The Structure of the Uncharged-Molecule Complex between a Dinaphthopyridino-18-crown-6 Host and Acetonitrile (1:2)

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Abstract. Single crystal X-ray analysis of a 1:2 complex between the dinaphthopyridino-18-crown-6 host (1) and acetonitrile is reported. Crystals of the complex are monoclinic, $P2_1/c$ with $a = 12.178(5)$, $b = 8.186(1)$, $c = 30.873(1)$ Å, $\beta = 96.86(1)°$, and $D_c = 1.25$ g cm^{-3} for $Z = 4$. The host molecule reveals an approximate mirror symmetry and exists in a so-called 'dentist's chair' conformation. One of the acetonitrile guest molecules is involved in possible weak interactions to two oxygen atoms of the host macroring, while the other fills free lattice space only.

Key words. Crown compound, acetonitrile, crown solvent complex, crystal structure.

1. Introduction

Complexes between crown compounds and acetonitrile (MeCN) have recently been shown to have different structures [1–4]. The argument is whether or not they should be understood as hydrogen-bonded host–guest species. The debatable point came from the 1:2 complexes of 18-crown-6 [2, 4] and dibenzo-18-crown-6 [1, 3] with MeCN.

Both are rather unstable species at ambient conditions [1, 5, 6]. Consequently, it is difficult to obtain good quality crystals and reasonably good X-ray data in order to deduce the mode of interaction. High resolution crystal structures at low temperature [2, 3] have now thrown more light upon the matter. They favour weak C—H···O type interactions [7] in both complexes. On the other hand, *ab initio* calculations [8] including MeCN and a single oxygen binding site (H$_2$O) does not favour H-bond interactions, which is reasonable because of the relatively low acidity of MeCN (p$K_a = 25$ [9]).

In order to clarify the confusion more structural details are desirable. In this context, complexes between MeCN and analogous pyridino crown compounds [10] are of interest. They provide more basic N sites for possible hydrogen bonding and,

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if aryl condensation is a contributing factor, also a higher shielding factor. We recently determined the crystal structure of the MeCN complex (1:2) of a rigid 21-membered tribenzopyridino crown [11, 12]. Unexpectedly, a H-bond interaction between MeCN and the basic N site was not observed.

The present study is aimed at obtaining the crystal structure of the 1:2 (host:guest) complex between pyridino crown compound **1** and MeCN. The host is probably more flexible than the previously studied 21-membered tribenzopyridino crown [11, 12], has two highly shielding 2,3-naphthylene units and, by ring size, it relates directly to 18-crown-6 or dibenzo-18-crown-6.

2. Experimental

The method for preparation of the host compound **1** and of the title complex,
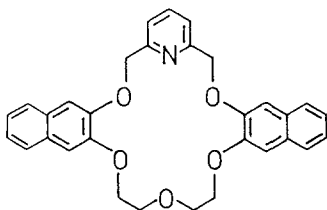
1*

*Systematic name (phane nomenclature) of **1**: 1,4,7,16,25-Pentaoxa [7] (2,3)naphthalino [2] (2,6)pyridino [2] (2,3)naphthalinophane

1 · 2 MeCN, have been described earlier [13]. A colourless crystal of the complex of dimensions $0.4 \times 0.3 \times 0.3$ mm was used. Preliminary studies of the cell dimensions and space group were carried out by photographic methods. More accurate cell dimensions were obtained using a Nonius CAD4 diffractometer equipped with CuK_α radiation and a graphite monochromator by least-squares fit of the 2Θ values of 20 general reflections ($20° < 2\Theta < 40°$).

2.1. CRYSTAL DATA

$C_{31}H_{27}NO_5 \cdot 2\,CH_3CN$, $FW = 575.7$, monoclinic, $P2_1/c$; $a = 12.178(5)$, $b = 8.186(1)$, $c = 30.873(1)$ Å, $\beta = 96.86(1)°$, $V = 3055.7$ Å^3, $Z = 4$, $D_c = 1.25$ g cm^{-3}, $\lambda(CuK_\alpha) = 1.5418$ Å, $\mu = 6.5$ cm^{-1}, $F(000) = 1216$, $T = 296$ K. Three dimensional data of 4905 reflections were collected, 2751 considered observed with $I > 2\sigma > (I)$, CuK_α radiation, max. $2\Theta = 120°$, $\omega - 2\Theta$ scan, data collection range: $h = 0$ to 13, $k = 0$ to 9, and $l = -34$ to 34. Lp^{-1} corrections were applied. An empirical absorption correction based on a series of psi-scans was applied to the data. Relative transmission coefficients ranged from 0.749 to 0.998 with an average value of 0.823.

The structure was solved by MULTAN 80 [14]. It gave the positions of most of the non-hydrogen atoms and the remaining non-hydrogens were located from a difference Fourier map. Refinement was carried out by full-matrix least-squares

(SDP/VAX Computer systems). Most of the H atoms were obtained from a difference Fourier map computed at an R of 0.10 and the remaining H atoms were fixed by stereochemical considerations. The H atoms were included in the structure factors for the final cycles of refinement. The refinement converged at an $R = 0.057$, $R_w = 0.055$, $S = 1.50$, and $(\Delta/\sigma)\text{max.} = 0.05$; $R = \Sigma (|F_o| - |F_c|)/ \Sigma |F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/ \Sigma w|F_o|^2]^{1/2}$; the quantity minimized was $\Sigma w[|F_o|^2 - (1/K)|F_c|^2]^2$, where the weight $w = 4|F_o|^2/\sigma(|F_o|)^2$ and $(\sigma|F_o|^2) = [\sigma^2(I) + (0.05 I)^2]/Lp$, where K is the scale factor, and $\sigma(I)$ is the standard deviation in the intensity I based on counting statistics. Maximum and minimum peak heights in the final difference Fourier map are 0.19 and -0.20 e Å^{-3}, respectively. Scattering factors were taken from [15]. All calculations were performed on a VAX 730 computer using SDP/VAX [16].

3. Results and Discussion

The final atomic coordinates of the non-hydrogen atoms are listed in Table I; atom labelling is in accordance with Figure 1. Table II shows bond distances and angles,
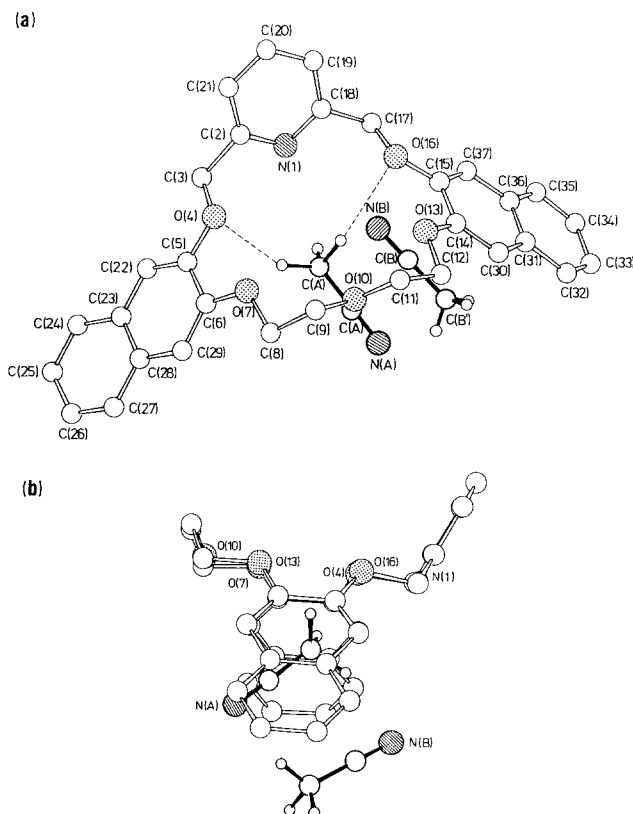

Fig. 1. Molecular structure of the 1·2 MeCN complex: (a) top view giving the numbering scheme for the atoms, (b) side view. The guest molecules are marked by bold lines; heteroatoms are shaded (O atoms dotted, N atoms hatched). In (a) the dotted lines represent the possible weak interactions.

Table I. Final fractional coordinates and equivalent thermal parameters for the non-hydrogen atoms of 1·2 MeCN (e.s.ds are in parentheses).

Atom	x/a	y/b	z/c	$B_{eq}(\text{Å}^2)$
N(1)	1.0367(3)	0.2214(5)	0.0327(1)	3.68(8)
C(2)	0.9612(3)	0.2148(6)	−0.0027(1)	3.72(9)
C(3)	0.8597(3)	0.1140(6)	0.0025(1)	4.2(1)
O(4)	0.7920(2)	0.2093(4)	0.02858(9)	4.18(7)
C(5)	0.7034(3)	0.1272(6)	0.0420(1)	3.69(9)
C(6)	0.6492(3)	0.2155(6)	0.0733(1)	4.0(1)
O(7)	0.6927(2)	0.3661(4)	0.08393(9)	4.66(7)
C(8)	0.6487(4)	0.4512(7)	0.1186(1)	5.0(1)
C(9)	0.7109(4)	0.6098(7)	0.1252(2)	5.2(1)
O(10)	0.8189(2)	0.5742(3)	0.14619(9)	4.76(7)
C(11)	0.8823(4)	0.7193(6)	0.1555(2)	5.01(1)
C(12)	0.9903(4)	0.6708(7)	0.1811(1)	5.2(1)
O(13)	1.0559(2)	0.5888(4)	0.15175(8)	4.66(7)
C(14)	1.1542(3)	0.5232(6)	0.1706(1)	4.1(1)
C(15)	1.2153(3)	0.4376(6)	0.1413(1)	3.9(1)
O(16)	1.1656(2)	0.4315(4)	0.09921(8)	4.48(7)
C(17)	1.2092(3)	0.3181(6)	0.0705(1)	4.4(1)
C(18)	1.1289(3)	0.3119(6)	0.0299(1)	3.77(9)
C(19)	1.1481(4)	0.3934(6)	−0.0078(1)	4.4(1)
C(20)	1.0696(4)	0.3829(7)	−0.0441(1)	4.9(1)
C(21)	0.9748(4)	0.2898(6)	−0.0418(1)	4.6(1)
C(22)	0.6674(3)	−0.0218(6)	0.0281(1)	4.1(1)
C(23)	0.5737(3)	−0.0946(6)	0.0440(1)	4.2(1)
C(24)	0.5329(4)	−0.2482(6)	0.0294(2)	5.2(1)
C(25)	0.4418(4)	−0.3173(7)	0.0452(2)	6.4(1)
C(26)	0.3904(4)	−0.2329(7)	0.0770(2)	6.3(1)
C(27)	0.4270(4)	−0.0816(7)	0.0915(2)	5.6(1)
C(28)	0.5202(3)	−0.0093(6)	0.0755(1)	4.4(1)
C(29)	0.5601(3)	0.1473(7)	0.0896(1)	4.6(1)
C(30)	1.1932(4)	0.5357(6)	0.2137(1)	4.4(1)
C(31)	1.2948(4)	0.4589(6)	0.2300(1)	4.4(1)
C(32)	1.3342(4)	0.4645(7)	0.2751(1)	5.5(1)
C(33)	1.4305(4)	0.3849(8)	0.2906(2)	6.2(1)
C(34)	1.4918(4)	0.3021(8)	0.2618(2)	6.6(1)
C(35)	1.4562(4)	0.2971(7)	0.2179(2)	5.7(1)
C(36)	1.3563(4)	0.3756(6)	0.2010(1)	4.4(1)
C(37)	1.3141(4)	0.3676(6)	0.1562(1)	4.4(1)
N(A)	0.9528(6)	0.203(1)	0.2094(2)	13.1(2)
C(A)	0.9477(5)	0.1969(8)	0.1729(2)	6.9(1)
C(A′)	0.9441(5)	0.1934(8)	0.1269(2)	7.0(2)
N(B)	1.2152(5)	−0.0435(8)	0.1564(2)	11.1(2)
C(B)	1.2214(5)	−0.0195(8)	0.1930(2)	8.3(2)
C(B′)	1.2283(6)	0.013(1)	0.2387(2)	10.0(2)

and Table III gives a selection of torsion angles. Lists of anisotropic thermal parameters (Table IV), coordinates of the H atoms (Table V), and structure factors have been deposited. The molecular structure of the complex 1·2 MeCN is shown in Figure 1 and the packing diagram is illustrated in Figure 2.

3.1. MOLECULAR STRUCTURE

3.1.a. *Host Conformation*

The host reveals an approximate mirror symmetry, passing through the N(1) and C(20) atoms. Individual torsion angles are as usually observed for benzo crown compounds [17]: *anti* (for C—X—C—C, X = O, N), ±*gauche* (for O—C—C—O) and *syn* (at *ortho* substituted aryl groups). Starting from the N(1)—C(2) bond, the macrocycle has the conformation $ag^+aasaag^-aag^+aasaag^-a$, which gives rise to a so-called 'dentist's chair' like shape of the molecule (Figure 1b). A similar ring conformation was found earlier for the analogous dibenzopyridino crown in its ethanol inclusion complex [18].

3.1.b. *Bond Distances and Angles*

There are two aliphatic CH—CH bonds in this structure [C(8)—C(9) and C(11)—C(12)], the mean value of which is significantly shorter [1.505(6) Å] com-

Table II. Bond distances (Å) and bond angles (°) for 1·2 MeCN (e.s.ds are in parentheses).

Atoms	Distance (Å)	Atoms	Distance (Å)
N(1)—C(2)	1.342(5)	C(18)—C(19)	1.385(6)
N(1)—C(18)	1.355(5)	C(19)—C(20)	1.385(6)
C(2)—C(3)	1.512(6)	C(20)—C(21)	1.392(7)
C(2)—C(21)	1.384(6)	C(22)—C(23)	1.425(6)
C(3)—O(4)	1.447(5)	C(23)—C(24)	1.406(7)
O(4)—C(5)	1.376(5)	C(23)—C(28)	1.418(6)
C(5)—C(6)	1.429(6)	C(24)—C(25)	1.385(7)
C(5)—C(22)	1.349(6)	C(25)—C(26)	1.408(8)
C(6)—O(7)	1.367(6)	C(26)—C(27)	1.373(8)
C(6)—C(29)	1.369(6)	C(27)—C(28)	1.420(7)
O(7)—C(8)	1.434(6)	C(28)—C(29)	1.421(7)
C(8)—C(9)	1.505(7)	C(30)—C(31)	1.425(6)
C(9)—O(10)	1.425(5)	C(31)—C(32)	1.418(6)
O(10)—C(11)	1.427(6)	C(31)—C(36)	1.411(7)
C(11)—C(12)	1.505(6)	C(32)—C(33)	1.377(7)
C(12)—O(13)	1.444(6)	C(33)—C(34)	1.403(8)
O(13)—C(14)	1.377(5)	C(34)—C(35)	1.373(7)
C(14)—C(15)	1.423(6)	C(35)—C(36)	1.419(6)
C(14)—C(30)	1.361(5)	C(36)—C(37)	1.418(6)
C(15)—O(16)	1.367(4)	N(A)—C(A)	1.124(7)
C(15)—C(37)	1.362(6)	C(A)—C(A')	1.416(7)
O(16)—C(17)	1.429(5)	N(B)—C(B)	1.140(9)
C(17)—C(18)	1.495(5)	C(B)—C(B')	1.43(1)

Table II continued

Atoms	Angle (°)	Atoms	Angle (°)
C(2)—N(1)—C(18)	117.6(3)	C(18)—C(19)—C(20)	118.7(4)
N(1)—C(2)—C(3)	115.2(4)	C(19)—C(20)—C(21)	119.3(4)
N(1)—C(2)—C(21)	123.5(4)	C(2)—C(21)—C(20)	118.2(4)
C(3)—C(2)—C(21)	121.3(3)	C(5)—C(22)—C(23)	120.8(4)
C(2)—C(3)—O(4)	107.0(4)	C(22)—C(23)—C(24)	122.1(4)
C(3)—O(4)—C(5)	115.0(3)	C(22)—C(23)—C(28)	118.9(4)
O(4)—C(5)—C(6)	113.5(4)	C(24)—C(23)—C(28)	119.0(4)
O(4)—C(5)—C(22)	125.6(4)	C(23)—C(24)—C(25)	121.4(5)
C(6)—C(5)—C(22)	120.9(4)	C(24)—C(25)—C(26)	119.1(5)
C(5)—C(6)—O(7)	114.9(4)	C(25)—C(26)—C(27)	121.1(5)
C(5)—C(6)—C(29)	119.6(4)	C(26)—C(27)—C(28)	120.3(5)
O(7)—C(6)—C(29)	125.5(4)	C(23)—C(28)—C(27)	119.1(5)
C(6)—O(7)—C(8)	116.7(3)	C(23)—C(28)—C(29)	119.1(4)
O(7)—C(8)—C(9)	107.0(4)	C(27)—C(28)—C(29)	121.8(4)
C(8)—C(9)—O(10)	107.9(4)	C(6)—C(29)—C(28)	120.8(4)
C(9)—O(10)—C(11)	111.6(4)	C(14)—C(30)—C(31)	120.0(4)
O(10)—C(11)—C(12)	107.7(4)	C(30)—C(31)—C(32)	120.7(4)
C(11)—C(12)—O(13)	107.8(3)	C(30)—C(31)—C(36)	119.5(4)
C(12)—O(13)—C(14)	115.7(3)	C(32)—C(31)—C(36)	119.8(4)
O(13)—C(14)—C(15)	114.6(3)	C(31)—C(32)—C(33)	120.0(5)
O(13)—C(14)—C(30)	124.6(4)	C(32)—C(33)—C(34)	120.3(4)
C(15)—C(14)—C(30)	120.7(4)	C(33)—C(34)—C(35)	120.7(5)
C(14)—C(15)—O(16)	114.7(3)	C(34)—C(35)—C(36)	120.4(5)
C(14)—C(15)—C(37)	120.0(4)	C(31)—C(36)—C(35)	118.8(4)
O(16)—C(15)—C(37)	125.3(4)	C(31)—C(36)—C(37)	118.9(4)
C(15)—O(16)—C(17)	117.3(3)	C(35)—C(36)—C(37)	122.2(4)
O(16)—C(17)—C(18)	106.7(3)	C(15)—C(37)—C(36)	120.9(4)
N(1)—C(18)—C(17)	115.5(4)	N(A)—C(A)—C(A′)	177.9(7)
N(1)—C(18)—C(19)	122.7(3)	N(B)—C(B)—C(B′)	179.2(7)
C(17)—C(18)—C(19)	121.9(4)		

pared to the normal value of 1.537 Å; this behaviour is frequently seen in crown complexes [17]. The mean C—C bond length of the napthaleno moieties is 1.400(6) Å, while the mean $C(sp^2)$—O and $C(sp^3)$—O bonds are 1.372(5) Å and 1.434(6) Å, respectively. The $C(sp^2)$—N bonds at the pyridine ring differ slightly [1.342(5) Å and 1.355(5) Å] but not significantly. There is good agreement of bond lengths and angles with those of the dibenzopyridino analogue mentioned above [18] and a related crown compound [19]. The intramolecular distances between heteroatoms are: N(1)—O(4) = 2.970(4) Å, N(1)—O(16) = 2.978(4) Å, O(4)—O(7) = 2.554(4) Å, O(7)—O(10) = 2.872(4) Å, O(10)—O(13) = 2.873(3) Å, and O(13)—O(16) = 2.568(4) Å. Out of the above non-bonded distances, the values of 2.554(4) Å and 2.568(4) Å are markedly shorter than the normal van der Waals O⋯O non-bonded contact distance of 2.8 Å which reflects conformational strain of the macrocycle. The mean value of bond angles at the heteroatoms are 115.3(3)° for C—O—C of the macrocycle and 117.6(3)° for C—N—C of the pyridine ring. Considerable ring strain can be seen at C(2), C(5),

Table III. Selected torsion angles (°) for 1·2 MeCN (e.s.ds are in parentheses).

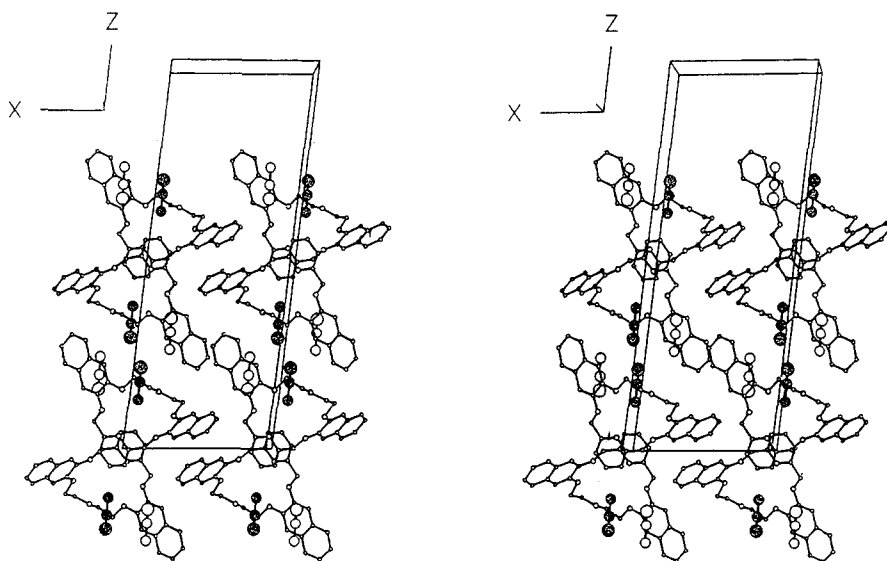| Atoms	Angle (°)
C(18)—N(1)—C(2)—C(3)	−179.2(4)
N(1)—C(2)—C(3)—C(4)	75.5(5)
C(2)—C(3)—O(4)—C(5)	−171.0(3)
C(3)—O(4)—C(5)—C(6)	170.4(3)
O(4)—C(5)—C(6)—O(7)	1.0(5)
C(5)—C(6)—O(7)—C(8)	−173.4(4)
C(6)—O(7)—C(8)—C(9)	178.4(4)
O(7)—C(8)—C(9)—O(10)	−73.7(4)
C(8)—C(9)—O(10)—C(11)	−177.4(3)
C(9)—O(10)—C(11)—C(12)	174.9(3)
O(10)—C(11)—C(12)—O(13)	72.0(4)
C(11)—C(12)—O(13)—C(14)	−174.7(4)
C(12)—O(13)—C(14)—C(15)	177.7(4)
O(13)—C(14)—C(15)—O(16)	−1.2(6)
C(14)—C(15)—O(16)—C(17)	−166.3(4)
C(15)—O(16)—C(17)—C(18)	169.4(4)
O(16)—C(17)—C(18)—N(1)	−78.1(5)
C(17)—C(18)—N(1)—C(2)	178.8(4)

Fig. 2. Crystal packing of the 1·2 MeCN complex (stereo view). The host molecules are represented by small, and the guest molecules by large circles; MeCN molecules involved in possible weak interactions are indicated by shading.

Table IV.   Anisotropic thermal parameters for the non-hydrogen atoms of 1·2MeCN (e.s.ds are in parentheses)

Anisotropic thermal parameters expression:

$$\exp[-0.25B_{11}h^2a^{*2} + B_{22}k^2B^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^*\cos\gamma^* + 2B_{13}hla^*c^*\cos\beta^*$$

$$+ 2B_{23}klb^*c^*\cos\alpha^*)]$$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N(1)	3.8(1)	4.5(2)	2.9(1)	0.4(1)	0.9(1)	−0.1(1)
C(2)	3.9(2)	4.3(2)	3.1(2)	1.1(2)	0.9(1)	−0.4(2)
C(3)	3.9(2)	4.7(2)	4.3(2)	0.3(2)	1.1(2)	−1.2(2)
O(4)	3.6(1)	4.7(1)	4.5(1)	0.3(1)	1.4(1)	−0.8(1)
C(5)	3.2(2)	4.5(2)	3.4(2)	0.4(2)	0.5(1)	−0.2(2)
C(6)	3.4(2)	4.9(2)	3.7(2)	0.2(2)	0.4(2)	−0.5(2)
O(7)	4.1(1)	5.4(2)	4.7(1)	−0.0(1)	1.5(1)	−1.4(1)
C(8)	3.9(2)	6.2(3)	5.0(2)	0.7(2)	1.1(2)	−2.2(2)
C(9)	4.0(2)	6.0(3)	5.5(2)	1.0(2)	−0.0(2)	−1.7(2)
O(10)	4.0(1)	5.4(2)	4.7(1)	0.8(1)	−0.1(1)	−0.9(1)
C(11)	4.3(2)	5.3(2)	5.3(2)	0.6(2)	0.3(2)	−1.9(2)
C(12)	4.6(2)	6.6(3)	4.5(2)	0.8(2)	0.9(2)	−2.4(2)
O(13)	4.1(1)	6.5(2)	3.4(1)	0.9(1)	0.5(1)	−1.1(1)
C(14)	3.3(2)	5.5(3)	3.5(2)	−0.3(2)	0.3(1)	−0.1(2)
C(15)	4.1(2)	4.5(2)	3.2(2)	−0.0(2)	0.7(1)	−0.0(2)
O(16)	4.6(1)	5.9(2)	2.9(1)	1.2(1)	0.4(1)	−0.7(1)
C(17)	3.6(2)	6.0(3)	3.7(2)	0.4(2)	0.9(1)	−1.5(2)
C(18)	4.1(2)	4.4(2)	3.0(2)	0.7(2)	1.0(1)	−0.3(2)
C(19)	4.6(2)	4.8(2)	4.0(2)	0.9(2)	1.6(2)	0.0(2)
C(20)	5.6(2)	5.8(3)	3.5(2)	1.3(2)	1.6(2)	0.3(2)
C(21)	4.8(2)	5.8(3)	3.2(2)	1.4(2)	0.8(2)	−0.2(2)
C(22)	3.7(2)	4.6(2)	4.1(2)	0.5(2)	−0.1(2)	−0.3(2)
C(23)	3.5(2)	4.7(2)	4.3(2)	0.3(2)	−0.5(2)	0.5(2)
C(24)	4.5(2)	5.1(3)	5.7(2)	−0.4(2)	−0.8(2)	0.2(2)
C(25)	5.3(2)	6.1(3)	7.2(3)	−0.8(2)	−1.2(2)	0.9(3)
C(26)	4.5(2)	7.5(3)	6.7(3)	−0.9(2)	0.2(2)	1.3(3)
C(27)	4.2(2)	7.8(3)	4.8(2)	−0.7(2)	0.0(2)	1.0(2)
C(28)	3.3(2)	6.2(3)	3.6(2)	−0.2(2)	−0.0(2)	0.7(2)
C(29)	3.6(2)	6.3(3)	3.8(2)	0.1(2)	0.5(2)	0.0(2)
C(30)	4.2(2)	5.6(3)	3.3(2)	−0.5(2)	0.2(2)	−0.4(2)
C(31)	4.3(2)	5.2(2)	3.6(2)	−1.1(2)	−0.0(2)	0.4(2)
C(32)	4.9(2)	7.4(3)	3.9(2)	−1.4(2)	−0.3(2)	0.5(2)
C(33)	6.3(3)	7.5(3)	4.6(2)	−1.7(3)	−0.8(2)	1.4(2)
C(34)	5.0(2)	8.0(3)	6.2(3)	−0.7(3)	−1.2(2)	1.1(3)
C(35)	4.1(2)	6.7(3)	6.0(2)	0.3(2)	−0.4(2)	0.5(3)
C(36)	4.1(2)	5.0(2)	4.2(2)	−0.5(2)	0.1(2)	0.5(2)
C(37)	3.9(2)	5.3(2)	3.9(2)	0.1(2)	0.5(2)	0.1(2)
N(A)	17.1(5)	17.3(6)	5.5(2)	−0.7(5)	4.3(3)	2.5(3)
C(A)	7.6(3)	8.3(4)	5.3(2)	−0.6(3)	2.4(2)	1.5(3)
C(A′)	8.6(3)	8.5(4)	3.9(2)	0.3(3)	0.6(2)	0.6(3)
N(B)	11.5(3)	10.7(4)	12.0(3)	0.8(3)	5.5(3)	−1.1(3)
C(B)	6.4(3)	6.9(4)	12.4(4)	0.6(3)	4.4(2)	−1.5(3)
C(B′)	9.4(4)	11.1(5)	10.1(4)	2.0(4)	3.1(3)	−0.0(4)

Table V. Atomic coordinates and isotropic thermal parameters for the hydrogen atoms of 1·2MeCN (e.s.ds are in parentheses)

Atom	x/a	y/b	z/c	B_{iso} (Å^2)
H(1C3)	0.880(4)	0.008(7)	0.019(2)	6.0
H(2C3)	0.816(4)	0.083(7)	−0.029(2)	6.0
H(1C8)	0.662(4)	0.379(7)	0.149(2)	6.9
H(2C8)	0.574(4)	0.469(7)	0.110(2)	6.9
H(1C9)	0.670(4)	0.706(7)	0.144(2)	6.8
H(2C9)	0.727(4)	0.660(7)	0.094(2)	6.8
H(1C11)	0.845(4)	0.813(7)	0.173(2)	6.7
H(2C11)	0.891(4)	0.769(7)	0.124(2)	6.7
H(1C12)	0.979(4)	0.608(7)	0.209(2)	7.2
H(2C12)	1.030(4)	0.766(7)	0.195(2)	7.2
H(1C17)	1.220(4)	0.204(7)	0.085(2)	6.4
H(2C17)	1.289(4)	0.370(7)	0.064(2)	6.4
H(C19)	1.215(4)	0.462(7)	−0.006(2)	5.9
H(C20)	1.089(4)	0.435(7)	−0.073(2)	6.6
H(C21)	0.925(4)	0.268(7)	−0.071(2)	6.1
H(C22)	0.699(4)	−0.082(7)	0.005(2)	5.5
H(C24)	0.571(4)	−0.308(7)	0.005(2)	7.1
H(C25)	0.417(5)	−0.433(8)	0.032(2)	8.9
H(C26)	0.334(5)	−0.287(8)	0.091(2)	8.4
H(C27)	0.390(5)	−0.010(8)	0.115(2)	8.1
H(C29)	0.519(4)	0.211(7)	0.115(2)	6.2
H(C30)	1.144(4)	0.602(7)	0.236(2)	6.3
H(C32)	1.287(4)	0.518(8)	0.298(2)	7.5
H(C33)	1.455(5)	0.387(8)	0.325(2)	8.8
H(C34)	1.555(5)	0.239(8)	0.276(2)	8.6
H(C35)	1.508(5)	0.229(8)	0.195(2)	7.9
H(C37)	1.360(4)	0.303(7)	0.137(2)	6.1
H(1CA′)	0.876(5)	0.175(9)	0.103(2)	9.3
H(2CA′)	0.979(5)	0.310(8)	0.119(2)	9.3
H(3CA′)	1.003(5)	0.098(8)	0.121(2)	9.3
H(1CB′)	1.287(6)	−0.03(1)	0.257(2)	12.5
H(2CB′)	1.219(6)	0.12(1)	0.249(2)	12.5
H(3CB′)	1.181(6)	−0.04(1)	0.254(2)	12.5

C(6), C(14), C(15), and C(18); maximum distortion (from 120°) is noted at C(5), C(6), C(14), and C(15).

3.2. HOST–GUEST INTERACTION AND CRYSTAL PACKING

There are two molecules of MeCN in the asymmetric unit constituting species with different host–guest interactions. One MeCN (labelled A) is involved *via* its methyl group in relatively short contacts to O(4) and O(16) of the macroring [C(A′)···O(4) = 3.346 Å, C(A′)···O(16) = 3.500 Å]. However, to designate these contacts as weak C—H···O hydrogen bonds (H(1CA′)···O(4) = 2.468 Å, C(A′)—H(1CA′)···O(4) = 149.0°; H(2CA′)···O(16) = 2.614 Å, C(A′)—H(2CA′)··· O(16) = 139.4°] is very doubtful [7, 20] and may not be warranted, at least for the

temperature conditions of this study. Thus, the situation is almost comparable to the MeCN complexes of 18-crown-6 [2, 4] and dibenzo-18-crown-6 [1, 3]. Interestingly, the fact that the basic pyridine N does not take part in any short contact to the guest molecule has recently been found for the MeCN complex of a related pyridino crown [11, 12] and occurs again here.

The other guest species of the present 1 : 2 complex (MeCN labelled B) shows neither short contacts to the host nor to the MeCN molecule discussed before. Instead it fills free lattice space in the crystal packing (Figure 2) and may be assigned as a clathrate-type [21] guest molecule. This fact is similar to the pyridino crown MeCN complex mentioned before [11, 12], although there is some evidence for short distance interaction between the two MeCN species in the former complex.

Nevertheless, the position of the two MeCN molecules in both the present and the former pyridino crown complex [11, 12] differs fundamentally from the MeCN complexes of 18-crown-6 [2, 4] and dibenzo-18-crown-6 [1, 3], though all have the same 1 : 2 stoichiometry. In the pyridino crown complexes both MeCN molecules have been located, and interact, on the same side of the host, while 18-crown-6 and dibenzo-18-crown-6 show MeCN molecules on both faces of the host. Moreover, the present pyridino crown uses the ring face for host–guest association which includes the pyridino N, while the former pyridino crown shows opposite behaviour. But both active faces feature the most concave region of the host. This is another reason which points to the fact that the pyridine N is not important for direct interaction in these complexes.

Intermolecular stacking between symmetry-related pyridine rings on the one hand and between the naphthalene units on the other hand (Figure 2) are certainly a stabilizing factor of the structure.

4. Conclusions

In conclusion, the present crystallographic results suggest that rather than the expected hydrogen bonding, the interaction between the host molecule **1** and MeCN in the solid-state is of a dipole–dipole nature and perhaps weaker than for the MeCN complexes of conventional crown compounds. Moreover it became apparent [13] that lateral naphthaleno groups may support the formation of interstitial lattice complexes. In view of the debate [1–4, 7, 8] raised at the beginning, it remains an interesting task for the future to study the structure of other complexes of **1** [13], e.g. its complex with nitromethane.

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