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Synthesis of Chiral Crown Ethers and Complexation with Chiral Protonated Amine Compounds: X-Ray Crystal and Nuclear Magnetic Resonance Studies of Perchlorate Salt of Chiral Benzo-Monoaza-15-Crown-5 and Chiral Monoaza-15-Crown-5

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Abstract

The X-ray crystal structure of **IX**, perchlorate salt of *R*-(−)-2-ethyl-N-benzyl-4,7,19,13-tetraoxa-8,9-benzo-1-azacyclopentadec-8-ene has been determined. In the molecule, the protonated nitrogen atom participates in two N—H· · ·O hydrogen bonds. The unusually high proton affinity of aza crown ether leads to the formation of diastreomer instead of complex formation with chiral R-(+)-1-phenyl ethyl ammonium perchlorate and S-(−)-1-phenyl ethyl ammonium perchlorate. The complex ability of host ethers was evaluated in terms of structural modification.

Introduction

Molecular recognition is an essential feature of biochemical systems. Structures such as receptors, antibodies, and enzymes must all recognise their reaction partners before they are able to proceed with their functions. Crown ethers, discovered in 1967 by Pedersen [1, 2], are macrocyclic polyethers which are able to form stable and selective complexes with alkali, alkaline-earth, and primary ammonium cations. In modern chemistry crown ethers are of great importance in biological studies, e.g., as enzyme models [3], in the synthesis for e.g., for phase- transfer catalysis [4], and in analytical chemistry. Chiral crown ethers possess a special interest in this manner because of their ability to discriminate between molecules, e.g., enantiomers. The study of enantiomeric recognition of amine and protonated amine compounds is significant since these compounds are the basic building blocks of biological molecules [5]. Among several types of the compounds studied, such as native or derivatized amino acids and cyclodextrins, proteins, and derivatized linear or branched carbohydrates (e.g., cellulose or amylose), chiral crown ethers have been recognised as the most successful selectors used in LC chiral stationary phases for resolution of primary amine-containing compounds [6]. Sutherland and co-workers studied properties of enantiomeric recognition of protonated amine compounds by several chiral aza-crown ether derivatives [7, 8]. In our earlier works [9–11] the synthesis of the building blocks of crown ethers **II** and **IV** has been described. The crystal structures of **III** and **V** complexes with sodium perchlorate have also been reported [11, 12].

Recently, our interest has been concerned with the interaction of chiral macrocycles with chiral organic ammonium salts to understand the enantiomeric recognition. For the first step to study enantiomeric recognition we have described the crystal structure of **VII** that is a complex between *R*-chiral monoaza-15-crown-5 and S-(-)-1-phenyl-ethyl-ammonium perchlorate [13]. The present contribution describes the structure of perchlorate salt of benzo-monoaza-15-crown-5 **IX**. In addition, ^{1}H NMR and ^{13}C NMR chemical shifts of **VI** with **III** are also summarized in the paper.

Experimental

Apparatus and chemicals

All chemicals were grade reagent unless otherwise specified. Melting points were determined with a Gallenkamp Model apparatus with open capillaries. Infrared spectra were recorded on a Midac-FTIR Model 1700 Spectrophotometer. The elemental analyses were obtained with Carlo-Erba Model 1108 apparatus. Optical rotations were recorded using a Atago DR Model 21949 polarimeter. ^{1}H-(400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker DPX-400 High Performance Digital FT-NMR spectrometer.

X-ray crystallographic measurements were carried out using an Enraf-Nonius CAD4 diffractometer with graphite monochromatised MoK_α radiation [λ(MoK_α) = 0.71073 Å] and $\omega/2\theta$ scan mode to $2\theta = 51.28°$ at room temperature.

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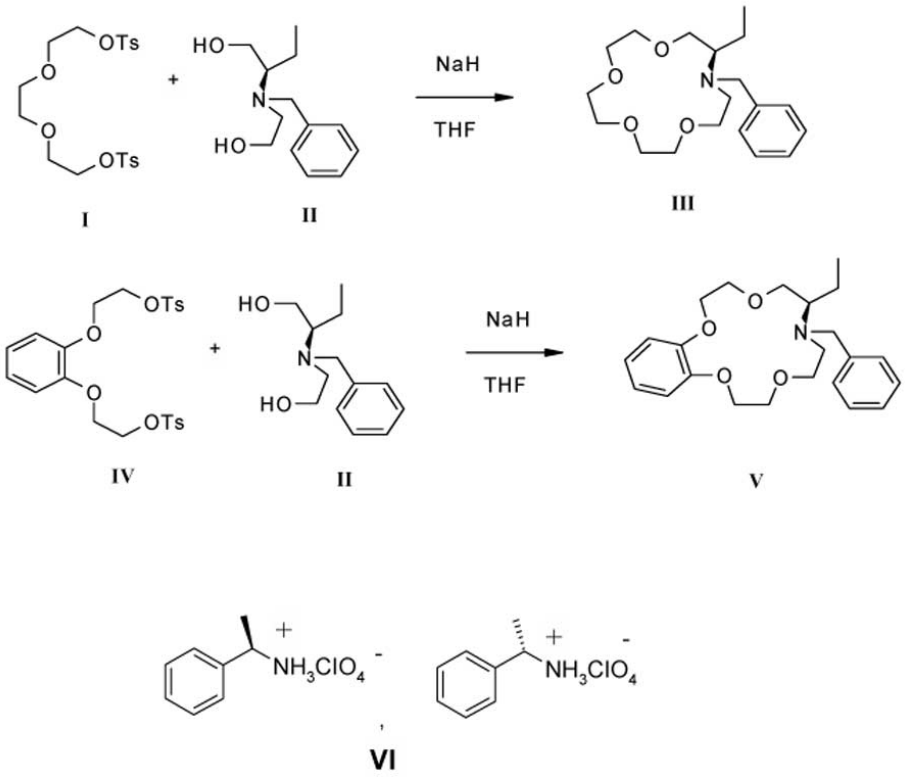
Synthesis



Scheme 1.

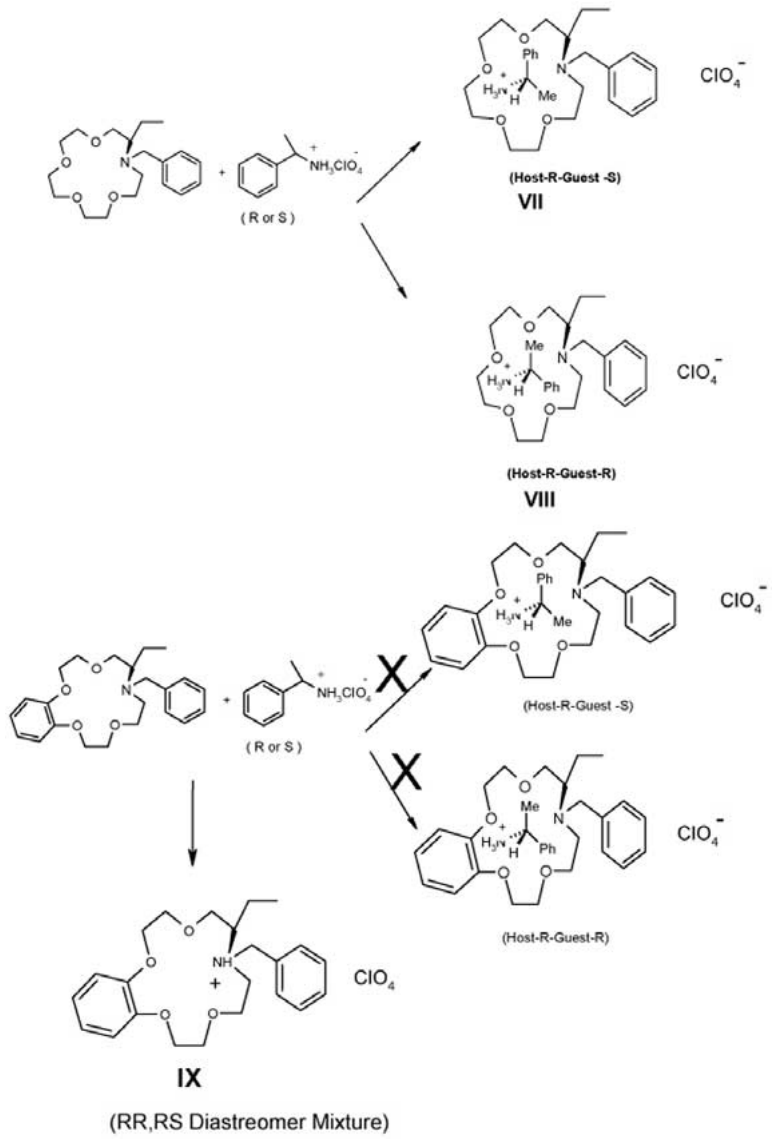
Table 1. ^{1}H and ^{13}C chemical shifts ppm) of *S*-(−)-1-phenyl ethyl ammonium perchlorate, *R*-(+)-1-phenyl ethyl ammonium perchlorate with **III** at 25 °C in $CDCl_3$

^{1}H NMR	Free	**III**-*R*-**VI**	$\Delta\delta(R)$	**III**-(*S*)-**VI**	$\Delta\delta(S)$	$\Delta\Delta\delta(S-R)$
CH3	1.61	1.50	0.11	1.52	0.09	0.02
CH	4.52	4.27	0.25	4.23	0.29	0.04
N + H3	6.25	5.89	0.36	6.17	0.12	0.24
^{13}C NMR						
Aromatic	137.03	141.26	4.23	141.32	4.29	0.06
Methine	53.31	54.96	1.65	55.25	1.94	0.29
Methyl	20.11	21.99	1.88	22.60	2.55	0.67

The chemical shifts were based on the spectrum of inclusion complexes of **III** with *R*-(+)-1- and *S*-(−)-1-phenyl ethyl ammonium percholorate.

*R-(−)-2-Ethyl-N-benzyl-4, 7, 10, 13-tetraoxa-1-azacyclopentadecane (***III***)*

To a solution of NaH (80% in mineral oil) 3.57 g (120 mmol) in dry THF (100 mL) in N_2 atmosphere , *R*-(−)-*N*-benzyl-4-hydroxymethyl-3-azahexzan-1-ol 6.62 g (30 mmol) in THF (100 mL) was added slowly at 0 °C. The mixture was heated slowly to 30–40 °C. The mixture then was kept at this temperature for 1.5 hours. Then triethylene glycol ditosylate 14.95 g (33 mmol) in THF (200 mL) was added slowly to the mixture. The mixture was stirred at 80 °C for five days. THF extract was evaporated and water (50 mL) was added to the remaining residue. Organic phase was extracted with $CHCl_3$ (3 × 50 mL) and combined organic phase was dried ($MgSO_4$) and evaporated. The product was dissolved in ethyl acetate (5 mL) and $NaClO_4H_2O$ 4.20 g (30 mmol) in ethyl acetate (5 mL) was added. The product recrystallised from ethanol to yield 9.20 g (65%), mp. 132–133 °C. $[\alpha]_D^{20} = -28.8$ (C = 0.04, EtOH). Mw. 477.5 g/mol (Found: C, 47.62; H, 6.86; N, 2.80. $C_{19}H_{31}NO_4{\cdot}NaClO_4{\cdot}H_2O$ requires: C, 47.74; H, 6.91; N, 2.93). IR (KBr, cm^{-1}): 3478, 3062, 3027, 1479, 1454, 1246, 1121, 741. ^{1}H NMR ($CDCl_3$): δ 0.86 (t, J = 7.21 Hz, 3H); 1.16 (bs, 1H); 1.56 (bs, 1H); 2.80–4.10 (m, 21H); 7.25–7.35 (m, 5H). ^{13}C NMR ($CDCl_3$): 12.05, 17.92, 68.51, 68.76, 68.96, 69.91, 127.31, 128.78, 128.94. The free ligand was recovered by passing the complex through a column on basic Al_2O_3. [Triethylamine-ethyl acetate-petroleum ether (40–60), 3:30:67 respectively as oil.]



Scheme 2.

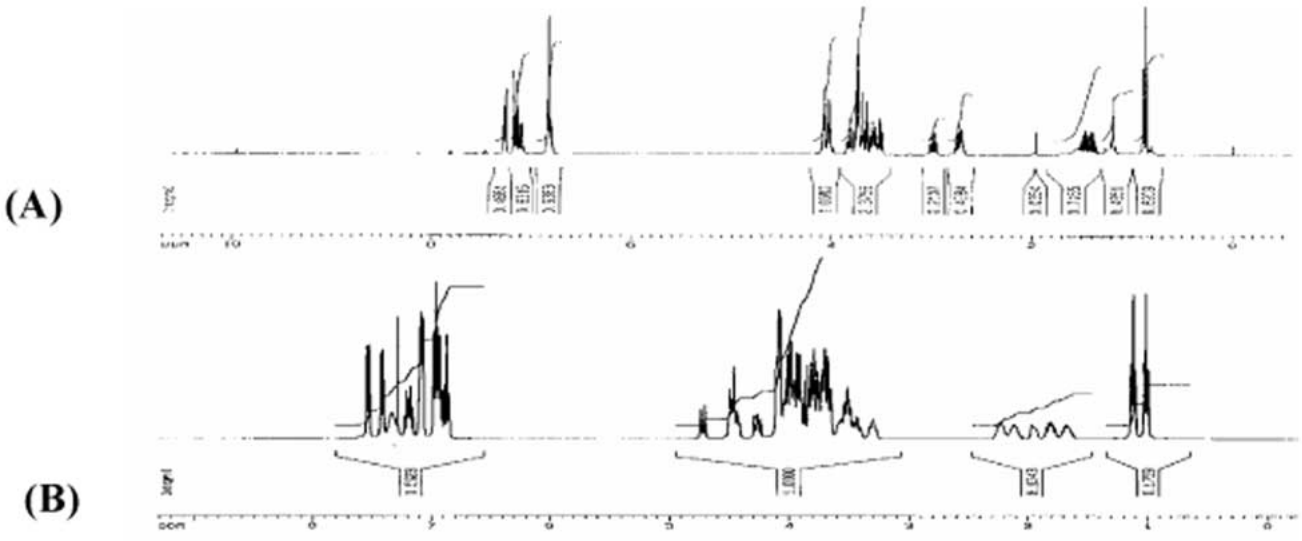


Figure 1. ^{1}H NMR spectra of **V**; (A) free **V**, (B) perchlorate salt of **V**.

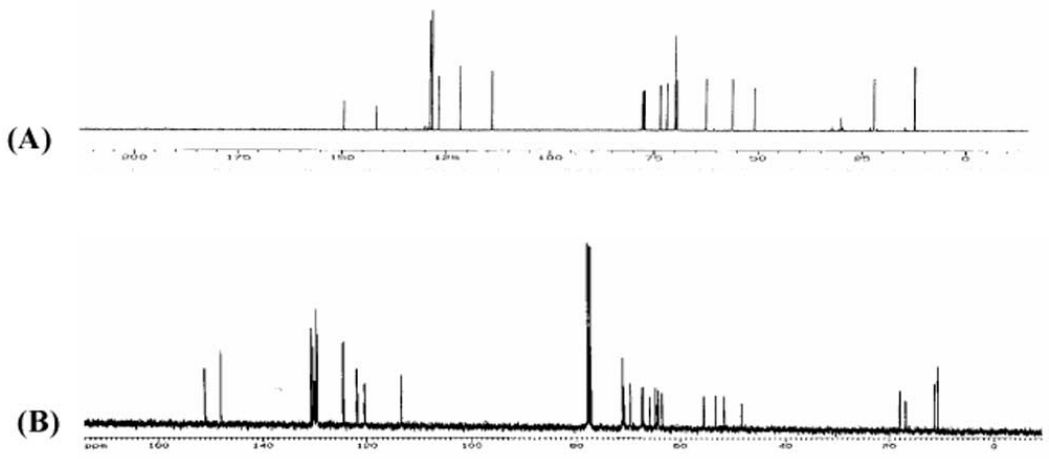


Figure 2. ^{13}C NMR spectra of **V**; (A) free **V**, (B) perchlorate salt of **V**.

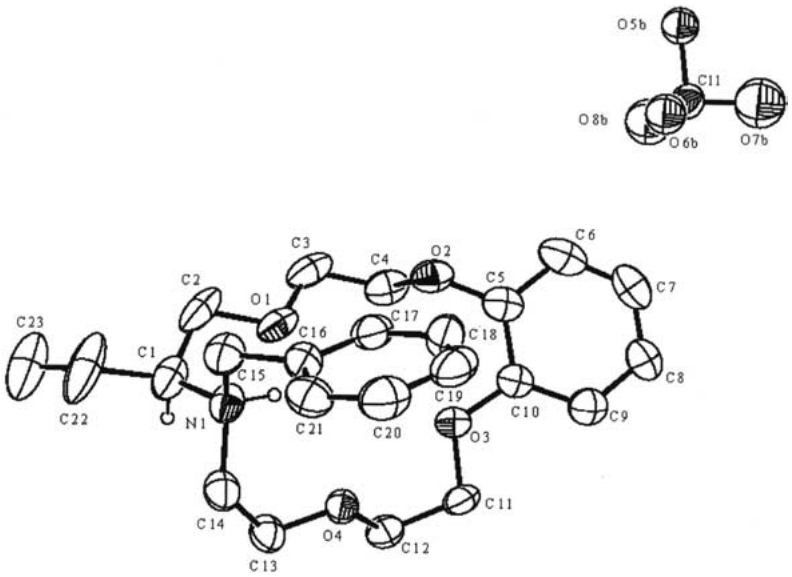


Figure 3. Ortep [16] drawing of the title compound with 25% probability displacement ellipsoids and the numbering scheme. Only H atoms of C1 and N1 are shown for clarity.

*R-(−)-2-Ethyl-N-benzyl-4, 7, 10, 13-tetraoxa-8, 9-benzo-1-azacyclopentadec-8-ene (***V***)*

To a solution of NaH (80% in mineral oil) 3.57 g (120 mmol) in dry THF (100 mL) in N_2 atmosphere, *R*-(−)-*N*-benzyl-4-hydroxymethyl-3-azahexzan-1-ol 6.62 g (30 mmol) in THF (100 mL) was added slowly at 0 °C. The mixture was heated slowly to 30–40 °C. The mixture then was kept at this temperature for 1.5 hours. 1,2-bis-(2-p-tolylsulphonylethoxy) benzene (**IV**) (16.7 g, 33 mmol) in THF (100 mL) was added dropwise to the mixture in 2 hours. The mixture was stirred at 80 °C for five days. THF extract was evaporated and water (50 mL) was added to the remaining residue. Organic phase was extracted with $CHCl_3$ (3 × 50 mL) and combined organic phase was dried ($MgSO_4$) and evaporated. The residual oil was purified by flash column chromatography on silica [triethylamine-ethyl acetate-petrolium ether (40–60), 3:17:80 and 3:30:67 respectively]. The product was obtained as a colourless oil, 6.25 g 49% of (**V**) M.w. 385 g/mol (Found: C, 71.54; H, 8.12; N, 3.68; $C_{23}H_{31}NO_4$ requires C, 71.68; H, 8.05; N, 3.63); IR (KBr): 3080, 3040, 2976, 2876, 1603, 1503, 1455, 1250, 1189, 1117, 1028, 928, 748, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (3H, t, J = 7.38 Hz), 1.37–1.50 (2H, m), 2.70–2.75 (2H, p), 2.97–3.00 (1H, m), 3.49–4.09 (14H, m), 6.79–7.27 (9H, m); ^{13}C NMR ($CDCl_3$) δ 12.33, 22.13, 30.12, 50.88, 56.16, 62.50, 69.50, 69.87, 69.98, 71.89, 73.47, 114.04, 121.64, 126.93, 128.45, 128.92, 141.80, 149.57.

*S(−)-1 phenyl ethyl ammonium percholorate complex of R-(−)-2-ethyl-N-benzyl-4, 7, 10, 13-tetraoxa-1-azacyclopentadecane (***VII***)*

To a solution of *R*-(−)-2-ethyl-*N*-benzyl-4, 7, 10, 13-tetraoxa-1-azacyclopentadecane, 0.53 g (1.6 mmol) in Et_2O (5 mL) , *S*(−)-1-phenyl ethyl ammonium cholorate 0.35 g (1.6 mmol) in ethyl acetate (5 mL) was added. The product crystallised from ethyl acetate, mp. 79–80 °C. M.w. = 558.5 g/mol (Found: C, 57.98; H, 7.68; N, 5.02, $C_{27}H_{43}N_2O_8Cl$ requires C, 58.01; H, 7.70; N, 5.01), IR (neat film): 3215, 3168, 3099, 3022, 2959, 2882, 1633, 1595,

Table 2. Crystal data and details of the structure determination for percholorate salt of *R*-(−)-2-ethyl-*N*-benzyl-4,7,10,13-tetraoxa-8,9-benzo-1-azacyclopentadec-8-ene (**IX**)

Crystal data:	
Formula	$C_{23}H_{32}O_8ClN$
Formula weight	485.95
Crystal system	Monoclinic
Space group	$P2_1$ (No. 4)
a, Å	10.849(2)
b, Å	8.783(2)
c, Å	13.907(3)
β, deg	104.77(2)
V, Å^3	1281.3(5)
Z	2
Dc, g cm^{-3}	1.26
$F(000)$	516
μ, cm^{-1}	19.4
Crystal size, mm	0.25 × 0.15 × 0.08
Data Collection:	
Temperature (K)	295
Radiation, λ	MoK$_\alpha$, $\lambda = 0.71073$ Å
Range of relative transm. factors, %	95.3–98.5
Range of *hkl*	−12:13; −10:0; −16:0
Scan type	$\omega/2\theta$
Number of collected reflections	2678 total, 2575 unique
Standard reflections	3 measured every 120 min
R_{int}	2.8%
Structure refinement:	
No. of reflections included	2575 on F^2
No. of refined parameters	265
Linear agreement factor	
$R = \Sigma\|\Delta F\|/\Sigma\|F_0\|$	0.0704
Weighted agreement factor	
$wR = [\Sigma w\|\Delta F\|^2/\Sigma w\|F_0\|^2]^{1/2}$	0.2065
Goodness of fit	1.031
Extinction coeff.	0.013(7)
Max. shift/error	0.00
Final $\Delta\rho_{\max}$, $\Delta\rho_{\min}$, e Å^{-3}	0.65, −0.20

Table 3. Selected interatomic distances (Å) and bond angles (°) for percholorate salt of *R*-(−)-2-ethyl-*N*-benzyl-4,7,10,13-tetraoxa-8,9-benzo-1-azacyclopentadec-8-ene (**IX**)

C3—C4	1.498(5)	C1—C2	1.483(14)
C4—O2	1.435(10)	C1—N1	1.504(10)
C5—O2	1.378(10)	C1—C22	1.565(14)
C5—C10	1.411(11)	C2—O1	1.455(11)
C11—O3	1.405(9)	C3—O1	1.398(12)
C13—O4	1.394(8)	C15—N1	1.506(10)
C13—C14	1.498(12)	C12—O4	1.423(9)
C14—N1	1.517(10)	C12—C11	1.486(11)
C15—C16	1.511(11)	C23—C22	1.383(16)
O3—C10	1.356(8)		
C2—C1—N1	108.1(6)	C23—C22—C1	116.4(2)
C2—C1—C22	114.4(10)	C1—N1—C15	113.3(6)
N1—C1—C22	112.0(9)	C1—N1—C14	112.2(6)
O3—C10—C9	126.8(7)	C15—N1—C14	112.1(7)
O2—C5—C6	120.7(8)	C13—C14—N1	111.4(7)
N1—C15—C16	110.7(6)	C15—C16—C17	119.3(7)

Table 4. Torsion angles in the benzo-monoaza-15-crown-5 ligand (°)

N1—C1—C2—O1	47.4(9)
C1—C2—O1—C3	174.8(7)
C4—C3—O1—C2	175.6(7)
O1—C3—C4—O2	−71.7(10)
C3—C4—O2—C5	168.2(7)
C10—C5—O2—C4	−76.8(8)
O2—C5—C10—O3	3.1(10)
C5—C10—O3—C11	−174.5(7)
C12—C11—O3—C10	−173.4(7)
C11—C12—O4—C13	179.1(6)
C14—C13—O4—C12	−170.0(7)
O4—C12—C11—O3	−64.2(9)
O4—C13—C14—N1	57.2(8)
C13—C14—N1—C1	84.3(8)
C2—C1—C22—C23	73.4(18)
C16—C15—N1—C14	72.2(9)
N1—C15—C16—C21	−115.7(9)
C2—C1—N1—C14	−154.0(7)
C1—N1—C15—C16	−159.6(7)

1523, 1454, 1250, 1115, 929, 764, 703, 618 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (3H, t, J = 7.47 Hz), 1.20–1.30 (1H, m), 1.52 (4H, d, J = 6.81), 3.069 (3H, m), 3.41–3.93 (18H, m), 4.23 (1H, q, J = 6.83), 6.16 (3H, s), 7.28–7.36 (10H, m); ^{13}C NMR ($CDCl_3$) δ: 18.78, 22.60, 49.64, 51.76, 55.25, 64.17, 66.80, 68.77, 68.98, 69.29, 69.35, 69.47, 69.92, 70.24, 126.99, 128.66, 128.78, 129.18, 129.30, 130.33, 135.64, 141.32.

*R(+)-1 phenyl ethyl ammonium percholorate complex of R-(−)-2-ethyl-N-benzyl-4,7,10,13-tetraoxa-1-azacyclopentadecane (***VIII***)*

To a solution of *R*-(−)-2-ethyl-*N*-benzyl-4,7,10,13-tetraoxa-1-azacyclopentadecane, 0.53 g (1.6 mmol) in Et_2O (5 mL), *R*(+)-1-phenyl ethyl ammonium chlorate 0.35 g (1.6 mmol) in ethyl acetate (5 mL) was added. The product crystallised from ethyl acetate, mp. 102–104 °C. M.w. = 558.5 g/mol (Found: C, 58.00; H, 7.67; N, 4.99, $C_{27}H_{43}N_2O_8Cl$ requires C, 58.01; H, 7.70; N, 5.01); IR (neat film): 3200, 3121, 3026, 2955, 2907, 2875, 1623, 1594, 1515, 1454, 1293, 1121, 1067, 930, 871, 774, 705, 623, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.84 (3H, t, J = 7.37 Hz), 1.12–1.35 (2H, m), 1.50 (3H, d, J = 6.82 Hz), 2.87–3.02 (3H, m), 3.39–3.82 (18H, m), 4.27 (1H, q, J = 6.81 Hz), 5.89 (3H, s), 7.23–7.46 (10H, m); ^{13}C NMR ($CDCl_3$) δ 18.99, 21.99, 49.00, 51.81, 54.96, 64.21, 66.71, 68.62, 69.09, 69.34, 69.50, 69.66, 69.82, 70.26, 127.41, 128.56, 128.93, 129.06, 129.35, 130.30, 135.65, 141.26.

*Percholorate salt of R-(−)-2-ethyl-N-benzyl-4,7,10,13-tetraoxa-8,9-benzo-1-azacyclopentadec-8-ene (***IX***)*

To a solution of *R*-(−)-2-ethyl-*N*-benzyl-4,7,10,13-tetraoxa-8,9- benzo-1-azacyclopentadec-8-ene, 0.53 g (1.6 mmol) in Et_2O (5 mL), *R*(+)-1-phenyl ethyl ammonium chlorate 0.35 g (1.6 mmol) in ethyl acetate (5 mL) was added and also same procedure was used for *S*(−)-1-phenyl ethyl ammonium chlorate. The product analysis revealed that no complexation occurred. The product was perchlorate salt of (**V**) and crystallised from ethyl acetate, mp. 181–182 °C. M.w. = 485.5 g/mol (Found: C, 56,35; H, 6,79; N, 2,86, $C_{23}H_{32}NO_8Cl$ requires C, 56,84; H, 6,59; N, 2,88) ; IR (KBr, cm^{-1}): 3442, 3129, 3061, 3035, 2932, 2908, 2873, 1596, 1496, 1450, 1256, 1088, 933, 759, 624. ^{1}H NMR ($CDCl_3$): δ 1.00 (t, J = 7.38, 1.5H); δ 1.11 (t, J = 7.35, 1.5H); δ 1.65–2.21 (m, 2H); δ 3.30–4.73 (m, 17H); δ 6.84–7.53 (m, 9H). ^{13}C NMR ($CDCl_3$): 10.73, 11.34, 16.90, 18.00, 48.30, 51.64, 53.18, 55.50, 63.50, 64.20, 64.32, 64.78, 65.82, 67.14, 67.20, 67.36, 69.58, 70.82, 70.96, 71.10, 113.28, 113.35, 120.27, 120.37, 121.83, 121.88, 124.46, 129.49, 129.66, 129.86, 130.10, 130.23, 130.30, 130.67, 147.94, 151.01, 151.04 ppm.

X-ray diffraction measurements

The crystal used for data collection was colourless and prismatic shaped. The cell constants and the orientation matrices for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centred reflections in the range $10.32° < 2\theta < 18.17°$. The data were corrected for Lorentz-polarisation effects and for absorption using empirical psi-scans. The structure was solved by direct methods (SHELXS-97 in WinGX program package [14]) and refined on F^2 with SHELXL-97 [15]. The structure solution revealed disordered oxygen atoms in ClO4 with occupancy factors of 0.360(6) for component A and 0.640(6) for component B. Thermal parameters for atoms within disordered ClO_4 molecules were restrained to be similar. In spite of this, several of these atoms exhibited unusual elongation, so the disordered O atoms were refined isotropically. In the final stages of refinement, the coordinates and displacement parameters of disordered oxygen atoms were fixed. The hydrogen atoms of C1 and N1 were found from the difference maps and refined isotropically in a few cycles and then the riding model was applied. All other H atoms were calculated to their idealised positions with isotropic temperature factors (1.3 Ueq of the bonded carbon atoms) and refined as riding atoms. All other non-H atoms were refined with anisotropic displacement parameters. Crystal data, a summary of the intensity data collection and structure refinement are given in Table 2 while the selected bond lengths and bond angles are listed in Table 3. The torsion angles of benzo-monoaza-15-crown-5 are given in Table 4.

Results and discussion

NMR spectral results

It is known that a primary requirement for enantiomeric recognition using chiral macrocyclic compounds as host molecules is that guest enantiomers form reasonably stable complexes with the hosts. No recognition is observed or is present if complexes are not formed. So to test this primary requirement we prepared complexes of **III** with **VI** according to procedure described in the experimental section, and the ^{1}H NMR and ^{13}C NMR chemical shifts (ppm) were summarised in Table 1. An interesting result was obtained in the preparation of complexes of **V** with **VI**. The product analyses revealed that no complexation occurred. Indeed the product was perchlorate salt of **V**. The benzo substitution on crown ether may probably lead to a highly symmetrical, hydrogen-bond stabilized structure which leads to a high proton affinity of aza crown ether. Thus molecular recognition of protonated amine compounds by **V** results in the aza crown ether stripping a proton off ammonium. These dramatic changes were observed in ^{1}H and ^{13}C NMR spectrum (Figures 1 and 2).

X-ray crystal structure studies

The molecular structure and the numbering scheme of (**IX**) are shown in Figure 3. The structure predicted from chemical and spectral analysis is confirmed by X-ray diffraction studies. From the ORTEP [16] plot and the torsion angles presented in Table 4, it is clear that the conformation of the macrocycle ring deviates from the expected conformation of 15-crown-5 type molecules. The deviation can be expected because of the presence of the aromatic phenyl ring in the macrocycle and also the replacement of one of the oxygens of the ring by nitrogen. Perhaps the most interesting feature is the conformational change brought about by the presence of the ethyl and benzyl groups bonded to the chiral carbon and the protonated nitrogen of the ether ring. However, all of the D-C-C-D torsion angles (D = oxygen and nitrogen donor) adopt the conformations g^-, g^+, g^-, g^+ (the exception is one *syn*-angle corresponding to the aromatic ring), and C-C *gauche*-angles are in the range 47.4(9)–71.7(10)°.

Most of the C-C-D-C torsion angles are close to the *anti*-conformation (154.0(7)–179.1(6)°) with the exception of C10—C5—O2—C4 and C13—C14—N1—C1 which are also gauche (76.8(8)° and 84.3(8)°, respectively). The given conformation is almost identical to that found in the $NaClO_4$ complex of the same ligand [12], where the macrocyclic ring differs in the signs of the *gauche*-angles and all C—O and C—N bonds are in the *anti*-conformation. A similar type of conformation was found in the benzo-15-crown-5 complex with 3,4-diamino-1,2,5-oxadiazole [17].

In the molecule, two oxygen atoms O1 and O3 are at one side of the mean plane defined by the four crown oxygens being at distances of −0.221(8) and −0.373(8) Å, respectively, while O2 and O4 are on the other side with deviations of 0.330(8) and 0.204(7) Å. The deviation of the N1 atom from the oxygen mean plane is 1.313(8)Å. The dihedral

Table 5. Hydrogen bonding geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1′···O1	0.9105	2.1151	2.656(10)	117.02
N1—H1′···O4	0.9105	2.3035	2.784(9)	112.68
C4—H4A···O3	0.9700	2.4767	3.011(10)	114.51
C1—H1···O6B^{i}	0.9804	2.2974	3.2194	156.30

Symmetry code: (i) $1-x, -1.2+y, 1-z$.

angle which the aromatic ring plane (C5—C10) makes with the plane of macrocycle oxygen atoms is 13.5(2)°. As shown in Figure 3, the ethyl group bonded to the chiral carbon atom C1, is oriented outwards from the macrocycle by the torsion angle of N1—C1—C22–C23 −162(1)°. The phenyl ring bonded to N1 is located under the best plane of the macrocycle and makes an angle of 50.5(3)° with this plane.

The protonated nitrogen atom participates in two N—H···O hydrogen bonds: N1···O1 = 2.656(10) and N1···O4 = 2.784(9) Å. Also, there is a relatively weak C—H···O interaction with the O3 oxygen, C4···O3 = 3.011(10) Å. The hydrogen bonding details are given in Table 5.

The geometry of (**IX**) is quite common and similar to that found in the related 15-membered-5 complexes [12, 13]. C—O and C—C distances of the macrocycle average 1.406 and 1.475 Å while the O—C—C and C—O—C angles average 108.8 and 115.3°, respectively. However, the geometric parameters including nitrogen atom of the macrocycle are rather distinct; the N—C distance averages to 1.511 Å whilst the C—N—C angle is 112.2(6)°. The phenyl rings in the molecule have the geometry of a rather regular hexagon.

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