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# Synthesis Of New Chromogenic Calix(8)arenes

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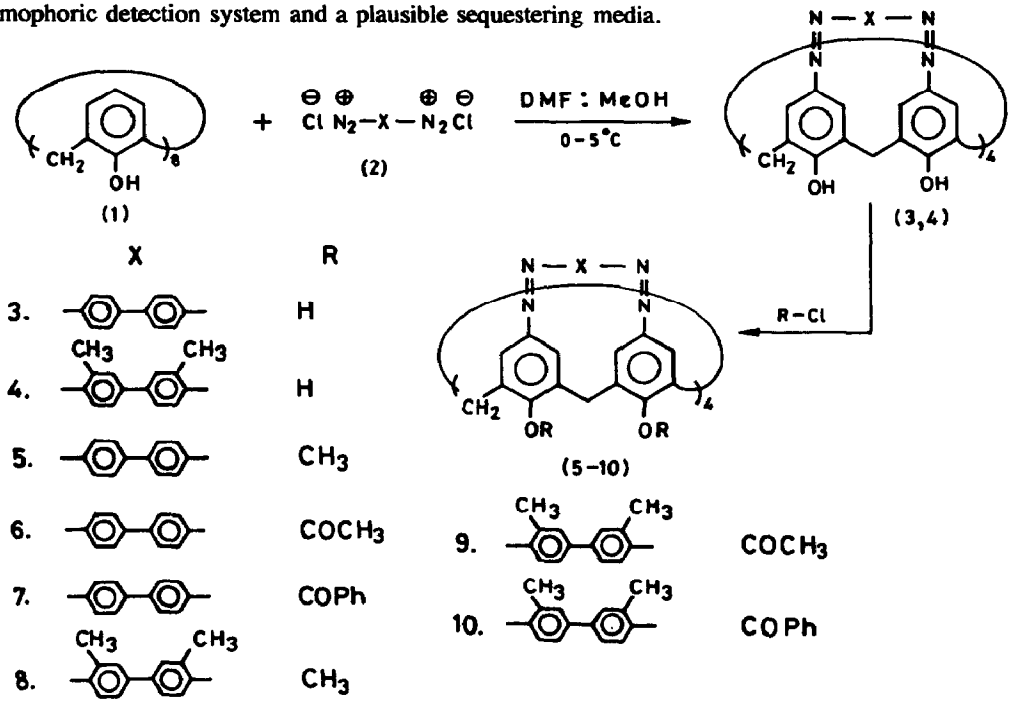
**Abstract** : *Synthesis of new chromogenic calix(8)arenes 3-10 through the coupling of diazotized 4,4'-diaminobiphenyl and octahydroxycalix(8)arenes is described. The synthesized derivatives provide an additional substructure and plausible sequestering media for detection of amines and metal ions.*

Though lot of work has been done on calix(4)arenes[1-5], relatively less attention has been paid to the derivatization of calix(6)arenes[6] and calix(8)arenes despite the fact that their hydroxyls have a comparatively larger difference in $pK_a$ values[7]. Our recent success[8] in calix(8)arene-cerium(IV) promoted biomimetic hydroxylation of simple phenols prompted us to obtain other calix(8)arene derivatives with selectively functionalized hydroxyl groups and additional chromophores. In line with these objectives, we report herein the first examples of chromogenic calix(8)arenes in which the opposite phenyl rings are bridged by the biphenyl bisazo linkage. The new derivatives not only provide an additional substructure but also a new chromophoric detection system and a plausible sequestering media.



Though diazotization and coupling of various amines (p-X-$C_6H_4$-$NH_2$, X = H, OMe, $NO_2$, Me) with Calix(n)arenes (n=4,6,8) did not give easily resolvable diazocalixes, the reaction was successful in the case of 4,4'-diaminobiphenyls. In a typical experiment 4,4'-diaminobiphenyls **2** were diazotised ($NaNO_2$/HCl, 0°C) and reacted with octahydroxycalix(8)arene **1** in DMF: $CH_3OH$ (8:5 V/V) at 0-5°C to yield red solids **3,4**. The analytical samples of these products were obtained by dissolving the dyes in pyridine and reprecipitating them with HCl followed by washing with water.

The synthesized chromogenic compounds gave typical $^1H$ NMR, IR and UV spectra (**Table 1**) which are indicative of the structures given in the reaction scheme. For instance **3** gave a deuterable broad singlet at $\delta$ 8.74 (-OH), two doublets at $\delta$ 7.80 (3,3',5,5'-biphenyl protons) and $\delta$ 7.49 (2,2',6,6'- biphenyl protons) and a multiplet at $\delta$ 6.90-6.81 (calixarene aromatic protons) in its $^1H$ NMR. The methylene protons of calix(8)arene moiety appeared as a singlet at $\delta$ 3.86. The azo (N=N) and hydroxy (-OH) linkages in **3** were observed at 1584 $cm^{-1}$ and 3260 $cm^{-1}$ respectively in its IR spectrum. The structures of **3** and **4** were confirmed by their conversion to **5-10**, by treatment with methyl iodide / NaH, acetyl chloride / pyridine and benzoyl chloride / pyridine respectively. The spectroscopic data for these new compounds are given in **Table 1.**

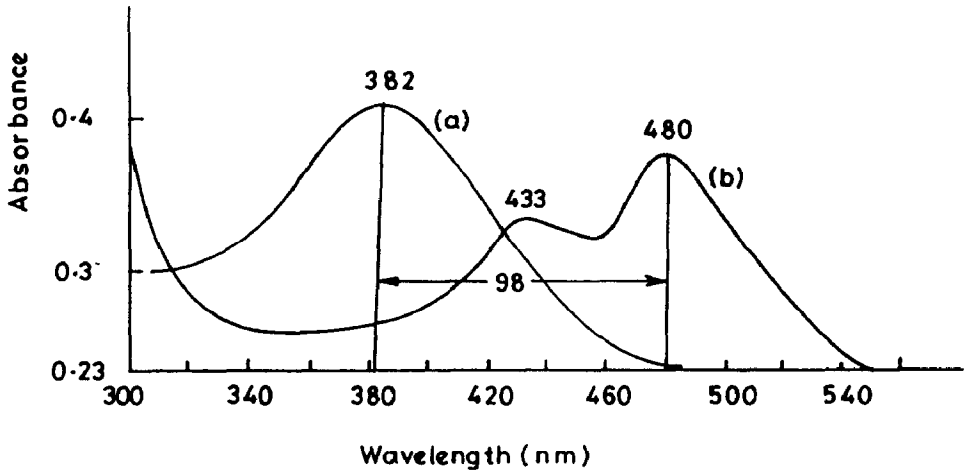



**Fig.1 :** Optical spectrum of **3** in DMSO:Water **(a)** in neutral medium **(b)** in alkaline medium (pH = 11.0) (Solvent effects were eliminated by using blanks)

**3** shows a strong absorption band (**Fig 1**) at $\lambda_{max}$: 382 *nm*, ($\epsilon$ = 5,800 $cm^2$ $mol^{-1}$) in its UV-VIS spectrum while the **5,6** and **7** show absorption bands at 329 *nm*, 342 *nm* and 334 *nm* respectively. When the solution of **3** was made alkaline (with NaOH), it turned red with a bathochromic shift of 98 *nm* along with an intense additional peak at 433 *nm*. No such bathochromic shift was observed in **5, 6** and **7** under alkaline conditions. This change in **3** is probably due to the ionization of hydroxyl groups since the original pale yellow colour was restored upon acidification.

**Table 1**: *Physical and spectroscopic data of new coompounds (3-10)*

| Compound | Colour | Yield (%) | Molecular formula (M.Wt)* | IR ($cm^{-1}$) | $^1H$ NMR ($\delta$) |
|---|---|---|---|---|---|
| 3 | Brownish red | 82 | $C_{104}H_{72}N_{16}O_8$ (1672) | 3260 (-OH) 1584 (N=N) | 8.74(s,8H,OH)7.80(d,16H, J=8Hz,ArH) 7.49 (d,16H, J=7Hz, ArH) 6.90-6.81(m, 16H,ArH) 3.86(s,16H, $ArCH_2Ar$) |
| 4 | Brownish red | 75 | $C_{112}H_{88}N_{16}O_8$ (1784) | 3260(-OH) 1585(N=N) | 8.75(s,8H,OH) 7.78-7.52(m,24H,ArH) 6.90-6.78(m,16H,ArH) 3.89(s,16H, $ArH_2Ar$) 2.52(s,24H,$CH_3$) |
| 5 | Yellow | 88 | $C_{112}H_{88}N_{16}O_8$ (1784) | 1582(N=N) | 7.82-7.59(m,16H,ArH) 7.22(d,16H,J=5Hz,ArH) 6.84(s,16H,ArH) 4.0(s,16H ,$ArCH_2Ar$)3.50(s,24H,$OCH_3$) |
| 6 | Pale Yellow | 70 | $C_{120}H_{88}N_{16}O_{16}$ (2008) | 1712(C=0) 1568(N=N) | 7.86-7.62(m,16H,ArH) 7.24(d,8H,J=9Hz,ArH)7 16 (s,16H,ArH) 6.99(s,8H, ArH)4.29(s,16H,$ArCH_2Ar$) 3.60(s,24H,CO-$CH_3$) |
| 7 | Orange | 65 | $C_{160}H_{104}N_{16}O_{16}$ (2504) | 1740(C=0) 1576(N=N) | 8.18-8.00(m,24H,ArH) 7.75-7.61(m,32H,ArH) 7.28 (s,8H,ArH) 7.24 (s, 8H,ArH) 6.92 (s,16H,ArH) 4.32 (s,16H,$ArCH_2Ar$) |
| 8 | Yellow | 92 | $C_{120}H_{104}N_{16}O_8$ (1896) | 1584(N=N) | 7.85-7.62(m,8H,ArH) 7.36-7.20(m,16H,ArH) 6.92(s,16H,ArH)4.05(s, 16H,$ArCH_2Ar$), 3.50 (s,24H, $OCH_3$), 2.56 (s,24H,-$CH_3$) |
| 9 | Reddish | 76 | $C_{128}H_{104}N_{16}O_{16}$ (2120) | 1715(C=0) 1570(N=N) | 7.8-7.51(m,16H,ArH) 7.32-7.15(m,16H,ArH).6 99 (s,8H,ArH)4.28(s,16H, $ArCH_2Ar$)3.62(s,24H, $COCH_3$)2.51 (s,24H,-$CH_3$) |
| 10 | Orange | 58 | $C_{168}H_{120}N_{16}O_{16}$ (2616) | 1740(C=0) 1594(N=N) | 8.24-8.12(m,16H,ArH) 7.65-7.51(m,24H,ArH) 7.38-7.23(m,16H,ArH)7.14 (s,8H,ArH)6.98(s,16H, ArH)4.35(s,16H,$ArCH_2Ar$) 2.53(s,24H,$CH_3$) |

* As measured by vapour pressure osmometry

These chromogenic derivatives can function as building blocks for new metal ion/organic molecule detection systems which are based upon their plausible complexation / sequestering properties. For example, **3** gives strong 1:1 molecular complexes with various amines [R-$NH_2$ where R=-$(CH_2)_xCH_3$, (x=1,2,3,4), -$CH_2CH(CH_3)CH_3$, -$C(CH_3)_3$ ] as evidenced by the UV-visible spectral analysis and continuous variation plots (For instance Fig.2.). Upon addition of these amines, the $\lambda_{max}$ of **3** was shifted from 382 *nm* to 420 *nm* possibly due to proton transfer (conductometric titrations[9] and other literature precedents[10]). **3** also forms black, brown and orange complexes with transition metal ions (e.g., $Ni^{+2}$, $Co^{+2}$, $Fe^{+2}$, $Cu^{+2}$). Detailed work on molecular /ion recognition by these compounds is under way.

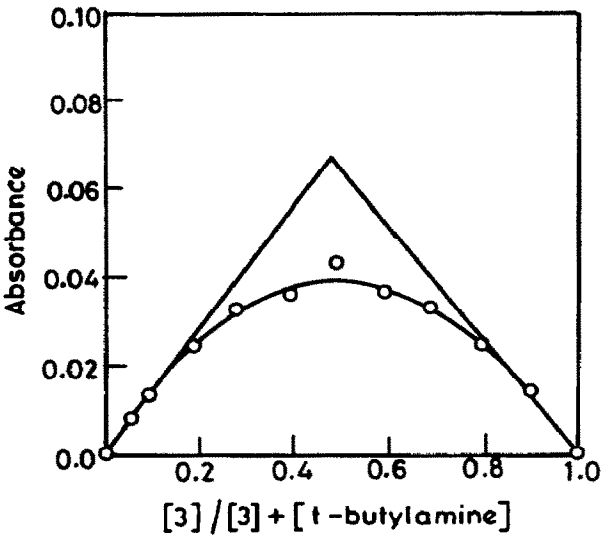



Fig.2 : Continous variation plot for the formation of **3**-t-butylamine complex. (25° DMSO, [**3**] + [amine] = $5.0 \times 10^{-5}$)

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