acceptors for exo-cavity water and adjacent host molecules in stabilizing the pseudo-capsular arrangements by O–H···O interactions. One of the iodines in the cavity of one host interacts with the phenyl ring of the **2-IPyNO** located in the cavity of the

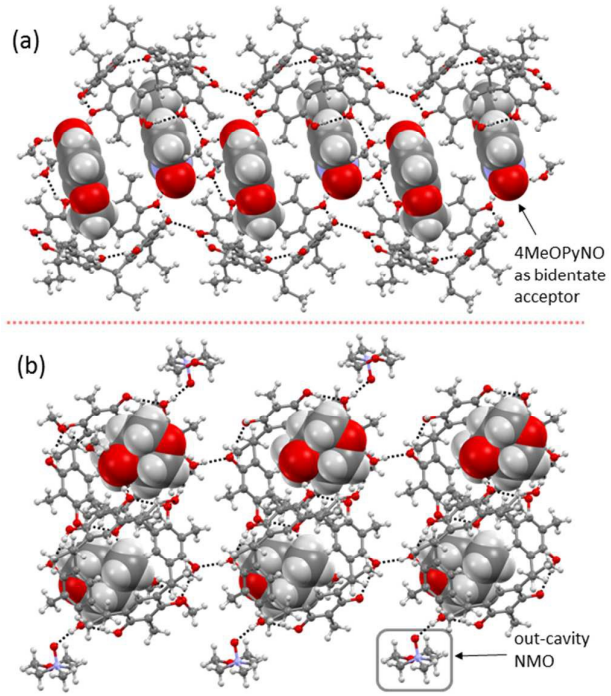

Fig. 4. (a) Section of the crystal packing in **4MeOPyNO@1** showing O–H···O interactions of **4MeOPyNO** and methanol molecules. (b) Top view of 2D polymeric structure in **NMO@1**. Black broken lines represent O–H···O interactions.

second host through intermolecular C–I···π contacts at distances of 3.549 Å [∠C-I···π(centroid), 161° and ∠C-I···π(plane), 155°]. The height of the capsule, defined as the distance between the centroids of the lower rim carbons is 13.479 Å (Fig S6),[8c] and in which the two **2-IPyNO** molecules are accommodated at heights of 2.720 Å and 3.153 Å. The hosts adopt a distorted crown conformations with centroid-to-centroid distances of 6.790/6.960 Å and 6.816/6.961 Å (Fig S7). The height and orientation of the **2-IPyNO** molecules increases the number of C–H···π interactions with the host aromatic ring. The **2-IPyNO** parallel to the host aromatic ring, and situated at a height of 3.153 Å is stabilized by two C–H···π interactions, while the non-parallel **2-IPyNO** situated deep in the cavity at a height of 2.720 Å is stabilized uniquely by three C–H···π interactions (Fig S7).

The orientation of the guest aromatic ring deep in the host cavity with N-O group pointing up has been a primary prerequisite to encapsulate the PyNOs by C_{ethyl}-2-methylresorcinarene **1**. As a consequence, the guest molecules become responsive by these interactions. As such, the self-assembly process can be controlled with respect to the guest interactions. To illustrate this, **2-IPyNO** was crystallised under similar solvent conditions to compare the nature of guest interactions in the absence of C_{ethyl}-2-methylresorcinarene **1**. The crystal structure of **2-IPyNO** (Fig. 6) displays classical intermolecular N-O···I-C XB at distances of 2.791 Å with XB ratio ($R_{XB} = d_{XB}/(X_{vdw}+B_{vdw})$) of 0.791.[14]

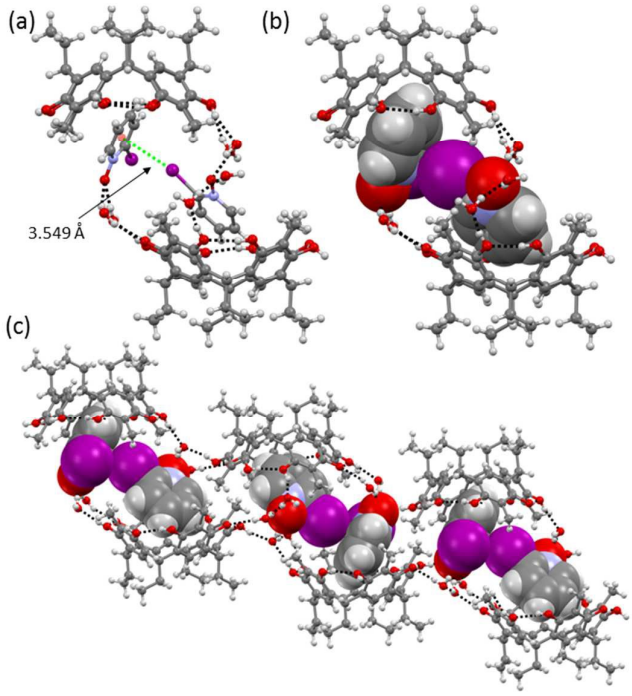

Fig. 5. Pseudo capsular arrangement of **2-IPyNO@1** with **2-IPyNO** guests shown in (a) ball and stick, and (b) CPK model. (c) Section of crystal packing to show O–H···O interactions templated **2-IPyNO@1** complexes. Black and green broken lines represent O–H···O and C-I···π interactions, respectively.

The type and strength of the electron withdrawing group attached to aromatic ring and its influence on hybridization of the aromatic ring affects the polarization of halogen atom (usually Br or I) to act either as electron donor or acceptor. Although, the iodine has weak interactions with *ortho*- carbons [*d*(C-I···C), 3.716 Å; ∠ C-I···C, 141.30°] and nitrogen [*d*(C-I···N), 3.649 Å; ∠C-I···N, 141.28°] of pyridine *N*-oxide ring; the centroid of the aromatic ring is influenced by shortest contact with distances of 3.549 Å. Thus, the iodine substituent clearly demonstrates the presence of weak C-I···π halogen type interactions which are enhanced inside the pseudo capsular arrangement.

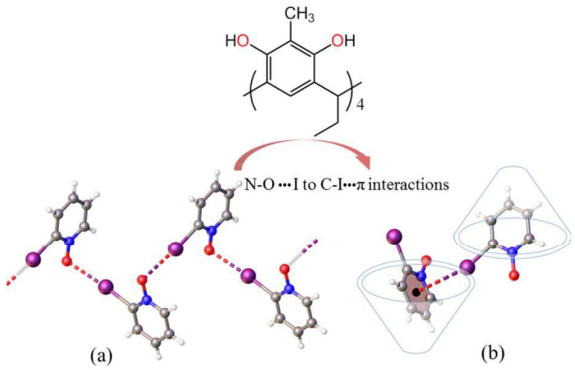

Fig. 6. (a) 1-D Polymeric N-O···I interactions based XB complex of **2-IPyNO**, and (b) confined C-I···π interactions between **2-IPyNO** by C_{ethyl}-2-methylresorcinarene **1** inside the complex **2-IPyNO@1**.

A CCDC search was carried out to survey the type and nature of molecules involved during intermolecular C-I···aromatic ring

interactions. The first search was limited to any 2-substituted iodo-aromatic compounds and their non-bonded interactions with adjacent aromatic ring. In total 22 hits were found,[13d,17] and of all the structures, one of the report constitutes a shortest distance of 3.321 Å.[17o] A search for perfluorinated iodobenzene related C-I···π interaction revealed zero hits. Consequently, individual survey were carried out on compounds that have neutral aprotic electron-withdrawing groups (-F, -Cl, -NO_2, -CN, -CF3, -CCl_3 and -COCl) and electron donating groups (alkyl and -NR_2) at 2-substituted position of iodo-aromatic compounds. Only chloro substituent retrieved one hit, which has a C-I···π distance of 3.537 Å.[18]

NMR Analyses

Solution studies between the C_{ethyl}-2-methylresorcinarene **1** as host, and **2MePyNO**, **3MePyNO**, **4MeOPyNO**, **NMO**, and **2-IPyNO** as guests were conducted *via* ^{1}H NMR experiments in CD_3OD at room temperature. In the experiments, 1:1 and 1:2 mixture of the host and guests were prepared, the ^{1}H NMR measured and the results compared with the free host (6.6 mM) and free guests (6.6 mM).

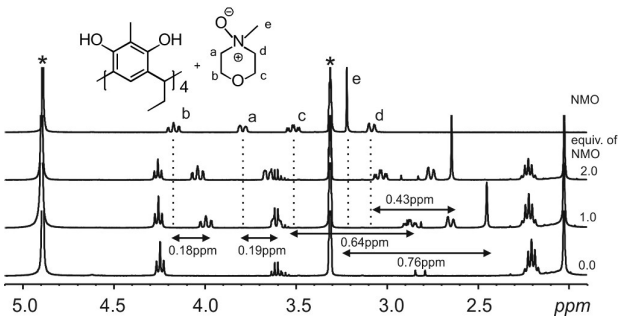

Fig. 7. Selected region of the ^{1}H NMR (CD_3OD, room temperature) after the addition of up to 2 equivalents of **NMO** to host **1**. Stars represent the residual CD_3OD. The shift changes of the guest signals in ppm are highlighted.

Significant complexation-induced shielding of the guests proton resonances were observed in all cases. The shielding effects of the aromatic rings of the bowl-shaped host cavity upon addition of the guest is responsible for this upfield shift and clearly points to a guest exchange fast on the NMR time scale. Taking the 1:1 mixture between the C_{ethyl}-2-methylresorcinarene **1** and **NMO** as an example (Fig. 7), the methyl group protons (e) are the most shielded (0.76 ppm). These shift changes clearly confirms the orientation of the guest in the host cavity. The large shift change for the methyl protons suggests the protons are situated deep in the cavity of the host. This is analogous to the X-ray structure (Fig. 4).

Analyses of the 1:1 mixture between the C_{ethyl}-2-methylresorcinarene **1** and **2-IPyNO** (Fig. 8) reveals the aromatic protons (*b, c*), to be the most shielded (0.67-0.72 ppm) with the proton next to the –NO group the least shielded (0.31 ppm). This supports the orientation of the guest within the host cavity as seen from the X-ray structures (Figs. 5 and 6). The analyses of the ^{1}H NMR results between the host and the other guests (**2MePyNO**, **3MePyNO** and **4MeOPyNO**) also confirm the orientation of the guests in the host cavity (Figs S1-S3) and support the structures observed from solid state analyses (Figs. 2 and 4). Additionally, the flexibility of the host when accommodating the guest is observed from small changes to the host upper rim methyl groups and the aromatic protons upon complex formation. This again supports the observation from solid-state studies.

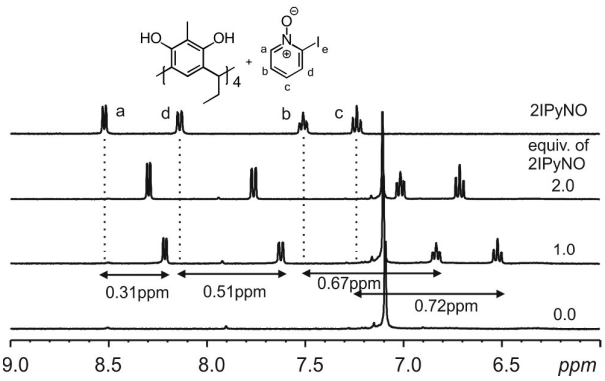

Fig. 8. Selected region of the ^{1}H NMR (CD_3OD, room temperature) after the addition of up to 2 equivalents of **2-IPyNO** to host **1**. Stars represent the residual CD_3OD. The shift changes of the guest signals in ppm are highlighted.

Conclusions

Five host-guest complexes between C_{ethyl}-2-methylresorcinarene (**1**) and five different N-oxides, three aromatic (**2MePyNO**, **3MePyNO**, and **4MeOPyNO**), one aliphatic (**NMO**) and an iodopyridine N-oxide (**2-IPyNO**) were obtained and analysed in the solid state and in solution *via* single crystal X-ray diffraction studies and ^{1}H NMR analyses respectively. Conformational flexibility of the host was observed when *ortho*- and *meta*- methylated guest molecules were utilized. All the aromatic guests were located in the cavity such that, the N-O groups points upwards (out of the cavity). However, the aliphatic analogue **NMO**, reveal the equatorial –N–CH_3 group to be located deep in the cavity of the host and greatly changing the cavity size and conformation of the host. The 1-D polymeric halogen bonded complex was disrupted in the presence of the host, resulting in a 2:2 host-guest pseudo capsular complex when 2-iodopyridine N-oxide (**2-IPyNO**) was used. Extra C–I···π interactions between the two **2-IPyNO** located in two different hosts help to glue the two capsule halves. In all the complexes, the binding of the N-oxides proceeds through multiple intra- and intermolecular hydrogen bonds, -C–H···π, π···π and -C–I···π interactions. The solution analyses through ^{1}H NMR measurements clearly support the structures observed in the solid state. Aromatic and aliphatic N-oxides are proving to be suitable guest compounds for the resorcinarene cavity when n the C_{4v} conformation. N-oxides have a huge potential with numerous applications as ligands in organo-metallic chemistry. Their ability to interact with resorcinarenes implies they ca be utilized in tandem to tune and construct functional assemblies.

Acknowledgments

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C_{ethyl}-2-Methylresorcinarene and aromatic *N*-oxides manifest host-guest chemistry by C-H···π interactions and halogen bonding, C-I···$^{-}$O-N^{+} halogen bond with iodopyridineoxide is broken by the in-cavity C-I···π interactions.