This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Investigation of Complexation of Sodium Cation by Anthracene Crown Ethers

Ryszard Ostaszewski[a]; Agnieszka Bozek[b]; Marcin Palys[b]; Zbigniew Stojek[b]
[a] Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Polan [b] Department of Chemistry, University of Warsaw, Warsaw, Poland

To cite this Article Ostaszewski, Ryszard , Bozek, Agnieszka , Palys, Marcin and Stojek, Zbigniew(2000) 'Investigation of Complexation of Sodium Cation by Anthracene Crown Ethers', Supramolecular Chemistry, 12: 1, 105 — 109

To link to this Article: DOI: 10.1080/10610270008029809

URL: http://dx.doi.org/10.1080/10610270008029809

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SUPRAMOLECULAR CHEMISTRY, Vol. 12, pp. 105-109
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Harwood Academic Publishers imprint,
part of the Gordon and Breach Publishing Group.
Printed in Malaysia

Investigation of Complexation of Sodium Cation by Anthracene Crown Ethers

RYSZARD OSTASZEWSKI[a*], AGNIESZKA BOŻEK[b], MARCIN PAŁYS[b] and ZBIGNIEW STOJEK[b]

[a]*Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01–224 Warsaw, Polan and* [b]*Department of Chemistry, University of Warsaw, Pasteura 1, 02–093 Warsaw, Poland*

Formation constants for complexes of sodium and anthracene crown ethers were determined using spectrophotometry and cyclic voltammetry. The complexation properties of the ligands examined depend significantly on alkyl substituents at 9 and 10-positions of the anthracene group and are strongly influenced by the solvent.

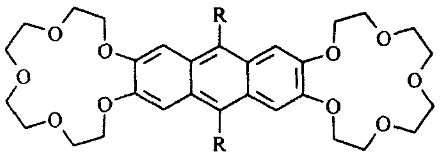
Among the interesting properties of the anthracene system, there are the fluorescence properties, which are utilised in, e.g., designing of luminescent photoinduced electron transfer sensors[1] according to the well known operation principles.[2] Quite recently, the interaction of the anthracene systems with biological polyanions (DNA, heparine), and particularly the intercalation of CT-DNA by diamino anthracene derivatives, have been reported.[3] Synthesis of anthracene-based sensor molecule can be realised by either an appropriate functionalization of crown ethers and cryptands with anthracene derivatives (simple anthracene crown ethers[4] and anthracene cryptands[5]) or direct synthesis based on functionalization of the anthracene group. The latter method is very difficult.[6] Preparation of anthracene bicyclic[7] and tricyclic cryptands[8] requires multistep synthesis.

During our studies directed towards synthesis of new anthracene crowns, we found that upon treatment of benzo-15-crown-5 or benzo-18-crown-6 with aliphatic aldehydes in the presence of sulphuric acid, the respective anthracene crowns **1** and **2** can be obtained in 15–71% yield.[9] These novel structures consist of two crown ethers sharing an anthracene ring system. Both crown ethers are potential binding sites for cations and the presence of alkyl groups in the 9 and 10- positions of the anthracene system can modify the recognition processes. The presence of two binding sites can lead to the formation of large structures, where sandwich-type complexes are formed, each cation being coordinated by two crowns belonging to different ligand molecules. To check out these possibilities, the binding properties of several of these new ionophores with respect to sodium cation were investigated using electrochemical and spectroscopic techniques.

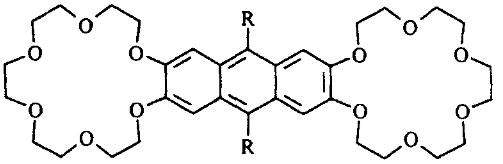
UV titration experiments were performed for sodium thiocyanate and ligand **1b** (Figs. 1 and 2). The values of the complex formation constants are collected in Table I. We have found that two complexes of 1:1 and 1:2 stoichiometries are (NaL and Na_2L) formed under the conditions applied.

---

[*] Author for correspondence.



1



2

1a, 2a R = CH_3CH_2-
1b R = $(CH_3)_2CHCH_2$-
1c R = $CH_3(CH_2)_3$-
1d R = $CH_3(CH_2)_6$-
1e R = $CH_3(CH_2)_8$-
1f R = $CH_3(CH_2)_{10}$-

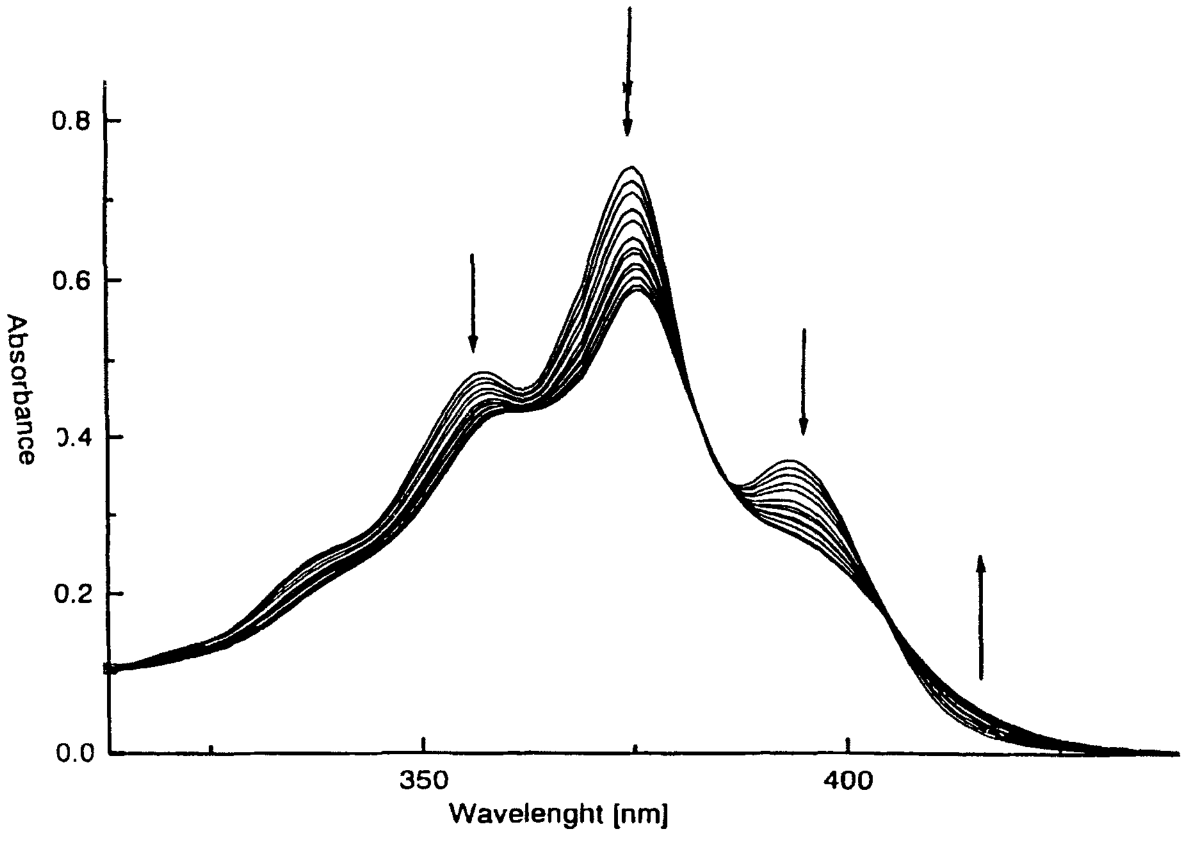


FIGURE 1 Change in the absorption spectrum of $6.86 \cdot 10^{-5}$ M solution of crown **1b** in chloroform-methanol mixture (8:2 v/v) upon increase of concentration of KSCN ($0 < C_{K^+} < 1.66 \cdot 10^{-3}$ M)

The same UV titrations were carried out for sodium and ligand **1a**. A large substituent effect was observed for the complexation of the second sodium cation. This effect is responsible for a decrease in the equilibrium constant by two orders of magnitude ($\log K_{Na_2L} = 1.94$). An

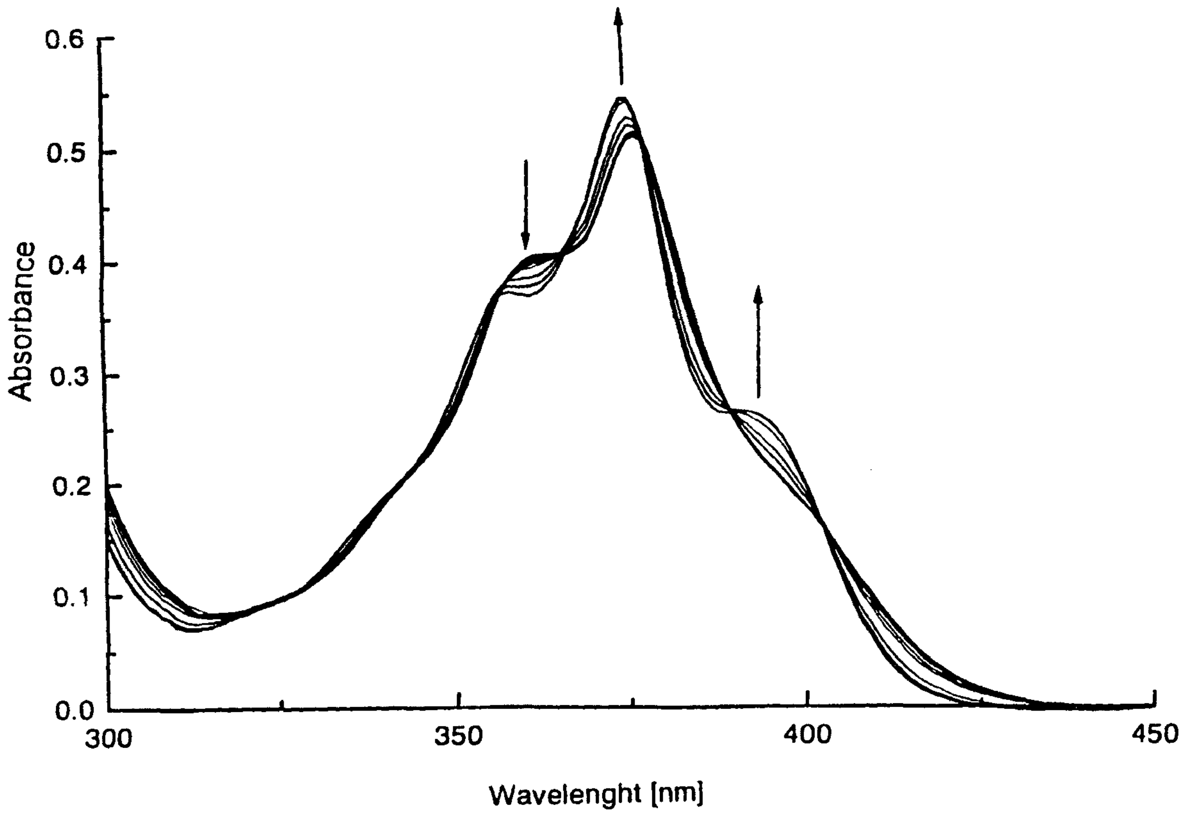


FIGURE 2 Change in the absorption spectrum of $6.86 \cdot 10^{-5}$ M solution of crown **1b** in chloroform-methanol mixture (8:2 v/v) upon increase of concentration of KSCN ($1.17 \cdot 10^{-3} < C_{K+} < 9.7 \cdot 10^{-3}$ M)

indirect voltammetric method was used to assess the complexation equilibria. The competitive cation (indicator) was the thallium(I) cation. Upon addition of the ligand, the voltammetric reduction peak of thallium shifts toward negative potentials. An addition of Na^+ decreases the shift by binding a fraction of the ligand and decomplexing thallium.

TABLE I Formation constants determined for sodium complexes of anthracene crown **1** in chloroform/methanol (9:1, v/v) mixture, at 20 °C for λ_{max}=375 nm

Compound	ε_1^b *(mol⁻¹dm³)*	$\log K_{NaL}$	ε_2^b *(mol⁻¹ dm³)*	$\log K_{Na_2L}$
1a	8560	4.40	6850	1.94
1b	10880	4.62	10620	3.67

The formation constants for the Na^+ complexes were determined by recording the voltammograms for free thallium ion (Tl^+), thallium ion with the ligand ($Tl^+ + L$) and thallium ion with ligand and the sodium ion ($Tl^+ + L + Na^+$).

The complex formation constants for thallium and sodium cations in dimethylformamide are presented in Table II.

An inspection of Table II shows that the formation constants of thallium and sodium complexes with anthracene crowns **1** clearly depend on the substituents at 9 and 10- positions of the anthracene group. The formation constants of sodium complexes of crown **1a** and **1b** in dimethylformamide (entries **1a** and **1b** in Table II) are smaller than those obtained in

$CHCl_3$/MeOH solvent mixture (Table I). Also, the trend in the formation constants of sodium complexes is reversed. In the $CHCl_3$/MeOH solvent mixture, the sodium complex of 1:1 stoichiometry with crown **1b** (isobutyl groups at 9 and 10- positions) is slightly stronger than that with the ethyl substituted ligand **1a** (Table I). In dimethylformamide, the formation constant decreased from $\log K_{NaL}=1.9$ for compound **1a** to $\log K_{NaL}=0.9$ for compound **1b**. The n-butyl substitued ligand **1c** has the value $\log K_{NaL}=2.0$, which is almost equal to that of the ethyl-substituted ligand **1a**. Further elongation of the aliphatic groups caused an increase in the formation constant to $\log K_{NaL}=3.2$ for compound **1d** (Table II), but the next extra carbon atom decreased the constant so strongly that it was not measurable under the experimental conditions. For the last compound studied, **1f**, which is substituted with dodecyl alkyl groups, the measured constant ($\log K_{NaL}= 1.9$) is equal to the one for crown **1a**, what indicates that the influence of both ethyl and dodecyl alkyl groups on the formation constant is very similar. The modulation effect of the alkyl groups on the formation constants is also observed for the thallium complexes. Again, the highest complexation constant was observed for the heptane and ethyl groups (entries **1a** and **1d** in Table II).

TABLE II Complex formation constants determined in voltammetric experiments at 20°C in dimethylformamide Estimated error is approx. 0.3 logK unit

Ligand	$logK_{TIL}{}^{+}$	$logK_{NaL}{}^{+}$
1a	2.8	1.9
1b	1.6	0.9
1c	1.3	2.0
1d	2.5	3.2
1e	1.9	a
1f	2.4	1.9
2a	4.9	4.4

a. the formation of the respective complex was not observed under experimental conditions

An enlargement of the crown ether groups by adding one ethylenoxy unit to form crown **2a** caused an increase of the complexation constants for both cations (last entry in Table II). An analysis of the spectrophotometric titration data presented in Table I leads to the conclusion that both crown ether rings can participate in the complexation. The complexation of the first cation can increase or decrease the binding of the second cation.

The complexation constants for the sodium cation and crown **1b** in the chloroform-methanol mixture, $\log K_{NaL}=4.62$ and $\log K_{Na_2L} = 3.67$, differ only by one order of magnitude. This system is characterised by a negative cooperation effect, since $K_{Na_2L}/k_{NaL} < 0.25$.[10] For compound **1a**, this difference in the complexation constants is even larger. Therefore, it is unlikely that the formation of a larger, self-assembly type structure, takes place.

The final conclusion is that the complexation and recognition properties of the studied anthracene crown ethers significantly depend on alkyl substituents and are strongly influenced by the solvent.

Acknowledgements

This work was supported by State Committee for Scientific Research Grant No. 3 TO9A 03317 and by the Department of Chemistry, University of Warsaw, Grant No. BW-1418/17/98.

References

1. A.P. de Silva, T. Gunnlaugsoon, T.E. Rice, *Analyst*, 1996, **121**, 1759.
2. A.P. de Silva, H.Q.N. Gunarante, T. Gunnlaugsoon, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, *Chem. Rev.*, 1997, **97**, 1515.
3. R. Ostaszewski, M. Wolszczak, E. Wolczynska, *Bioorg. Med. Chem. Lett.*, 1998, **8**, 2995.
4. (a) M.Y. Chae, X.M. Cherian, A.W. Czarnik, *J. Org. Chem.*, 1993, **58**, 5797.
   (b) A.P. De Silva, S.A. de Silva, *J. Chem. Soc., Chem. Commun.*, 1986, 1709.
   (c) L. Fabbrizzi, M. Licchelli, P. Pallavicini, A. Perotti, A. Taglietti, D. Sacchi, *Chem. Eur. J.*, 1996, **2**, 75.

5. P. Ghosh, P.K. Bharadwaj, S. Mandal, S. Ghosh, *J. Am. Chem. Soc.*, 1996, **118**, 1553.
6. J. Hinschberger, J.P. Desvergne, H. Bouas-Laurent, P. Marsau, *J. Chem. Soc. Perkin Trans.* **2**, 1990, 993.
7. (a) F. Fages, J.P. Desverge, H. Bouas-Laurent, P. Marsau, J.M. Lehn, F. Kotzyba-Hilbert, A.M. Gary, M. Al-Jubbeh, *J. Am. Chem. Soc.*, 1989, **111**, 8672.
   (b) J.P. Desverge, J. Laurent, H. Bouas-Laurent, P. Marsau, N. Lahrahar, H. Andrianatoandro, M. Cotrait, *Recl. Trav. Chim. Pays-Bas*, 1995, **114**, 504.
8. (a) F. Fages, J.P. Desverge, H. Bouas-Laurent, J.M. Lehn, J.P. Konopielski, P. Marsau, Y. Barrans, *J. Chem. Soc., Chem. Commun.*, 1990, 655.
   (b) F. Fages, J.P. Desverge, H. Bouas-Laurent, J.M. Lehn,, Y. Barrans, P. Marsau, M. Meyer, A.A. Albrecht-Gary, *J. Org. Chem.*, 1994, **59**, 5264.
9. R. Ostaszewski, *Tetrahedron*, 1998, **54**, 6902.
10. K. Kikukowa, G.X. Abe, T. Goto, R. Arata, T. Ikeda, F. Wada, T. Matsuda, *J. Chem. Soc., Perkin Trans.* 2, 1987, 135.