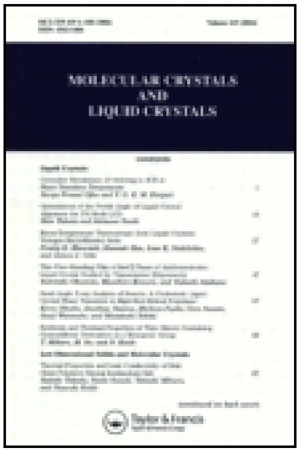

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Solid-State Structure and Spectroscopy of Chromoionophoric Acridinium Derivatives

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SOLID-STATE STRUCTURE AND SPECTROSCOPY OF CHROMOIONOPHORIC ACRIDINIUM DERIVATIVES

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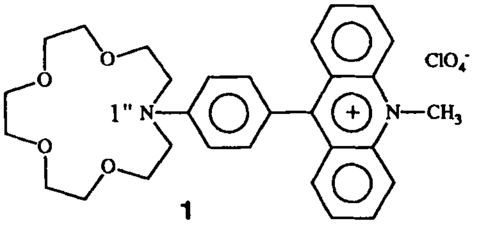
Abstract. A comparative study is presented of the chromoionophoric and fluoroionophoric behaviour of **1** and **2**, which both consist of an aza-crownether-ionophore integrated with a twisted 9-aryl-acridinium chromophore. In **2** the degree of ground state twisting in the chromophore is enhanced relative to that in **1**. While the cation induced spectral shifts (*i.e.* chromoionophoric effect) in **2** are not significantly different from those in **1**, the cation binding properties of **2** are enhanced significantly. This is explained in terms of better preorganisation of **2** and higher charge density of the anilino nitrogen in **2** as supported by X-ray data. In addition to their chromoionophoric properties, the non-fluorescing **1** and **2** show an acridinium-type of fluorescence upon binding of H^+ and Ag^+ ions. This fluoroionophoric effect is also significantly enhanced in **2** where restricted internal, rotational freedom allows for a higher fluorescence quantum yield of the complex.

INTRODUCTION

As demonstrated in earlier spectroscopic[1-3] and X-Ray structural[4] studies the spectral response of chromofluoroionophoric compound **1** upon metal-ion complexation is largely dominated[1-3] by the interaction between the metal-ion and the 'soft' nitrogen atom which forms part of the aza-crown ether of **1**. The X-ray structures of **1** and its complexes with metal-ions also revealed[2,3,4a-c] that the torsion angle, between the least square planes through the acridinium moiety and the aryl group, increases upon metal-ion complexa-



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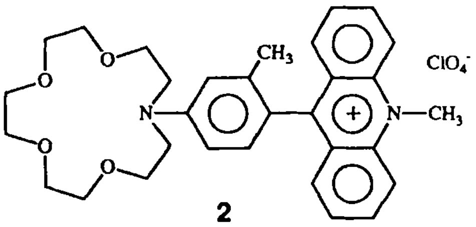

2

tion, *i.e.* from 57° in the uncomplexed **1** to *e.g.* 74° in the Ag^+-**1** complex.
These results inspired us to synthesize **2**. This molecule differs from **1** in that it has a methyl group introduced at the 2'-position of the aryl ring. From X-ray analyses[4e-f] of related 9-arylacridinium systems we know that this causes the torsion angle to increase to values around 70°-80° thus leading to a better preorganisation for complexation.

RESULTS AND DISCUSSION

Absorption spectra.

The absorption spectra of compounds **1** and **2** are given in Fig. 1. For both compounds three characteristic absorption bands are distinguishable; two structured bands at ≈ 360 nm and ≈ 420 nm respectively and one broad structureless band at ≈ 560 nm. The two short-wavelength transitions are typical[1,5] for the acridinium chromophore and are localised in this part of the molecule. The long-wavelength transition has been assigned[1] as an intramolecular Charge-Transfer (CT) transition, where Charge-Transfer occurs from the electron rich N-phenyl aza-crown ether (Donor) to the electron poor acridinium moiety (Acceptor). In accordance with its delocalised nature, the molar absorption of this CT transition, which does not vary with concentration (10^{-2}-10^{-5} M), is significantly lowered upon introduction of the methyl group, from 9800 $M^{-1}.cm^{-1}$ in **1** to 4210 in **2**. Protonation of the amino functionality leads to the loss of its electron donating properties and, as a consequence, to complete disappearance of the CT absorption band (see Fig. 1 and Table 1).

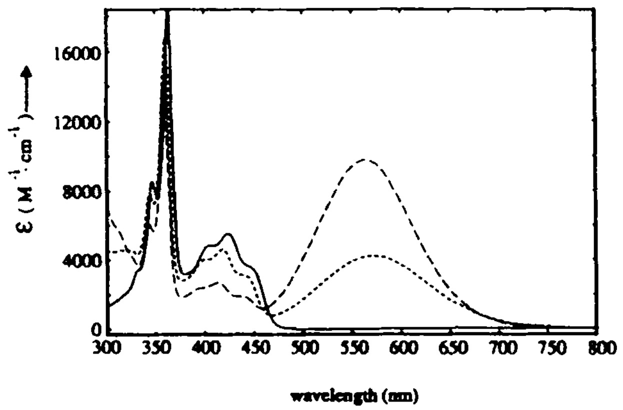

FIGURE 1 VIS/near UV spectra of **1**(– – – –), **2** (------) and protonated **2** (= **2**.$HClO_4$: ———) in acetonitrile at 20°C .

TABLE I Absorption characteristics of **1** and **2** and their complexes with several salts; the cation induced shifts of the first absorption maximum relative to uncomplexed **1** and **2** (in cm^{-1}).

Medium	Cation radius[a] [in Å] (coordn. no.)	λ_{max} (nm) [ε ($M^{-1}.cm^{-1}$)]		$\Delta\bar{\nu}$ (cm^{-1})	
		1	**2**	**1**	**2**
CH_3CN	-	412 [2700]; 562 [9800]	418 [4600]; 572 [4200]	0	0
$CH_3CN + HClO_4$	-	424 [5500]	424 [5700]	5791	6102
$CH_3CN + LiClO_4$	0.76 (6)	526 [6530]	529 [2580]	1217	1421
$CH_3CN + NaClO_4$	1.02 (6)	488 [5070]	± 488 [± 2000]	2698	3009
$CH_3CN + KClO_4$	1.37 (6)	530 [6530]	514 [2770]	1074	1972
$CH_3CN + Ca(ClO_4)_2$	1.06 (7)	428 [6270]	424 [6000]	5570	6102
$CH_3CN + Ba(ClO_4)_2$	1.47 (9)	442 [6670]	427 [6130]	4830	5936
CH_2Cl_2	-	420 [2700]; 604 [12570]	424 [4700]; 624 [5200]	0	0
$CH_2Cl_2 + AgClO_4$	1.15 (6)	459 [5430]	432 [5420]	5230	7122

a) from ref. 11.

UV/VIS reflection spectra (Fig. 2) of pulverised crystals of **1** and **2** (see experimental) show features quite similar to the spectra in solution (compare Figs. 1 and 2). X-ray analysis[4c,d] (see below) of these crystals provided the exact torsion angles between the aromatic moieties in **1** and **2**. These were found to be 57° (**1**)[4c] and 78° (**2**)[4d] respectively, while the intermolecular contact distances between Donor nitrogen N(1") and Acceptor nitrogen in the crystal were found to be larger than 6 Å. So it seems fair to conclude that, for **1** and **2**, the oscillator strength of the internal CT absorption band, in

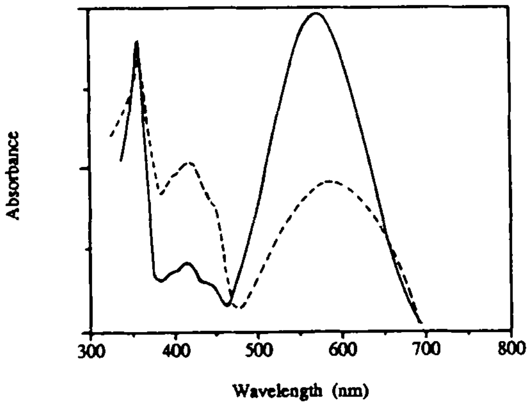

FIGURE 2 VIS/near UV reflection spectra of pulverised crystals of **1**(———) and **2** (– – – –).

solution as well as in the solid state is directly related to the torsion angle between Donor and Acceptor moieties.

Chromoionophoric behaviour of 1 and 2.

VIS/near-UV spectra of 2 and its complexes with H^+, Li^+, Na^+, K^+, Ca^{2+}, Ba^{2+} and Ag^+ are given in Figs. 1,3,4, while relevant data are summarized in Table I, together with data for 1 as obtained earlier[1,2].

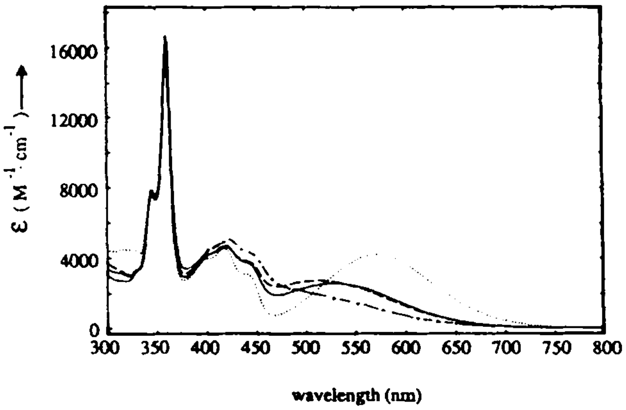

FIGURE 3 Effect of some alkali metal ions on the absorption of 2 in acetonitrile at 20°C : 2 (.......), 2+$LiClO_4$ (———), 2+ NaSCN (– · – · –), and 2+ KSCN (– – – –).

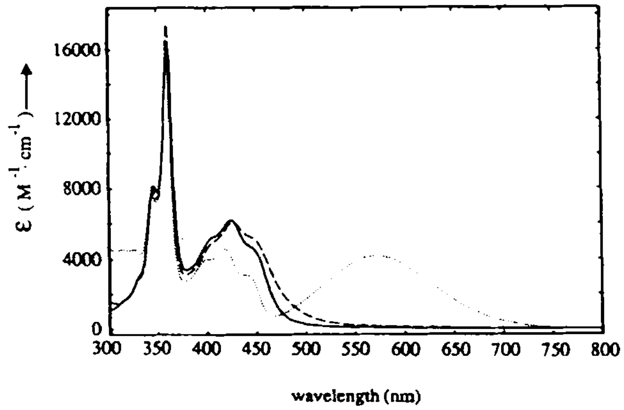

FIGURE 4 Effect of alkaline earth ions on the absorption of 2 in acetonitrile solution at 20°C : 2 (·······), 2+ $Ba(ClO_4)_2$ (– – – –), and 2+ $Ca(ClO_4)_2$ (———)

Table I shows that for **1** and **2** the cation induced shifts of the longest wavelength absorption band are roughly of the same magnitude, though the shifts are consistently somewhat larger for **2**, which is especially pronounced in the case of K^+. The introduction of the 2'-methyl group in **2** clearly has only minor effect on the position of the energy levels of **2** with respect to those of **1**, but is evident - as in the free ligand - from the decrease of transition probability of the CT absorption bands in the case of Li^+, Na^+ and K^+ (see Table I). In the case of Ca^{2+}, Ba^{2+} and Ag^+, the CT absorption band is hidden under the local absorption band, in both **1** and **2**, and since both bands borrow intensity from each other[3], the sum of their intensities will remain roughly the same.

Complexing ability of 1 and 2.

The improved complexation of **2**, which we anticipated, becomes evident from Table II. In this Table pK_a and log K values for complexation with Ca^{2+} and Ba^{2+} are summarized for **2**, together with the values of **1** determined[1] earlier. While the protonation equilibrium for **2** lies a factor 4.4 more towards the protonated species relative to that of **1**, this is a factor 2.5 for the complexation equilibrium with Ca^{2+} and Ba^{2+} ions.

TABLE II pK_a - values of **1** and **2** as determined from spectrophotometric (and fluorimetric) titration in water at 20°C, and log K values for complexes of **1** and **2** with $Ca(ClO_4)_2$, $Ba(ClO_4)_2$ and $Ba(SCN)_2 \cdot 3H_2O$ in dry acetonitrile at 20°C.

Compound	pK_a	log K		
		$Ca(ClO_4)_2$	$Ba(ClO_4)_2$	$Ba(SCN)_2 \cdot 3H_2O$
1	2.60 (2.52)	3.06 (± 0.03)	2.60 (± 0.06)	2.87 (± 0.02)
2	3.24 (3.18)	3.46 (± 0.08)	3.00 (± 0.04)	3.30 (± 0.02)

Fluoroionophoric behaviour of 1 and 2.

Both **1** and **2** are non-fluorescent due to the presence of a non-emitting (TI)CT-state[6] below the lowest excited state of the acridinium part. Cations that by complexation shift the TICT state to an energy above the locally, in the acridinium, excited state may thus induce fluorescence from the latter to become observable. Amongst the cations investigated only H^+ and Ag^+ create such a situation in both **1** and **2**. Results are given in Table III, which also shows that the fluorescence quantum yield of the complexed species is very significantly higher for **2** than for **1**. This phenomenon may readily be attributed to the reduced torsional freedom in **2**. Thus upon protonation the fluorescence quantum yield of **2** rises from 0 % → 100 % making **2** an extremely sensitive pH-probe in the pH 2-6 region, an acidity region present[7] in endosomes and lysosomes and for which a scarcity of sensitive probes appears to exist[8].

In analogy, the fluorescence quantum yield of $2\bullet AgClO_4$ was found to be much higher than that of $1\bullet AgClO_4$ (resp. 0.072 and 0.014, see Table III).

Table III Emission characteristics of the protonated compounds $1\bullet H^+$ and $2\bullet H^+$ in water at 20°C and of the complexes of **1** and **2** with $AgClO_4$ in dichloromethane at 20°C.

	$+HClO_4$ (H_2O)		$+AgClO_4$ (CH_2Cl_2)	
	ϕ^a	λ(nm)	ϕ^a	λ(nm)
1	0.24	509	0.014	508
2	1	501	0.072	508

a) Fluorescence quantum yields (excitation at 404 nm) were determined from the ratio of the integrated emission relative to that of 10-methylacridinium chloride, which has a known quantum yield of 1 (see ref. 2) and has similar absorption and emission characteristics.

Relation between spectral shifts and X-Ray structures.

For **1** and **2** and for most of their metal-ion complexes the structure in the solid state has been determined by single crystal X-ray diffraction. While we refer to the separate publications[2-4] for full details on these structures, we note here that an overall picture emerges which is consistent with the hypothesis that the cation induced spectral shifts of **1** and **2** in solution are governed by the binding strength between the cation and N(1") in these cation complexes. This binding strength, in turn, should be related to the configuration of N(1"), which will change from trigonal planar to pyramidal as a function of increasing cation - N(1") binding.

TABLE IV Relevant X-ray structural data (from refs. 2-4) for **1**, **2** and their cation complexes.

	Sum of bond angles at N(1")		Torsion angle acridinium-phenyl	
cation	**1**	**2**	**1**	**2**
none	359.6	359.2	57	78
Li	-	356	-	66
Na	344.5	347	63	82
K	-	351.6	-	85
Ba	342.6	340.5	73	78
Ag	337	-	57	78

The sum of the covalent bond angles at N(1") (=Σ) as taken from X-ray analyses (see Table IV), provides a measure for the degree of pyramidalization at N(1") in the solid state. In Fig. 5 we plot the spectral shift observed for various complexes of **1** and **2** as a function of this parameter. Evidently a strong correlation exists, especially for **2** where the spectral shifts deviate less than 600 cm^{-1} from those corresponding to the regression line that is given by :

$$\Delta v(2) = -294.16\,\Sigma + 105680 \quad (\text{in cm}^{-1})$$

Interestingly this correlation predicts a shift of $\Delta v(2) = 9048$ cm^{-1} for a tetrahedral configuration (328.5°), as expected to be approached upon protonation of N(1"). This would put the CT-absorption at 26531cm^{-1} (377 nm) and thus very much to the high energy side of the "local" acridinium absorption, thus providing additional credibility to our explanation for the fluorescent nature of $2{\bullet}H^+$ (as well as $1{\bullet}H^+$)

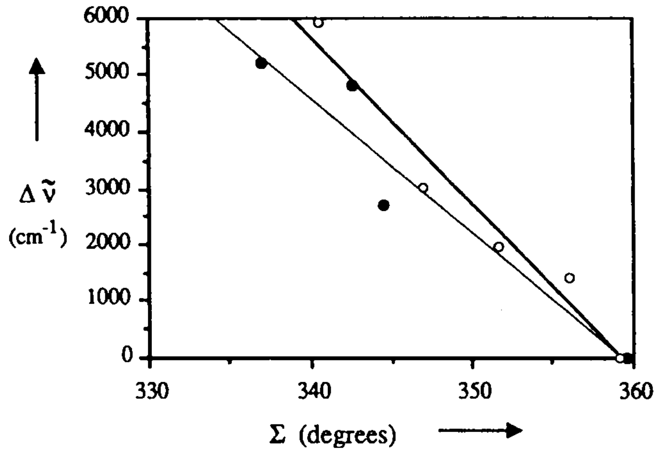

FIGURE 5 Relation between the cation induced shifts (Δυ) of the first absorption band and the sum (Σ) of the covalent bond angles at N(1") for **1** (•) and for **2** (o).

In conclusion, the X-ray data for **1**, **2** and their metal-ion complexes substantiate and enhance the correlation between the solid-state structural parameters and chromo(fluoro)ionophoric behaviour in solution as postulated earlier[1,2,3]. Thus, solid-state structural data provide a valuable guide in efforts to optimize chromo- and fluoroiono phoric systems via molecular engineering.

EXPERIMENTAL

Instrumentation

^{1}H NMR spectra were recorded on a Bruker AC 200 instrument. IR spectra were recorded on a Perkin Elmer 1310 spectrometer and UV-VIS spectra on a Hewlett-Packard HP 8451A diode array UV-VIS spectrophotometer or on a Cary 17D instrument. UV-VIS reflection spectra of pulverised crystals of **1** and **2** were taken on a Cary 14 instrument with a Cary model 1411 diffuse reflectance accessory. Crystals of **1** and **2** were pulverised and homogenised and spread on a solid support, which was previously coated with Kodak Lableader Analytical Standardwhite reflectance coating ($BaSO_4$; cat 118 1759). Corrected emission spectra were recorded on a SPEX-Fluorolog 2. Samples for emission spectroscopy were diluted to A(1cm) ≤ 0.1 at the wavelength of excitation and deoxygenated by purging for 15 minutes with argon. Determination procedures of the pK_a-value of **2** and the formation constants (K) of **2** with $Ca(ClO_4)_2$, $Ba(ClO_4)_2$, and $Ba(SCN)_2{\bullet}3H_2O$ have been extensively described in a previous paper[1].
Melting points were determined on a Reichert hot stage microscope and are uncorrected.

Materials

We wish to stipulate that perchlorates present a potential explosion hazard and should be handled with care and possibly only in small quantities! Li ClO_4, Na ClO_4, $KClO_4$, $Ba(ClO_4)_2$ were purchased from Merck, $Ca(ClO_4)_2$ and $Ba(SCN)_2{\bullet}3H_2O$, from Alfa, $AgClO_4$ from Fluka and KSCN and NaSCN from Janssen Chimica. These salts were used without further purification. For the determination of the stability constants, $Ca(ClO_4)_2$ and $Ba(ClO_4)_2$ were dried in very small amounts in an oven at 230°C and dissolved in dry acetonitrile. Acetonitrile (Janssen Chimica spectrograde) was dried under reflux over calcium hydride and subsequently distilled prior to each measurement.

Syntheses

The synthesis of *9-[4-(4,7,10,13-Tetraoxa-1-azacyclopentadecyl)-phenyl]-10-methylacridinium perchlorate* (**1**) has been previously described[1].

9-[2-Methyl, 4-(4,7,10,13-tetraoxa-1-azacyclopentadecyl)-phenyl]-10-methylacridinium perchlorate (**2**). Condensation of 1,8-dichloro-3,6-dioxaoctane (Fluka) with N,N-bis(2-hydroxyethyl)-m-toluidine (prepared according to *Ross*[9]) following the procedure of *Dix* and *Vögtle*[10] gave 1-(3-methylphenyl)-4,7,10,13-tetraoxa-1-azacyclopentadecane with a 12% Yield. ^{1}H NMR (200 MHz; $CDCl_3$) : δ 2.30 (s, 3H, CH_3), 3.6 - 3.8 (m, 20H, crown -CH_2O/CH_2N), 6.5 (m, 3H, phenyl-H2,4,6), 7.3 (t, 1H, phenyl-H5). M.p. 50-58 °C (uncomplexed); 159-162 °C ($NaClO_4$-complex). Compound **2** was synthesised from 10-methylacridinium iodide and 1-(3-methylphenyl)-4,7,10,13-tetraoxa-1-azacyclopentadecane following the same procedure[1] which was used for the synthesis of **1** (yield 19 %). Since crystals were not readily formed in this case, the complex was further purified via the $Ba(ClO_4)_2$-complex: **2** and a small excess of $Ba(ClO_4)_2$ were disolved in acetonitrile followed by addition of diethylether to the point of cloudening of the solution. Upon standing, orange crystals precipitated with m.p. 235-237 °C. Decomplexation of the complex could be achieved by dissolving the compound in water and subsequent extraction of the compound from the water layer with dichloromethane. The dichloromethane was washed 3 times with water. After concentration *in vacuo*, the raw meterial was dissolved in acetonitrile, followed by addition of diethylether to the point of cloudening. Upon standing dark purple crystals formed with m.p. 175 °C. This crystallization procedure was repeated three times. ^1H NMR (200 MHz; $CDCl_3$) : δ 1.87 (s, 3H, phenyl-CH_3), 3.7-3.9 (m, 20H, crown - CH_2O/CH_2N), 5.03 (s, 3H, N^+-CH_3), 6.73(m, 2H, phenyl-H3,5), 7.05 (d, 1H, phenyl-H6), 7.79 (t, 2H, Acridinium-H2,7), 8.09 (d, 2H, Acridinium-H1,8), 8.37 (t, 2H, Acridinium-H3,6), 8.71 (d, 2H, Acridinium-H4,5). IR (KBr): 1090-1140 cm^{-1} (CO), 1575, 1600 cm^{-1} (arom. C=C), 2870-3000 cm^{-1} (alif. CH), 3000-3030 cm^{-1} (arom. CH). Structure confirmed by X-ray analysis[4d].

ACKNOWLEDGEMENT

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