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Effect of the Medium Acidity on the Photophysical Characteristics of some 2-Aryl- and 2-Hetaryl-benzothiazoles

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ABSTRACT

The absorption and fluorescence spectral characteristics of 2-aryl- and 2-hetaryl-benzothiazoles and their protonated forms in solution were studied. The influence of structural modifications on the position of their absorption and fluorescence maxima, as well as interesting features with respect to competition in protonation between the benzothiazole and aniline or hetaryl nitrogen atom in the ground (S_0) *state has been studied. The influence of pH on the absorption and the emission spectra of all the compounds has been investigated in order to identify the ground state species present as a function of acidity.* © *1997 Elsevier Science Ltd*

Keywords: protonation, absorption, fluorescence,

INTRODUCTION

The pH dependence of the photophysical and photochemical behaviour of organic compounds has been studied by a number of authors in relation to the effect of substitution on ground and excited state acidity constants [1–3]. The interesting and often unusual photochemical and photophysical properties of compounds such as 2-arylbenzothiazoles could be attributed to the presence in their molecules of two different chromophores—the benzothiazole moiety and the substituted aromatic ring. The influence of the n-electrons of the N and S atoms in the azole ring leads to a substantial increase in

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the energy of the S, (nπ^*) excited state; the lowest energy excited singlet state becomes a π–π^* type and the spectral properties of 2-arylbenzothiazoles resemble these of stilbene.

2-Arylbenzothiazoles are used as organic luminophores, thermo- and LTV-stabilizers for polymer materials and diazotype materials [4–7].

Upon photoexcitation the acidity (basicity of the donor) acceptor groups of the compounds investigated increases in accordance to Forster's theory [8, 9]. The electron donating and electron withdrawing groups of these molecules in the ground state behave in a manner similar to those in monofunctional molecules. It has been observed however [10], that the increase in acidity of an electron donating group and the increase in basicity of an electron withdrawing group in the same electronically excited molecule are so large that the order of ionization of the two groups is reversed with respect to the normal order observed in the ground state. This could be due to the change in the charge densities at these functional groups in the excited singlet state. The effect of this change might be the selective protonation and the formation of a species in the excited state, which may be different to the species present in the ground state. In this respect, investigation of the spectral properties of the protonated forms of 2-arylbenzothiazoles is of great interest.

The absorption and fluorescence characteristics of some 2-aryl- and 2-hetarylbenzothiazoles in solution with respect to the nature of the substituents and the polarity of the solvents have been recently published [11].

The aims of the present work are:

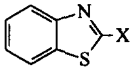
(a) (i) to study the effect of the medium acidity on the photophysical characteristics of 2-aryl- and 2-hetarylbenzothiazoles;
(b) (ii) to identify the various protonated species formed in solution;
(c) (iii) to determine the ground and excited state species present at various acidities as a function of the different basicity of the functional groups.

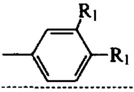
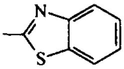
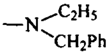
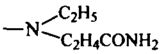
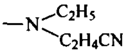
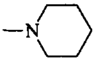
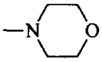
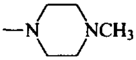
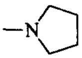
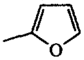
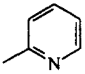
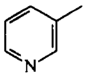
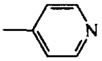
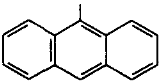
EXPERIMENTAL DETAILS

Table 1 shows the structure of the compounds investigated, synthesised according to [10].

The absorption spectra were recorded on Specord UV–Vis and Specord M40 (Carl Zeiss, Jena). The corrected fluorescence spectra were taken on a Spectrofluorimeter Perkin Elmer MPF44. The fluorescence quantum yields (Q_f) were measured relative to 3-aminophthalimide ($Q_f = 0.6$ in ethanol) [12]. The solvents used were of spectral grade.

TABLE 1
Compounds Investigated and Corresponding Substituents



No	X	R_1	R_2
			
1.		$-H$	$-H$
2.		$-CH_3$	$-H$
3.			$-H$
4.		$-N(CH_3)_2$	$-H$
5.		$-N(C_2H_5)_2$	$-H$
6.		 $-N(C_2H_5)(CH_2Ph)$	$-H$
7.		 $-N(C_2H_5)(C_2H_4CONH_2)$	$-H$
8.		 $-N(C_2H_5)(C_2H_4CN)$	$-H$
9.		$-NHCOCH_3$	$-H$
10.			$-H$
11.			$-H$
12.			$-H$
13.		$-O-CH_2-O-$	
14.			$-H$
15.			
16.			
17.			
18.			
19.			

RESULTS AND DISCUSSION

Absorption and fluorescence spectral characteristics in neutral solution

The absorption spectra of the investigated compounds in neutral solution consist of two absorption bands centered at around 210–230 nm (for all of them) and at 340–365 nm (for alkylamino substitution in the *p*-position of the phenyl ring if the 2-phenybenzothiazoles) (Fig. 1).

The position of the longest wavelength absorption maximum depends on the nature of the substituent in position 2 of the benzothiazole molecule [11] (Table 2). The reason for the substantial red shift in the investigated compounds, relative to those of unsubstituted 2-phenylbenzothiazole, is the strong inductive and conjugative effect of the amino and the dialkylamino substituent in the p-position of the phenyl ring. The bathochromic shift is relatable to the an increase of the molar absorptivity, this increase corresponding to the strength of the electron donating substituent.

All the studied compounds (except for N1) fluoresce in ethanol at room temperature (Table 3). Their fluorescence Franck–Condon transitions lie between 380 and 430 nm [11]. The excitation spectra are identical with the

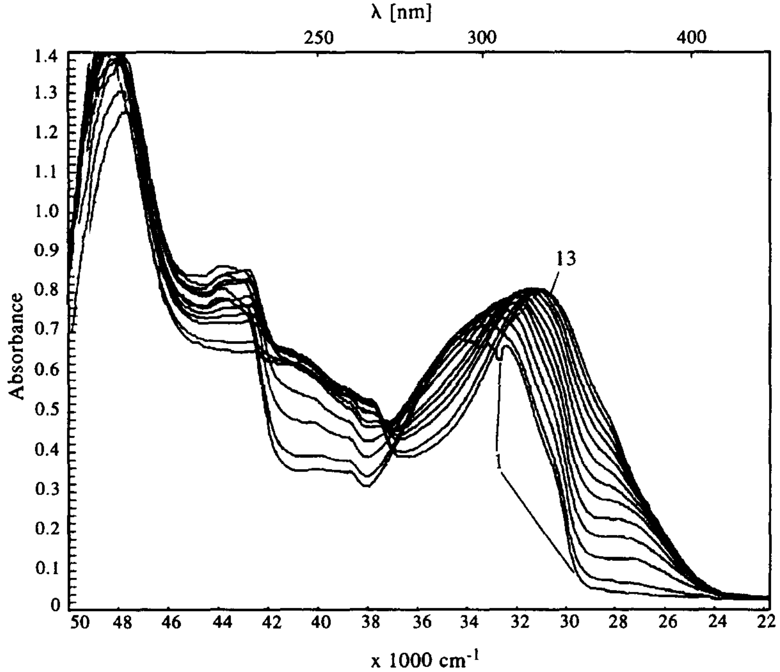


Fig. 1. Absorption spectrum of compound N1 in EtOH at room temperature, conc. 0.5×10^{-4} mol^{-1}; curve 1-without HCl curve 13-with 0.104 g HCl.

TABLE 2

Absorption Maxima of the Benzothiazoles in Neutral and Acid Medium. The Numbers of the Compounds Correspond to These Given in Table 1.

N	λ_{abs} *[nm] EtOH*	λ_{abs}*[nm] EtOH+HCl*	$\Delta\lambda_{abs}$ *[nm]*
1.	300	320	20
2.	305	331	26
3.	302	321	19
4.	359	312,440	81
5.	361	313,440	79
6.	361	315,438	77
7.	363	440	77
8.	347	310,426	79
9.	325	370	45
10.	355	307,436	81
11.	344	305,423	79
12.	347	340,409	62
13.	328	371	43
14.	365	320,438	73
15.	322	358	36
16.	308	330	22
17.	300	317	17
18.	301	342	41
19.	370	—	—

TABLE 3

Fluorescence Maxima of the Benzothiazoles in Neutral and Acid Medium. The Numbers of the Compounds Correspond to These Given in Table 1.

N	λ_{fl} *[nm] EtOH*	λ_{fl} *[nm] EtOH+HCl*	$\Delta\lambda_{fl}$ *[nm]*
3.	365	500	135
4.	428	480	52
8.	418	475	57
10.	430	480	50
11.	425	478	53
12.	422	480	58
16.	378	530	152
17.	370	530	160
18.	395	535	140

absorption spectra. The fluorescence quantum yield of the p-alkylamino substituted compounds is between 0.5 and 0.7. The 2-aryl-benzothiazoles in which the phenyl ring in position 2 is replaced by a pyridyl or an anthracenyl fragment have much lower $Q_f \sim 0.01$.

Effect of pH on the absorption and fluorescence spectra.

The absorption and fluorescence spectra of 2-aryl- and 2-hetarylbenzothiazoles in ethanol solutions containing various amounts of HCl were studied.

Figure 2 (parts a and b) show the changes in the absorption and fluorescence spectra of compound **16** in ethanol with increasing the amount of HCl. It can be seen from Fig. 1 and Fig. 2a that upon increasing the amount of HCl the absorption maximum at 360 nm characteristic of the starting 2-aryl- and 2-hetarylbenzothiazoles decreases, while new bands in the region 300–330 nm and 410–430 nm region appear.

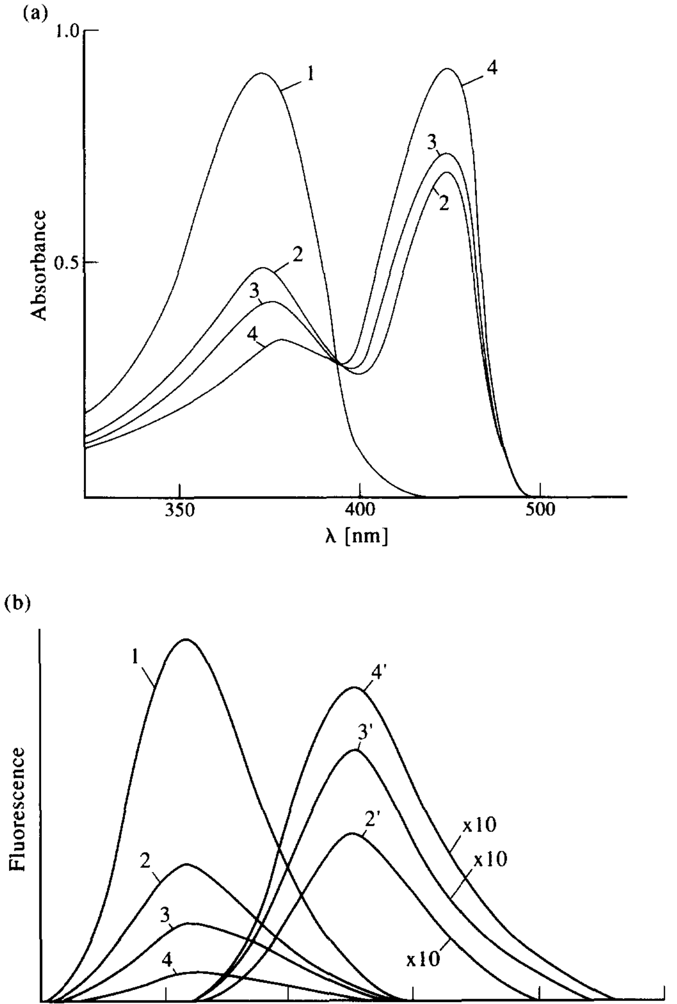


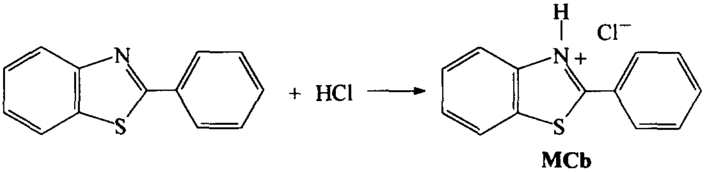
Fig. 2. a. Absorption spectrum of compound N14, conc. 0.5×10^{-4} mol.l^{-1}; curve 1-in EtOH; curve 2-in EtOH + 0.01 g HCl; curve 3-in EtOH + 0.02 g HCl curve 4-in EtOH + 0.04 g HCl.b. Fluorescence spectrum of compound N14, conc. 0.5×10^{-4} mol.l^{-1} curve 1-in EtOH; curve 2-in EtOH + 0.01 g HCl curve 3-in EtOH + 0.02 g HCl curve 4-in EtOH + 0.04 g HCl.

Simultaneously, the fluorescence band at around 430 nm disappears (Fig. 2b). Excitation at the newly arisen absorption band at 430 nm leads to the appearance of a new fluorescence maximum at around 480 nm for the p-alkylamino substituted compounds. Its intensity is approximately ten times lower in comparison to that at 430 nm, which is characteristic of the studied benzothiazoles in the absence of HCl (Fig. 2b). Upon neutralization of these solutions with 5% aqueous NaOH, the absorption and the fluorescence bands of the starting compounds appear again.

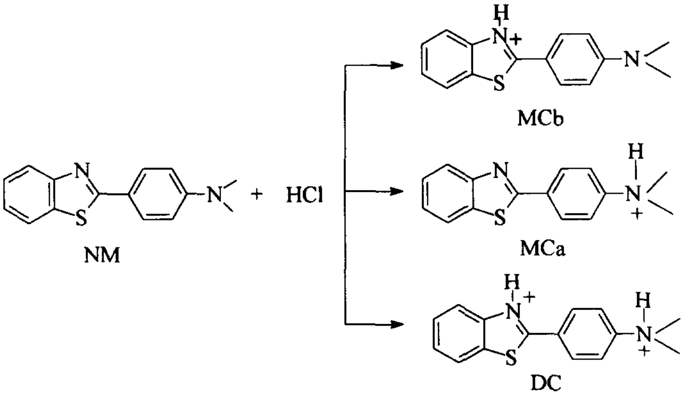
The observed changes in the position of the longest wavelength absorption band and of the fluorescence maxima with varying pH could be interpreted in terms of absorption and emission from protonated and unprotonated species.

The formation of three ground-state species—the neutral molecule I (NM), the monocation II (MC /a/ or /b/) and the dication III (DC) can be assumed. Two types of interactions could take place between benzothiazoles and HCl (Scheme 1 and Scheme 2).

The possibility the formation of the protonated forms $BH^+Cl^-$is associated with the different basicity of the nitrogen atoms: the first base center is the N-atom in the benzothiazole ring, and the second base center is the N-containing substituent in *p*-position of the phenyl ring.



Scheme 1



Scheme 2

The predominant factor responsible for the changes in the absorbance with increasing the amount of alcocholic HCl is the protonation of the basic centers in the molecules.

For compound **1** (2-phenylbenzothiazole) there is only one possibility for protonation, i.e., at the N atom in the benzothiazole ring, which is an electron acceptor (Scheme 1). For the p-alkylamino substituted benzothiazoles, another base center is present, and there are then two possibilities for protonation, one at the N atom in the benzothiazole fragment, and the other at the N atom in the alkylamino group (Scheme 2).

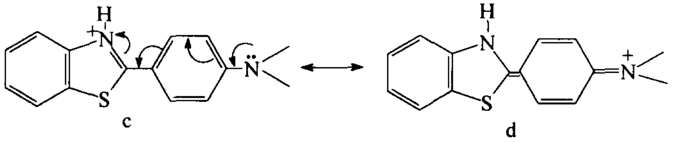
The red shift of the longest wavelength absorption maximum of the formed monocation in comparison to that of the neutral form shows (Table 2) that the first protonation in the ground state occurs at the benzothiazole N atom (MCb). This is in line with the theory that electron donating groups such as dialkylamino, increase the basicity of the molecule and, respectively, of the N atom in the benzothiazole fragment [13] (Scheme 3).

At the same time, the blue shift of the shorter wavelength absorption maximum of the investigated compounds shows (Table 2), that the second protonation step in the ground state occurs at the dialkylamino group (MCa). The protonation of the p-aromatic N atom eliminates the participation of the fragment, in conjugation (Scheme 4), and the absorption spectrum then becomes similar to that of the unsubstituted 2-phenylbenzothiazole (λ_{max} 300–320 nm).

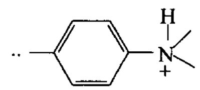
This shorter wavelength absorption band usually disappears with addition of HCl to the solution. This fact could be explained by the strong electron acceptor action of the protonated benzothiazole N atom, which could destroy the initially formed monocation (Scheme 5).

These results indicate that the monocations are involved in the equilibrium, as presented at Scheme 6.

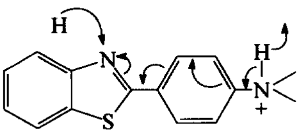
It could be supposed that the deprotonation equilibrium constant at the dialkylamino group is much larger than that of the protonated N-benzothiazole atom.



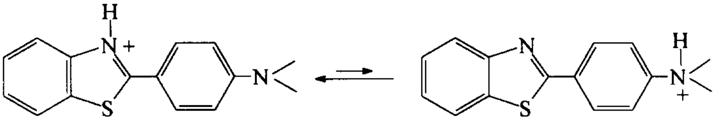
Scheme 3



Scheme 4



Scheme 5



Scheme 6

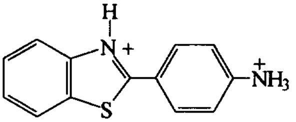
It is very important to note that the appearance of the shorter wavelength absorption band can be caused partly by disturbance of the coplanarity between the benzothiazole ring and the aromatic ring in the protonated form, according to Kiprianov [14] and, thus, by the impossibility of conjugation between both chromophoric parts.

The neutral species have fluorescence maxima at 400–430 nm [11]. In the presence of HCl this fluorescence band disappears and a new maximum with lower intensity appears between 480 and 500 nm (Table 3). Such a bathochromic shift of λ_{fl} is characteristic of the protonation of molecules in which H^+ is connected with the electron coupling of the heteroatom present in the conjugated double bond [15].

If the protonation of the starting compounds was at the dialkylamino group, similar to other aromatic amines,[16] the fluorescence maximum shoud have been blue shifted as was the absorption maximum. This result is understandable in terms of the above mentioned conclusions that emission occurs only from the protonated form MCb.

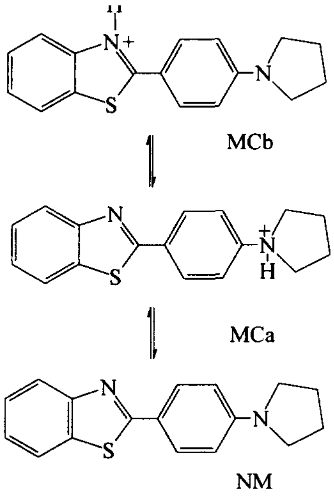
It could be assumed that the fluorescence maximum of the dication DC must be at shorter wavelenghth than that of the neutral molecule (400–430 nm), and also that of the monocation (480–500 nm). For example, λ_{fl} of the dication, presented in Scheme 7, is at 405 nm [17].

Our experimental results show that the DC is absent in the system. This is readily explicable, since the basicity of the imino fragment is very low.



Scheme 7

For compound **14**



Scheme 8

It is interesting to note the possibility of the existence of tautomerism. In the presence of HCl, in the S_0 state only the monocation MCb exists. The fluorescence spectrum has one maximum at around 480–500 nm, which corresponds to the presence of MCb. Simultaneously the presence of the absorption band at shorter wavelenghth region (300–330 nm) could be connected with MCa.

This indicates that there could be an equilibrium between these two species (the monocation and the dication) and the neutral form (Scheme 8).

The disappearance of the absorption maximum at 365 nm with adding HCl shows that the species (b) dissociate to the neutral form, and the dissociation, as could be expected, increases with increase in the hydrogen accepting tendency of the N atom in the benzothiazole fragment.

It was observed that the increase in acidity of the amino or dialkylamino groups, and in the basicity of the heterocyclic nitrogen atom, is so large that the order of protonation of these two groups is reversed with respect to the normal order in the ground state. Since both groups, the protonated dialkylamino group MCa and the nitrogen atom in the heterocycle MCb are widely separated, the tautomerism should be biprotonic.

There are clear structural effects on the absorption and fluorescence behaviour of the protonated benzothiazoles. The reason for this could be the simple structure of the monocation, and the impossibility for the substituents to influence the system.

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