New Fluorescent 1,3-Benzothiazoles by the Reaction of Heterocyclic Aldehydes with *ortho*-Aminobenzenethiol

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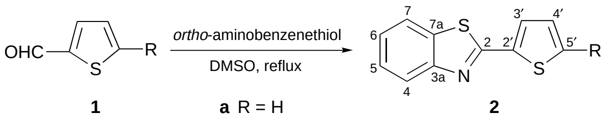
Fluorescent thienyl-1,3-benzothiazoles **2** and phenothiazinyl-1,3-benzothiazoles **5** are synthesised in 60–80% yields, characterised by spectroscopic means and their fluorescence properties evaluated.

Following our interest on synthesising reactive dyes[1] and applying them to fibres or analogous systems, we decided to prepare fluorescent compounds, which are largely used in scientific and industrial areas, as fluorescent brightening agents for textiles and plastics, additives in textile dyeing, lasers and biological stains.[2] The 1,3-benzothiazole moiety is present in many of the compounds currently used for these purposes.

1,3-Benzothiazoles are usually prepared from aldehydes[3] or carboxylic acids[4] by condensation with *o*-aminobenzenethiol and it was decided to follow this approach in the present work. The first series started with formylthiophenes **1** which were heated with *ortho*-aminobenzenethiol in DMSO for 30–60 min to afford the corresponding 2-(2-thienyl)-1,3-benzothiazoles **2a–f** in good yields (60–80%). The starting formylthiophenes were either commercially available (**1a**, **1b**, **1d**) or had to be prepared. From the nitration of 2-formylthiophene **1a**, 5-nitro-2-formylthiophene **1f** was obtained in 13% yield along with the 4-nitro derivative **1h** (46%) as the major compound and they were separated by column chromatography. Formylation of 2-methoxythiophene under Vilsmeier–Haack conditions[5] gave derivative **1c** in 27% yield. Another compound was isolated from the reaction in 26% yield and was identified as compound **1i**.[6] 5-Phenyl-2-formylthiophene **1e** was obtained in 35% yield from 3-chloro-3-phenylprop-2-enal by condensation with sodium sulfide and chloroacetaldehyde in DMF.[7] Compound **2g** was obtained by heating **2d** with copper cyanide in DMF (15% yield).

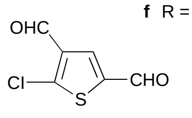


1

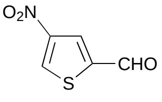
a R = H
b R = Me
c R = OMe
d R = Br
e R = Ph
f R = NO_2

2

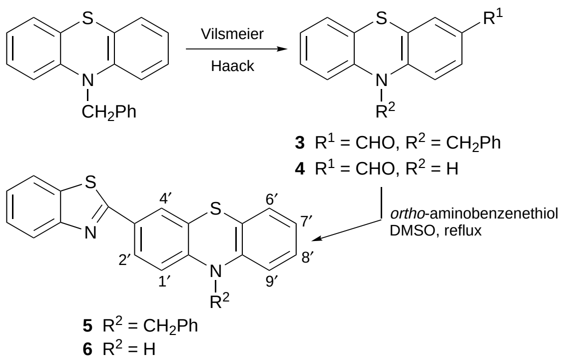
2g R = CN



1i



1h



3 R^1 = CHO, R^2 = CH_2Ph
4 R^1 = CHO, R^2 = H

5 R^2 = CH_2Ph
6 R^2 = H

Using the same procedure we also investigated the reactivity of formylphenothiazines. For this purpose, formylation of *N*-benzylphenothiazine led to the aldehyde **3** in 45% yield, together with a by-product, the phenothiazine **4**. Deprotection was observed during the formylation. Usually hydrogenation is the method of choice for debenzylation, but this has not previously been successful in this case.[8]

Condensation of the aldehydes with *ortho*-aminobenzenethiol gives the desired compounds **2a–f**, **5**, **6** and **9a–c** in good yields. The ^{1}H NMR spectra of the benzothiazoles showed the characteristic pattern corresponding to the homocyclic ring. The proton chemical shifts are not much influenced by the structure of the rest of the molecule and the observed chemical shifts are 0.4–0.6 ppm higher for 4- and 7-H as compared to 5- and 6-H.

In the UV–VIS spectra, a bathochromic shift was observed for the thiophene series when R = H was replaced by a substituent, this effect being more pronounced when R = NO_2. There is also an increase in the absorption intensity (ε) as the substituents change from electron-withdrawing to electron-donating. The fluorescence properties of the benzothiazoles, namely fluorescence spectra, wavelengths of maximum fluorescence and fluorescence quantum yields were obtained. The quantum yields (ϕ) were calculated using 9,10-diphenylanthracene in ethanol as standard ($\phi = 0.95$)[10] (Table 2).

The best fluorescence quantum yields in ethanol were observed for 2-(2-thienyl)-1,3-benzothiazoles substituted at the 5′-position with phenyl (**2e**) or methoxy (**2c**) groups. These compounds show fluorescence in the blue region. The phenothiazinylbenzothiazoles **5** and **6**, although having lower

Table 2 UV absorption and fluorescence data for the 1,3-benzothiazoles **2a–g**, **5**, **6**, **8** and **9a–c**

	Absorption		Fluorescence	
1,3-Benzothiazole	λ_{max}/nm	ε	λ_{max}/nm	ε
2a	316	22 800	397	0.14
2b	331	23 200	406	0.39
2c	347	23 200	417	0.55
2d	329	23 100	400	0.05
2e	359	31 800	426	0.63
2f	376	18 900	454	0.007
2g	342	20 200	402	0.10
5	304	28 000	527	0.22
6	307	22 600	534	0.19
8	282	30 900	315	0.004
9a	297	19 800	365	0.01
9b	302	22 200	371	0.02
9c	318	24 800	369	0.12

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fluorescence quantum yields, show exceptionally large Stokes' shifts with the wavelength of maximum fluorescence being displaced to the green region. To see how the introduction of a heterocyclic nucleus on the benzothiazole ring would affect the quantum yields, as opposed to a phenyl and a methyl substituent, 2-methyl-1,3-benzothiazole **8** and a series of known 2-substituted 1,3-benzothiazoles **9a–c** [**a** R = H; **b** R = OMe; **c** R = Br) were prepared. Replacement of the methyl group in the 2-methyl-1,3-benzothiazole moiety by a phenyl or thienyl nucleus causes an increase in the quantum yield (0.004→0.01→0.14) and there is also a difference in the quantum yields of the substituted phenyl- and thienyl-1,3-benzothiazoles, as seen in Table 2.

Compounds which exhibit $\phi > 0.5$ can be considered interesting for further synthetic studies.

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Techniques used: ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, UV–VIS, fluorescence spectrophotometry, elemental analysis

Table 1: ^{13}C NMR chemical shifts of the 1,3-benzothiazole ring for **2a–g**

Schemes: 3

References: 17

Figure 1: Fluorescence spectra of **2a–e** and **g**

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