On the coupling of aryldiazonium salts with *N*,*N*-disubstituted 2-aminothiophenes and some of their carbocyclic and heterocyclic analogues

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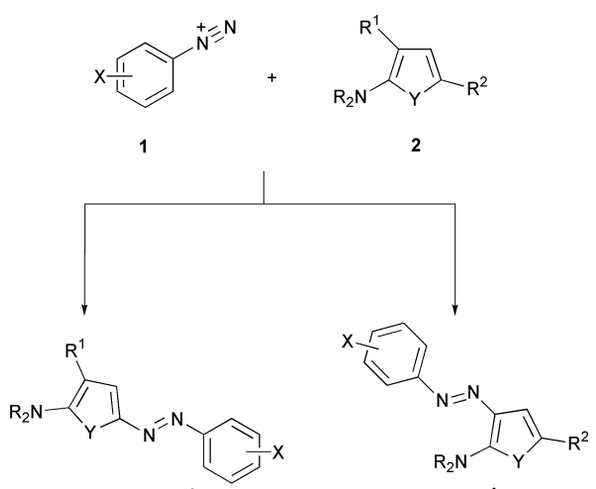
As exemplified with the morpholino derivatives **7**, *N*,*N*-disubstituted 2-aminothiophenes couple, depending on the substitution pattern at C(5), with aryldiazonium salts **1** either at their C(3) or C(5) position yielding the corresponding 3-arylazo-2-morpholinothiophenes **9** or, under elimination of the substituent at C(5), 5-arylazo-2-morpholinothiophenes **10**. This reaction contrasts to the behaviour of 5-morpholinothiazoles **8** and dimethylaniline **13** towards the same diazonium salts **1** which are unable to couple with these compounds if their C(5) or C(4) position, respectively, is not substituted by H, COOH or CHO.

Introduction

N,*N*-Dialkylanilines **2a** are known to be highly reactive towards electrophilic reagents. For example, with aryldiazonium salts **1** they yield deeply coloured 4-dialkylamino-substituted arylazobenzenes **3a** (Scheme 1).[1] A few of them are of some practical



1	X
a	4-NO_2
b	2,4-$(NO_2)_2$

2-4	Y
a	CH=CH
b	S

Scheme 1

interest, *e.g.* as acid–base indicators (C.I. Acid Orange 52) or as disperse dyes for dyeing synthetic fibres or plastics (C.I. Disperse Blue 354).[2] Very recently, 4-dialkylamino-substituted arylazobenzenes **3a** have been used as model compounds for materials with non-linear optical properties.[3]

The coupling reaction of aryldiazonium salts **1** with dialkylanilines **2a** giving rise to the formation of 4-dialkylamino-substituted diarylazobenzenes **3a** occurs only if the 4-position of **2a** is unsubstituted. Otherwise, no reaction occurs, meaning that the isomeric 2-dialkylamino-substituted diarylazobenzenes **4a**, which would be the alternative coupling products, are not available by this method. Because these 2-aminoazo compounds are of interest, *e.g.* as starting materials for preparing particular substituted benzimidazoles,[4] they have to be prepared by other synthetic routes.[5]

N,*N*-Disubstituted 2-aminothiophenes **2b** as heterocyclic analogues of the *N*,*N*-dialkylanilines **2a** exhibit a similar reactivity towards electrophilic reagents. Thus, with aryldiazonium salts **1** they are transformed, as long as their 5-position is unsubstituted, into *N*,*N*-disubstituted 2-amino-5-arylazothiophenes **3b**.[6] Otherwise, *e.g.* if they are substituted by a phenyl group at C(5), they yield, contrary to the *N*,*N*-dialkylanilines **2a**, *N*,*N*-disubstituted 2-amino-3-arylazothiophenes **4b**.[7] Obviously, the steric hindrance of an *ortho*-dialkylamino substituent to the attack of an electrophilic aryldiazonium salt **1** is significantly lower for the five-membered thiophene moiety than for the six-membered benzene ring.

A surprising result which contrasts this finding was reported by Russian authors. They observed the formation of 2-amino-5-arylazothiophenes **3b** if the 5-formyl derivatives of *N*,*N*-disubstituted 2-aminothiophenes **2b** (R^1 = CH=O) were allowed to react with aryldiazonium salts.[6a] Obviously, the 5-formyl group in the starting material **2b** split off in the course of the coupling reaction.

To see if this finding is peculiar to a particular substituted 2-dialkylaminothiophene derivative or a more general one the reaction of some aryldiazonium salts **1** towards a series of 2-dialkylaminothiophenes **2b** with different substituents at their 5-position was studied. As model compounds for this study the nitro-substituted benzenediazonium salts **1a** and **1b**[8] as well as the 2-morpholinothiophenes **7a**–**7p** are used. The 2-morpholino-substituted thiophenes **7b**–**7p** were prepared by known routes either from their corresponding parent compound **7a**[9] or from acyclic precursors, such as from the *N*-[3-amino(thioacryloyl)]morpholines **5**[10] and the halomethylcarbonyl compounds **6** (Scheme 2).[11]

To check the results of the reaction of the aryldiazonium salts **1** with the 5-substituted 2-morpholinothiophenes **7**, *e.g.* to see if isomeric products or mixtures of products were formed, not only were the products isolated and structurally characterised but the reaction mixture that resulted from the mixing of the components which were then left to stand for some time at room temperature was also monitored by TLC.

Results and discussion

Of the 5-substituted 2-morpholinothiophenes **7** studied not all reacted with the aryldiazonium salts **1**. Thus, a reaction

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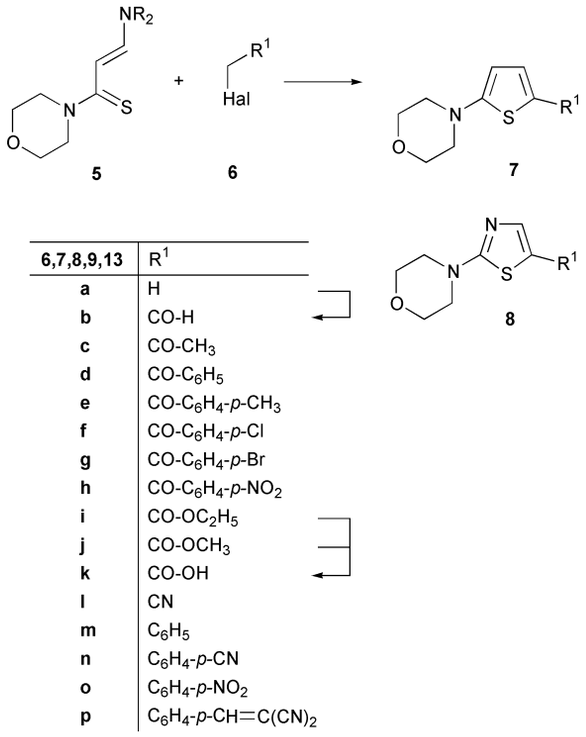


Scheme 2

was observed only with the 5-acyl- and 5-cyano-substituted 2-morpholinothiophenes **7b**–**7l** as well as with the 5-phenyl-substituted 2-morpholinothiophene **7m**. No reaction was observed with the 2-morpholinothiophenes **7n**–**7p** which are substituted at their C(5) position by an acceptor-substitued aryl or vinyl moiety, such as a 4-nitrophenyl or a dicyanovinyl moiety (Scheme 3).

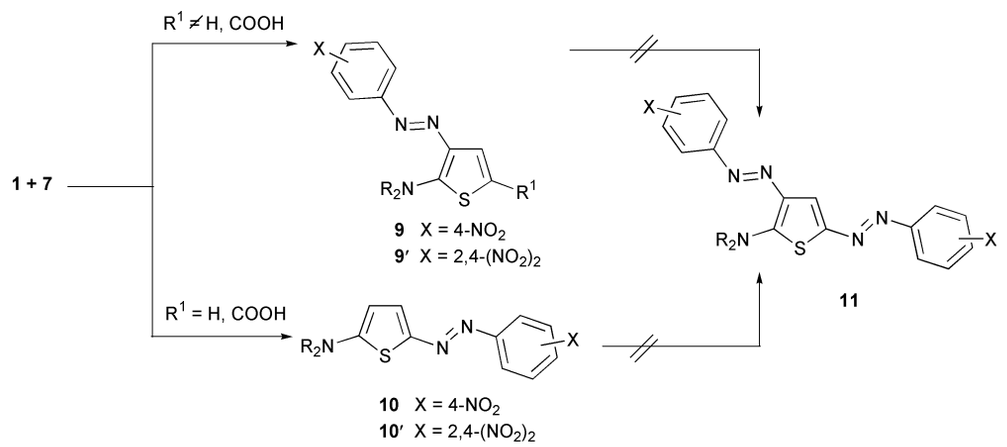
Whereas from **7c**–**7j** as well as from **7l** and **7m** the corresponding 3-arylazo-substituted 2-morpholinothiophenes **9c**–**9j**, **9l**, and **9m**, respctively, are formed, from **7a**–**7c** and **7k**, which was prepared from the corresponding alkyl 5-carboxylates **7i** or **7j** by saponification with sodium hydroxide in methanolic solution, the 5-arylazo-substituted 2-morpholinothiophenes **10** are formed. The latter compounds are also available from the parent 2-morpholinothiophene **7a** and the same aryldiazonium salts **1**. Due to the synthetic procedure for obtaining the corresponding azo compounds, namely allowing the required components to react in acetic acid containing some sulfuric acid and subsequent addition of methanol after the reaction, some azo compounds precipitate as hydrogen sulfates.

By checking the reaction mixtures by TLC it was found that from compounds **7a** and **7k** the corresponding 5-arylazo-substituted 2-morpholinothiophenes **10** are formed exclusively. However, from compounds **7b** and **7c** mixtures of two products are formed. Whereas from **7b** the 5-arylazo-substituted 2-morpholinothiophenes **10** are formed as the main products, from **7c** the 3-arylazo-substituted 5-acetyl-2-morpholinothiophenes **9c** are mainly formed. In the reaction of compound **7b** with the aryldiazonium salts **1** the corresponding 3-arylazo compound **9b** was obtained as a by-product. These products could be, as exemplfied with the 3-(4-nitrophenylazo)-substituted compound **9b**, isolated and unambiguously characterised. In the reaction of compound **7c** with the aryldiazonium salts **1** the corresponding 5-arylazo-substituted compounds **10a** are formed as by-products. Because they were only formed in trace amounts they were identified by TLC. Neither with compounds **7b** and **7c** nor with the other 5-substituted 2-morpholinothiophenes **7** studied, the conceivable bisarylazo-substituted 2-morpholinothiophenes **11** formed. Obviously, the introduction of one arylazo moiety in the thiophene ring prevents, similarly to an acceptor-substituted phenyl or vinyl moiety as mentioned before, a further coupling reaction giving rise to the formation of 3,5-bisarylazo-substituted thiophenes, even if the highly reactive 2,4-dinitrophenyl diazonium salt **1b** is used as diazo compound.

An interesting result was obtained, however, by studying the reaction of some of the 5-arylazo-substituted 2-morpholinothiophenes **10** prepared towards the nitrophenydiazonium salts **1**. Whereas no reaction was observed, as indicated by TLC, by allowing the 5-(2,4-dinitrophenylazo)-substituted 2-morpholinothiophene **10a′** to react with the 4-nitrophenyldiazonium salt **1a** a reaction was observed between the 5-(4-nitrophenylazo)-substituted 2-morpholinothiophene **10a** and the 2,4-dinitrophenyldiazonium salt **1b**. In this case the 5-(2,4-dinitrophenylazo)-substituted 2-morpholinothiophene **10a′** was formed. Obviously, the 4-nitrophenylazo moiety at C(5) of the starting thiophene derivative **10a** can be replaced by the more electrophilic 2,4-dinitrophenylazo moiety and not the 2,4-dinitrophenylazo moiety at the same position of compound **10a′** by the less electrophilic 4-nitrophenylazo moiety.

The formation of the above mentioned 3,5(bisarylazo)-substituted 2-morpholinothiophenes **11** was never observed. This means that an arylazo group at C(5) of a 2-morpholinothiophene moiety completely prevents the further attack of an aryldiazonium salt at C(3) of these products **10**, even if the reagents used are substituted by two strong electron accepting nitro groups.

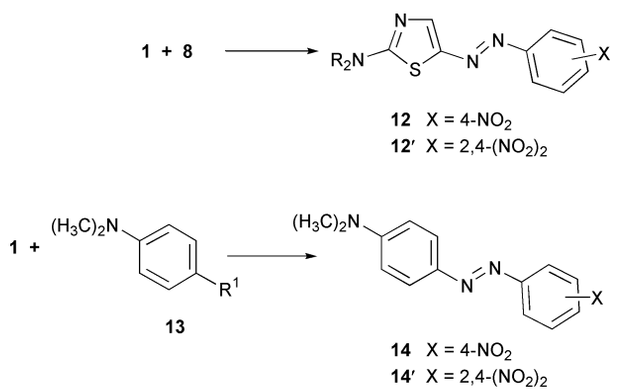
The previous results stimulated us to check the reactivity of some 5-substituted 2-morpholinothiazoles **8** and 4-substituted *N*,*N*-dimethylanilines **13** towards the aryldiazonium salts **1**. As model compounds the 2-morpholinothiazole derivatives **8a**–**8d**, **8o**, and **8p**, as well as the *N*,*N*-dimethylaniline derivatives **13a**, **13b**, **13k**, and **13l** were used. These heterocyclic thiazole derivatives were prepared in close analogy to the 5-substituted 2-morpholinothiophenes **7** from the halomethyl compounds **6**



Scheme 3

and the corresponding azaanalogues of the aminothioacrylamides **5**.[12]

The reactions were monitored by TLC as well as performed on a preparative scale. It was found that no reactions occur with the 2-morpholinothiazole derivatives **8b**–**8d**, **8o**, and **8p**, or with the 4-cyano-substituted dimethylaniline dervatives **13l**. In contrast, coupling reactions occur with the 2-morpholinothiazole derivatives **8a** and with the dimethylaniline derivatives **13a**, **13b**, and **13k**. Thus, in this way the 5-nitrophenyl-substituted 2-morpholinothiazoles **12** and the 4-dimethylamino-4′-nitroazobenzenes **14** are available. These compounds have been previously prepared from their unsubstituted parent compound **8a** or **13a**, respectively, by coupling with the nitrophenyldiazonium salts **1** (Scheme 4).[6c]



Scheme 4

The results obtained with the dimethylaniline derivatives **13** agree in some aspects with findings in the literature. Thus, it was reported that 4-dimethylaminobenzaldehyde **13b**[13] and 4-dimethylaminobenzoic acid **13k**[14] are able, analogously to their unsubstituted parent compound **13a**, to couple with (het)aryldiazonium salts.

All the prepared arylazo-substituted 2-morpholinothiophenes **9** and **10** are, similarly to the known 5-nitrophenyl-substituted 2-morpholinothiazoles **12** and 4-dimethylamino-4′-nitroazobenzene **14a**, deeply coloured compounds which exhibit intense absorptions in the visible range. Whereas the 3-arylazo-substituted thiophenes **9** are orange coloured products which absorb at about 500 nm, the 5-arylazo-substituted 2-morpholinothiophenes **10** are deeply magenta coloured compounds which exhibit, depending on the substitution pattern at their arylazo moiety and on the polarity of the solvent, intense absorption maxima at about 550 nm.[6c]

The structures of the arylazo compounds **9** and **10** were unambiguously confirmed by their analytical and spectral data. Thus, in all the ^{1}H NMR spectra of the 3-arylazo-substituted 2-morpholinothiophenes **9** a sharp singlet at about 7.00 ppm could be detected. This signal is attributed to the H(4) in the thiophene moiety. In contrast, in the ^{1}H NMR spectra of the 5-arylazo-substituted 2-morpholinothiophenes **10** two signals at about 7.00 and 8.00 ppm were detected. Both signals appear as doublets with coupling constants of 10–12 Hz indicating the presence of two adjacent protons at the corresponding thiophene moieties.

Experimental

Melting points were determined by means of a heating table microscope (Boetius). The ^{1}H NMR spectra were recorded with a Varian 300 MHz spectrometer Gemini 300 or with a JEOL 200 MHz spectrometer JNM FX 200. The UV/Vis spectra were recorded with a Perkin-Elmer spectrometer Lambda 900. The elemental analytical data were determined by means of a LECO analyser CHNS 932. The 2-morpholinothiophenes and 2-morpholinothiazoles **7** and **8**, respectively were prepared either as previously described in the reported literature (**7a**,[9c] **7b**,[9d] **7i** and **7j**,[15] **7k**,[16] **7m**,[17] **7n**–**7p**,[11a] **8a**,[18] **8b**,[19] **8d**,[12a] **8o**,[11e] and **8p**[11a]) or as follows.

5-Substituted 2-morpholinothiophenes 7c–7h and 7l–7p (general procedure)

A mixture of 3-[dimethylamino(thioacryloyl)]morpholide **5** (R = CH_3)[20] (10 mmol, 2.0 g) and the appropriate halomethyl compound **6** (10 mmol) in acetonitrile (25 mL) was refluxed for 2 min and subsequently mixed with triethylamine (10 mL). After cooling and dilution of the reaction mixture with water (5 mL) the precipitate formed was isolated by filtration and recrystallised.

The following 2-morpholinothiophenes **7** were so prepared.

5-Acetyl-2-morpholinothiophene 7c. (1.7 g, 80%) from chloroacetone **6c**; mp 114–116 °C (Found: C, 56.5; H, 6.2; N, 6.7. $C_{10}H_{13}NO_2S$ requires C, 56.9; H, 6.4; N, 6.7%); δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.41 (3H, s, CH_3CO), 3.25 (4H, t, NCH_2), 3.81 (4H, t, OCH_2), 6.03 (1H, d, C*H*), 7.43 (1H, d, C*H*).

5-Benzoyl-2-morpholinothiophene 7d. (2.3 g, 84%) from phenacyl bromide **6d**; mp 127–129 °C (Found: C, 66.0; H, 5.5; N, 5.3. $C_{15}H_{15}NO_2S$ requires C, 65.9; H, 5.5; N, 5.1%); δ_H(300 MHz; $CDCl_3$; Me_4Si) 3.32 (4H, t, NCH_2), 3.85 (4H, t, OCH_2), 6.09 (1H, d, C*H*), 7.39 (1H, d, C*H*), 7.42–7.52 (3H, m, C*H*), 7.75–7.77 (2H, m, C*H*).

5-(4-Methylbenzoyl)-2-morpholinothiophene 7e. (1.5 g, 52%) from 4-methylphenacyl bromide **6e**; mp 169–172 °C (Found: C, 66.5, H, 6.0; N, 4.7. $C_{16}H_{17}NO_2S$ requires C, 66.9; H, 5.9; N, 4.9%); δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.40 (3H, s, CH_3), 3.29 (4H, t, NCH_2), 3.83 (4H, t, OCH_2), 6.07 (1H, d, C*H*), 7.24 (2H, d, C*H*), 7.39 (1H, d, C*H*), 7.66 (2H, d, C*H*).

5-(4-Chlorobenzoyl)-2-morpholinothiophene 7f. (2.2 g, 72%) from 4-chlorophenacyl bromide **6f**; mp 168 °C (Found: C, 58.3; H, 4.7; N, 4.4. $C_{15}H_{14}ClNO_2S$ requires C, 58.6; H, 4.6; N, 4.6%); δ_H(300 MHz; $CDCl_3$; Me_4Si) 3.33 (4H, t, NCH_2), 3.85 (4H, t, OCH_2), 6.09 (1H, d, C*H*), 7.35 (1H, d, C*H*), 7.43 (2H, d, C*H*), 7.70 (2H, d, C*H*).

5-(4-Bromobenzoyl)-2-morpholinothiophene 7g. (2.9 g, 82%) from 4-bromophenacyl bromide **6g**; mp 170–171 °C (Found: C, 50.9; H, 4.0; N, 4.2. $C_{15}H_{14}BrNO_2S$ requires C, 51.1; H, 4.0; N, 4.0%); δ_H(300 MHz; $CDCl_3$; Me_4Si) 3.33 (4H, t, NCH_2), 3.85 (4H, t, OCH_2), 6.09 (1H, d, C*H*), 7.35 (1H, d, C*H*), 7.57–7.66 (4H, m, CH).

5-(4-Nitrobenzoyl)-5-morpholinothiophene 7h. (2.5 g, 79%) from 4-nitrophenacyl bromide **6h**; mp 205–206 °C (Found: C, 56.4; H, 4.4; N, 8.7. $C_{15}H_{14}N_3O_4S$ requires C, 56.6; H, 4.4; N, 8.8%); δ_H(300 MHz; DMSO-d^6; Me_4Si) 3.37 (4H, t, NCH_2), 3.76 (4H, t, OCH_2), 6.35 (1H, d, C*H*), 7.44 (1H, d, C*H*), 7.92 (2H, d, C*H*), 8.32 (2H, d, C*H*).

5-Cyano-2-morpholinothiophene 7l. (1.0 g, 52%) from chloroacetonitrile **6l**; mp 129 °C (Found: C, 55.2; H, 5.2; N, 14.2; S, 16.2. $C_9H_{10}N_2OS$ requires C, 55.7; H, 5.2; N, 14.4; S, 16.5%); δ_H(300 MHz; $CDCl_3$; Me_4Si) 3.21 (4H, t, NCH_2), 3.84 (4H, t, OCH_2), 6.01 (1H, d, C*H*), 7.34 (1H, d, C*H*).

5-Acetyl-2-morpholinothiazole. Analogously, by starting from 2-aza-3-morpholinothioacylmorpholide[11] and chloroacetone **6c**, 5-acetyl-2-morpholinothiazole **8c** (1.1 g, 56%) was prepared; mp 147 °C (Found: C, 55.3; H, 6.0; N, 14.1. $C_9H_{12}N_2OS$ requires C, 55.1; H, 6.1; N, 14.3%); δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.43 (3H, s, CH_3), 3.58 (4H, t, NCH_2), 3.80 (4H, t, OCH_2), 7.80 (1H, s, C*H*).

Coupling of the 2-morpholinothiophenes 7, 2-morpholinothiazoles 8, and *N*,*N*-dimethylanilines 13 with nitro-substituted benzenediazonium salts 1 (general procedure)

To a mixture of the appropriate 2-morpholinothiophene **7**, 2-morpholinothiazole **8** (10 mmol), or *N*,*N*-dimethylaniline **13** (10 mmol) in methanol or acetonitrile (25 mL) a solution of the nitro-substituted benzediazonium salt **1**, prepared by diazotisation of the appropriate nitroaniline (10 mmol) dissolved in a mixture of acetic acid (50 mL) and sulfuric acid (10 mL) with sodium nitrite (0.7 g, 10 mmol), was added dropwise at room temperature. After standing at room temperature for 2 h the resulting mixture was diluted with methanol (50 mL) and water (100 mL) and the product formed was isolated by filtration. The dried solution was evaporated and the remaining product was purified by column chromatography.

4-Nitrophenyldiazonium hydrogen sulfate 1a as diazo component. By using 4-nitrophenyldiazonium hydrogen sulfate **1a** as diazo component the following azo compounds or their hydrogen sulfates were prepared.

5-Formyl-2-morpholino-3-(4-nitrophenylazo)thiophene 9b. (0.7 g, 20%), plus 2-morpholino-5-(4-nitrophenylazo)thiophene **10a**, from 5-formyl-2-morpholinothiophene **7b**; mp 218–220 °C (Found: C, 52.2; H, 4.0; N, 16.3. $C_{15}H_{14}N_4O_4S$ requires C, 52.0; H, 4.1; N, 16.2%); $\lambda_{max}(CH_2Cl_2)$/nm 492 (ε/dm^3 mol^{-1} cm^{-1} = 17000); δ_H(300 MHz; DMSO-d^6; Me_4Si) 3.85 (4H, t, NCH_2), 4.02 (4H, t, OCH_2), 7.82 (2H, d, CH), 8.14 (1H, s, CH), 8.32 (2H, d, CH), 9.73 (1H, s, CH).

5-Acetyl-2-morpholino-3-(4-nitrophenylazo)thiophene hydrogen sulfate 9c·H_2SO_4. (2.6 g, 57%), plus 2-morpholino-5-(4-nitrophenylazo)thiophene **10a**, from 5-acetyl-2-morpholinothiophene **7c**; mp 217 °C (Found: C, 41.6, H, 4.1; N, 11.9; S, 13.6. $C_{16}H_{16}N_4O_4S{\cdot}H_2SO_4$ requires C, 41.9; H, 3.5; N, 12.1; S, 14.0%); $\lambda_{max}(CH_2Cl_2)$/nm 493 (ε/dm^3 mol^{-1} cm^{-1} = 21800); δ_H(300 MHz; DMSO-d^6; Me_4Si) 2.46 (3H, s, CH_3CO), 3.84 (4H, t, NCH_2), 3.99 (4H, t, OCH_2), 7.82 (2H, d, CH), 8.01 (1H, s, CH), 8.31 (2H, d, CH).

5-Benzoyl-2-morpholino-3-(4-nitrophenylazo)thiophene 9d. (2.2 g, 52%), from 5-benzoyl-2-morpholinothiophene **7d**; mp 222–224 °C (Found: C, 59.7; H, 4.7; N, 13.1. $C_{21}H_{18}N_4O_4S$ requires C, 59.7; H, 4.7; N, 13.3%); $\lambda_{max}(CH_2Cl_2)$/nm 498 (ε/dm^3 mol^{-1} cm^{-1} = 17400); δ_H(300 MHz; DMSO-d^6; Me_4Si) 3.87 (4H, t, NCH_2), 4.04 (4H, t, OCH_2), 7.55–7.66 (3H, m, CH), 7.76–7.82 (4H, m, CH), 7.81 (1H, s, CH), 8.29 (2H, d, CH).

2-Morpholino-3-(4-nitrophenylazo)-5-(4-methylbenzoyl)thiophene 9e. (2.9 g, 67%) from 2-morpholino-5-(4-methylbenzoyl)-thiophene **7e**; mp 225–227 °C (Found: C, 60.2, H, 4.5; N, 12.8. $C_{22}H_{20}N_4O_4S$ requires C, 60.6; H, 4.6; N, 12.8%); $\lambda_{max}(CH_2Cl_2)$/nm 498 (ε/dm^3 mol^{-1} cm^{-1} = 18600); δ_H(300 MHz; DMSO-d^6; Me_4Si) 2.42 (3H, s, CH_3), 3.86 (4H, t, NCH_2), 4.03 (4H, t, OCH_2), 7.38 (2H, d, CH), 7.68 (2H, d, CH), 7.77 (2H, d, CH), 7.81 (1H, s, CH), 8.30 (2H, d, CH).

5-(4-Chlorobenzoyl)-2-morpholino-3-(4-nitrophenylazo)thiophene 9f. (2.5 g, 55%) from 5-(4-chlorobenzoyl)-2-morpholinothiophene **7f**; mp 235–239 °C (Found: C, 54.9; H, 4.2; N, 12.1. $C_{21}H_{17}ClN_4O_4S$ requires C, 55.2; H, 3.7; N, 12.3%); $\lambda_{max}(CH_2Cl_2)$/nm 497 (ε/dm^3 mol^{-1} cm^{-1} = 19000); δ_H(300 MHz; DMSO-d^6; Me_4Si) 3.87 (4H, t, NCH_2), 4.04 (4H, t, OCH_2), 7.63 (2H, d, CH), 7.76 (1H, s, CH), 7.78–7.82 (4H, m, CH), 8.29 (2H, d, CH).

5-(4-Bromobenzoyl)-2-morpholino-3-(4-nitrophenylazo)thiophene 9g. (4.2 g, 84%) from 5-(4-bromobenzoyl)-2-morpholinothiophene **7g**; mp 260–265 °C (Found: C, 50.2; H, 3.5; N, 10.9. $C_{21}H_{17}BrN_4O_4S$ requires C, 50.3; H, 3.4; N, 11.2%); $\lambda_{max}(CH_2Cl_2)$/nm 498 (ε/dm^3 mol^{-1} cm^{-1} = 23400); δ_H(300 MHz; DMSO-d^6; Me_4Si) 3.87 (4H, t, NCH_2), 4.05 (4H, t, OCH_2), 7.76 (7H, m, CH), 8.29 (2H, d, CH).

2-Morpholino-5-(4-nitrobenzoyl)-3-(4-nitrophenylazo)thiophene 9h. (1.3 g, 28%) from 2-morpholino-5-(4-nitrobenzoyl)-thiophene **7h**; mp 262–264 °C (Found: C, 53.6; H, 4.1; N, 14.6. $C_{21}H_{17}N_5O_6S$ requires C, 54.0; H, 3.6; N, 15.0%); $\lambda_{max}(CH_2Cl_2)$/nm 498 (ε/dm^3 mol^{-1} cm^{-1} = 22400); δ_H(300 MHz; DMSO-d^6; Me_4Si) 3.87 (4H, t, NCH_2), 4.06 (4H, t, OCH_2), 7.75 (1H, s, CH), 7.80 (2H, d, CH), 7.99 (2H, d, CH), 8.29 (2H, d, CH), 8.38 (2H, d, CH).

5-(Ethoxycarbonyl)-2-morpholino-3-(4-nitrophenylazo)thiophene 9i. (2.5 g, 64%) from ethyl 2-morpholinothiophene-5-carboxylate **7i**; mp 199–201 °C (Found: C, 52.0; H, 4.9; N, 14.0. $C_{17}H_{18}N_4O_5S$ requires C, 52.3; H, 4.6; N, 14.4%); $\lambda_{max}(CH_2Cl_2)$/nm 491 (ε/dm^3 mol^{-1} cm^{-1} = 19500); δ_H(300 MHz; DMSO-d^6; Me_4Si) 1.29 (3H, t, CH_3), 3.84 (4H, t, NCH_2), 3.94 (4H, t, OCH_2), 4.27 (2H, q, OCH_2), 7.82 (2H, d, CH), 7.89 (1H, s, CH), 8.31 (2H, d, CH).

5-Cyano-2-morpholino-3-(4-nitrophenylazo)thiophene 9l. (2.5 g, 73%) from 5-cyano-2-morpholinothiophene **7l**; mp 260–262 °C (Found: C, 52.2; H, 3.9; N, 20.0; S, 9.3. $C_{15}H_{13}N_5O_3S$ requires C, 52.5; H, 3.8; N, 20.4; S, 9.3%); $\lambda_{max}(CH_2Cl_2)$/nm 479 (ε/dm^3 mol^{-1} cm^{-1} = 19500); δ_H(300 MHz; DMSO-d^6; Me_4Si) 3.84 (4H, t, NCH_2), 3.94 (4H, t, NCH_2), 7.81 (2H, d, CH), 8.01 (1H, s, CH), 8.32 (2H, d, CH).

2-Morpholino-3-(4-nitrophenylazo)-5-phenylthiophene hydrogen sulfate 9m·H_2SO_4. (3.2 g, 65%) from 5-phenyl-2-morpholinothiophene **7m**; mp 228–230 °C (Found: C, 47.4; H, 4.2; N, 10.7; S, 13.2. $C_{20}H_{18}N_4O_3S{\cdot}H_2SO_4$ requires C, 48.8; H, 3.7; N, 11.4; S, 13.0%); $\lambda_{max}(CH_2Cl_2)$/nm 536 (ε/dm^3 mol^{-1} cm^{-1} = 27000); δ_H(300 MHz; DMSO-d^6; Me_4Si) 3.86 (4H, t, NCH_2), 4.10 (4H, t, OCH_2), 7.44–7.86 (8H, m, CH), 8.22 (1H, d, CH), 8.30 (1H, d, CH).

2-Morpholino-5-(4-nitrophenylazo)thiophene 10a. (1.3 g, 41%) from 2-morpholinothiophene **7a**, (0.7 g, 22%) from 5-formyl-2-morpholinothiophene **7b**, (in a trace) from 5-acetyl-2-morpholinothiophene **7c**, (1.3 g, 41%) from 2-morpholinothiophene-5-carboxylic acid **7k**; mp 231 °C (lit.,[6c] 231 °C); $\lambda_{max}(CH_2Cl_2)$/nm 536 (ε/dm^3 mol^{-1} cm^{-1} = 15800).

2-Morpholino-5-(4-nitrophenylazo)thiazole 12a. (1.0 g, 31%) from 2-morpholinothiazole **7a**, (1.8 g, 56%) from 2-morpholinothiazole-5-carboxylic acid; mp 248–250 °C (lit.,[6c] 248–250 °C); $\lambda_{max}(CH_2Cl_2)$/nm 473 (ε/dm^3 mol^{-1} cm^{-1} = 13800).

***N*,*N*-Dimethyl-4-(4-nitrophenylazo)aniline 14a.** (2.0 g, 74%) from *N*,*N*-dimethylaniline **13a**, (2.2 g, 82%) from 4-dimethylaminobenzoic acid **13k**; mp 225–228 °C (lit.,[6c] 225–228 °C); $\lambda_{max}(CH_2Cl_2)$/nm 482 (ε/dm^3 mol^{-1} cm^{-1} = 11000).

2,4-Dinitrophenyldiazonium hydrogen sulfate 1b as diazo component. By using 2,4-dinitrophenyldiazonium hydrogen sulfate the following azo compounds were prepared.

5-Acetyl-3-(2,4-dinitrophenylazo)-2-morpholinothiophene 9c′. (2.0 g, 50%) from 5-acetyl-2-morpholinothiophene **7c**; mp 229 °C (Found: C, 47.1; H, 3.7; N, 17.1; S, 7.9. $C_{16}H_{15}N_5O_6S$ requires C, 47.5; H, 3.7; N, 17.3; S, 7.9%); $\lambda_{max}(CH_2Cl_2)$/nm 523 (ε/dm^3 mol^{-1} cm^{-1} = 25100); δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.45 (3H, s, CH_3CO), 3.85 (4H, t, NCH_2), 4.02 (4H, t, OCH_2), 7.80 (1H, s, CH), 8.45 (1H, d, CH), 8.47 (1H, d, CH), 8.78 (1H, d, CH).

3-(2,4-Dinitrophenylazo)-2-morpholino-5-(4-toluoyl)thiophene hydrogen sulfate 9e′·2/3 H_2SO_4. (2.3 g, 42%) from 2-morpholino-5-(4-toluoyl)thiophene **7e**; mp 215–220 °C (Found: C, 48.5; H, 3.6; N, 12.6. $C_{22}H_{19}N_5O_6S$·2/3 H_2SO_4 requires C, 48.3; H, 3.7; N, 12.8%); $\lambda_{max}(CH_2Cl_2)$/nm 528 (ε/dm^3 mol^{-1} cm^{-1} = 22400); δ_H(300 MHz; DMSO-d^6; Me_4Si) 2.42 (3H, s, CH_3), 3.87 (4H, t, NCH_2), 4.05 (4H, t, OCH_2), 7.37 (2H, d, CH), 7.62 (1H, s, CH), 7.66 (2H, d, CH), 7.79 (1H, d, CH), 8.44 (1H, dd, CH), 8.76 (1H, d, CH).

5-(Ethoxycarbonyl)-3-(2,4-dinitrophenylazo)-2-morpholinothiophene hydrogen sulfate 9i′·H_2SO_4. (2.6 g, 49%) from ethyl 2-morpholinothiophene-5-carboxylate **7i**; mp 192–195 °C (Found: C, 38.5; H, 3.4; N, 12.9. $C_{17}H_{17}N_5O_7S$·H_2SO_4 requires C, 38.3; H, 3.6; N, 13.1%); $\lambda_{max}(CH_2Cl_2)$/nm 523 (ε/dm^3 mol^{-1} cm^{-1} = 21400); δ_H(300 MHz; DMSO-d^6; Me_4Si) 1.28 (3H, t, CH_3), 3.84 (4H, t, NCH_2), 4.00 (4H, t, OCH_2), 4.27 (2H, q, OCH_2), 7.70 (1H, s, CH), 7.80 (1H, d, CH), 8.44 (1H, q, CH), 8.79 (1H, d, CH).

3-(2,4-Dinitrophenylazo)-5-(methoxycarbonyl)-2-morpholinothiophene hydrogen sulfate 9j′·H_2SO_4. (2.0 g, 48%) from methyl 2-morpholinothiophene-5-carboxylate **7j**; mp 199–202 °C (Found: C, 45.3; H, 3.7; N, 16.5. $C_{16}H_{15}N_5O_7S$·H_2SO_4 requires C, 45.6; H, 3.6; N, 16.6%); $\lambda_{max}(CH_2Cl_2)$/nm 520 (ε/dm^3 mol^{-1} cm^{-1} = 30200); δ_H(300 MHz; DMSO-d^6; Me_4Si) 3.81 (3H, s, OCH_3), 3.85 (4H, m, NCH_2), 3.99 (4H, m, OCH_2), 7.71 (1H, s, CH), 7.80 (1H, d, CH), 8.43 (1H, q, CH), 8.78 (1H, d, CH).

3-(2,4-Dinitrophenylazo)-5-cyano-2-morpholinothiophene 9l′. (3.3 g, 85%) from 5-cyano-2-morpholinothiophene **7l**; mp 231–233 °C (Found: C, 46.5; H, 3.2; N, 21.5; S, 8.3. $C_{15}H_{12}N_6O_5S$ requires C, 46.4; H, 3.1; N, 21.7; S, 8.3%); $\lambda_{max}(CH_2Cl_2)$/nm 508 (ε/dm^3 mol^{-1} cm^{-1} = 21800); δ_H(300 MHz; DMSO-d^6; Me_4Si) 3.84 (4H, t, NCH_2), 3.97 (4H, t, OCH_2), 7.84 (1H, s, CH), 8.45 (1H, d, CH), 8.48 (1H, d, CH), 8.79 (1H, d, CH).

5-(2,4-Dinitrophenylazo)-2-morpholinothiophene 10a′. (1.8 g, 50%) from 2-morpholinothiophene **7a**, (0.7 g, 19%) from 5-formyl-2-morpholinothiophene **7b**, (1.8 g, 50%) from 2-morpholinothiophene-5-carboxylic acid **7k**, (0.9 g, 25%) from *2-morpholino-5-(4-nitrophenylazo)thiophene* **10a**; mp 205–207 °C (lit.,[6c] 205–207 °C); $\lambda_{max}(CH_2Cl_2)$/nm 581 (ε/dm^3 mol^{-1} cm^{-1} = 56800).

5-(2,4-Dinitrophenylazo)-2-morpholinothiazole 12a′. (1.7 g, 38%) from 2-morpholinothiazole **8a**, (1.8 g, 41%) from 2-morpholinothiazole-5-carboxylic acid **8k**; mp 240 °C (lit.,[6c] 240 °C); $\lambda_{max}(CH_2Cl_2)$/nm 498 (ε/dm^3 mol^{-1} cm^{-1} = 16600).

***N*,*N*-Dimethyl-4-(2,4-dinitrophenylazo)aniline 14a′.** (1.6 g, 51%) from *N*,*N*-dimethylaniline **13a**, (1.3 g, 41%) from 4-dimethylaminobenzoic acid **13k**; mp 211 °C (lit.,[6c] 211 °C); $\lambda_{max}(CH_2Cl_2)$/nm 527 (ε/dm^3 mol^{-1} cm^{-1} = 18600).

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