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Crystal Engineering Studies of the Complexes of Ethyl Resorcinarene with Aromatic Nitrogen Heterocycles

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Five X-ray structures of complexes of ethyl resorcinarene with aromatic nitrogen heterocycles (imidazole, 1,2,4-triazole, pyridine, pyrazine, 2-pyridylmethanol and quinoline) show that ethyl resorcinarene spontaneously forms molecular inclusion complexes with five- and six-membered aromatic nitrogen heterocycles via π···π and CH···π interactions. However, with 10-membered quinoline, no molecular inclusion complex is formed. Instead, quinoline manifests crystal lattice inclusion.

Keywords: Crystal engineering; X-ray diffraction; Resorcinarenes; Complexation; Nitrogen heterocycles

INTRODUCTION

The complexation of organic molecules by artificial receptors via weak, non-covalent interactions such as hydrogen bonding and various π-interactions (CH···π, π···π interactions) has received increasing attention during the past decade due to the significant role of such interactions in recognition processes in biological systems [1]. N-Heterocyclic bases, such as imidazole, are widespread in nature

The Future of Supramolecular Chemistry

At present, Supramolecular Chemistry is greatly influenced by X-ray structure determinations of single crystals of supramolecular systems. Detailed structural information plays a crucial role in evaluation of weak intermolecular (e.g. supramolecular) intercations and functions and acts as a feedback to the synthesis planning and molecular design. These features will gain even more importance in the future when intelligent and functional nano-machines and -motors are to be designed, prepared and structurally characterized. The importance of supramolecular crystal engineering as a research area of its own will grow in the future since the first reports about dynamic behavior of close-packed crystal lattices have already been presented (*Science* **2002**, *298*, 1000). New functional crystalline materials will be developed, based on the increased knowledge on intermolecular interactions and the facts influencing the crystallization. Rational design of functional materials and devices will continue to rely on the expertise of crystal engineering and X-ray structural determinations.

Kari Rissanen was born in 1959. He undertook Chemistry studies at the University of Jyväskylä, 1980–1985 and remained there for his MSc in Organic Chemistry 1985, and PhD in Chemistry (Solid-state Structural Chemistry of Organic Compounds), 1990. He was Chemistry Assistant and Assistant Professor, at University of Jyväskylä, 1985–1993, and Research Fellow (1988–1991) and Senior Research Fellow (1991–1993), Finnish Academy. In 1993, he became Associate Professor, Organic Chemistry, University of Joensuu, Finland and in 1995 moved to his current position as Professor and Head of Laboratory of Organic Chemistry, University of Jyväskylä, Finland; since 1987, he has published ca. 200 publications in scientific journals, 14 patents/patent applications and >100 posters/lectures in scientific conferences in the field of Structural and Synthetic Supramolecular and Organic Chemistry.

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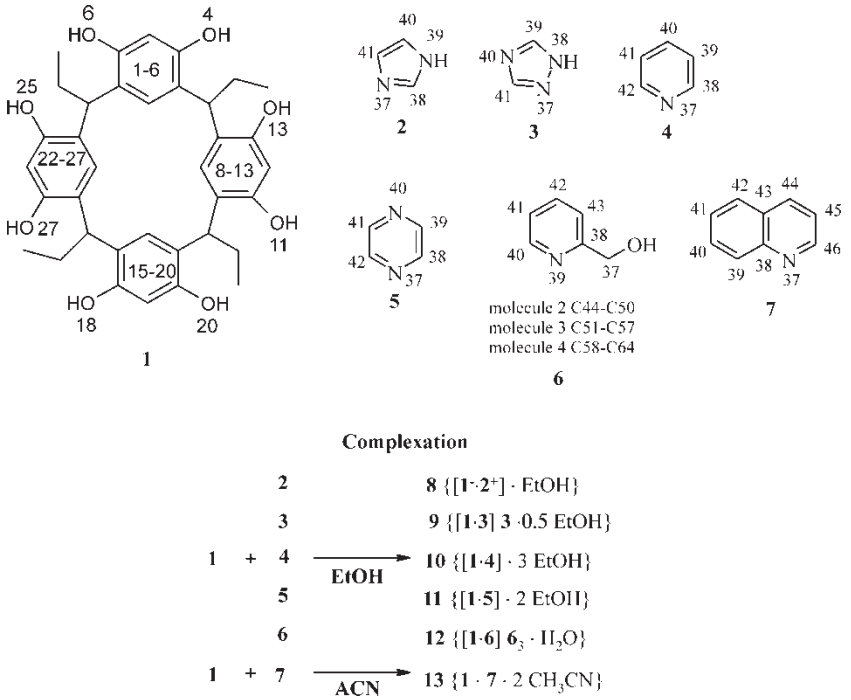

SCHEME 1 Structural formulae, relevant crystallographic numbering and complexation of ethyl resorcinarene and aromatic nitrogen heterocycles.

and of great biological importance. Thus, their complex formation properties in both neutral and cationic form with artificial receptors, especially with crown ethers, have been widely studied [2–9]. However, the utilization of ethyl resorcinarene in the complexation of aromatic nitrogen heterocycles has not been the subject of extensive studies, although its properties—the ability to form hydrogen bonds, the aromatic cavity—are obviously suitable for complexation of such compounds. Aromatic nitrogen heterocycles, such as 4,4′-bipyridine and pyridine, have mostly been used to build up multicomponent extended cavities with methyl resorcinarene, i.e. not in the role of guest but as a building block of multicomponent host [10–15]. In addition, some nucleosides and their model compounds have been used as guests for resorcinarenes in NMR titration experiments [16].

The purpose of our study was to explore the solid-state complexation and possible deprotonation of the ethyl resorcinarene (**1**) by the slightly basic aromatic nitrogen heterocycles as a continuation of our solid-state studies of crown ether and tetraphenylborate complexes of planar N-heteroaromatic cations [4–9] and complexes of resorcinarenes with melamine [17] and small alkyl ammonium cations [18,19], the latter showing formation of molecular capsules.

DISCUSSION

Crystallization experiments of selected aromatic nitrogen heterocycles were performed with a 1:1 host–guest molar ratio in ethanol solutions except for quinoline (**7**), the crystallization of which failed with ethanol. Instead, acetonitrile was used (Scheme 1).

Five-membered Heteroaromatic Rings Imidazole (2) and 1,2,4-Triazole (3)

Imidazole (**2**) and 1,2,4-triazole (**3**) spontaneously form inclusion compounds with ethyl resorcinarene **1**. In both cases, the conformation of the host **1** is a distorted crown typical for alkyl resorcinarenes in the solid state (the distances between the centroids of the opposite benzene rings are 6.15 and 7.34 Å in complex **8** {[**1**$^-$·**2**$^+$]·EtOH} and 6.13 and 7.40 Å in complex **9** {[**1**·**3**]·**3**·0.5EtOH}).[†] The conformations of the hosts are stabilized, as usual, via four intramolecular hydrogen bonds between the adjacent hydroxyl groups (Table I).

The guests are situated inside the cavity via π···π interactions to the narrow side of the cavity and via CH···π interactions to the wider side of the cavity. However, imidazole (**2**) is situated on the one corner of the cavity in complex **8**, while 1,2,4-triazole (**3**) is more in the middle of the cavity (Fig. 1) in **9**.

[†]The distances between the centroids of the opposite benzene rings are in accordance with earlier reported values of solid state structures of resorcinarenes in the crown conformation [18–20]. In the solid state, the conformation is usually not a perfect crown but slightly pinched.

TABLE I Hydrogen bonding presented as donor–acceptor distances

Complex	Intermolecular hydrogen bonds stabilizing the conformation of the host/Å	Intermolecular hydrogen bonds between guest and host/Å	Intermolecular hydrogen bonds from host to host/Å	Intermolecular hydrogen bonds to solvents/Å
8	2.577(2)*–2.766(2)	2.705(2), 2.753(2)	2.560(2)*–3.081(2)	2.726(2)
9	2.762(2)–2.988(3)	1,2,4-Triazole 1 (included): 2.732(3), 2.742(3) 1,2,4-Triazole 2 (outside): 2.923(3)	2.735(2)	Host–solvent: 3.204(5) Guest–solvent: 3.089(6)
10	2.735(3)–2.785(3)	2.650(3)	–	Host–solvent: 2.698(3)–3.299(3)
11	2.700(9)–2.763(7)	2.794(8), 2.852(9)	–	Host–solvent: 2.754(9)–3.18(1)
12	2.669(2)–2.830(2)	2-PyrMeOH 1 (included): 2.597(2) 2-PyrMeOH 3 and 4 (outside): 2.689(2), 2.743(2)	2.791(2)	Host–solvent: 2.825(2) Guest–solvent: 2.799(2)–2.829(2)
13	2.717(2)–2.814(2)	2.757(6), 2.62(2)†	2.682(2), 2.813(2)	Host–solvent: 2.744(3)

*The shortest bond is to the deprotonated hydroxyl group O18. †The guest is disordered. The latter distance is to the second position.

The distances between the centroid of the guest and the facing centroids of the aromatic rings of the host are Ct(guest)···Ct01 = 3.86 and Ct(guest)···Ct03 = 4.49 Å for **8** and Ct(guest)···Ct03 = 3.57 and Ct(guest)···Ct01 = 4.22 Å for **9**, indicating significant π···π interactions especially to the other facing aromatic ring.‡ The CH···π distances between the guest and the centroids of the aromatic rings (C41···Ct04 = 4.29 Å and C40···Ct02 = 3.20 Å for **8**; N38···Ct04 = 3.56 Å and C39···Ct02 = 3.66 Å for **9**) confirm the unsymmetrical placement of the imidazole and more symmetrical placement of 1,2,4-triazole inside the cavity. It is notable that the length of the closest distance between the imidazole and the host (C40···Ct02 = 3.20 Å) in complex **8** is almost in the range of conventional hydrogen bond.

There are two major differences of the solid-state complex structures of these two structurally very similar nitrogen heterocycles. First of all, interestingly, the imidazole (**2**) undergoes protonation into imidazolium cation during the crystallization, and simultaneously, one of the hydroxyl groups of the ethyl resorcinarene is deprotonated (O18). With 1,2,4-triazole (**3**), no protonation is observed, which is understandable on the basis of their pK_b values (7.05 for imidazole and 9.82 for 1,2,4-triazole in 25°C). The effect of the deprotonation is clearly seen in the lengths of the hydrogen bonds to adjacent hydroxyl group and to the opposing host, which are remarkably shorter than other respective hydrogen bonds (Table I).

The second major difference is that an additional molecule of 1,2,4-triazole is observed outside the cavity in complex **9**. The 1,2,4-triazole fills the interstice in the crystal lattice, but it seems to interact with the host by a hydrogen bond to a hydroxyl group (The hydrogen of hydroxyl group O18 is disordered over two positions. In one position, the hydrogen bond is direct towards the adjacent hydroxyl group of the host and in the other position, the hydrogen bond is to 1,2,4-triazole N37B.)

The packing of the complexes is fairly similar, despite the differences in the H-bond donor–acceptor properties of imidazole (**2**) and 1,2,4-triazole (**3**), and is governed by the hydrogen-bonding network between the hosts and guests and between the neighbouring hosts (Fig. 2). It is interesting to note that the hydrogen bonds of the guest are intercomplex by nature, i.e. they are directed to adjacent hosts and not to the host in whose cavity they are included, as was also observed with the complexes of planar N-heteroaromatic cations with crown ethers [4–9]. Thus, the hydrogen bonds from the guest to two facing hosts connect the hosts in continuous chains reinforced additionally by hydrogen bonds between the opposing hosts (Table I). The ethanol molecules play a role in packing by mediating the chain formation in **8** and in both structures by connecting the layers of chains *via* hydrogen bonds.

Six-membered Heteroaromatic Rings Pyridine (4), Pyrazine (5) and 2-Pyridylmethanol (6)

The complexation studies with unsubstituted six-membered heteroaromatics pyridine (**4**) and pyrazine (**5**) resulted in 1:1 complexes in which the ethyl resorcinarene (**1**) adopts a distorted crown conformation (the distances between the centroids of the opposite aromatic rings are 6.49 Å and 7.21 Å for complex **10** {[**1**·**4**]·3EtOH} and 6.56 Å and 7.15 Å for complex **11** {[**1**·**5**]·2EtOH}) stabilized by four

‡Ct01 = C1–C6, Ct02 = C8–C13, Ct03 = C15–C20, Ct04 = C22–C27.

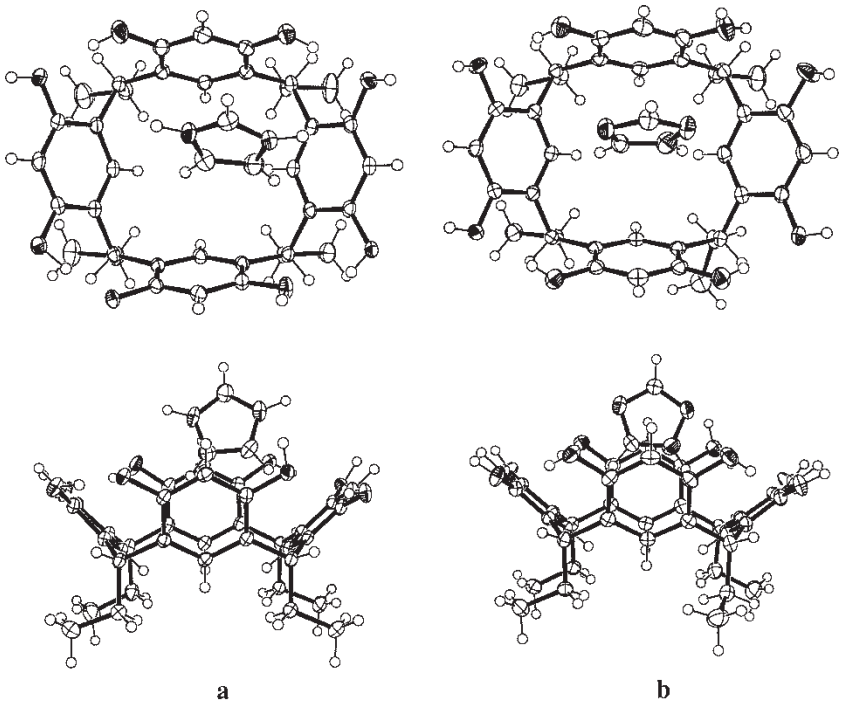

FIGURE 1 Top and side views of the crystal structures of **8** (a) and **9** (b). Solvents and another 1,2,4-triazole molecule are excluded for clarity.

intramolecular hydrogen bonds (Table I). However, the conformation is slightly more symmetrical than in complexes with five-membered rings probably because of the larger size of the guest, which forces the host molecule to adjust itself to the size of the guest.

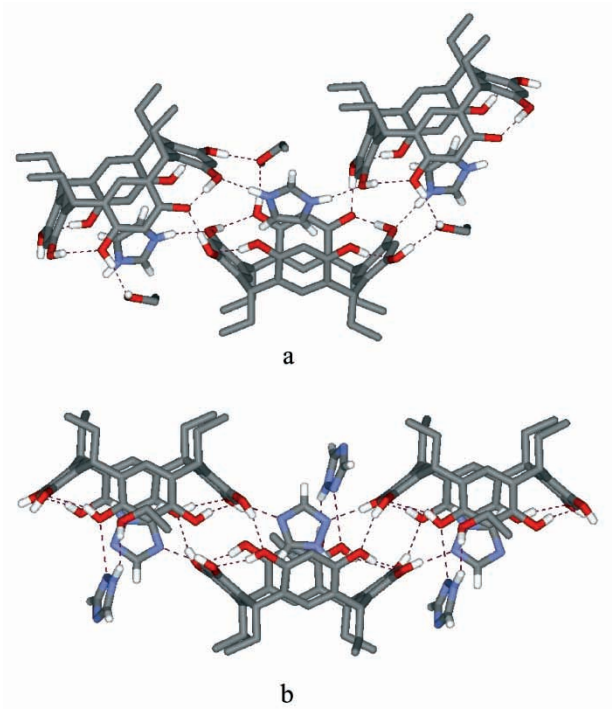

FIGURE 2 Crystal packing of **8** (a) and **9** (b). Non-hydrogen bonding hydrogens of hosts and solvent are excluded for clarity. Hydrogen bonds are shown as broken lines. (See colour plate 3 at the end of this issue.)

In both cases, the guests are located inside the cavity similarly to the 1,2,4-triazole (**3**) in **9** (Fig. 3). CH···π interactions (C38···Ct04 = 3.42 Å, C39···Ct01 = 3.66 Å, C40···Ct02 = 3.57 Å for **10**; C41···Ct02 = 3.65 Å and C42···Ct04 = 3.70 Å for **11**) to the wider side of the cavity and π···π interactions of length (from the centroid of the guest to the closest centroid of the aromatic ring of the host) 3.72 and 3.66 Å to the flattened side of the cavity stabilize the positioning of the pyridine (**4**) in complex **10** and pyrazine (**5**) in complex **11**, respectively. A slight difference is observed in the orientation of guests: one of the pyridine hydrogens (H39) points directly towards the bottom of the cavity optimizing the CH···π interactions to three aromatic rings of the host. The orientation of pyrazine in **11** is horizontal, i.e. no atom is pointing towards bottom. Neither of the guests is protonated owing to their weakness as base.

Both pyridine and pyrazine are able to act as hydrogen-bond acceptors, and this property governs the crystal packing of complexes, i.e. intercomplex hydrogen bonds connect opposing hosts to continuous chains as with five-membered rings (Table I; Fig. 4). The difference from imidazole and 1,2,4-triazole complexes **8** and **9** is the more zigzag nature of the chains in both vertical and horizontal directions, i.e. the facing hosts manifest a slipped packing motif. Another difference is the lack of direct hydrogen-bonding contact between the opposing

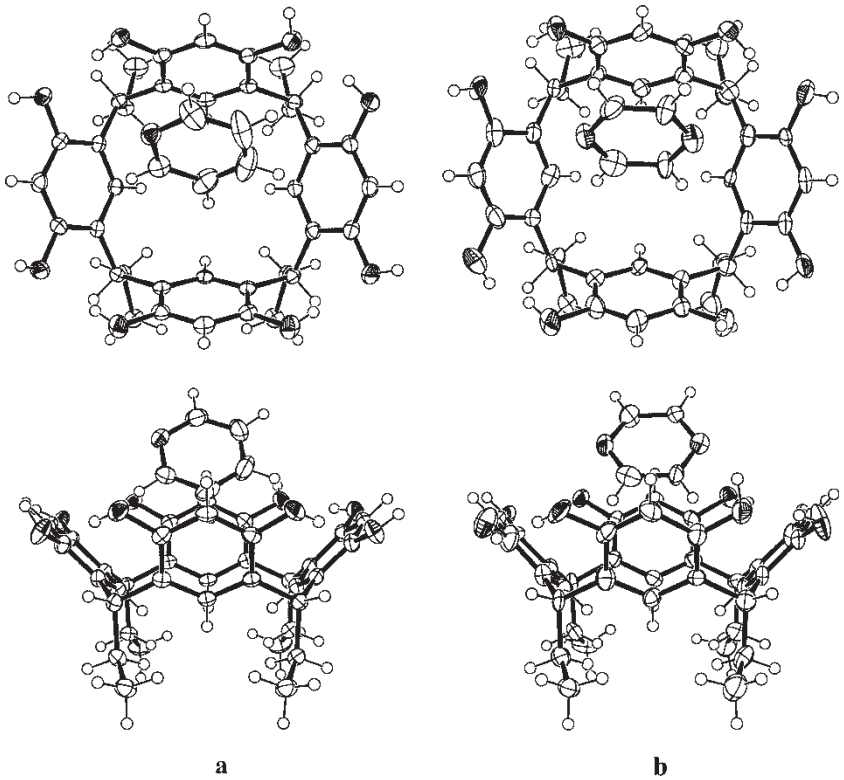

FIGURE 3 Top and side views of **10** (a) and **11** (b). Solvents are excluded for clarity.

hosts. This time hydrogen-bonding contacts between hosts are via solvent ethanols.

The obvious structural similarity of pyridine and pyrazine leads to a great similarity in the crystal structures of their complexes and even in crystallographic parameters of the complexes. The unit cells of two structures are not very far away from each other but still not isomorphous, mostly owing to the small difference in the orientation of the cation and in solvents.

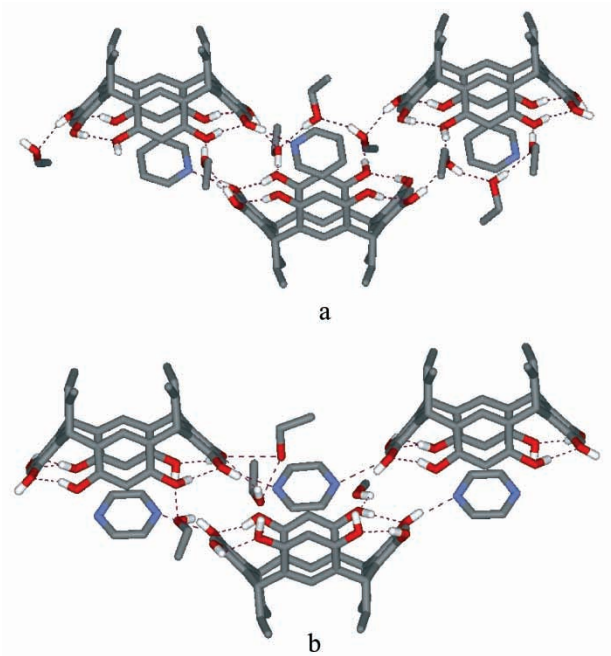

FIGURE 4 Crystal packing of **10** (a) and **11** (b). Non-hydrogen bonding hydrogens are excluded for clarity. Hydrogen bonds are shown as broken lines. (See colour plate 3 at the end of this issue.)

Earlier crystallization studies of alkyl resorcinarenes, mainly methyl resorcinarene, with pyridine have resulted in similar structures in which one of the pyridine molecules present in the structure is included in the cavity [10,11].

The third six-membered heteroaromatic compound 2-pyridylmethanol (**6**) contains an additional functionality, i.e. a $-CH_2OH$ group next to nitrogen, which gives a great deal of new possibilities in hydrogen bonding and thus in complexation and crystal packing. An excellent example of the possibilities of additional functionalities was the crystallization with melamine, which resulted in a conformational change in ethyl resorcinarene (1) [17]. This time, no conformational change occurs, but still there is some resemblance between these structures.

Although the crystallization was performed in a 1:1 molar ratio, the 1:4 complex **12** $\{[\mathbf{1}\cdot\mathbf{6}]\cdot\mathbf{6}_3\cdot H_2O\}$ crystallized out (Fig. 5). One of the guests is included in the cavity, two are hydrogen-bonded to hydroxyl groups similarly to melamine molecules in our previous study, and interestingly, one is bound between the lower rim ethyl chains. The cavity is

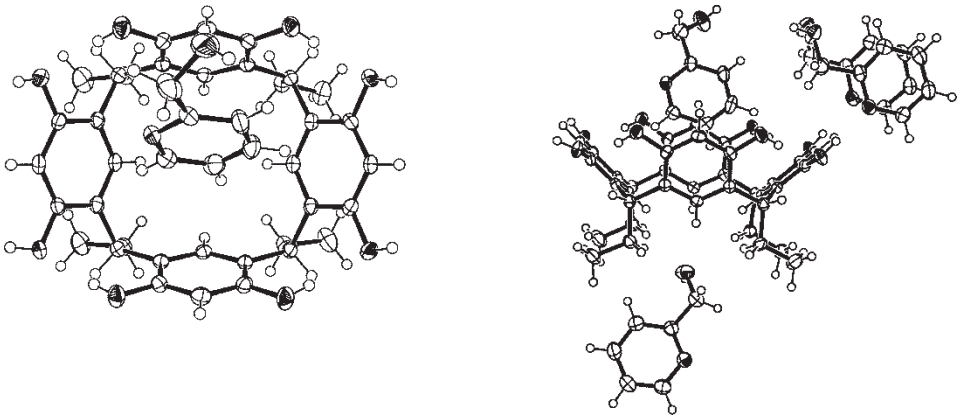

FIGURE 5 Top and side views of **12**. Non-included guests are excluded from top view picture for clarity. Water is excluded from both orientations.

again a pinched crown (the distances between the centroids of the opposite aromatic rings are Ct01···Ct03 = 6.24 Å and Ct02···Ct04 = 7.32 Å) and the included 2-pyridylmethanol (**6**) in **12** interacts with the host by π···π and CH···π interactions [Ct03···Ct(guest) = 3.67 Å; C55···Ct01 = 3.48 Å, C54···Ct02 = 3.50 Å, C56···Ct04 = 3.59 Å] like the other N-heteroaromatics. The orientation of the ring is the same as that of pyridine, but in this case, in addition to optimal CH···π interactions, the sterical reasons caused by the bulky $-CH_2OH$ group force the guest to adopt this orientation.

The location of the second guest between the lower rim ethyl chains indicates the suitability of simple alkyl resorcinarenes, at least in the solid state, to accommodate a guest also at the lower rim. Previously, we have observed the inclusion of spherical anions at the lower rim [18,19], but still, the binding of neutral, more complicated and larger systems, such as 2-pyridylmethanol (**6**), is quite surprising. The guest interacts with lower rim ethyl chains via weak CH···O hydrogen bonds of length 3.67–4.01 Å, i.e. the side chain $-CH_2OH$ is embedded between the alkyl chains. However, the alkyl chains are bent such that the hydrogen bonding of 2-pyridylmethanol to water is still possible. It is difficult to estimate whether the CH···O hydrogen bonds are the force which drive the guest to the lower rim or if the driving forces are the efficiency of packing and the sterical reasons.

Hydrogen bonding of two remaining 2-pyridylmethanol molecules resembles the binding of melamines in earlier determined crystal structure [17]. The molecules lie very close to each other (π-stacking; the distance between the centroids of the aromatic rings is 4.03 Å) and are hydrogen-bonded to the host (Table I) and to each other [O37···O44 = 2.717(2) Å]. With melamine, additional functionalities cause the conformational change because of the maximum amount of hydrogen bonds; this time, one hydroxyl group and aromatic nitrogen are not enough to change the conformation.

The crystal packing of 1:4 complex **12** is far more complicated than the packing of a simpler 1:1 complex. The guest is able to act as both hydrogen bond acceptor and donor, and it is larger and more flexible from its side chain, which gives it several possibilities for weak interactions and different orientations. Thus, no clear chain-like packing is observed but a complicated network of hosts and guests connected together by hydrogen bonds and various π interactions. All types of hydrogen bonds, i.e. host–host, host–guest, host–solvent and guest–solvent, are present in the structure (Fig. 6).

Ten-membered Heteroaromatic Ring Quinoline (7)

The largest N-heteroaromatic guest quinoline (**7**) appears to be too large to be included in the cavity of the ethyl resorcinarene (**1**), since the crystal structure

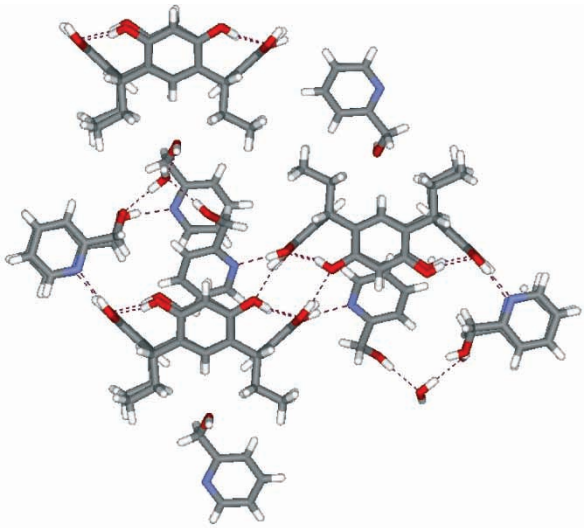

FIGURE 6 Crystal packing of **12**. Hydrogen bonds are shown as broken lines. (See colour plate 4 at the end of this issue.)

of complex **13** {1·7·2CH_3CN} reveals that quinoline is included in the crystal lattice, and the cavity is occupied by a solvent acetonitrile. However, the conclusion about the size being too large may not be totally unambiguous, since, according to our experience with crystallization of ethyl resorcinarene complexes, the affinity of ethyl resorcinarene (**1**) towards acetonitrile is quite significant, and other less competitive solvents might produce different results if the large guest adopts a suitable orientation in the cavity [20]. In this case, still, the crystallization from ethanol failed, but in the future, other possible solvents will be explored.

The earlier extensive studies with larger nitrogen heterocycles, such as the widely used bipyridines indicate that 4,4′-bipyridine is not usually included in the cavity but is hydrogen-bonded to hydroxyl groups and linking two hosts together, and the cavity is occupied by a smaller molecule, e.g. solvent [10,13–15]. 2,2′-Bipyridine [21] and nine-membered caffeine [22], however, are included in the cavity indicating that quinoline is not too large to fit the cavity.

One acetonitrile molecule is included in the cavity obliquely 56° from the normal of the vertical orientation via CH-π interactions (the distance between the methyl group and the centroids of the aromatic rings of the host is 3.50–3.63 Å). The second acetonitrile is situated between the lower-rim ethyl chains (Fig. 7) similarly to the 2-pyridylmethanol in complex **12** and spherical halogen anions in resorcinarene capsules [18,19]. The shortest distances between the nitrogen and surrounding ethyl chains vary from 3.77 Å to 3.89 Å and indicate CH···N

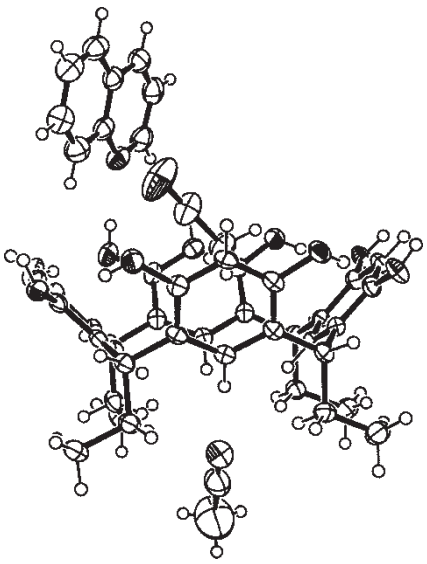

FIGURE 7 Side view of **13**. Quinoline (**7**) is hydrogen-bonded outside the cavity, and the cavity is occupied by a molecule of solvent acetonitrile. The second acetonitrile is situated in between lower-rim ethyl chains.

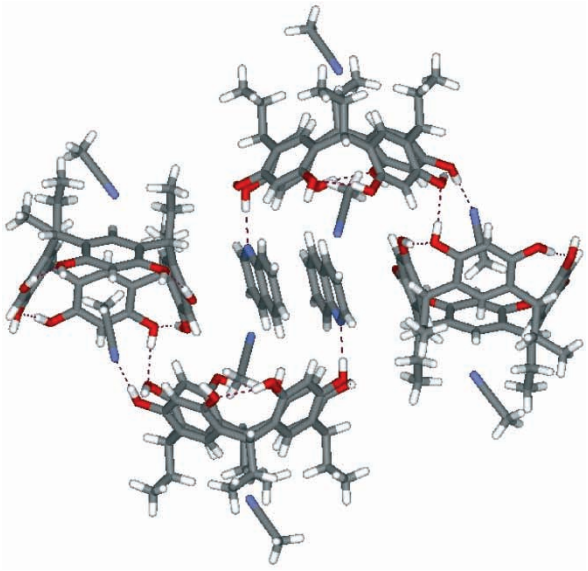

FIGURE 8 The crystal packing of **13**. Hydrogen bonds are shown as broken lines. (See colour plate 4 at the end of this issue.)

interactions as being the driving force for binding. The binding of acetonitrile at the lower rim further confirms the suitability of lower-rim alkyl chains in accommodating at least some electronegative groups or anionic species, while the π electron-rich cavity is suitable for binding neutral and cationic guests.

The quinoline is hydrogen-bonded to one host and π-stacked between the other host and adjacent quinoline molecule (Fig. 8), indicating that ethyl resorcinarene has some affinity for this large guest, even if the complexation may not occur by inclusion with its cavity. However, as mentioned earlier, the effect of the solvent is difficult to estimate without further investigations, so no clear conclusions about the largest possible guest can be drawn. The crystal packing is governed by the presence of the large guest in the crystal lattice, the intermolecular hydrogen bonding between opposing hosts and the H-bonding from included solvent to the opposing host.

CONCLUSIONS

Ethyl resorcinarene (**1**) has proven to be a suitable host for N-heteroaromatic five- and six-membered planar guests, such as imidazole (**2**), 1,2,4-triazole (**3**), pyridine (**4**), pyrazine (**5**) and 2-pyridylmethanol (**6**). A larger, 10-membered quinoline (**7**), however, may be too large for inclusion in the cavity. A definite conclusion about this cannot be drawn because of the competitive inclusion of acetonitrile in the cavity, and thus additional crystallization experiments in different solvents will be carried out to confirm the observation reported in this study.

TABLE II Crystal data for ethyl resorcinarene complexes **8**–**13**

Compound	**8**	**9**	**10**	**11**	**12**	**13**
Formula	$C_{36}H_{39}O_8^- \cdot C_3H_5N_2^+ \cdot C_2H_5OH$	$C_{36}H_{40}O_8 \cdot 2\,C_2H_3N \cdot 0.5\,C_2H_5OH$	$C_{36}H_{40}O_8 \cdot C_5H_5N \cdot 3\,C_2H_5OH$	$C_{36}H_{40}O_8 \cdot C_4H_4N_2 \cdot 2\,C_2H_5OH$	$C_{36}H_{40}O_8 \cdot 4\,C_6H_7NO \cdot H_2O$	$C_{36}H_{40}O_8 \cdot C_9H_7N \cdot 2\,CH_3CN$
Formula weight	714.83	761.86	817.98	772.94	1055.20	811.94
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1$ (No. 4)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a/Å	30.9353(3)	10.9695(3)	10.8118(3)	10.9992(4)	16.9095(3)	15.004(4)
b/Å	16.0663(4)	12.0019(4)	12.1679(2)	16.9882(4)	13.4250(3)	12.3010(2)
c/Å	18.0661(5)	16.6744(5)	17.1502(4)	11.9442(4)	24.4616(3)	24.2949(7)
α/°	90	109.480(1)	91.576(1)	90	90	90
β/°	123.980(1)	92.880(2)	91.330(1)	103.703(2)	100.433(1)	107.032(1)
γ/°	90	102.793(2)	103.468(1)	90	90	90
Volume/Å^{-3}	7445.8(3)	1999.8(1)	2192.33(9)	2168.3(1)	5461.2(2)	4287.3(2) Å^3
Z	8	2	2	2	4	4
Density (calc.)/Mg·m^{-3}	1.275	1.265	1.239	1.179	1.283	1.258
Abs. coefficient/mm^{-1}	0.090	0.090	0.087	0.083	0.090	0.085
Refl. collected/unique/R_{int}	18,950/8773/0.038	10,385/6876/0.019	11,818/7662/0.032	10,210/6780/0.030	26,308/9596/0.036	22,296/7563/0.047
Refl. used in refinement	6502	5839	6063	4870	7298	5269
Final R indices ($I > 2\sigma I$)	0.050/0.104	0.063/0.184	0.079/0.212	0.076/0.210	0.043/0.092	0.048/0.098
R indices (all data)	0.076/0.115	0.073/0.193	0.097/0.227	0.109/0.246	0.065/0.101	0.083/0.111

The inclusion of 2-pyridylmethanol (**6**) indicates that additional functionalities and small side chains do not prevent the complexation into the cavity but create a great diversity and complexity to crystal packing compared with simpler aromatic nitrogen heterocycles. Enhanced hydrogen-bonding possibilities also facilitate the complexation in a 1:4 host–guest molar ratio.

The binding of 2-pyridylmethanol and acetonitrile between the lower-rim ethyl chains supports the earlier observed binding of spherical halogen anions at the lower rim of resorcinarene capsules [18,19] and indicates the dual binding nature of the alkyl resorcinarenes: anionic or a molecule with some electronegative character may be bound between the lower-rim alkyl chains simultaneously when a neutral, cationic or partially positively charged molecule is bound in the π electron-rich cavity.

Deprotonation of the host and protonation of the guest were observed only with imidazole (**2**) as a guest. The reason for this is the relative basicity of the aromatic nitrogen heterocycles (which, in all tested cases, is quite weak), the only one strong enough being imidazole, as manifested by its ability to deprotonate the host ethyl resorcinarene.

The packing motifs of five- and six-membered guests are fairly similar, i.e. chain-like, except for 2-pyridylmethanol, the additional functionalities and different host-to-guest ratio of which complicate the packing. The larger size and different nature of complex **13** (clathrate-type) define the crystal packing of the quinoline complex. In all cases, however, the hydrogen bonding is also the driving force in packing.

Further investigations on the complexation of planar guests is required in the future, not only to explore how large planar guests could still be included in the cavity, but also to investigate the role of side chains and additional functionalities as well as complexation of N-heteroaromatic cations and the role of different anions in the complexation. Also, studies in solution will clarify the complexation phenomena.

EXPERIMENTAL

Suitable single crystals for X-ray analysis were obtained by slow evaporation of the ethanol (**8**, **9**, **10**, **11** and **12**) or acetonitrile (when the crystallization from ethanol failed, **13**) solutions. Host–guest molar ratios of 1:1 were used in all cases.

The X-ray crystallographic data for all complexes were recorded with a Nonius Kappa CCD diffractometer. Graphite monochromatized MoK_α radiation [$\lambda(MoK_\alpha) = 0.71073$ Å] and a temperature of 173.0 ± 0.1 K were used in all cases. The CCD data were processed with Denzo-SMN v0.93.0 [23], and all structures were solved by direct methods (SHELXS-97 [24]) and refined on F^2 using full-matrix least-squares techniques (SHELXL-97 [25]). The hydrogen atoms were calculated to their idealized positions with isotropic temperature factors (1.2 or 1.5 times the carbon temperature factor) and refined as riding atoms, except for hydrogen-bonding hydrogens, which were located from the difference Fourier, but in the final refinement also fixed similarly. Hydrogen atoms for water molecules in **12** were located from the difference Fourier and refined freely. Hydrogen atoms for disordered ethanol of **11** were not determined.

Solvent ethanol of **9** and two ethanol molecules of **11** were refined with the site occupation factor of 0.5. The quinoline in **13**, methyl group of the one of the ethanol molecule in **10** and hydroxyl group of one of the ethanols in **11** were disordered over two positions. The disordered ethanol in **11** was refined isotropically. The structure of **11** could also be solved in space group $P2_1/m$, but owing to the disorder of the solvents, the refinement could not be completed in this space group. Thus, a lower symmetry space group $P2_1$ was used.

The residual electron density below 1.20 e.Å^{-3} was found in **9** and **10** near the disordered ethanol molecules. See Table II for detailed crystallographic data.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-196105–CCDC-196110. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033 or deposit@ccdc.cam.ac.uk).

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