Anion- and Solvent-dependent Photochemical Decomplexation of Sodium Salt Complexes of a Calix[4]arene Tetraester

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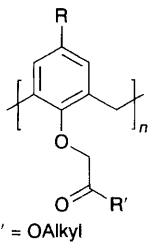
Sodium salt complexes of *p-tert*-butylcalix[4]arene tetraethyl acetate, where the anion is iodide, bromide, thiocyanate, perchlorate, tetraphenylborate, tetrafluoroborate or hexafluoroantimonate undergo a solvent-dependent decomplexation when irradiated with a low-pressure mercury lamp; photocleavage or photoisomerisation of the calixarene is not observed.

Calixarene esters of type **1** are known to form stable complexes with alkali cations.[1] The selectivity of complexation is determined by the size of the calixarene, the nature of the alkoxy residues of the ester and the solvent.[2] Esters in the tetramer series, *e.g.* **2**, in the cone conformation, favour Na^+, whereas the larger calix[6]arene esters show a distinct preference for Cs^+. Although there is no direct evidence for the structures of these complexes, NMR data for the tetramer derivatives suggest that the cation is bound within a polar cavity defined by the carbonyl oxygen atoms and the phenolic oxygen atoms of the calixarene substructure, the complex as a whole assuming C_{4v} symmetry.[2,3] The structure of a closely related tetraamide **3** complex with K^+, for which X-ray evidence is available, reveals this type of encapsulation of the cation.[4]

There have been several important studies of the effect on metal ion complexation in macrocyclic receptors, *e.g.* crown ethers, of photochemically induced isomerisation.[5] Cation complexation is sensitive to ligand geometry and binding equilibria can be effectively modulated by employing a photoexcitation which causes a conformational or geometric change, *e.g.* photoisomerisation, in the receptor. Most studies of photoresponsive systems have involved receptors with built-in azobenzene or stilbene units where the stability of the complex may be significantly changed by *cis*/*trans* isomerisation.[6,7] In a recent study Martin *et al.*[8] reported the photoejection of Li^+ and Ca^{2+} ion from mercocyanine–azacrown ether complexes and made the suggestion that a charge transfer from the nitrogen atom to the dicyanomethylene moiety in the ligand supplied the trigger for decomplexation. However, the fate of the ligand was not disclosed and it is unclear as to whether the process was in fact reversible or if the ligand suffered irreversible chemical change. To date there have been no clear-cut examples of decomplexation where the photoexcitation process disrupts the receptor–guest binding without modifying the ligand. A recent example of photoejection of alkali cations from their cryptates is in fact a photocleavage of a strategic bond in the receptor which robs it of its affinity for the cation: photodecomposition of the receptor ensues and the outcome is thus irreversible.[9]

We now report the first example of photochemical decomplexation of Na^+ complexes of *p-tert*-butylcalix[4]arene tetraethyl acetate **2** without either photocleavage or photoisomerisation of the receptor and show that the process is both counterion and solvent dependent, and reversible. If the binding ability of calixarene ionophores can be regulated by light in this way it may lead to the development of photocontrol of ion-transport systems. This preliminary study was conducted with NaI, NaBr, NaSCN, $NaClO_4$, $NaBPh_4$, $NaBF_4$ and $NaSbF_6$ salts of tetraester **2**. The individual salts were prepared and isolated as crystalline solids and it was confirmed by ^1H NMR measurements that the ester in each case was in the complexed state. Photochemical experiments were conducted using an Aldrich quartz photoreactor with a low-pressure mercury lamp. Initial experiments showed that decomposition of the calixarene occurred after short irradiation times. The use of a pyrex filter while significantly reducing the intensity of the light did allow clean decomplexation to occur. Dilute solutions of the individual Na^+ complexes in the chosen solvent were irradiated for 35 min while the solution was continuously purged with a stream of dry nitrogen. Since Na^+ forms kinetically stable complexes with **2** on the NMR timescale, it was relatively simple to estimate by ^1H integration the extent of decomplexation as a function of time, there being very diagnostic chemical shift differences between the spectrum of **2** and those of its complexes. For illustration, the spectra of **2** and **2**·NaI before and after *ca.* 20 min irradiation are shown in Fig. 1. The results of a series of experiments in methanol, acetonitrile, ethyl acetate, toluene, and chloroform are shown in Table 1.



1 R' = OAlkyl
2 R = Bu^t, R' = OEt, *n* = 4
3 R = Bu^t, R' = NEt_2, *n* = 4

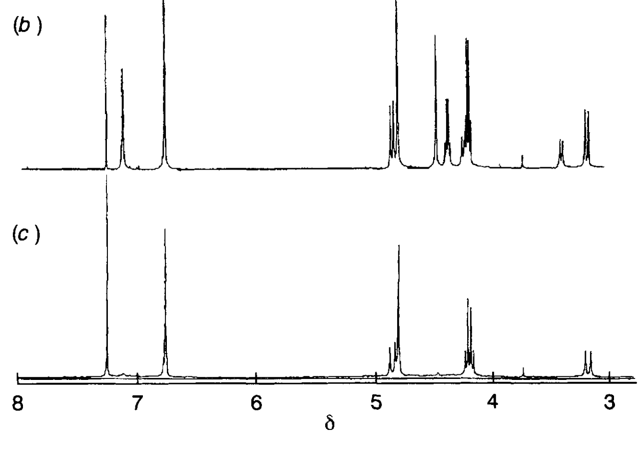


Fig. 1 (*a*) The ^1H NMR spectrum (δ 3.0–8.0) of the NaI complex of tetraester **2** in $CDCl_3$; (*b*) the spectrum of after 20 min irradiation; (*c*) the spectrum of the uncomplexed tetraester in $CDCl_3$

The principal observations are (*a*) photochemical decomplexation up to high levels can be achieved within 35 min; (*b*) the organic product of decomplexation is the free calixarene ester **2**, *cf.* Fig. 1(*a*), (*b*) there being no evidence of calixarene decomposition or conformational change. However, prolonged exposure did lead to decomposition of the ligand to as yet unidentified products; (*c*) addition of fresh sodium salt to the solution after 35 min irradiation with brief stirring showed that recomplexation had occurred; (*d*) the extent of decomplexation is solvent dependent with high levels with most salts in toluene and chloroform and no decomplexation in methanol or acetonitrile; (*e*) the extent of decomplexation is also anion dependent with iodide and thiocyanate the most labile in at least two solvents and perchlorate the least labile.

No simple explanation is apparent for what seems to be a very easy decomplexation. The UV–VIS spectrum of the calixarene shows two strong bands at *ca.* 280 nm. These bands have been assigned to π–π^* transitions of the phenolic units which would be accessible on mercury arc excitation. While intramolecular electronic energy transfer can be envisaged in the system possibly leading to decreased ligating ability towards Na^+, the fact that the decomplexation process is anion dependent may be of greater significance. In preliminary experiments with some of the anions, namely thiocyanate and iodide, we have found by IR spectroscopy and titration, respectively, that when decomplexation does occur these anions do not survive the irradiation process, suggesting that decomposition of the anion may be the trigger for decomplexation. This interpretation requires the formation of new anions which, together with Na^+, are not complexed by the tetraester. Preliminary UV measurements of the solution after decomplexation suggest that triiodide ion is among the new anions produced from the NaI complex of **2**. Addition of fresh NaI or NaSCN leads to recomplexation. Although the solvent effects are also not well understood, it may be significant that the more polar solvents, in which one would expect to have solvent separated ion-pairs, are also the solvents in which decomplexation occurs to the least extent. In contrast, toluene and chloroform, in which strong ion pairing would be expected, are solvents in which decomplexation is favoured. Although ethyl acetate is also a non-dissociating solvent, the failure to observe significant decomplexation may be due to the strong photoreactions associated with this solvent.

Table 1 Percentage decomplexation on photolysis of **2**·NaX in various solvents

	Anion $X^{a,b}$						
Solvent	I^-	Br^-	SCN^-	ClO_4^-	BPh_4^-	BF_4^-	SbF_6^-
MeOH/MeCN	0	0	0	0	0	0	0
EtOAc	20	0	0	0	0	4	0
PhMe	90	50	45	10	10	100	64
$CHCl_3$	70	10	70	0	40	0	0

[a] Exposure time 35 min in each case. [b] Average of 2 runs.

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