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# Photochemical synthesis of dibenzo-18-crown-6 ligands containing two 1-hydroxy-2-R-9,10-anthraquinone-9-imino side arms

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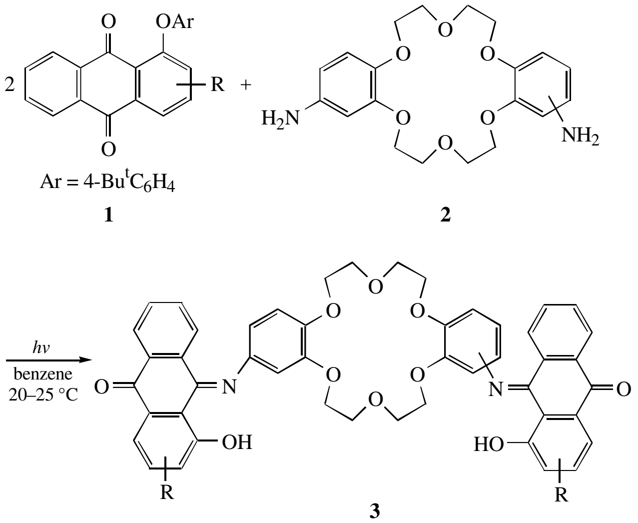
**4,4′- and 4,5′-Bis(1-hydroxy-2-R-9,10-anthraquinone-9-imino)dibenzo-18-crown-6 ethers (novel alkaline-earth cation chemosensors) were synthesised by the photochemical condensation of 1-aryloxy-2-R-9,10-anthraquinones with aromatic diamines containing a 18-crown-6 ether bridge in benzene at room temperature.**

The functionalization of crown ethers with additional ligating, proton-ionisable groups is an effective route to increase metal ion complexing ability and selectivity.[1,2] Double-armed aminophenol-substituted crown ethers can be interesting ionophores due to cooperation between amino and hydroxy groups in binding metal cations.[3] A key point of this investigation is the incorporation of additional proton-ionisable ligating groups with chromophoric abilities onto crown ethers to give complexes with metal ions having novel photophysical properties. In the course of our study on the photorearrangement of 1-aryloxy-9,10-anthraquinones in the presence of alkyl- and arylamines,[4] we have found that 1-aryloxy-2(4)-R-9,10-anthraquinones **1** undergo direct condensation with aromatic diamines containing 18-crown-6 **2** under irradiation, leading in a straightforward manner to 4,4′- and 4,5′-bis[1-hydroxy-2(4)-R-9,10-anthraquinone-9-imino]dibenzo-18-crown-6 ethers **3** (Scheme 1).




| R | | $NH_2$ | R | –N= | *t*/h | yield of **3** (%) |
|---|---|---|---|---|---|---|
| **1a** H | | **2a** 4,4′ | **3a** H | 4,4′ | 8 | 71 |
| **1b** 2-$NH_2$ | | **2a** 4,4′ | **3b** 2-$NH_2$ | 4,4′ | 11 | 68 |
| **1c** 2-NHCOPh | | **2a** 4,4′ | **3c** 2-NHCOPh | 4,4′ | 10 | 75 |
| **1c** 2-NHCOPh | | **2b** 4,5′ | **3d** 2-NHCOPh | 4,5′ | 10 | 78 |
| **1d** 4-NHCOPh | | **2a** 4,4′ | **3e** 4-NHCOPh | 4,4′ | 15 | 70 |

**Scheme 1**

Note that the use of starting compounds **1** with alkyl groups at phenoxy substituents, for example, ArO = 4-Bu$^t$C$_6$H$_4$O, enhances the solubility of these compounds in benzene.

The structure of **3a–e** was assigned on the basis of spectral data (IR, NMR and UV spectroscopy and mass spectrometry) and elemental analysis. The IR spectra of **3a–e** contain characteristic bands due to the vibration of N–H, C=O and C=N groups. Products **3a–e** are brown and have maximums in the visible spectrum region at 417–487 nm (depending on the character and position of the substituent).†

The mechanism of formation of **3** is depicted in Scheme 2. At the initial step, the irradiation of compound **1** gives intermediate 1,10-anthraquinone **4**,[4] which reacts with binucleophile **2** to form unstable compound **5**. Compound **5** eliminates two ArOH molecules to give bis(iminoanthraquinone) **3**.[4]

The interaction of ligands **3a–e** with Na$^+$, K$^+$, Mg$^{2+}$ and Ba$^{2+}$ was studied by UV-visible spectroscopy. In general, complexation with alkali and alkaline-earth metal ions causes small or no changes in ligand absorption spectra. The absorption maxima of free ligands **3a** and **3c** at 417 and 433 nm, respectively, are not shifted by Mg$^{2+}$. However, new absorption bands appeared for Mg$^{2+}$–**3a** and Mg$^{2+}$–**3c** complexes at 451 and 473 nm, respectively (Table 1).

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† The IR spectra were recorded on a Vector-22 spectrophotometer (Bruker) in KBr pellets. The electronic absorption spectra were measured on a Hewlett-Packard Agilent 8453 spectrophotometer (for 1×10$^{-4}$ M solutions in EtOH). The $^1$H and $^{13}$C NMR spectra were recorded in CDCl$_3$ solutions on a Bruker WP-200SY instrument with Me$_4$Si as the internal standard. The mass spectra were obtained on a Finnigan MAT-8200 instrument. The TLC analysis was performed on Silufol UV-254 plates using a 9:1 toluene–ethanol mixture as the eluent. Column chromatography was performed using silica gel (140–350 mesh). Solvents of reagent grade were dried before use. Starting materials **1a–d**, **2a**,**b** were synthesised according to the published procedures.[5,6]

*Typical procedure for the preparation of* **3a–e**. 1-(*p-tert*-Butylphenoxy)-2(or 4)-benzoylamino-9,10-anthraquinone **1a–d** (1.3 mmol) was dissolved in 0.5 l of dry benzene; then, diamine **2a** or **2b** (0.65 mmol) was added, and the solution was irradiated with sunlight for 8–15 h until the disappearance of initial compound **1a–d** (TLC monitoring). Photolysis was performed at 20–25 °C with the complete spectrum of a CVD-120A Hg lamp or with the sunlight. The reaction mixture was evaporated in a vacuum at 30 °C. The residue was washed with hexane, filtered off, purified by column chromatography in CHCl$_3$ and crystallised from a benzene–ethanol mixture (1:1).

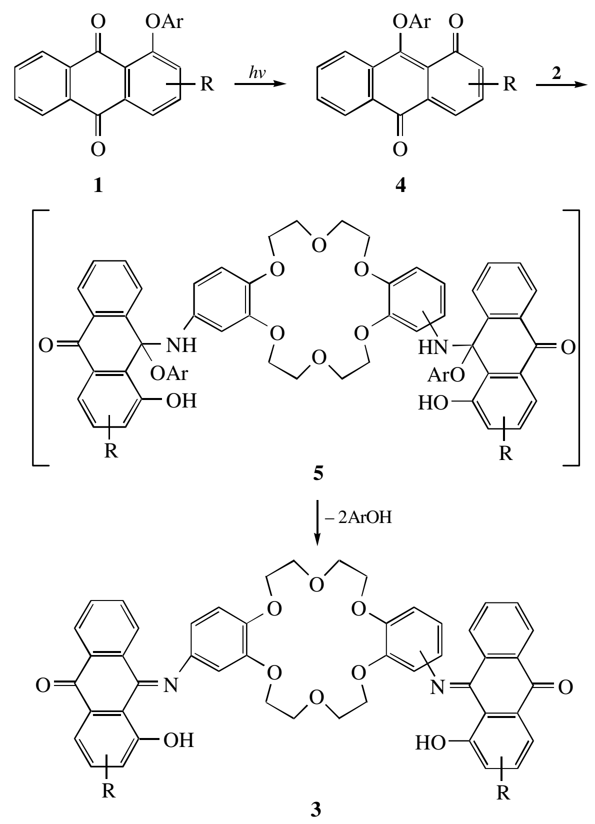
**3a**: mp 273–276 °C. $^1$H NMR, $\delta$: 3.75–4.15 (m, 16H, OCH$_2$CH$_2$), 6.87–8.00 (m, 18H, arom. H), 15.55 (s, 2H, OH). IR ($\nu$/cm$^{-1}$): 3432 (OH), 3073, 3067 (arom. CH), 2954, 2918 (CH$_2$), 1671, 1630 (C=O, C=N), 1604, 1591 (C=C). MS, *m/z*: 802 (M$^+$). Found (%): C, 72.36; H, 5.01; N, 3.73. Calc. for C$_{48}$H$_{38}$N$_2$O$_{10}$ (%): C, 71.81; H, 4.77; N, 3.49.

**3b**: mp 148–151 °C. $^1$H NMR, $\delta$: 3.89–4.17 (m, 16H, OCH$_2$CH$_2$), 4.73 (s, 4H, NH$_2$), 6.83–8.18 (m, 18H, arom. H), 16.61 (s, 2H, OH). IR (KBr, $\nu$/cm$^{-1}$) 3493 (OH), 3387 (NH$_2$), 3069, 3041 (arom. CH), 2965, 2938 (CH$_2$), 1665, 1660 (C=O, C=N), 1605, 1590 (C=C). MS, *m/z*: 832 (M$^+$). Found (%): C, 68.78; H, 4.61; N, 6.93. Calc. for C$_{48}$H$_{40}$N$_4$O$_{10}$ (%): C, 69.22; H, 4.84; N, 6.73.

**3c**: mp 173–176 °C. $^1$H NMR, $\delta$: 4.05–4.21 (m, 16H, OCH$_2$CH$_2$), 6.64–8.94 (m, 28H, arom. H), 9.25 (s, 2H, NH), 17.13 (s, 2H, OH). $^{13}$C NMR, $\delta$: 76.2–77.51 (m, OCH$_2$CH$_2$), 147.5 (s, C$^2$), 154.9 (s, C$^1$), 160.1 (s, C$^9$), 181.7 (s, C$^{10}$). IR (KBr, $\nu$/cm$^{-1}$): 3356 (NH), 3069, 3036 (arom. CH), 2962, 2928 (CH$_2$), 1682, 1662 (C=O, C=N), 1591, 1513 (C=C). MS, *m/z*: 1040 (M$^+$). Found (%): C, 71.37; H, 4.73; N, 5.09. Calc. for C$_{62}$H$_{48}$N$_4$O$_{12}$ (%): C, 71.53; H, 4.64; N, 5.38.

**3d**: mp 165–169 °C. $^1$H NMR, $\delta$: 3.95–4.19 (m, 16H, OCH$_2$CH$_2$), 6.16–8.83 (m, 28H, arom. H), 9.29 (s, 2H, NH), 17.19 (s, 2H, OH). IR ($\nu$/cm$^{-1}$): 3386 (NH), 3073 (arom. CH), 2962, 2930 (CH$_2$), 1673, 1657 (C=O, C=N), 1591 (C=C). MS, *m/z*: 1040 (M$^+$). Found (%): C, 71.14; H, 4.98; N, 5.45. Calc. for C$_{62}$H$_{48}$N$_4$O$_{12}$ (%): C, 71.53; H, 4.64; N, 5.38.

**3e**: mp 135–140 °C. $^1$H NMR, $\delta$: 3.90–4.18 (m, 16H, OCH$_2$CH$_2$), 6.88–9.13 (m, 28H, arom. H), 9.29 (s, 2H, NH), 13.24 (s, 2H, NH), 15.50 (s, 2H, OH). IR ($\nu$/cm$^{-1}$): 3446 (OH, NH), 3181, 3063 (arom. CH), 2982, 2941 (CH$_2$), 1671, 1633 (C=O, C=N), 1590 (C=C). Found (%): C, 72.03; H, 4.65; N, 5.61. Calc. for C$_{62}$H$_{48}$N$_4$O$_{12}$ (%): C, 71.53; H, 4.65; N, 5.38.



**Scheme 2**

A comparison of the spectral data for the $Mg^{2+}$–**3a**–**c** complexes shows that the presence of the donor 2-amino group in the anthraquinone moiety of $Mg^{2+}$–**3b** complex prevents from the appearance of new absorption peaks. On the other hand, a stronger electron-withdrawing group such as NHCOPh in the same position of the anthraquinone moiety of $Mg^{2+}$–**3c** complex leads to a significant change in the absorption bands (Table 1).

In summary, we developed a convenient method for the construction of dibenzo-18-crown-6 ligands containing two 1-hydroxy-2(4)-R-9,10-anthraquinone-9-imino side arms as new metal ion receptors. The spectral properties of **3a** and **3c** may make them useful selective sensors for $Mg^{2+}$.[2]

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**Table 1** Absorption maxima in UV-visible spectra of free and complexed **3a**–**d** with different metal ions $M^+$ in MeCN; [L]/[$M^+$] = 1:100.

| $M^+$ | $\lambda_{max}$ ($\Delta\lambda_{max}$)/nm | | | | |
|---|---|---|---|---|---|
| | **3a** | **3b** | **3c** | **3d** | **3e** |
| – | 417 | 461 | 433 | 436 | 487 |
| $Na^{+\,a}$ | 415 (–2) | 457 (–4) | 432 (–1) | 432 (–4) | 485 (–2) |
| $K^{+\,b}$ | 411 (–6) | 454 (–7) | 432 (–1) | 433 (–3) | 479 (–8) |
| $Mg^{2+\,a}$ | 416 (–1)<br>451 (+34) | 457 (–4) | 432 (–1)<br>473 (+40) | 437 (+1) | 487 (0) |
| $Ba^{2+\,a}$ | 414 (–3) | 452 (–9) | — | 427 (–7) | 471 (–16) |

[a]As perchlorate. [b]As thiocyanate.

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