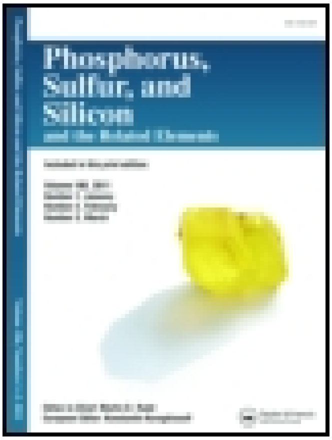


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

SYNTHESIS AND SOLVATOCHROMIC PROPERTIES OF 5-DICYANOVINYL-AND 5-TRICYANOVINYL-SUBSTITUTED 2-AMINO-THIAZOLES AND 2-AMINO-THIOPHENES

Katrin Eckert [a] , Cornelia Mokry [a] , Anke Schröder [a] & Horst Hartmann [a]
[a] Fachhochschule Merseburg , Geusaer Str., D-06217, Merseburg

To cite this article: Katrin Eckert , Cornelia Mokry , Anke Schröder & Horst Hartmann (1999) SYNTHESIS AND SOLVATOCHROMIC PROPERTIES OF 5-DICYANOVINYL-AND 5-TRICYANOVINYL-SUBSTITUTED 2-AMINO-THIAZOLES AND 2-AMINO-THIOPHENES, Phosphorus, Sulfur, and Silicon and the Related Elements, 152:1, 99-114, DOI: 10.1080/10426509908031622

To link to this article: http://dx.doi.org/10.1080/10426509908031622

Phosphorus, Sulfur and Silicon, 1999, Vol. 152, pp. 99-114
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS AND SOLVATOCHROMIC PROPERTIES OF 5-DICYANOVINYL- AND 5-TRICYANOVINYL-SUBSTITUTED 2-AMINO-THIAZOLES AND 2-AMINO-THIOPHENES

KATRIN ECKERT, CORNELIA MOKRY, ANKE SCHRÖDER and HORST HARTMANN*

Fachhochschule Merseburg, Geusaer Str., D-06217 Merseburg

(Received November 24, 1998; Revised January 24, 1999)

Starting from 2-morpholinothiazoles **6** and 2-morpholinothiophenes **7** and following known routes several 5-dicyanovinyl and 5-tricyanovinyl-substituted derivatives **10 – 13** have been prepared and their solvatochromic properties estimated.

Keywords: 2-Amino-5-(2,2-dicyanoethenyl)thiazoles; 2-Amino-5-(1,2,2-tricyanoethenyl)-thiazoles; 2-Amino-5-(2,2-dicyanoethenyl)thiophenes; 2-Amino-5-(1,2,2-tricyanoethenyl)-thiophenes; Solvatochromism

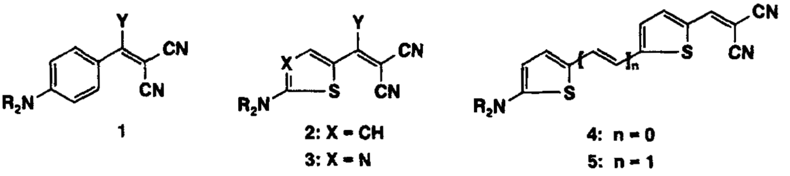
INTRODUCTION

Dicyanovinyl and tricyanovinyl anilines of the general structure **1** are easily available and, therefore, well-studied in their chemical and UV/VIS spectroscopic properties.[1] As colored compounds they exhibit intense long-wavelength absorption bands the positions of which are strongly influenced by the polarity of solvents.[2] Thus, the cyanovinyl compounds **1** exhibit pronounced solvatochromic properties.[3] Therefore, they can be used as model compounds for dyes with non-linear optical (NLO) properties.[4]

---

* correspondence Author.

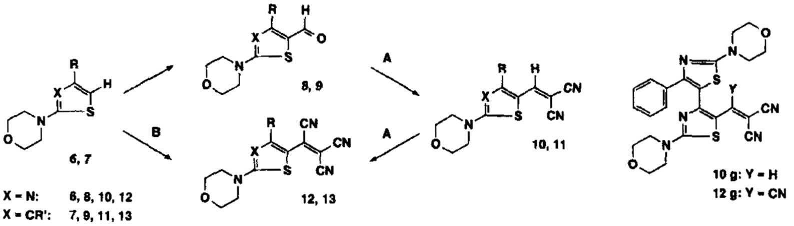
Similar properties should be also observed for their heterocyclic analogues **2** and **3**. However, such compounds are, in contrast to their vinylogues **4** and **5** which have been prepared and characterised very recently,[5] either unknown or, as far as they are known, spectroscopically not studied until now.



SCHEME 1

RESULTS AND DISCUSSION

Recently, we were able to synthesise a series of 4-heterofunctionalised 2-aminothiazoles and their formyl derivatives.[6] Therefore, it seems now possible to prepare, from these educts, several dicyanovinyl and tricyanovinyl derivatives and to study their UV/VIS spectroscopic properties. As model compounds 2-morpholino-substituted derivatives are chosen. These compounds have been prepared, as outlined in scheme 2, by the following routes starting from 5H-substituted 2-morpholinothiazoles **6**.



SCHEME 2

According to route A, 2-morpholinothiazoles **6**, differently substituted at C-4, were transformed, at first, by means of a Vilsmeier reaction into their formyl derivatives **8**[7], which have been subsequently condensed with malononitrile. From the resulting 2-morpholino-5-dicyanovinylthiazoles **10** the corresponding 5-tricyanovinyl derivatives **12** were prepared by means of an oxidative cyanation reaction using sodium cyanide and bromine or lead tetraacetate as addition and oxidation agent, respectively.[8] The 5-tricyanovinylthiazoles **12** were alternatively prepared, according to route B, by allowing to react tetracyanoethene with 5H-substituted 2-morpholinothiazoles **6**.[9]

For comparison, a few dicyanovinyl and tricyanovinyl-substituted thiophenes **11** and **13** have been also prepared by using the same synthetic routes as applied for the synthesis of the thiazole derivatives **10** and **12.** As educts 5H-substituted 2-morpholinothiophenes **7**[10] (route B) or their 5-formylderivatives **9**[11] (route A) were used.

Table I and II inform on the preparative results received as well as on the characteristic ^{1}H NMR and UV/VIS spectral data measured for the compounds prepared.

As can be seen, satisfactory yields were obtained only for most of the prepared dicyanovinyl compounds **10** and **11.** For the tricyanovinyl compounds **12** and **13,** however, the yields are generally low, obviously caused by oxidation reactions occurring with the educts used. Although a variety of products could be detected by means of thin-layer chromatography on silica their separation from the desired tricyanovinyl compounds **12** and **13** was not performed and, therefore, their structure have not been elucidated.

As can be seen from table I and II, all di- and tricyanovinyl compounds **10 – 13** depicted exhibit an intense long-wavelength absorption band in the visible spectral range. The positions of these bands are, as demonstrated in table III, in most cases strongly influenced by the polarity of solvents.

This influence can be quantified by plotting the reciprocal wavelengths of these bands with suitable solvent parameters, e.g., with the normalized E_T-values given by Dimroth and Reichardt[2] or with the π^*-values given by Kamlet and Taft,[12] by using equ. (1) and (2), resp., and taken the λ_{max} values in 10^{-5} m:

$$1/\lambda_{\text{max}} = \text{a} + \text{b} \cdot \text{E}_\text{T}^\text{N} \qquad (1)$$

$$1/\lambda_{\text{max}} = \text{a}' + \text{b}' \cdot \pi^* \qquad (2)$$

TABLE I 5-Dicyanovinyl-substiuted 2-Morpholinothiazoles **8** and 2-Morpholinothiophenes **10**

Nr.	*R*	*X*	*Educt [Ref.]*	*Yield [%]*	*m.p. [°C]*	*^1H NMR, δ-values in ppm (assignment)*	*λ_{max} in nm$^{a)}$ (log ε)*
10a	H	N	**8a**[17]	41	225 – 227	3.70 (s, 8H, CH_2), 8.12 (s, 1H, CH), 8.36 (s, 1H, CH) (DMSO-d_6)	480 (4.55)
10b	Cl	N	**8b**[7a]	39	172 – 173	3.69 (t, 4H, NCH_2), 3.81 (t, 4H, OCH_2), 7.77 (s, 1H, CH) ($CDCl_3$)	430 (4.51)
10c	C_6H_5	N	**8c**[17]	88	255 – 258	3.85 (d, 8H, CH_2), 7.30 – 7.56 (m, 5H, aromatic H), 7.70 (s, 1H, CH) ($CDCl_3$)	437 (4.57)
10d	p-C_6H_4-OCH_3	N	this work	19	274 – 275	3.76 (m, 4H, NCH_2), 3.82 (m, 4H, OCH_2), 3.88 (s, 3H, OCH_3), 7.0 (d, 2H, aromatic H), 7.49 (d, 2H, aromatic H), 7.65 (s, 1H, CH) ($CDCl_3$)	443 (4.52)
10e	p-C_6H_4-OH	N	this work	47	336 – 339	3.75 (m, 8H, CH_2), 6.92 (d, 2H, aromatic H), 7.52 (d, 2H, aromatic H), 7.76 (s, 1H, CH), 10.1 (s, 1H, OH) (DMSO-d_6)	441 (4.09)
10f	$N(C_2H_4)O$	N	this work	19	274 – 275	3.7 (m, 16H, CH_2), 7.63 (s, 1H, CH) (DMSO-d_6)	442 (4.75)
10g	b)	N	this work	60	289 – 290	3.66 (m, 8H, NCH_2), 3.82 (m,8H, OCH_2), 7.17 (s, 1H, CH), 7.4 (m, 3H, aromatic H), 7.57 (d, 2H, aromatic H) ($C_2D_2Cl_4$)	482 (4.29) 398 (4.25)
11a	H	CH	**9a**[10b]	71	212 – 213	3.49 (t, 4H, NCH_2), 3.73 (t, 4H, OCH_2), 6.57 (d, 1H, CH), 7.69 (d, 1H, CH), 8.05 (s, 1H, CH) (DMSO-d_6)	457 (4.67)
11c	C_6H_5	C-C_6H_5	**9b**[10b]	90	183 – 185	3.14 (t, 4H, NCH_2), 3.64 (t, 4H, OCH_2), 6.9 – 7.25 (m, 10H, aromatic H), 7.34 (s, 1H, CH) ($CDCl_3$)	466 (4.53)

[a] measured in dichloromethane
[b] 2-(4-morpholino)-4-phenyl-5-thiazolyl

TABLE II 5-Tricyanovinyl-substituted 2-Morpholinothiazoles **12** and 2-Morpholinothiophenes **13**

Nr.	*R*	*X*	*Educt [Ref.]*	*Yield [%] (Route)*	*m.p. [°C]*	*^1H NMR : δ-values in ppm (assignement)*	*λ_{max} in nm^a) (log ε)*
12a	H	N	**6a**[18]	22 (B)	233 – 235	3.76 (s, 8H, CH_2), 8.43 (s, 1H, CH) (DMSO-d_6)	480 (4.55)
12b	Cl	N	**8b**[7a]	48 (A)	209 – 211	3.8 (m, 8H, CH_2) ($CDCl_3$)	491 (4.55)
12c	C_6H_5	N	**6c**[19]	32 (B)	254 – 257	3.75 (s, 8H, CH_2), 7.52 (m, 5H, aromatic H) (DMSO-d_6)	504 (4.36)
12d	p-C_6H_4-OCH_3	N	this work	24 (B)	215 – 216	3.8 (m, 8H, CH_2), 3.84 (s, 3H, OCH_3), 6.97 (d, 2H, aromatic H), 7.5 (d, 2H, aromatic H) ($CDCl_3$)	513 (5.06)
12e	p-C_6H_4-OH	N	this work	37 (B)	250 (dec.)	3.74 (s, 8H, CH_2), 6.87 (d, 2H, aromatic H), 7.53 (d, 2H, aromatic H), 10.30 (s, 1H. OH) (DMSO-d_6)	510 (4.46)
12f	N(C_2H_4)O	N	**6f**[20]	11 (B)	222 – 224	3.78 (m, 16H, CH_2) ($CDCl_3$)	511 (4.58)
12g	b)	N	this work	63 (A)	288 – 291	3.5 – 3.7 (m, 16H, CH_2), 7.39 (m, 5H, aromatic H) (DMSO-d_6)	591 (4.15) 474 (4.26)
13a	H	H	**9a**[21] **7a**[22]	22 (A)	272 – 274	3.73 (m, 4H, NCH_2), 3.77 (m, 4H, OCH_2), 6.92 (d,1H, aromatic H), 7.9 (d, 1H, aromatic H) (DMSO-d_6)	524 (4.76)
13c	C_6H_5	C-C_6H_5	**9b**[11]	42 (A)	259 – 264 (dec.)	3.25 (t, 4H, NCH_2), 3.64 (t, 4H, OCH_2), 6.99 – 7.22 (m, 10H, aromatic H) ($CDCl_3$)	544 (4.60)

^{a}) measured in dichloromethane.
^{b}) 2-(4-morpholino)-4-phenyl-5-thiazolyl.

TABLE III Solvatochromic Properties of 5-Cyanovinyl-substituted 2-Morpholinothiazoles and 2-Morpholinothiophenes **10 – 13**

	Solvents^{a})								*regression and correlation coefficients of equ. (1)*			*regression and correlation coefficients of equ. (2)*		
	CH	*TE*	*TO*	*EtOH*^{b})	*MC*	*DMF*	*DMSO*							
π^*: (E_T^N)	*-0.02* *(0.006)*	*0.26* *(0.052)*	*0.53* *(0.099)*	*0.57* *(0.654)*	*0.78* *(0.309)*	*0.87* *(0.404)*	*1.01* *(0.444)*	$\Delta\lambda^{c}$)	*a* *[kcm^{-1}]*	*b* *[kcm^{-1}]*	*r*	*a′* *[kcm^{-1}]*	*b′* *[kcm^{-1}]*	*r*
10a	406	409	415	415	419	422	426	+ 30	24.50	- 2.36	- 0,9461	24.65	- 1.20	- 0.9910
10b	405	422	429	426	430	431	437	+ 27	24.09	- 2.66	- 0.7950	24.37	- 1.51	- 0.9346
10c	421	425	435	436	437	441	446	+ 25	23,58	- 2.48	- 0,9286	23.75	- 1.27	- 0.9822
10d	431	432	441	443	443	448	451	+ 20	23.14	- 2.11	- 0,9474	23.26	- 1.04	- 0.9662
10c	-	444	438	445	441	452	454	+ 16	22.83	- 1.50	- 0,7635	22.93	- 0.73	-0.6336
10f	442	445	445	441	442	440	441	- 01	22.51	+ 0.43	0,7521	22.53	+ 0.14	- 0.5050
10g	465	471	478	479	482	485	490	+ 25	21.35	- 2.01	- 0,9420	21.49	- 1.03	- 0.9955
	382	387	391	396	398	402	405	+ 23	26.04	- 3.00	- 0,9830	26.20	- 1.46	- 0.9855
12a	462	466	476	478	480	488	401$^{d)}$	+ 26	21.53	- 2.56	- 0.9408	21.69	- 1.26	- 0.9764
12b	470	474	485	487	491	498	449$^{d)}$	+ 28	21.17	- 2.73	-0.9477	21.33	- 1.34	- 0.9824
12c	486	488	499	501	504	512	512	+ 26	20.51	- 2.31	- 0.9603	20.64	- 1.13	- 0.9746
12d	487	498	508	511	513	520	521	+ 34	20.26	- 2.55	- 0,9280	20.43	- 1.3 1	- 0.9862

	Solvents^a)								regression and correlation coefficients of equ. (1)			regression and correlation coefficients of equ. (2)		
	CH	TE	TO	EtOH^b)	MC	DMF	DMSO							
π^*: (E_T^N)	- 0.02 (0.006)	0.26 (0.052)	0.53 (0.099)	0.57 (0.654)	0.78 (0.309)	0.87 (0.404)	1.01 (0.444)	$\Delta\lambda$^c)	a [kcm^{-1}]	b [kcm^{-1}]	r	a′ [kcm^{-1}]	b′ [kcm^{-1}]	r
12e	484	497	510	515	510	524	526	+ 42	20.34	- 3.00	- 0.9087	20.53	- 1.55	- 09281
12f	506	510	514	507	511	510	512	+ 06	19.63	- 0.20	- 0,3719	19.70	- 0.16	- 0.5620
12g	580	583	584	580	591	586	591	+ 11	17.20	- 0.58	- 0,855	17.26	- 0.30	- 0.7877
	448	455	464	472	474	483	489	+ 41	22.18	- 3.78	- 0,9803	22.38	- 1.83	- 0.9828
11a	436	442	449	457	457	462	466	+ 30	22,.78	- 2.95	- 0,9746	22.93	- 1.46	- 0.9783
11c	442	447	455	466	466	475	479	+ 37	22.54	- 3.70	- 0,9895	22.70	- 1.77	- 0.9895
13a	498	503	516	525	524	531	534	+ 36	19.35	- 2.81	- 0.9625	20.09	- 1.40	- 0.9696
13c	513	519	533	542	544	550	554	+ 41	19.30	- 2.90	- 0.9578	19.51	- 1.49	- 0.9791

[a] CH: cyclohexane, TE: tetrachloromethane, TO: toluene, EtOH: ethanol, MC: dichloromethane, DMF: *N,N*-dimethylformamide, DMSO: dimethylsulfoxide.

[b] not included in the regression analysis for the E_T^N -values.

[c] wavelength difference (measured in nm) between the absorption maximum measured in cyclohexane and DMSO.

[d] not included in the correlation with the E_T^N - and π^*-values.

As can be seen from the absorption maxima in table III, a bathochromic shift is usually observed for the dicyanovinyl and tricyanovinyl compounds **10** – **13** by increasing the solvent polarity (positive solvatochromism). This solvent-induced band shift can be, in most cases, satisfactorily linearly correlated with the given solvent parameters. In agreement with the solvatochromic properties of other series of dyes[13] a much better correlation, quantified by the corresponding regression coefficients r, is found by using the π^*-values and taken into account a polarizability correction term.[12c] Only in cases in which a weak or nearly no solvatochromism is observed, an insufficient linear correlation is found with both types of solvent parameters.

The largest positive solvatochromism is observed with the 5-dicyanovinyl-3,4-diphenyl-2-morpholino-thiophene **11c,** followed by 4-chloro-5-dicyanovinyl-2-morpholino-thiazole **10b.** Only in case of the 2,4-bis-morpholino-substituted compounds **10f** and **12f** nearly no or a slightly negative solvatochromism was observed. This observation shows that in these compounds, in contrast to the remaining compounds, nearly no change of the dipole moment arises by going from the ground to the first excited state of these compounds.

As generally known, such a missing or only weak negative solvatochromic effect is observed with compounds which contain either a typical polyenic or polymethinic chromophoric system.[14] Hence, due to the strong donator/acceptor substitution at both ends of the chromophoric system of the heterocyclic compounds studied here, a pronounced polymethinic character of the compounds **10f** and **12f** has to be claimed. This character is obviously caused, on the one hand, by the two morpholino groups attached at C-2 and C-4 and, on the other hand, by the dicyanovinyl or tricyanovinyl groups attached at C-5 of the corresponding thiazole moieties.

A peculiar spectroscopic effect is observed with compounds **10g** and **12g**, which have a 2-morpholino-4-phenyl-5-thiazolyl substituent at C-4 of their 5-cyanovinyl-substituted 2-morpholino-thiazole moieties. Due to a more extended π-system linked to this thiazole moiety, both of these compounds exhibit, other than the remaining compounds, in the visible spectral range two absorption maxima, from which only the shorter-wavelength absorption bands exhibit a pronounced positive solvatochromic shift which reaches that of the previous mentioned compounds

10b and **11c.** The longer-wavelength absorption bands exhibit, however, an opposite behaviour. Whereas the long-wavelength absorption band of compound **10g** exhibits a positive solvatochromic shift, the same band of compound **12g** exhibits nearly no solvatochromic shift.

From these findings it can be concluded that a rather large change of the electronic ground-state properties on going from the dicyanovinyl-substituted compound **10g** to the tricyanovinyl-substituted compound **12g** occurs. This change is, obviously, caused by replacing the weaker electron-accepting dicyanovinyl moiety by the stronger electron-accepting tricyanovinyl moiety which are, in these compounds, linked to the strong electron-donating 2-morpholino-4-(2-morpholino-4-phenyl-5-thiazolyl)-thiazole moiety. Hence, whereas for compound **10g** a chromophoric system with a large dipole moment change by going from the electronic ground to the first excited state is indicated, for compound **12g** a chromophoric system with a smaller change of the corresponding dipole moment is indicated.

In extreme cases, the solvatochromic shift observed can also be zero or sligthly negative. This is the case, e.g., for compounds **10f** and **12f.** These compounds attain, obviously, to the so-called charge-resonance limit.[16] Such a charge-resonance limit is characterised, as demonstrated recently by other authors,[15] by an extremely small difference in the dipole moments of the ground and first excited states of chromophores having a pronounced donator-acceptor substitution pattern.

In summary, the dicyanovinyl and tricyanovinyl substituted 2-morpholino-thiazole and 2-morpholino-thiophene compounds **10** – **13** studied in this work represent a peculiar class of chromophores which constitutes from two different fragments with a strong electron-donor and -acceptor character giving rise to a pronounced solvatochromism. The positive solvatochromic band shift usually observed reaches, in some cases, the shift observed with the 2-dimethylamino-4′-nitro-bithienyl which is one of the strongest positively solvatochromic compound known as yet.[15]

The structures of the new compounds were confirmed by their ^{1}H NMR spectra depicted in tables I and II, and by their elemental analytic data, compiled in table IV.

So far as the educts used were not reported in the literature, they have been synthesised as described in the following section.

TABLE IV Elemental Analytic Data of the Cyanovinyl Compounds **10** – **13** prepared

Nr.	*formula (m.w.)*	*calcd.found*	*% C*	*% H*	*% N*	*% S*	*% Cl*
10a	$C_{11}H_{10}N_4OS$		53.64	4.09	22.75	13.02	
	(246.3)		53.87	4.51	22.36	12.70	
10b	$C_{11}H_9ClN_4OS$		47.06	3.23	19.95	11.42	12.63
	(280.7)		47.27	3.52	19.62	11.62	12.99
10c	$C_{17}H_{14}N_4OS$		63.34	4.38	17.38	9.94	
	(322.4)		63.34	5.10	17.38	9.75	
10d	$C_{18}H_{16}N_4O_2S$		61.35	4.57	15.90	9.10	
	(352.4)		61.12	4.58	15.77	8.72	
10e	$C_{17}H_{14}N_4O_2S$		60.34	4.17	16.56	9.47	
	(338.4)		59.51	5.11	16.73	7.38	
10f	$C_{15}H_{17}N_5O_2S$		54.36	5.17	21.13	9.67	
	(331.4)		54.76	5.81	20.76	9.77	
10g	$C_{24}H_{22}N_6O_2S_2$		58.75	4.51	17.13	13.07	
	(490.6)		58.15	4.27	17.03	12.85	
11a	$C_{12}H_{11}N_3OS$		58.76	4.52	17.13	13.07	
	(245.3)		58.60	5.21	16.67	13.15	
11c	$C_{24}H_{19}N_3OS$		72.52	4.82	10.57	8.07	
	(397.5)		72.81	5.14	9.91	8.24	
12a	$C_{12}H_9N_5OS$		53.13	3.34	25.81	11.82	
	(271.3)		53.16	3.72	25.70	11.21	
12b	$C_{12}H_8ClN_5OS$		47.14	2.64	22.90	10.49	11.59
	(305.8)		47.67	2.97	22.34	10.55	11.62
12c	$C_{18}H_{13}N_5OS$		62.23	3.77	20.16	9.23	
	(347.4)		62.11	3.94	19.73	9.04	
12d	$C_{19}H_{15}N_5O_2S$		60.47	4.01	18.55	8.49	
	(377.4)		60.30	3.92	18.11	8.41	
12e	$C_{18}H_{13}N_5O_2S$		59.49	3.60	19.27	8.82	
	(363.4)		59.90	4.54	19.53	9.07	

Nr.	*formula (m.w.)*	*calcd.found*	*% C*	*% H*	*% N*	*% S*	*% Cl*
12f	$C_{16}H_{16}N_6O_2S$		53.92	4.52	23.58	8.99	
	(356.4)		54.23	4.50	23.26	9.23	
12g	$C_{25}H_{21}N_7O_2S_2$		58.23	4.10	19.01	12.44	
	(515.6)		57.59	4.40	18.15	12.04	
13a	$C_{13}H_{10}N_4OS$		57.76	3.73	20.73	11.86	
	(270.3)		57.74	4.04	19.87	11.71	
13c	$C_{25}H_{18}N_4OS$		71.07	4.29	13.26	7.59	
	(422.5)		71.04	4.61	13.30	7.56	

EXPERIMENTAL

Melting points were determined by means of a Boetius heating-table microscope and are uncorrected. The IR spectra were recorded in potassium bromide pellets with a Philips FTIR spectrometer PU 9624, the visible and near infrared spectra with a Shimadzu spectrometer UV 3101, and the NMR spectra with a Varian 300 MHz spectrometer Gemini 300 or with a JEOL 200 MHz spectrometer JNM FX 200. The elemental analytical data are estimated by means of a LECO analyser CHNS 932.

2-Morpholino-4-(4-methoxyphenyl)thiazole (6d)

A mixture of 4-methoxyphenyl-thiocyanatomethyl-ketone (22.8 g, 0.1 mol), prepared by heating of an equimolar mixture of 4-methoxyphenyl-bromomethyl-ketone and potassium rhodanide in acetone, morpholine (8.7 g, 0.1 mol), acetic acid (6.0 g, 0.1 mol), and ethanol (200 mL) was refluxed for 2h. After cooling, the mixture was diluted with ice water. The product, which precipitated as light-brown crystals, was isolated by filtration and recrystallized; yield 50 %, m.p. 121 – 122 °C (ethanol); ^1H NMR (deuteriochloroform): $\delta = 3.51$ (t, 4H, NCH_2), 3.80 (s, 3H, CH_3), 3.81 (t, 4H, OCH_2), 6.64 (s, 1H, thiazole-H), 6.88 (d, 2H, aromatic H), 7.75 (d, 2H, aromatic H).

Anal. Calcd. for $C_{14}H_{16}N_2O_2S$ (276.4): C, 60.84; H, 5.83; N, 10.14; S, 11.57. Found: C, 61.38; H, 5.86; N, 9.44; S, 11.38.

2-Morpholino-4-(4-hydroxyphenyl)thiazole Hydrobromide (6e·HBr)

2-Morpholino-4-(4-methoxyphenyl)thiazole **(6d)** (13.8 g, 0.05 mol) in aqueous hydrobromic acid (250 mL, 48 %) was refluxed for 10 h. After cooling the precipitate was isolated by filtration; yield 38 %, m.p. 232 – 238 °C; ir (KBr): ν_{OH} 3112 cm^{-1}; ^{1}H NMR (dimethylsulfoxide-d$_6$): $\delta = 3.53$ (t, 4H, NCH$_2$), 3.73 (t, 4H, OCH$_2$), 6.50 (s, 1H, OH), 6.81 (d, 2H, aromatic H), 7.05 (s, 1H, thiazole-H), 7.61 (d, 2H, aromatic H).

Anal. Calcd. for $C_{13}H_{15}BrN_2O_2S$ (343.2): C, 45.49; H, 4.40; N, 8.16; S, 9.34; Br, 23.28. Found: C, 45.39; H, 4.42; N, 8.12; S, 9.46; Br, 27.60.

2-(4-Morpholino)-4-phenyl-5[2-(4-morpholino)-4-thiazolyl]thiazole (6g)

A mixture of 5-chloroacetyl-2-morpholino-4-phenylthiazole[7b] (3.2 g, 0.01 mol) and morpholinothiourea (1.5 g, 0.01 mol) in ethanol (300 mL) was refluxed for 3h. After cooling triethylamine (2.0 g, 0.02 mol) was added to the resulting solution. The product, which precipitate as white crystals, was isolated by filtration and recrystallized; yield of 70 %, m.p. 196 – 198 °C (acetonitrile); ^{1}H NMR (deuteriochloroform): $\delta = 3.41$ (t, 4H, NCH$_2$), 3.49 (t, 4H, NCH$_2$), 3.77 (m, 8H, OCH$_2$), 6.10 (s, 1H, thiazole-H), 7.32 (m, 3H, aromatic H), 7.58 (d, 2H, aromatic H).

Anal. Calcd. for $C_{20}H_{22}N_4S_2O_2$ (414.5): C, 57.95; H, 5.35; N, 13.52; S, 15.47. Found: C, 57.78; H, 5.32; N, 13.56; S, 15.47.

Preparation of 5-formyl-thiazoles 8 (General procedure)

To a mixture of DMF (35 mL) and phosphorous oxytrichloride (9.2g, 0.06 mol) a solution of a 5H-substituted thiazole **6** (0,05 mol), dissolved in DMF (50 mL), was added under stirring at room temperature. The mixture was subsequently heated at 70 °C for 1 h and poured, after cooling, into ice water (400 ml). After alkalisation by addition of aqueous sodium hydroxide (pH 9 –10), the products formed were isolated by filtration.

5-Formyl-2-morpholino-4-(4-methoxyphenyl)thiazol (8d)

This compound was obtained from **6d** as green crystals in a yield of 80%; m.p. 196 – 198 °C (acetonitrile); ir (KBr): ν_{CO} 1625 cm^{-1}; ^{1}H NMR (deuteriochloroform): δ = 3.66 (t, 4H, NCH_2), 3.80 (t, 4H, OCH_2), 6.97 (d, 2H, aromatic H), 7.64 (d, 2H, aromatic H), 9.73 (s, 1H, CHO).

Anal. Calcd. for $C_{15}H_{16}N_2O_3S$ (304.4): C, 59.19; H, 5.30; N, 9.20; S, 10.54. Found: C, 58.62; H, 5.19; N, 8.92; S, 10.44.

5-Formyl-2-morpholino-4-(4-hydroxyphenyl)thiazol (8e)

This compound was obtained from **6e** as light-green crystals in a yield of 46 %; m.p. 284 - 288 °C (DMF, decomp.); ir (KBr): ν_{CO} 1606 cm^{-1}; ^1H NMR (dimethylsulfoxide-d_6): δ = 3.61 (t, 4H, NCH_2), 3.73 (t, 4H, OCH_2), 6.87 (d, 2H, aromatic H), 7.60 (d, 2H, aromatic H), 9.65 (s, 1H, CHO), 9.94 (s, 1H, OH).

Anal. Calcd. for $C_{14}H_{14}N_2O_3S$ (290.3): C, 57.92; H, 4.86; N, 9.65; S, 11.04. Found: C, 57.40; H, 5.04; N, 9.45; S, 10.97.

2,4-Bismorpholino-5-formylthiazole (8f)

To a mixture of N-methyl-formanilide (30 g, 0.22 mol) and phosphorous oxytrichloride (40.0 g, 0.26 mol) a solution of 2,4-bismorpholino-thiazole hydrotetrafluoroborate **6f**[6] in DMF (100 mL) was added under cooling with ice water. The mixture was stirred 24 h at room temperature and then 2 h at 50 °C. After cooling the solution was poured into ice water and neutralised by addition of 2N aqueous sodium hydroxide. The product which precipitates as colourless needles in a yield of 46 % was isolated by filtration and recrystallized; m.p. 196 - 197°C (acetonitrile); ^1H NMR (deuteriochloroform): δ = 3.55 (t, 4H, NCH_2), 3.69 – 3.79 (m, 12H, NCH_2, OCH_2), 9.57 (s, 1H, CHO).

Anal. Calcd. for $C_{12}H_{17}N_3O_3S$ (283.3): C, 50.88; H, 6.01; N, 14.84; S, 11.31. Found: C, 50.27; H, 6.67; N, 15.19; S, 11.50.

5-[5-Formyl-2-(4-morpholino)-4-thiazolyl]-2-(4-morpholino)-4-phenylthiazole (8g)

This compound was obtained from **6g** as luminously yellow crystals in a yield of 78%; m.p. 200 °C (acetonitrile); ir (KBr): ν_{CO} 1637 cm^{-1}; ^1H NMR (deuteriochloroform): δ = 3.74 (m, 8H, NCH_2), 3.80 (m, 8H,

OCH_2), 7.28 (m, 3H, aromatic H), 7.51 (d, 2H, aromatic H), 9.23 (s, 1H, CHO).

Anal. Calcd. for $C_{21}H_{22}N_4O_3S_2$ (442.5): C, 57.00; H, 5.01; N, 12.66; S, 14.49. Found: C, 57.33; H, 4.79; N, 12.60; S, 14.75.

Preparation of 5-(2,2-dicyanoethenyl)thiazoles 10 and 5-(2,2-dicyanoethenyl)thiophenes 11

Method A1

To a mixture of 5-formyl-thiazole **8** or 5-formyl-thiophene **9** (0.02 mol) and malononitrile (1.3 g, 0.02 mol) in methanol (20 mL) some drops piperidine were added. The mixture was stirred at room temperature for 1 h and the product precipitated was isolated by filtration and than recrystallized.

Method A2

This method is the same as method A1, but instead of methanol acetonitrile (100 mL) was used and the mixture was heated for 0.5 h at 60 °C.

Method A3

This method is the same as method A1, but instead of methanol and piperidine acetic anhydride (20 mL) and triethylamine (0.2 mL), resp., were used and the mixture was refluxed for 1 h.

The compounds so prepared are listed in table I.

Preparation of 5-(1,2,2-tricyanoethenyl)-thiazoles 12 and 5-(1,2,2-tricyanoethenyl)-thiophenes 13

Method A

Sodium cyanide (1.0 g, 0.02 mol), dissolved in water (2 mL), was added to a stirred solution of thiazole **10** or thiophene **11** (0.02 mol) in dimethylformamide (25 mL) acidified with hydrochloric acid at 0 – 5 °C; finally acetic acid (50 mL) and lead(IV) acetat (9.0 g, 0.02 mol) in small portions were added during 5 min. The mixture was stirred for 10 min, poured into icewater (400 ml), the precipitated product was filtered off, dried, and recrystallized.

Method B

To a solution of thiazole **6** or thiophene **7** (0.01 mol) in dichloromethane (50 mL), a solution of tetracyanoethene (1.4 g, 0.011 mol) in dichloromethane (60 mL), containing some trops of dimethylformamide, was added. The mixture was refluxed for 1 h and stirred at room temperature for 12 h. Then, the solvent was evaporated and the residue was recrystallized.

The compounds so prepared by means of the methods A or B are listed in table II.

Acknowledgements

The authors thanks the Deutsche Forschungsgemeinschaft and the CHEMTEC GmbH, Leuna, for generous financial support.

References

[1] 1a: D. N. Dhar, *Chem. Rev.* **67,** 611 (1967);
1b: F. Freeman, *Chem. Rev.* **69,** 591 (1969);
1c: K. Friedrich, W. Ertel, *Synthesis* **1970,** 23.

[2] 2a: C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry;* 2nd ed. VCH, Weinheim, 1988;
2b: P. Suppan, N. Ghoneim, *Solvatochromism;* Royal Society of Chemistry, Cambridge, U.K. 1997.

[3] S. R. Marder, J. W. Perry, G. Bourhill, C. B. Gorman, B. G. Tiemann, K. Mansour, *Science* **261,** 186 (1993).

[4] S. R. Marder, C. B. Gorman, F. Meyers, J. W. Perry, G. Bourhill, J. L. Brédas, B. M. Pirce, *Science* **265,** 632 (1994).

[5] 5a: A. K. Y. Jen, T. A. Chen, V. P. Rao, Y. Cai, Y. J. Liu, K. J. Drost, R. M. Mininni, L. R. Dalton, P. V. Bedworth, S. R. Marder, *Mat. Res. Soc., Symp. Proc.* **392,** 33 (1995);
5b: A. K. Y. Jen, Y. Cai, P. V. Bedworth, S. R. Marder, *Adv. Mater.* **9,** 132 (1997);
5c: P. V. Bedworth, Y. Cai, A. Jen, S. R. Marder, *J. Org. Chem.* **61,** 2242 (1996);
5d: I. D. L. Albert, T. J. Marks, M. A. Ratner, *J. Am. Chem. Soc.* **119,** 6575 (1997);
5e: V. P. Rao, A. K. Y. Jen, K. Y. Wong, K. J. Drost, *J. Chem. Soc., Chem. Commun.* **1993,** 1118;
5f: A. K. Y. Jen, V. P. Rao, K. Y. Wong, K. J. Drost, *J. Chem. Soc., Chem. Commun.* **1993,** 90;
5g: A. K. Y. Jen, K. J. Dost, V. P. Rao, Y. Cai, Y. J. Liu, R. M. Mininni, J. T. Kenney, E. S. Binkley, S. R. Marder, L. R. Dalton, C. Xu, *Polymer Prep.* **35,** 130 (1994);
5h: V. P. Rao, A. K. Y. Jen, K. Y. Wong, *Polymer Prep.* **35,** 168 (1994);
5i: S. Gilmour, R. A. Montgomery, S. R. Marder, L. T. Cheng, A. K.Y. Jen, Y. Cai, J. W. Perry, L. R. Dalton, *Chem. Mater.* **6,** 1603 (1994);
5j: S. Gilmour, S. R. Marder, J. W. Perry, L. T. Cheng; *Adv. Mater.* **6,** 494 (1994).

[6] 6a: R. Flaig, H. Hartmann, *Heterocycles* **45,** 875 (1997);
6b: R. Flaig, H. Hartmann, *Monatsh. Chem.* **128,** 1051 (1997).

[7] 7a: J. E. Israel, R. Flaig, H. Hartmann, *J. Prakt. Chem.* **338,** 51 (1996);
7b: C. Mokry, H. Hartmann, *J. Prakt. Chem,* **349,** 375 (1998);
7c: H. Hartmann, R. Radeglia, *J. Prakt. Chem.* **317,** 657 (1975);
7d: D. W. Gillon, I. J. Forrest, G. D. Meakins, M. D. Tirel, J. D. Wallis, *J. Chem. Soc., Perkin Trans. I* **1983,** 341 – 347.

[8] [8a]: B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffmann, H. F. Mower, *J. Am. Chem. Soc.* **80,** 2806 (1958);
[8b]: D. Berkesš, J. Kovac, *Collect. Czech. Chem. Commun.* **51,** (1986).

[9] [9a]: A. Medici, P. Pedrini, C. Venturolli, A. Dondoni, *J. Org. Chem.* **46,** 2790 (1981);
[9b]: R. Gompper, P. Kruck, J. Schelble, *Tetrahedron Lett.* **24,** 3563 (1983).

[10] [10a]: H. Hartmann, R. Mayer, *Z. Chem.* **6,** 28 (1966);
[10b]: H. Hartmann, S. Scheithauer, *J. Prakt. Chem.* **311,** 827 (1969).

[11] S. Scheithauer, H. Hartmann, J. Morgenstern; German Pat. (GDR) 82 715 (1970); *Chem. Abstr.* **77,** P 114421h (1972).

[12] [12a]: M. J. Kamlet, J.-L. M. Abboud, M. H. Abraham, R. W. Taft, *J. Org. Chem.* **48,** 2877 (1983);
[12b]: M. J. Kamlet, J.-L. M. Abboud, R. W. Taft, *J. Am. Chem. Soc.* **99,** 6027 (1977);
[12c]: R. W. Taft, M. J. Kamlet, *J. Am. Chem Soc.* **96,** 2886 (1976);
[12d]: R. W. Taft, M. J. Kamlet, *J. Chem. Soc., Perkin Trans. 2,* **1979,** 1723 – 1729.

[13] [13a]: E. Lippert, *Z. Elektrochem.* **61,** 962 (1957);
[13b]: W. Liptay, *Z. Naturforsch.* **20A,** 1441 (1955),
[13c]: S. R. Marder, C. B. Gorman, B. G. Tiemann, L. T. Cheng, *J. Am. Chem. Soc.* **115,** 3006 (1993).

[14] [14a]: S. R. Marder, C. B. Gorman, F. Meyers, J. W. Perry, G. Bourhill, J. L. Bredas, B. M. Pierce, *Science* **265,** 632 (1994);
[14b]: C. B. Gorman, S. R. Marder, *Chem. Mater.* **7,** 215 (1995),
[14c]: S. R. Marder, L. T. Cheng, B. G. Tiemann, A. C. Friedli, M. Blanchard-Desce, J. W. Perry, J. Skindhoj, *Science* **263,** 511 (1994);
[14d]: S. R. Marder, J. W. Perry, G. Bourhill, C. B. Gorman, B. G. Tiemann, K. Mansour, *Science* **261,** 186 (1993);
[14e]: S. R. Marder, C. B. Gorman, B. G. Tiemann, L. T. Cheng, *J. Am. Chem. Soc.* **115,** 3006 (1993);
[14f]: G. Bourhill, J. L. Bredas, L. T. Cheng, S. R. Marder, F. Meyers, J. W. Perry, B. G. Tiemann, *J. Am. Chem. Soc.* **116,** 2619 (1994).

[15] [15a]: F. Effenberger, F. Wuerthner, F. Steybe, *J. Org. Chem.* **60,** 2082 (1995);
[15b]: F. Effenberger, F. Wuerthner, *Angew. Chem.* **105,** 742 (1993); *Angew. Chem., Int. Ed. Engl.* **32,** 719(1993).

[16] F. Würthner, R. Wortmann, R. Matschiner, K. Lukaszuk, K. Meerholz, Y. DeNardin, R. Bittner, C. Bräuchle, R. Sens, *Angew. Chem.* **109,** 2933 (1997); *Angew. Chem., Int. Ed. Engl.* **36,** 2765 (1997).

[17] I. Sawhney, J. R. H. Wilson, *J. Chem. Soc., Perkin Trans. 1,* **1990,** 329.

[18] H. Grube, H. Suhr, *Chem. Ber.* **102,** 1570 (1969).

[19] J. Teller, H. Dehne, T. Zimmermann, W. Fischer, B. Olk, *J. Prakt. Chem.* **332,** 453 (1990).

[20] R. Flaig, H. Hartmann, *Heterocycles* **45,** 875 (1997).

[21] A. De, S. P. Bhattacharyya, J. S. A. Brunskill, K. K. Sidhu, D. F. Ewing, *J. Chem. Res. (S)* **1982,** 312.

[22] S. Scheithauer, H. Hartmann, R. Mayer, *Z. Chem.* **8,** 181 (1968).