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Synthesis and Absorption Spectral Properties of Substituted Phenylfurylbenzothiazoles and their Vinylogues

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Summary. A number of substituted 2-(5-aryl-2-furyl)benzothiazoles and their vinylogues were synthesized from corresponding 5-arylfurfurals by convenient methods. The yields of products and their UV/Vis spectroscopic properties are substituent-dependent.

Keywords. 2-(5-Aryl-2-furyl)benzothiazoles; 1-(5-Aryl-2-furyl)-2-(2-benzothiazolyl)ethenes; Absorption spectra.

Synthese und absorptionspektroskopische Eigenschaften von substituierten Phenylfurylbenzthiazolen und ihren Vinylogen

Zusammenfassung. Einige substituerte 2-(5-Aryl-2-furyl)benzthiazole und ihre Vinyloge wurden aus entsprechenden 5-Aryl-furfuralen synthetisiert. Die Ausbeuten an Produkten sowie ihre absorptionspektroskopischen Eigenschaften sind vom Substituenten abhängig.

Introduction

Continuing our previous studies on derivatives of benzothiazole [1, 2] in the present work we searched for synthetic ways to obtain polymethine dyes [3, 4] from this group of compounds. 2-Aryl- [5] and 2-heteroarylbenzothiazoles [6–8] are mostly colourless compounds and we tried to achieve a bathochromic shift in relation to 2-phenylbenzothiazole by incorporation of an ethylenic double bond or a furan ring (two double bonds) between the phenyl and the benzothiazolyl moiety of the parent compound. So some substituted 2-(5-aryl-2-furyl)benzothiazoles and their vinylogues were prepared.

We also studied the influence of substituents on the course of the reaction, yields and the spectroscopic properties of the obtained products.

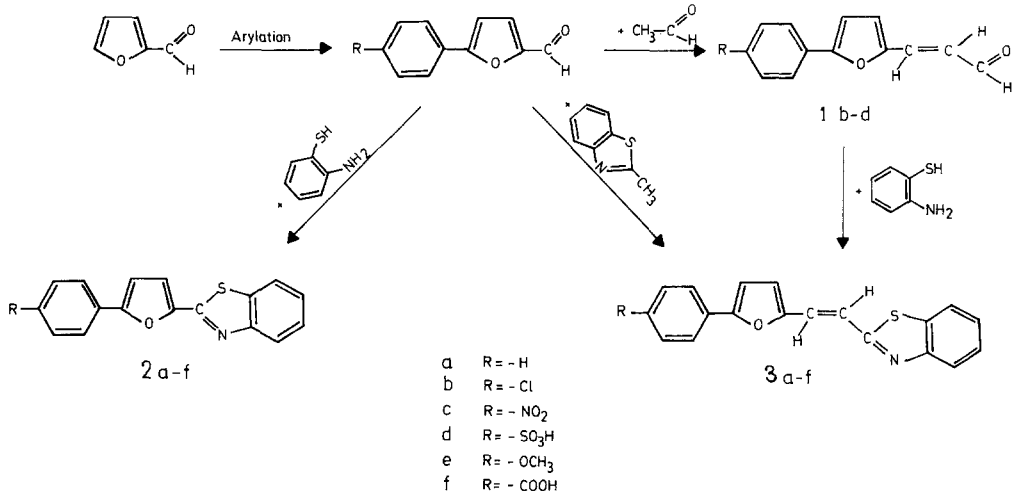
Results and Discussion

As starting materials for preparation of 2-(5-aryl-2-furyl)benzothiazoles **2a–f** and their vinylogues **3a–f** *p*-substituted 5-phenylfurfurals obtained by Meerwein arylation of furfural [9] were used. This arylation was investigated by many authors

mainly in searching for the reaction condition for better yields [10]. It was found that high yields could be obtained only in cases when an electron withdrawing group was attached to the phenyl ring, in other cases the yields were always low [11, 12]. In accordance to this, we obtained 5-arylfurfurals in very good yields when the substituents were Cl, NO_2, SO_3H and COOH groups. When there was no substituent at the phenyl ring and with OCH_3 as substituent the yields were very low.

The influence of these substituents was very similar in condensation reactions carried out with the above mentioned 5-arylfurfurals and *o*-aminothiophenole or 2-methylbenzothiazole. This will be discussed later as well as the influence of substituents on the UV spectroscopic properties of compounds **2a–f** and **3a–f**.

From 5-arylfurfurals we obtained the corresponding 2-(5-aryl-2-furyl)benzothiazoles **2a–f** and substituted furyl-benzothiazolylethenes **3a–f** according to the reaction scheme.



Formulae 1

Compounds **2a–f** were synthesized from appropriate 5-arylfurfural and *o*-aminothiophenole according to the modified method of condensation [13]. Among these compounds **2b** and **2c** were synthesized previously [14] but no spectroscopic data were reported. They were prepared by a modified procedure to study the influence of Cl and NO_2 in comparison with the other substituents, as well as to compare this compounds with their vinylogues **3b** and **3d**. During the first step of this reaction, a cyclisation leading to benzothiazoline [15] (not isolated from the reaction mixture) occurred. From this product benzothiazole was obtained by dehydrogenation. The course of dehydrogenation was not the same in all the cases. When an electron withdrawing group was attached to the phenyl ring (Cl, NO_2, SO_3H) this reaction occurred spontaneously after acidifying the solution. In other cases (without substituents and with COOH and OCH_3 as substituents) the benzothiazoline was more stable and the dehydrogenation was carried out by adding $FeCl_3$ to the reaction mixture. The yields of the products were influenced by substituents, better yields were obtained when Cl, NO_2, SO_3H or COOH were attached to the phenyl ring, lower with OCH_3 and without substituent.

In an attempt to obtain the substituted furylbenzothiazolylethenes starting with substituted 5-arylfurfurals two different synthetic ways were used. The first (Method A) was a two-step reaction in which substituted furylpropenals were obtained as intermediates. The other (Method B) was a condensation reaction with 2-methylbenzothiazol.

Expecting good yields with Cl, NO_2 and SO_3H as substituents substituted furylpropenals **1b–d** were synthesized according to the procedure reported for the preparation of furylacrolein [16]. Thus, the aldol condensation of 5-arylfurfurals with ethanal gave the appropriate unsaturated aldehydes **1b–d** in yields of 13 to 25%. As the yields were low, we did not try to use this method for the synthesis of compounds with other substituents.

The obtained *trans* furylpropenals **1b–d** (the *trans* configuration was confirmed by ^1H NMR spectra) were condensed with *o*-aminothiophenole by the same method as it was done with 5-arylfurfurals yielding 60–70% of **3b–d**. Much better yields on furyl-benzothiazolylethenes were obtained using the method of condensation of appropriate 5-arylfurfural with 2-methylbenzothiazole [17, 18] (Method B). The condensation was achieved by melting together the initial materials. The course of the reaction was independent of the kind of substituents and the yield was much lower in the cases when there was no substituent on the phenyl ring, and when the substituent was OCH_3 group, so the influence of substituents on the yield was the

Table 1. UV/Vis spectral data of substituted benzothiazoles **2a–f** and **3a–f** (in ethanol)

No.	R	λ_{max}/nm	lg ε	$\Delta\tilde{\nu}_{1/2}$/cm^{-1}
2a	H	258	4.17	4930
		355, 372 sh	4.69	
2b	Cl	258	4.14	4880
		355	4.69	
2c	NO_2	382	4.78	5051
2d	SO_3H	258	4.18	4850
		273	4.05	
		358, 376 sh	4.73	
2e	OCH_3	260	4.38	
		367	4.67	5170
2f	COOH	280	4.25	4870
		362, 382 sh	4.73	
3a	H	270	4.11	5540
		388	4.72	
3b	Cl	283	4.26	5054
		388, 410 sh	4.57	
3c	NO_2	412	4.83	5300
3d	SO_3H	288	4.45	5230
		398	4.81	
3e	OCH_3	282	4.51	5690
		401	4.62	
3f	COOH	297	4.16	5050
		392, 428 sh	4.75	

same as in the preparation of compounds **2a–f**. Substances **3b–d** prepared by this method were identical with the same compounds obtained from *trans* furylpropenals **1b–d**, so it can be concluded that compounds **3a–f** have a *trans* configuration although it could not be confirmed from their ^{1}H NMR spectra.

The influence of substituents and the extended conjugation on the position and intensity of the longwave absorption maxima have been studied (Table 1). Comparing the longwave absorption maxima of 2-(5-phenyl-2-furyl)benzothiazole **2a** with that of phenylbenzothiazolylbutadiene [19], it is evident that the furyl group incorporated between the phenyl and benzothiazolyl moiety exhibits the same bathochromic shift as two ethylenic double bonds. The vinylogues of substituted phenylfurylbenzothiazoles **3a–f** exhibit a bathochromic shift of about 30 nm in relation to the appropriate phenylfurylbenzothiazoles **2a–f** which is in agreement with the literature [19] for phenylbenzothiazole and its vinylogue. The absorption data for all investigated compounds show that an increase of the π-conjugation exhibits a bathochromic shift of the longwave maxima in relation to phenylbenzothiazole, but there is no significant change, neither of the molar absorption coefficient nor of the halfband width [20, 21]. It was found that the nitro group attached in the *para* position of the phenyl ring in compounds **2c** and **3c** exhibits a bathochromic shift of the longwave maximum of about 30 nm in relation to the unsubstituted compounds **2a** and **3a**, respectively. Other substituents such as Cl, SO_3H, OCH_3 and COOH have no significant influence on the position of the absorption maxima in the series of the prepared compounds **2a–f** and **3a–f**.

Experimental Part

Melting points were obtained with a Kofler block and are uncorrected. The UV/Vis spectra were taken on a Hitachi Perkin Elmer 124 spectrophotometer using ethanolic solutions. The IR spectra were recorded on a Perkin Elmer 297 spectrophotometer in KBr discs. The ^{1}H NMR spectra were recorded on a Joel JMM-FX-100 FT spectrometer with tetramethylsilane as the internal reference in *DMSO* solutions.

General Procedure for 3-(5-Aryl-2-furyl)propenals (**1b–d**)

Compounds **1b–d** were prepared by adding a 10% aqueous solution of NaOH to a stirred dioxane solution of 5-arylfurfural (10 mmol) and ethanal (15 mmol) at 15 °C. After the *pH* was adjusted to 9 the reaction mixture was stirred at room temperature for 7 h.

The compound **1d** precipitated from the reaction mixture and compounds **1b** and **1c** were extracted with petroleum ether, the extract dried over $MgSO_4$ and the solvent evaporated. The crude crystalline products were purified by repeated recrystallization from an appropriate solvent.

3-(5-p-Chlorophenyl-2-furyl)propenal (**1b**)

Yield: 0.58 g (25%), m.p. 111–113 °C from aq. acetone. IR (KBr): $\tilde{\nu} = 1660\,cm^{-1}$ (C=O), 1620 (C=C), 960 (=CH def.). UV (ethanol): λ_{max} (lg ε) = 370 nm (3.86). ^{1}H NMR (*DMSO*): $\delta = 6.62$ (dd, $J_{ald} = 7.8$ Hz, $J_{trans} = 15.8$ Hz, 1H, ethylen. H), 7.64 (d, $J_{trans} = 15.8$ Hz, 1H, ethylen. H), 7.28–7.90 (m, 6H, aromat. H and fur. H), 9.62 (d, $J = 7.7$ Hz, 1H, ald. H). $C_{13}H_9ClO_2$ (232.6): calcd. C 67.11, H 3.90; found C 67.26, H 3.78.

3-(5-p-Nitrophenyl-2-furyl)propenal (**1c**)

Yield: 0.36 g (15%), m.p. 177–180 °C from dioxane/petroleum ether. IR (KBr): $\tilde{\nu} = 1665\,cm^{-1}$ (C=O), 1620 (C=C), 965 (=CH def.). UV (ethanol): λ_{max} (lg ε) = 382 nm (3.99). ^{1}H NMR (*DMSO*): $\delta = 6.72$ (dd, $J_{ald} = 7.7$ Hz, $J_{trans} = 15.8$ Hz, 1H, ethylen. H), 7.28 (d, $J = 3.8$ Hz, 1H, fur. H), 7.39 (d, $J_{trans} = 15.8$ Hz, 1H, ethylen. H), 7.52 (d, $J = 3.8$ Hz, 1H fur. H), 8.06–8.41 (m, 4H, aromat. H), 9.66 (d, $J = 7.7$ Hz, 1H, ald. H). $C_{13}H_9NO_4$ (243.2): calcd. C 64.20, H 3.73; found C 64.41, H 3.55.

Na-Salt of 3-(5-p-Sulphophenyl-2-furyl)propenal (**1d**)

Yield: 0.39 g (13%), m.p. dec. > 250 °C from ethanol. IR (KBr): $\tilde{\nu} = 1640\,cm^{-1}$ (C=O), 1630 (C=C), 965 (=CH def.). UV (ethanol): λ_{max} (lg ε) = 370 nm (3.91). ^{1}H NMR (*DMSO*): $\delta = 6.60$ (dd, $J_{ald} = 7.6$ Hz, $J_{trans} = 15.8$ Hz, 1H, ethylen. H), 7.15 (s, 2H, fur. H). 7.55 (d, $J_{trans} = 15.8$ Hz, 1H, ethylen. H). 7.73–7.85 (m, 4H, aromat. H), 9.62 (d, $J = 7.6$ Hz, 1H, ald. H). $C_{13}H_9NaO_5S$ (300.2): calcd. C 52.00, H 3.02; found C 51.82, H 2.78.

General Procedure for 2-(5-Aryl-2-furyl)benzothiazoles (**2a–f**)

A solution of corresponding 5-arylfurfural (10 mmol) and *o*-aminothiophenole (10 mmol) in 15 ml pyridine was heated under reflux for 0.5 h. After cooling, the reaction mixture was acidified to *pH* 6 by addition of 2*M* HCl. On standing overnight in a refrigerator the crude product consisting of benzothiazoles in cases **2b–d** was worked up according to Method A, in other cases where benzothiazoline was obtained Method B was used.

Method A: The crystalline product was filtered off and recrystallized from an appropriate solvent. Pure product was obtained by repeated recrystallization.

Method B: The oily benzothiazolines (**2a, e, f**) were separated by decantation from the pyridine hydrochloride solution, washed with water, dissolved in ethanol and oxidized with a hot ethanolic solution of $FeCl_3$ (12 mmol). After boiling for some minutes, the reaction mixture was cooled and poured in 500 ml of cold water. The separated crystalline benzothiazole was purified by repeated recrystallization from an appropriate solvent.

2-(5-Phenyl-2-furyl)benzothiazole (**2a**)

Yield: 0.69 g (25%) (Method B), m.p. 145–146 °C from aq. ethanol. ^{1}H NMR (*DMSO*): $\delta = 7.12$ (d, $J = 3.8$ Hz, 1H, fur. H), 7.30 (d, $J = 3.8$ Hz, 1H, fur. H), 7.36–8.18 (m, 9H, aromat. H). $C_{17}H_{11}NOS$ (277.4): calcd. C 73.61, H 4.01; found C 73.89, H 4.21.

2-(5-p-Chlorophenyl-2-furyl)benzothiazole (**2b**)

Yield: 2.02 g (65%) (Method A), m.p. 182 °C (Ref. [14] 182 °C) from aq. ethanl. ^{1}H NMR (*DMSO*): $\delta = 7.34$ (d, $J = 3.7$ Hz, 1H, fur. H), 7.55 (d, $J = 3.7$ Hz, 1H, fur. H), 7.50–8.37 (m, 8H, aromat. H).

2-(5-p-Nitrophenyl-2-furyl)benzothiazole (**2c**)

Yield: 2.72 g (85%) (Method A), m.p. 209 °C (Ref. [14] 198 °C) from aq. ethanol/acetone. ^{1}H NMR (*DMSO*): $\delta = 7.32$ (d, $J = 3.7$ Hz, 1H, fur. H), 7.48 (d, $J = 3.7$ Hz, 1H, fur. H), 7.57–8.17 (m, 8H, aromat. H).

2-(5-p-Sulphophenyl-2-furyl)benzothiazole (**2d**)

Yield: 2.50 g (70%) (Method A), m.p. dec. > 250 °C from acetone/ethanol. ^{1}H NMR (*DMSO*): $\delta = 7.27$ (d, $J = 3.6$ Hz, 1H, fur. H), 7.47 (d, $J = 3.6$ Hz, 1H, fur. H), 7.54–8.16 (m, 8H, aromat. H). $C_{17}H_{11}NO_4S_2$ (357.4): calcd. C 57.12, H 3.11; found C 56.99, H 3.01.

2-(5-p-Methoxyphenyl-2-furyl)benzothiazole (**2e**)

Yield: 1.54 g (50%) (Method B), m.p. 180–182 °C from aq. acetone. ^{1}H NMR (*DMSO*): $\delta = 3.84$ (s, 3H, OCH_3), 6.47–7.12 (m, 10H, aromat. H and fur. H). $C_{18}H_{13}NO_2S$ (307.4): calcd. C 70.33, H 4.27; found C 70.49, H 4.10.

2-(5-p-Carboxyphenyl-2-furyl)benzothiazole (**2f**)

Yield: 2.25 g (70%) (Method B), m.p. 285 °C from aq. ethanol. IR (KBr): $\tilde{\nu} = 1710\,cm^{-1}$ (C=O). ^{1}H NMR (*DMSO*): $\delta = 7.38$ (d, $J = 3.5$ Hz, 1H, fur. H), 7.48 (d, $J = 3.5$ Hz, 1H, fur. H). 7.95–8.16 (m, 8H, aromat. H). $C_{18}H_{11}NO_3S$ (321.4): calcd. C 67.27, H 3.46; found C 67.41, H 3.55.

General Procedure for 1-(5-Aryl-2-furyl)-2-(2-benzothiazolyl)ethenes (**3a–f**)

Method A for compounds **3b–d**: The solution of 3-(5-aryl-2-furyl)propenal (10 mmol) and *o*-aminothiophenole (10 mmol) in pyridine was refluxed for 0.5 h. After cooling, the reaction mixture was acidified by addition of 2*M* HCl. On standing overnight in a refrigerator the crude product was filtered off and recrystallized from an appropriate solvent.

Method B for compounds **3a–f**: The corresponding 5-arylfurfural (10 mmol) and 2-methylbenzothiazole (10 mmol) with addition of anhydrous $ZnCl_2$ (0.5 g) was heated in an oil bath at 130 °C during 3 h. After cooling, the reaction mixture was triturated with 100 ml of ether or petroleum ether, the obtained crystalline product was filtered off and recrystallized from an appropriate solvent.

1-(5-Phenyl-2-furyl)-2-(2-benzothiazolyl)ethene (**3a**)

Yield: 0.45 g (15%) (Method B), m.p. 130–133 °C from aq. ethanol. IR (KBr): $\tilde{\nu} = 1620\,cm^{-1}$ (C=C), 940 (=CH def.). ^{1}H NMR (*DMSO*): $\delta = 6.61$ (d, $J = 3.6$ Hz, 1H, fur. H), 6.78 (d, $J = 3.6$ Hz, 1H, fur. H), 7.18–8.24 (m, 11H, aromat. H, ethylen. H). $C_{19}H_{13}NOS$ (303.4): calcd. C 75.21, H 4.32; found C 75.03, H 4.08.

1-(5-p-Chlorophenyl-2-furyl)-2-(2-benzothiazolyl)ethene (**3b**)

Yield: 3.01 g (89%) (Method A), m.p. 150–151 °C from aq. acetone IR (KBr): $\tilde{\nu} = 1630\,cm^{-1}$ (C=C), 938 (=CH def.). ^{1}H NMR (*DMSO*): $\delta = 7.12$ (d, $J = 3.5$ Hz, 1H, fur. H), 7.32 (d, $J = 3.5$ Hz, 1H, fur. H), 7.30–8.17 (m, 10H, aromat. H, ethylen. H). $C_{19}H_{12}ClNOS$ (337.8): calcd. C 67.54, H 3.58; found C 67.81, H 3.69.

1-(5-p-Nitrophenyl-2-furyl)-2-(2-benzothiazolyl)ethene (**3c**)

Yield: 2.78 g (80%) (Method A), m.p. 199–202 °C from *DMF*. IR (KBr) $\tilde{\nu} = 1590\,cm^{-1}$ (C=C). 935 (=CH def.). ^{1}H NMR (*DMSO*): $\delta = 7.07$ (d, $J = 3.5$ Hz, 1H, fur. H), 7.39 (d, $J = 3.5$ Hz, 1H, fur. H), 7.47–8.34 (m, 10H, aromat. H, ethylen. H). $C_{19}H_{12}N_2O_3S$ (348.4): calcd. C 65.50, H 3.47: found C 65.32, H 3.50.

1-(5-p-Sulphophenyl-2-furyl)-2-(2-benzothiazolyl)ethene (**3d**)

Yield: 2.30 g (60%) (Method A), m.p. dec. >250 °C from aq. DMF. IR (KBr): $\tilde{\nu} = 1645\,cm^{-1}$ (C=C), 980 (=CH def.). ^{1}H NMR (*DMSO*): $\delta = 7.04$ (d, $J = 3.5$ Hz, 1H, fur. H), 7.15 (d, $J = 3.5$ Hz, 1H, fur. H), 7.47–7.91 (m, 10H, aromat. H, ethylen. H). $C_{19}H_{13}NO_4S_2$ (383.4): calcd. C 59.51, H 3.42; found C 59.38, H 3.28.

1-(5-p-Methoxyphenyl-2-furyl)-2-(2-benzothiazolyl)ethene (**3e**)

Yield: 1.17 g (35%) (Method B), m.p. 189–191 °C from aq. ethanol. IR (KBr): $\tilde{\nu} = 1610\,cm^{-1}$ (C=C), 940 (=CH def.). ^1H NMR (*DMSO*): $\delta = 3.82$ (s, 3H, OCH_3), 6.69–8.14 (m, 12H, aromat. H, fur. H, ethylen. H). $C_{20}G_{15}NO_2S$ (333.4): calcd. C 72.04, H 4.53; found C 72.28, H 4.75.

1-(5-p-Carboxyphenyl-2-furyl)-2-(2-benzothiazolyl)ethene (**3f**)

Yield: 2.65 g (80%) (Method B), m.p. 286 °C from aq. *DMF*. IR (KBr) $\tilde{\nu} = 1700\,cm^{-1}$ (C=O), 1600 (C=C), 930 (=CH def.). ^1H NMR (*DMSO*): $\delta = 7.02$ (d, $J = 3.5$ Hz, 1H, fur. H), 7.24 (d, $J = 3.5$ Hz, 1H, fur. H), 7.32–8.10 (m, 10H, aromat. H, fur. H, ethylen. H). $C_{20}H_{13}NO_3S$ (347.4): calcd. C 69.15, H 3.8; found C 69.28, H 3.94.

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