PRACE NAUKOWE Akademii im. Jana Długosza w Częstochowie
Seria: CHEMIA I OCHRONA ŚRODOWISKA z. IX, 2005, ss. 115–124

Wanda Śliwa*
Barbara Dondela
Lidia Chrząstek
Jan Długosz University of Częstochowa, Institute of Chemistry and Environmental Protection
42-201 Częstochowa, Armii Krajowej Ave 13/15
***e-mail:** w. sliwa @ ajd. czest. pl*

PHYSICOCHEMICAL PROPERTIES AND APPLICATIONS OF QUATERNARY AZAAROMATICS

Abstract: In the paper physicochemical properties of selected quaternary azaaromatics are described, followed by their possible applications, pointing out the use of these compounds as synthons in chemical reactions.

Introduction

Quaternary azaaromatics [1–5] are intensively studied in view of their physicochemical properties [6–9] and variety of applications, e.g. as synthons in chemical reactions [10–12], as components of supramolecular systems [13–18] as well as ionic liquids [19], surfactants [20], catalysts [21] or DNA intercalators [3,22].

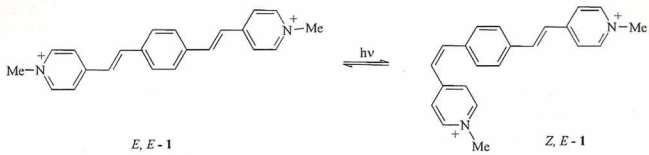
Numerous reports concern viologens [23–26] and azaaromatic betaines [27–30]; diazaphenanthrenes and their quaternary salts [1,31–33] are a research topic of our laboratory.

In the first part of the paper physicochemical properties of quaternary azaaromatics are briefly presented, and in the second one the use of these compounds as synthons in chemical reactions and their other application possibilities are described.

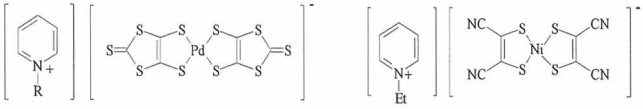
Since the amount of reports concerning quaternary azaaromatics is enormous, in the paper only selected examples of these species are taken into account.

1. Physicochemical properties of quaternary azaaromatics

In the study of the photoisomerization of distilbazolium **1** it was established that the presence of DNA favours formation of the *E,E* isomer [34].



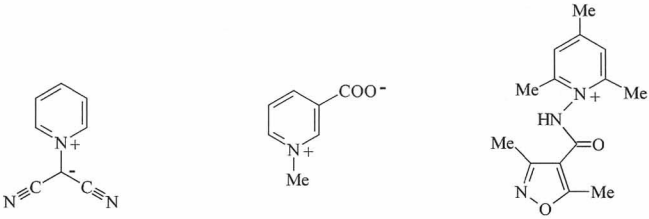
Electrochemical properties of CT complexes **2a,b** [35] and **3** [36,37] have been investigated.



	R
2 a	$C_{12}H_{25}$
b	$C_{18}H_{37}$

3

The structural examination of ylide **4** has been made using IR spectroscopy; experimental results are in accordance with those calculated by *ab initio* methods [38,39].

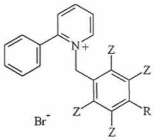


4 **5** **6**

The crystal structure of the complex of trigonelline **5** with perchloric acid $(\mathbf{5}\cdot HClO_4)_2$ was determined [40]. The observed values agree well with geometry data optimized by MP2/6-31G(d,p) and B3LYP/6-31G(d,p) approaches.

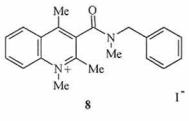
In the search for antibacterial isoxazole derivatives, compound **6** was synthesized and its structure investigated using DFT (B3LYP) calculations [41].

For pyridinium **7** [42,43] and quinolinium **8** [44] quaternary salts the crystalline structure has been determined, and for viologen derivative **9** [45] the results of ^{1}H NMR have been discussed.

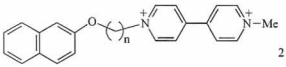


7

R	Z
H	H
OMe	H
CN	H
CF_3	H
CF_3	F
F	F

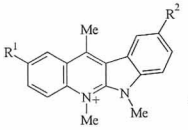


8 I^-



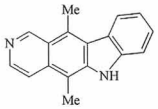
9 $2\,Cl^-$ n = 3, 5, 7, 9, 12

In the study of antineoplastic species, the structure of compounds **10**, which are analogues of ellipticine **11** has been investigated using ^1H and ^{13}C NMR spectroscopy[46,47].



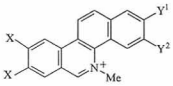
10 $MeSO_4^-$

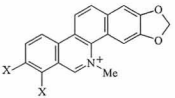
	R^1	R^2
a	H	H
b	Me	H
c	H	Me
d	Me	Me
e	OMe	H
f	H	OMe
g	F	H



11
ellipticine

These methods served also for analysis of quaternary benzo[c]phenanthridinium alkaloids – fagaronine, nitidine, chelerythrine and sanguinarine **12-15** and related compounds; their geometry was optimized using *ab initio* methods [48].



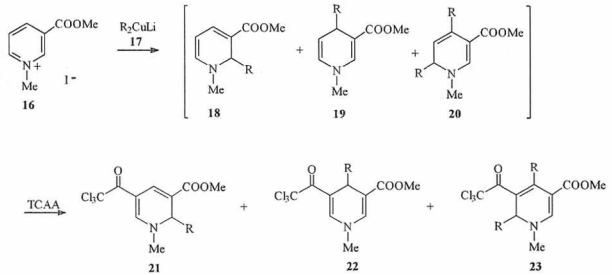


		X	Y^1	Y^2
12	fagaronine	OMe	OH	OMe
13	nitidine	OMe	$-OCH_2O-$	

		X	X
14	chelerythrine	OMe	OMe
15	sanguinarine	$-OCH_2O-$	

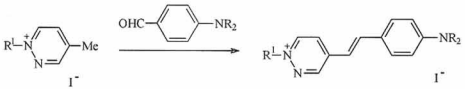
2. Application of quaternary azaaromatics as synthons in chemical reactions

It was established that pyridinium iodide **16** reacts with organocopper compounds **17** forming intermediates **18-20**, which were acylated with trichloroacetic anhydride to give dihydropyridines **21-23** [49].



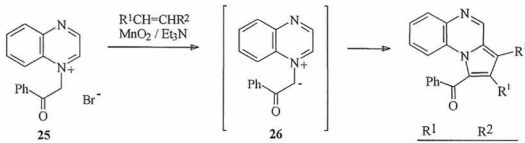
R = Me, Bu, CH_2=CH- , CH_2=CH-CH_2-

In the search for NLO (nonlinear optics) materials, following reaction leading to quaternary salts **24a-d** has been made; the products showed to have NLO properties, the best in the case of **24a** [50].



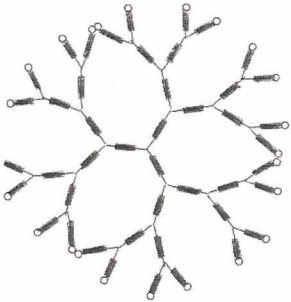
	R^1	R
a	Me	$C_{16}H_{33}$
b	$C_{18}H_{37}$	Me
24 c	$C_{18}H_{37}$	Et
d	$C_{18}H_{37}$	Bu

Quinoxalinium bromide **25** undergoes 1,3-dipolar cycloaddition with alkene derivatives in the presence of MnO_2. Reaction proceeds *via* the primarily formed ylide **26** affording pyrrolo[1,2-a]quinoxalines **27a-c** [51-53].



	R^1	R^2
a	H	CN
27 b	H	COOMe
c	COOEt	COOEt

In the study of dendrimers bearing redox groups [54,55], the viologen dendrimer **28** containing 45 4,4'-bipyridinium units has been obtained and investigated in view of the existing intramolecular CT interaction [56]. The synthesis begins with the reaction of mesitylene derivative **29**, serving as a core, with compound **30**, followed by the repetition process up to the formation of dendrimer **28**.



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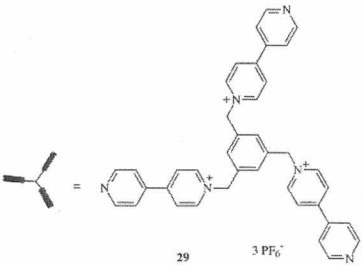
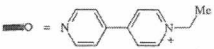
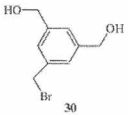


29 3 PF_6^-

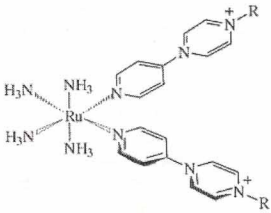




30

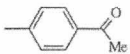
3. Other applications of quaternary azaaromatics

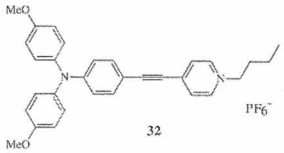
In the search for NLO chromophores it was established that the viologen derivatives **31** [57] as well as acetylenic compounds **32-35** [58] show such properties.



4 PF_6^-

31

a	Me
b	Ph
c	
d	



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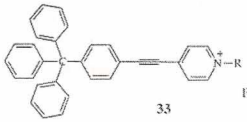

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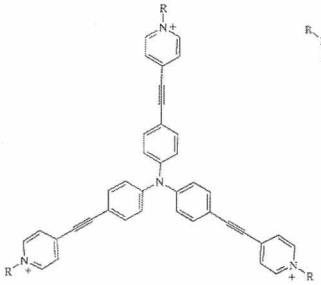
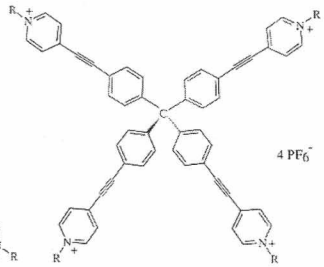


34 3 PF_6^-



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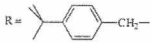
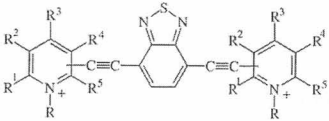


Bipyridinium salts **36** are useful as photocatalysts and luminescence materials [59].

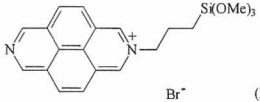


2 Br^-

R = alkyl, benzyl, $SiMe_3$

R^1-R^5 = H or C_1-C_{10} alkyl

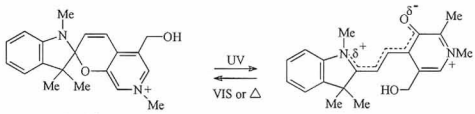
It was observed that 2,7-diazapyrenium salts **37** and **38** [60] may incorporate into silicon aerogels; the salt **37** is promising for the construction of luminescent sensors for oxygen [61].



37

38

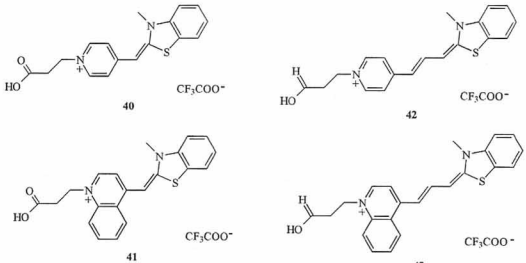
Photochromism of quaternary salt **39** has been investigated. Photochromic compounds are promising for possible applications in optoelectronic devices [62–64]. Irradiation of **39** leads to equilibrium between its closed and open forms, **39a** and **39b**, respectively[62–64].



closed form
39a

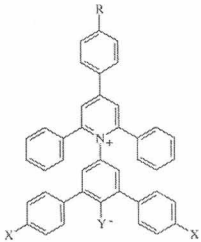
open form
39b

Four cyanine dyes **40-43** have been obtained by the solid-phase synthesis. They interact with DNA; upon intercalation the strong fluorescence enhancement occurs [65].



40 **42** **41** **43**

The Dimroth-Reichardt betaine **44a** used often for the determination of solvent polarity shows a strong negative solvatochromism, *i.e.* the blue shift of UV-VIS spectrum accompanying the increase of the solvent polarity [66].



		R	X	Y
	a	H	H	O
44	b	H	*t*-Bu	O
	c	H	H	S

The sulfur analogue of **44a**, *i.e.* **44c** shows more negative solvatochromism than **44a**, however, **44c** is unstable, readily forming disulfide which is not solvatochromic [66].

Other solvatochromic dyes bearing quaternary azaaromatic moieties have been investigated and the models of solute-solvent interaction are proposed [66].

Conclusion

Due to their interesting properties and promising application possibilities, quaternary azaaromatics are recently a topic of numerous reports [67-70]. In the above paper only selected, representative examples of these compounds have been described.

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Wanda Śliwa*
Barbara Dondela
Lidia Chrząstek

FIZYKOCHEMICZNE WŁAŚCIWOŚCI ORAZ MOŻLIWOŚCI ZASTOSOWAŃ CZWARTORZĘDOWYCH SOLI ZWIĄZKÓW AZAAROMATYCZNYCH

Streszczenie: W artykule przedstawiono właściwości fizykochemiczne wybranych czwartorzędowych soli związków azaaromatycznych oraz możliwości ich zastosowań, podkreślając ich użyteczność jako syntonów w reakcjach chemicznych.