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Photochromic Bis(monoaza-crown ether)s. Alkali-metal Cation Complexing Properties of Novel Diarylethenes

Stephen H. Kawai

Department of Chemistry, Bio-Méga Research Division, Boehringer Ingelheim (Canada) Ltd.,
2100 Cunard St., Laval, Québec, Canada H7S 2G5 Tel: (514) 682-4640 / Fax: (514) 682 8434

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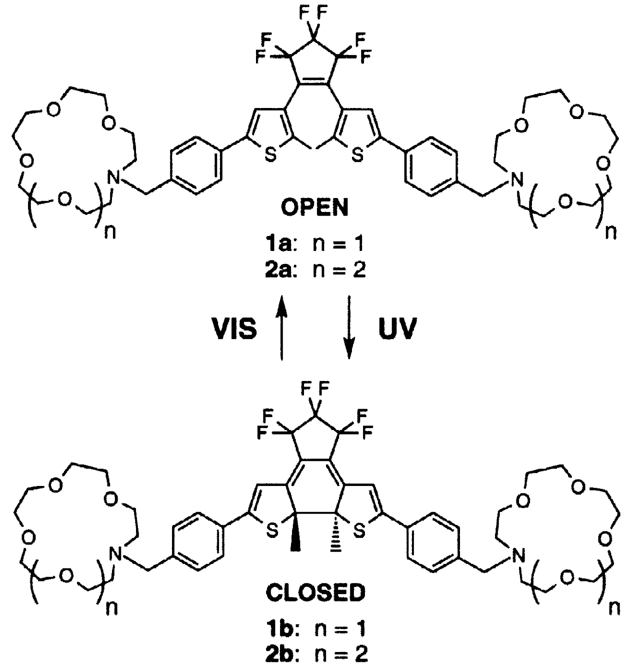
The novel bis(monoaza-crown ether) diarylethenes **1** and **2** have been synthesized and their photochromism and the ion-complexation properties of both photoisomers have been investigated.

Much attention is being devoted to molecules whose physical or chemical behaviour may be controlled by light [1]. This stems from their basic importance in fields as diverse as photobiology and molecular electronics [2], and has contributed to a renewed interest in organic photochromism [3]. Amongst the many systems which may be reversibly interconverted between distinct forms by irradiation, the diarylethenes [4] are receiving particular attention owing to their remarkable photofatigue-resistant photochromic properties. This work has, thus far, assumed two orientations. Largely responsible for the development of this class of compounds, Irie has focussed on fine tuning their properties for use in novel materials for optical data storage [5]. Meanwhile, Lehn has capitalized on the great differences in electronic conjugation between the photochromic states to develop an array of light-triggered molecular devices [6].

Of interest to us are the differences in molecular shape and conformational flexibility between the open and closed forms of the system in connection with molecular recognition properties. We herein describe the synthesis and behaviour of novel bis(aza-crown ether) photochromes **1** and **2** as well as the bis(triether) **4**. In the open form **a**, the conformational flexibility of the system, notably rotation about the thiophene-cyclopentene bonds, permits the crown ethers to act in concert in the binding of a metal cation. This "biscrown effect" is precluded once the system is converted to its essentially planar and rigid, cyclized photoisomer **b** in which the macrocycles are held apart. Such compounds may, therefore, exhibit ion complexation and/or selectivity which is light-



1a: n = 1
2a: n = 2

1b: n = 1
2b: n = 2

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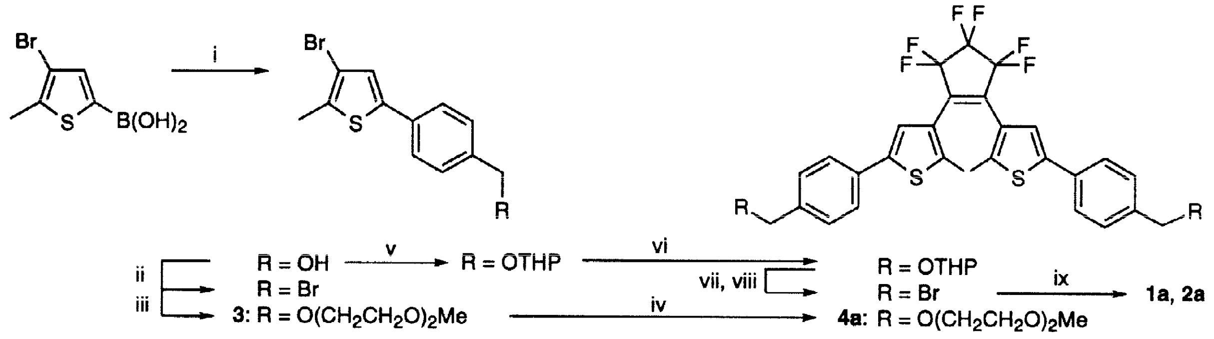

Scheme. *Reagents and conditions*: i, 4-bromobenzyl alcohol, $Pd(PPh_3)_4$, Na_2CO_3, H_20, THF, reflux (45%); ii, CBr_4, PPh_3, MeCN (89%); iii, $MeO(CH_2CH_2O)_2H$, NaH, THF, 0°C (89%); iv, *n*-BuLi, LiBr (2.5 equiv.), THF then C_5F_8, -78°C (72%); v, DHP, PPTS, CH_2Cl_2 (quant.); vi, as (iv) without LiBr (88%); vii, 2.5 N HCl, THF, 60°C (77%), viii, as (ii) (71%); ix, aza-crown ether, Na_2CO_3, THF, reflux (**1a**: 90%, **2a**: 87%).

regulated and be considered photoresponsive molecular tweezers. A variety of molecules which in some manner combine photochromic and cation-complexing behaviour have been studied [7], however, only very recently has a diarylethene-derived system been described [8]. Although similar in structure to **2**, its ion-complexation properties are quite different from those of the present systems which are reported herein.

The syntheses of the photochromes are outlined in the Scheme. Difficulties were encountered in generating the β-lithiated thiophene from **3** (step iv), resulting in starting bromide (1 equiv. *n*-BuLi) or butylated cyclopentenes (excess *n*-BuLi) rather than the photochrome **4a**. Reasoning that the alkyllithium was being sequestered by the triether chain, the lithiation was finally performed in the presence of LiBr followed by the addition of the fluorinated cycle which yielded **4a** in 72% yield. In light of these difficulties, an alternate approach in which the diarylethene is constructed prior to attachment of the macrocycles was followed, which provided the bis(aza crown)s **1a** and **2a** in very good yields.

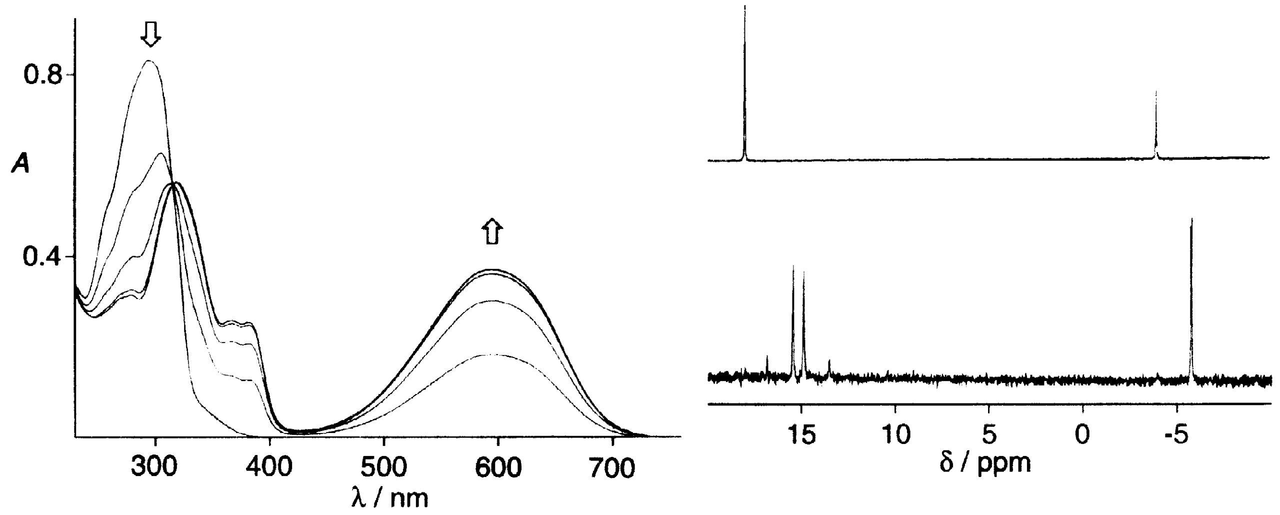

Figure. (left) Changes in absorption spectrum upon UV irradiation (312 nm) of **2a** after total irradiation times of 0, 3, 6, 12, 22 and 32 sec (2 x 10^{-5} mol dm^{-3} in CD_3OD); (right) ^{19}F NMR spectra (CD_3OD) of **2a** before (top) and after (bottom) UV irradiation.

All of the present diarylethenes exhibited pronounced photochromic properties, the behaviour of compound **2** being representative. Irradiation of the colourless open isomer **2a** with UV light (312 nm) resulted in the rapid appearance of a deep blue colour. By UV spectrophotometry, the process was observed as a decrease in a band at 294 nm and an increase in a broad absorption centered at 594 nm (Figure). The photostationary state of the process was determined by ^{1}H-NMR methods. In line with previously studied dithienyl systems lacking 4-substituents on the heterocycles [6], open **2a** could be converted nearly entirely to the coloured form **2b** upon UV irradiation (>98% conversion for **1**, **2** and **4**). Subsequent exposure to red (>600 nm) light returns it fully to the initial open state [9].

Table. Physical and Ion-Binding Properties of Photochromes 1, 2 and 4.

		4a (open)	**4b** (closed)	**1a** (open)	**1b** (closed)	**2a** (open)	**2b** (closed)
λ_{max}/nm ($\varepsilon \times 10^{-3}$)[a]		292(42)	590(18)	294(42)	594(19)	294(42)	594(19)
		-	318(31)	-	319(29)	-	318(28)
^{1}H-NMR[b]	(Me)	2.00	2.18	2.00	2.18	2.00	2.18
	(H)	7.35	6.80	7.33	6.80	7.33	6.81
^{19}F-NMR[c]	(central)	-3.89	-5.62	-3.91	-5.64	-3.91	-5.65
	(allylic)	18.04	14.50 / 15.86	18.06	14.52 / 15.87	18.05	14.52 / 15.89
% Metal picrate extracted[d]							
Li^+		<1	<1	3.9	2.8	3.7	3.7
Na^+		<1	<1	48.5	38.6	31.4	24.0
K^+		<1	<1	11.4	8.0	94.4	92.6
Rb^+		<1	1.2	6.7	5.3	87.1	84.1
Cs^+		1.1	<1	5.1	3.9	61.0	54.2

[a] In CH_2Cl_2. [b] In CD_3OD, δ (TMS) of thiophene methyl and proton signals. [c] In CD_3OD, ^{19}F-chemical shifts in ppm (external $C_6H_5CF_3$ assigned a shift of +63 ppm). [d] Composition of two-phase system: $CH_2Cl_2 = H_2O = 6.0$ mL, Aqueous phase: [Picric acid] = 7.0×10^{-5} M, [Metal hydroxide] = 0.1 M, Organic phase: [Diarylethene] = 3.5×10^{-4} M.

The open and closed isomers of the photochromes presented very distinct ^{19}F-NMR spectra (Figure and Table). For the former state **a**, two very finely split multiplets were observed. Upon photocyclisation to **b**, the downfield (allylic) signals evolved into AB quartets since the flourine atoms of these CF_2 groups become non-equivalent. The conserved equivalency of the central CF_2 fluorine atoms provides direct spectroscopic evidence for the *trans*-arrangement of thienyl methyl groups in the closed state **b** and the stereospecific (conrotatory) nature of the photocyclisation process.

Simple bis(azocrown)s [10,11] have been reported to exhibit enhanced cation binding (biscrown effect). Furthermore, evidence exists [11] that $(CH_2)_5$-linked bis(15- and 18-membered) systems form intramolecular sandwich complexes with Na^+. In light of this, we anticipated significant differences in ion-complexation between the open **a** and closed **b** forms of the present photochromes in favor of the former. The cation complexing abilities of **1**, **2** and **4** were evaluated by solvent extraction methods employing alkali-metal picrates [13] (Table). No ion-binding properties were observed for the bis(triether) **4** in either the open or closed states. The cation complexing properties of bis(azocrown)s **2a** and **2b** in both cases paralleled those reported for a simple alkyl-linked bis(aza-18-crown-6) system [11], extracting all ions except Li^+ and showing a preference for K^+. However, only slight differences in metal-picrate extraction were observed between the two photoisomers. The bis(15-membered) systems **1** in either state also exhibited parallel extraction properties, both showing marked preferences for a Na^+ cation. The open form exhibited a slightly greater Na^+-extracting capacity, however, whether this difference reflects formation of an Na^+-sandwich complex remains to be determined. The poor complexation of larger cations by **1a** is surprising in light of the pronounced biscrown effect reported [10] in this regard for simple bis(azocrown)s. Finally, comparing the present results for **2** with those reported [8] by Irie for a closely related bis(benzo-18-crown-6) dithienylethene reveals notable differences: the stronger and differential complexation of Na^+ by **2a/b** and the absence of photoswitching with respect to Cs^+-binding. It is hoped that a clearer understanding of photochromes of this type will eventually lead to cation-tweezers which truly exhibit all-or-nothing ion-binding which is subject to photocontrol.

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