LIGHT-SWITCHED IONOPHORIC CALIX[4] ARENES

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Abstract: Three bianthracene-substituted calix[4]arenes were synthesized and a novel attempt to use these two anthracene moieties as a "photochemical lid" for the ionophoric cavity was reported.

It has been established that ester derivatives of calix[4]arene (1) show the high affinity as well as the high selectivity toward Na⁺ ion.¹⁻⁴ The superb properties of 1 as ionophores stem from the ionophoric cavity size that exactly fits the size of Na⁺ and from the moderately-rigid calix[4]arene skeleton. Thus, applications of 1 as ion sensors, extractants, membrane carriers, etc. are now under intensive investigation.⁵ The sole defect, if any, is the slow complexation and decomplexation rate⁶: the slow exchange rate is related to the energetically-unfavorable comformational change in the relatively "rigid" calix[4]arene skeleton which occurs obligatorily upon



complexation or decomplexation of metal ions. Is there any practical method to "enforce" complexation with or decomplexation from $1/Na^+$? From careful examination of X-ray crystallographic pictures we noticed that in uncomplexed 1 four ester carbonyls are turned outward (exo-annulus direction) presumably to reduce electrostatic repulsion among carbonyl groups whereas in complexed 1 they are turned inward (endo-annulus direction) to bind Na⁺ in the cavity.⁷ This difference tells us that if one could "enforce" the carbonyl groups to turn outward, decomplexation of Na⁺ would be readily achieved. With these objects in mind, we introduced two photo-dimerizable anthracenes into the terminal alkyl groups: examination of their CPK molecular models suggests that dimerization of these two anthracenes can "enforce" the two carbonyl groups to turn outward.⁸

Compound **2a** was synthesized from 25,27-dihydroxy-26,28-dimethoxy-5,11,17,23-tetra-t-butylcalix[4]arene^{9,10} and 9-anthrylmethyl bromoacetate in refluxing benzene in the presence of metal sodium: mp 294 °C (decomposition), yield 91%. Compound **2b** was synthesized from 25,27-dimethoxy-26,28-bis(2hydroxyethoxy)-5,11,17,23-tetra-t-butylcalix[4]arene (prepared by LiAlH₄ reduction of 25,27-dimethoxy-26,28-bis(ethoxycarbonylmethoxy)-5,11,17,23tetra-t-butylcalix[4]arene) and anthracene-9-carbonyl chloride (prepared from anthracene-9-carboxylic acid and thionyl chloride): mp 254 °C, yield 83 %. Compound **2c** was synthesized from 25,27-dihydroxy-26,28-dipropoxy-5,11,17,23tetra-t-butylcalix[4]arene^{9,10} and 9-anthryloxyethyl bromoacetate in refluxing benzene in the presence of metal sodium: mp 196.5 °C, yield 77 %.The products were identified by ¹H NMR, FT-IR and mass spectral data in addition to elemental analysis data.



2c(4.93x10⁻⁵ mol dm⁻³): in tetrahydrofuran, at 25 °C.

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We first carried out two-phase solvent extraction of alkali picrates in order to estimate the ionophoric properties. The results (Table 1) indicate that **2a** shows the high but broad ion affinity toward alkali metal ions whereas **2c** shows the sharp ion selectivity toward Na⁺. The high Na⁺ selectivity observed for **2c** is attributable to the rigidly-delineated ionophoric cavity: in **2c** the rotation of four phenyl units is inhibited whereas in **2a** the rotation of two anisole units is still allowed.^{9,10} On the other hand, the ionophoricity of **2b** was relatively poor. This is due to the too-long spacer (CH₂CH₂O) between the phenolic oxygen and the ester carbonyl.

Photoreactions were carried out in tetrahydrofuran using a high-pressure Hg-lamp (450 W) through a cut-off filter UV-35 (λ >350 nm). Thermal dimer-tomonomer reactions were monitored by following the appearance of an absorption band at 365 nm at 25 °C. It was shown that the photoreaction of 2a was irreversible: although the spectral change occurred upon photoirradiation, the spectrum of 2a was not reproduced. We detected 9-hydroxymethylanthracene by HPLC. In 2b and 2c, in contrast, photochemical monomer-to-dimer conversion and thermal dimer-to-monomer conversion occurred reversibly (Fig. 1). Dimerto-monomer conversion could be accelerated by light shorter than 280 nm. The first-order rate constants for thermal dimer-to-monomer conversion were 2.13x10⁻³ s⁻¹ for 2b and 3.03x10⁻⁴ s⁻¹ for 2c. The Ex% values for dimeric 2c (>95% dimer purity) were estimated at -5 °C because at room temperature significant dimer-to-monomer conversion occurred during the extraction period. As shown in Table 1, the Ex% for Na+ was drastically reduced from 40.8% to 4.9%. The result indicates that the ionophoric cavity in dimeric 2c is photochemically "lidded".

Table 1. Extractabilities (Ex%) of alkali picrates^a

Metal	Extractant				
	2.8	2 b	20	2 එ	dimeric 2d
L1+	24.3	4.9	13.8	12.2	10.5
Na⁺	88.2	7.6	54.3	40.8	4.9
K*	94.1	21.5	2.0	2.1	3.0
Rb⁺	66.9	24.1	4.3	2.7	3.0
Cø†	70.6	<1	<1	<1	<1

^aAqueous phase (5cm³), [MOH]=0.10 mol dm⁻³, [MCl]=0.50 mol dm⁻³, [picric acid]=2.2x10⁻⁵ mol dm⁻³. Organic phase $(C_2H_2Cl_4:CH_2Cl_2=4:1 \text{ v/v}, 5 \text{ cm}^3):$ [2a]=9.63x10⁻⁶ mol dm⁻³, [2b]=9.93x10⁻⁶ mol dm⁻³. [2c]=3.00x10⁻⁵ mol dm⁻³. Extraction time 12 hours, extraction temperature 25 °C. ^bExtraction time 30 min, extraction temperature -5 °C.



The photoresponsive complexation-decomplexation process could be continuously monitored by electric conductivity because it sensitively reflects the dissociation of ionic species (Fig. 2). The Λ decrease occurring with photochemical dimerization is due to the squeezing-out of Na⁺ from 2c whereas the Λ increase with thermal dimer-to-monomer conversion is due to 2cinduced dissociation of NaClO₄.¹¹

In conclusion, the present study demonstrated that one can put a "lid" on the ionophoric cavity of calix[4]arene. The results are important in relation to a photochemical control of ionophoric properties in calix[4]arene and its analogs, which would be eventually led to photocontrol of ion extraction, ion transport, ion sensing, *etc*.

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