10.1071/CH10112_AC

Australian Journal of Chemistry, 2010, 63(9), 1348–1357

Supplementary Data

Synthesis, X-ray crystal studies and metal picrates extraction properties of lipophilic benzocrown ethers

Ewa Kowalska,[A,B] *Jaywant Phopase,*[A,B] *and Nicholas Gathergood*[A,C]

[A]Department of Chemical Sciences and National Institute of Cellular Biotechnology, Dublin City University, Glasnevin 9, Ireland.
[B]Both the authors contributed equally.
[C]Corresponding author. Email: nick.gathergood@dcu.ie

Contents Page

Table of contents 1
General Experimental 2
Preparation of metal picrate salts and binding study 3

Crystallographic data
X-ray data for 1,3-*bis*[2-(2-hydroxyethoxy)phenoxy]-*m*-xylene **(6)** 4
X-ray data for 1,2-*bis*[2-(2-hydroxyethoxy)phenoxy]-*o*-xylene **(7)** 13
X-ray data for 3,10,13,21,24,31-hexaoxapentacyclo [31.2.2.1^{15,19}.0^{4,9}.0^{25,30}]octatriaconta-1(35),4(9),5,7,15,17,19(38), 25(30),26,28,33,36-dodecaen-34-yl **(19)** 16
X-ray data for 3,10,13,21,24,31-hexaoxa-38-azapentacyclo [31.3.1.1^{15,19}.0^{4,9}.0^{25,30}]octatriaconta-1(36),4(9),5,7,15,17,19(38), 25(30),26,28,33(37),34-dodecaen-8-yl **(24)** 20
X-ray data for 3,10,13,21,24,31-hexaoxa-37,38-diazapentacyclo [31.3.1.1^{15,19}.0^{4,9}.0^{25,30}]octatriaconta-1(37),4(9),5,7,15(38),16,18, 25(30),26,28,33,35-dodecaen-16-yl **(26)** 25

Crystallographic summary 34

General Experimental

All chemicals were purchased from commercial suppliers, and used without further purification. THF was distilled from sodium with benzophenone as indicator under nitrogen. Dichloromethane was distilled from CaH_2, DMF and 1,4-dioxane were purchased anhydrous from Sigma-Aldrich.

Thin layer chromatography was performed on Fluka silica gel (60 F254) coated on aluminium plates. TLC plates were visualised by UV (254 nm) and/or developed using potassium permanganate. Davisil 60Å silica gel was used for column chromatography.

Melting point determinations were carried out using a Stuart, SMP3 melting point apparatus. Infrared spectra were recorded on an Perkin Elmer FT-IR system, spectrum GX spectrometer and reported in wavenumbers (cm^{-1}). High Resolution Mass Spectrometry was carried out on Liquid Chromatography Time of flight mass spectrometer from Micromass MS Technologies Centre by the Microanalytical Laboratory at University College Dublin. NMR spectra were obtained on a Bruker AC 400 NMR spectrometer operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. The ^{1}H and ^{13}C NMR shifts are expressed in ppm relative to tetramethylsilane and were internally referenced to the residual solvent signal. Coupling constants values (*J*) are in Hertz (Hz). Chemical-shift assignments for ^{1}H and ^{13}C spectra were assisted with COSY, DEPT and HMQC experiments. The splitting patterns for NMR spectra are designated as follows: s (singlet), d (doublet), t, (triplet), q, (quartet), p, (pentet), dd (doublet of doublets), ddd (doublet of doublet of doublets), dt (doublet of triplet) and m (multiplet).

Preparation of metal picrate salts and binding study.

Picric acid (0.77g. 65% suspension in water) was suspended in 20 mL of water and warmed to 70 °C to make a saturated solution. The metal carbonate was added slowly to the hot solution with stirring until evolution of CO_2 ceased. The solution was allowed to cool to 0 °C slowly and the yellow solid precipitated was isolated by gravity filtration, washed with 5 mL of cold water and allowed to air-dry. All the following metal picrates were synthesised according to the same method:

$LiC_6H_2N_3O_7$, $NaC_6H_2N_3O_7$, $KC_6H_2N_3O_7$, $CsC_6H_2N_3O_7$, $Mg(C_6H_2N_3O_7)_2$, $Ca(C_6H_2N_3O_7)_2$, $Ba(C_6H_2N_3O_7)_2$, $Zn(C_6H_2N_3O_7)_2$, $Co(C_6H_2N_3O_7)_2$, $Cu(C_6H_2N_3O_7)_2$, $Sr(C_6H_2N_3O_7)_2$, $Pb(C_6H_2N_3O_7)_2$, and $La(C_6H_2N_3O_7)_3$.

1000 mL of $7x10^{-5}$ M solutions of each of the picrate salts were made up in deionised water. The solutions of extracting agents (500 mL each) were made up to a concentration of $1.75x10^{-5}$ M in chloroform. Each metal picrate was extracted with each of the 13 macrocyclic structures and their precursors. 6 mL each of both the picrate solution and the macrocycle solution were transferred into a glass vial and shaken on an automatic shaker for 30 minutes and the same procedure was repeated 3 times. The UV absorption spectrum for each picrate salt was measured at 356 nm and then this was compared with the aqueous layer of each mixture after shaking.
Blank extractions with chloroform were carried out for each of the picrate solutions. The recorded absorbance for each case was oscillating around the same value recorded for deionised water. Blank experiments showed that no picrate extraction occurred in the absence of crown ethers or their precursors.
Picrate extraction studies were carried out and the % extraction values of various ions were calculated using the following equation:

$$\%E = 100 \cdot \left(\frac{\left(Mol_{picrate}\right)_0 - \left(Mol_{picrate}\right)_E}{Mol_{binding\ agent}} \right)$$

Where $(Mol\ picrate)_0$ is the number of moles of metal picrate in the aqueous layer originally, $(Mol\ picrate)_E$ is the number of moles of the picrate salt in the aqueous layer after extraction and $(Mol_{binding\ agent})$ is the number of moles of binding agent in the organic layer.
The calibration curves for each of the metal picrates were drawn according to data collected from standard solutions of metal picrates. The coefficient of determination (R^2 value) for each calibration curve was > 99 % and these records were used to calculate the percentage extraction of metal picrates into the organic layer.

Crystallographic data.

X-ray data for 1,3-*bis*[2-(2-hydroxyethoxy)phenoxy]-*m*-xylene (6)

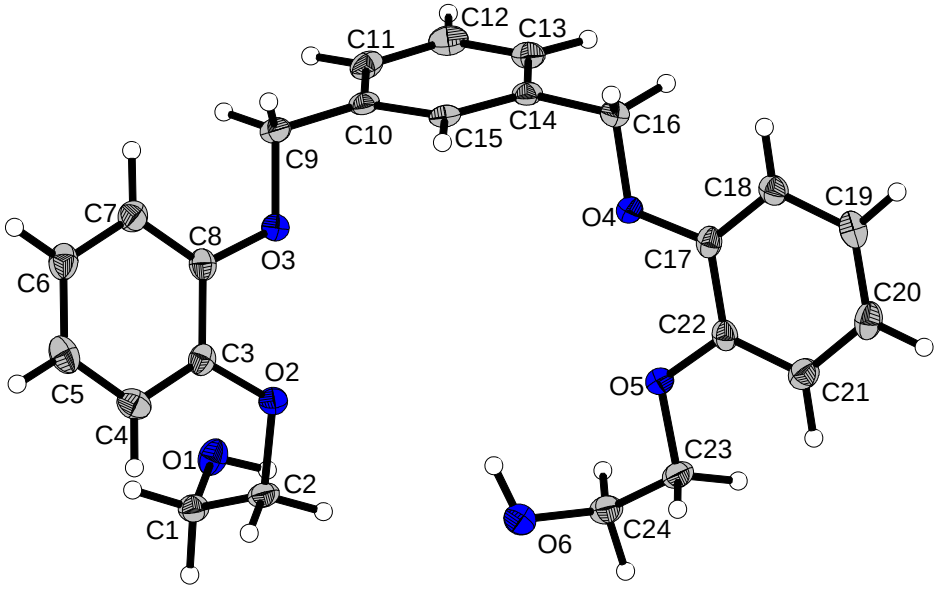

Fig. 1 1,3-*Bis*[2-(2-hydroxyethoxy)phenoxy]-*m*-xylene **(6)**, molecule; thermal ellipsoids are drawn on the 50% probability level

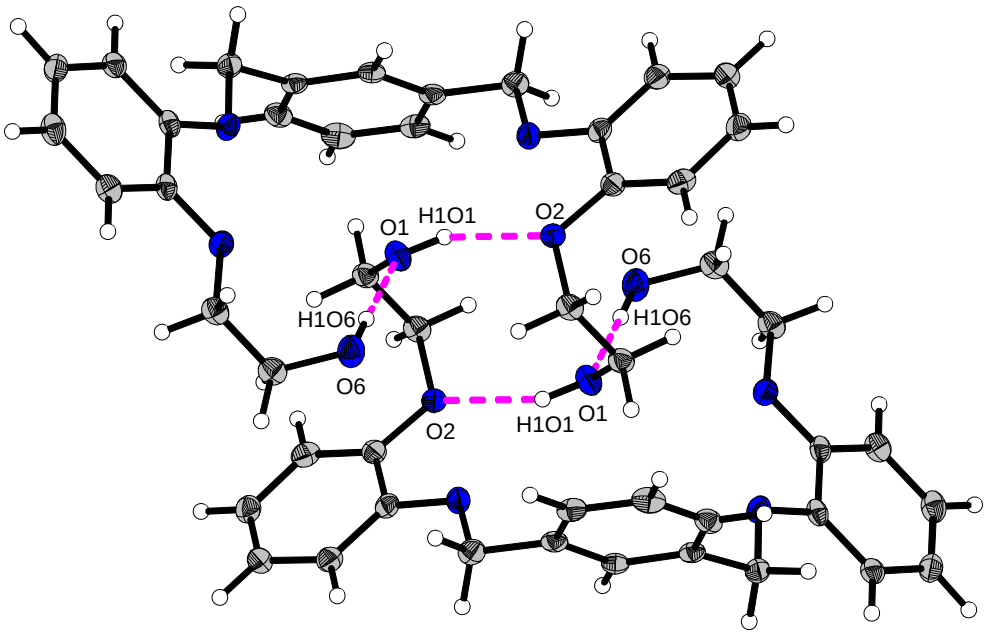

Fig. 2 Pair of hydrogen bond linked molecules; thermal ellipsoids are drawn on the 50% probability level **(6)**

Table 1. Crystal data and structure refinement for **6**.

Identification code	Gat04	
Empirical formula	$C_{24}\ H_{26}\ O_6$	
Formula weight	410.45	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$ (#14)	
Unit cell dimensions	a = 13.4964(16) Å	α= 90°.
	B = 7.0234(8) Å	β= 104.665(2)°.
	C = 22.476(3) Å	γ = 90°.
Volume	2061.2(4) $Å^3$	
Z	4	
Density (calculated)	1.323 Mg/m^3	
Absorption coefficient	0.095 mm^{-1}	
F(000)	872	
Crystal size	0.60 x 0.40 x 0.05 mm^3	
Theta range for data collection	1.87 to 26.00°.	
Index ranges	–16<=h<=16, –8<=k<=8, –27<=l<=27	
Reflections collected	17123	
Independent reflections	4056 [R(int) = 0.0359]	
Completeness to theta = 26.00°	100.0 %	
Absorption correction	Semi–empirical from equivalents	
Max. and min. transmission	0.9953 and 0.8160	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	4056 / 0 / 375	
Goodness–of–fit on F^2	1.018	
Final R indices [I>2sigma(I)]	R1 = 0.0372, wR2 = 0.0815	
R indices (all data)	R1 = 0.0490, wR2 = 0.0873	
Largest diff. peak and hole	0.246 and –0.167 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **6.** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	Y	z	U(eq)
O(1)	5961(1)	10091(2)	5822(1)	24(1)
C(1)	6336(1)	8211(2)	5790(1)	20(1)
C(2)	5842(1)	7240(2)	5192(1)	20(1)
O(2)	5978(1)	8296(1)	4667(1)	20(1)
C(3)	6945(1)	8442(2)	4584(1)	19(1)
C(4)	7746(1)	7222(2)	4831(1)	23(1)
C(5)	8705(1)	7519(2)	4718(1)	25(1)
C(6)	8852(1)	9033(2)	4361(1)	25(1)
C(7)	8042(1)	10243(2)	4099(1)	22(1)
C(8)	7086(1)	9948(2)	4203(1)	19(1)
O(3)	6231(1)	11013(1)	3960(1)	20(1)
C(9)	6365(1)	12632(2)	3595(1)	21(1)
C(10)	5329(1)	13491(2)	3330(1)	18(1)
C(11)	5091(1)	15302(2)	3506(1)	21(1)
C(12)	4131(1)	16089(2)	3260(1)	24(1)
C(13)	3399(1)	15049(2)	2845(1)	21(1)
C(14)	3620(1)	13234(2)	2666(1)	18(1)
C(15)	4590(1)	12477(2)	2903(1)	17(1)
C(16)	2801(1)	12086(2)	2243(1)	20(1)
O(4)	2458(1)	10692(1)	2614(1)	21(1)
C(17)	1664(1)	9557(2)	2319(1)	18(1)
C(18)	1204(1)	9599(2)	1695(1)	20(1)
C(19)	385(1)	8397(2)	1443(1)	23(1)
C(20)	32(1)	7138(2)	1810(1)	24(1)
C(21)	494(1)	7070(2)	2440(1)	22(1)
C(22)	1297(1)	8281(2)	2699(1)	18(1)
O(5)	1767(1)	8377(1)	3314(1)	20(1)
C(23)	1352(1)	7181(2)	3708(1)	21(1)
C(24)	1862(1)	7678(2)	4363(1)	23(1)
O(6)	2899(1)	7095(2)	4552(1)	27(1)

Table 3. Bond lengths [Å] and angles [°] for **6**.

O(1)–C(1)	1.4225(17)
O(1)–H(1O1)	0.867(19)
C(1)–C(2)	1.505(2)
C(1)–H(1A)	0.984(14)
C(1)–H(1B)	1.006(15)
C(2)–O(2)	1.4445(16)
C(2)–H(2A)	0.977(15)
C(2)–H(2B)	0.982(16)
O(2)–C(3)	1.3679(16)
C(3)–C(4)	1.381(2)
C(3)–C(8)	1.406(2)
C(4)–C(5)	1.396(2)
C(4)–H(4)	0.941(16)
C(5)–C(6)	1.378(2)
C(5)–H(5)	0.938(16)
C(6)–C(7)	1.392(2)
C(6)–H(6)	0.963(15)
C(7)–C(8)	1.384(2)
C(7)–H(7)	0.973(16)
C(8)–O(3)	1.3679(17)
O(3)–C(9)	1.4392(17)
C(9)–C(10)	1.500(2)
C(9)–H(9A)	0.989(15)
C(9)–H(9B)	0.995(17)
C(10)–C(15)	1.3919(19)
C(10)–C(11)	1.394(2)
C(11)–C(12)	1.388(2)
C(11)–H(11)	0.960(15)
C(12)–C(13)	1.384(2)
C(12)–H(12)	0.963(17)
C(13)–C(14)	1.392(2)
C(13)–H(13)	0.996(16)
C(14)–C(15)	1.388(2)
C(14)–C(16)	1.498(2)
C(15)–H(15)	0.961(15)
C(16)–O(4)	1.4370(16)
C(16)–H(16A)	0.979(15)
C(16)–H(16B)	0.980(16)
O(4)–C(17)	1.3644(16)
C(17)–C(18)	1.383(2)
C(17)–C(22)	1.4113(19)
C(18)–C(19)	1.393(2)
C(18)–H(18)	0.942(15)
C(19)–C(20)	1.374(2)
C(19)–H(19)	0.968(16)
C(20)–C(21)	1.396(2)
C(20)–H(20)	0.963(16)
C(21)–C(22)	1.384(2)
C(21)–H(21)	0.963(16)
C(22)–O(5)	1.3687(17)
O(5)–C(23)	1.4338(17)
C(23)–C(24)	1.500(2)
C(23)–H(23A)	0.984(15)
C(23)–H(23B)	0.992(17)
C(24)–O(6)	1.4155(18)
C(24)–H(24A)	0.991(15)
C(24)–H(24B)	0.999(15)
O(6)–H(1O6)	0.88(2)
C(1)–O(1)–H(1O1)	109.5(12)
O(1)–C(1)–C(2)	112.52(12)
O(1)–C(1)–H(1A)	107.2(8)
C(2)–C(1)–H(1A)	111.3(8)
O(1)–C(1)–H(1B)	110.4(9)
C(2)–C(1)–H(1B)	108.7(9)
H(1A)–C(1)–H(1B)	106.6(11)
O(2)–C(2)–C(1)	112.21(12)
O(2)–C(2)–H(2A)	103.8(9)
C(1)–C(2)–H(2A)	109.7(9)
O(2)–C(2)–H(2B)	111.4(8)

C(1)–C(2)–H(2B)	110.2(9)	C(11)–C(12)–H(12)	119.4(10)
H(2A)–C(2)–H(2B)	109.2(12)	C(12)–C(13)–C(14)	120.64(14)
C(3)–O(2)–C(2)	118.16(11)	C(12)–C(13)–H(13)	121.3(9)
O(2)–C(3)–C(4)	125.23(13)	C(14)–C(13)–H(13)	118.1(9)
O(2)–C(3)–C(8)	114.89(12)	C(15)–C(14)–C(13)	119.36(13)
C(4)–C(3)–C(8)	119.86(13)	C(15)–C(14)–C(16)	120.65(13)
C(3)–C(4)–C(5)	120.18(14)	C(13)–C(14)–C(16)	119.94(13)
C(3)–C(4)–H(4)	119.7(9)	C(14)–C(15)–C(10)	120.68(13)
C(5)–C(4)–H(4)	120.2(9)	C(14)–C(15)–H(15)	120.9(9)
C(6)–C(5)–C(4)	119.92(14)	C(10)–C(15)–H(15)	118.4(9)
C(6)–C(5)–H(5)	118.9(10)	O(4)–C(16)–C(14)	107.00(11)
C(4)–C(5)–H(5)	121.2(9)	O(4)–C(16)–H(16A)	107.9(9)
C(5)–C(6)–C(7)	120.25(14)	C(14)–C(16)–H(16A)	112.2(9)
C(5)–C(6)–H(6)	120.3(9)	O(4)–C(16)–H(16B)	110.8(9)
C(7)–C(6)–H(6)	119.4(9)	C(14)–C(16)–H(16B)	110.4(9)
C(8)–C(7)–C(6)	120.21(14)	H(16A)–C(16)–H(16B)	108.5(12)
C(8)–C(7)–H(7)	120.1(9)	C(17)–O(4)–C(16)	116.43(10)
C(6)–C(7)–H(7)	119.6(9)	O(4)–C(17)–C(18)	125.15(13)
O(3)–C(8)–C(7)	125.39(13)	O(4)–C(17)–C(22)	115.46(12)
O(3)–C(8)–C(3)	115.10(12)	C(18)–C(17)–C(22)	119.38(13)
C(7)–C(8)–C(3)	119.51(13)	C(17)–C(18)–C(19)	120.46(14)
C(8)–O(3)–C(9)	116.42(10)	C(17)–C(18)–H(18)	120.2(9)
O(3)–C(9)–C(10)	107.78(11)	C(19)–C(18)–H(18)	119.3(9)
O(3)–C(9)–H(9A)	109.6(9)	C(20)–C(19)–C(18)	120.31(14)
C(10)–C(9)–H(9A)	110.5(8)	C(20)–C(19)–H(19)	121.1(9)
O(3)–C(9)–H(9B)	109.1(9)	C(18)–C(19)–H(19)	118.6(9)
C(10)–C(9)–H(9B)	110.2(9)	C(19)–C(20)–C(21)	119.86(14)
H(9A)–C(9)–H(9B)	109.5(12)	C(19)–C(20)–H(20)	119.7(9)
C(15)–C(10)–C(11)	119.08(13)	C(21)–C(20)–H(20)	120.4(9)
C(15)–C(10)–C(9)	120.08(13)	C(22)–C(21)–C(20)	120.42(14)
C(11)–C(10)–C(9)	120.84(13)	C(22)–C(21)–H(21)	119.4(9)
C(12)–C(11)–C(10)	120.64(14)	C(20)–C(21)–H(21)	120.2(9)
C(12)–C(11)–H(11)	120.1(9)	O(5)–C(22)–C(21)	124.60(13)
C(10)–C(11)–H(11)	119.2(9)	O(5)–C(22)–C(17)	115.84(12)
C(13)–C(12)–C(11)	119.56(14)	C(21)–C(22)–C(17)	119.55(13)
C(13)–C(12)–H(12)	121.1(10)	C(22)–O(5)–C(23)	116.25(11)

O(5)–C(23)–C(24)	108.46(12)	C(23)–C(24)–H(24A)	109.7(8)
O(5)–C(23)–H(23A)	109.7(9)	O(6)–C(24)–H(24B)	107.6(8)
C(24)–C(23)–H(23A)	110.3(9)	C(23)–C(24)–H(24B)	107.6(9)
O(5)–C(23)–H(23B)	108.8(9)	H(24A)–C(24)–H(24B)	106.8(12)
C(24)–C(23)–H(23B)	110.8(9)	C(24)–O(6)–H(1O6)	108.0(13)
H(23A)–C(23)–H(23B)	108.7(12)		
O(6)–C(24)–C(23)	113.56(13)	Symmetry transformations used to generate equivalent atoms:	
O(6)–C(24)–H(24A)	111.4(8)		

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **6**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + \ldots\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	18(1)	23(1)	30(1)	–5(1)	7(1)	0(1)
C(1)	20(1)	21(1)	21(1)	3(1)	7(1)	1(1)
C(2)	22(1)	16(1)	24(1)	4(1)	8(1)	–2(1)
O(2)	19(1)	23(1)	18(1)	3(1)	5(1)	–1(1)
C(3)	18(1)	21(1)	17(1)	–5(1)	4(1)	–3(1)
C(4)	28(1)	22(1)	18(1)	0(1)	6(1)	2(1)
C(5)	22(1)	31(1)	20(1)	–2(1)	3(1)	7(1)
C(6)	18(1)	34(1)	22(1)	–3(1)	6(1)	0(1)
C(7)	21(1)	27(1)	18(1)	–1(1)	5(1)	–3(1)
C(8)	19(1)	21(1)	15(1)	–4(1)	2(1)	–1(1)
O(3)	17(1)	22(1)	21(1)	5(1)	4(1)	–1(1)
C(9)	22(1)	21(1)	20(1)	3(1)	6(1)	–5(1)
C(10)	21(1)	19(1)	16(1)	3(1)	8(1)	–4(1)
C(11)	26(1)	20(1)	18(1)	–4(1)	8(1)	–8(1)
C(12)	34(1)	17(1)	27(1)	–1(1)	14(1)	1(1)
C(13)	23(1)	20(1)	23(1)	5(1)	10(1)	3(1)
C(14)	21(1)	19(1)	15(1)	3(1)	7(1)	–2(1)
C(15)	22(1)	14(1)	17(1)	2(1)	9(1)	–2(1)
C(16)	19(1)	22(1)	18(1)	4(1)	5(1)	0(1)
O(4)	18(1)	23(1)	19(1)	4(1)	1(1)	–6(1)
C(17)	13(1)	16(1)	23(1)	–2(1)	4(1)	3(1)
C(18)	18(1)	21(1)	21(1)	2(1)	6(1)	4(1)
C(19)	20(1)	25(1)	20(1)	–4(1)	1(1)	5(1)

C(20)	19(1)	22(1)	29(1)	–7(1)	2(1)	–2(1)
C(21)	20(1)	19(1)	28(1)	0(1)	7(1)	–1(1)
C(22)	14(1)	17(1)	21(1)	0(1)	3(1)	4(1)
O(5)	19(1)	20(1)	20(1)	3(1)	3(1)	–3(1)
C(23)	21(1)	18(1)	27(1)	3(1)	8(1)	–3(1)
C(24)	24(1)	20(1)	26(1)	3(1)	8(1)	–1(1)
O(6)	24(1)	26(1)	30(1)	8(1)	4(1)	1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **6**.

Atom	x	y	z	U(eq)
H(1O1)	5299(15)	10060(30)	5750(8)	38(5)
H(1A)	7083(11)	8300(20)	5852(6)	13(3)
H(1B)	6217(11)	7410(20)	6138(7)	19(4)
H(2A)	5099(12)	7210(20)	5134(7)	18(4)
H(2B)	6098(11)	5930(20)	5193(6)	20(4)
H(4)	7645(11)	6200(20)	5079(7)	23(4)
H(5)	9259(12)	6710(20)	4887(7)	22(4)
H(6)	9518(12)	9270(20)	4292(7)	21(4)
H(7)	8154(11)	11310(20)	3846(7)	24(4)
H(9A)	6677(11)	12220(20)	3263(7)	17(4)
H(9B)	6822(12)	13570(20)	3863(7)	28(4)
H(11)	5601(11)	16010(20)	3799(7)	19(4)
H(12)	3986(12)	17350(30)	3382(7)	30(4)
H(13)	2699(12)	15570(20)	2669(7)	23(4)
H(15)	4761(11)	11230(20)	2785(6)	15(4)
H(16A)	2211(12)	12860(20)	2040(7)	19(4)
H(16B)	3072(11)	11470(20)	1926(7)	22(4)
H(18)	1433(11)	10460(20)	1438(7)	17(4)
H(19)	80(12)	8450(20)	1004(7)	23(4)
H(20)	–539(12)	6320(20)	1632(7)	25(4)
H(21)	253(11)	6180(20)	2699(7)	22(4)
H(23A)	608(12)	7380(20)	3625(7)	18(4)
H(23B)	1482(12)	5830(20)	3622(7)	26(4)

H(24A)	1791(11)	9060(20)	4429(6)	17(4)
H(24B)	1483(11)	7010(20)	4630(7)	20(4)
H(1O6)	3271(15)	7950(30)	4421(9)	48(6)

Table 6. Torsion angles [°] for **6**.

O(1)–C(1)–C(2)–O(2)	57.47(16)
C(1)–C(2)–O(2)–C(3)	67.41(16)
C(2)–O(2)–C(3)–C(4)	21.56(19)
C(2)–O(2)–C(3)–C(8)	–160.09(12)
O(2)–C(3)–C(4)–C(5)	–179.56(13)
C(8)–C(3)–C(4)–C(5)	2.2(2)
C(3)–C(4)–C(5)–C(6)	0.0(2)
C(4)–C(5)–C(6)–C(7)	–1.5(2)
C(5)–C(6)–C(7)–C(8)	0.8(2)
C(6)–C(7)–C(8)–O(3)	–178.45(13)
C(6)–C(7)–C(8)–C(3)	1.3(2)
O(2)–C(3)–C(8)–O(3)	–1.47(17)
C(4)–C(3)–C(8)–O(3)	176.98(12)
O(2)–C(3)–C(8)–C(7)	178.75(12)
C(4)–C(3)–C(8)–C(7)	–2.8(2)
C(7)–C(8)–O(3)–C(9)	–3.67(19)
C(3)–C(8)–O(3)–C(9)	176.56(12)
C(8)–O(3)–C(9)–C(10)	175.12(11)
O(3)–C(9)–C(10)–C(15)	–65.88(16)
O(3)–C(9)–C(10)–C(11)	113.91(14)
C(15)–C(10)–C(11)–C(12)	–0.1(2)
C(9)–C(10)–C(11)–C(12)	–179.91(13)
C(10)–C(11)–C(12)–C(13)	1.3(2)
C(11)–C(12)–C(13)–C(14)	–0.8(2)
C(12)–C(13)–C(14)–C(15)	–0.7(2)
C(12)–C(13)–C(14)–C(16)	176.70(13)
C(13)–C(14)–C(15)–C(10)	1.9(2)

C(16)–C(14)–C(15)–C(10)	–175.52(12)
C(11)–C(10)–C(15)–C(14)	–1.5(2)
C(9)–C(10)–C(15)–C(14)	178.33(12)
C(15)–C(14)–C(16)–O(4)	74.37(16)
C(13)–C(14)–C(16)–O(4)	–103.01(14)
C(14)–C(16)–O(4)–C(17)	176.38(11)
C(16)–O(4)–C(17)–C(18)	2.86(19)
C(16)–O(4)–C(17)–C(22)	–176.17(12)
O(4)–C(17)–C(18)–C(19)	–178.86(13)
C(22)–C(17)–C(18)–C(19)	0.1(2)
C(17)–C(18)–C(19)–C(20)	–0.8(2)
C(18)–C(19)–C(20)–C(21)	0.3(2)
C(19)–C(20)–C(21)–C(22)	0.9(2)
C(20)–C(21)–C(22)–O(5)	176.96(13)
C(20)–C(21)–C(22)–C(17)	–1.6(2)
O(4)–C(17)–C(22)–O(5)	1.49(17)
C(18)–C(17)–C(22)–O(5)	–177.59(12)
O(4)–C(17)–C(22)–C(21)	–179.85(12)
C(18)–C(17)–C(22)–C(21)	1.1(2)
C(21)–C(22)–O(5)–C(23)	–2.80(19)
C(17)–C(22)–O(5)–C(23)	175.78(12)
C(22)–O(5)–C(23)–C(24)	–172.13(12)
O(5)–C(23)–C(24)–O(6)	–71.02(16)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **6** [Å and °].

D–H…A	d(D–H)	d(H…A)	d(D…A)	<(DHA)
O(6)–H(1O6)…O(1)#1	0.88(2)	1.89(2)	2.7628(16)	175.6(19)
O(1)–H(1O1)…O(2)#1	0.867(19)	2.087(19)	2.8072(14)	140.0(16)

Symmetry transformations used to generate equivalent atoms:

#1 –x+1,–y+2,–z+1

1,2-*Bis*[2-(2-hydroxyethoxy)phenoxy]-*o*-xylene (7)

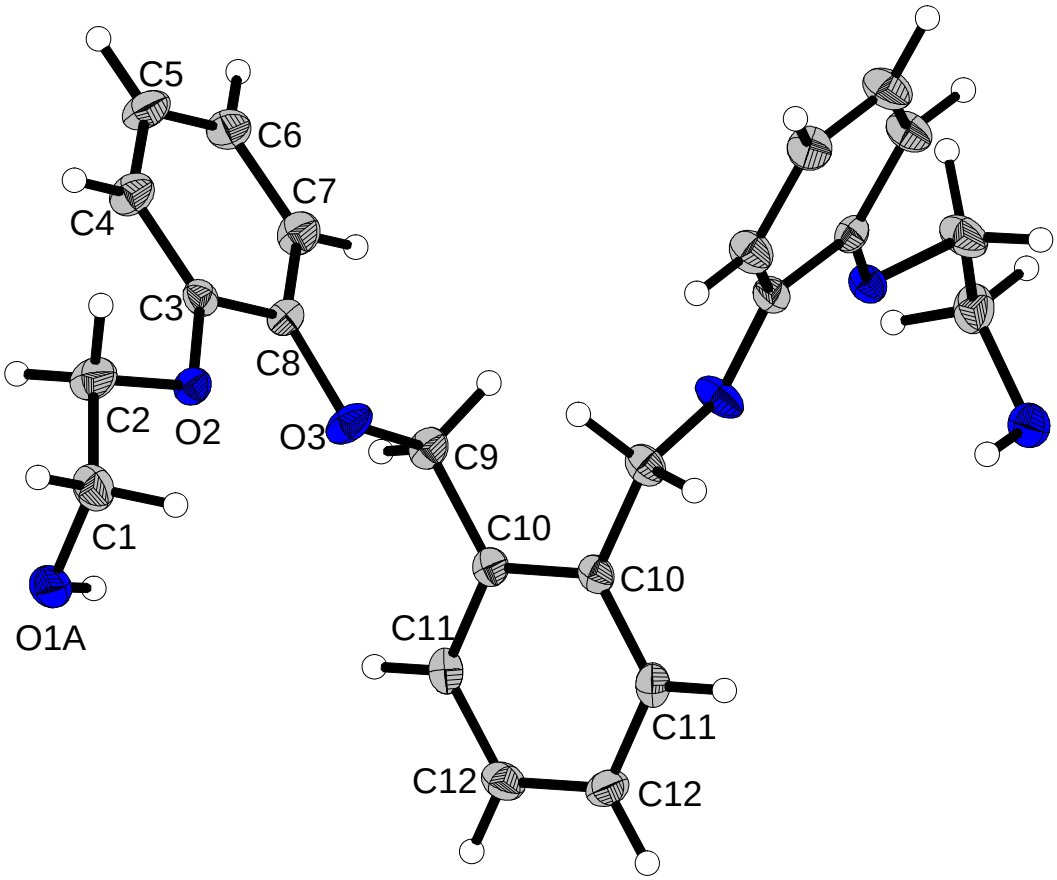

Fig. 3 X-ray crystal structure of 1,2-*bis*[2-(2-hydroxyethoxy)phenoxy]-*o*-xylene **7**

Table 8 Crystal data and structure refinement for **7**

Identification code	gat06
Empirical formula	C_{24} H_{26} O_6
Formula weight	410.45
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c (#15)
Unit cell dimensions	a = 26.492(4) Å α= 90°.
	B = 9.8112(15) Åβ= 106.831(3)°.
	C = 8.4897(13) Åγ = 90°.

Volume	2112.1(6) $Å^3$
Z	4
Density (calculated)	1.291 Mg/m^3
Absorption coefficient	0.092 mm^{-1}
F(000)	872
Crystal size	0.60 x 0.40 x 0.01 mm^3
Theta range for data collection	1.61 to 24.73°.
Index ranges	–31<=h<=31, –11<=k<=11, –9<=l<=9
Reflections collected	7805
Independent reflections	1794 [R(int) = 0.0263]
Completeness to theta = 24.73°	99.9 %
Absorption correction	Semi–empirical from equivalents
Max. and min. transmission	0.9991 and 0.8816
Refinement method	Full–matrix least–squares on F^2
Data / restraints / parameters	1794 / 0 / 148
Goodness–of–fit on F^2	1.024
Final R indices [I>2sigma(I)]	R1 = 0.0369, wR2 = 0.0851
R indices (all data)	R1 = 0.0452, wR2 = 0.0894
Largest diff. peak and hole	0.257 and –0.163 $e.Å^{-3}$

Table 9 Bond lengths [Å] and angles [°] for **7**

O(1A)–C(1)	1.505(3)	C(3)–C(8)	1.404(2)
O(1A)–H(1A)	0.8400	C(4)–C(5)	1.394(2)
C(1)–C(2)	1.485(2)	C(4)–H(4)	0.9500
C(1)–H(1A1)	0.9900	C(5)–C(6)	1.368(2)
C(1)–H(1A2)	0.9900	C(5)–H(5)	0.9500
C(1)–H(1B1)	0.9900	C(6)–C(7)	1.392(2)
C(1)–H(1B2)	0.9900	C(6)–H(6)	0.9500
O(1B)–C(1)	1.491(3)	C(7)–C(8)	1.382(2)
O(1B)–H(1B)	0.8400	C(7)–H(7)	0.9500
C(2)–O(2)	1.4289(17)	C(8)–O(3)	1.3809(17)
C(2)–H(2A)	0.9900	O(3)–C(9)	1.4457(17)
C(2)–H(2B)	0.9900	C(9)–C(10)	1.503(2)
O(2)–C(3)	1.3725(17)	C(9)–H(9A)	0.9900
C(3)–C(4)	1.376(2)	C(9)–H(9B)	0.9900

C(10)–C(11)	1.389(2)
C(10)–C(10)#1	1.405(3)
C(11)–C(12)	1.385(2)
C(11)–H(11)	0.9500
C(12)–C(12)#1	1.386(3)
C(12)–H(12)	0.9500
C(2)–C(1)–O(1A)	103.84(14)
C(2)–C(1)–H(1A1)	111.0
O(1A)–C(1)–H(1A1)	111.0
C(2)–C(1)–H(1A2)	111.0
O(1A)–C(1)–H(1A2)	111.0
H(1A1)–C(1)–H(1A2)	109.0
C(2)–C(1)–O(1B)	102.9(2)
C(2)–C(1)–H(1B1)	111.3
O(1B)–C(1)–H(1B1)	111.3
C(2)–C(1)–H(1B2)	111.3
O(1B)–C(1)–H(1B2)	111.3
H(1B1)–C(1)–H(1B2)	109.1
O(2)–C(2)–C(1)	108.83(12)
O(2)–C(2)–H(2A)	109.9
C(1)–C(2)–H(2A)	109.9
O(2)–C(2)–H(2B)	109.9
C(1)–C(2)–H(2B)	109.9
H(2A)–C(2)–H(2B)	108.3
C(3)–O(2)–C(2)	116.89(11)
O(2)–C(3)–C(4)	124.76(13)
O(2)–C(3)–C(8)	116.02(12)
C(4)–C(3)–C(8)	119.22(13)
C(3)–C(4)–C(5)	120.35(14)
C(3)–C(4)–H(4)	119.8
C(5)–C(4)–H(4)	119.8
C(6)–C(5)–C(4)	120.45(14)
C(6)–C(5)–H(5)	119.8
C(4)–C(5)–H(5)	119.8
C(5)–C(6)–C(7)	119.83(14)
C(5)–C(6)–H(6)	120.1
C(7)–C(6)–H(6)	120.1
C(8)–C(7)–C(6)	120.17(14)
C(8)–C(7)–H(7)	119.9
C(6)–C(7)–H(7)	119.9
O(3)–C(8)–C(7)	124.61(13)
O(3)–C(8)–C(3)	115.39(12)
C(7)–C(8)–C(3)	119.98(13)
C(8)–O(3)–C(9)	115.07(11)
O(3)–C(9)–C(10)	109.02(11)
O(3)–C(9)–H(9A)	109.9
C(10)–C(9)–H(9A)	109.9
O(3)–C(9)–H(9B)	109.9
C(10)–C(9)–H(9B)	109.9
H(9A)–C(9)–H(9B)	108.3
C(11)–C(10)–C(10)#1	119.11(8)
C(11)–C(10)–C(9)	119.78(13)
C(10)#1–C(10)–C(9)	121.07(8)
C(12)–C(11)–C(10)	121.23(14)
C(12)–C(11)–H(11)	119.4
C(10)–C(11)–H(11)	119.4
C(11)–C(12)–C(12)#1	119.67(9)
C(11)–C(12)–H(12)	120.2
C(12)#1–C(12)–H(12)	120.2

3,10,13,21,24,31-Hexaoxapentacyclo[31.2.2.1^{15,19}.0^{4,9}.0^{25,30}]octatriaconta-1(35),4(9),5,7,15,17,19(38),25(30),26,28,33,36-dodecaen-34-yl (19)

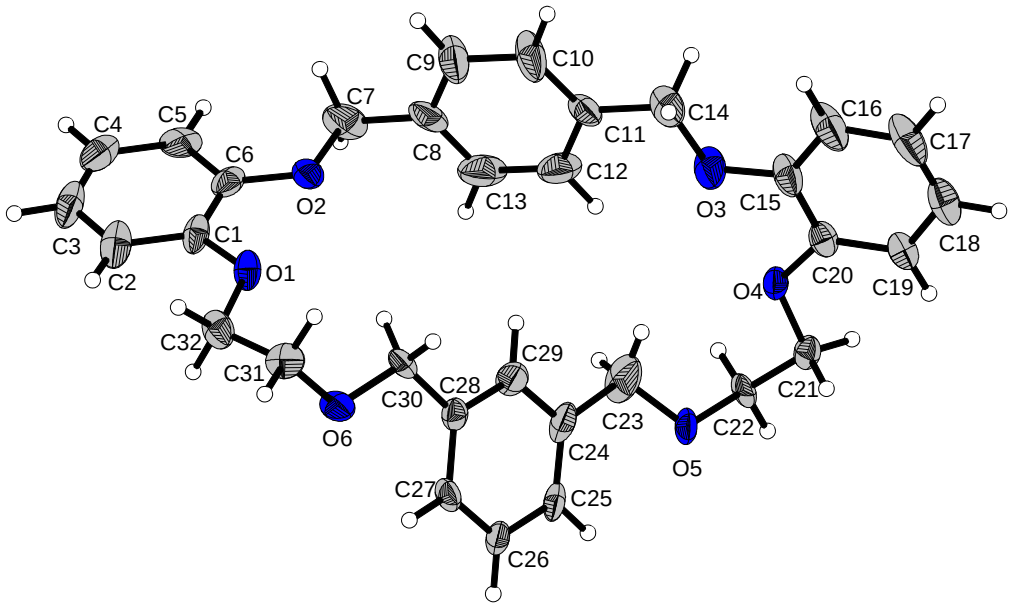

Fig. 4 X-ray crystal structure of 3,10,13,21,24,31-hexaoxapentacyclo[31.2.2.1^{15,19}.0^{4,9}.0^{25,30}]octatriaconta-1(35),4(9),5,7,15,17,19(38),25(30),26,28,33,36-dodecaen-34-yl (19)

Table 10 Crystal data and structure refinement for **19**

Identification code	gat15
Empirical formula	C_{32} H_{32} O_6
Formula weight	512.58
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$ (#14)
Unit cell dimensions	a = 4.606(3) Å α= 90°.
	B = 17.852(10) Å β= 93.071(11)°.
	C = 30.159(16) Å γ = 90°.
Volume	2476(2) Å^3
Z	4
Density (calculated)	1.375 Mg/m^3
Absorption coefficient	0.094 mm^{-1}

F(000)	1088
Crystal size	0.50 x 0.05 x 0.05 mm^3
Theta range for data collection	1.33 to 19.00°.
Index ranges	–4<=h<=4, –16<=k<=16, –27<=l<=27
Reflections collected	6108
Independent reflections	1979 [R(int) = 0.0606]
Completeness to theta = 19.00°	99.1 %
Absorption correction	Semi–empirical from equivalents
Max. and min. transmission	0.9953 and 0.7304
Refinement method	Full–matrix least–squares on F^2
Data / restraints / parameters	1979 / 348 / 343 [a)]
Goodness–of–fit on F^2	1.127
Final R indices [I>2sigma(I)]	R1 = 0.0811, wR2 = 0.1776
R indices (all data)	R1 = 0.1044, wR2 = 0.1868
Largest diff. peak and hole	0.322 and –0.248 e.$Å^{-3}$

DELU and SIMU restraints were applied to all thermal displacement parameters.

Table 11 Bond lengths [Å] and angles [°] for **19**

O(1)–C(1)	1.335(8)	C(8)–C(13)	1.364(11)
O(1)–C(32)	1.414(8)	C(9)–C(10)	1.367(11)
C(1)–C(6)	1.372(10)	C(9)–H(9)	0.9500
C(1)–C(2)	1.373(10)	C(10)–C(11)	1.347(10)
C(2)–C(3)	1.354(11)	C(10)–H(10)	0.9500
C(2)–H(2)	0.9500	C(11)–C(12)	1.370(10)
C(3)–C(4)	1.340(12)	C(11)–C(14)	1.480(10)
C(3)–H(3)	0.9500	C(12)–C(13)	1.369(11)
C(4)–C(5)	1.387(11)	C(12)–H(12)	0.9500
C(4)–H(4)	0.9500	C(13)–H(13)	0.9500
C(5)–C(6)	1.362(10)	C(14)–O(3)	1.404(8)
C(5)–H(5)	0.9500	C(14)–H(14A)	0.9900
C(6)–O(2)	1.360(8)	C(14)–H(14B)	0.9900
O(2)–C(7)	1.421(9)	O(3)–C(15)	1.359(9)
C(7)–C(8)	1.468(10)	C(15)–C(16)	1.351(10)
C(7)–H(7A)	0.9900	C(15)–C(20)	1.386(10)
C(7)–H(7B)	0.9900	C(16)–C(17)	1.362(11)
C(8)–C(9)	1.335(10)	C(16)–H(16)	0.9500

C(17)–C(18)	1.352(11)	C(31)–H(31B)	0.9900
C(17)–H(17)	0.9500	C(32)–H(32A)	0.9900
C(18)–C(19)	1.364(10)	C(32)–H(32B)	0.9900
C(18)–H(18)	0.9500		
C(19)–C(20)	1.378(9)	C(1)–O(1)–C(32)	117.7(6)
C(19)–H(19)	0.9500	O(1)–C(1)–C(6)	115.7(7)
C(20)–O(4)	1.342(8)	O(1)–C(1)–C(2)	125.7(8)
O(4)–C(21)	1.421(8)	C(6)–C(1)–C(2)	118.6(8)
C(21)–C(22)	1.479(9)	C(3)–C(2)–C(1)	120.4(9)
C(21)–H(21A)	0.9900	C(3)–C(2)–H(2)	119.8
C(21)–H(21B)	0.9900	C(1)–C(2)–H(2)	119.8
C(22)–O(5)	1.402(8)	C(4)–C(3)–C(2)	122.1(9)
C(22)–H(22A)	0.9900	C(4)–C(3)–H(3)	119.0
C(22)–H(22B)	0.9900	C(2)–C(3)–H(3)	119.0
O(5)–C(23)	1.365(8)	C(3)–C(4)–C(5)	118.0(9)
C(23)–C(24)	1.493(10)	C(3)–C(4)–H(4)	121.0
C(23)–H(23A)	0.9900	C(5)–C(4)–H(4)	121.0
C(23)–H(23B)	0.9900	C(6)–C(5)–C(4)	120.9(9)
C(24)–C(25)	1.356(10)	C(6)–C(5)–H(5)	119.6
C(24)–C(29)	1.368(10)	C(4)–C(5)–H(5)	119.6
C(25)–C(26)	1.382(10)	O(2)–C(6)–C(5)	125.4(8)
C(25)–H(25)	0.9500	O(2)–C(6)–C(1)	114.5(7)
C(26)–C(27)	1.362(9)	C(5)–C(6)–C(1)	120.1(8)
C(26)–H(26)	0.9500	C(6)–O(2)–C(7)	117.4(6)
C(27)–C(28)	1.372(9)	O(2)–C(7)–C(8)	106.7(6)
C(27)–H(27)	0.9500	O(2)–C(7)–H(7A)	110.4
C(28)–C(29)	1.381(9)	C(8)–C(7)–H(7A)	110.4
C(28)–C(30)	1.475(9)	O(2)–C(7)–H(7B)	110.4
C(29)–H(29)	0.9500	C(8)–C(7)–H(7B)	110.4
C(30)–O(6)	1.407(7)	H(7A)–C(7)–H(7B)	108.6
C(30)–H(30A)	0.9900	C(9)–C(8)–C(13)	117.4(8)
C(30)–H(30B)	0.9900	C(9)–C(8)–C(7)	121.1(8)
O(6)–C(31)	1.415(8)	C(13)–C(8)–C(7)	121.5(8)
C(31)–C(32)	1.467(10)	C(8)–C(9)–C(10)	120.6(8)
C(31)–H(31A)	0.9900	C(8)–C(9)–H(9)	119.7

C(10)–C(9)–H(9)	119.7
C(11)–C(10)–C(9)	123.3(8)
C(11)–C(10)–H(10)	118.4
C(9)–C(10)–H(10)	118.4
C(10)–C(11)–C(12)	116.3(7)
C(10)–C(11)–C(14)	121.4(7)
C(12)–C(11)–C(14)	122.3(7)
C(13)–C(12)–C(11)	120.3(8)
C(13)–C(12)–H(12)	119.9
C(11)–C(12)–H(12)	119.9
C(8)–C(13)–C(12)	122.1(8)
C(8)–C(13)–H(13)	119.0
C(12)–C(13)–H(13)	119.0
O(3)–C(14)–C(11)	108.1(6)
O(3)–C(14)–H(14A)	110.1
C(11)–C(14)–H(14A)	110.1
O(3)–C(14)–H(14B)	110.1
C(11)–C(14)–H(14B)	110.1
H(14A)–C(14)–H(14B)	108.4
C(15)–O(3)–C(14)	117.9(6)
C(16)–C(15)–O(3)	126.0(7)
C(16)–C(15)–C(20)	120.9(8)
O(3)–C(15)–C(20)	113.1(6)
C(15)–C(16)–C(17)	119.1(8)
C(15)–C(16)–H(16)	120.4
C(17)–C(16)–H(16)	120.4
C(18)–C(17)–C(16)	121.3(8)
C(18)–C(17)–H(17)	119.4
C(16)–C(17)–H(17)	119.4
C(17)–C(18)–C(19)	120.1(8)
C(17)–C(18)–H(18)	119.9
C(19)–C(18)–H(18)	119.9
C(18)–C(19)–C(20)	119.7(8)
C(18)–C(19)–H(19)	120.2
C(20)–C(19)–H(19)	120.2

O(4)–C(20)–C(19)	125.9(7)
O(4)–C(20)–C(15)	115.3(6)
C(19)–C(20)–C(15)	118.8(7)
C(20)–O(4)–C(21)	118.3(5)
O(4)–C(21)–C(22)	108.0(5)
O(4)–C(21)–H(21A)	110.1
C(22)–C(21)–H(21A)	110.1
O(4)–C(21)–H(21B)	110.1
C(22)–C(21)–H(21B)	110.1
H(21A)–C(21)–H(21B)	108.4
O(5)–C(22)–C(21)	113.1(6)
O(5)–C(22)–H(22A)	109.0
C(21)–C(22)–H(22A)	109.0
O(5)–C(22)–H(22B)	109.0
C(21)–C(22)–H(22B)	109.0
H(22A)–C(22)–H(22B)	107.8
C(23)–O(5)–C(22)	113.8(6)
O(5)–C(23)–C(24)	110.4(7)
O(5)–C(23)–H(23A)	109.6
C(24)–C(23)–H(23A)	109.6
O(5)–C(23)–H(23B)	109.6
C(24)–C(23)–H(23B)	109.6
H(23A)–C(23)–H(23B)	108.1
C(25)–C(24)–C(29)	118.7(7)
C(25)–C(24)–C(23)	124.0(7)
C(29)–C(24)–C(23)	117.2(8)
C(24)–C(25)–C(26)	120.5(7)
C(24)–C(25)–H(25)	119.7
C(26)–C(25)–H(25)	119.7
C(27)–C(26)–C(25)	120.8(7)
C(27)–C(26)–H(26)	119.6
C(25)–C(26)–H(26)	119.6
C(26)–C(27)–C(28)	118.9(7)
C(26)–C(27)–H(27)	120.5
C(28)–C(27)–H(27)	120.5

C(27)–C(28)–C(29)	119.8(7)
C(27)–C(28)–C(30)	122.1(6)
C(29)–C(28)–C(30)	118.1(7)
C(24)–C(29)–C(28)	121.2(7)
C(24)–C(29)–H(29)	119.4
C(28)–C(29)–H(29)	119.4
O(6)–C(30)–C(28)	110.9(6)
O(6)–C(30)–H(30A)	109.5
C(28)–C(30)–H(30A)	109.5
O(6)–C(30)–H(30B)	109.5
C(28)–C(30)–H(30B)	109.5
H(30A)–C(30)–H(30B)	108.1
C(30)–O(6)–C(31)	113.9(5)

O(6)–C(31)–C(32)	112.9(6)
O(6)–C(31)–H(31A)	109.0
C(32)–C(31)–H(31A)	109.0
O(6)–C(31)–H(31B)	109.0
C(32)–C(31)–H(31B)	109.0
H(31A)–C(31)–H(31B)	107.8
O(1)–C(32)–C(31)	107.7(6)
O(1)–C(32)–H(32A)	110.2
C(31)–C(32)–H(32A)	110.2
O(1)–C(32)–H(32B)	110.2
C(31)–C(32)–H(32B)	110.2
H(32A)–C(32)–H(32B)	108.5

3,10,13,21,24,31-Hexaoxa-38-azapentacyclo[31.3.1.1^{15,19}.0^{4,9}.0^{25,30}]octatriaconta-1(36),4(9),5,7,15,17,19(38),25(30),26,28,33(37),34-dodecaen-8-yl (24)

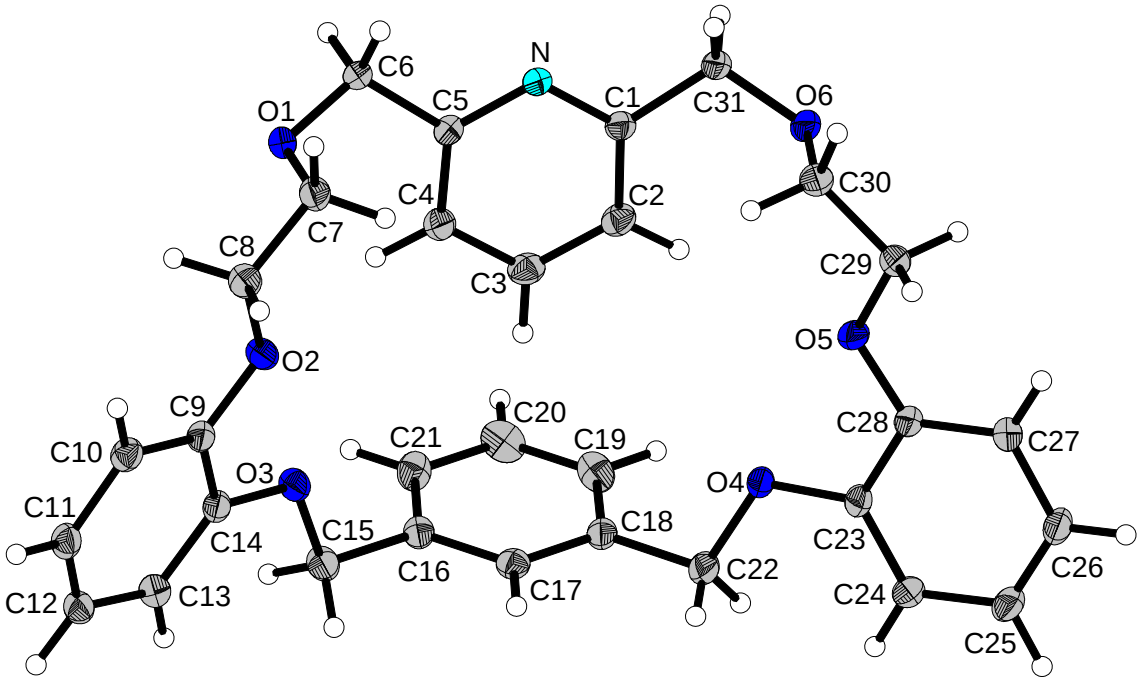

Fig. 5 X-ray crystal structure of *3,10,13,21,24,31-hexaoxa-38-azapentacyclo[31.3.1.1^{15,19}.0^{4,9}.0^{25,30}]octatriaconta-1(36),4(9),5,7,15,17,19(38),25(30),26,28,33(37),34-dodecaen-8-yl* **24**

Table 12 Crystal data and structure refinement for **24**

Identification code	gat23
Empirical formula	C_{31} H_{31} N O_6
Formula weight	513.57
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1$ (#4)
Unit cell dimensions	a = 14.6295(9) Å α= 90°.
	B = 5.2396(3) Å β= 107.767(1)°.
	C = 17.8162(11) Å γ = 90°.
Volume	1300.53(14) $Å^3$
Z	2
Density (calculated)	1.311 Mg/m^3
Absorption coefficient	0.091 mm^{-1}
F(000)	544
Crystal size	0.5 x 0.2 x 0.2 mm^3
Theta range for data collection	1.46 to 30.52°.
Index ranges	–20<=h<=20, –7<=k<=7, –25<=l<=23
Reflections collected	15434
Independent reflections	4361 [R(int) = 0.0242]
Completeness to theta = 30.52°	99.3 %
Absorption correction	Semi–empirical from equivalents
Max. and min. transmission	0.9821 and 0.8246
Refinement method	Full–matrix least–squares on F^2
Data / restraints / parameters	4361 / 1 / 343
Goodness–of–fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0420, wR2 = 0.1029
R indices (all data)	R1 = 0.0452, wR2 = 0.1052
Largest diff. peak and hole	0.361 and –0.216 $e.Å^{-3}$

N–C(5)	1.341(2)	C(15)–H(15A)	0.9900
N–C(1)	1.3412(19)	C(15)–H(15B)	0.9900
C(1)–C(2)	1.392(2)	C(16)–C(21)	1.388(3)
C(1)–C(31)	1.508(2)	C(16)–C(17)	1.396(2)
C(2)–C(3)	1.386(2)	C(17)–C(18)	1.393(2)
C(2)–H(2)	0.9500	C(17)–H(17)	0.9500
C(3)–C(4)	1.385(2)	C(18)–C(19)	1.392(3)
C(3)–H(3)	0.9500	C(18)–C(22)	1.499(2)
C(4)–C(5)	1.389(2)	C(19)–C(20)	1.378(3)
C(4)–H(4)	0.9500	C(19)–H(19)	0.9500
C(5)–C(6)	1.511(2)	C(20)–C(21)	1.390(2)
C(6)–O(1)	1.4206(18)	C(20)–H(20)	0.9500
C(6)–H(6A)	0.9900	C(21)–H(21)	0.9500
C(6)–H(6B)	0.9900	C(22)–O(4)	1.4310(19)
O(1)–C(7)	1.423(2)	C(22)–H(22A)	0.9900
C(7)–C(8)	1.503(2)	C(22)–H(22B)	0.9900
C(7)–H(7A)	0.9900	O(4)–C(23)	1.3719(18)
C(7)–H(7B)	0.9900	C(23)–C(24)	1.390(2)
C(8)–O(2)	1.4331(19)	C(23)–C(28)	1.406(2)
C(8)–H(8A)	0.9900	C(24)–C(25)	1.396(2)
C(8)–H(8B)	0.9900	C(24)–H(24)	0.9500
O(2)–C(9)	1.3647(18)	C(25)–C(26)	1.371(3)
C(9)–C(10)	1.388(2)	C(25)–H(25)	0.9500
C(9)–C(14)	1.412(2)	C(26)–C(27)	1.401(2)
C(10)–C(11)	1.403(2)	C(26)–H(26)	0.9500
C(10)–H(10)	0.9500	C(27)–C(28)	1.387(2)
C(11)–C(12)	1.375(3)	C(27)–H(27)	0.9500
C(11)–H(11)	0.9500	C(28)–O(5)	1.3678(17)
C(12)–C(13)	1.401(2)	O(5)–C(29)	1.4315(19)
C(12)–H(12)	0.9500	C(29)–C(30)	1.503(2)
C(13)–C(14)	1.389(2)	C(29)–H(29A)	0.9900
C(13)–H(13)	0.9500	C(29)–H(29B)	0.9900
C(14)–O(3)	1.3689(18)	C(30)–O(6)	1.421(2)
O(3)–C(15)	1.4390(19)	C(30)–H(30A)	0.9900
C(15)–C(16)	1.501(2)	C(30)–H(30B)	0.9900

O(6)–C(31)	1.4248(18)
C(31)–H(31A)	0.9900
C(31)–H(31B)	0.9900
C(5)–N–C(1)	118.05(13)
N–C(1)–C(2)	122.73(14)
N–C(1)–C(31)	114.71(13)
C(2)–C(1)–C(31)	122.55(14)
C(3)–C(2)–C(1)	118.35(14)
C(3)–C(2)–H(2)	120.8
C(1)–C(2)–H(2)	120.8
C(4)–C(3)–C(2)	119.60(15)
C(4)–C(3)–H(3)	120.2
C(2)–C(3)–H(3)	120.2
C(3)–C(4)–C(5)	118.11(15)
C(3)–C(4)–H(4)	120.9
C(5)–C(4)–H(4)	120.9
N–C(5)–C(4)	123.15(14)
N–C(5)–C(6)	115.32(14)
C(4)–C(5)–C(6)	121.52(14)
O(1)–C(6)–C(5)	112.37(12)
O(1)–C(6)–H(6A)	109.1
C(5)–C(6)–H(6A)	109.1
O(1)–C(6)–H(6B)	109.1
C(5)–C(6)–H(6B)	109.1
H(6A)–C(6)–H(6B)	107.9
C(6)–O(1)–C(7)	111.77(13)
O(1)–C(7)–C(8)	108.83(14)
O(1)–C(7)–H(7A)	109.9
C(8)–C(7)–H(7A)	109.9
O(1)–C(7)–H(7B)	109.9
C(8)–C(7)–H(7B)	109.9
H(7A)–C(7)–H(7B)	108.3
O(2)–C(8)–C(7)	107.40(13)
O(2)–C(8)–H(8A)	110.2
C(7)–C(8)–H(8A)	110.2
O(2)–C(8)–H(8B)	110.2
C(7)–C(8)–H(8B)	110.2
H(8A)–C(8)–H(8B)	108.5
C(9)–O(2)–C(8)	116.03(12)
O(2)–C(9)–C(10)	124.56(15)
O(2)–C(9)–C(14)	115.54(13)
C(10)–C(9)–C(14)	119.91(14)
C(9)–C(10)–C(11)	120.21(16)
C(9)–C(10)–H(10)	119.9
C(11)–C(10)–H(10)	119.9
C(12)–C(11)–C(10)	119.89(15)
C(12)–C(11)–H(11)	120.1
C(10)–C(11)–H(11)	120.1
C(11)–C(12)–C(13)	120.36(15)
C(11)–C(12)–H(12)	119.8
C(13)–C(12)–H(12)	119.8
C(14)–C(13)–C(12)	120.36(16)
C(14)–C(13)–H(13)	119.8
C(12)–C(13)–H(13)	119.8
O(3)–C(14)–C(13)	124.90(15)
O(3)–C(14)–C(9)	115.90(13)
C(13)–C(14)–C(9)	119.19(14)
C(14)–O(3)–C(15)	116.27(12)
O(3)–C(15)–C(16)	108.33(12)
O(3)–C(15)–H(15A)	110.0
C(16)–C(15)–H(15A)	110.0
O(3)–C(15)–H(15B)	110.0
C(16)–C(15)–H(15B)	110.0
H(15A)–C(15)–H(15B)	108.4
C(21)–C(16)–C(17)	119.40(15)
C(21)–C(16)–C(15)	119.92(15)
C(17)–C(16)–C(15)	120.68(16)
C(18)–C(17)–C(16)	120.79(16)
C(18)–C(17)–H(17)	119.6

C(16)–C(17)–H(17)	119.6
C(19)–C(18)–C(17)	119.03(16)
C(19)–C(18)–C(22)	119.25(16)
C(17)–C(18)–C(22)	121.69(18)
C(20)–C(19)–C(18)	120.26(16)
C(20)–C(19)–H(19)	119.9
C(18)–C(19)–H(19)	119.9
C(19)–C(20)–C(21)	120.78(18)
C(19)–C(20)–H(20)	119.6
C(21)–C(20)–H(20)	119.6
C(16)–C(21)–C(20)	119.73(16)
C(16)–C(21)–H(21)	120.1
C(20)–C(21)–H(21)	120.1
O(4)–C(22)–C(18)	108.86(13)
O(4)–C(22)–H(22A)	109.9
C(18)–C(22)–H(22A)	109.9
O(4)–C(22)–H(22B)	109.9
C(18)–C(22)–H(22B)	109.9
H(22A)–C(22)–H(22B)	108.3
C(23)–O(4)–C(22)	115.90(12)
O(4)–C(23)–C(24)	124.50(14)
O(4)–C(23)–C(28)	116.34(13)
C(24)–C(23)–C(28)	119.14(14)
C(23)–C(24)–C(25)	120.54(16)
C(23)–C(24)–H(24)	119.7
C(25)–C(24)–H(24)	119.7
C(26)–C(25)–C(24)	120.40(15)
C(26)–C(25)–H(25)	119.8
C(24)–C(25)–H(25)	119.8
C(25)–C(26)–C(27)	119.70(15)
C(25)–C(26)–H(26)	120.1
C(27)–C(26)–H(26)	120.1
C(28)–C(27)–C(26)	120.47(16)
C(28)–C(27)–H(27)	119.8
C(26)–C(27)–H(27)	119.8
O(5)–C(28)–C(27)	124.64(14)
O(5)–C(28)–C(23)	115.61(13)
C(27)–C(28)–C(23)	119.74(14)
C(28)–O(5)–C(29)	116.41(12)
O(5)–C(29)–C(30)	107.29(13)
O(5)–C(29)–H(29A)	110.3
C(30)–C(29)–H(29A)	110.3
O(5)–C(29)–H(29B)	110.3
C(30)–C(29)–H(29B)	110.3
H(29A)–C(29)–H(29B)	108.5
O(6)–C(30)–C(29)	109.29(14)
O(6)–C(30)–H(30A)	109.8
C(29)–C(30)–H(30A)	109.8
O(6)–C(30)–H(30B)	109.8
C(29)–C(30)–H(30B)	109.8
H(30A)–C(30)–H(30B)	108.3
C(30)–O(6)–C(31)	110.96(13)
O(6)–C(31)–C(1)	112.93(12)
O(6)–C(31)–H(31A)	109.0
C(1)–C(31)–H(31A)	109.0
O(6)–C(31)–H(31B)	109.0

Table 13 Bond lengths [Å] and angles [°] for **24**

3,10,13,21,24,31-Hexaoxa-37,38-diazapentacyclo[31.3.1.1^{15,19}.0^{4,9}.0^{25,30}]octatriaconta-1(37),4(9),5,7,15(38),16,18,25(30),26,28,33,35-dodecaen-16-yl (26)

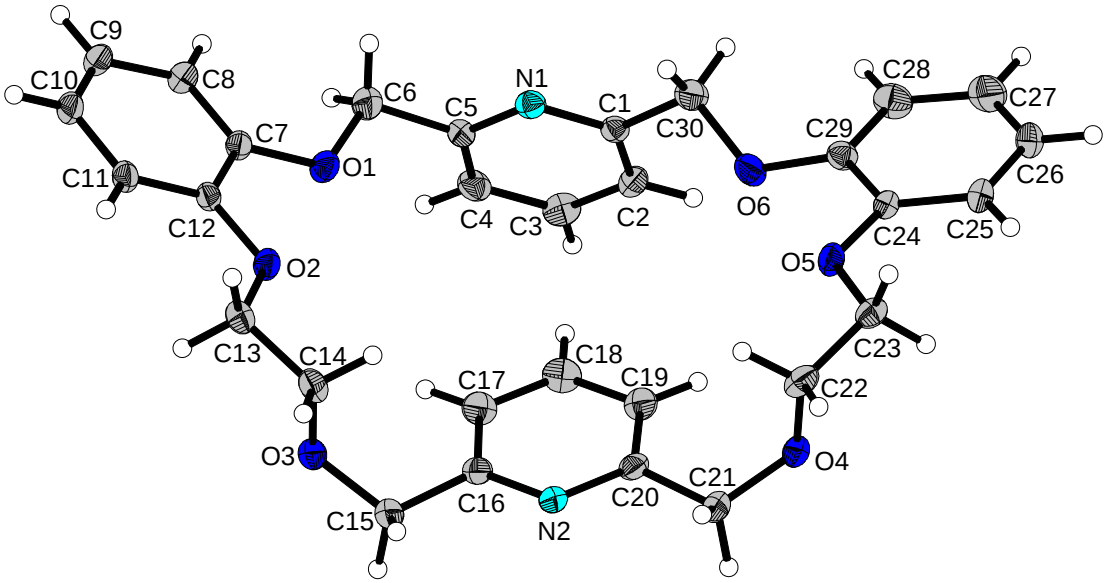

Fig. 6 X-ray crystal structure of *3,10,13,21,24,31-hexaoxa-37,38-diazapentacyclo[31.3.1.1^{15,19}.0^{4,9}.0^{25,30}]octatriaconta-1(37),4(9),5,7,15(38),16,18,25(30),26,28,33,35-dodecaen-16-yl* **26**

Table 14. Crystal data and structure refinement for **26**.

Identification code	gat21	
Empirical formula	$C_{30}\ H_{30}\ N_2\ O_6$	
Formula weight	514.56	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$ (#4)	
Unit cell dimensions	a = 15.080(2) Å	α= 90°.
	B = 5.4720(8) Å	β= 113.695(3)°.
	C = 17.191(2) Å	γ = 90°.
Volume	1299.0(3) Å^3	
Z	2	
Density (calculated)	1.316 Mg/m^3	
Absorption coefficient	0.092 mm^{-1}	

F(000)	544
Crystal size	0.50 x 0.30 x 0.20 mm^3
Theta range for data collection	1.29 to 24.11°.
Index ranges	–17<=h<=17, –6<=k<=6, –19<=l<=19
Reflections collected	9612
Independent reflections	2314 [R(int) = 0.0233]
Completeness to theta = 24.11°	99.9 %
Absorption correction	Semi–empirical from equivalents
Max. and min. transmission	0.9818 and 0.8775
Refinement method	Full–matrix least–squares on F^2
Data / restraints / parameters	2314 / 97 / 343 [a)]
Goodness–of–fit on F^2	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0385, wR2 = 0.0973
R indices (all data)	R1 = 0.0423, wR2 = 0.1006
Largest diff. peak and hole	0.336 and –0.209 e.$Å^{-3}$

a) DELU (rigid bond) restraints were applied to all themal displacement parameters.

Table 15. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **26**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
N(1)	3826(2)	5899(5)	3765(1)	56(1)
C(1)	4716(2)	6597(6)	3885(2)	50(1)
C(2)	4896(2)	8721(7)	3542(2)	61(1)
C(3)	4136(3)	10161(7)	3061(2)	73(1)
C(4)	3214(3)	9452(8)	2925(2)	73(1)
C(5)	3087(2)	7350(7)	3285(2)	62(1)
C(6)	2098(2)	6670(11)	3175(2)	91(1)
O(1)	1663(1)	5175(5)	2456(1)	68(1)
C(7)	764(2)	4213(6)	2300(2)	56(1)
C(8)	165(2)	5029(8)	2676(2)	71(1)
C(9)	–723(2)	3909(9)	2491(2)	77(1)
C(10)	–1002(2)	1974(8)	1948(2)	75(1)
C(11)	–413(2)	1156(7)	1560(2)	64(1)
C(12)	459(2)	2291(6)	1721(2)	53(1)
O(2)	1080(1)	1661(4)	1354(1)	63(1)

C(13)	815(2)	–338(7)	774(2)	63(1)
C(14)	1592(2)	–684(7)	463(2)	68(1)
O(3)	1574(1)	1234(6)	–91(1)	73(1)
C(15)	2388(2)	1140(10)	–310(2)	81(1)
C(16)	3309(2)	1994(7)	399(2)	60(1)
N(2)	4117(2)	935(6)	422(1)	58(1)
C(17)	3315(3)	3797(7)	963(2)	73(1)
C(18)	4181(3)	4536(7)	1565(2)	76(1)
C(19)	5021(2)	3473(7)	1601(2)	68(1)
C(20)	4961(2)	1683(7)	1017(2)	59(1)
C(21)	5842(2)	508(10)	967(2)	82(1)
O(4)	6678(1)	700(6)	1737(1)	74(1)
C(22)	6744(2)	–1154(7)	2324(2)	73(1)
C(23)	7473(2)	–448(7)	3176(2)	67(1)
O(5)	7036(1)	1351(5)	3508(1)	70(1)
C(24)	7605(2)	2654(6)	4201(2)	53(1)
C(25)	8598(2)	2397(9)	4625(2)	75(1)
C(26)	9104(2)	3885(12)	5303(2)	97(2)
C(27)	8646(3)	5598(11)	5568(3)	103(2)
C(28)	7650(3)	5855(8)	5154(2)	86(1)
C(29)	7126(2)	4388(6)	4479(2)	59(1)
O(6)	6156(2)	4591(6)	4016(1)	88(1)
C(30)	5531(2)	4992(9)	4437(2)	79(1)

Table 16. Bond lengths [Å] and angles [°] for **26**

N(1)–C(1)	1.329(3)	C(4)–H(4)	0.9300
N(1)–C(5)	1.347(4)	C(5)–C(6)	1.473(4)
C(1)–C(2)	1.379(4)	C(6)–O(1)	1.405(4)
C(1)–C(30)	1.499(4)	C(6)–H(6A)	0.9700
C(2)–C(3)	1.362(5)	C(6)–H(6B)	0.9700
C(2)–H(2)	0.9300	O(1)–C(7)	1.376(3)
C(3)–C(4)	1.370(5)	C(7)–C(8)	1.379(4)
C(3)–H(3)	0.9300	C(7)–C(12)	1.393(4)
C(4)–C(5)	1.356(5)	C(8)–C(9)	1.388(5)
		C(8)–H(8)	0.9300

C(9)–C(10)	1.361(6)	C(23)–H(23A)	0.9700
C(9)–H(9)	0.9300	C(23)–H(23B)	0.9700
C(10)–C(11)	1.382(4)	O(5)–C(24)	1.357(4)
C(10)–H(10)	0.9300	C(24)–C(25)	1.384(4)
C(11)–C(12)	1.378(4)	C(24)–C(29)	1.388(4)
C(11)–H(11)	0.9300	C(25)–C(26)	1.374(6)
C(12)–O(2)	1.367(3)	C(25)–H(25)	0.9300
O(2)–C(13)	1.425(4)	C(26)–C(27)	1.348(7)
C(13)–C(14)	1.482(4)	C(26)–H(26)	0.9300
C(13)–H(13A)	0.9700	C(27)–C(28)	1.387(6)
C(13)–H(13B)	0.9700	C(27)–H(27)	0.9300
C(14)–O(3)	1.410(4)	C(28)–C(29)	1.370(5)
C(14)–H(14A)	0.9700	C(28)–H(28)	0.9300
C(14)–H(14B)	0.9700	C(29)–O(6)	1.360(3)
O(3)–C(15)	1.422(3)	O(6)–C(30)	1.417(4)
C(15)–C(16)	1.507(4)	C(30)–H(30A)	0.9700
C(15)–H(15A)	0.9700	C(30)–H(30B)	0.9700
C(15)–H(15B)	0.9700		
C(16)–N(2)	1.336(4)	C(1)–N(1)–C(5)	117.4(3)
C(16)–C(17)	1.381(5)	N(1)–C(1)–C(2)	122.4(3)
N(2)–C(20)	1.337(4)	N(1)–C(1)–C(30)	116.7(3)
C(17)–C(18)	1.362(5)	C(2)–C(1)–C(30)	120.8(3)
C(17)–H(17)	0.9300	C(3)–C(2)–C(1)	119.0(3)
C(18)–C(19)	1.372(5)	C(3)–C(2)–H(2)	120.5
C(18)–H(18)	0.9300	C(1)–C(2)–H(2)	120.5
C(19)–C(20)	1.379(4)	C(2)–C(3)–C(4)	119.2(3)
C(19)–H(19)	0.9300	C(2)–C(3)–H(3)	120.4
C(20)–C(21)	1.508(4)	C(4)–C(3)–H(3)	120.4
C(21)–O(4)	1.419(4)	C(5)–C(4)–C(3)	118.9(3)
C(21)–H(21A)	0.9700	C(5)–C(4)–H(4)	120.6
C(21)–H(21B)	0.9700	C(3)–C(4)–H(4)	120.6
O(4)–C(22)	1.406(4)	N(1)–C(5)–C(4)	123.0(3)
C(22)–C(23)	1.485(4)	N(1)–C(5)–C(6)	118.4(4)
C(22)–H(22A)	0.9700	C(4)–C(5)–C(6)	118.5(4)
C(22)–H(22B)	0.9700	O(1)–C(6)–C(5)	110.5(3)
C(23)–O(5)	1.426(4)	O(1)–C(6)–H(6A)	109.5

C(5)–C(6)–H(6A)	109.5	C(14)–O(3)–C(15)	111.5(3)
O(1)–C(6)–H(6B)	109.5	O(3)–C(15)–C(16)	112.8(3)
C(5)–C(6)–H(6B)	109.5	O(3)–C(15)–H(15A)	109.0
H(6A)–C(6)–H(6B)	108.1	C(16)–C(15)–H(15A)	109.0
C(7)–O(1)–C(6)	118.0(2)	O(3)–C(15)–H(15B)	109.0
O(1)–C(7)–C(8)	124.3(3)	C(16)–C(15)–H(15B)	109.0
O(1)–C(7)–C(12)	116.4(2)	H(15A)–C(15)–H(15B)	107.8
C(8)–C(7)–C(12)	119.3(3)	N(2)–C(16)–C(17)	122.8(3)
C(7)–C(8)–C(9)	120.2(4)	N(2)–C(16)–C(15)	115.0(3)
C(7)–C(8)–H(8)	119.9	C(17)–C(16)–C(15)	122.2(3)
C(9)–C(8)–H(8)	119.9	C(16)–N(2)–C(20)	117.8(3)
C(10)–C(9)–C(8)	120.3(3)	C(18)–C(17)–C(16)	118.6(3)
C(10)–C(9)–H(9)	119.8	C(18)–C(17)–H(17)	120.7
C(8)–C(9)–H(9)	119.8	C(16)–C(17)–H(17)	120.7
C(9)–C(10)–C(11)	120.1(3)	C(17)–C(18)–C(19)	119.7(3)
C(9)–C(10)–H(10)	120.0	C(17)–C(18)–H(18)	120.2
C(11)–C(10)–H(10)	120.0	C(19)–C(18)–H(18)	120.2
C(12)–C(11)–C(10)	120.2(3)	C(18)–C(19)–C(20)	118.6(3)
C(12)–C(11)–H(11)	119.9	C(18)–C(19)–H(19)	120.7
C(10)–C(11)–H(11)	119.9	C(20)–C(19)–H(19)	120.7
O(2)–C(12)–C(11)	124.7(3)	N(2)–C(20)–C(19)	122.5(3)
O(2)–C(12)–C(7)	115.4(2)	N(2)–C(20)–C(21)	114.5(3)
C(11)–C(12)–C(7)	119.9(3)	C(19)–C(20)–C(21)	122.9(3)
C(12)–O(2)–C(13)	117.8(2)	O(4)–C(21)–C(20)	112.8(3)
O(2)–C(13)–C(14)	108.1(2)	O(4)–C(21)–H(21A)	109.0
O(2)–C(13)–H(13A)	110.1	C(20)–C(21)–H(21A)	109.0
C(14)–C(13)–H(13A)	110.1	O(4)–C(21)–H(21B)	109.0
O(2)–C(13)–H(13B)	110.1	C(20)–C(21)–H(21B)	109.0
C(14)–C(13)–H(13B)	110.1	H(21A)–C(21)–H(21B)	107.8
H(13A)–C(13)–H(13B)	108.4	C(22)–O(4)–C(21)	113.4(3)
O(3)–C(14)–C(13)	110.2(3)	O(4)–C(22)–C(23)	109.3(3)
O(3)–C(14)–H(14A)	109.6	O(4)–C(22)–H(22A)	109.8
C(13)–C(14)–H(14A)	109.6	C(23)–C(22)–H(22A)	109.8
O(3)–C(14)–H(14B)	109.6	O(4)–C(22)–H(22B)	109.8
C(13)–C(14)–H(14B)	109.6	C(23)–C(22)–H(22B)	109.8
H(14A)–C(14)–H(14B)	108.1	H(22A)–C(22)–H(22B)	108.3

O(5)–C(23)–C(22)	107.2(3)
O(5)–C(23)–H(23A)	110.3
C(22)–C(23)–H(23A)	110.3
O(5)–C(23)–H(23B)	110.3
C(22)–C(23)–H(23B)	110.3
H(23A)–C(23)–H(23B)	108.5
C(24)–O(5)–C(23)	118.9(2)
O(5)–C(24)–C(25)	125.3(3)
O(5)–C(24)–C(29)	115.3(2)
C(25)–C(24)–C(29)	119.3(3)
C(26)–C(25)–C(24)	120.1(4)
C(26)–C(25)–H(25)	120.0
C(24)–C(25)–H(25)	120.0
C(27)–C(26)–C(25)	120.9(3)
C(27)–C(26)–H(26)	119.6
C(25)–C(26)–H(26)	119.6
C(26)–C(27)–C(28)	119.6(4)
C(26)–C(27)–H(27)	120.2
C(28)–C(27)–H(27)	120.2
C(29)–C(28)–C(27)	120.8(4)
C(29)–C(28)–H(28)	119.6
C(27)–C(28)–H(28)	119.6
O(6)–C(29)–C(28)	124.4(3)
O(6)–C(29)–C(24)	116.1(3)
C(28)–C(29)–C(24)	119.3(3)
C(29)–O(6)–C(30)	119.6(2)
O(6)–C(30)–C(1)	108.2(2)
O(6)–C(30)–H(30A)	110.1
C(1)–C(30)–H(30A)	110.1
O(6)–C(30)–H(30B)	110.1
C(1)–C(30)–H(30B)	110.1
H(30A)–C(30)–H(30B)	108.4

Symmetry transformations used to generate equivalent atoms:

Table 17. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **26**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	62(2)	56(2)	53(1)	–5(1)	25(1)	–8(1)
C(1)	53(2)	51(2)	46(1)	–5(1)	21(1)	4(1)
C(2)	58(2)	63(2)	70(2)	–12(2)	34(2)	–8(2)
C(3)	97(2)	48(2)	83(2)	9(2)	46(2)	2(2)
C(4)	74(2)	82(2)	59(2)	11(2)	21(2)	24(2)
C(5)	50(2)	85(2)	46(1)	–5(2)	16(1)	0(2)
C(6)	62(2)	138(4)	71(2)	–21(3)	27(2)	–14(2)
O(1)	58(1)	80(2)	71(1)	–19(1)	32(1)	–20(1)
C(7)	44(1)	65(2)	57(2)	10(2)	19(1)	–1(1)
C(8)	60(2)	87(3)	70(2)	3(2)	31(2)	2(2)
C(9)	54(2)	110(3)	75(2)	17(2)	34(2)	9(2)

C(10)	47(2)	106(3)	71(2)	22(2)	22(2)	–10(2)
C(11)	45(1)	79(2)	61(2)	12(2)	14(1)	–12(2)
C(12)	40(1)	64(2)	50(1)	12(2)	12(1)	1(1)
O(2)	47(1)	72(2)	68(1)	–10(1)	22(1)	–11(1)
C(13)	56(2)	60(2)	61(2)	–1(2)	10(1)	–5(2)
C(14)	57(2)	72(2)	60(2)	–7(2)	8(1)	10(2)
O(3)	55(1)	101(2)	60(1)	9(1)	19(1)	20(1)
C(15)	55(2)	127(4)	58(2)	–1(2)	20(1)	13(2)
C(16)	60(2)	70(2)	52(2)	6(2)	25(1)	8(2)
N(2)	55(1)	73(2)	50(1)	–4(1)	26(1)	–3(1)
C(17)	80(2)	66(2)	71(2)	6(2)	30(2)	21(2)
C(18)	102(3)	49(2)	80(2)	–9(2)	39(2)	2(2)
C(19)	73(2)	62(2)	73(2)	–10(2)	33(2)	–22(2)
C(20)	60(2)	71(2)	57(2)	–6(2)	33(1)	–15(2)
C(21)	53(2)	131(4)	69(2)	–20(2)	31(2)	–9(2)
O(4)	50(1)	106(2)	69(1)	–6(1)	28(1)	–19(1)
C(22)	80(2)	72(2)	87(2)	–20(2)	55(2)	–15(2)
C(23)	67(2)	72(2)	74(2)	–3(2)	41(2)	7(2)
O(5)	45(1)	91(2)	74(1)	–23(1)	25(1)	1(1)
C(24)	45(1)	61(2)	55(2)	0(2)	23(1)	–4(1)
C(25)	46(2)	103(3)	77(2)	–2(2)	26(2)	–1(2)
C(26)	52(2)	157(5)	75(2)	–6(3)	18(2)	–36(2)
C(27)	101(3)	120(4)	82(2)	–31(3)	31(2)	–57(3)
C(28)	102(3)	75(3)	78(2)	–15(2)	33(2)	–10(2)
C(29)	63(2)	58(2)	54(2)	2(2)	22(1)	7(2)
O(6)	65(1)	133(2)	56(1)	–10(2)	15(1)	43(2)
C(30)	75(2)	98(3)	62(2)	7(2)	28(2)	29(2)

Table 18. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **26**.

Atom	x	y	z	U(eq)
H(2)	5527	9164	3637	73
H(3)	4242	11608	2828	88
H(4)	2685	10396	2592	88

H(6A)	2122	5807	3676	109
H(6B)	1713	8135	3111	109
H(8)	357	6333	3054	85
H(9)	–1129	4484	2738	92
H(10)	–1589	1201	1839	90
H(11)	–606	–165	1189	77
H(13A)	205	4	301	76
H(13B)	739	–1809	1055	76
H(14A)	2217	–719	941	81
H(14B)	1502	–2233	167	81
H(15A)	2261	2152	–806	97
H(15B)	2475	–527	–458	97
H(17)	2739	4492	933	87
H(18)	4204	5755	1949	91
H(19)	5618	3950	2010	82
H(21A)	5706	–1206	823	99
H(21B)	5971	1276	515	99
H(22A)	6934	–2678	2147	87
H(22B)	6119	–1393	2350	87
H(23A)	7662	–1861	3547	80
H(23B)	8046	215	3128	80
H(25)	8923	1217	4452	90
H(26)	9772	3708	5583	117
H(27)	8995	6601	6026	123
H(28)	7333	7038	5336	103
H(30A)	5882	5775	4981	94

Table 19. Torsion angles [°] for **26**.

C(5)–N(1)–C(1)–C(2)	0.3(4)	C(1)–N(1)–C(5)–C(4)	0.1(4)
C(5)–N(1)–C(1)–C(30)	178.7(3)	C(1)–N(1)–C(5)–C(6)	–177.3(3)
N(1)–C(1)–C(2)–C(3)	–0.1(4)	C(3)–C(4)–C(5)–N(1)	–0.7(5)
C(30)–C(1)–C(2)–C(3)	–178.4(3)	C(3)–C(4)–C(5)–C(6)	176.7(3)
C(1)–C(2)–C(3)–C(4)	–0.6(5)	N(1)–C(5)–C(6)–O(1)	–90.6(4)
C(2)–C(3)–C(4)–C(5)	1.0(5)	C(4)–C(5)–C(6)–O(1)	91.9(5)
		C(5)–C(6)–O(1)–C(7)	174.9(3)

C(6)–O(1)–C(7)–C(8)	15.4(5)
C(6)–O(1)–C(7)–C(12)	–164.6(3)
O(1)–C(7)–C(8)–C(9)	–178.7(3)
C(12)–C(7)–C(8)–C(9)	1.3(5)
C(7)–C(8)–C(9)–C(10)	1.1(5)
C(8)–C(9)–C(10)–C(11)	–1.8(5)
C(9)–C(10)–C(11)–C(12)	0.1(5)
C(10)–C(11)–C(12)–O(2)	–178.3(3)
C(10)–C(11)–C(12)–C(7)	2.3(5)
O(1)–C(7)–C(12)–O(2)	–2.5(4)
C(8)–C(7)–C(12)–O(2)	177.5(3)
O(1)–C(7)–C(12)–C(11)	177.0(3)
C(8)–C(7)–C(12)–C(11)	–2.9(4)
C(11)–C(12)–O(2)–C(13)	–1.1(4)
C(7)–C(12)–O(2)–C(13)	178.4(2)
C(12)–O(2)–C(13)–C(14)	–179.8(3)
O(2)–C(13)–C(14)–O(3)	–71.6(3)
C(13)–C(14)–O(3)–C(15)	172.1(3)
C(14)–O(3)–C(15)–C(16)	–75.2(4)
O(3)–C(15)–C(16)–N(2)	149.3(3)
O(3)–C(15)–C(16)–C(17)	–32.8(5)
C(17)–C(16)–N(2)–C(20)	–0.4(5)
C(15)–C(16)–N(2)–C(20)	177.5(3)
N(2)–C(16)–C(17)–C(18)	0.4(5)
C(15)–C(16)–C(17)–C(18)	–177.3(4)
C(16)–C(17)–C(18)–C(19)	–0.4(5)
C(17)–C(18)–C(19)–C(20)	0.5(5)
C(16)–N(2)–C(20)–C(19)	0.4(4)
C(16)–N(2)–C(20)–C(21)	–176.5(3)
C(18)–C(19)–C(20)–N(2)	–0.5(5)
C(18)–C(19)–C(20)–C(21)	176.2(4)
N(2)–C(20)–C(21)–O(4)	–160.7(3)
C(19)–C(20)–C(21)–O(4)	22.4(5)
C(20)–C(21)–O(4)–C(22)	84.8(4)
C(21)–O(4)–C(22)–C(23)	–164.8(3)
O(4)–C(22)–C(23)–O(5)	75.9(3)
C(22)–C(23)–O(5)–C(24)	–167.0(3)
C(23)–O(5)–C(24)–C(25)	0.2(5)
C(23)–O(5)–C(24)–C(29)	179.2(3)
O(5)–C(24)–C(25)–C(26)	177.6(3)
C(29)–C(24)–C(25)–C(26)	–1.4(5)
C(24)–C(25)–C(26)–C(27)	0.4(6)
C(25)–C(26)–C(27)–C(28)	0.3(7)
C(26)–C(27)–C(28)–C(29)	0.0(7)
C(27)–C(28)–C(29)–O(6)	–177.1(4)
C(27)–C(28)–C(29)–C(24)	–1.1(6)
O(5)–C(24)–C(29)–O(6)	–1.1(4)
C(25)–C(24)–C(29)–O(6)	178.0(3)
O(5)–C(24)–C(29)–C(28)	–177.4(3)
C(25)–C(24)–C(29)–C(28)	1.7(5)
C(28)–C(29)–O(6)–C(30)	–42.6(5)
C(24)–C(29)–O(6)–C(30)	141.2(3)
C(29)–O(6)–C(30)–C(1)	145.4(3)
N(1)–C(1)–C(30)–O(6)	132.5(3)
C(2)–C(1)–C(30)–O(6)	–49.1(4)

Symmetry transformations used to generate equivalent atoms:

Crystallographic summary

A summary of crystallographic data of **6**, **7**, **19**, **24** and **26** are presented in Table below.

	6	**7**	**19**	**24**	**26**
Molecular formula	C_{24} H_{26} O_6	C_{24} H_{26} O_6	C_{32} H_{32} O_6	C_{31} H_{31} N O_6	C_{30} H_{30} N_2 O_6
Formula weight	410.45	410.45	512.58	513.57	514.56
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	C2/c (no. 15)	$P2_1/n$ (no. 14)	$P2_1$ (no. 4)	$P2_1$ (no. 4)
a (Å)	13.4964(16)	26.492(4)	4.606(3)	14.6295(9)	15.080(2)
b (Å)	7.0234 (8)	9.8112(15)	17.852(10)	5.2396(3)	5.4720(8)
c (Å)	22.476 (3)	8.4897(13)	30.159(16)	17.8162(11)	17.191(2)
β (°)	104.665 (2)	106.831(3)	93.071(11)	107.767(1)	113.695(3)
Volume ($Å^3$)	2061.2 (4)	2112.1(6)	2476(2)	1300.53(14)	1299.0(3)
Z	4	4	4	2	2
$D_{calculated}$ (Mg/m^3)	1.323	1.291	1.375	1.311	1.316
μ (mm^{-1})	0.095	0.092	0.094	0.091	0.092
GOF on F^2	1.018	1.024	1.127	1.031	1.037
Final *R* indices*	0.0372/0.0815	0.0369/0.0851	0.0811/0.1776	0.0420/0.1029	0.0385/ 0.0973

* (*I* >2sigma*I*)

Diol macrocycle precursor **7** crystallizes in the monoclinic space group C2/c with four independent molecules per asymmetric unit (Fig. 3). Bond lengths within the phenyl rings are regular with C-C distances of 1.368 Å to 1.405 Å, mean 1.386 Å. The bond distances of O(2)–C(3) and C(8)–O(3) exhibit close values of 1.3725 (17) Å and 1.3809 (17) Å respectively, which are significantly shorter than C(2)–O(2), at 1.4289 (17) Å. The bond angles of O(3)–C(8)–C(3) and C(8)–O(3)–C(9) are identical, with values of 115.39 (12)° and 115.07 (11)° respectively. The torsion angle of the O(2)–C(3)–C(8)–O(3) is 0.45 and the torsion angle of C(8)–O(3)–C(9)–C(10) is -179.70(12)°. Refinement has shown that there are two types of disorder associated with **7**. The alcohol oxygen atom is disordered over the two sites O1A/O1B which differ in their orientation with respect to the alcohol chain moiety and with site occupancy factors subsequently fixed at 50 % (probability level) each. Crystallographic data for **7** provides constructive information about the arrangement of the aromatic rings and alcohol chains of **7** in the solid state. The measured distance between two hydrogens of the alcohol groups is 11.157 Å, which is too far apart compared with compound **6** (3.804 Å). Steric interactions between the *ortho*-xylene units might be hindering the molecule adopting a pseudo-cyclic structure resembling the macrocyclic precursor **6** (Fig. 1). The two alcohol groups of **7** are too far from each other to introduce another *meta*-, *para*- or especially *ortho*-xylene unit. This factor could perhaps shed some light on the unsuccessful results of ring closure reactions employing **7**. Even attempts to promote macrocyclization by introducing a *para*-xylene linker into the **7** failed, and also employment of a variety of templating agents (Li^+, Na^+, K^+, Cs^+) in that particular case did not promote the ring closure. In fact, only formation of oligomeric products was observed.

Crystals of **6** were grown by slow evaporation of a chloroform:hexane (2:1) mixture. Macrocycle **6** crystallizes in the monoclinic space group P21/c with four independent molecules per asymmetric unit. Bond lengths within the phenyl ring are normal, with C-C distances of 1.374 Å to 1.411 Å, mean 1.392 Å. The bond distances of C(2)–O(2) (1.4445 (16) Å) and O(5)–C(23) (1.4338 (17) Å) are similar to those of O(3)–C(9) (1.4392 (17) Å) and C(16)–O(4) (1.4370 (16) Å) and are in agreement with typical bond lengths for aliphatic ethers (1.430 Å). Furthermore the C-O bond in the phenol ring has been reported to be considerably shorter (1.37 Å)[1] and this includes bond lengths of C8-O3 (1.3679 (17) Å), C17-O4 (1.3644 (16) Å), C3-O2

(1.3679 (16) Å) and C22-O5 (1.368 (17) Å). The bond angles of O(3)–C(9)–C(10) and O(4)–C(16)–C(14) are practically identical and equal, 107.78 (11)° and 107.00 (11)° respectively, also C(15)–C(10)–C(9) and C(15)–C(14)–C(16) exhibit very similar values of 120.36°. The torsion angles of C(8)–O(3)–C(9)–C(10) and C(14)–C(16)–O(4)–C(17) between the two aromatic rings are 175.12° and 176.38° respectively, while O(2)–C(3)–C(8)–O(3) and O(4)–C(17)–C(22)–O(5) are –1.47° and 1.49° which emphasises the regularity of the structure **6** in the solid state.

Crystals of tetrabenzo-25-crown-6 **19** were grown by slow evaporation of a chloroform:hexane (2:1) mixture. Macrocycle **19** crystallizes in the monoclinic space group $P2_1/n$ with four independent molecules per asymmetric unit (Fig. 4). The bond length for C(7)–C(8) is 1.468 (10)Å and for C(11)–C(14) is 1.480 (10) Å, whereas for O(2)–C(7) it is 1.421 (9) Å and for C(14)–O(3) the bond length is slightly shorter at 1.404 (8) Å. Bonds C(6)–O(2) and O(3)–C(15) which are 1.360 (8) Å and 1.359 (9) Å are identical. The angle for O(2)–C(7)–C(8) is 106.7° and is close to O(3)–C(14)–C(11) angle of 108.1°. However, torsion angles for O(2)–C(7)–C(8)–C(13) and C(12)–C(11)–C(14)–O(3) are 84.7° and 2.3° respectively. This gives an indication that the compound is not completely symmetrical in the solid state. However, torsion angle values associated with the *meta*-xylene unit are similar and equal 166.7° for C(29)–C(28)–C(30)–O(6) and 157.0° for O(5)–C(23)–C(24)–C(29).

The crystals of **24** were grown by slow evaporation of a methanol/chloroform solution (1:1) and crystallizes in the monoclinic space group $P2_1/n$ with two independent molecules per asymmetric unit (Fig. 5). The bond length for C(14)–O(3) is 1.3689 (18) Å which is slightly shorter than the O(4)–C(23) which equals 1.3719 (18) Å, however both are shorter then O(1)–C(7) and C(30)–O(6) which are 1.423 (2) Å and 1.421 (2) Å respectively. Bond length of N–C(1) and N–C(5) are identical and equals 1.341 (2) Å, whereas C(16)–C(17) and C(17)–C(18) are as expected longer and equals 1.396 (2) Å and 1.393 (2) Å. A similar correlation to the crystal example of **26** (*vida supra*) have been observed in **24** for bonds C(15)–C(16) 1.501 (2) Å and C(18)–C(22) 1.499 (2) Å. These bonds are slightly shorter than the corresponding bonds on the pyridine ring C(5)–C(6), 1.511 (2) Å and C(1)–C(31), 1.508 (2) Å. The angles for O(1)–C(6)–C(5) and O(6)–C(31)–C(1) display very close values which are 112.37° and 112.93° respectively, and the angles for O(3)–C(15)–C(16), 108.33° and O(4)– C(22)–C(18), 108.86° are also very similar. The torsion angles for C(14)–O(3)–C(15)–C(16) and C(18)–C(22)–O(4)–C(23) are –171.04° and –176.41° respectively, whereas C(5)–C(6)–O(1)–C(7) is 69.51° and C(18)–C(22)–O(4)–C(23) is -73.83°, suggesting that **24** is also not completely symmetrical in the solid state.

Crystals of benzo-crown **26** were grown by slow evaporation of a chloroform solution. Macrocycle **26** crystallizes in the monoclinic space group $P2_1/n$ with two independent molecules per asymmetric unit. (Fig. 6) The bond length for O(1)–C(7) is 1.376 (3) Å which is slightly longer then the C(29)–O(6) which equals 1.360 (3) Å, however both are shorter then C(14)–O(3) and O(4)–C(22) which are 1.410 (4) Å and 1.406 (4) Å respectively. A similar correlation which highlights the influence of the aromatic rings was observed for bonds C(5)–C(6), 1.473 (4) Å and C(1)–C(30) 1.499 (4) Å. The angles for O(1)–C(6)–C(5) and O(6)–C(30)–C(1) display close values which are 110.5° and 108.2° respectively, and the angles for C(7)–O(1)–C(6) 118.0° and C(29)–O(6)–C(30) 119.6° are also similar. The angle of O(3)–C(15)–C(16) is 112.8 and is identical to O(4)–C(21)–C(20), while C(14)–O(3)–C(15) and C(22)–O(4)–C(21) differ slightly at 111.5° and 113.4°. The torsion angles for C(5)–C(6)–O(1)–C(7) and C(29)–O(6)–C(30)–C(1) are 174.9° and 145.4° respectively, whereas C(6)–O(1)–C(7)–C(8) is 15.4° and C(28)–C(29)–O(6)–C(30) is –42.6°. The torsion angles of C(14)–O(3)–C(15)–C(16) and C(20)–C(21)–O(4)–

C(22) are –75.2° and 84.8°, whereas the values for O(3)–C(15)–C(16)–C(17) and C(19)–C(20)–C(21)–O(4) are –32.8° and 22.4°, suggesting that **26** is not completely symmetrical in the solid state.

Reference:

1. Pauling, L. in *The Nature of the Chemical Bond*, 3d ed.; Cornell University Press: Ithaca, NY, **1960,** *pp.* 239-255.