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Pyridinium *N*-Phenoxide Betaines and Their Application to the Characterization of Solvent Polarities, XX<sup>[1]</sup>

## Synthesis, Solvatochromism, and Halochromism of Chromoionophoric Crown Ether-Substituted Pyridinium *N*-Phenolate Betaine Dyes<sup>[2]</sup>

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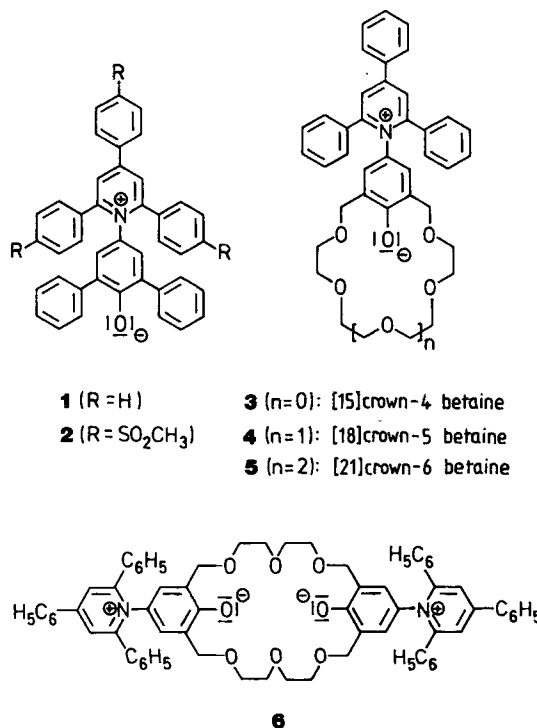
**Synthesis,** negative solvatochromism (Table 1, Figure 1), and negative halochromism (Tables 2–3, Figures 2–3) of the new crown ether-substituted pyridinium *N*-phenolate betaine dyes **3–6** are described. In contrast to other known chromoionophores, **3–5** exhibit a cation-selective negative halochromism, which manifests itself as a hypsochromic shift of the long-wavelength intramolecular charge-transfer (CT) absorption band of the betaine chromophore on addition of salts. As this

CT absorption band lies within the visible spectral region, the cation-induced colour change can be followed easily by eye, which suggests an application of these new chromoionophoric betaine dyes as cation indicators. The halochromism of **3–6** constitutes a new type of true halochromism, in contrast to the trivial halochromism first defined by Baeyer and Villiger in 1902.

The position of the longest-wavelength absorption band in the UV/Vis solution spectra of the pyridinium *N*-phenolate betaine dye **1** depends on the polarity of the solvent (solvatochromism), the temperature of the solution (thermochromism), the external pressure applied to the solution (piezochromism), the nature and concentration of added salts (halochromism), and possibly – in the case of chiral betaine dyes – on the configuration of enantiomerically pure, homochiral solvents (chiro-solvatochromism)<sup>[4,5]</sup>. The unusually large negative solvatochromism of **1** has been used to introduce spectroscopically derived empirical parameters of solvent polarity, the so-called  $E_T(30)$ -values<sup>[6]</sup>, which are known for numerous solvents and many binary solvent mixtures<sup>[4–6]</sup>. The use of the better water-soluble tris(methanesulfonyl)-substituted betaine dye **2** has enabled us recently to determine the  $E_T(30)$  values for aqueous electrolyte solutions<sup>[7]</sup>. The possibility of determining empirically the polarity of aqueous and nonaqueous electrolyte solutions by means of solvatochromic dyes such as **1** and **2** has recently led to many investigations by us<sup>[1,2,7,8]</sup> and others<sup>[9–17]</sup> of the halochromism of **1** and **2**, caused by the addition of inophores<sup>[18]</sup> to solutions of **1** and **2** at room temperature.

It has been shown<sup>[1,17]</sup> that the salt-induced negative halochromism<sup>[19]</sup> of **1** and **2** stems mainly from an ion-pairing between the cation, delivered from the salt added, and the phenoxide part of the betaine dye. There is even a linear correlation between the halochromic band shifts and the charge-to-size ratio (effective charge) of the cations, at least in acetonitrile as solvent<sup>[1,14]</sup>. This cation-influenced negative halochromism<sup>[19]</sup> should be enhanced and made more cation-selective by the introduction of crown ether rings into the phenolate moiety of **1**. For this reason, we have synthesized and UV/Vis-spectroscopically studied the new chromoionophoric<sup>[20]</sup> betaine dyes **3–6**, which have several advantages over the chromoionophoric dyes known to

date<sup>[21]</sup>. The crown ether-substituted betaine dyes **3–6** possess cavities capable of binding suitable guest species such as alkaline metal cations by means of ion/dipole interactions – with concomitant colour changes in the visible spectral range as desirable result. Because the intensity of the long-wavelength charge-transfer (CT) absorption band of **1**<sup>[22]</sup> (and of **2–5**) is rather low ( $\epsilon$  ca.  $300\text{--}800\text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ),



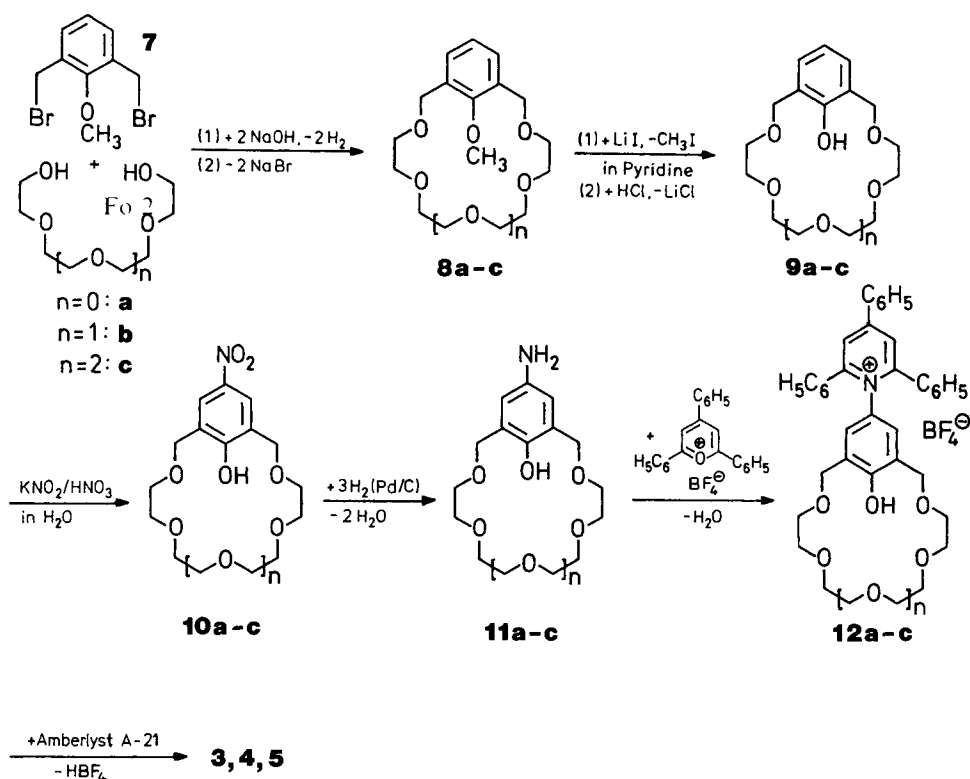


Table 1. Empirical parameters of solvent polarity,  $E_T(30)$ , long-wavelength intramolecular CT absorption maxima of dyes 3–6, and their corresponding transition energies,  $E_T$ , measured in 17 solvents of different polarity at 25°C

Solvents	$E_T(30)^a)$ $\text{kcal} \cdot \text{mol}^{-1}$	$\lambda_{\text{max}}(3)$ nm	$E_T(3)^b)$ $\text{kcal} \cdot \text{mol}^{-1}$	$\lambda_{\text{max}}(4)$ nm	$E_T(4)^b)$ $\text{kcal} \cdot \text{mol}^{-1}$	$\lambda_{\text{max}}(5)$ nm	$E_T(5)^b)$ $\text{kcal} \cdot \text{mol}^{-1}$	$\lambda_{\text{max}}(6)$ nm	$E_T(6)^b)$ $\text{kcal} \cdot \text{mol}^{-1}$
Water	63.1	428.7	66.7	433.0	66.0	430.5	66.4	433.0	66.0
Ethane-1,2-diol	56.3	473.2	60.4	469.9	60.8	472.8	60.5	445.0	64.2
Methanol	55.4	479.0	59.7	477.4	59.9	477.5	59.9	473.7	60.3
Propane-1,2-diol	54.1	–	–	–	–	–	–	476.6	60.0
Ethanol	51.9	494.6	57.8	484.5	59.0	497.5	57.5	479.6	59.6
1-Propanol	50.7	509.0	56.2	506.2	56.5	507.0	56.4	503.8	56.7
1-Butanol	50.2	515.3	55.5	512.2	55.8	512.1	55.8	511.5	55.9
3-Methyl-1-butanol	49.0	524.3	54.5	522.2	54.7	521.7	54.8	–	–
2-Propanol	48.4	537.0	53.2	532.2	53.7	533.5	53.6	520.2	55.0
2-Butanol	47.1	551.0	51.9	544.6	52.5	545.0	52.5	540.3	52.9
Acetonitrile	45.6	580.8	49.2	588.3	48.6	583.2	49.0	576.2	49.6
Dimethyl sulfoxide	45.1	600.2	47.6	603.0	47.4	608.8	47.0	605.9	47.2
Acetone	42.2	620.4	46.1	620.4	46.1	625.8	45.7	615.3	46.5
1-Methylpyrrolidin-2-one	42.2	615.7	46.4	630.7	45.3	637.4	44.8	–	–
1,2-Dichloroethane	41.3	643.2	44.4	642.5	44.5	647.4	44.2	627.1	45.6
Dichloromethane	40.7	647.0	44.2	646.8	44.2	649.9	44.0	626.3	45.6
Pyridine	40.5	653.8	43.7	662.6	43.1	662.7	43.1	653.7	43.7
Chloroform	39.1	665.9	42.9	667.9	42.8	661.8	43.2	659.2	43.4
Tetrahydrofuran	37.4	–	–	–	–	–	–	692.7	41.3
$\Delta\lambda^c)$ resp. $\Delta E_T^d)$	24.0	–237.2	23.8	–234.9	23.2	–231.3	23.2	–226.2	22.6

<sup>a)</sup>  $E_T(30)$  values were taken from ref. [4]. – <sup>b)</sup>  $E_T [\text{kcal} \cdot \text{mol}^{-1}] = 28591/\lambda_{\text{max}} [\text{nm}]$  [6]. – <sup>c)</sup>  $\Delta\lambda = \lambda_{\text{max}}(\text{H}_2\text{O}) - \lambda_{\text{max}}(\text{CHCl}_3)$ . – <sup>d)</sup>  $\Delta E_T = E_T(\text{H}_2\text{O}) - E_T(\text{CHCl}_3)$ .

the symmetric bis-chromophoric dye **6** has been prepared in order to overcome this drawback.

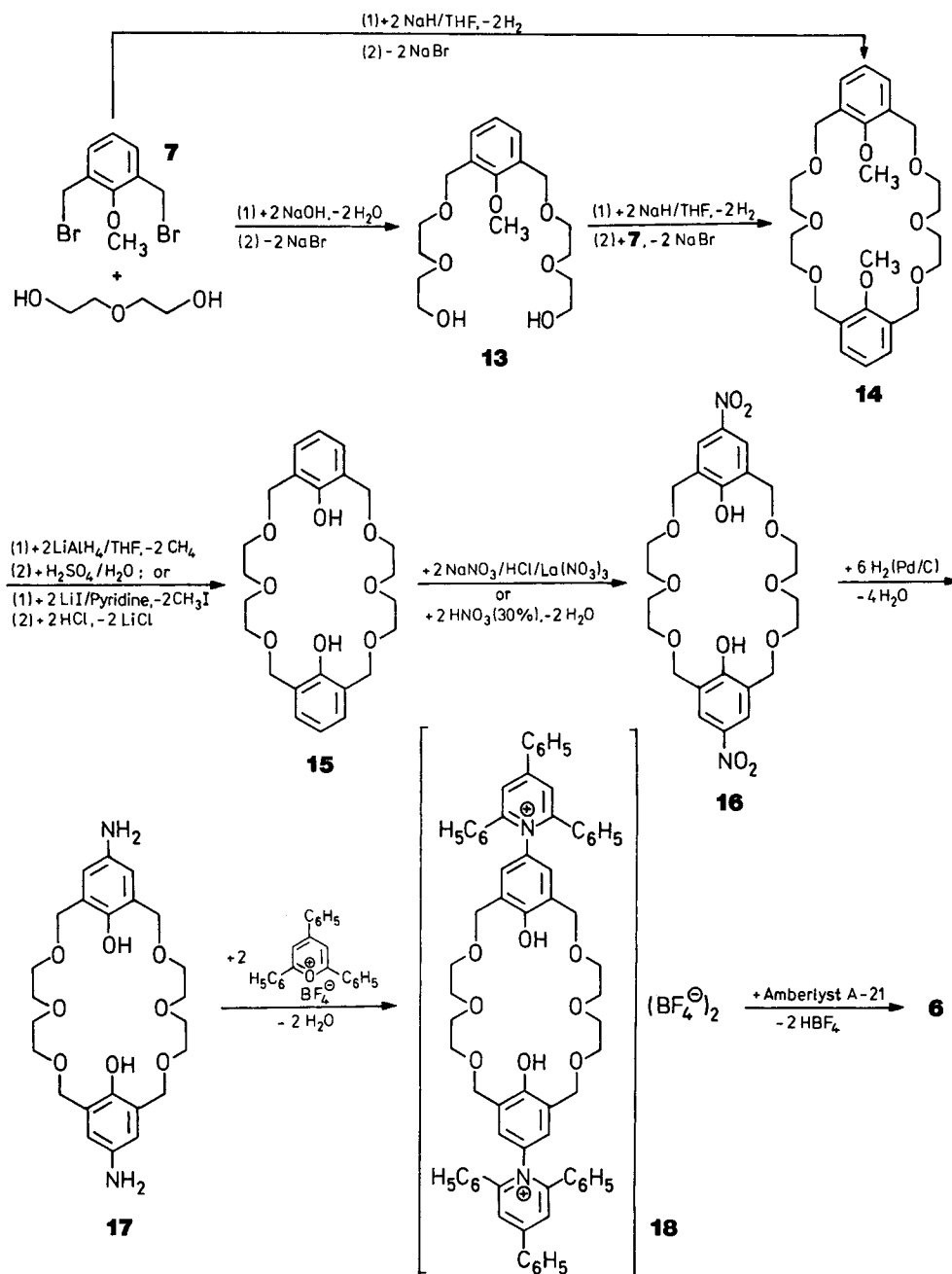
Based on recent work of McKervey et al. on phenolic crown ethers<sup>[23]</sup>, we have synthesized dyes **3–5** as depicted in the scheme.

A solution of 2,6-bis(bromomethyl)anisole (**7**)<sup>[24,25]</sup>, tri-, tetra- or pentaethylene glycol, and sodium hydride in THF is transformed into the crown ether-substituted anisoles **8a–c** (yields 37–52%), which are demethylated with lithium iodide in boiling pyridine<sup>[23,26]</sup> to give the phenols **9a–c** (yields 61–86%). Careful nitration of **9a–c** with potassium nitrite in dilute nitric acid at room temperature to the 4-nitrophenols **10a–c** (yields 67–86%), followed by catalytic reduction with hydrogen in methanol to the extremely oxygen-sensitive 4-aminophenols **11a–c** (yields 93–99%) and

treatment immediately thereafter with 2,4,6-triphenylpyrylium tetrafluoroborate<sup>[27]</sup> in dichloromethane/AcOH affords the 1-(4-hydroxyphenyl)pyridinium salts **12a–c** (yields 78–86%), which are deprotonated practically quantitatively to the betaine dyes **3–5** with a basic ion-exchange resin (Amberlyst A-21) suspended in dichloromethane. The normal deprotonation of **12a–c** with sodium methanolate in methanol<sup>[6]</sup> does not yield salt-free betaines **3–5** because of their excellent cation complexing properties.

The bis-betaine dye **6** is analogously prepared by starting with **7** and diethylene glycol to give the bis-anisole **14** either directly in low yield or better via the bis(hydroxyethoxymethyl)anisole **13** with satisfactory yield<sup>[28]</sup>.

The demethylation of **14** with lithium iodide in pyridine<sup>[23,26]</sup> gives the bis-phenol **15** in very low yield only.



More successful is the demethylation of **14** with  $\text{LiAlH}_4$  in boiling THF<sup>[29,30]</sup>. Because of the low solubility of **15** in water, its nitration to **16** is carried out in a 4:1 mixture of *n*-hexane and diethylene glycol diethyl ether, or better with sodium nitrate/concd. HCl and catalytic amounts of lanthanum(III) nitrate in a mixture of diethyl ether/dichloromethane/water<sup>[31]</sup>. Catalytic reduction of **16** with hydrogen to the bis-aminophenol **17**, followed immediately by treatment with 2,4,6-triphenylpyrylium tetrafluoroborate<sup>[27]</sup>, affords the bis-pyridinium salt **18**, the deprotonation of

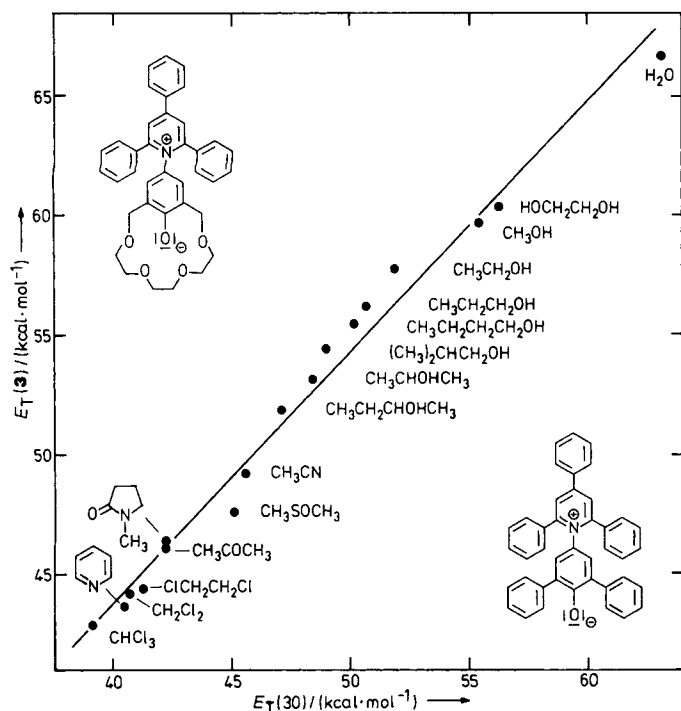


Figure 1. Linear correlation between the  $E_T(30)$  values of standard dye **1** and the  $E_T(3)$  values of [15]crown-4 betaine dye **3**, measured in 17 solvents of different polarity at 25 °C (cf. Table 1). Correlation equation:  $E_T(3) = 1.052 \cdot E_T(30) + 1.730$  (pairs of values  $n = 17$ , correlation coefficient  $r = 0.992$ , standard deviation of the estimate  $s = 0.927$ ). The corresponding correlation equations for [18]crown-5 betaine **4**, [21]crown-6 betaine **5**, and the bis-betaine **6** are:

$$E_T(4) = 1.072 \cdot E_T(30) + 0.828 \quad (n = 17, r = 0.984, s = 1.335)$$

$$E_T(5) = 1.074 \cdot E_T(30) + 0.572 \quad (n = 17, r = 0.987, s = 1.190)$$

$$E_T(6) = 1.078 \cdot E_T(30) + 1.241 \quad (n = 17, r = 0.981, s = 1.549)$$

Table 2. Long-wavelength UV/Vis absorption maxima of dyes **3–6** [ $c(\text{betaine}) = 1 \cdot 10^{-3} \text{ mol/l}$ ], measured in methanol and acetonitrile at 25 °C without and with added salts, as well as salt-induced band shifts [rounded values of  $\Delta\lambda = \lambda_{\text{max}}(\text{without salt}) - \lambda_{\text{max}}(\text{with salt})$  in parentheses] after the addition of various iodides [ $c(\text{salt}) = 1 \cdot 10^{-2} \text{ mol/l}$ ]

Salts <sup>[a]</sup>	$\lambda_{\text{max}}(3)/\text{nm}$		$\lambda_{\text{max}}(4)/\text{nm}$		$\lambda_{\text{max}}(5)/\text{nm}$		$\lambda_{\text{max}}(6)/\text{nm}$
	CH <sub>3</sub> OH	CH <sub>3</sub> CN	CH <sub>3</sub> OH	CH <sub>3</sub> CN	CH <sub>3</sub> OH	CH <sub>3</sub> CN	CH <sub>3</sub> CN
Without salt	479.0	580.8	477.4	588.3	477.5	583.2	576.2
+ ( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N <sup>+</sup> I <sup>−</sup>	470.7(8)	550.2(31)	470.2(7)	550.4(38)	473.8(4)	556.0(27)	—
+ CsI	475.5(4)	534.1(47)	463.5(14)	524.2(64)	457.3(20)	502.7(81)	574.3(2)
+ RbI	473.0(6)	537.1(44)	457.0(20)	515.7(73)	461.4(16)	527.8(55)	524.0(52)
+ KI	469.9(9)	524.8(56)	454.6(23)	—	472.1(5)	529.0(54)	482.3(94)
+ NaI	460.3(19)	488.8(92)	465.9(12)	464.3(124)	473.4(4)	475.7(108)	477.8(98)
+ LiI	—	—	—	—	—	—	409.8(166)
$\Delta\lambda$ is at maximum for	Na <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Na <sup>+</sup>	Cs <sup>+</sup>	Na <sup>+</sup>	Li <sup>+</sup>

<sup>[a]</sup> Salts in order of increasing effective charge (ratio ion charge/Pauling cation radius) of the corresponding cation.

which with a basic ion-exchange resin (Amberlyst A-21) leads to the bis-betaine dye **6** in satisfactory yields.

The structure of all new compounds has been proved by elemental analysis, UV/Vis, IR, mass, <sup>1</sup>H-, and <sup>13</sup>C-NMR spectra. The betaine dyes **3–6** are obtained as dark-red, powdery, hygroscopic crystals without sharp melting point, still containing some dichloromethane, even after drying in vacuo at elevated temperatures.

Like **1** and **2**, the dyes **3–6** show a pronounced negative solvatochromism, as measured in 17 solvents of different polarity (Table 1).

Table 3. Long-wavelength UV/Vis absorption maxima of dyes **3–5** [ $c(\text{betaine}) = 1 \cdot 10^{-3} \text{ mol/l}$ ], measured in methanol at 25 °C without and with added salts, as well as salt-induced band shifts [rounded values of  $\Delta\lambda = \lambda_{\text{max}}(\text{without salt}) - \lambda_{\text{max}}(\text{with salt})$  in parentheses] after the addition of various potassium salts [ $c(\text{salt}) = 1 \cdot 10^{-2} \text{ mol/l}$ ]

Salts <sup>[a]</sup>	$\lambda_{\text{max}}(3)/\text{nm}$	$\lambda_{\text{max}}(4)/\text{nm}$	$\lambda_{\text{max}}(5)/\text{nm}$
Without salt	479.0	477.4	477.5
+ KI	469.9(9)	454.6(23)	472.1(5)
+ KCl	471.2(8)	458.1(19)	470.6(7)
+ KF	470.9(8)	458.2(19)	470.3(7)

<sup>[a]</sup> Salts in order of increasing effective charge (ratio ion charge/Pauling anion radius) of the corresponding anion.

Thus, by changing the solvent from nonpolar chloroform to polar water, the long-wavelength UV/Vis absorption band of **3–6** undergoes a hypsochromic shift of about 230 nm (!), which corresponds to an increase of their molar transition energies  $E_T$ <sup>[6]</sup> of about 23 kcal/mol (Table 1). With increasing solvent polarity, the highly dipolar electronic ground state of these betaine dyes is increasingly stabilized by solvation, relative to the less dipolar excited state – with the observed hypsochromic band shift as consequence. The completely analogous solvent-dependent behaviour of the crown ether dyes **3–6** with respect to standard dye **1** is demonstrated by the linear correlation between the  $E_T(30)$  values of **1** and the corresponding  $E_T$  values of **3–6** (Table 1), as exemplarily shown for the [15]crown-4-betaine dye **3** in Figure 1.

The halochromism of dyes **3–6** has been studied in two solvents of different polarity, methanol and acetonitrile, after the addition of a tenfold excess of tetra-*n*-butylammonium iodide and alkaline halides with systematic variation of the cation (Table 2) and the anion (Table 3).

In all cases, a hypsochromic salt-induced band shift is obtained on the addition of electrolytes (ionophores) to solutions of **3–6** in both solvents. Whereas the anions of the added alkaline halides ( $F^-$ ,  $Cl^-$ , and  $I^-$ , as potassium salts) exert only a rather small influence on the observed halochromic band shifts ( $\Delta\lambda \approx 5\text{--}23\text{ nm}$ ; cf. Table 3), the corresponding halochromic band shifts caused by a variation of the cation ( $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $Rb^+$ ,  $Cs^+$ ,  $n\text{-Bu}_4N^+$ , as iodides) are much larger and strongly dependent on the nature of the cation ( $\Delta\lambda$  up to  $166\text{ nm}$ ; cf. Table 2). Obviously, the negative halochromism<sup>[19]</sup> of **3–6** is mainly determined by the nature (size, effective charge) of the cation. However, with tetra-*n*-butylammonium iodide in methanol and acetonitrile, a significantly smaller, but for all three dyes practically equally large, hypsochromic shift is obtained for **3–5**. This must be due to a more general nonspecific halochromism because tetraalkylammonium ions are not prone to ion-pairing for steric reasons<sup>[1]</sup>.

This cation-influenced negative halochromism has already been found with the betaine dyes **1**<sup>[1,2,10,13,16,17]</sup> and **2**<sup>[7]</sup>, the halochromic band shifts of both dyes being correlated

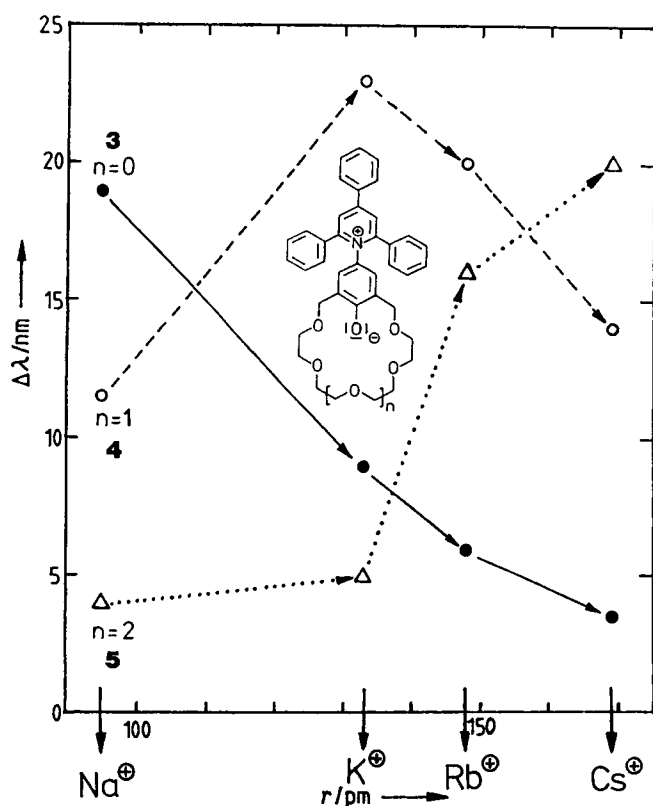


Figure 2. Cation-selective negative halochromism of dyes **3–5**, measured in methanol at  $25^\circ\text{C}$  as a function of Pauling's cation radius  $r$  of the corresponding alkali metal iodides NaI, KI, RbI, and CsI (betaine dye concentration ca.  $10^{-3}\text{ mol/L}$ ; salt concentration  $10^{-2}\text{ mol/L}$ ).  $\Delta\lambda = \lambda_{\text{max}}(\text{without salt}) - \lambda_{\text{max}}(\text{with salt})$

(sometimes linearly) with the effective charge of the cation (ion charge/Pauling's cation radius) of the alkali and alkaline earth salts added<sup>[1]</sup>. In addition to this more general halochromic behaviour, the crown ether dyes **3–5** exhibit a more cation-selective halochromism as shown in Figure 2 for solutions of **3–5** in methanol.

It follows from the dependence of the halochromic shifts ( $\Delta\lambda$ ) of **3–5** on the size of the alkali metal cation of the iodide salt added that [15]crown-4 betaine **3** complexes preferably  $Na^+$ , [18]crown-5 betaine **4**  $K^+$ , and [21]crown-6 betaine **5**  $Cs^+$ , at least in methanol. Treatment of the  $Na^+$ -selective dye **3** in methanol with a mixture of Na, K, Rb, and Cs iodide causes a hypsochromic band shift as if NaI alone were added. On addition of lithium<sup>[13]</sup> and alkaline earth metal salts to solutions of **3–5** in methanol or acetonitrile, the long-wavelength halochromic absorption band of **3–5** disappears, which corresponds to a more intense cation complexation with the phenolate moiety (formation of contact ion pairs), similar to the effect of protonation of **3–5** which also causes a disappearance of the absorption band in the visible range.

The long-wavelength UV/Vis absorption band of the betaines **1–6** is caused by an intramolecular charge-transfer (CT) transition, through which charge is transported from the electron-donating phenolate to the electron-accepting pyridinium moiety (interplanar angle between pyridinium and phenolate ring =  $65^\circ$ <sup>[32]</sup>). This follows from the dramatic decrease of the permanent ground-state dipole moment on excitation ( $\mu_g = 49 \cdot 10^{-30}\text{ Cm}$ <sup>[33a]</sup>  $\xrightarrow{h\nu}$   $\mu_e = 20 \cdot 10^{-30}\text{ Cm}$ <sup>[33b]</sup>;  $\Delta\mu = 29 \cdot 10^{-30}\text{ Cm} = 8.7\text{ D}$ ) and from recent quantum-chemical HMO calculations<sup>[34]</sup>. The position of such CT absorption bands depends on the ionization energy of the electron donor and on the electron affinity of the electron acceptor<sup>[35]</sup>. Thus, the introduction of electron-withdrawing substituents into the 4-phenylpyridinium ring of **1** increases its electron affinity and causes a bathochromic shift of the CT band of **1**<sup>[36]</sup>, whereas hydrogen-bond donor (HBD) solvents increase, by means of H bonding to the oxygen atom, the ionization energy of the phenoxide part of **1**, with a hypsochromic CT band shift as a consequence<sup>[36]</sup>.

In the same way, the crown ether-mediated complexation of the phenolate moiety of **3–5** by suitable cations results in a hypsochromic shift of the CT band, because the electrostatic  $O^-/M^+$  interaction increases the ionization energy of the electron donor part of the dye molecule, while the electron affinity of the electron acceptor moiety remains unaffected. The comparably small salt-induced band shifts observed with a variation of the anion (see Table 3) points to the fact that there is obviously no ion-pairing between the pyridinium ring of **3–5** and the anion of the salt added, presumably because of the high delocalization of the positive charge in the triphenylpyridinium moiety.

For the sodium-selective [15]crown-4 betaine dye **3**, the equilibrium constant  $K_c$  (using a molarity scale for concentrations) for the 1:1 cation/dye complexation has been determined UV/Vis-spectroscopically in acetonitrile with sodium and potassium iodide. Addition of increasing amounts of sodium iodide to a  $3 \cdot 10^{-4}\text{ M}$  solution of **3** in acetonitrile leads to a family of curves which meet at an isosbestic point (see Figure 3).

In accordance with an equilibrium  $M + L \rightleftharpoons ML$  between the metal cation  $M$  and the crown ether ligand  $L$ , the equilibrium constant  $K_c = c_{ML}/(c_M \cdot c_L)$  can be determined by means of equation

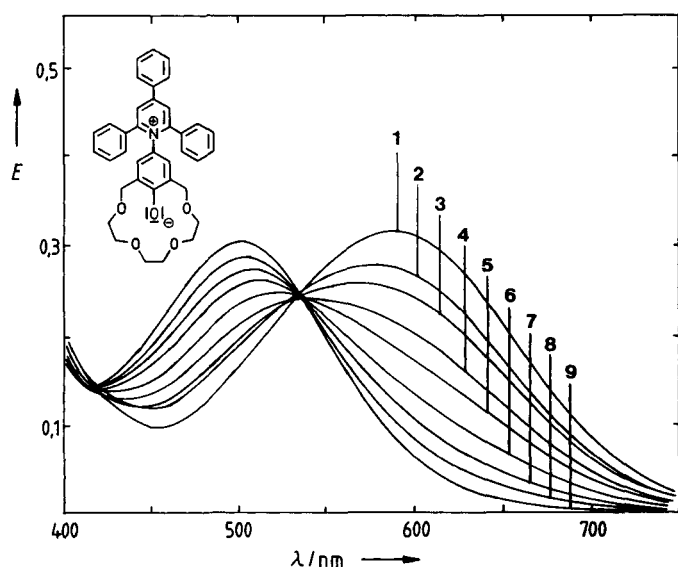


Figure 3. UV/Vis absorption spectra of [15]crown-4 betaine dye **3**, measured in acetonitrile at 20°C before [curve 1:  $\lambda_{\max} = 588$  nm,  $c(\mathbf{3}) = 3 \cdot 10^{-4}$  mol/l] and after the addition of sodium iodide:  $c(\text{NaI}) = 1 \cdot 10^{-5}$  mol/l (curve 2),  $2 \cdot 10^{-5}$  mol/l (curve 3),  $3 \cdot 10^{-5}$  mol/l (curve 4),  $4 \cdot 10^{-5}$  mol/l (curve 5),  $5 \cdot 10^{-5}$  mol/l (curve 6),  $6 \cdot 10^{-5}$  mol/l (curve 7),  $7 \cdot 10^{-5}$  mol/l (curve 8), and  $8 \cdot 10^{-5}$  mol/l (curve 9;  $\lambda_{\max} = 500$  nm). Isosbestic point at ca. 534 nm

(1)<sup>[37]</sup>), (which is valid only for  $c_M \gg c_L$ ; for details see ref.<sup>[3]</sup>), with  $A$  and  $A_0$  representing the absorbance of the free ligand  $L$  and the

$$\frac{A_0}{A_0 - A} = \frac{\varepsilon_L}{\varepsilon_L - \varepsilon_{ML}} \cdot \left( \frac{1}{K_c \cdot c_M} + 1 \right) \quad (1)$$

metal cation/ligand complex  $ML$  in solution at a given wavelength, as well as  $\varepsilon_L$  and  $\varepsilon_{ML}$  denoting the molar decadic extinction coefficients of the free ligand and the complex, respectively, and  $c_M$  the molar concentration of the metal cation. The variation in absorbance has been monitored at the wavelength of maximal absorption. Plotting  $A_0/(A_0 - A)$  against  $1/c_M$  yields a straight line with slope  $s$  and intercept  $p$ , and dividing  $p$  by  $s$  eventually gives the complex formation constant  $K_c$ <sup>[37]</sup>.

For (**3** + NaI) in acetonitrile, the resulting equilibrium constant  $K_c = 8008$  ( $\text{mol} \cdot \text{l}^{-1}$ )<sup>-1</sup> (average value from two independent determinations) is rather high, whereas the corresponding equilibrium constant for (**3** + KI) in acetonitrile amounts only to  $K_c = 4131$  ( $\text{mol} \cdot \text{l}^{-1}$ )<sup>-1</sup><sup>[3]</sup>. In agreement with the Na<sup>+</sup>-selective halochromism of **3** (see Figure 2), the complex formation constant of **3** with K<sup>+</sup> is only half as large as the corresponding constant obtained with **3** and Na<sup>+</sup>.

The pronounced cation-selective negative halochromism<sup>[19]</sup> of the new chromoionophoric<sup>[20]</sup> betaine dyes **3–5** can be exemplarily demonstrated by a simple test-tube experiment because of their light absorption within the visible range of the electromagnetic spectrum (see Figure 4): Treatment of a ca.  $10^{-3}$  M solution of the K<sup>+</sup>-selective [18]crown-5 betaine **4** in acetonitrile ( $\lambda_{\max} = 588$  nm, blue-violet solution) with ca.  $10^{-2}$  M potassium iodide causes a distinct color change from blue-violet to carmine-red ( $\lambda_{\max} = 529$  nm, salt-induced shift  $\Delta\lambda = -59$  nm).

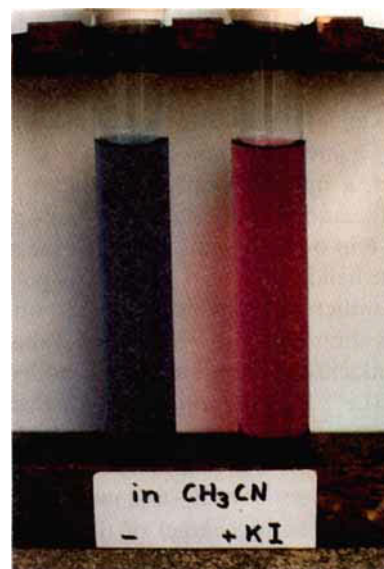


Figure 4. Visual representation of the negative, cation-selective halochromism of [18]crown-5 betaine dye **4**, dissolved in acetonitrile [ $c(\mathbf{4}) = 8 \cdot 10^{-3}$  mol/l] without (blue-violet solution,  $\lambda_{\max} = 588$  nm, left side) and with potassium iodide added [ $c(\text{KI})$  ca.  $10^{-2}$  mol/l; carmine-red solution,  $\lambda_{\max} = 529$  nm, right side]

The bis-betaine **6** has been synthesized in order to increase the absorption intensity which is rather low in the case of dyes **1–5** ( $\varepsilon_{\max} = \text{ca. } 300\text{--}800 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ). With  $\varepsilon_{\max} = 1420 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$  in acetonitrile, the absorption intensity of **6** is indeed nearly twice as large as that of the mono-betaines **1–5**. The bis-betaine **6** is also better soluble in water than **3–5**, leading to a yellow solution ( $\lambda_{\max} = 433$  nm). The negative solvatochromism of **6** is quite similar to that of **1–5** (see Table 1), and  $E_T(\mathbf{6})$  correlates linearly with  $E_T(\mathbf{30})$  (see legend to Figure 1). However, the negative halochromism of **6** does not show a cation-selective behaviour: on addition of alkali iodides to a solution of **6** in acetonitrile, a continuous increase of the halochromic shift ( $\Delta\lambda = 2 \rightarrow 166$  nm in going from CsI to LiI) with increasing effective charge of the cation added is obtained (see Table 2) – analogous to the halochromic behaviour of **1**<sup>[1]</sup>. The negative halochromism of **6** in methanol is too large to be fully measured, because the long-wavelength Vis absorption band is shifted hypsochromically to such an extent, that it is partly covered by the strong UV absorption band at  $\lambda_{\max} = 310$  nm, which stems from the  $\pi - \pi^*$  absorption of the two 2,4,6-triphenylpyridinium moieties of **6**.

The disappointingly missing cation-selective halochromism of **6** results presumably from the fact that **6** does not form a cavity suitable to host an alkali metal cation. Obviously, it is not planar and consists, for electrostatic reasons, of two antiparallel oriented, dipolar betaine molecules, linked by the two nonplanar polyether chains. So far, no crystals of **6** suitable for an X-ray analysis could be obtained.

To sum up, the crown ether-substituted betaine dyes **3–5** show, in contrast to several other chromoionophores<sup>[21]</sup>, a pronounced cation-selective negative halochromism<sup>[19]</sup>, caused by a hypsochromic shift of the long-wavelength, intramolecular CT absorption band of the pyridinium N-

phenolate chromophore on addition of alkali salts. As this absorption band lies in the visible spectral region, the alkali cation-induced colour changes can be followed easily by eye (Figure 4).

This negative halochromism of **3**–**5** stems mainly from the crown ether-mediated specific cation/dye interaction, thus reflecting salt-induced perturbations in the molecular-microscopic environment of the phenolate part of the betaine dye<sup>[1,17]</sup>. However, additional nonspecific halochromic effects due to salt-induced changes in the structure of the bulk solvent (i.e. interruption or reinforcement of intermolecular solvent/solvent interactions) are obviously also of importance, as shown by the halochromic band shifts induced on addition of tetra-*n*-butylammonium iodide (see Table 2), a salt not capable of specific cation/dye interactions. It seems to be very difficult to separate experimentally this nonspecific from the above-mentioned specific halochromic effect.

The term *halochromism* was first introduced by Baeyer and Villiger<sup>[38]</sup> and has been used until now to describe a colour change of a dissolved compound on addition of acid or base during which a chemical reaction transforms a colourless compound into a coloured one [e.g. (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>C–OH (colourless) + H<sub>3</sub>O<sup>+</sup> → (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>C<sup>+</sup> (yellow) + 2 H<sub>2</sub>O]. In contrast to this trivial halochromism (each chemical reaction leads to products with UV/Vis spectra which are different from that of the starting compounds), the salt-induced band shifts of **3**–**6** constitute a new type of true or genuine halochromism<sup>[1,7,8]</sup>. This true halochromism refers to a colour change on addition of an ionophore<sup>[18]</sup> to a dye solution *not* accompanied by a chemical alteration of the chromophore (see also footnote<sup>[19]</sup>). Other examples of this true halochromism can be found in refs.<sup>[39–45]</sup>.

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## Experimental

Melting points: Kofler-Mikroheiztisch (Fa. Reichert); corrected values. — Elemental analyses: Analytik-Servicelabor Marburg, CHN-Rapid (Fa. Heraeus). — UV/Vis: Spectrometer U-3410 (Fa. Hitachi), with thermostated 1-cm quartz cells. Commercial solvents of p.a. quality were used, sometimes after further purification by standard methods, particularly by filtration through alumina B – Super I (Fa. ICN Biomedicals) in order to remove traces of acids and water. The inorganic salts employed were of analytical reagent quality and were dried before use over P<sub>4</sub>O<sub>10</sub> in vacuo. — IR: Interferometer IFS 88 (Fa. Bruker), films for liquids and KBr discs for solids. — <sup>1</sup>H and <sup>13</sup>C NMR (TMS internal standard): NMR Servicelabor Marburg, with spectrometers AC-300 (Fa. Bruker) at 300.13 MHz and AM-400 (Fa. Bruker) at 400.13 MHz. — MS: MS-Servicelabor Marburg, with spectrometers MAT CH-7A (Fa. Varian) and electron-impact (EI) or MAT 711 (Fa. Varian) and field desorption (FD) ionization.

### 2,6-Bis(bromomethyl)anisole (7)

a) *2,6-Dimethylanisole*: Under nitrogen NaOH (40.0 g, 1.00 mol) was added to a solution of 2,6-dimethylphenol (119.7 g, 0.98 mol) in water (200 ml). After heating under reflux, dimethyl sulfate (100.0 ml, 133.0 g; 1.05 mol) was added dropwise to the stirred solution. Stirring under reflux under nitrogen was continued for 4 h. After cooling to room temp., the two phases were separated. The aqueous phase was extracted with diethyl ether (2 × 100 ml), and

the combined organic phases were washed with 2 N NaOH (4 × 100 ml) and dried with MgSO<sub>4</sub>. After distillation, finally in vacuo, 2,6-dimethylanisole (85.7 g; 64%) was obtained as colourless liquid with b.p. 79 °C/20 Torr (ref.<sup>[24]</sup> 65–66 °C/12 Torr).

b) **7**: A solution of 2,6-dimethylanisole (61.3 g, 0.45 mol), *N*-bromosuccinimide (160.2 g, 0.90 mol; dried with P<sub>4</sub>O<sub>10</sub>), and 0.5 g of azobisisobutyronitrile in tetrachloromethane (600 ml; dried with P<sub>4</sub>O<sub>10</sub>) was stirred and cautiously warmed up with irradiation (with a 300-Watt UV lamp) until the exothermic reaction starts (heavy boiling!). The reaction then continued for ca. 1.5 h even without further irradiation. After cooling to room temp., the succinimide (upper phase) was separated from the solution. After filtration, the volume of the filtrate was reduced by distillation under slightly reduced pressure (rotary evaporator). After standing for a few hours, the precipitate formed was filtered off and recrystallized from tetrachloromethane to give **7** (105.0 g; 79%) as colourless needles with m.p. 76 °C (ref.<sup>[25]</sup> 75 °C; ref.<sup>[23]</sup> 79.0–81.5 °C).

*18-Methoxy-3,6,9,12-tetraoxabicyclo[12.3.1]octadeca-1(18),14,16-triene (8a)*: Under nitrogen a solution of **7** (18.0 g, 61.0 mmol) and dry triethylene glycol (9.0 g, 60.0 mmol) in dry tetrahydrofuran (250 ml) was added dropwise during 6–8 h with stirring and boiling under reflux to a suspension of sodium hydride (6.0 g, 250 mmol) in dry tetrahydrofuran (350 ml), the latter being prepared from a NaH suspension (80%) in paraffin oil by filtration and washing with dry petroleum ether under nitrogen. The addition of **7** must be carried out very slowly, otherwise the yield of **8a** will be drastically reduced. After complete addition of **7**, the mixture was boiled under reflux for another 12 h, during which time its colour changed from milky-white to dark-brown. After cooling to room temp., water (40–50 ml) was added with stirring (H<sub>2</sub> development!). The precipitated inorganic salts were filtered off and washed with hot tetrahydrofuran (3 × 100 ml). Filtrate and THF extracts were combined, and the solvent was removed in vacuo in a rotary evaporator. The remaining dark-brown oil was dissolved in chloroform (200 ml) and the solution dried with MgSO<sub>4</sub>. After filtration and distilling off the solvent, the remaining oil was extracted by treatment with boiling *n*-heptane (500 ml) under reflux for ca. 5 min. The hot heptane solution was separated from the residue by decantation. After cooling to room temp., the *n*-heptane was distilled off from the extraction solution in a rotary evaporator, and the remaining oil was collected. The distilled *n*-heptane was again used for a second extraction of the residue, and this procedure was repeated four times. The oils, which remain after removal of the *n*-heptane, were combined to give altogether ca. 12 g of a pale-yellow oil, which again was extracted four times with hot *n*-heptane (400 ml) as described before. Eventually, **8a** (8.8 g; 52%) was obtained as nearly colourless oil, which was used without further purification for the following step (ref.<sup>[23]</sup> b.p. 115–116 °C/10<sup>–3</sup> Torr).

*3,6,9,12-Tetraoxabicyclo[12.3.1]octadeca-1(18),14,16-trien-18-ol (9a)*: Under dry nitrogen a solution of anhydrous lithium iodide (14.0 g, 104.6 mmol) and **8a** (14.1 g, 50.0 mmol) in dry, freshly distilled pyridine (100 ml) was heated under reflux with stirring for ca. 8 h. After cooling to room temp., the pyridine was removed by distillation under reduced pressure in a rotary evaporator, and then water (50 ml) was added to the dark-brown oily residue. The solvents were removed by distillation under reduced pressure, and this procedure (addition of water and distillation) was repeated three times. The oily residue was redissolved in water (50 ml), the solution was acidified with 2 N HCl, then extracted with chloroform (6 × 100 ml), and the combined extracts were dried with MgSO<sub>4</sub>. Removal of the solvent gave a dark-brown oil which, on standing for some time, crystallized. After recrystallization from *n*-hexane, **9a**



(11.5 g; 86%) was obtained as colourless needles with m.p. 66 °C (ref.<sup>[23]</sup> 66.0–66.5 °C).

**16-Nitro-3,6,9,12-tetraoxabicyclo[12.3.1]octadeca-1(18),14,16-trien-18-ol (10a):** A solution of potassium nitrite (3.4 g, 40.0 mmol) in concd. nitric acid (3 ml) was added at room temp. with stirring to a solution of **9a** (1.0 g, 3.7 mmol) in water (250 ml), and the stirring was continued for ca. 40 min. The aqueous solution was then extracted with chloroform (5 × 50 ml). The combined extracts were washed with water (3 × 50 ml) and dried with MgSO<sub>4</sub>. Removal of solvent gave crude **10a** (1.1 g; 94%), which was recrystallized from *n*-heptane/tetrachloromethane (3:1) to give 1.0 g (86%) light yellow needles with m.p. 106 °C (ref.<sup>[23]</sup> 105.5–106.0 °C). — <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 3.5–3.9 (m, 12H, –OCH<sub>2</sub>CH<sub>2</sub>O–), 4.69 (s, 4H, ArCH<sub>2</sub>O), 8.05 (s, 2H, aromatic H), 8.70 (s, broad, 1H, OH). — MS (70 eV, EI), *m/z* (%): 313 (29) [M<sup>+</sup>], 177 (14), 165 (21), 164 (10), 133 (22), 89 (42), 45 (100). Both spectra were in good agreement with those reported in ref.<sup>[23]</sup>

**16-Amino-3,6,9,12-tetraoxabicyclo[12.3.1]octadeca-1(18),14,16-trien-18-ol (11a):** A suspension of a palladium catalyst (10% Pd on charcoal; 40 mg) in a solution of **10a** (1.0 g; 3.2 mmol) in anhydrous methanol (40 ml) was reduced with hydrogen (H<sub>2</sub> absorption ca. 230 ml) at room temp. under normal pressure. Under nitrogen the catalyst was filtered off, and the solvent was removed in a rotary evaporator to give **11a** (0.9 g; 99%) as light yellow crystals, which immediately turned dark in air. Because of its sensitivity to oxygen, **11a** was immediately transformed into the pyridinium salt **12a** without further characterization.

**16-(2,4,6-Triphenyl-1-pyridinio)-3,6,9,12-tetraoxabicyclo[12.3.1]octadeca-1(18),14,16-trien-18-ol Tetrafluoroborate (12a):** Under nitrogen **11a** (0.90 g, 3.18 mmol) was added with stirring to a suspension of 2,4,6-triphenylpyrylium tetrafluoroborate<sup>[27]</sup> (0.79 g, 2.00 mmol) in anhydrous dichloromethane (5 ml) saturated with N<sub>2</sub>. Stirring at room temp. was continued for ca. 1.5 h. After the addition of acetic acid (0.1 ml) to the dark-red solution, stirring was continued for another 4 h. Then, diethyl ether (300 ml) was added dropwise with stirring and a yellow precipitate formed. After filtration and drying with P<sub>4</sub>O<sub>10</sub>, the pyridinium salt **12a** was dissolved in acetone (5 ml) and again precipitated with diethyl ether (15 ml). After filtration and drying, **12a** (1.10 g; 82%) was obtained as yellow microcrystalline powder with m.p. 207–209 °C. — IR (KBr):  $\tilde{\nu}$  = 3320 (OH), 1099 (C–O–C), 1060 cm<sup>–1</sup> (BF<sub>4</sub><sup>–</sup>). — UV/Vis (acetonitrile):  $\lambda_{\text{max}}$  (lg  $\epsilon$ ) = 306 nm (4.513). — <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 3.23–3.46 (m, 12H, –OCH<sub>2</sub>CH<sub>2</sub>O–), 4.37 (s, 4H, ArCH<sub>2</sub>O), 7.08 (s, 2H, phenol *m*-H), 7.26–7.81 (m, 15H, C<sub>6</sub>H<sub>5</sub>), 7.89 (s, 1H, OH), 7.97 (m, 2H, pyridinium *m*-H). — <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 68.87, 68.99, 69.53, 70.55 (four s, CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>Ar), 125.91–134.51 (several overlapping s, aromatic C), 157.00 (s, C–N<sup>+</sup>), 157.11 (s, C–OH). — MS (FD), *m/z* (%): 574 (100) [M<sup>+</sup> – BF<sub>4</sub><sup>–</sup>].

C<sub>37</sub>H<sub>36</sub>BF<sub>4</sub>NO<sub>5</sub>·0.5H<sub>2</sub>O (661.5 + 9.0 = 670.5)

Calcd. C 66.28 H 5.56 N 2.09

Found C 66.27 H 5.55 N 2.08

**16-(2,4,6-Triphenyl-1-pyridinio)-3,6,9,12-tetraoxabicyclo[12.3.1]octadeca-1(18),14,16-trien-18-olate, “[15]Crown-4 Betaine” (3):** At room temp., the ion-exchange resin Amberlyst A-21 (2.0 g) was added with stirring to a solution of **12a** (0.50 g, 0.75 mmol) in anhydrous dichloromethane (10 ml) saturated with N<sub>2</sub>. The colour of the solution changed to dark-blue, and stirring was continued for 3.5 h. After filtration and removal of the solvent in a rotary evaporator under reduced pressure, the remaining crystals were dried with P<sub>4</sub>O<sub>10</sub> at 35 °C/10<sup>–2</sup> Torr in a drying pistol to give **3** (0.41 g; 83%) as hygroscopic, dark-red crystals with m.p. 135–139 °C, still containing dichloromethane as solvent of crys-

tallization. — IR (KBr):  $\tilde{\nu}$  = 3380 (OH), 1083 cm<sup>–1</sup> (C–O–C). — UV/Vis (acetonitrile):  $\lambda_{\text{max}}$  (lg  $\epsilon$ ) = 580.8 nm (2.517), 305.2 (4.476), and Table 1. — <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 3.23–3.46 (m, 12H, –CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>O–), 4.37 (s, 4H, ArCH<sub>2</sub>O), 7.07 (s, 2H, phenolate *m*-H), 7.26–7.82 (m, 15H, C<sub>6</sub>H<sub>5</sub>), 8.03 (s, 2H, pyridinium *m*-H). — <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 68.79, 68.91, 69.55, 70.54 (four s, CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>Ar), 126.02–134.42 (several overlapping s, aromatic C), 157.10 (s, C–N<sup>+</sup>), 157.11 (s, C–O<sup>–</sup>). — MS (FD), *m/z* (%): 573 (100) [M<sup>+</sup>].

C<sub>37</sub>H<sub>35</sub>NO<sub>5</sub>·CH<sub>2</sub>Cl<sub>2</sub> (573.7 + 84.9 = 658.6)

Calcd. C 69.30 H 5.66 N 2.13

Found C 69.31 H 5.62 N 2.12

**21-Methoxy-3,6,9,12,15-pentaoxabicyclo[15.3.1]heneicosa-1(21),17,19-triene (8b):** 2,6-Bis(bromomethyl)anisole (**7**) (45.0 g, 153 mmol) and tetraethylene glycol (32.0 g, 165 mmol) were cyclized in anhydrous tetrahydrofuran (600 ml) containing sodium hydride (14.0 g, 583 mmol) according to the procedure given above for **8a**. The final extraction with *n*-heptane afforded **8b** (25.0 g; 51%) as viscous, colourless oil which crystallized on standing to give colourless needles with m.p. 50 °C (ref.<sup>[23]</sup> 50.0–50.5 °C).

**3,6,9,12,15-Pentaoxabicyclo[15.3.1]heneicosa-1(21),17,19-trien-21-ol (9b):** Analogous to the procedure described for **9a**, the crown ether-substituted anisole **8b** (17.0 g, 52.0 mmol) was demethylated with anhydrous lithium iodide (14.5 g, 108.0 mmol) in refluxing pyridine (100 ml) for 10 h. The crude product was purified by column chromatography on silica gel with *n*-hexane/chloroform (1:4), chloroform, and chloroform/methanol (1:1) as eluants. Recrystallization from *n*-hexane afforded **9b** (13.5 g; 83%) as colourless needles with m.p. 51 °C (ref.<sup>[23]</sup> 49.0–51.5 °C).

**19-Nitro-3,6,9,12,15-pentaoxabicyclo[15.3.1]heneicosa-1(21),17,19-trien-21-ol (10b):** Analogous to the procedure described for **10a**, a solution of the crown ether-substituted phenol **9b** (1.00 g, 3.2 mmol) in water (250 ml) was nitrated with potassium nitrite (3.00 g, 35.2 mmol) in concd. nitric acid (3 ml). The aqueous solution was extracted with chloroform (6 × 80 ml), and the united extracts were washed with water (4 × 50 ml). Removal of the solvent afforded a crude product (0.92 g) which was recrystallized from *n*-heptane/tetrachloromethane (3:1) to give **10b** (0.86 g; 75%) as yellow needles with m.p. 91 °C (ref.<sup>[23]</sup> 91.0–91.5 °C). — <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 3.6–3.8 (m, 16H, –OCH<sub>2</sub>CH<sub>2</sub>O–), 4.74 (s, 4H, ArCH<sub>2</sub>O), 8.09 (s, 2H, aromatic H), 9.10 (s, broad, 1H, OH). — MS (70 eV, EI), *m/z* (%): 357 (10) [M<sup>+</sup>], 340 (9), 165 (9), 164 (7), 133 (6), 89 (34), 45 (100). Both spectra were in good agreement with those reported in ref.<sup>[23]</sup>

**19-Amino-3,6,9,12,15-pentaoxabicyclo[15.3.1]heneicosa-1(21),17,19-trien-21-ol (11b):** According to the procedure described above for **11a**, the nitrophenol **10b** (1.00 g, 2.80 mmol), dissolved in anhydrous methanol (40 ml), was reduced with hydrogen (H<sub>2</sub> absorption ca. 205 ml) in the presence of a Pd/C catalyst (40 mg) to give **11b** (0.90 g; 98%) as light-yellow crystals which changed their colour immediately to dark-red when exposed to air. Therefore, **11b** was at once transformed into **12b** without further characterization.

**19-(2,4,6-Triphenyl-1-pyridinio)-3,6,9,12,15-pentaoxabicyclo[15.3.1]heneicosa-1(21),17,19-trien-21-ol Tetrafluoroborate (12b):** Analogous to the procedure described above for **12a**, 2,4,6-triphenylpyrylium tetrafluoroborate<sup>[27]</sup> (0.73 g, 1.84 mmol) in dichloromethane (5 ml) was treated with **11b** (0.90 g, 2.76 mmol) to give **12b** (1.10 g; 86%) as a nearly colourless, microcrystalline powder with m.p. 171–172 °C, still containing water of crystallization. — IR (KBr):  $\tilde{\nu}$  = 3352 (OH), 1083 (C–O–C), 1057 cm<sup>–1</sup> (BF<sub>4</sub><sup>–</sup>).

— UV (acetonitrile):  $\lambda_{\max}$  (lg  $\epsilon$ ) = 306 nm (5.501). —  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 3.34–3.70 (m, 16H,  $-\text{OCH}_2\text{CH}_2\text{O}-$ ), 4.45 (s, 4H,  $\text{ArCH}_2\text{O}$ ), 6.91 (s, 2H, phenol *m*-H), 7.07–7.56 (m, 15H,  $\text{C}_6\text{H}_5$ ), ca. 8.04 (two overlapping s, 1H and 2H, OH and pyridinium *m*-H). —  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 68.21, 68.79, 69.83, 70.35 (four s,  $-\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{Ar}$ ), 125.21–134.43 (several overlapping s, aromatic C), 157.00 (s, C–N $^{\oplus}$ ), 157.11 (s, C–OH). — MS (FD),  $m/z$  (%): 618 (100) [ $\text{M}^{\oplus} - \text{BF}_4^{\ominus}$ ].

$\text{C}_{39}\text{H}_{40}\text{BF}_4\text{NO}_6 \cdot 0.5\text{H}_2\text{O}$  (705.6 + 9.0 = 714.6)

Calcd. C 65.55 H 5.78 N 1.96

Found C 65.33 H 5.90 N 1.98

19-(2,4,6-Triphenyl-1-pyridinio)-3,6,9,12,15-pentaoxabicyclo[15.3.1]heneicos-1(21),17,19-trien-21-olate, “[18]Crown-5 Betaine” (4): According to the deprotonation procedure given above for 3, the reaction of the pyridinium salt 12b (0.50 g, 0.70 mmol) in dichloromethane (10 ml) afforded 4 (0.41 g; 80%) as hygroscopic, dark-red crystals with m.p. 107–110°C, still containing dichloromethane as solvent of crystallization. — IR (KBr):  $\tilde{\nu}$  = 3413 (OH), 1083  $\text{cm}^{-1}$  (C–O–C). — UV/Vis (acetonitrile):  $\lambda_{\max}$  (lg  $\epsilon$ ) = 588.3 nm (2.455), 305.1 (4.448), and Table 1. —  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 3.32–3.61 (m, 16H,  $-\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}-$ ), 4.43 (s, 4H,  $\text{ArCH}_2\text{O}$ ), 7.06 (s, 2H, phenolate *m*-H), 7.26–7.85 (m, 15H,  $\text{C}_6\text{H}_5$ ), 8.02 (s, 2H, pyridinium *m*-H). —  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 68.24, 68.78, 70.03, 70.51 (four s,  $-\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{Ar}$ ), 125.70–133.19 (several overlapping s, aromatic C), ca. 157.18 (two overlapping s, C–N $^{\oplus}$  and C–O $^{\ominus}$ ). — MS (FD),  $m/z$  (%): 617 (100) [ $\text{M}^{\oplus}$ ].

$\text{C}_{39}\text{H}_{39}\text{NO}_6 \cdot 1.3\text{CH}_2\text{Cl}_2$  (617.7 + 110.4 = 728.1)

Calcd. C 66.48 H 5.76 N 1.92

Found C 66.28 H 5.78 N 1.81

24-Methoxy-3,6,9,12,15,18-hexaoxabicyclo[18.3.1]tetracos-1(24),20,22-triene (8c): 2,6-Bis(bromomethyl)anisole (7) (20.0 g, 68 mmol) and pentaethylene glycol (16.2 g, 68 mmol) were cyclized in anhydrous tetrahydrofuran (600 ml) containing sodium hydride (9.6 g, 400 mmol) according to the procedure described above for 8a to give 8c (9.5 g; 37%) as colourless needles with m.p. 82°C (ref.<sup>[23]</sup> 82.0–82.5°C).

3,6,9,12,15,18-Hexaoxabicyclo[18.3.1]tetracos-1(24),20,22-trien-24-ol (9c): Analogous to the procedure described for 9a, the crown ether-substituted anisole 8c (6.0 g, 16.2 mmol) was demethylated with anhydrous lithium iodide (6.7 g, 50.0 mmol) in refluxing pyridine (100 ml). The crude product was purified by column chromatography on silica gel with *n*-hexane/chloroform (1:4), chloroform, and chloroform/methanol (1:1), to give 9c (3.5 g; 61%) as viscous, colourless oil (ref.<sup>[23]</sup>: viscous liquid which crystallizes at 0°C).

22-Nitro-3,6,9,12,15,18-hexaoxabicyclo[18.3.1]tetracos-1(24),20,22-trien-24-ol (10c): Analogous to the procedure described for 10a, a solution of the crown ether-substituted phenol 9c (1.00 g, 2.8 mmol) in water (250 ml) was nitrated with potassium nitrite (3.00 g, 35.2 mmol) in concentrated nitric acid (3 ml). The aqueous solution was extracted with chloroform (4  $\times$  50 ml), and the united extracts were washed with water (2  $\times$  30 ml). Removal of the solvent afforded a crude oily product (0.90 g) which solidified on standing. Recrystallization from *n*-hexane/tetrachloromethane (3:1) gave 10c (0.75 g, 67%) as light-yellow needles with m.p. 74°C (ref.<sup>[23]</sup> 73.0–73.5°C). —  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 3.4–3.8 (m, 20H,  $-\text{OCH}_2\text{CH}_2\text{O}-$ ), 4.66 (s, 4H,  $\text{ArCH}_2\text{O}$ ), 8.03 (s, 2H, aromatic H), 9.20 (s, broad, 1H, OH). — MS (70 eV, EI),  $m/z$  (%): 401 (9) [ $\text{M}^{\oplus}$ ], 384 (17), 165 (9), 164 (9), 133 (10), 89 (33), 87 (8), 45 (100). Both spectra were in good agreement with those reported in ref.<sup>[23]</sup>

22-Amino-3,6,9,12,15,18-hexaoxabicyclo[18.3.1]tetracos-1(24),20,22-trien-24-ol (11c): According to the procedure described above for 11a, the nitrophenol 10c (0.50 g, 1.25 mmol), dissolved in anhydrous methanol (30 ml), was reduced with hydrogen ( $\text{H}_2$  absorption ca. 91 ml) in the presence of a Pd/C catalyst (40 mg) to give 11c (0.43 g; 93%) as colourless crystals which immediately turned dark-red when exposed to air. Therefore, 11c was at once transformed into 12c without further characterization.

22-(2,4,6-Triphenyl-1-pyridinio)-3,6,9,12,15,18-hexaoxabicyclo[18.3.1]tetracos-1(24),20,22-trien-24-ol Tetrafluoroborate (12c): According to the procedure given above for 12a, 2,4,6-triphenylpyridinium tetrafluoroborate<sup>[27]</sup> (0.60 g, 1.51 mmol) in dichloromethane (5 ml) was treated with 11c (1.00 g, 2.70 mmol) to give 12c (0.90 g; 78%) as colourless needles with m.p. 113–115°C after recrystallization from ethanol/petroleum ether (b.p. 40–60°C) (3:1). — IR (KBr):  $\tilde{\nu}$  = 3343 (OH), 1101 (C–O–C), 1050  $\text{cm}^{-1}$  ( $\text{BF}_4^{\ominus}$ ). — UV (acetonitrile):  $\lambda_{\max}$  (lg  $\epsilon$ ) = 305.1 nm (4.458). —  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 3.41–3.70 (m, 20H,  $-\text{OCH}_2\text{CH}_2\text{O}-$ ), 4.46 (s, 4H,  $\text{ArCH}_2\text{O}$ ), 7.07 (s, 2H, phenol *m*-H), 7.27–7.81 (m, 15H,  $\text{C}_6\text{H}_5$ ), 7.96 (s, 2H, pyridinium *m*-H), 8.32 (s, broad, 1H, OH). —  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 69.03, 70.60, 70.85, 70.98 (four s,  $-\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{Ar}$ ), 125.41–134.52 (several overlapping s, aromatic C), 155.13 (s, C–N $^{\oplus}$ ), 157.10 (s, C–OH). — MS (FD),  $m/z$  (%): 663 (100) [ $\text{M}^{\oplus} - \text{BF}_4^{\ominus}$ ].

$\text{C}_{41}\text{H}_{44}\text{BF}_4\text{NO}_7 \cdot \text{H}_2\text{O}$  (749.6 + 18.0 = 767.6)

Calcd. C 64.15 H 6.04 N 1.82

Found C 64.24 H 5.77 N 1.74

22-(2,4,6-Triphenyl-1-pyridinio)-3,6,9,12,15,18-hexaoxabicyclo[18.3.1]tetracos-1(24),20,22-trien-24-olate, “[21]Crown-6 Betaine” (5): According to the deprotonation procedure given above for 3, the reaction of the pyridinium salt 12c (0.50 g, 0.66 mmol) in dichloromethane (10 ml) afforded 5 (0.42 g; 85%) as hygroscopic dark-red crystals with m.p. 98–102°C, still containing dichloromethane as solvent of crystallization. — IR (KBr):  $\tilde{\nu}$  = 3384 (OH), 1083  $\text{cm}^{-1}$  (C–O–C). — UV/Vis (acetonitrile):  $\lambda_{\max}$  (lg  $\epsilon$ ) = 583.2 nm (2.926), 304.6 (4.457); and Table 1. —  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 3.30–3.63 (m, 20H,  $-\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2-$ ), 4.37 (s, 4H,  $\text{ArCH}_2\text{O}$ ), 6.89 (s, 2H, phenolate *m*-H), 7.09–7.79 (m, 15H,  $\text{C}_6\text{H}_5$ ), 7.95 (s, 2H, pyridinium *m*-H). —  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 68.41, 68.63, 70.36, 70.63, 70.67 (five s,  $-\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{Ar}$ ), 125.56–134.21 (several overlapping s, aromatic C), 156.44 (s, C–N $^{\oplus}$ ), 157.08 (s, C–O $^{\ominus}$ ). — MS (FD),  $m/z$  (%): 663 (100) [ $\text{M}^{\oplus} + 2$ ].

$\text{C}_{41}\text{H}_{43}\text{NO}_7 \cdot \text{CH}_2\text{Cl}_2$  (661.8 + 84.9 = 746.7)

Calcd. C 67.56 H 6.07 N 1.88

Found C 66.74 H 6.30 N 1.93

2,6-Bis[2-(2-hydroxyethoxy)ethoxymethyl]anisole (13): 2,6-Bis(bromomethyl)anisole (7) (5.9 g, 20.0 mmol) was added with stirring to a suspension of NaOH (1.0 g, 25 mmol) in freshly distilled, anhydrous diethylene glycol (30 ml). The reaction mixture was heated up to 90°C for 30 min and then to 115°C for 5 h. After cooling to room temp., water (80 ml) was added and the mixture extracted with chloroform (3  $\times$  50 ml). The combined organic phases were washed with water (2  $\times$  20 ml) and dried with  $\text{MgSO}_4$ . After filtration and removal of the solvent in a rotary evaporator, the remaining yellow oil was shortly refluxed with *n*-hexane (300 ml). The hot *n*-hexane solution was decanted and the solvent was removed to give an oil. This procedure (extraction with hot *n*-hexane, removal of solvent) was repeated four times. The oils, which remained after removal of the *n*-hexane, were combined to give crude 13 (5.4 g; 78%) as viscous light-green oil, which was used for the next step without further purification. —  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  =

3.16–3.52 (m, 16H, HOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>O–), 3.60 (s, 3H, OCH<sub>3</sub>), 4.64 (s, 4H, ArCH<sub>2</sub>O), 6.95–7.26 (m, 3H, aromatic H). — <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 61.28–72.24 (several overlapping s, HOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>Ar and OCH<sub>3</sub>), 124.11 (s, anisole *o*-C), 129.67 (s, anisole *p*-C), 131.31 (s, anisole *m*-C), 156.70 (s, anisole *ipso*-C). — MS (70 eV, EI), *m/z* (%): 343 (15) [M<sup>+</sup>], 238 (39), 135 (82), 105 (22), 89 (32), 45 (100).

29,30-Dimethoxy-3,6,9,17,20,23-hexaoxatricyclo[23.3.1.1<sup>11,15</sup>]-trianta-1(29),11,13,15(30),25,27-hexaene (**14**)

a) *Preparation from 13*: A solution of 2,6-bis(bromomethyl)anisole (**7**) (5.0 g, 17.0 mmol) and the substituted anisole **13** (5.9 g, 17.1 mmol) in anhydrous tetrahydrofuran (350 ml) was slowly added dropwise within 12 h with stirring to a boiling suspension of sodium hydride (2.0 g, 83.0 mmol) in anhydrous tetrahydrofuran (500 ml), the latter being prepared from a NaH suspension (80%) in paraffin oil by filtration and washing with dry petroleum ether under nitrogen. After the addition had been completed, boiling under reflux was continued for another 10 h. After cooling to room temp., water (10 ml) was added with stirring (H<sub>2</sub> development!). The precipitated inorganic salts were filtered off and washed with tetrahydrofuran (3 × 50 ml). Filtrate and THF extracts were combined, and the solvent was removed in vacuo in a rotary evaporator. The remaining oil was dissolved in chloroform (100 ml) and the solution dried with MgSO<sub>4</sub>. After removal of solvent, the remaining oil was heated under reflux with *n*-heptane (500 ml) for ca. 10 min. The hot *n*-heptane solution was separated from the residue by decantation. After cooling to room temp., the *n*-heptane was distilled off, and the remaining oil was collected. The distilled *n*-heptane was again used for a second hot extraction of the residue, and this procedure was repeated five times. The remaining oils from each extraction were combined to give crude **14** (5.5 g) as a light-yellow oil, which was again purified by hot extraction with *n*-hexane (6 × 500 ml) as described before. The bis(anisole) **14** (4.5 g; 55%) was obtained as colourless oil, pure enough for the next synthetic step. For analytical purposes, **14** was further purified by column chromatography on silica gel with chloroform/ethanol (9:1) as the eluant. The analytical and spectral properties of the product obtained in this way were identical with those of the product obtained directly from **7** and diethylene glycol.

b) *Direct Preparation from 7 and Diethylene Glycol*: A solution of 2,6-bis(bromomethyl)anisole (**7**) (2.5 g, 8.5 mmol) and dry diethylene glycol (0.9 g, 8.5 mmol) in anhydrous tetrahydrofuran (50 ml) was added dropwise within 3 h with stirring to a boiling suspension of sodium hydride (1.0 g, 42.0 mmol) in anhydrous tetrahydrofuran (250 ml), the latter being prepared from a NaH suspension (80%) in paraffin oil by filtration and washing with dry petroleum ether under nitrogen. After cooling to room temp., water (10 ml) was added (H<sub>2</sub> development!). The precipitated inorganic salts were filtered off and washed with tetrahydrofuran (3 × 50 ml). Filtrate and THF extracts were combined, and the solvent was removed in vacuo in a rotary evaporator. The remaining dark-brown oil was dissolved in chloroform (100 ml) and the solution dried with MgSO<sub>4</sub>. After filtration and removal of solvent, the remaining oil was heated under reflux with *n*-heptane (500 ml) for ca. 10 min. The hot *n*-heptane solution was separated from the residue by decantation. After cooling to room temp., the *n*-heptane was distilled off, and the remaining oil was collected. The distilled *n*-heptane was again used for a second hot extraction of the residue, and this procedure was repeated five times. The remaining oils from each extraction were combined to give crude **14** (1.0 g) as a light-yellow oil, which was again purified by hot extraction with *n*-hexane (5 × 500 ml) as described before. The bis(anisole) **14** (0.4 g; 10%)

was obtained as a nearly colourless oil, which was further purified for analytical purposes by column chromatography on silica gel with chloroform/ethanol (9:1) as eluant. — IR (Film):  $\tilde{\nu}$  = 3030, 1096 cm<sup>-1</sup> (C–O–C). — <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 3.59–3.73 (m, 22H, –OCH<sub>2</sub>CH<sub>2</sub>O– and OCH<sub>3</sub>), 4.53 (s, 8H, ArCH<sub>2</sub>O–), 6.9–7.3 (m, 6H, aromatic H). — <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 62.47 (s, OCH<sub>3</sub>), 69.44 (s, Ar–CH<sub>2</sub>O), 70.29–70.33 (overlapping s, –OCH<sub>2</sub>CH<sub>2</sub>O–), 123.86 (s, anisole *o*-C), 129.61 (s, anisole *p*-C), 132.25 (s, anisole *m*-C), 154.69 (s, anisole *ipso*-C). — MS (70 eV, EI), *m/z* (%): 476 (26) [M<sup>+</sup>], 370 (27), 237 (49), 149 (72), 134 (100), 119 (90), 91 (76), 45 (97).

C<sub>26</sub>H<sub>36</sub>O<sub>8</sub> (476.6) Calcd. C 65.53 H 7.61  
Found C 64.02 H 7.34

3,6,9,17,20,23-Hexaoxytricyclo[23.3.1.1<sup>11,15</sup>]trianta-1(29),11,13,15(30),25,27-hexaene-29,30-diol (**15**)

a) *Demethylation with LiAlH<sub>4</sub>/THF*: Under nitrogen LiAlH<sub>4</sub> (0.95 g, 25.0 mmol) was added to a solution of bis(anisole) **14** (1.50 g, 3.1 mmol) in anhydrous tetrahydrofuran (60 ml) with stirring, and the mixture was boiled under reflux for 18 h. After cooling to 0°C, cooled diluted sulfuric acid (10%, 30 ml) was added with stirring and cooling (H<sub>2</sub> development!). At room temp., stirring was continued for ca. 20 h. The mixture was extracted with chloroform (150 ml), the extract was dried with MgSO<sub>4</sub>, and the solvent was removed in a rotary evaporator. The remaining light-yellow oil (ca. 1.2 g) was dissolved in anhydrous ethanol (20 ml), and the solvent was removed in a rotary evaporator. This procedure was repeated three times. The remaining light-yellow crystals (ca. 0.8 g) were recrystallized from *n*-hexane/ethanol (1:3) to give **15** (0.70 g; 49%) as colourless crystals with m.p. 112–114°C. The analytical and spectral properties of the product obtained in this way were identical with those of the product prepared from **14** with LiI/pyridine.

b) *Demethylation with LiI/Pyridine*: Under nitrogen anhydrous lithium iodide (4.5 g, 33.6 mmol) was added with stirring to a solution of **14** (4.0 g, 8.40 mmol) in anhydrous pyridine (30 ml), and the mixture was boiled under reflux for ca. 15 h. After cooling to room temp., the pyridine was removed in vacuo in a rotary evaporator. To the dark-brown oily residue water (20 ml) was added and then distilled off. This procedure was repeated three times in order to remove all the pyridine. To the oily residue water (20 ml) was added, the solution was acidified with 2 N HCl and then extracted with chloroform (6 × 50 ml). The combined chloroform extracts were dried with MgSO<sub>4</sub>, and the solvent was removed to give a dark-brown oil. This oil was dissolved in warm *n*-hexane/ethanol (1:4). After cooling of the solution, a yellow precipitate formed within a short period of time. Filtration and recrystallization from *n*-hexane/ethanol (1:3) gave **15** (0.20 g; 5%) as colourless crystals with m.p. 112–114°C. — IR (KBr):  $\tilde{\nu}$  = 3350 (OH), 3043, 1101 cm<sup>-1</sup> (C–O–C). — <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 3.66–3.77 (m, 16H, –OCH<sub>2</sub>CH<sub>2</sub>O–), 4.71 (s, 8H, ArCH<sub>2</sub>O), 6.81 (t, <sup>3</sup>J = 7.5 Hz, 2H, phenol *p*-H), 7.12 (d, <sup>3</sup>J = 7.4 Hz, 4H, phenol *m*-H), 7.91 (s, 2H, OH). — <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 69.45 (s, Ar–CH<sub>2</sub>O), 70.29–70.33 (several s, –OCH<sub>2</sub>CH<sub>2</sub>O–), 119.37 (s, phenol *o*-C), 124.35 (s, phenol *p*-C), 128.82 (s, phenol *m*-C), 154.69 (s, phenol *ipso*-C). — MS (70 eV, EI), *m/z* (%): 448 (9) [M<sup>+</sup>], 312 (57), 236 (74), 135 (61), 119 (86), 91 (70), 45 (100).

C<sub>24</sub>H<sub>32</sub>O<sub>8</sub> · 0.5 C<sub>2</sub>H<sub>5</sub>OH (448.5 + 23.0 = 471.5)  
Calcd. C 63.68 H 7.48 Found C 63.64 H 7.25

13,27-Dinitro-3,6,9,17,20,23-hexaoxatricyclo[23.3.1.1<sup>11,15</sup>]trianta-1(29),11,13,15(30),25,27-hexaene-29,30-diol (**16**)

a) *By Nitration with NaNO<sub>3</sub>/HCl/La(NO<sub>3</sub>)<sub>3</sub>*: At room temp., a mixture of sodium nitrate (0.30 g, 3.5 mmol), water (7 ml), and

concd. hydrochloric acid (1 ml) as well as a catalytic amount of lanthanum(III) nitrate were added with stirring to a solution of **15** (0.52 g, 1.1 mmol) in diethyl ether (15 ml) and dichloromethane (5 ml), and stirring was continued for ca. 15 h. After ca. 2 h, the red solution became cloudy, and a precipitate formed. The precipitate was filtered off, washed with water (not much) and *n*-hexane/diethyl ether (1:2), and recrystallized from *n*-hexane/ethanol (1:4) to give **16** (0.48 g, 81%) as light-yellow needles with m.p. 157–160°C. The analytical and spectral properties of the product obtained in this way were identical with those of the product prepared by the procedure described subsequently.

b) *By Nitration with HNO<sub>3</sub>*: A solution of bis(phenol) **15** (0.20 g, 0.42 mmol) in *n*-hexane (20 ml) and diethylene glycol diethyl ether (5 ml) was heated up to 65°C with stirring. To the stirred solution, diluted nitric acid (30%, 3 ml) was added dropwise at 60°C at such a rate that no nitrous gases developed. The yellow mixture was then stirred at 60°C for 1 h. After cooling to room temp. and stirring for further ca. 12 h, a precipitate slowly formed. The precipitate was filtered off, washed with water (not much) and *n*-hexane/diethyl ether (1:2), and recrystallized from *n*-hexane/ethanol (1:4) to give **16** (0.18 g, 80%) as light-yellow crystals with m.p. 155–158°C. — IR (KBr):  $\tilde{\nu}$  = 3284 (OH), 1524 and 1337 (NO<sub>2</sub>), 1092 cm<sup>-1</sup>. — <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 3.59–3.82 (m, 16H, —OCH<sub>2</sub>CH<sub>2</sub>O—), 4.70 (s, 8H, ArCH<sub>2</sub>O), 8.00 (s, 4H, aromatic H), 8.90 (s, broad, 2H, OH). — <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 69.56 (s, Ar—CH<sub>2</sub>O), 70.15 (s, Ar—CH<sub>2</sub>O—CH<sub>2</sub>—), 70.23 (s, ArCH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>O—), 123.28 (s, phenol *o*-C), 125.01 (s, phenol *m*-C), 140.30 (s, C—NO<sub>2</sub>), 159.38 (s, C—OH). — MS (FD), *m/z* (%): 538 (90) [M<sup>+</sup>].

C<sub>24</sub>H<sub>30</sub>N<sub>2</sub>O<sub>12</sub> (538.5) Calcd. C 53.53 H 5.61 N 5.20  
Found C 53.82 H 5.58 N 5.28

*13,27-Diamino-3,6,9,17,20,23-hexaoxatricyclo[23.3.1.1<sup>11,15</sup>]triaconta-1(29),11,13,15(30),25,27-hexaene-29,30-diol* (**17**): A suspension of a palladium catalyst (10% Pd on charcoal, 40 mg) in a solution of **16** (0.50 g, 0.93 mmol) in anhydrous methanol (40 ml) was reduced with hydrogen (H<sub>2</sub> absorption ca. 75 ml) at room temp. and under normal pressure for ca. 4 d. After filtration under nitrogen and removal of the solvent, **17** (0.41 g, 92%) was obtained as a yellow oil which in air changed its colour to dark-red because of its fast oxidation. Therefore, **17** was immediately transformed into the bis(pyridinium) salt **18** without further characterization.

*13,27-Bis(2,4,6-triphenyl-1-pyridinio)-3,6,9,17,20,23-hexaoxatricyclo[23.3.1.1<sup>11,15</sup>]triaconta-1(29),11,13,15(30),25,27-hexaene-29,30-diol Bis(tetrafluoroborate)* (**18**): Under nitrogen a suspension of 2,4,6-triphenylpyrylium tetrafluoroborate<sup>[27]</sup> (0.60 g, 1.51 mmol) in dichloromethane (5 ml) was added at room temp. with stirring to a solution of **17** (0.40 g, 0.84 mmol) in anhydrous dichloromethane saturated with N<sub>2</sub> (10 ml) and methanol (2 ml). After stirring at room temp. for ca. 4 h, acetic acid (0.1 ml) was added, and stirring was continued for another 3 h. To the dark-brown, slightly fluorescent solution diethyl ether (250 ml) was added dropwise with stirring, and a yellow precipitate formed. After filtration and drying with P<sub>4</sub>O<sub>10</sub>, the bis(pyridinium) salt was dissolved in anhydrous chloroform (30 ml). The solution was filtered, and diethyl ether (100 ml) was added dropwise with stirring to afford a yellow precipitate. This purification procedure was repeated three times to give **18** (0.62 g, 64%) as light-yellow powdery crystals with m.p. 120–124°C, still containing water of crystallization. — IR (KBr):  $\tilde{\nu}$  = 3353 (OH), 3058, 1084 (C—O—C), 1060 cm<sup>-1</sup> (BF<sub>4</sub><sup>-</sup>). — UV (acetonitrile):  $\lambda_{\max}$  (lg  $\epsilon$ ) = 311.2 nm (4.614). — <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  = 3.22–3.54 (m, 16H, —OCH<sub>2</sub>CH<sub>2</sub>O—), 4.31 (s, 8H, ArCH<sub>2</sub>O), 6.93 (s, 4H, phenol *m*-H), 7.30–8.00 (m, 30H, C<sub>6</sub>H<sub>5</sub>), 8.28 (s, 4H, pyridinium *m*-H). — <sup>13</sup>C NMR (CD<sub>3</sub>CN):  $\delta$  = 69.48–70.58 (several

s, Ar—CH<sub>2</sub>—O—CH<sub>2</sub>CH<sub>2</sub>O—), 126.16–134.88 (several overlapping s, aromatic C), 158.11 (two overlapping s, C—N<sup>+</sup> and C—OH). — MS (FD), *m/z* (%): 531 (34) [M<sup>2+</sup> — 2 BF<sub>4</sub><sup>-</sup>].

C<sub>70</sub>H<sub>64</sub>B<sub>2</sub>F<sub>8</sub>N<sub>2</sub>O<sub>8</sub> · 2H<sub>2</sub>O (1234.9 + 36.0 = 1270.9)  
Calcd. C 66.15 H 5.39 N 2.20  
Found C 66.95 H 5.06 N 2.17

*13,27-Bis(2,4,6-triphenyl-1-pyridinio)-3,6,9,17,20,23-hexaoxatricyclo[23.3.1.1<sup>11,15</sup>]triaconta-1(29),11,13,15(30),25,27-hexaene-29,30-diolate* (**6**): At room temp., the ion-exchange resin Amberlyst A-21 (2.0 g) was added with stirring to a solution of **18** (0.50 g, 0.40 mmol) in anhydrous dichloromethane saturated with N<sub>2</sub> (20 ml), and stirring was continued for 3.5 h. After filtration and removal of solvent, the remaining crystals were dried with P<sub>4</sub>O<sub>10</sub> at 35°C/10<sup>-2</sup> Torr in a drying pistol to give **6** (0.38 g, 80%) as hygroscopic, dark-red crystals with m.p. 88–90°C, which still contain dichloromethane as solvent of crystallization. — IR (KBr):  $\tilde{\nu}$  = 3345 (OH), 1100 cm<sup>-1</sup> (C—O—C). — UV/Vis (acetonitrile):  $\lambda_{\max}$  (lg  $\epsilon$ ) = 576.2 nm (3.153), 457.1 (3.132), 309.0 (4.587); and Table 1. — <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  = 3.24–3.55 (m, 16H, —OCH<sub>2</sub>CH<sub>2</sub>O—), 4.31 (s, 8H, ArCH<sub>2</sub>O), 6.95 (s, phenolate *m*-H), 7.41–8.14 (m, 30H, C<sub>6</sub>H<sub>5</sub>), 8.37 (s, 4H, pyridinium *m*-H). — <sup>13</sup>C NMR (CD<sub>3</sub>CN):  $\delta$  = 69.26–71.06 (several s, Ar—CH<sub>2</sub>—O—CH<sub>2</sub>CH<sub>2</sub>O—), 126.34 to 134.89 (several overlapping s; aromatic C), 158.11 (two overlapping s, C—N<sup>+</sup> and C—O<sup>-</sup>). — MS (FD), *m/z* (%): 1059 (100) [M<sup>+</sup>].

C<sub>70</sub>H<sub>62</sub>N<sub>2</sub>O<sub>8</sub> · 1.5CH<sub>2</sub>Cl<sub>2</sub> (1059.3 + 127.4 = 1186.7)  
Calcd. C 72.37 H 5.52 N 2.36  
Found C 72.32 H 5.94 N 2.34

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- [18] *Ionophores* are ionic compounds (e.g.  $\text{Na}^+\text{Cl}^-$ ) which, in contrast to *ionogens*, consist of ions in the crystal, in the melt, and in solution. *Ionogens* (e.g.  $\text{H}-\text{Cl}$ ) are compounds with molecular crystal lattices which produce ions only when dissolved in appropriate solvents; see R. M. Fuoss, *J. Chem. Educ.* **1955**, *32*, 527; and refs.<sup>[13,20]</sup>
- [19] We have suggested the term “negative (positive) halochromism” for a hypsochromic (bathochromic) shift of the UV/Vis absorption band of a dissolved compound on increasing electrolyte (ionophore) concentration, when this band shift is *not* caused by a change in chemical structure of the chromophore; see refs.<sup>[1,8]</sup>
- [20] *Chromoionophores* are dye molecules which contain chromophoric and ionophoric units. Such a chromoionophore can complex ions with concomitant change in colour; see [20a] J. P. Dix, F. Vögtle, *Chem. Ber.* **1981**, *114*, 638–651 (cf. footnote 3 in this paper), and [20b] A. Villiger, W. E. Morf, W. Simon, *Helv. Chim. Acta* **1983**, *66*, 1078–1089. In this context, ionophores are considered as neutral macrocyclic molecules (or parts of molecules) which form complexes with ions and as carriers transport them through biological membranes; see B. C. Pressman, “Alkali Metal Chelators – the Ionophores”, *Inorg. Biochem.* **1973**, *1*, 203–226; *Chem. Abstr.* **1975**, *83*, 23537h. This term was chosen somewhat unfortunately, because previously ionophores referred to ionic compounds which, in contrast to ionogens, consist of ions in the crystal, in the melt, and in solution; see ref.<sup>[18]</sup>
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