Crystal Structure of an Uncomplexed 25-Crown-7 Comprising One 2,6-Pyridino and Two 1,4-Benzo Condensations*

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Abstract. Single crystal X-ray analysis of the uncomplexed crown macroring **1** is reported. Crystals are triclinic, $P\bar{1}$, with $a = 10.809(1)$, $b = 10.945(1)$, $c = 10.256(1)$ Å, $\alpha = 107.85(1)$, $\beta = 104.15(1)$, $\gamma = 87.27(1)°$, $D_c = 1.318$ g cm^{-3}, $Z = 2$. Three torsion angles in the macrocycle take up *gauche* conformations in contrast to the usual *anti* conformation. The crystal structure is stabilized by intramolecular van der Waals forces and weak C–H...O and C–H...N hydrogen bond attractions. Stacking of pyridine rings is a noticeable packing feature in the crystal lattice.

Key words: (1,4)Dibenzo(2,6)pyridino-25-crown-7, X-ray crystal structure analysis.

1. Introduction

Host compounds capable of selective complex formation with uncharged organic molecules have generated considerable interest in the past few years [2]. A family of aryl-condensed pyridino crowns [3], including **1–4**, is an example of this development due to the high potential for molecular complexation provided by this type of macrocycle [4].

Nevertheless, host behaviour in this class of compounds depends very much on structural parameters, including ring size as well as the nature and position of the condensed aromatic and heteroaromatic constituents (ref. [1] and previous papers [3, 4]).

While crown compound **3** readily yields a crystalline complex with acetonitrile [5], the analogous compounds **1** and **2**, having 1,4- and 1,3- instead of 1,2-lateral

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* Macroring Uncharged Molecule Complexation. Part 20. For Part 19 of this series see Ref. [1].
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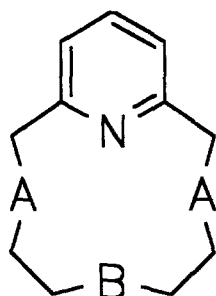
	A	B
1	O⟨⟩O	OCH_2CH_2O
2		OCH_2CH_2O
3		OCH_2CH_2O
4	O⟨⟩O	

benzo condensations, showed no host properties towards organic molecules [6]. Moreover, macrocycle **4**, unlike **1**, is very efficient in complex formation with organic guests [1, 6]. The difference between **1** and **4** is that the former lacks the 1,2-benzo condensation diametrical to the pyridino constituent.

In order to rationalize the very different host properties of macrocycles **1** and **4** (or **1** and **3**), **1** being an inefficient host [6], we have carried out a crystal structure determination of uncomplexed crown compound **1**, Here, we report the results of this study, considering potential guidelines for future host design.

2. Experimental

2.1. SAMPLE PREPARATION AND DATA COLLECTION

The title compound, **1**, was obtained as described [6]. A crystal of dimension $0.45 \times 0.26 \times 0.2$ mm was used and the accurate cell parameters of the compound were obtained using a Enraf-Nonius CAD4 diffractometer equipped with CuK_α

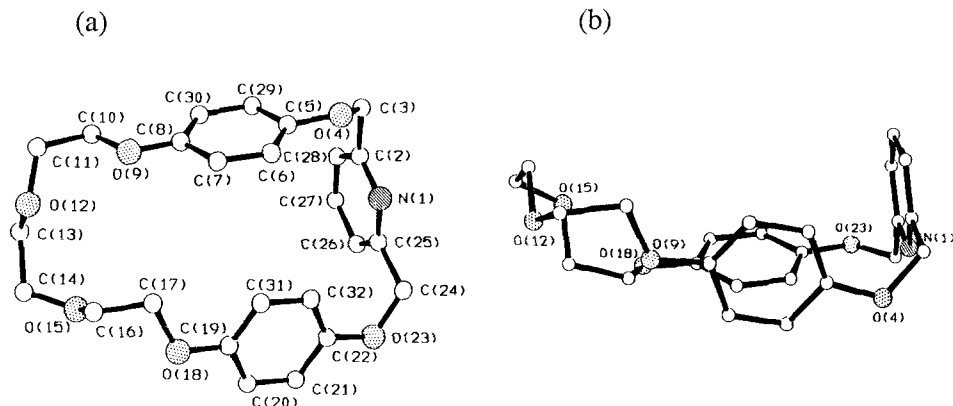(a)   (b)

Fig. 1. Molecular structure of **1**: (a) top view giving the numbering scheme for the atoms; (b) side view showing the distorted boat conformation. H atoms are omitted; heteroatoms are shaded.

radiation.

Crystal Data. $C_{25}O_6NH_{27}$, F_w = 437.5, triclinic $P\bar{1}$, a = 10.809(1), b = 10.945(1), c = 10.256(1) Å, α = 107.85(1), β = 104.15(1), γ = 87.27(1)°, V = 1119.4 Å^3, Z = 2, D_c = 1.318 g cm^{-3}, $F(000)$ = 464.0, T = 296 K.

2.2. STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved by the 'direct method' using SHELX86. All the non hydrogen atoms were refined anisotropically and all the hydrogens (Table IV), except two, were refined isotropically. The final refinement converged at R = 0.049, R_w = 0.051. Maximum and minimum peak heights in the difference maps are 0.17 and –0.23 e Å^{-3}, respectively. Atomic scattering factors were taken from [7]. The coordinates of the basic atoms are shown in Table I; atom labelling is in accordance with Figure 1.

3. Results and Discussion

3.1. MOLECULAR STRUCTURE

Chemically equivalent bond lengths and bond angles in the present macrocycle **1** (Table II) compare well with the mean values of those observed in other crown compounds [1, 8, 9], including the enlarged C–O–C angles (by 2–3°) relative to O–C–C [10], or are normal [11].

The macroring has an approximate twofold symmetry passing through the N(1) and C(27) atoms and bisecting the opposite C(13)–C(14) bond [Figure 1(a)]. Nevertheless, the C(11)–O(12)–C(13)–C(14)–O(15)–C(16) unit deviates greatly from

TABLE I. Final fractional atomic coordinates and equivalent thermal parameters ($\times 10^4$) Å for non-hydrogens of **1** (e.s.d.s are in parentheses).

Atom	x/a	y/b	z/c	U_{eq}
N(1)	0.3523(2)	0.7237(2)	−0.1666(2)	499(7)
C(2)	0.2951(2)	0.7099(3)	−0.0705(2)	593(10)
C(3)	0.2426(2)	0.8293(3)	0.0124(3)	740(12)
O(4)	0.3369(2)	0.9306(2)	0.0785(2)	689(7)
C(5)	0.4370(2)	0.9156(2)	0.1857(2)	572(9)
C(6)	0.5488(3)	0.9833(2)	0.2063(3)	620(10)
C(7)	0.6506(2)	0.9822(2)	0.3176(3)	593(9)
C(8)	0.6451(2)	0.9121(2)	0.4080(2)	564(9)
O(9)	0.7516(2)	0.9195(2)	0.5147(2)	658(8)
C(10)	0.7511(2)	0.8458(2)	0.6078(2)	606(11)
C(11)	0.8746(3)	0.8740(3)	0.7180(2)	635(10)
O(12)	0.9850(2)	0.8411(2)	0.6639(2)	623(7)
C(13)	1.0084(3)	0.7068(2)	0.6286(3)	653(11)
C(14)	1.1050(2)	0.6770(3)	0.5417(3)	668(10)
O(15)	1.0537(2)	0.6802(2)	0.4015(2)	696(7)
C(16)	1.0655(2)	0.8025(3)	0.3827(3)	628(10)
C(17)	0.9609(2)	0.8125(2)	0.2618(2)	587(9)
O(18)	0.9848(1)	0.7280(2)	0.1331(2)	636(7)
C(19)	0.8843(2)	0.7033(2)	0.0170(2)	504(8)
C(20)	0.8944(2)	0.5976(2)	−0.0977(2)	550(9)
C(21)	0.7949(2)	0.5620(2)	−0.2157(2)	556(8)
C(22)	0.6841(2)	0.6315(2)	−0.2222(2)	544(9)
O(23)	0.5893(2)	0.5870(2)	−0.3455(2)	739(7)
C(24)	0.4679(2)	0.6454(3)	−0.3485(2)	642(10)
C(25)	0.4027(2)	0.6209(2)	−0.2424(2)	554(8)
C(26)	0.3974(3)	0.5018(3)	−0.2269(4)	893(15)
C(27)	0.3378(4)	0.4884(4)	−0.1269(5)	1106(21)
C(28)	0.2856(3)	0.5930(3)	−0.0489(4)	869(15)
C(29)	0.4297(2)	0.8445(3)	0.2742(3)	647(10)
C(30)	0.5343(2)	0.8433(3)	0.3851(3)	624(10)
C(31)	0.7751(2)	0.7746(2)	0.0084(2)	529(8)
C(32)	0.6738(2)	0.7384(2)	−0.1115(2)	545(9)

the twofold symmetry. Also, the torsion angles about the C(2)–C(3) and C(24)–C(25) bonds are not related by the twofold symmetry, with the corresponding torsion angles about them being −54 and 134°, respectively (Table III). Four of the heteroatoms O(4), O(9), O(12) and O(15) are coplanar within ±0.04 Å, and the deviation of N(1) and O(23) from the mean plane is −0.756 and 0.109 Å, respectively. Starting from the N(1)–C(2) bond, the macrocycle has the conformation $ag^-g^-aasaaag^-g^-ag^-gag^-aaasaag^-aa$ which gives rise to a distorted

TABLE II. Bond distances (Å) and bond angels (°) involving non-hydrogen atoms of **1** (e.s.d.s are in parentheses).

Atoms	Distance	Atoms	Distance
N(1)–C(2)	1.332(4)	O(15)–C(16)	1.425(4)
N(1)–C(25)	1.334(3)	C(16)–C(17)	1.488(3)
C(2)–C(3)	1.496(4)	C(17)–O(18)	1.435(3)
C(2)–C(28)	1.376(5)	O(18)–C(19)	1.367(2)
C(3)–O(4)	1.427(3)	C(19)–C(20)	1.397(3)
O(4)–C(5)	1.385(3)	C(19)–C(31)	1.383(3)
C(5)–C(6)	1.385(4)	C(20)–C(21)	1.374(3)
C(5)–C(29)	1.382(4)	C(21)–C(22)	1.387(3)
C(6)–C(7)	1.381(4)	C(22)–O(23)	1.387(3)
C(7)–C(8)	1.385(4)	C(22)–C(32)	1.380(3)
C(8)–O(9)	1.367(3)	O(23)–C(24)	1.430(3)
C(8)–C(30)	1.377(3)	C(24)–C(25)	1.525(4)
O(9)–C(10)	1.427(4)	C(25)–C(26)	1.366(4)
C(10)–C(11)	1.498(3)	C(26)–C(27)	1.383(7)
C(11)–O(12)	1.422(4)	C(27)–C(28)	1.366(5)
O(12)–C(13)	1.428(3)	C(29)–C(30)	1.397(3)
C(13)–C(14)	1.495(5)	C(31)–C(32)	1.397(3)
C(14)–O(15)	1.420(4)		

Atoms	Angle	Atoms	Angle
C(2)–N(1)–C(25)	118.5(2)	C(16)–C(17)–O(18)	109.2(2)
N(1)–C(2)–C(28)	121.9(2)	C(17)–O(18)–C(19)	116.1(2)
N(1)–C(2)–C(3)	115.8(2)	O(18)–C(19)–C(31)	124.2(2)
C(3)–C(2)–C(28)	122.3(2)	O(18)–C(19)–C(20)	116.5(2)
C(2)–C(3)–O(4)	112.1(2)	C(20)–C(19)–C(31)	119.3(2)
C(3)–O(4)–C(5)	117.8(2)	C(19)–C(20)–C(21)	120.3(2)
O(4)–C(5)–C(29)	124.7(2)	C(20)–C(21)–C(22)	120.2(2)
O(4)–C(5)–C(6)	115.5(2)	C(21)–C(22)–C(32)	120.3(2)
C(5)–C(6)–C(7)	119.7(2)	C(21)–C(22)–O(23)	115.6(2)
C(6)–C(5)–C(29)	119.7(2)	O(23)–C(22)–C(32)	124.1(2)
C(6)–C(7)–C(8)	121.6(2)	C(22)–O(23)–C(24)	117.0(2)
C(7)–C(8)–C(30)	118.3(2)	O(23)–C(24)–C(25)	112.8(2)
C(7)–C(8)–O(9)	116.0(2)	N(1)–C(25)–C(24)	115.2(2)
O(9)–C(8)–C(30)	125.7(2)	C(24)–C(25)–C(26)	121.8(2)
C(8)–O(9)–C(10)	117.8(2)	N(1)–C(25)–C(26)	123.0(2)
O(9)–C(10)–C(11)	107.7(2)	C(25)–C(26)–C(27)	118.0(3)
C(10)–C(11)–O(12)	114.4(2)	C(26)–C(27)–C(28)	119.4(4)
C(11)–O(12)–C(13)	113.0(2)	C(2)–C(28)–C(27)	119.1(3)
O(12)–C(13)–C(14)	109.1(2)	C(5)–C(29)–C(30)	119.7(2)
C(13)–C(14)–O(15)	112.5(2)	C(8)–C(30)–C(29)	121.0(2)
C(14)–O(15)–C(16)	114.2(2)	C(19)–C(31)–C(32)	120.4(2)
O(15)–C(16)–C(17)	108.4(2)	C(22)–C(32)–C(31)	119.4(2)

TABLE III. Selected torsion angles (°) involving non-hydrogen atoms of **1** (e.s.d.s are in parentheses).

Atoms	Angle	Atoms	Angle
C(25)–N(1)–C(2)–C(3)	179.0(2)	C(13)–C(14)–O(15)–C(16)	90.7(3)
N(1)–C(2)–C(3)–O(4)	–54.2(3)	C(14)–O(15)–C(16)–C(17)	–153.2(2)
C(2)–C(3)–O(4)–C(5)	–67.3(3)	O(15)–C(16)–C(17)–O(18)	–70.5(3)
C(3)–O(4)–C(5)–C(6)	154.2(2)	C(16)–C(17)–O(18)–C(19)	165.3(2)
O(4)–C(5)–C(6)–C(7)	175.1(2)	C(17)–O(18)–C(19)–C(20)	–163.7(2)
C(5)–C(6)–C(7)–C(8)	1.6(4)	O(18)–C(19)–C(20)–C(21)	176.6(2)
C(6)–C(7)–C(8)–O(9)	–179.5(2)	C(19)–C(20)–C(21)–C(22)	0.6(3)
C(7)–C(8)–O(9)–C(10)	–178.3(2)	C(20)–C(21)–C(22)–O(23)	–179.6(2)
C(8)–O(9)–C(10)–C(11)	–177.7(2)	C(21)–C(22)–O(23)–C(24)	171.9(2)
C(9)–C(10)–C(11)–O(12)	–60.9(3)	C(22)–O(23)–C(24)–C(25)	–64.3(3)
C(10)–C(11)–O(12)–C(13)	–78.2(3)	O(23)–C(24)–C(25)–N(1)	134.4(3)
C(11)–O(12)–C(13)–C(14)	166.4(2)	C(24)–C(25)–N(1)–C(2)	–179.2(2)
O(12)–C(13)–C(14)–O(15)	–73.9(3)		

boat conformation [Figure 1(b)]. The possible intramolecular contacts for O and N atoms are 2.855(3) Å for N(1)...O(4), 2.856(3) Å for O(9)...O(12), 2.974(3) Å for O(12)...O(15) and 2.872(3) Å for O(15)...O(18), with 2.974(3) Å for O(12)...O(15) being significantly larger than the van der Waals O...O nonbonded contact distance of 2.8 Å [12].

From a more detailed inspection, one can see the following. The torsion angles about C(3)–O(4), C(11)–O(12) and C(14)–O(15) take up *gauche* conformations (Table III) in contrast to the usual *anti* conformation [8]. These abnormal rotations about the bonds may be due to the necessity to direct one or more oxygen atoms away from the cavity and to a bending of the pyridine ring in order to point the N atom away from the cavity. It is also interesting to note that the torsion about C(24)–C(25) of **1** is 135°, i.e. it lies between *gauche* and *anti* conformations. Strictly speaking, the torsion angles of the macrocycle **1** adjust themselves so that the dihedral angles between the pyridine and benzene rings amount to 103.3 and 111.6°, respectively.

Moreover, a comparison shows that conformations of **1** and of the closely related macrocycle **4** in its benzonitrile complex [1] are roughly similar, although two of the C–C–O–C angles change from *gauche* in molecule **1** to *anti* in complexed **4**, whereas the remaining torsion angles are of the same type in both macrorings, but corresponding ones may differ by as much as 25° and the signs may be reversed. This ultimately makes the pyridine and the benzene rings perpendicular to each other in **4** (as the benzonitrile complex), in contrast to **1**.
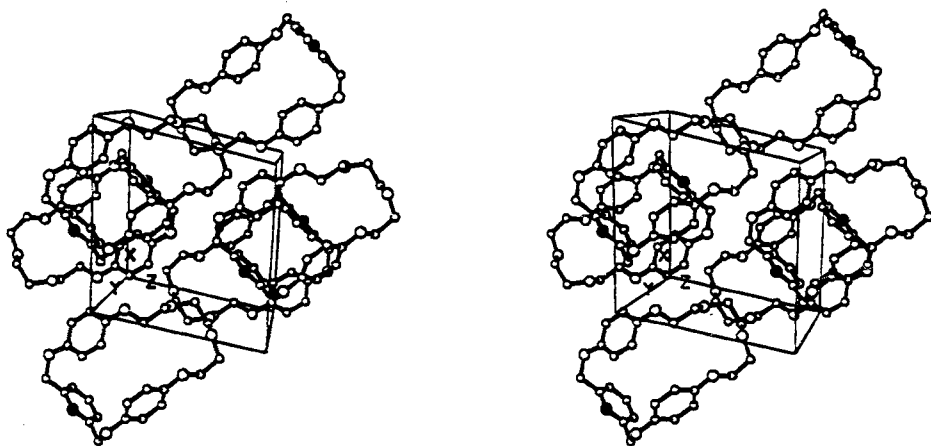
Fig. 2. Crystal packing of **1** in the unit cell (stereo view down the y-axis).

3.2. CRYSTAL PACKING

As seen from the packing diagram of compound **1** (Figure 2), there is stacking between pyridine nuclei of the molecules. This type of macro structure is frequently found in the packing of pyridino crowns including their crystalline complexes [6, 9]. Buckling of the O(12)–C(13)–C(14)–O(15)–C(16) unit is another noticeable packing feature in the crystal lattice of **1**.

As well as the stacking interaction, the molecules are held together by weak C–H...O and C–H...N hydrogen bond attractions with O(12), N(1) and O(23) as acceptor sites. Possible nonbonded intermolecular contacts include C(24)...O(23) = 3.318(3), C(14)...N(1) = 3.142(3), H(2C14)...N(1) = 2.743(2) and H(2C24)... O(23) = 2.44(4) Å.

Thus, the crystal structure of **1** is stabilized by intermolecular stacking interactions between the pyridine rings, C–H...O and C–H...N type of interactions and intramolecular van der Waals forces.

4. Conclusion

Crown compound **1** is capable of forming a suitably close crystal packing by itself, accounting for its lack of host properties [6]. By way of contrast, **4**, with an extra 1,2-benzo condensation in diametrical opposition to the pyridine ring is an efficient host for organic guest molecules [1, 6].

A possible conclusion for future design of hosts is as follows. One single peripheral 1,2-benzo unit, if properly condensed to a basic crown macroring, might be a vital design parameter for a potentially active host molecule in the crystalline state.

Acknowledgements

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