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X-ray Structure Analysis Online

Crystal Structure of 2-[2-(2-Aminophenoxy)ethoxy]-*N*-[(1*E*)-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-ylmethylene]aniline

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The title compound, $C_{29}H_{34}N_2O_7$, is a substituted monotopic benzo-15-crown-5-ether ligand. It belongs to the space group $P2_1/a$ with cell parameters a = 8.9857(6), b = 25.0353(17), c = 12.6979(9)Å and β = 109.730(1)°. The intermolecular N–H···O hydrogen bonds are dominantly effective in stabilizing the crystal structure. The N–H···O intermolecular hydrogen bonds link the molecules, forming infinite one-dimensional chains running approximatelly parallel to the *a*-axis. The relative macrocyclic inner-hole size is estimated to be 1.44 Å. The substituent and benzocrown ether precursors about the C=N imine bond reveals a *trans* planar (1*E*) configuration.

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Monotopic benzocrown ether ligands with additional donor atom(s) in the side-arm(s) have been prepared in order to alter the cation binding ability and the selectivity of the parent crown ethers.[1] These types of ligands with different ring sizes and different numbers and types of substituents have been used to synthesize a large number of alkali, alkaline earth cations and neutral molecular complexes as quests.[2] The title molecule may be a potential selective reagent for some alkali and alkaline earth metal cations and some neutral polar molecules. A structure analysis was carried out in order to estimate the macrocyclic ring hole size, which is very important for ion selectivity. The title ligand was prepared from the condensation reaction of 4′-formylbenzo-15-crown-5 and 1,2-bis(2-aminophenoxy)ethane, according to a literature method.[3] It was crystallized from methanol (yield 0.57 g, 65%, m.p. 408 K).

The X-ray analysis results are given in Tables 1 – 4. The H atoms were located by a difference synthesis and refined isotropically. The molecular structure of the title compound are shown in Fig. 2. It consists of a benzo-15-crown-5 ring and 1,2-bis(2-aminophenoxy)ethane side-arm, which contains one imine, one NH_2 and two etheric oxygen donors. The intramolecular C1···C6 [6.116(4)], C4···C9 [6.229(3)], O1···O3 [4.486(3)], O1···O4 [4.276(3)], O2···O4 [4.312(3)], O2···O5 [4.397(3)] and O3···O5 [4.520(3)Å] distances may indicate the

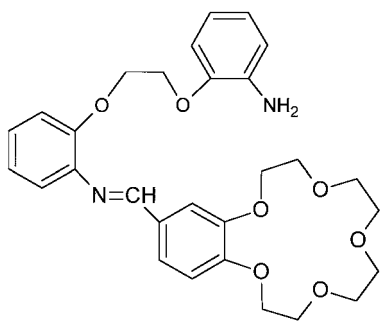

Fig. 1 Chemical diagram.

Table 1 Crystal and experimental data

Formula: $C_{29}H_{34}N_2O_7$	
Formula weight: 522.58	
Crystal system: monoclinic	
Space group: $P2_1/a$	$Z = 4$
a = 8.9857(6)Å	
b = 25.0353(17)Å	
c = 12.6979(9)Å	
β = 109.730(1)°	
V = 2688.8(3)Å^3	
D_x = 1.291 g/cm^3	
μ(Mo K_α) = 0.092 mm^{-1}	
T = 273 K	
Crystal color: colorless	
Crystal size: 0.09 × 0.22 × 0.43 mm	
λ(Mo K_α) = 0.71073 Å	
R = 0.0539	wR = 0.1131
No. of reflections measured = 6444	
No. of reflections used = 3957 [$I > 2\sigma(I)$]	
No. of parameters = 479	
Goodness-of-fit = 1.042	
$(\Delta/\sigma)_{max}$ = 0.000	
$(\Delta\rho)_{max}$ = 0.152 eÅ^{-3}	
$(\Delta\rho)_{min}$ = –0.197 eÅ^{-3}	
$2\theta_{max}$ = 56.64°	
Measurements: Bruker 1000 CCD area-detector diffractometer	
Program system: Bruker Software	
Structure determination: SHELXS-97	
Refinement: full matrix	

CCDC 294121contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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Table 2 Final atomic coordinates and equivalent isotropic thermal parameters

Atom	*x*	*y*	*z*	U_{eq}(Å^2)
O1	0.83936(14)	0.37795(5)	0.17442(10)	0.0557(3)
O2	0.89250(16)	0.36108(5)	0.39992(11)	0.0675(4)
O3	0.60302(17)	0.32504(6)	0.41651(12)	0.0753(4)
O4	0.47743(15)	0.27410(6)	0.20342(12)	0.0685(4)
O5	0.57448(14)	0.33525(5)	0.05481(10)	0.0571(3)
O6	1.21032(15)	0.43751(5)	-0.18001(11)	0.0650(4)
O7	1.32761(15)	0.46584(5)	0.05141(10)	0.0588(3)
N1	1.05539(18)	0.34000(6)	-0.22175(12)	0.0553(4)
N2	1.5060(3)	0.40938(8)	0.2258(2)	0.0792(6)
C1	0.9913(2)	0.38652(11)	0.25673(17)	0.0647(6)
C2	0.9647(3)	0.40310(10)	0.36198(18)	0.0702(6)
C3	0.8364(3)	0.37571(10)	0.48746(18)	0.0693(6)
C4	0.7445(3)	0.33023(12)	0.5085(2)	0.0768(7)
C5	0.5372(3)	0.27307(10)	0.3988(2)	0.0763(7)
C6	0.4076(3)	0.27142(12)	0.2885(2)	0.0739(6)
C7	0.3724(2)	0.29094(9)	0.09976(18)	0.0601(5)
C8	0.4578(2)	0.29435(8)	0.01768(17)	0.0546(5)
C9	0.6890(2)	0.33756(6)	0.00629(14)	0.0463(4)
C10	0.6697(2)	0.31942(8)	-0.10049(16)	0.0573(5)
C11	0.7919(2)	0.32372(8)	-0.14266(16)	0.0558(5)
C12	0.9343(2)	0.34583(7)	-0.07936(14)	0.0469(4)
C13	0.9545(2)	0.36392(7)	0.02846(15)	0.0471(4)
C14	0.8330(2)	0.36021(6)	0.07174(14)	0.0445(4)
C15	1.0648(2)	0.35322(7)	-0.12310(16)	0.0512(4)
C16	1.1796(2)	0.35276(8)	-0.26239(14)	0.0523(4)
C17	1.2177(3)	0.31643(10)	-0.33130(18)	0.0720(6)
C18	1.3289(3)	0.32785(13)	-0.3801(2)	0.0875(8)
C19	1.4009(3)	0.37641(12)	-0.36398(19)	0.0817(7)
C20	1.3653(2)	0.41423(10)	-0.29738(17)	0.0667(6)
C21	1.2557(2)	0.40245(8)	-0.24570(14)	0.0518(4)
C22	1.3061(3)	0.48264(9)	-0.13600(18)	0.0624(5)
C23	1.2634(3)	0.50249(8)	-0.03922(17)	0.0609(5)
C24	1.3114(2)	0.47791(6)	0.15301(15)	0.0489(4)
C25	1.2163(3)	0.51759(9)	0.16990(19)	0.0656(6)
C26	1.2082(3)	0.52629(10)	0.2753(2)	0.0768(7)
C27	1.2947(3)	0.49499(10)	0.3624(2)	0.0712(6)
C28	1.3908(2)	0.45527(9)	0.34650(18)	0.0601(5)
C29	1.4033(2)	0.44610(7)	0.24224(15)	0.0490(4)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (\boldsymbol{a}_i \cdot \boldsymbol{a}_j)$.

Table 3 Selected bond distances (Å) and angles (°)

O1	C1	1.428(2)	O5	C8	1.427(2)
O1	C14	1.3602(19)	O5	C9	1.3678(19)
O2	C2	1.404(2)	O6	C21	1.365(2)
O2	C3	1.415(2)	O6	C22	1.416(2)
O3	C4	1.412(3)	O7	C23	1.432(2)
O3	C5	1.416(3)	O7	C24	1.380(2)
O4	C6	1.422(2)	N1	C15	1.270(2)
O4	C7	1.401(2)	N1	C16	1.415(2)
C1-O1-C14		118.12(14)	C8-O5-C9		117.53(13)
C2-O2-C3		113.83(17)	C21-O6-C22		119.14(15)
C4-O3-C5		115.30(18)	C23-O7-C24		118.03(14)
C6-O4-C7		113.42(16)	C15-N1-C16		120.16(16)

macrocyclic hole size.

The relative macrocyclic inner-hole size,[4] which is a 15-membered macroring, is estimated to be 1.44 Å. This value can be compared with the 15-membered (1.57 Å)[5] multidentate ligand hole size.

The intermolecular N–H···O hydrogen bonds (Table 4) are dominantly effective in stabilization of the crystal structure; they result in sittings of atoms N2 on the 15-crown-5 holes. The N–H···O intermolecular hydrogen bonds link the molecules, forming infinite one-dimensional chains running approximatelly parallel to the *a*-axis (Fig. 3). The ϕ_{CN} torsion angle [C12–C15–N1–C16] is 174.00(16)°, showing that the configuration about the N1–C15 bond is *trans* planar [*anti*(1*E*)].

Table 4 Hydrogen bonding geometry (Å, °)

D-H···A	D-H	H···A	D···A	D-H···A
N2-H21···O5^{i}	0.84(2)	2.40(2)	3.072(3)	138.1(18)
N2-H22···O3^{i}	0.79(2)	2.34(2)	3.108(3)	165.9(19)

Symmetry codes: (i) 1 + *x*, *y*, *z*

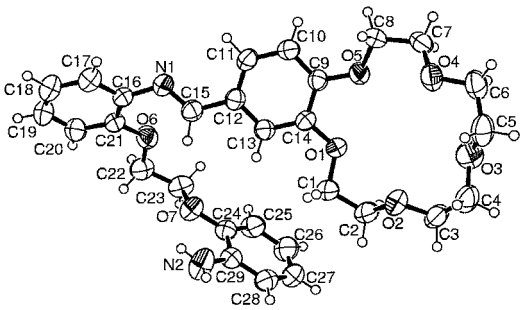

Fig. 2 Molecular structure of the title compound with the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

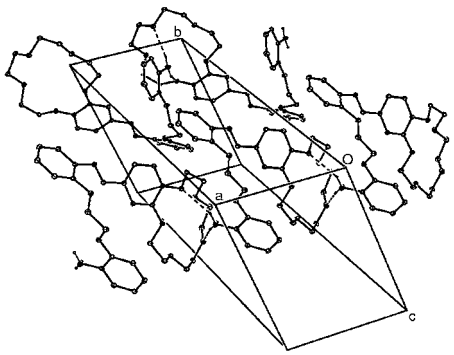

Fig. 3 Packing diagram. The dashed lines indicate hydrogen bonds. H atoms not involved in hydrogen bonds have been omitted.

Acknowledgements

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