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Synthesis and characterisation of methine dyes derived from *N,N*-disubstituted 2-aminoselenazoles and some of their heterocyclic sulfur analogues

Dietmar Keil[a], Ronald Flaig[b,1], Anke Schroeder[b], Horst Hartmann[b,*]

[a]*SYNTEC Gmbh, ChemiePark Bitterfeld Wolfen, Arial A, Werkstattstrasse 10, D-06766 Wolfen, Germany*
[b]*Fachbereich Chemie, Fachhochschule Merseburg, Geusaer Str., D-06217 Merseburg, Germany*

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Abstract

By reaction of *N,N*-disubstituted 2-aminoselenazoles **4** and *N,N*-disubstituted 2-aminothiazoles **3** with the methine forming reagents **5** and **6** a series of new methine dyes **7–12** have been prepared and their spectral properties recorded and compared with the spectral properties of methine dyes **13–15** derived from *N,N*-disubstituted 2-aminothiophenes **2**

Keywords: *N,N*-disubstituted 2-aminoselenazoles; *N,N*-disubstituted 2-aminothiazoles; Methine dyes; UV/Vis spectral data

1. Introduction

In the last three decades *N,N*-disubstituted 2-aminothiophenes **2** and 2-aminothiazoles **3** received a lot of interest. As heteroanalogues of the well-known *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-aminothiophenes **2** [2] could by successfully transformed, especially if they are unsubstituted at their 5-position, e.g. in azo dyes [3], methine and azomethine dyes [2b,4], or squarylium [5] and croconium dyes [6]. Analogously, *N,N*-disubstituted 2-aminothiazoles **3** [7] have been transformed into the corresponding azo dyes [8], methine and azamethine dyes [9], as well as squarylium dyes [10] (Scheme 1).

Recently *N,N*-disubstituted 2-aminoselenazoles **4** have become of interest as starting materials for preparing different types of dyes. They could be prepared accordingly to the well-known Hantzsch method from *N,N*-disubstituted selenoureas [11] and have been converted successfully into corresponding azo dyes [12] and squarylium dyes [13]. This result stimulates us to convert these compounds also into methine dyes which are unknown as yet.

2. Results and discussion

A simple method for transforming the mentioned selenazoles **4** into methine dyes, their reaction with

* Corresponding author. Tel.: +49-3461-462025; fax: +49-3461-462192.
E-mail address: horst.hartmann@cui.fh-merseburg.de (H. Hartmann).
[1] Present address: DyStar Textilfarben GmbH & Co. Deutschland KG, Postfach 100480, D-51304 Leverkusen, Germany.

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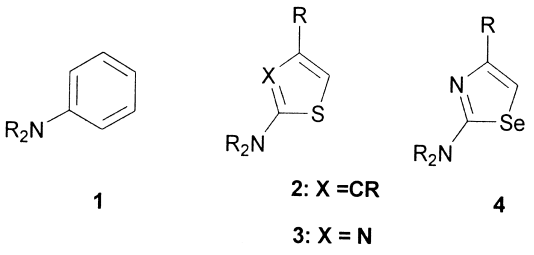


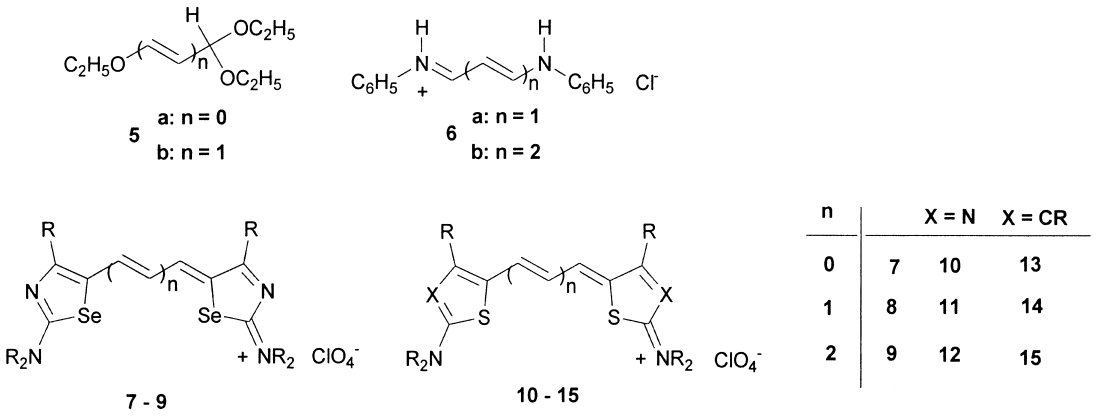
Scheme 1.

certain methine forming reagents, such as triethyl orthoformiate **5a**, 3-ethoxyacrolein-diethylacetal **5b**, malonic dialdehyde dianile hydrochloride **6a** or glutaconic dialdehyde dianile hydrochloride **6b**, has been performed. Thus, by heating a *N,N*-disubstituted 2-aminoselenazole **4** with triethyl orthoformiate **5a** in acetic anhydride in presence of some magnesium perchlorate at elevated temperatures corresponding monomethines **7** could be prepared. Analogously, by heating a *N,N*-disubstituted 2-aminoselenazole **4** with 3-ethoxyacrolein-diethylacetal **5b** or with malonic dialdehyde dianile hydrochloride **6a** in the same solvent under the same conditions, the corresponding trimethines **8** were obtained. Finally, by heating a *N,N*-disubstituted 2-aminoselenazole **4** with glutaconic dialdehyde dianile hydrochloride **6b** the corresponding pentamethines **9** were obtained. In all cases, the products formed precipitated from their reaction mixture after cooling, sometimes only after adding some diethyl ether. They could be isolated by filtration and purificated, if necessary, by recrystallisation (Scheme 2).

The simple formation of the methine dyes **7**–**9** from the *N,N*-disubstituted 2-aminoselenazoles **4** is surprising because *N,N*-disubstituted anilines **1** as the carbocyclic analogues of these heterocyclic amines are, as we checked, unable to react with the same methine forming reagents **5** and **6** under the same reaction conditions. In this respect, the reactivity of *N,N*-disubstituted 2-aminoselenazole **4** is strongly related to the reactivity of *N,N*-disubstituted 2-aminothiazole **3** and *N,N*-disubstituted 2-aminothiophenes **4** which can react with a variety of electrophilic reagents, such as with the mentioned methine forming reagents **5** and **6**, to yield appropriate products, such as the methine dyes **10**–**15** [3,7].

It is worth mentioning that the yields of the methine dyes **7**–**9** are mostly moderate, except when starting from 4-*tert*-butyl-substituted 2-aminoselenazole **4**. These compounds are unable to form, obviously from steric reasons, corresponding monomethine dyes (**7**, R = *tert*-butyl). In the course of the synthesis of selenazolyl-substituted pentamethines **9**, a surprising fact has been observed. By starting from glutaconic dialdehyde dianile hydrochloride **6b** and *N,N*-disubstituted 2-aminoselenazoles **4**, besides the expected pentamethines **9**, the formation of side-products was observed. Accordingly to the absorptions in the visible spectral region as well as to the NMR data these side-products their formation during the reaction could be monitored by thin-layer chromatography were identified as corresponding trimethine dyes **8**. Obviously, a splitting of the pentamethine chain in course of the dye-forming process occurs. This splitting was explained, as depicted in Scheme 3, as an attack of the nucleophilic 2-aminoselenzole compound **4** used as educt for the methine dye synthesis at one of the positive charged methine moiety in the pentamethine dye **9**. The existence of alternating positively as well as negatively charged CH-moieties in the chain of polymethines was demonstrated by other authors earlier and was taken as criterion for a typical polymethine structure [14,15]. Following these findings it has to be assumed that a *N,N*-disubstituted 2-aminoselenazole **4** can act as a strong nucleophilic compound which is able to attack a postively charged methine group of the methine chain in a pentamethine dyes **9** primarily formed to give rise, via **16**, to the formation of an intermediate adduct **17**. This intermediate can split, after deprotonation, into a trimethine dye **8** and in a ethylene-substituted selenazole derivative **18** its isolation was not performed, at yet. In this context it is worth mentioning, that by allowing the reaction of a pentamethine dye **9** with a *N,N*-substituted 2-aminoselenazole **4** in acetic anhydride the corresponding trimethine dye **8** is formed in moderate yield also.

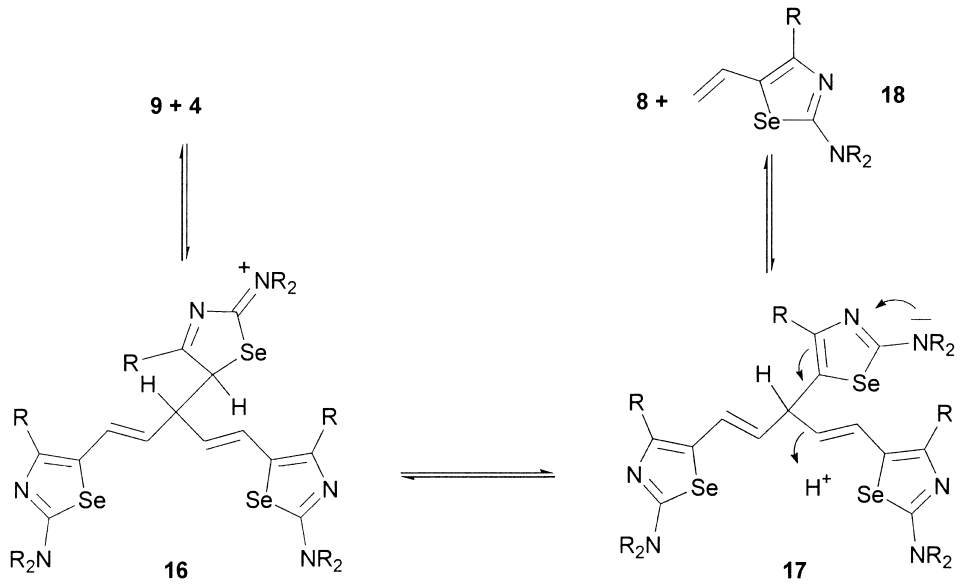
All the prepared selenzole-substituted methine dyes **7**–**9** are deeply coloured compounds their hue is originated from an intense absorption band in the visible spectral region. The position of this band



Scheme 2.

and, hence, the colour of the compound depend, as seen from the data depicted in Table 1, on the substitution pattern at the appropriate selanzole moiety and, in a especial manner, from the length of their methine chain. Thus, the monomethines **7** absorb at about 580 nm. The trimethines **8** exhibit intense absorptions at about 680 nm, and the pentamethines **9** absorb in the near infrared region at about 780 nm.

To see if this spectral behaviour is normal for one of the methine dyes derived from amino-substituted heterocyclic compounds, a comparison to the spectral absorption of the methine dyes derived from *N,N*-disubstituted 2-aminothiophenes **2** and *N,N*-disubstituted 2-aminothiazoles **3** seems necessary. Whereas corresponding methine dyes **13–15** derived from *N,N*-disubstituted 2-aminothiophenes **2** have been prepared and studied spectroscopically in detail some decades earlier [2b,4a] the methine dyes **10–12** derived from *N,N*-disubstituted 2-aminothiazoles **3** have not been studied extensively in this respect



Scheme 3.

as yet. Although such dyes have been described, e.g. in the patent literature [9a], no detailed information on their spectral properties have been reported. Therefore, we have prepared some of such methine dyes starting from *N,N*-disubstituted 2-aminothiazoles **3** and using the same methine forming reagents **5** and **6** as used for the preparation of the selenazolyl-substituted methines **7–9**. Thus, from *N,N*-disubstituted 2-aminothiazoles **3** and triethyl orthoformiate **5a** the corresponding monomethines **10** were obtained. Analogously, from 3-ethoxyacrolein-diethylacetal **5b** and glutaconic dialdehyde dianile hydrochloride **6b** the corresponding trimethines **11** and pentamethines **12**, respectively, have been obtained in satisfactory yield mostly.

Analogously to the formation of the selenazolyl-substituted pentamethines **9** from their educts **4** and **6b,** the formation of the thiazolyl- and thienyl-substituted pentamethines **12** and **15** from their corresponding educts **2**, **3**, and **6a** is accompanied by the one of corresponding trimethines **11** and **14**, respectively, their presence in the reaction mixture could be unambiguously detected by TLC and by means of UV/Vis spectroscopy.

By comparing the spectral data of the methine dyes **7–9** derived from the *N,N*-disubstituted 2-aminoselenazoles **4** with the spectral data of the methine dyes **10–12** and **13–15** derived from the *N,N*-disubstituted 2-aminothiazoles **3** and 2-aminothiophenes **2**, respectively, a certain similarity was found (see Fig. 1 and Table 2). Identically substituted compounds of the selenazole and thiazole series absorb nearly at the same wavelength. In contrast, the same compounds absorb in the thiophene series at about a 40 nm longer wavelength. Typically for all compounds the spectral shift observed by going from a monomethine dye to an

Table 1
Longest-wavelength absorption data of the bis-(2-amino-5-selenazolyl)-substituted methines **7–9**

No.	R_2N	R	*n*	λ_{max} (log ε)
7a	Dimethylamino	Phenyl	0	584 (4.95)
7b	Pyrrolidino	Phenyl	0	588 (4.94)
7c	Piperidino	Phenyl	0	596 (4.95)
7d	Morpholino	Phenyl	0	595 (4.97)
8a	Dimethylamino	Phenyl	1	677 (5.26)
8b	Dimethylamino	*tert*-Butyl	1	685 (5.10)
8c	Diethylamino	Phenyl	1	684 (5.29)
8d	Pyrrolidino	Phenyl	1	680 (5.27)
8e	Piperidino	Phenyl	1	688 (5.27)
8f	Methylanilino	Phenyl	1	695 (5.09)
8g	Dibenzylamino	Phenyl	1	690 (5.31)
8h	Morpholino	Phenyl	1	686 (5.26)
9a	Dimethylamino	Phenyl	2	780 (5.38)
9b	Dimethylamino	*tert*-Butyl	2	759 (5.41)
9c	Diethylamino	*tert*-Butyl	2	766 (5.42)
9d	Pyrrolidino	*tert*-Butyl	2	764 (5.38)
9e	Piperidino	*tert*-Butyl	2	771 (5.39)
9f	Morpholino	Phenyl	2	787 (5.36)
9g	Morpholino	*tert*-Butyl	2	766 (5.39)
9h	Dibenzylamino	Phenyl	2	795 (5.39)

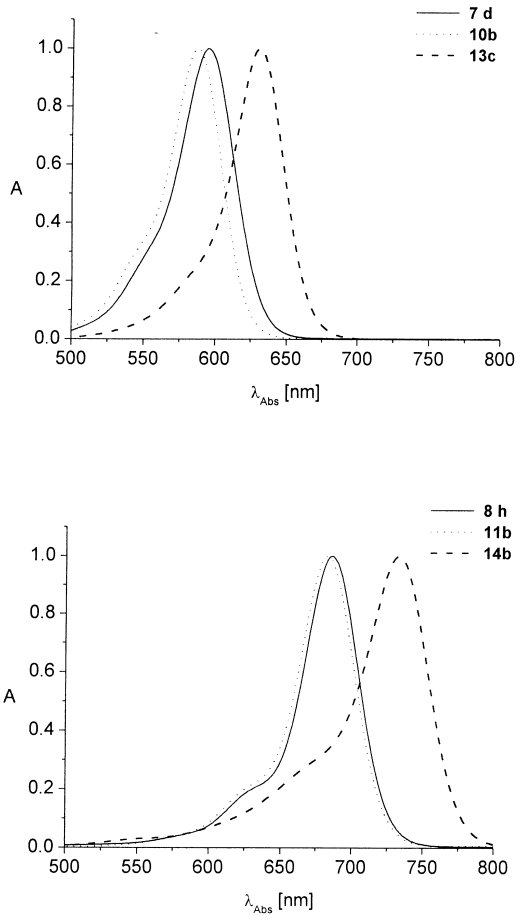


Fig. 1. Absorption spectra of the (a) monomethines **7d**, **10b**, and **13c**, (b) trimethines **8h**, **11b**, and **14b**.

Table 2
Longest-wavelength absoprtion data of the sulphur-containing methines **10**–**15**

No.	R_2N	R	*n*	X	λ_{max} (log ε)	Ref.
10a	Morpholino	H	0	N	552 (4.93)	
10b	Morpholino	Phenyl	0	N	586 (4.95)	
10c	Piperidino	4-Tolyl	0	N	593 (4.98)	
10d	Morpholino	4-Chlorophenyl	0	N	596 (4.96)	
11a	Morpholino	H	1	N	642 (5.08)	
11b	Morpholino	Phenyl	1	N	680 (5.23)	
11c	Dimethylamino	*tert*-Butyl	1	N	653 (5.31)	
11d	Piperidino	*tert*-Butyl	1	N	665 (5.33)	
11e	Piperidino	4-Tolyl	1	N	690 (5.18)	
11f	Morpholino	4-Chlorophenyl	1	N	690 (5.17)	
12a	Dimethylamino	*tert*-Butyl	2	N	753 (5.39)	
12b	Piperidino	*tert*-Butyl	2	N	765 (5.37)	
12c	Diethylamino	*tert*-Butyl	2	N	761 (5.42)	
13a	Dimethylamino	H	0	CH	591 (5.11)	[2b]
13b	Morpholino	H	0	CH	599 (5.16)	[2b]
13c	Morpholino	Phenyl	0	$C(C_6H_5)$	630 (4.94)	[4a]
14a	Morpholino	H	1	CH	692 (5.27)	[2b]
14b	Morpholino	Phenyl	1	$C(C_6H_5)$	728 (5.25)	[4a]
15a	Morpholino	Phenyl	2	$C(C_6H_5)$	840 (5.15)	[4a]

identically substituted trimethine dye is to be mentioned. It has with ca. 100 nm nearly the same as by going from a trimethine dye to a pentamethine dye [16].

The structures of all the new methine dyes prepared follow from their analytical and from some of their spectroscopic data, such as from their ^{1}H NMR data (see Table 3).

Thus, in the ^{1}H NMR spectra of the methines **7**–**12** all signals for the appropriate H-atoms at the amino substituents and at the substituents R in the heterocyclic moieties could be detected and assigned. Moreover, all the signals for the protons at the methine chain of the dyes **7**–**12**, as far as they are not hidden under the signals of the protons of the substituents R, could be detected and assigned also. For instance, the protons at the methine chain in the monomethines **7** and **10** were found as singlets with a chemical shift between 8.10 and 8.40 ppm. Contrarily, the protons at the methine chain in the trimethines **8** and **11,** as well as in the pentamethines **9** and **12** were recorded as multiplets. Thus, the signals of the methine protons adjacent to the corresponding heterocycles were found as doublets between 7.95 and 8.60 ppm in the trimethine series **8** and **11**, and as doublets at about 7.90 ppm in the pentamethine series **9** and **12**. The protons at the *meso*-position in the methine chain were found as triplets between 6.00 and 6.80 ppm in the trimethines **8** and **11** and at about 7.50 ppm in the pentamethines **9** and **12**. The observed differences in the chemical shift of the protons at different positions of the methine chain confirm the above-mentioned different charge distribution along the conjugated π-system in the corresponding methine dyes and demonstrate that the methine positions adjacent to the heterocyclic moieties are the most positive charged ones. In contrast, the methine positions adjacent to these α-positions are the lowest positive charged methine positions.

3. Experimental

Melting points were determined by means of a Boëtius heating table microscope. The NMR spectra were recorded with a Varian 300 MHz spectrometer Gemini 300 and the UV/Vis spectra with a Perkin-Elmer spectrometer Lambda 900. The elemental analytical data were determined by means of a LECO analyser CHNS 932 (Table 4).

3.1. Preparation of bis-(2-amino-5-selenazolyl)-substituted monomethines 7

3.1.1. General procedure

A mixture of a *N,N*-disubstituted 2-aminoselenazole **4** (10 mmol), triethyl orthoformiate (1 ml), and magnesium perchlorate (2.2 g, 10 mmol) in acetic anhydride (50 ml) was heated for 5 min at 100 °C. After cooling and addition of diethyl ether to the reaction mixture the product formed was isolated by filtration.

*3.2. Prepartion of bis-(2-amino-5-thiazolyl)-substituted monomethines **10***

3.2.1. General procedure

The preparation procedure was the same as before, however, instead of a *N,N*-disubstituted 2-aminoselenazole **4** an equivalent amount of a *N,N*-disubstituted 2-aminothiazole **3** was used.

Table 3
^{1}H NMR spectral data of the methines **7**–**12**

No.	^{1}H NMR δ-values, in ppm (assignment)	Solvent
7a	3.42 (*s*, 6H, CH_3), 3.53 (*s*, 6H, CH_3), 7.56 (*m*, 6H, CH), 7.78 (*m*, 4H, CH), 8.26 (*s*, 1H, CH)	DMSO-d_6
7b	2.12 (*m*, 8H, CH_2), 3.67 (*t*, 4H, NCH_2), 3.95 (*t*, 4H, NCH_2), 7.57 (*m*, 6H, CH), 7.78 (*m*, 4H, CH), 8.27 (*s*, 1H, CH)	DMSO-d_6
7c	1.74 (*m*, 12H, CH_2), 3.71 (*m*, 4H, CH_2), 4.12 (*m*, 4H, CH_2), 7.55 (*m*, 6H, CH), 7.77 (*m*, 4H, CH), 8.28 (*s*, 1H, CH)	DMSO-d_6
7d	3.84 (*m*, 12H, CH_2), 4.11 (*m*, 4H, CH_2), 7.57 (*d*, 6H, CH), 7.79 (*d*, 4H, CH), 8.34 (*s*, 1H, CH)	DMSO-d_6
8a	3.41 (*m*, 12H, CH_3), 6.59 (*t*, J = 11.7 Hz, J = 12.6 Hz, 1H, CH), 7.54–7.72 (*m*, 10 H, CH), 8.08 (*d*, 2H, J = 12.3 Hz, CH)	DMSO-d_6
8b	1.49 (*s*, 18H, CH_3), 3.35 (*s*, broad, 12H, NCH_3), 5.96 (*t*, J = 12.0 Hz, 1H, CH), 8.58 (*d*, J = 12 Hz, 2H, CH)	DMSO-d_6
8c	1.33 (*s*. 12H, CH_3), 3.65 (*m*, 4H, NCH_2), 3.92 (*m*, 4H, NCH_2), 6.55 (*t*, J = 11.7 Hz, J = 12.6 Hz, 1H, CH), 7.52–7.73 (*m*, 10H, CH), 8.10 (*d*, J = 12 Hz, 2H, CH)	DMSO-d_6
8d	2.09 (*m*, 8H, CH_2), 3.59 (*m*, 4H, NCH_2), 3.89 (*m* 4H, NCH_2), 6.62 (*t*, 1H, CH), 7.57–7.69 (*m*, 10H, CH), 8.05 (*d*, 2H, CH)	DMSO-d_6
8e	1.73 (*m*, 12H, CH_2), 3.86 (*m*, 8H, NCH_2), 6.47 (*t*, J = 12 Hz, J = 12 Hz, 1H, CH), 7.52–7.72 (*m*, 10H, CH), 8.09 (*d*, J = 12 Hz, 2H, CH)	DMSO-d_6
8f	3.76 (*s*, 6H, NCH_3), 6.63 (*t*, J = 12 Hz, J = 15 Hz, 1H, CH), 7.56–7.75 (*m*, 20H, CH), 8,09 (*d*, J = 12 Hz, 2H, CH)	DMSO-d_6
8g	4.89 (*s*, 4H, NCH_2), 5.23 (*s*. 4H, NCH_2), 6.67 (*t*, J = 12.3 Hz, J = 12.6 Hz, 1H, CH), 7.37–7.75 (*m*, 30H, CH), 8.15 (*d*, J = 12 Hz, 2H, CH)	DMSO-d_6
8h	3.82 (16H, NCH_2, OCH_2), 6.61 (*t*, J = 12 Hz, J = 12 Hz, 1H, CH), 7.54–7.73 (*m*, 10H, CH), 8.14 (*d*, J = 12.3 Hz, 2H, CH)	DMSO-d_6
9a	3.46 (*s*, 12H, NCH_3), 6.58 (*t*, 2H, CH), 7.42–7.77 (*m*, 13H, CH)	CD_3NO_2
9b	1.49 (*s*, 18H, CH_3), 3.41 (*s*, 12H, NCH_3), 6.40 (*t*, 2H, CH), 7.44 (*t*, 1H, CH), 7.93 (*d*, 2H, CH)	$CDCl_3$
9c	1.37 (*t*, 12H, CH_3), 1.49 (*s*, 18H, CH_3), 3.73 (*m*, 8H, NCH_2), 6.41 (*t*, 2H, CH), 7.44 (*t*, 1H, CH), 7.94 (*d*, 2H, CH)	$CDCl_3$
9d	1.49 (*s*, 18H, CH_3), 2.17 (*m*, 8H, CH_2), 3.74 (*m*, 8H, NCH_2), 6.40 (*t*, 2H, CH), 7.42 (*t*, 1H, CH), 7.91 (*d*, 2H, CH)	$CDCl_3$
9e	1.47 (*s*, 18H, CH_3), 1.78 (*m*, 12H, CH_2), 3.78 (*m*, 8H, NCH_2), 6.38 (*t*, 2H, CH), 7.42 (*t*,1H, CH), 7.92 (*d*, 2H, CH)	$CDCl_3$
9f	3.82–3.85 (*m*, 16H, CH_2), 6.77 (*t*, 2H, CH), 7.55–7.71 (*m*, 13H, CH)	DMSO-d_6
9g	1.47 (*s*, 18H, CH_3), 3.86 (*m*, 16H, CH_2), 6.55 (*t*, 2H, CH), 7.44 (*t*, 1H, CH), 7.95 (*d*, 2H, CH)	$CDCl_3$
9h	4.69–5.00 (*m*, 8H, NCH2), 6.74 (*t*, 2H, CH), 7.27–7.70 (*m*, 33H, CH)	$CDCl_3$
10a	3.87 (*m*, 8H, CH_2), 3.96 (*m*, 8H, CH_2), 8.41 (*s*, 2H, CH), 8.42 (*s*, 1H, CH)	CD_3NO_2
10b	3.83 (*m*, 12H, CH_2), 3.90–4.20 (*m*, 4H, CH_2), 7.58–7.60 (*m*, 6H, CH), 7.82–7.85 (*m*, 4H, CH), 8.19 (*s*, 1H, CH)	DMSO-d_6
10c	1.74 (*m*, 12H, CH_2), 2.41 (*s*, 6H, CH_3), 3.93 (*m*, 8H, CH_2), 7.40 (*d*, J 8.1 Hz, 4H, CH), 7.72 (*d*, J = 8.1 Hz, 4H, CH), 8.17 (*s*, 1H, CH)	DMSO-d_6
10d	3.36 (*m*, 8H, CH_2), 3.84 (*m*, 8H, CH_2), 7.75 (*d*, J = 6.6 Hz, 4H, CH), 7.89 (*d*, J = 6.6 Hz, 4H, CH), 8. 14 (*s*, 1H, CH)	DMSO-d_6
11a	3.41 (*m*, 8H, CH_2), 3.82 (*m*, 8H, CH_2), 6.76 (*t*, J = 13.2 Hz, 1H, CH), 8. 18 (*d*, J = 13.2 Hz, 2H, CH), 8.60 (*s*, 2H, CH)	DMSO-d_6
11b	3.81 (*m*, 8H, CH_2), 3.87 (*m*, 8H, CH_2), 6.58 (*t*, 1H, CH), 7.56 (*t*, 4H, CH), 7.62 (*t*, 2H, CH), 7.75 (*d*, 4H, CH), 8.23 (*d*, 2H, CH)	DMSO-d_6
11c	1.52 (*s*, 18H, CH_3), 3.46 (*s*, 12H, NCH_3), 6.28 (*t*, 1H, CH), 7.95 (*d*, 2H, CH)	$CDCl_3$
11d	1.51 (*s*, 18H, CH_3), 1.79 (*m*, 12H, CH_2), 3.87 (*m*, 8H, NCH_2), 6.22 (*t*, 1H, CH), 7.94 (*d*, 2H, CH)	$CDCl_3$
11e	1.72 (*m*, 12 H, CH_2), 3.85 (*m*, 8H, CH_2), 6.47 (*t*, J = 12.3 Hz, 1H, CH), 7.38 (*d*, J = 8.1 Hz, 4H, CH), 7.67 (*d*, J = 8.1 Hz, 4H, CH), 8.13 (*d*, J = 12.3 Hz, 2H, CH)	DMSO-d_6
11f	3.83 (*m*, 8H, CH), 3.89 (*m*, 8H, CH), 6.61 (*t*, J = 12.3 Hz, 1H, CH), 7.64 (*d*, J = 8.7 Hz, 4H, CH), 7.78 (*d*, J = 8.7 Hz, 2H, CH), 8.19 (*d*, J = 12.3 Hz, 2H, CH)	DMSO-d_6
12a	1.48 (*s*, 18H, CH_3), 3.42 (*s*, 12H, NCH_3), 6.51 (*t*, 2H, CH), 7.53 (*t*, 1H, CH), 7.90 (*d*, 2H, CH)	$CDCl_3$
12b	1.47 (*s*, 18H, CH_3), 1.78 (*m*, 12H, CH_2), 3.81 (*m*, 8H, NCH_2), 6.48 (*t*, 2H, CH), 7.50 (*t*, 1H, CH), 7.89 (*d*, 2H, CH)	$CDCl_3$
12c	1.35 (*t*, 12H, CH_3), 1.48 (*s*, 18H, CH_3), 3.72 (*q*, 8H, NCH_2), 6.47 (*t*, 2H, CH), 7.57 (*t*, 1H, CH), 7.93 (*d*, 2H, CH)	$CDCl_3$

Table 4
Characteristic substance data of compounds **7–12**

No.	Yield (%)	m.p. (°C)	Formula (m.w.)	Calcd. found			
				C	H	N	S
7a	25	223–224	$C_{23}H_{23}ClN_4O_4Se_2$	45.04	3.75	9.14	
			(612.8)	44.91	3.72	9.31	
7b	32	282–283	$C_{27}H_{27}ClN_4O_4Se_2$	48.73	4.06	8.42	
			(664.9)	48.52	4.11	8.66	
7c	40	269 (dec.)	$C_{29}H_{31}ClN_4O_4Se_2$	50.22	4.47	8.08	
			(693.0)	49.65	4.88	8.13	
7d	50	294–297	$C_{27}H_{27}ClN_4O_6Se_2$	46.49	3.87	8.04	
			(696.9)	46.13	3.87	7.77	
8a	20	273–274	$C_{25}H_{25}ClN_4O_4Se_2$	47.00	3.94	8.77	
			(638,9)	46.59	4.03	8.49	
8b	25	304–305	$C_{21}H_{33}ClN_4O_4Se_2$	42.08	5.51	9.35	
			(598.9)	42.18	5.25	9.40	
8c	20	218–222	$C_{29}H_{33}ClN_4O_4Se_2$	50.12	4.79	8.06	
			(695,0)	49.70	4.84	7.84	
8d	20	267–268	$C_{29}H_{29}ClN_4O_4Se_2$	50.41	4.23	8.11	
			(691.0)	50.23	4.25	7.88	
8e	50	264–265	$C_{31}H_{33}ClN_4O_4Se_2$	51.79	4.63	7.79	
			(719.0)	51.81	4.62	7.78	
8f	45	189–191	$C_{35}H_{29}ClN_4O_4Se_2$	55.10	3.83	7.34	
			(763.0)	55.38	3.96	7.04	
8g	45	233–235	$C_{49}H_{41}ClN_4O_4Se_2$	62.39	4.38	5.94	
			(943,3)	61.90	4.39	5.73	
8h	50	293–295	$C_{29}H_{29}ClN_4O_6Se_2$	48.18	4.04	7.75	
			(723.0)	48.44	4.07	7.54	
9a	35	223–228	$C_{27}H_{27}ClN_4O_4Se_2$	48.77	4.09	8.43	
			(665.0)	48.64	4.20	8.20	
9b	20	258–264	$C_{23}H_{35}ClN_4O_4Se_2$	44.21	5.65	8.97	
			(625.0)	44.10	5.65	8.87	
9c	20	162–164	$C_{27}H_{43}ClN_4O_4Se_2$	47.62	6.36	8.23	
			(681.0)	47.54	6.49	8.04	
9d	35	255–257	$C_{27}H_{39}ClN_4O_4Se_2$	47.90	5.81	8.28	
			(677.0)	47.88	5.86	7.52	
9e	20	213–215	$C_{29}H_{43}ClN_4O_4Se_2$	49.40	6.15	7.95	
			(705.07)	49.21	6.25	7.59	
9f	25	266–267	$C_{31}H_{31}ClN_4O_6Se_2$	49.71	4.17	7.48	
			(749.9)	48.66	4.12	7.45	
9g	15	252–254	$C_{27}H_{39}ClN_4O_4Se_2$	45.74	5.54	7.90	
			(709.0)	45.69	5.51	7.93	
9h	15	209–213	$C_{51}H_{43}ClN_4O_6Se_2$	63.20	4.47	5.78	
			(969.3)	63.30	4.53	5.78	
10a	74	268–270	$C_{15}H_{19}ClN_4O_6S_2$	39.95	4.22	12.43	14.20
			(450.5)	40.42	4.93	11.99	14.13
10b	98	285–286	$C_{27}H_{27}ClN_4O_6S_2$	53.77	4.48	9.29	10.62
			(602.5)	53.17	5.28	8.52	10.02
10c	80	285–286	$C_{31}H_{37}ClN_4O_4S_2$	59.31	5.90	8.93	10.20
			(627.2)	59.46	5.60	8.24	10.29
10d	72	320–321	$C_{27}H_{25}Cl_3N_4O_6S_2$	48.21	3.72	8.33	9.52
			(672.0)	48.37	4.10	7.66	9.49
11a	36	224–226	$C_{17}H_{21}ClN_4O_6S_2$	42.81	4.41	11.75	13.43
			(476.5)	42.81	4.54	10.65	12.72

(*continued on next page*)

Table 4 (*continued*)

No.	Yield (%)	m.p. (°C)	Formula (m.w.)	Calcd. found			
				C	H	N	S
11b	64	287–290	$C_{29}H_{29}ClN_4O_6S_2$	55.37	4.61	8.91	10.18
			(628.5)	54.44	5.16	8.83	9.71
11c	20	250–251	$C_{21}H_{33}ClN_4O_4S_2$	49.94	6.59	11.09	12.70
			(505.1)	49.99	6.28	10.71	12.87
11d	20	244–246	$C_{27}H_{41}ClN_4O_4S_2$	55.41	7.06	9.57	10.96
			(585.2)	55.35	6.71	9.28	11.08
11e	37	217–221	$C_{33}H_{37}ClN_4O_4S_2$	60.62	5.66	8.57	9.80
			(653.3)	60.46	5.83	9.06	9.02
11f	60	273–274	$C_{29}H_{27}Cl_3N_4O_6S_2$	49.86	3.87	8.02	9.17
			(698.0)	49.93	4.19	8.03	8.45
13a	30	255–257	$C_{23}H_{35}ClN_4O_4S_2$	52.01	6.64	10.55	12.07
			(531.1)	52.25	6.29	10.25	12.34
12b	25	236–238	$C_{29}H_{43}ClN_4O_4S_2$	56.98	7.09	9.17	10.49
			(611.3)	57.03	7.28	8.95	10.22
12c	25	180–182	$C_{27}H_{43}ClN_4O_4S_2$	55.22	7.38	9.54	10.92
			(587.3)	55.01	6.97	9.17	10.95

3.3. Preparation of 1,3-bis-(2-amino-5-selenazolyl)-substituted trimethines ***8***

3.3.1. Method A

A mixture of a *N,N*-disubstituted 2-aminoselenazole **4** (10 mmol), malonic aldehyde dianile hydrochloride (1.37 g, 5.3 mmol), and magnesium perchlorate (2.2 g, 10 mmol) in acetic anhydride (50 ml) was heated for 5 min at 100 °C. After cooling and addition of diethyl ether to the reaction mixture the product formed was isolated by filtration.

3.3.2. Method B

A mixture of a 1,5-bis-(2-amino-5-selenazolyl)-substituted pentamethine **9** (1 mmol) and a 2-aminoselenazole **4** (4 mmol) in acetic anhydride (10 ml) was heated at 100 °C for about 20 min. In this time the reaction was monitored by thin layer chromatography or by UV/Vis spectroscopy. After cooling and addition of diethyl ether to the reaction mixture the product formed was isolated by filtration.

3.4. Preparation of 1,3-bis-(2-amino-5-thiazolyl)-substituted trimethines ***11***

3.4.1. General procedure

A mixture of a *N,N*-disubstituted 2-aminothiazole **3** (10 mmol), 3-ethoxyacroleine diethylacetal (1 ml), and magnesium perchlorate (2.2 g, 10 mmol) in acetic anhydride (50 ml) was heated for 5 min at 100 °C. After cooling and addition of diethyl ether to the reaction mixture the product formed was isolated by filtration.

3.5. Preparation of 1,5-bis-(2-amino-5-selenazolyl)-substituted pentamethines ***9***

3.5.1. General procedure

A mixture of a *N,N*-disubstituted 2-aminoselenazole **4** (10 mmol), glutaconic aldehyde dianile hydrochloride (1.5 g, 5.3 mmol), and magnesium perchlorate (2.2 g, 10 mmol) in acetic anhydride (50 ml) was heated for 5 min at 100 °C. After cooling and addition of diethyl ether to the reaction mixture the product formed was isolated by filtration.

3.6. Preparation of 1,5-bis-(2-amino-5-thiazolyl)-substituted pentamethines ***12***

3.6.1. General procedure

The preparation procedure was the same as before, instead of a *N,N*-disubstituted 2-aminoselenazole **4** an equivalent amount of a *N,N*-disubstituted 2-aminothiazole **3** was used.

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