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Synthesis and Metal Ion Complexing Properties of Novel Chromogenic Cryptands

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Abstract. Four novel chromogenic benzocryptands and one side-armed chromogenic cryptand have been synthesized and their complexing abilities for alkali metal cations are described.

Key words. Cryptands, benzocryptands, chromogenic, alkali metal cation complexation.

1. Introduction

Crown ether-based chromogenic compounds which allow selective determination of alkali metal and alkaline earth cations have been known for more than a decade [1–4]. The need to incorporate a bicyclic structure into a chromoionophore as a means of increasing selectivity and sensitivity was discussed some time ago [5]. Surprisingly, only a few chromoionophores which employ a bicyclic unit have been reported. These include the cryptand azophenols 1 [6] and a structure-controlled azo dye 2 [7].

In this paper, we report the synthesis and complexation characteristics of four new ionizable chromoionophores **3–6** which incorporate a benzocryptand unit and also cryptand **7** which has a pendant chromogenic unit.

2. Experimental

2.1. PREPARATION OF CHROMOGENIC CRYPTAND 3

To commercially-available benzo[2.2.2]cryptand (1.00 g, 2.35 mmol) dissolved in glacial acetic acid (17 mL) and chloroform (20 mL), 3.2 mL of concentrated nitric acid was added dropwise at room temperature. The solution was stirred for 24 h and was neutralized with sodium bicarbonate. The organic layer was separated and evaporated *in vacuo*. The residue was extracted several times with chloroform and the combined extracts were evaporated *in vacuo* to give a light-brown semi-solid which was passed through a column of Dowex 1X8 ion exchange resin (OH form)

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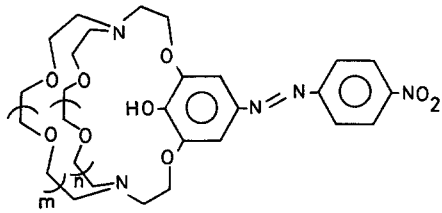

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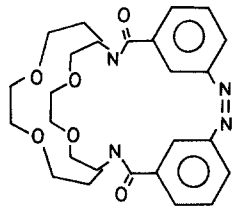

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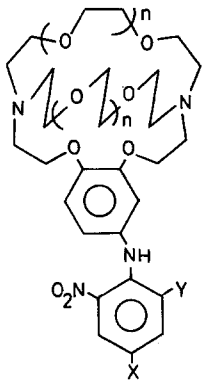
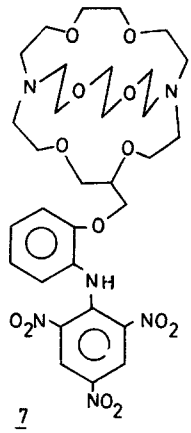


	n	X	Y
3	1	NO_2	CF_3
4	1	CF_3	NO_2
5	2	NO_2	NO_2
6	2	NO_2	CF_3



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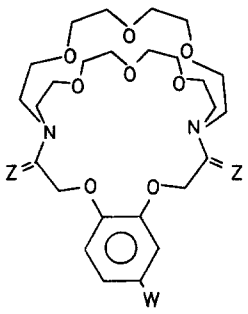
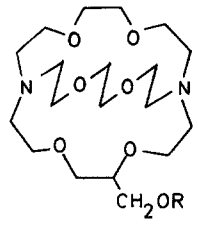
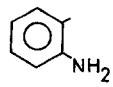
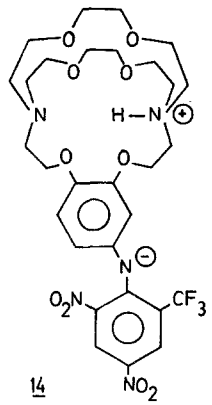


	Z	W
8	O	NO_2
9	H_2	NO_2
10	H_2	NH_2



	R
11	H
12	Ts
13	



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to provide the nitrated benzocryptand as a light-brown oil (1.09 g, 98% yield). ^{1}H-NMR ($CDCl_3$): $\delta = 2.55-3.25$ (*m*, 12H), 3.60 (*br s*, 16H), 3.85–4.4 (*m*, 4H), 6.95–7.9 (*m*, 3H). IR (neat): 1514, 1506, 1338 (NO_2), 1126 (C—O) cm^{-1}. The nitrated benzocryptand (0.80 g, 1.70 mmol) in dry DMF (15 mL) with 0.20 g of 10% Pd/C was hydrogenated at room temperature under 40 psi of hydrogen. The catalyst was filtered and the solvent was evaporated *in vacuo* to give 0.80 g of crude amino benzo cryptand which was dissolved in dry methanol (8 mL) and 0.17 g of sodium bicarbonate and 0.51 g of 1-chloro-2,4-dinitro-6-trifluoromethylbenzene were added. The mixture was refluxed overnight and the methanol was removed *in vacuo*. The residue was chromatographed on alumina with ethyl acetate and ethyl acetate–methanol (20:1) as eluents to afford 0.22 g (18% overall yield from benzo[2.2.2]cryptand) of **3** as a dark-red solid with mp 130°C (dec). ^{1}H-NMR ($CDCl_3$): $\delta = 2.45-3.05$ (*m*, 12H), 3.3–3.85 (*m* + *s*, 16H), 3.9–4.25 (*m*, 4H), 6.25–7.0 (*m*, 4H), 8.2 (*m*, 1H), 8.65 (*m*, 1H). IR (deposit from chloroform): 3400 (N—H), 1531, 1346 (NO_2), 1124, 1102 (C—O) cm^{-1}. Calcd: C, 51.71; H, 5.68. Found: C, 51.60; H, 5.49.

2.2. PREPARATION OF CHROMOGENIC CRYPTAND 4

The crude 4′-aminobenzo[2.2.2]cryptand described above was reacted with 1-chloro-2,6-dinitro-4-trifluoromethylbenzene in methanol in the presence of sodium bicarbonate. Chromatography on alumina with ethyl acetate–methanol (20:1) as eluent afforded the product as a sodium bicarbonate complex. Yield 64%, deep-red solid, mp 53–55°C. ^{1}H-NMR ($CDCl_3$): $\delta = 2.2-4.4$ (*m*, 32H), 6.4–7.0 (*m*, 3H), 7.98 (*s*, 1H), 8.31 (*s*, 2H). IR (deposit from chloroform): 3312 (N—H), 1543, 1512 (NO_2), 1134, 1103 (C—O) cm^{-1}. Calcd. ($\times NaHCO_3$): C, 47.56; H, 5.19. Found: C. 47.90; H, 5.23.

2.3. PREPARATION OF CRYPTAND DIAMIDE 8

Solution A (100 mL) was prepared by dissolving 1,2-bis(oxyacetyl chloride)-4-nitrobenzene [8] (2.20 g, 7.12 mmol) in toluene. Triethylamine (2.25 mL) and

1,13-diaza-24-crown-8 [9] (2.50 g, 7.12 mmol) were dissolved in toluene to make 100 mL of solution B. Solutions A and B were added simultaneously over 6 h to 250 mL of vigorously-stirred toluene at 0°C. The reaction mixture was stirred overnight at room temperature, filtered and evaporated *in vacuo*. The residue was chromatographed on alumina with chloroform–ethanol (50 : 1) as eluent to afford 2.60 g (63%) of **8** as a hygroscopic, colorless oil. ^{1}H-NMR ($CDCl_3$): $\delta = 2.7–5.6$ (*m*, 36H), 7.0–8.2 (*m*, 3H). IR (mull): 1651 (C=O), 1462 (NO_2), 1140–1031 (C—O) cm^{-1}. Calcd. (hydrate): C, 51.74; H, 6.85. Found: C, 51.62; H, 6.52.

2.4. PREPARATION OF NITROCRYPTAND 9

Cryptand diamide **8** (1.70 g, 2.75 mmol) was dissolved in dry THF (30 mL) and 1.45 mL of 10 M borane–dimethyl sulfide complex was added and the mixture was refluxed for 8 h. Water was added carefully and the solvent was removed *in vacuo*. The residue was extracted with chloroform and the chloroform was evaporated *in vacuo*. The residue was dissolved in 6N hydrochloric acid (30 mL) and refluxed for 8 h. The water was evaporated *in vacuo* and the residue was passed through a Dowex 1X8 ion exchange column (OH form) to give 1.17 g (73%) of **9** as a yellow oil. ^{1}H-NMR ($CDCl_3$): $\delta = 2.6–4.5$ (*m*, 30H), 6.9–7.0 (*d*, 1H), 7.6–8.2 (*m*, 2H). IR (neat): 1114 (C—O) cm^{-1}. Calcd: C, 56.00; H, 7.77. Found: C, 55.77; H, 7.76.

2.5. PREPARATION OF AMINOCRYPTAND 10

Nitrocryptand **9** (1.17 g, 2.10 mmol) in dry DMF (20 mL) with 10% Pd/C (0.20 g) was hydrogenated under 50 psi hydrogen pressure for 24 h at room temperature. The catalyst was filtered and the solvent was removed *in vacuo*. The residue was chromatographed on alumina with chloroform–ethanol (50 : 1) as eluent to produce 0.78 g (71%) of **10** as a colorless, viscous liquid. ^{1}H-NMR ($CDCl_3$): $\delta = 2.6–3.3$ (*m*, 12H), 3.3–4.4 (*m*, 30H), 5.9–6.5 (*m*, 2H), 6.75 (*d*, 1H). IR (neat): 3439, 3352, 3200 (N—H), 1128 (C—O) cm^{-1}. Calcd: C, 59.18; H, 8.60. Found: C, 58.90; H, 8.45.

2.6. PREPARATION OF CHROMOGENIC CRYPTAND 5

Aminocryptand **10** was reacted with picryl chloride in methanol in the presence of triethylamine to give a 62% yield of **5** as a dark-red oil. ^{1}H-NMR ($CDCl_3$): $\delta = 2.3–3.2$ (*m*, 12H), 3.3–4.5 (*m*, 29H), 6.3–7.1 (*m*, 3H), 8.70 (*br s*, 2H). IR (neat): 3520, 3300 (N—H), 1122 (C—O) cm^{-1}. Calcd. ($\times$ 0.6 $CHCl_3$): C, 48.00; H, 5.97. Found: C, 48.32; H, 5.80.

2.7. PREPARATION OF CHROMOGENIC CRYPTAND 6

Aminocryptand **10** was reacted with 1-chloro-2,4-dinitro-6-trifluoromethylbenzene in methanol in the presence of triethylamine to give **6** as a red oil in 48% yield. ^{1}H-NMR ($CDCl_3$): $\delta = 2.4–3.3$ (*m*, 12H), 3.4–4.5 (*m*, 29H), 6.2–7.0 (*m*, 3H), 8.30 (*d*, 1H), 8.60 (*d*, 1H). IR (neat): 3506, 3346 (N—H), 1116 (C—O) cm^{-1}. Calcd. ($\times$ 0.4 $CHCl_3$): C, 49.40, H, 5.60. Found: C, 49.74; H, 5.80.

2.8. PREPARATION OF (TOSYLOXY)METHYL[2.2.2]CRYPTAND **12**

A solution of hydroxymethyl[2.2.2]cryptand (**11** [10, 11], 1.20 g, 2.40 mmol) in pyridine (5 mL) was cooled to $-10°C$ and a solution of *p*-toluenesulfonyl chloride in pyridine (8 mL) was added. The mixture was stirred at $-10°C$ for 1 h and left in a refrigerator overnight. The pyridine was removed *in vacuo* without heating and the residue was chromatographed on basic alumina with chloroform-ethanol (20 : 1) as eluent to afford 0.81 g (61%) of **12** as a colorless oil. ^{1}H-NMR ($CDCl_3$): $\delta = 2.3–3.1$ (*m*, 15H), 3.25–4.4 (*m*, 25H), 7.3–7.9 (*ABq*, 4H). This material was used in the next step without further purification.

2.9. PREPARATION OF (*o*-AMINOPHENOXY)METHYL[2.2.2]CRYPTAND **13**

Sodium hydride (0.05 g of 50% dispersion in mineral oil, 10 mmol) was washed with pentane and suspended in dry THF (10 mL). *o*-Aminophenol (0.14 g, 1.30 mmol) in THF (10 mL) was added dropwise with stirring and the mixture was stirred under nitrogen for 1 h. A solution of cryptand tosylate **12** (0.60 g, 1.10 mmol) was added and the mixture was refluxed for 48 h. The solvent was evaporated *in vacuo* and the residue was chromatographed on alumina with chloroform–ethanol (50 : 1) as eluent to produce 0.53 g (96%) of **13** as a light orange oil. ^{1}H-NMR ($CDCl_3$): $\delta = 2.2–3.0$ (*m*, 12H), 3.2–4.35 (*m*, 27H), 6.77 (*s*, 1H). IR (neat): 3460, 3350, 3198 (N—H), 1101 (C—O) cm^{-1}. Calcd: C, 60.34; H, 8.71. Found: C, 60.24; H, 8.56.

2.10. PREPARATION OF CHROMOGENIC CRYPTAND **7**

Substituted cryptand **13** (0.24 g, 0.48 mmol), lithium carbonate (0.10 g, 1.35 mmol), and picryl chloride (0.15 g, 0.61 mmol) in 15 mL of dry methanol was stirred for 72 h at room temperature. The solvent was evaporated *in vacuo* and the residue was chromatographed on alumina with ethyl acetate-methanol (50 : 1) as eluent to give 0.23 g (67%) of a dark red solid with mp 208–210°C. ^{1}H-NMR ($CDCl_3$): $\delta = 2.1–3.05$ (*m*, 12H), 3.2–4.35 (*m*, 27H), 6.65–7.0 (*m*, 4H), 8.52 (*s*, 2H), IR (deposit from chloroform): 3580, 3380 (N—H), 1530 (NO_2), 1101 (C—O) cm^{-1}. Calcd. (lithium amide hydrate): C, 50.81; H, 6.19. Found: C, 50.52: H, 6.01.

When **13** was reacted with picryl chloride in methanol in the presence of triethylamine, a red-brown solid with mp 42–50°C was obtained in 99% yield. ^{1}H-NMR ($CDCl_3$): $\delta = 2.1–3.05$ (*m*, 12H), 3.2–4.35 (*m*, 27H), 6.85 (*s*, 4H), 8.52 (*s*, 2H). IR (deposit from chloroform): 3583, 3373 (N—H), 1531 (NO_2), 1101 (C—O) cm^{-1}. Calcd. (hydrate): C, 51.23; H, 6.38. Found: C, 50.94; H, 6.29.

2.11. IONIZATION OF CHROMOGENIC CRYPTANDS

The pK_a values for the chromogenic cryptands in aqueous dioxane solutions were determined by the spectrophotometric method [12] based on the absorptivities of individual acid/base forms of the chromogenic cryptands. A combination pH electrode having a silver-chloride reference and a leak junction was used to measure the pH in 50% aqueous dioxane. The results were uncorrected for dioxane concentration or liquid junction potential effects.

3. Results and Discussion

3.1. SYNTHESIS OF CHROMOGENIC COMPOUNDS 3–7

Nitration of commercially-available benzo[2.2.2]cryptand with concentrated nitric acid in chloroform-glacial acetic acid gave 4′-nitrobenzo[2.2.2]cryptand in 98% yield. The nitrated benzo cryptand was hydrogenated over 10% Pd/C in DMF to afford a cryptand amine which was directly coupled with 1-chloro-2,4-dinitro-6-trifluoromethylbenzene in the presence of sodium bicarbonate in methanol to give chromogenic benzo cryptand **3** in an 18% overall yield from the benzo[2.2.2]cryptand. Similar reaction of 4′-aminobenzo[2.2.2]cryptand with 1-chloro-2,6-dinitro-4-trifluoromethylbenzene produced chromogenic compound **4** as a sodium bicarbonate complex (64% yield) and a small amount of the free ligand.

Chromoionophores **5** and **6** were prepared by a different route. Thus, high dilution cyclization of 1,2-bis(oxyacetyl chloride)-4-nitrobenzene with 1,13-diaza-24-crown-8 in toluene gave cryptand diamide **8** in 63% yield. Reduction of **8** with borane-dimethyl sulfide in THF afforded a 73% yield of nitro cryptand **9** which was hydrogenated over 10% Pd/C in DMF to form cryptand amine **10** in 71% yield. Coupling of **10** with picryl chloride in the presence of triethylamine produced chromogenic benzo cryptand **5** in 62% yield. Similar reaction of **10** with 1-chloro-2,4-dinitro-6-trifluoromethylbenzene gave a 48% yield of chromogenic cryptand **6**.

For the preparation of chromoionophore **7** which bears a pendant, proton-ionizable chromogenic group, hydroxymethyl[2.2.2]cryptand (**11**) was reacted with *p*-toluenesulfonyl chloride to give tosylate **12** in 61% yield. Subsequent reaction of *o*-aminophenol with sodium hydride and **12** in THF provided a 96% yield of **13**. Coupling of **13** with picryl chloride in methanol in the presence of lithium carbonate afforded a lithium cryptate of chromogenic cryptand **7** in 67% yield. When the coupling was carried in the presence of triethylamine, **7** was isolated as a monohydrate in an almost quantitative yield.

3.2. COMPLEXATION BEHAVIOR

Interactions of chromogenic cryptand **3**, which was isolated and characterized as the free ligand, with alkali metal cations were probed by a solvent extraction technique. Chloroform solutions of **3** were shaken with aqueous alkali metal hydroxide solutions. Changes in the ultraviolet-visible spectrum of the chloroform layers were monitored.

The absorption maximum for chromogenic cryptand **3** in chloroform ($\lambda_{max} = 453$ nm, $\varepsilon = 19{,}400$) revealed that the chromophore unit was already in its ionized form. Shaking chloroform solutions of **3** with aqueous solutions of lithium, sodium or potassium hydroxides changed neither the position nor the extinction coefficient of the absorption maximum. Complexation of an appropriately-sized alkali metal cation within the cryptand cavity would be expected to affect both the absorption frequency and intensity of the chromoionophore.

Both the ionized form of the free ligand and its lack of response to the presence of alkali metal cations may be rationalized if chromogenic cryptand **3** exists in the form of a zwitterion **14**. A positive charge on the protonated cryptand would inhibit

alkali metal cation complexation by charge repulsion. The proton itself may be located within the cryptand cavity where hydrogen bonding can take place.

The pK_a values for the chromophore N—H group of **3** in 50% and 70% aqueous dioxane were determined to be 9.3 and 9.5, respectively. Reported pK_a values for diprotonated [2.2.2]cryptand in 95% methanol–5% water are 6.65 and 9.85 [13]. This suggests that the cryptand amine nitrogens of **3** have approximately the same basicity as the amine nitrogen of the chromophore and lends support to the proposal that **3** exists in the zwitterion from **14**.

In an attempt to decrease the acidity of the chromophore unit [15], preparation of an analogous compound **4** was attempted in which the trifluoromethyl group has been shifted to the 4-position. However, the synthesis yielded almost exclusively a 1 : 1 complex of **4** and sodium bicarbonate. A small portion of the product which was isolated as the free ligand exhibited ^{1}H-NMR and IR spectra which were very similar to those shown by **3** for which the zwitterion form **14** is postulated.

Chromogenic cryptand **7** contains the same type of chromophore unit as do **3** and **4**, but now the less substituted benzene ring is separated from the cryptand framework. When the synthesis of **7** was attempted using lithium carbonate as the base for coupling of cryptand amine **10** with picryl chloride, the product obtained was the lithium cryptand complex. Subsequent attempts to produce the free ligand **7** by treatment with mineral acid were unsuccessful. When triethylamine was used in the coupling reaction instead of lithium carbonate, the free ligand was obtained as a monohydrate. However, analysis of **7** by ^{1}H-NMR, IR and UV-visible spectroscopy were again consistent with a zwitterion form. In agreement, the UV-visible spectrum of **7** in chloroform was unaffected after shaking with aqueous sodium and potassium hydroxide solutions.

A potential solution to the problem of 'internal ionization' of the chromophore unit is to utilize larger cryptands which have less basic bridgehead nitrogen atoms. Reported pK_2 values for parent cryptands [2.2.2], [3.2.2], [3.3.2] and [3.3.3] in water are 9.60, 8.50, 8.16 and 7.70, respectively [14]. To investigate this approach, two chromogenic cryptands **5** and **6** based on benzo[3.3.2]cryptand were synthesized. Analytical evaluation did indeed reveal that these two chromogenic cryptands have structures **5** and **6** rather than the zwitterion forms which were observed for **3**, **4** and **7**.

Electronic spectra for the HL and L^- forms of chromogenic cryptands **3**, **5** and **6** in 50% aqueous dioxane are shown in Figure 1. Absorption maxima and extinction coefficients for the HL and L^- forms of all five chromogenic cryptands are collected in Table I. The $\Delta\lambda_{max}$ valued for dissociation of the chromophore amine protons of **3**–**7** are 87, 145, 72, 88, and 47 nm, respectively.

Spectral responses of chromogenic cryptands **3**, **5** and **6** to sodium and potassium ions in 50% aqueous dioxane at pH = 9.5 and 10.0 are recorded in Table II. Chromophore pK_a values in 50% aqueous dioxane in the absence and presence of sodium and potassium ions are given in Table III.

The UV-visible spectrum of chromogenic cryptand **3** in 50% aqueous dioxane remained unchanged in the presence of sodium and potassium ions. The chromophore pK_a value of 9.3 was constant for all three forms (L^-, NaL and KL) of **3**.

The picryl group-containing chromogenic cryptands **5** exhibited a greater spectral response to potassium ions than to sodium ions. The chromophore pK_a value for **5**

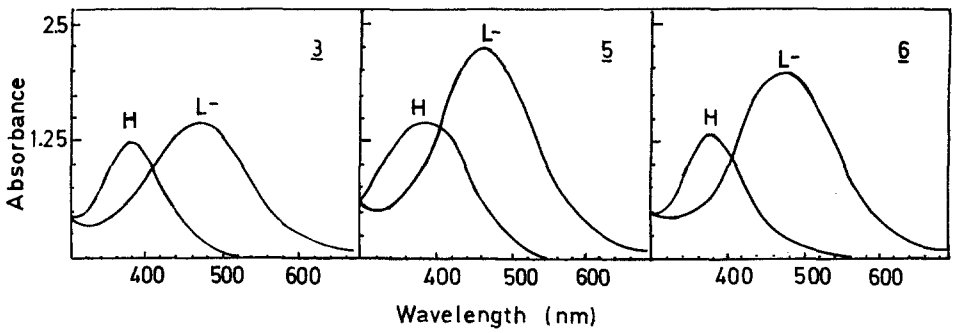

Fig. 1. Electronic spectra of chromogenic cryptands **3**, **5** and **6** in 50% aqueous dioxane (HL = acid form in 0.10N HCl; L^- = base form in 0.10N TMAH).

was diminished in the presence of sodium ions and reduced even further by the presence of potassium ions.

Chromogenic cryptand **6**, which is the same as **5** except for replacement of the 6-nitro group with a 6-trifluoromethyl (6TF) group, gave greater spectral responses to the presence of sodium ions ($\Delta\lambda_{max} = 33$ nm) and potassium ions ($\Delta\lambda_{max} = 54$ nm) at pH = 9.5 (Figure 2) than at 10.0 (Table II). Again the chromophore pK_a value was lowered in the presence of sodium ions and decreased even further in the presence of potassium ions (Table III). A set of potassium ion

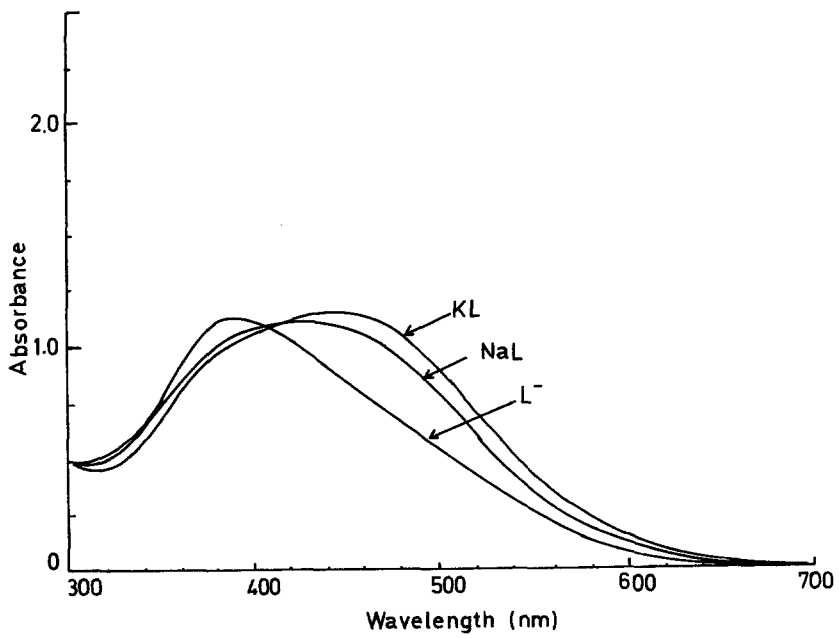

Fig. 2. Potassium and sodium ion responses of chromogenic cryptand **6** at pH 9.5 in 50% aqueous dioxane (0.11mM **6** and 25.0mM M^+).

Table I. Wavelength maxima and extinction coefficients for chromogenic cryptands **3**–**7** in 50% aqueous dioxane

Compound	HL		L^-	
	λ_{max}(nm)	$\varepsilon \times 10^4$	λ_{max}(nm)	$\varepsilon \times 10^4$
3	379	1.03	466	1.25
4	416	0.43	561	0.29
5	388	1.34	460	2.05
6	380	1.22	468	1.78
7	366	1.57	413	1.44

Table II. Spectral responses of chromogenic cryptands **3**, **5** and **6** to sodium and potassium ions at pH 9.5 and 10.0 in 50% aqueous dioxane

	$\frac{\lambda_{max}(nm)}{(\varepsilon \times 10^4)}$					
	pH 9.5[a]			pH 10.0[a]		
Compound	L^-	NaL	KL	L^-	NaL	KL
3	444 (0.95)[b]	445 (0.98)[b]	447 (1.01)[b]	459 (1.13)[b]	460 (1.13)[b]	462 (1.27)[b]
5	412 (0.02)[c]	423 (1.05)[c]	429 (1.18)[c]	429 (1.13)[c]	442 (1.35)[c]	445 (1.53)[c]
6	391 (0.68)[d]	424 (0.80)[d]	445 (0.96)[d]	452 (1.13)[d]	458 (1.41)[d]	461 (1.46)[d]

[a]0.10 M CHES [2-(*N*-cyclohexylamino)ethanesulfonic acid], adjusted with tetramethylammonium hydroxide.
[b]$\varepsilon_{\lambda max}$; [c]$\varepsilon_{\lambda 460}$; [d]$\varepsilon_{\lambda 468}$

Table III. Chromophore pK_a values for compounds **3**, **5** and **6**

Compound	pK_a		
	L^-	NaL	KL
3	9.28	9.28	9.30
5	10.00	9.77	9.65
6	9.80	9.54	9.34

response curves for **6** in 50% aqueous dioxane is shown in Figure 3. Comparison of the data obtained for chromoionophores **5** and **6** clearly shows that the latter is superior for the spectrophotometric determination of sodium and potassium ions. Similar superiority of the 6TF chromophore has been observed earlier with chromogenic crown ethers [15].

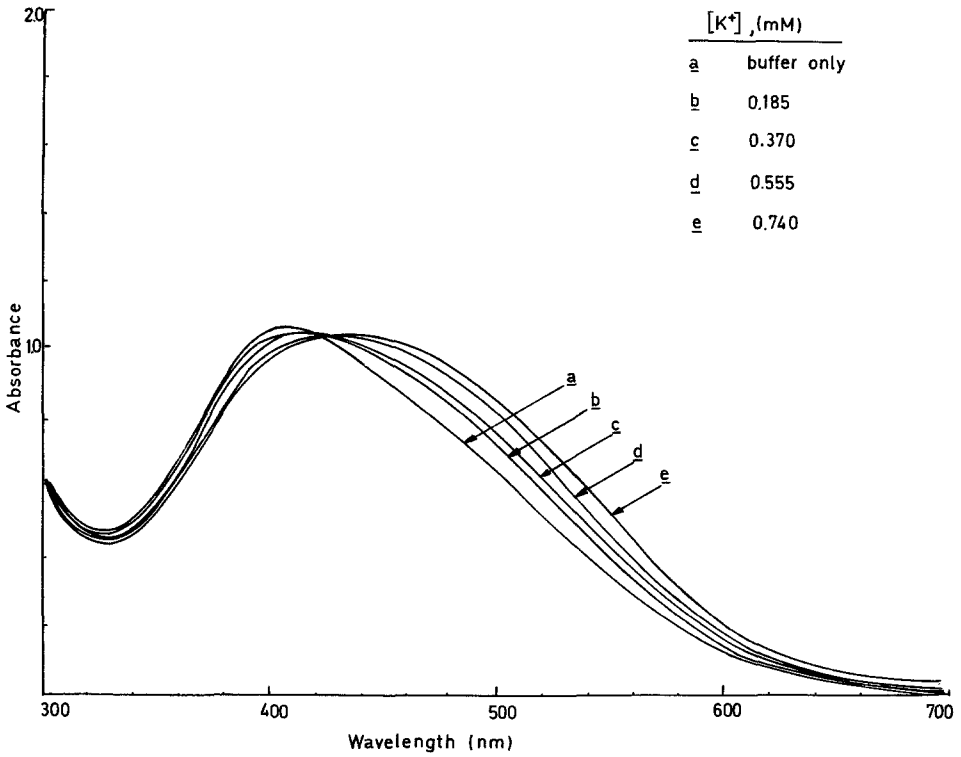

Fig. 3. Potassium ion response curves for 0.11mM **6** at pH 9.5 in 50% aqueous dioxane.

3.3. CONCLUSIONS

Five novel chromogenic cryptands which incorporate substituted diphenylamine chromophores have been prepared. Potential chromoionophores **3**, **4** and **7**, which are based on benzo[2.2.2]cryptand or [2.2.2]cryptand itself, did not respond to the presence of potassium or sodium ions due to an apparent existence of the chromogenic cryptands in zwitterion forms. Thus, the substituted diphenylamine chromophore is ionized with transfer of the proton to one of the cryptand nitrogen atoms. On the other hand, chromogenic cryptands **5** and **6**, which are based upon benzo[3.3.2]cryptand, exhibit spectrophotometric sensitivity to the presence of potassium and sodium ions with a greater influence of potassium ions. Thus the lower basicity of the bridgehead nitrogen atoms in **5** and **6** precludes zwitterion formation and allows the spectrophotometric response to be altered by the presence of potassium and sodium ions.

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