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Lariat Ethers with Pendant Phenanthridine Units. Synthesis and Complexation of Na- and K-Picrate.

*Sulejman Alihodžić and Mladen Žinić**

Laboratory for Supramolecular and Nucleoside Chemistry, Department of Organic Chemistry and Biochemistry, Rudjer Bošković Institute, P.O.B. 1016, HR–10001, Zagreb, Croatia

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Lariat ethers **12** and **13** with appended phenanthridine fluorophoric units have been prepared as potential fluorescent chemosensor molecules for alkaline metal salts possessing aromatic anions. The starting 8-ethyloxycarbonylamino-6-methylphenanthridine (**1**) was converted *via* **2**, **3**, **6** and **7** to *N*-(2-tosylethyl)-derivatives **4** and **8** suitable for *N*-alkylations of diaza- and aza-18-crown-6. However, the alkylations failed, giving the 2-oxazolidinone derivative **5** formed by intramolecular cyclization of phenanthridine *N*-carbamate derivatives **4** and **8** in basic conditions. The phenanthridine derivative **10** having benzyl instead carbamate protection on 8-amino group successfully alkylated mono- and diaza-crown ethers, giving lariats **12** and **14**. Subsequent removal of benzyl protection groups in acidic conditions gave lariats **13** and **15**. Lariat **12** was found to form unique Na- and K-picrate complexes with the metal cation bound in the crown cavity and picrate anion intercalated between phenanthridine units.

Key words: crown ethers, lariate ethers, phenanthridine, complexes, sodium picrate

INTRODUCTION

The basic principle of fluorescent chemosensors rests on fluorescence "reading out" of the molecular or ion recognition process.[1] This principle is best corroborated by numerous cases of successful fluorescent sensing of

* Author to whom correspondence should be addressed. (E-mail: zinic@rudjer.irb.hr)

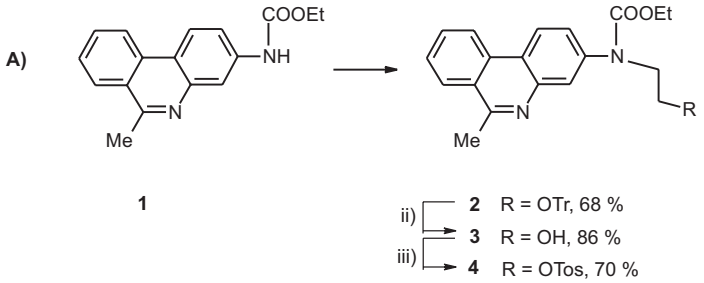
metal cations by receptor molecules constructed from crown ethers and various fluorophoric units.[2] On the other hand, fluorescence sensing of anionic species is much less developed.[3] Since anions play a fundamental role in many biological and chemical transformations and some anions are dangerous environmental pollutants, the development of various fluorescent anion chemosensors appears of high importance.[3-5]

RESULTS AND DISCUSSION

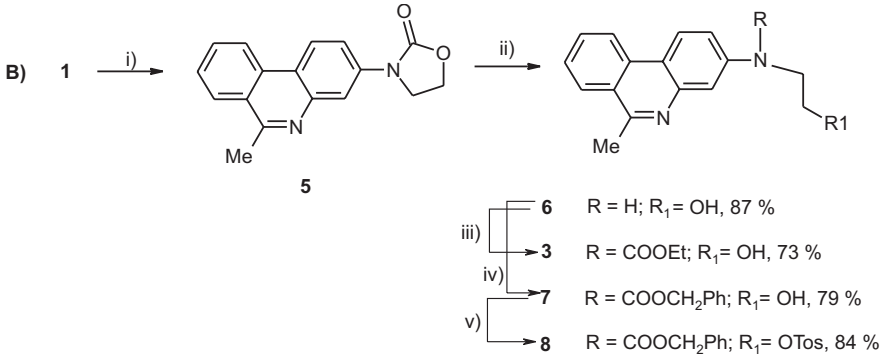
Here, we report on the synthesis of phenanthridine lariat ether derivatives **12**–**15** as potential fluorescent chemosensors for aromatic anions. Lariat ethers are well known as crown ether derivatives with appended flexible alkylether or alkylamino sidearms.[6] Such derivatives bind alkaline cations in the macrocyclic cavity with the participation of the side arm donors. Compounds **12**–**15** (Scheme 2) are constructed from *N*-(2-aminoethyl)-appended diaza- or monoaza-lariat ether as the metal cation recognition site and two fluorophoric phenanthridine units attached onto sidearm amino donors. The complexes that may be anticipated to form between, for example, **12** and an inorganic or organic non-aromatic (Figure 1, A) or an aromatic (Figure 1, B) alkaline metal salt are shown schematically in Figure 1. For the first case (A), only binding of a cation should affect the fluorescence properties of phenthridine units, mostly through the electronic effects including photoinduced electron transfer processes.[3] For the second case (B), however, in addition to the electronic effects of cation binding, the aromatic π-stacking interactions between phenanthridine units and aromatic anion may occur, which should result in quenching of phenanthridine fluorescence.[7] In other words, a different fluorescence response may be expected for the binding of an alkaline metal salt with inorganic or organic non-aromatic anion compared to an aromatic one by this type of lariat ethers. Thus, simultaneous fluorescent sensing of a cation and an aromatic anion may be expected to occur by such lariat molecules. In this paper, in addition to the synthesis of phenanthridine lariat ethers, we report on **12**- and **13**-Na- and K-picrate complexes and provide NMR evidence that the B type complex is formed between **12** and K- and Na-picrate.

Synthesis

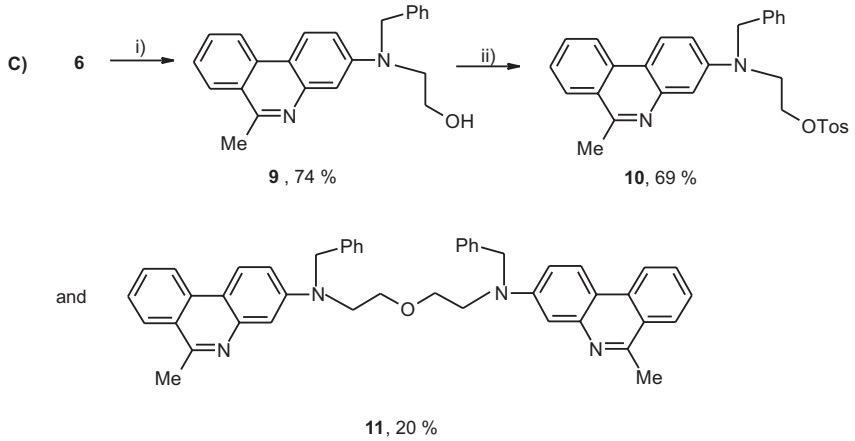
The synthesis of phenanthridine appended lariat ethers is based on preparation of phenanthridine 8-(2-tosylethyl)amino derivative suitable for *N*-alkylations of 4,13-diaza-18-crown-6 and aza-18-crown-6 (Schemes 1 and 2). In the first attempt, 8-(ethyloxycarbonylamino)-6-methylphenanthridine



i) $BrCH_2CH_2OTr$, K_2CO_2, CH_3CN, 40–50 °C; ii) 80% CH_3COOH, reflux;
iii) TosCl, Py, CH_2Cl_2, 0 °C



i) ethylene carbonate, NaOH, 130–140 °C; ii) 70 % H_2SO_4, 130–140 °C;
iii) EtOCOCl, H_2O, DMF, $CHCl_3$, rt.; iv) $PhCH_2OCOCl$, H_2O, DMF, $CHCl_3$, rt.;
v) TosCl, Py, CH_2Cl_2, 0 °C.



i) $PhCH_2Cl$, Na_2CO_3, EtOH, 70 °C; ii) TosCl, Py, CH_2Cl_2, 0 °C.

Scheme 1

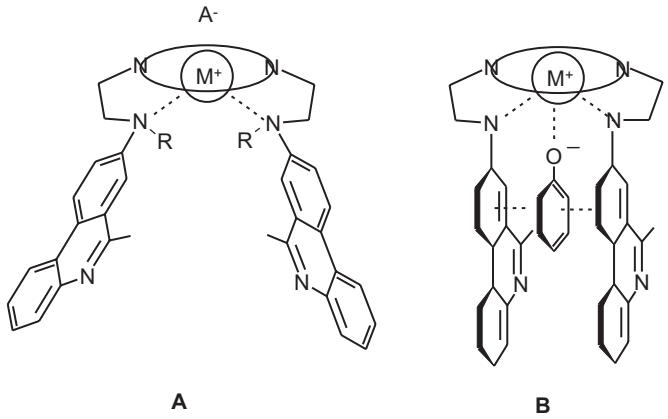
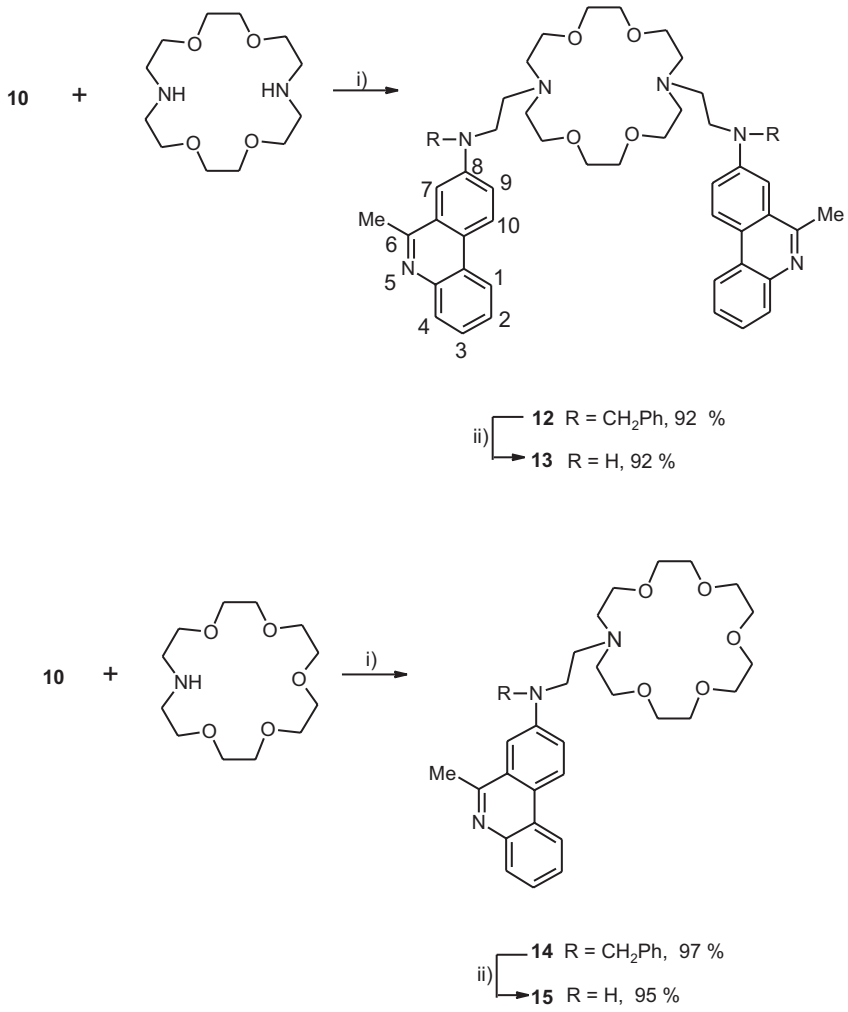


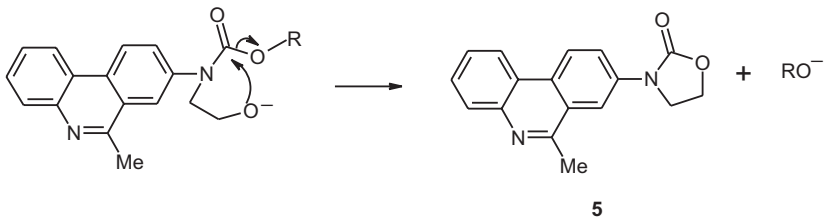
Figure 1. Schematic presentation of possible structures for complexes between **12** and an alkaline metal salt with non-aromatic (**A**) and aromatic (**B**) anion.

(**1**)[8] was treated with 1-bromo-2-trityloxyethane and K_2CO_3 at 40–50 °C in DMF. In the very slow reaction, compound **2** was formed in 68% yield after 10 days. Removal of the ethyloxycarbonyl protection group in acidic media gave **3**, which was then tosylated to **4.** In order to avoid very long reaction time needed for the preparation of **2**, we next examined the possibility of using ethylene carbonate in strongly basic conditions to introduce 2-hydroxyethyl fragment onto nitrogen of 8-(ethyloxycarbonyl)amino group of **1**. However, instead of 8-*N*-(2-hydroxyethyl) derivative, the 2-oxazolidinone derivative **5** was obtained in high yield (86%). The 2-oxazolidinone ring opening in acidic conditions gave 2-hydroxyethyl derivative **6**. Reprotection of phenanthridine 8-amino group using ethyl or benzyl chloroformate gave **3** and **7**, respectively, which upon tosylation gave the respective tosylates **4** and **8**. Both *N*-protected phenanthridine tosylates, **4** and **8**, have been used for *N*-alkylations of 4,13-diaza-18-crown-6, however in each case 2-oxazolidinone derivative **5** was obtained as the exclusive product together with unreacted diazacrown ether. Apparently, the presence of carbamate type of protection and 2-tosylethyl group on phenanthridine 8-nitrogen favours, in basic conditions, an intramolecular cyclization into 2-oxazolidinone derivative. The exact mechanism of this intramolecular transformation is not known at present. However, it seems plausible that formation of **5** from **1** and also from both **4** and **8** in basic conditions shares the same intermediate having on phenanthridine 8-amino the carbamate group and 2-ethyloxy anion. The intramolecular ethoxyd attack on carbamate carbonyl gives 2-oxazolidinone **5** (Scheme 3). To avoid formation of 2-oxazolidinone derivatives, the *N*-benzyl protected phenanthridine derivative **9** has been prepared. Tosylation of **9** gave **10** as major product (69%) together with dimmeric by-pro-



i) Na_2CO_3, CH_3CN, 60 °C, 4 days; ii) conc. HCl, 70% H_2SO_4,50 °C, 24 hours.

Scheme 2



Scheme 3

duct **11** (20%). The *N*-alkylations of diaza-18-crown-6 and aza-18-crown-6 using the phenanthridine derivative **10** proceeded smoothly, giving **12** and **14** in 92 and 97% yield, respectively. The *N*-deprotected bis(phenanthridine) and mono-phenanthridine lariat ethers **13** and **15** were obtained in high yields from **12** by acid treatment.

Formation of Na- and K-Picrate Complexes.

Extraction of Na- or K-picrate aqueous solution with dichloromethane solution of **12** or **13** and evaporation of organic solvent gave the respective complexes. However, lariat **14** having one phenanthridine unit failed to extract any picrate under the same conditions. Integration of picrate and phenanthridine resonances in the ^{1}H NMR spectra of the complexes gives in each case the 1:1 complex stoichiometry. Comparison of ^{1}H NMR spectra ($CDCl_3$) of free ligands with those of the complexes reveals considerable chemical shift differences for **12** (Figure 2), particularly in the region of phenanthridine protons, and only minor differences for **13**. The phenanthridine resonances in the spectra of free ligands as well as in those of their complexes have been unambiguously assigned from their 2D COSY maps. The fact that phenanthridines are substituted in position 8 allows identification of H7 resonance, appearing as the doublet with small *metha*-coupling of 1–2 Hz. Also the phenanthridine H1 and H10 doublets are identified on the basis of large *ortho*-couplings of 8.85–9.24 Hz. The assignation of the remaining phenanthridine resonances is then straightforward from 2D-COSY

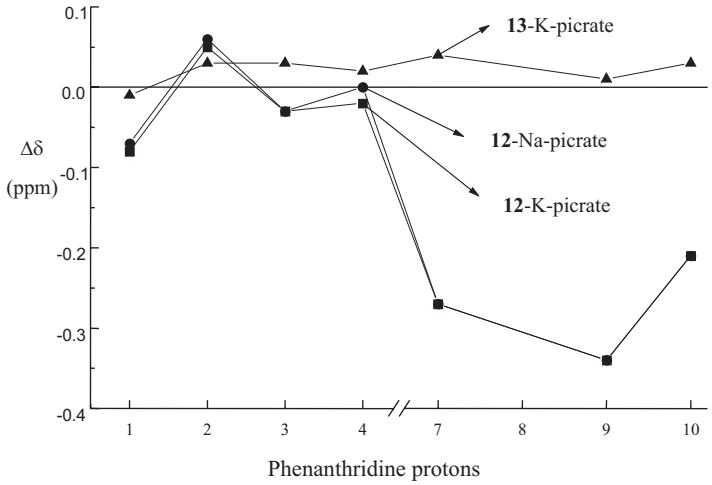


Figure 2. Graphical presentation of complexation induced shifts (CIS, δ/ppm) for phenanthridine protons in **12-** and **13-** Na- and K-picrate complexes.

maps. Thus achieved full assignation of all phenanthridine resonances in free ligands and in complexes allowed determination of the complexation induced shifts (CIS, $\Delta\delta_{H_i} = \delta_{H_i\ free} - \delta_{H_i\ compl.}$, in ppm) of phenanthridine protons (Figure 2). The CIS values are expected to gain valuable structural information on formed complexes. As shown in Figure 2 for Na- and K-picrate complexes of **12**, the phenanthridine H7, H9 and H10 protons are considerably shielded and therefore shifted upfield. In addition, the signal of picrate protons appears considerably more upfield in the spectra of **12**-Na- and **12**-K-picrate complexes (δ 8.07 and 8.04 ppm, respectively) compared to its position in the spectra of both diaza-18-crown-6-K-picrate and **13**-K-picrate complexes (δ 8.70 ppm). Thus, strong shielding of phenanthridine H7, H9, H10 and picrate protons in **12**-Na- and **12**-K-picrate complexes suggests mutual interaction between these π-systems. The ^{1}H NMR data for **12**-Na- or K-picrate complexes are in accord with the structure of C_2 symmetry in each case, due to the equivalence of picrate H3, H5 and the corresponding protons of both phenanthridine units. Therefore, in the complexes, the picrate anion must be intercalated between phenanthridine phenyl rings closest to ethylene spacers with phenanthridine units related by C_2 axes. Besides the upfield shifts of phenanthridine and picrate resonances, broadening of crown methylene resonances shows cation binding in the macrocycle cavity.

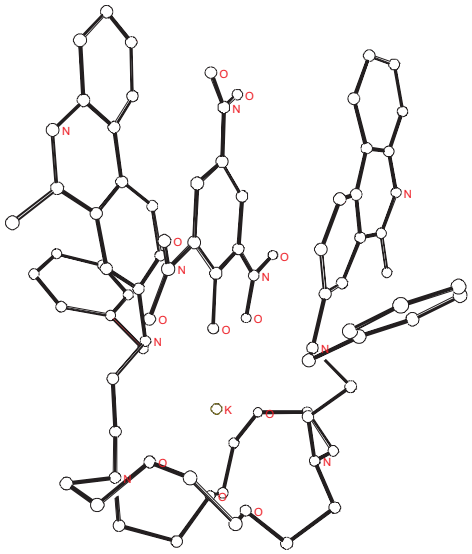


Figure 3. Minimized structure of **12**-K-picrate complex (SYBYL molecular modelling software of TRIPOS INC.). Hydrogens omitted for clarity. In calculations, K^+-O,N distance constrains from the x-ray structure of diaza-18-crown-6-K-picrate complex[6] were used. Onto minimized structure of **12**, the picrate anion was docked and the resulting low energy complex was minimized.

Remarkably, also the benzylic methylene protons are shifted upfield by 0.3 ppm and broadened while the signal of benzyl aromatic protons is split into two multiplets. Both latter observations suggest participation of phenanthridine *tertiary* 8-amino donors in binding of Na^+ or K^+ located in the diazacrown ring. This results in diminished conformational freedom of benzylic groups. The fully minimised structure of **12**-K-picrate complex in accordance to spectroscopic data is shown in Figure 3.

In contrast, the phenathridine protons in the spectra of **13**-Na- and K-picrate complexes are only slightly shifted downfield (Figure 2, CIS for **1**-K--picrate shown), apparently due to the absence of picrate-phenanthridine interactions. Neither shift changes nor splitting of benzylic CH_2 and aromatic protons could be found in the spectra of the complexes of **13**. Apparently, in **13**, the phenanthridine secondary 8-amino atoms are less efficient donors for the metal cation and they do not participate in cation binding.

In conclusion, we present spectroscopic evidence that the complexes between **12** and picrate salts possess the anticipated structure B (Figure 1). Therefore, the lariats of type **12** seem to be good candidates for the development of new fluorescent chemosensors for simultaneous sensing of aromatic anions and alkaline metal cations. The fluorescence studies aimed at evaluating their sensing potential are in progress.

EXPERIMENTAL

General

^1H and ^{13}C NMR spectra were recorded at 300 MHz on a Varian Gemini-300 instrument. Chemical shifts are expressed in ppm downfield from TMS as internal standard. *J* values are given in Hz. IR spectra (KBr or film) were recorded on the Perkin Elmer 297 spectrophotometer. TLC and column chromatography using Merck Kiselgel F_{254} plates and Kiselgel 0.005–0.02 mm were performed using solvent mixtures A: CH_2Cl_2 : MeOH = 9:1; B: CH_2Cl_2 : MeOH = 9.5:10.5 and C: CH_2Cl_2 : MeOH = 9.8: 0.2. Compounds 1-bromo-2-triphenylmethyloxyethane,[9] 6-chloromethylphenanthridine,[10] 4,13-diaza-18-crown-6[11] and 8-(ethyloxycarbonylamino)-6-methylphenanthridine (**1**)[8] have been prepared according to the literature procedures.

*8-*N*-(Ethyloxycarbonyl)-*N*-(2-triphenylmethyloxyethyl)amino-6--methyl-phenanthridine (**2**)*

1-Bromo-2-triphenylmethyloxyethane (1.18 g, 3.21 mmol) and K_2CO_3 (1.48 g, 10.70 mmol) were added to DMF (40 mL) solution of 8-(ethyloxycarbonyl)amino-6-methyl-phenanthridine (**1**) (0.30 g, 1.07 mmol) and the reaction mixture was heated at 40–50 °C under argon for 10 days. After 4 days, additional quantities of 1-bromo-2-triphenylmethyloxyethane (0.59 g, 1.60 mmol) and K_2CO_3 (0.74 g, 5.34 mmol) were added and the same was repeated with half quantities of both reactants after 7 days. After 10 days, the formed precipitate was filtered off and the solvent was evaporated under reduced pressure. The oily residue was dissolved in EtOAc (50 mL), washed

with water (50 mL) and dried over Na_2SO_4. The evaporation of the solvent and purification of oily residue by column chromatography using solvent mixture CH_2Cl_2 : EtOAc 9.5 : 0.5 for elution gave **2** (0.41 g; 68% yield): R_f 0.23 (B); m.p. 143–144 °C (recrystallized from CH_2Cl_2 / ether mixture); IR ν/cm^{-1}: 3060, 2920, 1700, 1610, 1570, 1530, 1480, 1380, 1340, 1290; ^{1}H NMR δ/ppm: 1.24 (t, 3H, J = 7.19, CH_3CH_2), 2.38 (s, 3H, Phen.–CH_3), 3.37 (t, 2H, J = 5.38, NCH_2), 4.20 (t, 2H, J = 5.38, OCH_2), 4.20 (q, 2H, J = 7.19, CH_2CH_3), 7.19 (m, 9H, Tryt.), 7.33 (m, 6H, Tryt.), 7.63 (m, 1H, Phen. H3), 7.72 (m, 1H, Phen.-H2), 7.74 (dd, 1H, J = 9.13, Phen.H9), 8.06 (d, 1H, J = 1.28, Phen.-H7), 8.11 (dd, 1H, J = 8.20 and 1.28, Phen.-H4), 8.51 (dd, 1H, J = 8.86 and 1.07, Phen.-H1), 8.54 (d, 1H, J = 9.13, Phen.H10); ^{13}C NMR δ/ppm: 14.50, 22.97, 40.40, 61.45, 61.45, 86.46, 121.50, 122.58, 122.92, 123.59, 125.85, 126.02, 128.11, 128.96, 129.57, 130,03, 141.14, 143.17, 155.01, 126.58, 127.32, 128.11, 143.34, 155.01. *Anal*. Calcd. for $C_{38}H_{34}N_2O_3$: C, 80.54, H, 6.05, N, 5.02; found: C, 80.62, H, 6.14, N, 5.02.

8-N-*(Ethyloxycarbonyl)*-N-*(2-hydroxyethyl)amino-6-methylphenanthridine (**3**)*

The solution of **2** (0.116 g, 0.21 mmol) in 80% acetic acid (5 mL) was heated under reflux for 0.5 hours. The oily residue obtained after removal of acetic acid under reduced pressure was purified by preparative TLC using solvent mixture B. Recristallization from ether gave **3** (57 mg, 86% yield): R_f 0.48 (A); m.p. 179–180 °C; IR ν/cm^{-1}: 3300, 2980, 1700, 1615, 1590, 1530, 1480, 1440, 1380, 1300; ^{1}H-NMR δ/ppm: 1.23 (t, 3H, J = 7.08, CH_3CH_2), 3.01 (s, 3H, Phen.-CH_3), 3.90 (t, 2H, J = 5.00, NCH_2), 3.99 (t, 2H, J = 5.00, CH_2OH), 4.21 (q, 2H, J = 7.08, CH_2CH_3), 7.63 (m, 1H, Phen.-H3), 7.71 (m, 1H, Phen.-H2), 7.76 (dd, 1H, J = 8.77, Phen.-H9), 8.12 (dd, 1H, J = 7.17 and 1.70, Phen.-H4), 8.13 (d, 1H, J = 2.01,Phen.-H7), 8.47 (dd, 1H, J = 8.08 and 1.90, Phen.-H1), 8.56 (d, 1H, J = 8.77, Phen.-H10); ^{13}C NMR δ/ppm: 14.29, 22.60, 53.01, 61.47, 62.00, 121.76, 122.97, 123.09, 123.90, 126.02, 126.48, 128.53, 128.60, 130.08, 130,58, 141.11, 142.80, 156.08, 158.31. *Anal*. Calcd. for $C_{19}H_{20}N_2O_3$: C, 70.35, H, 6.21, N, 8.64; found: C, 70.55, H, 6.41, N, 8.70.

8-N-*(Ethyloxycarbonyl)*-N-*(2-p-toluensulfonyloxyethyl)amino-6-methyl-phenanthridine (**4**)*

The solution of **3** (0.218 g, 0.67 mmol) in the mixture of CH_2Cl_2 (9.0 mL) and pyridine (2.0 mL) was added dropwise (2 hours) into the ice cooled solution of TosCl (0.27 g, 1.92 mmol) in pyridine (4 mL) under vigorous stirring and argon. After 48 hours at room temperature, water was added (25 mL) and the mixture was stirred for additional 0.5 hours. Dichloromethane layer was separated, aqueous layer was extracted with dichloromethane (10 mL) and combined extracts were dried with Na_2SO_4. Removal of solvent and purification by preparative TLC using solvent mixture C, gave **4** (0.24 g, 75% yield); R_f 0.30 (B); m.p. 56–58 °C (recristallized from MeOH); IR ν/cm^{-1}: 2980, 1710, 1580, 1490, 1360, 1300; ^{1}H NMR δ/ppm: 1.21 (t, 3H, J = 7.08, CH_3CH_2), 2.33 (s, 3H, Tos–CH_3), 2.99 (s, 3H, Phen.–CH_3), 4.05 (t, 2H, J = 5.00, NCH_2), 4.17 (q, 2H, J = 7.08, CH_2CH_3), 4.34 (t, 2H, J = 5.00, OCH_2), 7.18 (d, 2H, J = 8.08, Tos-H), 7.65 (d, 2H, J = 8.08, Tos-H), 7.66 (m, 1H, Phen.-H3), 7.70 (m, 1H, Phen.-H2), 7.73 (dd, 1H, J = 8.93, Phen.-H9), 8.06 (d, 1 H, J = 2.02, Phen.-H7), 8.11 (dd, 1 H, J = 8.14 and 1.28, Phen.-H4), 8.51 (dd, 1H, J = 8.08 and 1.71, Phen.-H1), 8.55 (d, 1 H, J = 8.93, Phen.-H10); ^{13}C NMR δ/ppm: 14.19, 21.26, 23.03, 49.78, 62.09, 67.31, 121.92, 123.24, 123.42, 124.27, 126.31, 126.56, 129.28, 129.34, 130.95, 140.80, 143.59, 144.94, 155.23, 127.67, 128.71, 128.79, 132.58, 158.54. *Anal*. Calcd. for $C_{26}H_{26}N_20_5S$: C, 65.25, H, 5.48, N, 5.85; found: C, 65.3, H, 5.73, N, 5.79.

*3-(6-Methylphenanthridine-8-yl)-2-oxazolidinone (**5**)*

Mixture of **1** (5.00 g, 17.84 mmol), ethylene carbonate (31.42 g, 0.36 mol) and NaOH (0.71 g, 17.84 mmol) was stirred at 140 °C under argon for 6 hours. After cooling to 90 °C, MeOH (25 mL) was added through reflux condenser and the mixture was heated under reflux for 15 min. Upon cooling to room temp., precipitation of unreacted **1** occurred. After removal of **1**, addition of water precipitated chromatographically pure **5** (4.30 g, 86% yield): R_f 0.22 (EtOAc); m.p. 229–230 °C (recrystallized from acetonitrile); IR ν/cm^{-1}: 1755, 1480, 1450, 1405, 1395, 1215, 1120, 1040, 770; ^{1}H NMR δ/ppm: 2.97 (s, 3H, Phen.-CH_3), 4.13 (t, 2H, J = 7.98, NCH_2), 4.54 (t, 2H, J = 7.98, OCH_2), 7.59 (m, 1 H, Phen.-H3), 7.67 (m, 1 H, Phen.-H2), 8.05 (dd, 1H, J = 8.20 and 1.37, Phen.-H4), 8.07 (d, 1H, J = 2.38, Phen.-H7), 8.10 (d, 1H, J = 9.78, Phen.-H9), 8.41 (dd, 1 H, J = 8.12 and 1.42, Phen.-H1), 8.51 (d, 1 H, J = 9.78, Phen.-H10); ^{13}C NMR δ/ppm: 23.42, 45.06, 61.37, 113.66, 121.17, 121.69, 123.28, 123.38, 126.12, 126.55, 128.31, 128.51, 129.29, 137.20, 143.19, 155.17, 158.18. *Anal*. Calcd. for $C_{17}H_{14}N_2O_2$: C, 73.36, H, 5.07, N, 10.07; found: C, 73.42, H, 5.27, N, 9.82.

*8-*N*-(2-Hydroxyethyl)amino-6-methylphenanthridine (**6**)*

The solution of **5** (2.98 g, 10.70 mmol) in 70% sulfuric acid was heated at 130–140 °C for 4 hours. To ice cooled reaction mixture, aqueous ammonia was added until pH 8 was reached. The formed yellow precipitate was collected and purified by column chromatography by elution with solvent mixture A. The product **6** (2.33 g, 86% yield) was recristallized from EtOH – ether mixture; R_f 0.23 (A); m.p. 172–173 °C; IR ν/cm^{-1}: 3300, 2980, 1620, 1570, 1550, 1460, 1390, 1355, 1300, 1260; ^{1}H NMR δ/ppm: 2.94 (s, 3H, Phen.-CH_3), 3.47 (t, 2H, J = 5.18, NCH_2), 3.98 (t, 2H, J = 5.18, OCH_2), 5.23 (br, 1 H, NH), 7.17 (d, 1 H, J = 2.20, Phen.-H7), 7.20 (dd, 1H, J = 8.77, Phen.-H9), 7.55 (m, 1 H, Phen.-H3), 7.58 (m, 1 H, Phen.-H2), 8.04 (dd, 1 H, J = 6.94 and 2.20, Phen.-H4), 8.38 (dd, 1 H, J = 6.59 and 2.25, Phen.-H1), 8.40 (d, 1 H, J = 8.77, Phen.-H10); ^{13}C NMR ($CDCl_3$ /: CD_3OD 1:1) δ/ppm: 21.69, 45.17, 59.79, 104.25; 119.95; 120.68, 123.00, 123.73, 124.12, 125.99, 126.31, 127.08, 127.42, 140.84, 147.62, 157.81. *Anal*. Calcd. for: $C_{16}H_{16}N_2O$: C, 76.16, H, 6.39, N, 11.10; found: C, 76.12, H, 6.48, N, 11.05.

*Conversion of **6** to **3***

Aqueous $NaHCO_3$ (0.504 g, 6.00 mmol) solution was added to the solution of **6** (0.252 g, 1.00 mmol) in the mixture of chloroform (30 mL) and DMF (5 mL) and to this mixture ethyl chloroformate (0.285 mL, 3.00 mmol) was added dropwise during 20 min. The reaction mixture was stirred for 17 hours at room temperature. Organic layer was separated and aqueous layer was extracted with chloroform(2×15 mL). Combined extracts were dried (Na_2SO_4), and the solvent was removed under reduced pressure. Purification of the residue by preparative TLC using the solvent mixture B gave **3** (0.236 g, 73% yield).

*8-*N*-(Benzyloxycarbonyl)-*N*-(2-hydroxyethyl)amino-6-methylphenanthridine (**7**)*

The solution of $NaHCO_3$ (0.400g, 4.76 mmol) in water (30 mL) was added to the solution of **6** (0.213 g, 0.85 mmol) in the mixture of THF (30 mL) and DMF (5 mL). To the cooled solution (bellow 0 °C), the 50% solution of benzyl chloroformate in toluene (0.85 mL, 2.53 mmol) was added during 30 min. under vigorous stirring. After additional 17 hours of stirring at room temperature, the organic layer was separated, the aqueous layer was extracted with ether (2×20 mL) and combined extracts

were dried (Na_2SO_4). Removal of solvent and purification by preparative TLC using solvent mixture B gave **7** (0.260 g, 79% yield); R_f 0.44 (A); m.p. 59–61 °C; IR ν/cm^{-1}: 3350, 1700, 1620, 1580, 1530, 1480, 1440, 1390, 1350, 1290; ^{1}H NMR δ/ppm: 2.92 (s, 3H, Phen.-CH_3), 3.89 (t, 2H, J = 5.00, NCH_2), 4.00 (t, 2H, J = 5.00, $HOCH_2$), 5.19 (s, 2H, Ph-CH_2), 7.27 (s, 5H, Ph-H), 7.61 (m, 1 H, Phen.-H3), 7.71 (m, 1 H, Phen.-H2), 7.74 (dd, 1 H, J = 8.87, Phen.-H9), 8.08 (d, 1H, J = 1.31, Phen.-H7), 8.08 (dd, 1H, J = 6.97 and 1.4, Phen.-H4), 8.45 (dd, 1H, J = 8.22 and 1.26, Phen.-H1), 8.54 (d, 1H, J = 8.87, Phen.-H10); ^{13}C NMR δ/ppm: 22.98, 53.26, 60.81, 67.63, 121.85, 123.13, 123.21, 124.21, 126.16, 126.50, 128.71, 129.02, 129.86; 130.84, 140.82, 143.31, 156.04, 127.68, 128.04, 128.38, 130.84, 158.29. *Anal*. Calcd. for $C_{24}H_{22}N_2O_3$: C, 74.59, H, 5.76, N, 7.25; found: C, 74.43, H, 5.67, N, 7.15.

8-N-*(Benzyloxycarbonyl)*-N-*(2*-p-*toluenesulfonyloxyethyl)amino-6-methyl-phenanthridine (**8**)*

The solution of **7** (0.190 g, 0.49 mmol) in the mixture of dichloromethane (18 mL) and pyridine (4 mL) was added to ice cooled solution of *p*-toluenesulfonylcloride (0.186 g, 0.98 mmol) in pyridine (4 mL) under vigorous stirring. After 48 hours of stirring at room temperature, water (25 mL) was added and stirred for additional 0.5 hours. Dichloromethane layer was separated and aqueous layer was extracted with 10 mL of the same solvent. Drying (Na_2SO_4) of the combined extracts, and removal of the solvent and purification of the residue by column chromatography using the solvent mixture C gave **9** (0.240 g; 84% yield); R_f 0.50 (B); m.p. 38–40 °C; IR ν/cm^{-1}: 2980, 1710, 1580, 1490, 1440, 1360, 1300, 1230, 1190, 1150; ^{1}H NMR δ/ppm: 2.33 (s, 3H, Tos-CH_3), 2.96 (s, 3H, Phen.-CH_3), 4.07 (t, 2H, J = 5.00, NCH_2), 4.34 (t, 2H, J = 5.00, OCH_2), 5.16 (s, 2H, Ph-CH_2), 7.18 (d, 2H, J = 8.07, Tos-H), 7.28 (s, 5H, Ph-H), 7.63 (d, 2H, J = 8.07, Ts-H), 7.67 (m, 1 H, Phen.-H3), 7.71 (m, 1 H, Phen.-H2), 7.74 (dd, 1H, J = 8.88, Phen.-H9), 8.07 (d, 1H, J = 1.84, Phen.-H7), 8.14 (dd, 1H, J = 8.14 and 1.28, Phen.-H4), 8.50 (dd, 1H, J = 7.93 and 1.30, Phen.-H1), 8.55 (d, 1 H, J = 8.88, Phen.-H10); ^{13}C NMR δ/ppm: 21.36, 22.66, 49.88, 64.38, 67.70, 121.88, 123.09, 123.30, 124.54, 125.98, 126.76, 128.50, 128.96, 130.20, 131.04, 140.50, 144.85, 154.85, 127.54, 127.66, 129.62, 132.37, 127.54, 128.08, 128.40, 130.20, 158.56. *Anal*. Calcd. for C_{31},$H_{28}N_2O_5$ S : C, 68.87, H, 5.22, N, 5.18; found: C, 68.63, H, 5.33, N, 5.15.

8-N-*(Benzyl)*-N-*(2-hydroxyethyl)amino-6-methylphenanthridine (**9**)*

Compound **6** (0.420 g, 1.66 mmol), Na_2CO_3 (0.530 g, 4.98 mmol) and benzylbromide (0.40 mL; 4.98 mmol) in dry ethanol (25 mL) were heated stirred at 70 °C for 20 hours. Ethanol was removed under reduced pressure, the residue was taken in EtOAc (25 mL) and extracted with water (50 mL). After removal of EtOAc, the oily residue was dissolved in conc. hydrochloric acid and extracted with ether to remove the unreacted benzylbromide. The water solution was made alkaline with 10% aqueous NaOH (pH 8–9) and extracted with EtOAc. After drying and removal of EtOAc, the oily residue was purified by column chromatography using the solvent mixture A for elution**.** Crystallization from CH_2Cl_2 – ether mixture gave **8** (0.42 g, 74%); R_f 0.44 (A); m.p. 166–167 °C; IR ν/cm^{-1}: 3400, 3240, 2920, 1620, 1590, 1540, I500, 1460, 1410, 1360; ^{1}H NMR δ/ppm: 2.41 (s, 3H, Phen.-CH_3), 3.75 (t, 2H, J = 5.30, NCH_2), 4.01 (t, 2H, J = 5.30, OCH_2), 4.34 (s, 2H, Ph-CH_2), 6.71 (d, 1 H, J = 2.60, Phen.-H7), 7.04 (d, 2H, J = 6.90, Ph-H), 7.21 (m, 3H, Ph-H), 7.28 (dd, 1H, J = 9.10, Phen.-H9), 7.54 (m, 1H, Phen.-H3), 7.57 (m, 1 H, Phen.-H2), 8.01 (dd, 1 H, J = 6.78 and 2.07,

Phen.-H4), 8.27 (d, 1 H, J = 9.10, Phen.-H10), 8.32 (dd, 1 H, J = 6.90 and 1.86, Phen.-H1); ^{13}C NMR δ/ppm: 22.72, 53.54, 54.86, 59.80, 106.16, 117.97, 120.93, 122.98, 123.27, 124.21, 126.20, 126.62, 127.13, 128.83, 141.73, 147.35, 158.25, 126.31, 127.00, 128.68, 137.78. *Anal*. Calcd. for $C_{23}H_{22}N_2O$: C, 80.67, H, 6.48, N, 8.18; found: C, 80.75, H, 6.66, N 8.11.

8-N-*(Benzyl)*-N-*(2*-p-*toluenesulfonyloxyethyl)-6-methylphenanthridine (**10**)*

By the same procedure as described for preparation of **9**, the tosyl derivative **10** (0.480 g, 68% yield) was obtained from **8** (0.490 g; 1.42 mmol) and *p*-toluenesulfonylcloride (0.540 g, 2.84 mmol). The crude product was purified column chromatography by using the solvent mixture B for elution. Crystallization from dichloroethane – ether mixture gave pure **10,** yellow crystals; R_f 0.34 (B); m.p. 139–140 °C; IR ν/cm^{-1}: 2920, 1610, 1570, 1530, 1480, 1450, 1400, 1380, 1360, 1300; ^{1}H NMR δ/ppm: 2.23 (s, 3H, TosCH_3), 2.81 (s, 3H, Phen.-CH_3), 3.91 (t, 2H, J = 5.85, NCH_2), 4.32 (t, 2H, J = 5.85, OCH_2), 4.67 (s, 2H, Ph-CH_2), 7.14 (d, 2H, J = 8.18, Tos-H), 7.17 (d, 1 H, J = 2.25, Phen.-H7), 7.25–7.31 (m, 5H, Ph-H), 7.31 (dd, 1H, J = 9.05, Phen.-H9), 7.58 (m, 1H, Phen.-H3), 7.58 (m, 1H, Phen.-H2), 7.67 (d, 2H, J = 8.18, Tos-H), 8.02 (dd, 1H, J = 7.48 and 1.80, Phen.-H4), 8.34 (dd, 1H, J = 7.02 and 2.09, Phen.-H1), 8.35 (d, 1H, J = 9.05, Phen.-H10); ^{13}C NMR δ/ppm: 21.21, 23.14, 49.91, 54.99, 66.38, 106.69, 117.82, 120.92, 123.60, 123.79, 123.94, 126.22, 126.89, 127.21, 129.15, 142.25, 146.59, 157.98, 127.72, 129.68, 132.51, 145.00, 126.48, 127.32, 128.83, 137.37. *Anal*. Calcd. for $C_{23}H_{22}N_20$: C, 72.56, H, 5.68, N, 5.64; found: C, 72.50, H, 5.61, N, 5.50. From the filtrate after crystallization of **10**, a dimmerization product **11** was isolated by preparative TLC using solvent mixture C. **11** (0.090 g, 20% yield); R_f 0.36 (B); m.p. 146–147 °C; IR ν/cm^{-1}: 2920,1620, 1580, 1540, 1490, 1470, 1450, 1400, 1370, 1360; ^{1}H NMR δ/ppm: 2.84 (s, 6H, Phen.-CH_3), 3.76 (t, 4H, J = 7.12, NCH_2), 2.96 (t, 4H, J = 7.12, OCH_2), 4.76 (s, 4H, Ph-CH_2), 7.25 (d, 2H, J = 1.77, Phen.-H7), 7.28–7.33 (m, l0H, Ph-H), 7.31 (dd, 1H, J = 9.10, Phen.-H9), 7.52 (m, 2H, Phen.-H3), 7.57 (m, 2H, Phen.-H2), 8.02 (dd, 1H, J = 6.68 and 1.67, Phen.-H4), 8.35 (dd, 1H, J = 6.49 and 1.80, Phen.-H1), 8.41 (d, 1H, J = 9.10, Phen.-H10); ^{13}C NMR δ/ppm: 23.01, 40.27, 53.29, 59.09, 106.59, 117.76, 120.94, 123.76, 123.84, 123.98, 126.24, 126.89, 127.35, 128.99, 142.06, 146.58, 157.98, 126.45, 127.29, 128.85, 137.56.

*7,16-bis{2-[*N-*Benzyl*-N-*(6-methylphenanthridine-8-yl)]aminoethyl}-7,16-diaza1,4,10,13-tetraoxacyclooctadecane (**12**)*

To the solution of 7,16-diaza-18-crown-6 (55 mg, 0.21 mmol) in acetonitrile (15 mL), Na_2CO_3 (66, mg; 0.62 mmol) and **10** (228 mg, 0.46 mmol) were added and the reaction mixture was stirred under argon at 60 °C for 4 days. The precipitate was filtered off and the solvent evaporated under reduced pressure. The oily residue was taken in dichloromethane (20 mL) and washed with water. Drying and evaporation of the solvent gave crude **12.** Purification by column chromatography on silica gel (solvent mixture A; R_f 0.30) gave **12**, 167 mg, (91.6%), m.p. 50–52 °C; IR ν/cm^{-1}: 3080, 2920, 2860, 1615, 1575, 1580, 1490, 1470, 1450, 1400, 1350, 1300, 1220, 1110, 1070, 1030; ^{1}H NMR δ/ppm: 2.84 (s, 6H, Phen.-CH_3), 2.86 (t, 8H, J = 5.04, NCH_2CH_2O), 2.86 (t, 4H, J = 6.20, NCH_2), 3.59 (s, 8H, OCH_2CH_2O), 3.62 (t, 8H, J = 5.04, CH_2O), 3.71 (t, 4H, J = 6.20, Phen.-NCH_2), 4.71 (s, 4H, PhCH_2), 7.21–7.30 (m, 10H, Ph), 7.22 (d, 2H, J = 1.58, Phen.-H7), 7.30 (dd, 2H, J = 9.24, Phen.-H9), 7.50 (m, 2H, Phen.- H2), 7.54 (m, 2H, Phen.-H3), 8.00 (dd, 2H, J = 7.32, J = 1.90, Phen.-H4), 8.32 (dd, 2H, J = 7.08 and J = 1.66, Phen.-H1), 8.38 (d, 2H, J = 9.24,

Phen.-H10); ^{13}C NMR δ/ppm: 23.20, 50.11, 52.46, 54.50, 55.01, 70.00, 70.67, 105.83, 117.66, 120.83, 123.03, 123.56, 124.18, 126.10, 126.51, 127.44, 129.08, 142.07, 147.35, 157.97, 126.51, 127.10, 128.72, 138.21. *Anal*. Calcd. for $C_{58}H_{66}N_6O_4$: C, 76.45, H, 7.30 N, 9.22; found: C, 76.38 H, 7.24 N, 9.08.

*7,16-Bis{2-[*N*-(6-Methylphenanthridine-8-yl)]aminoethyl}-7,16-diaza-1,4,10,13-tetraoxacyclooctadecane (**13**)*

The solution of **12** (100 mg, 0.11 mmol) in the mixture of concentrated hydrochloric acid (5 mL) and 70% sulfuric acid (1 mL) was stirred at 50 °C for 24 hours. The cooled solution was diluted with water (5 mL) and extracted with ether (30 mL) to remove benzyl chloride. The aqueous layer was made alkaline (pH 8–9) by addition of conc. ammonia and extracted with CH_2Cl_2 (30 mL). After drying and evaporation of the solvent, the oily residue was obtained. The preparative tlc by using the solvent mixture A gave **13** (82 mg, 92%); R_f 0.30; m.p. 57–59 °C; IR ν/cm^{-1}: 3260, 2980, 1615, 1570, 1540, 1490, 1470, 1460, 1440, 1400 , 1360, 1300, 1260, 1230, 12I0, 1130, 1100, 1060; ^{1}H NMR δ/ppm: 2.92 (s, 6H, Phen.-CH3), 2.83 (t, 8H, J = 5.36 Hz, N-CH_2CH_2-O), 2.83 (t, 4H, J = 5.03 Hz, N-CH_2), 3.21 (t, 4H, J = 5.03 Hz, Phen.-NCH_2), 3.65 (m, 16H, CH_2-O), 5.22 (br, 2H, NH) 7.09 (d, 2H, J = 2.21, Phen.-H7), 7.21 (dd, 2H, J = 8.85, Phen.-H9), 7.49 (m, 2H, Phen.-H3), 7.54 (m, 2H, Phen.-H2), 8.02 (dd, 2H, J = 7.80, and 1.38, Phen.-H4), 8.31 (dd, 2H, J = 7.43 and 1.96, Phen.-H1), 8.33 (d, 2H, Phen.-H10); ^{13}C NMR δ/ppm: 23.20, 41.10, 53.37, 54.14, 69.70, 70.51, 104.71, 119.91, 120.77, 123.15, 123.76, 124.31, 125.91, 126.33, 127.51, 128.96, 141.98, 147.86, 157.79. *Anal*. Calcd. for $C_{44}H_{54}N_6O_4$: C, 72.30 H, 7.45, N, 11.50; found: C, 72.39, H, 7.61, N, 11.31.

*16-{2-[*N*-Benzyl-*N*-(6-Methylphenanthridine-8-yl)]aminoethyl}-16-aza-1,4,7,10,13-pentaoxacyclooctadecane (**14**)*

Using the experimental procedure as described for preparation of **12**, 16-aza-18-crown-6 (0.190 g, 0.72 mmol), Na_2CO_3 (0.270 g, 2.58 mmol) and **10** (0.430 g, 0.86 mmol) in acetonitrile (15 mL) gave **14**, oil, (0.410 g, 96.9%) after column chromatography on silica gel (solvent mixture A; R_f 0.16); IR ν/cm^{-1}: 3060, 3030, 2900, 1620, 1570, 1535, 1475, 1450, 1400, 1350, 1225, 1120, 1030; ^{1}H NMR δ/ppm: 2.84 (s, 3H, Phen.-CH3), 2.87 (t, 4H, J = 5.87, N-CH_2CH_2-O), 2.91 (t, 2H, J = 7.09, N-CH_2CH_2 N), 3.66 (m, 20H, O-CH_2), 3.74 (t, 2H, J = 7.09, Phen.-N-CH_2), 4.71 (s, 2H, Ph-CH_2), 7.26–7.30 (m, 5H, Ph), 7.23 (d, 1H, J = 2.40, Phen.-H7), 7.33 (dd, 1 H, J = 9.24, Phen.-H9), 7.52 (m,1 H, F-H2), 7.54 (m, 1 H, Phen.H-3), 8.00 (dd, 1H, J = 6.81, and J = 2.40, Phen.-H4), 8.33 (dd, 1 H, J = 6.93 and J = 2.25, Phen.-H1), 8.40 (d, 1 H, J = 9.24, Phen-H 10); ^{13}C NMR δ/ppm: 23.14, 50.05, 52.56, 54.49, 54.91, 69.87, 70.18, 70.49, 70.53, 70.69, 105.70, 117.59, 120.75, 122.84, 123.44, 124.13, 125.97, 126.36, 127.65, 129.00, 141.99, 147.31, 157.92 126.42, 126.96, 128.62, 138.21. *Anal*. Calcd. for $C_{35}H_{45}N_3O_5$: C, 71.52 H, 7.72 N, 7.15; found: C, 71.74 H, 7.46 N, 7.22.

*16-[2-*N*-(6-Methylphenanthridine-8-yl)aminoethyl]-16-aza-1,4,7,10,13-pentaoxacyclooctadecane (**15**)*

As described for **13**, from **14** (88 mg, 0.15 mmol), conc. hydrochloric acid (7 mL) and 70% sulfuric acid (1 mL) **15** (71 mg, 95%, yellow oil) was obtained after preparative tlc (CH_2Cl_2/MeOH 8:2; R_f 0.12); IR ν/cm^{-1}: 3340, 3060, 2920, 2860, 1620, 1580, 1540, 1500, 1470, 1440, 1395, 1355, 1300, 1260, 1210, 1140; ^{1}H NMR δ/ppm: 2.83 (t, 4H, J = 5.08, N-CH_ZCH_Z-O), 2.90 (t, 2H, J = 4.96, NCH_2), 2.96 (s, 3H, Phen.-CH3),

3.66 (m, 20H, CH_2-O), 5.29 (br, 1H, NH) 7.14 (d, 1H, J = 1.44 Hz, Phen.-H7), 7.29 (dd, 1H, J = 8.85, Phen.-H9), 7.53 (m, 1H, Phen.-H3), 7.57 (m, 1H, Phen.-H2), 8.02 (dd, 1 H, J = 7.62, and J = 1.38, Phen.-H4), 8.39 (dd, 1 H, J = 8.85 and J = 1.96, Phen.-H1), 8.39 (d, 1H, J = 8.85, F-H10). ^{13}C NMR δ/ppm: 23.33, 41.26, 53.40, 54.18, 69.64, 70.12, 70.52, 70.65, 70.77, 104.72, 112.29, 120.88, 123.22, 123.88, 124.46, 125.97, 126.39, 127.65, 129.08; 142.10, 148.12, 157.95. *Anal*. Calcd. for $C_{44}H_{54}N_6O_4$: C, 67.58 H, 7.90 N, 8.44; found: C, 67.41 H, 7.79 N, 8.40.

*Complexation of Na- and K-picrates by **12** and **13***

The dichloromethane solutions of **12** or **13** containing approximately 10 mg of each compound in 5 mL of the solvent were vigorously shaken with conc. aqueous solutions (5 mL) of each M-picrate for 30 min. After standing for one hour, the organic layer was separated and the solvent was removed under reduced pressure. The solid residue was taken in $CDCl_3$ and ^{1}H NMR spectrum δ/ppm was recorded: **12-K-picrate**: 2.75 (s, 6H, Phen.-CH_3), 2.78 (m, 8H, CH_2NCH_2), 2.78 (m, 4H, $(CH_2)_2$ N-CH_2, 3.61 (m, 8H, CH_2-O and 4H, Phen.-N-CH_2), 3.73 (s, 8H, OCH_2CH_2-O), 4.37 (s, 4H, Ph-CH_2), 7.04 (d, 4H, J = 6.67, Ph-H), 7.15 (m, 6H, Ph-H), 6.95 (s, 2H, Phen.-H7), 6.96 (d, 2H, J = 8.90, Phen.-H9), 7.55 (m, 2H, Phen.-H2), 7.51 (m, 2H, Phen.-H3), 7.98 (d, 2H, J = 7·62, Phen.-H4), 8.07 (s, 2H, picrate-H) 8.17 (d, 2H, J = 8.90, Phen.-H10), 8.24 (d, 2H, J = 7.50, Phen.-H1); **12-Na-picrate**: 2.76 (s, 6H, Phen.- CH3), 2.78 (m, 8H, CH_2NCH_2 and 4H, $(CH_2)_2$ N-CH_2, 3.62 (m, 8H, CH_2-O and 4H, Phen.-N-CH_2), 3.74 (s, 8H, O-CH_2CH_2-O), 4.38 (s, 4H, Ph-CH2), 7.04 (d, 4H, J = 6.83, Ph-H), 7.18 (m, 6H, Ph-H), 6.95 (s, 2H, Phen.-H7), 6.96 (d, 2H, J = 9.08, Phen.-H9), 7.51 (m, 2H, Phen.-H3), 7.56 (m, 2H, Phen-H2), 8.00 (d, 2H, J = 7.38, Phen.-H4), 8.03 (s, 2H, Picrate-H.) 8.17 (d, 2H, Phen.-H10), 8.24 (d, 2H, J = 7.38, Phen.-H l); **13-K-picrate**: 2.67 (m, 8H, CH_2NCH_2), 2.78 (t, 4H, J = 4.23, $(CH_2)_2$ N-CH_2, 2.91 (s, 6H, Phen.-CH_3), 3.30 (t, 4H, J = 4.23 Hz, Phen.-N-CH2), 3.54- 3.62 (m, 16H, CH_2-O), 4.91 (br, 2H, NH) 7.06 (s, 2H, Phen.-H7), 7.21 (d, 2H, J = 8.49, Phen.-H9), 7.52 (m, 2H, Phen.-H3), 7.57 (m, 2H, Phen.-H2), 8.01 (d, 2H, J = 7.79, Phen.-H4), 8.31 (d, 2H, J = 7.70, Phen.-H l), 8.30 (d, 2H, Phen.-H10), 8.71 (s, 2H, picrate-H).

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SAŽETAK

Lariat-eteri s fenantridinskim jedinicama. Sinteza i kompleksiranje Na- i K-pikrata.

Sulejman Alihodžić i Mladen Žinić

Sintetizirani su lariat-eteri **12** i **13** s fenantridinskim jedinicama kao potencijalni fluorescentni kemosenzori za alkalijske soli kiselih aromatskih spojeva. Polazni 8-etiloksikarbonilamino-6-metilfenantridin preveden je preko intermedijara **2**, **3**, **6** i **7** u *N*-(2-tosiletil)-derivate **4** i **8** pogodne za *N*-alkilaciju diaza- i monoaza-18-krune-6. Pokušaji *N*-alkilacije dali su 2-oksazolidinon **5** umjesto očekivanog produkta. Spoj **5** nastaje intramolekulskom ciklizacijom fenantridinskih karbamata **4** i **8** u baznim uvjetima. Fenantridinski derivat **10** s benzilnom umjesto karbamatne zaštite na amino-skupini u položaju 8 uspješno je primijenjen za *N*-alkilaciju mono- i diaza-krunastih etera. Na taj su način sintetizirani lariat-eteri **12** i **14** koji skidanjem zaštitne benzilne skupine daju lariate **13** i **15**. Lariat **12** tvori komplekse s Na- i K-pikratom u kojima je kation vezan u krunastom eteru a pikratni anion interkaliran izmedu fenantridinskih jedinica.