### A Versatile Route to *N*,*N*′-Tetraaryl-Substituted 2,5-Diaminothiophenes

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Received 20 June 2011; revised 21 July 2011

Dedicated to Prof. Dr. Dr. h. c. mult. Siegfried Hünig on the occasion of his 90th birthday

**Abstract:** By reaction of N,N'-tetraaryl-substituted succinic diamides with Lawesson's reagent, a series of N,N'-tetraaryl-substituted 2,5-diaminothiophenes was prepared. The N,N'-tetrakis(4-bromophenyl)-2,5-diaminothiophene, thus available, was used as an educt for the synthesis of N,N'-tetrakis(4-diphenylaminophenyl)-2,5-diaminothiophene by reaction with four equivalents of diphenylamine in the presence of palladium as catalyst. Both the N,N'-tetrakis(4-diphenylaminophenyl)-2,5-diaminothiophenes and the N,N'-tetrakis(4-diphenylaminophenyl)-2,5-diaminothiophene can be electrochemically oxidised in a stepwise manner via the corresponding radical cations into relatively stable dications. The latter compounds can also be oxidised into tetracationic species.

**Key words:** amides, hiophenes, heterocycles, Lawesson's reagent, oxidation

*N*,*N*'-Peraryl-substituted 1,4-phenylenediamines and their phenylene homologues of type **A** have received a lot of interest because of their ability to form amorphous glasses in which the cationic species generated by oxidation have a high mobility. Such compounds can be used as hole transport materials, for example, for building optoelectronic devices, such as OFET,<sup>2</sup> OLED,<sup>3</sup> OSOL,<sup>4</sup> photocopiers,<sup>5</sup> and others. The same applies to the *N*,*N*'-perarylsubstituted 2,5-diaminothiophenes and their thienylene homologues **B**.<sup>6</sup> Similar to the carbocyclic compounds **A**, the heterocyclic analogues **B** have been prepared by heavy-metal catalysed C–N coupling reactions starting from diarylamines **3** and appropriate dihalo-arylenes **1** or 2,5-dihalothiophenes and homologues **2**, respectively (Scheme 1).<sup>7</sup>

In contrast to the preparation of the N,N'-peraryl-substituted 1,4-phenylenediamines and their homologues **A**, the N,N'-peraryl-substituted 2,5-diaminothiophene analogues **B** were frequently obtained in low yields by using such heavy-metal catalysed procedures;<sup>8</sup> clearly, undesirable deactivation of the catalysts by the sulphur-containing reactants occurred in these cases.

To overcome this disadvantage, we have searched for heavy-metal-free synthetic routes with which to prepare such sulphur-containing compounds. One of these routes, which allows N,N'-peraryl-substituted 5,5'-diamino-2,2'-bithienyles (**B**; n = 2) to be prepared in satisfactory yields, consists of an oxidative coupling reaction<sup>9</sup> of *N*-diaryl-

substituted 2-aminothiophenes, which are easily available by a heavy-metal-free heterocyclisation method starting from *N*-diaryl-substituted thioacetamides and haloketones.<sup>10</sup> Here, we report a simple synthetic route to *N*,*N*'peraryl-substituted 2,5-diaminothiophenes **6** (**B**; n = 1) that also avoids the use of heavy-metal catalysts.



Scheme 1

The first step of this new route is similar to the C–N coupling reactions mentioned above from diarylamines **3**, but these starting materials are transformed by reaction with succinic dichloride **4** into the corresponding *N*,*N'*-peraryl-substituted succinic diamides **5**, from which the target compounds **6** are available by reaction with Lawesson's reagent (LR)<sup>11</sup> according to the well-known Paal–Knorr procedure (Scheme 2).<sup>12</sup>

For the preparation of the N,N'-peraryl-substituted succinic diamides **5**, the interaction of one equivalent of succinic dichloride **4** with two equivalents of an appropriate diarylamine **3** in dioxane at reflux temperature, was successful. After cooling the reaction mixture, the precipitated N,N'-peraryl-substituted succinic diamides **5** could be isolated by suction, mostly in satisfactory yields. For the preparation of the N,N'-peraryl-substituted 2,5-diaminothio-phenes **6**, the reaction of succinic diamides **5** with the LR in either 1,4-dioxane or 1,2-dimethoxyethane proved to be successful. The reaction yields the 2,5-diaminothiophenes **6** in satisfactory yields, generally without the formation of detectable by-products. Unfortunately, little evidence for the mechanism of the reaction has, as yet, be gained, however, because thioamides are the usual reaction products

SYNTHESIS 2011, No. 20, pp 3375–3378 Advanced online publication: 18.08.2011 DOI: 10.1055/s-0030-1260178; Art ID: T47011SS © Georg Thieme Verlag Stuttgart · New York





of N,N-disubstituted amides with LR,<sup>11</sup> it can be assumed that the first reaction step involves the formation of the corresponding thioamides from the starting succinic diamides **5**. Such compounds can be transformed, when particular structural requirements are satisfied, into the appropriate N,N-disubstituted 2-aminothiophene derivatives.<sup>13</sup>

It is worth mentioning that the synthesis of the N,N'-tetrakis(4-diphenylaminophenyl)-substituted 2,5-diaminothiophene 7 from the corresponding N,N'-tetrakis(4diphenylaminophenyl)-substituted succinic diamide using the Paal–Knorr procedure was not efficient because the preparation of the necessary and commercially unavailable 4,4'-bis-(diphenylamino)diphenylamine starting material is performed on the corresponding carbamide derivative, which has to be transformed subsequently into the free amine.<sup>14</sup> Therefore, the synthetic route to 7 described in Scheme 3 seems to be the most effective alternative.

The structures of both the succinic diamides 5 and the N,N'-peraryl-substituted 2,5-diaminothiophenes 6 were



Scheme 3

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unambiguously confirmed from the analytic data. Thus, all the prepared compounds give the expected elemental analyses and mass spectra. In the <sup>1</sup>H NMR spectra of the N,N'-peraryl-substituted succinic diamides 5, characteristic signals at  $\delta = 4$  ppm and between 7–9 ppm were measured that could be assigned to the protons in the aliphatic methylene groups and in the aryl moieties, respectively. In the <sup>1</sup>H NMR spectra of the N,N'-peraryl-substituted 2,5diaminothiophenes **6**, characteristic singlets at  $\delta = 6$  ppm and multiplets between 7-9 ppm were detected that could be assigned to the protons at the 2,5-diaminothiophene moieties as well as at the N-linked aryl groups, respectively. In the <sup>1</sup>H NMR spectra of the N,N'-naphthyl-substituted succinic diamide 5d and the 2,5-diaminothiophenes 6c and 6d as well as in the spectra of the tetrahydroquinolylsubstituted compounds 5f and 6f certain signals of the aromatic protons appear as doublets or triplets indicating the existence of certain rotamers in the corresponding samples.

The *N*,*N*'-peraryl-substituted 2,5-diaminothiophenes **6**, thus prepared, are rather stable as solids under anaerobic conditions but are easily oxidised in solution. As demonstrated earlier<sup>7a</sup> and further documented by electrochemical measurements depicted in Table 1 and Figure 1, all *N*,*N*'-peraryl-substituted 2,5-diaminothiophenes **6** can be electrochemically oxidised to relatively stable radical cations **6**<sup>+</sup> and dications **6**<sup>2+</sup>. Remarkably, the *N*,*N*'-bis(2-naphthyl)-*N*,*N*'-diphenyl-2,5-diaminothiophene (**6d**) exhibits an additional irreversible peak at approximately 0.83 V, indicating a further oxidative transformation.

**Table 1**Electrochemical Data of the *N*,*N'*-Peraryl-Substituted 2,5-Diaminothiophenes 6 and 7

Compd.1st Ox [V]			2nd Ox [V]		3rd Ox [V]	
	$E_{1/2}{}^a$	E <sub>1/2</sub> (Fc) <sup>b</sup>	$E_{1/2}{}^a$	E <sub>1/2</sub> (Fc) <sup>b</sup>	$E_{1/2}{}^a$	E <sub>1/2</sub> (Fc)
6a	0.31	-0.07	0.74	0.36	-	-
6b	0.48	0.09	0.85	0.46	-	_
6c	0.34	-0.05	0.57	0.18	0.83°	0.42 <sup>c</sup>
6d	0.33	-0.04	0.71	0.34	-	-
6e	0.48	0.11	0.83	0.46	-	-
6f	0.26	-0.16	0.68	0.26	-	-
7	0.17	-0.24	0.40	0.00	1.02	0.62

<sup>a</sup> Measured vs. Ag/AgCl.

<sup>b</sup>  $E_{1/2}(Fc/Fc^+) = 0.40 \text{ V}.$ 

<sup>c</sup> Irreversible.

The N,N'-tetrakis(4-diphenylaminophenyl)-substituted 2,5-diaminothiophene **7**, which was obtained in satisfactory yield by reaction of the tetrabromo-compound **6b** with an excess of diphenylamine **3a** in the presence of Pd(OAc)<sub>2</sub> and P(*tert*-Bu)<sub>3</sub> as catalyst, could be electrochemically transformed in several well-separated steps



Figure 1 Cyclic voltammograms of some of the N,N'-persubstituted 2,5-diaminothiophenes 6 and 7

into the corresponding radical cation  $7^{+}$ , dication  $7^{2+}$ , and tetracation  $7^{4+}$  at 0.17, 0.40 and 1.02 V, respectively.

Further efforts to study the chemical nature and the electronic properties of the oxidised species of the N,N'-peraryl-substituted 2,5-diaminothiophenes 6 and 7 are in progress and will be reported later.

<sup>1</sup>H NMR spectra were recorded with a Bruker DRX 500 P instrument at 500.13 MHz. Elemental analyses were performed with a Eurovektor Hekatech EA-3000 elemental analyzer. Mass spectra were recorded in MeOH with a Bruker Esquire-LC 00084 instrument, operating at 10 V with electrospray ionisation. Melting points were measured with a Boetius heating-table microscope. Cyclic voltammetry was conducted with a Metrohm µ-Autolab potentiostat in a single-component cell under a nitrogen atmosphere. A typical three-electrode configuration was used with an inlaid platinum disk as working electrode, platinum wire as counter electrode, and a silver rod electrochemically coated with AgCl. Potentials were measured versus a Ag/AgCl electrode and referenced to ferrocene (Fc) as an internal standard. The measurements were performed with a scan rate of 100 mV  $\cdot s^{-1}$  in  $CH_2Cl_2$  under a nitrogen atmosphere and with tetra-n-butylammonium hexafluorophosphate (0.1 M) as electrolyte. No reduction peaks were observed between 0 and -2.3 V.

#### Preparation of N,N'-Tetrasubstituted Succinic Diamides 5; General Procedure

To a mixture of a diarylamine 3 (0.1 mol) and zinc chloride (0.27 g, 2 mmol) in dioxane (150 mL), succinyl dichloride 4 (7.75 g, 0.05 mol) was added dropwise and the resulting solution was heated at reflux for 4 h. The product precipitated by cooling was separated by suction and air-dried. Because the products, thus obtained, contained variable amounts of dioxane, analytical samples were typically recrystallised from toluene.

#### N,N'-Tetraphenyl-succinic Diamide (5a)

Yield: (80%); mp 233 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 2.58 (s, 4 H, CH<sub>2</sub>), 7.17–7.46 (m, 20 H, ArH).

Anal. Calcd for  $C_{28}H_{24}N_2O_2{:}$  C, 79.98; H, 5.75; N, 6.66. Found: C, 80.22; H, 5.82; N, 6.13.

#### *N,N*′-**Tetrakis(4-bromophenyl)succinic Diamide (5b)** Yield (78%); mp 230–232 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.52 (s, 4 H, CH<sub>2</sub>), 7.48 (m, 16 H, ArH).

Anal. Calcd for  $C_{28}H_{20}Br_4N_2O_2:$  C, 45.69; H, 2.74; Br, 43.42; N, 3.81. Found: C, 45.45; H, 2.50; Br, 43.70; N, 4.12.

# $N,\!N'\text{-Bis}(1\text{-naphthyl})\text{-}N,\!N'\text{-diphenyl-succinic Diamide (5c)}$ Yield (60%); mp 242–245 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.18–2.76 (m, 4 H, CH<sub>2</sub>), 7.17 (s, 2 H, ArH), 7.26–7.33 (m, 4 H, ArH), 7.44–7.49 (m, 12 H, ArH), 7.86–7.92 (m, 4 H, ArH), 8.04–8.12 (m, 2 H, ArH).

Anal. Calcd. for  $C_{36}H_{28}N_2O_2$ : C, 83.05; H, 5.42; N, 5.38. Found: C, 83.20; H, 5.12; N, 5.33.

#### *N,N*'-**Bis(2-naphthyl)**-*N,N*'-**diphenyl-succinic Diamide (5d)** Yield (68%); mp 250 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.65 (br s, 4 H, CH<sub>2</sub>), 6.95–7.12 (t, 2 H, ArH), 7.18–7.50 (m, 16 H, ArH), 7.62–7.65 (d, 2 H, ArH), 7.71–7.74 (d, 4 H, ArH).

Anal. Calcd for  $C_{36}H_{28}N_2O_2{:}$  C, 83.05; H, 5.42; N, 5.38. Found: C, 83.27; H, 5.04; N, 5.00.

#### **1,4-Bis**(*N*-**phenothiazinyl**)**butane-1,4-dione (5e)** Yield (75%); mp 286 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.50 (s, 2 H, CH<sub>2</sub>), 2.78 (br s, 2 H, CH<sub>2</sub>), 7.17–7.22 (m, 4 H, ArH), 7.27–7.32 (m, 4 H, ArH), 7.40 (d, J = 10.0 Hz, 4 H, ArH), 7.56 (d, J = 10.4 Hz, 4 H, ArH).

Anal. Calcd for  $C_{28}H_{20}N_2O_2S_2$ : C, 69.97; H, 4.19; N, 5.83; S, 13.34. Found: C, 70.14; H, 4.06; N, 6.11; S, 13.84.

#### **1,4-Bis**(*N***-tetrahydroquinolyl)butane-1,4-dione** (5f) Yield (82%); mp 77 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 1.94 (m, 4 H, CH<sub>2</sub>), 2.70 (t, 4 H, CH<sub>2</sub>), 2.84 (s, 4 H, CH<sub>2</sub>), 3.77 (t, 4 H, CH<sub>2</sub>), 7.13 (m, 8 H, ArH).

Anal. Calcd for  $C_{22}H_{24}N_2O_2{:}$  C, 75.83; H, 6.94; N, 8.04. Found: C, 76.05; H, 7.11; N, 8.24.

# Preparation of N,N'-Tetrasubstituted 2,5-Diaminothiophenes 6; General Procedure

A mixture of appropriate N,N'-tetraaryl-substituted succinic diamide **5** (0.1 mol) and Lawesson's reagent (50 g, 0.12 mol) in either dioxane or 1,2-dimethoxyethane (250 mL) was heated at reflux under stirring for 24 h. After cooling, the reaction mixture was neutralised by addition of aqueous NaOH (10%) under stirring, and the precipitated products were isolated by suction, washed with water and air-dried.

#### *N,N'*-Tetraphenyl-2,5-diaminothiophene (6a) from 5a

Yield (70%); mp 148 °C (Lit.<sup>7b</sup> 144–145 °C).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.44 (s, 2 H, CH<sub>th</sub>), 6.9–7.02 (m, 4 H, ArH), 7.14–7.26 (m, 8 H, ArH), 7.25–7.30 (m, 8 H, ArH).

MS (ESI, 70 eV): m/z calcd for C<sub>28</sub>H<sub>22</sub>N<sub>2</sub>S: 418.55; found: 419.2.

Anal. Calcd for  $C_{28}H_{22}N_2S$ : C, 80.35; H, 5.30; N, 6.69; S, 7.66. Found: C, 80.63; H, 5.18; N, 7.02; S, 7.50.

### *N*,*N*'-Tetrakis(4-bromophenyl)-2,5-diaminothiophene (6b) from 5b

Yield (78%); mp 142–145 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.46 (s, 2 H, CH<sub>th</sub>), 6.99 (d, *J* = 8.9 Hz, 8 H, ArH), 7.36 (d, *J* = 8.9 Hz, 8 H, ArH).

MS (ESI, 70 eV): m/z calcd for  $C_{28}H_{18}Br_4N_2S$ : 734.14; found: 734.8.

Anal. Calcd for  $C_{28}H_{18}Br_4N_2S$ : C, 45.81; H, 2.47; Br, 43.54; N, 3.82; S, 4.37. Found: C, 46.02; H, 2.50; Br, 44.24; N, 3.71; S, 4.84.

## *N*,*N*′-Bis(1-naphthyl)-*N*,*N*′-diphenyl-2,5-diaminothiophene (6c) from 5c

Yield (72%); mp 173 °C (Lit.7b 120-125 °C).

 $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.73 (d, 2 H, CH\_th), 6.84 (t, 2 H, ArH), 6.87–6.92 (m, 6 H, ArH), 7.17 (t, 2 H, ArH), 7.43 (t, 2 H, ArH), 7.47–7.51 (m, 6 H, ArH), 7.80 (d, 2 H, ArH), 7.90 (d, 2 H, ArH), 8.04 (d, 2 H, ArH).

MS (ESI, 70 eV): m/z calcd for  $C_{36}H_{26}N_2S$ : 518.67; found: 519.2.

Anal. Calcd for  $C_{36}H_{26}N_2S$ : C, 83.36; H, 5.05; N, 5.40; S, 6.18. Found: C, 83.12; H, 4.89; N, 5.85; S, 6.26.

# $N,\!N'\text{-}\mathsf{Bis}(2\text{-}\mathsf{naphthyl})\text{-}N,\!N'\text{-}\mathsf{diphenyl-}2,\!5\text{-}\mathsf{diaminothiophene}\,(\mathsf{6d})$ from 5d

Yield (66%); mp 119 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.41 (d, *J* = 10.0 Hz, 2 H, CH<sub>th</sub>), 6.85 (t, *J* = 10.0 Hz, 2 H, ArH), 7.05 (t, *J* = 9.5 Hz, 4 H, ArH), 7.14–7.16 (m, 4 H, ArH), 7.24–7.27 (m, 4 H, ArH), 7.35–7.41 (m, 4 H, ArH), 7.47 (br s, 2 H, ArH), 7.49–7.54 (m, 2 H, ArH), 7.64 (br s, 2 H, ArH).

MS (ESI, 70 eV): m/z calcd for  $C_{36}H_{26}N_2S$ : 518.67; found: 519.3.

Anal. Calcd for  $C_{36}H_{26}N_2S$ : C, 83.36; H, 5.05; N, 5.40; S, 6.18. Found: C, 82.96; H, 5.00; N, 5.27; S, 6.38.

#### 2,5-Bis(N-phenothiazyl)thiophene (6e) from 5e

Yield (97%); mp 215 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.90 (dd, *J* = 8.2, 0.9 Hz, 4 H, ArH), 6.94 (dt, *J* = 8.6, 1.1 Hz, 4 H, ArH), 7.07 (s, 2 H, CH<sub>th</sub>), 7.06 (m, 4 H, ArH), 7.10 (dd, *J* = 7.6, 1.3 Hz, 4 H, ArH).

MS (ESI, 70 eV): m/z calcd for  $C_{28}H_{18}N_2S_3$ : 478.65; found: 481.1.

Anal. Calcd for  $C_{28}H_{18}N_2S_3$ : C, 70.26; H, 3.79; N, 5.85; S, 20.10. Found: C, 70.02; H, 4.03; N, 6.12; S, 20.56.

#### 2,5-Bis(N-tetrahydroquinolyl)thiophene (6f) from 5f

Yield (82%); mp 111-113 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.08 (m, 4 H, CH<sub>2</sub>), 2.85 (t, *J* = 6.3 Hz, 4 H, CH<sub>2</sub>), 3.64 (t, *J* = 5.6 Hz, 4 H, CH<sub>2</sub>), 6.59 (s, 2 H, CH<sub>th</sub>), 6.73 (t, 2 H, ArH), 6.88 (d, 2 H, ArH), 7.02 (m, 4 H, ArH).

MS (ESI, 70 eV): m/z calcd for  $C_{22}H_{22}N_2S$ : 346.49; found: 347.2. Anal. Calcd for  $C_{22}H_{22}N_2S$ : C, 76.26; H, 6.40; N, 8.08; S, 9.25. Found: C, 76.00; H, 6.40; N, 8.00; S, 9.00.

#### Preparation of *N*,*N*,*N*',*N*'-[Tetrakis(4-diphenylamino)phenyl]thiophene-2,5-diamine (7)

To an argon-degassed solution of N,N,N',N'-tetrakis(4-bromophenyl)-2,5-diaminothiophene (**6b**; 3.67 g, 0.05 mol) and diphenylamine (**3a**; 3.72 g, 0.022 mol) in *p*-xylene (50 mL), palladium diacetate (22.45 mg, 0.001 mol), tri-*tert*-butylphosphine in xylene (27%, 0.001 mol, 0.82 mL), and sodium *tert*-butylate (2.4 g, 0.025 mol) were successively added and the resulting mixture was heated at reflux for 15 min. After cooling to r.t., the mixture was diluted with MeOH (200 mL) and stirred for 30 min. The precipitated product was filtrated, washed with MeOH (100 mL) and dried.

Yield (96%); mp 229–234 °C.

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 6.46 (s, 2 H, CH<sub>th</sub>), 6.87 (t, *J* = 7.3 Hz, 8 H, ArH), 7.01 (d, *J* = 8.9 Hz, 8 H, ArH), 7.08 (m, 16 H, ArH), 7.14 (d, *J* = 8.9 Hz, 8 H, ArH), 7.24 (m, 16 H, ArH).

MS (ESI, 70 eV): *m/z* calcd for C<sub>76</sub>H<sub>58</sub>N<sub>6</sub>S: 1087.38; found: 1087.7.

Anal. Calcd for  $C_{76}H_{58}N_6S$ : C, 83.95; H, 5.38; N, 7.73; S, 2.95. Found: C, 84.00; H, 5.00; N, 7.73; S, 3.00.

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