Formation of Azolo[1,2,4]triazinium Salts by Reaction of Heterocyclic-substituted 1-Azo-naphthalen-2-ols with Strong Acids

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By reaction of heterocyclic-substituted 1-azo-naphth-2-ols with the Vilsmeier reagent or with strong acids polycyclic azolo[1,2,4]triazinium salts are formed in good yields. The azolo[1,2,4] triazinium salts exhibit similar UV/Vis absorption properties as the starting azo compounds, but in contrast to those the fluorescence appears in the visible range.

Key words: 1-Arylazo-2-naphthols, Benzo[*b*]naphtho[2,1-*e*]thiazolo[2,3-*c*][1,2,4]triazinium Salts, Naphtho[2,1-*e*]thiazolo[2,3-*c*][1,2,4]triazinium Salts, Naphtho[2,1-*e*][1,3,4]thiadiazolo [2,3-*c*][1,3,4]triazinium Salts, Vilsmeier Reaction

Introduction

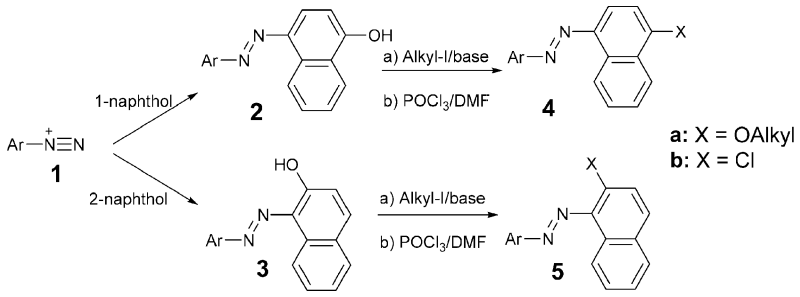
Aromatic diazonium salts **1**, readily available from primary aromatic amines by reaction with alkali nitrites in acidic solution [1, 2], can be coupled with different electron-rich aromatic or heteroaromatic compounds (Scheme 1). Thus, with 1- or 2-naphthols, 1-arylazonaphthalen-4-ols **2** or naphthalene-2-ols **3**, respectively, are formed [3 – 5]. These pH-sensitive compounds can be easily functionalized at their hydroxyl group. For instance, by reaction with certain alkylating agents in the presence of non-nucleophilic bases the corresponding 1-arylazo-4-alkoxynaphthalenes **4a** or 2-alkoxy-naphthalenes **5a** are formed [6, 7], whereas with $POCl_3$ in the presence of DMF 1-arylazo-4-chloronaphthalenes **4b** or 2-chloronaphthalenes **5b** are obtained [8].

In analogy to the reaction of aromatic diazonium salts **1**, the heterocylic diazonium salts **6**, similarly available by reaction of 2-aminobenzthiazoles with alkali nitrites in strong acidic solution [1], are also readily coupled with 1- or 2-naphthols to yield the corresponding 1-(2-benzthiazolylazo)-naphthalen-4-ols **9** or 1-(2-benzthiazolylazo)-naphthalen-2-ols **12** [9, 10] (Scheme 2). In contrast to the 1-arylazo-naphthols **2** and **3**, these heterocyclic azo compounds **9** and **12** react with alkylating agents at the heterocyclic N-atom forming the corresponding quaternary salts **10** and **13** which can be transformed by reaction with bases into pH-sensitive and strongly solvatochromic 1,2- or 1,4-naphthoquinone monohydrazones **11** and **14**, respectively [11]. Non-solvatochromic heterocyclic quaternary salts **8** are obtained, however, when the 1-(2-benzthiazolylazo)-naphthalen-4-ols **9** are transformed first by reaction with $POCl_3$ in presence of DMF under Vilsmeier conditions into the 1-(2-benzthiazolylazo)-4-chloronaphthalenes **7** and subsequent reaction with an appropriate methylating agents [12].

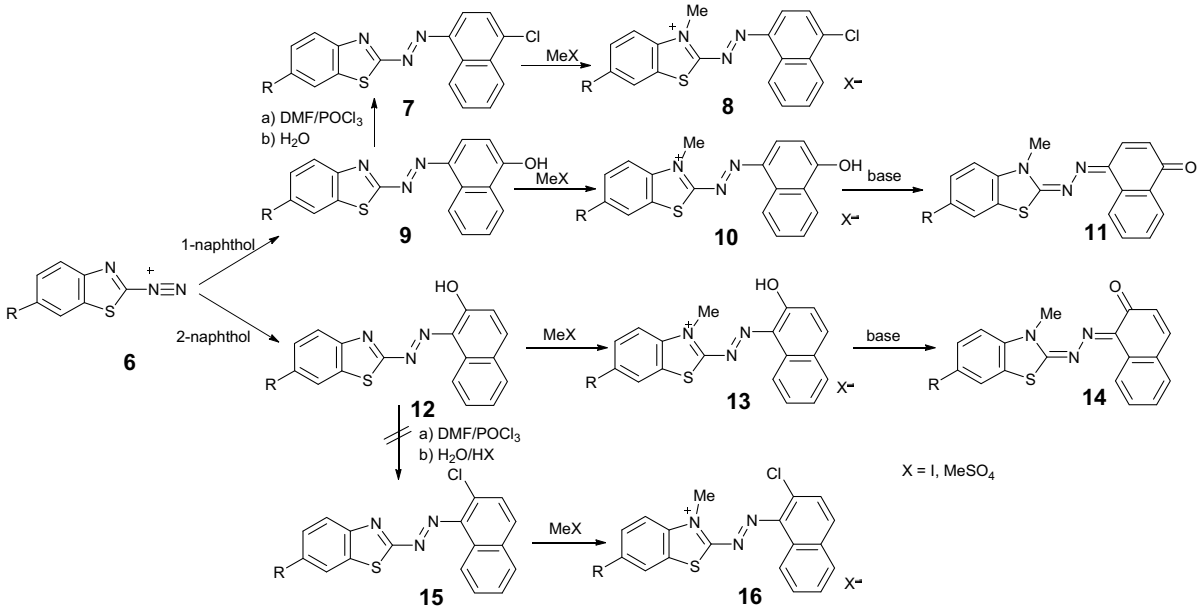
To our surprise, the same reaction sequence to transform the isomeric 1-(2-benzthiazolylazo)-2-chloronaphthalenes **15** into the appropriate quaternary salts **16** failed because the necessary starting compounds **12** react with the Vilsmeier reagent in a quite different way. Instead of non-ionic 1-(2-benzthiazolylazo)-2-chloronaphthalenes **15**, cationic compounds with a naphtho[2,1-e]thiazolo[2,3-*c*][1,2,4]triazinium structure **17** were obtained.

Results and Discussion

By studying the last-mentioned reaction in more detail, we found that the transformation of the 1-



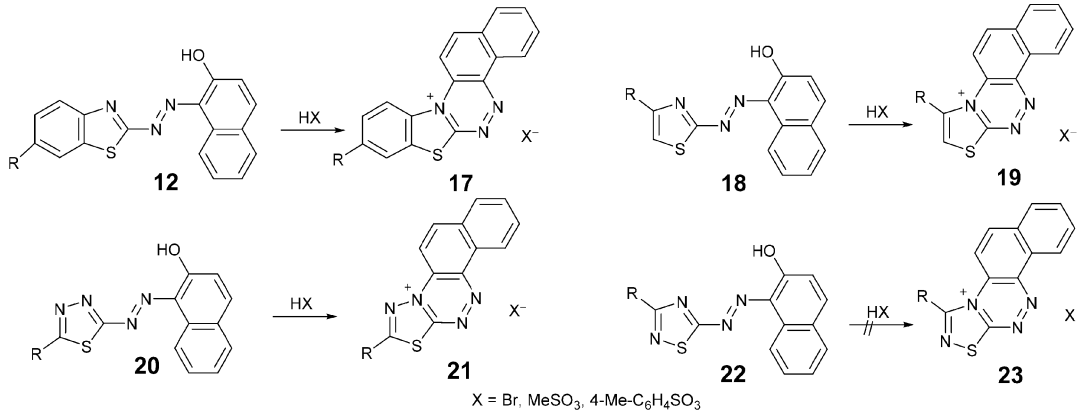
Scheme 1.



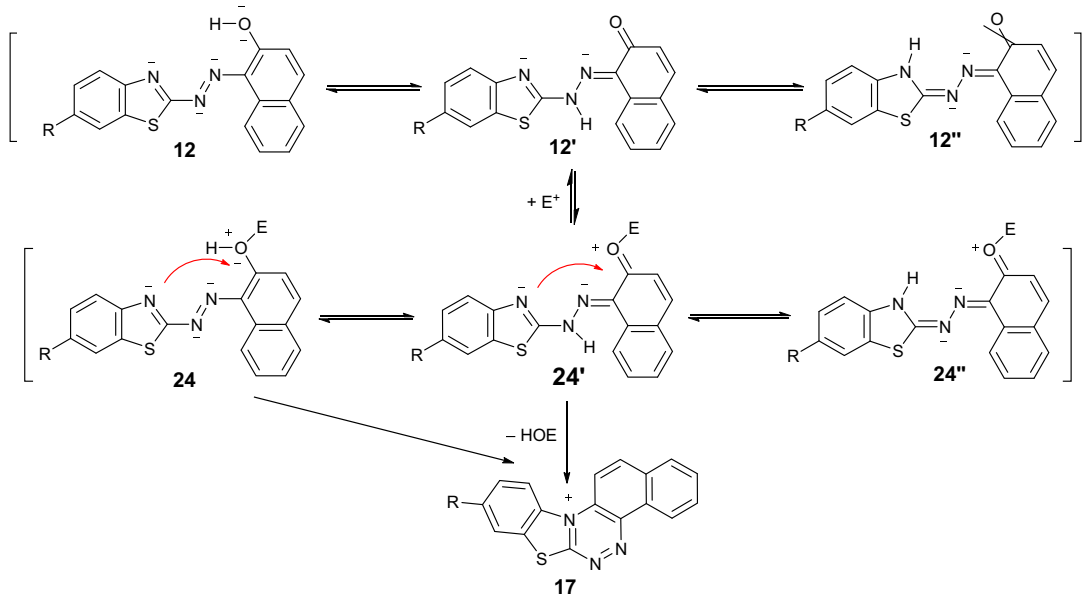
Scheme 2.

(2-benzthiazolylazo)-naphthalen-2-ols **12** into the naphtho[2,1-e]thiazolo[2,3-*c*][1,2,4]triazin-4-ium salts **17** can be performed not only with the Vilsmeier reagent but also, more simply, by heating of the 1-azo-naphthalen-2-ols **12** with strong acid, preferably in acetic acid as solvent. Thereby, naphtho[2,1-*e*]thiazolo[2,3-*c*][1,2,4]triazin-12-ium salts **17** with different anions can be prepared without difficulties (Scheme 3). Thus, by refluxing a 1-(2-benzthiazolylazo)-naphthalen-2-ol **12** with perchloric acid, methanesulfonic acid or *p*-toluenesulfonic acid in acetic acid the corresponding benzo[*b*]naphtho[2,1-*e*]thiazolo[2,3-*c*][1,2,4]triazin-12-ium perchlorates **17a** and **17b**, methanesulfonates **17a′** and **17b′** and tosylates **17a″** and **17b″**, respectively, were obtained mostly in satisfactory yields.

The analogous transformation of heterocyclic-substituted 1-azo-naphthalen-2-ols into polycyclic quaternary salts can be performed also by using vanadinyl perchlorate [13] or by starting from certain other 1-(hetarylazo)naphthalen-2-ols. Thus, by heating of 1-(thiazol-2-ylazo)naphthalen-2-ols **18** or 1-([1,3,4]thiadiazol-2-ylazo)naphthalen-2-ol **20** with perchloric acid, methanesulfonic acid or *p*-toluenesulfonic acid in acetic acid the corresponding naphtho[2,1-*e*]thiazolo[2,3-*c*][1,2,4]triazin-4-ium salts **19** and naphtho[2,1-*e*][1,3,4] thiadiazolo[2,3-*c*][1,3,4]triazin-4-ium salts **21**, respectively, were



Scheme 3.



Scheme 4. (color online)

obtained in satisfactory yields. Surprisingly, attempts of an analogous transformation of 1-{[1,2,4]thiadiazol-5-ylazo}naphthalen-2-ols **22** into the corresponding naphtho[2,1-*e*][1,3,4]thiadiazolo[2,3-*c*][1,2,4]triazin-4-ium salts **23** failed. Neither the unsubstituted 1-{[1,2,4]thiadiazol-5-ylazo}naphthalen-2-ol **22a** nor the 4-methyl-substuituted derivative **22b** gave rise to the expected naphtho[2,1-*e*][1,3,4]thiadiazolo[2,3-*c*][1,2,4]triazin-4-ium salts **23a** or **23b**. Probably, the N-S bond in these compounds is broken in the course of the heterocyclization to yield acylic products, the structures of which have not been elucidated.

The structures of the new penta- or tetracyclic quaternary salts **17**, **19** and **21** were confirmed by mass spectral and ^{1}H NMR data. Thus, all salts prepared exhibit in the mass spectra the expected molecular ion peak for their cationic part. In the ^{1}H NMR spectra of the salts **17**, **19** and **21** characteristic signals between $\delta = 8.0$ and 10.0 ppm were detected. They can be attributed to the protons at

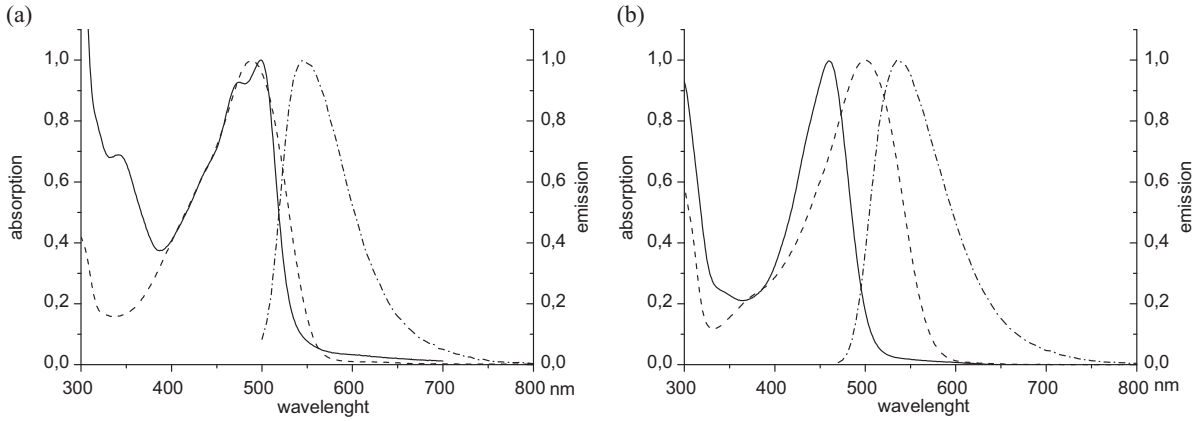


Fig. 1. Absorption spectra (–) and emission spectra (-·-·-·) of compound **17a** (left) and compound **19b** (right) shown with the absorption spectra (- - - - -) of the starting azo compounds **12a** (left) and **18b** (right).

Table 1. Absorption and emission data of the azolo[1,2,4] triazinium salts **17**, **19** and **21**.

Compound	R	λ_{max} (abs) in nm (lg ε)	λ_{max} (Fl) in nm
17a	H	499 (4.41)	548
17b	Me	498 (4.39)	545
17c	MeO	497 (4.44)	545
19a	H	452 (4.50)	545
19b	C_6H_5	461 (4.30)	535
21a	H	409 (4.58)	530
21b	Me	423 (4.97)	530

the (hetero)aromatic moieties. Additional signals for methyl or methoxy groups attached at the appropriate heterocyclic moieties and for the methyl groups in the methanesulfonate or *p*-toluenesulfonate anions were found at about $\delta = 2.0$, 4.0, 3.0 and 2.2 ppm, respectively.

The transformation of the starting heterocyclic 1-hetarylazonaphthalen-2-ols into the cationic heterocyclic compounds **17**, **19** and **21** is accompanied in most cases with only small changes in the UV/Vis absorptions. Thus, the long-wavelength absorption bands of the 1-hetarylazonaphth-2-ols **12**, **18** and **20** are, as shown in Fig. 1, narrow and found nearly at the same wavelength as in the corresponding cationic compounds **17**, **19** and **21**, respectively (see Table 1). However, a significant change in the emission spectra was observed. In contrast to the starting azo compounds, which are non-fluorescent, the cationic compounds **17**, **19** and **21** exhibit a fluorescence at about 540 nm. The Stokes shifts of the fluorescence maxima range from 47 nm in compound **17b** up to 121 nm in compound **21a**.

Concerning the mechanism of the formation of the thiazolo[2,3-*c*][1,2,4]triazinium salts, *e. g.* of **17**, it can be assumed that the electrophilic reagent E^+ used (E^+ = H or Cl-CH=NMe_2^+) attacks the starting thiazoloazo compound **12**, which can exist in different tautomeric forms **12**, **12′** and **12″**, *inter alia* at the naphthalene-based hydroxy group yielding the intermediates **24**-**24″**. From the latter, elimination of HOE can occur giving rise to the final product **17** (Scheme 4).

Experimental Section

Melting points were determined with a Netzsch STA 449C instrument. ^{1}H NMR spectra were recorded in $CDCl_3$, [D_6]DMSO or trifluoroacetic acid with a Bruker DRX 500 P (^{1}H: 500.13 MHz) instrument. Elemental analyses data were obtained with a Eurovektor Hekatech EA-3000 elemental analyzer, and the mass spectra with a Bruker Esquire-LC 00084 instrument. The UV/Vis absorption and emission spectra were recorded in dichloromethane with a Perkin Elmer Lambda 25 spectrometer and with an Edinburgh spectrometer, respectively.

*Preparation of the 1-hetarylazonaphth-2-ols **12**, **18**, **20**, and **22** (general procedure)*

To a solution of 2-naphthol (0.01 mol, 1.4 g) in methanol (50 mL) a freshly prepared solution of the appropriate diazonium salt **6**, prepared by addition of nitrosylsulfuric acid (5 mL, 2 molar) to a solution of the corresponding amino-substituted azole (0.01 mol) in a 5:1 mixture of acetic

acid/propionic acid (25 mL) and phosphoric acid (5 mL) at 0 °C, was added under vigorous stirring and cooling. After a few minutes, the mixture was diluted with a saturated aqueous sodium acetate solution until the azo compound formed a precipitate. The product was isolated by filtration, washed repeatedly with water and dried in air. Finally, the products obtained were purified by recrystallization from a toluene/acetic acid mixture.

The following 1-hetarylazonaphthalen-2-ols were prepared according to this procedure:

*1-(2-Benzthiazolylazo)-naphthalen-2-ol (**12a**)* from 2-naphthol and benzthiazole-2-diazonium hydrogensulfate in a yield of 2.05 g (67 %); m. p. 173 – 174 °C. – ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 6.82$ (d, $J = 9.6$ Hz, 1H), 7.38 (t, $J = 7.7$ Hz, 1H), 7.48 (t, $J = 7.5$ Hz, 1H), 7.52 (t, $J = 7.5$ Hz, 1H), 7.64 (t, $J = 7.4$ Hz, 1H), 7.76 (d, $J = 7.7$ Hz, 1 H), 7.85 (d, $J = 8.0$ Hz, 1H), 8.00 (d, $J = 9.6$ Hz, 1H), 8.03 (d, $J = 7.8$ Hz, 1H), 8.29 (d, $J = 8.0$ Hz, 1H), 15.44 (s, 1H) ppm.

*1-(6-Methyl-2-benzthiazolylazo)-naphthalen-2-ol (**12b**)* from 2-naphthol and 6-methyl-benzthiazole-2-diazonium hydrogensulfate in a yield of 1.63 g (51 %); m. p. 194 °C. – ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 2.44$ (s, 3H), 6.91 (d, $J = 9.5$ Hz, 1H), 7.33 (d, $J = 7.5$ Hz, 1H), 7.55 (t, $J = 7.2$ Hz, 1H), 7.68 (t, $J = 6.9$ Hz, 1H), 7.77 – 7.82 (m, 2H), 7.85 (s, 1H), 8.06 (d, $J = 9.5$ Hz, 1H), 8.37 (d, $J = 8.0$ Hz, 1H), 15.32 (s, 1H) ppm.

*1-(6-Methoxy-2-benzthiazolylazo)-naphthalen-2-ol (**12c**)* from 2-naphthol and 6-methoxy-benzthiazole-2-diazonium hydrogensulfate in a yield of 2.41 g (72 %); m. p. 235 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 3.90$ (s, 3H), 6.88 (d, $J = 13.9$ Hz, 1H), 7.09 (dd, $J = 8.9$ Hz, $J = 2.2$ Hz, 1H), 7.29 (d, $J = 2.2$ Hz, 1H), 7.47 (t, $J = 7.5$ Hz, 1H), 7.58 – 7.61 (m, 2H), 7.77 (d, $J = 9.4$ Hz, 1H), 7.85 (d, $J = 8.9$ Hz, 1H), 8.47 (d, $J = 8.0$ Hz, 1H), 15.31 (s, 1H) ppm.

*1-(Thiazol-2-ylazo)-naphthalen-2-ol (**18a**)* from 2-naphthol and thiazole-2-diazonium hydrogensulfate in a yield of 2.02 g (79 %); m. p. 131 – 133 °C. – ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 7.07$ (d, $J = 9.3$ Hz, 1H), 7.51 (dt, $J = 8.0$ Hz, $J = 1.0$ Hz, 1H), 7.67 (dt, $J = 8.2$ Hz, $J = 1.1$ Hz, 1H), 7.76 (d, $J = 3.3$ Hz, 1H), 7.86 (d, $J = 7.8$ Hz, 1H), 7.91 (d, $J = 3.3$ Hz, 1H), 8.08 (d, $J = 9.3$ Hz, 1H), 8.41 (d, $J = 8.3$ Hz, 1H), 14.64 (s, 1H) ppm.

*1-(4-Phenyl-thiazol-2-ylazo)-naphthalen-2-ol (**18b**)* from 2-naphthol and 4-phenyl-thiazole-2-diazonium hydrogensulfate in a yield of 1.36 g (41 %); m. p. 203 °C. – ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 7.10$ (d, $J = 9.3$ Hz, 1H), 7.40 (t, $J = 7.4$ Hz, 1H), 7.49 (t, $J = 7.5$ Hz, 2 H), 7.56 (t, $J = 7.8$ Hz, 1H), 7.71 (t, $J = 8.1$ Hz, 1H), 7.89 (d, $J = 7.8$ Hz, 1H), 8.03 (d, $J = 7.2$ Hz, 2H), 8.15 (d, $J = 9.3$ Hz, 1 H), 8.18 (s, 1H), 8.47 (d, $J = 8.2$ Hz, 1H), 14.82 (s, 1H) ppm.

*1-(1,3,4-Thiadiazol-2-ylazo)-naphthalen-2-ol (**20a**)* from 2-naphthol and 1,3,4-thiadiazole-2-diazonium hydrogensulfate in a yield of 1.78 g (70 %); m. p. 194 – 199 °C. – ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 6.94$ (d, $J = 9.4$ Hz, 1H), 7.53 (t, $J = 7.6$ Hz, 1H), 7.66 (t, $J = 8.0$ Hz, 1H), 7.81 (d, $J = 7.7$ Hz, 1H), 8.06 (d, $J = 9.5$ Hz, 1H), 8.39 (d, $J = 8.1$ Hz, 1H), 9.44 (s, 1H), 14.90 (s, 1H) ppm.

*1-(5-Methyl-1,3,4-thiadiazol-2-ylazo)-naphthalen-2-ol (**20b**)* from 2-naphthol and 5-methyl-1,3,4-thiadiazole-2-diazonium hydrogensulfate in a yield of 1.54 g (69 %); m. p. 192 – 194 °C (dec.). – ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 2.76$ (s, 3H), 7.07 (d, $J = 9.2$ Hz, 1H), 7.56 (t, $J = 7.0$ Hz, 1H), 7.69 (t, $J = 6.9$ Hz, 1H), 7.88 (d, $J = 7.4$ Hz, 1H), 8.13 (d, $J = 9.0$ Hz, 1H), 8.39 (d, $J = 8.0$ Hz, 1H), 14.51 (s, 1H) ppm.

*1-(1,2,4-Thiadiazol-5-ylazo)-naphthalen-2-ol (**22a**)* from 2-naphthol and 1,2,4-thiadiazole-5-diazonium hydrogensulfate in a yield of 1.56 g (61 %); m. p. 145 – 150 °C. – ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 6.50$ (d, $J = 9.8$ Hz, 1 H), 7.39 – 7.42 (m, 1 H), 7.47 – 7.50 (m, 2 H), 7.74 (d, $J = 9.8$ Hz, 1 H), 8.14 – 8.16 (m, 1 H), 8.51 (s, 1 H) ppm.

*1-(3-Methyl-1,2,4-thiadiazol-5-ylazo)-naphthalen-2-ol (**22b**)* from 2-naphthol and 3-methyl-1,2,4-thiadiazole-5-diazonium hydrogensulfate in a yield of 1.26 g (47 %); m. p. 159 – 161 °C. – ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 2.49$ (s, 3H), 6.61 (d, $J = 9.7$ Hz, 1H), 7.50 (t, $J = 7.4$ Hz, 1H), 7.58 (t, $J = 7.1$ Hz, 1H), 7.67 (d, $J = 7.5$ Hz, 1H), 7.91 (d, $J = 9.6$ Hz, 1H), 8.20 (broad, 1H), 15.38 (s, 1H) ppm.

*Preparation of **17**, **19** and **21** (general procedure)*

Method A: To a solution of the appropriate 1-hetarylazo-substituted naphthalen-2-ol (0.01 mol) in DMF (25 mL) $POCl_3$ (2 mL) was added with cooling and the resulting mixture warmed at 90 °C for 3 h. After cooling to room temperature, the mixture was carefully poured in methanol (50 mL) containing perchloric acid (2 mL, 70 %), and the precipitate was isolated by filtration with suction.

Method B: To a solution of the appropriate 1-hetarylazo-substituted naphthalen-2-ol (0.025 mol) in acetic acid (25 mL) a strong acid (2 mL) was added and the resulting mixture refluxed for 3 h. After cooling and addition of diethyl ether the precipitate was isolated by filtration with suction and recrystallized, after drying in air, from acetic acid.

The following azolo[1,2,4]triazinium salts were prepared according to this procedure:

*Benzo[4,5]thiazolo[2,3-c]naphtho[2,1-e][1,2,4]triazin-12-ium perchlorate (**17a**)* from 1-(2-benzthiazolylazo)-naphthalen-2-ol (**12a**) and perchloric acid as a yellow solid in a yield of 2.0 g (53 %) according to method A and in a yield of 0.81 g (83 %) according to method B; m. p. 332 – 334 °C. – ^{1}H NMR (500 MHz, CF_3COOH): $\delta = 8.08 – 8.11$ (m, 2H),

8.14 – 8.21 (m, 2H), 8.29 (d, $J = 7.9$ Hz, 1H), 8.41 (d, $J = 8.0$ Hz, 1H), 9.05 (d, $J = 8.7$ Hz, 1H), 9.12 (d, $J = 8.9$ Hz, 1H), 9.21 (d, $J = 8.6$ Hz, 1H) 9.68 (d, $J = 8.3$ Hz, 1H) ppm. – ESI (70 eV): $m/z = 288.1$ (calcd. 288.06 for $[C_{17}H_{10}N_3S]^+$). – $C_{17}H_{10}ClN_3O_4S$ (387.80): calcd. C 52.65, H 2.60, Cl 9.14, N 10.84, S 8.27; found C 52.47, H 2.69, Cl 9.38, N 10.66, S 8.50.

*Benzo[4,5]thiazolo[2,3-c]naphtho[2,1-e][1,2,4]triazin-12-ium methanesulfonate (**17a′**)* from 1-(2-benzthiazolylazo)-naphthalen-2-ol (**12a**) and methanesulfonic acid as a yellow solid in a yield of 0.87 g (91 %) according to method B; m. p. 125 – 135 °C; an additional ^{1}H NMR signals was found at $\delta = 2.92$ (s, 3H, $MeSO_3$) ppm.

*Benzo[4,5]thiazolo[2,3-c]naphtho[2,1-e][1,2,4]triazin-12-ium tosylate (**17a″**)* from 1-(2-benzthiazolylazo)-naphthalen-2-ol (**12a**) and *p*-toluenesulfonic acid as a yellow solid in a yield of 1.01 g (88 %) according to method B; m. p. 143 – 153 °C; additonal ^{1}H NMR signals were found at $\delta = 2.26$ (s, 3H, CH_3), 7.13 (d, $J = 7.3$ Hz, 2 arom. H), 7.57 (d, $J = 7.4$ Hz, 2 arom. H) ppm.

*9-Methylbenzo[4,5]thiazolo[2,3-c]naphtho[2,1-e][1,2,4]triazin-12-ium perchlorate (**17b**)* from 1-(6-methylbenzthiazol-2-ylazo)-naphthalen-2-ol (**12b**) and perchloric acid as a yellow solid in a yield of 3.2 g (80 %) according to method A and in a yield of 0.79 g (78 %) according to method B; m. p. 315 – 317 °C (dec.). – ^{1}H NMR (500 MHz, CF_3COOH): $\delta = 2.67$ (s, 3H, CH_3), 7.96 (d, $J = 8.7$ Hz, 1H), 8.07 (t, $J = 7.5$ Hz, 1H), 8.16 (t, $J = 7.3$ Hz, 2H), 8.27 (d, $J = 7.9$ Hz, 1H), 9.00 – 9.08 (m, 2H), 9.65 (d, $J = 8.2$ Hz, 1H) ppm. – ESI (70 eV): $m/z = 302.0$ (calcd. 302.37 for $[C_{18}H_{12}N_3S]^+$). – $C_{18}H_{12}ClN_3O_4S$ (401.82): calcd. C 53.80, H 3.01, Cl 8.82, N 10.46, S 7.89; found C 53.84, H 3.12, Cl 8.66, N 10.76, S 8.02.

*9-Methylbenzo[4,5]thiazolo[2,3-c]naphtho[2,1-e][1,2,4]triazin-12-ium methanesulfonate (**17b′**)* from 1-(6-methylbenzthiazol-2-ylazo)-naphthalen-2-ol (**12b**) and methanesulfonic acid as a yellow solid in a yield of 0.94 g (95 %) according to method B; m. p. 90 – 100 °C; additional ^{1}H NMR signals were found at $\delta = 3.06$ (s, 3H, $MeSO_3$) ppm.

*9-Methylbenzo[4,5]thiazolo[2,3-c]naphtho[2,1-e][1,2,4]triazin-12-ium tosylate (**17b″**)* from 1-(6-methyl-benzthiazol-2-ylazo)-naphthalen-2-ol (**12b**) and *p*-toluenesulfonic acid as a yellow solid in a yield of 1.01 g (86 %) according to method B; m. p. 130 – 150 °C; an additional ^{1}H NMR signal was found at $\delta = 2.27$ (s, 3H, CH_3), 7.95 (d, $J = 8.0$ Hz, 2 H), 7.89 (d, $J = 8.0$ Hz, 2 H) ppm.

*9-Methoxybenzo[4,5]thiazolo[2,3-c]naphtho[2,1-e][1,2,4]triazin-12-ium perchlorate (**17c**)* from 1-(6-methoxybenzthiazol-2-ylazo)-naphthalen-2-ol (**12b**) and perchloric acid as a red solid in a yield of 3.5 g (83 %) according to method A and in a yield of 0.97 g (94 %) according to method B; m. p. 349 – 351 °C. – ^{1}H NMR (500 MHz, CF_3COOH): $\delta = 3.86$ (s, 3H, OCH_3), 6.52 (d, $J = 9.8$ Hz, 1H), 7.18 (dt, $J = 2.2$ Hz, $J = 9.1$ Hz, 1H), 7.36 – 7.40 (m, 2H), 7.44 – 7.51 (m, 2H), 7.66 (d, $J = 9.1$ Hz, 1H), 7.72 (d, $J = 9.8$ Hz, 1H), 8.21 (d, $J = 7.8$ Hz, 1H) ppm. – ESI (70 eV): $m/z = 318.1$ (calcd. 318.37 for $[C_{18}H_{12}N_3OS]^+$). – $C_{18}H_{12}ClN_3O_5S$ (417.82): calcd. C 51.74, H 2.89, Cl 8.49, N 10.06, S 7.67; found C 51.65, H 2.80, Cl 8.65, N 10.00, S 7.88.

*9-Methoxybenzo[4,5]thiazolo[2,3-c]naphtho[2,1-e][1,2,4]triazin-12-ium methanesulfonate (**17c′**)* from 1-(6-methoxybenzthiazol-2-ylazo)-naphthalen-2-ol (**12b**) and methanesulfonic acid as a red solid in a yield of 0.99 g (96 %) according to method B; m. p. 87 – 99 °C; an additional ^{1}H NMR signal was found at $\delta = 2.96$ (s, 3H, $MeSO_3$) ppm.

*9-Methoxybenzo[4,5]thiazolo[2,3-c]naphtho[2,1-e][1,2,4]triazin-12-ium tosylate (**17c″**)* from 1-(6-methoxybenzthiazol-2-ylazo)-naphthalen-2-ol (**12b**) and *p*-toluenesulfonic acid as a red solid in a yield of 1.19 g (97 %) according to method B; m. p. 140 – 144 °C; additional ^{1}H NMR signals were found at $\delta = 2.27$ (s, 3H, CH_3), 7.15 (d, $J = 8.0$ Hz, 2 arom. H), 7.60 (d, $J = 8.2$ Hz, 2 arom. H) ppm.

*Naphtho[2,1-e]thiazolo[2,3-c][1,2,4]triazinium perchlorate (**19a**)* from 1-(thiazolylazo)-naphthalen-2-ol (**18a**) and perchloric acid as a pale-yellow solid in a yield of 0.76 g (90 %) according to method B; m. p. 284 – 287 °C. – ^{1}H NMR (500 MHz, CF_3COOH): $\delta = 8.04$ (dt, $J = 0.9$ Hz, 7.2 Hz, 1 H), 8.15 (dt, $J = 1.0$ Hz, 7.2 Hz, 1H), 8.24 (d, $J = 8.1$ Hz, 1H), 8.51 (d, $J = 9.2$ Hz, 1H), 8.77 (d, $J = 4.4$ Hz, 1H), 8.88 (d, $J = 9.2$ Hz, 1H), 9.36 (d, $J = 4.5$ Hz, 1H), 9.64 (d, $J = 8.4$ Hz) ppm. – ESI (70 eV): $m/z = 238.9$ (calcd. 238.04 for $[C_{13}H_8N_3S]^+$). – $C_{13}H_8ClN_3O_4S$ (337.74): calcd. C 46.23, H 2.39, Cl 10.50, N 12.44, S 9.49; found C 46.17, H 2.29, Cl 10.68, N 12.40, S 9.82.

*Naphtho[2,1-e]thiazolo[2,3-c][1,2,4]triazin-4-ium methanesulfonate (**19a′**)* from 1-(thiazol-2-ylazo)-naphth-2-ol (**18a**) and methanesulfonic acid as a pale-yellow solid in a yield of 0.8 g (95 %) according to method B; m. p. 168 – 170 °C (dec.); an additional ^{1}H NMR signal was found at $\delta = 3.04$ (s, 3H, $MeSO_3$) ppm.

*Naphtho[2,1-e]thiazolo[2,3-c][1,2,4]triazin-4-ium tosylate (**19a″**)* from 1-(thiazol-2-ylazo)-naphthalen-2-ol (**18a)** and *p*-toluenesulfonic acid as a yellow solid in a yield of 1.02 g (100 %) according to method B; m. p. 217 – 227 °C (dec.); additional ^{1}H NMR signals were found at $\delta = 2.24$ (s, 3H, CH_3), 7.09 (d, $J = 8.1$ Hz, 2 arom. H), 7.56 (d, $J = 8.3$ Hz, 2 arom. H) ppm.

*9-Phenyl-naphtho[2,1-e]thiazolo[2,3-c][1,2,4]triazin-4-ium perchlorate (**19b**)* from 1-(4-phenylthiazol-2-ylazo)-naphth-2-ol (**18a**) and perchloric acid as an orange solid in a yield of 0.45 g (43 %) according to method B; m. p. 165 – 170 °C. – ^{1}H NMR (500 MHz, CF_3COOH): $\delta = 7.50$

(d, J = 9.5 Hz, 1 H), 7.60 – 7.65 (m, 4 H), 7.74 (t, J = 7.5 Hz, 1 H), 7.97 (t, J = 7.5 Hz, 1 H), 8.05 – 8.10 (m, 2 H), 8.35 (d. J = 9.5 Hz, 1 H), 8.48 (s, 1 H), 9.62 (d, J = 8.3 Hz, 1 H) ppm. – ESI (70 eV): m/z = 314.1 (calcd. 314.07 for $[C_{19}H_{12}N_3S]^+$). – $C_{19}H_{12}ClN_3O_4S$ (413.83): calcd. C 55.14, H 2.92, Cl 8.57, N 10.15, S 7.75; found C 55.22, H 2.80, Cl 8.66, N 10.17, S 7.93.

*9-Phenyl-naphtho[2,1-e]thiazolo[2,3-c][1,2,4]triazin-4-ium methanesulfonate (**19b′**)* from 1-(4-phenylthiazol-2-ylazo)-naphth-2-ol (**18a**) and methanesulfonic acid as an orange solid in a yield of 0.81 g (79 %) according to method B; m. p. 115 – 125 °C; an additional ^{1}H NMR signal was found at δ = 2.98 (s, 3H, $MeSO_3$) ppm.

*9-Phenyl-naphtho[2,1-e]thiazolo[2,3-c][1,2,4]triazin-4-ium tosylate (**19b″**)* from 1-(4-phenylthiazol-2-ylazo)-naphth-2-ol (**18a**) and *p*-toluenesulfonic acid as an orange solid in a yield of 0.93 g (64 %) according to method B; m. p. 120 – 128 °C; additional ^{1}H NMR signals found at δ = 2.25 (s, 3H, CH_3), 7.14 (d, J = 8.0 Hz, 2 H), 7.63 (d, J = 8.1 Hz, 2 H) ppm.

*Naphtho[2,1-e][1,3,4]thiadiazolo[2,3-c][1,2,4]triazin-4-ium perchlorate (**21a**)* from 1-(1,3,4-thiadiazol-2-ylazo)-naphthalen-2-ol (**20a**) and perchloric acid as a pale-yellow solid in a yield of 2.8 g (83 %) according to method A and 0.76 g (90 %) according to method B; m. p. 262 – 264 °C. – ^{1}H NMR (500 MHz, CF_3COOH): δ = 8.13 (dt, J = 1.0 Hz, J = 7.3 Hz, 1H), 8.21 (dt, J = 1.0 Hz, J = 7.3 Hz, 1H), 8.30 (d, J = 8.0 Hz, 1H), 8.76 (d, J = 9.1 Hz, 1H), 8.98 (d, J = 9.1 Hz, 1H), 9.69 (d, J = 8.2 Hz, 1H) ppm. – ESI (70 eV): m/z = 238.9 (calcd. 239.04 for $[C_{12}H_7N_4S]^+$). – $C_{12}H_7ClN_4O_4S$ (338.73): calcd. C 42.55, H 2.08, Cl 10.47, N 16.54, S 9.47; found C 42.36, H 2.15, Cl 10.55, N 16.44, S 9.77.

*Naphtho[2,1-e][1,3,4]thiadiazolo[2,3-c][1,2,4]triazin-4-ium methanesulfonate (**21a′**)* from 1-(1,3,4-thiadiazol-2-ylazo)-naphthalen-2-ol (**20a**) and methanesulfonic acid as a pale-yellow solid in a yield of 2.4 g (70 %) according to method A; m. p. 155 – 165 °C; an additional ^{1}H NMR signal was found at δ = 3.00 (s, 3H, $MeSO_3$) ppm.

*Naphtho[2,1-e][1,3,4]thiadiazolo[2,3-c][1,2,4]triazin-4-ium tosylate (**21a″**)* from 1-(1,3,4-thiadiazol-2-ylazo)-naphthalen-2-ol (**20a**) and *p*-toluenesulfonic acid as a pale-yellow solid in a yield of 0.97 g (95 %) according to method B; m. p. 150 – 163 °C; additional ^{1}H NMR signals found at δ = 2.27 (s, 3H, CH_3), 7.16 (d, J = 7.2 Hz, 2 H), 7.61 (d, J = 7.3 Hz, 2 H) ppm.

*2-Methylnaphtho[2,1-e][1,3,4]thiadiazolo[2,3-c][1,2,4]triazin-4-ium perchlorate (**21b**)* from 1-(5-methyl-1,3,4-thiadiazol-2-ylazo)-naphth-2-ol (**20b**) and perchloric acid as a yellow solid in a yield of 0.69 g (78 %) according to method B; m. p. 270 – 273 °C. – ^{1}H NMR (500 MHz, CF_3COOH): δ = 3.03 (s, 3H, CH_3), 8.10 (t, J = 7.5 Hz, 1H), 8.18 (t, J = 7.5 Hz, 1H), 8.26 (d, J = 7.9 Hz, 1H), 8.68 (d, J = 9.0 Hz, 1H), 8.93 (d, J = 8.9 Hz, 1H), 9.65 (d, J = 8.2 Hz, 1H) ppm. – ESI (70 eV): m/z = 253.0 (calcd. 253.30 for $[C_{13}H_9N_4S]^+$). – $C_{13}H_9ClN_4O_4S$ (352.75): calcd. C 44.26, H 2.57, Cl 10.05, N 15.88, S 9.09; found C 44.34, H 2.66, Cl 10.18, N 15.68, S 8.96.

*10-Methylnaphtho[2,1-e][1,3,4]thiadiazolo[2,3-c][1,2,4]triazin-4-ium methanesulfonate (**21b′**)* from 1-(5-methyl-1,3,4-thiadiazol-2-ylazo)-naphth-2-ol (**20b**) and methanesulfonic acid as a yellow solid in a yield of 0.85 g (98 %) according to method B; m. p. 95 – 105 °C; an additional ^{1}H NMR signal was found at δ = 3.16 (s, 3H, $MeSO_3$) ppm.

*10-Methylnaphtho[2,1-e][1,3,4]thiadiazolo[2,3-c][1,2,4]triazin-4-ium tosylate (**21b″**)* from 1-(5-methyl-1,3,4-thiadiazol-2-ylazo)-naphth-2-ol (**20b**) and *p*-toluenesulf onic acid as a yellow solid in a yield of 1.03 g (97 %) according to method B; m. p. 160 – 170 °C; additional ^{1}H NMR signals were found at δ = 2.28 (s, 3H, CH_3), 7.18 (d, J = 8.1 Hz, 2 H), 7.62 (d, J = 8.2 Hz, 2 H) ppm.

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