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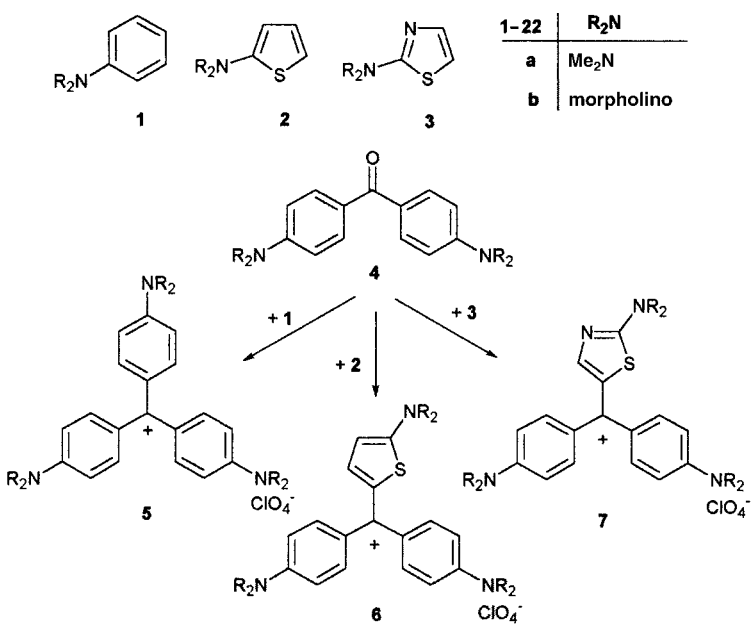
Synthesis and Spectral Characterization of a New Class of Heterocyclic Analogues of Crystal Violet Dyes**

Antje Noack, Anke Schröder, and Horst Hartmann*

Dedicated to Professor Siegfried Hünig on the occasion of his 80th birthday

Crystal Violet **5a** is a classical representative of synthetic dyes that is to some extent still used today. It attracted considerable attention immediately after its discovery by von Hofmann in 1873, because such a beautiful and colorfast dye was unknown.[1] The dye can be synthesized by various methods usually starting from dimethylaniline (**1a**).[2] Some of these routes utilize Michler's ketone **4a** that is readily accessible from **1a** and phosgene (see Scheme 1).



Scheme 1. Synthesis of the Crystal Violet dyes **5**–**7**.

To improve the coloristic properties of Crystal Violet numerous experiments were performed to synthesize structurally modified derivatives. Among others, sulfonation leading to more water soluble, acidic Crystal Violet dyes, or the replacement of the benzenoidic rings by polycyclic or heterocyclic groups were tried succesfully. Further attempts to make the dyes more colorfast by substituting the N-alkyl groups by different types of aryl substituents were carried out.[3] With most of these dyes practical applications were rather limited, but from a theoretical point of view some of these compounds were of great importance.[4] A few years ago it was shown that Crystal Violet derivatives with an extended π system exhibit extraordinarily high quadrupol-induced nonlinear optical (NLO) coefficients through a multidirectional intramolecular charge transfer from the periphery to the center of the molecule that makes them promising candidates for the synthesis of materials with NLO properties.[5]

In recent years 2-dialkylaminothiophenes **2**[6] and 2-dialkylaminothiazoles **3**[7] have received special attention as heterocyclic analogues of the dialkylanilines **1**, since they are also able to form a large variety of different dyes. Thus, these heterocyclic amines can be used for, among other things, the preparation of diazo dyes,[8, 9] methine and azomethine dyes,[10, 11] as well as squaraine acid and croconine dyes.[12, 13] They can also be used for the preparation of a series of compounds that, because of their donor–acceptor character, possess an intense absorption in the visible spectral range and a high dipolarity. Thus, compounds of this type can be used as indicators for the determination of solvent polarities[14] or for the preparation of materials with NLO properties.[15] However, to our knowledge, compounds of type **2** and **3** have not

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[**] This work has been financially supported by the Deutsche Forschungsgemeinschaft.

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yet been used in the preparation of heterocyclic analogues of triphenylmethane dyes.

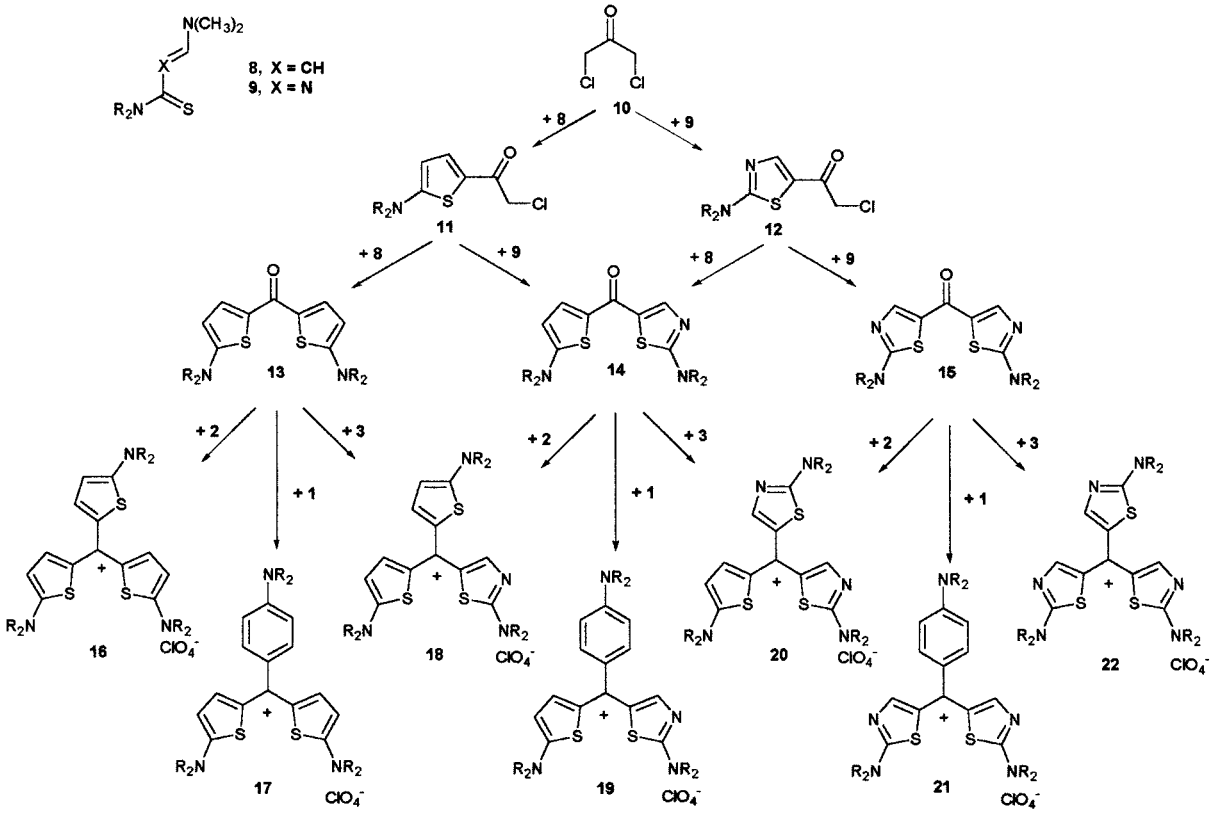
We found that this preparation can be carried out successfully if Michler's ketone (**4a**; or one of its derivatives which, like the bis(morpholino) derivative **4b**, is structurally modified at the nitrogen atoms) is treated either with one of the heterocyclic compounds **2** or **3** (which were generally used as their 2-morpholino derivatives) in presence of an acidic condensation agent such as $POCl_3$ or treated with a derivative of these aminoheterocycles that is lithiated at the 5 position. Whereas in the former case the reaction proceeds via a bis[4-(*N*,*N*-alkylanilino)]chloromethinium chloride, in the latter case it proceeds via the corresponding bis[(*N*,*N*-dialkylanilino)]-substituted carbinols[2] from which the hitherto unknown heterocyclic Crystal Violet analogues **6** and **7**, which we isolated as perchlorates were obtained (Scheme 1, Table 1).

With both these methods further heterocyclic analogues of Crystal Violet can be prepared as long as suitable heterocyclic analogues of **4** are available. Such compounds are unknown at yet, but can be synthesized according to a method for the synthesis of 2-aminothiophenes and 2-aminothiazoles that are acceptor-substituted in the 5 position, recently described by us.[16] This synthesis starts from N,N′-persubstituted thioacrylamides **8**[17] or their aza analogues **9**[18] which are allowed to react with 1,3-dichloroacetone (**10**) in the presence of a suitable auxiliary base. Depending on the reaction stoichiometry and conditions either N,N-disubstituted 2-amino-5-(chloroacetyl)thiophenes **11**, 2-amino-5-(chloroacetyl)thiazoles **12**, or N,N′-persubstituted bis(2-amino-5-thienyl)-ketones **13** as well as bis(2-amino-5-thiazolyl)ketones **15** were obtained. The two latter types of compounds are, as well as the N,N′-persubstituted (2-amino-5-thiazolyl)-(2-amino-5-thienyl)ketones **14**, optionally accessible through the reaction of the 5-chloroacetyl-substituted 2-aminothiophenes and 2-aminothiazoles **11** and **12**, respectively, with the corresponding thioacrylamide derivative **8** or **9**.

By using one of the routes described above, the new heterocyclic Michler's-ketone analogues **13**–**15** were converted into the corresponding heterocyclic Crystal Violet analogues **16**–**22**. Thus, a complete series of thiophene and thiazole analogues of Crystal Violet is now accessible (Scheme 2, Table 1).

The identity of all the heterocyclic Crystal Violet analogues **6**, **7**, and **16**–**22** synthesized by us could be confirmed by their elemental analysis and NMR spectra (Table 1).[19] The ^1H and ^{13}C NMR spectra are rather straight forward in the aromatic region. Thus, in the ^1H NMR spectra only doublets or singlets (as in the case of thiazolyl-substituted derivatives) could be found. In the ^{13}C NMR spectra the signals for the central methine atoms are found between $\delta = 140$ and 160 depending on the nature of the corresponding carbo- or heterocyclic moieties.

All heterocyclic Crystal Violet analogues **6**, **7**, and **16**–**22** described here are, as expected, deeply colored compounds with intensive absorption in the visible range of the spectrum (Table 1). Similar to the Crystal Violet derivative **5b** obtained by the reaction of three equivalents of *N*-(4-lithio-phenyl)-morpholine with one equivalent of diethyl carbonate and subsequent treatment with perchloric acid, **6**, **7**, and **16**–**22** usually have only one absorption band in the visible region (Figure 1), which is in contrast to the triphenylmethane dye, Malachite Green, which has only two dimethylamino groups on its three phenyl moieties. With the exception of **7b**, this



Scheme 2. Synthesis of the Crystal Violet dyes **16**–**22**.

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Table 1. Characteristic data of the heteroanalogous Crystal Violet perchlorates **5b**–**7b** and **16b**–**22b**.

5b: m.p. >350 °C; UV/Vis (CH_2Cl_2): $\lambda_{max}(\lg\varepsilon)=597$ nm (4.97); ^{1}H NMR ([D$_6$]DMSO): $\delta=3.63$ (t, 12H, CH_2), 3.77 (t, 12H, CH_2), 7.21 (d, 6H, CH), 7.32 (d, 6H, CH); ^{13}C NMR ([D$_6$]DMSO): $\delta=46.56$, 65.64, 113.42, 127.29, 139.25, 155.44, 176.53

6b: m.p. 161–163 °C; UV/Vis (CH_2Cl_2): $\lambda_{max}(\lg\varepsilon)=582$ nm (4.77); ^{1}H NMR ([D$_6$]DMSO): $\delta=3.37$ (t, 8H, CH_2), 3.75 (t, 8H, CH_2), 3.83 (t, 4H, CH_2), 7.07 (d, 4H, CH), 7.19 (d, 2H, CH), 7.34 (d, 2H, CH), 7.43 (d, 1H, CH), 7.86 (d, 1H, CH); ^{13}C NMR ([D$_6$]DMSO): $\delta=46.72$, 52.09, 65.17, 65.74, 113.43, 119.66, 127.61, 130.14, 134.23, 148.91, 158.81, 171.43, 179.66

7b: m.p. 180–185 °C; UV/Vis (CH_2Cl_2): $\lambda_{max}(\lg\varepsilon)=579$ nm (4.92); ^{1}H NMR ([D$_6$]DMSO): $\delta=3.56$ (t, 8H, CH_2), 3.76 (t, 8H, CH_2), 3.81 (t, 4H, CH_2), 3.85 (t, 4H, CH_2), 7.16 (d, 4H, CH), 7.45 (d, 4H, CH), 8.18 (s, 1H, CH); ^{13}C NMR ([D$_6$]DMSO): $\delta=46.49$, 49.61, 65.11, 65.61, 113.46, 126.51, 129.25, 136.79, 154.97, 162.86, 179.96, 179.99

16b: m.p. >370 °C; UV/Vis (CH_2Cl_2): $\lambda_{max}(\lg\varepsilon)=615$ nm (4.97); ^{1}H NMR ([D$_6$]DMSO): $\delta=3.51$ (t, 12H, CH_2), 3.77 (t, 12H, CH_2), 6.79 (d, 3H, CH), 7.68 (d, 3H, CH); ^{13}C NMR ([D$_6$]DMSO): $\delta=49.85$, 65.15, 110.18, 123.23, 142.38, 142.89, 171.02

17b: m.p. 206–209 °C; UV/Vis (CH_2Cl_2): $\lambda_{max}(\lg\varepsilon)=609$ nm (4.83); ^{1}H NMR ([D$_6$]DMSO): $\delta=3.32$ (t, 4H, CH_2), 3.63 (t, 8H, CH_2), 3.76 (m, 12H, CH_2), 6.90 (d, 2H, CH), 7.07 (d, 2H, CH), 7.33 (d, 2H, CH), 7.55 (d, 2H, CH); ^{13}C NMR ([D$_6$]DMSO): $\delta=46.99$, 50.52, 65.26, 65.96, 112.54, 113.50, 125.13, 127.02, 133.17, 145.03, 152.82, 171.80, 173.56

18b: m.p. 235–242 °C; UV/Vis (CH_2Cl_2): $\lambda_{max}(\lg\varepsilon)=623$ (4.77), 541 nm (4.42); ^{1}H NMR ([D$_6$]DMSO): $\delta=3.62$ (t, 12H, CH_2), 3.76 (t, 12H, CH_2), 6.92 (d, 2H, CH), 7.74 (s, 1H, CH), 7.83 (d, 2H, CH); ^{13}C NMR ([D$_6$]DMSO): $\delta=48.26$, 50.45, 65.27, 112.48, 122.52, 124.18, 139.99, 144.25, 150.36, 172.90, 174.82

19b: m.p. 163–165 °C; UV/Vis (CH_2Cl_2): $\lambda_{max}(\lg\varepsilon)=582$ nm (4.50); ^{1}H NMR ([D$_6$]DMSO): $\delta=3.33$ (t, 4H, CH_2), 3.64 (t, 4H, CH_2), 3.75 (m, 8H, CH_2), 3.81–3.86 (m, 8H, CH_2), 6.92 (d, 1H, CH), 7.09 (d, 2H, CH), 7.34 (d, 2H, CH), 7.55 (d, 1H, CH), 7.66 (s, 1H, CH); ^{13}C NMR ([D$_6$]DMSO): $\delta=46.67$, 48.36, 51.87, 65.08, 65.68, 66.17, 113.42, 124.99, 126.16, 131.33, 132.95, 133.41, 148.27, 152.88, 168.29, 175.58, 177.62, 179.56

20b: m.p. 265–268 °C; UV/Vis (CH_2Cl_2): $\lambda_{max}(\lg\varepsilon)=600$ nm (4.44); ^{1}H NMR ([D$_6$]DMSO): $\delta=3.64$ (m, 8H, CH_2), 3.75 (m, 8H, CH_2), 3.84 (8H, m, CH_2), 7.30 (d, 1H, CH), 7.87 (s, 2H, CH), 8.12 (d, 1H, CH); ^{13}C NMR ([D$_6$]DMSO): $\delta=48.30$, 51.80, 65.15, 104.54, 118.18, 122.82, 127.51, 147.58, 151.66, 175.05, 176.72

21b: m.p. 114–115 °C; UV/Vis (CH_2Cl_2): $\lambda_{max}(\lg\varepsilon)=558$ nm (4.24); ^{1}H NMR ([D$_6$]DMSO): $\delta=3.25$ (t, 4H, CH_2), 3.76 (t, 8H, CH_2), 3.80–3.82 (m, 12H, CH_2), 7.31 (d, 2H, CH), 7.58 (d, 2H, CH), 8.18 (s, 2H, CH); ^{13}C NMR ([D$_6$]DMSO): $\delta=46.37$, 49.36, 65.06, 65.60, 113.40, 125.07, 126.99, 134.79, 154.29, 161.65, 169.28, 178.28

22b: m.p. 171–173 °C; UV/Vis (CH_2Cl_2): $\lambda_{max}(\lg\varepsilon)=570$ nm (4.42); ^{1}H NMR ([D$_6$]DMSO): $\delta=3.78$ (m, 24H, CH_2), 8.35 (s, 3H, CH); ^{13}C NMR ([D$_6$]DMSO): $\delta=49.02$, 65.09, 124.63, 142.93, 158.74, 177.18

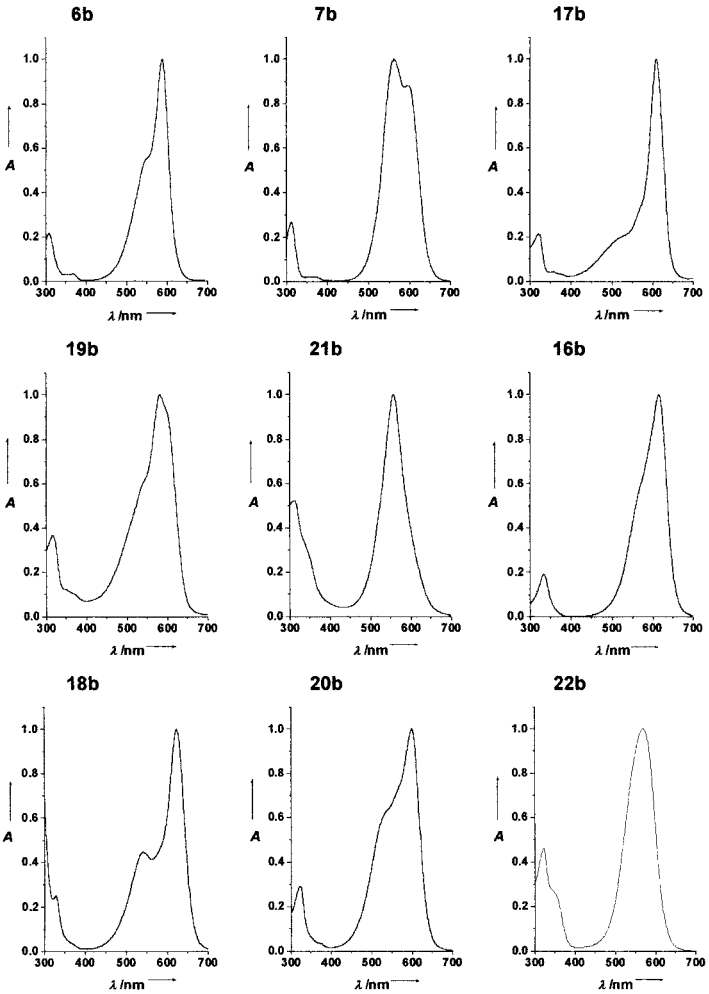

Figure 1. Absorption spectra of heteroanalogous Crystal Violet derivatives.

single band in the visible region usually has a more or less well-defined shoulder towards shorter wavelengths; for **7b** there is a shoulder on the longer wavelength side as well. The position of the maximum of these bands is independent of the substituents on the amino groups, but markedly dependent on the heterocyclic moieties. From a theoretical point of view these absorption bands arise from two transitions polarized perpendicularly to each other.[4] Clearly, in all the compounds (the heterocyclic analogues and Crystal Violet) these transitions have very similar energies. Thus, even compounds that have two or three (e.g. **19**) different side groups, display comparatively small band splittings.

Because of the small size of the crystals obtained it was not possible to determine the structures of the Crystal Violet analogues by X-ray analysis. Therefore, no unambiguous description of the three-dimensional arrangement of the side groups can be given. However, force-field calculations[20] demonstrate that, because of the smaller steric demand of a heterocyclic five-membered ring compared to a carbocyclic six-membered ring, all the compounds that possess two heterocyclic side groups have them in a coplanar conformation. Thus, the heterocyclic derivatives differ from Crystal Violet **5a**, which has, following force-field calculations performed by us and in agreement with the published X-ray data,[21] a propellerlike structure, and also from the recently published structures of tris(bithienyl)methinium and tris(trithienyl)methinium ions that are also of the propeller type.[22]

To illustrate these findings the molecular structures of Crystal Violet **5a** and the tris(2-dimethylamino-5-thienyl)methinium ion **16a** calculated using the MM2 method are given in Figure 2. As can be seen **5a** has a propellerlike structure with almost identical torsion angles for the three dimethylamino-substituted phenyl groups relative to the central trimethylene methane unit, whereas the heterocyclic Crystal Violet analogue **16a** exhibits an almost planar bis(2-dimethylamino-5-thienyl)methinium unit and a 2-dimethylamino-5-thienyl unit almost perpendicular to it. Because force-field calculations have some uncertainties with large π-systems,

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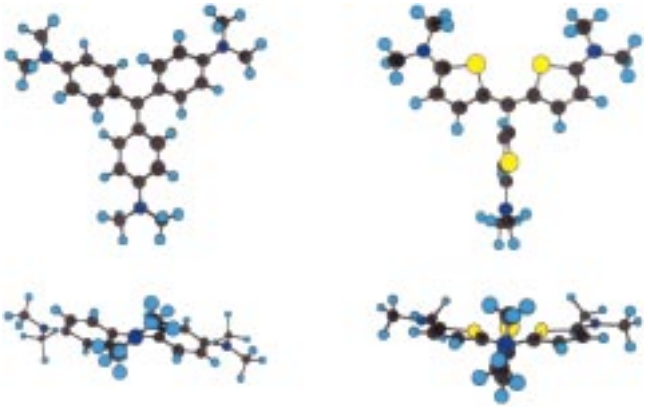

Figure 2. MM2-optimized structures of the cation of Crystal Violet **5a** (left) and of the tris(2-dimethylamino-5-thienyl) methinium ion **16a** (right).

quantum-chemical ab initio calculations were performed. The results obtained demonstrate the existence of flat energy minima between different conformers of the sulfur-containing compounds which makes it more difficult to find the global energy minimum and, hence, to find the most-stabilized conformation.[23]

It has to be seen whether the unusual structures of the heterocyclic analogues of Crystal Violet dyes described here have a marked effect on their NLO behavior, which is determined by the molecular symmetry and the character of the excited states of the compounds.[24] According to theoretical studies molecules with two energetically almost degenerate electronic transitions that are perpendicular to each other should display a special NLO behavior indicative of an octopolar charge distribution in the corresponding molecular system.[25]

Experimental Section

General: The UV/Vis absorption spectra were recorded with a UV-2501 spectrometer, Shimadzu, Tokyo, and the NMR spectra with a Gemini 300 spectrometer, Varian, Zurich.

Synthesis of the bis(heteroaryl)ketones **13b**–**15b** and their precursors **11b** and **12b**: To 3-dimethylaminothioacrylmorpholide (**8b**; 10 mmol) or *N*-(dimethylaminomethylene)morpholino thiourea (**9b**; 10 mmol) in acetonitrile (50 mL) were added 1–5 equivalents of 1,3-dichloroacetone (**10**), the mixture was then heated to boiling for a short time. The mixture was cooled to room temperature, triethylamine (30 mmol) was added then the mixture was heated to boiling again before being poured into water (100 mL). The precipitate was collected by filtration and recrystallized from ethanol or DMF: **11b**: yield 23%; m.p. 156–158 °C (ethanol); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.29$ (t, 4H, CH_2), 3.81 (t, 4H, CH_2), 4.40 (s, 2H, CH_2Cl), 6.05 (d, 1H, CH), 7.54 (d, 1H, CH); **12b**: yield 63%; m.p. 164–166 °C (ethanol); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.59$ (t, 4H, CH_2), 3.78 (t, 4H, CH_2), 4.39 (s, 2H, CH_2Cl), 7.91 (s, 1H, CH); **13b**: yield 74%; m.p. 286 °C (DMF); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.28$ (t, 8H, CH_2), 3.84 (t, 8H, CH_2), 6.10 (d, 2H, CH), 7.61 (d, 2H, CH); **14b**: yield 98%; m.p. 306–307 °C (DMF); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.29$ (t, 4H, CH_2), 3.60 (t, 4H, CH_2), 3.83 (m, 8H, CH_2), 6.10 (d, 1H, CH), 7.60 (d, 1H, CH), 7.90 (s, 1H, CH); **15b**: quantitative yield; m.p. 312–313 °C (DMF); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.57$ (t, 8H, CH_2), 3.73 (t, 8H, CH_2), 8.11 (s, 2H, CH).

Synthesis of the heterocyclic Crystal Violet analogues **16b**–**22b**: To a cooled suspension, prepared by addition of a solution of butyllithium (1.6 M) in hexane (10 mL) to a solution of 2-morpholinothiophene **2b** or 2-morpholinothiazole **3b** (10 mmol), respectively, in absolute 1,4-dioxane (50 mL), a bis(heteroaryl)ketone **13b**–**15b** (10 mmol) was added under argon and the resulting mixture heated for 8 h on a water bath at 90 °C. After cooling to room temperature the mixture was filtered and perchloric acid (70%, 0.5 mL) added to the filtrate. The resulting precipitate was collected by filtration, dried, and recrystallized from glacial acetic acid.

The Crystal Violet analogues **6b** and **7b** were prepared similarly by the reaction of *N*-(4-lithio-phenyl)morpoline with methyl 2-morpholinothiophene-5-carboxylate or 2-morpholinothiazole-5-carboxylate,[17c] respectively.

Received: February 26, 2001 [Z16675]

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