Synthesis of New Chromogenic Calix[4]arenes Bridged at the Upper Rim through Bisazobiphenyl Linkages

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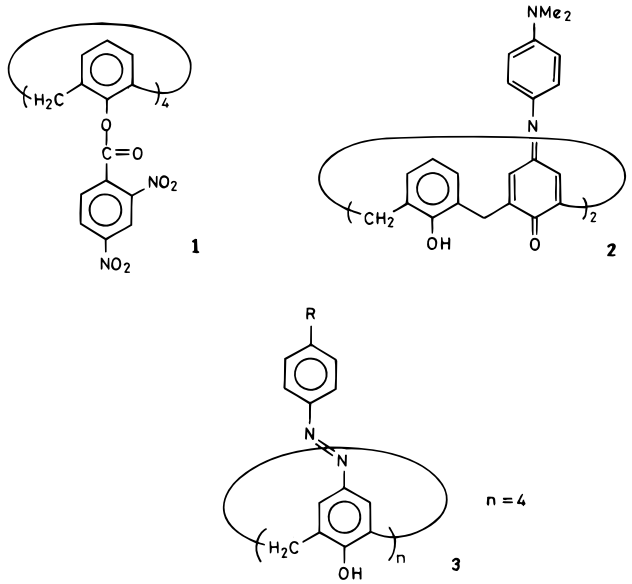
Synthesis of new chromogenic calix[4]arenes through the coupling of diazotized 4,4′-diaminobiphenyls and calix[4]arenes at the upper rim is described. Analysis of the synthesized bisazobiphenyl-bridged calixarenes by NMR and CPK models suggest that the bisazobiphenyl linkage is on the transannular phenyl groups of the calixarene moiety in the 1,3-alternate conformation.

Calix[*n*]arenes are obtained by the condensation of *p*-alkyl-substituted phenols and formaldehyde in the presence of alkali.[1] The cavity size of calix[*n*]arenes can be varied (*e.g.*, $n = 4-8$), and they possess many characteristics analogous to those of crown ethers and cyclodextrins.[2] Due to their molecular architecture, easily manipulable cavity dimensions, and application in recognition of organic molecules[3] and metal ions,[4] they have been recently named as *third-generation molecular receptors*.[5] Current studies on the synthesis of calixarene derivatives have promised the development of optical sensors,[6] ion-selective electrodes,[7] and spectrofluorometric[8] and NMR[9] assay systems. However, there is still a need for systems that can exhibit color changes as a consequence of ionic or molecular interactions, and there are only a few reports[10,11] on chromogenic calix[4]arenes in the literature. The known chromogenic calixarenes have the primary chromophores appended at the lower rim (*e.g.*, **1**) or at the upper rim (*e.g.*, **2** and **3**) and are of limited utility as the phenolic hydroxyls are protected (*e.g.*, **1**) or are obtained in low yield (*e.g.*, **2** and **3**). In this paper, we present our work on obtaining good yields of new chromogenic bisazobiphenyl bridged calix[4]arenes that have free hydroxyl groups.



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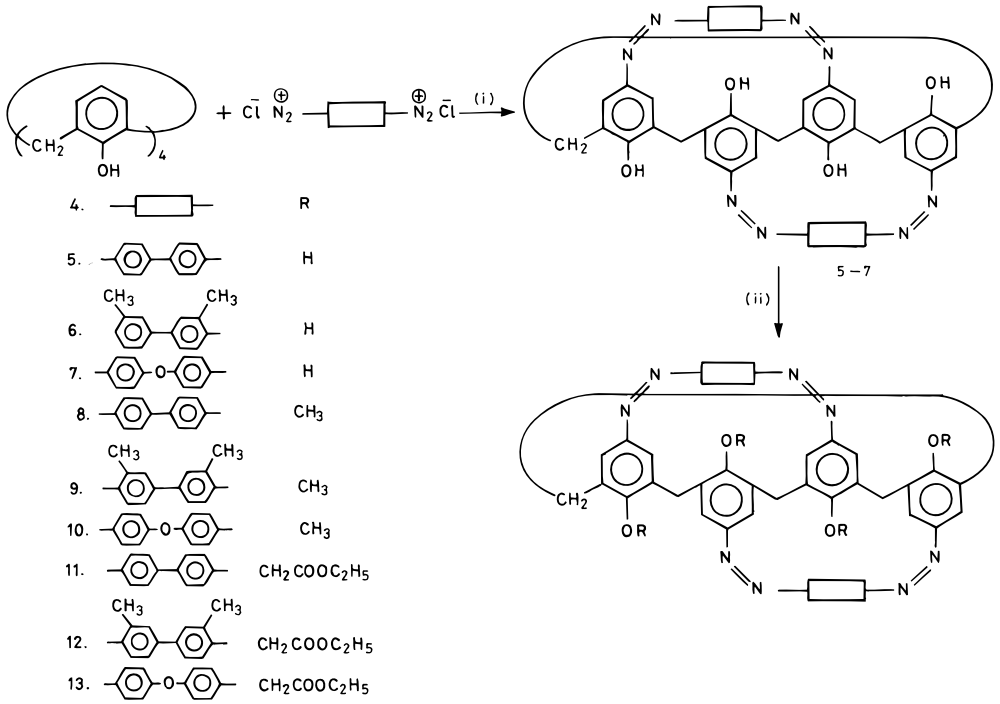
Scheme 1. Synthetic Route to Bisazobiphenylcalix[4]arenes



Results and Discussion

Synthesis of red bisazobiphenyl-bridged calix[4]arenes **5**−**7** was accomplished by coupling the calix(4)arene **4** with diazotized 4,4′-diaminobiphenyls (Scheme 1), and the products were identified by spectral characterization, elemental analysis, and molecular weight determination. For example, the ^{1}H NMR spectrum of **5** exhibited a prominent deuterable broad singlet at δ 9.55 for the hydroxyl protons, two doublets at δ 8.02 (3,3′,5,5′-biphenyl protons) and δ 7.37 (2,2′,6,6′-biphenyl protons), and two singlets at δ 7.59 (calixarene aromatic protons) and δ 3.89 (methylene bridges of calixarene moiety). The molecular weight obtained (vapor pressure osmometry) for **5** was 846 (as against the calculated value of 836 for $C_{52}H_{36}N_8O_4$), which ruled out the likelihood of possible formation of biscalix[4]arenes[12] (Figure 1). In a similar fashion, **6** and **7** were determined to have the structures as indicated on the basis of spectra, analysis, and osmometric molecular weight measurements.

The synthesized calix[4]arenes **5**−**7** could theoretically have bisazobiphenyl linkages across phenyl rings at the 1,2- or 1,3-positions of the calixarene unit (Figure 1). Among the possible intramolecular proximal (1,2) and transannular (1,3) bisazobiphenyl linkages, the synthesized compounds were identified to have the transannular (1,3) bridges on the basis of analysis by CPK models. The presence of only one singlet for the methylene protons (*e.g.*, δ 3.89 for **5**) in the ^{1}H NMR spectrum of the synthesized bisazobiphenyl-capped calix[4]arenes **5**−**7**, clearly established that the bisazobiphenyl calix[4]arenes are in the 1,3-alternate conformation.[2] Since the synthesized bisazo compounds **5**−**7** were too insoluble for meaningful ^{13}C NMR spectroscopic analysis,[13] they were converted to their methyl **(8**−**10**) and (ethoxycarbonyl)methyl **(11**−**13**) derivatives by reacting them with CH_3I/NaH and $BrCH_2COOC_2H_5$/NaH in DMF, respectively. The examination of ^{13}C NMR spectra of **8**−**13** gave the methylene carbon signal around δ 36.5 (Table 1, Figure 2), thereby confirming the 1,3-alternate conformation of the synthesized bisazocalix[4]arenes. These findings are in consonance with the recent reports on crown ether-bridged calix[4]arenes.[14]

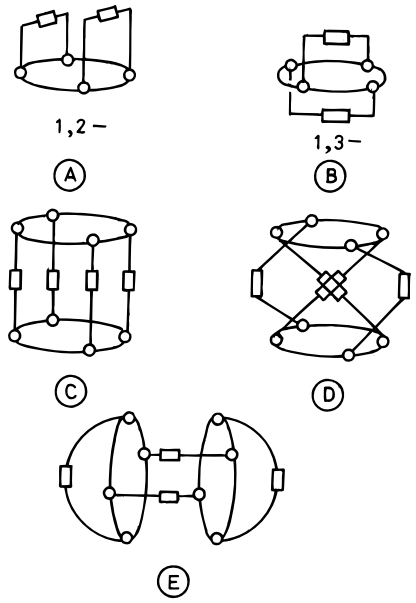


Figure 1. Possible regioisomers of bisazobiphenyl-bridged calix[4]arenes **5**−**7**: (A) intramolecular 1,2-bridged isomer; (B) intramolecular 1,3-bridged isomer; (C) intermolecular symmetrically bridged isomer; (D) and (E) intermolecular unsymmetrically bridged isomers.

(12) We thank the reviewer for suggesting the possibility of unsymmetrical coupling of two calix[4]arene units in bisazo biscalixarenes.

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Table 1. ^{13}C NMR Spectral Data for Methylene Carbons of the Synthesized Bisazocalixarenes 8−13

compd	position of methylene carbon (δ)
8	36.59
9	36.52
10	35.97
11	36.69
12	36.48
13	36.23

Table 2. Change in Color and Absorption Maxima of 5 on Addition of Amines

serial no.	amine added	change in color	λ_{max} of **5** (shift, nm)
1		yellow	410
2	ethylamine	yellow to red	490 (80)
3	diethylamine	yellow to red	490 (80)
4	triethylamine	yellow to red	494 (84)
5	*tert*-butylamine	yellow to red	494 (84)
6	aniline	no change	412 (2)
7	*p*-nitroaniline	no change	412 (2)
8	*N*-methylaniline	no change	416 (4)

Derivatives **8**−**13** also exhibited singlets for the methylene bridge protons of calixarenes in their ^{1}H NMR spectrum (Figure 3), thereby demonstrating that all the compounds synthesized have been immobilized by the bisazobiphenyl bridge in the 1,3-alternate conformation. These observations are in agreement with recent findings[15] by Shinkai *et al.* on transannularly stapled calixarenes at the upper rim.

Chromogenic Nature of Synthesized Calixarenes. Effect of Addition of Alkali. Bisazocalixarenes **5**−**7** exhibit prominent absorption bands at λ_{max} 410 nm (ϵ = 7200 cm^2 mol^{-1}), 408 nm(ϵ = 8680 cm^2 mol^{-1}), and 405 nm (ϵ = 9220 cm^2 mol^{-1}), respectively, in their UV−vis spectrum while methyl derivatives **8**, **9** and **10** show absorption bands at λ_{max} 389, 390, and 392 nm, respectively. When the yellow DMSO solution of bisazocalixarenes (*e.g.*, **5**, 2.5 × 10^{-4} M) was made alkaline with NaOH (2.5 × 10^{-4} M), the solution turned deep red with a bathochromic shift of 88 nm. No such bathochromic shift was observed when the parent bisazocalixarenes were replaced by their methyl derivatives (*e.g.*, **8**) under identical conditions. This change in color of **5** on addition of alkali is probably due to the ionization of hydroxy groups of bisazobiphenyl-bridged calixarenes since the original yellow color was restored upon acidification of the alkaline solution.

Effect of Addition of Aliphatic and Aromatic Amines. As the calixarenes have been reported to complex with amines,[16−18] the synthesized bisazocalixarenes were preliminarily examined for their interaction with them (Table 2) by UV−vis spectral analysis.

In a representative study it has been observed that the bisazocalixarene **5** exhibited a λ_{max} at 410 nm, while the studied amines (Table 2) did not absorb at this wavelength. When a dilute solution of various amines in DMSO (Table 2, 2.5 × 10^{-4}M) was added to the DMSO solution of bisazocalixarene **5** (2.5 × 10^{-4}M), it shifted its λ_{max} to 494 nm with a distinct color change from yellow to red. For instance, addition of 2.5 × 10^{-4} M DMSO solution of *tert*-butyl amine to **5** (2.5 × 10^{-4}M, DMSO) changed its color from yellow to red with a bathochromic shift of 84 nm (Figure 4). On the other hand, when aromatic amines were used in place of aliphatic amines, they did not show any color change or shift in the absorption maxima of the amines or bisazocalixarene, thereby providing a clue that the reagent synthesized could be used for visual discrimination of aliphatic and aromatic amines. Similar addition of amines to methoxy derivative **8** did not show any color change or shift in absorption maxima.

Since the original pale yellow color was restored upon acidification of a solution of **5**−*tert*-butylamine complex, the color change could be attributed to the ionization of hydroxyl groups of **5**, which was further evidenced by conductometric titration of **5** (2.5 × 10^{-4} M, DMSO) with a DMSO solution of *tert*-butylamine where conductivity of the mixture continuously increased until it reached a plateau at equimolar concentration of amine. Further work to understand the nature of complexation is in progress.

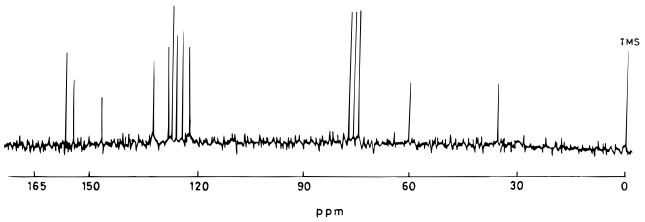

Figure 2. ^{13}C NMR spectrum of bisazocalix[4]arene **8**.

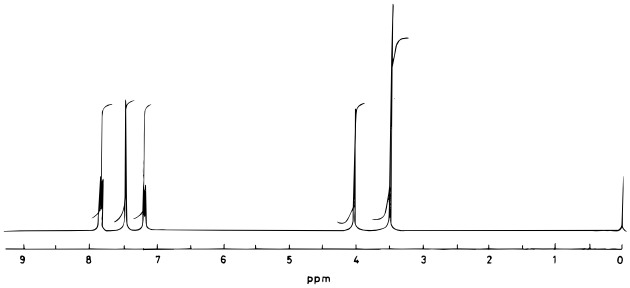

Figure 3. ^{1}H NMR spectrum of bisazocalix[4]arene **8**.

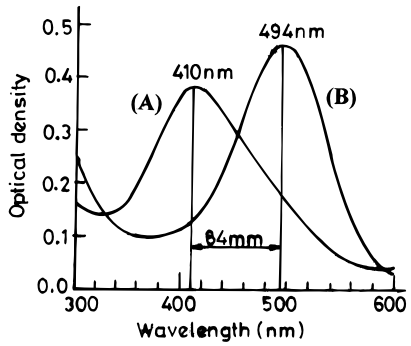

Figure 4. Optical spectrum of bisazocalix[4]arene (2.5 × 10^{-4} M, DMSO) (A) without addition of amine and (B) with addition of *tert*-butylamine (2.5 × 10^{-4} M, DMSO).

Experimental Section

General Method for Coupling of 4 with Diazotized 4,4′-Diaminobiphenyls. A solution of 4,4′-biphenyldiazonium

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chloride prepared from 4,4′-diaminobiphenyl (10 mmol), sodium nitrite (20 mmol), and concd HCl (5 mL) in water (25 mL) was added slowly into an ice-cold (0−5 °C) solution of calix[4]arene **4** (2.36 mmol) and sodium acetate trihydrate (4 g) in DMF−CH_3OH (50 mL, 5:8, v/v) to give a red suspension. After the suspension was allowed to stand at room temperature for 3 h, it was made acidic with aqueous HCl (150 mL, 2.5%), and the mixture was warmed to 60 °C for 30 min to produce bisazocalixarenes in nearly quantitative yields as red solids that were filtered and subsequently washed with water and methanol in succession.

The analytical samples of **5**−**7** were obtained by dissolving the crude products in pyridine followed by neutralization of the resultant solution with dilute HCl (2.5%). The precipitated solid thus obtained by filtration was washed with a solution of $NaHCO_3$ followed by water, methanol, and diethyl ether.

5: yield 0.83 g (42%); mp >300 °C dec; UV (DMSO) 410 nm; IR (KBr) 3220, 1585 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.55 (brs, 4H, D_2O exchanged), 8.02 (d, J = 9 Hz, 8H), 7.59 (s, 8H), 7.37 (d, J = 9 Hz, 8H), 3.89 (s, 8H); molecular mass 846 (vapor pressure osmometry, $CHCl_3$, calcd 836). Anal. Calcd for $C_{52}H_{36}N_8O_4$: C, 74.64; H, 4.30; N, 13.40. Found: C, 74.66; H, 4.37; N, 13.39.

6: yield 0.95 g (45%); mp 320 °C dec; UV (DMSO) 408nm; IR (KBr) 3212, 1580 cm^{-1}; ^1H NMR (DMSO-d_6) δ 9.62 (brs, D_2O exchanged, 4H), 8.13−7.4 (m, 20H); molecular mass 858 (vapor pressure osmometry, DMSO, calcd 882). Anal. Calcd for $C_{56}H_{44}N_8O_4$: C, 75.34; H, 4.93; N, 12.55. Found: C, 75.30; H, 4.76; N, 12.20

7: yield 1.03 g (48%); mp 300 °C dec; UV(DMSO) 405 nm; IR (KBr) 3210, 1582 cm^{-1}; ^1H NMR (DMSO-d_6) δ 9.65 (brs, D_2O exchanged, 4H) 7.96 (d, $J \approx$ 8 Hz, 8H), 7.48 (s, 8H), 7.10 (d, $J \approx$ 8 Hz, 8H) 3.89 (brs, 8H); molecular mass 853 (vapor pressure osmometry, DMSO, calcd 868). Anal. Calcd for $C_{52}H_{36}N_8O_6$; C, 71.89; H, 4.15; N, 12.90. Found: C, 71.80; H, 4.35; N, 12.92.

General Procedure for Derivatization of Bisazocalixarenes 5−7. A mixture of bisazocalix[4]arene **5**−**7** (8 mmol), NaH (8 mmol) and methyl iodide (1.7 g, 12 mmol) or $BrCH_2COOC_2H_5$ (2.0 g, 12 mmol) in dry DMF (50 mL) was stirred at 60 °C for 20 h. The reaction mixture was cooled and poured into 200 mL of ice-cold water. The yellow precipitate was collected by suction filter, and the residue was subjected to spectral analysis.

8: yield 0.36 g (40%); mp 255−258 °C; UV ($CHCl_3$) 389 nm; IR (KBr) 1582 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.86(d, $J \approx$ 9 Hz, 8H), 7.50 (s, 8H), 7.21 (*d*, $J \approx$ 9 Hz, 8H), 4.03 (s, 8H), 3.51 (s, 12H); ^{13}C NMR ($CDCl_3$) δ 158.6, 156.4, 148.9, 134.0, 129.2, 128.8, 126.3, 124.5, 123.9, 60.57, 36.59; molecular mass 908 (vapor pressure osmometry, $CHCl_3$, calcd 892). Anal. Calcd for $C_{56}H_{44}N_8O_4$: C, 75.34; H, 4.93; N, 12.55. Found: C, 75.25; H, 4.82; N, 12.56.

9: yield 0.54 g (55%); mp 262−264 °C; UV ($CHCl_3$) 390 nm; IR (KBr) 1585 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.72−7.23 (m, 20H), 3.98 (s, 8H), 3.53 (s, 12H), 2.45 (s, 12H); ^{13}C NMR ($CDCl_3$) δ 159.2, 156.8, 149.2, 133.6, 129.5, 128.6, 126.6, 124.5, 123.8, 122.2, 60.0, 36.5, 20.2; molecular mass 962 (vapor pressure osmometry, $CHCl_3$, calcd 948). Anal. Calcd for $C_{60}H_{52}N_8O_4$: C, 75.95; H, 5.49; N, 11.91. Found: C, 75.85; H, 5.40; N, 11.78.

10: yield 0.37 g (40%); mp 250−252 °C; UV ($CHCl_3$) 392 nm; IR (KBr) 1585 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.82(d, $J \approx$ 9 Hz, 8H), 7.48 (s, 8H), 7.09 (d, $J \approx$ 9 Hz, 8H), 4.02 (s, 8H), 3.56 (s, 12H); ^{13}C NMR ($CDCl_3$) δ 159.1, 158.2, 151.8, 148.5, 135.3, 130.6, 129.0, 128.2, 126.6, 124.9, 123.3, 60.5, 35.9; molecular mass 916 (vapor pressure osmometry, $CHCl_3$, calcd 924). Anal. Calcd for $C_{56}H_{44}N_8O_6$: C, 72.73; H, 4.76; N, 12.12. Found: C, 71.63; H, 4.72; N, 12.02.

11: yield 0.38 g (32%); mp 278−280 °C; UV ($CHCl_3$) 384 nm; IR (KBr) 1742, 1585 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.85 (d, $J \approx$ 8 Hz, 8H), 7.33 (d, $J \approx$ 8 Hz, 8H), 7.26 (s, 8H), 4.62 (s, 8H), 4.2−3.82 (m, 16H), 1.23 (t, 12H); ^{13}C NMR ($CDCl_3$) δ 192.5, 190.2, 160.2, 159.1, 149.2, 136.2, 135.2, 129.3, 128.5, 127.7, 125.3, 124.6, 123.2, 71.5, 60.8, 36.6, 14.2; molecular mass 1198 (vapor pressure osmometry, $CHCl_3$, calcd 1180). Anal. Calcd for $C_{68}H_{60}N_8O_{12}$: C, 69.15; H, 5.08; N, 9.49. Found: C, 69.01; H, 5.18; N, 9.36.

12: yield 0.43 g (35%); mp 285−288 °C; UV ($CHCl_3$) 382 nm; IR (KBr) 1740, 1585 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.62−7.30 (m, 12H), 7.19 (s, 8H), 4.58 (s, 8H), 4.2−3.65 (m, 16H), 2.43 (s, 12H), 1.25 (t, 12H); ^{13}C NMR ($CDCl_3$) δ 191.6, 190.3, 161.0, 159.9, 149.3, 136.6, 134.9, 130.1, 129.3, 128.6, 127.3, 125.1, 124.0, 70.9, 60.2, 36.4, 20.2, 14.3; molecular mass 1254 (vapor pressure osmometry, $CHCl_3$, calcd 1236). Anal. Calcd for $C_{72}H_{72}N_8O_{12}$: C, 69.68; H, 5.08; N, 9.03. Found: C, 69.58; H, 5.60; N, 8.99.

13: yield 0.37 g (30%); mp 262−265 °C; UV ($CHCl_3$) 382 nm; IR (KBr) 1740, 1580 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.75−7.35 (m, 16H), 6.89 (s, 8H), 4.80 (s, 8H), 4.26−3.66 (m, 16H), 1.18 (t, 12H); ^{13}C NMR ($CDCl_3$) δ 193.5, 191.8, 161.3, 159.9, 151.2, 149.2, 135.1, 134.3, 130.5, 129.6, 128.6, 127.3, 125.1, 70.5, 60.6, 36.2, 14.1; molecular mass 1243 (vapor pressure osmometry, $CHCl_3$, calcd 1212). Anal. Calcd for $C_{68}H_{60}N_8O_{16}$: C, 65.59; H, 4.82; N, 9.00. Found: C, 65.72; H, 4.68; N, 9.00.

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