Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

New Macrocycle Synthesis, Part VIII [1]. The Synthesis of Dibenzo(3 k +2(crown- k And Cationic Recognition With Fluorescence Spectroscopy

Hülya Tuncer[a]; Çakil Erk[a]
[a] Chemistry Department, I ˙ stanbul Technical University, I ˙ stanbul, Turkey

Online publication date: 29 October 2010

To cite this Article Tuncer, Hülya and Erk, Çakil(2002) 'New Macrocycle Synthesis, Part VIII [1]. The Synthesis of Dibenzo(3 k +2(crown- k And Cationic Recognition With Fluorescence Spectroscopy', Supramolecular Chemistry, 14: 1, 27 — 32
To link to this Article: DOI: 10.1080/10610270290006556
URL: http://dx.doi.org/10.1080/10610270290006556

Supramolecular Chemistry, 2002 Vol. 14 (1), pp. 27–32

New Macrocycle Synthesis, Part VIII [1]. The Synthesis of Dibenzo(3*k*+2(crown-*k* And Cationic Recognition With Fluorescence Spectroscopy

HÜLYA TUNCER and ÇAKIL ERK*

Chemistry Department, İstanbul Technical University, Maslak, 80626, İstanbul, Turkey

(Received 21 September 2000; Revised 19 December 2000; In final form 20 February 2001)

Macrocycles of dibenzo(3*k*+2(crown-*k*, ($k = 6–9$) were synthesised from the condensation of bis(3-hydroxyphenoxy)glycols with polyglycol dihalides or ditosylates in the presence of alkali carbonates/DMSO. Bis(3-hydroxyphenoxy) ended glycols were obtained from resorcinol and dihalides of mono or diethylene glycols in water/-NaOH in good yields. The products were identified with IR, high-resolution EI and FAB mass spectrometry, ^{1}H and ^{13}C-NMR spectroscopy. The binding properties of macrocycles with K^+, Na^+ and Li^+ were investigated with the steady state fluorescence spectroscopy in acetonitrile at room temperature. Macrocycles exhibited complexation enhanced quenching with alkali perchlorates while showing complexation enhanced fluorescence spectra with alkali thiocyanates to give association constants. They mostly displayed better Na^+ binding selectivity compared to those of K^+ and Li^+ ions.

INTRODUCTION

Dibenzo(3*k*+2(crown-*k* type of bismetaphenylene derived macrocycles, among the others, have received brief attention [2]. The oligomers, $k = 10$ or larger, have been, in particular, studied by Stoddart [3,4]. Gibson has reported on the bismetaphenylene-macrocycle polymers [5]. Dibenzocrowns with *o*- and *m*-dioxa moieties have been prepared by Weber [6]. Thomas has reported on the use of such structures as ion selective receptors [7]. Biernat has reported on the formation and binding roles of bis-1,3-benzocrowns obtained from resorcinol [8].

Our continuing work on the synthesis of macrocycles deals with *m*-phenylene moiety of macrocycles for their stereochemistry and the related cationic recognition [9–17]. Such macrocycles are interesting, in particular, due to the macrocyclic conformations of *m*-dioxo-phenylene moieties [3,6,19]. We now report the synthesis of new dibenzo(3*k*+2(crown-*k* oligomers where $k = 6–9$ starting from bis(3-hydroxyphenoxy) glycols which were obtained from resorcinol and bis-dihalides of mono or diethylene glycols in alkaline water in good yields. The cation binding behaviour of the macrocycles were estimated from the steady state fluorescence spectroscopy [9,20,21].

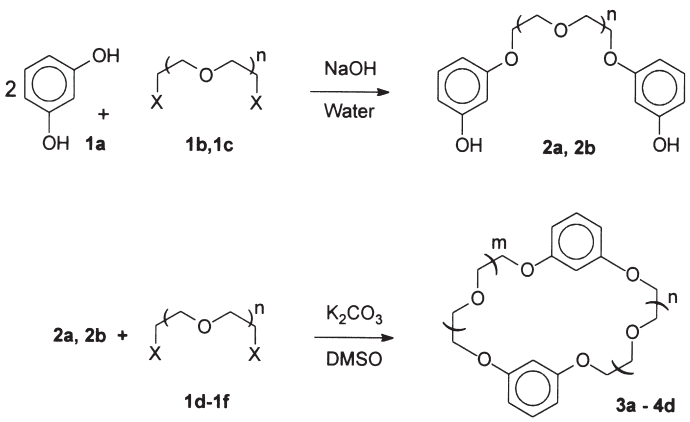
RESULTS AND DISCUSSION

Synthesis

The syntheses of macrocycles were started from resorcinol condensing with glycols. However, we developed a new synthetic route to prepare the novel macrocyclic oligomer structures of dibenzo(3*k*+2 (crown-*k* where $k = m + n + 4$, $n = 0, 1$ and $m = 1–4$, Scheme 1. The syntheses of such molecules were conducted in two steps, and we first obtained bis(3-hydroxyphenyl) ended ethylene glycols in good yields, Scheme 1. The earlier reports for large macrocycles have been based on the hydrogenation of benzyl derivatives to form free hydroxy groups for the macrocyclic condensation [6]. The macrocyclic condensations of such podands with the bispolyethylene glycol dihalides in DMSO/alkali carbonates yielded the macrocycles shown in Scheme 1. In all

*Corresponding author.

ISSN 1061-0278 print/ISSN 1029-0478 online © 2002 Taylor & Francis Ltd
DOI: 10.1080/10610270290006556



	n	m	X
1b	0	-	Br
1c	1	-	Cl
2a	0	-	-
2b	1	-	-
1d	2	-	Cl
1e	3	-	Cl
1f	4	-	TsO
3a	0	2	-
3b	0	3	-
3c	0	4	-
4a	1	1	-
4b	1	2	-
4c	1	3	-
4d	1	4	-

SCHEME 1

steps of synthesis, we tried different solvents, temperatures, reaction periods, basic mediums, as well as column chromatography separations. The macrocycle condensations using bis-polyglycol dihalides gave also better yields compared to polyglycol ditosylate condensations tried at the same experimental conditions [13–15].

The bis(3-hydroxyphenoxy)glycols were obtained in water/NaOH. Reaction of **1a** with **1b** and **1c** afforded **2a** and **2b** in good yields. The cyclic condensation of **2a** with **1d**, **1e** and **1f**, in DMSO/alkali carbonates afforded the moderate yields of **3a**, **3b** and **3c**, respectively. The reaction of **2a** with **1c**, however, yielded polymeric material. The cyclic condensation of **2b** with **1d**, **1e** and **1f** in DMSO/alkali carbonates afforded moderate yields of **4b**, **4c** and **4d**. The reaction of **2b** with **1c** gave a rather low yield macrocycle, **4a** [18].

Cation Binding With Fluorescence Spectroscopy

The macrocycles with aromatic fluorescent moieties have received more attention recently. In particular, the perturbed fluorescence spectra of cation bound macrocycles have been used to study the mechanism and the power of the cationic recognition [9,13–17,21].

K^+, Na^+ and Li^+ binding properties of products **3a–4d** in AN were investigated with steady state fluorescence that display induced changes in triplet energy relative to ground, $T_1 \rightarrow S_0$ and excited singlet state, $S_1 \rightarrow T_1$ energies upon the cationic recognition [20]. The fluorescence emission maxima, I, of the complexed macrocycle at $\lambda = 475$ nm, was observed with the excitation maxima, at $\lambda = 335$ nm in the presence of various cation concentrations, [M], at room temperature. The ion binding constants, K_b were estimated from the equation, $(I - I_f)/(I_b - I) = K_b[M]$ where I_b is the emission intensity of the 1:1 ratio of the complex, and I_f is the intensity of free macrocycle, Tables I and II and Fig. 1A and B [20,21]. The binding order, $Na^+ > K^+ > Li^+$ was found for the macrocycles. However, thiocyanate salts displayed complexing enhanced fluorescence spectra, CEFS, Fig. 1A and Table I, while complexing enhanced quenching spectra, CEQFS was observed with perchlorate salts due to the photophysical balance of decay rates, Fig. 1B, and Table II [20]. The changes in fluorescence emission properties governed are by fluorescence, φ_f and phosphorescence, φ_p quantum yields [9]. Therefore, the macrocycle ligand–cation interactions may give different results due to the computation between the φ_f and φ_p of the lumophore macrocycles. The binding powers observed are limited to structural and

TABLE I The 1:1 cation binding constants, K_b with CEF spectra at room temp in AN

*Compound**	*Salt*	I_b†	I_f‡	K_b	$\log K_b$	$-\Delta G$¶
3a	NaSCN	117	57	433	2.68	14.97
3a	KSCN	104	60	294	2.47	14.02
3b	NaSCN	116	50	632	2.80	15.90
3b	KSCN	106	58	388	2.59	14.70
4c	NaSCN	116	54	548	2.74	15.55
4c	KSCN	106	57	332	2.52	14.32

* $0.24.10^{-3}$ mol/l. † Intensity of complex. ‡ Intensity of free crown. ¶ kJ/mol at 298 K.

TABLE II The 1:1 cation binding constants, K_b with CEQF spectra at room temp in AN

*Compound**	*Salt*	I_b†	I_f‡	K_b	$\log K_b$	$-\Delta G$¶
3a	$LiClO_4$	70	170	110	2.04	11.06
3a	$NaClO_4$	70	170	243	2.84	12.85
3b	$LiClO_4$	45	160	81	1.91	10.35
3b	$NaClO_4$	100	160	600	2.78	15.06
3c	$LiClO_4$	50	90	78	1.89	10.24
3c	$NaClO_4$	60	90	231	2.36	12.80
4c	$LiClO_4$	60	170	81	1.91	10.33
4c	$NaClO_4$	85	170	175	2.24	12.14
4d	$LiClO_4$	55	91	103	2.01	10.92
4d	$NaClO_4$	63	91	165	2.22	12.03
DB18C6§	$LiClO_4$	70	160	107	2.03	10.97
DB18C6§	$NaClO_4$	70	160	99	2.00	10.73

* $0.66.10^{-3}$ mol/l. † Complex intensity. ‡ Crown intensity. ¶ kJ/mol at 298 K. § Dibenzo[18]crown-6.

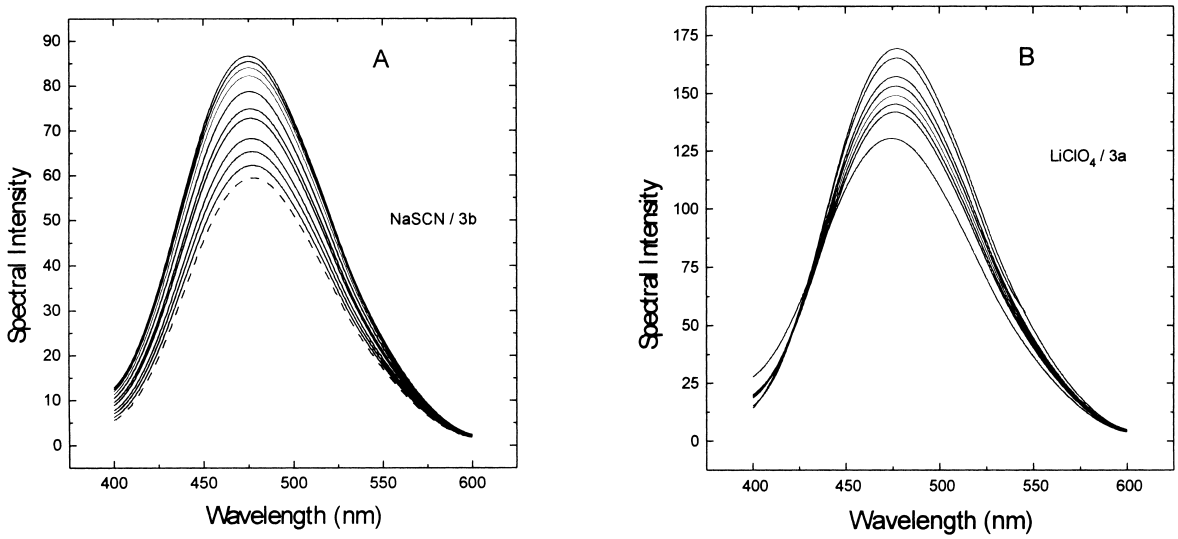


FIGURE 1 (A) Emission CEF spectra of **3b** (0.20×10^{-3} mol/l, lowest peak) in the presence of various amounts of NaSCN (0.2, 0.3, 0.6, 0.8, 0.9, 1.1, 1.2, 1.4, 1.5, 1.7×10^{-3} mol/l, increasing peak maxima), excitation $\lambda = 335$ nm.. (B) Emission CEQF spectra of **3a** (1.33×10^{-3} mol/l, highest peak) in the presence of various amounts of $LiClO_4$ (0.7, 1.3, 1.8, 2.4, 2.9, 3.4, 3.8 and 10.0×10^{-3} mol/l, lowering order of peak maxima), excitation $\lambda = 335$ nm.

conformational restrictions, as expected, and it is to note that Na^+ is mostly better complexed compared to those of K^+ and Li^+ due to the preferred macrocycle size and conformation. Solvent polarity of AN stabilised the polar structure of macrocycles, although, the marked solute–solvent interactions deactivate the non-radiative fluorescence process. The good selectivity of **3b** for both cases responded in a wide concentration range despite its small size. Anion depended spectral results, in particular, proved the ion-macrocycle interactions switching the photophysical effects of lumophore ligands where the more charge delocalised counterions caused the CEFS [22].

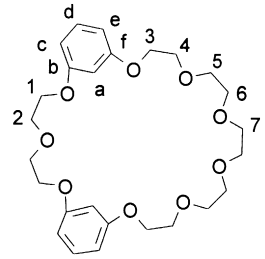
The cationic recognition conducted with steady state fluorescence spectroscopy displayed the 1:1 binding constants, K_b, Tables I and II [9–18,20,21]. However, the Na^+ binding role of dibenzo[18]-crown-6 found in this work is interestingly not better than those of **3a–c** and **4d** at the similar measurement conditions. The low symmetry macrocycles, however, have been reported mostly to exhibit the better binding with Na^+ if the cavities are large for Li^+ or too small for K^+ [6–19]. We reported only the 1:1 stoichiometry of cation binding constants, K_b but no other stoichiometry due to the restriction to the presented calculation methods, Tables I and II [20,21]. In particular, $n = 0$ group of **3a–c** are not better complexed, compared to those of $n = 1$ group of **4c–d**, Tables I and II. This is because of the preferred encapsulation of cations by the long bridge side of bis-*m*-phenylene macro rings where the *anti*, ±*gauche*, *anti* conformational unit sequences of OCH_2CH_2 groups may exist in the complexed macrocycle backbone.

Experimental

Melting points were uncorrected. Resorcinol, **1a**, mono and diethylene glycol dihalides, **1b** and **1c**, were from Merck. However, **1d** and **1e** were available from our earlier studies, [9] and **1f** was from Fluka, Scheme 1. IR spectra were recorded as KBr discs using JASCO spectrometer model-5300. ^{1}H-NMR and ^{13}C-NMR and two-dimensional NMR spectra were recorded on a 400 MHz NMR spectrometer, Bruker model AVANCE CPX 400. The ^{1}H vicinal coupling constants reported are rough values due to non equivalence of proton in methylene groups as well as, stereochemical effects. ^{13}C-NMR spectra separately display the assigned NMR lines corresponding to the structures in Table III were obtained from two-dimensional HETCOR spectra. The exact high-resolution relative molecular EI mass spectra were recorded on a Fisons VG-ZabSpec including FAB mass spectra. However, no elemental analysis were reported beside **2a** and **2b** since the crystalline macrocycles were mostly hygroscopic which was detected with FAB mass spectra.

The emission and excitation fluorescence spectra were obtained with Perkin Elmer luminescence spectrometer, model LS-50 in a 10 mm quartz cell with 10 nm bandwidth at room temperature. Intensity measurements with the various cation concentrations, [M], were made in the presence of constant macrocycle concentration in dry acetonitrile at room temperature using the standard software of the spectrometer, Fig. 1A and B. The intensities of free, I_f and complexed I, aliquots measured from the smoothed peak maxima were used in equation, $(I - I_f)/(I_b - I) = K_b[M]$. However, K_b values were obtained from the slope of linear least

TABLE III Structural assignment of **2a–b**, **3a–c** and**4a–d** to 100 MHz ^{13}C-NMR data in $CDCl_3$/TMS



	1	2	3	4	5	6	7	a	b	c	d	e	f	
2a	67.3	–	–	–	–	–	–	103.4	161.2	106.5	131.1	109.6	160.2
2b	68.3	70.7	–	–	–	–	–	103.4	161.3	106.9	130.9	109.4	159.7
3a	68.1	–	67.8	71.2	70.8	–	–	103.5	160.8	108.6	130.3	108.7	160.6
3b	67.6	–	67.8	70.9	70.9	69.5	–	103.2	160.5	108.1	130.3	108.5	160.6
3c	67.7	–	67.8	70.8	70.9	69.5	69.3	103.0	160.5	108.0	130.2	108.6	160.6
4a	68.7	70.9	68.7	70.9	–	–	–	104.0	161.3	108.6	129.3	108.6	161.3
4b	67.6	89.9	67.2	70.0	70.9	–	–	101.9	160.6	107.6	130.3	107.6	160.6
4c	67.6	70.9	67.5	70.7	69.9	69.8	–	101.9	160.6	107.4	130.2	107.4	160.6
4d	67.6	70.9	67.5	70.7	70.0	69.7	69.6	101.9	160.6	102.5	130.2	107.7	160.6

squares calculation of spectral data by simulating the I_b to reach a highest correlation coefficient and a minimum-y intercept, (see Fig. 2) [1,13–17].

1,4-Bis(3-hydroxyphenyl)-1,4-dioxabutane (2a)

Resorcinol, **1a**, (22.02 g, 200 mmol), 1,2-dibromoethane, **1b**, (9.40 g, 50 mmol) and NaOH (4.0 g, 100 mmol) were boiled in a flask (1.0 l) in water (250 ml) under a reflux condenser whilst vigorously stirring for 24–26 h. The warm solution was filtered and allowed to stand for 24 h and then the crystals formed were recrystallized from hot water; 8.70 g, m.p. 162°C, **2a**, yield 70–71%; (HRMS Found: m/z 246.0892. $C_{14}H_{14}O_4$ requires: 246.0825); MS m/z (% Rel int): 246 (97, M^+), 137 (95, $C_8H_9O_2^+$), 136 (100, M^+-110, $C_6H_6O_2^+$), 123 (43, $C_7H_7O_2^+$); IR (KBr) $\nu =$ 3269 (OH), 2942, 2866 (CH_2), 1610, 1588 (Ar), 1283, 1147 (COC) cm^{-1}; ^{1}H-NMR ($CDCl_3$/TMS, 400 MHz): $\delta_H = 4.22$ (4H, s, C_2H_4O), 6.42 (6H, m, Ar), 7.03(2H, t, $J = 8.05$ Hz, Ar), 9.03(2H, s, OH); Calcd for $C_{14}H_{14}O_4$: C 68.28; H 5.73, Found: C 68.36: H 5.65.

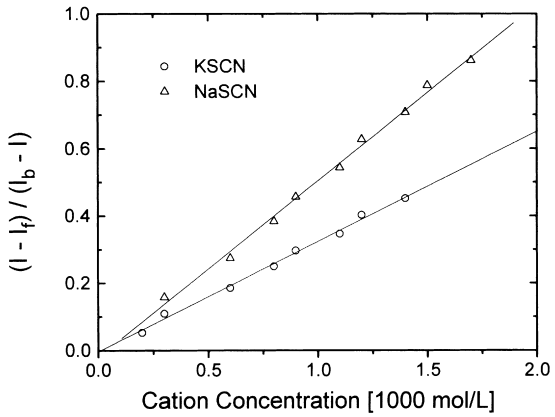


FIGURE 2 The estimation of K_b of **4c**/NaSCN and KSCN complexes from equation $(I - I_f)/(I_b - I) = K_b[M]$.

1,7-Bis(3-hydroxyphenyl)-1,4,7-trioxaheptane (2b)

Resorcinol, **1a**, (22.02 g, 200 mmol), β,β′-dichlorodiethyl ether, **1c**, (7.15 g, 50 mmol) and KOH (5.61 g, 100 mmol) in boiling water (300 ml) in 90 h at above given conditions afforded white large crystals from $CHCl_3$, 5.35 g, m.p. 130°C, **2b**, yield 36.9%; (HRMS found: m/z 290.1091. $C_{16}H_{18}O_5$ requires: 290.1154); MS m/z (% Rel int): 290 (85, M^+), 137 (90, $C_8H_9O_2^+$), 136 (60, $C_8H_8O_2^+$), 123 (40, $C_7H_7O_2^+$); IR (KBr) $\nu =$ 3422 (OH), 2944, 2877 (CH_2), 1580 (Ar), 1177, 1055 (COC) cm^{-1}; ^{1}H-NMR ($CDCl_3$/TMS, 400 MHz) $\delta_H =$ 3.82 (4H, t, $J = 4.5$ Hz, CH_2O), 4.04(4H, t, $J = 4.5$ Hz, CH_2O), 6.41(6H, m, Ar), 6.93(2H, t, $J = 8.9$ Hz, Ar), 8.32(2H, s, OH); Calcd for $C_{16}H_{18}O_5$: C 66.20 H 6.25, Found: C 66.26: H 6.15.

1,5,8,12,15,18-hexaoxa-(2,4-9,11-[1,3] Dibenzeno)cycloeicosa-2,9-diene (3a)

1,4-Bis(3-hydroxyphenyl)-1,4-dioxabutane, **2a**, (1.23 g, 5.0 mmol), 1,8-dichloro-3,6-dioxa-octane, **1d**, (0.935 g, 5.0 mmol), K_2CO_3 (1.38 g, 10.0 mmol) and DMSO (45 ml) were heated at 95°C for 100–110 h whilst stirring. Cooled mixture was diluted with water (100 ml) and acidified with HCl (5 ml, 2N) then extracted with $CHCl_3$ (4 × 50 ml) and organic residue eluted on basic alumina (40 g, Merck, pH:10) with CH_2Cl_2 (100 ml) gave oily products. Further elution of the column with methanol (2 × 25 ml) gave colourless crystals, 0.45 g, m.p. 152°C, **3a**, yield 25.0%; (HRMS Found: m/z 360.1510. $C_{20}H_{24}O_6$ requires: 360.1572); FABMS m/z 361; Mass m/z (% Rel int): 360 (99, M^+), 162 (33, $C_{10}H_{10}O_2^+$), 137 (93,

$C_8H_9O_2^+$), 136 (70, $C_8H_8O_2^+$); IR (KBr) $\nu = 2922, 2877$ (CH_2), 1480, 1450 (Ar), 1183, 1061 (COC) cm^{-1}; ^{1}H-NMR ($CDCl_3$/TMS, 400 MHz) $\delta_H = 3.73$ (4H, s, C_2H_4O), 3.84(4H, t, $J = 5.0$ Hz, CH_2O), 4.11(4H, t, $J = 5.0$ Hz, CH_2O), 4.37(4H, s, C_2H_4O), 6.55(4H, m, ArH), 6.69(2H, m, ArH), 7.16(2H, t, $J = 9.2$ Hz, ArH).

1,5,8,12,15,18,21-heptaoxa-(2,4-9,11-[1,3] Dibenzeno)cyclotricosa-2,9-diene (3b)

1,4-Bis(3-hydroxyphenyl)-1,4-dioxabutane, **2a**, (1.23 g, 5.0 mmol), 1,11-dichloro-3,6,9-trioxaundecane, **1e**, (1.15 g, 5 mmol), K_2CO_3 (1.38 g, 10.0 mmol) and DMSO (40 ml) were heated at 90–95°C for 110–120 h whilst stirring. Cooled mixture was acidified with HCl (5 ml, 2N). The separated oil was extracted with CH_2Cl_2 (4 × 50 ml) and combined extracts was eluted on basic alumina (25 g) to give oily products with CH_2Cl_2 (3 × 25 ml). Further elution with methanol (2 × 25 ml) yielded a fraction of colourless crystals, 0.43 g, m.p. 85°C, **3b**, yield 21.0%; (HRMS Found: m/z 404.1831. $C_{22}H_{28}O_7$ requires: 404.1835); FABMS 405; MS m/z (% Rel int): 404 (60, M^+), 162 (30, $C_{10}H_{10}O_2^+$), 137 (100, $C_8H_9O_2^+$), 136 (70, $C_8H_8O_2^+$); IR(KBr) $\nu = 2922, 2877$ (CH_2), 1483, 1450 (Ar), 1183, 1061 (COC) cm^{-1}; ^{1}H-NMR ($CDCl_3$/TMS, 400 MHz) $\delta_H = 3.68$ (8H, m, C_2H_4O), 3.99(4H, m, CH_2O), 4,24(4H, s, CH_2O), 6.56(6H, m, ArH), 7.17(2H, t, $J = 8.2$ Hz, ArH).

1,5,8,12,15,18,21,24-octaoxa(2,4-9,11-[1,3] Dibenzeno)cyclohexacosa-2,9-diene (3c)

1,4-Bis(3-hydroxyphenyl)-1,4-dioxabutane,**2a**, (1.23 g, 5.0 mmol), 1,14-bis(*p*-toluene sulphonyl)-3,6,9,12-tetraoxatetradecane, **1f**, (2.73 g, 5.0 mmol), K_2CO_3 (1.38 g, 10.0 mmol) and DMSO (40–45 ml) were heated at 85–90°C for 140–142 h whilst stirring. Cooled mixture diluted with with HCl (100 ml, 0.02N) then extracted with CH_2Cl_2 (4 × 50 ml). Evaporated extracts were chromatographed on basic alumina (25 g) to give oily products with CH_2Cl_2 (3 × 25 ml). Further elution with methanol (2 × 25 ml) yielded a colourless oil, 0.18 g, d.p. 235°C, **3c**, yield 8.0%; (HRMS Found: m/z 448.1999. $C_{24}H_{32}O_8$ requires: 448.2097); FABMS m/z 449; MS m/z (% Rel int): 448 (67, M^+), 162 (54, $C_{10}H_{10}O_2^+$), 137 (100, $C_8H_9O_2^+$), 136 (70, $C_8H_8O_2^+$); IR (KBr) $\nu = 2923$, 2872 (CH_2), 1597, 1488, (Ar), 1142, 1066 (COC) cm^{-1}; ^{1}H-NMR ($CDCl_3$/TMS, 400 MHz) $\delta_H = 3.68$ (12H, m, C_2H_4O), 3.99(4H, m, CH_2O), 4.24(4H, s, CH_2O), 6.57(6H, m, ArH), 7.16(2H, t, $J = 8.2$ Hz, ArH).

1,5,8,11,15,18-hexaoxa(2,4-12,14-[1,3] Dibenzeno)cycloeicosa-2,12-diene (4a)

1,7-Bis(3-hydroxyphenyl)-1,4,7-trioxaheptane,**2b**, (0.93 g, 3.2 mmol), β,β′-dichlorodiethyl ether, **1c**, (0.46 g, 3.2 mmol) and Na_2CO_3 (0.68 g, 6.4 mmol) in DMSO (50 ml) were heated at 95°C whilst stirring for six days. The product after HCl (5 ml, 2N) addition was extracted with $CHCl_3$. Major product was isolated and purified with chromatography using basic alumina/benzene (20 g/100 ml). Crystallized from ether, 0.09 g, m.p. 46°C, **4a**, yield 7.80%; (HRMS Found: m/z 360.1517. $C_{20}H_{24}O_6$ requires: 360.1522); FABMS m/z 361; MS m/z (% Rel int): 360 (50, M^+), 180 (35, M^+-180, $C_{10}H_{12}O_3^+$), 137 (90, $C_8H_9O_2^+$), 109 (30, $C_6H_5O_2^+$); IR (KBr) $\nu = 2933$, 2877 (CH_2), 1594, 1488 (Ar), 1127, 1055 (COC) cm^{-1}; ^{1}H-NMR ($CDCl_3$/TMS, 400 MHz) $\delta_H = 3.83$ (4H, m, CH_2O), 4.03(4H, m, CH_2O), 6.47(6H, m, ArH), 7.14(2H, t, $J = 9.0$ Hz, ArH).

1,5,8,11,15,18,21-heptaoxa(2,4-12,14-[1,3]dibenzeno) cyclotricosa-2,12-diene (4b)

1,7-Bis(3-hydroxyphenyl)-1,4,7-trioxaheptane, **2b**, (1.15 g, 4 mmol), 1,8-dichloro-3,6-dioxaoctane, **1d**, (0.75 g, 4 mmol) and K_2CO_3 (1.10 g, 8.0 mmol) in DMSO (40 ml) were heated at 95°C whilst stirring for 100 h. The product separated after HCl (5 ml, 2N) addition was extracted with CH_2Cl_2 and eluted on basic alumina (25 g) with CH_2Cl_2 (3 × 25 ml) gave oily products. Further elution with methanol, (2 × 25 ml) yielded a fraction, crystals, 0.49 g, m.p. 75°C, **4b**, yield 33.0%; (HRMS Found: m/z 404.1829. $C_{22}H_{28}O_7$ requires: 404.1835); FABMS m/z 405; MS m/z (% Rel int): 404 (86, M^+), 180 (30, $C_{10}H_{12}O_3^+$), 137 (85, $C_8H_9O_2^+$), 109 (30, $C_6H_5O_2^+$); IR (KBr) $\nu = 2923$, 2876 (CH_2), 1492, 1453, (Ar), 1138, 1030 (COC), cm^{-1}; ^{1}H-NMR ($CDCl_3$/TMS, 400 MHz) $\delta_H = 3.73$ (4H, m, C_2H_4O), 3.83 (4H, m, CH_2O), 3.89(4H, m, CH_2O), 4.10(8H, m, C_2H_4O), 6.51(6H, m, ArH), 7.13(2H, m, ArH).

1,5,8,11,15,18,21,24-octaoxa(2,4-12,14-[1,3] dibenzeno)cyclohexacosa-2,12-diene (4c)

1,7-Bis(3-hydroxyphenyl)-1,4,7-trioxaheptane,**2b**, (1.3 g. 4.5 mmol) 1,11-dichloro-3,6,9-trioxaundecane, **1e**, (1.04 g, 4.5 mmol) and K_2CO_3 (1.24 g, 9 mmol) in DMSO (50 ml) were heated at 95°C whilst stirring for six days. The oil separated with HCl (5 ml, 2N) addition was extracted with $CHCl_3$ that eluted on basic alumina (25 g) to give oily by products with CH_2Cl_2 (2 × 25 ml). Further elution with methanol (2 × 25 ml) yielded a fraction, crystals, 0.42 g, m.p. 65°C, **4c**, yield 21.0%; (HRMS Found: m/z 448.2069. $C_{24}H_{32}O_8$ requires: 448.2097); FABMS m/z 449; MS m/z (% Rel int): 448 (99, M^+), 180 (20, $C_{10}H_{12}O_3^+$), 137 (90, $C_8H_9O_2^+$), 109 (27, $C_6H_5O_2^+$); IR (KBr) $\nu = 2922$, 2866 (CH_2), 1483, 1450 (Ar), 1183, 1061 (COC) cm^{-1}; ^{1}H-NMR ($CDCl_3$/TMS, 400 MHz) $\delta_H = 3.71$ (8H, m, C_2H_4O), 3.85(4H, m, CH_2O), 3.90(4H, m, CH_2O),

4.07(8H, m, ArH), 6.54(6H, m, ArH), 7.16 (2H, m, ArH).

1,5,8,11,15,18,21,24,27-heptaoxa(2,4-12,14-[1,3] dibenzeno)cyclononacosa-2,12-diene (4d)

1,7-Bis(3-hydroxyphenyl)-1,4,7-trioxaheptane,**2b**, (1.33 g, 4.6 mmol), K_2CO_3 (1.27 g, 9.2 mmol) and 1,14-bis(p-toluenesulphonyl)-3,6,9,12-tetraoxatetradecane, **1f**, (2.51 g, 4.6 mmol) in DMSO (50 ml) were heated at 95°C whilst stirring for six days. The oily product separated after HCl (5 ml, 2N) addition was extracted with $CHCl_3$. Residue was eluted on basic alumina, (25 g) to give by products with CH_2Cl_2, (3×25 ml). Further elution with methanol (2×25 ml) yielded a fraction of a colourless oil, 0.26 g, d.p. 245°C, **4d**, yield 11.5%; (Found: m/z 492.2377. $C_{24}H_{32}O_8$ requires: 492.2359), FAB mass m/z 493; Mass m/z (% Rel int): 492 (65, M^+), 180 (20, $C_{10}H_{12}O_3^+$), 137 (90, $C_8H_9O_2^+$), 109 (25, $C_6H_5O_2^+$); IR (KBr) $\nu = 2923$ (CH_2), 1488, 1454 (Ar), 1125, 1066 (COC) cm^{-1}; ^{1}H-NMR ($CDCl_3$/TMS, 400 MHz) $\delta_H =$ 3.73 (12H, m, C_2H_4O), 3.85(4H, m, CH_2O), 3.90(4H, m, CH_2O), 4.07(8H, m, ArH), 6.54(6H, m, ArH), 7.16(2H, m, ArH).

Acknowledgements

The author, H.T. acknowledges the support of İTU Research Foundation for the PhD work. The authors are grateful to Turkish Scientific and Technological Research Council, TUBITAK, supporting the present work.

References

[1] Part, VII, Erk, Ç., Bulut, M. and Göçmen, A. (2000), *J. Incl. Phenom.* **37**, 441.
[2] Izatt, R.M., Pawlak, K., Bradshaw, J.S. and Bruening, R.L. (1995), *Chem. Rev.* **95**, 2529.
[3] Colquhon, H.M., Goodings, E.P., Maud, J.M., Stoddart, J.F., Williams, D.J. and Wolsstenholme, J.B. (1983), *J.C.S. Chem. Commun.*, 1140.
[4] Stoddart, J.F. (1988), *Pure Appl. Chem.* **60**, 467.
[5] Delaviz, Y. and Gibson, H.W. (1992), *Macromolecules*, 4859.
[6] Weber, E., Köhler, H.-J., Panneerselvam, K., Chacko, K.K. and J, C.S. (1990), *Perkin Trans. 1*, 1599.
[7] Thomas, J.D.R. (1991), *Analyst*, 1211.
[8] Luboch, E., Fonari, S., Simonov, Yu.A., Belski, V.K. and Biernat, J.F. (1995), *Russian Chem. Bull.* **44**, 2353.
[9] Erk, Ç., Göçmen, A. and Bulut, M. (1998), *J. Incl. Phenom.* **31**, 319.
[10] Erk, Ç., Göçmen, A. and Bulut, M. (1999), *Supramol. Chem.* **11**, 49.
[11] Erk, Ç. and Erbay, E. (2000), *J. Incl. Phenom.* **36**, 229.
[12] Erk, Ç. and Göçmen, A. (2000), *Talanta* **44**, 81.
[13] Tuncer, H., Erk, Ç. (1997) Ninth Int. Symp. Macromole. -Metal Complexes, Leiden.
[14] Tuncer, H., Erk, Ç. (1998) Tenth Int. Symp. on Inclusion & Mole. Recogn., Warsaw.
[15] Tuncer, H., Erk, Ç. (1999) 24th Int. Symp. on Macrocyclic Chemistry, Barcelona.
[16] Tuncer, H. and Erk, Ç. (2000), *Dyes Pigments* **44**, 81.
[17] Japanese Patent, C.A. 97, 47.203 (1982).
[18] Bozkurtoğlu, N. and Erk, Ç. (1998) In: Coleman, A.W., ed, Molecular recognition and inclusion (Kluwer, Dordrecht).
[19] Buchanan, G.W. (1999), *Prog. NMR Spectrosc.* **34**, 327.
[20] Prasanna de Silva, A., Gunaratne, Q.N., Gunnlaugsson, T., Huxley, A.J.M., McCoy, C.P., Rademacher, R.T. and Rice, T.E. (1997), *Chem. Rev.* **97**, 1515.
[21] Bourson, J., Pouget, J. and Valeur, B. (1993), *J. Phys. Chem.* **97**, 4552.
[22] Smid, J. (1972) In: Szwarc, M., ed, Ions and Ion Pairs in Organic Reactions (Wiley, London) **1**, p 130.