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Preparation and X-ray structures of two crystalline complexes between macrocyclic pyridino hosts and benzonitrile

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The preparations of solid-state benzonitrile complexes of two oligoaryl-condensed crown hosts are described and their crystal structures are reported. Benzo-di[(2,3)naphtho]-(2,6)pyridino-21-crown-7 (1) forms a crystalline 1:3 (host:guest) complex (1a) while benzo-di[(1,4)benzeno]-(2,6)pyridino-25-crown-7 (2) forms a 2:1 crystalline complex (2a) with PhCN. Crystal data: 1a [$P\bar{1}$, $a = 13.455(3)$, $b = 15.313(2)$, $c = 13.371(4)$ Å, $\alpha = 103.75(2)$, $\beta = 109.00(2)$, $\gamma = 103.63(2)°$, $Z = 2$], **2a** [$C2/c$, $a = 37.105$, $b = 17.410(8)$, $c = 8.598(3)$ Å, $\beta = 90.89(2)°$, $Z = 4$]. **Both compounds are lattice-type complexes showing no significant host-guest contacts. The crystal structures are stabilized by dipole-dipole, stacking and van-der-Waals interactions.**

INTRODUCTION

Crystalline complex formation between crown compounds and CH-acidic organic molecules is well documented.[1–3] These complexes show characteristic host-guest H-bonding modes. Complexation of alcohols in the solid state is typical of a particular family of semi-rigid pyridino-crowns.[1,4] Depending on the bulk of substituents and aryl condensations, these latter crown compounds are also capable of complexing aprotic organic molecules such as DMF[5] or dioxane[6] in a cavitate[7] or lattice-type (clathrate)[8] inclusion manner. Complexation of aryl-containing guest molecules by using a semi-rigid pyridino crown has been successful only recently.[9] Since many aromatic solvents are considered environmental pollutants,[10] their complexation or inclusion is of fundamental and practical interest. Hosts with corresponding inclusion properties are thus potentially useful to develop chemical sensors[11] and absorptive materials[12] for toxicant aromatic compounds such as benzonitrile.[10]

In this context, the crystalline complexes **1a** and **2a** formed of pyridino crowns **1**[6] and **2**[13] with benzonitrile, respectively, aroused our interest. Structural studies of **1a** and **2a** were undertaken to rationalize the crystalline complexation behavior of macrocycles **1** and **2** to benzonitrile, and to uncover structural parameters for future design of macrocyclic hosts destined for the complexation of this and other aromatic solvents. Here we report preparation and complete X-ray structural results of the two complexes **1a** and **2a** showing very different macrocyclic host: benzonitrile guest stoichiometric ratios (1:3 or 2:1).

RESULTS AND DISCUSSION

Synthesis

The host macrorings **1** and **2** were synthesized from 2,6-bis(chloromethyl) pyridine and the corresponding diphenol constituents using known ring closure reactions.[6,13] The crystalline complexes **1a** and **2a** were obtained by slow concentration of benzonitrile solutions of **1** and **2**, whereas usual recrystallization conditions from hot solutions yielded the unsolvated host compounds (in nonsuitable crystal quality for X-ray analysis).

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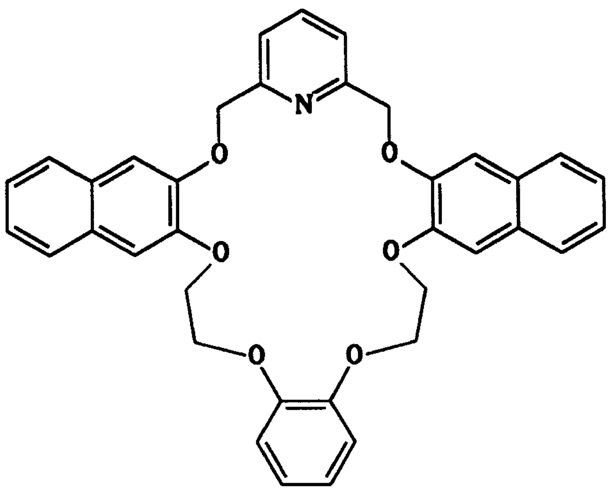
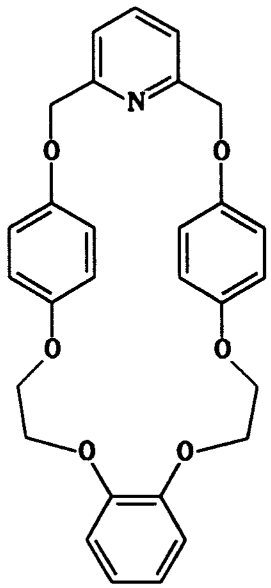


1 1a : 1 · 3 PhCN



2 2a : $(2)_2$ · PhCN

X-ray analysis

(1) Structure description of 1a [1·PhCN (1:3)]. *Molecular structure.* A perspective view along with the atom labels of the complex is shown in Fig 1. The bond parameters of the present macrocycle exhibit no anomalies except that the C(ar)-C(ar) bonds at the fusion of naphthalene groups are slightly lengthened [C(5)-C(6) 1.432 Å, C(17)-C(18) 1.432 Å]. A similar fact was observed for an analogous dinaphthopyridino crown in its acetonitrile complex[14] which may be a result of strong O···O repulsions. In the present complex the nonbonded intramolcular O···O short contacts, O(4)···O(7), O(10)···O(13) and O(16)···O(19) are 2.547(5), 2.605(4) and 2.541(5) Å, respectively, that is significantly less than the sum of their van-der-Waals radii (2.8 Å),[15] which imposes severe strain in the conformation of the macrocycle.

The macrocycle (1) has an approximate mirror running through the atoms N(1) and C(23) of the pyridine ring and bisecting the opposite phenylene ring with the exception of the torsion angles about the bond O(10)-C(11) and C(12)-O(13) (endocyclic torsion angles in Table 1). The overall conformation of the macrocycle is *ag*$^+$*aasaag*$^-$*aasaag*$^+$*aasaag*$^-$*a*, starting from the N(1)-C(2) bond. As a result, the macrocycle exhibits a conformation which has two concave faces (Figure 1): one of the concave faces (*A*) is flanked by the two highly shielding naphthalene groups while the other concave face (*B*) is flanked by the pyridino and benzo moieties. The concave face (*A*) has a conformation similar to a boat with the hetero atoms O(4), O(7), O(16) and O(19) lying in a plane whose maximum deviation from planarity is 0.067(4) Å and forming the base of the boat. The dihedral angle between the two naphthalene planes is 72.8(1)°. The other concave face (*B*) has a rough appearance of a cradle with the hetero atoms O(4), O(10), O(13) and O(19) being nearly planar, the maximum deviation from planarity is −0.043(3) Å. The dihedral angle between the pyridino and benzo moieties is 27.7(2)°. The diameter of the macrocycle is about 5.3 Å, in principle large enough for the benzonitrile guest to fit in via its rod-like nitrile group.

Table 1 Endocyclic torsion angles (deg) observed in 1a

Atoms	*Angle*
C(21)-N(1)-C-2)-C(3)	−178.1(5)
N(1)-C(2)-C(3)-O(4)	94.9(5)
C(2)-C(3)-C(4)-C(5)	−167.5(5)
C(3)-O(4)-C(5)-C(6)	176.7(5)
O(4)-C(5)-C(6)-O(7)	5.0(7)
C(5)-C(6)-O(7)-C(8)	177-1(4)
C(6)-O(7)-C(8)-C(9)	−170.9(4)
O(7)-C(8)-C(9)-O(10)	−74.1(5)
C(8)-C(9)-O(10)-C(11)	178.6(4)
C(9)-O(10)-C(11)-C(12)	−172.9(4)
O(10)-C(11)-C(12)-O(13)	−1.1(6)
C(11)-C(12)-O(13)-C(14)	−6.1(4)
C(12)-O(13)-C(14)-C(15)	−178.4(4)
O(13)-C(14)-C(15)-O(16)	78.0(5)
C(14)-C(15)-O(16)-C(17)	164.7(4)
C(15)-O(16)-C(17)-C(18)	−178.8(4)
O(16)-C(17)-C(18)-O(19)	−3.9(7)
C(17)-C(18)-O(19)-C(20)	−177.7(5)
C(18)-O(19)-C(20)-C(21)	157.6(5)
O(19)-C(20)-C(21)-N(1)	−81.3(6)
C(20)-C(21)-N(1)-C(2)	176.1(5)

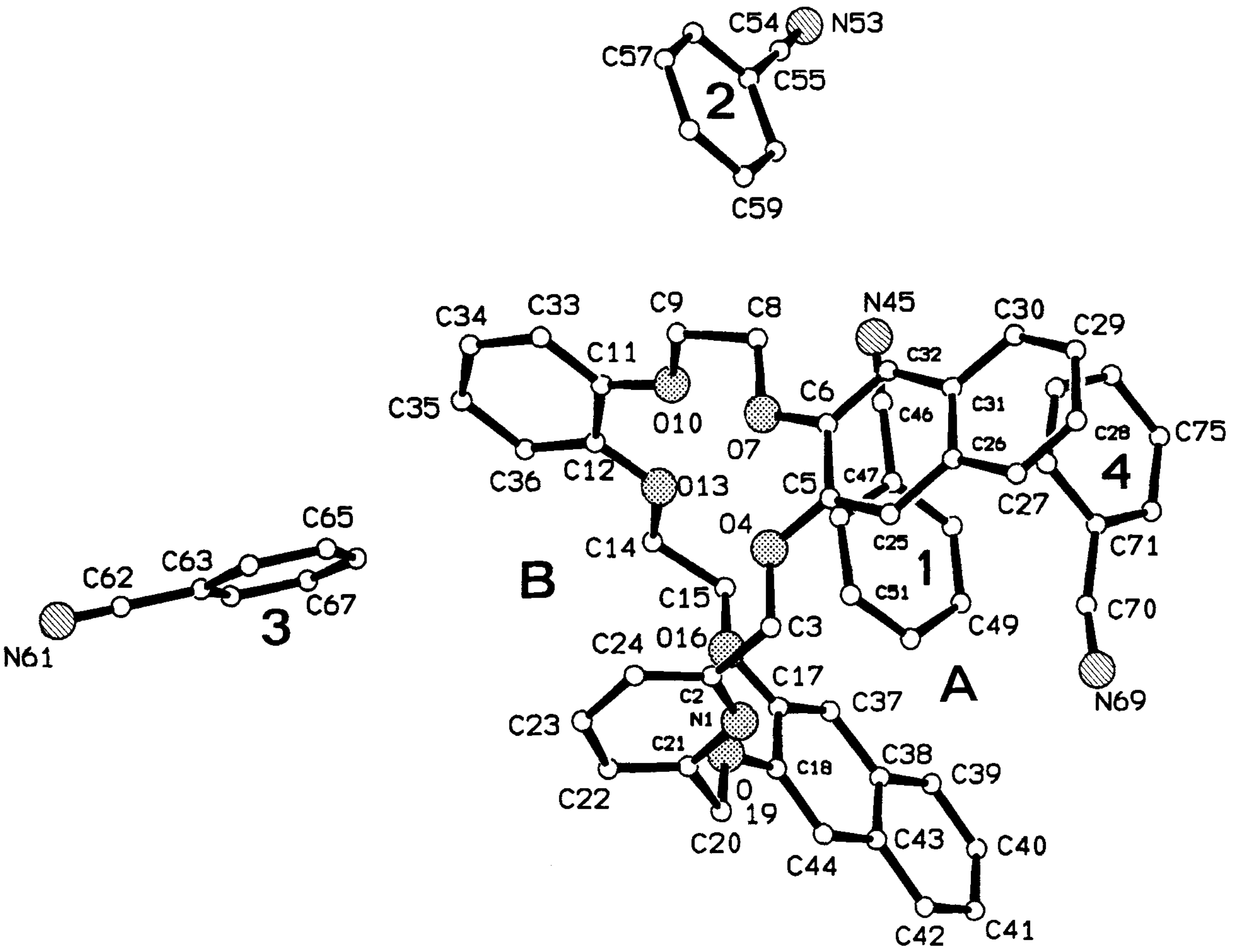


Figure 1 Perspective view and atom numbering scheme of **1a** [1·PhCN (1:3)] showing the two disordered PhCN molecules (*3*) and (*4*). H atoms are omitted; heteratoms are shaded.

Packing structure. A stereoview of the molecular packing in the unit cell viewed down the *c*-axis is shown in Fig 2. There are three benzonitrile molecules (*cf.* Fig 1) in the asymmetric unit with one of the benzonitrile guests being disordered about the centers of inversion [(*3*) 1.0, 0.5, 0.5 and (*4*) 1.0, 0.5, 0.0]. These disordered guest molecules (*3* and *4*) do not have any interaction with the macrocycle. In fact, the guest molecules *3* and *4* occupy open inter-host channels aligned parallel to the *c*-axis and centred around (0, 0.5, *z*). Among the other two benzonitrile guests (*1* and *2*), *1* lies on the side of the concave face *A* of the host with its nitrogen atom N(45) pointing away from the macrocycle. On the other hand, the aromatic ring of benzonitrile *1* is disposed towards the macrocycle, with its carbon atom C(52) interacting with the oxygen atom O(7) of the macrocycle through a C-H···O type of interaction[16] [C(52)···O(7) = 3.327(8) Å, H(36)···O(7) = 2.53 Å, C(52)···O(7) = 126(5)°] (Table 2). The pyridine nitrogen [N(1)] points toward the concave face *A* but it does not interact with any of the guest molecules. Unlike *1*, the benzonitrile guest *2* does not participate in any significant interaction with the host macrocycle, however, it interacts weakly with the translationally related macrocycles and with the translationally related benzonitrile guest *1*.

The complex is unstable when removed from solvent and this may be due to the slow evaporation of the disordered benzonitrile guests *3* and *4* that occupy the open inter-host channels, while the structural environment of guests *1* and *2* is more restricted. Intermolecular stacking interactions between the centrosymmetrically related pyridine rings, on one hand, and between the naphthalene rings (Fig 2), on the other hand, provide additional stability to the crystal structure.

(2) Structure description of 2a [2·PhCN (2:1)]. *Molecular structure.* A perspective view including the atom numbering scheme of the present complex is shown in Fig 3.

As for **1a**, the bond parameters of the crown

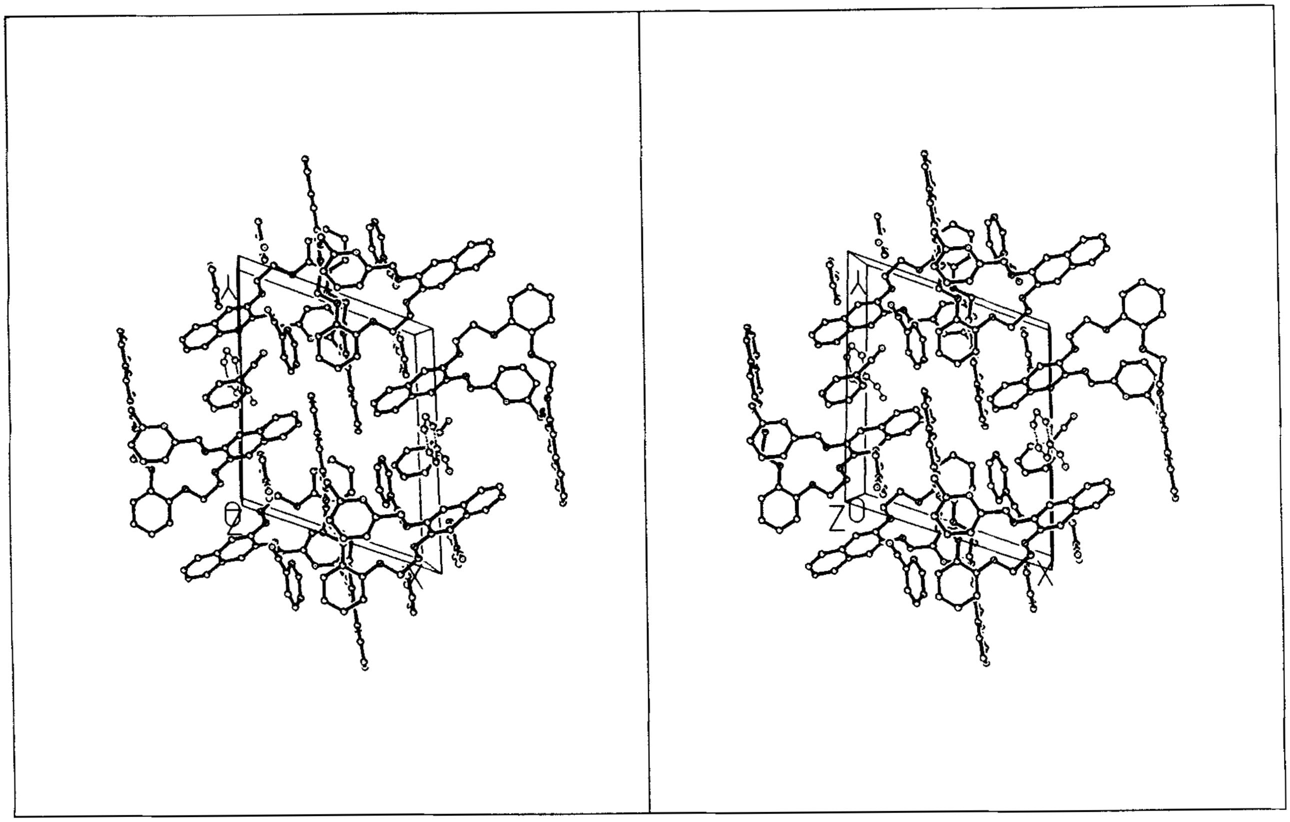


Figure 2 Stereoscopic packing diagram of **1a** [**1**·PhCN (1:3)]. The disordered molecules of PhCN are specified by normal and thin line drawing.

Table 2 C-H···O type of interactions observed in 1a

Donor-H (Å)	*Donor···Acceptor* (Å)	*H···Acceptor* (Å)	*Donor-H···Acceptor* (deg)
C(52)-H(36) 1.14(7)	C(52)···O(7) i 3.327(8)	H(36)···O(7) 2.53(7)	C(52)-H(36)···O(7) 126(5)
C(14)-H(8) 1.08(4)	C(14)···O(13) ii 3.401(6)	H(8)···O(13) 2.71(5)	C(14)-H(8)···O(13) 122(3)
C(24)-H(15) 1.10(6)	C(24)···O(16) ii 3.435(7)	H(15)···O(16) 2.73(6)	C(24)-H(15)···O(16) 121(4)
C(23)-H(14) 1.09(5)	C(23)···O(16) iii 3.417(6)	H(14)···O(16) 2.75(5)	C(23)-H(14)···O(16) 119(3)

Equivalent positions: i x, y, z
ii $-x+1, -y, -z+1$
iii $-x+1, -y, -z$

compound in **2a** are also normal and correspond to related macrocycles[13,17] with some minor exceptions, e.g. the bond lengths C(5)-C(29) 1.344(5) Å of 1,4-phenylene ring *B*, and C(sp^3)-O bonds C(3)-O(4) 1.413(5) and C(24)-O(23) 1.419(5) Å are remarkably short.

The macroring (**2**) adopts a conformation with the torsion code $ag^+g^+sasaaag^-aasaag^+aaasasg^+aa$, starting from the N(1)-C(2) bond (endocyclic torsion angles in Table 3). The two ethyleneoxy groups [O(9)-C(10)-C(14)-O(15) and O(15)-C(16)-C(17)-O(18)] are conform to the expected ±*gauche*.[18] On the other hand, the torsion angles about C(3)-O(4) and O(23)-C(24) deviate from the usual *anti*[18] due to the steric hindrance between the pyridine ring and the two flanking 1,4-phenylene groups. The torsion angles in this section of the macrocycle adjust such that the pyridine and the two 1,4-phenylene rings are

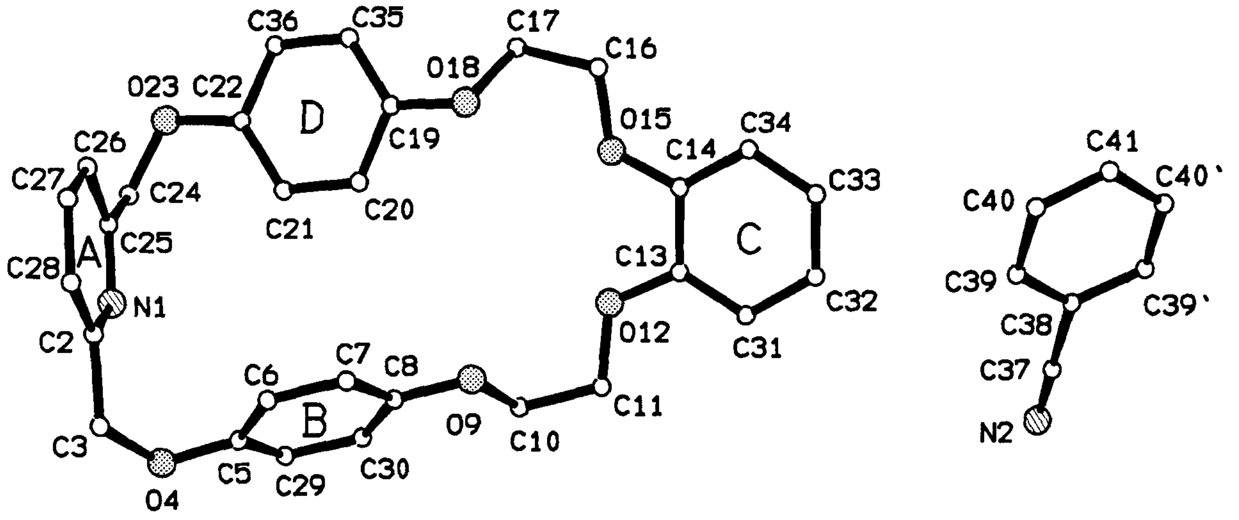


Figure 3 Perspective view and atom numbering of **2a** [2·PhCN (2:1)]. H atoms are omitted; heteroatoms are shaded.

Table 3 Endocyclic torsion angles (deg) observed in 2a

Atoms	*Angle*
C(25)-N(1)-C(2)-C(3)	−179.1(4)
N(1)-C(2)-C(3)-O(4)	34.8(5)
C(2)-C(3)-O(4)-C(5)	57.5(5)
C(3)-O(4)-C(5)-C(6)	19.3(5)
O(4)-C(5)-C(6)-C(7)	179.3(3)
C(5)-C(6)-C(7)-C(8)	−0.1(6)
C(6)-C(7)-C(8)-O(9)	−179.0(3)
C(7)-C(8)-O(9)-C(10)	172.4(3)
C(8)-O(9)-C(10)-C(11)	−174.2(3)
O(9)-C(10)-C(11)-O(12)	−74.0(3)
C(10)-C(11)-O(12)-C(13)	174.4(3)
C(11)-O(12)-C(13)-C(14)	−165.9(3)
O(12)-C(13)-C(14)-O(15)	−1.8(5)
C(13)-C(14)-O(15)-C(16)	160.1(3)
C(14)-O(15)-C(16)-C(17)	−178.8(3)
O(15)-C(16)-C(17)-O(18)	58.6(3)
C(16)-C(17)-O(18).C(19)	−167.5(3)
C(17)-O(18)-C(19)-C(20)	143.7(3)
O(18)-C(19)-C(20)-C(21)	174.4(3)
C(19)-C(20)-C(21)-C(22)	0.2(5)
C(20)-C(21)-C(22)-O(23)	−179.6(4)
C(21)-C(22)-O(23)-C(24)	5.8(5)
C(22)-O(23)-C(24)-C(25)	68.2(4)
O(23)-C(24)-C(25)-N(1)	−146.6(4)
C(24)-C(25)-N(1)-C(2)	178.8(4)

approximately perpendicular to each other with the dihedral angles between them being 75.4(1)° for rings *A* and *B*, 97.2(1)° for *A* and *D*, and 77.2(1)° for rings *B* and *D*. Among the nonbonded O···O distances, O(12)···O(15) 2.546(3) and O(15)···O(18) 2.664(5) Å are relative short (sum of the van-der-Waals radii 2.8 Å).[15] Also, the *gauche* torsion angles of 34.8(5) and 57.5(5)° about C(2)-C(3) and C(3)-O(4), respectively, give rise to a relative short nonbonded N···O distance, N(1)···O(4) 2.762(4) Å. The other nonbonded N···O distance [N(1)···O(23)] is 3.589(4) Å. Short O···O and N···O distances of the given range are not unusual for crown compounds.[2,9,18]

Packing structure. A stereoview of the molecular packing in the unit cell projected down the *c*-axis is shown in Fig 4. The macrocycles are arranged in the crystal lattice such that they form a close packing and there is no macrocyclic cavity available for molecular inclusion. On the contrary, such an arrangement has given rise to channels parallel to the *c*-axis at the corners and the centre of the *ab*-face, where the benzonitrile guests are located in nearly perpendicular orientation relative to the *c*-axis. The pyridine nitrogen [N(1)] is in a favorable position for dipole-dipole interaction giving rise to a weak contact between N(1) and C(40) of the benzonitrile guest [C(40)···N(1) $(0.5-x,\ 0.5+y,\ 0.5-z)=3.523(8)$ Å]. Other dipole-dipole interactions which stabilize the crystal are C(26)···O(23) 2.873(5) Å; C(26)-H(17)···O(23) 94(3)° and C(30)···O(15) 3.360(4) Å; C(30)-H(21)···O(15) 142(5)°. In addition to this, stacking interactions between the symmetry related guest molecules and between the centrosymmetrically related pyridine rings are seen in the packing.

CONCLUSIONS

The incorporation of aryl condensations in specified positions of a crown ring involves significant changes of the conformation and leads to particular solid state

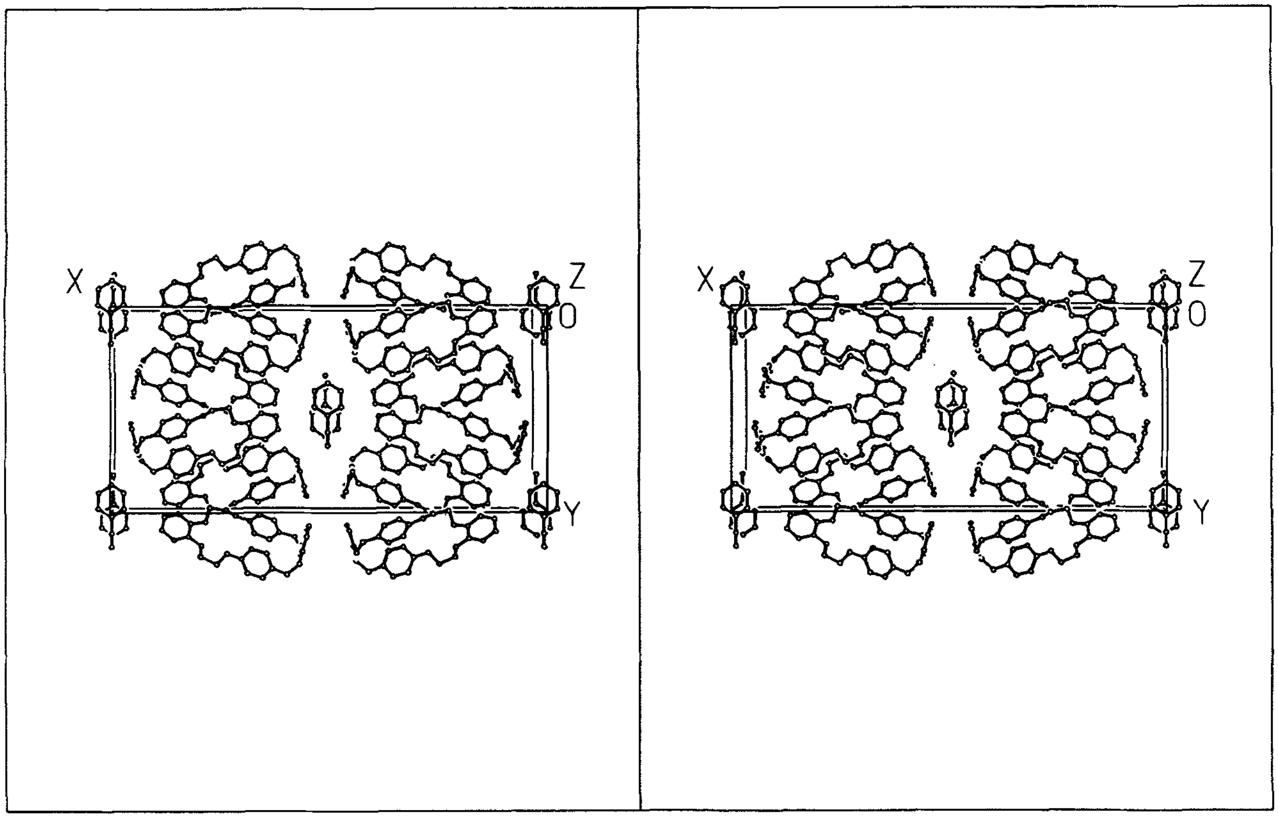


Figure 4 Stereoscopic packing diagram of **2a** [2·PhCN (2:1)].

complexation properties towards uncharged organic molecules. In the present case, the crown compounds 1 and 2 are two of the rare examples of macrocycles yielding crystalline complexes with benzonitrile.[6,9]

The structural study of the 1:3 complex between benzodinaphthopyridino-21-crown-7 (**1**) and benzonitrile reveals that the substitution of sterically demanding naphthalene groups at the flanking positions of the macrocycle gives rise to a biconcave surface which is differentiated by the guest molecules. That is, the host-guest association with one of the benzonitrile guests is through the concave face shielded by the two naphthalene units. The other benzonitriles are included in lattice cavities (Figs 1 and 2).

Incorporation of 1,4-phenylene building blocks into a crown ring, such as in **2**, is shown to have an adverse effect on the crystal conformation of an expected active host molecule. Unlike **1**, the macrocycle **2** in the crystal lattice of its complex with PhCN (**2a**) is arranged such as to form a close packing and there is no macrocyclic cavity available for molecular inclusion. Instead, the benzonitrile guests are located in channels at the corners and centre of the *ab*-face of the unit cell (Figs 3 and 4).

The pyridine nitrogen, though available in **1** and **2**, does not participate in the host-guest interaction neither in **1a** nor in **2a**. Similar observations were noted for the acetonitrile complexes of analogous aryl-condensed pyridino crowns.[14,19] This suggests that the pyridine nitrogen is not an important binding site for the interaction with dipolar aprotic guest molecules. On the other hand, oligoaryl-condensed crown compounds encourage both molecular inclusion and lattice type inclusion[1,8] depending on the kind of aromatic units and its positions in the frame.

EXPERIMENTAL SECTION

Compound preparation

The macrocycles **1** and **2** were synthesized as described previously.[6,13] Single crystals of **1a** [1·PhCN (1:3)] and **2a** [2·PhCN (2:1)] were obtained by slow concentration of benzonitrile solutions of **1** and **2**.

Crystallography

(a) Data collection. The selected single crystals of

Table 4 Crystal data

compound	**1a**	**2a**
formula unit	$C_{37}H_{31}NO_6{\cdot}3(C_6H_5CN)$	$(C_{29}H_{27}NO_6)_2{\cdot}C_6H_5CN$
formula wt	895.02	1074.19
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$
cell dimensions		
a, Å	13.455(3)	37.105(13)
b, Å	15.313(2)	17.410(8)
c, Å	13.371(4)	8.598(3)
α, deg	103.75(2)	90
β, deg	109.00(2)	90.89(3)
γ, deg	103.64(2)	90
V_c· Å^3	2378.9(11)	5553.6(37)
D_c, g cm^{-3}	1.249	1.285
D_m, g cm^{-3}	1.25(1)	1.29(1)
Z	2	4
μ, cm^{-1}	6.16 (CuKα)	0.87 (MoKα)
$F(000)$	940.0	2264.0
No. of coll. reflect.	5071	3576
No. of sign. reflect.	4388	2977
Limit of signific.	$I > 3\sigma(I)$	$I > 3\sigma(I)$
R $[=\sum\lvert\Delta F\rvert/\sum\lvert F_0\rvert]$	0.072	0.057
R_w $[=\sum w\lvert F\rvert^2/\sum w\lvert F_0\rvert^2]^{1/2}$	0.080	0.056
Weighting: g in SHELX[a]	0.00012	0.001946
S [goodness of fit]	3.06	0.965
No. of param. refined	658	404
Max./min. peak height in the final Fourier map, e$^-$Å^{-3}	0.58/−0.51	0.20/−0.15

[a] Weights in SHELX[21,22] are estimated as $w=[\sigma^2(F_0)+g|F_0|^2]^{-1}$.

reasonable quality of **1a** and **2a** were put in glass capillaries in order to protect them from possible evaporation during the data collection. Intensity data were obtained with a Enraf-Nonius CAD-4 diffractometer at room temperature, using graphite-monochromatized CuKα radiation ($\lambda = 1.5418$ Å, $2\Theta_{max} = 110°$) for **1a** and MoKα radiation ($\lambda = 0.71073$ Å, $2\Theta_{max} = 55°$) for **2a**. The data were collected by using ω-2Θ scan technique. During the data collection, three standard reflections were monitored every hundred reflections. The maximum intensity variation was less than 4%. The data reduction included corrections for background, Lorentz and polarization effects.[20]

Preliminary photographs on the Weissenberg camera indicated triclinic and monoclinic crystal systems for **1a** and **2a**, respectively. The accurate cell parameters, listed in Table 4, were determined by least-squares refinement of 2Θ values of 25 high angle ($60 < 2\Theta < 90°$) reflections for **1a**, and 20 reflections ($30 < 2\Theta < 40°$) for **2a**.

(b) Structure analysis and refinement. The structure solutions were performed by direct methods using SHELX86.[21] In **2a**, four atoms of the benzonitrile guest were sitting in the special positions *0, y, 0.25*. Both structures were refined by full-matrix least-squares method using SHELX76.[22]

One of the guest molecules of **1a** occurs in two centrosymmetrically related disorder positions with occupancies of 0.5, and was later subjected to constrained least-squares refinement with predetermined geometry. Difference Fourier maps gave all hydrogen positions in both structures, except those of the disordered guest in **1a**, which were neither located nor geometrically fixed. The non-hydrogen atoms of **1a** and **2a**, except those of disordered guest in **1a**, were refined together with their anisotropic thermal parameters. The non-hydrogens of the disordered guest of **1a** as well as hydrogen positions in both structures were refined isotropically. Final R values and other details of refinement calculations are shown in Table 4.

The atomic scattering factors of the non-hydrogen[23] and hydrogen atoms[24] were taken from the literature. Tables V and VI give fractional atomic coordinates and thermal parameters of the non-hydrogen atoms for **1a** and **2a**, respectively. Lists of final atomic coordinates for the hydrogen atoms, bond distances and angles, torsion angles, selected least-squares planes, anisotropic thermal parameters of the non-hydrogen atoms and intermolecular contacts are available from E.W.

Table 5 Final fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2) for nonhydrogen atoms of 1a

Atoms	*x/a*	*y/b*	*z/c*	*Ueq*
N(1)	0.4023(3)	−0.1897(3)	−0.1221(3)	0.058(2)
C(2)	0.3433(4)	−0.1390(3)	−0.1692(4)	0.058(2)
C(3)	0.2204(4)	−0.1842(4)	−0.2135(4)	0.073(3)
O(4)	0.1860(3)	−0.1443(2)	−0.1259(3)	0.065(2)
C(5)	0.0797(4)	−0.1891(3)	−0.1399(4)	0.058(2)
C(6)	0.0527(4)	−0.1497(3)	−0.0479(4)	0.052(2)
O(7)	0.1340(2)	−0.0702(2)	0.0330(2)	0.056(1)
C(8)	0.1071(4)	−0.0264(3)	0.1239(4)	0.056(2)
C(9)	0.1984(4)	0.0682(3)	0.1944(4)	0.055(2)
O(10)	0.2969(2)	0.0524(2)	0.2591(2)	0.052(2)
C(11)	0.3875(3)	0.1335(3)	0.3260(3)	0.046(2)
C(12)	0.4870(3)	0.1170(3)	0.3793(3)	0.045(2)
O(13)	0.4804(2)	0.0238(2)	0.3601(2)	0.049(1)
C(14)	0.5816(3)	0.0089(3)	0.4214(3)	0.050(2)
C(15)	0.5637(4)	−0.0957(3)	0.3902(4)	0.052(2)
O(16)	0.5690(2)	−0.1296(2)	0.2837(2)	0.054(2)
C(17)	0.5811(3)	−0.2157(3)	0.2546(4)	0.050(2)
C(18)	0.5882(4)	−0.2449(3)	0.1479(4)	0.057(2)
O(19)	0.5743(3)	−0.1826(2)	0.0910(3)	0.062(2)
C(20)	0.5757(4)	−0.2070(4)	−0.0196(4)	0.068(3)
C(21)	0.5145(4)	−0.1512(3)	−0.0733(4)	0.057(2)
C(22)	0.5711(4)	−0.0624(4)	−0.0820(4)	0.065(3)
C(23)	0.5066(5)	−0.0130(3)	−0.1329(4)	0.067(3)
C(24)	0.3930(5)	−0.0519(4)	−0.1755(4)	0.065(3)
C(25)	0.0025(4)	−0.2659(4)	−0.2302(4)	0.072(3)
C(26)	−0.1040(4)	−0.3122(3)	−0.2317(4)	0.067(3)
C(27)	−0.1872(5)	−0.3947(4)	−0.3251(5)	0.089(3)
C(28)	−0.2863(5)	−0.4373(4)	−0.3203(6)	0.096(4)
C(29)	−0.3093(4)	−0.4017(4)	−0.2270(6)	0.085(3)
C(30)	−0.2318(4)	−0.3237(4)	−0.1379(5)	0.075(3)
C(31)	−0.1284(4)	−0.2762(3)	−0.1384(4)	0.062(3)
C(32)	−0.0483(4)	−0.1926(3)	−0.0467(4)	0.060(3)
C(33)	0.3858(4)	0.2251(3)	0.3421(4)	0.058(3)
C(34)	0.4844(4)	0.3031(3)	0.4106(4)	0.067(3)
C(35)	0.5826(4)	0.2887(3)	0.4620(4)	0.072(3)
C(36)	0.5834(4)	0.1949(3)	0.4464(4)	0.058(3)
C(37)	0.5865(4)	−0.2732(3)	0.3183(4)	0.056(2)
C(38)	0.6031(4)	−0.3618(3)	0.2798(5)	0.064(3)
C(39)	0.6122(4)	−0.4227(4)	0.3470(5)	0.078(3)
C(40)	0.6299(5)	−0.5062(4)	0.3076(7)	0.093(4)
C(41)	0.6408(5)	−0.5343(4)	0.2067(7)	0.100(4)
C(42)	0.6332(5)	−0.4767(4)	0.1404(5)	0.086(3)
C(43)	0.6140(4)	−0.3893(3)	0.1770(5)	0.064(3)
C(44)	0.6063(4)	−0.3284(3)	0.1102(4)	0.063(3)
N(45)	0.1575(6)	−0.1494(6)	0.3572(7)	0.144(5)
C(46)	0.1916(6)	−0.1905(6)	0.2997(7)	0.098(5)
C(47)	0.2334(5)	−0.2407(5)	0.2291(5)	0.071(3)
C(48)	0.2397(5)	−0.3299(5)	0.2303(6)	0.085(4)
C(49)	0.2788(6)	−0.3776(5)	0.1622(7)	0.102(4)
C(50)	0.3106(6)	−0.3382(6)	0.0862(7)	0.103(5)
C(51)	0.3031(5)	−0.2497(5)	0.0861(6)	0.089(4)
C(52)	0.2656(5)	−0.1996(4)	0.1559(5)	0.072(4)
N(53)	0.1351(8)	0.0866(8)	0.8314(8)	0.202(7)
C(54)	0.1326(7)	0.1001(8)	0.7483(9)	0.143(6)
C(55)	0.1277(6)	0.1193(7)	0.6456(6)	0.098(4)
C(56)	0.1109(7)	0.2018(7)	0.63767(8)	0.122(6)
C(57)	0.1035(8)	0.2179(8)	0.5371(11)	0.147(8)
C(58)	0.1167(7)	0.1553(8)	0.4557(8)	0.125(6)
C(59)	0.1360(6)	0.0741(6)	0.4655(6)	0.104(5)
C(60)	0.1419(5)	0.0531(6)	0.5642(7)	0.097(4)
N(61)[a]	1.1241(5)	0.6478(13)	0.4786(22)	0.258(12)
C(62)[a]	1.0720(2)	0.5830(4)	0.4926(4)	0.130(6)
C(63)[a]	1.0000	0.5000	0.5000	0.142(2)
C(64)[a]	0.8912(4)	0.4535(7)	0.4188(8)	0.104(2)

Table 5 *Continued*

Atoms	*x/a*	*y/b*	*z/c*	*Ueq*
C(65)[a]	0.8228(5)	0.3734(8)	0.4265(9)	0.152(2)
C(66)[a]	0.8613(7)	0.3384(7)	0.5125(9)	0.087(2)
C(67)[a]	0.9717(8)	0.3875(8)	0.5957(9)	0.144(2)
C(68)[a]	1.0394(6)	0.4677(8)	0.5881(8)	0.151(2)
N(69)[a]	1.0772(6)	0.4291(12)	−0.1453(24)	0.330(19)
C(70)[a]	1.0506(2)	0.4720(4)	−0.0792(4)	0.146(6)
C(71)[a]	1.0000	0.5000	0.0000	0.137(2)
C(72)[a]	0.9784(10)	0.5855(5)	0.0174(8)	0.116(2)
C(73)[a]	0.9335(10)	0.6117(7)	0.0957(9)	0.100(2)
C(74)[a]	0.9169(10)	0.5565(8)	0.1613(8)	0.115(2)
C(75)[a]	0.9428(11)	0.4723(8)	0.1462(8)	0.127(2)
C(76)[a]	0.9853(6)	0.4453(5)	0.0663(7)	0.086(2)

[a] These atoms were given isotropic thermal parameters during refinement.

Table 6 Final fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2) for nonhydrogen atoms of 2a

Atoms	*x/a*	*y/b*	*z/c*	*Ueq*
N(1)	0.4360(1)	0.7825(3)	0.2592(1)	0.076(3)
C(2)	0.4389(1)	0.8056(2)	0.1105(4)	0.075(1)
C(3)	0.4310(1)	0.7481(3)	−0.0130(5)	0.098(2)
O(4)	0.4033(1)	0.6964(1)	0.0207(3)	0.101(1)
C(5)	0.3694(1)	0.7231(2)	0.0650(4)	0.075(1)
C(6)	0.3570(1)	0.7966(2)	0.0239(4)	0.071(1)
C(7)	0.3226(1)	0.8175(2)	0.0659(4)	0.062(1)
O(8)	0.3007(1)	0.7684(1)	0.1455(3)	0.054(1)
C(9)	0.2668(1)	0.7931(1)	0.1806(2)	0.062(1)
C(10)	0.2430(1)	0.7384(2)	0.2458(3)	0.062(1)
C(11)	0.2062(1)	0.7747(2)	0.2601(3)	0.059(1)
O(12)	0.2079(1)	0.8276(1)	0.3868(2)	0.064(1)
C(13)	0.1779(1)	0.8712(2)	0.4092(3)	0.057(1)
C(14)	0.1833(1)	0.9342(2)	0.5097(3)	0.060(1)
O(15)	0.2170(1)	0.9404(1)	0.5718(3)	0.073(1)
C(16)	0.2288(1)	1.0114(2)	0.6319(4)	0.066(1)
C(17)	0.2670(1)	0.9984(1)	0.6873(3)	0.065(1)
O(18)	0.2870(1)	0.9734(1)	0.5597(2)	0.081(1)
C(19)	0.3209(1)	0.9436(2)	0.5904(3)	0.062(1)
C(20)	0.3308(1)	0.8833(2)	0.4966(3)	0.065(1)
C(21)	0.3656(1)	0.8533(2)	0.5084(3)	0.065(1)
C(22)	0.3896(1)	0.8857(2)	0.6169(4)	0.071(1)
O(23)	0.4256(1)	0.8618(2)	0.6412(3)	0.095(1)
C(24)	0.4382(1)	0.8053(2)	0.5362(4)	0.094(2)
C(25)	0.4423(1)	0.8320(2)	0.3752(4)	0.073(1)
C(26)	0.4518(1)	0.9083(2)	0.3430(5)	0.090(2)
C(27)	0.4551(1)	0.9309(3)	0.1896(6)	0.104(2)
C(28)	0.4488(1)	0.8801(3)	0.0733(5)	0.092(2)
C(29)	0.3485(1)	0.6750(2)	0.1461(4)	0.075(1)
C(30)	0.3138(1)	0.6956(2)	0.1869(4)	0.068(1)
C(31)	0.1443(1)	0.8569(2)	0.3445(4)	0.069(1)
C(32)	0.1157(1)	0.9057(2)	0.3748(5)	0.086(2)
C(33)	0.1213(1)	0.9682(2)	0.4691(5)	0.087(2)
C(34)	0.1546(1)	0.9827(2)	0.5352(4)	0.078(1)
C(35)	0.3440(1)	0.9725(2)	0.7008(4)	0.077(1)
C(36)	0.3785(1)	0.9432(2)	0.7152(4)	0.081(1)
N(2)	0.0000(0)	0.8250(3)	0.2500(0)	0.119(3)
C(37)	0.0000(0)	0.8907(4)	0.2500(0)	0.096(3)
C(38)	0.0000(0)	0.9742(3)	0.2500(0)	0.075(2)
C(39)	0.0303(1)	1.0137(2)	0.2100(6)	0.110(2)
C(40)	0.0297(1)	1.0942(3)	0.2124(7)	0.131(2)
C(41)	0.0000(0)	1.1337(4)	0.2500(0)	0.121(3)

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