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Azocalixarenes.7: Synthesis and study of the absorption properties of novel *mono*-azo substituted chromogenic calix[4]arenes

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Eight new *mono*-azo substituted chromogenic calix[4]arenes (**1**-**8**) were synthesized by diazo-coupling reactions in which 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri-(*tert*-butyl)calix[4]arene and diazonium salts (2-, 3-, and 4-nitroaniline; 4-phenyl azoaniline; 3- and 4-chloroaniline; or 2- and 4-methylaniline) formed the corresponding *mono*-azo substituted derivatives in high yields. The *mono*-azo substituted calix[4]arenes were characterized by UV-Vis, FT-IR, and ^{1}H-NMR spectroscopic techniques. Elemental analysis was also carried out. In addition, the effects of varying pH levels and solvents upon the absorption ability of azocalix[4]arenes substituted with electron-donating and electron-withdrawing groups at their *o*-, *m*-, and *p*-positions were studied. The results proved that the absorption maxima of the prepared compounds showed large bathochromic effects in comparison with analog compounds containing aromatic amine residue. Furthermore, concentration effects on the visible absorption maxima of the azocalix[4]arene compounds studied were also reported.

Key Words: Calixarene, azocalix[4]arenes, *mono*-azo substituted, diazo-coupling reaction, solvent effect, substituent effect, absorption properties

Introduction

Calix[n]arenes, which are accessible by the base-catalyzed condensation of *para*-substituted phenols with formaldehyde, are ideal frameworks for the development of chromogenic ionophores in the molecular recognition of ionic species of chemical and biological interest, since the calixarene results in a tailored chromogenic

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receptor.[1] Selective signaling of heavy metal ions is a very important topic for the detection and treatment of the toxic metal ions in various chemical systems, including living systems.[2] In this field, calixarenes are currently subjects of interest as chemical sensors[3] and selective receptors[4] due to their important functionalization properties. A variety of compounds based upon calixarene having nitrophenol,[5] nitrophenylazophenol,[6] azophenol,[7] indophenol,[8] and indoaniline[9] functional groups have been successfully designed and have exhibited a pronounced chromogenic behavior toward Na^+, K^+, Cs^+, Ca^{2+}, and UO_2^{2+} cations, and even chiral amines.

Shinkai et al. synthesized a calix[4]arene with a 4-(4'-nitrophenyl azo)phenol unit and 3 ethyl ester residues on the lower rim. They observed the lithium sensitivity of the ionophore.[10] Toth et al. reported the sodium selectivity of similar azophenol derivatives.[11] Lu et al. also reported the synthesis of a water-soluble azocalixarene derivative, detecting highly selective chromogenic ionophores for the recognition of chromium(III) ions.[12]

Recently, various derivatives of calix[4]arene[13−15] and their complexes,[16] polymeric calix[n]arene derivatives[17] and azocalix[n]arenes,[18−22] have been synthesized by the authors. We examined the selective extraction of the Fe^{3+} ion from the aqueous phase into the organic phase, as well as the liquid-liquid extraction of transition metal ions,[23] using diazo-coupled calix[n]arenes. However, there is still an important system that can exhibit color changes due to ionic or molecular interactions.

We are mainly interested in the development of a new class of chromogenic azocalix[n]arene dyes. The aim of this study was to synthesize 8 new diazo-coupled *mono*-azo substituted calix[4]arenes by substituted aniline derivative subunits **1-8** (Figure 1) and investigate their properties. There have not been any reports on azocalix[4]arene-based selective chromoionophores or the visible absorption properties of their compounds until now.

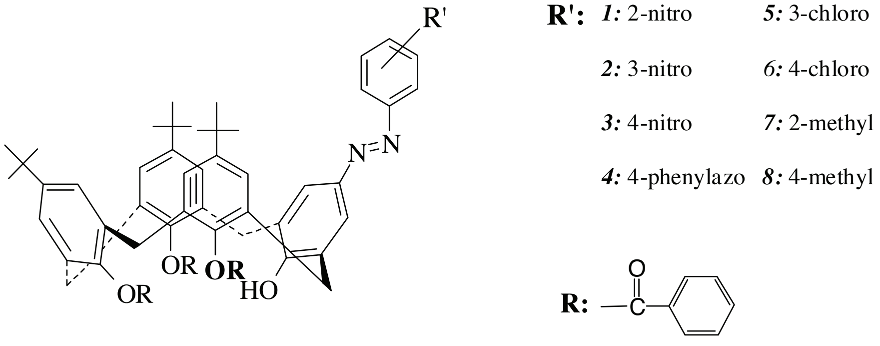

Figure 1. Diazo-coupled *mono*-azo substituted calix[4]arene derivatives **1-8**.

Experimental

General

All solvents and compounds were commercially graded reagents used without further purification. Melting points were measured with an Electrothermal IA9100 digital melting point apparatus in capillaries sealed under nitrogen and are uncorrected. The UV-Vis spectra were obtained with a Shimadzu 1601 UV-Visible recording spectrophotometer. The IR spectra were recorded with a Mattson 1000 FT-IR spectrometer as KBr pellets. The ^{1}H-NMR spectra, referenced to tetramethylsilane (TMS) at 0.00 ppm as an internal standard, were recorded on a Bruker 400 MHz spectrometer at room temperature (25 ± 1 °C). The elemental analyses were performed at the laboratory of the Scientific and Technological Research Council of Turkey (TÜBİTAK).

The solvent of crystallization was retained in some of the analytical samples and affected the elemental analysis results. In such cases, best fits between the analytical values and appropriate fractional increments of solvents were used.

Preparation of the ligands

p-*tert*-Butylcalix[4]arene,[24] 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17,23-tetra-(*tert*-butyl)calix[4]arene,[25] and 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri-(*tert*-butyl) calix[4]arene[25] were synthesized as described by a previously reported method.

Preparation of *mono*-phenylazocalix[4]arenes (1-8)

Diazotization of the various carbocyclic amines was effected with concentrated HCl. Compound 1 was as follows: 25,26,27-Tribenzoyloxy-28-hydroxy-5,11,17-tri-(*tert*-butyl)-23-(3-nitrophenylazo)calix[4]arene (**2**), 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri-(*tert*-butyl)-23-(4-nitrophenylazo)calix[4]arene (**3**), 25,26,27-tribenzoyl oxy-28-hydroxy-5,11,17-tri-(*tert*-butyl)-23-(4-phenylazophenylazo)calix[4]arene (**4**), 25,26,27-tri benzoyloxy-28-hydroxy-5,11,17-tri-(*tert*-butyl)-23-(3-chlorophenylazo)calix[4]arene (**5**), 25,26,27-tribenzoyloxy-28-hydroxy-5,11, 17-tri-(*tert*-butyl)-23-(4-chlorophenylazo)calix[4]arene (**6**), 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri-(*tert*-butyl)-23-(2-methyl phenylazo)calix[4]arene (**7**), and 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri-(*tert*-butyl)-23-(4-methylphenylazo)calix[4]arene (**8**) were obtained by applying the described method, and the yield was 60%-96%. The obtained compounds were purified by crystallization using DMF/MeOH and analyzed, respectively.

All of the *mono*-substituted azocalix[4]arenes were soluble in EtOH, diethyl ether, acetic acid, benzene, acetone, $CHCl_3$, and DMSO, and insoluble in water, 10% HCl, and 10% NaOH.

The synthesis of 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri-(*tert*-butyl)-23-(2-nitrophenylazo) calix[4]arene (1)

A solution of 2-nitrophenyldiazonium chloride, prepared from 2-nitroaniline (0.21 g, 1.50 mmol), sodium nitrite (0.12 g, 1.50 mmol), and concentrated HCl (0.35 mL) in water (3 mL), was added slowly to a cold (5 °C) solution of 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri-(*tert*-butyl)calix[4]arene (1.0 g, 1.10 mmol) and sodium acetate trihydrate (0.40 g, 3.00 mmol) in DMF/MeOH (13 mL, 8:5, v/v) to give a yellow suspension. After standing for 2 h at room temperature, the suspension was acidified with aqueous HCl (50 mL, 0.25%). The resulting mixture was first warmed to 60 °C and kept at that temperature for 30 min to give **1** (yield: 1.01 g, 87%) as a yellow solid, and then filtered and washed with water and MeOH, respectively. A typical sample for analysis was obtained as follows: **1** was dissolved in 100 mL of hot aqueous $NaHCO_3$ (4.20 g) solution, after which 1 g of activated charcoal was added to the solution. After the charcoal was filtered, the filtrate was cooled to room temperature and acidified with concentrated HCl (1 or 2 mL). The solution was heated to 60 °C and kept at that temperature, then cooled down. The resulting solid was filtered, washed with water, and dried. Recrystallization from the DMF/MeOH mixture gave a yellow product. Yield 0.86 g (87%), mp 265 °C; [Found: C: 76.02; H: 6.18; N: 3.57]; $C_{67}H_{63}N_3O_9$ requires C: 76.33; H: 6.02; N: 3.98. IR (KBr) υ: 3450 cm^{-1} (-OH), 1720 cm^{-1} (-C = O), 1490 cm^{-1} (-N = N), 1255 cm^{-1} (C-O). ^{1}H-NMR (DMSO-d$_6$, 25 °C) δ_H: 1.0 (27H, s, $t-$bu), 3.5-3.9 (8H, d, J = 13.2 Hz, Ar-CH$_2$-Ar), 5.9 (1H, s, OH), 6.8-7.4 (8H, m, Ar-H), 7.5-7.8 (15H, m, ArH-CO), 7.9-8.3 (4H, m, ArH-NO$_2$).

The synthesis of 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri-(*tert*-butyl)-23-(3-nitrophenylazo) calix[4]arene (2)

Azocalix[4]arene **2** was prepared using 3-nitroaniline in water/HCl and obtained as a pale brown solid, which was filtered and washed with water and MeOH, and dried as described above. The resulting solid was recrystallized from the DMF/MeOH mixture, which gave a pale brown product. Yield 0.76 g (65%), mp 269 °C; [Found: C: 76.42; H: 6.12; N: 3.67]; $C_{67}H_{63}N_3O_9$ requires C: 76.33; H: 6.02; N: 3.98. IR (KBr) υ: 3450 cm^{-1} (-OH), 1740 cm^{-1} (-C = O), 1495 cm^{-1}(-N = N), 1250 cm^{-1} (C-O). ^{1}H-NMR (DMSO-d$_6$, 25 °C) δ_H: 1.0 (27H, s, $t-$bu), 3.5-4.1 (8H, d, J = 13.3 Hz, Ar-CH$_2$-Ar), 5.7 (1H, s, OH), 6.6-7.3 (8H, m, Ar-H), 7.5-7.8 (15H, m, ArH-CO), 7.9-8.2 (4H, m, ArH-NO$_2$).

The synthesis of 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri-(*tert*-butyl)-23-(4-nitrophenylazo) calix[4]arene (3)

Azocalix[4]arene **3** was prepared using 4-nitroaniline in water/HCl and was obtained as an ivory solid, which was filtered and washed with water and MeOH, and dried as described above. The resulting solid was recrystallized from the DMF/MeOH mixture, which gave an ivory product. Yield 0.92 g (69%), mp 249 °C; [Found: C: 75.92; H: 6.21; N: 3.59]; $C_{67}H_{63}N_3O_9$ requires C: 75.92; H: 6.21; N: 3.59. IR (KBr) υ: 3450 cm^{-1} (-OH), 1700 cm^{-1} (-C = O), 1490 cm^{-1}(-N = N), 1250 cm^{-1} (C-O). ^{1}H-NMR (DMSO-d$_6$, 25 °C) δ_H: 1.0 (27H, s, $t-$bu), 3.5-4.2 (8H, d, J = 13.1 Hz, Ar-CH$_2$-Ar), 5.7 (1H, s, OH), 6.5-7.2 (8H, m, Ar-H), 7.4-7.8 (15H, m, ArH-CO), 7.9-8.2 (4H, m, ArH-NO$_2$).

The synthesis of 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri-(*tert*-butyl)-23-(4-phenylazophenylazo)calix[4]arene (4)

Azocalix[4]arene **4** was prepared using 4-phenylazoaniline in water/HCl and was obtained as a dark red solid, which was filtered and washed with water and MeOH, and dried as described above. The resulting solid was recrystallized from the DMF/MeOH mixture, which gave a dark red product. Yield 1.16 g (96%), mp 232 °C; [Found: C: 78.25; H: 6.42; N: 4.85]; $C_{73}H_{68}N_4O_7$ requires C: 78.75; H: 6.16; N: 5.03. IR (KBr) υ: 3495 cm^{-1} (-OH), 1760 cm^{-1} (-C = O), 1495 cm^{-1} (-N = N), 1250 cm^{-1} (C-O). ^{1}H-NMR (DMSO-d$_6$, 25 °C) δ_H: 1.3 (27H, s, $t-$bu), 3.7-3.9 (8H, d, J = 13.5 Hz, Ar-CH$_2$-Ar), 5.8 (1H, s, OH), 6.7-6.9 (8H, m, Ar-H), 7.0-7.7 (9H, m, ArH), 7.7-7.9 (15H, m, ArH-CO).

The synthesis of 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri-(*tert*-butyl)-23-(3-chlorophenylazo)calix[4]arene (5)

Azocalix[4]arene **5** was prepared using 3-chloroaniline in water/HCl and was obtained as a pale yellow solid, which was filtered and washed with water and MeOH, and dried as described above. The resulting solid was recrystallized from the DMF/MeOH mixture, which gave a pale yellow product. Yield 0.80 g (71%), mp 279 °C; [Found: C: 76.82; H: 6.12; Cl: 3.15; N: 2.49]; $C_{67}H_{63}ClN_2O_7$ requires C: 77.10; H: 6.08; Cl: 3.40; N: 2.68. IR (KBr) υ: 3510 cm^{-1} (-OH), 1735 cm^{-1} (-C = O), 1480 cm^{-1} (-N = N), 1260 cm^{-1} (C-O). ^{1}H-NMR (DMSO-d_6, 25 °C) δ_H: 1.2 (27H, s, $t-$bu), 3.5-4.2 (8H, d, J = 13.2 Hz, Ar-CH_2-Ar), 5.7 (1H, s, OH), 6.4-7.5 (8H, m, Ar-H), 6.9-7.6 (4H, m, Ar-Cl), 7.8-8.1 (15H, m, ArH-CO).

The synthesis of 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri-(*tert*-butyl)-23-(4-chlorophenylazo)calix[4]arene (6)

Azocalix[4]arene **6** was prepared using 4-chloroaniline in water/HCl and was obtained as a yellow solid, which was filtered and washed with water and MeOH, and dried as described above. The resulting solid was recrystallized from the DMF/MeOH mixture, which gave a yellow product. Yield 0.68 g (60%), mp 280 °C; [Found: C: 77.42; H: 6.35; Cl: 3.20; N: 2.47]; $C_{67}H_{63}ClN_2O_7$ requires C: 77.10; H: 6.08; Cl: 3.40; N: 2.68. IR (KBr) υ: 3500 cm^{-1} (-OH), 1736 cm^{-1} (-C = O), 1480 cm^{-1} (-N = N), 1260 cm^{-1} (C-O). ^{1}H-NMR (DMSO-d_6, 25 °C) δ_H: 1.0 (27H, s, $t-$bu), 3.2-4.3 (8H, d, J = 13.2 Hz, Ar-CH_2-Ar), 5.6 (1H, s, OH), 6.5-7.5 (8H, m, Ar-H), 6.9-7.6 (4H, m, Ar-Cl), 7.7-8.1 (15H, m, ArH-CO).

The synthesis of 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri-(*tert*-butyl)-23-(2-methylphenylazo)calix[4]arene (7)

Azocalix[4]arene **7** was prepared using 2-methylaniline in water/HCl and was obtained as an ivory solid, which was filtered and washed with water and MeOH, and dried as described above. The resulting solid was recrystallized from the DMF/MeOH mixture, which gave an ivory product. Yield 0.68 g (60%), mp 269 °C; [Found: C: 79.42; H: 6.32; N: 2.67]; $C_{68}H_{66}N_2O_7$ requires C: 79.82; H: 6.50; N: 2.74. IR (KBr) υ: 3523 cm^{-1} (-OH), 1735 cm^{-1} (-C = O), 1481 cm^{-1} (-N = N), 1268 cm^{-1} (C-O). ^{1}H-NMR (DMSO-d_6, 25 °C) δ_H: 1.1 (27H, s, $t-$bu), 1.7 (3H, s, CH_3), 3.5-4.1 (8H, d, J = 13.2 Hz, Ar-CH_2-Ar), 5.8 (1H, s, OH), 6.6-7.2 (8H, m, ArH), 7.2-7.9 (4H, m, ArH-CH_3) 7.9-8.3 (15H, m, ArH-CO).

The synthesis of 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri-(*tert*-butyl)-23-(4-methylphenylazo)calix[4]arene (8)

Azocalix[4]arene **8** was prepared using 4-methylaniline in water/HCl and was obtained as an ivory solid, which was filtered and washed with water and MeOH, and dried as described above. The resulting solid was recrystallized from the DMF/MeOH mixture, which gave an ivory product. Yield 0.70 g (64%), mp 276 °C; [Found: C: 79.30; H: 6.85; N: 2.43]; $C_{68}H_{66}N_2O_7$ requires C: 79.82; H: 6.50; N: 2.74. IR (KBr) υ: 3450 cm^{-1} (-OH), 1740 cm^{-1} (-C = O), 1495 cm^{-1} (-N = N), 1250 cm^{-1} (C-O). ^{1}H-NMR (DMSO-d_6, 25 °C) δ_H: 1.1 (27H, s, $t-$bu), 1.6 (3H, s, CH_3), 3.5-4.1 (8H, d, J = 13.2 Hz, Ar-CH_2-Ar), 5.7 (1H, s, OH), 6.5-7.3 (8H, m, Ar-H), 7.4-8.0 (4H, m, ArH-CH_3), 8.1-8.3 (15H, m, ArH-CO).

Results and discussion

Synthesis and characterizations

In our previous studies, the absorption properties of the carbocyclic and heterocyclic amine substituted azocalix[4]arenes, as simple bathochromic and hypsochromic effects, were investigated. In this study, we focused on calix[n]arene-based diazonium salts as precursors for a new group of macrocyclic oligomeric ligands. Based on thorough studies of calix[n]arenes as ligands for transition metal complexes,[23] the following basic building principle should be pursued: A calix[4]arene skeleton may serve as a platform to attach -N = N- ligands. Because of the typical geometry[26] of calix[4]arenes, it is easier to identify different functional sites on the calix[n]arene. The *upper* (wide) rim of the macrocycle may serve to place ligands at discrete positions. Variation of both the number and the relative geometry of the ligands can be easily adjusted to fit the needs imposed by the catalytic task. Functionalization of the calix[4]arene at the *lower* (narrow) rim with benzoyl groups fixes the *cone* conformation and enhances its solubility in organic solvents.

Recently, we reported the synthesis of various azocalix[4]arenes through diazo-coupling with carbocyclic and heterocyclic amines.[18−22] Azocalix[4]arenes have proven to be versatile substrates in diazo-coupling reactions, allowing the preparation of several new donor-acceptor substituted carbocyclic amine derivatives.

In this work, 8 new azo compounds were synthesized from 2-, 3-, and 4-nitroaniline, 4-phenylazoaniline, 3- and 4-chloroaniline, and 2- and 4-methylaniline, and their properties were investigated. These azocalix[4]arene compounds (**1-8**) are outlined in Figure 2. This functionalization was achieved by reacting 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri-(*tert*-butyl)calix[4]arene with aryldiazonium salts in DMF/methanol for 2 h at 5 °C.

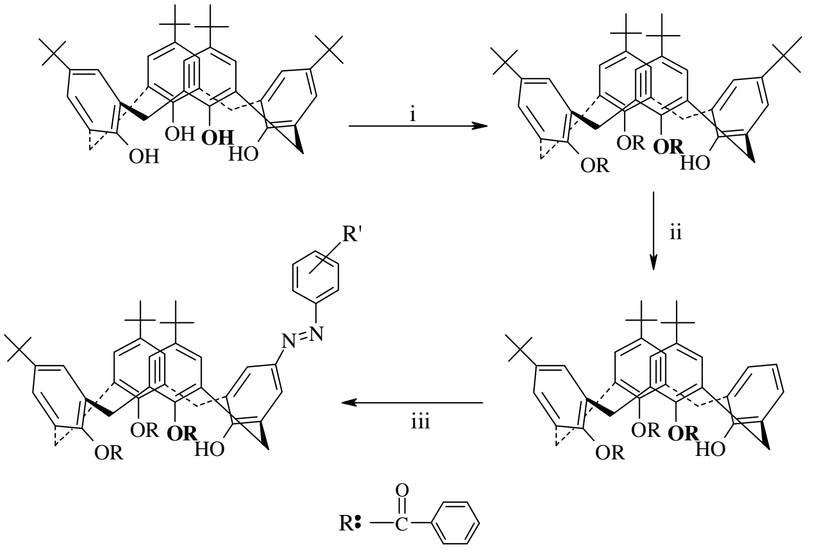

Figure 2. The synthesis of *mono*-azo substituted calix[4]arene derivatives **1**-**8**. i) benzoylchloride/pyridine, ii) $AlCl_3$/toluene, iii) $NaNO_2$/HCl and carbocyclic amine derivatives.

The *mono*-azocalix[4]arene derivatives (**1**–**8**) were prepared by coupling 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri-(*tert*-butyl)calix[4]arene with diazotized carbocyclic amines in $NaNO_2$/HCl. The *mono*-azo substituted calix[4]arenes may exist in 4 possible tautomeric forms in solutions, namely the azo-phenol form (A), the quinone-hydrazone form (B), and their deprotonated anions (C) and (D), respectively. These results are in agreement with the work of Ertan[27] and our recent paper.[18–22]

Diazo-coupling was accomplished selectively at the *p*-position of the calix[4]arene ring to give compounds in moderate to excellent yields (60%-96%). These results, which are in accordance with the greater nucleophilicity of the carbocyclic amine ring, were observed earlier in the case of the formulation of carbocyclic amine derivatives. The structures of the azocalix[4]arenes were unambiguously confirmed by their analytical and spectral data.

The infrared spectra of all of the azocalix[4]arenes (in KBr) show broad bands within the range of 3523-3450 cm^{-1}, corresponding to υ_{OH}. The FT-IR spectra also showed a strong band located at 1495-1480 cm^{-1}, which can be assigned to -N = N-. The other $\upsilon_{\max}$ values, at 1760-1700 and 1268-1250 cm^{-1}, can be assigned to $\upsilon_{C=O}$ and υ_{C-O}, respectively. It can be suggested that these azocalix[4]arenes do not exist as the keto-hydrazo form B or its anionic form D in the solid state (Figure 3).

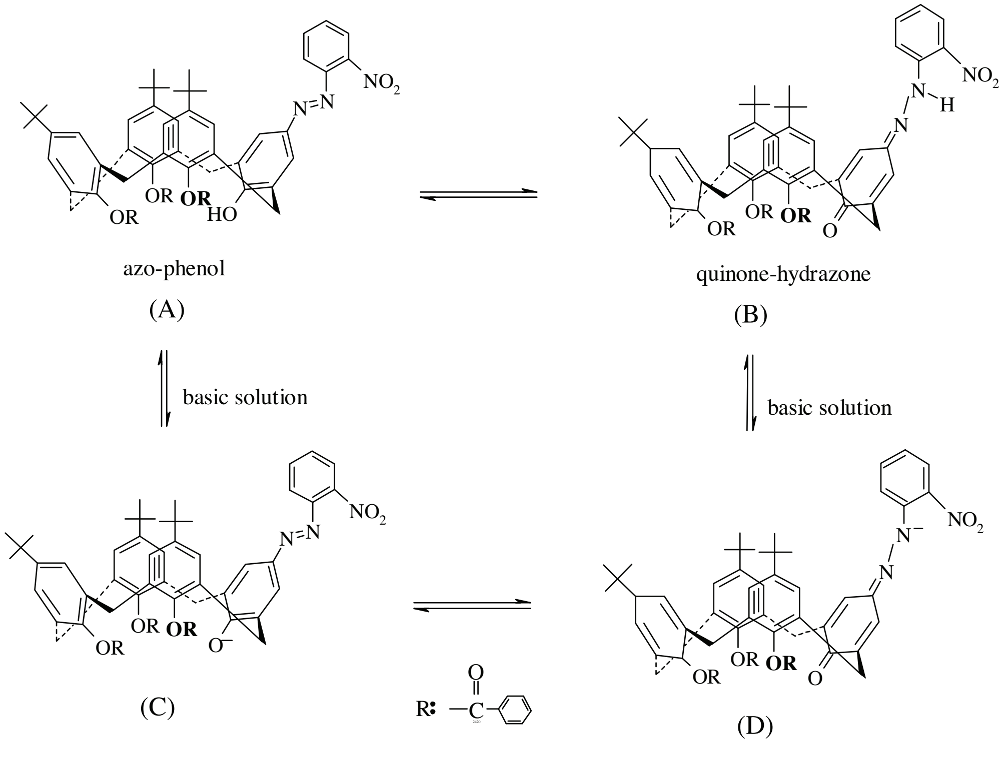

Figure 3. The tautomeric forms of diazo-coupled *mono*-azo substituted calix[4]arene **1**.

According to ^{1}H NMR in DMSO, the structure of azocalix[4]arene derivatives **1-8** not only impose the *cone* conformation in the liquid state, but also provide evidence for asymmetric structural features. Each of the derivatives has 2 pairs of doublets around 3.2 and 4.2 ppm, which indicates a *cone* conformation with nonequivalent methylene bridges in the neighboring and remote positions relative to the *p*-substituted arene moiety. However, the *cone* conformation of flexible calixarenes (**1-8**) could be stabilized by intramolecular H-bonding involving the OH group. Consecutively, the partial *cone* conformation may be formed with DMSO by breaking the H-bonds, resulting in a similar pattern of Ar-CH$_2$-Ar protons signals. As previously reported,[1,24,25] this can be explained by the presence of chiral substituents and indicates a significant degree of structural rigidity. In the ^{1}H NMR spectrum of the azocalix[4]arenes, signals of the aromatic hydroxyl and imine proton shifted upfield, which suggests that the hydrogen bonds involved in the *mono*-azo substituted calix[4]arenes are more important than in azocalix[4]arenes.

The ^{1}H NMR spectra measured in DMSO-d_6 at 25 °C showed a multiplet from 8.3 to 7.7 ppm for substituted aromatic protons (ArH-X), a multiplet from 7.9 to 7.0 ppm for benzoyl aromatic protons (ArH-CO), a multiplet from 7.5 to 6.4 ppm for calix[4]arene aromatic protons (Ar-H), a broad peak from 5.9 to 5.6 ppm for hydroxyl protons (-OH), and a singlet at 1.0 ppm for *tert*-butyl protons. These results indicate that azocalix[4]arene, rather than the *mono*-azo substituted one, may exist as a mixture of several tautomeric forms in DMSO. Such an observation in ^{1}H-NMR can be easily explained by the C$_{2v}$ symmetry of the bridge protons in trisubstituted azocalix[4]arenes **1-8**. *Mono*-azo substituted azocalix[4]arenes are in favor of the predominantly single tautomeric form in DMSO.

Absorption properties

The design and synthesis of organic chromophores as nonlinear optical (NLO) materials has attracted much attention in recent years.[28] They have great potential, especially in optical communication, information processing, frequency doubling, and integrated optic fields. Organic NLO materials have many advantages over inorganic materials, including large nonlinear optical coefficients, great ease of synthetic design, easy preparation, and low cost. It has been shown that the second order hyperpolarizabilities (β) of heterocyclic chromophores are often higher than those of carbocyclic amine analogs. Recently, we also demonstrated that donor-acceptor substituted azocalix[4]arenes have many favorable features as NLO materials.[18-22]

Electronic absorption spectra of azocalix[4]arenes showed an intense lowest energy charge-transfer absorption band in the UV-Vis region. Dramatic differences in energy occur upon arylazo substitution of azocalix[4]arenes. For example, the wavelength of the lowest energy charge transfer band of azocalix[4]arene **4** was shifted upfield by 176 nm upon arylazo substitution (azocalix[4]arene **6**, 325 nm) (Table). The influence of the strength of acceptor groups, such as nitro- and chloro-, is demonstrated by comparison of the absorption maxima of compounds **1**, **2**, **3**, **5**, and **6** as the longest wavelengths. The shift in the transition of azocalix[4]arene **1** (404 nm) to azocalix[4]arene **3** (331 nm) in methanol (Table) can be attributed to the stabilization of LUMO by the electron-withdrawing groups.[29] A distinct spectral effect could be also caused by the substituent at the nitrogen atom of the aromatic amine ring. The influence of the substituent on the nitrogen atom of the aromatic amine ring was demonstrated by comparison of the absorption maxima of azocalix[4]arenes **2** and **3** as the longest wavelengths. In addition, a shift in transition was observed from azocalix[4]arene **2** to azocalix[4]arene **3** in methanol (Table), at 481 and 331 nm, respectively.

Solvent effects

Mono-azo substituted calix[4]arene derivatives **1-8** showed characteristic absorption patterns. The appearance of the azocalix[4]arene absorption band at a relatively high wavelength may be attributed to the presence of electron-withdrawing groups, such as nitro- and chloro-, and electron-donating groups, such as azo- and methyl-. The electronic absorption spectra of azocalix[4]arene derivatives **1-8** exhibited an absorption band and a shoulder in the range of 325-404 nm corresponding to $\pi - \pi^*$ and n-π^* transitions, which are in accordance with typical diazo spectra.

The visible spectral properties of the *mono*-azo substituted calix[4]arene derivatives were compared with respect to positions of substitutions. Electron-withdrawing groups, such as nitro- and chloro- groups, and electron-donating groups, such as azo- and methyl- groups, exerted a bathochromic effect as substituents in the aryl ring.

The absorption spectra of azocalix[4]arenes **1-8** were recorded in various solvents at concentrations of approximately 10^{-6} to 10^{-8} M (Table). The visible absorption spectra of these azocalix[4] arenes were found to exhibit strong solvent dependency, which did not show regular variation with the polarity of the solvents.

Table. Influence of solvent on $\lambda_{\max}$ (nm) of azocalix[4]arenes.

Compounds	DMSO		DMF		Acetonitrile		Chloroform + Piperidine	Methanol		Acetic Acid	
	conc.	dil.	conc.	dil.	conc.	dil.	conc.	conc.	dil.	conc.	dil.
1	416	416	411	411	401	399	397 347	404	404	398	397
2	439 588 s	435 567 s	494 326 s	493 327 s	480	480	335	481 s	413s	324	325
3	575s 378	380	375	375	364	364	353	331	331	361	357
4	427	421	413	412	394	394	336	401	403	403	402
5	495	495	320s 355s	319 s 355 s	321	324	335 489 s	334	333	335	332
6	330 s	329 s	363 s	363 s	387 s	380 s	382 s 323 s	325 s	325 s	326 s	326 s
7	347 s	347 s	370 s	370 s	330 s	330 s	323	364 s	364 s	-	-
8	333	333 417 s	337	336	333	332	334	401	403	403	403

s: shoulder

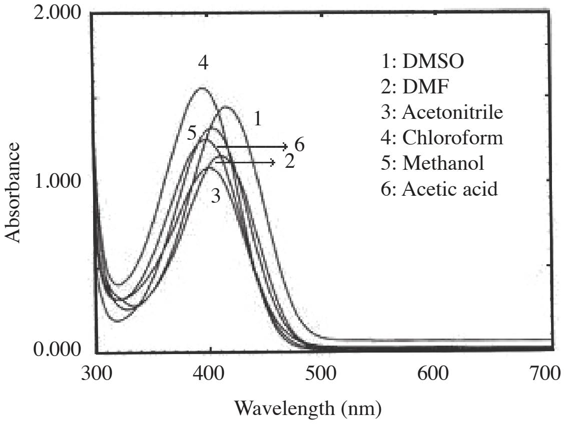

Figure 4. Absorption spectra of azocalix[4]arene **1** in various solvents.

Strong evidence for the existence of these azocalix[4]arenes in an equilibrium is provided by the isosbestic points in the visible spectra of, for example, azocalix[4]arene **1** in different solvents (Figure 4). This equilibrium may exist among tautomeric forms. The equilibrium depends on the basicity of the solvents used; with proton-accepting solvents such as DMSO, DMF, acetonitrile, and chloroform, the azocalix[4]arenes displayed a red shift of λ_{max}. Moreover, in a proton-donating solvent such as methanol or acetic acid, the λ_{max} of the azocalix[4]arenes did not significantly change with respect to the absorption spectra in chloroform, with the exception of azocalix[4]arene **1**. Similar approaches and suggestions have also been reported by Ertan[28] and Deligöz.[18−22]

The λ_{max} of azocalix[4]arene **4** in methanol showed bathochromic shifts when 0.1 M KOH was added. The λ_{max} of this compound in methanol showed both hypsochromic shifts and slight bathochromic shifts when 0.1 M HCl was added. A typical example for azocalix[4]arene **4** is shown in Figure 5. These results indicate that azocalix[4]arenes **1-8** exist in the anion form.

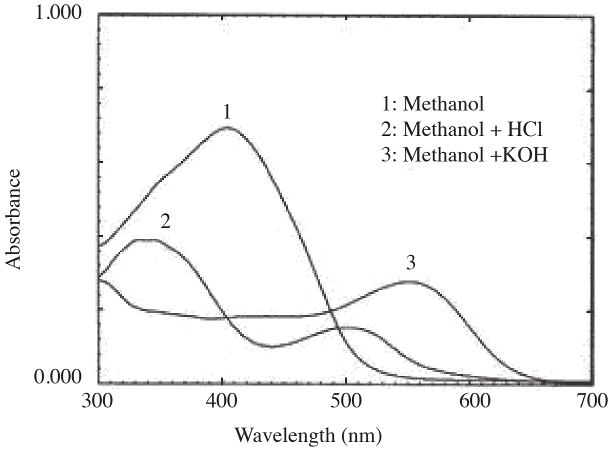

Figure 5. Absorption spectra of azocalix[4]arene **4** in acidic and basic solutions.

Substituent effects

As shown in the Table, the introduction of electron-withdrawing nitro- and chloro- groups and electron-donating azo- and methyl- groups into the carbocyclic rings resulted in bathochromic shifts in all solvents. However, the introduction of electron-donating azo- and methyl- groups into the benzene rings resulted in hypsochromic shifts in DMSO and DMF, but produced bathochromic shifts in acetonitrile, methanol, acetic acid, and chloroform. The introduction of nitro- and chloro- groups into the benzene rings imparted the greatest bathochromic shift of all groups. No group's position showed a regular variation in all solvents.

The visible absorption maxima (λ_{max}) in all solvents are given in the Table. Inspection of the Table shows that azocalix[4]arene derivatives **1**, **2**, **3**, **5**, and **6**, derived from nitro- and chloro- carbocyclic amines containing electron-withdrawing nitro- and chloro- groups, and azocalix[4]arenes **1-8** did not have uniform bathochromic shifts of about 48-165 nm relative to the corresponding azocalix[4]arene derivatives **4**, **7**, and **8**, from azo- and methyl- carbocyclic amines containing one-electron-donating azo- and methyl- groups. Thus, azocalix[4]arenes **1** and **3**, with an *o*- and *p*- nitro substituent in the diazo component, absorbed at 416 and 378 nm. When the nitro group was in the *m*-position (**2**), the absorption shifted to 439 nm in DMSO.

Concentration effects

The effect of concentration on the absorption maxima of compounds **1-8** is given in the Table. As can be seen, all azocalix[4]arenes had concentration-independent $\lambda_{\max}$ values of compounds, indicating that the azocalix[4]arenes existed in their tautomeric form in all solvents used. The $\lambda_{\max}$ of no compound changed with compound concentration.

Conclusions

Eight new calixarene-based receptors with benzoyl groups immersed in a large cavity were synthesized. The synthesis of all diazo-coupled compounds was achieved using the method of Morita.[30] These reactions produced the corresponding azo compounds in good yield. Diazo-coupling reactions are shown in Figure 2. This pathway was a convenient way to achieve the best yield of azocalix[4]arene compounds. We studied the diazo-coupling reactions of calix[4]arene with benzenediazonium chloride; 2-, 3-, and 4-nitroaniline; 4-phenyl azoaniline; 3- and 4-chloroaniline; or 2- and 4-methylaniline.

The *o*-, *m*-, and *p*-substituted groups dissociated progressively in solution with increasing pH, thus forming the azo-phenol form and quinone-hydrazone form species, with characteristic changes in the visible absorption spectra.

The azocalix[4]arene **4** derived from calix[4]arene and substituted aniline showed a pronounced color change from pale yellow to dark red in dry $CHCl_3$, and could be used as an analytical indicator. As both the neutral and mono-anionic forms of azocalix[4]arene derivatives were nonfluorescent, these compounds could be used as pH indicators.

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