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MOLECULAR CLIPS BASED ON BENZOAZA-15-CROWN-5 AND DIPHENYLGLYCOLURIL: SYNTHESIS AND COMPLEXATION WITH ALKALI AND ALKALINE EARTH METAL CATIONS

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New molecular clips were obtained by reacting benzoaza-15-crown-5 derivatives with diphenylglycoluril bis-ether in polyphosphoric acid. In the case of benzoaza-15-crown-5 with an unsubstituted nitrogen atom, a low yield of the target product was obtained. The introduction of substituents at the nitrogen atom allows the yield to be increased to 40–42%. It has been demonstrated that the complexing properties of the synthesized compounds depend on the nature of the substituent at the nitrogen atoms of the crown ether fragments. The unsubstituted clip interacts weakly with alkali metal cations but forms very stable 2:1 (L:M) complexes with alkaline earth metal cations. Among the alkali metal cations, the N–Me derivative forms the most stable complexes with K^+ and Rb^+, whereas the clip containing an ester group forms the most stable complex with the sodium cation.

Keywords: supramolecular chemistry, molecular clips, diphenylglycoluril, benzoaza-15-crown-5, complexing properties, spectrophotometry.

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Introduction

Glycoluril and its derivatives are among the most commonly used fragments in the construction of synthetic receptors [1–6]. It should be noted that all glycoluril-based receptors contain methylene (bridging) bonds, due to which they have a U-shape, which provides the formation of a pseudocavity. In 1991, Sijbesma et al. [7] called such receptors molecular clips. We have previously obtained a series of molecular clips based on diphenylglycoluril and benzo(dibenzo)crown ethers and studied their complexation with alkali metal cations and paraquat [8–12]. Among the obtained crown ethers, benzoazacrown ethers have received relatively little attention. The advantage of these compounds is the possibility of introducing substituents with different nature at the nitrogen atom, which should lead to a change in their complexation properties. To date, no molecular clips with benzoazacrown ether fragments have been demonstrated. Only one bis(benzoaza-15-crown-5) has been described, in which the crown ether rings are connected by a trimethylene linker [13]. The subject of this work was the synthesis of molecular clips based on diphenylglycoluril and benzoaza-15-crown-5 derivatives.

Experimental

Materials and equipment

The ^1H and ^{13}C NMR spectra were obtained from 10% solutions in chloroform-d on a Bruker Advance DRX 500 spectrometer using tetramethylsilane as internal reference. Fast atom bombardment (FAB) mass spectrometry was performed on a VG 70-70EQ mass spectrometer, equipped with an argon primary atom beam, and an m-nitrobenzyl alcohol matrix was utilized. Absorption spectra in the UV region (200–310 nm) were recorded using a spectrophotometer SPECORD 250 Plus. All of the metal chlorides were of analytical grade. Benzo-15-

crown-5 **1** was prepared according to the procedure described in ref. [14].

Synthesis

N-(Methoxycarbonylmethyl)benzoaza-15-crown-5 (**2**)

A 0.03 mol (3.2 mL) of bromomethyl acetate was added to a solution of 0.02 mol (5.35 g) of crown ether **1** and 0.04 mol (5.56 mL) of triethylamine in 50 mL of methyl alcohol, and the reaction mixture was boiled for 24 h. The solvent was evaporated under reduced pressure to dryness, the resulting residue was recrystallized from heptane. An oily substance; yield 78%. ^{1}H NMR: δ 6.91–6.86 (m, 4H, ArH), 4.17–4.12 (m, 8H, CH_2–CH_2O), 3.96 (t, 2H, CH_2–CH_2O), 3.87 (t, 2H, CH_2–CH_2O), 3.49 (c, 2H, N–CH_2CO), 2.97 (m, 7H, CH_3, CH_2N). ^{13}C NMR: δ 171.58, 148.82, 121.18, 113.59, 70.94, 70.50, 68.83, 59.16, 58.70, 51.93. FAB-MS (+): m/z (%): 354 $[M+H]^+$ (100).

N-Methylbenzoaza-15-crown-5 (**3**)

A 10.5 mmol (0.483 g) of formic acid (99.5%, d 1.22) and 5.25 mmol (0.1575 g) of a 40% formalin solution were added to 5.0 mmol (1.336 g) of benzoaza-15-crown-5 **1**. The reaction mixture was heated in a water bath for 8 h, cooled, neutralized with a saturated sodium carbonate solution, and the pH was adjusted to 9. The product was extracted with chloroform (3×50 mL). The combined chloroform extracts were dried over anhydrous $MgSO_4$. Chloroform was evaporated under reduced pressure, the product was extracted from the obtained residue with boiling hexane with the addition of 10–15% ethyl acetate (3×70 mL). After evaporation of the solvents, the product was additionally recrystallized from hexane with the addition of ethyl acetate. White solid; yield 72%. ^{1}H NMR: δ 6.61–6.70 (m, 4H, ArH), 4.13 (t, 4H, CH_2O), 3.67 (t, 4H, CH_2O), 3.39 (t, 4H, OCH_2CH_2N), 3.25 (t, 4H, CH_2N), 2.34 (s, 3H, CH_3). ^{13}C NMR: δ 148.80, 121.16, 113.67, 70.94, 70.49, 67.85, 59.15, 45.53. FAB-MS (+): m/z (%): 282 $[M+H]^+$ (100).

Synthesis of clips

The mixture of 2.65 mmol (1g) bis(ether) **7** and 5.42 mmol of the corresponding benzoazacrown ether **1**–**3** in PPA was intensively stirred at 85–90°C until the reagents were completely dissolved and for another 40 min. The cooled mixture was poured into water (150 mL) and stirred for 2–3 h. The precipitate was filtered, and an aqueous solution of Li_2CO_3 was added. The resulting oily suspension was extracted with chloroform (2×50 mL). The combined chloroform solutions were dried over $MgSO_4$, and the chloroform was distilled off under reduced pressure. Further processing was performed as described below.

Clip **4**

Benzene (50 mL) was added to the oily residue with stirring. The crystalline product was filtered off. Yield 27%. Mp: 248–249°C. ^{1}H NMR: δ 7.28–7.14 (m, 10H, Ph), 7.06 (s, 4H, ArH), 5.85 (s, 2H, NH), 4.63 (d, J=16.1 Hz, 4H, N–CH_2), 4.12–3.73 (m, 28H, O–CH_2CH_2–O, N–CH_2), 2.78–2.75 (m, 8H, O–CH_2CH_2–N). ^{13}C NMR: δ 160.05, 1467.84, 137.29, 127.71, 127.69, 126.83, 124.88, 110.37, 86.52, 71.50, 70.98, 70.50, 65.84, 57.61. FAB-MS (+): m/z (%): 877 $[M+H]^+$ (100).

Clips **5** *and* **6**

The residue was dissolved in benzene, washed with water (250 mL), and the benzene was distilled off under reduced pressure. The crystalline residue was dried in a vacuum at 60–70°C. Beige solid; yield 40% for clip **5**, 42% for clip **6**.

Clip **5**: Mp: 172–173°C. ^{1}H NMR: δ 7.11–7.04 (m, 10H, Ph), 6.76 (s, 4H, ArH), 4.65 (d, J=16.1 Hz, 4H, NCH_2), 4.14–3.70 (m, 28H, O–CH_2CH_2–O, N–CH_2), 2.73–2.70 (m, 8H, O–CH_2CH_2–N), 2.33 (s, 6H, N–CH_3).^{13}C NMR: δ 157.72, 147.51, 133.77, 129.90, 128.58, 128.21, 115.31, 85.35, 69.62, 69.34, 69.13, 56.68, 44.93, 44.13. FAB-MS (+): m/z (%): 905 $[M+H]^+$ (100).

Clip **6**: Mp: 121–122°C. ^{1}H NMR: δ 7.36–7.10 (m, 10H, Ph), 6.78 (s, 4H, ArH), 4.68 (d, J=15.74 Hz, 4H, N–CH_2), 4.13 (d, J=15.74 Hz, 4H, N–CH_2), 4.06–3.93 (m, 24H, 6H, O–CH_2CH_2–N, O–CH_2CH_2–O, N–CH_2), 3.81 (s, 6H, $COOCH_3$), 3.28–3.09 (m, 8H, O–CH_2CH_2–O), 2.79 (br.s, 4H, CH_2–$COOCH_3$). ^{13}C NMR: δ 157.70, 147.34, 133.61, 129.85, 128.69, 128.55, 128.24, 128.15, 115.17, 85.32, 69.25, 69.19, 68.90, 56.63, 56.37, 44.85, 43.82. FAB-MS (+): m/z (%): 1021 $[M+H]^+$ (100).

Stability constant determination

UV-vis titration experiments. A solution of molecular clip **4**–**6** (concentration about $1\cdot10^{-5}$–$5\cdot10^{-5}$ M) in methanol was treated with increasing amounts of alkali metal chloride solution (concentration about $2\cdot10^{-3}$ M) containing proper molecular clip of the same concentration at 20°C. The host concentration was maintained constant and the molar ratio of guest increased with respect to the host over the range 0.1:1 to 30:1 during the titration. The obtained solutions were leaving at room temperature for 12–15 h to achieve equilibrium. The absorbance measurements were carried out at four wavelengths, at which spectral changes were the most notable (200–310 nm) simultaneously, and sets of the obtained experimental values (4×30 points) were used for joint computer processing. The data were processed with the nonlinear least squares fitting MatLab

software [15].

Results and discussion

Alkylation of crown ether **1** with bromomethyl acetate in methanol in the presence of triethylamine gave derivative **2** with a 76% yield. Alkylation of **1** with formalin in 99.5% formic acid gives the N-methylbenzoaza-15-crown-5 **3** with a 72% yield (Scheme 1).

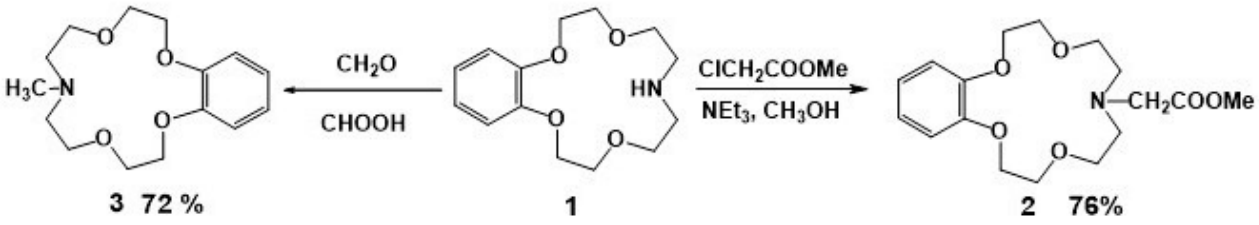
For the synthesis of molecular clips **4**–**6**, we used the previously developed method for obtaining clips with fragments of benzocrown ethers, based on heating 2.1 equivalents of crown ether with one equivalent of bis-ether **7** in polyphosphoric acid (PPA) [8] (Scheme 2).

It should be noted that in the case of crown ether **1**, complete conversion of the reagents required the reaction to be carried out at a higher temperature (85–90^{0}C instead of 80^{0}C). The total reaction time is 3–4 hours, during which the reagents are completely dissolved, plus an additional 40 minutes of stirring. In the original method [8], the total reaction time is 40 minutes. The yield of molecular clip **4** was less than expected (27%). To increase the yield of the product, the nitrogen atom of crown ether **1** was protected with a trifluoroacetyl group (Scheme 3). The reaction was carried out in trifluoroacetic anhydride in the presence of triethylamine.

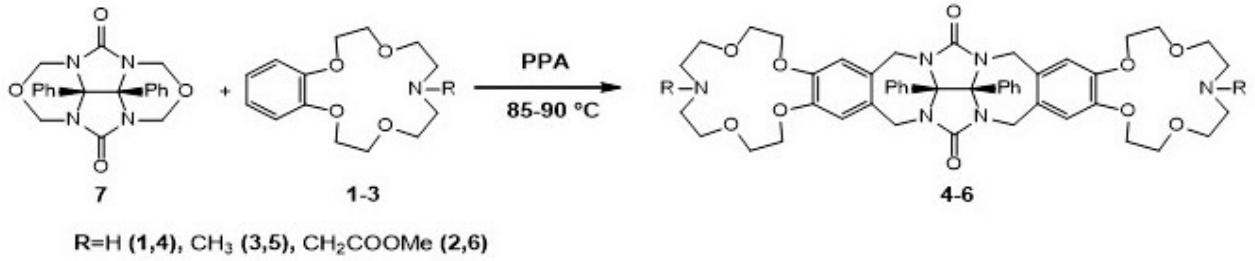
It should be noted that the interaction of derivative **8** with bis(ether) **7** in polyphosphoric acid does not lead to the formation of the target product, probably due to the destruction of the crown ether cycle under these conditions.

The yields of clips **5** and **6** were 40–42%. Clip **6** was isolated from the reaction medium in the form of a sodium complex that is difficult to destroy. Such a strong interaction may indicate the participation of oxygen atoms of the ester group in coordination with the sodium ion. Therefore, we changed the product isolation procedure and used Li_2CO_3 instead of NaOH.

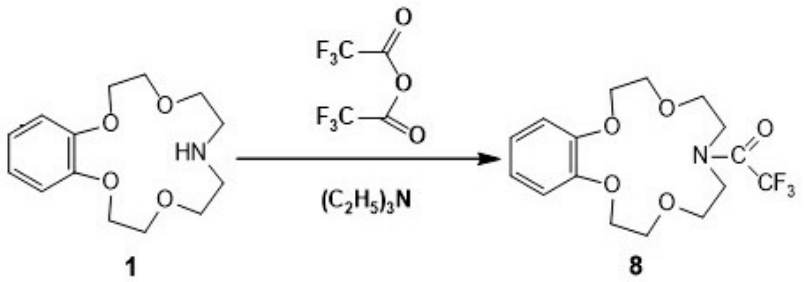
The stability of complexes of molecular clips **4**–**6** with alkali and alkaline earth metal cations was determined by spectrophotometric titration (Table). Data for clip **9** (Scheme 4) with a fragment of benzo-15-crown-5 are given for comparison [9]. Typical



Scheme 1. Synthesis of benzoaza-15-crown-5 derivatives **2** and **3**



Scheme 2. Synthesis of molecular clips **4**–**6**



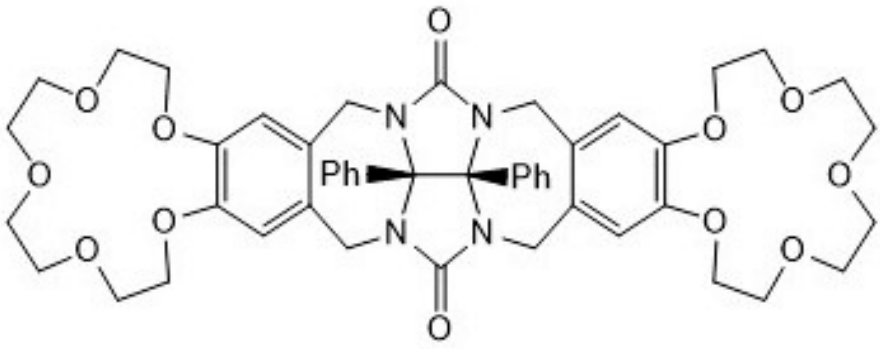
Scheme 3. Introduction of a protective group at the nitrogen atom of crown ether **1**

changes in the electronic absorption spectra and the titration curve are presented in Figure.

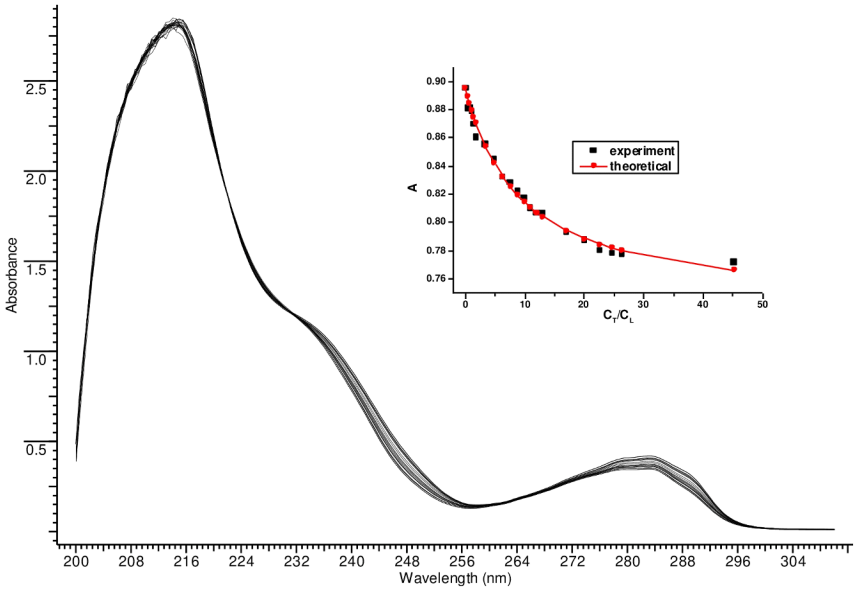
As follows from the data given in Table, the complexing properties of molecular clips **4**–**6** strongly depend on the nature of the substituent at the nitrogen atom. The tendency of selectivity toward to cations of alkaline metals, which is demonstrated by clips **5** and **9** coincides. This suggests the formation of intramolecular sandwich complexes in the case of potassium and rubidium ions. However, the observed constants for clip **5** are significantly lower (up to 3 orders of logarithmic units for potassium and rubidium). Molecular clip **4** with unsubstituted nitrogen atoms interacts very weakly with alkali metal cations. It was possible to calculate the stability constant only for the sodium ion. Much stronger interactions with alkaline earth metal cations for clip **4** are observed. With large cations of strontium and barium, very stable complexes of composition 2:1 (L:M) are formed ($\log K_{21}$>7 for Ba^{2+}). Clip **6** with an ester group at nitrogen atom, as expected, forms the most stable complex among alkaline cations with sodium ion. The stability constant value of this complex is an order of magnitude higher than for the other two clips, and is close to the value observed for clip **9**. Among alkaline earth cations, the stability of the complexes increases with increasing cation size. Moreover, the formation of stable complexes of both 1:1 and 2:1 compositions were observed with the barium ion.

Conclusions

New molecular clips with fragments of diphenylglycoluril and benzoaza-15-crown-5 have been obtained. It have been demonstrated that their complexation depends on the nature of the substituent at the nitrogen atom. In general, clips with benzoaza-15-crown-5 form less stable complexes with alkali metal cations than their analogue with the benzo-15-



Scheme 4. Clip **9**



Changes in the absorption spectrum and titration curve of molecular clip **5** with potassium chloride in methanol at 20^{0}C

crown-5 fragment. With large alkaline earth cations, very stable complexes of composition 2:1 (L:M) are formed.

REFERENCES

1. *Basket-shaped* hosts with semi-flexible handles / Smeets J.W.H., Visser H.C., Kaats-Richters V.E.M., Nolte R.J.M. // Recl. Trav. Chim. Pays-Bas. – 1990. – Vol.109. – No. 3. – P.147-153.

2. *Assaf K.I., Nau W.M.* Cucurbiturils: from synthesis to high-affinity binding and catalysis // Chem. Soc. Rev. – 2015. – Vol.44. – No. 2. – P.394-418.

3. *Rivera J.M., Martin T., Rebek Jr.J.* Chiral softballs: synthesis and molecular recognition properties // J. Am. Chem. Soc. – 2001. – Vol.123. – No. 22. – P.5213-5220.

4. *Synthesis* of novel molecular clips based on diethoxycarbonyl glycoluril / Yin G., Wang Z., Chen Y, Wu A., Pan Y. // Synlett. – 2006. – No. 1. – P.49-52.

5. *Glycoluril-derived* crown clips as new ditopic receptors / Rahimizadeh M., Seresht E.R., Bakavoli M., Pordel M. // Can. J. Chem. – 2007. – Vol.85. – No. 11. – P.964-968.

6. *Self-sorting* molecular clips / Ghosh S., Wu A., Fettinger J.C., Zavalij P.Y., Isaacs L. // J. Org. Chem. – 2008. – Vol.73. – No. 15. – P.5915-5925.

7. *Sijbesma R.P., Kentgens A.P.M., Nolte J.M.* Binding of dihydroxybenzenes in a synthetic molecular clip. Effect of hydrogen bonding and π-stacking // J. Org. Chem. – 1991. – Vol.56. – No. 10. – P.3199-3201.

8. *Synthesis*, crystal structure and alkali metal picrate extraction capabilities of molecular clips based on diphenylglycoluril and benzocrown ethers / Bogaschenko T.Yu., Lyapunov A.Yu., Kikot' L.S., Mazepa A.V., Botoshansky M.M., Fonari M.S., Kirichenko T.I. // Tetrahedron. – 2012. – Vol.68. – No. 24. – P.4757-4764.

9. *Molecular* clips based on diphenylglycoluril and benzocrown ethers: promising complexing agents for the alkali metal cations / Kikot' L.S., Lyapunov A.Yu., Kulygina C.Yu., Bogaschenko T.Yu., Zubatyuk R.I., Shishkin O.V., Kirichenko T.I. // J. Incl. Phenom. Macrocycl. Chem. – 2014. – Vol.79. – No. 3-4. – P.343-348.

10. *Complexation* of molecular clips containing fragments of diphenylglycoluril and benzocrown ethers with paraquat and its derivatives / Kikot' L.S., Kulygina C.Yu., Lyapunov A.Yu., Shishkina S.V., Zubatyuk R.I., Bogaschenko T.Yu., Kirichenko T.I. // Beilstein J. Org. Chem. – 2017. – Vol.13. – P.2056-2067.

11. *Synthesis* and complexation of molecular clips based on diphenylglycoluril and dibenzocrown ethers with alkali metal cations and paraquat / Kikot L.S., Kulygina C.Yu., Lyapunov A.Yu., Shishkina S.V., Zubatyuk R.I., Bogashchenko T.Yu., Kirichenko T.I. // Tetrahedron. – 2018. – Vol.74. – No. 39. – P.5725-5732.

12. *Synthesis* and complexation of molecular clips based on diphenylglycoluril and halogenated dibenzocrown ethers with paraquat / Kikot L.S., Kulygina C.Yu., Lyapunov A.Yu., Shishkina S.V., Vaksler Y.A., Bogashchenko TYu, Kirichenko T.I. // Tetrahedron Lett. – 2020. – Vol.61. – No. 18. – Art. No. 151839.

13. *Substitution* effect, absorption, and fluorescence behaviors of 11,12-benzo-1,7,10,13-tetraoxa-4-aza-cyclopentadec-11-ene (benzoaza-15-crown-5) derivatives upon cation complexation in solvent extraction / Nakamura M., Yokono H., Tomita K., Ouchi M., Miki M., Dohno R. // J. Org. Chem. – 2002. – Vol.67. – No. 10. – P.3533-3536.

14. *Lu T., Wu Ch.* Studies on azacrown ethers. VII. An improved method for synthesis of 2,3-benzo-10-aza-1,4,7,13-tetraoxa-cyclopentadeca-2-ene // Chin. J. Org. Chem. – 1985. – Vol.4. – P.312-314.

15. *Thordarson P.* Determining association constants from titration experiments in supramolecular chemistry // Chem. Soc. Rev. – 2011. – Vol.40. – No. 3. – P.1305-1323.

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Stability constants (lg*K*) of the complexes of clips 4–6, 9 with alkali and alkaline earth metal cations in MeOH at 20°C

Compound	Stability constant							
	lg*K*	Na^+	K^+	Rb^+	Cs^+	Ca^{2+}	Sr^{2+}	Ba^{2+}
4	lgK_{11}	2.94	**	**	**	2.36	0.86	–
	lgK_{21}	–	–	–	–	–	6.86	>7
5	lgK_{11}	2.87	3.18	3.31	2.79	3.18	3.40	3.23
6	lgK_{11}	3.90	3.51	3.69	2.99	2.88	3.99	5.57
	lgK_{21}	–	–	–	–	–	–	6.33
9*	lgK_{11}	4.13	6.25	6.34	3.74			

Notes: * – studied with alkali metal ions only; ** – too small changes in spectra.

МОЛЕКУЛЯРНІ КЛІПСИ НА ОСНОВІ БЕНЗОАЗА-15-КРАУН-5 І ДИФЕНІЛГЛІКОЛЬУРИЛУ: СИНТЕЗ І КОМПЛЕКСОУТВОРЕННЯ З КАТІОНАМИ ЛУЖНИХ І ЛУЖНОЗЕМЕЛЬНИХ МЕТАЛІВ

К.Ю. Кулигіна, Т.І. Кириченко

Взаємодією похідних бензоаза-15-краун-5 з біс-етером дифенілгліколькурилу в поліфосфатній кислоті отримані нові молекулярні кліпси. Використання бензоаза-15-краун-5 із незаміщеним атомом азоту дає низький вихід цільового продукту. Введення замісників по атому азоту дозволяє підвищити вихід до 40–42%. Продемонстровано залежність комплексоутворювальних властивостей синтезованих сполук від природи замісника у атома азоту краун-етерного фрагменту. Незаміщена кліпса слабко взаємодіє з катіонами лужних металів, однак утворює дуже стійкі комплекси складу 2:1 (ліганд:метал) з катіонами лужноземельних металів. N–Me похідне серед катіонів лужних металів утворює найбільш стійкі комплекси з K^+ і Rb^+, а кліпса, яка містить естерну групу, утворює найбільш стійкій комплекс з катіоном натрію.

Ключові слова: супрамолекулярна хімія; молекуляоні кліпси; дифенілгліколькурил; бензоаза-15-краун-5; комплексоутворювальні властивості; спектрофотометрія.

MOLECULAR CLIPS BASED ON BENZOAZA-15-CROWN-5 AND DIPHENYLGLYCOLURIL: SYNTHESIS AND COMPLEXATION WITH ALKALI AND ALKALINE EARTH METAL CATIONS

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New molecular clips were obtained by reacting benzoaza-15-crown-5 derivatives with diphenylglycoluril bis-ether in polyphosphoric acid. In the case of benzoaza-15-crown-5 with an unsubstituted nitrogen atom, a low yield of the target product was obtained. The introduction of substituents at the nitrogen atom allows the yield to be increased to 40–42%. It has been demonstrated that the complexing properties of the synthesized compounds depend on the nature of the substituent at the nitrogen atoms of the crown ether fragments. The unsubstituted clip interacts weakly with alkali metal cations but forms very stable 2:1 (L:M) complexes with alkaline earth metal cations. Among the alkali metal cations, the N–Me derivative forms the most stable complexes with K^+ and Rb^+, whereas the clip containing an ester group forms the most stable complex with the sodium cation.

Keywords: supramolecular chemistry; molecular clips; diphenylglycoluril; benzoaza-15-crown-5; complexing properties; spectrophotometry.

REFERENCES

1. Smeets JWH, Visser HC, Kaats-Richters VEM, Nolte RJM. Basket-shaped hosts with semi-flexible handles. *Recl Trav Chim Pays-Bas*. 1990; 109: 147-153. doi: 10.1002/recl.19901090303.

2. Assaf KI, Nau WM. Cucurbiturils: from synthesis to high-affinity binding and catalysis. *Chem Soc Rev*. 2015; 44: 394-418. doi: 10.1039/C4CS00273C.

3. Rivera JM, Martin T, Rebek Jr J. Chiral softballs: synthesis and molecular recognition properties. *J Am Chem Soc*. 2001; 123(22): 5213-5220. doi: 10.1021/ja004080i.

4. Yin G, Wang Z, Chen Y, Wu A, Pan Y. Synthesis of novel molecular clips based on diethoxycarbonyl glycoluril. *Synlett*. 2006; (1): 49-52. doi: 10.1055/s-2005-922761.

5. Rahimizadeh M, Seresht ER, Bakavoli M, Pordel M. Glycoluril-derived crown clips as new ditopic receptors. *Can J Chem*. 2007; 85(11): 964-968. doi: 10.1139/v07-115.

6. Ghosh S, Wu A, Fettinger JC, Zavalij PY, Isaacs L. Self-sorting molecular clips. *J Org Chem*. 2008; 73(15): 5915-5925. doi: 10.1021/jo8009424.

7. Sijbesma RP, Kentgens APM, Nolte JM. Binding of dihydroxybenzenes in a synthetic molecular clip. Effect of hydrogen bonding and π-stacking. *J Org Chem*. 1991; 56(10): 3199-3201. doi: 10.1021/jo00010a001.

8. Bogaschenko TYu, Lyapunov AYu, Kikot' LS, Mazepa AV, Botoshansky MM, Fonari MS, et al. Synthesis, crystal structure, and alkali metal picrate extraction capabilities of molecular clips based on diphenylglycoluril and benzocrown ethers. *Tetrahedron*. 2012; 68: 4757-4764. doi: 10.1016/j.tet.2012.04.009.

9. Kikot' LS, Lyapunov AYu, Kulygina CYu, Bogaschenko TYu, Zubatyuk RI, Shishkin OV, et al. Molecular clips based on diphenylglycoluril and benzocrown ethers: promising complexing agents for the alkali metal cations. *J Incl Phenom Macrocycl Chem*. 2014; 79: 343-348. doi: 10.1007/s10847-013-0357-3.

10. Kikot' LS, Kulygina CYu, Lyapunov AYu, Shishkina SV, Zubatyuk RI, Bogaschenko TYu, et al. Complexation of molecular clips containing fragments of diphenylglycoluril and benzocrown ethers with paraquat and its derivatives. *Beilstein J Org Chem*. 2017; 13: 2056-2067. doi: 10.3762/bjoc.13.203.

11. Kikot LS, Kulygina CYu, Lyapunov AYu, Shishkina SV, Zubatyuk RI, Bogashchenko TYu, et al. Synthesis and complexation of molecular clips based on diphenylglycoluril and dibenzocrown ethers with alkali metal cations and paraquat. *Tetrahedron*. 2018; 74: 5725-5732. doi: 10.1016/j.tet.2018.08.008.

12. Kikot LS, Kulygina CYu, Lyapunov AYu, Shishkina SV, Vaksler YA, Bogashchenko TYu, et al. Synthesis and complexation of molecular clips based on diphenylglycoluril and halogenated dibenzocrown ethers with paraquat. *Tetrahedron Lett*. 2020; 61: 151839. doi: 10.1016/j.tetlet.2020.151839.

13. Nakamura M, Yokono H, Tomita K, Ouchi M, Miki M, Dohno R. Substitution effect, absorption, and fluorescence behaviors of 11,12-benzo-1,7,10,13-tetraoxa-4-aza-cyclopentadec-11-ene (benzoaza-15-crown-5) derivatives upon cation complexation in solvent extraction. *J Org Chem*. 2002; 67(10): 3533-3536. doi: 10.1021/jo0107148.

14. Lu T, Wu Ch. Studies on azacrown ethers. VII. An improved method for synthesis of 2,3-benzo-10-aza-1,4,7,13-tetraoxa-cyclopentadeca-2-ene. *Chin J Org Chem*. 1985; 4: 312-314.

15. Thordarson P. Determining association constants from titration experiments in supramolecular chemistry. *Chem Soc Rev*. 2011; 40: 1305-1323. doi: 10.1039/C0CS00062K