Preparation and Characterisation of Several New *N*-Disubstituted 2-Aminoselenophene Derivatives*

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Dedicated to Prof. Dr. Bärbel Schulze on the occasion of her 60th birthday

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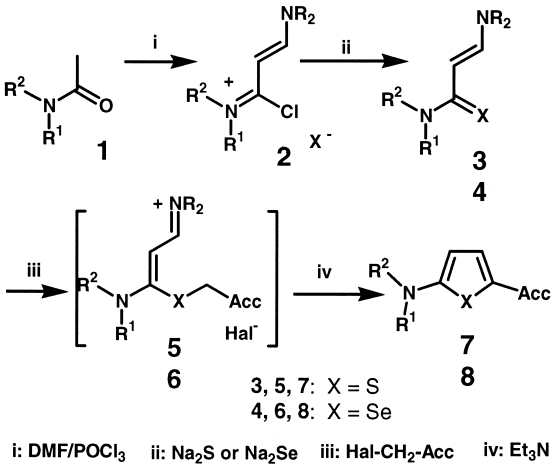
N-Disubstituted 2-Aminoselenophenes, 1-Chlorovinamidinium Salts, Solvatochromism

N,N′-Persubstituted selenoacrylamides (**4**), easily available by reaction of 1-chlorovinamidinium salts (**2**) with sodium selenide, were transformed by means of acceptor-substituted halomethyl compounds (**9**–**14**) into new 2-aminoselenophene derivatives (**15**–**20**). Their UV/vis data are presented, and the positive solvatochromism of 2-R_2N-5-acceptor-substituted selenophenes is reported.

Introduction

N,N′-Persubstituted 3-aminothioacrylamides of the general structure **3** are well-known as versatile synthons in organic chemistry [1]. They are easily available by several different routes [2], *e.g.*, from simple *N*-disubstituted acetamides **1** *via* corresponding 1-chlorovinamidinium salts **2** [3], and are highly reactive towards a lot of preferably electrophilic reagents which are able to transform these educts with their S-C-C-C moiety into a variety of products. For instance, they can be transformed, by reaction with halomethylcarbonyl compounds as well as with nitro- or dicyanovinyl-substituted (het)arylmethyl halides, *via* corresponding 1-mercapto-substituted vinamidinium salts of the general structure **5**, into 5-aceptor-substituted 2-aminothiophenes **7**. Examples of the latter include 5-acyl- or 5-alkoxycarbonyl-substituted 2-aminothiophenes [4], 5′-nitro- or 5′-dicyanovinyl-substituted 5-amino-2,2′-bithiophenes and 4′-nitro- or 4′-dicyanovinyl-substituted 5-phenyl-2-aminothiophenes [5]. Whereas the 5-acyl- and 5-alkoxycarbonyl-substituted 2-aminothiophenes raise some interest as starting materials for preparing deeply coloured methine dyes [6], the nitro- and dicyanovinyl-substituted 5-amino-2,2′-bithiophenes and 2-amino-5-phenylthiophenes are of practical interest as strongly solvatochromic compounds useful for measuring the polarity of organic solvents [7, 8] or for manufacturing of materials with high non-linear optical properties [9].



Scheme 1.

Starting from the same 1-chloro-substituted vinamidinium salts **2**, the *N,N′*-persubstituted 3-aminoselenoacrylamides **4**, as the selenium-analogues of the thioacrylamides **3**, have also been prepared recently [3]. Their use as starting materials for preparing *N*-disubstituted 2-aminoselenophenes is, however, rarely not documented as yet.

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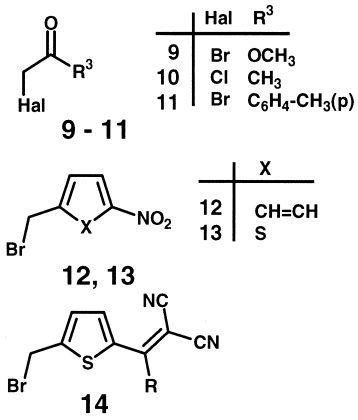
Only their transformation into strongly solvatochromic selenophenes of the general structure **8** by their reaction with some acceptor-substituted halomethyl compounds was recently exemplified [7]. Now we report on further examples of the transformation of the *N,N′*-persubstituted 3-aminoselenoacrylamides **4** into 5-acceptor-substituted derivatives of *N*-disubstituted 2-aminoselenophenes.

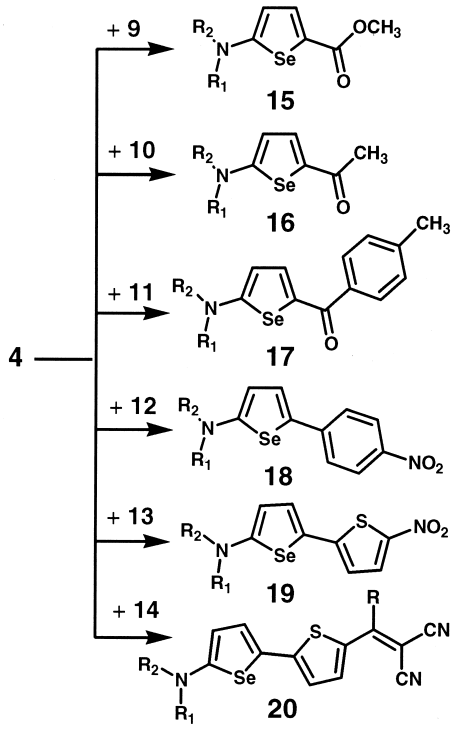
Results and Discussion

As reagents for this transformation the halomethyl compounds **9**–**14** have been used. As far as they are not commercially available they have been synthesised as described recently [6].



Scheme 2.

The transformation of the *N,N′*-persubstituted 3-aminoselenoacrylamides **4** into 5-acceptor-substituted 2-aminoselenophenes can be performed, analogously to the transformation of the *N,N′*-persubstituted 3-aminothioacrylamides **3** into the 5-acyl-substituted 2-aminothiophenes **5**, by allowing to react these compounds with one equivalent of the appropriate acylmethyl halide in a polar solvent, such as acetonitrile, and subsequent addition of a base, such as triethylamine, to the reaction mixture at slightly elevated temperature. The reactions proceed, analogously to the reaction of *N,N′*-persubstituted thioacrylamides **3** with halomethyl compounds [5, 10], *via* intermediate 1-seleno-substituted vinamidinium salts of the general structure **6** and give rise to the formation of the *N,N*-disubstituted 2-aminoselenophenes of the structure **15**–**20** (see Table 1).



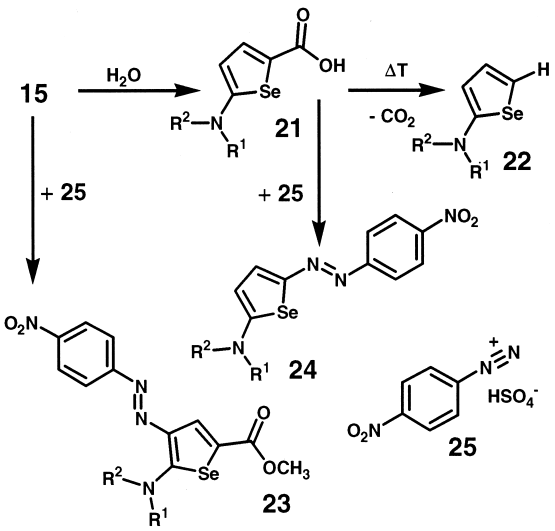
Scheme 3.

Similarly to their sulfur analogues [11], some of the *N*-disubstituted 2-aminoselenophenes prepared were used as starting materials for some further 2-aminoselenophene derivatives. Thus, the alkyl 2-aminoselenophene-5-carboxylates **15** can easily be transformed by saponification with aqueous bases into their corresponding 2-aminoselenophene-5-carboxylic acids **21**. These acids and their esters **15** are able, by analogy to corresponding 2-amino-5-thiophenecarboxylates [12], to react with arenediazonium salts. Whereas the alkyl 2-amino-5-selenophenecarboxylates **15** were transformed by this reaction, as exemplified with the 4-nitrophenyldiazonium salt **25**, into corresponding alkyl 2-amino-3-arylazo-5-selenophenecarboxylates **23**, the 2-amino-5-selenophenecarboxylic acids **21** yield *N*-disubstituted 2-amino-5-arylazoselenophenes **24**. Obviously, in the course of the azo coupling reaction a decarboxylation reaction of **21** occurs. Such a decarboxylation reaction can also be achieved, as checked by DSC measurements, by heating the carboxylic acids **21** at their melting points. Efforts to obtain the 5-unsubstituted 2-aminoselenophenes **22** on a preparative scale by

Table 1. Characteristic physical data of the 2-aminoselenophenes prepared.

Compound	R^1R^2N	Yield [%]	M.p. [°C]	Formula calcd. (m.w.) found	C	H	N
15a	dimethylamino	70	135–136	$C_8H_{11}NO_2Se$	41.39	4.78	6.03
				(232.1)	41.21	5.00	5.93
15b	diethylamino	–	Oil	$C_{10}H_{15}NO_2Se$	46.12	5.67	5.38
				(260.2)	–	–	–
15c	morpholino	80	127–128	$C_{10}H_{13}NO_3Se$	43.80	4.74	5.11
				(274,2)	43.82	4.82	4.95
15d	piperidino	67	97	$C_{11}H_{15}NO_2Se$	48.53	5.51	5.15
				(272.2)	48.52	5.55	4.95
15e	diphenylamino	85	68–69	$C_{18}H_{15}NO_2Se$	60.68	4.24	3.93
				(356.3)	60.52	4.36	4.11
15f	*N*-phenothiazino	15	135–137	$C_{18}H_{13}NO_2SSe$	55.96	3.39	3.63
				(386.3)	56.12	3.57	3.72
15 g	*N*-indolenino	–	Oil	$C_{14}H_{13}NO_2Se$	54.87	4.25	4.57
				(306.2)	–	–	–
16c	morpholino	38	127–129	$C_{10}H_{13}NO_2Se$	46.52	5.08	5.43
				(258.2)	46.69	5.28	5.49
16e	diphenylamino	70	73–74	$C_{18}H_{15}NOSe$	63.53	4.44	4.12
				(340.3)	63.33	4.64	4.28
17c	morpholino	38	169–170	$C_{16}H_{17}NO_2Se$	57.49	5.13	4.19
				(334.3)	57.29	5.33	4.31
17e	diphenylamino	40	140–141	$C_{24}H_{19}NOSe$	69.23	4.60	3.36
				(416.4)	69.22	4.80	3.52
18a	dimethylamino	55	220–221	$C_{12}H_{12}N_2O_2Se$	48.82	4.10	9.49
				(295.2)	48.64	4.22	9.55
18c	morpholino	10	201–204	$C_{14}H_{14}N_2O_3Se$	49.86	4.18	8.31
				(337.3)	49.72	4.32	8.45
18e	diphenylamino	44	131–133	$C_{22}H_{16}N_2O_3Se$	63.01	3.85	6.68
				(419.4)	62.89	4.01	6.88
19a	dimethylamino	75	206–207	$C_{10}H_{10}N_2O_2SSe$	39.87	3.35	9.30
				(301.2)	39.98	3.33	9.47
19c	morpholino	68	210–212	$C_{12}H_{12}N_2O_3SSe$	41.99	3.52	8.16
				(343.3)	42.12	3.55	8.10
19e	diphenylamino	97	147	$C_{20}H_{14}N_2O_2SSe$	56.47	3.32	6.59
				(425.4)	56.31	3.55	6.76
20c	morpholino	78	208–209	$C_{16}H_{13}N_3OSSe$	51.34	3.50	11.23
				(374.3)	51.54	3.34	11.11
20e	diphenylamino	20	181–183	$C_{24}H_{15}N_3SSe$	63.16	3.31	9.21
				(456.4)	62.98	3.42	9.12
21b	diethylamino	36	93	$C_9H_{13}NO_2Se$	43.90	5.28	5.69
				(246.2)	44.12	5.32	5.84
21c	morpholino	65	200	$C_9H_{11}NO_3Se$	41.54	4.23	5.38
				(260.2)	41.50	4.45	5.22
21d	piperidino	89	137	$C_{10}H_{13}NO_2Se$	46.51	5.04	5.43
				(258.2)	46.66	5.06	5.22
21e	diphenylamino	87	142	$C_{17}H_{13}NO_2Se$	59.66	3.83	4.09
				(342.3)	59.52	3.89	4.15
21 g	*N*-indolenino	35	128	$C_{13}H_{11}NO_2Se$	53.42	3.77	4.79
				(292.2)	53.61	3.85	4.71
23a	dimethylamino	65	223–225	$C_{14}H_{14}N_4O_4Se{\cdot}H_2SO_4$	35.04	3.37	11.69
				(479.3)	34.87	3.45	11.51
23c	morpholino	63	216–218	$C_{16}H_{16}N_4O_5Se{\cdot}H_2SO_4$	36.86	3.48	10.75
				(521.7)	36.52	3.62	10.50
24b	diethylamino	31	117–120	$C_{14}H_{16}N_4O_2Se$	47.87	4.59	15.95
				(351.3)	47.61	4.74	15.71
24c	morpholino	32	267–269	$C_{14}H_{14}N_4O_3Se$	46.03	3.84	15.34
				(365.3)	46.05	4.01	15.22
24d	piperidino	35	180–185	$C_{15}H_{16}N_4O_2Se$	49.59	4.44	15.42
				(442.2)	49.33	4.61	15.21
24e	diphenylamino	37	168–170	$C_{22}H_{16}N_4O_2Se$	59.07	3.61	12.52
				(447.4)	58.96	3.75	12.48

this route were not very successfully as yet, but they are continued.



Scheme 4.

The structure of the *N*-disubstituted 2-aminoselenophenes **15**–**24** prepared were confirmed by elemental analysis, mass spectroscopy, and ^{1}H NMR measurements. Thus, all 2-aminoselenophenes **15**–**24** with the exception of the 3-arylazo derivatives **23** exhibit in their ^{1}H NMR spectra characteristic doublets at ~ 7.0 and 8.0 ppm confirming the presence of the heteroaromatic seleneophene subunits (see Table 2).

In the UV/vis spectra of almost all *N*-disubstituted 2-aminoselenophenes prepared intense absorptions were recorded. The positions of the appropriate absorption maxima strongly depend on the substitution pattern at the selenophene moieties as well as, in some cases, on the polarity of solvents. Therefore, some of the prepared 5-acceptor-substituted 2-aminoselenophenes can be used, as recently demonstrated briefly for the compounds **18** and **19** [8] and further confirmed in Table 3, as indicators for measurement of the polarity of solvents. This solvatochromism can be quantified by plotting the reciprocal wavelength of the longest-wavelength absorption bands of the corresponding 2-aminoselenophene derivative versus the π^* values introduced by Kamlet and Taft [13] accordingly to Equation (1):

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

As seen from Table 3, in which the UV/vis spectral data of some selected 2-aminoselenophenes **18**, **19**, **20**, and **24** as well as the correlation parameter *a* and *b* of equation (1) and the regression coefficient *r* as measure for the quality of the corresponding correlation are given, they exhibit a pronounced positive solvatochromism indicated by the negative sign of the coefficient *b*. The extent of solvatochromism, quantified by the *b* values, exceeds the one of analogously substituted 2-aminothiophenes in most cases [7]. The highest *b* values measured in the series of 5-acceptor-substituted 2-aminoselenophenes is found with compound **19a**. Therefore, especially this 2-aminoselenophene derivative can be used as a much better indicator for a rather precise measurement of the polarity of solvents. It is worth mentioning that the 2-amino-5-(4-nitrophenylazo)selenophenes **24** exhibit, besides of their relative long-wavelength absorptions, only a low solvatochromic sensitivity.

Experimental Section

Melting points were determined on a Boetius heating-table microscope and are uncorrected. The UV/VIS spectra were recorded in dichloromethane with a Perkin-Elmer spectrometer Lambda 900, and the NMR spectra with a Varian 300 MHz spectrometer Gemini 300. The extinctions in the UV/VIS spectra were measured in the dimension $m^2\ mol^{-1}$ and for shortness recorded as logarithmic values. The elemental analytical data were obtained by means of a LECO analyzer CHNS 932.

The preparation of the *N,N′*-persubstituted 1-chlorovinamidinium salts **2** and *N,N′*-persubstituted 3-aminoselenoacrylamides **4** used as educts for the synthesis of the 2-aminoseleophenes was reported in ref. [3]. The following educts hitherto not described were prepared analogously: *3-(dimethylamino)selenoacryl-N-diethylamide* (**4b**) from *N*-[3-chloro-3-(diethylamino)-2-propenylidene]dimethyliminium perchlorate (**2b**) and sodium selenide as an oil in a yield of 20%; *3-dimethylamino-1-selenoacrylpiperidide* (**4d**) from *N*-[3-chloro-3-(1-piperidino)-2-propenylidene]-dimethyliminium perchlorate (**2d**) and sodium selenide in a yield of 86% ; m.p. 93–95 °C; ^{1}H NMR (in $CDCl_3$): δ = 1.59 (m, 6H, CH_2), 2.89 (m, 6H, NCH_3), 3. 93 (m, 4H, NCH_2), 5.24 (d, 1H, CH), 8.27 (d, 1H, CH); *N,N-dimethyl-N-[3-(10H-phenothiazin-10-yl)-3-selenoxo-1-propenyl]amine* (**4f**) from *N*-[3-chloro-3-(phenothiazinyl)-2-propenyli-

Table 2. Selected spectral data of the 2-aminoselenophenes prepared.

Compound	λ_{max} (log ε) [nm] in MC	^{1}H NMR, δ-values in ppm in $CDCl_3$ or [a] in D_6-DMSO
15a	–	3.00 (s, 6H, CH_3), 3.70 (s, 3H, OCH_3), 5.89 (d, 1H, CH), 7.68 (d, 1H, CH)
15c	–	3.19 (t, 4H, NCH_2), 3.78–3.83 (m, 7H, OCH_2, OCH_3), 6.06 (d, 1H, CH), 7.76 (d, 1H, CH)
15d	–	1.61 (m, 2H, CH_2), 1.74 (m, 4H, NCH_2), 3.23 (t, 4H, OCH_2), 3.78 (s, 3H, OCH_3), 6.10 (s. 1H, CH), 7.75 (s, 1H, CH)
15e	–	3.70 (s, 3H, OCH_3), 6.32 (d, 1H, CH), 7.24–7.31 (m, 6H, CH), 7.40 (t, 4H, CH), 7.70 (d, 1H, CH)
15f	–	3.75 (s, 3H, OCH_3), 6.70 (d, 1H, CH), 7.26 (m, 2H, CH), 7.37 (m, 2H, CH), 7.47 (m, 4H, CH), 7.78 (d, 1H, CH)
16c	369 (4.32)	2.34 (s, 3H, CH_3), 3.26 (t, 4H, NCH_2), 3.73 (t, 4H, OCH_2), 6.23 (d, 1H, CH), 7.79 (d, 1H, CH) [a]
16e	392 (4.40)	2.36 (s, 3H, CH_3), 6.30 (d, 1H, CH), 7.25–7.34 (m, 6H, CH), 7.43 (m, 4H, CH), 7.78 (d, 1H, CH) [a]
17c	3.87 (4.38)	2.39 (s, 3H, CH_3), 3.32 (t, 4H, NCH_2), 3.75 (t, 4H, OCH_2), 6.28 (d, 1H, CH), 7.30 (d, 2H, CH) [a]
17e	410 (4.42)	2.39 (s, 3H, CH_3), 6.30 (d, 1H, CH), 7.28–7.49 (m, 13H, CH), 7.59 (m, 2H, CH) [a]
18a	474 (4.30)	3.04 (s, 6H, CH_3), 5.86 (d, 1H, CH), 7.38 (d, 1H, CH), 7.43 (d, 2H, CH), 8.10 (d, 2H, CH)
18c	445 (4.30)	3.21(t, 4H, NCH_2), 3.76 (t, 4H, OCH_2), 6.28 (d, 1H, CH), 7.61 (d, 2H, CH), 7.66 (d, 1H, CH), 8.12 (d, 2H, CH) [a]
18e	460 (4.25)	6.61 (d, 1H, CH), 7.16–7.26 (m, 6H, CH), 7.39 (m, 4H, CH), 7.68 (m, 3H, CH), 8.13 (m, 2H, CH) [a]
19a	544 (4.26)	3.04 (s, 6H, CH_3), 5.79 (d, 1H, CH), 6.66 (d, 1H, CH), 7.32 (d, 1H, CH), 7.76 (d, 1H, CH),
19c	505 (4.19)	3.20 (m 4H, NCH_2), 3.85 (m, 4H, OCH_2), 6.06 (d, 1H, CH), 6.74 (d, 1H, CH), 7.30 (d, 1H, CH), 7.78 (d, 1H, CH)
19e	522 (4.33)	6.49 (d, 1H, CH), 7.12 (d, 1H, CH), 7.20–7.29 (m, 6H, CH), 7.40 (m, 4H, CH), 7.54 (d, 1H, CH), 7.97 (d, 1H, CH)
20c	544 (4.08)	3.23 (t, 4H, NCH_2), 3.85 (t, 4H, OCH_2), 6.10 (d, 1H, CH), 6.93 (d, 1H, CH), 7.40 (d, 1H, CH), 7.51 (d, 1H, CH), 7.63 (s, 1H, CH)
20e	562 (4.53)	6.48 (d, 1H, CH), 7.21–7.31 (m, 7H, CH), 7.43 (m, 4H, CH), 7.53 (d, 1H, CH), 7.80 (d, 1H, CH), 8.42 (s, 1H, CH) [a]
21b	–	1.16 (t, 6H, CH_3), 3.34 (q, 4H, CH_2), 5.84 (d, 1H, CH), 7.57 (d, 1H, CH), 11.70 (s, 1H, OH) [a]
21c	–	3.16 (t, 4H, NCH_2), 3.71 (t, 4H, OCH_2), 6.18 (d, 1H, CH), 7.63 (d, 1H, CH), 12.19 (s, 1H, OH) [a]
21d	–	1.60 (m, 6H, CH_3), 3.21 (t, 4H, CH_2), 6.07 (d, 1H, CH), 7.59 (d, 1H, CH), 11.79 (s, 1H, OH) [a]
21e	–	6.33 (d, 1H, CH), 7.20–7.29 (m, 6H, CH), 7.40 (t, 4H, CH), 7.62 (d, 1H, CH), 12.49 (s, 1H, OH) [a]
21 g	–	3.23 (t, 2H, CH_2), 4.06 (t, 2H, NCH_2), 6.51 (d, 1H, CH), 6.91 (m, 1H, CH), 7.19 (m, 3H, CH), 7.75 (d, 1H, CH), 12.13 (s, 1H, OH) [a]
23a	495 (4.28)	3.56 (s, 6H, CH_3), 3.81 (s, 3H, OCH_3), 7.73 (d, 2H, CH), 8.28 (d, 2H, CH), 8.32 (s, 1H, CH) [a]
23c	490 (4.25)	3.79 (s, 3H, OCH_3), 3.84 (t, 4H, NCH_2), 3.98 (t, 4H, OCH_2), 7.79 (d, 2H, CH), 8.28 (t, 3H, CH) [a]
24b	570 (4.34)	1.27 (t, 6H, CH_3), 3.61 (q, 4H, NCH_2), 6.56 (d, 1H, CH), 7.54 (d, 2H, CH), 7.87 (d, 1H, CH), 8.16 (d, 2H, CH) [a]
24c	552 (4.67)	3.60 (t, 4H, NCH_2), 3,77 (t, 4H, NCH_3), 6.68 (d, 1H, CH), 7.62 (d, 2H, CH), 7.93 (d, 1H, CH), 8.20 (d, 2H, CH) [a]
24d	575 (4.56)	1.68 (m, 6H, CH_2), 3.63 (m, 4H, CH_2), 6.68 (d, 1H, CH), 7.55 (d, 2H, CH), 7,88 (d, 1H, CH), 8.17 (d, 2H, CH) [a]
24e	566 (4.66)	6.73 (d, 1H, CH), 7.39–7.53 (m, 10H, CH), 7.69 (d, 2H, CH), 7.96 (d, 1H, CH), 8.25 (d, 2H, CH), [a]

Table 3. Solvatochromism of some 2-aminoselenophenes prepared; UV/Vis absorptions [nm], correlation parameters *a*, *b*, and regression coefficients *r* according to eq. (1).

Compound	Solvent[a]	CH	TE	TO	ET	MC	DMF	DMSO	*a*	*b*	*r*
	π*[b]	−0.02	0.26	0.53	0.57	0.78	0.87	1.01	[10^{-5} m^{-1}]	[10^{-5} m^{-1}]	
18a		437	446	459	468	474	483	492	22.965	− 2.53	−0.9898
18c		418	425	434	438	445	454	464	24.059	− 2.26	−0.9806
18e		416	426	436	439	445	455	461	24.077	− 2.25	−0.9901
19a		478	497	517	538	544	562	574	20.918	− 3.47	−0.9868
19c		460	471	488	501	505	525	538	21.876	− 3.06	−0.9798
19e		478	490	497	509	522	527	534	21.017	− 2.23	−0.9770
20c		513	524	530	541	544	553	562	19.517	− 1.61	−0.9797
24b		535	544	552	565	570	581	588	18.805	− 1.71	−0.9656
24c		515	524	538	555	552	574	585	19.567	− 2.28	−0.9591
24d		533	545	556	572	575	588	600	18.859	− 2.05	−0,9717
24e		541	550	552	556	566	567	574	18.617	− 1.04	−0.8007

[a] CH: cyclohexane, TE: tetrachloromethane, TO: toluene, ET: ethanol, MC: dichloromethane, DMF: dimethylformamide, DMSO: dimethylsulfoxide; [b] values taken from ref. [13].

dene]dimethyliminium perchlorate (**2f**) and sodium selenide in a yield of 75%; m.p. 156–159 °C; ^{1}H NMR (in [D_6]-DMSO): δ = 2.12 (s, 6H, NCH_3), 5.50 (d, 1H, CH), 7.27–7.41 (m, 2H, CH), 7.52–7.67 (m, 4H, CH), 7.73 (m, 2H, CH), 8.26 (d, 1H, CH); *3-dimethylamino-1-(N-indoleninyl)selenoacrylamide* (**4 g**) from *N*-[3-chloro-3-(*N*-indoleninyl)-2-propenylidene]-dimethyliminium perchlorate (**2 g**) and sodium selenide as an oil in a yield of 65%; ^{1}H NMR (in $CDCl_3$): δ = 1.95 (s, 2H, CH_2), 3.00 (m, 6H, NCH_3), 4.60 (t, 2H, NCH_2), 5.95 (d, 1H, CH), 6.97 (t, 1H, CH), 7.10 (m, 2H, CH), 7.16 (d, 1H, CH), 8.30 (d, 1H, CH).

The bromomethyl compounds **9**–**14**, as far as commercially not available, were prepared as described in ref. [5].

N-Disubstituted methyl 2-aminoselenophene-5-carboxylates (**15**)

General procedure

A mixture of a *N,N′*-persubstituted selenoacrylamide **4** (0.02 mol) and methyl bromoacetate (0.02 mol, 3.0 g) in methanol (50 ml) was refluxed for 15 min. After cooling triethylamine (10 ml) was added and the mixture was diluted with water. Solid products were isolated by filtration, liquid products were extracted with dichloromethane. After drying with $CaCl_2$ the solvent was evaporated and the residue left standing at r.t. until crystallisation occurs. For the products so obtained see Table 1.

N-Disubstituted 5-acetyl-2-aminoselenophenes (**16**)

General procedure

By analogy to the previous procedure a mixture of an *N,N′*-persubstituted selenoacrylamide **4** (0.02 mol) and 1-chloro-2-propanone (0.025 mol, 2.3 g) in acetonitrile (50 ml) was allowed to react with triethylamine (10 ml). For the products obtained see Table 1.

N-Disubstituted 2-amino-5-(4-methylbenzoyl)-selenophenes (**17**)

General procedure

By analogy to the previous procedure a mixture of an *N,N′*-persubstituted selenoacrylamide **4** (0.02 mol) and 2-bromo-1-(4-tolyl)ethanone (0.02 mol, 4.0 g) in acetonitrile (50 ml) was allowed to react with triethylamine (10 ml). See Table 1 for products.

N-Disubstituted 2-amino-5-(4-nitrophenyl)-selenophenes (**18**)

General procedure

By analogy to the previous procedure a mixture of an *N,N′*-persubstituted selenoacrylamide **4** (0.02 mol) and 4-nitrobenzylbromide (0.02 mol, 4.3 g) in acetonitrile (50 ml) was allowed to react with triethylamine (10 ml). See Table 1 for products.

N-Disubstituted 2-amino-5-(5-nitro-2-thienyl)-selenophenes (**19**)

General procedure

By analogy to the previous procedure a mixture of an *N,N′*-persubstituted selenoacrylamide **4** (0.02 mol) and 2-bromomethyl-5-nitrothiophene (0.02 mol, 4.2 g) in acetonitrile (50 ml) was allowed to react with triethylamine (10 ml). See Table 1 for products.

N-Disubstituted 2-amino-5-[5-(2-dicyanoethenyl)-2-thienyl]selenophenes (**20**)

General procedure

By analogy to the previous procedure a mixture of an *N,N′*-persubstituted selenoacrylamide **4** (0.02 mol) and 2-bromomethyl-5-(2-dicyanoethenyl)thiophene [5] (0.02 mol, 5.1 g) in acetonitrile (50 ml) was allowed to react with triethylamine (10 ml). See Table 1 for products.

N-Disubstituted 2-aminoselenophene-5-carboxylic acids (**21**)

General procedure

A mixture of a methyl 2-aminoselenophene-5-carboxylate **15** (0.02 mol) and sodium hydroxide (0.05 mol, 2,0 g) in ethanol (100 ml) was refluxed for 1 h. After cooling the reaction mixture was neutralized with acetic acid and diluted with water (100 ml). The product crystallized was isolated by filtration and washed with water. See Table 1 for products.

Methyl 2-(dialkylamino)3-(4-nitrophenylazo)-selenophen-carboxylates (**23**) *and N-disubstituted 2-amino-5-(4-nitrophenylazo)selenophenes* (**24**)

General procedure

To a mixture of methyl 2-(dialkylamino)selenophene-5-carboxylate **15** (0.01 mol) or 2-(dialkylamino)selenophene-5-carboxylic acid **21** (0.01 ml) in methanol (50 ml) an accordingly to ref. [14] freshly prepared solution of 4-nitrophenyldiazonium hydrosulphate (0.02 mol) was added under stirring at 20 °C. After some standing the reaction mixture was diluted with methanol (200 ml) and the product formed isolated by filtration.

See Table 1 for products.

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[1] J. Liebscher, B. Abegaz, A. Knoll, Phosphorus and Sulfur **35**, 5 (1988).
[2] J. Liebscher, A. Knoll, Z. Chem. **27**, 8 (1987).
[3] H. Hartmann, C. Heyde, I. Zug, Synthesis 805 (2000).
[4] C. Heyde, I. Zug, H. Hartmann, Eur. J. Org. Chem. 3273 (2000).
[5] K. Eckert, A. Schröder, H. Hartmann, Eur. J. Org, Chem. 1327 (2000).
[6] A. Noack, A. Schröder, H. Hartmann, Angew. Chem. **113**, 3097 (2001); Angew. Chem. Int. Ed. Engl. **40**, 3008 (2001).
[7] H. Hartmann, K. Eckert, A. Schröder, Angew. Chem. **112**, 567 (2000); Angew. Chem. Int. Ed. Engl. **39**, 556 (2000); K. Eckert, C. Mockry, A. Schröder, H. Hartmann, Phosphorus, Sulfur and Silicon **152**, 99 (1999).
[8] F. Effenberger, F. Würthner, Angew. Chem. **105**, 742 (1993); Angew. Chem. Int. Ed. Engl. **32**, 719 (1993); F. Effenberger, F. Würthner, F. Steybe, J. Org. Chem. **60**, 2082 (1995).
[9] V. P. Rao, A. K-Y. Jen, K. Y. Wong, K. J. Drost, J. Chem. Soc., Chem. Commun. 1118 (1993); A. K-Y. Jen, V. P. Rao, K. J. Drost, Y. Cai, R. M. Mininni, J. T. Kenney, E. S. Binkley, L. R. Dalton, S. R. Marder, SPIE **2143**, 30 (1994); A. K-Y. Jen, V. P. Rao, K. Y. Wong, K. J. Drost, J. Chem. Soc., Chem. Commun. 90 (1993); V. P. Rao, A. K-Y. Jen, K. Y. Wong, K. J. Drost, Tetrahedron Lett. **34**, 1747 (1993).
[10] A. Noack, H. Hartmann, Tetrahedron **58**, 2137 (2002).
[11] H. Hartmann, P. Gerstner, D. Rohde, Org. Lett. **3**, 1673 (2001).
[12] H. Hartmann, I. Zug, J. Chem. Soc., Perkin Trans. 1, 4316 (2000).
[13] M. J. Kamlet, J.-L. M. Abboud, R. W. Taft, J. Org. Chem. **48**, 2877 (1983); M. J. Kamlet, J.-L. M. Abboud, R. W. Taft, J. Am. Chem. Soc. **99**, 6027 (1977); R. W. Taft, M. J. Kamlet, J. Am. Chem. Soc. **96**, 2886 (1976); R. W. Taft, M. J. Kamlet, J. Chem. Soc., Perkin Trans. 2, 1723 (1979).
[14] H. G. O. Becker, Organikum, Johann Ambrosius Barth Leipzig, Edition Deutscher Verlag der Wissenschaften, 19th edit., Berlin (1993).