Preparation and Characterization of 3,4-Diaryl-Substituted 2-Diarylaminothiophenes

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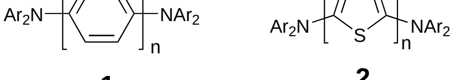
Abstract: Starting from *N*,*N*,*C*-triarylacetamides and 1-aryl-2-bromoethanones a series of new 3,4-diaryl-substituted 2-diarylaminothiophenes have been prepared and characterized spectroscopically.

Key words: amines, cyclization, heterocycles, oxidations

Recently, *N*,*N*-diaryl-substituted 2-aminothiophenes **3** received a lot of interest. They have not only been used for the synthesis of highly stable dyes with pronounced nonlinear optical or elctrophotographic properties,[1] but also for the synthesis of α,α′-bisdiarylamino-capped oligothiophenes (Figure 1) $\mathbf{2_n}$.[2] These compounds were employed, similar to their carbocyclic analogues $\mathbf{1_n}$,[3] as starting materials for the preparation of compounds with tuneable electric conductivity,[4] Due to the ease with which they form amorphous glasses from their melts, radical cations generated by their oxidation have a high stability and large mobility.[5] Such compounds can be used for manufacturing electrooptical and microelectronic devices, e.g., as photocopiers,[6] organic light emitting diodes,[7] organic field-effect transistors,[8] or organic solar cells.[9]

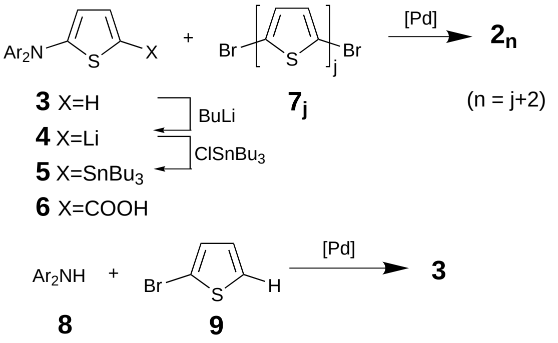


$\mathbf{1_n}$ $\mathbf{2_n}$

Figure 1

The transformation of *N*,*N*-disubstituted 2-aminothiophenes **3** into 5,5′-bisdiarylamino-capped oligothiophenes $\mathbf{2_n}$ was performed by a palladium-catalyzed coupling reaction of metallated 2-aminothiophenes **4** or **5** with the dibromothiophenes $\mathbf{7_j}$ (Scheme 1).[10] The metallated thiophenes **4** or **5** were available by standard metallation methods from their 5*H*-substituted parent compounds **3**.[11] Compounds **3** were prepared, in turn, either from diarylamines **8** and 2-bromothiophene **9** by a palladium-catalyzed coupling reaction[1,12] or by decarboxylation of 2-diarylaminothiophene-5-carboxylic acid **6**. Their synthesis can be carried out by carboxylation of **4** or, via their corresponding alkyl carboxylates, by a simple ring-closure reaction.[13]

Since it has been demonstrated in several series of oligothiophenes that the electronic properties of the appropriate compounds can be strongly influenced by introducing special substiuents in their 3,4-positions,[14] it seems of interest to synthesize such derivatives in the α,α′-diarylamino-capped oligothiophene series $\mathbf{2_n}$. For instance, aryl substituents in these positions should influence not only the stability of the cationic species generated by their oxidation but also the intramolecular interaction of the molecules in the solid state affecting a better migration of the corresponding charge carriers from one molecular unit to its adjacent units.



Scheme 1

Certain 2-(*N*,*N*-diarylamino)thiophenes with aryl groups in 3- and 4-positions should be versatile staring materials to prepare α,α′-diarylamino-capped oligothiophenes with additional aryl groups in these positions. However, such compounds are almost unknown. To prepare these compounds a simple ring-closure reaction starting from *N*,*N*,*C*-triaryl-subtituted thioacetamides **10** and 1-aryl-2-bromoethanones **11** can be employed (Scheme 2). This synthetic method was previously applied to the synthesis of 3,4-diaryl-substituted 2-dialkylaminothiophenes[15] and for some 5,5′-dialkylamino- and 5,5′-diarylamino-2,2′-bithiophenes.[16]

The ring-closure reaction was performed by allowing **10** and **11** to react in a solvent, such as dichloromethane, at room temperature followed by addition of triethylamine to the reaction mixture. The reaction proceeds via inter-

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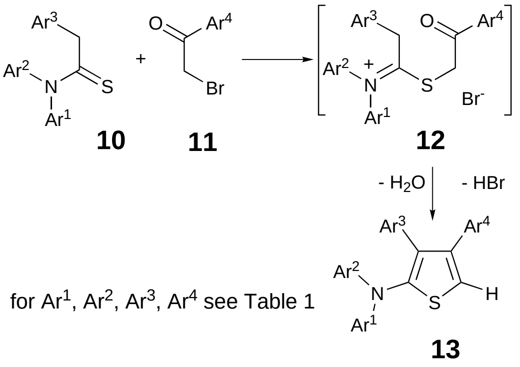
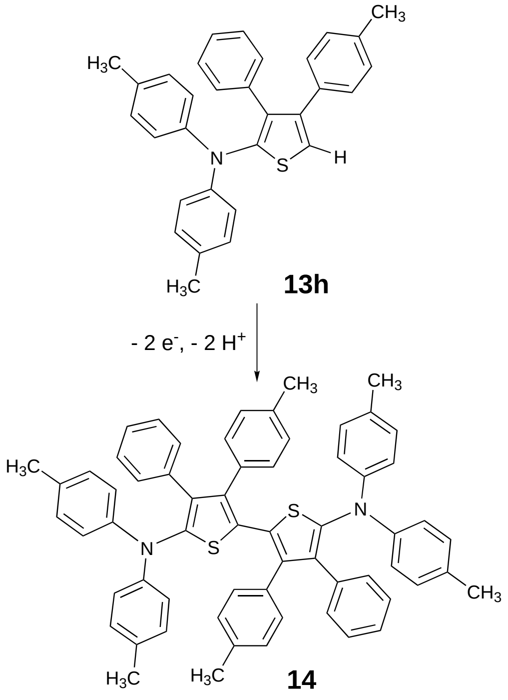


Scheme 2

mediate thioamidinium salts **12** and gives the products **13** in satisfactory yields. The 3,4-diarylamino-substituted 2-diarylaminothiophenes **13** so prepared are depicted in Table 1.

They are colorless, air-stable compounds whose structures were unambiguously determined by elemental analysis, mass spectra, and NMR measurements. Some of these data are recorded in Table 2.

In contrast to the ^{13}C NMR spectra, the ^{1}H NMR spectra of the aryl-substituted 2-aminothiophenes **13** are less indicative since only unresolved multiplets were found between 6.75 and 7.95 ppm. These multiplets originate from the aryl protons. The signals of the thiophene protons at C(5) are usually hidden under these multiplets. Only protons of aliphatic groups, if present, can be detected by their signals in the expected range.



Scheme 3

As expected, the *N*,*N*,3,4-tetraaryl-substituted 2-aminothiophenes **13** can be used as starting materials for the preparation of *N*,*N*′-peraryl-substituted 5,5′-diamino-2,2′-bithiophenes and their homologues (Scheme 3). This transformation can be performed by using several oxidizing reagents and certain preparative methods which will

Table 1 3,4-Diaryl-substituted 2-(*N*,*N*-Diarylamino)thiophenes **13** Prepared

Compd	Ar^1Ar^2N	Ar^3	Ar^4	Yield (%)	Mp (°C)
13a	$(C_6H_5)_2N$	C_6H_5	C_6H_5	62	108–110
13b	$(C_6H_5)_2N$	C_6H_5	$4-C_6H_5-C_6H_4$	69	151–152
13c	$(C_6H_5)_2N$	C_6H_5	$4-CH_3-C_6H_4$	75	175–176
13d	$(C_6H_5)_2N$	C_6H_5	$4-CH_3O-_6H_4$	76	128–129
13e	$(C_6H_5)_2N$	C_6H_5	$1-C_{10}H_7$	68	110–112
13f	$(C_6H_5)_2N$	C_6H_5	$2-C_{10}H_7$	70	148–150
13g	$(4-CH_3-C_6H_4)_2N$	C_6H_5	C_6H_5	68	145
13h	$(4-CH_3-C_6H_4)_2N$	C_6H_5	$4-CH_3-C_6H_4$	72	137–138
13i	$(4-CH_3-C_6H_4)_2N$	$4-CH_3-C_6H_4$	$4-CH_3-C_6H_4$	69	197
13j	$(4-CH_3O-C_6H_4)_2N$	$4-CH_3O-C_6H_4$	$4-CH_3O-C_6H_4$	63	147
13k	$1-C_{10}H_7-(C_6H_5)N$	C_6H_5	C_6H_5	62	153–154
13l	$1-C_{10}H_7-(C_6H_5)N$	C_6H_5	$1-C_{10}H_7$	64	167–169
13m	$2-C_{10}H_7-(C_6H_5)N$	C_6H_5	C_6H_5	59	168–169
13n	$2-C_{10}H_7-(C_6H_5)N$	C_6H_5	$2-C_{10}H_7$	65	125–127

Table 2 Spectroscopic Data of the 3,4-Diaryl-Substituted 2-(*N*,*N*-Diarylamino)thiophenes **13** Prepared[a]

Compd	*m*/*z*	^{1}H NMR ($CDCl_3$), δ (ppm)	^{13}C NMR ($CDCl_3$), δ (ppm)
13a	403	6.88–7.23 (m, 20 H$_{\text{arom}}$), 6.92 (s, 1 H$_{\text{heteroarom.)}}$	120.33, 122.31, 122.89, 127.46, 127.48, 128.46, 128.72, 129.45, 129.51, 130.52, 135.59, 137.54, 139.94, 142.22, 146.84, 148.14
13b	479	6.89–7.58 (m, 24 Harom., 1 H$_{\text{heteroarom.)}}$	119.60, 121.59, 122.18, 126.63, 126.77, 126.85, 127.17, 127.79, 128.67, 128.77, 129.00, 129.82, 134.86, 135.75, 137.18, 139.36, 140.56, 140.97, 146.23, 147.37
13c	417	2.31 (s, 3 H, CH_3), 6.89–7.2 (m, 19 H$_{\text{arom.}}$, 1 H$_{\text{hetarom.}}$)	21.77, 119.86, 122.25, 122.81, 127.37, 128.41, 129.24, 129.42, 129.46, 130.48, 134.63: 135.68, 137.08, 137.93, 142.12, 146.69, 148.11
13d	433	3.78 (s, 3 H OCH_3) 6.75–7.22 (m, 19 H $_{\text{arom.}}$, 1 H$_{\text{hetarom.)}}$	55.78, 114.15, 119.35, 122.23, 122.81, 127.37, 128.42, 129.45, 130.12, 130.47, 130.48, 135.69, 137.88, 141.75, 146.66, 148.10, 159.21
13e	453	6.81–7.95 (m, 22 H$_{\text{arom}}$, 1 H$_{\text{hetarom.}}$)	121.34, 121.63, 122.26, 125, 125.57, 125.81, 126.08, 126.52, 127.41, 127.63, 128.03, 128.12, 128.86, 129.13, 132.35, 133.52, 134.59, 135.06, 138.49, 139.81, 145.5, 147.46
13f	453	6.86–7.74 (m, 22 H$_{\text{arom.}}$, 1 H$_{\text{hetarom.)}}$	120.01, 121.55, 122.18, 125.73, 125.95, 126.79, 127.08, 127.32, 127.33 127.51, 127.80, 127.94, 128.8, 129.77, 132.19, 133.27, 134.37, 134.76, 137.24, 141.34, 146.22, 147.35
13g	431	2.26 (s, 6 H, CH_3), 6.85–7.22 (m, 18 H$_{\text{arom.}}$, 1 H$_{\text{hetoarom.}}$)	20.66, 119.42, 121.42, 126.64, 126.68, 127.69, 127.96, 128.72, 129.35, 129.83, 131.43, 134.94, 136.85, 136.91, 141.37, 145.27, 146.6
13h	445	2.27 (s, 6 H, CH_3), 2.3 (s, 3 H, CH_3), 6.84–7.11 (m, 17 H $_{\text{arom.}}$), 7.13 (s, 1 H$_{\text{hetarom.}}$)	20.66, 21.09, 118.98, 121.42, 126.59, 127.67, 128.55, 128.70, 129.33, 129.84, 131.39, 134.06, 135.09, 136.32, 136.89, 141.31, 145.3, 146.47
13i	459	2.24 (s, 3 H, CH_3), 2.27 (s, 6 H, CH_3), 2.30 (s, 3 H CH_3), 6.83–7.08 (m, 16 H$_{\text{arom.}}$), 7.12 (s, 1 H$_{\text{heteroarom.}}$)	20.66, 21.12, 21.18, 119.16, 121,35, 128,41, 128.53, 128,69, 129.33, 129.64, 131.30, 131.99, 134.20, 136.09, 136.23, 137.13, 141.32, 145.39, 146.02
13j[b]	523	3.71 (s, 3 H, OCH_3), 3.73 (s, 6 H, OCH_3), 3.75 (s, 3 H OCH_3), 6.62–7.08 (m, 16 H$_{\text{arom.}}$), 7.06 (s, 1 H$_{\text{hetarom.}}$)	55.38, 55.47, 55.77, 113.51, 113.70, 114.46, 118.52, 122.94, 127.87, 130.06, 130.16, 131.33, 136.36, 141.47, 141.97, 147.01, 155.34, 158.83, 158.94
13k	453	6.79–7.79 (m, 22 H$_{\text{arom.}}$, 1 H$_{\text{hetarom.)}}$	117.68, 119.09, 120.22, 124.54, 125.43, 125.62, 125.71, 125.88, 126.43, 126.68, 127.75, 127.93, 127.95, 128.00, 128.65, 128.74, 129.93, 130,00, 134.73, 135.17, 136.67, 136.82, 141.40, 142.56, 147.23, 150.15
13l	503	6.76–7.95 (m, 24 H$_{\text{arom.}}$, 1 H$_{\text{hetarom.}}$)	117.53, 120.18, 120.87, 124.54, 124.92, 125.51, 125.71, 125.73, 125.79, 125.95, 126.09, 126.46, 126.55, 127.40, 127.42, 127.52, 127.96, 128.05, 128.09, 128.81, 129.34, 130.03, 132.33, 133.42, 134.82, 134.91, 135.03, 138.02, 139.74, 142.64, 146.44, 150.27
13m	453	6.92–7.74 (m, 22 H$_{\text{arom.}}$, 1 H$_{\text{hetarom.}}$)	117.61, 119.74, 121.87, 121.98, 122.45, 124.21, 126.17, 126.78, 126.80, 126.97, 127.48, 127.75, 128.01, 128.50, 128.72, 128.83, 129.67, 129.76, 134.13, 134.78, 136.74, 137.31, 141.50, 145.14, 146.04, 147.27
13n	503	6.94–7.8 (m, 24 H$_{\text{arom.}}$, 1 H$_{\text{hetarom.}}$)	117.41, 119.56, 121.69, 121.76, 122.31, 124.04, 125.57, 125.78, 126.01, 126.65, 126.76, 126.88, 127.15, 127.17, 127.28, 127.31, 127.62, 127.74, 128.34, 128.67, 129.49, 129.57, 132.04, 133.09, 133.95, 134.15, 134.56, 137.15, 141.21, 144.95, 145.00, 147.07

[a] All compounds gave satisfactory elemental analysis C±0.25, H±0.22, N±0.2, S±0.21.

[b] Measured in CD_2Cl_2.

be described in detail elsewhere.[17] The course of this transformation can be studied by cyclic voltammetry.

As exemplified in Figure 2 for compound **13h**, its oxidation starts at about +0.45 V, the other thiophene compounds **13** are similar. Due to the irreversibility of this process the formation of a rather unstable radical cation **13h**$^{\cdot+}$ can be assumed. It dimerizes immediately upon formation giving rise to the formation of a corresponding *N*,*N*′-peraryl-substituted 5,5′-diamino-2,2′-bithiophene **14** as consequence of a radical-radical dimerization or radical-substrate coupling process.[18] The formation of the 5,5′-diamino-2,2′-bithiophene **14** during the electrochemical process is indicated by a reversible peak appearing at about +0.06 V. Its intensity increases continuously with the number of scans and its potential is measured in the same range as is found for the 5,5′-diamino-2,2′-bithiophene reference compound **14** prepared from the same precursor **13h** by its reaction with bromine as oxidizing reagent.

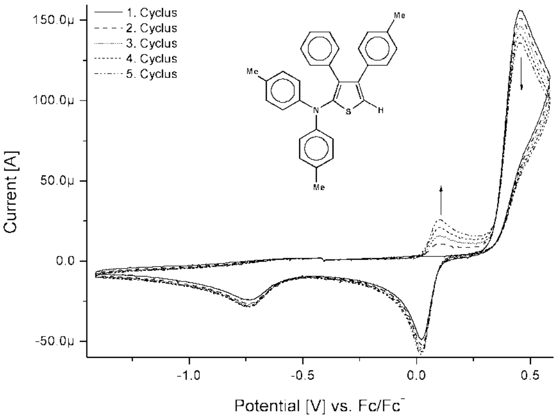


Figure 2 Cylic voltammogramm of compound **13h**

The following instruments and analytical techniques were used: melting points: Kofler hot-stage microscope, corrected; NMR: Inova 500 'max 2', Varian 300 MHz spectrometer, Gemini 300, with $CDCl_3$ as solvent; elemental analysis: LECO analyzer CHNS 932; MS: AMOspectrometer 402 (70 eV, EI); mass spectra: ESI, LCQ, Finnigan MAT.

Cyclic voltammetry: Autolab instrument PGSTAT 20. The measurements were performed under N_2 in benzonitrile containing Bu_4NPF_6 as supporting electrolyte with a scan rate of 0.1 V/s using a stationary working platinum electrode, a platinum counter electrode, and a stationary platinum reference electrode. Standard redox potentials have been estimated versus ferrocene/ferrocenium in benzonitrile as reference redox system for a nearly reversible electrode processes.

N,N-Diarylamino-Substituted 3,4-Diarylthiophenes 13; General Procedure

A solution of a *N,N*-disubstituted thioacetamide (**10**, 0.01 mol) and a bromoketone (**11**, 0.01 mol) in EtOH (100 mL) was refluxed for 6 h. After cooling, the mixture was diluted with ice-water (200 mL) and the precipitate was isolated by filtration, followed by recrystallization from EtOH or HOAc.

Bis-5,5′[(4-toly)amino-4-phenyl-3(4-tolyl)]2,2′-bithiophene (14)

A solution of Br_2 (6.39g, 40 mmol) in dichloroethane (20 mL) was added at ambient temperature under stirring to a solution of 2-bis-[(4-tolyl)amino]-3-phenyl-4-(4-tolyl)thiophene (**13h**, 4.46g, 10 mmol) in dichloroethane (60 ml) and refluxed for 0.5 h. After cooling, the dark blue precipitate was separated by filtration und washed with Et_2O. The product was dissolved in acetone (100 mL), $NaBH_4$ (0.86g) was added and the solution heated to reflux until it became colorless. The solution was concentrated and the product precipitated with MeOH and recrystallized from MeCN.

Yield: 3.65g, (82%); mp 224–225 °C.

^1H NMR($CDCl_3$): δ = 2.25 (s, 12 H, CH_3), 2.28 (s, 6 H, CH_3), 6.70–7.00 (m, 34 $H_{arom.}$).

^{13}C NMR($CDCl_3$): δ = 20.64, 21.25, 121.35, 126.30, 127.36, 127.71, 128.13, 129.22, 129.79, 130.57, 131.30, 132.66, 135.10, 136.02, 137.55, 140.57, 144.96, 145.86.

MS: *m*/*z* (%) = 888 (100), 444 (26).

Anal. Calcd for $C_{62}H_{52}N_2S_2$ (889.23): C, 83.74; H, 5.91; N, 3.15; S, 7.20. Found: C, 83.80; H, 5.72; N, 3.06; S, 7.17.

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