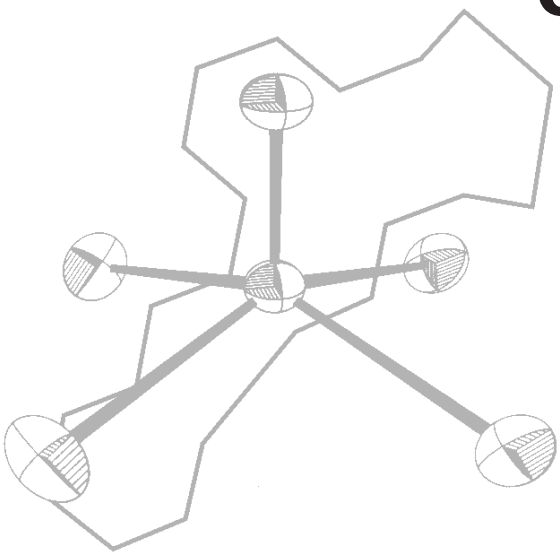
CSIRO PUBLISHING

Australian Journal of Chemistry



Volume 52, 1999

A journal for the publication of original research
in all branches of chemistry and chemical technology

www.publish.csiro.au/journals/ajc

All enquiries and manuscripts should be directed to
The Managing Editor
Australian Journal of Chemistry
CSIRO PUBLISHING
PO Box 1139 (150 Oxford St)
Collingwood Telephone: 61 3 9662 7630
Vic. 3066 Facsimile: 61 3 9662 7611
Australia Email: john.zdysiewicz@publish.csiro.au

Published by **CSIRO** PUBLISHING
for CSIRO Australia and
the Australian Academy of Science

Aust. J. Chem., 1999, **52**, 1055–1059

New Macrocyclic Ligands. IX*
N-Benzylated Macrocycles Incorporating O_2N_2-, O_3N_2- and O_2N_3-Donor Sets†

Jeong Kim,[A,B] *Youngran Lee,*[A] *Shim Sung Lee,*[C]
Leonard F. Lindoy[B,D] *and Tania Strixner*[E]

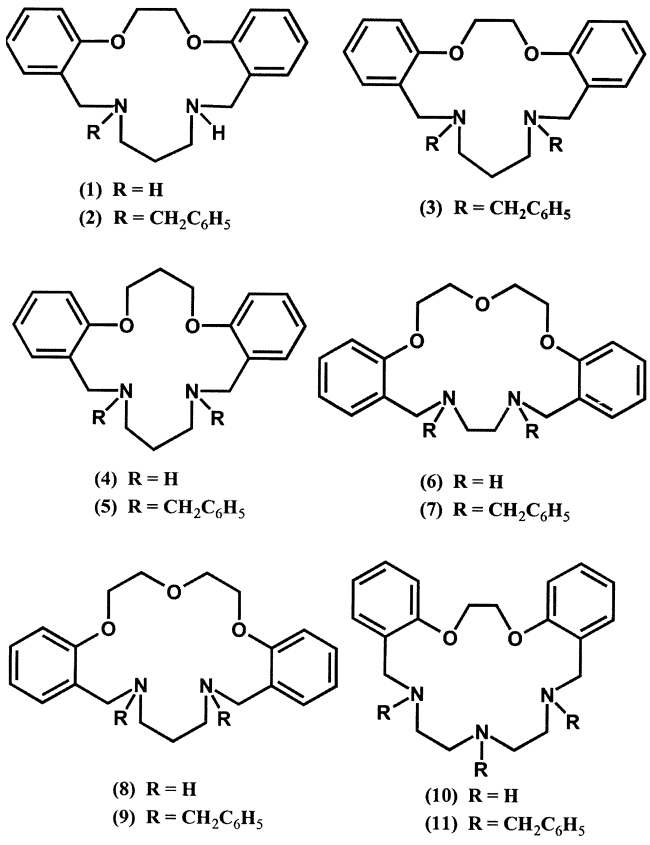
[A] Department of Chemistry, Seonam University, Namwon 590-711, Korea.
[B] Authors to whom correspondence should be addressed.
[C] Department of Chemistry, Gyeongsang National University, Chinju 660-701, Korea.
[D] School of Chemistry, University of Sydney, N.S.W. 2006.
[E] School of Biomedical and Molecular Sciences, James Cook University, Townsville, Qld. 4811.

The syntheses of *N*-benzylated macrocyclic ligands incorporating O_2N_2-, O_3N_2- and O_2N_3-donor sets, and ring sizes from 15- to 18-membered, is described. The new derivatives were obtained by benzylation of the previously reported parent macrocycles with benzyl bromide in acetonitrile containing suspended sodium carbonate or bicarbonate. The X-ray structure determination of a tribenzylated product containing a 17-membered, O_2N_3-donor macrocyclic ring is described.

Introduction

As part of an investigation of the factors underlying metal-ion recognition,[1] we have synthesized new mixed-donor, nitrogen-containing macrocycles incorporating benzyl groups attached to the macrocyclic ring nitrogen donors. These derivatives were required for a systematic investigation of a 'new' discrimination mechanism observed by us. In this, the addition of *N*-appended bulky groups has, in particular cases, been observed to lead to selective 'detuning' of the affinity of a parent (unsubstituted) macrocyclic ring for some metal ions but not others. As a consequence, enhanced metal-ion discrimination has been induced; for example, in this manner we have been successful in achieving greatly enhanced discrimination for silver(I) in the presence of a number of other transition and post-transition metal ions.[2]

Although isolated examples of *N*-benzylated derivatives of aza-containing macrocycles exist,[3] and most notably the tetrabenzylated derivative of 1,4,8,11-tetraazacyclotetradecane (cyclam),[4] few studies of the effects of *N*-benzylation of mixed-donor macrocyclic ligands on their heavy metal ion discrimination behaviour have been carried out.[5] We now describe the synthesis of new *N*-benzylated derivatives, prepared for use in studies of this latter type.



Results and Discussion

Strategies for preparing macrocyclic systems incorporating pendant groups may be divided into two categories: those

* Part VIII, *Aust. J. Chem.*, 1999, **52**, 351.
† In commemoration of the contributions of Professors W. R. Jackson, J. T. Pinhey, R. W. Rickards, S. Sternhell and W. C. Taylor to organic chemistry.

Manuscript received 9 August 1999 10.1071/CH99098 0004-9425/99/111055

involving direct derivatization of the preformed parent macrocycle and those in which appropriately substituted precursors are employed directly in the cyclization reaction.[6] Both strategies have been used for the synthesis of *N*-benzylated derivatives of aza-containing macrocycles.[3]

In the work now described we have employed direct *N*-alkylation of the preformed parent O_2N_2-, O_3N_2- and O_2N_3-donor macrocycles (1), (4), (6), (8) and (10)[7,8] to yield the benzylated products (2), (3), (5), (7), (9) and (11). This involved reaction of benzyl bromide with the corresponding cyclic precursor in the presence of sodium carbonate (or sodium hydrogen carbonate) suspended in acetonitrile under the conditions defined in the Experimental section. After workup, yields in the range 43–50% were achieved. It is noted that we have previously described related alkylations of O_2N_2-donor macrocyclic rings to produce a range of 'pendant-arm' ligands incorporating additional donor functionality in the arms.[9]

The monobenzylated and dibenzylated derivatives (2) and (3) were obtained by performing the respective benzylation reactions under stoichiometric conditions [1 : 1 and 1 : 2 ratios of (1) to benzyl bromide]. The crude monobenzylated species (2) was purified by dissolution in dilute hydrochloric acid, washing this solution with dichloromethane, adjusting the pH of the aqueous phase to 14, then extracting the neutral macrocyle from this solution with dichloromethane. Final purification involved recrystallization from acetonitrile.

A modification of the above procedure was required to purify the crude dibenzylated and tribenzylated macrocycles (3), (5), (7), (9) and (11). Each of these products was also treated with dilute hydrochloric acid; this was found to dissolve preferentially any starting macrocyle as well as any incompletely benzylated species present—presumably reflecting the lower lipophilicities of their corresponding hydrochloride salts (relative to those of the fully benzylated products). In each case the undissolved hydrochloride salt

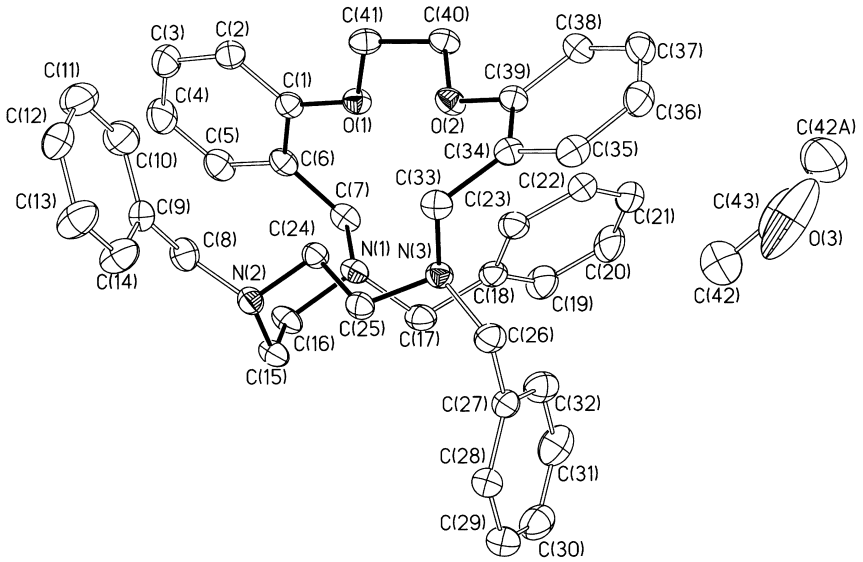


Fig. 1. X-Ray structure of the acetone solvate of the tribenzylated macrocycle (11). Thermal ellipsoids are scaled to 20% probability.

Table 1. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for the tribenzylated macrocycle (11), $C_{41}H_{45}N_3O_2[0.5(CH_3)_2CO]$

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Atom	*x*	*y*	*z*	U_{eq}	Atom	*x*	*y*	*z*	U_{eq}	Atom	*x*	*y*	*z*	U_{eq}
O(1)	665(1)	9579(1)	–238(1)	55(1)	C(11)	1461(1)	6379(3)	–1985(1)	98(1)	C(28)	2205(1)	5528(3)	1708(1)	78(1)
O(2)	384(1)	7063(1)	245(1)	58(1)	C(12)	1718(1)	5296(3)	–1979(1)	82(1)	C(29)	2474(1)	6270(4)	2050(1)	97(1)
O(3)	0	4045(5)	2500	266(4)	C(13)	2051(1)	5128(3)	–1602(1)	101(1)	C(30)	2303(1)	7382(4)	2260(1)	98(1)
N(1)	1577(1)	10156(2)	381(1)	53(1)	C(14)	2132(1)	6048(3)	–1220(1)	90(1)	C(31)	1856(1)	7768(3)	2129(1)	95(1)
N(2)	2010(1)	7730(2)	–239(1)	54(1)	C(15)	2233(1)	8658(2)	120(1)	62(1)	C(32)	1585(1)	7014(3)	1789(1)	77(1)
N(3)	1297(1)	5763(2)	724(1)	52(1)	C(16)	2042(1)	10025(2)	132(1)	62(1)	C(33)	945(1)	5000(2)	434(1)	58(1)
C(1)	893(1)	10306(2)	–620(1)	54(1)	C(17)	1623(1)	10243(2)	969(1)	68(1)	C(34)	469(1)	5082(2)	680(1)	52(1)
C(2)	807(1)	10220(2)	–1170(1)	67(1)	C(18)	1167(1)	10238(2)	1267(1)	60(1)	C(35)	286(1)	4115(2)	1005(1)	66(1)
C(3)	1041(1)	11010(3)	–1530(1)	85(1)	C(19)	1067(1)	11158(3)	1655(1)	84(1)	C(36)	–162(1)	4194(3)	1216(1)	74(1)
C(4)	1358(1)	11890(3)	–1342(1)	93(1)	C(20)	647(1)	11114(4)	1939(1)	103(1)	C(37)	–429(1)	5253(3)	1109(1)	73(1)
C(5)	1444(1)	11976(2)	–796(1)	76(1)	C(21)	333(1)	10162(4)	1840(1)	98(1)	C(38)	–259(1)	6238(2)	790(1)	64(1)
C(6)	1221(1)	11189(2)	–423(1)	58(1)	C(22)	428(1)	9237(3)	1457(1)	79(1)	C(39)	189(1)	6151(2)	575(1)	51(1)
C(7)	1330(1)	11280(2)	171(1)	60(1)	C(23)	840(1)	9282(3)	1172(1)	68(1)	C(40)	90(1)	8043(2)	34(1)	57(1)
C(8)	1974(1)	8202(2)	–787(1)	69(1)	C(24)	1575(1)	7181(2)	–26(1)	51(1)	C(41)	327(1)	8682(2)	429(1)	59(1)
C(9)	1884(1)	7155(2)	–1203(1)	58(1)	C(25)	1687(1)	6100(2)	371(1)	57(1)	C(42)	413(2)	5900(6)	372(2)	197(2)
C(10)	1547(1)	7329(3)	–1590(1)	91(1)	C(26)	1460(1)	5064(2)	1205(1)	65(1)	C(43)	0	5201(6)	2500	138(2)
					C(27)	1757(1)	5885(2)	1570(1)	60(1)					

remaining was then taken up in dichloromethane. The aqueous phase was also extracted with dichloromethane and both dichloromethane phases were combined. After washing the combined solution well with base, removal of the solvent yielded the respective fully benzylated products. A final recrystallization from acetonitrile yielded colourless crystals in each case.

The new derivatives were characterized from their ^{1}H and ^{13}C n.m.r. spectra, their mass spectra and their microanalytical data. For (11), an X-ray structure determination was also undertaken. In all cases the data were in accordance with the proposed structures.

The X-ray structure of (11), crystallized from acetone, is shown in Fig. 1; isolated in this way, the compound crystal-

Table 2. Bond lengths (Å) and angles (degrees) for the tribenzylated macrocycle (11), $C_{41}H_{45}N_3O_2$ [0.5$(CH_3)_2CO$]

Atoms[A]	Distance	Atoms	Angle	Atoms[A]	Angle
O(1)–C(1)	1.372(2)	C(1)–O(1)–C(41)	117.06(17)	C(19)–C(18)–C(17)	121.2(2)
O(1)–C(41)	1.422(2)	C(39)–O(2)–C(40)	117.97(15)	C(23)–C(18)–C(17)	120.6(2)
O(2)–C(39)	1.367(2)	C(7)–N(1)–C(17)	110.36(17)	C(18)–C(19)–C(20)	120.3(3)
O(2)–C(40)	1.419(2)	C(7)–N(1)–C(16)	111.35(17)	C(21)–C(20)–C(19)	120.4(3)
O(3)–C(43)	1.197(6)	C(17)–N(1)–C(16)	109.75(16)	C(20)–C(21)–C(22)	119.9(3)
N(1)–C(7)	1.458(3)	C(8)–N(2)–C(15)	112.27(18)	C(21)–C(22)–C(23)	119.9(3)
N(1)–C(17)	1.458(3)	C(8)–N(2)–C(24)	114.11(17)	C(22)–C(23)–C(18)	121.2(2)
N(1)–C(16)	1.472(3)	C(15)–N(2)–C(24)	114.24(17)	N(2)–C(24)–C(25)	109.81(16)
N(2)–C(8)	1.441(3)	C(25)–N(3)–C(26)	110.98(16)	N(3)–C(25)–C(24)	113.60(16)
N(2)–C(15)	1.455(3)	C(25)–N(3)–C(33)	111.30(17)	N(3)–C(26)–C(27)	112.63(18)
N(2)–C(24)	1.466(2)	C(26)–N(3)–C(33)	110.35(16)	C(28)–C(27)–C(32)	117.7(2)
N(3)–C(25)	1.459(3)	O(1)–C(1)–C(2)	123.6(2)	C(28)–C(27)–C(26)	121.6(2)
N(3)–C(26)	1.466(3)	O(1)–C(1)–C(6)	116.1(2)	C(32)–C(27)–C(26)	120.7(2)
N(3)–C(33)	1.467(3)	C(2)–C(1)–C(6)	120.3(2)	C(29)–C(28)–C(27)	121.4(3)
C(1)–C(2)	1.379(3)	C(1)–C(2)–C(3)	120.4(2)	C(30)–C(29)–C(28)	120.5(3)
C(1)–C(6)	1.399(3)	C(4)–C(3)–C(2)	119.9(3)	C(29)–C(30)–C(31)	119.5(3)
C(2)–C(3)	1.383(3)	C(3)–C(4)–C(5)	119.7(3)	C(30)–C(31)–C(32)	119.9(3)
C(3)–C(4)	1.367(4)	C(4)–C(5)–C(6)	122.0(3)	C(27)–C(32)–C(31)	121.0(3)
C(4)–C(5)	1.372(4)	C(5)–C(6)–C(1)	117.6(2)	N(3)–C(33)–C(34)	113.47(17)
C(5)–C(6)	1.386(3)	C(5)–C(6)–C(7)	121.0(2)	C(35)–C(34)–C(39)	117.7(2)
C(6)–C(7)	1.501(3)	C(1)–C(6)–C(7)	121.4(2)	C(35)–C(34)–C(33)	122.6(2)
C(8)–C(9)	1.514(3)	N(1)–C(7)–C(6)	113.42(17)	C(39)–C(34)–C(33)	119.73(18)
C(9)–C(14)	1.350(3)	N(2)–C(8)–C(9)	113.82(19)	C(36)–C(35)–C(34)	121.6(2)
C(9)–C(10)	1.369(3)	C(14)–C(9)–C(10)	117.4(2)	C(37)–C(36)–C(35)	119.7(2)
C(10)–C(11)	1.406(4)	C(14)–C(9)–C(8)	122.7(2)	C(36)–C(37)–C(38)	120.5(2)
C(11)–C(12)	1.342(4)	C(10)–C(9)–C(8)	119.9(2)	C(37)–C(38)–C(39)	119.7(2)
C(12)–C(13)	1.344(4)	C(9)–C(10)–C(11)	120.9(3)	O(2)–C(39)–C(38)	124.0(2)
C(13)–C(14)	1.361(4)	C(12)–C(11)–C(10)	118.9(3)	O(2)–C(39)–C(34)	115.10(18)
C(15)–C(16)	1.519(3)	C(11)–C(12)–C(13)	120.3(3)	C(38)–C(39)–C(34)	120.8(2)
C(17)–C(18)	1.502(3)	C(12)–C(13)–C(14)	120.6(3)	O(2)–C(40)–C(41)	109.14(17)
C(18)–C(19)	1.380(3)	C(9)–C(14)–C(13)	121.9(3)	O(1)–C(41)–C(40)	110.35(18)
C(18)–C(23)	1.383(3)	N(2)–C(15)–C(16)	117.96(18)	O(3)–C(43)–C(42)#1	120.6(3)
C(19)–C(20)	1.391(4)	N(1)–C(16)–C(15)	114.79(18)	O(3)–C(43)–C(42)	120.6(3)
C(20)–C(21)	1.357(4)	N(1)–C(17)–C(18)	114.07(18)	C(42)#1–C(43)–C(42)	118.8(7)
C(21)–C(22)	1.373(4)	C(19)–C(18)–C(23)	118.2(2)		
C(22)–C(23)	1.374(3)				
C(24)–C(25)	1.521(3)				
C(26)–C(27)	1.503(3)				
C(27)–C(28)	1.378(3)				
C(27)–C(32)	1.379(3)				
C(28)–C(29)	1.376(4)				
C(29)–C(30)	1.354(4)				
C(30)–C(31)	1.380(4)				
C(31)–C(32)	1.385(4)				
C(33)–C(34)	1.494(3)				
C(34)–C(35)	1.387(3)				
C(34)–C(39)	1.392(3)				
C(35)–C(36)	1.386(3)				
C(36)–C(37)	1.365(3)				
C(37)–C(38)	1.378(3)				
C(38)–C(39)	1.392(3)				
C(40)–C(41)	1.486(3)				
C(42)–C(43)	1.422(5)				
C(43)–C(42)#1	1.422(5)				

[A] Symmetry transformations used to generate equivalent atoms: #1 $-x,y,-z+1/2$.

lized with four molecules of acetone per unit cell, one-half of a molecule of solvent (disposed on a crystallographic *2* axis) and one molecule of (11), devoid of crystallographic symmetry, comprising the asymmetric unit of the structure. The atomic coordinates are listed in Table 1 and bond lengths and angles are given in Table 2. In contrast to the X-ray structure of the corresponding (unsubstituted) 17-membered ring (10),[10] which crystallizes in an unfolded configuration, the structure of (11) shows a very convoluted geometry. There is an absence of pseudo-symmetry relating equivalent 'halves' of the molecule, while reasonable agreement between bond lengths for chemically equivalent bonds in each 'half' is evident. As is well documented for other structures containing $–OCH_2CH_2O–$ strings,[11] the C–C bond between the ether oxygens in (11), at 1.486(3) Å, appears slightly shorter than the average C–C length of 1.524(15) Å for straight-chain alkane derivatives contained in the Cambridge Structural Data Base.[12] In this context, it is noted that such shortening has been suggested to be largely an artefact, with the 'real' component of the shortening being quite minor.[13] Other bond lengths in the structure appear unremarkable.

Experimental

^{1}H and ^{13}C n.m.r. spectra were recorded in (D)chloroform solution on a Varian Unity 400 spectrometer at 400 and 100 MHz, respectively. The e.i. mass spectra of (2) and (9) and positive-ion f.a.b. mass spectra of (3), (5), and (11) were determined by using JEOL-DX 300/303 spectrometers. The e.s. mass spectrum of (7) was obtained on a Finnigan LCQ-8 spectrometer. Melting points are uncorrected. The precursor macrocycles (1), (4), (6), (8) and (10) used in the benzylation reactions were prepared by literature procedures.[1,7,10,14]

X-Ray Crystallographic Data Collection and Structure Determination

$C_{41}H_{45}N_3O_2{\cdot}0.5(CH_3)_2CO$, M 640.84. Orthorhombic, space group *Pbcn*, a 28.646(2), b 10.3600(8), c 24.664(2) Å, γ 7319.7(10) Å^3. $D_c(Z=8)$ 1.163 g cm^{-3}; $F(000)$ 2752. μ_{Mo} 0.072 mm^{-1}; specimen 0.2 by 0.3 by 0.4 mm. $2\theta_{max}$ 56.74°; N_{tot} 46061, N_{ind} 9114 (R_{int} = 0.0964), N_o 3613; R_1 0.0519, wR_2 0.1218 for 434 parameters. Largest difference peak and hole 0.265 and –0.233 e Å^{-3}.

Colourless crystals of (11) suitable for X-ray diffraction were crystallized from acetone solution over 5 days. A suitable crystal was mounted on a Bruker SMART diffractometer equipped with a graphite-monchromatized Mo Kα (λ 0.71073 Å) radiation source and a CCD detector; 45 frames of two-dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. Data collection was performed at 298(2) K. A total of 1271 frames of two-dimensional diffraction images were collected, each of which was exposed for 30 s. The structure was solved by direct methods and refined by full matrix least squares using SHELXTL software;[15] the quantity $\Sigma w(F^2_{obs}–F^2_{calc})^2$ was minimized, with $w = [\sigma^2(F_{obs})^2+(0.0855P)^2+P]^{-1}$, where $P = (F^2_{obs}+2F^2_{calc})/3$. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas the hydrogen atoms were constrained at estimated positions. Material deposited comprises hydrogen coordinates, torsion angles and anisotropic displacement parameters and structure factors.*

Ligand Synthesis

Macrocycle (2). Benzyl bromide (1.71 g, 0.01 mol) and (1) (3.12 g, 0.01 mol) were dissolved in acetonitrile (100 ml) and sodium carbonate (5.29 g, 0.05 mol) was added. The mixture was heated at the reflux overnight and then cooled and filtered. The solvent was removed on a rotary evaporator and then dilute hydrochloric acid (0.1 mol dm^{-3}, 100 ml) was added to the resulting oil to yield a colourless solution. The solution was washed with dichloromethane (3×100 ml) and then its pH was adjusted to 14 with sodium hydroxide. The solution was allowed to cool. It was then extracted with dichloromethane (2×50 ml). The combined dichloromethane phases were then washed with water (3×50 ml), dried over anhydrous sodium sulfate, then filtered. The solvent was removed in a rotary evaporator. The *product* that remained was recrystallized from acetonitrile to yield colourless needle-like crystals (1.9 g, 47%), m.p. 134.6–134.9°C (Found: C, 77.4; H, 7.4; N, 7.2. $C_{26}H_{30}N_2O_2$ requires C, 77.6; H, 7.5; N, 7.0%). Mass spectral (e.i.) parent peak, *m/z* 402. ^{1}H n.m.r. δ 1.79, 2H, q, $NCH_2C\mathbf{H_2}CH_2N$; 2.46, 2H, t, $CH_2C\mathbf{H_2}NH$; 2.61, 2H, t, $CH_2C\mathbf{H_2}NCH_2C_6H_5$; 2.92, 1H, br, NH; 3.38, 2H, s, $ArC\mathbf{H_2}NH$; 3.49, 2H, s, $ArC\mathbf{H_2}NCH_2C_6H_5$; 3.68, 2H, s, $C\mathbf{H_2}C_6H_5$; 4.31, 4H, s, $OC\mathbf{H_2}$; 6.9–7.3, m, arom. ^{13}C n.m.r. δ 26.5, $NCH_2\mathbf{C}H_2CH_2N$; 47.2, $Ar\mathbf{C}H_2NH$; 49.1, $Ar\mathbf{C}H_2NCH_2C_6H_5$; 51.5, $CH_2\mathbf{C}H_2NH$; 53.5, $CH_2\mathbf{C}H_2NCH_2C_6H_5$; 58.4, $\mathbf{C}H_2C_6H_5$; 65.6, OCH_2; 110.0, 119.8, 120.5, 128.4, 131.1, 133.0, 156.9, 157.4, arom., macrocycle; 126.3, 127.7, 128.9, 139.6, arom., benzyl.

Macrocycle (3). Benzyl bromide (3.42 g, 0.02 mol) and (1) (3.12 g, 0.01 mol) were dissolved in acetonitrile (100 ml) containing sodium carbonate (5.29 g, 0.05 mol). The mixture was heated at the reflux overnight and then cooled and filtered. The solvent was removed on a rotary evaporator then dilute hydrochloric acid (0.1 M, 100 ml) was added to the residue with stirring. Undissolved residue was dissolved in dichloromethane (50 ml). The acid/aqueous solution was extracted with dichloromethane (3×100 ml). Both organic fractions were combined and the resulting solution was washed with aqueous sodium hydroxide (2×50 ml), dried over anhydrous sodium sulfate, filtered, and the solvent removed on a rotary evaporator. The *product* that remained was recrystallized from acetonitrile to yield colourless crystals (2.2 g, 45%), m.p. 123.8–124.5°C (Found: C, 80.3; H, 7.6; N, 5.7. $C_{33}H_{36}N_2O_2$ requires C, 80.5; H, 7.4; N, 5.7%). Mass spectral parent peak (f.a.b.), *m/z* 493 (LH^+). ^{1}H n.m.r. δ 1.72, 2H, q, $NCH_2C\mathbf{H_2}CH_2N$; 2.50, 4H, t, $NC\mathbf{H_2}CH_2$; 3.53, 4H, s, $ArC\mathbf{H_2}N$; 3.63, 4H, s, $C\mathbf{H_2}C_6H_5$; 4.38, 4H, s, OCH_2; 6.9–7.3, m, arom. ^{13}C n.m.r. δ 23.5, $NCH_2\mathbf{C}H_2CH_2N$; 51.1, $Ar\mathbf{C}H_2N$; 51.8, $N\mathbf{C}H_2CH_2$; 58.0, $\mathbf{C}H_2C_6H_5$; 66.4, OCH_2; 110.8, 120.3, 128.0, 128.1, 132.5, 157.2, arom., macrocycle; 126.5, 127.1, 128.8, 140.6, arom., benzyl.

Macrocycle (5). In a similar manner to that described above, benzyl bromide (3.42 g, 0.02 mol) and (4) (3.26 g, 0.01 mol) gave the crude *product* which was recrystallized from acetonitrile to yield colourless crystals (2.2 g, 43%), m.p. 107.4–107.7°C (Found: C, 80.8; H, 7.6; N, 5.6. $C_{34}H_{38}N_2O_2$ requires C, 80.6; H, 7.6; N, 5.5%). Mass spectral parent peak (f.a.b.), *m/z* 507 (LH^+). ^{1}H n.m.r. δ 1.56, 2H, q, $NCH_2C\mathbf{H_2}CH_2N$; 2.28, 2H, m, $OCH_2C\mathbf{H_2}CH_2O$; 2.30, 4H, t, $NC\mathbf{H_2}CH_2$; 3.51, 4H, s, $ArC\mathbf{H_2}N$); 3.55, 4H, s, $C\mathbf{H_2}C_6H_5$; 4.29, 4H, s, OCH_2; 6.9–7.3, m, arom. ^{13}C n.m.r. δ 23.7, $NCH_2\mathbf{C}H_2CH_2N$; 29.1, $OCH_2\mathbf{C}H_2CH_2O$; 51.7, $Ar\mathbf{C}H_2N$; 52.0, $N\mathbf{C}H_2CH_2$; 59.2, $C_6H_5\mathbf{C}H_2$; 64.8, OCH_2; 113.0, 120.7, 128.0, 128.8, 131.8, 157.2, arom., macrocycle; 126.5, 128.0, 128.9, 140.0, arom., benzyl.

Macrocycle (7). In a similar manner to that described above, benzyl bromide (3.42 g, 0.02 mol) and (6) (3.42 g, 0.01 mol) yielded the *product* (2.6 g, 50%) as colourless crystals after recrystallization from acetonitrile, m.p. 98.5–98.8°C (Found; C, 78.0; H, 7.3; N, 5.4. $C_{34}H_{38}N_2O_3$ requires C, 78.1; H, 7.3; N, 5.4%). Mass spectral (e.s.) parent peak, *m/z* 523 (LH^+). ^{1}H n.m.r. δ 2.69, 4H, s, $NC\mathbf{H_2}C\mathbf{H_2}$; 3.50, 4H, s, $ArC\mathbf{H_2}$; 3.64, 4H, s, $C\mathbf{H_2}C_6H_5$; 3.97, 4H, m, OCH_2; 4.16, 4H, m, $OC\mathbf{H_2}$; 6.9–7.3, m, arom. ^{13}C n.m.r. δ 50.8, $Ar\mathbf{C}H_2N$; 52.1, NCH_2CH_2N; 58.2, $\mathbf{C}H_2C_6H_5$; 68.2, 70.0, OCH_2; 111.6, 120.5, 128.0, 131.5, 157.3, arom., macrocycle; 126.5, 127.9, 128.0, 140.2, arom., benzyl.

Macrocycle (9). In a similar manner to that described above, benzyl bromide (3.42 g, 0.02 mol) and (8) (3.56 g, 0.01 mol) yielded the *product* (2.4 g, 45%) as colourless crystals after recrystallization from acetonitrile, m.p. 92.1–92.5°C (Found: C, 78.3; H, 7.4; N, 5.2. $C_{35}H_{40}N_2O_3$ requires C, 78.3; H, 7.5; N, 5.2%). Mass spectral (e.i.) parent peak, *m/z* 536. ^{1}H n.m.r. δ 1.85, 2H, q, $NCH_2C\mathbf{H_2}CH_2N$; 2.39, 4H, t, CH_2N; 3.54, 4H, s, $ArC\mathbf{H_2}$; 3.70, 4H, s, $C\mathbf{H_2}C_6H_5$; 4.04, 4H, m,

* Copies are available (until 31 December 2004) from the Australian Journal of Chemistry, P.O. Box 1139, Collingwood, Vic. 3066.

OCH_2; 4.16, 4H, m, OCH_2; 6.9–7.3, m, arom. ^{13}C n.m.r. δ 22.2, $NCH_2\mathbf{C}H_2CH_2N$; 51.6, $Ar\mathbf{C}H_2N$, $\mathbf{C}H_2NCH_2Ar$; 58.1, $\mathbf{C}H_2C_6H_5$; 68.2, 70.3, OCH_2; 111.4, 120.4, 127.9, 131.2, 157.2, arom., macrocycle; 126.5, 128.0, 128.7, 140.3, arom., benzyl.

Macrocycle (11). In a similar manner to that described above, benzyl bromide (4.27 g, 0.025 mol) and (10) (3.41 g, 0.01 mol) yielded the *product* as colourless crystals (2.7 g, 43%), on recrystallization from acetonitrile, m.p. 94.4–95.2°C (Found: C, 80.4; H, 7.5; N, 6.8. $C_{41}H_{45}N_3O_2$ requires C, 80.5; H, 7.4; N, 6.9%). Mass spectrum (f.a.b.) *m/z* 612 (LH^+). ^1H n.m.r. δ 2.56, 8H, m, NCH_2; 3.30, 2H, s, $C\mathbf{H}_2C_6H_5$ (centre); 3.54, 4H, s, $ArC\mathbf{H}_2$; 3.76, 4H, s, $C\mathbf{H}_2C_6H_5$; 4.39, 4H, s, OCH_2; 6.9–7.3, m, arom. ^{13}C n.m.r. δ 51.1, NCH_2; 52.6, $Ar\mathbf{C}H_2$; 58.9, $\mathbf{C}H_2C_6H_5$; 66.6, OCH_2; 110.9, 120.5, 126.5, 130.5, 132.8, 156.9, arom., macrocycle; 127.6, 127.9, 128.0, 128.5, 128.7, 139.7, 140.1, arom., benzyl.

Acknowledgments

J.K. wishes to acknowledge the financial support of the Korea Research Foundation made in the program year of 1997 and for support from its 'Faculty Research Abroad' Fund. We thank Dr A. J. Leong for experimental assistance.

References

[1] Davis, C. A., Duckworth, P. A., Leong, A. J., Lindoy, L. F., Bashall, A., and McPartlin, M., *Inorg. Chim. Acta*, 1998, **273**, 372.

[2] Lindoy, L. F., *Pure Appl. Chem*., 1997, **69**, 2179.

[3] Bradshaw, J. S., Krakowiak, K. E., and Izatt, I. M., 'Aza-Crown Macrocycles' (John Wiley: New York 1993).

[4] Tsukube, H., *J. Chem. Soc., Chem. Commun.,* 1983, 970; *Chem. Lett*., 1984, 1961; *J. Chem. Soc*., *Perkin Trans*. *1*, 1985, 615; Tsukube, H., Tagaki, K., Higashiyama, T., Iwachido, T., and Hayama, N., *J. Chem. Soc*., *Perkin Trans. 1*, 1986, 1033.

[5] Izatt, R. M., Bradshaw, J. S., Nielsen, S. A., Lamb, J. D., Christensen, J. J., and Sen, D., *Chem. Rev.*, 1985, **85**, 271; Izatt, R. M., Pawlak, K., Bradshaw, J. S., and Bruening, R. L., *Chem. Rev.*, 1991, **91**, 1712; Izatt, R. M., Pawlak, K., and Bradshaw, J. S., *Chem. Rev.*, 1995, **95**, 2529.

[6] Kaden, T. A., *Top. Curr. Chem*., 1984, **121**, 157; Lindoy, L. F., 'The Chemistry of Macrocyclic Ligand Complexes' (Cambridge University Press: Cambridge 1989).

[7] Grimsley, P. G., Lindoy, L. F., Lip, H. C., Smith, R. J., and Baker, J. T., *Aust. J. Chem.*, 1977, **30**, 2095.

[8] Davis, C. A., Leong, A. J., Lindoy, L. F., Kim, J., and Lee, S.-H, *Aust. J. Chem*., 1998, **51**, 189, and references therein.

[9] Chia, P. S., Ekstrom, A., Liepa, I., Lindoy, L. F., McPartlin, M., Smith, S. V., and Tasker, P. A., *Aust. J. Chem.,* 1991, **44**, 737; Lindoy, L. F. , Skelton, B. W., Smith, S. V., and White, A. H., *Aust. J. Chem.*, 1993, **46**, 363.

[10] Adam, K. R., Leong, A. J., Lindoy, L. F., Lip, H. C., Skelton, B. W., and White, A. H., *J. Am. Chem. Soc*., 1983, **105**, 4645.

[11] Bush, M. A., and Truter, M. R., *J. Chem. Soc. B*, 1971, 1440; Dunitz, J. D., Dobler, M., Sieler, P., and Phizackerley, R. P., *Acta Crystallogr., Sect. B*, 1974, **30**, 2733; Izatt, R. M., and Christensen, J. J., (Eds) 'Synthetic Multidentate Macrocyclic Compounds' p. 240 (Academic Press: New York 1978); Hilgenfeld, R., and Saenger, W., in 'Host Guest Complex Chemistry II' (Ed. F. Vögtle) p. 39 (Springer: Berlin 1982).

[12] Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G., and Taylor, R., *J. Chem. Soc., Perkin Trans. 2*, 1987, 12, S1.

[13] Adam, K. R., Davies, R. L., Kennard, C. L. H., Calos, N. J., Lindoy, L. F., and McCool, B. J., *J. Chem. Soc., Chem. Commun.,* 1990, 1784.

[14] Adam, K. R., Lindoy, L. F., Lip, H. C., Rea, J. H., Skelton, B. W., and White, A. H., *J. Chem. Soc., Dalton Trans*., 1981, 74.

[15] SHELXTL v5, Siemens Analytical X-Ray Systems Inc., Madison, Wisconsin, U.S.A., 1994.