

## NEWS

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A. Tukibayeva <sup>1</sup>, Ł. Tabisz <sup>2</sup>, B. Łęska <sup>2</sup>, N. Abylkasymov <sup>2</sup>, S. Saparbayeva <sup>3</sup><sup>1</sup>M. Auezov South Kazakhstan state university, Shymkent, Kazakhstan;<sup>2</sup>Adam Mickiewicz University in Poznan, Poland;<sup>3</sup>Academic Innovation University, *Shymkent, Kazakhstan***RESEARCH OF SYNTHESIS OF NOVEL DIPODAL SYSTEMS  
CONTAINING CONJUGATED PYRIDINIUM – IMINE MOTIFS**

**Abstract.** In this paper the results of the investigation of **novel dipodal systems containing conjugated pyridinium – imine motifs are given.** Comparison of the 3-dimensional structure and <sup>1</sup>H NMR spectra of organosilicon (podand 1) and purely organic (podand 2) dipodal bromide salts derived from 3-pyridinecarboxaldehyde and quaternized using benzyl bromide are given. The results of NMR spectroscopic and ESI-MS analysis confirm the composition and portion of target compounds.

Despite this fact, characterization by means of NMR techniques was impossible due to the multitude of signals present. In all cases, although siloxane dipodands were found to be somewhat more susceptible to degradation, they offer a wider assortment of compatible solvents and have better solubilities overall. All compounds are potent allergens and should be handled with gloves.

**Key words:** supramolecular chemistry, podands, complexes, **dipodal system**, NMR measurements.

**Introduction**

Both the fields of supramolecular chemistry and hybrid material science are relatively young disciplines, or rather unexplored until a few decades ago, but now a field of fierce competition and breaking ground for scientific novelty with new approaches and discoveries being published every week in some of the best international journals. Navigating each of those subjects requires vast interdisciplinary knowledge base, qualified staff and specific equipment.

Supramolecular science has become one of the more prominent research fields in the last few decades [1-3]. Partially due to the broad spectrum of problems that can be explained, or at least discussed from a supramolecular point of view, and partially because of the apparent shift of interest towards green processes, biocompatibility and the important subject of biomimetics [4], the chemistry of non-covalent interactions is now regarded as significant as the classical chemistry of the covalent bond.

Podands are a family of molecular receptors from the latter side of that spectrum; they encompass the simple ethylenediamine bidendate ligand as well as diethylene triamine pentaacetic acid. Lacking a rigid structure of a macrocycle, they cannot discriminate between guests of different sizes to such extent as crown ethers; synthetically they are however less demanding and offer the possibility of a non-symmetrical design [5]. As the prerequisite for industrial implementation is economic viability, the search for effective, but simple podand receptors for macro-scale applications proceeds in parallel to the development of somewhat more sophisticated systems designed for more specialized uses.

One way to force preorganization in a podal host is to introduce bulky substituents and double- or triple-bonded fragments in its structure, which hinder the rotation of podand's arms [6-8]. Alternatively,

because of their relative simplicity and flexibility, podal hosts can form supramolecular architectures of higher order, in some cases even non-covalently bound cage-like structures that form complexes with guests in a concerted manner [9-11]. The third possibility is to combine a flexible organic ligand with a highly rigid matrix. This can be either an organic, cross-linked polymer [12,13], metal sheets and particles [14,15] or an inorganic, porous material, such as zeolite [16], carbon [17] or silica [18,19]. These two interdisciplinary fields - supramolecular and material sciences - are being actively employed in creating new receptor-functionalized hybrid materials, usable in sensing and solid-phase extraction.

Anions are presented in many biological processes and chemicals, medicine and environmental protection. Receptors anionic molecules can be positively charged or neutral molecules capable of binding anion. There are two main groups of synthetic receptor anionic receptors: the positively charged, and that bind anions through electrostatic interaction of the ammonium groups or guanidine (also can bind via hydrogen bonding) and receptors electrically neutral, that bind anions, mainly by hydrogen bonding, the donor can be an amide group, urea, thiourea and the -NH group of the pyrrole ring. Binding different anions commonly used bio- and chemosensors usually accompanied by a change of color or fluorescence of the analyte at milimolar to nanomolar concentrations. To develop a strategy for the synthesis of molecular receptors capable of binding anions is not an easy task, but allows to obtain molecular receptor molecules with specific characteristics and abilities (ie. the host molecules) to selectively recognize molecules complexed (ie. guests). Most of supramolecular chemistry research is focusing on the development of bio- or chemosensors. The novelty anionic receptors that play an important role in increasing the dissociation of the lithium salt in high-voltage, high-energy lithium ion batteries or anionic receptors used as additives in the electrolyte solvents such as dimethyl carbonate (DMC) and propylene carbonate (PC), solubilizing agents, lithium fluoride or lithium oxide ( $\text{Li}_2\text{O}$ ,  $\text{Li}_2\text{O}_2$ ) and help maintain the stable solid electrolytic interface on the electrode surfaces [20]. The structure of synthesized experiment quaternary salts can distinguish specific binding  $\text{CH} = \text{N}^-$ .

Containing compounds, azomethine ( $-\text{CH} = \text{N}-$ ), known as Schiff bases, they are prepared by condensing the primary amine with a carbonyl compound. They were first described by Hugo Schiff [21] in 1864, and from the name which later adopted the name. These compounds are colored yellow, orange or red, generally easy to obtain in the crystalline form.

The general formula is as follows:  $\text{R}_3\text{R}_2\text{C} = \text{NR}_1$ , wherein the substituents  $\text{R}_2$  and  $\text{R}_3$  may be alkyl, aryl, heterocyclic, hydrogen or a metal (typically silicon, aluminum, boron or tin) [21]. The Schiff bases derived from aliphatic carbonyl compounds are relatively unstable and easily polymerized, and Schiff bases synthesized from aromatic carbonyl compounds are more stable because of having a conjugated double bond system. Due to the existence of free electron pair orbital, azomethine nitrogen atom of  $\text{sp}^2$  hybridized, these compounds have a particularly important chemical and biological properties [22]. The N-substituted imine is one of the most common ligand coordination chemistry. Di-, tri- or tetra-macrocyclic ligands of the structure or chain capable of forming highly stable complexes with transition metals are used as chiral catalysts for organic reactions, ie. Asymmetric synthesis or oxidation reactions or polymerization also have interesting magnetic properties. [23-25] The metal complexes of Schiff bases are an important class of compounds in the field of medicine and pharmacy due to the broad spectrum of biological activity, including antibacterial, herbicides, anti-fungal and anti-tumor effect [26]. Have a wide range of applications in the preparation of consumer identification, detection and determination of aldehydes and ketones, purification and amino carbonyl groups and protection of the complex and sensitive reactions. They also represent the fundamental units of certain dyes [23].

Quaternary pyridinium salts and their derivatives are an important and thoroughly researched group of products of the chemical industry. The possibility to generate the desired physical and chemical properties of a molecule by attaching a suitable substituent is used on both laboratory and industrial scale. This work discusses the characteristics of a few novel potential anion receptors, in dependence on their structure. For this purpose a synthetic strategy for the quaternization of pyridines-Schiff bases with alkyl halides was developed. Spectral analyses were performed, and the changes in respective chemical shifts of the signals between substrates and obtained products as well as between the products with different substituents were characterized.

In previously works we have established that a novel siloxane dipodand, *1,3-bis-(3-guanidylpropyl)-tetramethyldisiloxane*, can be effectively used to precipitate nitrate ions from aqueous solutions. The

obtained salt has remarkably different properties from the original hydrochloride, which suggests a supramolecular arrangement of the ions into a larger aggregate than derived from simple stoichiometric formula [27-28]. In adherence to the original plan, we have decided to focus on similar compounds in the project's second year, and establish whether these properties are shared by dipodands with and without siloxane backbone, and more elaborate functional arms, originating from biogenic compounds (e.g. amino acids) [29-31].

## Experimental

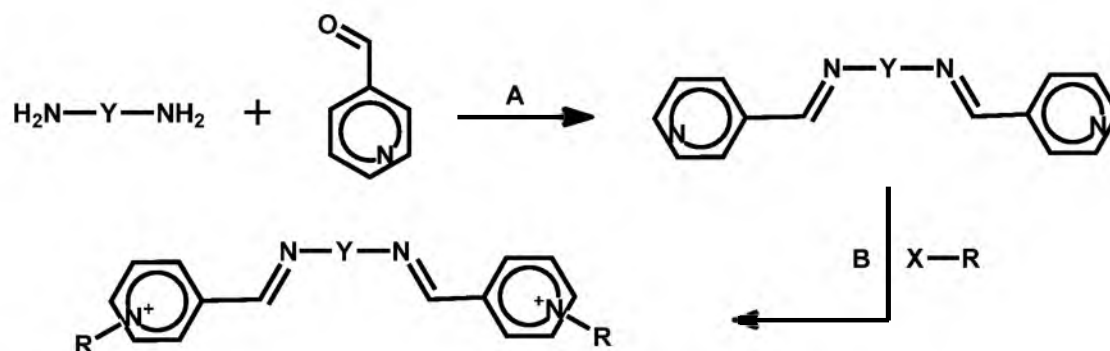
A. In a 10 mL reactor vessel 5 mmol of diamine, 3 mL of anhydrous ethanol and 10 mmol of freshly distilled pyridinecarboxaldehyde are mixed and stirred until one homogenous layer forms (this step is fairly exothermic). The vessel is then irradiated in a microwave reactor (CEM Discover®) using a three-step programme to avoid overheating: 50°C, 30 s; 75°C, 30 s; 100°C, 10 min (for disiloxane diamine) or 15 min (for hexamethylenediamine). Afterwards the solution is poured into a 25 mL round-bottom flask and evaporated under reduced pressure to a constant mass; the liquid solidifies on repeated cooling and warming to an off-white solid. It can be recrystallized (large, white needles) from petroleum ether (temperatures of around -25°C are needed to obtain higher yields).

B. In a 10 mL round-bottom flask 0.5 mmol of bis-pyridine Schiff base and 1 mmol of halide are dissolved in 2.5 mL of dried THF. The flask is filled with argon, sealed and stored at room temperature and in darkness. After 1-2 days, when the amount of precipitate or residue stops to accumulate, the product is either quickly filtered (powder), washed with diethyl ether twice and immediately returned to the flask, or the remaining THF is decanted and the residue is washed in the flask (using an ultrasonic bath) with diethyl ether twice. Afterwards the product is evaporated under reduced pressure and lyophilized, if needed, to constant mass. In some cases, a fair amount of product can be obtained from supernatant after mixing with diethyl ether.

**NMR measurements.** The NMR spectra were recorded in CD<sub>3</sub>CN using a Varian Gemini 300 MHz spectrometer. All spectra were locked to deuterium resonance of CD<sub>3</sub>CN. The error in parts per million values was 0.01. All <sup>1</sup>H NMR measurements were carried out at the operating frequency 600 MHz; T ¼ 293.0 K and TMS as the internal standard. No window function or zero filling was used. Digital resolution was 0.2 Hz/point. <sup>13</sup>C NMR spectra were recorded at the operating frequency 75.454 MHz; pw ¼ 608; sw ¼ 19,000 Hz; at ¼ 1.8 s; d1 ¼ 1.0 s; T ¼ 293.0 K and TMS as the internal standard. Line broadening parameters were 0.5 or 1 Hz.

## Results and discussion

We received 16 new compounds, according to Scheme 1 (and Table 1)



Scheme 1 - General scheme of synthesis

A – EtOH 1mL/mmol, MW, 100C, 10-15min

B – THF 1.5mL/mmol, RT, 1-2 days

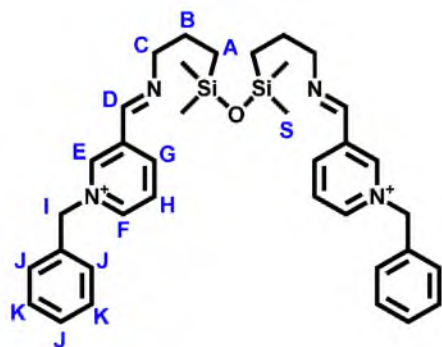
Table 1 – Characteristics of synthesized compounds

Y	Compound			Yield	Stability	Form	Color
	Pyridine isomer	X	R				
1	2	3	4	5	6	7	8
-(CH <sub>2</sub> ) <sub>6</sub> -	3	I	-CH <sub>3</sub>	85%	H	powder	yellow
-(CH <sub>2</sub> ) <sub>6</sub> -	3	Br	-Bn	73%	M	waxy solid	light brown
-(CH <sub>2</sub> ) <sub>6</sub> -	3	Br	-AcOMe	~30%, P	-	-	*dark orange
-(CH <sub>2</sub> ) <sub>6</sub> -	3	Br	-Bzh	-	-	-	-
-(CH <sub>2</sub> ) <sub>6</sub> -	4	I	-CH <sub>3</sub>	87%	M	powder	bright yellow
-(CH <sub>2</sub> ) <sub>6</sub> -	4	Br	-Bn	65%	L	low-melting solid	brown
-(CH <sub>2</sub> ) <sub>6</sub> -	4	Br	-AcOMe	P	-	-	*dark red
-(CH <sub>2</sub> ) <sub>6</sub> -	4	Br	-Bzh	P	-	-	*red
-(CH <sub>2</sub> ) <sub>3</sub> -Si(CH <sub>3</sub> ) <sub>2</sub> -O-Si(CH <sub>3</sub> ) <sub>2</sub> -(CH <sub>2</sub> ) <sub>3</sub> -	3	I	-CH <sub>3</sub>	69%	M	hard foam	orange
-(CH <sub>2</sub> ) <sub>3</sub> -Si(CH <sub>3</sub> ) <sub>2</sub> -O-Si(CH <sub>3</sub> ) <sub>2</sub> -(CH <sub>2</sub> ) <sub>3</sub> -	3	Br	-Bn	66%	L	waxy foam	brown
-(CH <sub>2</sub> ) <sub>3</sub> -Si(CH <sub>3</sub> ) <sub>2</sub> -O-Si(CH <sub>3</sub> ) <sub>2</sub> -(CH <sub>2</sub> ) <sub>3</sub> -	3	Br	-AcOMe	P	-	-	*red
-(CH <sub>2</sub> ) <sub>3</sub> -Si(CH <sub>3</sub> ) <sub>2</sub> -O-Si(CH <sub>3</sub> ) <sub>2</sub> -(CH <sub>2</sub> ) <sub>3</sub> -	3	Br	-Bzh	P	-	-	*dark orange
-(CH <sub>2</sub> ) <sub>3</sub> -Si(CH <sub>3</sub> ) <sub>2</sub> -O-Si(CH <sub>3</sub> ) <sub>2</sub> -(CH <sub>2</sub> ) <sub>3</sub> -	4	I	-CH <sub>3</sub>	71%	M	hard foam	dark yellow
-(CH <sub>2</sub> ) <sub>3</sub> -Si(CH <sub>3</sub> ) <sub>2</sub> -O-Si(CH <sub>3</sub> ) <sub>2</sub> -(CH <sub>2</sub> ) <sub>3</sub> -	4	Br	-Bn	70%	L	waxy foam	brownish-red
-(CH <sub>2</sub> ) <sub>3</sub> -Si(CH <sub>3</sub> ) <sub>2</sub> -O-Si(CH <sub>3</sub> ) <sub>2</sub> -(CH <sub>2</sub> ) <sub>3</sub> -	4	Br	-AcOMe	P	-	-	*brownish-red
-(CH <sub>2</sub> ) <sub>3</sub> -Si(CH <sub>3</sub> ) <sub>2</sub> -O-Si(CH <sub>3</sub> ) <sub>2</sub> -(CH <sub>2</sub> ) <sub>3</sub> -	4	Br	-Bzh	P	-	-	*dark red

P – polymerisation products dominating, disappearance of imine 1H NMR signals; H – high; weakly hygroscopic, slowly decomposes by hydrolysis; M – medium; medium hydrolysis speed, some decomposition on dry air (redox-based); L – low; fast hydrolysis speed, fast decomposition even when stored under inert gas when not refrigerated and/or exposed to light.

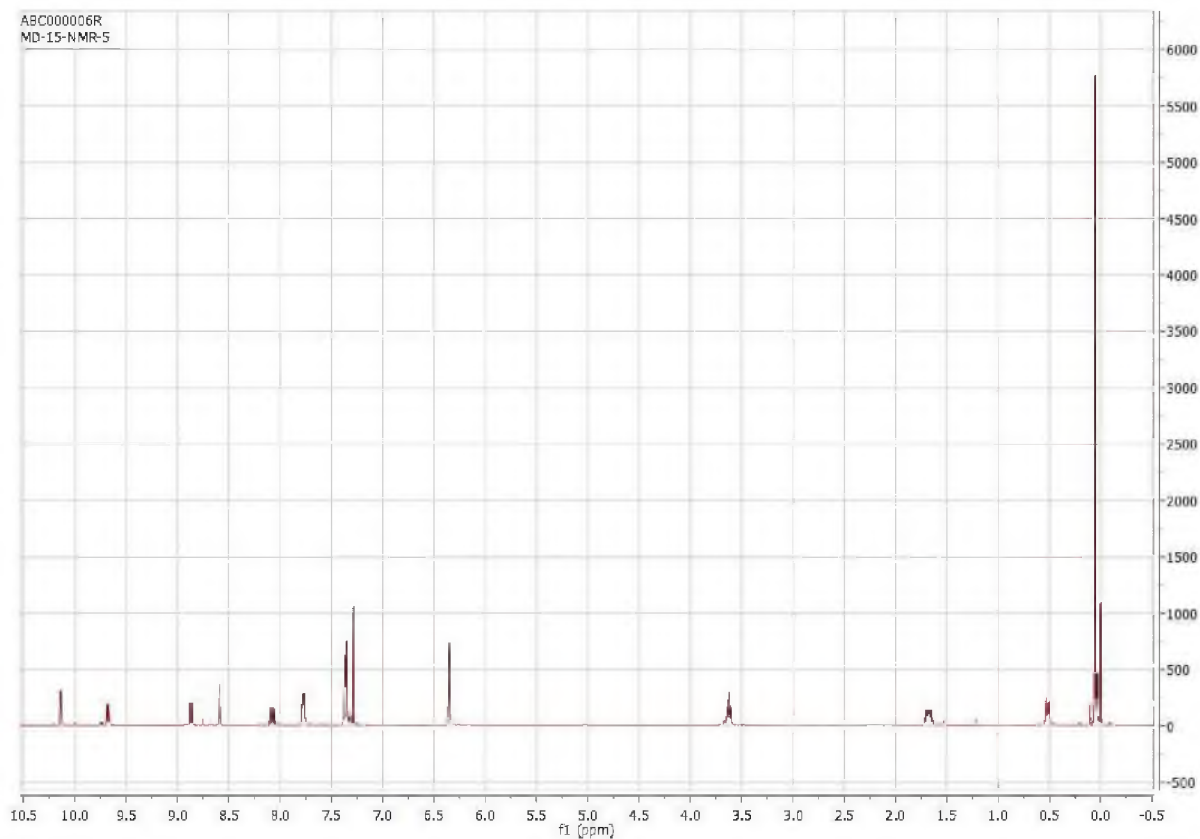
\* - denotes the color of polymerized, high-weight products

Comparison of the 3-dimensional structure and <sup>1</sup>H NMR spectra of organosilicon (podand 1) and purely organic (podand 2) dipodal bromide salts derived from 3-pyridinecarboxaldehyde and quaternized using benzyl bromide is shown below (Figures 1-3):



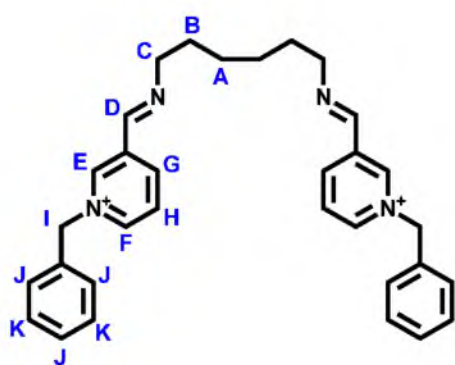
(podand 1)



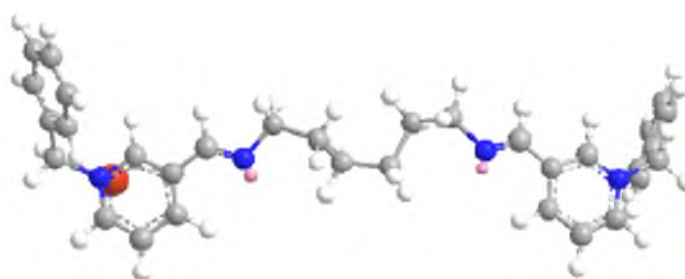


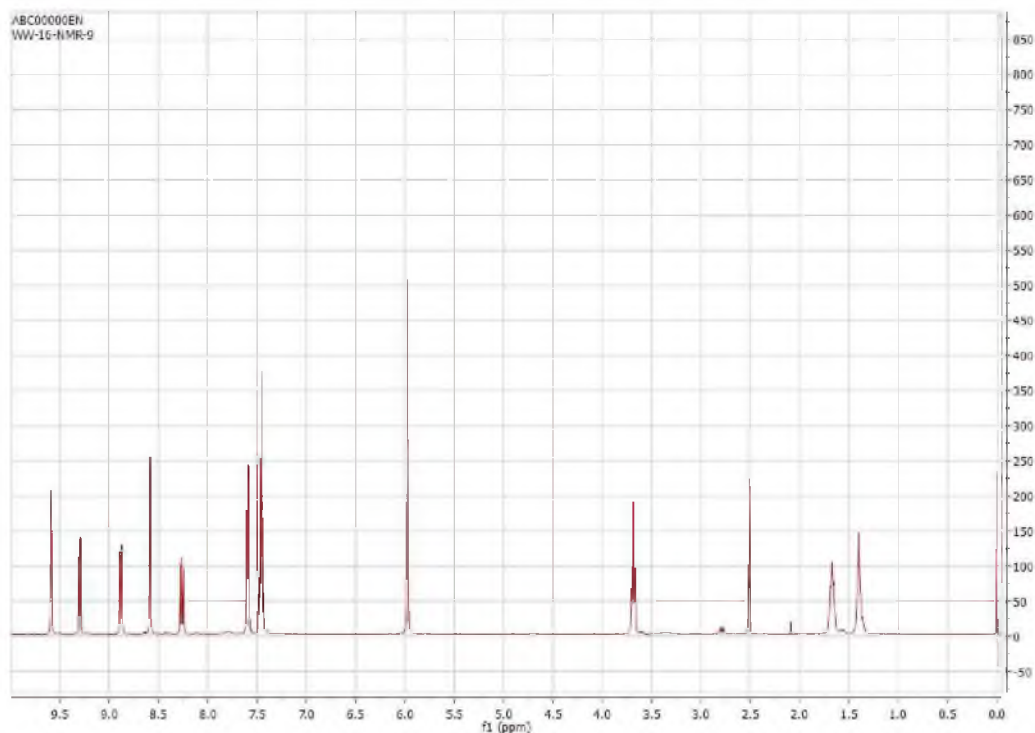
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =0.05 (s, 12H, S); 0.51 (m, 4H, A); 1.68 (m, 4H, B); 3.62 (t,  $J$  = 6.6 Hz, 4H, C); 6.35 (s, 4H, I); 7.37 (m, 6H, J); 7.77 (m, 4H, K); 8.08 (dd,  $J$  = 8.2, 1.2 Hz, 2H, H); 8.59 (s, 2H, D); 8.87 (dt,  $J$  = 8.1, 6.1 Hz, 2H, G); 9.68 (dt,  $J$  = 6.0, 1.2 Hz, 2H, F); 10.14 (s, 2H, E)

Figure 1 -  $^1\text{H}$  NMR spectra of purely organic (podand 1) dipodal bromide salts



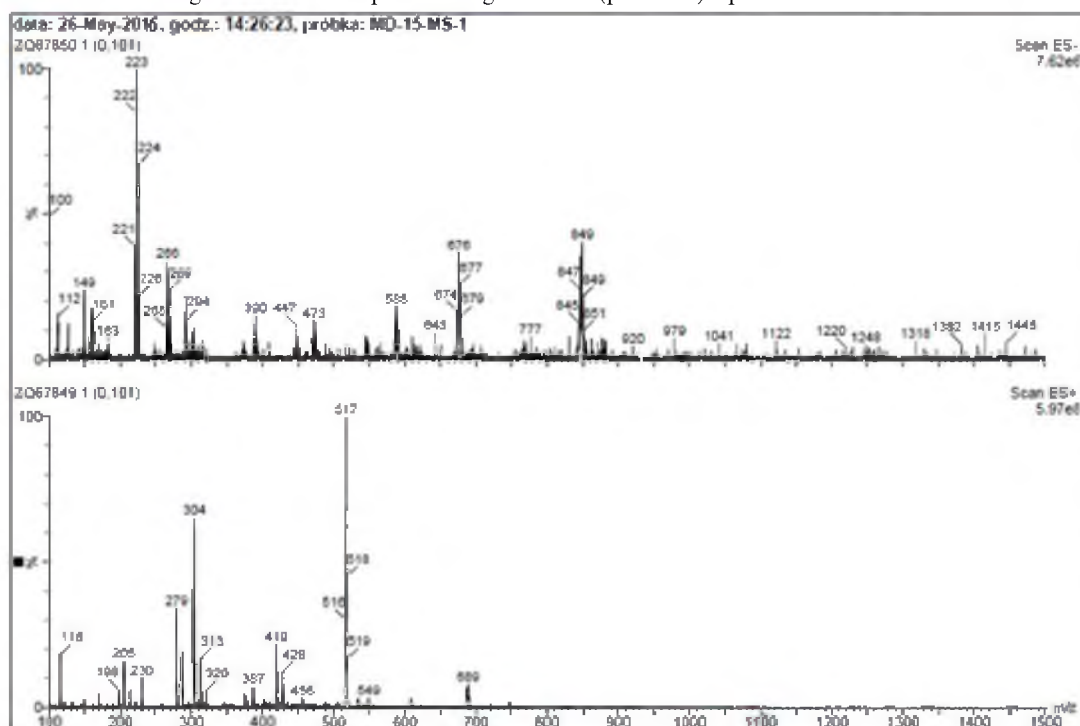
(podand 2)





$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$ =1.40 (m, 4H, A); 1.67 (m, 4H, B); 3.68 (t,  $J$  = 6.5 Hz, 4H, C); 5.97 (s, 4H, I); 7.41-7.53 (m, 6H, J); 7.56-7.63 (m, 4H, K); 8.26 (dd,  $J$  = 8.0, 6.1 Hz, 2H, H); 8.58 (s, 2H, D); 8.88 (dt,  $J$  = 8.1, 1.3 Hz, 2H, G); 9.29 (dd,  $J$  = 6.1, 1.2 Hz, 2H, F); 9.59 (s, 2H, E)

Figure 2 -  $^1\text{H}$  NMR spectra of organosilicon (podand 2) dipodal bromide salts



MS (ESI):  $m/z$  = 304 [ $\text{M}^{2+}$ ] $^{2+}$ ; 687/689 [ $\text{M}^{2+}+\text{Br}^-$ ] $^+$ ; 847/849/851 [ $\text{M}^{2+}+3\text{Br}^-$ ]

Figure 3 – Results of comparison of the 3-dimensional structure

### Conclusion

1. Dipodal Schiff bases readily form complexes with transition metals (copper, zinc, silver, cadmium). These complexes are polymeric in nature and poorly soluble; in some cases more than one product is possible, depending on stoichiometry. Siloxane complexes display much higher solubilities (best in medium-polarity solvents, e.g. ethanol, acetone).

2. Zinc complexes are the most stable and do not react with halides as free pyridines do. Silver complexes, though near-insoluble, react fast, but produce only polymeric products lacking the imine moiety, even with reagents that normally form stable or semi-stable salts.

3. It appears that the more nucleophilic the  $\alpha$  carbon next to pyridinium nitrogen, the less stable the compound. This in turn suggests that the decomposition is started with the appearance of ylide species.

4. Susceptibility to nucleophilic attack by the ylide species can be the reason for apparent lower stability of siloxane analogues.

5. All of the polymerization, complex products were uniquely soluble in DMSO. Despite this fact, characterization by means of NMR techniques was impossible due to the multitude of signals present.

6. In all cases, although siloxane dipodands were found to be somewhat more susceptible to degradation, they offer a wider assortment of compatible solvents and have better solubilities overall.

7. All compounds are potent allergens and should be handled with gloves. Despite being non-volatile themselves, volatile solvents have the potential to transfer them onto skin (e.g. when heated near boiling point, allowed to creep out of the vessel or shaken, producing a mist)

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**А.С. Тукибаева<sup>1</sup>, Л. Табиш<sup>2</sup>, Л. Богуслава<sup>2</sup>, Н. Абылкасымов<sup>1</sup>, С. Сапарбекова<sup>3</sup>**

<sup>1</sup>М.Әуезов атындағы Оңтүстік Қазақстан мемлекеттік университеті, Шымкент қ., Қазақстан;

<sup>2</sup>Познаньдағы Адама Мицкевич университеті, Познань қ., Польша;

<sup>3</sup>Академиялық инновациялық университеті, Шымкент қ., Қазақстан

### **ЖАҢА ДИПОДОЛ СИНТЕЗ ЖҮЙЕСІН ЗЕРТТЕУ, ҚҰРАМЫНДА ПИРИДИНИЯ БАР - ИМИНДІ ҚАЛДЫҚТАР**

**Аннотация.** Жұмыста құрамында қабысқан пиридиний-имин қалдықтары бар жаңа диподол жүйеслерін зерттеу нәтижелері ұсынылған. 3-пиридинкарбоксальдегид және кватернизирленген бензилбромидтен алынған кремнийорганикалық (поданд 1) және таза органикалық (поданд 2) пдал бромид тұзарының үшөлшемді құрылымы мен <sup>1</sup>H ЯМР-спектроскопиясын салыстыру нәтижелері келтірілген. ЯМР-спектроскопия және ESI-МС анализ нәтижелері мақсатты қосылыстардың құрамы мен үлесін растайды. Осы деректерге қарамастан, көптеген сигналдардың болуының салдарынан ЯМР тәсілдердің көмегімен сипаттау мүмкін болмады. Дегенмен де барлық жағдайларда силоксанды диподандтар анықталып отырды, олар ыдырауға анағұрлым бейім, және салыстырмалы жоғары ерігіштікке ие. Барлық қосылыстар күшті аллергияға және қолғаппен жұмыс істеуді талап етеді.

**Тірек сөздер:** кремнийорганикалық химия, подандтар, комплекстер, диподол жүйесі, ЯМР-өлшеулер.

**А.С. Тукибаева<sup>1</sup>, Л. Табиш<sup>2</sup>, Л. Богуслава<sup>2</sup>, Н. Абылкасымов<sup>1</sup>, С. Сапарбекова<sup>3</sup>**

<sup>1</sup>Южно-Казахстанский государственный университет им.М.Ауезова, Шымкент,

<sup>2</sup>Университет Адама Мицкевича в Познани, Польша

<sup>3</sup>Академический инновационный университет, Шымкент

### **ИССЛЕДОВАНИЕ СИНТЕЗА НОВЫХ ДИПОДОЛ СИСТЕМЫ, СОДЕРЖАЩИХ СОПРЯЖЕННЫЕ ПИРИДИНИЙ - ИМИНОВЫЕ ОСТАТКИ**

**Аннотация.** В данной работе представлены результаты исследования новых диподол систем, содержащие сопряженные пиридиний - иминовые остатки. Приведены результаты сравнения 3-мерной структуры и <sup>1</sup>H ЯМР спектров кремнийорганических (поданд 1) и чисто органических (поданд 2) диподол бромидов, полученные из 3-пиридинкарбоксальдегида и кватернизированного бензилбромида. Результаты ЯМР-спектроскопии и ESI-МС анализа подтверждают состав и долю целевых соединений.

Несмотря на этот факт, охарактеризовать с помощью ЯМР методов было невозможно из-за присутствия множества сигналов. Хотя во всех случаях были обнаружены силоксановые диподанды, которые могут быть несколько более восприимчивыми к разложению и представляют более широкий ассортимент совместимых растворителей и обладают относительно лучшей растворимостью. Все соединения являются сильными аллергенами и требуют работать в перчатках.

**Ключевые слова:** кремнийорганическая химия, поданды, комплексы, диподол система, ЯМР- измерения.