Preparation and Characterization of Cyanovinyl-Substituted 2-Aminothiophenes and 2-Aminothiazoles and Some of Their Heterooligomers

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Dedicated to Professor Heinz-Günter Viehe on the occasion of his 70th birthday

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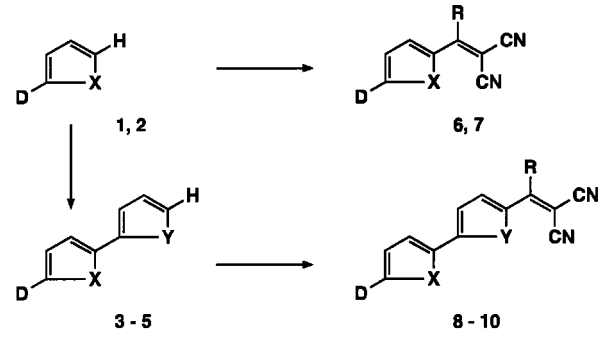
The reaction of 2,2-dicyanoethenyl- and 1,2,2-tricyanoethenyl-substituted bromoalkanes, bromomethyl benzenes, thiophenes, and furans **19–22** with 3-aminothioacrylamides and their 2-azaanalogues **23** and **24** gives a series of 5-dicyanoethenyl- and 5-tricyanoethenyl-substituted 2-aminothiophenes, 2-aminothiazoles and their (hetero)benzologous analogues **25–32**. The solvatochromism, which is a characteristic feature of these donor-acceptor substituted heterocyclic compounds, was studied in detail and correlated with the Kamlet-Taft solvent parameters.

Introduction

In the last few years the donor (D) substituted dicyanovinyl and tricyanovinyl compounds of general structure **6–10** (Scheme 1) have received a lot of interest. Due to their strong solvatochromic properties, which mainly originate from their donor-acceptor substitution, they can be used as model compounds for dyes with strong nonlinear optical (NLO) properties.[1] Such dyes have found applications for manufacturing new materials capable of generating special electrooptical effects, such as frequency doubling or wave mixing.[2]



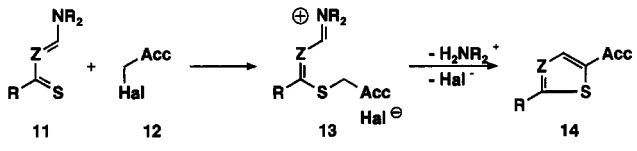
	X	Y
1,3,6	CH=CH	S
2,4,7	S	CH=CH
5,8	S	S

6 - 10	R
a	H
b	CN

Scheme 1

Usually, the dicyanovinyl and tricyanovinyl compounds **6–10** are prepared by functionalization of their acceptor-free precursors **1–5** by different methods, for example, by a Knoevenagel condensation starting from the corresponding formyl derivatives of the compounds **1–5** and malononitrile[3] or by a tricyanovinylation reaction starting from the parent heterocycles **1–5** and TCNE.[4] The corresponding starting compounds **1–5** are either commercially available or can be prepared by simple methods. For example, the strong donor-substituted 2-dialkylaminothiophenes **2** (D = R_2N) can be prepared by reaction of 2-mercaptothiophene with secondary amines.[5] The phenyl-thienyl and bis-thienyl derivatives **3** and **5** can be prepared from the donor-substituted starting materials **1** or **2** and their donor-group-free parent compounds by a (hetero)aryl-hetaryl coupling reaction mediated by heavy or pseudo metals.[1t,6]

Here we report on a new and versatile route for preparing the dicyanovinyl and tricyanovinyl compounds of the general structure **6–10**, as well as some further compounds with a similar structure and the same donor-acceptor substitution pattern. Contrary to the above-mentioned methods, the main strategy of this route is to synthesize one of the heterocyclic moieties in the course of a ring-closure reaction starting from the appropriately substituted acylic precursors. This method has been used by us for several years[7] and has been subsequently extended by Liebscher at al.[8] This modification consists of the reaction of an aminoethenyl-thioketone precursor **11a** or its aza analogue **11b** with an acceptor-substituted halomethyl compound **12** (Acc = acceptor) giving rise to the initial formation of imin-



11, 13, 14	Z
a	CH
b	N

Scheme 2

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ium salts of general structure **13**, which can be cyclized by the addition of base to the thiophenes **14a** or thiazoles **14b** (Scheme 2). Until now however, this method has not been applied to the synthesis of donor-acceptor substituted thiophene and thiazole derivatives **14** with a dicyanovinyl or tricyanovinyl moiety.

Results and Discussion

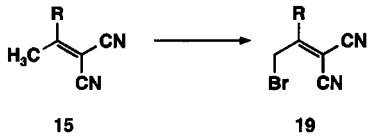
To extend the mentioned method to the preparation of such thiophene and thiazole derivatives as well as for some of their heteroanalogues, the dicyano- and tricyanovinyl-substituted halomethyl compounds such as **19–22** were necessary (Scheme 3). However, these compounds are either unknown or not commercially available, except for a couple of exceptions.[9]

The best method for their synthesis consists of the bromination of the corresponding methyl compounds **15–18** with elemental bromine or NBS in tetrachloromethane.[10] The required methyl compounds **15–18** were available either by a Knoevenagel condensation from the corresponding carbonyl compounds and malononitrile,[3] or by reaction of the resulting dicyanovinyl compounds **16a–18a** with sodium cyanide, and subsequent oxidation of the initially formed tricyanoethane derivatives with $Pb(OAc)_4$ in acetic acid.[4]

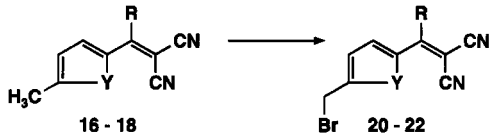
In Table 1 some characteristic preparative and spectroscopic data of the prepared dicyano- and tricyanovinyl-substituted bromomethyl compounds **19–22** are listed. As a special feature of these compounds their lachrymatory properties, which restrict their handling in a laboratory environment, should be emphasised.

As co-reagents for the heterocyclization reaction, the amino-substituted thioacrylamides **23** and their aza analogues **24** were used (Scheme 4). These compounds are easily available by known methods, e.g., by starting from *N,N*-disubstituted thioacetamides or thioureas.[11]

The transformation of the mentioned dicyano- and tricyanovinyl-substituted bromomethyl compounds **19–22** and thioacrylamides **23** and **24** into corresponding products **25–32** was performed, in general, by heating an equimolar mixture of these starting materials in ethanol or acetonitrile solution, and subsequent addition of a suitable base such as triethylamine or sodium methoxide (Scheme 5). They were isolated by filtration and, when necessary, purified by recrystallization.



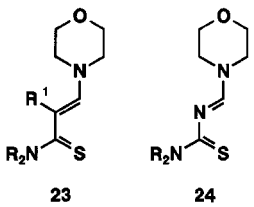
15, 19	R
a	CH_3
b	C_6H_5



	Y
16, 20	CH=CH
17, 21	S
18, 22	O

16 - 18 20 - 22	R
a	H
b	CN

Scheme 3

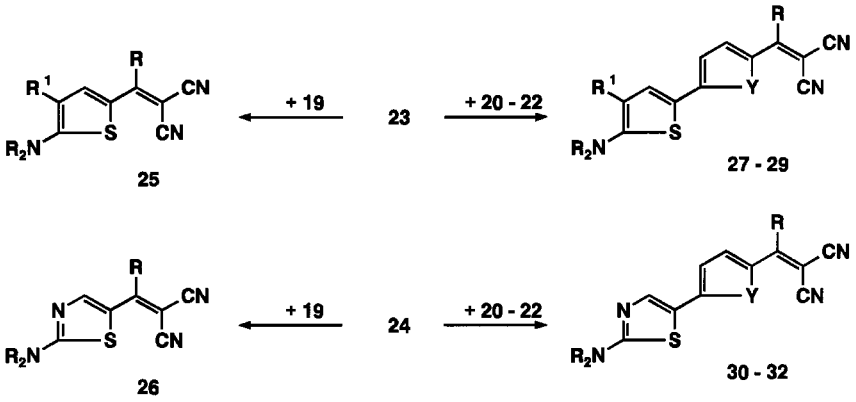


23, 24	R_2N	R^1
a	morpholino	H
b	morpholino	C_6H_5
c	dimethylamino	H
d	diethylamino	H
e	diphenylamino	H

Scheme 4

Table 1. Bromomethyl compounds **19–22**

	Y	R	yield [%] (route)	m.p. [°C] b.p. (Torr)	formula (m.w)	^{1}H NMR, δ [ppm] in $CDCl_3$	ν_{CN} [cm^{-1}]	ref.
19a	–	CH_3	40 (A)	b.p. 86–90 (2)	$C_6H_5BrN_2$ (185.0)	2.44 (s, 3 H, CH_3), 4.22 (s, 2 H, CH_2Br)	2235	[9a]
19b	–	C_6H_5	61 (A)	117–119 (EtOH)	$C_{11}H_7BrN_2$ (247.1)	4.56 (s, 2 H, CH_2Br), 7.52–7.65 (m, 5 H, CH)	2233	[9a]
20a	CH=CH	H	79 (A)	77–80 (MeOH)	$C_{11}H_7BrN_2$ (247.1)	4.50 (s, 2 H, CH_2Br), 7.55 (d, 2 H, CH), 7.76 (s, 1 H, CH), 7.88 (d, 2 H, CH)	2223	[9b]
20b	CH=CH	CN	52 (B)	100–102 (MeOH)	$C_{12}H_6BrN_3$ (272.1)	4.51 (s, 2 H, CH_2Br), 7.63 (d, 2 H, CH), 7.99 (d, 2 H, CH)	2235	
21a	S	H	72 (A)	98–101 (MeOH)	$C_9H_5BrN_2S$ (253.1)	4.70 (s, 2 H, CH_2Br), 7.23 (d, 1 H, CH), 7.62, (d, 1 H, CH), 7.80 (s, 1 H, CH)	2225	
21b	S	CN	44 (B)	83–87 (MeOH)	$C_{10}H_4BrN_3S$ (278.1)	4.68 (s, 2 H, CH_2Br), 7.30 (d, 1 H, CH), 7.96 (d, 1 H, CH)	2225	
22a	O	H	69 (B)	81 (MeOH)	$C_9H_5BrN_2O$ (237.1)	4.49 (s, 2 H, CH_2Br), 6.67 (d, 1 H, CH), 7.33 (d, 1 H, CH),7.47 (s, 1 H, CH)	2225	
22b	O	CN	88 (B)	oil	$C_{10}H_4BrN_3O$ (262.6)	4.50 (s, 2 H, CH_2Br), 6.80 (d, 1 H, CH), 7.50 (d, 1 H, CH)	2227	



	Y
27, 30	CH=CH
28, 31	S
29, 32	O

25, 26	R_2N	R^1	R
a	morpholino	H	CH_3
b	morpholino	H	C_6H_5
c	morpholino	C_6H_5	CH_3
d	morpholino	C_6H_5	C_6H_5
e	dimethylamino	H	CH_3
f	dimethylamino	H	C_6H_5
g	diphenylamino	H	CH_3
h	diphenylamino	H	C_6H_5

27 - 32	R_2N	R^1	R
a	morpholino	H	H
b	morpholino	H	CN
c	morpholino	C_6H_5	H
d	morpholino	C_6H_5	CN
e	dimethylamino	H	H
f	dimethylamino	H	CN
g	diethylamino	H	H
h	diethylamino	H	CN
i	diphenylamino	H	H
j	diphenylamino	H	CN

Scheme 5

In Table 2 the prepared dicyanovinyl- and tricyanovinyl-substituted thiophenes and thiazoles **25** and **26**, as well as their heterooligomers **27–32** are depicted. From these compounds only compounds **28e** and **28f** have previously been described in the literature; they were prepared by a heteroaryl-heteroaryl coupling reaction.[11t]

The structures of all compounds prepared have been elucidated by their elemental analytical and spectroscopic data. Some of these data are listed in Tables 2, 3 and 4.

The bromomethyl compounds **19–22** exhibit intense signals at about 2220 cm^{-1} in their IR spectra which can be unambiguously attributed to the CN moieties. The same compounds exhibit characteristic signals at about 4.20–4.70 ppm and 6.60–8.00 ppm in their ^1H NMR spectra. The first set of signals can be attributed to the protons of the bromomethyl groups, and the second set to the protons of the carbocyclic or heterocyclic moieties. In contrast to the tricyanovinyl compounds **20b–22b**, the dicyanovinyl compounds **20a–22a** exhibit an additional signal at about 7.30 ppm which can be attributed to the protons of the vinyl moieties.

In the IR spectra of the dicyanovinyl- and tricyanovinyl-substituted heterocycles **27–32**, the characteristic signals of the CN groups are found at about 2200 cm^{-1}. In the ^1H NMR spectra these compounds exhibit characteristic signals at about 1.20–4.00 ppm, 6.30–7.70 ppm, and 7.90–8.40 ppm. Whereas the first set of signals can be attributed to the protons of the *N*-bound alkyl and alkylene groups, the second and third sets of signals can be unambiguously attributed to the protons of the heterocyclic and vinylic moieties, respectively.

As a characteristic feature of all the dicyanovinyl- and tricyanovinyl-substituted heterocycles **25–32** their light absorption in the visible range should be mentioned. Representative data are depicted in Table 2. As can be seen, all the compounds studied exhibit an intense absorption band in the visible range whose position is strongly influenced by the structure of the compounds, for example, by the substitution pattern in the donor and acceptor moieties or by the number and kind of rings, as well as by the polarity of the solvents. Thus, the monocyclic compounds **25** and **26** absorb at shorter wavelength than the bicyclic compounds **27–32** with the same substitution pattern at their donor and acceptor moieties. A similar relation is observed by comparing the thiophene compounds **25** and **27–29** with the thiazole compounds **26** and **30–32**. The latter compounds absorb at shorter wavelength than their thiophene analogues with the same substitution pattern. For all the compounds

Table 2. Di- and tricyanovinyl compounds **25**–**32**

	R_2N	Y	R	R^1	yield [%]	m.p. [° C] (recryst.)	λ_{max} [nm]	lg ε in MC	ν_{CN} [cm^{-1}]	^{1}H NMR, δ [ppm] in [D$_6$]DMSO
25a	morph	–	CH_3	H	33	220–221 (CH_3CN)	463	4.62	2188 2205	2.52 (s, 3 H, CH_3) 3.46 (t, 4 H, NCH_2), 3.76 (t, 4 H, OCH_2), 6.55 (d, 1 H, CH), 7.97 (d, 1 H, CH)
25b	morph	–	C_6H_5	H	66	179–180	466	4.65	2184 2198	3.46 (t, 4 H, NCH_2), 3.73 (t. 4H. OCH_2), 6.58 (d, 1 H, CH), 7.32 (d, 1 H, CH), 7.44 (m, 2 H, CH), 7.55 (m, 3 H, CH)
25c	morph	–	CH_3	C_6H_5	54	183–184 (DMF)	452	4.53	2210	2.59 (s, 3 H, CH_3), 3.12 (t, 4 H, NCH_2), 3.68 (t, 4 H, OCH_2), 7.35–7.58 (m, 5 H, CH), 8.0 (s,1 H, CH)
25d	morph	–	C_6H_5	C_6H_5	74	194–196	466	4.52	2210	3.11 (t, 4 H, NCH_2), 3.65 (t, 4 H, OCH_2), 7.42–7.60 (m, 11 H, CH)
25e	Me_2N	–	CH_3	H	75	184	465	4.76	2202	2.48 (s, 3 H, CH_3), 3.17 (s, 6 H, CH_3), 6.37 (d, 1 H, CH), 7.94 (d, 1 H, CH)
25f	Me_2N	–	C_6H_5	H	69	150	470	4.77	2198	3.17 (s, 6 H, CH_3), 4.40 (s, 1 H, CH), 7.39–7.54 (m, 6 H, CH)
25g	Ph_2N	–	CH_3	H	61	139–141	475	4.64	2210	2.50 (s, 3 H, CH_3), 6.38 (d, 1 H, CH), 7.34–7.51 (m, 10 H, CH), 7.92 (d, 1 H, CH)
25h	Ph_2N	–	C_6H_5	H	58	154 (CH_3CN)	485	4.50	2210	6.34 (d, 1 H, CH), 7.29 (d, 1 H, CH), 7.34–7.53 (m, 15 H, CH)
26a	morph	–	CH_3	–	88	203–204 (CH_3CN)	418	4.55	2214	2.57 (s, 3 H, CH_3), 3.66 (t, 4 H, NCH_2), 3.74 (t, 4 H, OCH_2), 8.31 (s, 1 H, CH
26b	morph	–	C_6H_5	–	68	152–154	429	4.57	2214	3.66 (t, 4 H, NCH_2), 3.72 (t, 4 H, OCH_2), 7.41 (s, 1 H, CH) 7.50–7.63 (m, 5 H, CH)
27a	morph	CH=CH	H	H	51	226–228 (DMF)	491	4.53	2221	3.20 (t, 4 H, NCH_2), 3.75 (t, 4 H, OCH_2), 6.30 (d, 1 H, CH), 7.55 (d, 1 H, CH), 7.67 (d, 2 H, CH), 7.90 (d, 2 H, CH), 8.31 (s, 1 H, CH)
27b	morph	CH=CH	CN	H	24	283–285 (DMF)	602	4.44	2214	3.27 (t, 4 H, NCH_2), 3.76 (t,4 H,OCH_2), 6.36 (d, 1 H, CH) 7.66 (d, 1 H, CH), 7.73 (d, 2 H, CH), 7.94 (d,2 H,CH)
27c	morph	CH=CH	H	C_6H_5	36	178–182	466	4.41	2225	2.94 (t, 4 H, NCH_2), 3.70 (t, 4 H, OCH_2), 7.29 (t, 1 H, CH), 7.44 (t, 2 H, CH), 7.81 (m, 5 H, CH), 7.96 (d, 2 H, CH), 8.37 (s,1 H,CH)
27d	morph	CH=CH	CN	C_6H_5	22	186–189	583	4.07	2359	2.97 (t, 4 H, NCH_2), 3.71 (t, 4 H, OCH_2), 7.30–8.00 (m, 10 H, CH)
28a	morph	S	H	H	80	190–193 (DMF)	536	4.54	2206	3.26 (t, 4 H, NCH_2), 3.75 (t, 4 H, OCH_2), 6.31 (d, 1 H, CH) 7.31 (d, H, CH), 7.46 (d,1 H, CH), 7.8 (d, 1 H, CH), 8.38 (s, 1 H, CH)
28b	morph	S	CN	H	75	285–290 dec (DMF)	681	4.69	2205	3.44 (t, 4 H, NCH_2), 3.76 (t, 4 H, OCH_2), 6.53 (d, 1 H, CH), 7.46 (d, 1 H, CH), 7.82 (d, 1 H, CH), 7.90 (d, 1 H, CH)
28c	morph	S	H	C_6H_5	59	193–194 (DMF)	508	4.48	2215	2.93 (t, 4 H, NCH_2), 3.69 (t, 4 H, OCH_2), 7.30–7.86 (m, 8 H, CH), 8.47 (s, 1 H, CH)
28d	morph	S	CN	C_6H_5	68	176–178 (DMF)	630	4.51	2212	3.05 (t, 4 H, NCH_2), 3.69 (t, 4 H, OCH_2), 7.33–8.00 (m, 8 H, CH)
28e	Me_2N	S	H	H	90	245–247 (241–247)[6b]	572	4.56	2208	3.05 (s, 6 H, CH_3), 6.07 (d, 1 H, CH), 7.24 (d, 1 H, CH), 7.47 (d, 1 H, CH), 7.76 (d, 1 H, CH), 8.29 (s, 1 H, CH)
28f	Me_2N	S	CN	H	55	285 (275)[1t] (DMF)	704	4.85	2202	3.21 (s, 6 H, CH_3), 6.43 (d, 1 H, CH), 7.42 (d,1 H, CH), 7.82 (d, 1 H, CH), 7.87 (d, 1 H, CH)
28g	Et_2N	S	H	H	60	168–170 (CH_3CN)	588	4.71	2214	1.19 (t, 6 H, CH_3), 3.41 (q, 4 H, CH_2), 6.07 (d, 1 H, CH), 7.21 (d, 1 H, CH), 7.46 (d, 1 H, CH), 7.74 (d, 1 H, CH), 8.27 (s,1 H,CH)
28h	Et_2N	S	CN	H	46	264–265 (DMF)	718	4.91	2198	1.23 (t, 6 H, CH_3), 3.55 (q, 4 H, CH_2), 6.50 (d, 1 H, CH), 7.43 (d, 1 H, CH), 7.80 (d, 1 H, CH), 7.91 (d, 1 H, CH)
28i	Ph_2N	S	H	H	43	145–147 (CH_3CN)	548	4.47	2214	6.50 (d, 1 H, CH), 7.03 (d, 1 H, CH), 7.13–7.24 (m, 7 H, CH), 7.30–7.37 (m, 4 H,CH), 7.40 (d, 1 H, CH), 7.66 (s, 1 H, CH)[a][a] In $CDCl_3$
28j	Ph_2N	S	CN	H	43	242–244 (CH_3CN)	685	4.72	2210	6.45 (d, 1 H, CH), 7.07 (d, 1 H, CH), 7.22–7.33 (m, 6 H, CH), 7.33–7.42 (m, 5 H, CH), 7.87 (d, 1 H, CH)[a]
29a	morph	O	H	H	67	193–194 (CH_3CN)	527	4.51	2213, 2200	3.25 (t, 4 H, NCH_2), 3.75 (t, 4 H, OCH_2), 6.37 (d, 1 H, CH), 6.94 (d, 1 H, CH), 7.46 (d, 1 H, CH), 7.51 (d, 1 H, CH), 7.88 (s,1 H, CH)
29b	morph	O	CN	H	47	290–295 dec (DMF)	661	4.57	2202	3.44 (t, 4 H, NCH_2), 3.77 (t, 4 H, OCH_2), 6.61 (d, 1 H, CH), 7.25 (d, 1 H, CH), 7.75 (d, 1 H, CH), 7.85 (d, 1 H, CH)
29c	morph	O	H	C_6H_5	60	247 (DMF)	497	4.49	2219	2.95 (t, 4 H, NCH_2), 3.69 (t, 4 H, OCH_2), 7.11 (d, 1 H, CH),7.31 (t, 1 H, CH), 7.42–7.75 (m, 6 H, CH), 8.00 (s, 1 H, CH)
29d	morph	O	CN	C_6H_5	68	226–228 (DMF)	632	4.54	2210	3.05 (t, 4 H, NCH_2), 3.69 (t, 4 H, OCH_2), 7.35–7.46 (m, 4 H, CH), 7.64 (d, 2 H, CH), 7.80 (d, 1 H, CH), 7.92 (s, 1 H, CH)
30a	morph	CH=CH	H	–	40	261–264	448	4.45	2223	3.51 (t, 4 H, NCH_2), 3.74 (t, 4 H, OCH_2), 7.70 (d, 2 H, CH), 7.93 (s, 3 H, CH), 8.40 (s, 1 H, CH)
30b	morph	CH=CH	CN	–	82	228–230	549	4.42	2218	3.53 (t, 4 H, NCH_2), 3.75 (t, 4 H, OCH_2), 7.75 (d, 2 H, CH), 7.96 (d, 2 H, CH), 7.99 (s, 1 H, CH)
31a	morph	S	H	–	80	210–212	495	4.53	2219	3.56 (t, 4 H, NCH_2), 3.83 (t, 4 H, OCH_2), 7.05 (d, 1 H, CH), 7.58 (s,d,2 H, CH), 7.67 (s,1 H,CH)[a]

[a] In $CDCl_3$.

Table 2. *(Continued)*

	R_2N	Y	R	R^1	yield [%]	m.p. [° C] (recryst.)	λ_{max} [nm]	lg ε in MC	ν_{CN} [cm^{-1}]	^1H NMR, δ [ppm] in [D_6]DMSO
31b	morph	S	CN	–	89	270–272 (DMF)	593	4.62	2208	3.60 (t, 4 H, NCH_2), 3.75 (t, 4 H, OCH_2), 7.56 (d, 1 H, CH), 8.03 (d,1 H, CH), 8.11 (s, 1 H, CH)
32a	morph	O	H	–	59	235–237 (DMF)	486	4.53	2207	3.53 (t, 4 H, NCH_2), 3.74 (t, 4 H, OCH_2), 7.00 (d, 1 H, CH), 7.48 (d, 1 H, CH), 7.86 (s, 1 H, CH), 7.99 (s,1 H,CH)
32b	morph	O	CN	–	61	278–280 (DMF)	584	4.61	2214	3.58 (t, 4 H, NCH_2), 3.74 (t, 4 H, OCH_2), 7.28 (d, 1 H, CH), 7.81 (d, 1 H, CH), 8.1 (s, 1 H, CH)

studied the dicyanoethenyl compounds absorb at shorter wavelength than their tricyanoethenyl analogues. In the bicyclic series the compounds **28** with di- and tricyanoethenyl-linked thiophene moieties absorb at longer wavelength than the compounds **27** and **29** with furan or benzene moieties.

A distinct spectral effect is also caused by the substituents at the amino groups or at their adjacent ring C-atom. Thus, a diphenyl substitution at the amino group in the monocyclic compounds **25** causes a longer wavelength absorption than an alkyl substitution at the same position. The reverse effect is observed for the bicyclic compounds **28**. Here, a diphenylamino moiety causes a hypsochromic effect relative to the dimethylamino or diethylamino moieties. A similar effect is observed with a phenyl substituent in the 3-position of the 2-aminothiophene moiety. In the compounds **27** and **28** this substituent causes a hypsochromic shift relative to the absorption wavelength of the corresponding 3H-substituted derivatives (compare, for example, the absorption wavelength of compounds **27c** and **27d** with the ones of compounds **27a** and **27b**), whereas it has nearly no influence on the wavelength of the longest absorption maxima in the monocyclic compounds **25**.

With respect to the influence of the solvent on the absorption properties of the compounds studied, a bathochromic shift of the longest wavelength bands is observed mostly by increasing the solvent polarity (positive solvatochromism). This solvent-induced shift can be quantified by plotting the reciprocal wavelength (1/λ) of the longest wavelength absorption band, measured in 10^{-5} m, against suitable solvent parameters, for example, the E_T values given by Dimroth and Reichardt[12] or, more precisely, with the π* values introduced by Kamlet and Taft[13] and modified by Effenberger, Würthner and Steybe[6b] for which Equation 1 was applied:

$$1/\lambda = a + b \cdot \pi^* \quad (1)$$

The measured spectral data in a series of different solvents and the correlation parameters *a* and *b* of Equation (1), as well as the corresponding correlation coefficients *r*, are depicted in Table 3. Usually, a good correlation, indicated by correlation coefficients *r* larger than 0.95, is observed. Only in cases in which a weak or no solvatochromism is measured are the correlation coefficients *r* significantly lower.

For the monocyclic compounds **25** and **26** it was found that the strongest solvatochromic effect, indicated by a large negative **b** value, is observed in the 3H-substituted 2-aminothiophene series, followed by the 3-phenyl-substituted 2-aminothiophene series, and the 2-aminothiazole series. With respect to the acceptor moieties, the strongest solvatochromism is caused by the 1-methyl-2,2-dicyanoethenyl substituents.

For the solvatochromism in the series of bicyclic compound **27–32** the strongest solvatochromic effect is generally caused by the tricyanoethenyl substituents. For the heterocyclic moieties linked with the cyano-substituted acceptor groups the thiophene derivatives **28** and **31** exhibit the largest solvatochromic effect, followed (with some exceptions in the thiophene series **27–29**) by the furan derivatives **29** and **32** and the benzene derivatives **27** and **30**.

In the series of bicyclic thiophene compounds **27–29** the 3H-substituted 2-aminothiophenes generally exhibit a stronger solvatochromic effect than their 3-phenyl-substituted analogues. This effect probably originates from a distortion of the 2-amino moieties from the plane of their adjacent π-systems by the phenyl group. This is supported by the solvatochromic effects observed in the series of the bicyclic thiazole derivatives **30–32**. Usually, these compounds exhibit a stronger solvatochromism than their thiophene analogues with a phenyl moiety in the 3-position.

Remarkably, a few tricyanoethenyl-substituted compounds of the bicyclic series, namely the compounds **27c**, **27d**, and **30b**, exhibit a weak positive or a pronounced negative solvatochromism. From this fact it can be concluded that the polarity of these compounds is not significantly changed, as is the case for most of the other compounds, by going from the electronic ground state to the first excited state. Therefore, these compound seem to be not as well-suited as the other ones as active compounds for manufacturing materials with nonlinear optical properties, for which a strong alteration of the polarity of the compounds on

Table 3. Solvatochromic data of the di- and tricyanovinyl compounds **25**–**32**

Solvents[a]	CH	TE	TO	ET	DMF	DMSO	*a*	*b*	*r*
π*	−0.02	0.26	0.53	0.57	0.87	1.01			
25a	433	440	449	460	466	469	23.083	−1.84	−0.9741
25b	442	450	458	470	476	479	22.598	−1.72	−0.9604
25c	431	439	445	451	460	464	23.193	−1.58	−0.9842
25d	443	450	456	460	475	480	22.656	−1.70	−0.9803
25e	445	451	458	466	469	472	22.437	−1.28	−0.9703
25f	449	456	464	472	476	479	22.225	−1.37	−0.9703
25g	461	467	469	472	472	474	21.605	−0.57	−0.9310
25h	471	477	479	483	482	484	21.142	−0.55	−0.9154
26a	399	406	413	413	422	426	25.036	−1.51	−0.9977
26b	413	418	424	426	433	437	24.228	−1.28	−0.9946
27a	462	473	478	483	492	496	21.583	−1.45	−0.9914
27b	573	579	587	596	606	614	17.509	−1.16	−0.9817
27c	454	460	459	450	455	458	21.954	−0.16	−0.2326
27d	550	562	555	547	546	549	18.005	+0.24	+0.4611[b]
28a	503	517	523	527	546	551	19.866	−1.65	−0.9883
28b	–	620	628	670	691	698	16.826	−2.65	−0.9229
28c	487	494	496	497	502	500	20.452	−0.63	−0.8496
28d	587	596	601	628	632	633	17.045	−1.36	−0.9194
28e	535	547	552	567	578	587	18.708	−1.60	−0.9762
28f	637	651	661	702	724	740	15.826	−2.21	−0.9517
28g	553	562	566	582	592	600	18.131	−1.41	−0.9652
28h	651	664	674	722	734	746	15.445	−2.01	−0.9341
28i	527	535	530	535	539	544	18.961	−0.58	−0.8057
28j	639	651	646	676	679	686	15.666	−1.12	−0.8859
29a	503	510	518	524	531	539	19.900	−1.26	−0.9879
29b	–	607	628	659	677	688	17.055	−2.57	−0.9522
29c	482	488	491	492	499	500	20.725	−0.74	−0.9920
29d	592	599	599	618	627	631	16.952	−1.15	−0.9138
30a	437	445	447	435	446	448	22.798	−0.45	−0.5866
30b	535	537	534	551	535	532	18.653	+ 0.10	+0.6414[c]
31a	471	480	486	476	491	497	21.216	−1.04	−0.8913
31b	–[d]	574	575	586	598	604	17.834	−1.24	−0.9506
32a	474	477	480	475	486	488	21.151	−0.62	−0.8882
32b	–[d]	575	578	579	598	605	17.846	−1.18	−0.9136

[a] CH: cyclohexane, TE: tetrachloromethane, TO: toluene, ET: ethanol, MC: dichloromethane, DMF: dimethylformamide, DMSO: dimethyl sulfoxide, for values in dichloromethane ($\pi^*_{(MC)} = +0.78$) see Table 2. – [b] Value in MC neglected. – [c] Value in ET and ET neglected.

going from the electronic ground state to the excited states is a requirement.

In summary, both the positions of the longest-wavelength absorption bands of the compounds studied as well as their solvatochromism are strongly influenced by the structure of the compounds. The effects observed depend on the length of the conjugated system, its substitution pattern, and its heteroatom modification in a rather sensitive manner. At first glance, from the data presented, it seems impossible to derive a simple increment scheme which is suitable for a correct numerical prediction of the spectral effects measured as well as to derive a simple concept for creating a synthetic route to effectively synthesize compounds exhibiting pronounced nonlinear optical effects.

Experimental Section

General: Melting points were determined by means of a Boetius heating-table microscope and are corrected. – IR spectra were recorded in KBr pellets with a Philips PU 9624 FT-IR spectrometer, while UV/Visible spectra were recorded with a Perkin–Elmer Lamba 900 UV/Vis/NIR spectrometer. – NMR spectra were recorded with a 300 MHz Varian Gemini 2000 spectrometer. Elemental analytical data were obtained with a LECO CHNS 932 analyzer.

Preparation of Cyanovinyl-Substituted Bromomethyl Compounds 19–22 (General Procedure). – Method A: To a mixture of a cyanovinyl-substituted methyl or methyl(hetero)aryl compound **15**–**18** (0.1 mol) in tetrachloromethane (100 mL) was added dropwise bromine (0.1 mol, 16.0 g) under stirring at reflux temperature. After the colour of the reaction mixture changed from red-brown to a pale orange the solution was concentrated in vacuum. Solid products were isolated by filtration and recrystallized from methanol or ethanol, liquid products were purified by distillation.

Method B: A mixture of a cyanovinyl-substituted methyl or methyl(hetero)aryl compound **15**–**18** (0.1 mol) and *N*-bromosuccinimide (0.1 mol, 18.0 g) in tetrachloromethane (100 mL) was refluxed for about 12 h and then cooled to room temperature. Finally, the mixture was filtered and the filtrate was concentrated in vacuum. Solid products were isolated by filtration and recrystallized from methanol or ethanol, liquid products were purified by distillation.

In Table 1 the products obtained by both the methods A and B are depicted.

Preparation of Cyanovinyl-Substituted Thiophenes 25 and 27–29 (General Procedure): A mixture of a cyanovinyl-substituted bromomethyl compound **19–22** (0.1 mol) and 3-morpholino-thioacrylamide (**23**; 0.1 mol) in acetonitrile (100 mL) or methanol (100 mL) was refluxed for 10 min. After cooling, triethylamine (for reactions

Table 4. Analytical data of the cyanovinyl compounds **25**–**32**

	Empirical formula (mol. mass)	calcd. (found)			
		C	H	N	S
25a	$C_{13}H_{13}N_3OS$ (259.3)	60.21 (60.35)	5.05 (5.50)	16.20 (16.25)	12.36 (12.64)
25b	$C_{18}H_{15}N_3OS$ (321.4)	67.27 (67.33)	4.70 (4.83)	13.07 (12.85)	9.98 (9.83)
25c	$C_{19}H_{17}N_3OS$ (335.4)	68.03 (68.07)	5.11 (5.08)	12.53 (12.57)	9.56 (9.82)
25d	$C_{24}H_{19}N_3OS$ (397.5)	72.52 (72.63)	4.82 (4.92)	10.57 (10.37)	8.07 (7.95)
25e	$C_{11}H_{11}N_3S$ (217.3)	60.80 (60.23)	5.10 (5.11)	19.34 (19.24)	14.76 (15.08)
25f	$C_{16}H_{13}N_3S$ (279.4)	68.79 (68.79)	4.69 (4.80)	15.04 (14.60)	11.48 (11.74)
25g	$C_{21}H_{15}N_3S$ (341.4)	73.87 (72.95)	4.43 (4.50)	12.39 (12.24)	9.39 (9.63)
25h	$C_{26}H_{17}N_3S$ (403.5)	77.39 (76.92)	4.25 (4.42)	10.41 (10.20)	7.95 (8.21)
26a	$C_{12}H_{12}N_4OS$ (260.3)	55.37 (55.58)	4.65 (4.79)	21.52 (21.30)	12.32 (12.52)
26b	$C_{17}H_{14}N_4OS$ (322.4)	63.33 (63.52)	4.38 (4.58)	17.38 (17.31)	9.95 (9.90)
27a	$C_{18}H_{15}N_3OS$ (321.4)	67.27 (67.79)	4.70 (5.06)	13.07 (13.01)	9.98 (9.99)
27b	$C_{19}H_{14}N_4OS$ (346.4)	65.88 (65.49)	4.07 (4.50)	16.17 (16.11)	9.26 (9.25)
27c	$C_{24}H_{19}N_3OS$ (397.5)	72.45 (72.50)	4.82 (5.36)	10.57 (10.07)	8.06 (8.14)
27d	$C_{25}H_{18}N_4OS$ (422.5)	71.07 (70.94)	4.29 (4.52)	13.26 (12.96)	7.59 (7.71)
28a	$C_{16}H_{13}N_3OS_2$ (327.4)	58.69 (58.59)	4.00 (4.00)	12.83 (12.76)	19.59 (19.55)
28b	$C_{17}H_{12}N_4OS_2$ (352.4)	57.93 (57.68)	3.43 (3.46)	15.90 (15.89)	18.19 (17.98)
28c	$C_{22}H_{17}N_3OS_2$ (403.5)	65.48 (64.92)	4.25 (4.49)	10.41 (10.27)	15.89 (15.90)
28d	$C_{23}H_{16}N_4OS_2$ (428.5)	64.46 (64.36)	3.76 (4.46)	13.07 (13.16)	14.97 (14.25)
28e	$C_{14}H_{11}N_3S_2$ (285.4)	58.92 (59.06)	3.88 (4.12)	14.72 (14.43)	22.47 (23.28)
28f	$C_{15}H_{10}N_4S_2$ (310.4)	58.04 (57.64)	3.25 (3.75)	18.05 (18.02)	20.66 (20.77)
28g	$C_{16}H_{15}N_3S_2$ (313.5)	61.31 (61.27)	4.82 (4.85)	13.40 (13.18)	20.46 (20.29)
28h	$C_{17}H_{14}N_4S_2$ (338.5)	60.33 (60.36)	4.17 (4.39)	16.55 (16.20)	18.95 (18.63)
28i	$C_{24}H_{15}N_3S_2$ (409.5)	70.39 (70.83)	3.69 (3.92)	10.26 (10.35)	15.66 (15.68)
28j	$C_{25}H_{14}N_4S_2$ (434.5)	69.10 (69.10)	3.25 (3.43)	12.89 (12.95)	14.76 (14.74)
29a	$C_{16}H_{13}N_3O_2S$ (311.4)	61.72 (61.86)	4.21 (4.29)	13.50 (13.51)	10.30 ()10.37
29b	$C_{17}H_{12}N_4O_2S$ (336.4)	60.70 (61.19)	3.59 (4.03)	16.66 (16.68)	9.53 (9.74)
29c	$C_{22}H_{17}N_3O_2S$ (387.5)	68.20 (68.21)	4.42 (4.47)	10.84 (10.84)	8.28 (8.49)
29d	$C_{23}H_{16}N_4O_2S$ (412.5)	66.97 (66.38)	3.91 (4.17)	13.58 (13.35)	7.77 (7.83)
30a	$C_{17}H_{14}N_4OS$ (322.4)	63.33 (62.93)	4.38 (4.69)	17.38 (16.91)	9.95 (9.84)
30b	$C_{18}H_{13}N_5OS$ (347.4)	62.23 (62.20)	3.77 (4.27)	20.16 (19.28)	9.23 (9.31)
31a	$C_{15}H_{12}N_4OS_2$ (328.4)	54.86 (54.86)	3.68 (3.68)	17.06 (16.75)	19.53 (19.85)
31b	$C_{16}H_{11}N_5OS_2$ (353.4)	54.37 (54.15)	3.14 (3.18)	19.81 (19.77)	18.15 (18.34)
32a	$C_{15}H_{12}N_4O_2S$ (312.4)	57.68 (57.35)	3.87 (3.80)	17.94 (17.64)	10.27 (10.20)
32b	$C_{16}H_{11}N_5O_2S$ (337.4)	56.96 (56.97)	3.29 (3.33)	20.76 (20.72)	9.50 (9.69)

in acetonitrile; 0.25 mol, 26.0 g) or sodium methoxide (for reactions in methanol; 0.25 mol, 13.5 g) was added to the reaction mixture which was refluxed for a further 10 min. The resulting mixture was cooled again and diluted with water (250 mL). The precipitate formed was isolated by filtration and recrystallized, if required, from acetonitrile or DMF.

The products thus obtained are depicted in Table 2. Their analytical data are recorded in Table 4.

Preparation of Cyanovinyl-Substituted Thiazoles 26 and 30–32 (General Procedure): The procedure is the same as before, but instead of a 3-morpholino-thioacrylamide **(23)** its aza analogous thiourea derivative **(24**; 0.1 mol) is used. The products thus obtained are depicted in Table 2. Their analytical data are recorded in Table 4.

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