NIR Absorbing Squaraines by Extension of the Conjugation with (Aminothiazolyl)ethenyl Groups

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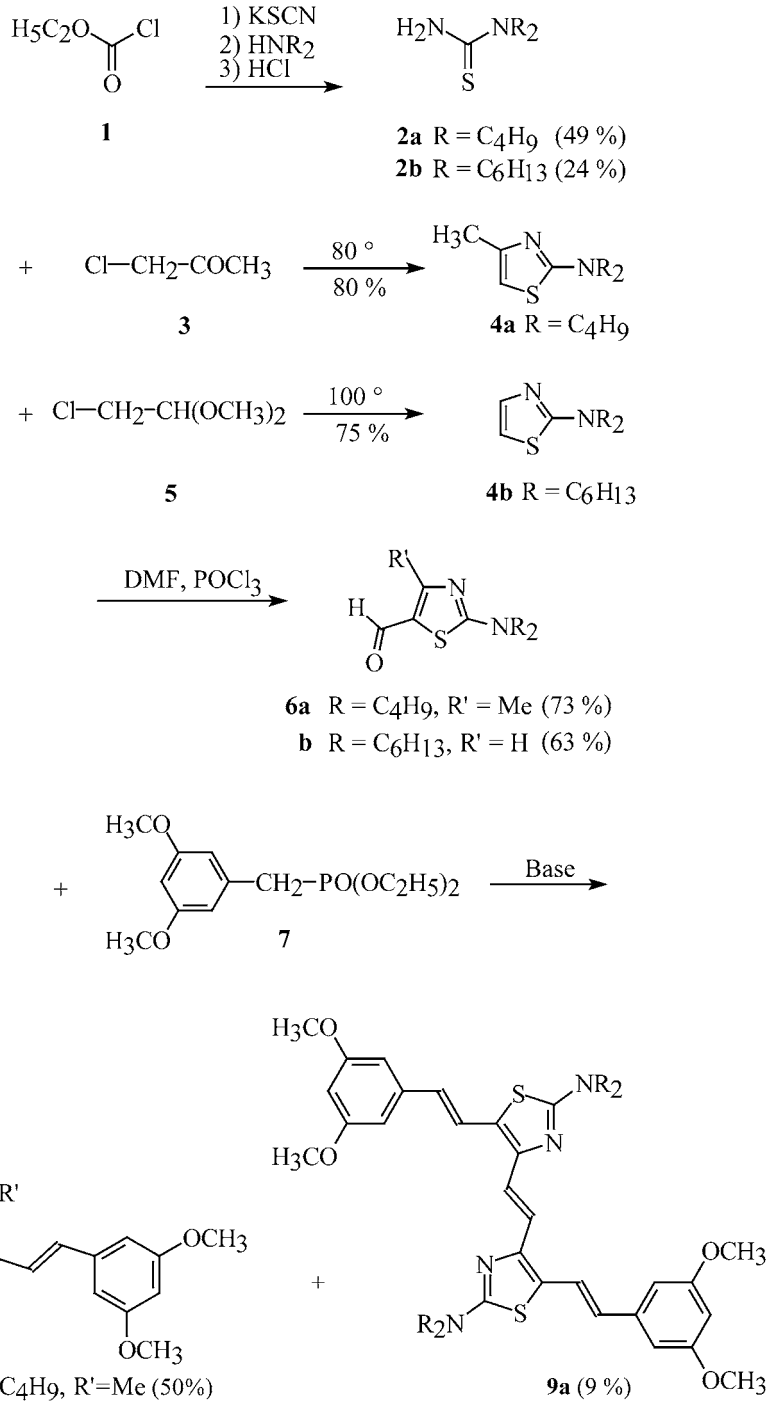
The bis{4-{2-[2-(dialkylamino)thiazol-5-yl]ethenyl}-2,6-dihydroxyphenyl}squaraines **12a**,**b** were synthesized from ethyl carbonochloridate (**1**) in six steps (*Scheme*). The donor–acceptor–donor systems **12a**,**b** are dark blue dyes with absorption maxima in the NIR region, unless the measurements are performed in the presence of EtOH. In the latter case, the long-wavelength band disappears, and the absorption in the UV region is strongly enhanced. The λ_{max} values in $CHCl_3$ and $CHCl_3$/EtOH differ by more than 450 nm. The completely reversible effect can be rationalized by the reversible degradation of intramolecular H-bonds and a consequent torsion between the acceptor and the donor moieties.

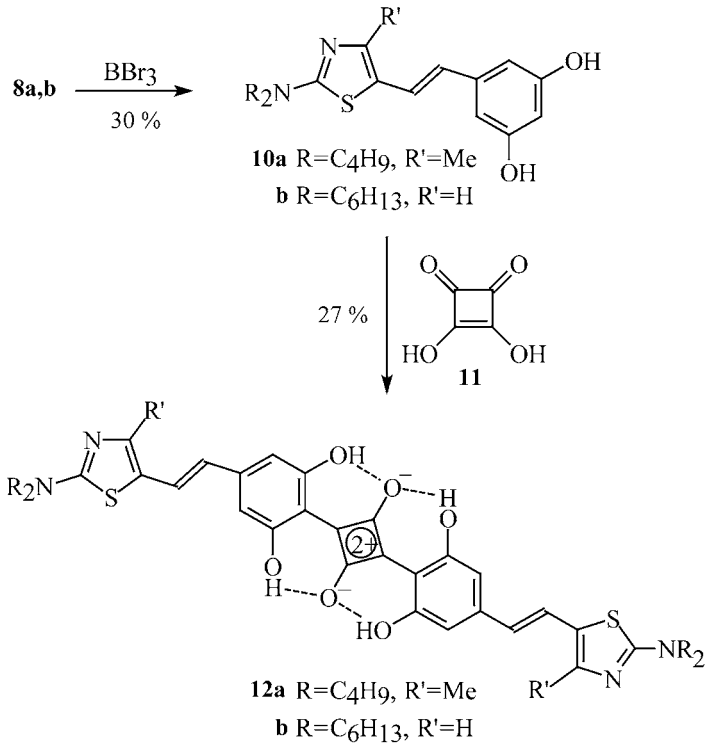
Introduction. – Squaraines (for reviews, see [1]) attract considerable interest in electrophotography (see [1a–c] and ref. cit. therein), nonlinear optics [2–5], optical-data storage [6], conversion of solar energy [7][8], and as fluorescence markers [9]. In contrast to 1,3-diarylsquaraines, which represent blue or blue-green pigments or dyes, we prepared some time ago 1-aryl-3-stilbenyl- and 1,3-bis(stilbenyl)squaraines, which absorb in the near infrared (NIR) [10–13]. It turned out that the extension of the conjugation provokes first a strong bathochromic effect, but surprisingly further extension of the conjugation leads to a hypsochromic effect [10]. Thus, a donor–acceptor distance as in stilbenoid moieties seems to be highly appropriate for an absorption in the NIR region, which is characterized by a strong intramolecular charge transfer (ICT). We studied in this context 2-(dialkylamino)thiazol-5-yl substituents, which are bound *via* ethenediylphenylene segments to the squaraine center. The heterocyclic building blocks were chosen to improve the photoconductivity induced by NIR radiation. Squaraines exhibit normally a good hole transport [1b]. The heterocyclic moieties should ameliorate the efficiency for the electron transport.

Results and Discussion. – The synthesis of the target compounds started with dialkylthiourea **2a**,**b** which were prepared from ethyl carbonochloridate (**1**) by an established method [14]. Reaction of **2a** with chloroacetone (**3**) and of **2b** with the dimethyl acetal **5** of chloroacetaldehyde led to the corresponding 2-(dialkylamino)-thiazoles **4a**,**b** in good yields (*Scheme*). *Vilsmeyer* formylation furnished the corresponding 5-carboxaldehydes **6a**,**b** which were subjected to the subsequent *Wittig–Horner* reaction with the phosphonate **7**. In the case of the 4-methyl compound **6a**, the yield of **8a** was somewhat lower because of the unexpected generation of by-product **9a**. Obviously, the activated Me groups of two molecules **6a** form an (*E*)-

Scheme. *Preparation of the Squaraines* **12a**,**b**



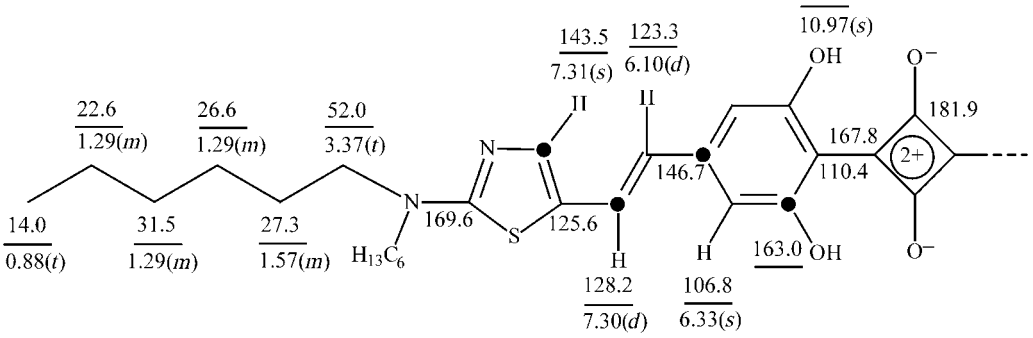
Scheme (cont.)



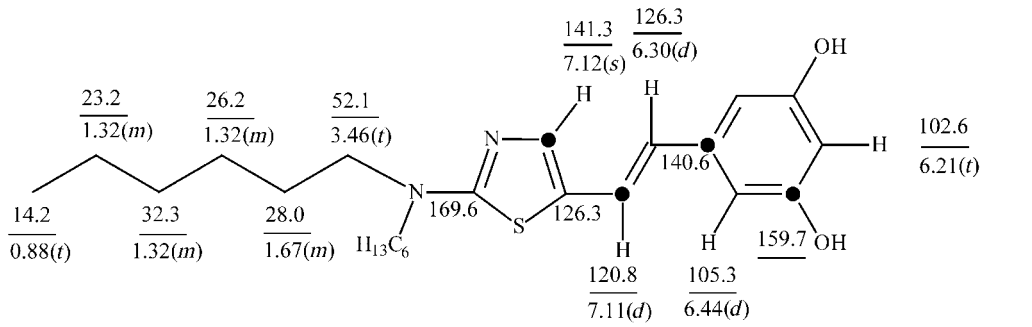
configured olefinic C=C bond under the reaction conditions. Since the *Wittig–Horner* reaction with resorcinols (= benzene-1,3-diols) gives poor yields, the OH groups were protected for this step. Subsequent deprotection by methyl ether cleavage with BBr_3 proved to be difficult because of partial decomposition. Optimization of this process gave 30% of **10a**,**b** which were coupled to squaric acid (**11**) in the final step. The C,C coupling represents an electrophilic attack of **11** at the activated position of **10a**,**b**. Squaric acid reacts selectively at its 1,3-positions. The formation of intramolecular H-bonds in the resulting squaraines **12a**,**b** facilitates the reaction; the dimethoxy compounds **8a**,**b** do not give such a substitution!

The detailed spectroscopic characterization of the novel compounds is given in the *Exper. Part*. *Fig. 1* shows as an example the ^{1}H- and ^{13}C-NMR data of squaraine **12b** in comparison to its precursor **10b**. The donor–acceptor–donor system causes a polarization of the bonds along the conjugated chain. Especially the dotted positions exhibit significant low-field shifts and indicate the delocalization of the positive charge. The (*E*) configuration of the olefinic C=C bond is established by the vicinal coupling constant ($^3J = 16.4$ Hz).

The absorption spectra of **12a**,**b** in the VIS/NIR region revealed pronounced solvatochromic effects. The long-wavelength λ_{max} of **12b**, *e.g.*, varies between 813 nm in heptane and 861 nm in CH_2Cl_2. *Fig. 2* shows the wavenumbers of the measured maxima



12b



10b

Fig. 1. *Comparison of the* ^1H- (lower values) *and* ^{13}C-*NMR data* (upper values) *of* **12b** *and* **10b** *indicating the impact of the push-pull effect.* The assignment of the signals is based on NOE measurements and $^{13}C,^1H$ couplings.

in relation to the $E_T(30)$ and π^* values of the corresponding solvents. In contrast to earlier results [1a][15], the *Taft* parameter π^* [16], which is a solvent polarity-polarizability parameter that provides a measure of the ability of the medium to stabilize charges, does not give a linear correlation with the $\tilde{\nu}_{max}$ values. The analogous statement can be made for the $E_T(30)$ values [17]; at most, a certain trend can be recognized in both cases.

The selection of solvents listed in *Fig. 2* does not contain alcohols because the interaction of alcohols with the squaraines **12a**,**b** gives a totally unexpected result. *Fig. 3* depicts the absorption of **12b** in $CHCl_3$ and $CHCl_3$/EtOH mixtures.

The spectrum in $CHCl_3$ contains an intense band with λ_{max} 851 nm and a weak absorption between 300 and 400 nm. The addition of EtOH provokes a steady decrease of the long-wavelength band in the NIR region and an increase of the band in the UV region. The VIS region between 500 and 700 nm is a constant gap in the absorption – irrespective of the solvent mixture. The effect is much too strong for a usual solvatochromic behavior.

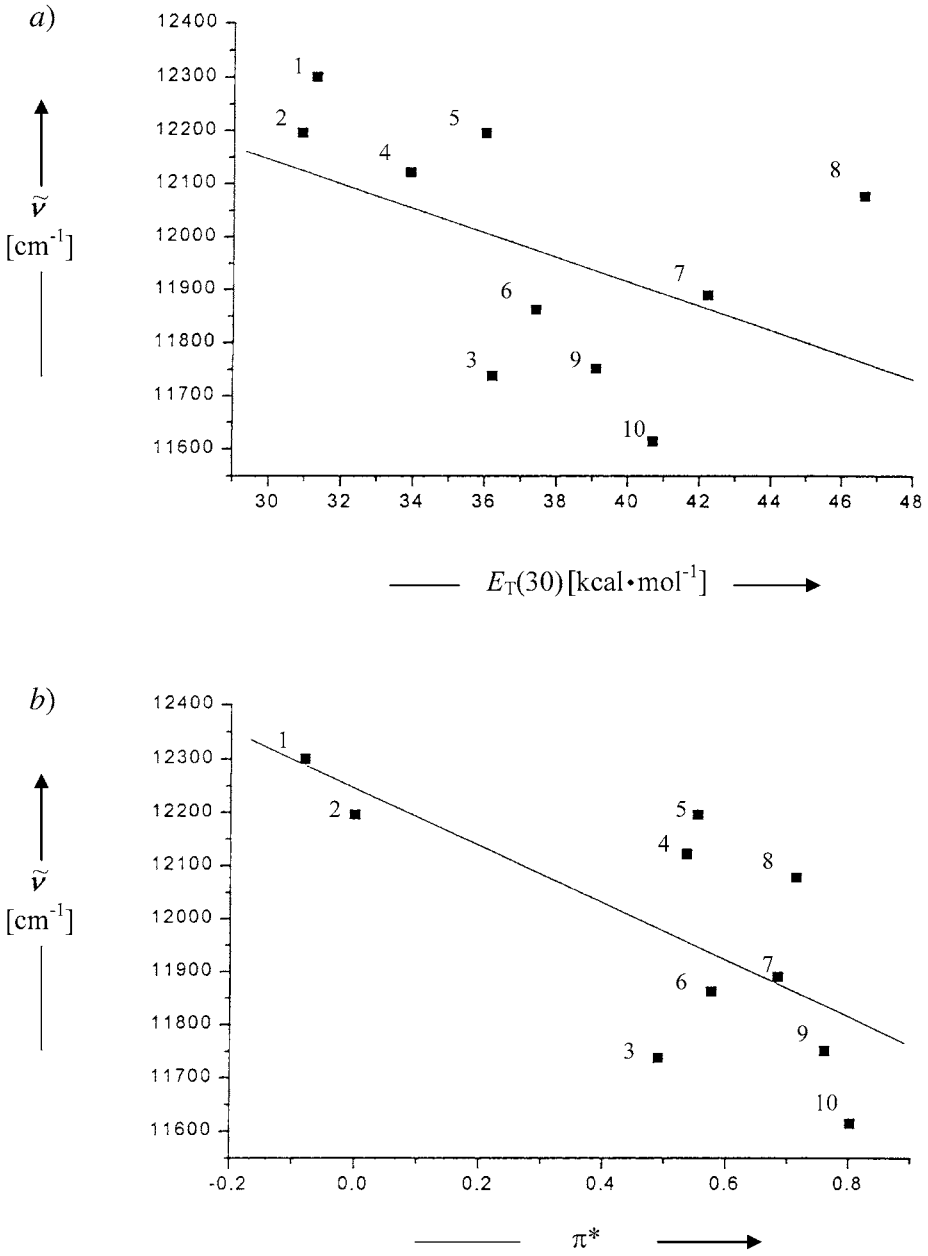


Fig. 2. *Wavenumbers of the absorption maxima of squaraine* **12b** *in different solvents correlated to* a) *the* $E_T(30)$ *values and* b) *the* π^* *parameters.* 1: Heptane, 2: cyclohexane, 3: 1,1,1-trichloroethane, 4: toluene, 5: 1,4-dioxane, 6: THF, 7: acetone, 8: MeOH, 9: $CHCl_3$, 10: CH_2Cl_2.

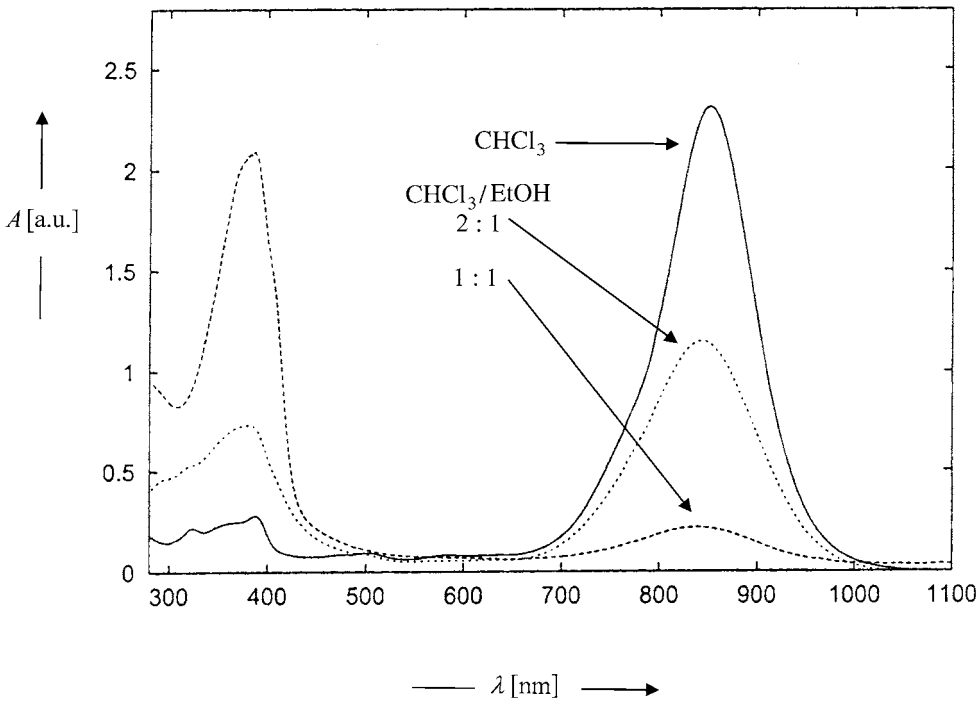
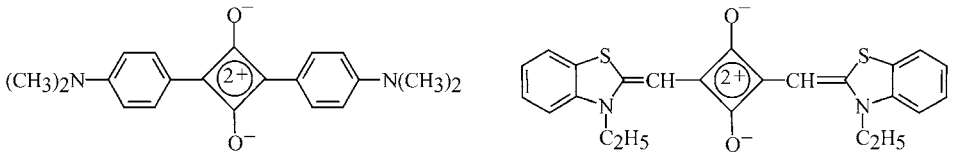


Fig. 3. *Absorbance of squaraine* **12b** *in* $CHCl_2$ *and* $CHCl_3$*/EtOH mixtures*

For bis[4-(dimethylamino)phenyl]squaraine **13** (*Fig. 4*) and related compounds, a bathochromic shift was reported for the complexation with alcohol solvents [18]; for the benzothiazole system **14** on the other hand, the interaction with alcohol solvents induced a hypsochromic effect [15]. However, the size of the effect is in both cases relatively small and not comparable to the measurement shown in *Fig. 3*.



13 **14**

Fig. 4. *Squaraines* **13** *and* **14** *used for comparison of solvent effects on the absorption*

The shift of the absorption of **12b** from the NIR to the UV region caused by the addition of EtOH indicates a change of the absorbing chromophore; either the push-pull character of the donor–acceptor–donor system is decreased because of the interaction with the EtOH molecules or the aggregation (see, *e.g.*, [19]) is fundamentally changed. Such a pronounced hypsochromic shift would correspond to the formation of H aggregates in which the long-wavelength absorption is forbidden.

Protonation of **12b** with a small amount of CF_3COOH in $CHCl_3$ leads to a small hypsochromic shift from λ_{max} 851 nm to 815 nm. Further addition of CF_3COOH causes the complete disappearance of this absorption, and a new band at λ_{max} 670 nm arises. The absorption between 300 and 400 nm is hardly affected by the protonation. In accordance with [20], we assume that the first protonation occurs at the squaraine O-atom and the second protonation at the aminothiazole moiety. However, the protonation cannot explain the effect measured in the presence of EtOH. Either the before-mentioned generation of H aggregates or the total decoupling between the donor and acceptor parts has to be responsibel for the NIR → UV shift. The latter effect can be due to the replacement of the intramolecular H-bonds in **12a**,**b** by intermolecular H-bonds between **12a**,**b** and EtOH. Thus, a torsion (of ideally 90°) between the 4-membered ring and the benzene ring could induce a total breakdown of the intramolecular charge transfer in the transition $S_0 \rightarrow S_1$. Dilution does not affect the measurement; therefore, we favor the explanation on the basis of the torsion.

Conclusion. – The squaraines **12a**,**b**, which contain 4-{2-[2-(dialkylamino)thiazol-5-yl]ethenyl}-2,6-dihydroxyphenyl groups could be prepared by C,C coupling reactions of the corresponding resorcinols **10a**,**b** with squaric acid (**11**). Due to the extended conjugation, these compounds exhibit absorption maxima in the NIR region. A pronounced solvatochromic effect can be observed for **12a**,**b** which does not correlate with the usual solvent parameters π^* or $E_T(30)$. A special situation is given in the presence of EtOH, where the long-wavelength absorption in the NIR region disappears and the absorption in the UV region is strongly enhanced. Obviously, the charge-transfer character of the electron transition $S_0 \rightarrow S_1$ in this donor–acceptor–donor compounds is blocked by EtOH – an effect, which can be rationalized by degradation of intramolecular H-bonds and a consequent torsion between the acceptor and the donor moieties. The hypsochromic shift is completely reversible.

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Experimental Part

General. Melting points (uncorrected): *Büchi* apparatus. UV/VIS/NIR Spectra [nm]: *Zeiss MCS-224* and *Perkin-Elmer Lambda-20*. IR Spectra [cm^{-1}]: *Beckman Acculab-4*. NMR Spectra (^1H, ^{13}C; δ [ppm], J [Hz]): *Bruker AM-400*; $CDCl_3$ as solvent if not otherwise specified, $SiMe_4$ as internal standard. MS: *Varian MAT-CH7A* (EI, 70 eV) and *Finnigan MAT-95* (FD technique); in *m/z* (rel. %).

Dibutylthiourea (**2a**) *and Dihexylthiourea* (**2b**). As described in [14].

Data of **2a**: Yield 49% ([14]: 42%). Colorless crystals. M.p. 58° ([14]: 57–58°).

Data of **2b**: Yield 24%. Colorless oil. IR (neat): 3270, 3170, 2910, 1600, 1500, 1455, 1355, 1300, 985. ^1H-NMR (CD_3SOCD_3): 0.85 (*t*, 2 Me); 1.24 (*m*, 12 H, CH_2); 1.49 (*m*, 4 H, CH_2); 3.45 (br. *t*, 2 CH_2N); 7.10 (*s*, NH_2). ^{13}C-NMR (CD_3SOCD_3): 13.8 (Me); 21.9, 25.7, 26.9, 30.9 (CH_2); 50.0 (CH_2N); 180.5 (CS). FD-MS: 244 (100, $M^{+\cdot}$). Anal. calc. for $C_{13}H_{28}N_2S$ (244.2): C 63.88, H 11.55, N 11.46, S 13.21; found C 63.61, H 11.75, N 11.43, S 13.18.

N,N-*Dibutyl-4-methylthiazol-2-amine* **(4a)**. As described in [21]. Yield 80% ([21]: 80%). Colorless oil. B.p. 75°/1 Pa ([21]: 163°/2.3 kPa. ^1H-NMR: 0.92 (*t*, 2 Me); 1.26 (*m*, 4 H, CH_2); 1.57 (*m*, 4 H, CH_2); 2.20 (*s*, Me–C(4)); 3.36 (*t*, 2 CH_2N); 5.95 (*s*, H–C(5)).

N,N-*Dihexylthiazol-2-amine* (**4b**). For 18 h, **2b** (24.4 g, 0.10 mol) and 2-chloro-1,1-dimethoxyethane (**5**; 15.0 g, 0.12 mol) were stirred in boiling H_2O (60 ml). After addition H_2O (200 ml) and neutralization with K_2CO_3, the aq. phase was extracted with Et_2O (2 × 200 ml). The org. phase was dried ($MgSO_4$) and purified by

filtration through silica gel 8 × 25 cm; petroleum ether (40–70°)/AcOEt 20:1): 20.5 g (75%) **4b**. Colorless oil. IR (neat): 2930, 1535, 1465, 1320, 1130. ^{1}H-NMR: 0.86 (*t*, 2 Me); 1.28 (*m*, 12 H, CH_2); 1.59 (*m*, 4 H, CH_2); 3.36 (*t*, 2 CH_2N); 6.39 (*d*, ^3J = 3.9, H–C(5)); 7.11 (*d*, ^3J = 3.9, H–C(4)). ^{13}C-NMR: 14.0 (Me); 22.6, 26.6, 27.4, 31.6 (CH_2); 51.7 (CH_2N); 105.1 (C(5)); 139.1 (C(4)); 170.9 (C(2)). EI-MS: 268 (17, $M^{+\bullet}$), 197 (20), 127 (69), 113 (80), 41 (100). Anal. calc. for $C_{15}H_{28}N_2S$ (268.5): C 67.10, H 10.51, N 10.43; found: C 67.33, H 10.85, N 10.11.

2-(Dibutylamino)-4-methylthiazole-5-carboxaldehyde (**6a**). To a soln. of **4a** (16.0 g, 70.6 mmol) in DMF (61.3 g, 840 mmol), $POCl_3$ (10.8 g, 70.0 mmol) was slowly added. The temp. raised from 0 to 20° during the addition. After stirring for 1 h at 20° and for 3 h at 80°, the reaction was quenched with H_2O (200 ml) and the mixture neutralized with K_2CO_3. Extraction with Et_2O (3 × 100 ml) furnished an org. phase, which was dried ($MgSO_4$) and purified by filtration through silica gel (10 × 16 cm; toluene/AcOEt 10:1): 13.1 g (73%) of **6a**. Pale yellow oil. IR (neat): 2930, 1625, 1530, 1365, 1320, 1235, 900. ^{1}H-NMR: 0.88 (*t*, 2 Me); 1.28 (*m*, 4 H, CH_2); 1.58 (*m*, 4 H, CH_2); 2.42 (*s*, Me–C(4)); 3.41 (*t*, 2 CH_2N); 9.67 (*s*, CHO). ^{13}C-NMR: 13.8 (Me); 16.2 (*Me*–C(4)); 20.0, 29.1 (CH_2); 51.4 (CH_2N); 122.1 (C(5)); 164.2 (C(4)); 173.5 (C(2)); 179.4 (CHO). FD-MS: 254 (100, $M^{+\bullet}$). Anal. calc. for $C_{13}H_{22}N_2OS$ (254.4): C 61.37, H 8.72, N 11.01, S 12.61; found: C 61.54, H 8.94, N 11.14, S 12.90.

2-(Dihexylamino)thiazole-5-carboxaldehyde (**6b**). As described for **6a**: 61% of **6b**. Pale yellow oil. IR (neat): 2955, 1650, 1545, 1515, 1460, 1380, 1335, 1225, 780. ^{1}H-NMR: 0.85 (*t*, 2 Me); 1.28 (*m*, 12 H, CH_2); 1.63 (*m*, 4 H, CH_2); 3.44 (*t*, 2 CH_2N); 7.81 (*s*, H–C(4)); 9.62 (*s*, CHO). ^{13}C-NMR: 14.0 (Me); 22.5, 26.5, 27.0, 31.5 (CH_2); 52.1 (CH_2N); 127.9 (C(5)); 153.9 (C(4)); 175.2 (C(2)); 180.3 (CHO). EI-MS: 296 (25, $M^{+\bullet}$), 155 (74), 141 (59), 42 (100). Anal. calc. for $C_{16}H_{28}N_2OS$ (296.5): C 64.81, H 9.52, N 9.44, S 10.82; found: C 64.55, H 9.60, N 9.81, S 10.42.

N,N-*Dibutyl-5-[(*1E*)-2-(3,5-dimethoxyphenyl)ethenyl]-4-methylthiazole-2-amine* (**8a**) *and 4,4′-[(*1E*)-Ethene-1,2-diyl]bis[*N,N-*dibutyl-5-[(*1E*)-2-(3,5-dimethoxyphenyl)ethenyl]thiazol-2-amine]* (**9a**). A soln. of diethyl (3,5-dimethoxybenzyl)phosphonate (**7**) (5.79 g, 20.0 mmol) [22] in dry 1,2-dimethoxyethane (20 ml) was dropped to a suspension of NaH (60% in hexane; 3.3 g, 83.0 mmol) in dry 1,2-dimethoxyethane (60 ml). After 10 min, a soln. of **6a** (5.08 g, 20.0 mmol) in 1,2-dimethoxyethane (20 ml) was added and the mixture refluxed for 3 h and then quenched with H_2O (100 ml). Extraction with CH_2Cl_2 (2 × 250 ml) furnished an org. phase, which was dried ($MgSO_4$) and purified by filtration through silica gel (6 × 25 cm; toluene/AcOEt 25:1): 3.89 g (50%) of **8a**. Pale yellow oil. IR (neat): 2945, 1580, 1530, 1450, 1360, 1320, 1200, 1150, 1060, 930. ^{1}H-NMR: 0.94 (*t*, 2 Me); 1.34 (*m*, 4 H, CH_2); 1.62 (*m*, 4 H, CH_2); 2.28 (*s*, Me–C(4)); 3.34 (*t*, 2 CH_2N); 3.79 (*s*, 2 MeO); 6.26 (*d*, ^3J = 16.6, CH=C(5)); 6.31 (*t*, ^3J = 2.3, 1 arom. H); 6.54 (*d*, ^3J = 2.3, 2 arom. H); 7.06 (*d*, ^3J = 16.6, CH=C*H*–C(5)). ^{13}C-NMR: 13.9 (Me); 15.7 (*Me*–C(4)); 20.2, 29.5 (CH_2); 50.8 (CH_2N); 55.3 (MeO); 98.9, 103.7 (arom. CH); 118.3 (quat. C); 120.3, 123.9 (olef. CH); 140.1, 149.2, 160.9, 167.2 (quat. C). FD-MS: 388 (100, $M^{+\bullet}$). Anal. calc. for $C_{22}H_{32}N_2O_2S$ (388.6): C 68.00, H 8.30, N 7.21, S 8.26; found: C 68.40, H 8.01, N 7.23, S 8.50.

A further small fraction consisted of 0.70 g (9%) of **9a**. Colorless solid. M.p. 178°. IR (KBr): 2935, 1570, 1535, 1340, 1190, 1140. ^{1}H-NMR: 0.98 (*t*, 4 Me); 1.39 (*m*, 8 H, CH_2); 1.68 (*m*, 8 H, CH_2); 3.47 (*t*, 4 CH_2N); 3.78 (*s*, 4 MeO); 6.32 (*t*, ^3J = 2.0, 2 arom. H); 6.36 (*d*, ^3J = 15.6, 2 CH=C*H*–C(5)); 6.56 (*d*, ^3J = 2.0, 4 arom. H); 7.37 (*d*, ^3J = 15.6, 2 olef. H); 7.47 (*s*, 2 olef. H). ^{13}C-NMR: 13.9 (Me); 20.2, 29.6 (CH_2); 50.9 (CH_2N); 55.3 (MeO); 99.4, 103.8 (arom. CH); 119.5, 121.6, 125.6 (olef. CH); 123.6, 139.7, 149.4, 161.0, 166.2 (quat. C). FD-MS: 772 (100, $M^{+\bullet}$). Anal. calc. for $C_{44}H_{60}N_4O_4S_2$ (773.1): C 68.35, H 7.82, N 7.24, S 8.30; found: C 68.09, H 7.89, N 7.25, S 8.25.

N,N-*Dihexyl-5-[(1*E*)-2-(3,5-dimethoxyphenyl)ethenyl]thiazol-2-amine* (**8b**). *t*-BuOK (11.2 g, 100 mmol) in dry DMF (100 ml) was added to phosphonate **7** (6.1 g, 21.1 mmol) in dry DMF (50 ml). After cooling to 0°, **6b** (6.25 g, 21.1 mmol) in dry DMF (20 ml) was added, and the mixture was stirred for 5 h at r.t. Workup as described for **8a** with petroleum ether (40–70°) for the silica gel filtration yielded 7.3 g (81%) of **8b**. Yellow oil. IR (neat): 2930, 1590, 1540, 1460, 1370, 1295, 1205, 1155, 1130, 1060, 940, 845. ^{1}H-NMR: 0.88 (*t*, 2 Me); 1.30 (*m*, 12 H, CH_2); 1.64 (*m*, 4 H, CH_2); 3.39 (*t*, 2 CH_2N); 3.78 (*s*, 2 MeO); 6.30 (*t*, ^3J = 2.0, 1 arom. H), 6.35 (*d*, ^3J = 15.6, C*H*=CH–C(5)); 6.53 (*d*, ^3J = 2.0, 2 arom. H); 7.05 (*d*, ^3J = 15.6, CH=C*H*–C(5)); 7.12 (*s*, H–C(4)). ^{13}C-NMR: 14.0 (Me); 22.6, 26.7, 27.3, 31.6 (CH_2); 51.6 (CH_2N); 55.3 (MeO); 99.3, 103.8, (CH arom.); 120.5 (quat. C); 125.2, 125.2 (olef. CH); 139.7 (quat. C); 140.4 (C(4)); 161.0, 169.1 (quat. C). EI-MS: 430 (100, $M^{+\bullet}$), 289 (21), 275 (23), 127 (22), 113 (23), 42 (80). Anal. calc. for $C_{25}H_{38}N_2O_2S$ (430.7): C 69.72, H 8.89, N 6.50, S 7.44; found: C 70.07, H 8.78, N 6.53, S 7.71.

*5-{(1*E*)-2-[2-(Dibutylamino)-4-methylthiazol-5-yl]ethenyl}benzene-1,3-diol* (**10a**) *and 5-{(1*E*)-2-[2-(Dihexylamino)-4-methylthiazol-5-yl]ethenyl}benzene-1,3-diol* (**10b**). The dimethoxy compounds **8a**,**b** (5.0 mmol) were slowly treated in dry CH_2Cl_2 (150 ml) at –78° with 2.1 equiv. of 1M BBr_3 in hexane. After 4 h, the temp. was raised to 20° and the mixture stirred for additional 18 h, quenched with H_2O and neutralized with K_2CO_3. Extraction with $CHCl_3$ (2 × 100 ml) gave, after evaporation, yellow to ochre solids.

Data of **10a**: Yield 30%. M.p. 105°. IR (KBr): 2930, 1580, 1520, 1310, 1140, 995, 930. ^{1}H-NMR (CD_3SOCD_3): 0.90 (*t*, 2 Me); 1.28 (*m*, 4 H, CH_2); 1.56 (*m*, 4 H, CH_2); 2.20 (*s*, Me–C(4)); 3.37 (*t*, 2 CH_2N); 6.06 (*t*, ^3J = 1.8, 1 arom. H); 6.09 (*d*, ^3J = 15.6, C*H*=CH–C(5)); 6.30 (*d*, ^3J = 1.8, 2 arom. H); 7.03 (*d*, ^3J = 15.6, CH=C*H*–C(5)); 9.14 (*s*, 2 OH). ^{13}C-NMR (CD_3SOCD_3): 13.5 (Me); 15.2 (Me–C(4)); 19.4, 28.9 (CH_2); 50.1 (CH_2N); 101.4, 103.7 (arom. CH); 117.8 (quat. C); 119.0, 124.0 (olef. CH); 139.1, 148.3, 158.3, 165.9 (quat. C). FD-MS: 360 (100 $M^{+\cdot}$). Anal. calc. for $C_{20}H_{28}N_2O_2S$ (360.5): C 66.62, H 7.83, N 7.77, S 9.01; found: C 66.59, H 7.91, N 7.91, S 9.18.

Data of **10b**: Yield 30%. M.p. 80° (dec.). IR (KBr): 2920, 1580, 1530, 1440, 1360, 1295, 1145, 940. ^{1}H- and ^{13}C-NMR: see *Fig. 1*. EI-MS: 402 (100, $M^{+\cdot}$), 261 (32), 245 (30), 127 (21), 114 (43), 42 (80). Anal. calc. for $C_{23}H_{34}N_2O_2S$ (402.6): C 68.61, H 8.51, N 7.43, S 7.70; found: C 68.43, H 8.48, N 7.23, S 7.50.

*1,3-Bis{4-{(1*E*)-2-[2-(dibutylamino)-4-methylthiazol-5-yl]ethenyl}-2,6-dihydroxyphenyl}squaraine* (=*2,4-Bis{4-{(1*E*)-2-[2-(dibutylamino)-4-methylthiazol-5-yl]ethenyl}-2,6-dihydroxyphenyl}-3-oxocyclobut-4-en-2-ylium-1-olate*; **12a**) *and 1,3-Bis{(4-{(1*E*)-2-[2-(dihexylamino)thiazol-5-yl]ethenyl}-2,6-dihydroxyphenyl}squaraine* (=*2,4-Bis{4-{(1*E*)-2-[2-(dihexylamino)thiazol-5-yl]ethenyl}-2,6-dihydroxyphenyl}-3-oxocyclobut-4-en-2-ylium-1-olate*; **12b**). For 3 h, **10a** or **10b** (0.1 mmol), squaric acid (**11**; 0.06 mmol), BuOH (1.5 ml), and toluene (2.5 ml) were refluxed. The H_2O generated in the reaction was removed by Na_2SO_4 on a filter between the reaction vessel and the cooler. Evaporation of the volatile parts led to a residue, which was washed with MeOH, acetone, and petroleum ether (40–70°) in the case of **12a** and with acetone and Et_2O in the case of **12b**.

Data of **12a**: Yield 27%. Blue-green powder. M.p. 250° (dec.). IR (KBr): 2920, 1615, 1570, 1500, 1400, 1200, 1155, 1020, 900. ^{1}H-NMR ($CDCl_3$): 0.95 (*t*, 4 Me); 1.35 (*m*, 8 H, CH_2); 1.63 (*m*, 8 H, CH_2); 2.35 (*s*, 2 Me–C(4)); 3.43 (*t*, 4 CH_2N); 6.08 (*d*, ^3J = 15.4, C*H*=CH–C(4)); 6.40 (*s*, 4 arom.); 7.43 (*d*, ^3J = 15.4, C*H*=CH–C(4)); 11.00 (*s*, 4 OH). The solubility of **12a** was not sufficient for a ^{13}C-NMR measurement. FD-MS: 799 (100, $M^{+\cdot}$). Anal. calc. for $C_{44}H_{54}N_4O_6S_2$ (799.1): C 66.13, H 6.81, N 7.01, S 8.03; calc. for 1% H_2O included[1]): C 65.48, H 6.86, N 7.01; found: C 65.06, H 7.01, N 6.99.

Data of **12b**: Yield 27%. Blue-violet crystals. M.p. 240° (dec.). IR (KBr): 2920, 1590, 1510, 1460, 1420, 1260, 1150. ^{1}H- and ^{13}C-NMR: see *Fig. 1*. FD-MS: 883 (100, $M^{+\cdot}$). Anal. calc. for $C_{50}H_{66}N_4O_6S_2$ (883.2): C 68.00, H 7.53, N 6.34; calc. for 1% H_2O included[1]) [24]: C 67.33, H 7.57, N 6.28; found: C 67.52, H 7.58, N 6.31.

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