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 electrophotographic properties,\(^1\) but also for the synthesis of \(\alpha,\alpha'\)-bisdiarylaminocapped oligothiophenes (Figure 1) 2\(\text{n}\).\(^2\) These compounds were employed, similar to their carbocyclic analogues 1\(\text{n}\),\(^3\) 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.\(^9\)

The transformation of \(N,N\)-disubstituted 2-aminothiophenes 3 into 5,5'-bisdiarylamino-capped oligothiophenes 2\(\text{n}\) was performed by a palladium-catalyzed coupling reaction of metallated 2-aminothiophenes 4 or 5 with the dibromothiophenes 7\(\text{j}\) (Scheme 1).\(^10\) The metallated thiophenes 4 or 5 were available by standard metallation methods from their 5\(\text{H}\)-substituted parent compounds 3.\(^11\) Compounds 3 were prepared, in turn, either from diarylmines 8 and 2-bromo thiophene 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 substituents in their 3,4-positions,\(^14\) it seems of interest to synthesize such derivatives in the \(\alpha,\alpha'\)-diarylamino-capped oligothiophene series 2\(\text{n}\). 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.

Certain 2-(\(N,N\)-diarylamino)thiophenes with aryl groups in 3- and 4-positions should be versatile staring materials to prepare \(\alpha,\alpha'\)-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-substituted thiocetamides 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-
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 13C NMR spectra, the 1H 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.

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

<table>
<thead>
<tr>
<th>Compd</th>
<th>( Ar^1Ar^2N )</th>
<th>( Ar^3 )</th>
<th>( Ar^4 )</th>
<th>Yield (%)</th>
<th>Mp (°C)</th>
</tr>
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<tbody>
<tr>
<td>13a</td>
<td>(C₆H₅)₂N</td>
<td>C₆H₅</td>
<td>C₆H₅</td>
<td>62</td>
<td>108–110</td>
</tr>
<tr>
<td>13b</td>
<td>(C₆H₅)₂N</td>
<td>C₆H₅</td>
<td>4-C₆H₄C₆H₄</td>
<td>69</td>
<td>151–152</td>
</tr>
<tr>
<td>13c</td>
<td>(C₆H₅)₂N</td>
<td>C₆H₅</td>
<td>4-CH₃C₆H₄</td>
<td>75</td>
<td>175–176</td>
</tr>
<tr>
<td>13d</td>
<td>(C₆H₅)₂N</td>
<td>C₆H₅</td>
<td>4-CH₃O-C₆H₄</td>
<td>76</td>
<td>128–129</td>
</tr>
<tr>
<td>13e</td>
<td>(C₆H₅)₂N</td>
<td>C₆H₅</td>
<td>1-C₁₀H₇</td>
<td>68</td>
<td>110–112</td>
</tr>
<tr>
<td>13f</td>
<td>(C₄H₉)₂N</td>
<td>C₆H₅</td>
<td>2-C₁₀H₇</td>
<td>70</td>
<td>148–150</td>
</tr>
<tr>
<td>13g</td>
<td>(4-CH₃C₆H₄)₂N</td>
<td>C₆H₅</td>
<td>C₆H₅</td>
<td>68</td>
<td>145</td>
</tr>
<tr>
<td>13h</td>
<td>(4-CH₃C₆H₄)₂N</td>
<td>C₆H₅</td>
<td>4-CH₃C₆H₄</td>
<td>72</td>
<td>137–138</td>
</tr>
<tr>
<td>13i</td>
<td>(4-CH₃C₆H₄)₂N</td>
<td>4-CH₃C₆H₄</td>
<td>4-CH₃C₆H₄</td>
<td>69</td>
<td>197</td>
</tr>
<tr>
<td>13j</td>
<td>(4-CH₃O-C₆H₄)₂N</td>
<td>4-CH₃O-C₆H₄</td>
<td>4-CH₃O-C₆H₄</td>
<td>63</td>
<td>147</td>
</tr>
<tr>
<td>13k</td>
<td>1-C₁₀H₇(C₆H₅)N</td>
<td>C₆H₅</td>
<td>C₆H₅</td>
<td>62</td>
<td>153–154</td>
</tr>
<tr>
<td>13l</td>
<td>1-C₁₀H₇(C₆H₅)N</td>
<td>C₆H₅</td>
<td>1-C₁₀H₇</td>
<td>64</td>
<td>167–169</td>
</tr>
<tr>
<td>13m</td>
<td>2-C₁₀H₇(C₆H₅)N</td>
<td>C₆H₅</td>
<td>C₆H₅</td>
<td>59</td>
<td>168–169</td>
</tr>
<tr>
<td>13n</td>
<td>2-C₁₀H₇(C₆H₅)N</td>
<td>C₆H₅</td>
<td>2-C₁₀H₇</td>
<td>65</td>
<td>125–127</td>
</tr>
</tbody>
</table>

Scheme 2

Scheme 3
be described in detail elsewhere. 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+ can be assumed. It dimerizes immediately upon formation giving rise to the formation of a corresponding N,N'-perylenyl-substituted 5,5'-diamino-2,2'-bithiophene 14 as consequence of a radical-radical dimerization or

| Table 2 Spectroscopic Data of the 3,4-Diaryl-Substituted 2-(N,N-Diarylamino)thiophenes 13 Prepareda |
|------------------|------------------|------------------|
| Compd | m/z | 1H NMR (CDCl3, δ (ppm)) | 13C NMR (CDCl3, δ (ppm)) |
| 13a | 403 | 6.88–7.23 (m, 20 H arom.), 6.92 (s, 1 H 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 H arom., 1 H 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, CH3), 6.89–7.2 (m, 19 H arom., 1 H heteroarom.) | 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, 138.32, 142.12, 146.66, 148.10, 149.81 |
| ... | ... | ... | ... |

*All compounds gave satisfactory elemental analysis Ce0.25, He0.22, Ne0.2, Ss0.21.*

b Measured in CD2Cl2.
radical-substrate coupling process. 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.

The following instruments and analytical techniques were used: melting points: Kofer 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 4 NPF 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 CDCl 3 as solvent; elemental analysis: LECO analyzer CHNS 932; NMR: Inoven Instrument 500 MHz, Varian 300 MHz spectrometer, Gemini 300, with 1H NMR(CDC13): δ = 2.25 (s, 12 H, CH 3 ), 2.28 (s, 6 H, CH 3 ), 6.70–7.00 (m, 34 H arom.).

13C NMR(CDC13): 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, 144.96, 145.86. MS: m/z (%) = 888 (100), 444 (26).

Anal. Calcd for C 62 H 52 N 2 S 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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References

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Figure 2  Cyclic voltammogram of compound 13h