

Preparation and UV/Vis Spectroscopic Characterization of *N,N*-Disubstituted 2-Amino-5-arylazoselenazoles and Some of Their Carbocyclic and Heterocyclic Analogues

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Abstract. By coupling of aryldiazonium salts **5** with *N,N*-disubstituted 2-amino-5*H*-selenazoles **4** deeply coloured 5-aryazo-substituted 2-amino-selenazoles **6a–6l** have been prepared and their solvatochromic properties determined by

means of UV/Vis spectroscopy, and compared with the ones of several other arylazo-substituted *N,N*-dialkylanilines **7a–7d**, 2-(*N,N*-dialkylamino)-thiophenes **8a–8e**, and 2-(*N,N*-dialkylamino)-thiazoles **9a–9c**.

In the last three decades *N,N*-disubstituted 2-amino-thiophenes **2** and 2-amino-thiazoles **3** received a lot of interest. As heteroanalogues of *N,N*-disubstituted anilines **1**, which are important starting compounds for the synthesis of organic dyes [1], they have been used as versatile educts for preparing different types of organic dyes also. Thus, *N,N*-disubstituted 2-amino-thiophenes **2** could be successfully transformed, especially if they are unsubstituted in their 5-position, *e.g.*, into azo dyes [2], methine dyes [3], and squarylium and croconium dyes [4]. Analogously, *N,N*-disubstituted 2-amino-thiazoles **3** have been transformed into corresponding azo dyes [5], methine and azomethine dyes [6], and squarylium dyes [7].

ly [10], here we will report on their transformation into corresponding phenylazo compounds **6**.

Results and Discussion

The synthesis of *N,N*-disubstituted 2-amino-5-aryazo-4-phenylselenazoles **6** was performed either by addition of an 2-amino-4-phenyl-selenazole **4** to an arene diazonium salt **5**, *e.g.* a diazonium tetrafluoroborate, in

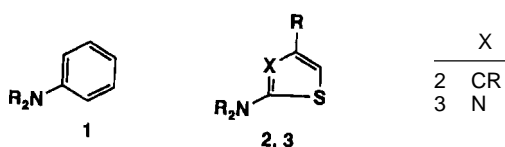
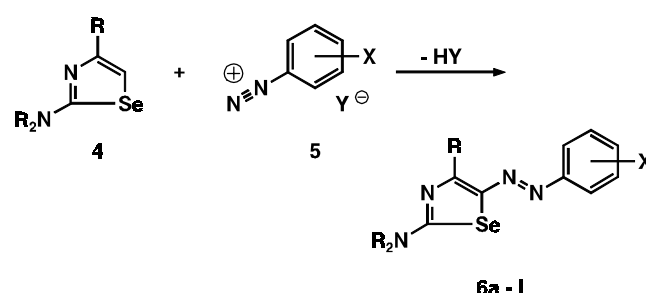


Fig. 1 Structural formulas of *N,N*-disubstituted anilines and their heterocyclic analogues

In contrast to the mentioned thiophenes **2** and thiazoles **3**, *N,N*-disubstituted 2-amino-selenazoles **4** have not found such attention hitherto, because they were nearly unknown as yet [8]. However, recently we have described a simple route for the synthesis of 4-phenyl-substituted derivatives [9], so that their use as dye educts can be now checked more in detail. Whereas on the transformation of the new *N,N*-disubstituted 2-amino-4-phenylselenazoles **4** ($R = C_6H_5$) into corresponding selenazolyl-substituted squaranyl dyes was reported recent-



6a - l			
Nr.	R ₂ N	R	X
6a	dimethylamino	phenyl	4-NO ₂
6b	diethylamino	phenyl	4-NO ₂
6c	dibenzylamino	phenyl	4-NO ₂
6d	pyrrolidino	phenyl	4-NO ₂
6e	piperidino	phenyl	4-NO ₂
6f	morpholino	phenyl	4-NO ₂
6g	dimethylamino	phenyl	2,4-(NO ₂) ₂
6h	diethylamino	phenyl	2,4-(NO ₂) ₂
6i	dibenzylamino	phenyl	2,4-(NO ₂) ₂
6j	pyrrolidino	phenyl	2,4-(NO ₂) ₂
6k	piperidino	phenyl	2,4-(NO ₂) ₂
6l	morpholino	phenyl	2,4-(NO ₂) ₂

Scheme 1 Synthetic route to *N,N*-disubstituted 2-amino-5-aryazo-selenazoles **6**

DMSO (method A) or in acetic acid solution (method B), or by addition of a methanolic solution of the carbocyclic or heterocyclic amine to a sulfuric acid solution of an aryl diazonium salt **5** prepared in the usual way [11] from a corresponding aromatic amine and nitrous acid (method C).

The resulting 5-phenylazo-substituted 2-amino-selenazoles **6** are deeply coloured compounds with intense

absorption bands in the visible range. Their structure follows unambiguously from the elemental analysis and ^1H NMR spectroscopic data (see Table 1). Thus, in the ^1H NMR spectra characteristic signals at about 3.0–4.0 ppm and 7.0–8.0 ppm were found. Whereas the first set of signals can be attributed to the protons attached at their 2-amino group, the second one to the protons at their 4-phenyl and 5-arylamino moieties.

Table 1 Spectroscopic data of the *N,N*-disubstituted 2-Amino-5-arylamino-4-phenylselenazoles **6a–6l**

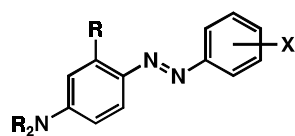
Nr.	^1H NMR (δ /ppm) measured in (a) CDCl_3 , (b) $\text{DMSO}-D_6$	λ_{max} /nm (lg ϵ) (in CH_2Cl_2)
6a	3.36 (s, 6H, NCH_3), 7.48–7.50 (m, 3H, CH), 7.74 (d, 2H, $^1J = 9$ Hz, CH), 8.27 (d, 2H, $^1J = 9.3$ Hz, CH), 8.29–8.33 (m, 2H, CH), (a)	527 (4.56)
6b	1.38 (t, 6H, CH_3), 3.70 (broad, 4H, NCH_2), 7.48–7.50 (m, 3H, CH), 7.73 (d, 2H, $^1J = 9.3$ Hz, CH), 8.26 (d, 2H, $^1J = 9.3$ Hz, CH), 8.30–8.33 (m, 2H, CH), (a)	534 (4.59)
6c	4.61 (broad, 2H, NCH_2), 5.15 (broad, 2H, NCH_2), 7.3–7.43 (m, 10H, CH), 7.49–7.54 (m, 3H, CH), 7.77 (d, 2H, $^1J = 9$ Hz, CH), 8.27 (d, 2H, $^1J = 9.3$ Hz, CH), 8.32–8.35 (m, 2H, CH), (a)	525 (4.56)
6d	2.15 (m, 4H, CH_2), 3.51 (m, 2H, NCH_2), 3.95 (m, 2H, NCH_2), 7.47–7.49 (m, 3H, CH), 7.73 (d, 2H, $^1J = 9.3$ Hz, CH), 8.26 (d, 2H, $^1J = 9$ Hz, CH), 8.28 (m, 2H, CH), (a)	532 (4.58)
6e	1.78 (m, 6H, CH_2), 3.79 (m, 4H, NCH_2), 7.47–7.49 (m, 3H, CH), 7.73 (d, 2H, $^1J = 9$ Hz, CH), 8.26 (d, 2H, $^1J = 9.3$ Hz, CH), 8.28–8.32 (m, 2H, CH), (a)	534 (4.58)
6f	3.86–3.87 (m, 8H, CH_2), 7.48–7.50 (m, 3H, CH), 7.76 (d, 2H, $^1J = 9.3$ Hz, CH), 8.28 (d, 2H, $^1J = 9$ Hz, H), 8.26–8.29 (m, 2H, CH), (a)	523 (4.55)
6g	3.29 (broad, 3H, NCH_3), 3.54 (broad, 3H, NCH_3), 7.50–7.52 (m, 3H, CH), 7.84 (dd, 1H, $^1J = 9.6$ Hz, $^3J = 0.3$ Hz, CH), 8.29–8.32 (m, 2H, CH), 8.33 (dd, 1H, $^1J = 9$ Hz, $^2J = 2.7$ Hz, CH), 8.59 (dd, 1H, $^1J = 2.7$ Hz, $^3J = 0.3$ Hz, CH), (a)	563 (4.61)
6h	1.32 (t, 6H, CH_3), 3.64 (q, 2H, NCH_2), 3.97 (q, 2H, NCH_2), 7.54–7.62 (m, 3H, CH), 7.84 (d, 1H, $^1J = 9$ Hz, CH), 8.27–8.31 (m, 2H, CH), 8.41 (dd, 1H, $^1J = 9$ Hz, $^2J = 2.4$ Hz, CH), 8.74 (d, 1H, $^2J = 2.4$ Hz, CH), (b)	569 (4.64)
6i	4.86 (broad, 2H, NCH_2), 5.24 (broad, 2H, NCH_2), 7.35–7.42 (m, 10H, CH), 7.56–7.59 (m, 3H, CH), 7.86 (d, 1H, $^1J = 9$ Hz, CH), 8.29–8.32 (m, 2H, CH), 8.44 (dd, 1H, $^1J = 9$ Hz, $^2J = 2.4$ Hz, CH), 8.76 (d, 1H, $^2J = 2.4$ Hz, CH), (b)	562 (4.62)
6j	2.07–2.10 (m, 4H, CH_2), 3.59 (broad, 2H, NCH_2), 3.95 (broad, 2H, NCH_2), 7.55–7.61 (m, 3H, CH), 7.84 (d, 1H, $^1J = 9.3$ Hz, CH), 8.28–8.30 (m, 2H, CH), 8.41 (dd, 1H, $^1J = 9.2$ Hz, $^2J = 2.7$ Hz, CH), 8.73 (d, 1H, $^2J = 2.7$ Hz, CH), (b)	568 (4.65)
6k	1.80 (broad, 6H, CH_2), 3.57 (broad, 2H, NCH_2), 4.15 (broad, 2H, NCH_2), 7.47–7.54 (m, 3H, CH), 7.83 (d, 1H, $^1J = 9.3$ Hz, CH), 8.28–8.34 (m, 2H, CH), 8.32 (dd, 1H, $^1J = 9.1$ Hz, $^2J = 2.4$ Hz, CH), 8.58 (d, 1H, $^1J = 2.4$ Hz, CH), (a)	572 (4.63)
6l	3.70 (broad, 2H, NCH_2), 3.79 (m, 4H, OCH_2), 4.16 (broad, 2H, NCH_2), 7.52–7.61 (m, 3H, CH), 7.85 (d, 1H, $^1J = 9.3$ Hz, CH), 8.29–8.32 (m, 2H, CH), 8.43 (dd, 1H, $^1J = 9$ Hz, $^2J = 2.7$ Hz, CH), 8.75 (d, 1H, $^2J = 2.4$ Hz, CH), (b)	562 (4.60)

Table 2 Absorption maxima (in nm) of the carbocyclic and heterocyclic arylazo compounds **6–9**, measured in several solvents of different polarity and correlation coefficients of equation (1)

Nr.	$R_2\text{N/R}^b$	Solvent ^{a)} X	CH π^*	TE –0.02	DN +0.26	TO +0.52	ET +0.53	ET +0.57	AN +0.78	MC +0.78	DMF +0.87	DMSO +1.01	a	b	r
6a	dimethylamino	4- NO_2	503	510	516	519	519	523	527	534	538	19.940	–1.27	–0.9834	
6b	diethylamino	4- NO_2	510	517	519	522	524	527	532	537	541	19.677	–1.10	–0.9677	
6c	dibenzylamino	4- NO_2	510	517	519	522	524	527	532	537	541	19.677	–1.10	–0.9677	
6d	pyrrolidino	4- NO_2	510	519	521	524	528	531	534	537	543	19.626	–1.14	–0.9806	
6e	piperidino	4- NO_2	509	515	515	516	519	519	525	528	533	19.711	–0.81	–0.9806	
6f	morpholino	4- NO_2	505	508	514	515	518	521	523	532	537	19.944	–1.17	–0.9552	
6g	dimethylamino	2,4-(NO_2) ₂	534	542	547	550	556	556	563	562	537	18.790	–1.26	–0.9643	
6h	diethylamino	2,4-(NO_2) ₂	540	547	548	554	560	560	569	565	574	18.572	–1.08	–0.9568	
6i	dibenzylamino	2,4-(NO_2) ₂	540	547	548	554	560	560	569	570	574	18.579	–1.12	–0.9702	
6j	pyrrolidino	2,4-(NO_2) ₂	544	551	553	556	562	565	572	571	576	18.439	–1.05	–0.9601	
6k	piperidino	2,4-(NO_2) ₂	538	547	546	548	558	551	562	556	563	18.557	–0.76	–0.8787	
6l	morpholino	2,4-(NO_2) ₂	538	542	547	549	554	556	562	565	570	18.690	–1.07	–0.9672	
7a	dimethylamino	4- NO_2	446	454	464	464	477	478	482	492	500	22.580	–2.43	–0.9725	
7b	dimethylamino	2,4-(NO_2) ₂	486	497	507	520	516	520	527	530	537	20.520	–1.91	–0.9772	
7c	diethylamino	4- NO_2	552	529	536	536	545	550	555	560	567	19.282	–1.55	–0.9715	
7d	diethylamino	2,4-(NO_2) ₂	570	582	582	586	593	594	603	601	605	17.527	–1.02	–0.9560	
8a	morpholino	4- NO_2	501	508	525	520	534	542	536	555	567	20.152	–2.29	–0.9623	
8b	morpholino	2,4-(NO_2) ₂	540	550	564	563	585	589	581	604	611	18.649	–2.18	–0.9529	
8c	morpholino	4- NO_2	509	518	528	526	535	548	545	558	568	19.817	–2.03	–0.9677	
8d	morpholino	2,4-(NO_2) ₂	554	565	579	574	590	607	603	616	624	18.199	–2.12	–0.9677	
8e	morpholino	2,4-(CN) ₂	543	549	559	554	566	570	569	576	582	18.491	–1.25	–0.9664	
9a	morpholino	4- NO_2	452	458	467	468	463	472	473	484	489	22.246	–1.61	–0.9566	
9b	morpholino	4- NO_2	495	501	505	507	508	512	515	522	526	20.285	–1.16	–0.9716	
9c	morpholin	2,4-(NO_2) ₂	526	533	538	539	541	546	550	554	558	19.062	–1.09	–0.9856	

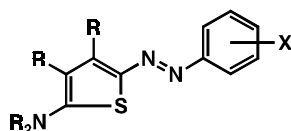
^{a)} CH: cyclohexane, TE: tetrachloromethane, DN: 1,4-dioxane, TO: toluene, ET: ethanol, AN: acetonitrile, MC: dichloromethane, DMF: *N,N*-dimethylformamide, DMSO: dimethylsulfoxide; ^{b)} R = phenyl for **6a–1**, **8c,d,e**, **9b**, and **9c**; R = H for **7a**, **7b**, **8a**, **8k**, and **9a**; R = diethylamino for **7c** and **7d**

As characteristic feature of the *N,N*-disubstituted 2-amino-5-arylazoselenazoles **6** the strong solvent dependence of their longest-wavelength absorptions is to be mentioned. Especially if their phenylazo moieties are substituted by one or more electron-accepting groups, like a nitro group, pronounced solvatochromic properties were observed. In this respect, the 5-nitrophenylazo-substituted 2-amino-selenazoles **6** exhibit, as documented in Table 2, a solvatochromic behaviour analogous to that of substituted arylazo compounds of the structures **7–9**. Although some of these azo compounds are already known, their solvatochromic properties were not studied as yet. Therefore, they have been prepared analogously to the 5-arylazo-substituted 2-amino-4-phenylselenazoles **6** by coupling of the before-mentioned carbocyclic and heterocyclic amines **1–3** with an ap-



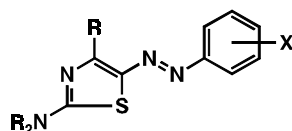
7a - 7d

Nr.	R ₂ N	R	X
7a	dimethylamino	H	4-NO ₂
7b	dimethylamino	H	2,4-(NO ₂) ₂
7c	diethylamino	diethylamino	4-NO ₂
7d	diethylamino	diethylamino	2,4-(NO ₂) ₂



8a - 8e

Nr.	R ₂ N	R	X
8a	morpholino	H	4-NO ₂
8b	morpholino	H	2,4-(NO ₂) ₂
8c	morpholino	phenyl	4-NO ₂
8d	morpholino	phenyl	2,4-(NO ₂) ₂
8e	morpholino	phenyl	2,4-(CN) ₂



9a - 9c

Nr.	R ₂ N	R	X
9a	morpholino	phenyl	4-NO ₂
9b	morpholino	phenyl	4-NO ₂
9c	morpholin	phenyl	2,4-(NO ₂) ₂

Scheme 2 Structural formulas of carbocyclic and heterocyclic arylazo compounds

propriate arenediazonium salt and their solvatochromic properties were compared with that of the selenazole analogues **6**.

As seen from Table 2, a bathochromic shift is generally observed by increasing the solvent polarity (positive solvatochromism). This solvent-induced band shift can be quantified by plotting the reciprocal wavelength $1/\lambda$ (λ measured in 10^{-5} m) of the longest-wavelength absorption bands with suitable solvent parameters, e.g., with the $E_T(30)$ values given by Dimroth and Reichardt [12] or, more precisely, with the π^* values given by Kamlet and Taft [13] using Equation (1). Usually, with the π^* values a good correlation, indicated by correlation coefficients r larger than 0.95, is observed.

$$1/\lambda_{\max} = a + b \cdot \pi^* \quad (1)$$

As can be seen from the determined parameters **b** of Equation 1, which are a measure of the solvent sensitivity of the absorption bands of the studied arylazo compound **6–9**, they exhibit generally a pronounced solvatochromism. The largest solvatochromic effects are observed with the azo compounds **7** and **8**. To the contrary, the lowest solvatochromic effects are observed with the heterocyclic azo compounds **6** and **9**. They contain an *N*-atom in their heterocyclic moieties. Obviously, the *N*-atom containing heterocyclic azo compounds **6** and **9** exhibit, so far as they have the same substitution pattern at their chromophoric framework, a less pronounced solvatochromism as their *N*-atom free analogues. Nevertheless, all azo compounds studied are highly dipolar compounds whose dipolarity is strongly altered by going from the electronic ground to their first electronic excited states [14]. In this respect the studied arylazo compounds **6–9**, especially the heterocyclic azo compounds **6** and **8**, seem good candidates for manufacturing materials with pronounced non-linear optical [15] or photorefractive properties [16]. Detailed studies in this direction are performed and will be published soon.

The authors thank Mrs. C. Koenig for measuring the NMR spectra

Experimental

Melting points were determined by means of heating table microscope (Boëtius). The ¹H NMR spectra were recorded with a Varian 300 MHz spectrometer Gemini 300 or with a JEOL 200 MHz spectrometer JNM FX 200. The elemental analytical data were determined by means of a LECO analyser CHNS 932. The preparation of the phenylazo starting compounds used is documented in the following papers: the *N,N*-disubstituted 2-amino-selenazoles **4** [9], the *N,N*-disubstituted 2-amino-thiophenes **2** [17], and the *N,N*-disubstituted 2-amino-thiazoles **3** [7a]. They are also available from the Syntec GmbH, Wolfen, Germany.

***N,N*-Disubstituted 2-amino-5-phenylazoselenazoles 6a–l**

Method A: The *N,N*-disubstituted 2-amino-4-phenylselenazole **4** (0.02 mol) was dissolved in acetic acid (20 mL) and dropwise mixed under stirring and cooling with a solution of 4-nitrophenyldiazonium tetrafluoroborate (0.021 mol, 4.97 g) in a mixture of water (5 mL) and acetic acid (5 mL). The product precipitated from the solution was isolated by filtration, washed with methanol, and recrystallized from a *n*-butanol/DMF mixture.

Method B: The *N,N*-disubstituted 2-amino-4-phenylselenazole **4** (0.02 mol) was dissolved in DMSO (15 mL) and dropwise mixed under stirring and cooling with a solution of 2,4-dinitrophenyldiazonium tetrafluoroborate (0.021 mol, 5.92 g) in DMSO (15 mL). The product formed either precipitates immediately or was forced to precipitate from the solution by addition of water after 60 min. It was isolated by filtration, washed with methanol, and recrystallized from a *n*-butanol/DMF mixture.

2-(N,N-Dimethylamino)-5-(4-nitrophenylazo)-4-phenylselenazole (6a)

yield 2.8 g (35%, method A); *m.p.* 226–228 °C (dec.).
 $C_{17}H_{15}N_5O_2Se$ Calcd.: C 51.11 H 3.78 N 17.50
 (400.3) Found: C 51.15 H 3.87 N 17.43.

2-(N,N-Diethylamino)-5-(4-nitrophenylazo)-4-phenylselenazole (6b)

yield 4.6 g (53%, method A); *m.p.* 185–186 °C.
 $C_{19}H_{19}N_5O_2Se$ Calcd.: C 53.28 H 4.47 N 16.35
 (428.4) Found: C 53.54 H 4.50 N 16.15.

2-(N,N-Dibenzylamino)-5-(4-nitrophenylazo)-4-phenylselenazole (6c)

yield 6.0 g (55%, method A); *m.p.* 240–243 °C.
 $C_{29}H_{23}N_5O_2Se$ Calcd.: C 63.04 H 4.20 N 12.68
 (552.5) Found: C 62.66 H 4.40 N 12.02.

5-(4-Nitrophenylazo)-4-phenyl-2-pyrrolidinoselenazole (6d)

yield 2.0 g (23%, method A); *m.p.* 163–165 °C (dec.).
 $C_{19}H_{17}N_5O_2Se$ Calcd.: C 53.53 H 4.02 N 16.43
 (426.3) Found: C 53.51 H 4.10 N 16.14.

5-(4-Nitrophenylazo)-4-phenyl-2-piperidinoselenazole (6e)

yield 4.6 g (53%, method A); *m.p.* 243–244 °C.
 $C_{20}H_{19}N_5O_2Se$ Calcd.: C 54.55 H 4.35 N 15.90
 (440.4) Found: C 54.30 H 4.58 N 15.88.

2-Morpholino-5-(4-nitrophenylazo)-4-phenylselenazoles (6f)

yield 3.2 g (37%, method A); *m.p.* 280–282 °C.
 $C_{19}H_{17}N_5O_3Se$ Calcd.: C 51.59 H 3.87 N 15.83
 (442.3) Found: C 51.44 H 4.38 N 15.81.

2-(N,N-Dimethylamino)-5-(2,4-dinitrophenylazo)-4-phenylselenazole (6g)

yield 1.4 g (15%, method B); *m.p.* 262–263 °C.
 $C_{17}H_{14}N_6O_4Se$ Calcd.: C 45.85 H 3.17 N 18.87
 (445.3) Found: C 45.72 H 3.71 N 18.70.

2-(N,N-Diethylamino)-5-(2,4-dinitrophenylazo)-4-phenylselenazole (6h)

yield 2.6 g (28%, method B); *m.p.* 225–227 °C.

$C_{19}H_{18}N_6O_4Se$ Calcd.: C 48.21 H 3.83 N 17.75
 (473.4) Found: C 47.81 H 4.35 N 17.52.

2-(N,N-Dibenzylamino)-5-(2,4-dinitrophenylazo)-4-phenylselenazole (6i)

yield 1.8 g (15%, method B); *m.p.* 241–242 °C.
 $C_{29}H_{22}N_6O_4Se$ Calcd.: C 58.30 H 3.71 N 14.07
 (597.5) Found: C 58.16 H 4.47 N 13.85.

5-(2,4-Dinitrophenylazo)-4-phenyl-2-pyrrolidinoselenazole (6j)

yield 2.3 g (24%, method B); *m.p.* 233–235 °C.
 $C_{19}H_{16}N_6O_4Se$ Calcd.: C 48.42 H 3.42 N 17.83
 (485.4) Found: C 48.41 H 3.55 N 17.84.

5-(2,4-Dinitrophenylazo)-4-phenyl-2-piperidinoselenazole (6k)

yield 1.3 g (13%, method B); *m.p.* 217–218 °C.
 $C_{20}H_{18}N_6O_4Se$ Calcd.: C 49.49 H 3.74 N 17.31
 (485.4) Found: C 49.05 H 3.75 N 16.45.

5-(2,4-Dinitrophenylazo)-2-morpholino-4-phenylselenazole (6l)

yield 1.2 g (12%, method B); *m.p.* 232–234 °C.
 $C_{19}H_{16}N_6O_5Se$ Calcd.: C 46.83 H 3.31 N 17.24
 (487.3) Found: C 46.96 H 3.99 N 17.19.

***N,N*-Disubstituted-4-phenylazoanilines 7a–d, *N,N*-Disubstituted 2-amino-5-phenylazothiophenes 8a–e, and *N,N*-Disubstituted 2-amino-5-phenylazothiazoles 9a–c**

Method C: The aromatic amine (0.01 mol) was dissolved in a mixture of acetic acid (50 mL) and conc. sulphuric acid (20 mL) and dropwise mixed under stirring and cooling with a solution of sodium nitrite (0.01 mol, 0.7 g) in water (2.5 mL). After 30 min the resulting diazonium salt solution was poured in a mixture of a *N,N*-disubstituted aniline, 2-aminothiophene, or 2-aminothiazole as coupling component (0.01 mol), dissolved in methanol (50 mL), and subsequently diluted with water (200 mL). The product precipitated was filtrated, washed with methanol, dried, and recrystallized from *n*-butanol.

***N,N*-Dimethyl-4-(4-nitrophenylazo)aniline (7a)**

yield 2.0 g (75%); *m.p.* 225–228 °C. – 1H NMR (in $CDCl_3$): δ /ppm = 3.12 (s, 6H, NCH_3), 6.73 (d, 2H, CH), 7.90 (m, 4H, CH), 8.31 (d, 2H, CH).
 $C_{14}H_{14}N_4O_2$ Calcd.: C 62.22 H 5.19 N 20.75
 (270.0) Found: C 61.96 H 5.35 N 20.56.

***N,N*-Dimethyl-4-(2,4-dinitrophenylazo)aniline (7b)**

yield 1.6 g (50%); *m.p.* 211 °C (dec.). – 1H NMR (in $CDCl_3$): δ /ppm = 3.15 (s, 6H, NCH_3), 6.73 (d, 2H, CH), 7.88 (m, 3H, CH), 8.40 (d, 1H, CH), 8.66 (s, 1H, CH).
 $C_{14}H_{13}N_5O_4$ Calcd.: C 53.33 H 4.13 N 22.22
 (315.0) Found: C 52.25 H 4.60 N 21.97.

***N,N*-Diethyl-3-(*N,N*-diethylamino)-4-(4-nitrophenylazo)aniline (7c)**

yield 2.5 g (67%); *m.p.* 108–110 °C. – 1H NMR (in DMSO- D_6): δ /ppm = 1.13–1.21 (m, 12H, CH_3), 3.45 (m, 4H, NCH_2), 3.59 (m, 4H, NCH_2), 5.90 (s, 1H, CH), 6.32 (d, 1H, CH), 7.69

(d, 2H, CH), 7.81 (d, 1H, CH), 8.28 (d, 2H, CH).

$C_{20}H_{27}N_5O_2$ Calcd.: C 65.05 H 7.32 N 18.97
(369.0) Found: C 64.89 H 7.38 N 19.10.

N,N-Diethyl-3-(*N,N*-diethylamino)-4-(2,4-dinitrophenylazo)aniline (**7d**)

yield 1.4 g (34%); *m.p.* 207 °C. – 1H NMR (in DMSO- D_6): δ /ppm = 1.07–1.25 (m, 12H, CH₃), 3.49 (m, 4H, NCH₂), 3.68 (m, 4H, NCH₂), 5.78 (s, 1H, CH), 6.43 (d, 1H, CH), 7.63 (d, 1H, CH), 7.73 (d, 1H, CH), 8.37 (dd, 1H, CH), 8.69 (d, 1H, CH).

$C_{20}H_{26}N_6O_4$ Calcd.: C 57.97 H 6.28 N 20.29
(414.0) Found: C 57.30 H 6.67 N 19.88.

2-Morpholino-5-(4-nitrophenylazo)thiophene (**8a**)

yield 1.3 g (40%); *m.p.* 231 °C. – 1H NMR (in CDCl₃): δ /ppm = 3.43 (m, 4H, NCH₂), 3.84 (m, 4H, OCH₂), 6.37 (d, 1H, CH), 7.65 (d, 1H, CH), 7.74 (d, 2H, CH), 8.25 (d, 2H, CH).

$C_{14}H_{14}N_4O_3S$ Calcd.: C 52.83 H 4.40 N 17.61 S 10.06
(318.0) Found: C 52.42 H 4.59 N 16.86 S 10.60.

5-(2,4-Dinitrophenylazo)-2-morpholinothiophene (**8b**)

yield 1.8 g (49%); *m.p.* 205–207 °C. – 1H NMR (in CDCl₃): δ /ppm = 3.84 (m, 4H, NCH₂), 4.00 (m, 4H, OCH₂), 7.77 (d, 1H, CH), 7.84 (d, 1H, CH), 8.42 (d, 1H, CH), 8.44 (d, 1H, CH), 8.78 (dd, 1H, CH).

$C_{14}H_{13}N_5O_5S$ Calcd.: C 46.28 H 3.58 N 19.28
(363.0) Found: C 46.18 H 3.81 N 18.57.

3,4-Diphenyl-2-morpholino-5-(4-nitrophenylazo)thiophene (**8c**)

yield 1.9 g (40%); *m.p.* 238–240 °C. – 1H NMR (in CDCl₃): δ /ppm = 3.11 (m, 4H, NCH₂), 3.66 (m, 4H, OCH₂), 7.14–7.24 (m, 10H, CH), 7.64 (d, 2H, CH), 8.18 (d, 2H, CH).

$C_{26}H_{22}N_4O_3S$ Calcd.: C 66.38 H 4.68 N 11.91 S 6.81
(470.0) Found: C 65.74 H 4.81 N 11.73 S 6.76.

5-(2,4-Dinitrophenylazo)-3,4-diphenyl-2-morpholinothiophene (**8d**)

yield 2.6 g (51%); *m.p.* 207 °C. – 1H NMR (in CDCl₃): δ /ppm = 3.27 (m, 4H, NCH₂), 3.66 (m, 4H, OCH₂), 7.13 (m, 4H, CH), 7.26 (m, 9H, CH), 7.58 (d, 1H, CH), 8.20 (d, 1H, CH), 8.55 (s, 1H, CH).

$C_{26}H_{21}N_5O_5S$ Calcd.: C 60.59 H 4.08 N 13.59 S 6.21
(515.0) Found: C 60.89 H 4.46 N 12.96 S 7.14.

5-(2,4-Dicyanphenylazo)-3,4-diphenyl-2-morpholinothiophene (**8e**)

yield 0.8 g (17%); *m.p.* 244–247 °C. – 1H NMR (in CDCl₃): δ /ppm = 3.25 (m, 4H, NCH₂), 3.66 (m, 4H, OCH₂), 7.11–7.27 (m, 10H, CH), 7.50 (d, 1H, CH), 7.57 (d, 1H, CH), 7.87 (s, 1H, CH).

$C_{28}H_{21}N_5OS$ Calcd.: C 70.74 H 4.42 N 14.74 S 6.74
(475.0) Found: C 69.75 H 5.24 N 13.72 S 6.47.

2-Morpholino-5-(4-nitrophenylazo)thiazole (**9a**)

yield 1.9 g (60%); *m.p.* 248–250 °C. – 1H NMR (in CDCl₃): δ /ppm = 3.72 (m, 4H, NCH₂), 3.83 (m, 4H, OCH₂), 7.80 (d, 2H, CH), 8.11 (s, 1H, CH), 8.27 (d, 2H, CH).

$C_{13}H_{13}N_5O_3S$ Calcd.: C 48.90 H 4.07 N 21.94 S 10.03
(319.0) Found: C 48.74 H 4.23 N 21.47 S 9.93.

2-Morpholino-5-(4-nitrophenylazo)-4-phenylthiazole (**9b**)

yield 3.0 g (77%); *m.p.* 279–280 °C. – 1H NMR (in CDCl₃): δ /ppm = 3.81 (m, 4H, NCH₂), 3.84 (m, 4H, OCH₂), 7.84 (m, 3H, CH), 8.27 (m, 4H, CH).

$C_{19}H_{17}N_5O_3S$ Calcd.: C 57.72 H 4.30 N 17.72 S 8.10
(395.0) Found: C 58.06 H 4.62 N 17.61 S 8.01.

5-(2,4-Dinitrophenylazo)-2-morpholino-4-phenylthiazole (**9c**)

yield 1.7 g (38%); *m.p.* 240 °C. – 1H NMR (in CDCl₃): δ /ppm = 3.86 (m, 8H, CH₂), 7.51 (m, 3H, CH), 7.82 (d, 1H, CH), 8.25 (d, 2H, CH), 8.36 (d, 1H, CH), 8.58 (d, 1H, CH).

$C_{19}H_{16}N_6O_5S$ Calcd.: C 51.82 H 3.64 N 19.09 S 7.27
(440.0) Found: C 51.93 H 3.80 N 18.96 S 7.33.

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