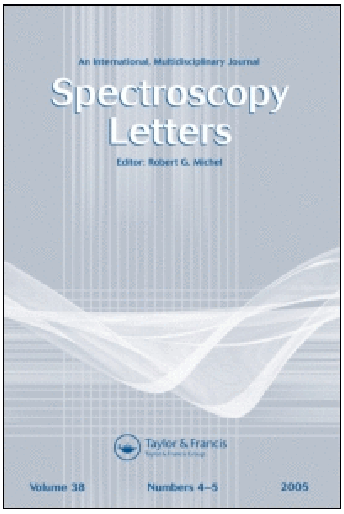

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Tralić-Kulenović, Vesna , Racanè, Livio and Karminski-Zamola, Grace(2003) 'Absorption and Fluorescence Properties of Some Substituted 2-Furylbenzothiazoles and Their Vinylogues in Various Solvents', Spectroscopy Letters, 36: 1, 43 — 50

To link to this Article: DOI: 10.1081/SL-120021172

URL: http://dx.doi.org/10.1081/SL-120021172

SPECTROSCOPY LETTERS
Vol. 36, Nos. 1 & 2, pp. 43–50, 2003

Absorption and Fluorescence Properties of Some Substituted 2-Furylbenzothiazoles and Their Vinylogues in Various Solvents

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ABSTRACT

Absorption and fluorescence emission spectra of six substituted 2-(2-furyl) benzothiazoles and their vinylogues have been studied in different solvents at room temperature. It was found that both the kind of the substituent and the solvent polarity influenced the spectral properties. The ethylenic double bond between the furyl and benzothiazolyl moiety caused a bathochromic shift in the longwave absorption maxima of 1927–3182 cm^{-1} as well as a bathochromic shift in the fluorescence maxima of 2646–3338 cm^{-1}. For substituted 2-(2-furyl)benzothiazoles

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DOI: 10.1081/SL-120021172
0038-7010 (Print); 1532-2289 (Online)

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a linear relationship between solvent polarity and Stokes shift was observed. This group of compounds exhibited higher relative fluorescence quantum efficiency than their vinylogues. The most fluorescent compound among them was 2-(5-phenyl-2-furyl)benzothiazole.

Key Words: Benzothiazole; Fluorescence; Quantum efficiency.

INTRODUCTION

The benzothiazole nucleus has been incorporated into a wide variety of therapeutically important drugs. Among the most promising drugs are sequence-specific ligands such as substituted benzothiazoles.[1,2] These compounds, designed to fit within the structure of DNA, are capable of recognizing DNA sequences. Interaction between drugs and DNA include methods such as intercalation and groove binding. The interactions between these drugs and DNA molecules have been studied using different techniques such as UV-vis absorption spectroscopy, fluorescence spectroscopy and others. Synthetic oligopeptides and oligonucleotides, in their interactions with compounds examined here, induce significant shifts in the UV-vis spectra and large changes in fluorescence intensity.[3] In connection with our recent studies on the synthesis of potential antitumor active heterocyclically substituted benzothiazoles,[4] we have continued studies on the UV-vis absorption and fluorescent properties of substituted benzothiazoles.[5,6] In these papers, we reported on the fluorescence characteristics of some 2-substituted benzothiazoles. It was found that some parameters characterizing the fluorescence of 2-aryl- and 2-heteroaryl-benzothiazoles show a linear relationship against the solvent polarity. Moreover, solvent and substituent effects upon the fluorescence of 2-arylbenzothiazoles and their vinylogues are remarkable, and compounds of the phenyl series exhibit larger fluorescence quantum efficiency then their vinylogues. Therefore, continuing our studies on the fluorescence, in the present work we investigated the effect of solvents on the absorption and emission properties of some previously described 2-(2-furyl)benzothiazoles and their vinylogues.

EXPERIMENTAL

All the benzothiazole derivatives (Figure 1) were previously prepared in our laboratory using the described procedures. Substituted 2-(2-furyl) benzothiazoles (**1**–**6**) were synthesized from corresponding aldehydes and *o*-aminothiophenole, while substituted 1-(2-benzothiazolyl)-2-(2-furyl)ethenes

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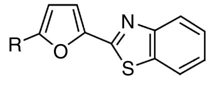		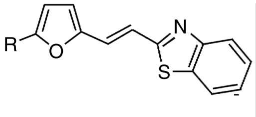	
No.	R	No.	R
1	H	**7**	H
2	CH_3	**8**	CH_3
3	Ph	**9**	Ph
4	Br	**10**	Br
5	I	**11**	I
6	NO_2	**12**	NO_2

Figure 1. Formulae of substituted 2-(2-furyl)benzothiazoles (**1–6**) and their vinylogues (**7–12**).

(**7–12**) were obtained by condensation of corresponding aldehydes with 2-methylbenzothiazole.

Analytical grade ethanol (EtOH), dichloromethane (DCM), dioxane (DX) and cyclohexane (CH) were used for spectroscopic measurements. Ultraviolet absorption spectra were determined on a Perkin-Elmer M-124 spectrophotometer with freshly prepared solutions of 10^{-5} mol dm^{-3} concentrations. Fluorescence spectra, obtained at room temperature on a fluorescence-spectrometer Perkin-Elmer 3000 with 10^{-6}–10^{-7} mol dm^{-3} concentrations of freshly prepared solutions, were corrected using appropriate standards (2-naphthol in Merck acetate buffer[7] or quinine sulphate in perchloric acid[8]). Relative fluorescence quantum efficiencies ϕ_r were calculated relative to quinine sulphat in 0.5 mol dm^{-3} sulphuric acid ($\phi = 0.546$) or antranilic acid in ethanolic solution ($\phi = 0.588$).[9]

RESULTS AND DISCUSSION

The absorption and fluorescence spectral data of substituted 2-(2-furyl)benzothiazoles (**1–6**) and their vinylogues (**7–12**) are given in Table 1 and Table 2. The long wave absorption maxima of compounds (**1–6**) apply from 317–367 nm, and of compounds (**7–12**) from 348–367 nm, in all the solvents that were examined. From the data summarized in both tables it is apparent that both electron-withdrawing and electron-donating groups attached to the furan ring affect the absorption bathochromic shift, in comparison with compounds without the substituent on the furan ring. The ultraviolet absorption maxima of substituted benzothiazolylfurylethenes (**7–12**) are shifted bathochromicaly by 1927–3182 cm^{-1}, in comparison

Table 1. Absorption and emission data for substituted

	Ethanol					Dichlormethane				
No.	λ_{max} (abs) (nm)	ε_{max}	λ_{ex} (nm)	λ_{em} (nm)	ϕ_r	λ_{max} (abs) (nm)	ε_{max}	λ_{ex} (nm)	λ_{em} (nm)	ϕ_r
1	317	34500	315	365	0.093	319	51000	315	363	0.052
						335sh				
2	225	22000	329	378	0.171	328	50500	329	376	0.140
	328	42000				342sh				
3	258	52000	350	410	0.457	355	68000	350	395	0.285
	355	52000				375sh			410	
4	323	46000	325	375	0.084	327	23000	325	375	0.102
						343sh				
5	331	25500	331	380	0.018	331	48000	331	388	0.008
6	220	17800				367	20000	345	400	0.0001
	275	7800	345	405	0.007					
	361	17000								

λ_{max} = absorption maxima; sh = shoulder; ε_{max} = molar absorbtivity; λ_{ex} = excitation maxima;

Table 2. Absorption and emission data for substituted

	Ethanol					Dichlormethane				
No.	λ_{max} (abs) (nm)	ε_{max}	λ_{ex} (nm)	λ_{em} (nm)	ϕ_r	λ_{max} (abs) (nm)	ε_{max}	λ_{ex} (nm)	λ_{em} (nm)	ϕ_r
7	218	35000	335	405	0.0003	353	74500	335	415	0.0003
	352	49000								
8	220	22300	350	420	0.0002	365	47000	350	440	0.0004
	365	30200								
9	270	23500	390	475	0.0013	390	63000	390	440	0.0015
	388	40000				415sh				
	410sh									
10	220	44500	350	420	0.0006	360	94000	350	430	0.0007
	360	61500								
11	362	24500	355	430	0.0011	365	38000	375	440	0.0012
12	300	17000	no fluorescence			395	41000	no fluorescence		
	388	29300								

λ_{max} = absorption maxima; sh = shoulder; ε_{max} = molar absorbtivity; λ_{ex} = excitation maxima;

2-(2-furyl)benzothiazoles in various solvents.

Dioxane					Cyclohexane				
λ_{max} (abs) (nm)	ε_{max}	λ_{ex} (nm)	λ_{em} (nm)	ϕ_r	λ_{max} (abs) (nm)	ε_{max}	λ_{ex} (nm)	λ_{em} (nm)	ϕ_r
319	26000	315	363	0.052	316	75000	315	358	0.017
335sh					332	59000			
327	45000	329	370	0.151	310sh				
342sh					324	63000	329	365	0.100
					340	38000			
355	42500	350	387	0.259	335sh				
375sh			405		352	50000	350	380	0.196
					372	43000		400	
327	41000	325	368	0.044	226	34000			
343sh					323	54800	325	360	0.022
					340	41700			
330	51500	331	375	0.005	329	62000	331	380	0.003
			395					400	
367	28000	345	400	0.0003	345sh		no fluorescence		
					361	36500			
					381	29000			

λ_{em} = emission maxima; ϕ_r = relative fluorescence quantum efficiency.

1-(2-benzothiazolyl)-(2-furyl)ethenes in various solvents.

Dioxane					Cyclohexane				
λ_{max} (abs) (nm)	ε_{max}	λ_{ex} (nm)	λ_{em} (nm)	ϕ_r	λ_{max} (abs) (nm)	ε_{max}	λ_{ex} (nm)	λ_{em} (nm)	ϕ_r
355	51000	335	410	0.0011	348	56000	335	400	0.002
360	35000	350	425	0.0008	357	23500	350	415	0.0026
390	63000	390	440	0.0028	385	66000	390	420	0.0004
412sh					410sh			445	
358	67000	350	425	0.0002	355	63000	350	415	0.005
362	33000	340	420	0.0033	360	60000	340	420	0.0029
393	37000	no fluorescence			368sh		no fluorescence		
					387	73000			
					410sh				

λ_{em} = emission maxima; ϕ_r = relative fluorescence quantum efficiency.

with the corresponding maxima of 2-furylbenzothiazoles (**1–6**). No significant influence of the solvent on the position of absorption maxima is observed, but changing the solvent polarity changes the shapes of absorption curves. Therefore in nonpolar cyclohexane, compounds (**1–4**) and (**6**) exhibit a new absorption maximum at a longer wavelength. The excitation maxima for the compounds of the 2-furyl series (**1–6**) are at 315–350 nm, the emission maxima are at 358–410 nm in all solvents. In ethenyl derivatives (**7–12**) excitation maxima occur at 335–390 nm and emission maxima at 358–410 nm. All substituents in both series of benzothiazoles move the emission maxima bathochromically. A large bathochromic shift (2646–3338 cm^{-1}) is observed by comparing the emission maxima of substituted benzothiazolylfurylethenes (**7–12**) with compounds without an ethylenic bond (**1–6**). With increased solvent polarity the emission maxima of substituted 2-furylbenzothiazoles are moved bathochromically, and in the series of corresponding vinylogues the solvent polarity affects the change of emission maxima, but without any regularity.

Stokes shifts, ν_{ss}, are influenced by changes of solvent polarity Δf. A linear relationship exists that shows correlation between Δf and ν_{ss} for substituted 2-furylbenzothiazoles. With increasing Δf, Stokes shifts are increased; the exception is the iodo-substituted compound (**5**). In the series of benzothiazolylfurylethenes (**7–12**) there is no linear relationship between Δf and Stokes shift (Figure 2), but for all compounds except 1-(2-benzothiazolyl)-2-(5-phenyl-2-furyl)ethene (**9**) the Stokes shift is the largest

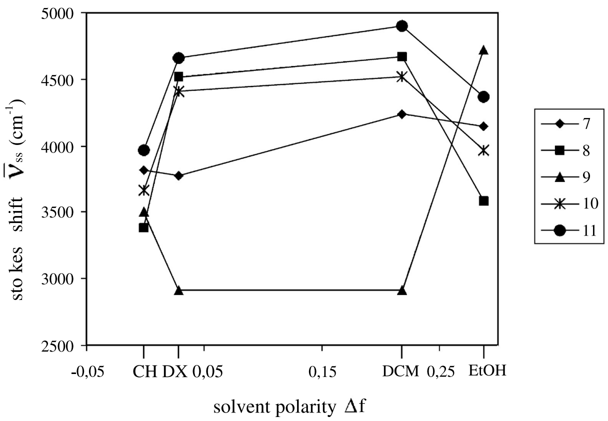

Figure 2. Correlation diagram between Stokes shifts ($\overline{\nu_{ss}}$) and solvent polarity parameters (Δf) of substituted 1-(2-benzothiazolyl)-2-(2-furyl)ethenes (compounds **7–11**, as defined in Figure 1) in cyclohexane (CH), dioxane (DX), dichloromethane (DCM) and ethanol (EtOH).

in dichloromethane. A comparison of relative fluorescence quantum efficiency (ϕ_r) of the compounds under investigation (Table 1 and Table 2) shows that the compounds of the series of 2-furylbenzothiazoles (**1–6**) exhibit higher ϕ_r values than their vinylogues (**7–12**). The reason for this lack of emission in the series of corresponding ethenic derivatives (as in the case of 2-styrylbenzothiazoles[6,10]) appears to be that in the process of excitation followed by deexcitation the torsional motion competes favorably with fluorescence. The electron-withdrawing NO_2 group in compound (**6**) diminishes the fluorescence compared with other furylbenzothiazoles (**1–5**) in ethanol, dichloromethane and dioxane, while in nonpolar cyclohexane an absence of fluorescence is observed. The vinylogue of the above-mentioned compound (**12**) does not fluoresce at all. This is in agreement with the principal finding that nitro-substitution modify, radically, the photochemical and photophysical properties of nitroaromatics.

The present investigation has shown a distinction between fluorescent properties of substituted 2-furylbenzothiazoles and their vinylogues as well as between nitro-substituted compounds and all other compounds of the corresponding series.

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Received October 9, 2002
Accepted January 12, 2003