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CHEMISTRY OF QUATERNARY AZAAROMATICS AND RELATED SPECIES

Abstract: In the present review dealing with quaternary azaaromatics three first chapters concern their syntheses, reactivity and physicochemical properties. The fourth and fifth chapters are devoted to viologens and to selected examples of supramolecular systems, respectively. In three final chapters the possible applications and biological activities of quaternary azaaromatics are presented along with porphyrins bearing quaternary azaaromatic moieties.

Introduction

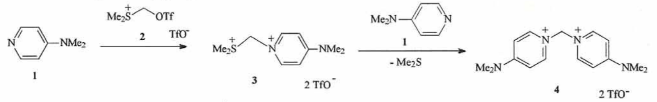
Quaternary azaaromatics are a topic of numerous reports due to their interesting properties and application possibilities [1]. The present paper is connected with works of our research group concerning benzonaphthyridinium quaternary salts [2–10]. Since the amount of reports on quaternary azaaromatics is enormous, only selected examples are presented here.

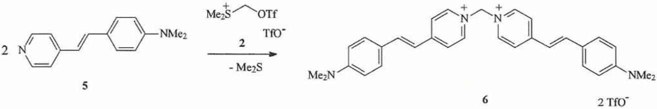
The review consists of eight chapters, the first ones deal with syntheses, reactivity and physicochemical properties of quaternary azaaromatics, and the next ones are devoted to viologens and supramolecular systems. In the final chapters application possibilities and biological activities of these species are described, along with porphyrins bearing quaternary azaaromatic units.

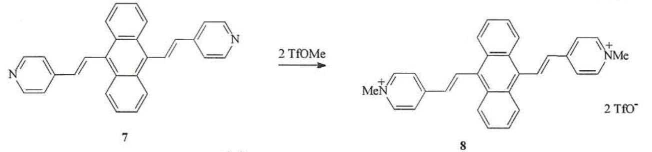
1. Syntheses of quaternary azaaromatics

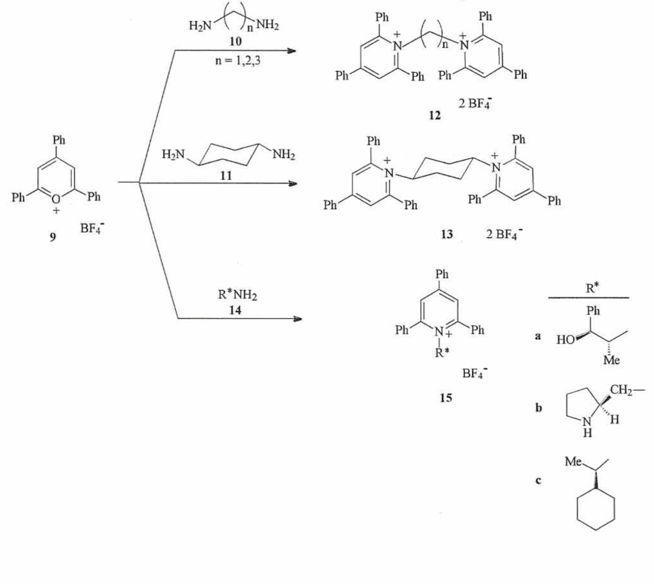
For the synthesis of quaternary azaaromatics usually two general methods are used – quaternization of azaaromatics and reaction of pyrylium salts with primary amines. As an example of quaternization of azaaromatics may serve reaction of N,N-dimethylaminopyridine (**1**) with sulfonium salt (**2**), leading to **3**; this species reacts with the second molecule of **1** to give dipyridinium salt (**4**) [11]. Similar reaction of stilbazole (**5**) affords dipyridinium salt (**6**). Compounds (**4**) and (**6**) are dyes which may be used as ylide precursors [11]. To syntheses involving quaternization belongs also reaction of **7** with methyl triflate leading to **8** which is a potential DNA intercalator [12].

As examples of syntheses of quaternary azaaromatics from pyrylium salts and amines may be mentioned reactions of 2,4,6-triphenylpyrylium tetrafluoroborate (**9**) with diamines (**10**) and (**11**) affording dipyridinium salts (**12**) and (**13**) [13], as well as reaction with amine (**14**) bearing chiral substituents R*, giving rise to chiral quaternary pyridinium salts (**15**a – **c**) [14].





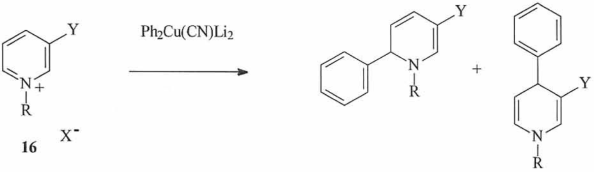




2. Reactivity of quaternary azaaromatics

Quaternary azaaromatics are highly reactive [15–18]; their selected reactions are presented below. Compounds (**16**) undergo reduction to 1,2- and 1,4-dihydropyridine derivatives (**17**) and (**18**) by treatment with copper organometallics. This reaction affords predominantly 1,4-dihydropyridines (**18**) serving as starting materials for alkaloid syntheses [19].

For example the stereoselective synthesis of alkaloids (+)-16-epivinoxin and (-)vinoxin begins with the addition of the chiral species (**19**) to quaternary salt (**20**), and proceeds *via* formation of 1,4-dihydropyridine and cyclization [20]. The obtained diastereomeric mixture was separated by chromatography, assigning to the major product the (+)-**21** configuration. The subsequent hydrolysis of (+)-**21** with HCl and reduction gave **22**, which upon transesterification with bromomethoxymagnesium, enabling the removal of chiral system, afforded (+)-16-epivinoxin. This compound treated with potassium *t*-butoxylate in methanol undergoes epimerization leading to (-)vinoxin.

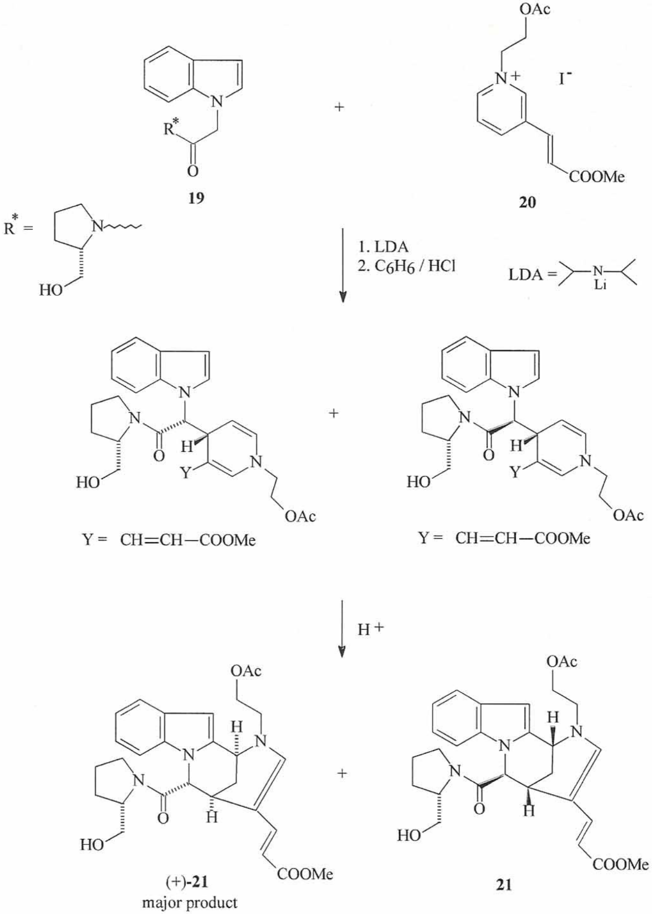


16 **17** **18**

Y = NO_2, CN, CHO, COOH

R = Me, $PhCH_2$

X = Cl, I


OAc
N+
I⁻
N
R*
O
+
COOMe
19
20
R* =
N
HO
1. LDA
2. C6H6 / HCl
LDA =
N
Li
N
N
H
O
N
Y
HO
OAc
Y = CH=CH—COOMe
+
N
N
H
O
N
Y
HO
OAc
Y = CH=CH—COOMe
H+
OAc
H
N
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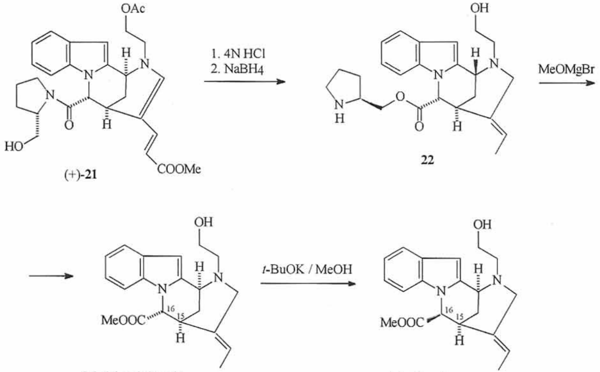
HO
COOMe
21



(+)-**21**

22

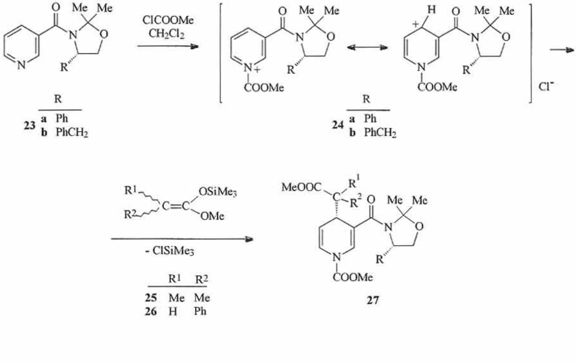
(+)-16-epivinoxin

(−)-vinoxin

Pyridines (**23a,b**) react with methyl chloroformate to give pyridinium salts (**24a,b**). It was observed that in **24b** both rings – pyridine and phenyl rings are parallel, enabling interaction of pyridinium cation with electrons of phenyl ring; in free pyridine (**23b**), however, the rings are not parallel. The reaction of **24** with ketene silylacetals (**25**) and (**26**), serving as nucleophiles gives chiral 1,4 adducts (**27**) [21], which are alkaloid synthons [22] and may be used as NADH models [23].

It was established that the first step in the asymmetric total synthesis of (+)-cannabisativine (**28**) is the reaction of chiral 1-acylpyridinium salt (**29**) with zinc enolate (**30**) affording dihydropyridone (**31**) [24].

The Zincke salt (**32**) by treatment with (R)-(-)-2-phenylglycynol (**33**) was converted into a chiral compound (**34**); its oxidation with $K_3Fe(CN)_6$ in alkaline medium leads to alkylpyridones (**35**) and (**36**) [25].

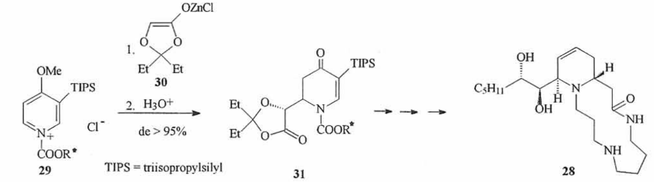


	R
23 a	Ph
b	PhCH$_2$

	R
24 a	Ph
b	PhCH$_2$

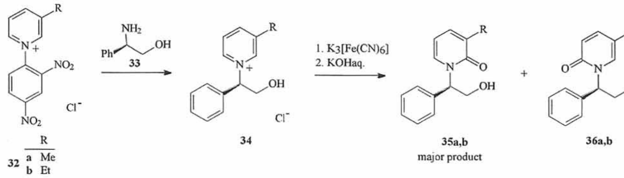
	R1	R2
25	Me	Me
26	H	Ph

27



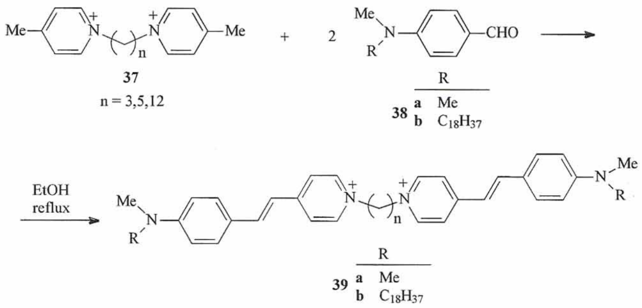
R* = (+)-TCC

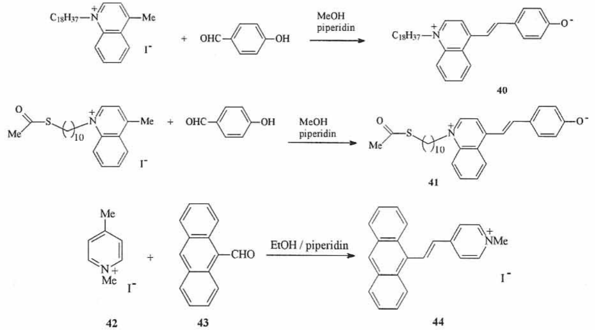
TCC = *trans*-2-(α-cumyl)cyclohexyl



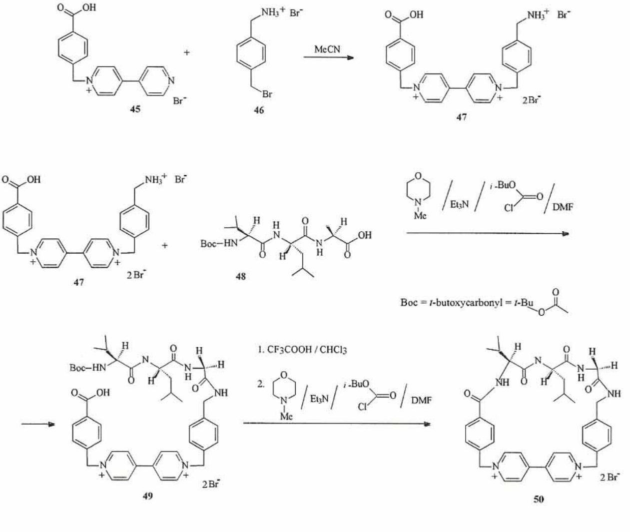
It was observed that dipyridinium salts (**37**) react with aldehydes (**38**) to give dimeric stilbazolium dyes (**39a,b**) exhibiting NLO (nonlinear optics) properties [26–28]. Similar procedure leads to merocyanines (**40**) and (**41**). They undergo a smooth protonation, accompanied by a color change and due to this property may be used as sensors for acids and bases [29].

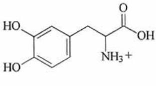
In the search for quaternary azaaromatic intercalators of DNA undergoing photoizomerization, the reaction of **42** with aldehyde (**43**), leading to **44** has been made [12].





Quaternization of the compound (**45**) by benzyl bromide (**46**) affords the dipyridinium system (**47**), undergoing condensation with protected tripeptide (*S*)-(Val-Leu-Ala) (**48**) in the presence of N-methylmorpholine, triethylamine and *i*-butyl chlorocarbonate. The formed **49** was deprotected and subjected to the next condensation to give the chiral cyclophane (**50**) [30]. As guest molecules of cyclophane (**50**) may serve pharmacologically important DOPA (**51**) (two enantiomers) and nadolol (**52**) (a racemate) [30].





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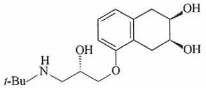
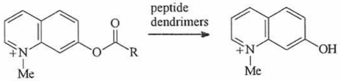


52

In the study of enzymatic catalysis, the hydrolysis of N-methylquinolinium salts (**53–56**) leading to fluorescent **57** has been performed using peptide dendrimers composed of histidine, aspartate and serine [31–34].

The synthesis of oxazoline dihydropyridines (**58**) proceeds *via* quaternary salt (**59**) formed from pyridine (**60**) and nitriles of α- and β-acetylene-γ-hydroxyacids (**61**) [35]. It should be pointed out that this annelation proceeds under mild conditions, without solvent or catalysts.

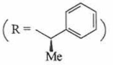
Reaction of the phenanthridinium quaternary salt (**62**) with primary amines affords in a simple one-pot procedure tetracyclic compounds (**63**) showing DNA affinities and high cytotoxic activities [36]. Process begins with nucleophilic attack of primary amine on the heteroaromatic ring of **62**; the subsequent cyclization and hydride loss lead to compounds (**63**). The above method may be also applied to quinolinium and quinazolinium starting materials.



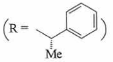
57

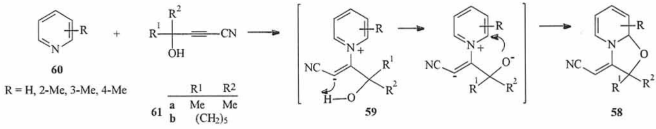
	R
53	Me
54	C_5H_{11}
55	*i*-Pr

(*R*)-**56**



(*S*)-**56**





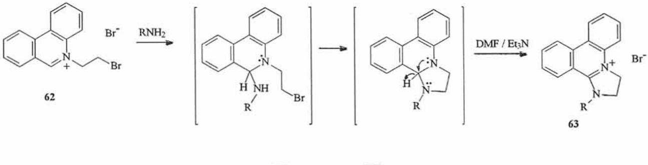
60

R = H, 2-Me, 3-Me, 4-Me

61	R1	R2
a	Me	Me
b	$(CH_2)_5$	

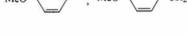
59

58



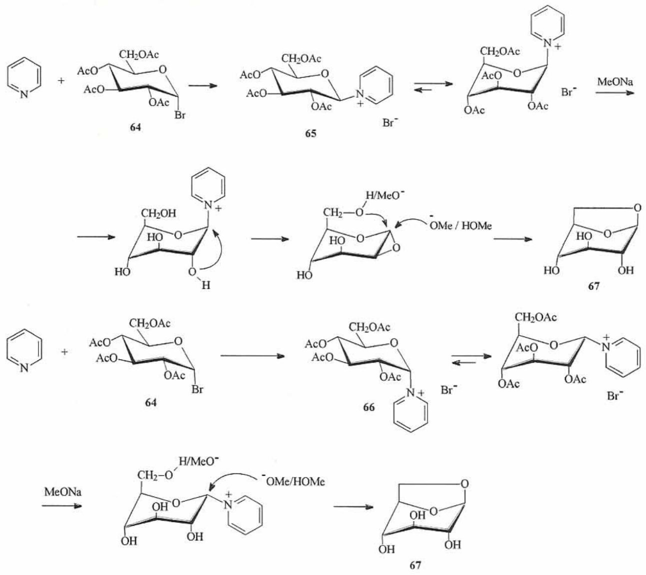
62

63



R = *i*-Pr, cyclopropyl, $HOCH_2CH_2$–, Ph, MeO–C_6H_4–, MeO–C_6H_4–CH_2 and other

Quaternization of pyridine with compound (**64**) leads to N-glucopyranosylpyridinium salts (**65**) and (**66**) which undergo 1,6-cyclization affording 1,6-anhydro-D-glucopyranoside **67** [37]. The crystalline structure of glucopyranosylpyridinium salts has been examined; they cocrystallize with water molecules.



64

65

67

64

66

67

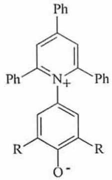
3. Physicochemical properties of quaternary azaaromatics

Physicochemical properties of quaternary azaaromatics are intensively studied [38–41], for example it was observed that Reichardt's betaines (**68**) show solvato- and termochromism. These properties have been examined experimentally and theoretical calculations have been made using AM1 and PM3 / COSMO methods [42]. It was found that complexes of quaternary azaaromatics (**69**) with ytterbium exhibit chemiluminescence and are less cytotoxic than the salts (**69**) themselves [43].

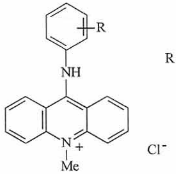
Excited-state proton transfer, electron transfer and solvent relaxation processes in **70** and **71** have been studied in acid and basic solutions. It was observed that hydroxyl group behaves like a superacid in the excited state, the deprotonation rates of **70** and **71** $(2\ \mathrm{ps})^{-1}$ and $(4.5\ \mathrm{ps})^{-1}$, respectively, are among the fastest observed to date in intermolecular proton transfer to water molecules [44].

The photolysis of quaternary salts (**72**) has been made and the interaction of formed radicals with parent cations was investigated using NIR and EPR spectroscopies [45]. The analysis of IR and UV spectra and Raman spectra of monolayers of betaine (**73**) on solid surfaces was also performed [46].

Quaternary diazabenzoperylenium salt (**74**) shows an intense fluorescence. The examination of crystalline structure of this compound indicates a 25° twist of central hexagonal ring, resulting in atropoisomerism [47].

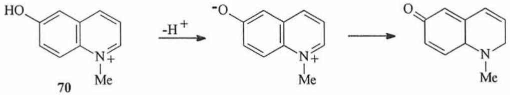


		R
68	**a**	H
	b	Ph



R = OH, COOH

69



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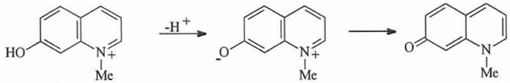

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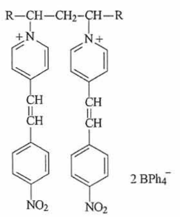
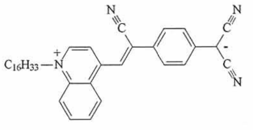


		R
72	**a**	H
	b	Me



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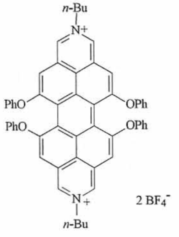


74

Derivatives of acridanecarboxylic acid (**75**) show chemiluminescence; this property is useful for the sensitive detection of peroxidase [48]. They are obtained from acridine (**76**) by quaternization with methyl triflate and subsequent reduction.

Compounds (**75**) undergo an enzymatic oxidation affording chemiluminescent quaternary acridinium salts. For example **75a** affords quaternary salt (**77**), reacting with peroxides to give dioxetanone (**78**) which decomposes affording N-methylacridone. The process is accompanied by the light emission.

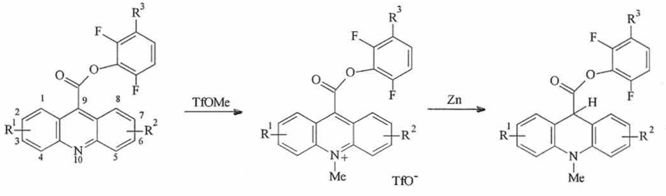
The presence of suitable leaving groups, *e.g.* difluorophenoxyl or trifluorophenoxyl accelerates reaction, in this case the light emission achieves maximum in a shorter time. As peroxides H_2O_2 and $NaBO_3$ were used, and as peroxidase enhancers served phenol derivatives, *e.g.* *p*-iodophenol, *p*-bromophenol or *p*-phenylphenol [48].

In the study of peroxyoxalate-chemiluminescence, the reaction of bis(2,4,6-trichlorophenyl)oxalate (**79**) with hydrogen peroxide in the presence of acriflavine has been examined [49]. Acriflavine is an orange dye consisting of 3,6-diamino-10-methylacridinium chloride (**80**) and 3,6-diaminoacridinium chloride (**81**).

In the first step **79** reacts with H_2O_2 to give the C_2O_4 intermediate, containing the necessary excitation energy. Then the excitation of acriflavine occurs; due to the C_2O_4 intermediate the chemical energy is converted into electronic excitation energy. The final step involves the emission of light energy, accompanied by the return of the excited acriflavine molecule to the ground state.

The dependence of chemiluminescence intensity on concentration of **79**, H_2O_2 and acriflavine was investigated. The influence of H_2O_2 concentration on the peroxyoxalate-chemiluminescence of acriflavine was studied in the presence and in the absence of sodium salicylate. In both reactions the linear relationship was found, however in the former case the chemiluminescence intensity is higher, indicating the catalytic effect of sodium salicylate.

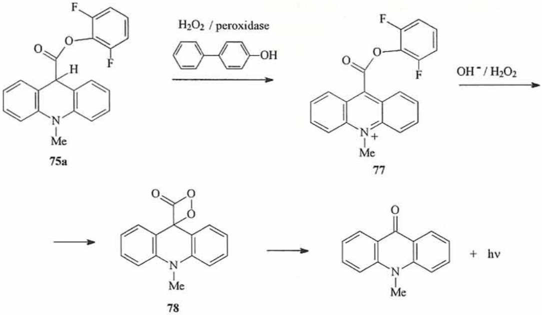
The structure of pyridinium methylides (**82–84**) has been determined using ^{13}C NMR spectroscopy and DFT (density functional theory) method [50], and the stability of pyridinium cations (**85a**) has been studied [51]. The crystal and single molecule structures of **85b** have also been determined and the X-ray and B3LYP characterization of this compound is presented [52].



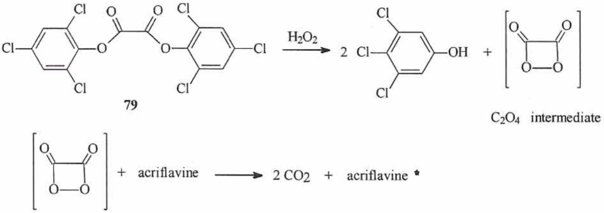
76

75

	R1	R2	R3
a	H	H	H
b	H	H	F
c	3-OMe	H	F
d	1-OMe	6-OMe	F

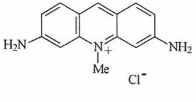


75a **77** **78**

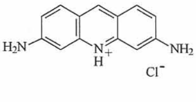


79

acriflavine * $\longrightarrow$ acriflavine + hν



80



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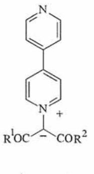

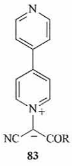

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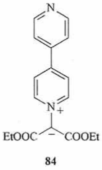

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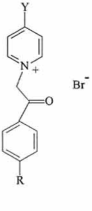


82

	R^1	R^2
a	Me	Et
b	Me	Ph
c	Et	Ph
d	Et	NHPh
e	Ph	Ph
f	Ph	NHPh

R = Me, Et, Ph, NHPh

85

	Y	R
a	H	H, Cl, Br, NO_2, OMe
b	CN	H

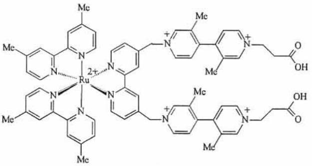
4. Viologens

Viologens, *i.e.* 1,1'-dimethyl-4,4'-bipyridinium dichloride and its derivatives are the subject of a number of works [53–57]. These redox systems are intensively studied in view of their applications in design of electronic devices; as an example may serve the redox – switchable compound (**86**), containing viologen as an electron acceptor and $[Ru(bpy)_3]^{2+}$ as an electron donor [58].

In the study of photosynthesis the formation of supramolecular assemblies of **87** and **88** with crown ethers (**89–91**) has been investigated [59]. Such systems, interesting as models for the photosynthetic reaction center [59] are promising for biomedical applications [60].

The photoinduced electron transfer from $[Ru(bpy)_3]^{2+}$ incorporated into zeolite K^+Y to viologen (**92**) has been examined [61]. The addition of crown ethers (**93–95**) results in the increased yield of radical cation ($\mathbf{92}^{\cdot+}$) proportional to increase of formation constant of complexes of crown ethers with K^+ ions, in the **93** < **94** < **95** order. This behavior results from the release of K^+ ions from the zeolite to solution during interfacial electron transfer from the photoexcited $[Ru(bpy)_3]^{2+}$ complex to viologen (**92**).

The photoinduced system of the hydrogen evolution, containing hydrogenase has been designed; compound (**96**) consisting of viologen and lysine produces hydrogenase and serves as an electron carrier, while porphyrin (**97**) is a photosensitizer [62]. It was established that the complex $\mathbf{96}^{\cdot+}$·hydrogenase forms efficiently, leading to more intense hydrogen evolution than in the case of methyl viologen [62].



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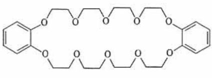

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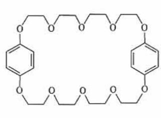

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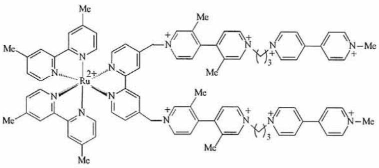

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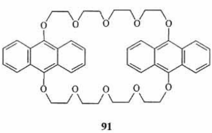

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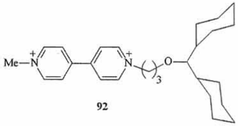

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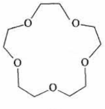

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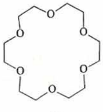

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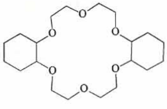

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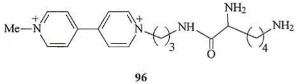

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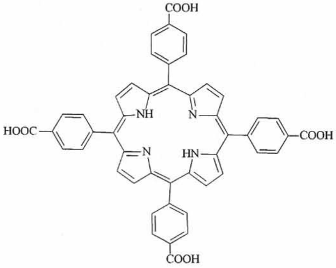

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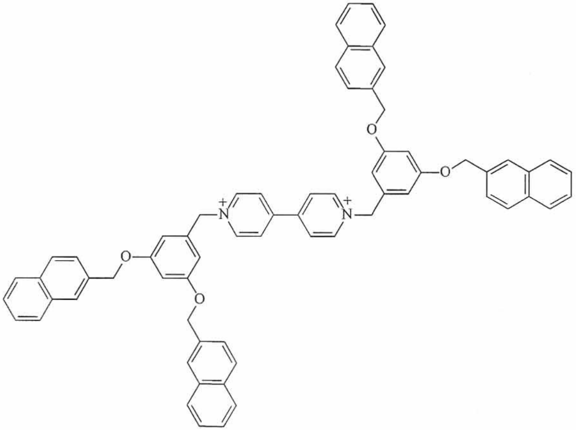
Dendrimers (**98–100**) containing a viologen core are synthetic redox models, mimeting natural light storage systems [63].



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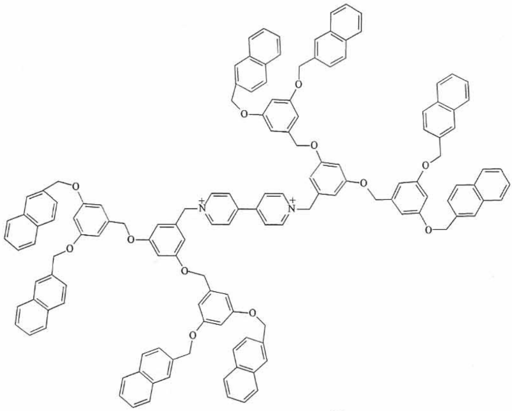

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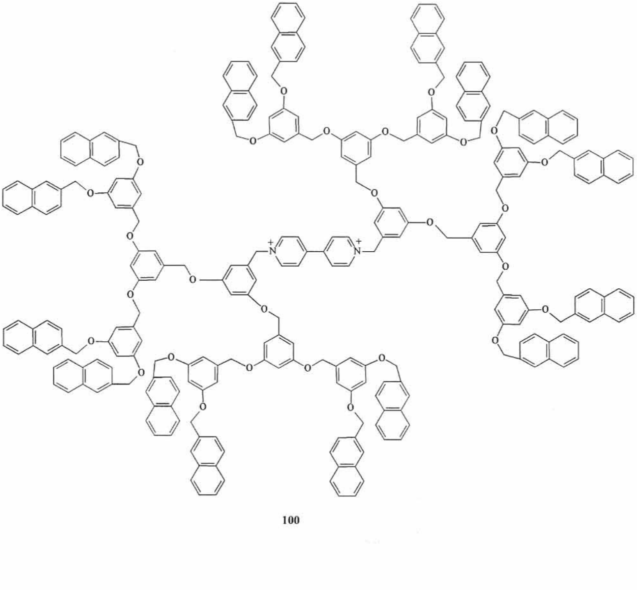


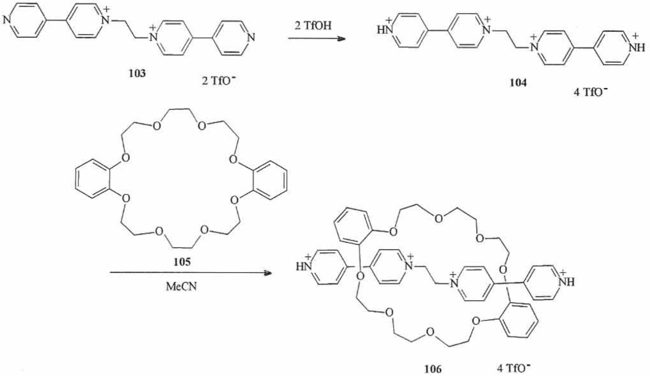
100

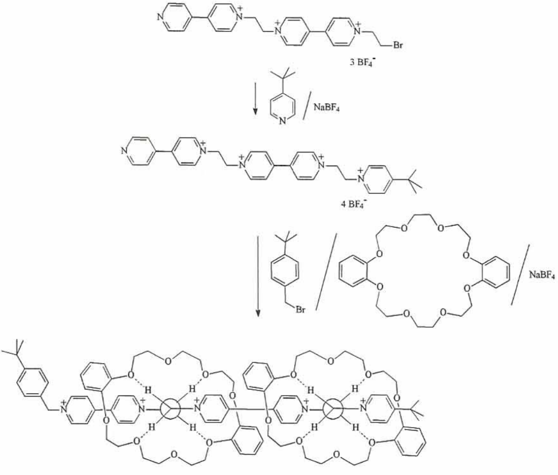
5. Supramolecular systems containing azaaromatic moieties

A special attention is paid today to supramolecular systems [64–67]. In the search of solid-state materials [68, 69] combining ideas of molecular machines systems and crystal engineering, the synthesis of two pseudopolyrotaxanes (**101**) and (**102**) [70, 71] has been made. For this purpose bis(dipyridinium)ethane (**103**) [71] was converted into its diprotic form (**104**) using trifluoromethanesulfonic acid; **104** reacts with crown ether (**105**) affording pseudorotaxane (**106**). The slow evaporation of the obtained solution leads to formation of two crystalline pseudopolyrotaxanes (**101**) and (**102**).

In the pseudopolyrotaxane (**101**), *i.e.* [(**106**/**105**)$(H_2O)_2$/**105**)][OTf]$_4$·$4H_2O$ the hydrogen bonds are present, whereas **102**, *i.e.* [(**106**/**105**)(**105**)$_2$][OTf]$_4$·$4H_2O$ is held by π interactions between electron rich benzene rings of crown ether and electron deficient pyridinium units [70].

In investigation of systems promising for design of electronic devices, two [3]rotaxanes (**107**) and (**108**) have been synthesized [72]. In rotaxanes (**107**) and (**108**) the hydrogen bonds occur, this fact being established by ^1H NMR analysis in CD_3CN solution. Examination of crystalline structure of **108** has confirmed the presence of hydrogen bonds C-H···O and charge transfer interactions between electron donors, *i.e.* oxygen atoms of crown ethers and electron acceptors, *i.e.* pyridinium units.





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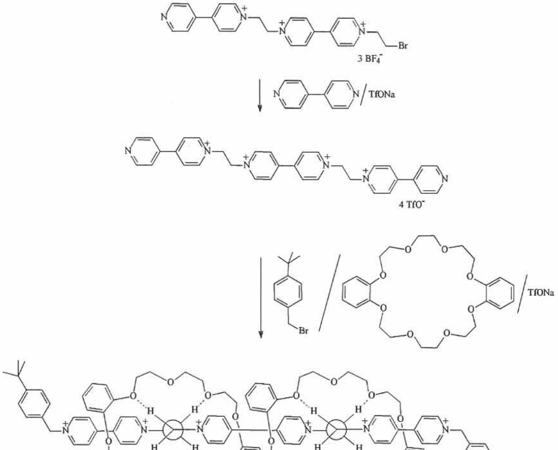
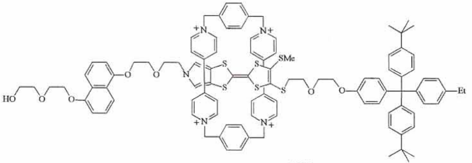


108

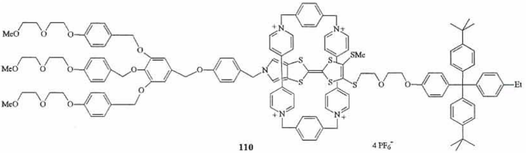
Syntheses of pseudorotaxane (**109**) [73], and rotaxane (**110**) [73] containing pyrrolotetrathiafulvalene moieties have been made. The LB (Langmuir-Blodgett) monolayers of **109** and **110** may be used in molecular electronic systems [73].

Numerous redox compounds are promising for construction of devices [74]. For example the redox species tetrathiafulvalene (TTF) may exist in three oxidation states – as TTF$^{(0)}$, TTF$^{•+}$ and TTF $^{2+}$. The neutral TTF$^{(0)}$ molecule in the presence of two receptors – cyclophane (**111**$^{4+}$) and crown ether (**112**) forms a strong complex with **111**$^{4+}$ (A), however as TTF$^{•+}$ it does not bind **111**$^{4+}$ nor **112** , and as TTF $^{2+}$ forms complex with crown ether (**112**) (B).

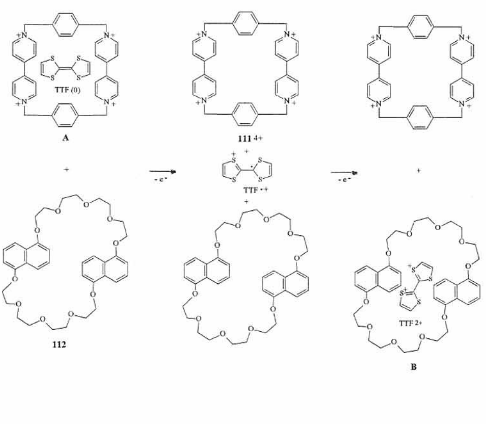
The interaction of cyclophane (**111**$^{4+}$) with TTF derivative (**113**) forming monolayer on the gold electrode in MeCN solution was investigated. On the electrode surface the complex of **111**$^{4+}$ with derivative (**113**) is formed, which upon oxidation of TTF to radical cation undergoes a decomposition [74].

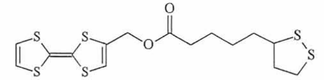


109 4 PF_6^-



110 4 PF_6^-

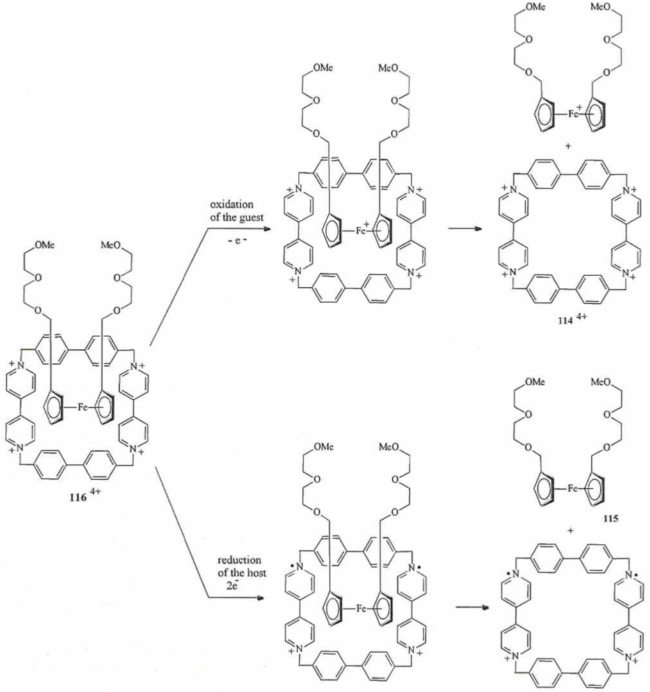


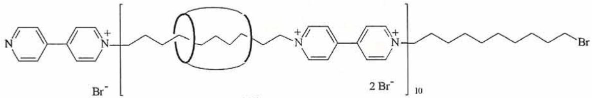


113

It was observed that cyclophane (**114^{4+}**) (the host) and the ferrocene derivative (**115**) (the guest) which have redox properties, form in acetonitrile strong complex (**116^{4+}**), in which two polyether chains of ferrocene (**115**) are localized at one side of the host. In the case of guest oxidation or the host reduction, the complex decomposes [74].

The water soluble pseudopolyrotaxane (**117**), consisting of a thread incorporating viologen unit and of [6]cucurbituril, *i.e.* CB[6], has been synthesized [75]. As an example of a host-guest system may be mentioned **118** in which viologen (**119**) is a guest, and CB[7] serves as a host [76].





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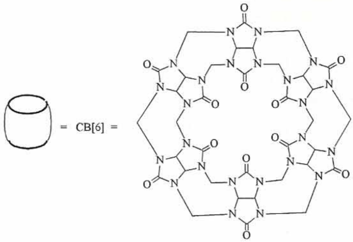
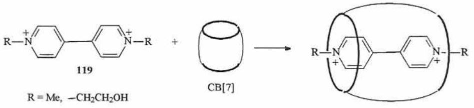




118

6. Applications of quaternary azaaromatics

Quaternary azaaromatics are promising for a number of applications such as sensors [77, 78], electrooptic chromophores [79], hydrogels [80], surfactants [81] or corrosion inhibitors [82]; among examples it should be noted that compound (**120**) [83] shows NLO properties and quaternary salts (**121**) and (**122**) [84] are dyes.

In the search for optical sensors for glucose useful in the diabetes treatment, the ability of systems containing boronic acid moieties to reversible formation of complexes with monosaccharides was applied. In these methods the saccharide concentration is determined by fluorescence intensity changes [85].

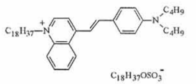
It was observed that viologen (**123**) efficiently quenches fluorescence of the dye pyranin (**124**). Viologen (**123**) and pyranin (**124**) in the absence of saccharide form the 1:1 complex which is not fluorescent. However when **123** binds to saccharide the complex decomposes, and as a result the fluorescence appears. This method is convenient due to the absorption in visible region in aqueous solution at pH 7.4 at physiological glucose concentrations.

Another glucose sensor is the water soluble quaternary salt (**125**), obtained in the reaction of protected 3-pyridineboronic acid (**126**) with anthracene derivative (**127**) [86]. The quaternary salt (**128**) formed was deprotected by treatment with aqueous acetone.

The obtained boronic acid derivative (**129**), crystallizing with one acetone molecule was recrystallized from methanol. The formed ester (**130**) upon hydrolysis affords the quaternary salt **125**.

The aqueous solution of **125** and glucose forms 1:1 complex, showing stronger fluorescence than that of **125** itself. The selectivity of the sensor (**125**) towards glucose is higher than in the case of fructose and galactose [86].

It was established that the salt (**131**) may be used as a receptor of ammonium and carboxylic groups of α-aminoacids. This behavior enables the transport of amino acids through a liquid $CHCl_3$ membrane [87].



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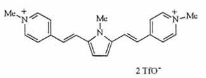

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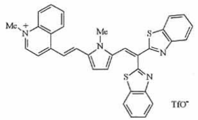

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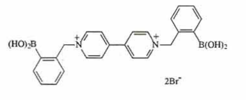

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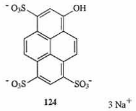

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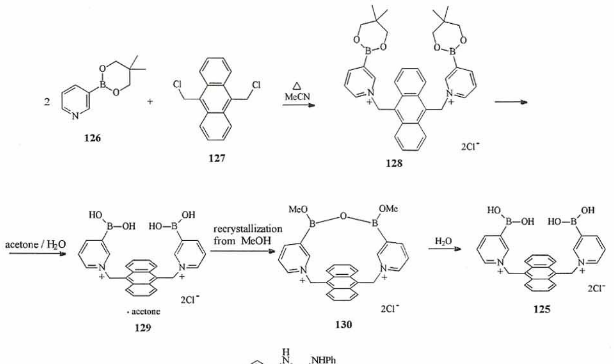
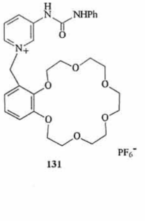


126 **127** **128** **129** **130** **125**



131

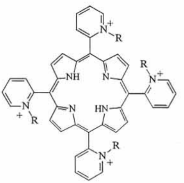
7. Porphyrins bearing quaternary azaaromatics

Due to their various applications, porphyrins containing quaternary groups in their molecule are now intensively studied [88–92]. These compounds are obtained by quaternization of pyridylporphyrins, so free bases as metallopyridylporphyrins. Some quaternary manganese pyridylporphyrins are model systems for enzymes; among them one should mention derivatives of **132** [93] for haloperoxidase, derivatives of **133** [94] for peroxide dismutase, and derivatives of **134** [95] for P450.

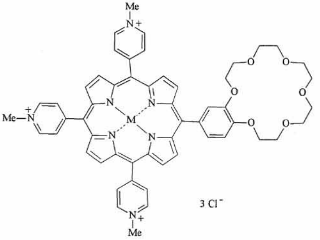
It was established that water soluble quaternary pyridinioporphyrins **135a-c**, bearing a crown ether moiety are receptors of peptides, *e.g.* Gly, Gly; Gly, Phe; Gly, Gly, Gly; Gly, Gly, Phe; Gly, Phe, Gly; Gly, Gly, Gly, Gly [96].

Systems of two porphyrins (**136**) and (**137**), forming ion pairs may serve as artificial models of photosynthesis; an example is the double system (**138**), consisting of two molecules of porphyrins (**136**) and (**137**) bearing differently charged substituents [97].

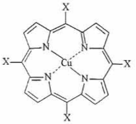
In the search for receptors of anions, the double porphyrinic system (**139**) was synthesized; it has two centers binding anions, each of them bearing a pair of quaternary pyridinium groups [98]. The dianion of tartrate (**140**) was used as a guest molecule [98]. The circular dichroism spectroscopy analysis has shown that **139** forms with **140** a 1:2 complex. Such systems are promising for the construction of molecular switches.

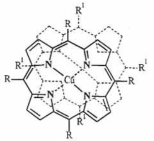


	R
132	Me
133	Et
134	$C_{14}H_{29}$



		M
	a	2H
135	**b**	Zn
	c	Cu





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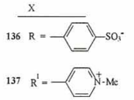

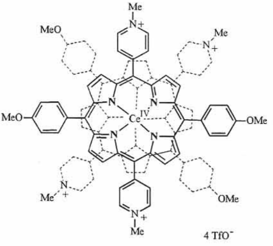

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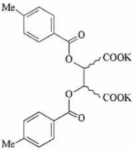


140

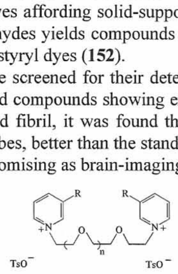
8. Biological activities of quaternary azaaromatics

Numerous works concern biological activities of quaternary azaaromatics [99–102], for example compounds (**141**) and (**142**) showing antituberculous activities [103] were investigated, and the synthesis of ceftazidime (**143**) and its derivatives has been reported [104].

In the study of syntheses and biological activities of bispyridinium cyclophanes as choline kinase (Cho K) inhibitors it was established that compound (**144**) is a potent human ChoK inhibitor (IC_{50} of 0.3 μM) [105]. Bisquaternary oximes (**145**) are reactivators of cyclosarin-inhibited acetylcholinesterase, among them **145b** showing a higher activity [106].

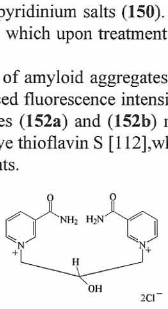
In the search for amyloid sensors, a library of 320 fluorescent styryl dyes was prepared by solid-phase chemistry [107]. Amyloids result from protein misfolding leading to fibrillar deposits in tissues; they cause a large number of protein-misfolding diseases [108, 109]. The solid-phase synthesis of styryl dyes was performed using 2-chlorotrityl resin (**146**) which with thionyl chloride affords **147**. Its treatment with aminoalcohols leads to alcohols (**148**) which were mesylated to give **149**. They react with pyridine derivatives affording solid-supported pyridinium salts (**150**). The condensation of **150** with aldehydes yields compounds (**151**) which upon treatment with TFA release from the resin as styryl dyes (**152**).

The dyes were screened for their detection of amyloid aggregates [110, 111]. From among 13 selected compounds showing enhanced fluorescence intensities upon addition of insulin amyloid fibril, it was found that dyes (**152a**) and (**152b**) may serve as convenient assay probes, better than the standard dye thioflavin S [112],whereas dyes (**152c**) and (**152d**) are promising as brain-imaging agents.



	R	n
a	H	1
b	$CONH_2$	0 - 2

141



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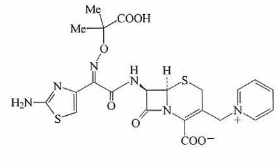

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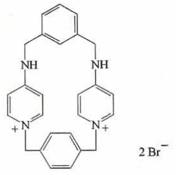

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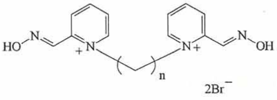
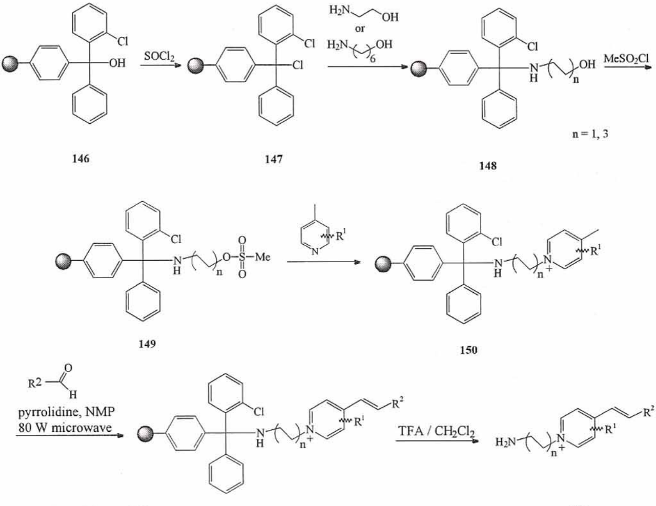


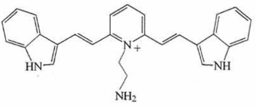
	n
a	1
b	2

145

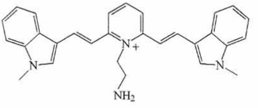


146 **147** **148** **149** **150** **151** **152**

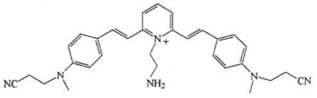
NMP = N-methylpyrrolidine



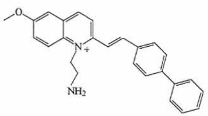
152a



152b



152c



152d

Conclusion

The chemistry of quaternary azaaromatics is studied intensively, the rapid development of this research area has its reflection in numerous works [113–120]. Having in view the enormous number of reports concerning quaternary azaaromatics, the present review only highlights the main features of investigation of this class.

One should point out the important role of quaternary azaaromatics as building blocks of rotaxanes [3] and catenanes [2] promising in the design of molecular machines, viologens [116, 117] deserving here a special attention.

Quaternary azaaromatics binding DNA [118], among them porphyrins [119, 120], are of a great interest, as well as compounds showing biological activities which may find application as drugs [100].

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Małgorzata Deska

CHEMIA CZWARTORZĘDOWYCH ZWIĄZKÓW AZAAROMATYCZNYCH I POKREWNYCH UKŁADÓW

Streszczenie: W artykule na temat czwartorzędowych związków azaaromatycznych w pierwszych trzech rozdziałach omówiono ich syntezy, reaktywność

i właściwości fizykochemiczne; w czwartym i piątym rozdziale przedstawiono wiologeny i wybrane przykłady supramolekularnych układów. W końcowych rozdziałach opisano możliwości zastosowań i czynność biologiczną czwartorzędowych związków azaaromatycznych oraz scharakteryzowano porfiryny zawierające takie układy.