Tetrahedron Letters, Vol.32, No.50, pp 7419-7420, 1991
Printed in Great Britain

0040-4039/91 \$3.00 + .00
Pergamon Press plc

NEW CHROMOIONOPHORES BASED ON INDOANILINE DYES CONTAINING CALIX[4]ARENE

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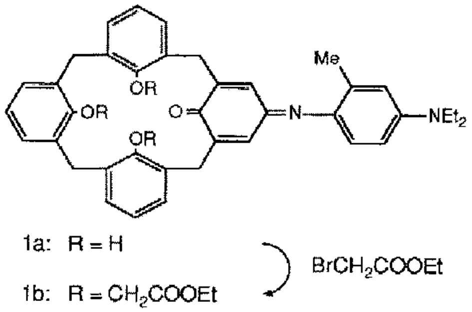
Summary: A new set of chromoionophores having indoaniline and calix[4]arene segments have been prepared, the ethylacetate derivative of which shows a high selectivity for Na^+. Sodium ion binding induces a bathochromic shift in the absorption spectrum of this chromoionophore leading to the suggestion that this class of compounds could have potential use as an optical sensor for Na^+ detection.

Recently, particular emphasis has been devoted to developing spectrophotometric methods for Na^+ and K^+ detection that are ready adoptable to clinical analysis. Thus, synthetic chromoionophores which show alkali - cations induced color change could be of great value.[1] The indoaniline chromophore system might be one of important candidates because the optical property can be perturbed significantly by chemical stimuli. To date, a set of crown ether-derived indoanilines have been synthesized.[2] Although this system shows cations induced color change, no high cation selectivity was observed. To obtain compounds which would show better selectivity, we designed a new type of indoaniline-derived dyes containing calix[4]arene **1**.

Condensing calix[4]arene[3] with 4-diethylamino-2-methylaniline hydrochloride under alkaline conditions in the presence of $K_3Fe(CN)_6$ at room temperature afforded the mono-substituted product, 23-(4'-diethylamino-2'-methylphenylimino)-26,27,28-trihydroxypentacyclo$[19.3.1.1^{3,7}1^{9,13}.1^{15,19}]$octacosa-1(24),3,5,7(28),9,11,13(27),15,17,19(26),21-undecaen-25-one, **1a**[4] in 74% yield, followed by ethoxycarbonylmethylation to give the ethylacetate derivative **1b**[5] in 40% yield. The molecules **1a** and **1b** absorb visible light at 661 nm (ε_{max} 45,000) and 574 nm (ε_{max} 13,000) in n-butyl acetate, respectively. The absorption property of **1a** appears influenced by an *intramolecular hydrogen bonding interaction*. Here, we thought that a metal ion, which is encapsulated in the cavity constructed with $-OCH_2COO-$ groups for **1b**, could cause some change in the absorption maximum. In fact, addition of NaSCN (30 equiv.) to **1b** in 99% EtOH solution caused a bathochromic shift of 42 nm with an increase in absorption intensity compared to **1b** (Figure 1). Use of the continuous variation method[6] indicated the formation of a 1:1 Na^+ - **1b** complex. However, the addition of $LiI \cdot 2H_2O$, KSCN, RbI, and CsSCN caused minor or no changes in the absorption



1a: R = H

1b: R = CH$_2$COOEt

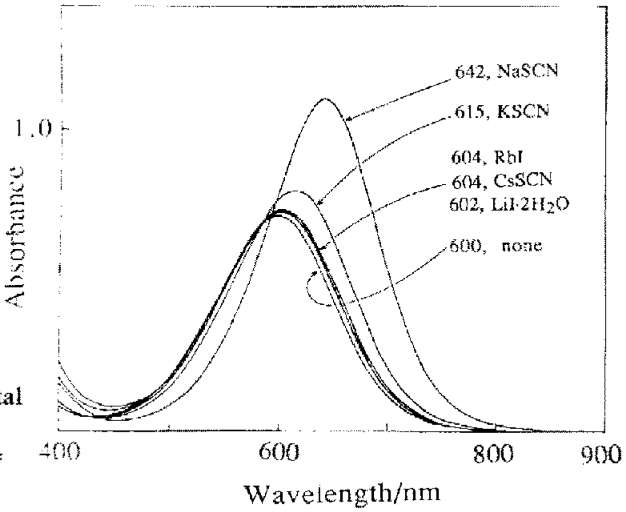


Figure 1. Influence of added alkali metal ions on the absorption spectra of **1b** in 99% EtOH; [metal salt]/[**1b**] = 30, [**1b**] = 5.0×10^{-5} mol dm^{-3}.

spectrum. From these results, **1b** exhibits a high selectivity for Na$^+$. It has been well-known that the tetraester-derived calix[4]arene forms an encapsulated complex with Na$^+$ ion.[7] Here, the rather specific Na$^+$ ion induced bathochromic shift observed for **1b** could be explained on the basis of the well-tailored electrostatic interactions existing between Na$^+$ cation surrounded by -OCH$_2$COO- groups and the indoaniline carbonyl oxygen segment. The excited state of the chromophore might be more stabilized by the cation than the grand state.

In conclusion, this study demonstrates that **1b** could behave as a new type of chromogenic host molecule and have potential applications as a sensor for Na$^+$ detection.

Y. K. acknowledges Prof. Jonathan L. Sessler of the University of Texas for helpful discussions.

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5. **1b**, ^{1}H n.m.r.(CDCl$_3$, 90MHz) δ 0.92-1.33 (15H, m), 2.26 (3H, s), 3.05-4.63 (24H, m), and 6.07-7.18 (14H, m); mass: m/z 858(M$^+$ + 2); elemental analysis: Found: C, 71.4; H, 7.3; N, 2.8. $C_{51}H_{56}N_2O_{10}$ requires C, 71.5; H, 6.6; N, 3.3.
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(Received in Japan 17 September 1991)