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SUPRAMOLECULAR EFFECTS ON PHOTOCHROMISM—PROPERTIES OF CROWN ETHER-MODIFIED DIHYDROINDOLIZINES*

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Photochromic molecules such as dihydroindolizines (DHI) containing crown ether units can be 'tuned', as far as their properties are concerned, by supramolecular ion binding. Inclusion of the ion in the crown ether cavity yields a new supramolecular species. This species shows special properties of the excited state after guest addition: (a) bathochromic shifts of the photochromic crown ethers and also hyperchromic effects in the UV spectra; (b) fluorescence intensity of one of the photochromic crown ethers is either increased (crown excitation) or decreased (DHI excitation) after addition of alkali metal ions; and (c) in the ground state a large change in reaction rate for the reaction 1,5-electrocyclization betaine (coloured form) to dihydroindolizine is observed in the supramolecular complexes.

INTRODUCTION

Supramolecular systems have been intensively investigated recently,[1] and the 'tuning' of thermal and photochemical properties in such species is of great current interest.[2] To achieve this goal, supramolecular systems may be used to influence both ground-state and excited-state properties. For example, binding of crown ethers and bipyridinium systems shows interesting selectivity.[3] Excited-state properties may be changed by salt effects[4] and chemical reactivity can be controlled in supramolecular systems.[5] The combination of supramolecular effects, which can be geared by light switching, is a field receiving considerable interest.[6] The systems studied in Ref. 6 involve light-sensitive enzymes or enzyme analogues showing selective binding in the on and off state.

In this context, photochromic systems may be tailored in such a way as to allow supramolecular structures to undergo selective ion binding, leading to assemblies with new properties.[7] Little is known in this field, however, and very few studies of supramolecular photochromic systems are available.[6,8,9] Effects on emission data have been studied, but in non-photochromic metal ion cryptands.[10–13]

In this paper, we present (a) tuning of photophysical properties of the excited state in supramolecular photochromic systems, (b) effects on chemical reactivity of supramolecular species and (c) some results of molecular modelling studies of the host systems.

TUNING OF PHOTOPHYSICAL PROPERTIES

UV spectra/excited state

The photochromic crown ethers **1a–f** studied are shown in Scheme 1. Their synthesis has been reported elsewhere.[7]

The photochromism in spirodihydroindolizines (DHI) **1** is based on the reaction shown in Scheme 2. The conversion **1** → **2** is thus a unimolecular photochromic system.[9]

The supramolecular effects on the excited state were probed with the colourless spirodihydroindolizines **1** and the coloured form, the betaines **2** by both UV (absorption) and fluorescence (emission) spectroscopy.

Alkali and alkaline earth metal ions were employed as guests for the spirodihydroindolizine (**1**) and betaine

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* Dedicated to Professor H. G. O. Becker on the occasion of his 70th birthday.

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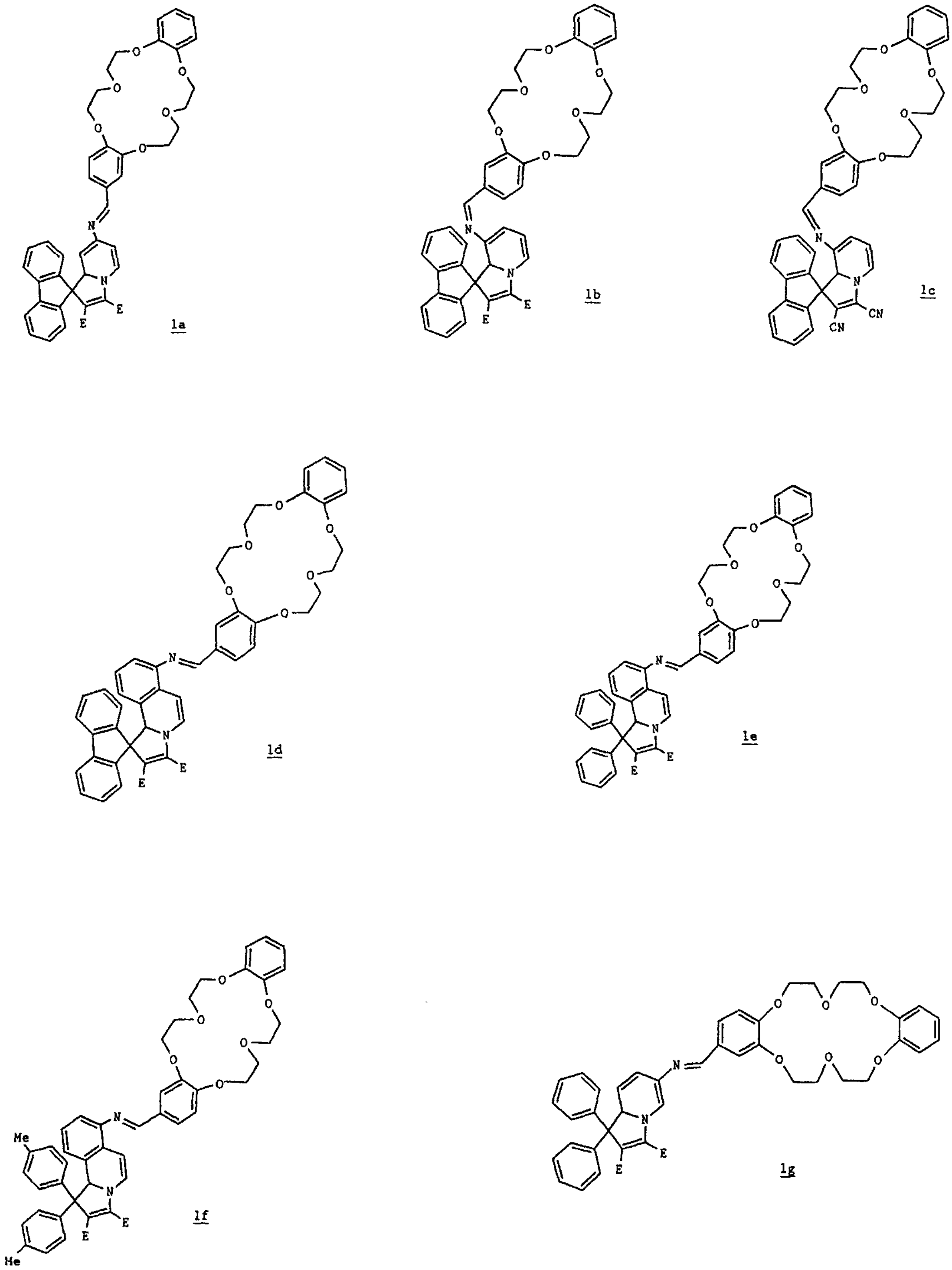
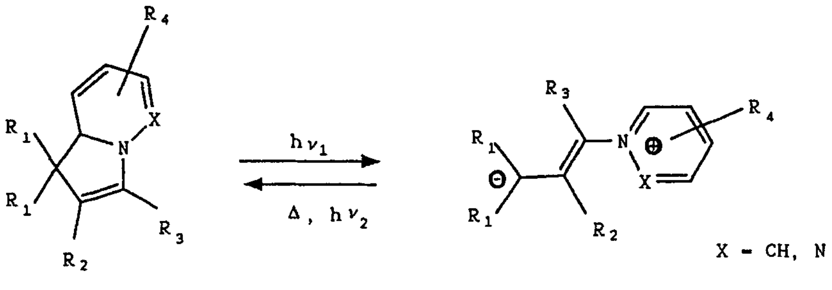


Scheme 1



1 2

Scheme 2

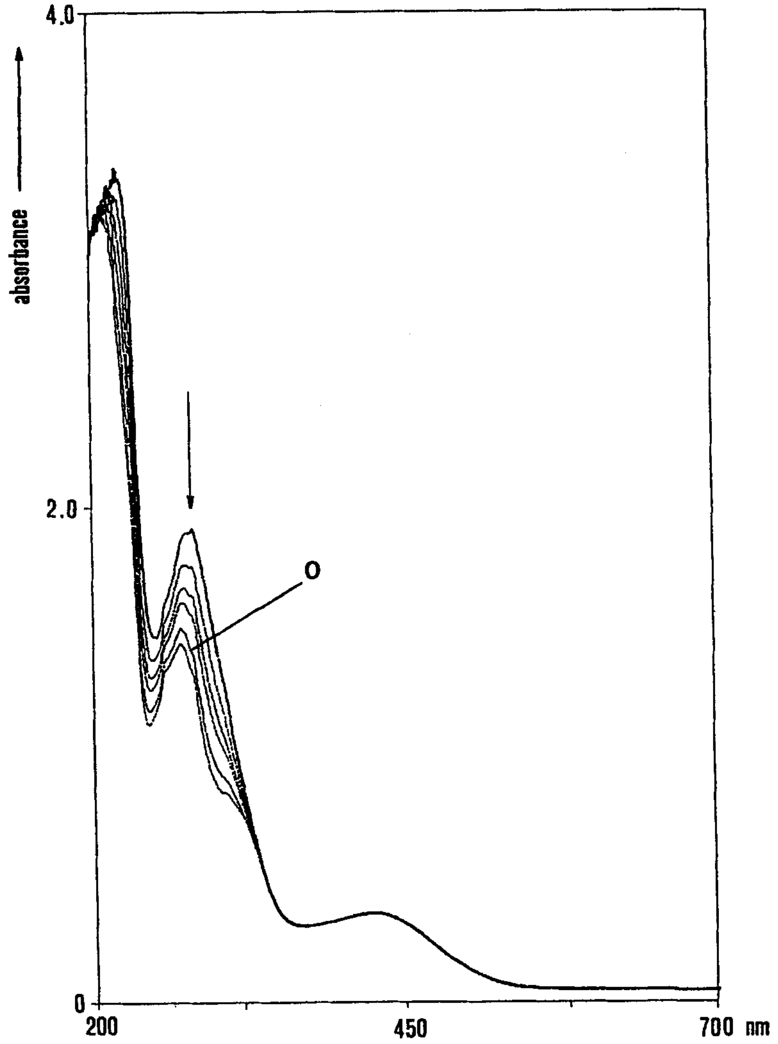


Figure 1. Change in UV spectrum of DHI **1b** (host) with increasing addition of K^+I^- (guest). c_{DHI} **1b** : K^+ = 1 : 0·6–1·4 (O : no salt added)

Table 1. Effects on UV spectra (λ_{max}) of supramolecular ion binding of **1a** and **2a** [in CH_2Cl_2–MeOH (2 : 1)]

	1a				**2a**	
Cation	λ_{max_1} (nm)	Log ε	λ_{max_2} (nm)	Log ε	λ_{max} (nm)	
Salt-free	324	4·34	269	4·49	621	459
Li^+	320	4·29	240	4·66	609	457
Na^+	355[a]	4·19	238	4·66	621	458
K^+	357	4·22	264	4·58	624	459
Rb^+	313[b]	4·38	252	4·73	623	459
Mg^{2+}	354[c]	4·03	264	4·62	605	458
Cal^{2+}	362	4·62	264	4·58	–	–
Sr^{2+}	358	4·14	264	4·63	615	459
Ba^{2+}	361	4·18	264	4·70	605	460

[a] Shoulder 321 nm (10 $\varepsilon = 4{\cdot}24$).
[b] Shoulder 359 nm 10 $\varepsilon = 4{\cdot}19$).
[c] Shoulder 277 nm (10 $\varepsilon = 4{\cdot}58$).

(**2**) hosts. The non-complexed photochromic model compounds are included in Table 1, which gives the spectral data.

Figure 1 shows a typical example of the effect of increasing amounts of ions (see Experimental). The complexation of K^+ by the photochromic crown ether can be seen by the appearance of a new peak at 280 nm (arrow; see also Ref. 10a).

From Figures 1–3 and Table 1, it can be concluded that supramolecular effects can be easily detected in the dihydroindolizines **1a**. In **1a** a bathochromic shift (with the exception of Li^+ and Rb^+) of the band at 324 nm occurs on guest addition (Table 1). In the other photochromic molecules **1b–d** only weak changes in the long-wavelength region of the spectrum are observed. In **1e** and (see Figure 2) a hyperchromic effect after adding metal ions is obvious. In the betaine **2f** a hypochromic shift is seen (Figure 3).

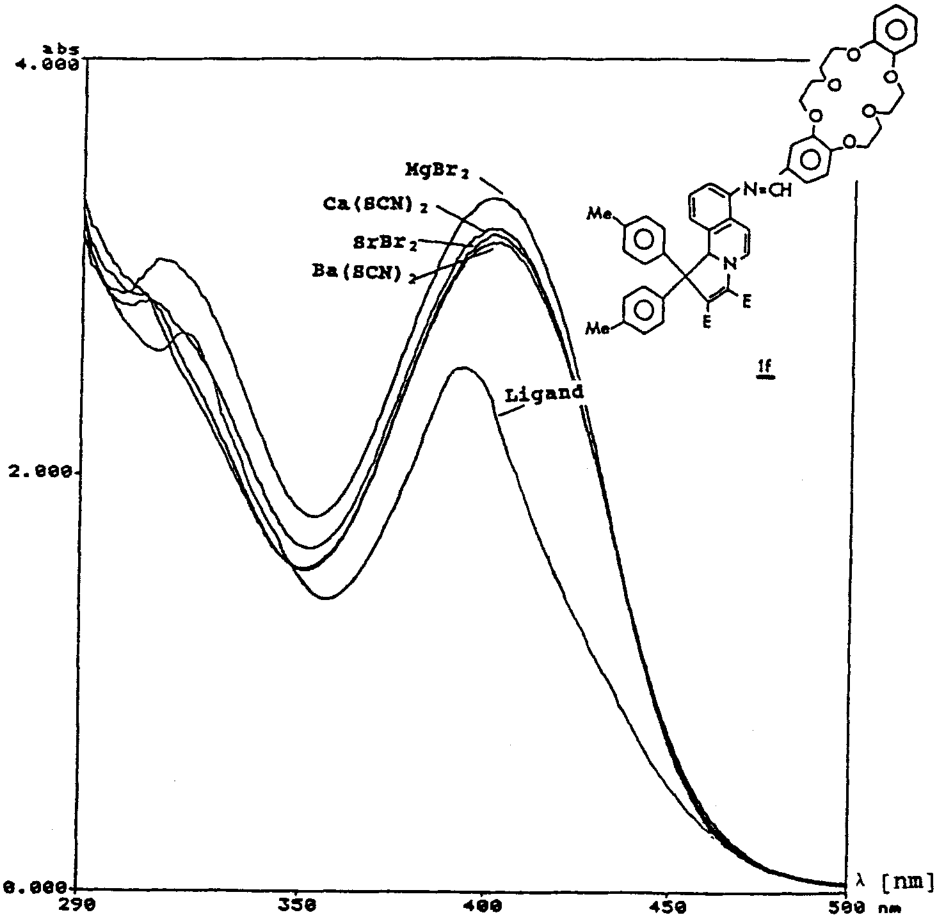


Figure 2. Absorption spectra of **1f** in dichloromethane– methanol (2 : 1) with addition of alkaline earth metal ions. Concentrations of DHI **1f** : salt < 0·01; ligand = **1f**

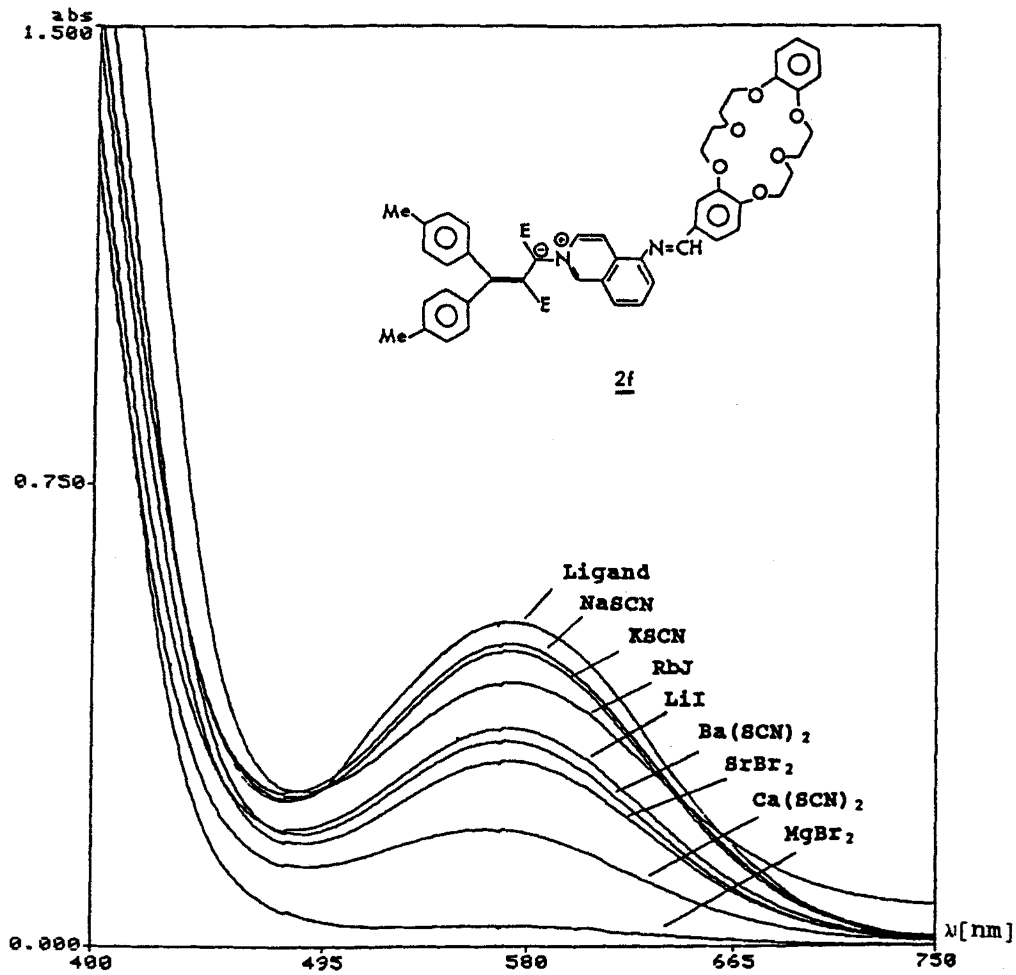


Figure 3. Absorption spectra of **2f** in dichloromethane– methanol (2 : 1) after addition of alkali and alkaline earth metal salts. Concentration of DHI **2f** : salt < 0·1; ligand = **2f**

Emission spectra

In a study of **1b** by emission spectroscopy using solutions of 5×10^{-5} M **1b** (reference) plus $2{\cdot}5 \times 10^{-5}$ M alkali metal iodides in methanol (1 : 5), the effect of alkali metal ions was investigated. The fluorescence spectra of the complexes **1b** + Me^+ did not show significant changes in wavelength compared with the spectra of the reference compound **1b**. Excitation at 260 nm (crown excited) results in a fluorescence maximum at $\lambda_{em} = 389$ nm, whereas excitation at 394 nm (DHI bond) gives rise to fluorescence at $\lambda_{em} = 504$ nm. However, the fluorescence intensity is enhanced by the addition of alkali metal ions if excitation occurs at 260 nm. Similar results were found by Shizuka *et al.*,[14] who reported fluorescence enhancement of dibenzo-18-crown-6 after addition of alkali metal cations. Excitation of the π–π^* transition of the DHI **1b** ($\lambda = 394$ nm) causes the fluorescence intensity to decrease. We assume that the fluorescence of the DHI **1b** is simply quenched by the metal ions.

SUPRAMOLECULAR EFFECTS ON REACTIVITY: 1,5-ELECTROCYCLIZATION

Photoinduced ring opening of DHI **1** affords the coloured betaine **2**. This molecule can undergo a concerted 1,5-electrocyclization to give **1**.[15] It was of interest if (concerted) cyclization and thus reactivity can be tuned by supramolecular effects. To study this problem, **1c** was investigated in the presence of alkali and alkaline earth metal ions. The reaction rate for the cyclization of the betaine **2** → DHI **1** can be described by the half-life,

$t_{1/2} = \ln 2/k$, where k = cyclization rate. A slow cyclization $\mathbf{2} \rightarrow \mathbf{1}$ is equivalent to a large $t_{1/2}$ value. To see clearly the effect of added metal ions on the reaction rate or $t_{1/2}$, we introduced a new value, $t'_{1/2}$: $t'_{1/2} = t_{1/2}(\mathrm{DHI} + \mathrm{M}^{n+})/t_{1/2}(\mathrm{DHI})$ where $t_{1/2}$ $(\mathrm{DHI} + \mathrm{M}^{n+})$ = half-life in the presence of metal (M) ions and $t_{1/2}(\mathrm{DHI})$ = half-life in the absence of metal ions.

The parameter equals $t'_{1/2} = 1$ if there is no salt or supramolecular effect. Table 2 shows the half-lives for the coloured form **2c** ($t_{1/2} = \ln 2/k$).

Figure 4 gives plots of the $t'_{1/2}$ data at 25 °C. It can be seen that especially K^+ and Ba^{2+} ions produce the largest decrease in $t'_{1/2}$ of **2c** values [Figure 4(a)]. Alkali metal ions give rise to larger effects on $t'_{1/2}$ than alkaline

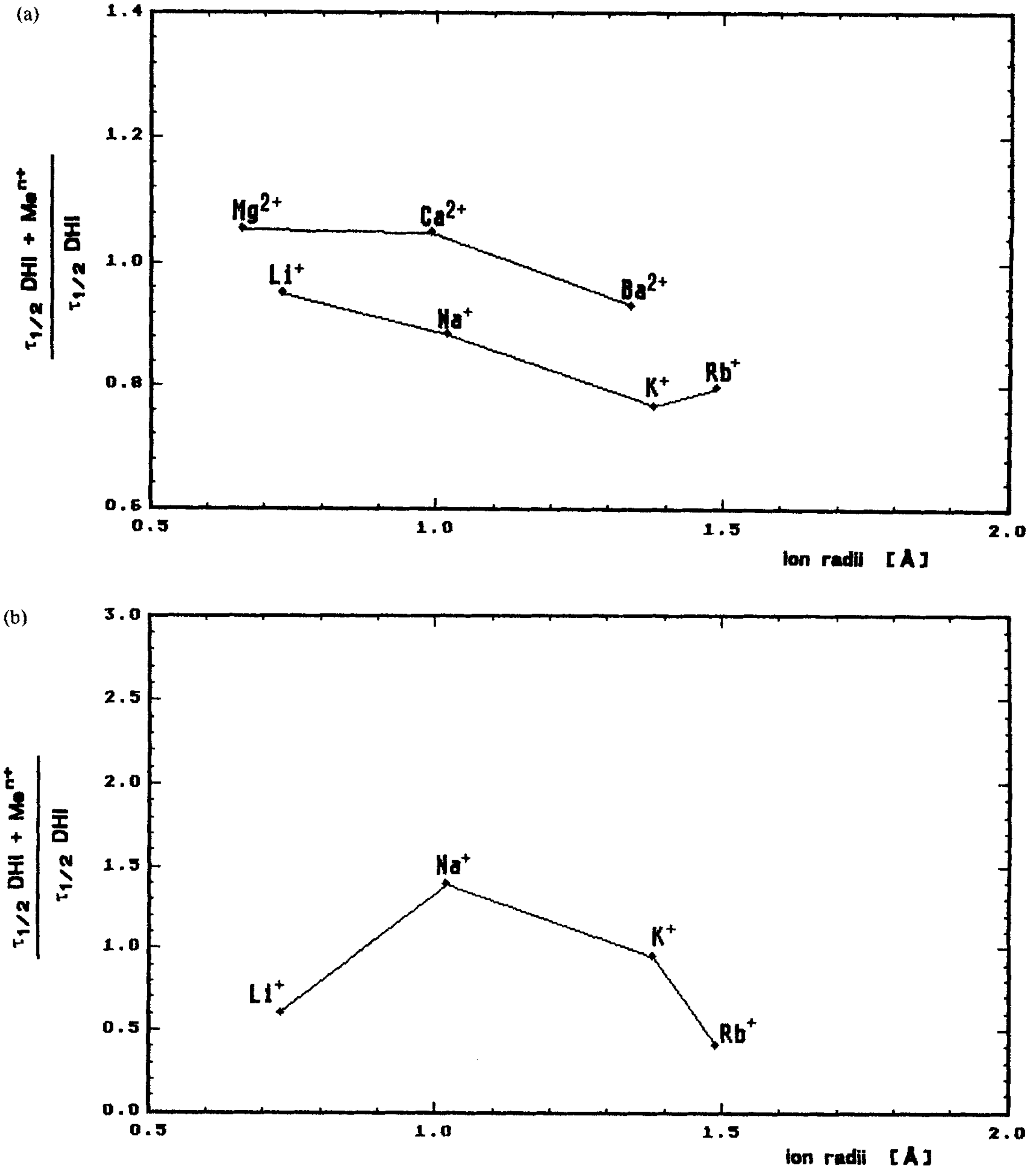


Figure 4. Plot of $t'_{1/2}$ values of coloured species (a) **2c** (b) **2e** and (c) **2f** depending on guest added.

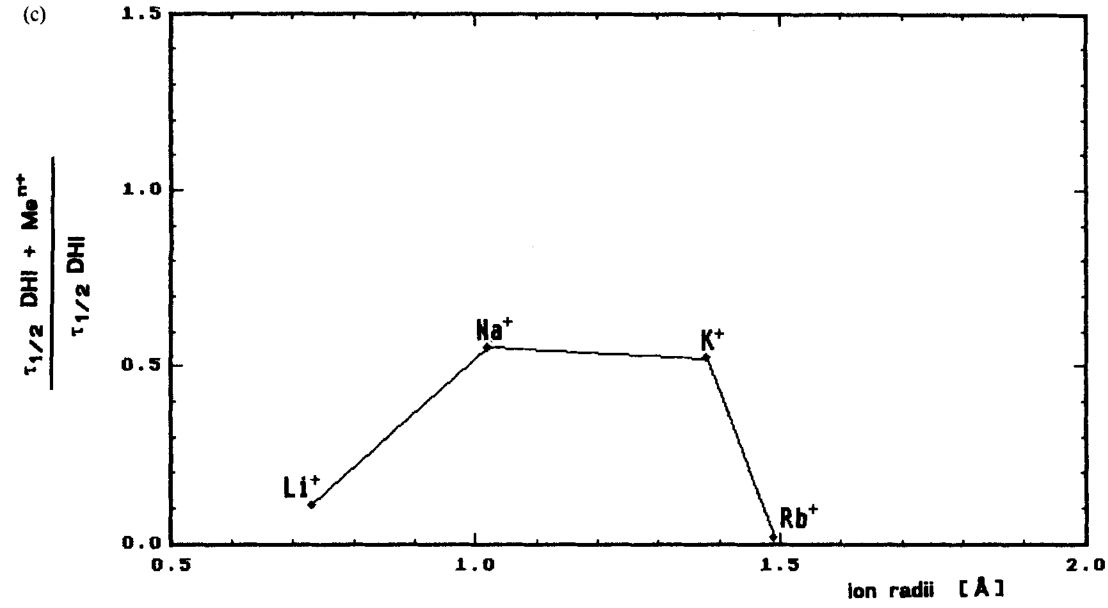


Figure 4. (*Continued*)

Table 1. Half-lives of cyclization of coloured betaine **2c** to the colourless DHI **1c** as a function of temperature and added ion concentration [in CH_2Cl_2–MeOH (2 : 1); $t_{1/2}$: see text]

	$t_{1/2}$ (min)		
Cation	25 °C	30 °C	35 °C
Salt-free	123.0	75.2	45.6
Li^+	117.1	70.5	37.1
Na^+	108.9	61.5	35.4
K^+	94.4	53.5	32.0
Rb^+	98.0	63.0	37.2
Mg^{2+}	129.8	78.8	48.8
Ca^{2+}	129.1	78.8	48.0
Ba^{2+}	114.6	74.4	44.3

earth metal ions. Increasing temperature reduces this effect. This means that ion binding of K^+ and Ba^{2+} by the crown-DHI **1c** generates a conformational change increasing the rate constant for cyclization. The more stable the complex, the larger is the effect, as is evident from Table 2.

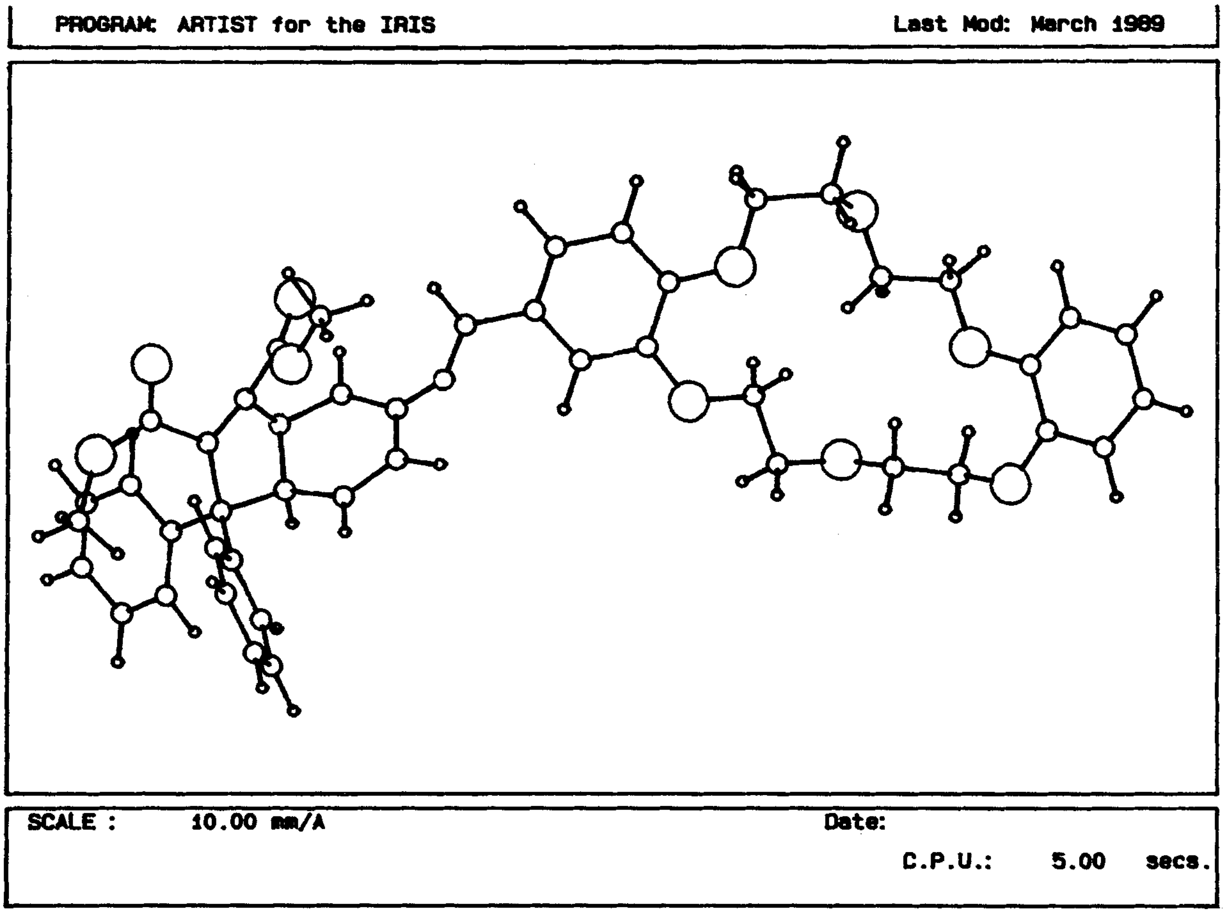
DISCUSSION

The properties of the photochromic system DHI **1** ⇌ betaine **2**[15] containing crown ether units can be affected by ions. The effects on the excited state can be seen in the UV spectra of **1**. Both bathochromic shifts and hyperchromic effects are observed. Alkali metal cations cause a fluorescence enhancement. The binding of ions in the crown ether cavity is possible in both the colourless form **1** and the coloured form **2**, as is demonstrated by the spectral data. The conformational changes due to complexation are most sensitively felt, however, in the electrocyclization **2** → **1**. To understand the conformational changes involved, we carried out force-field calculations for photochromic DHI **1** and their corresponding betaines **2**. The results are given in Figure 5.

Model calculations were performed for with diphenyl-crowns such as **1g** and the corresponding betaine **2g** (CHARM calculations were carried out on with the program of Polygen Corp., version 2[16]). As the calculations clearly show, metal ions such as K^+ or Ba^{2+} can be easily incorporated in the cavity of the DHI **1g**. The crown unit's six oxygen atoms are also fairly close to the optimum conformation for binding.

However, the most relaxed conformation for the betaine **2g** shows a heavily distorted geometry. Only four oxygen of the crown unit are arranged for reasonable binding. To have good binding with all oxygens, the conformation of **2g** has to be altered.

It is clear that in the betaine **2**, not all oxygens of the crown are oriented properly for complexation. Inclusion of an ion (M^{n+}) in the cavity of **2g** brings about a conformational change, which we believe makes the supramolecular structure tighter. This more



(a)

Figure 5. CHARM Force-field calculations (CHARM = Chemistry Harvard molecular modelling) of (a) a typical DHI crown ether (**1g**) and (b) its corresponding betaine (**2g**)

rigid complex may transfer more easily positive charge to the photochromic unit. The positive charge in the pyridinium or isoquinolinium group of **2** is thus destabilized by the positive charge of the cation in the supramolecular crown ether. Higher rigidity and additional positive charges in the crown of **2** seem to favour 1,5-electrocyclization.

CONCLUSION

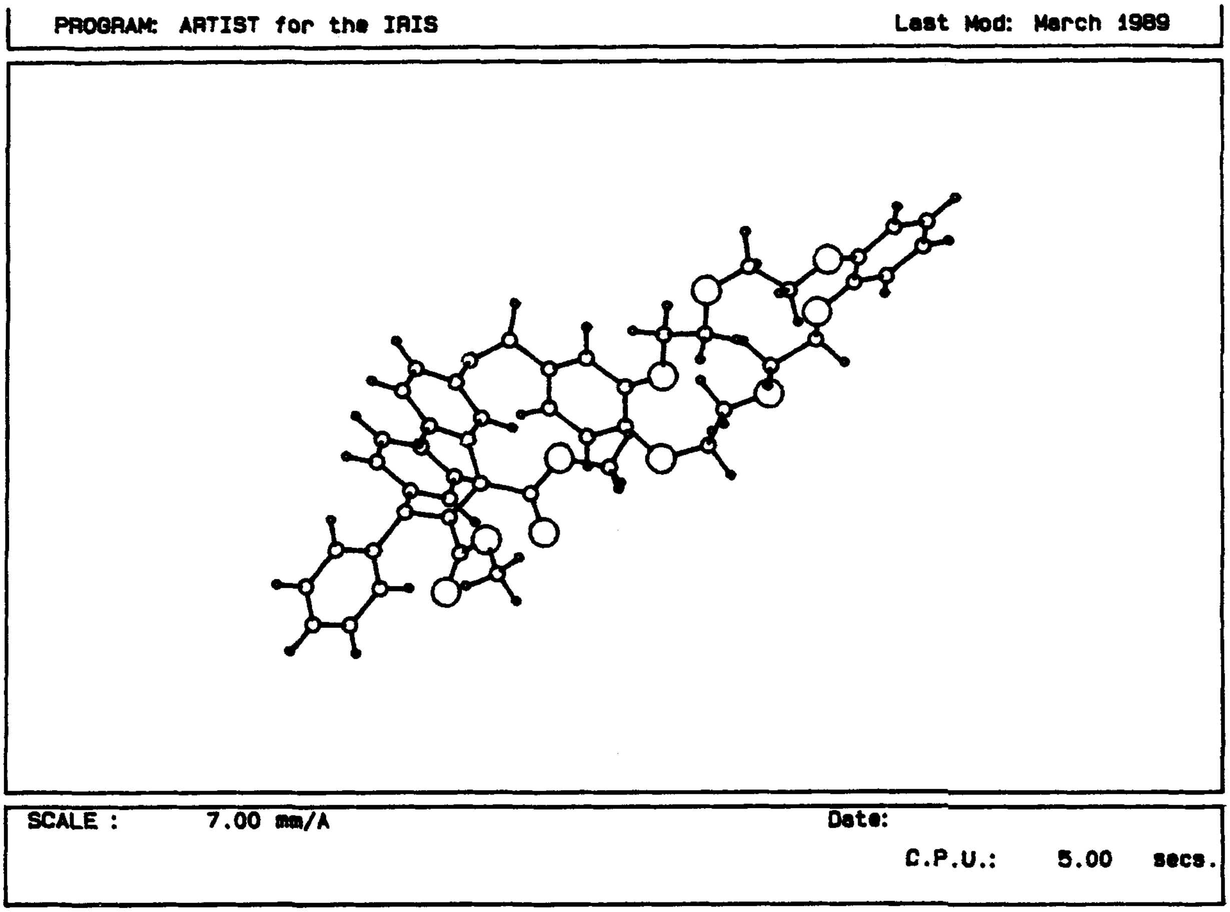
It has been shown that the excited state of the photochromic crown ethers **1** and **2** can be tuned by supramolecular effects. Ion binding in the photochromic crown ethers **1** leads to bathochromic shifts and hyperchromic effects in the UV spectra, to changes in the fluorescence spectra after addition of ions and to a decrease or increase in reaction rates for 1,5-electrocyclization.

EXPERIMENTAL

All measurements were carried out on a Kontron Uvikon 860 spectrophotometer at 25 °C. The supramolecular effects of the cations Li^+, Na^+, K^+, Rb^+ with the DHI host **1** were measured by UV spectrophotometry. The following guest alkali and alkaline earth metal ions were used in methanolic solutions:

0·10 M $LiI\cdot 2H_2O$, NaSCN and KSCN, 0·05 M RbI, 0·10 M $MgBr_2\cdot 6H_2O$ and $Ca(SCN)_2\cdot 3H_2O$ and 0·05 M $Ba(SCN)_2\cdot 3H_2O$. The counter ions employed were chosen to show large (a) polarizability, (b) high stability of the complexes and (c) good solubility in organic solvents.

The measurements were carried out using 1 ml of a



(b)

Figure 5. (*Continued*)

methanolic salt solution, to which 2 ml of a 1×10^{-4}–5×10^{-5} M crown ethers **1a–f** solution in dichloromethane were added and stirred until equilibrium was reached (maximum 24 h, room temperature, without light). An excess of salt to coronand **1** of 500 or 250 : 1 was employed. The solvent composition was therefore methanol–dichloromethane (1 : 2).

Fluorescence spectra were measured at 25 °C with a Hitachi F-3000 spectrofluorimeter. Solutions 5×10^{-5} M DHI plus $2{\cdot}5 \times 10^{-5}$ M alkali metal iodides ($LiI_2 \cdot 2H_2O$, NaI, KI, RbI) were prepared and stirred until complexation equilibrium was reached. All samples were intensively purged with nitrogen before measurement.

Calculations were carried out using the force-field and MINDO/3 CHARM programs, version 2.1.89.1031(e)[16] on a Silicon Graphics Workstation.

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