Polish J. Chem., **75**, 1947–1951 (2001) **COMMUNICATION**

Spectroscopic and Kinetic Characterization of Aza-15-crown-5 Ether O←N Styryl Pyridine as Polyfunctional Receptor

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(Received April 25th, 2001; revised manuscript August 28th, 2001)

Depending on external conditions, a molecular receptor can exhibit different structures as electron density, *cis*-*trans* conformation, and *etc*. [1–5]. It is connected with possibility of information transfer. Until now many types of these arrangements have been synthesized and two most important features can be decidive: a high affinity and selectivity for the substrate used. The molecular receptors are characterized by sensitivity to light, pH, the concentration and kind of some metal ions, the presence of donor or acceptor reagents in solution.

A new molecular receptor – the derivative of aza-15-crown-5 ether and O N styryl pyridine has been synthesized and characterized by spectroscopic and kinetic studies. This compound comprises three functional groups: the crown ether donor group, capable of cation complexation, the nucleophilic – donor group, in the form of N–O and the photochemically active double bond. Scheme 1 presents different reaction pathways of the receptor in solution. The receptor was synthesized by the method described in [6] and [7] with phenyl-aza-15-crown-5 as starting material and the product was obtained in the *trans* form. Under UV-irradiation this isomer evolved and its conformation changed into the *cis* one in different solvents. Cessation of UV-irradiation causes a slow transformation of the isomer *cis* into the thermodynamically stable isomer *trans*. *Trans* and *cis* isomers also differ from each other in absorption electron UV-Vis spectra. The solvents influence strongly the kind of cation complexation, the form of the substrate and the structure of the product of nucleophilic substitution. It is very interesting to note that this influence is rather important and these changes are observed for monovalent (Li^+, Na^+, CH_3CO^+, $(CH_3)_4N^+$) as well as for divalent cation (Mg^{2+}, Ni^{2+}). The values of $_{max}$ of the receptor in different systems are collected in Table 1.

For different pH in water solution, the pKa for protonated in crown ether ring of *trans* isomer of receptor was calculated giving 3.60 0.05.

We studied these isomers and metal cation complexes by ^1H NMR using Varian 300 spectrometer. The stoichiometry of receptor complexes with metal cations was established on the basis of ^{23}Na NMR titration of sodium perchlorate solvent by receptor solvent. In Figure 1 the changes of the half-intensity width and also chemical shifts in dependence on the molar ratio cation/receptor are observed. The complex of ratio 1:1 is formed (max. and min. in Figure 1).

In order to characterize the binding of complex metal cations (Na^+ and Li^+) to the receptor *trans*-*cis* isomers, ^1H NMR measurements with different molar ratio of the receptor to the given cation were performed (Table 2).

Scheme 1

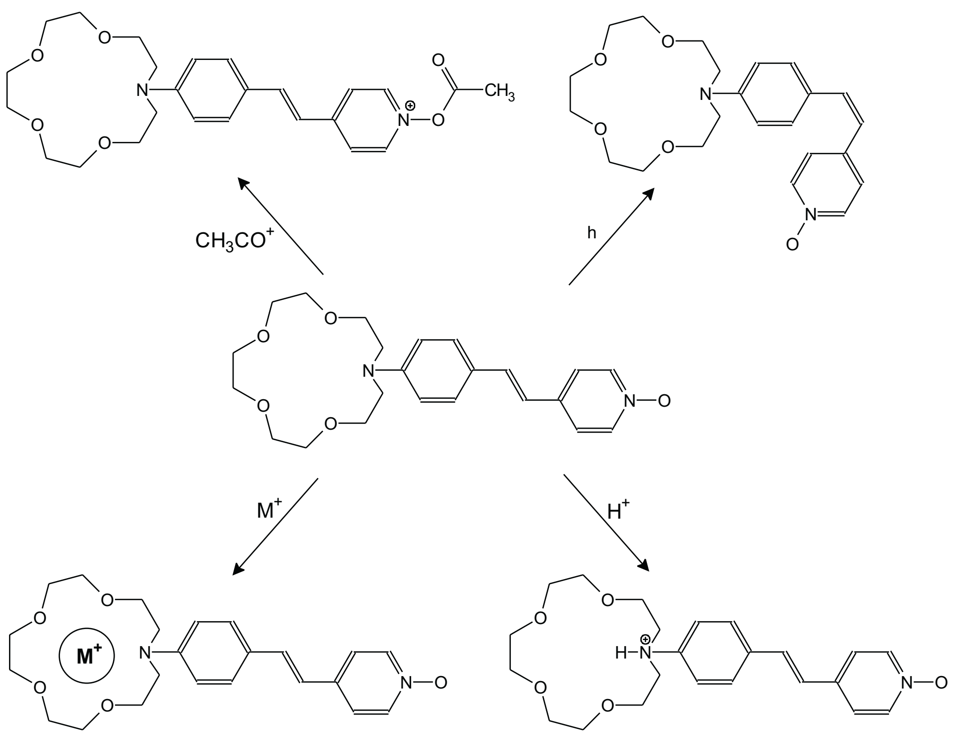


Table 1. The influence of different cations on $_{max}$ values of receptor in different solvents.

System	$_{max}$ [nm]	
	CH_3CN	EtOH
Receptor-*trans*	392 (= 40 400)	404 (= 39 900)
Receptor-*cis*	289 (= 39 100)	312 (= 38 500)
Receptor-*trans* + H^+	328	330
Receptor-*trans* + $(CH_3)_4N^+$	396	404
Receptor-*trans* + Li^{+-}	376	404
Receptor-*trans* + Na^+	368	408
Receptor-*trans* + Mg^{2+}	416	404
Receptor-*trans* + Ni^{2+}	430	420
Receptor-*trans* + CH_3CO^+	508	508

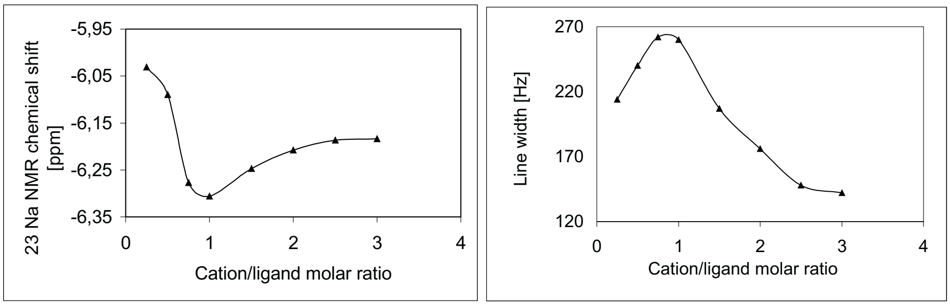


Figure 1.

Table 2. Chemical shifts ^{1}H NMR for the *trans*/*cis* receptor isomers in the presence of different cations in CD_3CN.

Proton	*trans*	*trans*+Li$^+$	*trans*+Li$^+$	*trans*+Na$^+$	*trans*+Na$^+$	*trans*+H$^+$	*cis*	*cis*+Li$^+$	*cis*+Na$^+$
		(1:1)	(1:10)	(1:1)	(1:10)	(1:1)		(1:10)	(1:10)
H-2	6.69	6.88	6.92	7.00	7.04	7.90	6.57	6.83	7.00
H-3	7.36	7.40	7.54	7.33	7.49	7.90	7.12	7.20	7.24
H-2	7.98	7.97	8.17	7.83	8.07	8.64	7.92	8.10	8.05
H-3	7.40	7.48	7.68	7.36	7.55	8.02	7.20	7.41	7.31
H-*alfa*	7.17	7.26	7.43	7.11	7.31	7.74	6.62	6.80	6.79
H-*beta*	6.85	6.91	7.05	6.85	7.03	7.45	6.23	6.41	6.45

In the case of H-2 we could observe a relatively big change in the chemical shift values for Na$^+$ as well as Li$^+$ cation complexation in the ratio of receptor to cation (1:1). However, for H-2 proton in the ratio of receptor to cation (1:1), the changes are comparatively small. For ratios of 1 to 5 and 1 to 10 the changes in chemical shifts increased and this could be explained by the fact that the excess of cations could be also act on the N-oxide oxygen atom. Lithium ion being characterized by a larger polarizability, stronger than the sodium ion bonds with the NO group. This caused a larger change of the chemical shift values of H-2 and H-3 protons in pyridine part of molecule. For complexes 1:1 the FT-IR spectra in acetonitrile were taken and the characteristic signal of the NO bond in the receptor (1255 cm^{-1}) was changing to 1260 cm^{-1}. This took place for all cases, for complexes with Na$^+$, Li$^+$, and Mg^{2+}. It shows that all used cations form with this receptor the same type of complexes. The metal cation is located in the crown ether cave.

The second order rate constants for sodium ion transport from crown ether cavity of receptor to ethanol solution were determined by temperature-jump methods [8,9] and these values at 21.5 C, 30.5 C and 39.5 C are 2344, 2909, 3314 dm^3 mol^{-1} s^{-1}, respectively. The values of activation parameters for decomplexation reactions are H = 12.25 1.87 kJ mol^{-1}, S = –196 6 J mol^{-1} K^{-1} and G = 70.75 1.87 kJ mol^{-1}. Entropy solvatation effects control the process of sodium ions transport.

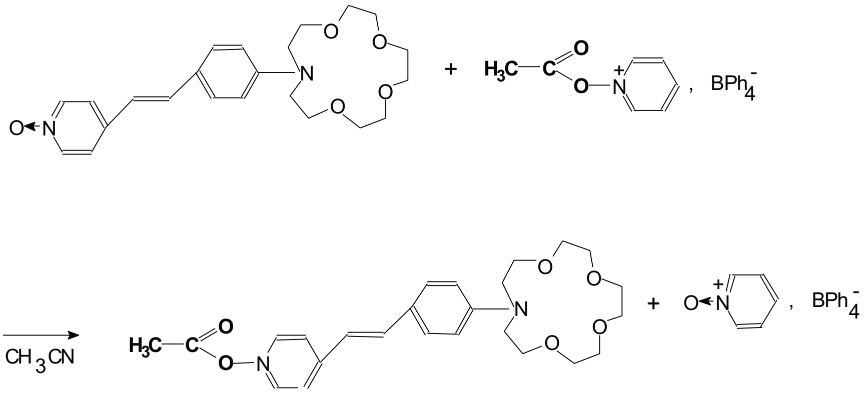
The influence of metal cations on the yield of *trans*-*cis* isomerization process in acetonitrile solution is presented in Table 3.

Table 3. The ratio of *cis*/*trans* isomers formations under UV-irradiation.

Arrangements	Ratio *cis*:*trans* isomers
receptor in $CDCl_3$	45:55
receptor in CD_3CN	58:42
receptor – Li^+ (1:10) in CD_3CN	63:36
receptor – Na^+ (1:10) in CD_3CN	71:28

The relation between *trans* and *cis* isomers was changing depending on cations used. The solvent influenced also the isomerization process. The nucleophilic properties of N–O group in the receptor were studied in reaction between the molecule and benzyl chloride in acetonitrile solution using stopped flow method [10,11]. The second order rate constants for this reaction with substituent of amino crown ethers and for reaction with substituent of aliphatic amine [6,7] were similar (k_{25} 4 000 [$dm^3mol^{-1}s^{-1}$]), but the addition of cations to solutions caused important changes in these values. The presence of cations that create the complexes with amino crown ethers, decreased the rate constant, because of changes of the electronic density on the nucleophilic centre. This relation is also typical for other nucleophilic reactions (Table 4).

Table 4. The second order rate constants at 25 C for acyl group transfer reactions in acetonitrile.



Salts	k [$dm^3mol^{-1}s^{-1}$]
————	4485 15
$Me_4N^+ClO_4$	3150 20
$LiCiO_4$	1105 20
$NaClO_4$	1752 25

The compound studied can be used as multifunctional molecular receptor that reacts not only on the presence of cations but also on pH and UV-Vis light.

Acknowledgment

The authors kindly acknowledge the financial support by the Polish State Committee for Scientific Research (grant No. 7T09A04721).

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