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Absorption and Fluorescence Characteristics of some 2-Aryl- and 2-Hetaryl-Benzothiazoles

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ABSTRACT

The absorption and fluorescence characteristics of some 2-aryl- and 2-hetaryl-benzothiazoles were studied with respect to the nature of the substituents and the polarity of the solvents. The longest wavelength absorption maximum of these compounds is in the region 27 000–34 000 cm^{-1}. The PPP-SCF-CI quantum chemical calculations show that they result from a singlet π–π^* transition. The fluorescence Franck–Condon transition is between 19 000 and 28 000 cm^{-1}. The fluorescence quantum yield of most of the investigated benzothiazoles exceeds 0·5. The compounds do not phosphoresce in frozen ethanol solutions at 77 K.

1 INTRODUCTION

2-Arylbenzothiazoles are widely used as organic luminophores,[1] thermo- and UV-stabilizers for polymer materials[2–4] and diazotype materials.[5] An improved method for the synthesis of 2-aryl- and 2-hetaryl-benzothiazoles has been recently published.[6]

The aim of this work is to study the absorption and fluorescence

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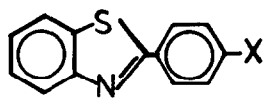
characteristics of benzothiazoles substituted in the 2-position with respect to the nature of the substituents and the polarity of the solvents. Investigations of their photochemical and photophysical properties in a polymer matrix are in progress. Some of the benzothiazoles have been described in Ref. 6. These compounds are also of interest as organic luminophores.[7,8]

TABLE 1
Compounds Investigated and Corresponding Substituents



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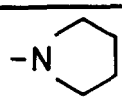
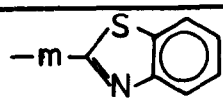
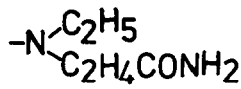
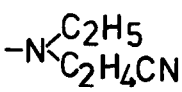
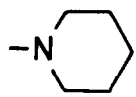
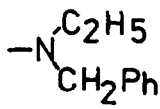
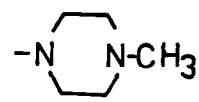
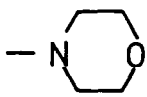
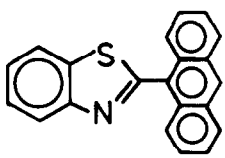
1.		6.	
2.		7.	$-N(CH_3)_2$
3.		8.	$-N(C_2H_5)_2$
4.		9.	
5.		10.	
		11.	$-NHCOCH_3$



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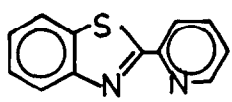

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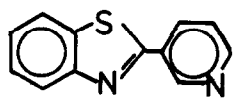

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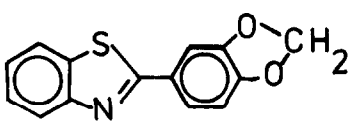

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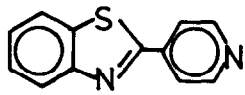

16.

2 EXPERIMENTAL

Table 1 shows the structure of the compounds investigated (synthesized according to Ref. 6) and the corresponding substituents. Compounds 1–6 are newly synthesized.[6]

Absorption spectra were recorded on Specord M40 (Carl-Zeiss, Jena). Fluorescence spectra were recorded on a Perkin Elmer MPF 44 spectrofluorimeter. The fluorescence quantum yields Q_f were determined relative to 3-aminophthalimide ($Q_f = 0{\cdot}6$ in ethanol[9]). The natural lifetimes were calculated from the decay curves, measured on a nanosecond spectrofluorimeter PRA-2000 at 293 K. The solvents used were of spectral grade. The PPP-SCF-CI quantum-chemical calculations were done with standard parametrisation.[10,11]

3 RESULTS AND DISCUSSION

2-Arylbenzothiazoles are π-isoelectronic with stilbene.[1] The azole cycle contributes, with its C=N bond, to the π-electron system. The interaction of the n-electrons of the S and the N atoms in the azole ring leads to a substantial increase in the energy of the $n \rightarrow \pi^*$ excited state; the lowest-energy excited singlet state is of a π–π^* nature and the spectral properties of 2-arylbenzothiazoles resemble these of stilbene. Their electronic spectra change in a similar way on elongation of the π-electron system.

The 2-aryl- and 2-hetaryl-benzothiazoles investigated in this present paper have two absorption maxima in the region 43 000–45 000 cm^{-1} and 27 000–34 000 cm^{-1}. The PPP-SCF-CI quantum chemical calculations show that these result from singlet π–π^* transitions. The computed transition energies of some of the investigated compounds (13, 14, 16) are in good agreement with the experimental ones (Table 2). The PPP-SCF-CI quantum chemical calculations were performed with standard parameterisation,[10,11] taking into account all singly excited configurations. There are no substantial changes in the numerical results if the real geometry, determined by crystallographic studies,[12] is taken into account.

The electronic spectra of compound 3 in ethanol and the results of the PPP-SCF-CI quantum chemical calculations are presented in Fig. 1. The vertical lines denote the computed energies of the singlet π–π^* transitions. The heights of the corresponding lines are proportional to the computed oscillator strengths f.

The effect of the substituent X on the longest wavelength absorption maxima, as well as on the energy of the Franck–Condon fluorescence transitions and the fluorescence quantum yield, can be evaluated from the spectral data of compounds 1–16 (Table 3).

TABLE 2

Experimental and Computed Energies in eV of the Longest Wavelength π–π^* Singlet Transitions of 2-Pyridyl-Benzothiazoles. The Numbers Correspond to those in Table 1

Compound	ΔE_{exp}	ΔE_{calc}
13	4·019[a]	3·935
	4·024[b]	
14	4·132[a]	3·971
	4·177[b]	
16	4·114[a]	3·975
	4·193[b]	

[a] In ethanol.
[b] In acetonitrile.

The longest wavelength absorption band of 2-phenyl-benzothiazole is around 33 000 cm^{-1}.[13] As the electron-donating properties of pyridine are similar to those of benzene, it could be expected that the longest wavelength absorption maxima of compounds 13, 14 and 16 (2-pyridyl-benzothiazoles) will be in the same region. The results show (Table 3) that these bands are at about 32 000–33 000 cm^{-1}. The same holds also for compound 6, in which the substituent is in *m*-position of the phenyl ring and does not lead to a prolongation of the conjugated system. The longest wavelength absorption Franck–Condon transitions of compound 6 and 2-phenyl-benzothiazole in ethanol have practically the same energy (33 000 cm^{-1}).

Replacement of the H atom in the *p*-position of the phenyl ring by electron donating substituents leads to a significant bathochromic shift of the longest wavelength absorption band (approximately 4500 cm^{-1}). The

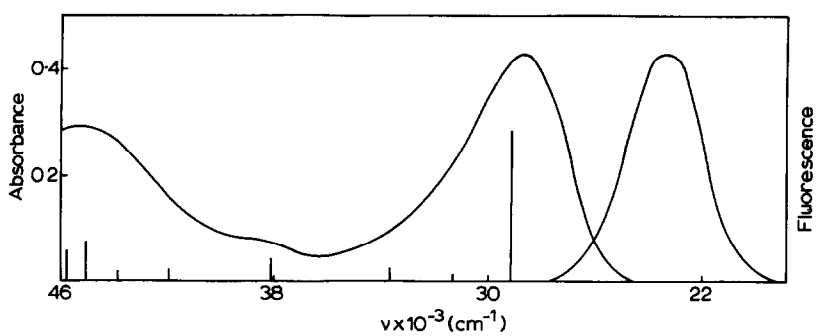

Fig. 1. Electronic spectra of compound 3 in ethanol at 293 K. The vertical lines denote the computed energy of the singlet transitions and the corresponding oscillator strengths.

TABLE 3

Experimental Spectral Characteristics of the Investigated Compounds; the Numbers of the Compounds Correspond to those in Table 1; ν, Frequencies of the Longest Wavelength Absorption and Fluorescence Franck–Condon Transitions in cm^{-1}; Q_f, Fluorescence Quantum Yield; ε, Molar Absorptivity, $[\varepsilon]$ = litre mol^{-1} cm^{-1}; (/), very Poor Solubility

No.	*Ethanol*				*Acetonitrile*			*Cyclohexane*		
	ν^{abs}	ε	ν^{fl}	Q_f	ν^{abs}	ν^{fl}	Q_f	ν^{abs}	ν^{fl}	Q_f
1	27412	43380	23360	0·60	27540	23810	0·52	28380	25000	0·37
2	27578	42930	23530	0·70	27780	23810	0·56	28540	25000	0·35
3	28220	34820	23920	0·72	28380	24390	0·68	29170	25640	0·38
4	28140	32430	23260	0·63	28260	23260	0·50	28940	25000	0·35
5	28850	29760	23700	0·50	28780	23810	0·43	29260	25130	0·28
6	33090	35320	27400	0·26	33210	27030	0·22	33040	27780	0·11
7	27900	40270	23530	0·54	28060	23700	0·53	28780	25320	0·30
8	27730	39360	23700	0·57	27580	23520	0·55	28380	25000	0·31
9	27730	36740	23530	0·64	27980	23810	0·57	28570	25000	0·35
10	29100	36050	23530	0·52	29100	23520	0·51	29580	25130	0·28
11	30730	16580	25970	0·20	30700	26460	0 20	30700	25980	0·12
12	27220	—	19230	0·01	25850	19610	0·01	25850	20000	0·01
13	32420	11790	26320	0·01	32460	26320	0·01	32330	27030	0·01
14	33330	11660	26670	0·01	33690	27030	0·01	32330	28170	0·01
15	30570	22970	25970	0·22	29930	26320	0·14	30660	27030	0·14
16	33180	24170	25640	0·01	33820	25640	0·01	34060	27780	0·01

compound with an anthracene ring in position 2 has a longer conjugated system in comparison with that with a phenyl substituent, and hence its longest wavelength absorption transition is of much lower energy (around $27\,000\,cm^{-1}$).

The effect of solvent polarity on the position of the longest wavelength absorption band is less pronounced than that of the nature of the substituent in the *p*-position of the phenyl ring. Passing from ethanol to cyclohexane, a hypsochromic shift of about $1000\,cm^{-1}$ is observed (Table 3).

The energy of the Franck–Condon fluorescence transitions and the fluorescence quantum yield also depend on the solvent polarity and the nature of the substituent.

Increase of the solvent polarity, as well as replacement of the electron acceptor substituent with an electron-donating one leads to a bathochromic shift of the fluorescence maxima and to higher values of the relative fluorescence quantum yield (Table 3).

Compounds 12, 13, 14 and 16, in which the phenyl ring in position 2 is replaced by a pyridyl- or anthracenyl-group have the lowest fluorescence quantum yields. This could be explained by rotation around the C—C bond between the benzothiazole and the pyridyl-(anthracenyl-) parts of the molecule in the excited state. This rotation could lead to an increase in the probability for non-radiative deactivation of the S_1 (π–π^*) state and, thus, decreasing Q_f. In order to confirm this assumption, quantum-chemical PPP-SCF-CI calculations were made. However, these did not indicate a decrease in the C—C bond order in the first excited π–π^* state, which could lead to easier rotation around it.

The fluorescence quantum yield of 2-pyridyl- and 2-anthracenyl benzothiazoles is not significantly enhanced in frozen ethanol solution at 77°K and in a polymer matrix, when the compounds have a fixed planar structure. Consequently, rotation around the C—C bond in compounds 12, 13, 14 and 16 cannot account for their low Q_f.

The lifetimes τ of the S_1 (π–π^*) state of 2-aryl-benzothiazoles, computed from the fluorescence decay curve, fitted to a monoexponential linear function $I(t) = A \exp(-t/\tau)$ are between 1 and 3 ns.

No phosphorescence was observed for any of the compounds investigated in frozen ethanol solutions at 77 K.

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