Journal of Inclusion Phenomena and Molecular Recognition in Chemistry **28:** 223–244, 1997.

Synthesis, Characterisation and UV-Vis Properties of *Azo*calix[4]crowns

M. SAADIOUI, Z. ASFARI and J. VICENS
ECPM, Laboratoire de Chimie Analytique et Minérale, URA 405 du CNRS, 1, rue Blaise Pascal, Strasbourg, F-67008 France.

N. REYNIER and J. F. DOZOL
CEA-Cadarache, Saint-Paul-Lez-Durance, F-13108 France.

(Received: 12 June 1996; in final form: 1 October 1996)

Abstract. This article describes the synthesis, structure and UV properties of *azo*calixcrowns in which the photoresponsive *trans-cis azo benzene* unit has been introduced in the glycolic chains of the calix[4]crowns. The synthesis proceeded via the selective-1,3*O*-dialkylation of calix[4]arene with glycolic chains terminated by nitrophenyl residues. After reduction of the nitro groups into amino functions, intramolecular oxidative coupling produced the capping of the calixarene. The synthetic approaches and the *cis-trans* structure of these new ligands are discussed and full details on syntheses and structural data are given. A preliminary example of cesium complexation by one of the ligands is proposed.

Key words: Calix[4]arene, calixcrowns, *cis-trans azo benzene* unit.

1. Introduction

Many systems are described in the literature in which the photoresponsive *trans-cis azo benzene* (Chart I(a)) has been introduced in macrocyclic structures in order to change the cavity shape of the receptors leading to a photocontrol of ion complexation, extraction and cation transport [1]. On the other hand, calixarenes (Chart I(b)) have been proved to be versatile building blocks to design and synthesize a large variety of selective ligands by chemical transformations of the parent cyclic oligomers with appropriate binding functions [2]. In the peculiar case of calix[4]arenes, the observed selectivities are not only dependent on the introduced ligating sites, but on the conformation of the calix unit [2]. Among the functionalized calix[4]arenes, calix[4]crowns refer to a family of macropolycyclic compounds, combining in their structure calix[4]arene and polyether elements, aimed at the selective complexation of alkali cations [3]. In the present paper we expand upon that investigation and present the synthesis, structure and UV properties of *azo*calixcrowns in which the photoresponsive *trans-cis azo benzene* unit has been introduced in the glycolic chains of calix[4]crown [4].

Chawla and Srinivas [5] have designed new chromogenic calix[8]arenes in which azobenzene units are directly created at the upper rim of the calix unit as

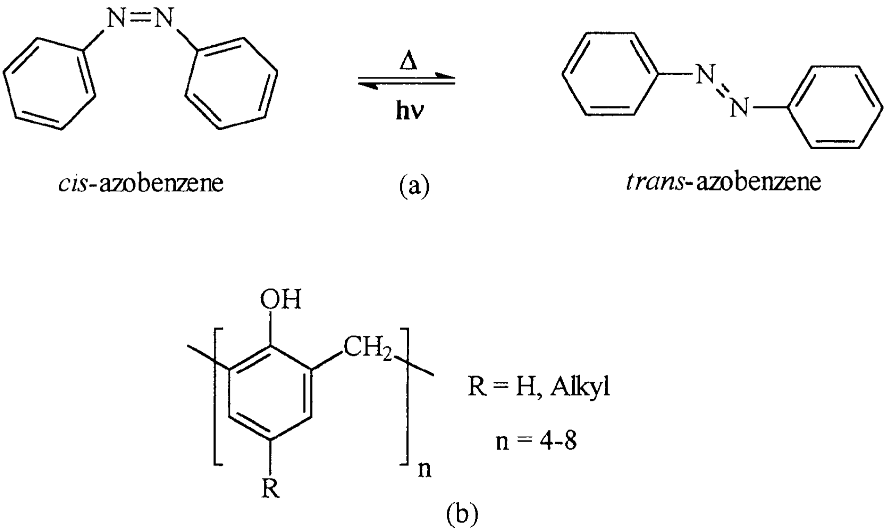


Chart I.

potential reagents for amines. A very recent example has been reported by Hamada *et al.* [6] of a photoregulated metal binding by a calix[4]arene in which the azo benzene unit capped the calix through ester linkages.

2. Experimental

2.1. GENERAL

The solvents and all compounds were commercial reagents and were used without further purification. Melting points were measured with a Büchi 500 apparatus in capillaries sealed under nitrogen. Chromatography columns were prepared from Kieselgel Merck (Art. 9385). TLC was performed on 250 μm silica gel plates containing a fluorescent indicator. ^{1}H-NMR spectra were recorded at 200 MHz on a Bruker SY200 spectrometer and the chemical shifts are reported as δ values referenced to tetramethylsilane (TMS) at $\delta = 0.00$ as an internal standard. UV-Vis spectra recorded at different institutions were measured on Cary 13 E (Varian) and Shimadzu UV-2101/3101PC instruments. The FAB mass spectra were obtained on a VG-analytical ZAB HF apparatus. Elemental analyses were provided by the Service de Microanalyse of the Institut de Chimie de Strasbourg. Solvent of crystallization was retained in some of the analytical samples and affected the elemental analysis. In such cases, best fits between the analytical values and appropriate increments of solvents were used.

2.1.1. *Preparation (**1–6**)*

2-(p-Nitrophenoxy)ethanol (**1**). In a 2-L round-bottomed flask, equipped with a condenser was placed *p*-nitrophenol (25.00 g, 180.00 mmol) and K_2CO_3 (37.32 g, 270.00 mmol) in CH_3CN (1500 mL). The reaction mixture was stirred at room temperature (r.t.) for 3 h in an atmosphere of N_2. 2-Chloroethanol (21.74 g, 270.00 mmol) was added and the mixture was refluxed for 7 days. On completion of the reaction (as indicated by TLC) the reaction mixture was cooled to r.t., and the solvents were removed under reduced pressure on a rotary evaporator to afford a residue which was dissolved in CH_2Cl_2 (600 mL) and 1 N HCl (600 mL) was added under stirring to neutralize the excess of K_2CO_3. The organic layer was separated and the water layer was extracted with CH_2Cl_2 (200 mL). The combined extract was dried (Na_2SO_4) and the filtered solution concentrated and precipitated in Et_2O to yield pure **1** as a white solid: 24.00 g.

2-[2-(p-Nitrophenoxy)ethoxy]ethanol (**2**). Same as **1**; *p*-nitrophenol (22.50 g, 161.74 mmol), K_2CO_3 (44.70 g, 323.48 mmol), 2-(2-chloroethoxy)ethanol (40.28 g, 323.48 mmol) in CH_3CN (1500 mL); 48 h; white solid from Et_2O: 26.00 g.

2-[(2-(p-Nitrophenoxy)ethoxy)ethoxy]ethanol (**3**). Same as **1**; *p*-nitrophenol (2.78 g, 20.00 mmol), K_2CO_3 (8.29 g, 60.00 mmol), 2-[2-(2-chloroethoxy)ethoxy]ethanol (3.37 g, 20.00 mmol) in CH_3CN (150 mL); 3 days; transparent oil: 4.70 g.

Tosylate of 2-(p-nitrophenoxy)ethanol (**4**). In a 2-L round-bottomed flask, equipped with a condenser, **1** (24.00 g, 131.03 mmol) and *p*-toluene-sulfonyl chloride (37.47 g, 194.00 mmol) were dissolved in CH_2Cl_2 (1000 mL) and then triethylamine (53.83 g, 533.00 mmol) was added dropwise over 1 h at 0 °C. The reaction mixture was stirred at r.t. for 24 h in an atmosphere of N_2. On completion of the reaction (as indicated by TLC) the excess of triethylamine was neutralized with 1N HCl. The organic layer was separated and the water layer was extracted with CH_2Cl_2 (200 mL). The combined extract was dried (Na_2SO_4), the filtered solution was concentrated at reduced pressure and precipitated with methanol to yield pure **4** as a white solid: 36.78 g.

Tosylate of 2-[2-(p-nitrophenoxy)ethoxy]ethanol (**5**). Same as **4**; **2** (6.00 g, 26.40 mmol), *p*-toluene-sulfonyl chloride (5.03 g, 26.40 mmol) in CH_2Cl_2 (300 mL), triethylamine (10.66 g, 105.60 mmol); 24 h; white solid: 7.03 g.

Tosylate of 2-[(2-(p-nitrophenoxy)ethoxy)ethoxy]ethanol (**6**). Same as **4**; **3** (4.60 g, 16.90 mmol), *p*-toluene-sulfonyl chloride (6.46 g, 33.90 mmol) in CH_2Cl_2 (250 mL), triethylamine (6.84 g, 67.8 mmol); 24 h; chromatography on a silica column using 95 : 5 chloroform:acetone as eluent; transparent oil 4.30 g.

2.1.2. *Preparation of p-nitrophenoxy calixarenes (**7–15**)*

25,27-Bis[2-(p-nitrophenoxy)ethoxy]-26,28-dihydroxy-calix[4]arene (**7**). In a 250 mL round-bottomed flask, equipped with a condenser, K_2CO_3 (2.05 g, 14.84 mmol) was added to a solution of calix[4]arene (6.00 g, 14.13 mmol) in CH_3CN (100 mL) and stirred at r.t. for 24 h in an atmosphere of N_2. Then, a solution of **4** (9.53 g, 28.26 mmol) in CH_3CN (50 mL) was added dropwise. The reaction mixture was refluxed for 19 days. On completion of the reaction (as indicated by TLC) the reaction mixture was cooled to r.t. and the solvents were removed under reduced pressure on a rotary evaporator to afford a residue which was dissolved in CH_2Cl_2 (300 mL). 1N HCl (100 mL) was added under stirring to neutralize the unreacted K_2CO_3. The organic layer was separated and the water layer was extracted with CH_2Cl_2 (200 mL). The combined extract was dried (Na_2SO_4), the filtered solution was concentrated and chromatographed on a silica column using chloroform as eluent to yield pure **7** as a white solid after precipitation with methanol: 6.65 g.

25,27-Bis[2-(2-(p-nitrophenoxy)ethoxy)ethoxy]-26,28-dihydroxy-calix[4]arene (**8**). Same as **7**; calix[4]arene (12.00 g, 28.26), K_2CO_3 (4.10 g, 29.67 mmol), **5** (21.55 g, 56.52 mmol) in CH_3CN (750 mL); 4 days; chromatography on silica column using 98 : 2 chloroform:acetone as eluent; precipitation with hexane-methanol to yield **8** as a white solid: 12.00 g.

25,27-Bis[2-[2-(2-(p-nitrophenoxy)ethoxy)ethoxy)ethoxy]-26,28-dihydroxy-calix[4]arene (**9**). Same as **7**; calix[4]arene (4.00 g, 9.42 mmol), K_2CO_3 (1.36 g, 9.89 mmol), **6** (8.01 g, 18.84 mmol) in CH_3CN (300 mL); 10 days; chromatography on silica column using 98 : 2 dichloromethane : acetone as eluent to yield **9** as a transparent oil: 4.17 g.

25,27-Bis[2-(p-nitrophenoxy)ethoxy]-26,28-di-[2-(2-methoxyethoxy)ethoxy]-calix[4]arene (**10**). In a 250 mL round-bottomed flask, equipped with a condenser, K_2CO_3 (5.49 g, 39.74 mmol) was added to a stirred solution of **7** (3.00 g, 3.97 mmol) in CH_3CN (100 mL) and stirring was continued at r.t. for 24 h in an atmosphere of N_2. Then a solution of 2-(2-methoxyethoxy)ethanol-*p*-toluenesulfonate (3.27 g, 11.92 mmol) in CH_3CN (50 mL) was added dropwise, and the reaction mixture was refluxed for 8 days. After cooling to r.t. the solvents were removed under reduced pressure to afford an oil which was dissolved in CH_2Cl_2 (200 mL) and 1 N HCl (200 mL) was added under stirring to neutralize the unreacted K_2CO_3. The organic layer was separated and the water layer was extracted with CH_2Cl_2 (200 mL). The combined extract was dried (Na_2SO_4), the filtered solution was concentrated and chromatographed on a silica column by using dichloromethane as eluent to yield pure **10** as a white solid after precipitation in methanol: 1.10 g.

25,27-Bis[2-(2-(p-nitrophenoxy)ethoxy)ethoxy]-26,28-di-[2-(2-methoxyethoxy) ethoxy-calix[4]arene (**11**). Same as **10**, K_2CO_3 (11.06 g, 80.00 mmol), **8** (6.75 g, 8.00 mmol), 2-(2-methoxyethoxy)ethanol-*p*-toluenesulfonate (4.94 g, 18.00 mmol) in CH_3CN (250 mL); chromatography on silica column using 96 : 4 chloroform:acetone as eluent; white solid: 2.50 g.

25,27-Bis[2-(2-(2-(p-nitrophenoxy)ethoxy)ethoxy)ethoxy]-26,28-di-[2-(2-methoxyethoxy)ethoxy]-calix[4]arene (**12**). Same as **10**, K_2CO_3 (5.92 g, 42.90 mmol), **9**, (4.00 g, 4.29 mmol), 2-(2-methoxyethoxy)ethanol-*p*-toluenesulfonate (3.53 g, 12.87 mmol) in CH_3CN (200 mL), chromatography on silica column using 95 : 5 dichloromethane : acetone as eluent; transparent oil: 2.20 g.

25,26,27,28-Tetrakis[2-(p-nitrophenoxy)ethoxy]-calix[4]arene (**13**). In a 500 mL round-bottomed flask, equipped with a condenser, K_2CO_3 (9.75 g, 70.60 mmol) was added to a stirred solution of calix[4]arene (3.00 g, 7.06 mmol) in CH_3CN (200 mL) and stirring was continued at r.t. for 24 h in an atmosphere of N_2. Then a solution of **4** (11.90 g, 35.26 mmol) in CH_3CN (50 mL) was added dropwise. The reaction mixture was refluxed for 12 days. The same quantity of K_2CO_3 was added and the reflux was continued for 13 additional days. After cooling to r.t. the solvents were removed under reduced pressure to afford a residue which was dissolved in CH_2Cl_2 (600 mL) and 1N HCl (300 mL) was added under stirring to neutralize the unreacted K_2CO_3. The organic layer was separated, and the water layer was extracted with CH_2Cl_2 (200 mL). The solution was concentrated and a precipitate was formed which was filtered to give **13′** as an insoluble white solid (1.80 g) [7]. The filtrate solution was dried (Na_2SO_4), filtered and concentrated. The compound **13** was precipitated with dichloromethane–methanol as a white solid: 4.50 g.

25,26,27,28-Tetrakis[2-(2-(p-nitrophenoxy)ethoxy)ethoxy]-calix[4]arene (**14**). Same as **13**, K_2CO_3 (5.80 g, 42.00 mmol), calix[4]arene (1.78 g, 4.20 mmol), **5** (8.00 g, 20.97 mmol) in CH_3CN (150 mL); the same quantities of K_2CO_3 were added after 6 days: total reflux time 12 days; insoluble white solid: 2.50 g.

25,26,27,28-Tetrakis[2-(2-(2-(p-nitrophenoxy)ethoxy)ethoxy)ethoxy]calix[4] arene (**15**). Same as **13**, K_2CO_3 (9.72 g, 70.33 mmol), calix[4]arene (1.49 g, 3.51 mmol), **6** (6.00 g, 14.10 mmol) in CH_3CN (150 mL). The same quantities of K_2CO_3 was added after 4 days: total reflux time 10 days; chromatography on silica column using 98 : 2 dichloromethane:acetone as eluent, transparent oil: 2.27 g.

2.1.3. *Preparation of the p-aminophenoxy calixarenes (***16**–**23***)*

25,27-Bis[2-(p-aminophenoxy)ethoxy]-26,28-dihydroxy-calix[4]arene (**16**). In a 250 mL 2-necked round-bottomed flask, equipped with a condenser, **7** (3.00 g, 3.97 mmol) was dissolved in absolute ethanol (80 mL) and graphite (4.00 g) was added under stirring at r.t. for 2 h under an atmosphere of N_2. Then, a solution of hydrazine monohydrate (4.00 g, 79.90 mmol) in absolute ethanol (20 mL) was added dropwise and the reaction mixture was refluxed for 3 days. On completion of the reaction (as indicated by TLC) the mixture was cooled to r.t., filtered over celite and washed with dichloromethane. The solvents were evaporated under reduced pressure and the diamine **16** was precipitated with methanol to give a white solid: 2.40 g.

25,27-Bis[2-(2-(p-aminophenoxy)ethoxy)ethoxy]-26,28-dihydroxy-calix[4] arene (**17**). Same as **16**; **8** (6.00 g, 7.12 mmol), hydrazine monohydrate (3.56 g, 71.20 mmol), graphite (6.00 g) in absolute ethanol (150 mL), 2 days of reflux, chromatography on a silica column using 95 : 5 chloroform acetone as eluent; transparent oil: 4.87 g.

25,27-Bis[2-(2-(2-(p-aminophenoxy)ethoxy)ethoxy)ethoxy]-calix[4]arene (**18**). Same as **16**; **9** (4.17 g, 4.48 mmol), hydrazine monohydrate (4.48 g, 89.49 mmol), graphite (8.00 g) in absolute ethanol (150 mL), 1 day of reflux, viscous oil: 3.80 g.

25,27-Bis[2-(p-aminophenoxy)ethoxy]-26,28-di-[2-(2-methoxyethoxy)ethoxy]-calix[4]arene (**19**). Same as **16**; **10** (1.00 g, 1.04 mmol), hydrazine monohydrate (4.00 g, 79.90 mmol), graphite (4.00 g) in absolute ethanol (100 mL), reflux for 2 days, precipitation with methanol to give **19** as a white solid: 0.89 g.

25,27-Bis[2-(2-(p-aminophenoxy)ethoxy)ethoxy]-26,28-di-[2-(2-methoxy-ethoxy)ethoxy]-calix[4]arene (**20**). Same as **16**; **11** (2.00 g, 1.90 mmol), hydrazine monohydrate (1.90 g, 38.90 mmol), graphite (7.60 g) in absolute ethanol (70 mL), reflux for 3 days, purification by chromatography on a silica column 80 : 20 dichloromethane : acetone as eluent to leave a viscous oil 1.01 g.

25,27-Bis[2-(2-(2-(p-aminophenoxy)ethoxy)ethoxy)ethoxy]-26,28-di-[2-(2-methoxyethoxy)ethoxy]-calix[4]arene (**21**). Same as **16**; **12** (3.79 g, 3.34 mmol), hydrazine monohydrate (3.34 g, 66.72 mmol), graphite (8.00 g) in absolute ethanol (150 mL), reflux for 4 days; transparent oil: 3.50 g.

25,26,27,28-Tetrakis[2-(2-(p-aminophenoxy)ethoxy)ethoxy]-calix[4]arene (**22**). Same as **16**; **14** (2.00 g, 1.58 mmol), hydrazine monohydrate (16.00 g, 319.61 mmol), graphite (8.00 g) in absolute ethanol (150 mL), reflux for 2 days, purification by precipitation with methanol to give a white solid :1.30 g.

25,26,27,28 Tetrakis[2-(2-(2-(p-aminophenoxy)ethoxy)ethoxy)ethoxy]-calix [4]arene (**23**). Same as **16**; **15** (1.50 g, 1.04 mmol), hydrazine monohydrate (4.00 g, 79.90 mmol), graphite (8.00 g) in absolute ethanol (70 mL), reflux for 3 days; transparent oil: 1.02 g.

2.1.4. *Preparation of azocalixcrowns (**24**–**31**)*

25,27-(p,p′-azobenzene)-26,28-dihydroxy-calix[4]-crown-4 (**24**). In a 500 mL round-bottomed flask equipped with a condenser and a Dean-Stark water separator, were placed a mixture of **16** (2.00 g, 2.80 mmol) and activated MnO_2 (10.00 g, 115.02 mmol) in dry benzene (150 mL). The heterogeneous mixture was stirred vigorously at reflux for 7 days. On completion (TLC analysis indicated complete conversion of **16**) the reaction mixture was filtered through celite and the residue was washed with CH_2Cl_2 (200 mL). The combined layers and washings were concentrated under reduced pressure, diluted with CH_2Cl_2 and dried ($MgSO_4$). After filtration and evaporation of the solvents, the dark oily residue was purified by chromatography using 97 : 3 dichloromethane : acetone as eluent to afford a yellow solid: 0.200 g.

25,27-(p,p′-azobenzene)-26,28-dihydroxy-calix[4]-crown-6 (**25**). Same as **24**; **17** (1.56 g, 2.00 mmol), activated MnO_2 (3.47 g, 40.00 mmol) in dry benzene (60 mL), 5 days of reflux, 96 : 4 chloroform : acetone as eluent; yellow solid: 0.144 g.

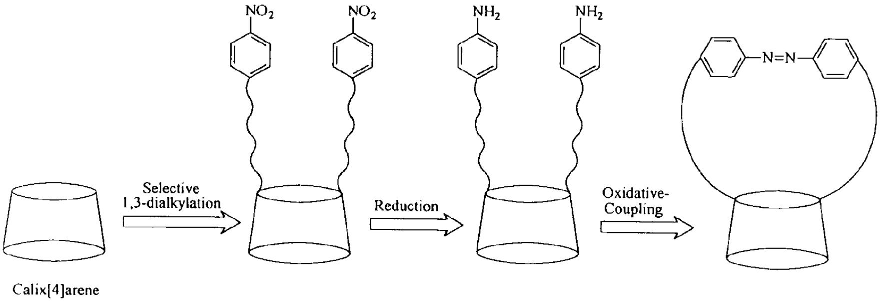
25,27-(p,p′-azobenzene)-26,28-dihydroxy-calix[4]-crown-8 (**26**). Same as **24**; **18** (3.80 g, 4.36 mmol), activated MnO_2 (28.00 g, 322.06 mmol) in dry benzene (350 mL), 8 days of reflux, 90 : 10 dichloromethane : acetone as eluent of chromatography; red solid: 0.616 g.

25,27-di-[2-(2-methoxyethoxy)ethoxy]-26,28-(p,p′-azobenzene)-calix[4]-crown-4 (**27**). Same as **24**; **19** (1.50 g, 1.67 mmol), activated MnO_2 (7.00 g, 80.51 mmol) in dry benzene (250 mL), 1 day of reflux, 95 : 5 dichloromethane : acetone as eluent of chromatography, precipitated with methanol to afford red microcrystals: 0.823 g.

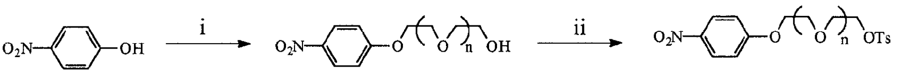
26,28-di-[2-(2-methoxyethoxy)ethoxy]-26,28-(p,p′-azobenzene)-calix[4]-crown-6 (**28**). Same as **24**; **20** (1.80 g, 1.82 mmol), activated MnO_2 (7.00 g, 80.51 mmol) in dry benzene (150 mL), 2 days of reflux, 93 :7 dichloromethane : acetone as eluent of chromatography; crystallised from CH_2Cl_2–CH_3OH to afford yellow microcrystals: 0.522 g.

26,28-di-[2-(2-methoxyethoxy)ethoxy]-26,28-(p,p′-azobenzene)-calix[4]-crown-8 (**29**). Same as **24**; **21** (2.00 g, 1.86 mmol), activated MnO_2 (7.00 g, 80.51 mmol) in dry benzene (150 mL), 2 days of reflux, 95 : 5 dichloromethane : acetone as eluent of chromatography; yellow oil: 0.309 g.

1,3-(p,p′-azobenzene)-calix[4]-bis-crown-6 (**30**). Same as **24**; **22** (1.58 g, 1.38 mmol), activated MnO_2 (15.00 g, 172.53 mmol) in dry benzene (150 mL), 7 days of reflux, 95 : 5 dichloromethane : acetone as eluent of chromatography; yellow solid: 0.105 g.



Scheme 1. General synthesis of azocalixcrowns.



1-3 (n = 0,1,2)

4-6 (n = 0,1,2)

i- $K_2CO_3.ClCH_2CH_2(OCH_2CH_2)_nOH.CH_3CN$. ii-$Et_3N.TsCl.CH_2Cl_2$

Scheme 2. Synthesis of tosylates **4–6**.

1,3-(p,p′-azobenzene)-calix[4]-bis-crown-8 (**31**). Same as **24**; **23** (1.02 g, 0.77 mmol), activated MnO_2 (10.00 g, 115.02 mmol) in dry benzene (150 mL), 10 days of reflux, 90 : 10 dichloromethane : acetone as eluent of chromatography; yellow oil: 0.027g.

3. Results and Discussion

3.1. GENERAL SYNTHESIS

As depicted in general Scheme 1, calix[4]arene was first functionalized by glycolic chains terminated by nitrophenyl residues via selective-1,3-*O*-dialkylation [8] to give the corresponding calixarene podands. After reduction of the nitro groups into amino functions, oxidative coupling of the amino functions was performed to produce the capping of the calixarene. By this mean, the *azo benzene* chromophores were produced in the final step so that the exposure of *azo* linkages to synthetic conditions can be avoided.

We have prepared *azo* calix crowns **24–31**. Their detailed syntheses presented herein are described in Schemes 2 and 3.

3.2. PREPARATION OF ALKYLATING AGENTS **4–6**

As shown in Scheme 2, p-nitrophenol was treated with 2-chloroethanol ($n = 0$) or 2-(2-chloroethoxy)ethanol ($n = 1$) or 2-[2-(2-chloroethoxy)]ethanol ($n = 2$) in the presence of K_2CO_3 with reflux in acetonitrile under nitrogen to give **1–3** (n

Table I. Physical and spectroscopic data of **1–23**.

Compound	Yield (%)	m.p. (°C)	^{1}H NMR (200 MHz)(CDCl$_3$/TMS) δ, J(Hz)	FAB-MS m/z (%)
1[a]	73	133–134	8.22 (d, 2H, J = 9.2, ArH), 6.99 (d, 2H, J = 9.2, ArH), 4.19 (t, 2H, J = 4.5, ArOCH$_2$), 4.12–3.98 (m, 2H, CH$_2$), 2.01 (t, 1H, J = 6.1, OH exchange with D$_2$O)	
2[b]	71	86–87	8.21 (d, 2H, J = 9.2, ArH), 7.00 (d, 2H, J = 9.2, ArH), 4.24 (t, 2H, J = 4.7, CH$_2$), 3.91 (t, 2H, J = 4.7, CH$_2$), 3.77 (t, 2H, J = 4.6, CH$_2$), 3.68 (t, 2H, J = 4.8, CH$_2$), 2.02 (t, 1H, J = 6.0, OH exchange with D$_2$O)	
3[c]	87	oil	8.19 (d, 2H, J = 9.2, ArH), 6.98 (d, 2H, J = 9.2, ArH), 4.22 (t, 2H, J = 4.6, CH$_2$), 3.89 (t, 2H, J = 4.6, CH$_2$), 3.79–3.59 (m, 8H, CH$_2$), 2.36 (s broad, 1H, OH exchange with D$_2$O)	
4[d]	83	122–123	8.17 (d, 2H, J = 9.2 ArH), 7.81 (d, 2H, J = 8.3, TsH), 7.34 (d, 2H, J = 8.1, TsH), 6.85 (d, 2H, J = 9.2, ArH), 4.43–4.36 (m, 2H, CH$_2$), 4.30–4.23 (m, 2H, CH$_2$), 2.45 (s, 3H, CH$_3$)	
5[e]	70	65–66	8.22 (d, 2H, J = 9.2, ArH), 7.78 (d, 2H, J = 8.3, TsH), 7.30 (d, 2H, J = 8.1, TsH), 6.92 (d, 2H, J = 9.2, ArH), 4.21–4.14 (m, 4H, CH$_2$), 3.85–3.75 (m, 4H, CH$_2$), 2.42 (s, 3H, CH$_3$)	
6[f]	60	oil	8.20 (d, 2H, J = 9.2, ArH), 7.79 (d, 2H, J = 8.3, TsH), 7.33 (d, 2H, J = 8.4 TsH), 7.00 (d, 2H, J = 9.2, ArH), 4.23–4.13 (m, 4H, CH$_2$), 3.87 (t, 2H, J = 4.6, CH$_2$), 3.72–3.60 (m, 6H, CH$_2$), 2.43 (s, 3H, CH$_3$)	
7[g]	62	246–248	8.21 (d, 4H, J = 9.2, ArH), 7.62 (s, 2H, ArOH exchange with D$_2$O), 7.07 (d, 4H, J = 7.5, calix-ArH), 6.98 (d, 4H, J = 9.2, ArH), 6.92 (d, 4H, J = 7.1, calix-ArH), 6.77 (t, 2H, J = 7.5, calix-ArH), 6.68 (t, 2H, J = 7.5, calix-ArH), 4.38–4.33 (m, 12H, ArCH$_2$Ar and CH$_2$), 3.38 (d, 4H, J = 13.0, ArCH$_2$Ar)	
8[h]	50	175–176	8.08 (d, 4H, J = 9.2, ArH), 7.62 (s, 2H, ArOH exchange with D$_2$O), 7.04 (d, 4H, J = 7.5, calix-ArH), 6.87–6.75 (m, 8H, calix- ArH and ArH), 6.68 (t, 2H, J = 7.5, calix-ArH), 6.66 (t, 2H, J = 7.5, calix-ArH), 4.37 (d, 4H, J = 13.1, ArCH$_2$Ar), 4.31–4.26 (m, 4H, CH$_2$), 4.20–416 (m, 4H, CH$_2$), 4.07–3.97 (m, 8H, CH$_2$), 3.34 (d, 4H, J = 13.1, ArCH$_2$Ar)	843,6 (MH$^+$, 100)
9[i]	48	oil	8.16 (d, 4H, J = 9.2, ArH), 7.66 (s, 2H, ArOH exchange with D$_2$O), 7.05 (d, 4H, J = 7.5, calix-ArH), 6.90–6.84 (m, 8H, calix-ArH and ArH), 6.72 (t, 2H, J = 7.5, calix-ArH), 6.66 (t, 2H, J = 7.4, calix-ArH), 4.40 (d, 4H, J = 13.0, ArCH$_2$Ar), 4.17 (t, 4H, J = 4.7, CH$_2$), 4.04–3.94 (m, 8H, CH$_2$), 3.89–3.79 (m, 12H, CH$_2$), 3.34 (d, 4H, J = 13.0, ArCH$_2$Ar)	

10[j]	29	188-189	8.19 (d, 4H, *J* = 9.2, ArH), 7.12 (d, 4H, *J* = 7.5, calix-ArH), 6.99 (d, 4H, *J* = 7.5, calix-ArH), 6.96 (d, 4H, *J* = 9.2, ArH), 6.72 (t, 2H, *J* = 7.5, calix-ArH), 6.49 (t, 2H, *J* = 7.5, calix-ArH), 4.17 (t, 4H, *J* = 4.6, CH_2), 3.97 (t, 4H, *J* = 4.6, CH_2), 3.85 (t, 4H, *J* = 5.2, CH_2), 3.73–3.57 (m, 20H, $ArCH_2Ar$ and CH_2), 3.43 (s, 6H, OCH_3)
11[k]	30	146–147	8.18 (d, 4H, *J* = 9.2, ArH), 7.08 (d, 4H, *J* = 7.5, calix-ArH), 7.06 (d, 4H, *J* = 7.5, calix-ArH), 6.98 (d, 4H, *J* = 9.2, ArH), 6.64 (t, 2H, *J* = 7.5, calix-ArH), 6.58 (m, 2H, *J* = 7.4, calix-ArH), 4.28 (t, 4H, *J* = 4.7, CH_2), 3.94–3.83 (m, 12H, CH_2), 3.78–3.63 (m, 16H, CH_2), 3.59 (s, 8H, $ArCH_2Ar$), 3.42 (s, 6H, OCH_3)
12[l]	45	oil	8.16 (d, 4H, *J* = 9.2, ArH), 7.06 (d, 4H, *J* = 7.5, calix-ArH), 7.05 (d, 4H, *J* = 7.5, calix-ArH), 6.92 (d, 4H, *J* = 9.2, ArH), 6.66–6.56 (m, 4H, calix-ArH), 4.21 (t, 4H, *J* = 4.7, CH_2), 3.94–3.61 (m, 36H, CH_2), 3.57 (s, 8H, $ArCH_2Ar$), 3.42 (s, 6H, OCH_3)

---

[a] Anal. calcd. for $C_8H_9NO_4$: C, 52.46; H, 4.95; found C, 52.32; H, 4.96

[b] Anal. calcd. for $C_{10}H_{13}NO_5$: C, 52.86; H, 5.77; found C, 52.72; H, 5.45

[c] Anal. calcd. for $C_{12}H_{17}NO_6.C_6H_{13}O_3C1.$: C, 50.76; H, 7.10; found C, 50.50; H, 6.87

[d] Anal. calcd. for $C_{15}H_{15}NO_6S$: C, 53.41; H, 4.48; found C, 53.44; H, 5.55

[e] Anal. calcd. for $C_{17}H_{19}NO_7S$: C, 53.54; H, 5.02; found C, 53.73; H, 5.03

[f] Anal. calcd. for $C_{19}H_{23}NO_8S$: C, 53.64; H, 5.45; found C, 53.36; H, 5.57

[g] Anal. calcd. for $C_{44}H_{38}N_2O_{10}$: C, 70.02; H, 5.07; found C, 69.83; H, 5.07

[h] Anal. calcd. for $C_{48}H_{46}N_2O_{12}$: C, 68.40; H, 5.50; found C, 68.41; H, 5.77

[i] Anal. calcd. for $C_{52}H_{54}N_2O_{14}$: C, 67.09, H, 5.85; found C, 67.25; H, 5.59

[j] Anal. calcd. for $C_{54}H_{58}N_2O_{14}$: C, 67.61, H, 6.10; found C, 67.59; H, 6.15

[k] Anal. calcd. for $C_{58}H_{66}N_2O_{16}.CH_3OH$: C, 65.66, H, 6.54; found C, 65.78; H, 6.42

[l] Anal. calcd. for $C_{62}H_{74}N_2O_{18}.H_2O$: C, 64.57, H, 6.66; found C, 64.39; H, 6.63

Table I. Continued.

Compound	Yield (%)	m.p. (°C)	^{1}H NMR (200 MHz)($CDCl_3$/TMS) δ, J(Hz)	FAB-MS m/z (%)
13^m	59	184–185 (partial cone)	8.20 (d, 2H, J = 9.2, ArH), 8.09 (d, 4H, J = 9.2, ArH), 7.99 (d, 2H, J = 9.2, ArH), 7.40 (d, 2H, J = 7.5, calix-ArH), 7.15 (d, 2H, J = 7.2, calix-ArH), 7.04–6.40 (m, 16H, calix-ArH and ArH), 4.34 (t, 2H, J = 4.6, CH_2), 4.20–3.86 (m, 16H, $ArCH_2Ar$ and CH_2), 3.80 (s, 4H, $ArCH_2Ar$), 3.14 (d, 2H, J = 13.3, $ArCH_2Ar$)	
14^n	47	205–206	Insoluble	
15^o	45	oil	8.15 (d, 8H, J = 9.2, ArH), 7.04 (d, 8H, J = 7.5, calix-ArH), 6.91 (d, 8H, J = 9.2, ArH), 6.59 (t, 4H, J = 7.5, calix-ArH), 4.20 (t, 8H, J = 4.7, CH_2), 3.91 (t, 8H, J = 4.7, CH_2), 3.84–3.72 (m, 32H, CH_2), 3.54 (s, 8H, $ArCH_2Ar$)	1459.5 ($MH^+ + Na^+$, 23)
16^p	87	200–201	7.98 (s, 2H, ArOH exchange with D_2O), 7.05 (d, 4H, J = 7.4, calix-ArH), 6.93 (d, 4H, J = 7.3), calix-ArH), 6.82 (d, 4H, J = 8.8, ArH), 6.75–6.60 (m, 8H, calix-ArH and ArH), 4.44 (d, 4H, J = 13.0, $ArCH_2Ar$), 4.30–4.24 (m, 8H, CH_2), 3.42 (s, 4H, $ArNH_2$ exchange with D_2O), 3.36 (d, 4H, J = 13.0, $ArCH_2Ar$)	
17^q	87	oil	7.84 (s, 2H, ArOH exchange with D_2O), 7.07 (d, 4H, J = 7.5, calix-ArH), 6.89 (d, 4H, J = 7.4, calix-ArH), 6.76–6.55 (m, 12H, calix-ArH and ArH), 4.43 (d, 4H, J = 13.0, $ArCH_2Ar$), 4.21–3.97 (m, 18H, CH_2), 3.38 (s, 4H, $ArNH_2$ exchange with D_2O), 3.36 (d, 8H, J = 13.0, $ArCH_2Ar$)	
18^r	97	oil	7.78 (s.broad, 2H, ArOH exchange with D_2O), 7.05 (d, 4H, J = 7.5, calix-ArH), 6.87 (d, 4H, J = 7.2, calix-ArH), 6.74–6.56 (m, 12H, calix-ArH and ArH), 4.41 (d, 4H, J = 13.0, $ArCH_2Ar$), 4.17 (t, 4H, J = 4.7, CH_2), 4.00–3.74 (m, 20H, CH_2), 3.36 (s, 4H, $ArNH_2$ exchange with D_2O), 3.34 (d, 4H, J = 13.0, $ArCH_2Ar$)	
19^s	95	161–162	7.09 (d, 4H, J = 7.5, calix-ArH), 7.07 (d, 4H, J = 7.5, calix-ArH), 6.82 (d, 4H, J = 8.7, ArH), 6.70–6.63 (m, 6H, calix-ArH and ArH), 6.57 (t, 2H, J = 7.5, calix-ArH), 4.03 (t, 4H, J = 4.5, CH_2), 3.96 (t, 4H, J = 4.5, CH_2), 3.86 (t, 4H, J = 4.5, CH_2), 3.73–3.63 (m, 20H, $ArCH_2Ar$ and CH_2), 3.43 (s.broad, 10H, OCH_3 and $ArNH_2$ exchange with D_2O)	

20[t]	96	oil	7.08 (d, 8H, *J* = 7.5, calix-ArH), 6.79 (d, 4H, *J* = 8.8, ArH), 6.67–6.60 (m, 8H, calix-ArH and ArH), 4.11 (t, 4H, *J* = 4.7, CH_2), 6.84 (t, 12H, *J* = 5.0, CH_2), 3.73–3.61 (m, 24H, $ArCH_2Ar$ and CH_2), 3.42 (s, 6H, OCH_3), 1.66 (s.broad, 4H, $ArNH_2$ exchange with D_2O)
21[u]	97	oil	7.05 (d, 8H, *J* = 7.3, calix-ArH), 6.76–6.59 (m, 12H, calix-ArH and ArH), 3.86–3.65 (m, 36H, CH_2), 3.58 (s, 8H, $ArCH_2Ar$), 3.42 (s, 6H, OCH_3), 1.63 (s.broad, 4H, $ArNH_2$ exchange with D_2O)
22[v]	72	147–149	7.08 (d, 8H, *J* = 7.5, calix-ArH), 6.78 (d, 8H, *J* = 8.8, ArH), 6.69–6.60 (m, 12H, calix-ArH and ArH), 4.11 (t, 8H, *J* = 4.7, CH_2), 3.83 (t, 16H, *J* = 4.7 CH_2), 3.67 (t, 8H, *J* = 4.7, CH_2), 3.63 (s, 8H, $ArCH_2Ar$), 3.42 (s.broad, 8H, $ArNH_2$ exchange with D_2O)
23[w]	74	oil	7.06 (d, 8H, *J* = 7.5, calix-ArH), 6.76–6.58 (m, 20H, calix-ArH and ArH), 4.06 (t, 8H, *J* = 4.7, CH_2), 3.86–3.66 (m, 40H, CH_2), 3.57 (s, 8H, $ArCH_2Ar$), 3.48 (s.broad, 8H, $ArNH_2$ exchange with D_2O)

---

[m] Anal. calcd. for $C_{60}H_{52}N_4O_{16}.CH_3OH$: C, 65.58, H, 5.05; found C, 65.66; H, 5.01

[n] Anal. calcd. for $C_{68}H_{68}N_4O_{20}$: C, 64.75; H, 5.43; found C, 64.57; H, 5.33

[o] Anal. calcd. for $C_{76}H_{84}N_4O_{24}$: C, 63.49; H, 5.89; found C, 63.63; H, 5.74

[p] Anal. calcd. for $C_{44}H_{42}N_2O_62H_2O$: C, 72.31; H, 6.34; found C, 72.28; H, 6.19

[q] Anal. calcd. for $C_{48}H_{50}N_2O_8$: C, 73.57; H, 6.44; found C, 73.80; H, 6.20

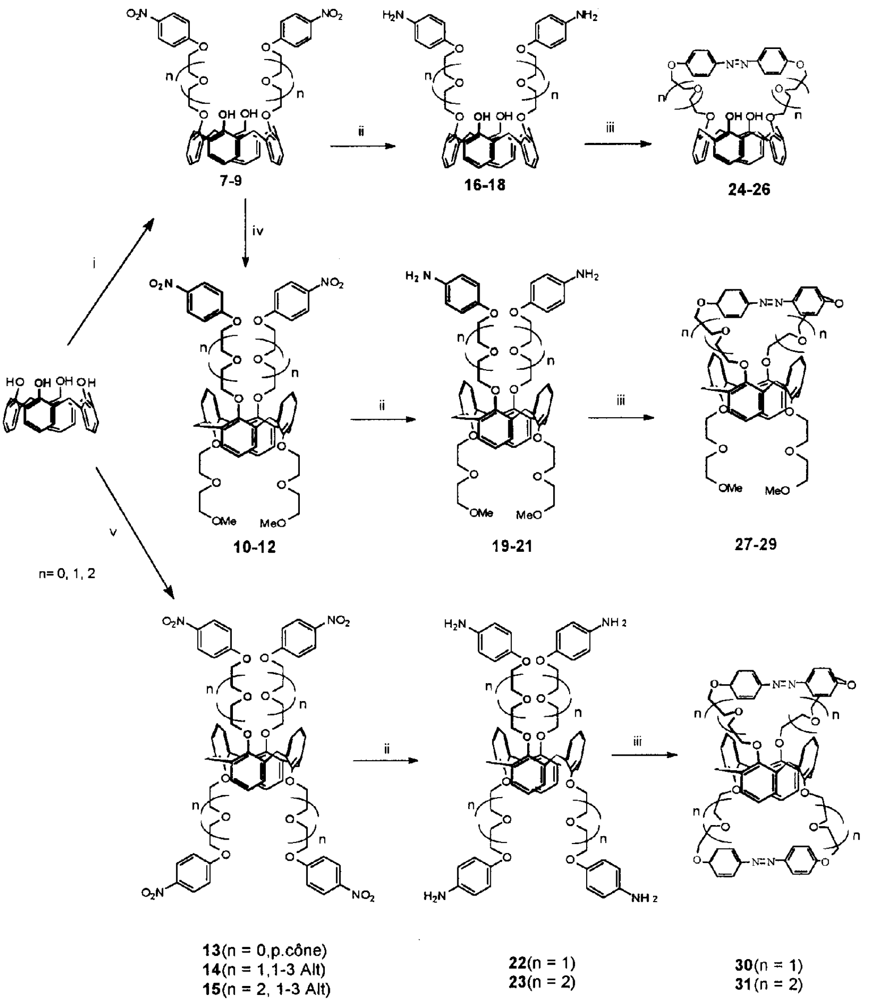
[r] Anal. calcd. for $C_{52}H_{58}N_2O_{10}.2H_2O$: C, 68.86; H, 6.89; found C, 68.59; H, 6.39

[t] Anal. calcd. for $C_{58}H_{70}N_2O_{12}$: C, 70.57; H, 7.15; found C, 70.65; H, 7.26

[u] Anal. calcd. for $C_{62}H_{78}N_2O_{14}.H_2O$: C, 67.01; H, 7.44; found C, 67.08; H, 7.13

[v] Anal. calcd. for $C_{68}H_{76}N_4O_{12}.H_2O$: C, 70.45; H, 6.78; found C, 70.83; H, 6.83

[w] Anal. calcd. for $C_{76}H_{92}N_4O_{16}.H_2O$: C, 68.35; H, 7.09; found C, 68.31; H, 7.08



i - K_2CO_3.2eq of **4-6**.CH_3CN. ii- $NH_2NH_2.H_2O$ .Graphite. EtOH abs .
iii- MnO_2.Benzène. iv-K_2CO_3.TsO$(CH_2CH_2O)_2$Me.CH_3CN.
v-K_2CO_3.5eq of **4-6**.CH_3CN.

Scheme 3. Synthesis of azocalixcrowns **24**–**31**.

= 0, 1, 2 respectively). The yields ranged from 71 to 87%. Then, nitrophenyl glycols **1**–**3** were treated with *p*-toluene-sulfonyl chloride in the presence of NEt_3 in dichloromethane at 0 °C for 1 h and at room temperature for 24 h. After neutralization with HCl, the corresponding nitrophenyl glycol tosylates **4**–**6** were obtained in 60–83% yields. Physical and spectroscopic data of **1**–**6** are given in Table I.

3.3. SELECTIVE 1,3-O-DIALKYLATIONS OF CALIX[4]ARENE [8]

According to Scheme 3, calix[4]arene was treated with two equivs of nitrophenyl glycol tosylates **4**–**6** in the presence of K_2CO_3 in refluxing acetonitrile to yield, after neutralization with HCl and chromatography on a silica column, 1,3-O-dialkylated calix[4]arenes **7**–**9** as white solids in yields ranging from 48 to 62%. 1,3-O-Dialkylation and cone conformation were deduced from ^{1}H-NMR spectra of **7**–**9** presenting two distinct triplets for the aromatic *para* protons of the phenyl ring and a characteristic AB system corresponding to the ArCH_2Ar protons in the calix macroring as usually deduced for calixes [2, 3]. Yields, physical and spectroscopic data of **7**–**9** are given in Table I.

Reaction at room temperature of **7**–**9** with the tosylate of 2-(2-methoxyethoxy)ethanol in the presence of K_2CO_3 in acetonitrile for 24 h afforded after chromatography on a silica column 2 + 2′ tetraalkylated calixes **10**–**12**. ^{1}H-NMR spectra of **10**–**12** revealed that dialkylation occured with a change from the cone conformation of **7**–**9** into 1,3-alternate in **10**–**12** due to the presence of one singlet (see Table I) for the ArCH_2Ar protons in the macrorings **10**–**12** as usually deduced for calixes [2, 3]. Yields, physical and spectroscopic data of **10**–**12** are given in Table I.

The alkylation of calix[4]arene with five equivs of **4**–**6** under similar conditions lead to the formation of tetraalkylated calix[4]arenes **13** in a partial cone conformation [8] and **14** and **15** in the 1,3-alternate conformation as deduced from their ^{1}H-NMR spectra. Yields, physical and spectroscopic data of **13-15** are given in Table I.

3.4. REDUCTIONS OF THE NITRO GROUPS

Reduction of the nitro groups into amino functions was conducted according to literature [9]. Derivatives **7**–**15** (except **13**) were transformed in very good yields (74–97%) into the corresponding amino compounds **16**–**23** by reduction with $NH_2NH_2 \cdot H_2O$ in the presence of graphite in refluxing absolute ethanol. It was noticed that the reaction did not alter the conformation of the calixes. From ^{1}H-NMR it was observed that **16**–**18** adopted the cone conformation whereas **19**–**23** maintained the 1,3-alternate one. Amino functions were evidenced by proton-exchange with D_2O. Yields, physical and spectroscopic data of **16**–**23** are given in Table I.

3.5. OXIDATIVE AZO-COUPLING

The coupling of diamino functions into *azo* benzene chromophores was performed by treating **16**–**23** with activated MnO_2 in dry benzene according to the described procedure [10]. *Monoazo* calixes **24**–**29** were purified by chromatography on a silica column. The orange or red powders obtained were analysed by TLC (Merck Kieselgel 60F254). We observed two orange spots corresponding to the *trans* and

Table II. TLC of **24–31**.

Calixarene	Solvent v/v $CH_2Cl_2 : CH_3COCH_3$	R_f^*
24	97.3	0.62 *t* 0.50 *c*
25	95 : 5	0.73 *t* 0.45 *c*
26	90 : 10	0.58 *t* 0.32 *c*
27	95 : 5	0.76 *t* 0.50 *c*
28	97 : 3	0.54 *t* 0.36 *c*
29	90 : 10	0.70 *t* 0.53 *c*
30	95 : 5	0.58 *tt* 0.47 *tc* 0.32 *cc*
31	90 : 10	0.48 *tt* 0.35 *tc* 0.30 *cc*

* *t = trans, c = cis.*

cis isomers. The R_f values and eluents are given in Table II. By watching the intensity of each spot we concluded the *cis* isomer to be mainly formed for **24** and **27** and the *trans* isomer for **25**, **26**, **28** and **29**. This was also in agreement with the ^{1}H-NMR spectra of **24–29** (see Figures 1 and 2). *Trans* and *cis* forms were interpreted from ^{1}H-NMR data as in reference [11] where the authors noticed a *ca.* 0.7 ppm shift at higher field of the AA′–BB′ spin system of the *cis* form compared to the *trans* in a series of dithiadiaza[n.2]paracyclophane-enes.

Orange powders of *diazo* calix[4]crowns **30** and **31** showed three orange spots corresponding to the *trans-trans, cis-cis* and *trans-cis* isomers (Table II). ^{1}H-NMR (Figure 3) and TLC were in agreement to indicate *trans-trans* isomers were formed probably because the *azo benzene* units are introduced in too large glycolic chains to constrain to the *cis* isomer.

3.6. UV-VIS STUDIES

Figure 4 shows the typical UV-Vis spectra of *cis*-**24** and *trans*-**26** in 1,2-dichlorobenzene at 10^{-4} mol L^{-1}. Assuming that our compounds are similar to the photoresponsive *azo*-crown ethers reported by Shinkai *et al.* [12], we evaluated the *trans/cis* composition and determined molar absorption coefficients of **24–29**

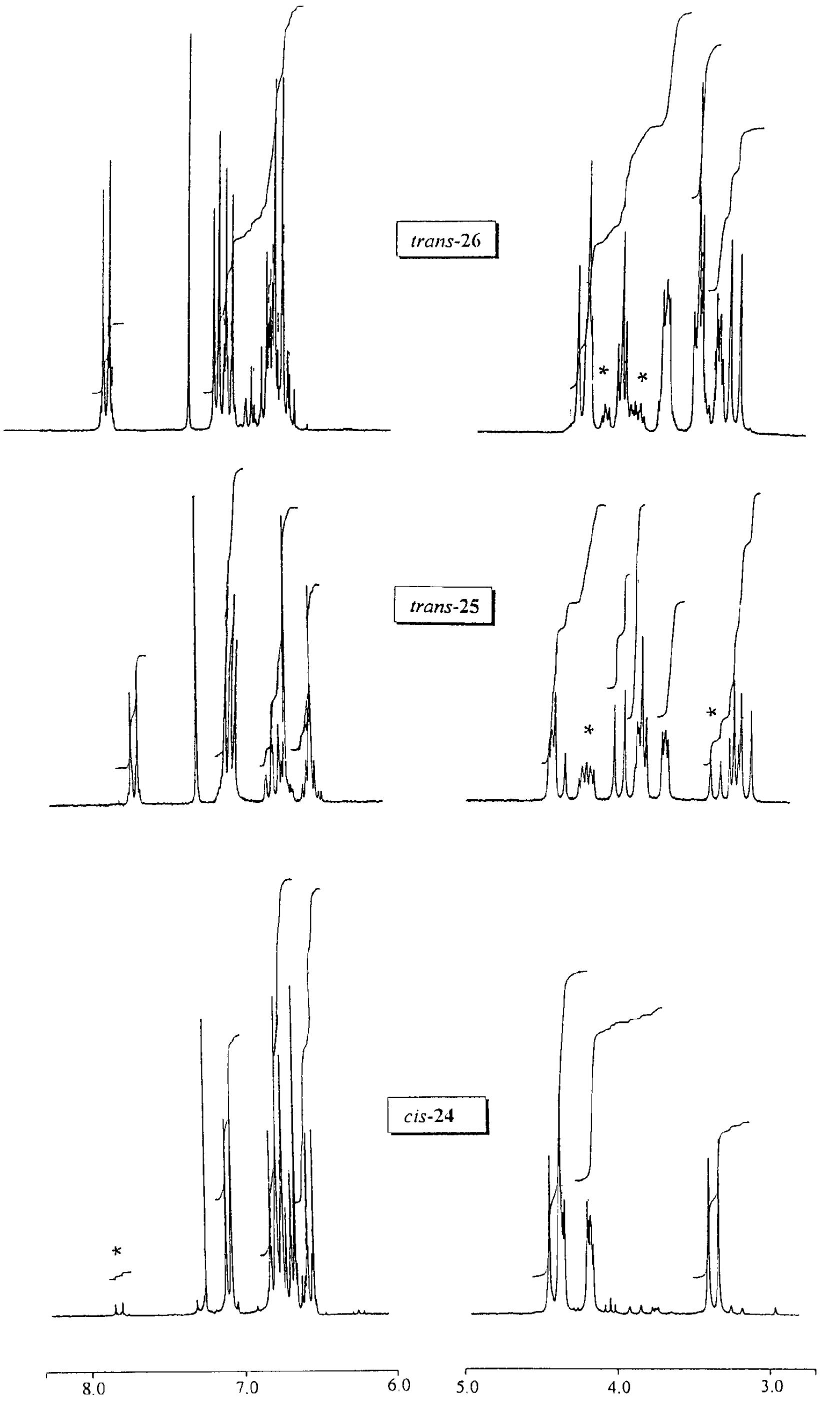


Figure 1. ^{1}H-NMR (200 MHz) of azocalixcrowns *cis*-**24**, *trans*-**25** and *trans*-**26** in $CDCl_3$. The star (*) denotes the other isomer.

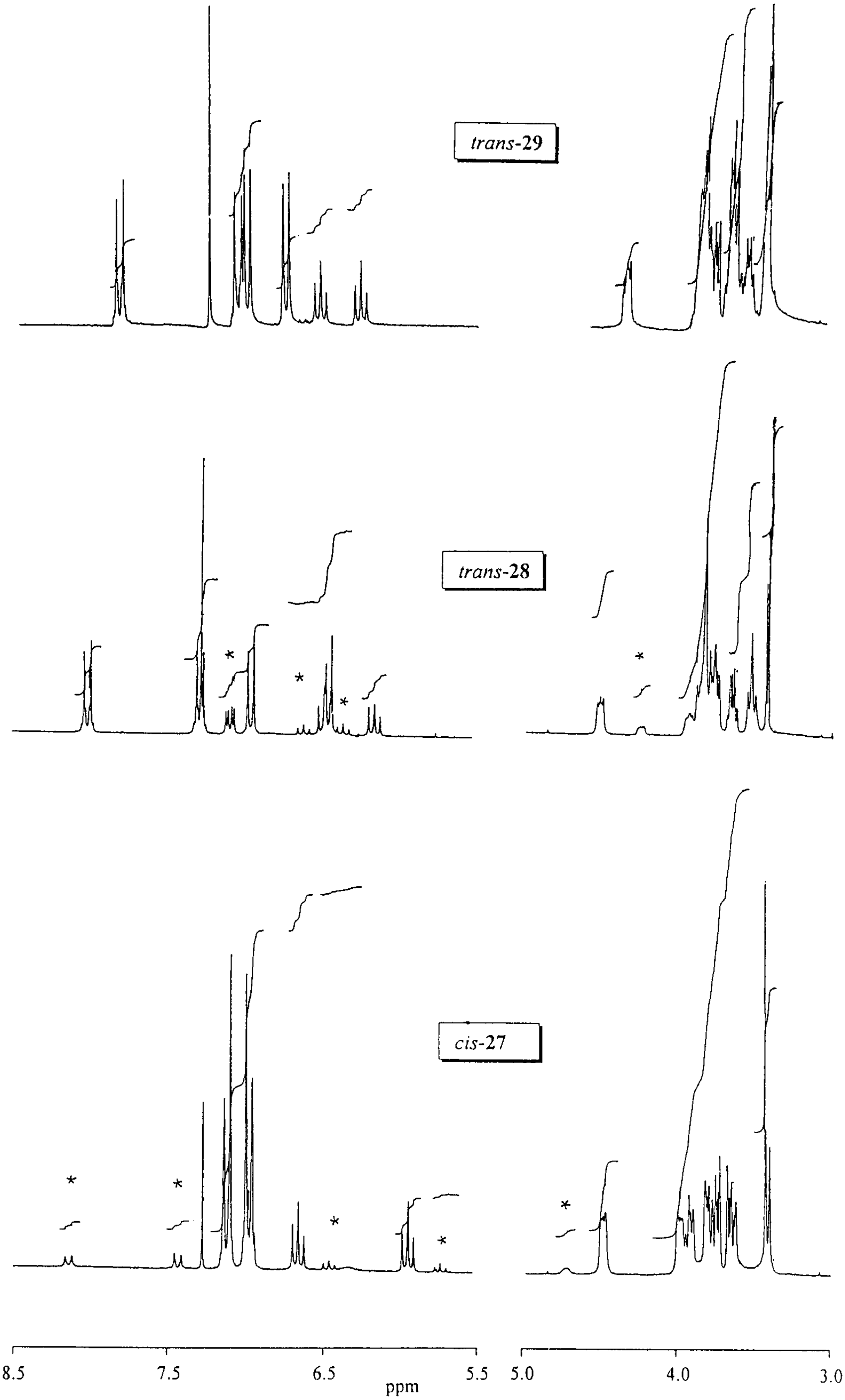


Figure 2. ^{1}H-NMR (200 MHz) of azocalixcrowns *cis*-**27**, *trans*-**28** and *trans*-**29** in $CDCl_3$. The star (*) denotes the other isomer.

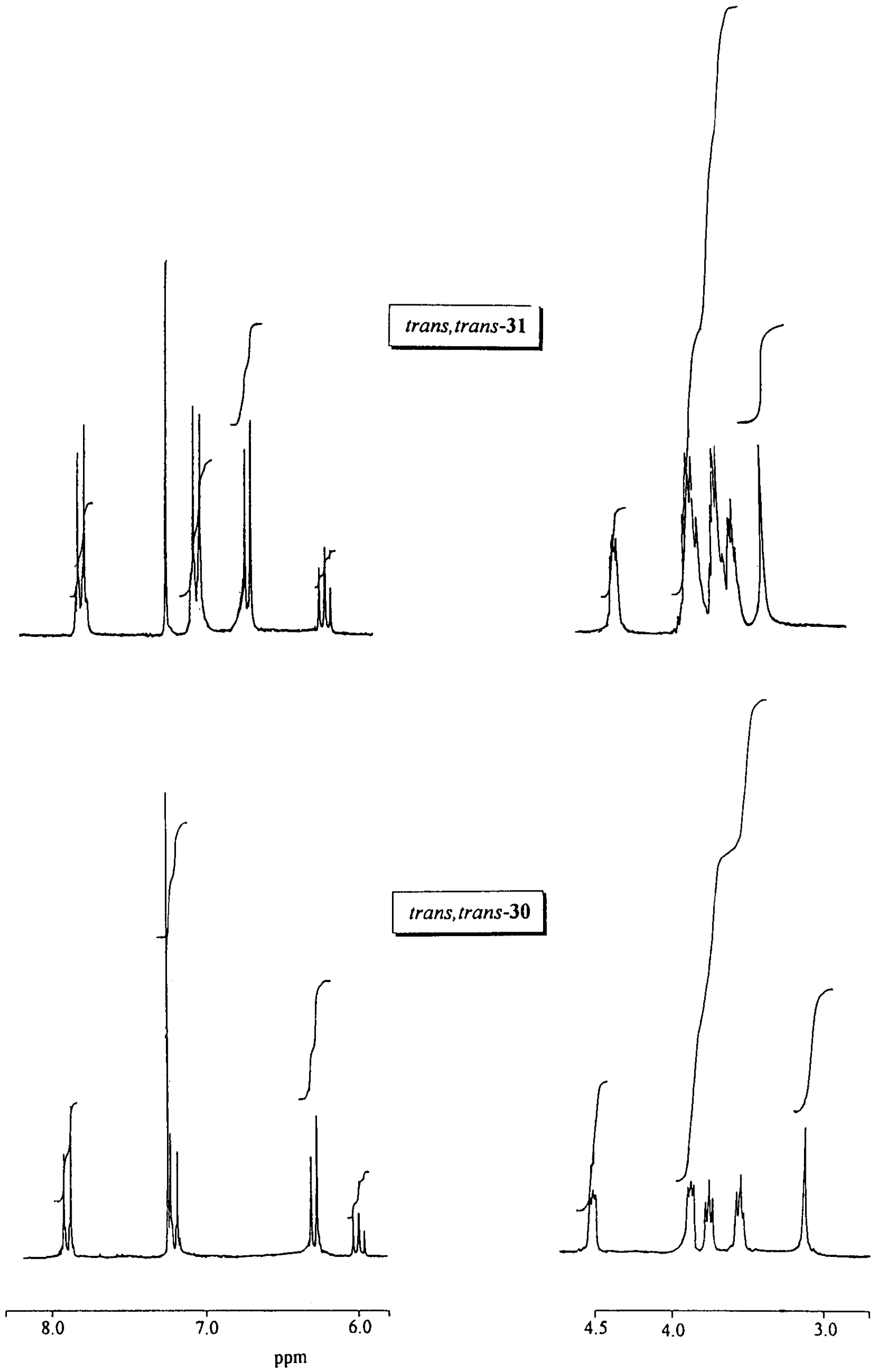


Figure 3. ^{1}H-NMR (200 MHz) of azocalixcrowns *trans, trans*-**30** and *trans, trans*-**31** in $CDCl_3$.

Table III. Physical and spectroscopic data of **24**–**31**.

Compound	Yield (%)	m.p. (°C)	^{1}H NMR (200 MHz) δ, J (Hz)	FAB-MS m/z (%)
24[a]	10	284–285	7.10 (d, 4H, J = 7.5, calix-ArH), 6.83–6.53 (m, 18H, calix-ArH, ArH and ArOH exchange with D_2O), 4.44 (d, 4H, J = 13.3, $ArCH_2Ar$), 4.37 (t, 4H, J = 4.7, CH_2), 4.20 (t, 4H, J = 4.7, CH_2), 3.38 (d, 4H, J = 13.3, $ArCH_2Ar$)	691.2 (MH^+, 100)
25[b]	9	233–234	7.68 (d, 4H, J = 8.8, ArH), 7.06 (d, 4H, J = 8.4, ArH), 7.03 (d, 8H, J = 7.2, calix-ArH), 6.92–6.47 (m, 6H, calix-ArH and ArOH exchange with D_2O), 4.44–4.40 (m, 4H, CH_2), 3.98 (d, 4H, J = 13.6, $ArCH_2Ar$), 3.83 (t, 8H, J = 5.9, CH_2), 3.21 (t, 4H, J = 5.9, CH_2), 3.13 (d, 4H, J = 13.6, $ArCH_2Ar$)	779.4 (MH^+, 70)
26[c]	16	106–107	7.82 (d, 4H, J = 8.9, ArH), 7.07 (d, 4H, J = 7.5, calix-ArH), 6.98 (d, 4H, J = 8.9, ArH), 6.77–6.55 (in, 10H, calix-ArH and ArOH exchange with D_2O), 4.35–4.26 (in, 8H, $ArCH_2Ar$ and CH_2), 4.05 (t, 4H, J = 5.5, CH_2), 3.81–3.74 (m, 4H, CH_2), 3.60–3.53 (m, 8H, CH_2), 3.44–3.34 (m, 4H, CH_2), 3.30 (d, 4H, J = 13.4, $ArCH_2Ar$)	867.4 (MH^+, 100)
27[d]	55	69–70	7.10 (d, 8H, J = 7.9, calix-ArH), 6.96 (d, 8H, J = 8.0, ArH), 6.64 (t, 2H, J = 7.5, calix-ArH), 5.93 (t, 2H, J = 7.5, calix-ArH), 4.50–4.47 (m, 4H, CH_2), 4.01–3.47 (m, 28H, $ArCH_2Ar$ and CH_2), 3.43 (s, 6H, OCH_3)	895.2 (MH^+, 100)
28[e]	29	132–133	8.01 (d, 4H, J = 9.0, ArH), 7.27 (d, 4H, J = 9.0, ArH), 6.93 (d, 4H, J = 7.5, calix-ArH), 6.50–6.42 (m, 6H, calix-ArH), 6.14 (t, 2H, J = 7.5, calix-ArH), 4.49 (t, 4H, J = 3.9, CH_2), 3.89–3.74 (m, 28H, $ArCH_2Ar$ and CH_2), 3.67–3.62 (m, 4H, CH_2), 3.52 (t, 4H, J = 5.3, CH_2), 3.41 (s, 6H, OCH_3)	983.2 (MH^+, 100)
29[f]	15	oil	7.85 (d, 4H, J = 8.9, ArH), 7.08 (d, 4H, J = 8.9, ArH), 7.02 (d, 4H, J = 7.6, calix-ArH), 6.74 (d, 4H, J = 7.5, calix-ArH), 6.54 (t, 2H, J = 7.5, calix-ArH), 6.28 (t, 2H, J = 7.5, calix-ArH), 4.35 (t, 4H, J = 4.3, CH_2), 3.95–3.45 (m, 44H, $ArCH_2Ar$ and CH_2), 3.43 (s, 6H, OCH_3)	1071.5 (MH^+, 100)
30[g]	6	297–298	7.92 (d, 8H, J = 8.9, ArH), 7.22 (d, 8H, J = 8.9, ArH), 6.30 (d, 8H, J = 7.5, calix-ArH), 6.01 (t, 4H, J = 7.5, calix-ArH), 4.53–4.48 (m, 8H, CH_2), 3.88–3.84 (in, 8H, CH_2), 3.74 (t, 8H, J = 5.0, CH_2), 3.53 (t, 8H, J = 5.0, CH_2), 3.10 (s, 8H, $ArCH_2Ar$)	1133.5 (MH^+, 100)
31[h]	2	oil	7.82 (d, 8H, J = 8.9, ArH), 7.05 (d, 8H, J = 8.9, ArH), 6.72 (d, 8H, J = 7.5, calix-ArH), 6.22 (t, 4H, J = 7.5, calix-ArH), 4.36–4.24 (m, 8H, CH_2), 3.88–3.54 (m, 40H, CH_2), 3.36 (s, 8H, $ArCH_2Ar$)	1309.4 (MH^+, 65)

[a] Anal. calcd. for $C_{44}H_{38}N_2O_6$: C, 76.49; H, 5.55; found C, 76.35; H, 5.57

[b] Anal. calcd. for $C_{48}H_{46}N_2O_8.2H_2O$: C, 70.75; H, 6.18; found C, 70.36; H, 6.16

[c] Anal. calcd. for $C_{52}H_{54}N_2O_{10}$: C, 72.02; H, 6.28; found C, 72.16; H, 6.31

[d] Anal. calcd. for $C_{54}H_{58}N_2O_{10}.CH_3OH$: C, 71.25; H, 6.74; found C, 71.42; H, 6.36

[e] Anal. calcd. for $C_{58}H_{66}N_2O_{12}$: C, 70.84; H, 6.77; found C, 71.07; H, 6.83

[f] Anal. calcd. for $C_{62}H_{74}N_2O_{14}$: C, 69.50; H, 6.97; found C, 69.31; H, 7.02

[g] Anal. calcd. for $C_{68}H_{68}N_4O_{12}.2H_2O$: C, 69.85; H, 6.21; found C, 69.34; H, 6.44

[h] Anal. calcd. for $C_{76}H_{84}N_4O_{16}$: C, 69.69; H, 6.47; found C, 69.50; H, 6.58

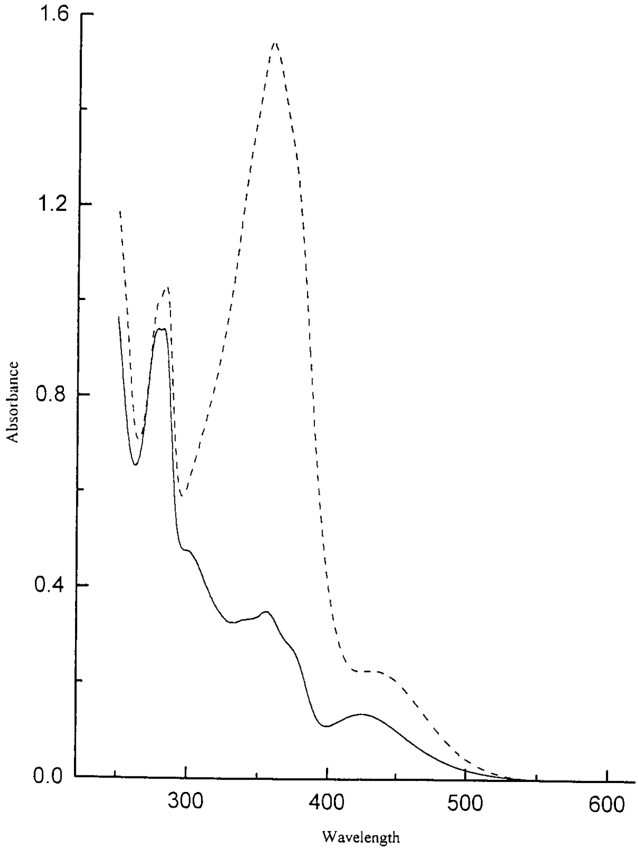


Figure 4. UV-Vis absorption spectra of *cis*-**24** (——) and *trans*-**26** (– – – –) in 1,2-dichlorobenzene (1×10^{-4} mol l^{-1}).

in the same manner. Table IV reports the molar absorption coefficients of **24**–**29** at 360 nm [13]. The data were approximately in agreement with the ^{1}H-NMR results.

All these data were rationalized by assuming the *cis* isomer to be formed for the shortest glycolic chain, the *trans* form for the longest one. We note that the ratio between *trans* and *cis* isomers was not affected by the conformation of the calix unit. This is probably due to the fact that both conformations (cone and 1,3-alternate) are flexible in the same manner.

3.7. PRELIMINARY COMPLEXATION STUDY

A preliminary complexation study was realised by means of ^{1}H-NMR and FAB(+) mass spectrometry. After 24 hours reaction between solid cesium picrate and a chloroform solution of **28**, the ratio of metal to ligand in solution as estimated by integration of the picrate proton resonance versus those of glycolic chains was 1 : 3. The formation of a complex was evidenced by FAB(+)-MS data presenting

Table IV. Molar absorption coefficients of **24-29** at 360 nm in 1,2-dichlorobenzene.

Compound	C_T (mol L^{-1})	$A_{\max}$	% *trans*	% *cis*	λ_{trans} (nm) ε_{trans} (L mol^{-1} cm^{-1})	λ_{cis} (nm) ε_{cis} (L mol^{-1} cm^{-1})
24	10^{-4}	0.35	0	100	355	423
					25974	3510
25	10^{-4}	1.82	95	5	362	434
					19174	2591
26	10^{-4}	2.10	98	2	359	433
					21463	2900
27	10^{-4}	0.24	0	100	363	425
					19382	2421
28	10^{-4}	2.03	100	0	360	421
					20373	2553
29	10^{-4}	2.24	100	0	361	434
					22429	30031

M^+ = 983.2 (53%) for the free ligand and M^+ + Cs^+ = 1115.1(30%) for the 1 : 1 complex.

4. Conclusion

The present paper reports on the synthesis, characterisation and UV-Vis studies of a series of azocalixcrown compounds. We have shown that the *trans*/*cis* composition of the calixcrowns produced is dependent on the length of the glycolic chain capping the calix[4]arene unit. We have determined the molar absorption coefficients which are going to be used for further studies in photocontrolled complexation.

Further studies of the complexation properties of these new ligands are currently under investigation and will be presented in full in due course. Our objectives include: (a) photocontrolled transport of metal cations through synthetic membranes; and (b) preparing calixarene ligands in the 1,3-alternate conformation and containing both crown ether and azobezene crown ether to provide allosteric systems.

References

1. For comprehensive reviews see M. Tagaki and K. Ueno: *Top. Curr. Chem.* **121**, 39 (1984); S. Shinkai and O. Manabe: *Top. Curr. Chem.* **121**, 67 (1984); M. Okahara and Y. Nakatsuji: *Top. Curr. Chem.* **128**, 37 (1985); and also N. Tamaoki, K. Koseki and T. Yamaoka: *Tetrahedron Lett.* 3309 (1990); and also N. Tamaoki, K. Koseki and T. Yamaoka: *Angew. Chem. Int. Ed. Engl.* **29**, 105 (1990); S. Shinkai, H. Nakayama and O. Manabe: *J. Chem. Soc. Perkin Trans. 2* 1905 (1990).
2. For comprehensive reviews and books see C.D. Gutsche: *Acc. Chem. Res.* **97**, 332 (1983); C.D. Gutsche: *Calixarenes*, Monographs in Supramolecular Chemistry, J.F. Stoddart (Ed.), The Royal Society of Chemistry, Cambridge, U.K. (1989); Vol. 1; J. Vicens and V. Böhmer (Eds.): *;Calixarenes: A Versatile Class of Macrocyclic Compounds*, Kluwer Academic Publishers, Dor-

drecht, The Netherlands (1991); J. Vicens, Z. Asfari and J.M. Harrowfield (Eds.); *Calixarenes 50th Anniversary: Commemorative Issue*, Kluwer Academic Publishers, Dordrecht, The Netherlands (1994); V. Böhmer: *Angew. Chem. Int. Ed. Engl.* **34**, 713 (1995); P. Lhotak and S. Shinkai: *J. Synth. Org. Chem., Jpn.* **53**, 963 (1995).

3. For comprehensive reviews see R. Ungaro and A. Pochini: in *Frontiers in Supramolecular Chemistry and Photochemistry*, H.J. Schneider and H. Dürr (Eds.), VCH, Weinheim, pp. 57–81 (1991); R. Ungaro, A. Arduini, A. Casnati, O. Ori, A. Pochini and F. Ugozzoli: in *Computational Approaches in Supramolecular Chemistry*, G. Wipff (Ed.), Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 277–300 (1994); Z. Asfari, S. Wenger and J. Vicens: *Pure Appl. Chem.* **67**, 1037 (1995); Z. Asfari, S. Wenger and J. Vicens: *J. Incl. Phenom.* **19**, 137 (1994); Z. Asfari, M. Nierlich, P. Thuéry, V. Lamare, J.F. Dozol, M. Leroy and J. Vicens: *Anal. Quim.* **92**, 260 (1996).
4. Several examples have been reported of chromogenic calixarenes based on azo arene units: S. Shinkai, K. Araki, J. Shibata, D. Tsugawa, and O. Manabe: *J. Chem. Soc. Perkin Trans. 1* 3333 (1990); N. Ehlinger, S. Lecocq, R. Perrin, and M. Perrin: *Supramol. Chem.* **2**, 77 (1993); M.-l. Yeh, Fa-s. Tang, S.-L. Chen, W.-C. Liu, and L.-G. Lin: *J. Org. Chem.* **59**, 754 (1994); Y. Kubo, S. Maeda, M. Nakamura and S. Tokita: *J. Chem. Soc., Chem. Commun.* 1725 (1994); H. Yamamoto, K. Uedo, K.R.A. Samankura Sandanayake, and S. Shinkai: *Chem. Lett.* 497 (1995); J.L.M. Gordon, V. Böhmer and W. Vogt: *Tetrahedron Lett.* 2445 (1995).
5. H.M. Chawla and K. Srinivas: *Tetrahedron Lett.* 2925 (1994); H.M. Chawla and K. Srinivas: *J. Chem. Soc., Chem. Commun.* 2593 (1994).
6. F. Hamada, T. Masuda, and Y. Kondo: *Supramol. Chem.* **5**, 129 (1995).
7. Accompanying **13** in a partial cone conformation we isolated in 24% yield a white solid **13**$'$ melting at 270–272 °C with an elemental analysis corresponding to an isomer of **13**. This isomer was probably isolated because it is insoluble in organic solvents.
8. S. Wenger, Z. Asfari, and J. Vicens: *J. Incl. Phenom.* **20**, 293 (1994).
9. B.H. Han, D.H. Shin, and, S.Y. Cho: *Tetrahedron Lett.* 6233 (1985).
10. H. Firouzabadi, and Z. Mostafavipoor: *Bull. Chem. Soc. Jpn.* **56**, 914 (1983); M.Z. Barakat, M.F.A. Wahab, and M.M. El-Sadr: *J. Chem. Soc.* 4685 (1956); O.H. Wheeler and D. Gonzalez: *Tetrahedron* **20**, 189 (1964).
11. U. Funke and H.-F. Grützmacher: *Tetrahedron* **43**, 3787 (1987).
12. S. Shinkai, T. Nakaji, T. Ogawa, K. Shigematsu, and O. Manabe: *J. Am. Chem. Soc.* **103**, 111 (1981).
13. N. Reynier: *Nouvelle Thèse*, Université de Strasbourg (May 1996).