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Complexation and structural studies of a sulfonamide aza-15-crown-5 derivative

Marie Ioannidis, Alexander S. Gentleman, Lam Ho, Stephen F. Lincoln *, Christopher J. Sumby *

School of Chemistry and Physics, The University of Adelaide, Adelaide, SA 5005, Australia

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ABSTRACT

An aza-15-crown-5 derivative, *N*-[4-(phenyldiazo)benzenesulfonyl]-aza-15-crown-5, **1** was synthesised from commercially available starting materials in 55% yield. Compound **1**, which contains a sulfonamide link between the crown ether macroring and the azobenzene, readily binds alkali metals in buffered ethanol–water (75:25 v/v, pH 6.66). Titration data for both sodium and potassium were readily fitted to a 1:1 metal ion/ligand binding model to obtain stability constants (log *K*) of 4.7 ± 0.4 and 4.8 ± 0.2 $dm^3\ mol^{-1}$, respectively. We also investigated the structures of **1** and the sodium perchlorate salt of **1**, $[Na(\mathbf{1})(H_2O)]_2(ClO_4)_2$, which were determined by X-ray crystallography. $[Na(\mathbf{1})(H_2O)]_2(ClO_4)_2$ is a dimer in the solid state whereby a sulfonamide oxygen atom from one of the $[Na(\mathbf{1})(H_2O)]$ cations provides solvation of the adjacent macroring bound sodium cation. In the crystal structure, binding of a water molecule to the sodium cation is supported by hydrogen bonding to the sulfonamide oxygen, which represents a supramolecular lariat ether-like interaction.
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Studies into the host–guest chemistry of crown ether systems have been a longstanding and very fruitful area of research [1]. For example, aza-15-crown-5 has been incorporated into a large range of colorimetric and fluorometric sensors for alkali and alkali earth cations [2]. The ionophore aza-15-crown-5 has been shown to readily and effectively bind alkali and alkali earth cations [1,2]. Ionophores of this type, possessing aromatic groups appended to the nitrogen of the azacrown ether have also been the focus of studies into cation···π interactions in solution and the solid state [3]. These studies have illustrated the importance of cation···π interactions in cation receptor design and biology [3]. Covalently attaching further ether oxygen donors to the nitrogen of the aza-15-crown-5 ether macroring also improves the binding ability of this ionophore for alkali cations [1]. This class of compounds, called lariat ethers, were first reported by Gokel [4,5] and consist of azacrown derivatives containing a flexible arm of electron donor groups appended on the nitrogen atom of the crown. The binding data for 15-membered ring lariat ethers containing between zero and eight additional oxygen atoms in the side arm were obtained in methanol solutions for sodium cations. The lariat ether containing a total of six oxygen donors binds sodium with the highest binding constant [4,5].

We have an established interest in investigating novel biomedical and environmental sensors, for example the Zn^{2+} selective fluorophores Zinquin-A and Zinquin-E [6a–e] and fluorescent alkali metal complexes of azacrown ethers [6f]. As part of our recent studies on new sensors for metal ions, we investigated the synthesis and properties of *N*-[4-(phenyldiazo)benzenesulfonyl]-aza-15-crown-5, **1**. Compound **1** attracted our attention because of the one-step synthetic approach to prepare the compound and the presence of a sulfonamide link between the azacrown ether binding unit and the azobenzene group. As far as we are aware, there are no examples of sulfonamide linked systems of this type in the literature. Herein, we describe the synthesis and photophysical properties of **1**, binding constants for Na^+ and K^+, and crystal structures of **1** and its sodium complex.

Compound **1** was synthesised from commercially available 4-phenyldiazobenzenesulfonyl chloride and aza-15-crown-5 in 55% yield (Scheme 1, see Supplementary material). The crown derivative was isolated as a 95:5 mixture of *E/Z* isomers and characterised by ^1H and ^{13}C NMR spectroscopy, mass spectrometry and absorption spectroscopy. Heating the sample at 40 °C in the dark for 24 h ensured complete conversion to the *E*-isomer, which simplified characterisation by NMR spectroscopy. The electrospray mass spectrum of **1** indicated the ability of **1** to readily bind alkali cations, with a peak at *m/z* 486 corresponding to $[Na(\mathbf{1})]^+$. The visible absorption spectrum for **1** was measured in buffered ethanol–water (75:25 v/v, pH 6.66), with constant ionic strength ($I = 0.1$ mol dm^{-3}, NEt_4ClO_4). Compound **1** gives bright orange coloured solutions and displays a broad absorption in the visible range with a maximum of 439 nm. Compound **1** is very weakly fluorescent (excitation 439 nm, emission at 505 nm), consistent with related flexible azobenzene derivatives [7].

Further confirmation of the structure of compound **1** was obtained by X-ray crystallography. Crystals of **1** were obtained by slow evaporation of an ethanol solution of **1** and crystallised in the

* Corresponding authors. Lincoln is to be contacted at Tel.: +61 8 8303 5559; fax: +61 8 8303 4358. Sumby, Tel.: +61 8 8303 7406; fax: +61 8 8303 4358.
E-mail addresses: stephen.lincoln@adelaide.edu.au (S.F. Lincoln), christopher.sumby@adelaide.edu.au (C.J. Sumby).

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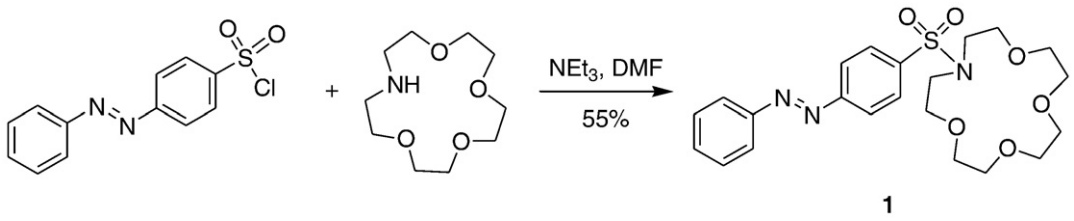

Scheme 1. Synthesis of 1.

monoclinic space group $P2_1/n$ with one complete molecule in the asymmetric unit [8]. The crystal structure confirms the structure proposed on the basis of NMR spectroscopy, mass spectrometry and CHN combustion analysis. Several features of the structure are worthy of further discussion (Fig. 1). The *E*-isomer is a thermodynamically more stable isomer and the major isomer isolated from the reaction was assigned as this structure. This was confirmed by the crystal structure which shows the *E*-isomer.

Within compound **1** the diazo moiety is not completely planar; the torsion angles involving N9–N8–C5–C4 and C15–C10–N9–N8 are 23.0(1) and 28.3(1)°, respectively. Consequently, the twist between the two phenyl rings in the azo moiety is 51.3(1)°. The sulfonamide nitrogen atom (N18) is approximately perpendicular to the central phenyl ring, with an angle of 107.5(1)° which is close to the expected tetrahedral arrangement. The crown is then extended close to the plane of the azo region of the molecule due to the flexible nature of the moiety. The outcome is that the molecule is almost flat in the solid state, which optimises the crystal packing.

Several groups have previously studied the incorporation of an amide into an aza-15-crown-5 and the effect this has on the structure of the macrocycle by X-ray crystallography [9]. Amide groups were shown to rigidify the crown ether and diminish the donor ability of the nitrogen. In the amide-containing aza-15-crown-5 compounds the amide nitrogen is nearly planar. In the case of **1** the nitrogen atom of the sulfonamide crown is similarly close to a trigonal planar geometry with angles of 117.6(2) (C32–N18–C19), 118.1(2) (C32–N18–S1) and 116.3(2)° (C19–N18–S1). As the crystal structure of **1** demonstrates, in the crystal form observed here, the cavity of the crown moiety does not contain any solvent or guests molecules. To get around this, the crown forms two weak intramolecular hydrogen bonds (Fig. 1) which further stabilize the conformation observed. The distances between the hydrogen and the oxygen atoms are 2.84 Å (O21) and 2.98 Å (O24), while the distances between the carbon and oxygen atoms are 3.44(1) Å and 3.89(1) Å, which lie in the range expected for weak hydrogen bonding interactions. Crystal packing of **1** was completed by further weak intermolecular hydrogen bonding interactions of the crown moiety with other molecules of compound **1**.

The known binding preferences of the aza-15-crown-5 moiety [1] led us to investigate the binding of **1** with alkali metal cations. Binding

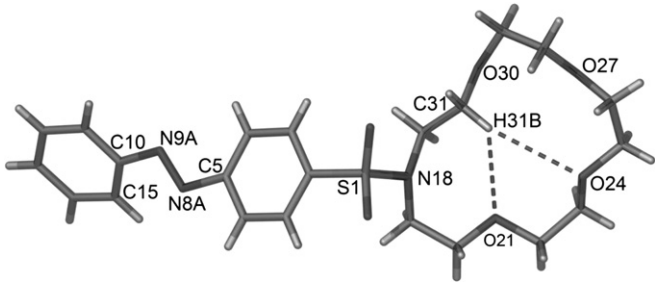

Fig. 1. A perspective view of **1** with selected atom labeling. The weak CH···O hydrogen bonds are shown by dashed bonds and the disorder of the azo moiety (a second *E* form) is not shown.

constants for complexes of **1** with sodium and potassium were determined by monitoring changes in absorption of **1** at 439 nm upon titrating **1** with standardized $MClO_4$ [10] solutions (M = Na, K) in buffered ethanol–water (75:25 v/v, pH 6.66). The titration data for both sodium and potassium was readily fitted to a 1:1 metal ion/ligand binding model (see Supplementary materials) to obtain stability constants (log *K*) of 4.7 ± 0.4 and 4.8 ± 0.2 $dm^3\ mol^{-1}$, respectively (Table 1). In the titration, a linear response was observed upon addition of the metal ion, up to a sharp end point where the concentration of the M^+ is equal to that of the ligand, after which no further change in absorbance was observed. This indicates that nearly stoichiometric complexation occurs upon addition of one equivalent of M^+, and that the resulting 1:1 complexes are stable.

The measured stability constants obtained for **1** with sodium and potassium were higher than anticipated, particularly as the aza-15-crown-5 macroring possesses only four oxygen donors and an electron deficient sulfonamide nitrogen, and the measurements were carried out in a coordinatively competitive solvent mixture (Table 1). The values obtained for **1** contrast markedly with those reported for the parent aza-15-crown-5, [4] which binds sodium and potassium in methanol much less efficiently than 15-crown-5 or *N*-methylaza-15-crown-5 [4]. As shown in Table 1, the binding constants obtained for **1** are more consistent with values obtained for sodium and potassium binding by lariat ethers rather than parent 1-aza-15-crown-5 derivatives such as *N*-methylaza-15-crown-5 [4]. This led us to further investigate the binding of **1** and alkali cations.

Based on chemical models of compound **1** bound to a sodium cation and the crystal structure of **1** we wondered if the oxygen atom(s) of the sulfonamide derivative were also involved in binding to the alkali metal. The trigonal planar sulfonamide nitrogen atom would allow the oxygen atoms of the sulfonamide to protrude slightly over the cavity of the crown that could allow these donors to form electrostatic interactions with an alkali metal atom (Fig. 2a). A further possibility was the interaction of the azo-dye moiety of **1** with the alkali metal, a cation···π-interaction (Fig. 2b), although this would only occur for the less stable *Z*-isomer of the sulfonamide.

Table 1
Binding constants for 1-aza-15-crown-5 derivatives and lariat ether analogues.

Crown ether derivative	Cation	Log *K* ($dm^3\ mol^{-1}$)	T (°C)	Solvent	Reference
15-crown-5	Na^+	3.32 ± 0.12	25	MeOH	[11,12]
	K^+	3.5 ± 0.2	25	MeOH	[12]
Aza-15-crown-5	Na^+	1.70	25	MeOH	[4]
	K^+	2.72	25	MeOH	[1]
N-Methylaza-15-crown-5	Na^+	3.39	25	MeOH	[4]
N-[2-(10-Ethyl-9-anthryl) ethyl]aza-15-crown-5	Na^+	4.97	25	CH_3CN	[6]
	K^+	4.23	25	CH_3CN	[6]
N-(3,6-dioxaheptyl)-aza-15-crown-5	Na^+	4.54	25	MeOH	[4]
	K^+	4.42	25	MeOH	[1]
1	Na^+	4.7 ± 0.4	25	75:25 EtOH/water	This work
	K^+	4.8 ± 0.2	25	75:25 EtOH/water	This work

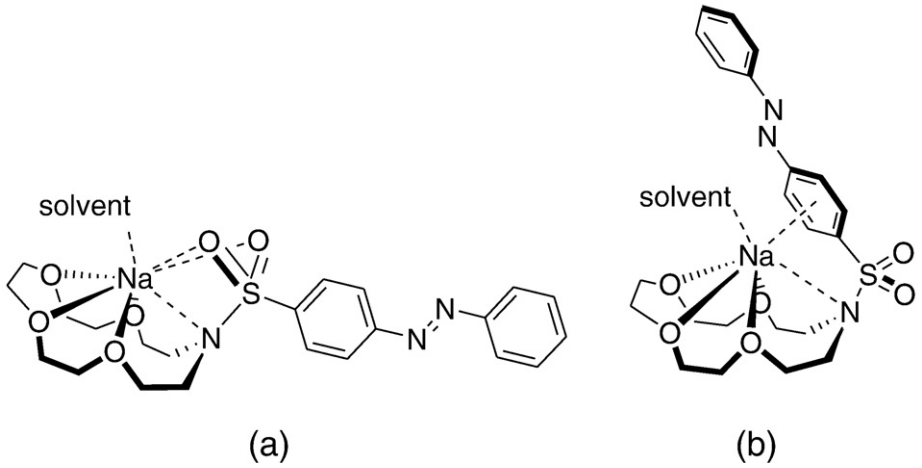

Fig. 2. Representations of two potential modes of binding for **1** with Na^+: (a) with an additional contact with one or two sulfonamide oxygen atoms and (b) a cation···π-interaction.

NMR spectra of **1** and **1** with added sodium perchlorate in methanol-d_4 (Fig. 3b and a, respectively) revealed limited changes due to binding of sodium. The most significant changes in chemical shift are observed for the hydrogen atoms of the azacrown, while little or no change was observed for the protons of the azobenzene moiety of **1**. This suggests that a cation···π interaction does not play a significant role in binding the sodium cation, particularly in polar solvents.

Neither of the possibilities outlined in Fig. 2 were shown to occur in the solid state. In the crystal structure of the sodium complex of **1** a dimeric structure $[Na(\mathbf{1})(H_2O)]_2(ClO_4)_2$ was obtained whereby a water molecule bound to the sodium is hydrogen-bonded to a sulfonamide oxygen atom of **1**. Crystals of **1** bound to sodium were obtained by slowly evaporating an ethanol–water 75:25 v/v solution of **1** and sodium perchlorate (1:2 excess of sodium). The structure of $[Na(\mathbf{1})(H_2O)]_2(ClO_4)_2$ crystallises in the monoclinic space group $P2_1/n$ with the sodium cation sitting in the crown cavity of a molecule of **1** and also bound to a water molecule (disordered over two sites) [13]. The asymmetric unit is completed by a non-coordinated perchlorate counterion. The dimeric cationic unit in the crystal structure $[Na(\mathbf{1})(H_2O)]_2$ (Fig. 4) sits on a centre of inversion.

The seven coordinate sodium cation sits approximately 1.12 Å above the centroid of the donors of the crown ether moiety. There are four typical Na–O bond lengths and, as expected, a much longer bond to the sulfonamide nitrogen atom with a bond length of 2.9672(15) Å. The sulfonamide nitrogen atom of **1** in $[Na(\mathbf{1})(H_2O)]_2(ClO_4)_2$ has a geometry that is a closer to tetrahedral, with bond angles of 113.9(1) (C32–N18–C19), 114.6(1) (C32–N18–S1) and 114.6(1)° (C19–N18–S1). A coordinated water molecule and the sulfonamide oxygen atom of another molecule of **1** complete the coordination of the sodium. In the crystal structure, the sodium complex forms a dimeric cationic structure $[Na(\mathbf{1})(H_2O)]_2$ in which one of the sulfonamide oxygen atoms coordinates to the sodium cation with a bond distance of 2.4209(13) Å. A very similar arrangement was observed for a sodium iodide salt of amide derivative of monoaza-18-crown-6 [9]. The azobenzene groups are located on opposite sides of the $[Na(\mathbf{1})(H_2O)]_2$ assembly and, within the extended structure, lie over the crown moiety of other dimeric dications. As noted, the coordinated water molecule in the structure is hydrogen-bonded to the sulfonamide oxygen atom (an O33–H33B···O16 distance of 2.27 Å and an O33···O16 distance of 3.00 Å). This arrangement represents what we have likened to a supramolecular lariat ether-like interaction (Fig. 5), where instead of having a covalently tethered ether oxygen in a lariat ether type structure, a hydrogen-bonded water molecule provides additional oxygen donors.

The unexpected arrangement observed in the crystal structure of $[Na(\mathbf{1})(H_2O)]_2(ClO_4)_2$ led us to further consider the behavior of **1** and alkali metal cations. The Gaussian '03 suite of programs [14,15] was

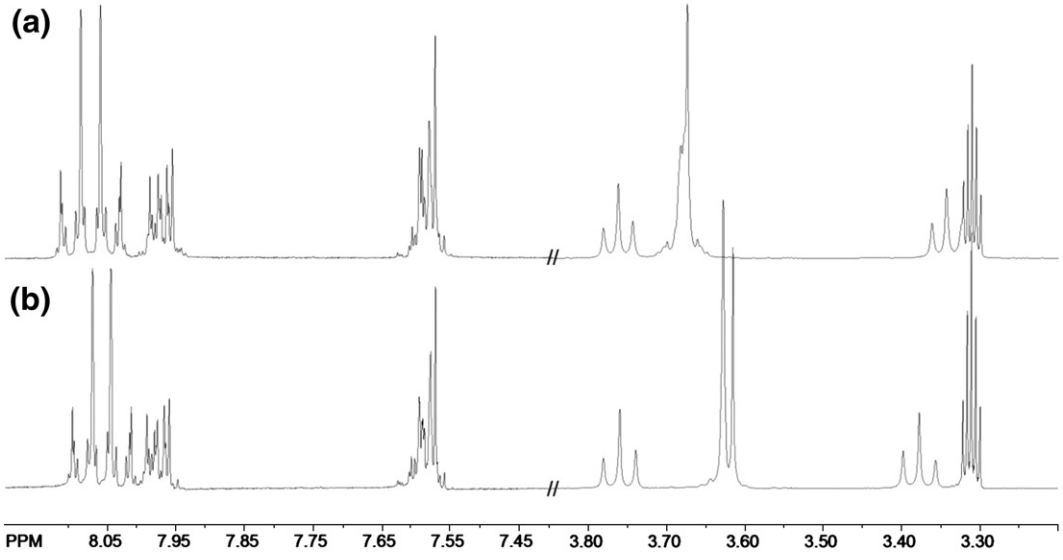

Fig. 3. ^1H NMR spectra in methanol-d_4 of (a) the sodium complex of **1**, $[Na(\mathbf{1})]^+$, and (b) **1**.

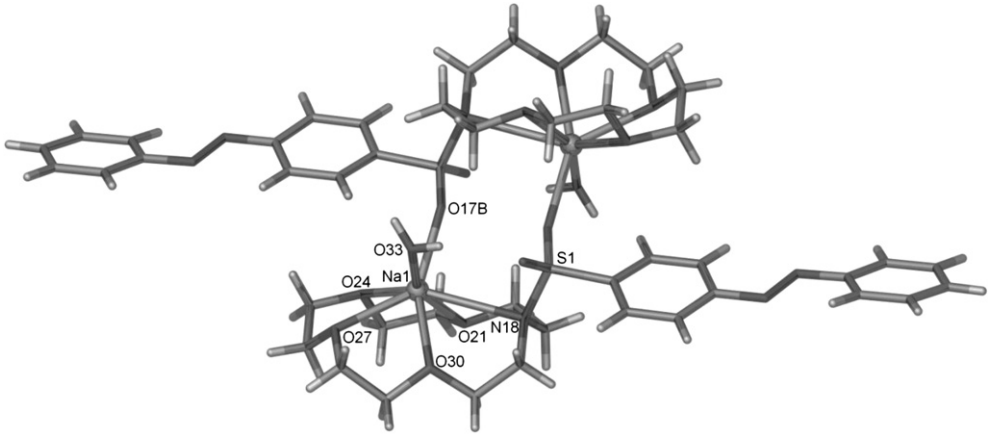

Fig. 4. A perspective view of the cationic moiety ($[Na(\mathbf{1})(H_2O)]_2$) in the crystal structure of $[Na(\mathbf{1})(H_2O)]_2(ClO_4)_2$. The disorder of the coordinated water molecule is not shown. Selected bond lengths: Na1 O34 2.284(6), Na1 O33 2.3015(18), Na1 O17B 2.4209(13), Na1 O21 2.4365(14), Na1 O30 2.4415(13), Na1 O24 2.4457(15), Na1 O27 2.4822(15), and Na1 N18 2.9672(15).

used to investigate the relative energies of various conformations for the sodium crown-ether assembly. Two starting configurations were considered for compound $[Na(\mathbf{1})]^+$. The first configuration represents a proposed cation···π-interaction between the sodium cation and the azobenzene functional group (*Z*-isomer of the sulfonamide). The second configuration considered has the azobenzene functional group directed away from the macroring to represent the potential interaction of the sodium cation with the two sulfonamide oxygen atoms (*E*-Isomer). Both configurations were optimised at the HF and B3LYP level to determine which method would be most suitable to perform further computational investigations on the compound.

Fig. 6 shows the structures of the two minima obtained from the HF and B3LYP calculations (Structures **1a** and **1b**, respectively). Both methods show that the *E*-isomer (Structure **1a**) is the more energetically favourable configuration (energy differences between the optimised structures: $\Delta E_{HF} = 0.36$ eV, $\Delta E_{B3LYP} = 0.25$ eV). This is consistent with the preferred conformation of **1** in solution and in the solid state, as well as the NMR data, which indicates that a cation···π interaction does not play a role in the binding of the sodium cation in polar solvents. In addition to this, the azobenzene functional group in structure **1a** appears to pivot slightly around the sulfonamide bond so that one of the oxygen atoms interacts with the sodium cation. This is not surprising as sodium is highly oxophilic, making the interaction between the sulfonamide oxygen atom and the sodium cation more favourable than the cation···π interaction.

To determine which method was more reliable to perform additional calculations on compound $[Na(\mathbf{1})]^+$, the lengths of the sulfonamide bond calculated from the HF and B3LYP methods were compared to the value obtained from the crystal structure. This bond length was chosen as the deciding factor due to the azobenzene functional group possessing the ability to pivot around this bond to afford the two possible configurations mentioned earlier. From the B3LYP structure, the bond length was determined to be 1.903 Å and in the HF structure, the bond length was determined to be 1.754 Å. In the crystal structure, the bond length was 1.644(1) Å. As clearly observed, the bond length determined using the HF method compares better with the crystal structure bond length than that determined using the B3LYP method. Therefore, the HF method was deemed more suitable than the B3LYP method to perform additional calculations with.

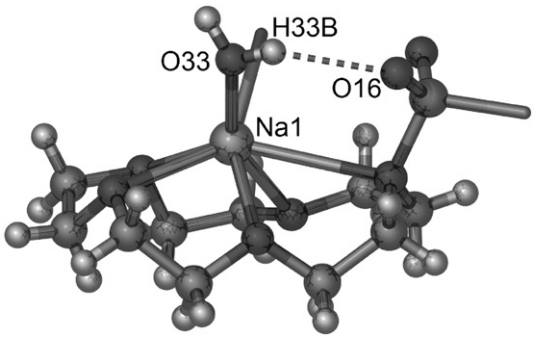

Fig. 5. A view of the crystal structure showing hydrogen bonding of the sulfonamide oxygen to a water molecule that is also bound to the sodium.

As the crystal structure of $\{[Na(\mathbf{1})(H_2O)]_2\}^{2+}$ reveals, additional oxygen donors can bind to the sodium cation. Therefore, two water molecules were made to interact with structure **1a** in order to demonstrate that they can easily be accommodated around the sodium cation. Fig. 7 shows the structure of the sodium aza-15-crown-5 derivative with two water molecules bound around the sodium cation optimised at the HF/6–31 g level. As observed in Fig. 7, both water molecules can bind quite easily to the sodium cation via their oxygen atoms ($Na–O_W = 2.385$ Å, $Na–O_{W'} = 2.386$ Å). In addition to this, hydrogen bonds are also formed between the hydrogen atoms on the water molecules and the two sulfonamide oxygen atoms ($O–H_W = 1.892$ Å, $O'–H_{W'} = 1.900$ Å). As a consequence of these interactions, the twisting of the azobenzene functional group around the sulfonamide bond, as observed in structure **1a**, has been inhibited as the water molecules have competitively bound to the sodium cation. All bond distances mentioned previously, as well as other Na–O and Na–N bond distances, are similar to those observed in the crystal structure for the coordinated water molecule.

Herein we have reported the synthesis of an aza-15-crown-5 derivative, *N*-[4-(phenyldiazo)benzenesulfonyl]-aza-15-crown-5, **1** containing a sulfonamide link between the crown ether macroring and the azobenzene. Compound **1** was synthesised from commercially available starting materials in 55% yield and, as expected, readily binds alkali metals in buffered ethanol–water (75:25 v/v, pH 6.66). Visible absorption titration data for both sodium and potassium was fitted to a 1:1 metal ion/ligand binding model to obtain stability constants (log *K*) of 4.7 ± 0.4 and 4.8 ± 0.2 $dm^3\ mol^{-1}$, respectively.

We have described the structures of **1** and the sodium perchlorate salt of **1**, $[Na(\mathbf{1})(H_2O)]_2(ClO_4)_2$, in the solid state. $[Na(\mathbf{1})(H_2O)]_2(ClO_4)_2$ is a dimer in the solid state whereby a sulfonamide oxygen atom from one of the $[Na(\mathbf{1})(H_2O)]$ cations provides solvation of the adjacent macroring bound seven coordinate sodium cation. In the crystal structure of $[Na(\mathbf{1})(H_2O)]_2(ClO_4)_2$, binding of a water molecule to the sodium cation is supported by hydrogen bonding to the sulfonamide oxygen, which represents a supramolecular lariat ether-like interaction. While the solvation of the crown ether bound sodium cation in the solution is not known, a calculated structure was examined, which

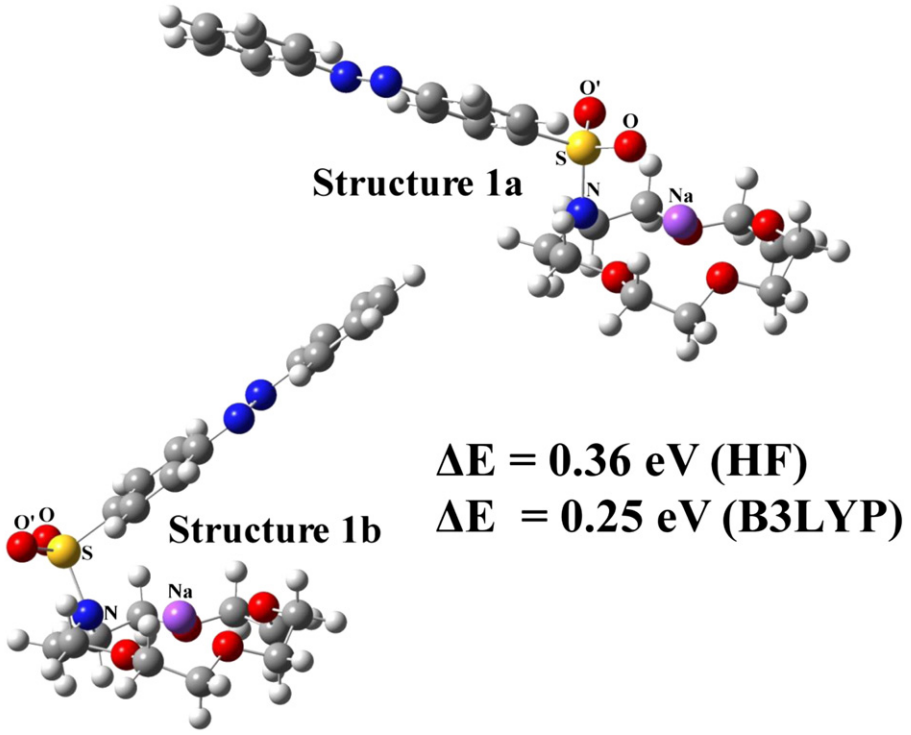

Fig. 6. The structures of the minima obtained for the two isomers of $[Na(\mathbf{1})]^+$ from the HF and B3LYP calculations (Structures **1a** and **1b**, respectively).

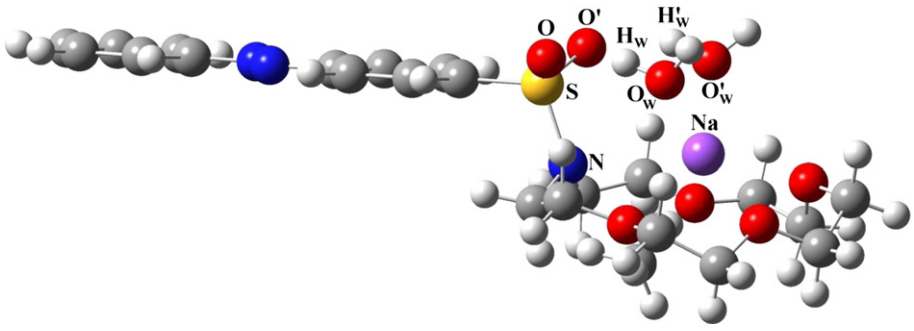

Fig. 7. A calculated structure demonstrating that the supramolecular 'lariat ether' interaction is possible for $[Na(\mathbf{1})(H_2O)_2]^+$.

illustrates that two water molecules bound to the sodium cation can form hydrogen bonds with the oxygen atoms of the sulfonamide group. An alternative binding mode was also observed *in silico* whereby the sulfonamide group pivots around the N–S bond to allow one of the oxygen atoms of the sulfonamide group to form a bond to the oxophilic sodium cation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2010.02.011.

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[8] Selected details of data collection and structure refinement for compound 1: Formula $C_{22}H_{29}N_3O_6S$, monoclinic, space group $P2_1/n$, Mr 463.54, orange rod, $0.88\times0.16\times0.16$ mm, $a=10.916(2)$, $b=9.564(1)$, $c=22.350(3)$ Å, $\beta=101.314(6)$, $V=2288.1(5)$ Å^3, $Z=4$, $D_{calcd}=1.346$ g cm^{-3}, $\mu=0.185$ cm^{-1}, θ range $=2.86$–$27.00°$ data collected 22268, unique data 4970 ($R_{int}=0.032$), obs. data [$I>2\sigma(I)$] 4425, no. parameters 308, no. restraints 2, R_1 0.0460 (obs. data), wR_2 0.1097 (all data), GOF 1.047. The azo moiety of the structure is disordered with another E form of the structure present in the crystal (major component 68%; minor component 32%). The two restraints are used to maintain appropriate distances for the minor disorder component.

[9] (a) C.F. Martens, A.P.H.J. Schenning, M.C. Feiters, R.J.M. Nolte, G. Beurskens, P.T. Beurskens, Inorg. Chim. Acta 190 (1991) 163;
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[10] Caution! Whilst no problems were encountered in the course of this work, perchlorate salts are strong oxidising agents and are potentially explosive and should be handled on a small scale with appropriate care.

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[13] Selected details of data collection and structure refinement for compound $[Na(1)(H_2O)]_2(ClO_4)_2$: Formula $C_{22}H_{31}ClN_3NaO_{11}S$, monoclinic, space group $P2_1/n$, Mr 604.00, orange rod, $0.30\times0.10\times0.10$ mm, $a=10.202(3)$, $b=25.310(7)$, $c=10.439(3)$ Å, $\beta=96.411(4)$, $V=2678.7(12)$ Å^3, $Z=4$, $D_{calcd}=1.498$ g cm^{-3}, $\mu=0.301$ cm^{-1}, $2\theta=55°$ data collected 20598, unique data 6089 ($R_{int}=0.031$), obs. data [$I>2\sigma(I)$] 5048, no. parameters 353, no. restraints 2, R_1 0.0355 (obs. data), wR_2 0.0846 (all data), GOF 1.045. The coordinated water molecule in the structure was modeled as being disordered over two sites (O33, 80%; O34, 20%).

[14] Geometry optimisations and harmonic vibrational frequency calculations were performed using the *ab-initio* Hartree–Fock (HF) method and the B3LYP density functional in the Gaussian '03 suite of programs.[16] The harmonic vibrational frequency calculations were performed to ensure that the optimised structures were indeed true minima (0 imaginary frequencies). All atoms were treated with the split-valence double-zeta 6–31 g Pople-type basis set. Calculations involving the addition of diffuse and polarisation functions to this basis set were also performed on the E and Z-Isomers of compound $[Na(1)]^+$, but were found to yield very similar results to the 6–31 g basis set. Due to this and the large increase in calculation time upon the addition of these functions to the basis set, further calculations were performed with the standard 6–31 g basis set.

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