

## Synthesis, electronic spectra and conformational properties of some N-substituted aza-crown ethers

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The preparation and the electronic (absorption and fluorescence) spectra of some newly synthesized N-substituted C15 and C18 diaza-crown ethers are reported. Dynamic and conformational simulations at the semiempirical PM3 MO level show relatively weak interactions of the small Mg<sup>2+</sup> ions with the ether macrocycle as well as with the aromatic chromophore. The PM3 calculations indicate a clear preference for this ion of the smaller C15-diazacrown cycle. The calculated ring deformation energies, required to accommodate Mg<sup>2+</sup> by C18-diazacrowns, are about 25 kcal/mol higher than by C15 rings. This result is in line with the known weak selectivity of C18-crowns for small divalent metal ions in solution. Substituents at the N-atom affect the complexation properties not only through interaction with the charge density of the metal cation, but also through hindering the access of metal cations to the ionophore cavity.

**Key words:** diaza crown ethers, electronic absorption and fluorescence, PM3 conformational analysis, PM3 molecular dynamics.

### INTRODUCTION

Macrocyclic organic molecules, containing heteroatoms, are widely recognized as important components of the rapidly increasing variety of host-guest complexes. The simplest crown ethers and their derivatives are used as ion selective reagents in a number of separation and catalytic processes and as model reagents for molecular recognition [1]. Studies of ion complexation by these reagents are most often carried out using spectroscopic methods, among the latter electronic spectroscopy [2–4]. Crown ethers with specific chromophoric and/or fluorophoric substituents are of particular interest in photophysical studies of ion complexation. Data on the structure, spectral and analytical properties of N-phenylaza-15-crown-5 derivatives (A15C5 **1**, Scheme 1) with *p*-azomethine substituents, as well as their complexes with alkaline metal ions, with Be<sup>2+</sup> and Mg<sup>2+</sup> have been reported in a series of earlier papers [5–11].

The dansyl (Dns, 1-dimethylamino-5-naphthalenesulfonyl) fluorophore is widely used as a label in amino acid and protein chemistry because of its convenient attachment to amine functionalities. Spectroscopic analyses of ion-macrocyclic interactions of dansyl derivatives of monoaza A15C5 and A18C6 have been performed [4, 12]. Weak binding of Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup> to **3** has been discussed on

the basis of the known solid state structure of the free crown [4] pointing at the necessity of conformational and/or molecular dynamics studies of compound **3** [4] in order to understand its cation binding properties. Solvent polarity dependence of the position of the fluorescence emission maximum of **3**,  $\nu_{\max}$  vs. ET(30), has been reported as well [4].

Scheme 1. Structures and notation of bis-dansyl aza-crown ethers

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In this paper we report the synthesis and electronic spectra, and discuss the cation binding properties of *bis*-dansyl derivatives of 4,13-diaza-15-crown-5, **2**, and 4,13-diaza-18-crown-6, **3** [12] (Scheme 1), as well as N-phenyl A15C5 crown ether derivatives of barbituric acids **4** (Scheme 2). The compounds **2** and **4** have not yet been described, while the compound **3** is already known [12].

Scheme 2. Structures and notation in 5-[4-(1,4,7,10-tetraoxa-13-azacyclopentadec-13-yl)-benzylidene]-pyrimidine-2,4,6-triones **4**.

## METHODOLOGIES AND ANALYTICAL DATA

*Synthesis of bis-Dns crown ethers 2 and 3:* We use a general procedure, in which to a solution of 1.39 mmol diaza-crown ether and 0.39 ml (2.78 mmol) dry triethylamine in 5 ml dry CH<sub>2</sub>Cl<sub>2</sub> we add dropwise an excess of dansyl chloride (3.26 mmol, 0.85 g) solution in 7 ml CH<sub>2</sub>Cl<sub>2</sub>. The resulting mixture is stirred for 24 hours at room temperature. The reaction mixture is then washed with water, reextracted with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic extracts are dried over Na<sub>2</sub>SO<sub>4</sub>. The product is then isolated by evaporation of the solvent and recrystallised from ethylacetate. The purity of bis-Dns derivatives is verified by thin layer chromatography (TLC). The obtained thermo-analytical data for **3**, Table 1, are close to the results reported earlier [4]. Our <sup>1</sup>H NMR data for **3** (Table 2) are similar to the known values [13] as well. UV/Vis spectral data are given in Table 4.

**Table 1.** Thermoanalytical data of compounds **2**, **3** and **4**.

	Yield, %	Formula (mol. mass)	M.p., °C	C, %		H, %		N, %	
				Calc.	Found,	Calc.	Found	Calc.	Found
<b>2</b>	61	C <sub>34</sub> H <sub>44</sub> N <sub>4</sub> O <sub>7</sub> S <sub>2</sub> (684)	168–169	59.65	59.99	6.48	6.66		
<b>3</b>	46	C <sub>36</sub> H <sub>48</sub> N <sub>4</sub> O <sub>8</sub> S <sub>2</sub> (728)	170–171	59.30	59.28	6.59	6.83		
<b>4a</b>	42	C <sub>21</sub> H <sub>27</sub> N <sub>3</sub> O <sub>7</sub> (433.5)	212–213	58.19	57.65	6.28	6.30	9.70	9.55
<b>4b</b>	63	C <sub>23</sub> H <sub>31</sub> N <sub>3</sub> O <sub>7</sub> (461.5)	206–207	59.85	59.72	6.77	6.93	9.11	9.09
<b>4c</b>	71	C <sub>25</sub> H <sub>35</sub> N <sub>3</sub> O <sub>6</sub> S (505.6)	227–229	59.34	59.30	6.92	6.54	8.30	8.74

**Table 2.** <sup>1</sup>H-NMR spectral data of compounds **2** and **3** in CDCl<sub>3</sub>. For atom notations, see Scheme 1.

	N(CH <sub>3</sub> ) <sub>2</sub>	O(CH <sub>2</sub> ) <sub>2</sub> -a,b,d,e	O(CH <sub>2</sub> ) <sub>2</sub> -c	1-H, 4-H	2-H, 5-H	3-H, 6-H
<b>2</b>	2.86 (s, 6H)	3.42–3.66 (m, 16H)	3.54 (s, 4H)	7.15 (dd, 2H) 8.13 (dd, 2H)	7.49 (dd, 2H) 7.53 (dd, 2H)	8.29 (dt, 2H) 8.51 (dt, 2H)
<b>3</b>	2.83 (s, 6H)	3.59 (s, 16H)	3.48 (s, 8H)	7.18 (dd, 2H) 8.14 (dd, 2H)	7.51 (dd, 2H) 7.54 (dd, 2H)	8.29 (dt, 2H) 8.51 (dt, 2H)

**Table 3.** <sup>1</sup>H-NMR data of compounds **4a–c** in CDCl<sub>3</sub>. For atom notations, see Scheme 2.

	R	O(CH <sub>2</sub> ) <sub>2</sub> -e	O(CH <sub>2</sub> ) <sub>2</sub> -a,b,c,d	2H	3-H	-CH=
<b>4a<sup>a</sup></b>	10.93 (s, 1H)	3.50	3.53–3.58	6.80	8.41	8.14
	11.06 (s, 1H)	(s, 4H)	(m, 8H) 3.69(s, 8H)	(m, 2H)	(m, 2H)	(s, 1H)
<b>4b</b>	3.36 (s, 3H, CH <sub>3</sub> )	3.62	3.63–3.83	6.71	8.38	8.42
	3.39 (s, 3H, CH <sub>3</sub> )	(s, 4H)	(m, 16H)	(m, 2H)	(m, 2H)	(s, 1H)
<b>4c</b>	1.31 (t, 3H, CH <sub>3</sub> )	3.66	3.70–3.84	6.74	8.40	8.41
	1.32 (t, 3H, CH <sub>3</sub> )	(s, 4H)	(m, 16H)	(m, 2H)	(m, 2H)	(s, 1H)
	4.53–4.61 (m, 4H, CH <sub>2</sub> )					

a- DMSO-d<sub>6</sub>

*Synthesis of 5-[4-(1,4,7,10-tetraoxa-13-azacyclopentadec-13-yl)-benzylidene]-pyrimidine-2,4,6-tri-ones 4:* Warm solutions of 0.4 g (1.24 mmol) of 4-(1,4,7,10-tetraoxa-13-azacyclopentadec-13-yl) benzaldehyde [13] in 5 ml glacial AcOH and 1.24 mmol of the corresponding barbituric acid (1,3-H-1,3-dimethyl-1,3-diethyl-2-thio) in 5 ml glacial AcOH are mixed and then refluxed for 2 hours. The product crystallizes upon cooling, and is purified by recrystallisation from AcOH. The product purity is verified by TLC. <sup>1</sup>H NMR data are listed in Table 3 and UV/Vis spectral data in ethanol are given in Table 4.

**Table 4.** UV-VIS absorption and fluorescence spectral characteristics of the studied substituted aza-crown compounds in ethanol.

Compound	$\nu_{\text{Abs}}$ , $\text{cm}^{-1}$	$\nu_{\text{Fl}}$ , $\text{cm}^{-1}$	$\Delta\nu_{\text{Stokes}}$ , $\text{cm}^{-1}$
<b>2</b>	29600	18700	10900
<b>4a</b>	21500	19100	2400
<b>4b</b>	21400	18900	2500
<b>4c</b>	20100	17700	2400

#### Electronic spectra

The absorption and emission UV spectra of compounds **2** and **4a–c** have been recorded in ethanol, respectively, on a Specord UV-VIS spectrophotometer and a MPF-44 Perkin-Elmer spectrofluorimeter (Table 4).

The absorption spectrum of **2** consists of three bands of diminishing intensity at 220, 253 and 338 nm. The observed similarity in shape and position of the bands of both the absorption and fluorescence spectra of **2** to those, reported for 1-(dimethylamino)-5-naphthalenesulfonic acid [4, 23] suggests absence of significant interaction between the crown ether moiety and the basic dansyl chromophore, as previously found in the case of dansyl substituted monoaza crown ethers [4, 12]. The observed anomalous Stokes shift of **2**, by analogy to the basic dansyl fluorophore, 1-(dimethylamino)-5-naphthalenesulfonic acid, can be interpreted in terms of large increase of the dipole moment in polar solvents upon excitation, due to a change of the emitting state upon increasing the solvent polarity [17].

The absorption spectra of compounds **4a–c** consist of an intense CT band in the visible region (see Table 4) and a series of low intensity bands at shorter wavelengths.

#### Molecular modeling

The geometries of N-substituted aza-crown ethers **2** and **3** have been optimized without constraints using MOPAC 93 [18] and the PM3 [19]

hamiltonian as implemented in this program. In addition, dynamic geometry changes of Dns-aza-crown15 **2** have been calculated using the dynamic reaction coordinate approach, DRC [20], and the same PM3 semi-empirical MO approximation.

## RESULTS AND DISCUSSION

*Conformations of the studied crown ethers and conformational changes upon binding metal ions:* Free crown ethers possess multiple conformational minima, the preferred ones of which are those with the heteroatoms as much apart as possible, as shown both experimentally and by molecular mechanics [21] and quantum chemical MO [22] calculations. In contrast to it, in metal complexes of crown ethers the heteroatoms are pointing to the inside of the ring [21–23], as they are attracted more or less strongly by the ion positive charge(s). The conformational changes in case of metal ion coordination require significant amounts of energy, which are part of the ion – crown stabilization energy. In the case of aza-crown ethers there is some uncertainty concerning the preference of specific metal ions to oxygen or nitrogen atoms of the ligand. Therefore, we attempt to shed some light on this problem by MO calculations of crown complexes.

According to the PM3 dynamic calculations (Figure 1) the Dns-substituent in the aza-crown ether does not drastically change the known features of the macro-heterocycle.

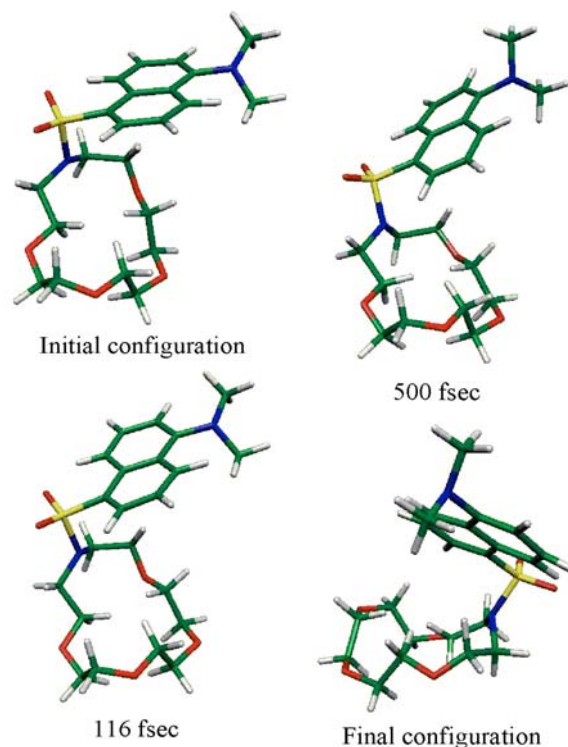


Fig. 1. Molecular dynamics, with time marks, of Dns-A15C5 **2**, PM3.

However, a PM3 conformational analysis, performed separately, shows that the dansyl fragment in Dns-A15C5 **2** rotates around the N–S(O<sub>2</sub>) bond practically freely (barrier for rotation is not higher than 3.5 kcal/mol), see Figure 2, and can hinder the access of metal ions to the internal crown cavity.

The partial hindering of ionophore cavity by the rotating dansyl moiety can be the reason for the observed reduced interaction of monoaza crown ethers carrying the dansyl fluorophore with alkaline metal ions [4, 12]. Bis-dansyl crown ethers may be expected to show more of this hindrance effect, even though the rotation of fluorescent fragments in Dns<sub>2</sub>-A18C6 **3** is significantly limited by the relatively broad zones of forbidden conformations (see Figure 3).

Compared to the known very stable magnesium hexahydrate complex these complexes are, however, significantly less stable. This result predicts a negligible selectivity of the studied crown ethers with respect to Mg<sup>2+</sup>, even with the necessary reservations against the used PM3 approximation in present calculations. The conformation energy loss by ring deformation is relatively small, ca. 20 kcal/mol – see column 4, entries **2**, **4a** and **4c** of Table 5 (the 1SCF calculations).

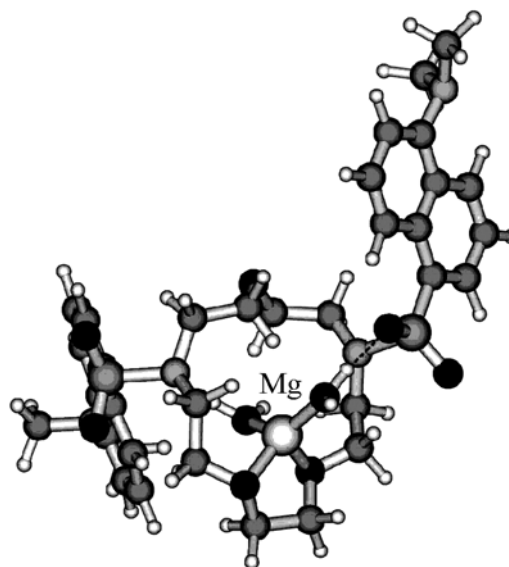


Fig. 2. Energy profile for the dansyl rotation in Dns-A15C5 **2**, PM3 calculation.

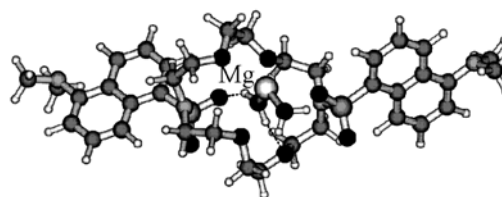
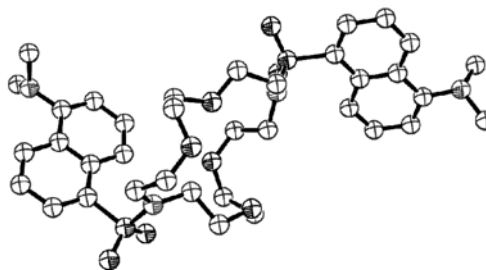


Fig. 3. Energy profile for the dansyl rotation in Dns-A18C6 **3**, PM3 calculation.

The complex formation of aza-crown ethers with divalent metal ions is studied by PM3 calculations of the respective Mg<sup>2+</sup> complexes. The results, listed in Table 5, indicate that the A15C5 crowns **4a** and **4c** form stronger complexes with the small magnesium cation than the A18C6 crown **3**.

Fig. 4. Mg<sup>2+</sup>·2H<sub>2</sub>O complexes of bis-dansyl crown ethers C15A2 (top) and C18A2 (bottom), PM3 calculations.

The structure of the free compound **3** is given for comparison, with the heteroatoms as shaded circles.

As it was expected, the PM3 calculations show that the complexes of the larger A18C6 crown **3** with Mg<sup>2+</sup> are even less stable than those of **2**, **4a** and **4c**, and indeed compared to Mg<sup>2+</sup>(H<sub>2</sub>O)<sub>6</sub>. The latter result is evidently due to the larger cavity size of **3**, as is the resulting larger loss of conformational

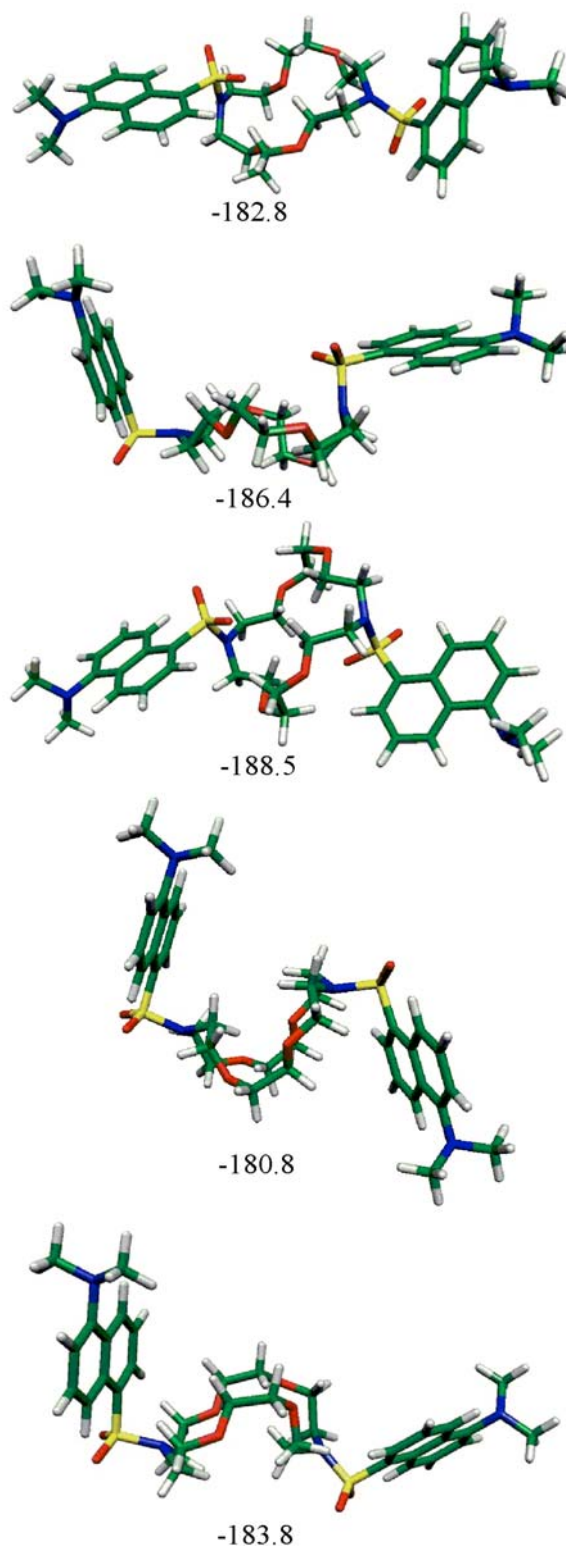
energy upon metal ion binding, almost 50 kcal/mol versus 21–26 kcal/mol for the C15 ligands (see Table 5). Indeed, the absolute values of the calculated PM3 stabilization energies of the studied aza-crown–Mg<sup>2+</sup> complexes are of little significance due to the strong exaggeration of Mg<sup>2+</sup>–O interaction energies by the used valence electron MO approximation. However, the calculated order of macrocycle deformation energies is in line with the preference of 15-membered crown ethers for smaller mono and divalent main group metal ions known from experimental data. Moreover, the results clearly indicate, that crown ethers **4a–c** are expected to form much stronger complexes with Mg<sup>2+</sup> than the widely studied dansyl derivatives of crown ethers. The PM3 calculations additionally indicate preference of Mg<sup>2+</sup> ions for oxygen rather than nitrogen atoms of crown ligands (see Figure 4). This result is in line with the known preference of “hard” Mg<sup>2+</sup> ions for oxygen rather than nitrogen atoms in protein complexes [24]. In addition, calculations (as well as the X-ray data) show that the traditional symmetric formulae of crown ethers and their metal complexes do not present correctly their structures. In fact, the symmetric configurations of studied diaza-crowns ethers **2** and **3**, and their metal complexes are not stationary points on the respective potential energy surfaces.

**Table 5.** PM3 heats of formation  $H_f$  in kcal/mol of substituted aza-crown ethers and complexes with Mg<sup>2+</sup>. Reference heats of formation are: Mg<sup>2+</sup>, 555.1; H<sub>2</sub>O, –53.4; Mg<sup>2+</sup>(H<sub>2</sub>O)<sub>6</sub>, –68.9,  $\Delta H_f = -303.6$  kcal/mol, PM3.

Aza-crown ether	Free crown	+ Mg <sup>2+</sup> $\Delta H_f$	– Mg <sup>2+</sup> / 1SCF $\Delta H_f$	– Mg <sup>2+</sup> / opt $\Delta H_f$	+ Mg <sup>2+</sup> + 2H <sub>2</sub> O $\Delta H_f$
<b>2</b>	–149.9	290.4	–123.2	–147.8	67.9
		–114.8	26.7	2.1	–230.5
<b>3</b>	–184.7	207.5	–139.5	–182.8	21.8
		–162.9	45.2	0.5	–241.8
<b>4a</b>	–229.5	132.6	–208.1	–227.7	–29.6
		–193.0	21.4	1.8	–248.4
<b>4c</b>	–157.4	206.4	–135.8	–158.2	44.2
		–191.3	21.6	–0.8	–246.7

As regarding the “approximately perpendicular” orientation of dansyl fragments against the macrocyclic aza-ether, observed in the solid state X-ray studies of **3** [4], the PM3 calculations indicate that these conformations are well within the broad zones of free rotation around N–S bonds and could only be limited by inversion processes of aza-nitrogen atoms and the macrocycle (see Figure 5). We did not try to calculate barriers to these processes, but found that energy differences between some of the possible conformers were again within a few kcal.mol<sup>–1</sup>. Thus, the observed crystal structures [4] can well be

the result of crystal lattice interactions beyond the scope of our study.



**Fig. 5.** PM3 Heats of formation of rotamers arising from dansyl rotation around the axial sulfamide bond N–S, the dihedral rotation angle defined as  $\langle C-N-S-O$ . Exo- and endo-axial dansyl substituents of Dns<sub>2</sub>-A18C6 **3** are shown at the top. “Perpendicular conformers” with diequatorial dansyl substituents are shown at the bottom.

## CONCLUSIONS

A number of factors are commonly recognized in the literature to affect the binding ability and selectivity of crown ether ligands to metal ions. Among them the size of the crown ether cavity and the size and charge density of the metal ion are recognized as the most important ones, most often the size match being considered the key factor. Substituents in the crown ether have also been considered in some cases to affect the complexation properties through interaction with the charge density of the metal cation.

In the present study we observe all the mentioned effects. The calculated order of macrocycle deformation energies is in line with the preference of 15-membered crown ethers for smaller mono and divalent main group metal ions, compared to the 18-membered crown known from experimental data. The compounds **4** form more stable complexes with  $Mg^{2+}$  than the compounds **2** and **3**, presumably for two reasons: first, because the *p*-substituted benzylidene-pyrimidine moiety is more sensitive to the high charge density of  $Mg^{2+}$  than the dansyl fragment, and second, because the *p*-substituted benzylidene-pyrimidyl fragment does not hinder the access of metal cations to the ionophore cavity. Both reasons originate from the capability of *p*-substituted benzylidene-pyrimidyl to participate in  $\pi$ -electron conjugation, a property that the dansyl fragment does not possess. Our results confirm the suggested participation of the dansyl fluorescent label in hindering the access of metal ions to the ionophore cavity – an additional factor, which ought to be considered in interpretations of experimental data concerning ligands bearing flexibly bound indicator fragments.

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## ЕЛЕКТРОННИ СПЕКТРИ И КОНФОРМАЦИОННИ СВОЙСТВА НА НЯКОИ N-ЗАМЕСТЕНИ АЗА-КОРОННИ ЕТЕРИ И ТЕХНИ КОМПЛЕКСИ С ЙОНИ НА АЛКАЛОЗЕМНИ МЕТАЛИ

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(Резюме)

Описани са синтезът и електронните абсорбционни и флуоресцентни емисионни спектри на новосинтезирани N-данзил-заместени C15 и C18 аза-коронни етери. Извършено е динамично и конформационно моделиране на полуемпирично PM3 MO ниво, което сочи относително слаби взаимодействия на малкия двувалентен йон Mg<sup>2+</sup> както с етерния макроцикъл, така и с ароматния флуорофор. Споменатите PM3 пресмятания сочат ясно предпочитание на магнезиевите йони към по-малките C15 от изследваните макроцикли. Изчислените енергии за деформация на макроцикъл C18 при образуване на изследваните йонни комплекси са от порядъка на 25 ккал/мол и са по-неизгодни от съответните стойности за C15. Този резултат е в съответствие с известната слаба селективност на C18 краун етери към малки двувалентни йони в разтвор. Заместителите при азотния атом влияят върху комплексообразуването не само чрез взаимодействие със зарядовата плътност на металния катион, но и посредством запречване на достъпа на метални йони до кухината на йонофора.