

Naphthotriazole derivatives: synthesis and fluorescence properties

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ABSTRACT

Eight fluorescent compounds containing a naphthotriazole moiety substituted at position 2 by a (vinylsulfonyl)aryl group or its precursors, containing hydroxyl or sulphonic groups or *N*-methylglycine, were prepared and characterized. The products were recovered in moderate yields after column chromatography or recrystallization and identified by proton and carbon nuclear magnetic resonance spectroscopy. Double resonance, heteronuclear multiple quantum coherence and heteronuclear multiple bond correlation experiments were carried out for complete assignment of proton and carbon signals. Absorption and emission spectra were obtained, in acetonitrile, for all the compounds and the fluorescence quantum yields determined. All compounds are promising fluorescent probes due to their high fluorescence quantum yields.

Keywords: Nitrogen heterocycles; Naphthotriazole; Vinylsulphone; Azo coupling; Fluorescence spectra; Quantum yield of fluorescence.

1. Introduction

Compounds containing the 1,2,3-triazole unit have attracted attention as intermediates for the synthesis of several products with industrial application, namely, fluorescent compounds used either as dyes [1] or as optical brighteners [2]. In particular, naphthotriazoles, have been used as fluorescent whiteners [3,4] and show a potential as fluorescent markers [5].

Sulphonated derivatives of 2*H*-naphthotriazoles are well-known in the textile industry [6]. In fact, dyes with a vinylsulfonyl group, or its precursors are useful for wool or cotton dyeing [7-9] since they react with a nucleophilic group of a fibre by α,β -addition. These compounds may form a reactive vinyl sulfone moiety by a β -elimination reaction.

Vinyl sulfones may be prepared by dehydration of the corresponding alcohols with mesyl chloride, in CH_2Cl_2 and triethylamine. Our group published recently some results on the use of vinyl sulfones as Michael acceptors [10]. In general, dyes with vinylsulfonyl groups are applied in a protected form (e.g. as 2-sulfato-ethyl sulfones) which are stable in storing under standard conditions and the reactive vinylsulfonyl group (bonded to a chromophore) is formed in the dyeing bath. They were originally developed for the reactive dyeing of wool by Hoechst researchers [11].

A water soluble secondary amine such as *N*-methyltaurine may be used to protect the vinylsulfonyl group (e.g. in Procilan E dyes from ICI). *N*-Methylglycine (sarcosine), an amino acid containing a secondary amino group, was developed as a reactive group [12] and it is assumed that the mechanism of fixation on the fibre is as described by Zollinger [13] and later improved by Lewis [14], the reactive vinyl form is obtained from the sulphate derivative in “dye-bath” in basic medium. In the case of derivatives containing sarcosine the vinyl group is obtained in the dye-bath by action of acids [12].

In the work described in this manuscript several derivatives containing a naphthotriazole moiety were synthesized and their fluorescence properties were evaluated.

2. Results and discussion

2.1. Synthesis

The compounds described contain a naphthotriazole moiety and various substituents at position 2 of the triazole ring (Figure 1). The triazole ring is obtained in low overall yields by diazotization of an aniline derivative [15] and azo coupling of the diazonium salt with an aminonaphthalene derivative followed by oxidation with copper acetate in DMF or similar organic solvent at high temperature (Scheme 1) [6].

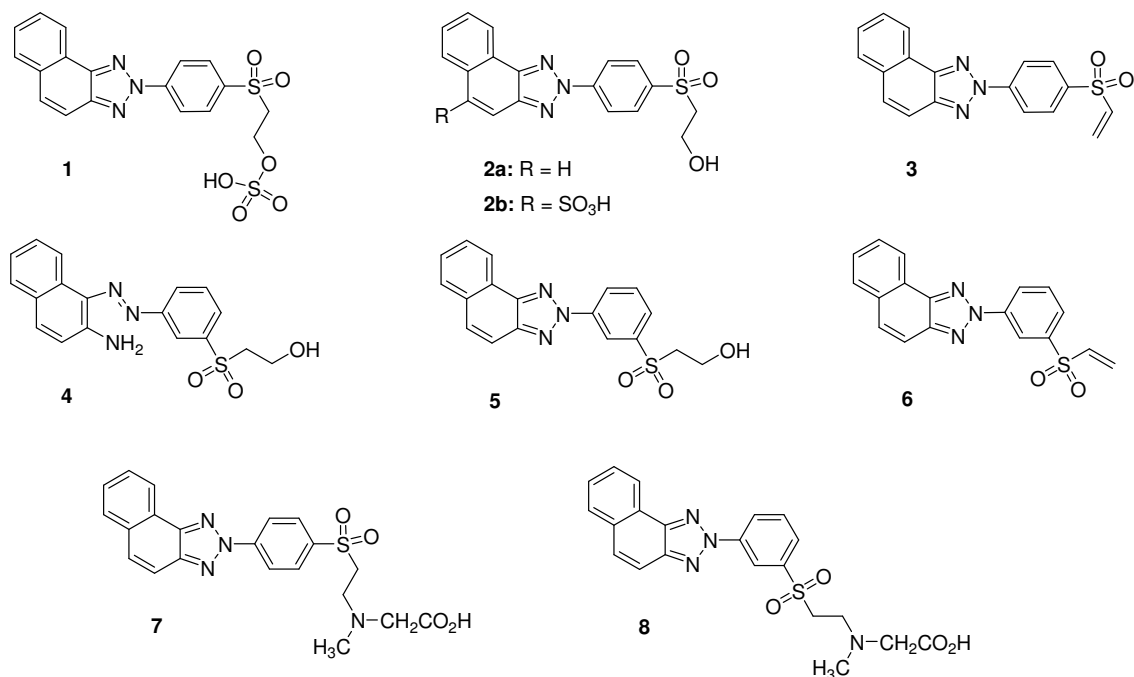
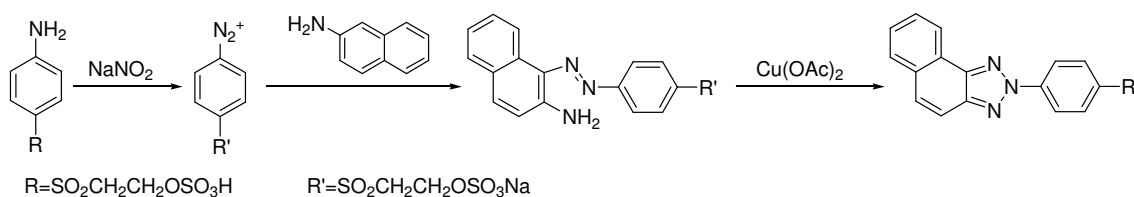


Figure 1. Structures of compounds **1-8**.

During the preparation of compound **1** from 2-aminonaphthalene, a mixture of three compounds was obtained. Chromatographic purification of this mixture gave compound **1** (49%) and the alcohol **2a** (10%) which is explained by hydrolysis. In the ¹H-NMR of the crude mixture the characteristic pattern of the vinyl protons for compound **3**, formed by elimination, could be observed. This third compound, however, was not isolated by chromatography, as it was present in trace amounts.



Scheme 1. Synthesis of compound **1**

When the above impure mixture was treated with triethylamine and mesyl chloride [16] vinyl compound, **3**, was obtained in 20% yield, the same treatment on alcohol **2a**

gave **3** in 22% yield. The formation of the vinyl sulfone was readily confirmed by ^1H NMR spectrum which showed the expected splitting pattern for the vinyl protons.

Diazotization of 2-[(3-aminophenyl)sulfonyl]-1-ethanol and coupling (pH 7) with 2-aminonaphthalene afforded dye **4** which was not characterized. Alcohol **5** was obtained by cyclisation of **4** with copper acetate in a mixture of pyridine and water.

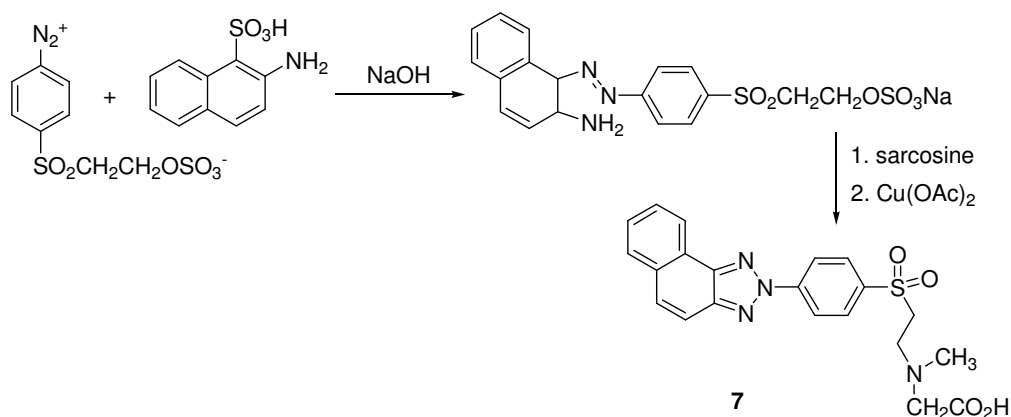
The procedure described above [16] was also used to prepare vinyl compound **6** from alcohol **5** in 33% yield.

Compound **2b** was prepared by the same method starting from 3-aminonaphthalene-1-sulfonic acid and 2-[(4-aminophenyl)sulfonyl]ethyl hydrogen sulphate in low overall yield (9%).

Cyclisation with copper acetate in a mixture of pyridine and water of the intermediate obtained by *ipso*-coupling between the 4-[(2-sulphatoethyl)-sulfonyl] benzenediazonium sodium salt and 2-aminonaphthalene-1-sulfonic acid followed by the addition of sarcosine, originated compound **7** (Scheme 2).

Compound **8** was obtained (55%) by addition of sarcosine to vinyl derivative **6**.

The NMR data for all compounds were in accordance with the expected structures.



Scheme 2. Synthesis of compound **7**: 2-aminonaphthalene-1-sulfonic acid as secondary component (*ipso*-coupling).

2.2. Spectral data

The shape of absorption and emission spectra for all the compounds is very similar to the spectrum of compound **3** (Figure 2). The first absorption band of triazoles

consists of two vibronic bands. The long-wave absorption maxima are at ~ 360 nm for *p*-derivatives, and at ~ 355 for *m*- derivatives.

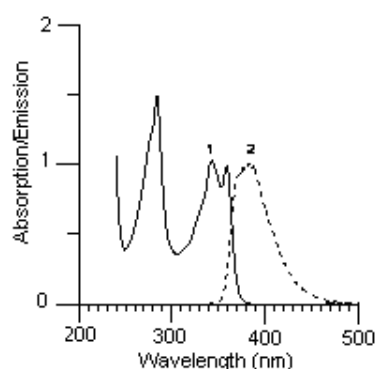
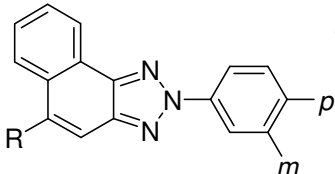


Figure 2. UV/vis absorption (1) and fluorescence (2) spectra of compound **3** in CH₃CN. Fluorescence spectrum was excited at 340 nm.

The positions of fluorescence maxima are also practically of the same value: ~380 nm for *p*-derivatives and ~360 nm for *m*-derivatives. The q_F of all substances under study is very high (Table 1), nonetheless, there is a decrease of fluorescence quantum yield in the case of sarcosine derivatives.

Table 1

Absorption maxima (A_{max}), fluorescence maxima (F_{max}) and fluorescence quantum yields (q_F) of derivatives of 2*H*-naphto[1,2-*d*][1,2,3]triazol-2-yl)benzene in acetonitrile

	^a	A_{max} (nm)	F_{max} (nm)	λ_{excit} (nm)	q_F (%)
-SO ₂ CH ₂ CH ₂ OSO ₃ H (<i>p</i>)	(1)	360	380	340	82
-SO ₂ CH ₂ CH ₂ OSO ₃ H (<i>p</i>) R=SO ₃ H (2b)		360	380	340	80
-SO ₂ CH ₂ CH ₂ OH (<i>p</i>)	(2a)	360	375	340	83
-SO ₂ CH ₂ CH ₂ OH (<i>m</i>)	(5)	353	362	340	81
-SO ₂ CHCH ₂ (<i>p</i>)	(3)	360	380	340	82
-SO ₂ CHCH ₂ (<i>m</i>)	(6)	354	363	340	81
-SO ₂ CH ₂ CH ₂ N(CH ₃)CH ₂ CO ₂ H (<i>p</i>)	(7)	360	380	340	62
-SO ₂ CH ₂ CH ₂ N(CH ₃)CH ₂ CO ₂ H (<i>m</i>)	(8)	354	362	340	54

^a R=H, except otherwise indicated

3. Experimental

3.1. General

Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. ^1H NMR (300 MHz) and ^{13}C NMR (75.4 MHz) spectra were recorded on a Varian Unity Plus Spectrometer at 298 K or on a Bruker Avance III 400 spectrometer (400 MHz for ^1H and 100.6 MHz for ^{13}C). Chemical shifts are reported in ppm relative to solvent peak or TMS. Coupling constants (J) are given in Hz. Double resonance, HMQC (heteronuclear multiple quantum coherence) and HMBC (heteronuclear multiple bond correlation) experiments were carried out for complete assignment of ^1H and ^{13}C signals in the NMR spectra. The IR spectra were recorded on a Perkin Elmer FTIR 1600. High-resolution mass spectra (EI) were obtained on an AutoSpec E spectrometer and ESI mass spectrum on a LC-MS Finnigan LXQ spectrometer. UV/vis spectral data were measured in acetonitrile solutions in 1-cm quartz cuvette. Absorption spectra were recorded using a Perkin-Elmer Lambda 35 spectrophotometer. Fluorescence emission spectra were recorded using a Perkin-Elmer LS 55 spectrophotometer; excitation wavelength was 340 nm. Fluorescence emission spectra were corrected for characteristics of the emission monochromator and the photomultiplier response. Fluorescence quantum yields q_F of triazoles were referred to 1-aminonaphthalene as fluorescence standard ($q_F = 0.39$ [17]). TLC was carried out on plates coated with silica gel 60 F₂₅₄. Column chromatography was performed on silica gel (230-400 mesh) with light petroleum-ethyl acetate mixtures of increasing polarity, unless other conditions are described. Light petroleum refers to the fraction boiling in the range 40-60 °C.

3.2. General procedures for the synthesis of compounds **1**, **2b**, **5** and **7**

3.2.1. Diazotization

To a solution of 2-[(4-aminophenyl)sulfonyl]ethyl hydrogen sulphate (5.7, 10 and 6 mmol for compounds **1**, **2b**, **7**, respectively) or 2-[(3-aminophenyl)sulfonyl]ethan-1-ol (6 mmol, for compound **5**) in H₂O (13.0 mL), concentrated HCl (2.8 mL; 25 mmol) was slowly added. The reaction mixture was cooled to 0-5°C and 5 M NaNO₂ (0.27 mL mmol⁻¹ of substrate) was added dropwise; the mixture was stirred for 30 min. The excess HNO₂ (I₂-starch test) was destroyed using amidosulfuric acid.

3.2.2. Azo coupling

To a solution of 2-aminonaphthalene (for compounds **1** and **5**) (7 mmol) in H₂O (10.0 mL), concentrated HCl (1.0 mL; 9 mmol) was added and the mixture heated for 10 min. After cooling, in an ice-acetone bath, the diazonium salt solution (2.2.1) was added dropwise, pH was adjusted to 5 using a 5 M NaOH solution, and the mixture stirred for 1 h. When the coupling was complete (H-acid test), pH was adjusted to 7, the precipitated dye was filtered off and used in the next step without drying.

For compound **2b** to a solution of 3-aminonaphthalene-1-sulfonic acid (2.23 g; 10 mmol) in H₂O (10 mL), 5 M NaOH (2.0 mL; 10 mmol) was added. After cooling in an ice-acetone bath, the diazonium salt solution was added dropwise and the work up procedure was the same as described above

3.2.3. Oxidation with copper acetate

To the above dye (2.2.2), pyridine (5.0 mL), H₂O (2.0 mL) and Cu(OAc)₂ (2.5 g; 13.8 mmol) were added, the mixture was refluxed (15 min for compounds **1** and **2b**; 30 min. for compound **5**) and poured into water. The precipitated solid was filtered off and dried. Recrystallization from hot ethanol afforded the final compound.

3.3. Synthesis and characterization of compounds **1-8**

3.3.1. 2-[[4-(2H-Naphtho[1,2-d][1,2,3]triazol-2-yl)phenyl]sulfonyl]ethyl hydrogen sulphate (**1**).

Yield: 1.2 g, 49%, m.p. 169-172 °C. UV $\lambda_{\max}(\epsilon)$: 284 (2.55 x 10⁴), 342 (1.72 x 10⁴), 358 (1.66 x 10⁴) nm. ¹H NMR (300 MHz, DMSO-*d*₆): δ = 3.55 (t, *J* = 6.0 Hz, 2H, SO₂CH₂), 3.75 (t, *J* = 6.3 Hz, 2H, CH₂O), 7.71-7.80 (m, 2H (H-7, H-8), 7.91 (d, *J* = 9.3 Hz, 1H, H-4), 7.94 (d, *J* = 9.0 Hz, 1H, H-5), 8.08 (dd, *J* = 2.1, 6.6 Hz, 1H, H-9), 8.16 (d, *J* = 9.0 Hz, 2H, H-2', H-6'), 8.54 (d, *J* = 9.0 Hz, 2H, H-3', H-5'), 8.55 (dd, *J* = 2.1, 6.6 Hz, 1H, H-6). ¹³C NMR (75.4 MHz, DMSO-*d*₆): δ = 55.08 (CH₂OSO₃H), 57.76 (SO₂CH₂), 116.20 (C-4), 120.04 (C-3', C-5'), 122.93 (C-6), 123.75 (C-9a), 128.27 and 128.50 (C-7, C-8), 129.40 (C-9), 129.91 (C-2', C-6'), 130.94 (C-5), 132.23 (C-5a), 139.57 (C-4'), 142.67 (C-1'), 142.83 (C-9b), 143.66 (C-3a). HRMS calcd for C₁₈H₁₅N₃S₂O₆: 433.0402. Found: (M-1)⁺ 432.0313.

The mother liquor was extracted with ethyl acetate and the combined organic extracts were dried (anhydrous MgSO₄) and the oily residue obtained was subjected to column chromatography (EtOAc/light petroleum 5:1) yielding compound **2a** (0.2 g, 10%, m.p. 201-202 °C).

3.3.2. 2-{[4-(2H-Naphtho[1,2-d][1,2,3]triazol-2-yl)phenyl]sulfonyl}ethan-1-ol (**2a**)

UV $\lambda_{\max}(\epsilon)$: 284 (2.60 x 10⁴), 342 (1.74 x 10⁴), 358 (1.70 x 10⁴) nm. ¹H NMR (300 MHz, acetone-*d*₆): δ = 3.58 (t, *J* = 6.3 Hz, 2H, SO₂CH₂), 3.96-4.08 (m, 3H, CH₂OH and OH), 7.74-7.85 (m, 2H, H-7, H-8), 7.88, 7.91, 7.94 and 7.97 (AB q, *J* = 9.3 Hz, 2H, H-5, H-4), 8.07-8.12 (m, 1H, H-9), 8.25 (d, *J* = 9.0 Hz, 2H, H-2', H-6'), 8.66 (d, *J* = 9.0 Hz, 2H, H-3', H-5'), 8.63-8.7 (m, 1H, H-6). ¹³C NMR (75.4 MHz, acetone-*d*₆): δ = 56.74 (CH₂OH), 59.20 (SO₂CH₂), 117.08 (C-4), 120.87 (C-3', C-5'), 123.94 (C-6), 125.39 (C-9a), 128.91 and 129.19 (C-7, C-8), 130.16 (C-9), 130.87 (C-2', C-6'), 131.71 (C-5), 133.60 (C-5a), 140.95 (C-4'), 144.23 (C-1'), 144.30 (C-3a), 144.99 (C-9b). HRMS calcd for C₁₈H₁₆N₃SO₃: 354.0912 (M+1)⁺. Found: (M+1)⁺ 354.0913.

3.3.3. 2-{4-[(2-Hydroxyethyl)sulfonyl]phenyl}-2H-naphtho[1,2-d][1,2,3]triazole-5-sulfonic acid (**2b**)

Yield: 0.39 g, 9%, m.p. 172-175 °C. UV $\lambda_{\max}(\epsilon)$: 283 (2.50 x 10⁴), 342 (1.70 x 10⁴), 358 (1.64 x 10⁴) nm. ¹H NMR (300 MHz, DMSO-*d*₆): δ = 3.55 (t, *J* = 6.0 Hz, 2H, SO₂CH₂), 3.73 (apparent q, *J* = 6.0 Hz, 2H, CH₂OH), 4.92 (t, *J* = 6.0 Hz, 1H, OH), 7.70-7.79 (m, 2H, H-7, H-8), 8.29 (s, 1H H-4), 8.16 (d, *J* = 9.0 Hz, 2H, H-3', H-5'), 8.54-8.59 (m, 3H, H-9, H-2', H-6'), 8.95 (dd, *J* = 7.2, 2.0 Hz, 1H, H-6). ¹³C NMR (75.4 MHz, DMSO-*d*₆): δ = 55.13 (CH₂OH), 57.84 (SO₂CH₂), 114.35 (C-4), 120.24 (C-2', C-6'), 122.82 (C-9), 124.17 (C-9a), 127.95 and 127.97 (C-7, C-8), 128.99 (C-5a), 129.76 (C-6), 139.64 (C-3a), 129.97 (C-3', C-5'), 142.40 (C-4'), 142.71 (C-1'), 143.38 (C-9b), 146.78 (C-5). HRMS calcd for C₁₈H₁₅N₃S₂O₆: 433.0402. Found: (M-1)⁺ 432.0313.

3.3.4. 2-[4-(Vinylsulfonyl)phenyl]-2H-naphtho[1,2-d][1,2,3]triazole (**3**)

To a dichloromethane (3.2 mL) solution of alcohol **2a** (0.32 g; 0.9 mmol) maintained at 0 °C, triethylamine (0.35 mL; 2.5 mmol) and mesyl chloride (0.1 mL; 1.3 mmol) were added and the mixture was kept stirring for 10 min. The solution was washed with

saturated ammonium chloride, dried (anhydrous MgSO_4) and concentrated in vacuum. The residue was purified by crystallization from chloroform/diethyl ether yielding the title compound as a light brown solid (0.068 g, 22%), m.p. 195-196 °C (dec). UV $\lambda_{\text{max}}(\epsilon)$: 284 (2.55×10^4), 342 (1.72×10^4), 358 (1.66×10^4) nm. ^1H NMR (300 MHz, CDCl_3): δ = 6.10 (d, J = 9.6 Hz, 1H, = CH , *trans* SO_2), 6.50 (d, J = 16.5 Hz, 1H, = CH , *cis* SO_2), 6.71 (dd, J = 16.5, 9.6 Hz, 1H, SO_2CH), 7.56-7.74 (m, 2H, H-7, H-8), 7.71, 7.74, 7.75, 7.78 (AB q, J = 9.0 Hz, 2H, H-4, H-5), 7.87 (dd, J = 7.5, 1.5 Hz, 1H, H-6), 8.05 (d, J = 9.0 Hz, 2H, H-2', H-6'), 8.54 (d, J = 9.0 Hz, 2H, H-3', H-5'), 8.55 (d, J = 7.5 Hz, H-9). ^{13}C NMR (75.4 MHz, CDCl_3): δ = 116.07 (C-4), 120.13 (C-1'), 120.24 (C-3', C-5'), 123.34 (C-9), 124.50 (C-9a), 127.77 and 128.09 (C-7, C-8), 128.30 (=CH₂), 128.97 (C-6), 129.41 (C-2', C-6'), 130.79 (C-5), 138.11 ($\text{SO}_2\text{C}=\text{C}$), 132.46 (C-5a), 143.60 (C-9b), 143.70 (C-4'), 144.17 (C-3a). HRMS calcd for $\text{C}_{18}\text{H}_{13}\text{N}_3\text{SO}_2$: 335.0728. Found: (M)⁺ 335.0725.

3.3.5. 2-[[3-(2H-Naphtho[1,2-d][1,2,3]triazol-2-yl)phenyl]sulfonyl]ethan-1-ol (**5**)

Yield: 0.86 g, 41%, m.p. 158-159 °C. UV $\lambda_{\text{max}}(\epsilon)$: 282 (2.52×10^4), 338 (1.69×10^4), 355 (1.63×10^4) nm. ^1H NMR (300 MHz, $\text{DMSO-}d_6$): δ = 3.61 (t, J = 6.0 Hz, 2H, SO_2CH_2), 3.76 (t, J = 6.0 Hz, 2H, CH_2OH), 7.60-7.80 (m, 2H, H-7, H-8), 7.80-8.00 (m, 3H, H-4, H-5, H-5'), 8.00-8.15 (m, 2H, H-6', H-6), 8.57 (dd, J = 7.5, 1.2 Hz, 1H, H-9), 8.63 (dd, J = 7.8, 1.2 Hz, 1H, H-4'), 8.74 (t, J = 1.2 Hz, 1H, H-2'). OH not observed. ^{13}C NMR (75.4 MHz, $\text{DMSO-}d_6$): δ = 55.01 (CH_2OH), 57.61 (SO_2CH_2), 116.12 (C-4), 118.55 (C-2'), 122.86 (C-9), 123.69 (C-9a), 124.17 (C-4') 127.66 (C-6'), 128.16 and 128.31 (C-7, C-8), 129.29 (C-6), 130.64 (C-5), 131.24 (C-5'), 132.11 (C-5a), 139.65 (C-3'), 141.85 (C-1'), 142.50 (C-9b), 143.34 (C-3a). HRMS calcd for $\text{C}_{18}\text{H}_{15}\text{N}_3\text{SO}_3$: 353.0834. Found: (M)⁺ 353.0845.

3.3.6. 2-[3-(Vinylsulfonyl)phenyl]-2H-naphtho[1,2-d][1,2,3]triazole (**6**)

To a dichloromethane (4.7 mL) solution of alcohol **5** (0.52 g; 1.47 mmol) maintained at 0 °C, triethylamine (0.51 mL, 3.7 mmol) and mesyl chloride (0.14 mL; 1.8 mmol) were added and the mixture was stirred for 10 min. The solution was washed with a saturated ammonium chloride solution, dried (anhydrous MgSO_4) and then concentrated under vacuum. The oily residue was purified by flash column

chromatography (chloroform: methanol, 10:1). The first fraction gave the title product as a light-brown solid (0.16 g, 33%), m.p. 167-168 °C. UV $\lambda_{\text{max}}(\epsilon)$: 281 (2.22×10^4), 339 (1.39×10^4), 354 (1.30×10^4) nm. ^1H NMR (300 MHz, CDCl_3): δ = 6.16 (d, J = 9.6 Hz, 1H, = $\underline{\text{CH}}$, *trans* SO_2), 6.60 (d, J = 16.5 Hz, 1H, = $\underline{\text{CH}}$, *cis* SO_2), 6.78 (dd, J = 16.5, 9.6 Hz, 1H, SO_2CH), 7.60-7.75 (m, 2H, H-7, H-8), 7.71-7.80 (m, 3H, H-4, H-5, H-5'), 7.86-7.98 (m, 2H, H-6, H-6'), 8.58-8.68 (m, 2H, H-9, H-4'), 8.92 (t, J = 1.8 Hz, 1H, H-2'). ^{13}C NMR (75.4 MHz, CDCl_3): δ = 116.18 (C-4), 119.23 (C-2'), 123.40 (C-9), 124.46 (C-4'), 124.66 (C-9a), 126.95 (C-6' or C-6), 127.78 and 127.98 (C-7, C-8), 128.87 (C-6' or C-6), 128.98 (=CH₂), 130.55 and 130.58 (C-5, C-5'), 137.99 (SO_2CH), 132.48 (C-5a), 140.95 (C-1'), 141.30 (C-3'), 143.38 (C-9b), 143.96 (C-3a). HRMS calcd for $\text{C}_{18}\text{H}_{14}\text{N}_3\text{SO}_2$: 336.0807. Found: $(\text{M}+1)^+$ 336.0812.

3.3.7. 2-[[4-(2H-Naphtho[1,2-d][1,2,3]triazol-2-yl)phenyl]sulfonyl]ethyl (methyl)carbamic acid (7)

To a suspension of 2-aminonaphthalene-1-sulfonic acid (1.37 g; 6 mmol) in H_2O (10.0 mL), 5 M NaOH (1.2 mL) was added. The solution obtained was cooled to 0-5 °C, and the diazonium salt solution (2.2.1) was added portionwise, keeping the temperature below 5 °C and pH 8 by addition of 5 M NaOH. The azo coupling was finished after ca 2 h (H-acid test) and pH of the reaction mixture was lowered to 4 with HCl. The azo dye formed was collected by filtration.

The moist dye was suspended in water (12 mL), sarcosine (0.71 g; 8 mmol) was added, and pH was adjusted to 8 by addition of 5 M NaOH. The mixture was heated at 60 °C for 2 h, then cooled to 5 °C, its pH was adjusted to 5 with HCl, the dye obtained was salted out by addition of 3 g NaCl and collected by filtration.

The filter cake was dissolved in pyridine (5.0 mL) and water (5.0 mL). Cupric acetate (2.5 g; 13.8 mmol) was added with stirring and the mixture was heated at 60 °C for 4 h. After cooling it was poured into 100 mL cold water and the precipitate was collected and dried at 30 °C. The crude product **7** was obtained in 94% yield (2.40 g). A pure sample of **7** for spectroscopic analysis was obtained by repeated thorough mixing with acidified water (pH 1) and filtration, which removed the remaining pyridine and copper salts; m.p. 180-181 °C. UV $\lambda_{\text{max}}(\epsilon)$: 282 (2.30×10^4), 338 (1.40×10^4), 355 (1.29×10^4) nm. ^1H NMR (300 MHz, $\text{DMSO}-d_6$): δ = 2.28 (s, 3H, CH_3), 3.22 (s, 2H,

$\text{CH}_2\text{CO}_2\text{H}$), 3.82 (t, $J = 6.0$ Hz, 2H, NCH_2), 4.11 (t, $J = 6.0$ Hz, 2H, SO_2CH_2), 7.72-7.75 (m, 2H, H-7, H-8), 7.89-7.93 (m, 2H, H-4, H-5), 8.06-8.08 (m, 1H, H-9), 8.18-8.22 (m, 2H, H-2', H-6'), 8.50-8.53 (m, 3H, H-3', H-5', H-6), the OH was not observed. ^{13}C NMR (75.4 MHz, $\text{DMSO}-d_6$): $\delta = 39.6$ (CH_3), 48.0 (CH_2N), 51.3 (SO_2CH_2), 55.6 (CH_2COOH), 118.9 (C-4), 119.0 (C-3', C-5'), 126.5 (C-6), 127.2 (C-9a), 128.3 and 128.5 (C-7, C-8), 129.6 (C-9), 136.3 (C-5), 136.6 (C-2', C-6'), 137.6 (C-5a), 141.3 (C-4'), 141.8 (C-1'), 144.3 (C-3a), 145.1 (C-9b), 170.3 (COOH).

3.3.8. 2-[[3-(2H-Naphtho[1,2-d][1,2,3]triazol-2-yl)phenyl]sulfonyl]ethyl (methyl)carbamic acid (**8**)

The pH of a solution of sarcosine (0.029 g; 0.33 mmol) in H_2O (3.0 mL) was adjusted to 8-9 by addition of NaOH (0.014 g; 0.35 mmol) and added to a solution of 2-(3-(vinylsulfonyl)phenyl)-2H-naphtho[1,2-d][1,2,3]triazole, **6**, (0.111 g; 0.33 mmol) in acetone (3.0 mL). The reaction mixture was heated under reflux for 2 h. After cooling the mixture in an ice bath the pH was adjusted to 7 by addition of a 1 M HCl solution. The solid precipitated was filtered off and dried, affording the titled compound (0.077 g; 55%); m.p. 256-258 °C.

^1H NMR (400 MHz, $\text{DMSO}-d_6$): $\delta = 2.20$ (s, 3H, CH_3), 2.93 (t, $J = 5.4$ Hz, 2H, CH_2N), 3.14 (s, 2H, $\text{CH}_2\text{CO}_2\text{H}$), 3.67 (t, $J = 5.4$ Hz, 2H, SO_2CH_2), 7.70-7.80 (2H, m, H-7, H-8), 7.93 (apparent t, $J = 8.4$ Hz, 3H, H-4, H-5, H-5'), 8.04-8.11 (2H, m, H-4', H-6'), 8.58 (d, $J = 6.6$ Hz, 1H, H-6), 8.64 (d, $J = 6.6$ Hz, 1H, H-9), 8.77 (t, $J = 1.5$ Hz, 1H, H-2'), OH not observed. ^{13}C NMR (100.6 MHz, $\text{DMSO}-d_6$): 40.87 (CH_3), 49.13 (CH_2N), 52.49 (SO_2CH_2), 52.67 (CH_2COOH), 116.18 (C-4), 118.62 (C-2'), 122.90 (C-9), 123.77 (C-9a), 124.27 (C-6), 127.61 (C-6'), 128.17 and 128.31 (C-7, C-8), 129.33 (C-4'), 130.65 (C-5), 131.22 (C-5'), 132.16 (C-5a), 139.73 (C-3'), 141.42 (C-1'), 142.55 (C-9b), 143.39 (C-3a), 171.68 (C=O). MS, ESI^+ : 425.33 ($(\text{M}+1)^+$, 3%); 379.25 [$(\text{M}+1)^+ - \text{CO}_2\text{H}$, 100%].

4. Conclusions

A series of compounds derived from naphthotriazole were synthesised and characterised. Due to their high fluorescence quantum yields, all compounds are promising fluorescent markers (probes). The compounds described can be used as

photochemically stable UV protectors and weak optical brighteners in cellulose or animal fibres and synthetic polyamides.

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