



Synthesis, Characterization and X-Ray Crystal Structure of Macrocyclic Ligand Based on 2,2-Methylene-bis[(6-formyl)-4-tert-butylphenol] and 1,2-bis-(2-aminoethoxy)ethane

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A new macrocyclic compound based on 2,2-methylene-bis[(6-formyl)-4-tert-butylphenol] and 1,2-bis-(2-aminoethoxy) ethane has been prepared by stirring and refluxing equimolar quantities of ethanolic solution of 2,2-methylene-bis[(6-formyl)-4-tert-butylphenol] and 1,2-bis-(2-aminoethoxy)ethane overnight in a basic media. The synthesis of this macrocyclic ligand involves Schiff-base condensation. This macrocyclic ligand exists in a crystalline solid of yellow colour. The ligand crystallizes in the monoclinic space group $P 2(1)/c$, with unit cell dimensions, $a = 21.2761(17) \text{ \AA}$, $b = 26.038(2) \text{ \AA}$, $c = 10.0873(8) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 93.7090(10)^\circ$, $\gamma = 90^\circ$, $Z = 8$, $V = 5576.6(8) \text{ \AA}^3$. Unit cell contains 8 molecules of macrocyclic ligand. The macrocyclic ligand was characterized by using single crystal X-ray spectroscopy, $^1\text{H NMR}$, IR-spectroscopy and mass spectrophotometry.

Keywords: 2,2-Methylene-bis[(6-formyl)-4-tert-butylphenol], 1,2-bis-(2-aminoethoxy) ethane, Schiff-base Condensation.

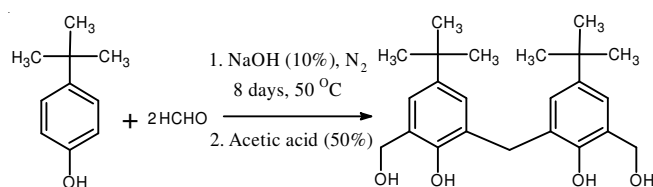
INTRODUCTION

Macrocyclic complexes by Schiff-base condensation have got much attention since the early 1980s and several reviews covering this field of research have appeared¹⁻⁷. Template Schiff-base condensations between dicarbonyl compounds and diamines are among the simplest and most popular methods for macrocycle synthesis. Structure of the condensation products is controlled by the size and preferred coordination geometry of the metal ion^{8,9}. During the last three decades, it has been great interested to design and synthesize a range of amines, both for intrinsic interest and because of the possibilities of extending them by the formation of open-chain and macrocyclic Schiff-bases complexes¹⁰.

Special attention has been paid on the recognition of guest molecules by artificial macrocycles in order to mimic specific functions of naturally occurring supramolecular hosts, such as enzyme and receptors¹¹. Furthermore, the chemists are facing a continuous challenge to synthesize a medium and large sized cyclic systems because such systems are widespread, ranging from naturally occurring compounds to macrocyclic synthetic receptors or ligands. For this study, a large number of macrocyclic host molecules have been synthesized¹². Template effect has been seen very useful in many cases to fascinate macrocyclic structures¹³.

EXPERIMENTAL

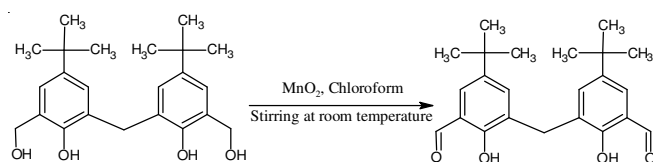
Synthesis of 2,2-methylene-bis-[(6-hydroxymethyl)-4-tert-butylphenol] (H_2mhtbp): 45 g (0.30 mol) of freshly ground 4-tert-butylphenol and 60 mL of 37 % formaldehyde (0.80 mol) were taken in three neck flask under an atmosphere of N_2 . Then NaOH solution (0.35 moles; 14 g NaOH in 140 mL of H_2O) was added and mixture was heated for 8 days at 50°C under a nitrogen atmosphere. The resulting yellowish resinous precipitates were filtered off and dissolved in 50 mL of acetone. The white solid precipitating from acetone solution was removed by filtration. The acetone solution was acidified by the addition of 200 mL of 50 % acetic acid that turned its colour into milky. Then it was diluted with 100 mL of water and extracted several times by 300 mL of Et_2O and 300 mL of ethyl acetate. The organic extracts were combined and washed with 200 mL of water and dried over anhydrous Na_2SO_4 . The solvents were rotary evaporated to get 30 g of oil which was re-dissolved in toluene [make sure that oil has completely dissolved in toluene otherwise you will have oil at the end rather than having your right product. So it is better to use excess toluene and stir to ensure that oil has completely dissolved in toluene] and precipitated by addition of light petroleum ether (**Scheme-I**). The turbid solution was left in a fridge overnight. 16.32 g of 4-tert-butyl phenol dimer (H_2mhtbp) was collected



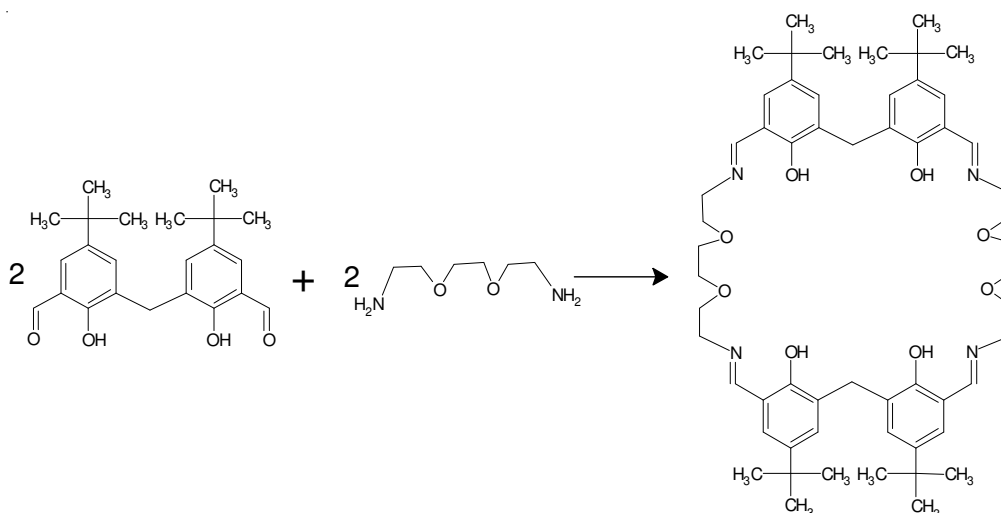
Scheme-I

by filtration under vacuum. Yield: 29.25 %. m.p.: 145-147 °C. TLC R_f = 0.30 in chloroform:acetone 5:1 (V/V). $^1\text{H NMR}$ (d- CHCl_3), δ (ppm): 1.3 (s, 18H, $\text{C}(\text{CH}_3)_3$), 3.9 (s, 2H, CH_2), 4.7 (s, 4H, CH_2OH), 6.96 (s, 2H, Ar), 7.29 (s, 2H, Ar), 8.45 (s, 2H, ArOH). EI-MS (relative intensity) and (peak assignment calc.): 395 (100 %) ($\text{H}_2\text{mhtbp} + \text{Na}$) $^+$. CHN Calculated: C 74.16 %, H 8.66 % for ($\text{C}_{23}\text{H}_{32}\text{O}_4$) and Found: C 74.14 %, H 8.94 %. IR, (KBr, ν_{max} , cm^{-1}): 2962 (s, OH); 1205 (s, ArOH);

Oxidation of 2, 2-methylene-bis-[(6-hydroxymethyl)-4-tert-butylphenol] (H_2mhtbp) to 2,2-methylene-bis[(6-formyl)-4-tert-butylphenol] (H_2mftbp): Manganese dioxide (10 g) was suspended in 500 mL of chloroform and stirred for 0.5 h. To the suspension, 2 g of H_2mhtbp was added and the mixture was stirred for 5 h at room temperature. The MnO_2 was filtered off and the filter cake was washed with 300 mL of chloroform followed by 100 mL of acetone. The filtrate was evaporated in rotary evaporator to dryness and washed with hot EtOH to yield 1 g of yellow H_2mftbp upon cooling (Scheme-II). Yield is 50 %. m.p.: 182-185 °C. TLC R_f : 0.74 in chloroform. $^1\text{H NMR}$ (d- CHCl_3), δ (ppm): 1.22(s, 18H, $\text{C}(\text{CH}_3)_3$), 3.96 (s, 2H, CH_2), 7.30 (s, 2H, ArH), 7.57 (s, 2H, ArH), 9.79 (s, 2H, ArOH), 11.11 (s, 2H, CHO). ESI-MS (relative intensity) and (peak assignment calc.): 391 (100 %) ($\text{H}_2\text{mftbp} + \text{Na}$) $^+$. CHN Calculated: C 74.97 %, H 7.66 % for ($\text{C}_{23}\text{H}_{28}\text{O}_4$) and Found: C 74.57 %, H 7.72 %. IR (KBr, ν_{max} , cm^{-1}): 2967 (s, OH), 1660 (s, C=O), 1271 (s, ArOH).



Scheme-II



Scheme-III

Synthesis of macrocyclic ligand based on 2,2-methylene-bis[(6-formyl)-4-tert-butylphenol] and 1,2-bis-(2-aminoethoxy)ethane: 0.1 g (0.27 mmol) 2,2-methylene-bis[(6-formyl)-4-tert-butylphenol] was added in a 250 mL round-bottomed flask containing 60 mL ethanol/methanol and refluxed for 0.5 h to dissolve 2,2-methylene-bis[(6-formyl)-4-tert-butylphenol] completely. To this clear solution, 0.04023 g (0.27 mmol) 1,2-bis-(2-aminoethoxy)ethane was added and refluxed overnight to get a clear yellow solution. This clear yellow solution was left for slow evaporation and after one week from this solution, yellow powder was filtered and from the filtrate, yellow crystal was characterized by single crystal x-ray (Scheme-III). Yield is 0.078 g, 63.06 %.

Elemental analysis calculated for $\text{C}_{58}\text{H}_{80}\text{O}_8\text{N}_4$: C 72.47 %; H 8.39 %; N 5.83 %. Observed: C 72.18 %; H 8.77 %; N 5.72. $^1\text{H NMR}$ (d- CHCl_3), δ [ppm]: 1.27 (s, 36H, $\text{C}(\text{CH}_3)_3$), 2.2 (s, 4H, Ph- CH_2 -Ph), 3.22 (t, 8H, $-\text{CH}_2-$), 3.49 (t, 8H, $-\text{CH}_2-$), 3.53 (t, 8H, $-\text{CH}_2-$), 7.04 (s, 4H, ArH), 7.4 (s, 4H, ArH), 8.1 (s, 4H, N=CH), 13.48 (br, 4H, ArOH). ESI-MS (m/z , rel. intensity, assignment): 983.5847 [$\text{C}_{58}\text{H}_{80}\text{O}_8\text{N}_4 + \text{Na}$] $^{+1}$. IR (KBr, ν_{max} , cm^{-1}): 3401.12 (v O-H), 2956.51, 2902.93, 2861.73, 1634.14 (v C=N), 1470.81, 1393.2, 1362.1, 1344.38, 1278.25, 1223.19, 1128.44, 1018.58, 998.15, 936.54, 918.54, 875.35, 823.68, 790.33, 758.92, 743.23, 701.46, 626.94, 591.35, 509.4.

RESULTS AND DISCUSSION

Macrocyclic ligand was prepared by the condensation reaction of 2,2-methylene-bis[(6-formyl)-4-tert-butylphenol] and 1,2-bis-(2-aminoethoxy)ethane based on both templated and non-templated high dilution methods. This macrocyclic compound was prepared by stirring and refluxing equimolar quantities of ethanolic solution of 2,2-methylene-bis[(6-formyl)-4-tert-butylphenol] and 1,2-bis-(2-aminoethoxy)-ethane overnight in a basic media. Schiff-base condensation reaction was involved in the synthesis of this macrocyclic ligand. This macrocyclic ligand was obtained in a yellow crystalline solid form. The ligand crystallizes in the monoclinic space group $P 2(1)/c$, with unit cell dimensions, $a = 21.2761(17) \text{ \AA}$, $b = 26.038(2) \text{ \AA}$, $c = 10.0873(8) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 93.7090(10)^\circ$, $\gamma = 90^\circ$, $Z = 8$, $V = 5576.6(8) \text{ \AA}^3$. Unit cell has $Z = 8$, i.e. unit cell contains 8

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT
FOR SYNTHESIZED MACROCYCLIC LIGAND

Identification code	ce5
Empirical formula	C ₂₉ H ₄₀ N ₂ O ₄
Formula weight	480.63
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 21.2761(17) Å α = 90° b = 26.038(2) Å β = 93.7090(10)° c = 10.0873(8) Å γ = 90°
Volume	5576.6(8) Å ³
Z	8
Density (calculated)	1.145 Mg/m ³
Absorption coefficient	0.076 mm ⁻¹
F(000)	2080
Crystal size	0.27 × 0.19 × 0.10 mm ³
Crystal description	yellow block
Theta range for data collection	1.56 to 26.43°
Index ranges	-26 < = h < = 26, -32 < = k < = 32, -12 < = l < = 12
Reflections collected	49624
Independent reflections	11456 [R(int) = 0.0702]
Completeness to theta = 26.43°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9925 and 0.9799
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	11456/0/659
Goodness-of-fit on F ²	1.014
Final R indices [I>2σ(I)]	R1 = 0.0581, wR2 = 0.1353
R indices (all data)	R1 = 0.1181, wR2 = 0.1629
Largest diff. peak and hol	0.408 and -0.228 e.Å ⁻³

molecules of macrocyclic ligand. ¹H NMR study shows the peak at δ [ppm]: 8.1 (s, 4H, N=CH) to ensure the Schiff-base conden-

sation and confirms the formation of -N=C. Proton signals at 13.48 ppm for the phenolic hydroxyl group gives the indication about the presence of hydrogen bonds. Hydrogen bond is between phenolic hydrogen and nitrogen of the imine linkage of the same molecule.

In mass spectrum, singly charged peak at *m/z* 983.5847 indicates the presence of [(2 + 2)Na⁺] macrocycle. Two molecules of 2,2-methylene-bis[(6-formyl)-4-*tert*-butylphenol] and two molecules of 1,2-bis-(2-aminoethoxy)ethane combine by Schiff-base condensation to make a (2 + 2) macrocycle with molecular formula C₅₈H₈₀N₄O₈.

IR Analysis reveals intense ν(C=N) bands and broad ν(O-H) bands at 1634.14 and 3401.12 cm⁻¹, respectively. Intramolecular hydrogen bonding is present between phenolic hydrogen and nitrogen (Table-3).

Conclusion

Macrocycles can be produced by both template Schiff-base condensation and non-template Schiff-base condensation methods. Macrocyclic hydrogen bonding is between phenolic hydrogen and nitrogen of the imine linkage of the same molecule. π-π stacking is present within the molecule between aromatic rings of the same molecule.

Single-crystal X-ray analysis: Structure determination and refinement was done on a Bruker Smart Apex II diffractometer using MoKα radiation (k = 0.71073 Å). The APEX2^{14,15} program package was used for cell refinements and data reductions. The structure was solved by direct methods using SHELXL-2012¹⁶ with the WinGX¹⁷ graphical user interface. An empirical absorption correction (SADABS)¹⁸ was applied to the data. Structural refinements were carried out using SHELXL-97^{19,20}. All the non-hydrogen atoms were refined using anisotropic atomic displacement parameters and

TABLE-2
BOND LENGTHS [Å] AND ANGLES [°] FOR SYNTHESIZED MACROCYCLIC LIGAND

N(1)-C(1)	1.275(3)	C(13)-C(14)	1.391(3)
N(1)-C(1)	1.275(3)	C(13)-C(14)	1.391(3)
N(1)-C(24)	1.470(3)	C(13)-C(22)	1.395(3)
N(2)-C(23)	1.274(3)	C(14)-C(15)	1.398(3)
N(2)-C(27)	1.459(3)	C(15)-C(20)	1.387(3)
O(1)-C(11)	1.352(3)	C(15)-C(16)	1.536(3)
O(2)-C(22)	1.357(3)	C(16)-C(18)	1.523(4)
O(3)-C(25)	1.418(3)	C(16)-C(17)	1.528(4)
O(3)-C(26)	1.430(3)	C(16)-C(19)	1.529(4)
O(4)-C(28)	1.402(3)	C(20)-C(21)	1.393(3)
O(4)-C(29)	1.425(3)	C(21)-C(22)	1.410(3)
C(1)-C(2)	1.457(3)	C(21)-C(23)	1.460(3)
C(2)-C(3)	1.401(3)	C(24)-C(25)	1.506(4)
C(2)-C(11)	1.405(3)	C(26)-C(29)#1	1.485(4)
C(3)-C(4)	1.382(3)	C(27)-C(28)	1.504(4)
C(4)-C(9)	1.400(3)	C(29)-C(26)#1	1.485(4)
C(4)-C(5)	1.536(3)	N(1A)-C(1A)	1.278(3)
C(5)-C(6)	1.524(4)	N(1A)-C(24A)	1.454(3)
C(5)-C(8)	1.530(3)	N(2A)-C(23A)	1.273(3)
C(5)-C(7)	1.536(4)	N(2A)-C(27A)	1.445(3)
C(11)-C(10)	1.407(3)	O(1A)-C(11A)	1.354(3)
C(10)-C(9)	1.379(3)	O(2A)-C(22A)	1.356(3)
C(10)-C(12)	1.515(3)	O(3A)-C(25A)	1.414(3)
C(12)-C(13)	1.519(3)	O(3A)-C(26A)	1.429(3)
O(4A)-C(28A)	1.420(3)	C(10A)-C(12A)	1.519(3)
O(4A)-C(29A)	1.428(3)	C(12A)-C(13A)	1.510(3)

C(1A)-C(2A)	1.458(3)	C(13A)-C(22A)	1.403(3)
C(2A)-C(3A)	1.403(3)	C(15A)-C(20A)	1.381(3)
C(2A)-C(11A)	1.404(3)	C(15A)-C(16A)	1.537(4)
C(3A)-C(4A)	1.383(3)	C(16A)-C(19A)	1.523(4)
C(4A)-C(14A)	1.409(3)	C(16A)-C(18A)	1.534(4)
C(4A)-C(5A)	1.531(3)	C(16A)-C(17A)	1.537(4)
C(5A)-C(6A)	1.529(4)	C(20A)-C(21A)	1.403(3)
C(5A)-C(7A)	1.540(4)	C(21A)-C(22A)	1.411(3)
C(5A)-C(8A)	1.551(4)	C(21A)-C(23A)	1.457(3)
C(9A)-C(13A)	1.388(3)	C(24A)-C(25A)	1.505(4)
C(9A)-C(15A)	1.415(4)	C(26A)-C(29A)#2	1.502(4)
C(10A)-C(14A)	1.389(3)	C(27A)-C(28A)	1.507(4)
C(10A)-C(11A)	1.401(3)	C(29A)-C(26A)#2	1.502(4)
C(1)-N(1)-C(24)	117.1(3)	C(6)-C(5)-C(4)	112.2(2)
C(23)-N(2)-C(27)	119.1(2)	C(8)-C(5)-C(4)	110.0(2)
C(25)-O(3)-C(26)	114.6(2)	C(6)-C(5)-C(7)	108.7(2)
C(28)-O(4)-C(29)	113.0(2)	C(8)-C(5)-C(7)	108.7(2)
N(1)-C(1)-C(2)	123.0(3)	C(4)-C(5)-C(7)	109.2(2)
C(3)-C(2)-C(11)	119.3(2)	O(1)-C(11)-C(2)	121.2(2)
C(3)-C(2)-C(1)	119.7(2)	O(1)-C(11)-C(10)	119.0(2)
C(11)-C(2)-C(1)	121.1(2)	C(2)-C(11)-C(10)	119.8(2)
C(4)-C(3)-C(2)	122.1(2)	C(9)-C(10)-C(11)	118.2(2)
C(3)-C(4)-C(9)	116.8(2)	C(9)-C(10)-C(12)	121.6(2)
C(3)-C(4)-C(5)	122.9(2)	C(11)-C(10)-C(12)	120.2(2)
C(9)-C(4)-C(5)	120.3(2)	C(10)-C(9)-C(4)	123.7(2)
C(6)-C(5)-C(8)	108.0(2)	C(10)-C(12)-C(13)	112.67(19)
C(14)-C(13)-C(22)	119.0(2)	O(3)-C(25)-C(24)	108.0(2)
C(14)-C(13)-C(12)	121.1(2)	O(3)-C(26)-C(29)#1	114.6(2)
C(22)-C(13)-C(12)	119.9(2)	N(2)-C(27)-C(28)	112.7(2)
C(13)-C(14)-C(15)	123.1(2)	O(4)-C(28)-C(27)	109.5(2)
C(20)-C(15)-C(14)	116.3(2)	O(4)-C(29)-C(26)#1	109.6(2)
C(20)-C(15)-C(16)	120.9(2)	C(1A)-N(1A)-C(24A)	117.2(2)
C(14)-C(15)-C(16)	122.7(2)	C(23A)-N(2A)-C(27A)	118.9(2)
C(18)-C(16)-C(17)	107.9(2)	C(25A)-O(3A)-C(26A)	114.2(2)
C(18)-C(16)-C(19)	108.7(2)	C(28A)-O(4A)-C(29A)	113.28(19)
C(17)-C(16)-C(19)	109.2(2)	N(1A)-C(1A)-C(2A)	122.7(2)
C(18)-C(16)-C(15)	112.1(2)	C(3A)-C(2A)-C(11A)	119.6(2)
C(17)-C(16)-C(15)	110.0(2)	C(3A)-C(2A)-C(1A)	119.8(2)
C(19)-C(16)-C(15)	109.0(2)	C(11A)-C(2A)-C(1A)	120.6(2)
C(15)-C(20)-C(21)	123.0(2)	C(4A)-C(3A)-C(2A)	122.0(2)
C(20)-C(21)-C(22)	118.9(2)	C(3A)-C(4A)-C(14A)	116.7(2)
C(20)-C(21)-C(23)	120.9(2)	C(3A)-C(4A)-C(5A)	123.0(2)
C(22)-C(21)-C(23)	120.3(2)	C(14A)-C(4A)-C(5A)	120.2(2)
O(2)-C(22)-C(13)	118.6(2)	C(6A)-C(5A)-C(4A)	112.3(2)
O(2)-C(22)-C(21)	121.7(2)	C(6A)-C(5A)-C(7A)	108.2(2)
C(13)-C(22)-C(21)	119.7(2)	C(4A)-C(5A)-C(7A)	109.4(2)
N(2)-C(23)-C(21)	122.4(2)	C(6A)-C(5A)-C(8A)	109.0(2)
N(1)-C(24)-C(25)	111.2(2)	C(4A)-C(5A)-C(8A)	108.4(2)
C(7A)-C(5A)-C(8A)	109.5(2)	C(10A)-C(11A)-C(2A)	119.9(2)
C(13A)-C(9A)-C(15A)	123.6(2)	C(13A)-C(12A)-C(10A)	111.25(19)
C(14A)-C(10A)-C(11A)	118.5(2)	C(9A)-C(13A)-C(22A)	118.0(2)
C(14A)-C(10A)-C(12A)	121.7(2)	C(9A)-C(13A)-C(12A)	122.6(2)
C(11A)-C(10A)-C(12A)	119.8(2)	C(22A)-C(13A)-C(12A)	119.3(2)
O(1A)-C(11A)-C(10A)	119.0(2)	C(10A)-C(14A)-C(4A)	123.2(2)
O(1A)-C(11A)-C(2A)	121.1(2)	C(20A)-C(15A)-C(9A)	116.4(2)
C(20A)-C(15A)-C(16A)	120.2(3)	C(22A)-C(21A)-C(23A)	120.4(2)
C(9A)-C(15A)-C(16A)	123.3(2)	O(2A)-C(22A)-C(13A)	118.8(2)
C(19A)-C(16A)-C(18A)	108.0(3)	O(2A)-C(22A)-C(21A)	120.9(2)
C(19A)-C(16A)-C(17A)	109.0(3)	C(13A)-C(22A)-C(21A)	120.3(2)
C(18A)-C(16A)-C(17A)	108.8(3)	N(2A)-C(23A)-C(21A)	122.7(2)
C(19A)-C(16A)-C(15A)	112.2(3)	N(1A)-C(24A)-C(25A)	112.9(2)
C(18A)-C(16A)-C(15A)	109.8(2)	O(3A)-C(25A)-C(24A)	109.5(2)
C(17A)-C(16A)-C(15A)	109.0(2)	O(3A)-C(26A)-C(29A)#2	113.1(2)
C(15A)-C(20A)-C(21A)	122.6(2)	N(2A)-C(27A)-C(28A)	110.4(2)
C(20A)-C(21A)-C(22A)	118.9(2)	O(4A)-C(28A)-C(27A)	107.9(2)
C(20A)-C(21A)-C(23A)	120.6(2)	O(4A)-C(29A)-C(26A)#2	109.5(2)

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y + 1, -z + 1$ #2 $-x, -y + 1, -z + 1$

TABLE-3
HYDROGEN BONDS FOR SYNTHESIZED MACROCYCLIC LIGAND [Å AND °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...N(1)	0.86(3)	1.81(4)	2.610(3)	153(3)
O(2)-H(2)...N(2)	0.90(3)	1.74(3)	2.590(3)	156(3)
O(1A)-H(2A)...N(1A)	1.04(3)	1.64(3)	2.593(3)	151(3)
O(2A)-H(1A)...N(2A)	1.04(3)	1.60(3)	2.579(3)	154(3)

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y + 1, -z + 1$ #2 $-x, -y + 1, -z + 1$

hydrogen atoms bonded to carbon were inserted at calculated positions using a riding model. Crystallographic data is shown in Tables 1-3.

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