SHORT PAPER

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The synthesis and properties of some novel azo group containing calix[*n*]arene derivatives[†]

Hasalettin Deligöz* and Halil Çetişli

Pamukkale University, Faculty of Science-Arts, Department of Chemistry, 20017, Denizli-Turkey

Two different azo derivatives of *p-tert*-butylcalix[4 and 6]arene **5a**, **5b** have been synthesised; treatment of the monomers (phenol and *p-tert*-butyl phenol) with diazonium chloride (**3**) provided corresponding compounds **4a**, **4b**.

Keyword: calixarenes, azo calix[n]arenes, azo compounds, identification of azo calixarenes

Calix[*n*]arenes are readily converted into a wide range of derivatives by alkylation of the phenolic groups at the lower rim.[1,2] This type of chemical modification, first introduced by Gutsche[1] as part of conformational studies in calix[n]arenes,[3] has since then been widely used by several groups to produce pendant ether,[4] carboxylate,[5] ester,[6,7] amide,[8] phosphine,[9,10] *vic*-dioxime,[11–13] and keto[14] derivatives. Azo compounds are the most widely used class of dyes due to their versatile application in various fields such as the dyeing of textile fibre and the colouring of different materials, and for plastics, biomedical studies, and advanced applications in organic synthesis.[15–18]

Calix[*n*]arenes as cavity-containing molecules, are readily prepared in good yields from the base-induced condensation of *p-tert*-butylphenol and formaldehyde,[1] and are employed as putative hosts. When appropriately modified, they provide attractive platforms for metal ion complexation. Shimuzu *et al*. synthesised a chromogenic calix[4]arene which has within the molecule a calix[4]aryl triester moiety as a metal binding site and an azophenol moiety as a coloration site.[19] Diazo coupling reactions of calix[4]arene were studied, and their NMR spectra were described by Morita *et al*. and Shinkai *et al*.[20,21] Our recent work described the synthesis of a *vic*-dioxime derivative of calix[*n*]arene and its complexes,[22,23] polymeric calix[*n*]arene derivatives[24,25] and selective extraction of transition metal cations with these calix[*n*]arene derivatives.[26–29]

The present work describes the synthesis of novel azo compounds either as free ligands (**4a** and **4b**) or as analogues of calix[n]arenes (**5a** and **5b**).

Experimental

All compounds were purified by recrystallisation. The melting points of the compounds were determined with an Electrothermal IA 9100 digital melting point apparatus and are uncorrected. Absorption spectra in DMF were determined on a Shimadzu 160A UV-vis spectrophotometer. IR spectra were recorded on a Mattson 1000 FTIR spectrometer calibrated with polystyrene film using the KBr pellets, ^{1}H-NMR spectra were recorded on a Bruker 200 MHz spectrometer with deuterium dimethyl sulfoxide as solvent and TMS as internal standard. The elemental analyses were performed in the TUBITAK laboratories. (The Scientific and Research Council of Turkey).

Preparation of p-*nitrodiazonium chloride:* A mixture of *p*-nitroaniline (2.48 g, 18 mmol), water (10 ml) and concentrated hydrochloric acid (4.50 ml, 54 mmol) was heated to 40–45 °C while being stirred until a clear solution was obtained. This solution was cooled to 0–5 °C, and a solution of sodium nitrite (1.24 g, 18 mmol) in 2 ml of water was then added dropwise, maintaining the temperature below 5 °C. The resulting mixture was stirred for an additional 30 min. in an ice bath, and excess nitrite was destroyed by addition of urea.[30] This solution was buffered with solid sodium acetate.

*Synthesis of 2-(*p-*nitrodiazophenyl)-4-*tert-*butylphenol* (**1**)*: p-tert*-Butylphenol (2.70 g, 18 mmol) in 5 ml of EtOH with sodium acetate was cooled to 0–5 °C in an ice bath. This solution was gradually added to the solution of the cooled *p*-nitrodiazonium chloride, and the resulting mixture was continually stirred at 0–5 °C for 60 min. The pale orange crude precipitate was filtered and washed several times with water. The resulting product was recrystallised from glacial acetic acid and then dried under vacuum to yield orange crystals **(1)** (4.41 g, 82%), m.p. 142–143 °C. (Found: C; 63.97; H, 5.77; N, 14.38. $C_{16}H_{17}O_3N_3$ requires C, 64.21; H, 5.68; N, 14.05%).

*Synthesis of 2-(*p-*aminodiazophenyl)-4-*tert-*butylphenol* (**2**)*:* A solution of 4.20 g (14 mmol) of 2-(*p*-nitrodiazophenyl)-4-*tert*-butylphenol and 3.16 g (14 mmol) of $SnCl_2.2H_2O$ in 40 ml MeOH was refluxed 4 h. The solution was cooled, poured onto ice, neutralised (pH 7–8) by the addition of 1% NaOH, and extracted three times with CH_2Cl_2. The organic phase was separated, washed with brine and dried (Na_2SO_4) and evaporated to leave a dark red solid. Trituration with 75 ml of CH_3OH followed by crystallisation of the insoluble material from *i*-PrOH gave 3.63 g (96%) of pale orange crystals (**2**), m.p. 132–133 °C. (Found: C, 71.12; H, 7.23; N, 15.74. $C_{16}H_{17}O_3N_3$ requires C, 71.37; H, 7.06; N, 15.99%).

Synthesis of o-(4-hydroxydiazophenyldiazophenyl)-p-tert-butylphenol (**4a**)*:* general procedure.[20] A solution of 2-(*p*-diazonium-chloridediazophenyl)-4-*tert*-butyl phenol, which was prepared from 2.70 g (10 mmol) of 2-(*p*-aminodiazophenyl)-4-*tert*-butyl phenol, 0.69 g (10 mmol) sodium nitrite and 7 ml conc. HCl in 25 ml of water, was added slowly into a cold (5 °C) solution of 0.94 g (10 mmol) of phenol and 4.08 g (30 mmol) of sodium acetate trihydrate in 26 ml of MeOH-DMF (5:8, v/v) to give a red-brown suspension. After being allowed to stand for 2 h at room temperature, the suspension was made acidic with 150 ml of 0.25% aqueous HCl. The mixture was warmed to 60 °C for 30 min. to produce (**4a**) in quantitative yield as a brownish solid. The resulting solid was filtered and washed with water and MeOH, and dried. The yield was 2.54 g (68%) of brownish crystals (**4a**), m.p. 85 °C, ^{1}H NMR (DMSO, 25 °C): δ: 12.40 (1H, s, –OH), 9.14 (1H, s, –OH), 6.68–7.15 (11H, m, Ar–H), 1.26 (9H, s, CMe_3). For analysis see Table 1.

This compound (**4a**) was soluble in EtOH, acetone, acetic acid, $CHCl_3$, DMSO, and slightly soluble in diethyl ether, and insoluble in water.

*Synthesis of bisdiazo(1-hydroxy-4-*tert-*butylphenyl)benzene* (**4b**)*:* Compound (**4b**) was prepared as described above, using *p-tert*-butyl phenol and obtained as a pale brown solid, which was filtered and washed with water and MeOH. Yield was 2.75 g (64%) of pale brown crystals (**4b**), m.p. 180 °C, ^{1}H NMR (DMSO, 25 °C): δ: 13.25 (2H, s, –OH), 7.01–7.88 (10H, m, Ar–H), 1.28 (18H, s, CMe_3). For analysis see Table 1.

This compound (**4b**) was soluble in EtOH, acetone, acetic acid, DMSO, and slightly soluble in $CHCl_3$, diethyl ether, and insoluble in water.

Synthesis of p-(2-hydroxy-5-tert-butylphenylazophenylazo) calix[4]arene (**5a**)*:* Compound (**5a**) was prepared as described above, using calix[4]arene and obtained as a dark brown solid, which was filtered and washed with water and MeOH. Yield was 2.98 g (77%) of dark brown crystals (**5a**), m.p. 230 °C, ^{1}H NMR (DMSO, 25 °C): δ: 10.23 (4H, s, –OH), 9.12 (4H, s, –OH), 7.14 (28H, s, Ar–H), 6.68 (8H, s, Ar–H), 3.36 (8H, broad, Ar–CH_2–Ar), 1.22 (36H, s, CMe_3). For analysis see Table 1.

This compound (**5a**) was soluble in acetic acid, $CHCl_3$, DMSO, and slightly soluble in EtOH, acetone, diethyl ether, and insoluble in water.

*Synthesis of p-(2-hydroxy-5-*tert-*butylphenylazophenylazo) calix[6]arene* (**5b**)*:* Compound (**5b**) was prepared as described above,

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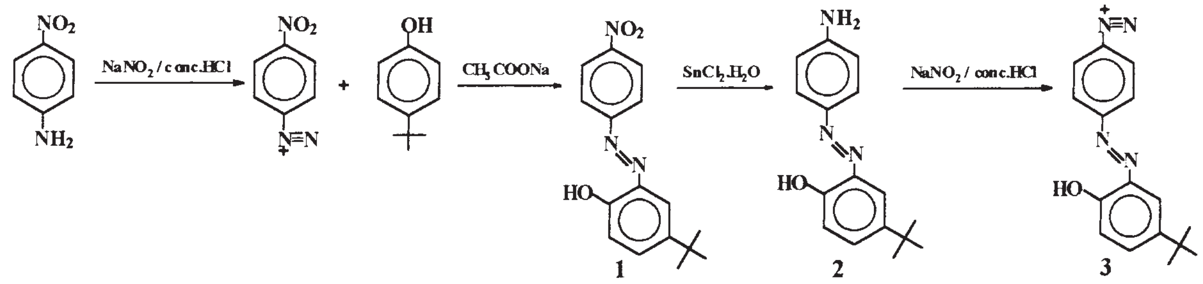
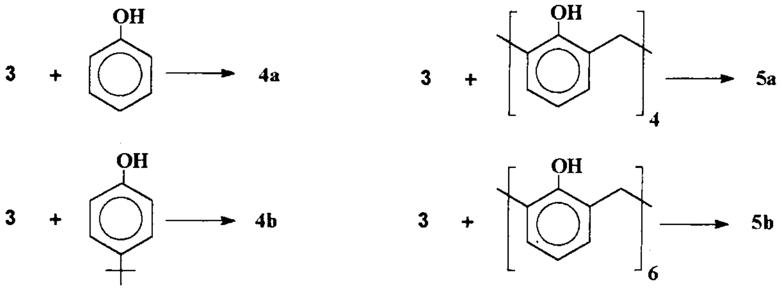
* To receive any correspondence. E-mail: hdeligoz@pamukkale.edu.tr

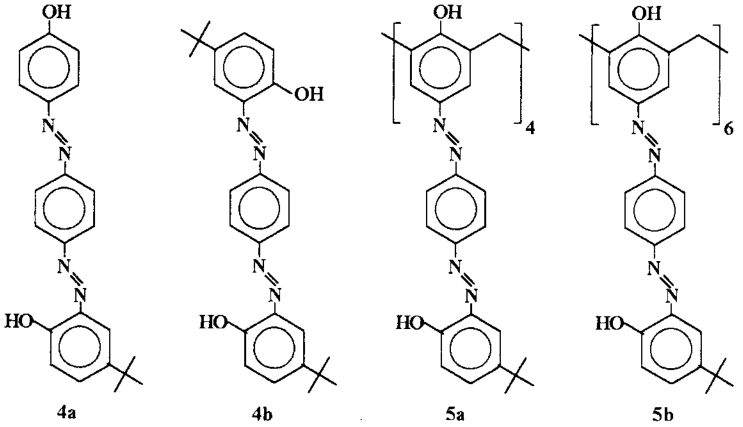
[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*



Scheme 1



Scheme 2



Scheme 3

using calix[6]arene and was obtained as a pale brown solid, which was filtered off and washed with water and MeOH. Yield was 2.36 g (61%) of pale brown crystals (**5b**), m.p. >360 °C, ^{1}H NMR (DMSO, 25 °C): δ: 10.14 (6H, s, –OH), 9.16 (6H, s, –OH), 7.13 (42H, s, Ar–H), 6.69 (12H, s, Ar-H), 3.38 (12H, broad, Ar–CH$_2$–Ar), 1.12-1.31 (54H, s, CMe$_3$). For analysis see Table 1.

This compound (**5b**) was soluble in acetic acid, DMSO, and slightly soluble in EtOH, acetone, diethyl ether, CHCl$_3$, and insoluble in water.

Results and discussion

The substituted azo compounds (**4** and **5**) were characterised by spectroscopic techniques and elemental analysis. The results are summarised in Tables 1–3.

The ^{1}H NMR spectra for all the azo compounds exhibited a sharp singlet signal in the range of 1.12–1.31 ppm, attributed to the *tert*-butyl groups. These compounds have *tert*-butyl groups of the same environments and gave singlet peaks. The compounds **4a**, **5a** and **5b** showed peaks locating in the range of 9.12–9.19 ppm which could be attributed to the hydroxyl groups. The lower field signals of hydroxyl group of the all compounds resonate the *ca* 9.12–12.40 ppm range and these are typical for intramolecular hydrogen bonding protons as reported in the literature.[18] However, for compound **4b** this resonance shifted to 13.25 ppm due to the presence of the hydrogen bond. It was evident that this strong intramolecular hydrogen bond tends to keep the molecule planar. In addition, there are no intermolecular contacts other than van der Waals force between the molecules which caused them to be present as isolated individuals within the crystal. The phenyl protons were also observed as multiplets at 6.68–7.88 ppm. The methylene resonances, which could appear as an AB quartet or doublet of doublets in cone conformation compounds in NMR measurements[1,20] were detected as a broad resonance at 3.36–3.38 in DMSO for compounds **5a** and **5b**.

Table 1 Colours, yields, m.p. and elemental analyses of ligands

Compounds	MW (Calcd.)	Colour	m.p. /°C	Yield /%	Calcd. (Found)		
					C	H	N
4a CH_3OH	406	Brownish	85	68	67.98 (67.93)	6.40 (6.18)	13.79 (13.75)
4b CH_3OH	462	Pale brown	180	64	70.13 (70.02)	7.36 (7.07)	12.12 (12.33)
5a CH_3OH	1576	Dark brown	230 (dec.)	77	70.81 (70.52)	5.84 (6.03)	14.21 (14.09)
5b CH_3OH	2348	Pale brown	>360 (dec.)	61	71.04 (70.72)	5.79 (5.93)	14.31 (14.03)

Table 2 Characteristic IR Bands of ligands as KBr pellets (cm^{-1})

Compounds	$\nu_{(O\text{-}H)}$	$\nu_{(C\text{-}H)(\text{-}Bu^t)}$	$\nu_{(C=C)}$	$\nu_{(N=N)}$
4a CH_3OH	3495–3420	2966	1625	1465
4b CH_3OH	–	2977	1625	1470
5a CH_3OH	3450–3445	2977	1625	1495
5b CH_3OH	3450–3445	2976	1625	1495

In the IR spectra of the compounds, characteristic vibrational bands were observed at 1465–1495 cm^{-1} for –N=N– groups which is in agreement with the literature values.[18] The hydroxyl groups in the compound **4b** do not form an intramolecular hydrogen bonding between hydroxyl group and the azo nitrogen. This was confirmed by very low field signals at 13.25 ppm in the ^1H NMR spectra which are typical for hydroxyl protons involved in intramolecular hydrogen bonds. All the compounds showed hydroxyl vibrational bands between 3495 and 3420 cm^{-1}.

Table 3 The electronic spectra of the ligands (in DMSO)

Compounds	Wavelength in nm (log ε)	
4a CH_3OH	330 (4.280)	
4b CH_3OH	335 (4.320)	
5a CH_3OH	308 (4.150)	424 (3.875)
5b CH_3OH	304 (3.980)	354 (3.635)

The UV spectral behaviours of the compounds were investigated in DMSO. Comparing the UV spectra, it was found that all spectra show strong absorption maxima in the 304–424 nm range with high extinction coefficients. As can be seen from Table 3, the compounds **5a** and **5b** represented two absorption bands; one of which was a $\pi \rightarrow \pi^*$ and the other a $n \rightarrow \pi^*$ transition. However, the other compounds **4a** and **4b** showed only the a $\pi \rightarrow \pi^*$ band because of forbidden $n \rightarrow \pi^*$ transition. Similar results were reported by Zollinger.[30]

None of the four compounds dissolve in water and MeOH, but all are soluble in acetic acid and DMSO. However, they are soluble in 10% HCl and 10% NaOH. Although compounds **4a** and **4b** dissolve in EtOH and acetone easily, compounds **5a** and **5b** are only slightly soluble in these solvents.

Consequently, the results suggested that the structure consists of isolated molecules with van der Waals contacts and that the molecule was essentially planar in the solid state containing a strong intramolecular hydrogen bond between the hydroxyl and azo groups.

The synthesis of compounds by diazo coupling reactions has been defined in the literature,[19] which molecular design of chromogenic calix[4]arene. However, these compounds are of interest among azo group-containing compounds because of their properties as having binding sites for complexation or as chromophores of dyes. We are currently studying these calix[*n*]arene derivatives containing azo groups for their binding properties for metal ions.

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