# Synthesis and Characterization of Some Heterocyclic Analogues of *N*,*N*'-Perarylated Phenylene-1,4-diamines and Benzidines as a New Class of Hole Transport Materials

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Received 5 March 2002

Abstract: Starting from N,N-diarylsubstituted thioureas **20** and thioacetamides **21** a series of heterocyclic analogous of N,N'-perarylated phenylene-1,4-diamines and benzidines was obtained. These compounds represent, as studied by DSC measurements, a new class of hole transporting materials with high thermal stability and high tendency to form stable amorphous states. Moreover, some of the new compounds are, as measured by cyclic voltammetry, easily reversibly oxidized indicating the formation of persistent radical ions. Such compounds, which are, in general, completely substituted by aryl groups at their heterocyclic moieties, have been successfully used as hole-transport materials in OLEDs.

**Key words:** heterocyclization, hole transport materials, *N*-perarylated 2-aminothiophenes, *N*-perarylated 2-aminothiazoles

Because of their electrical properties N,N',N''-perarylated 1,3,5-triaminobenzene of the so-called starburst series<sup>1</sup> and N,N'-perarylated phenylene-1,4-diamines **9**<sup>2</sup> and benzidines **10**<sup>3</sup> are of interest for organic light-emitting diodes (OLEDs),<sup>4</sup> organic field-effect transistors,<sup>5</sup> organic solar cells,<sup>6</sup> or organic recording and storage media.<sup>7</sup>



#### Scheme 1

For all applications materials with excellent glass-forming tendency and easy formation of radical ions are advantageous. Both properties correlate to the molecular structure. Thus, the glass-forming tendency can be increased by increasing the number of conformers.<sup>8</sup> In this respect substituted aryl moieties, such as *m*-tolyl or naphthyl, were used. Usually, these moieties were introduced in the core of the molecule during synthesis, which usually requires catalysis by heavy metals. Thus, the *N*,*N*'-perarylated 1,4-phenylene-1,4-diamines **9** and benzidines **10** (Scheme 1) were prepared, e.g., from substituted aryl halides **1** and *N*,*N*'-diaryl-substituted phenylene-1,4-diamines **3** or benzidines **4** or, alternatively, from diarylamines **2** and 1,4-dihalobenzenes **5** or 4,4'-dihalobiphenyls **6** by means of a C–N coupling reaction accomplished by copper<sup>9</sup> or palladium<sup>10</sup> catalysts.

Another concept favoring the amorphous state consists in replacing aryl or phenylene groups in compounds **9** and **10** by heterocyclic moieties, such as thienyl or thienylene. Thus, *N*,*N*'-perarylated 2,5-diaminothiophenes **11**<sup>11</sup> and 5,5'-diamino-2,2'-bithiophenes **12**<sup>12</sup> as heterocyclic analogues of the 1,4-phenylenediamines **9** and benzidines **10** were prepared from diarylamines **2** and 2,5-dibromothiophene (**7**) or 5,5'-dibromo-2,2'-bithiophene (**8**) using palladium catalysts.

Although metal-catalyzed coupling reactions reach, in common, high yields they lack from residual metal impurities. This is detrimental to electric and optical properties. Purification is an urgent need but a time and cost consuming procedure.

Therefore a simple heavy metal-free synthesis for N,N'perarylated diamines 9 and 10 or their heterocyclic analogues **11** and **12** is highly favoured. Although such routes for the carbocyclic compounds 9–10 are not in sight today we will present a simple route to several derivatives of their heterocyclic sulphur analogues. This route allows the synthesis of thiophene analogues 11 and 12 of the phenylene-1,4-diamine and benzidine derivatives 9 and 10, as well as the synthesis of hitherto unknown thiazole analogues. The route is based on well-known methods for preparing amino-substituted thiophenes and thiazoles by heterocyclization procedures and requires dedicated educts, such as halomethyl ketones, like the compounds 13–15, as well as N-diarylamines and N,N'-(diaryl)diamines of the general structure 2-4. Whereas the amines 2, 3 and 4 used are commercially available, the halomethyl ketones 13–15 have to be synthesized, as far as possible from commercially available, simple halo-free precursors.

Synthesis 2002, No. 9, 01 07 2002. Article Identifier: 1437-210X,E;2002,0,09,1268,1276,ftx,en;C11102SS.pdf. © Georg Thieme Verlag Stuttgart · New York ISSN 0039-7881

Thus, the dibromodiketones 14 and 15 were prepared from 1,2-dibenzoylethylene or 1,4-diacetylbenzene, respectively, by reaction with elemental bromine in acetic acid.<sup>13</sup>





Products were obtained as depicted in Scheme 2. Thus, the diarylamines 2 were allowed to react with pivaloylisothiocyanate 16, simply prepared in situ from pivaloyl chloride and potassium rhodanide. This reaction gave rise to the formation of intermediate *N*-pivaloylthioureas **18** from which the *N*-diarylthioureas **20** were obtained by reaction with concentrated aqueous hydrochloric acid. The subsequent reaction of these thioureas **20** with the bromoketones **13–15** (Figure 1), performed in ethanol, DMF, or acetic anhydride, yields *N*-disubstituted 2-aminothiazoles **22** as well as bisthiazoles **23** and **24**, respectively.

By an analogous sequence, the reaction of the diarylamines 2 with acetyl chlorides of the general structure 17 gave rise to the formation of *N*-diarylsubstituted acetamides 19. These compounds were transformed by reaction with  $P_2S_5$  or Lawesson's reagent to their corresponding *N*diarylsubstituted thioacetamides 21 and, subsequently, into corresponding bithiophenes 25 and 26 as well as into *N*-disubstituted 2-aminothiophenes 27 by reaction with the bromoketones 13–15. The last step of this reaction sequence was performed in ethanol, DMF, or acetic anhydride and has a strong analogy to the simple Hantzsch



Scheme 2

Synthesis 2002, No. 9, 1268–1276  $\,$  ISSN 0039-7881  $\,$  © Thieme Stuttgart  $\cdot$  New York

route for the synthesis of thiazoles.<sup>14</sup> This method was applied for the time by us for the synthesis of *N*-dialkylsubstituted 2-aminothiophenes more than four decades ago.<sup>15</sup>

By means of these procedures the *N*-diaryl-substituted 2aminothiazoles **22** and 2-aminothiophenes **27** as well as the *N*,*N*'-peraryl-substituted 2,2'-diamino-5,5'-bithiazoles **23**, 5,5'-diamino-2,2'-bithiophenes **26**, 1,4-bis[(2-amino-1,3-thiazol)-4-yl]benzenes **24** and 1,4-bis(2-amino-thien-4-yl)benzenes **25** have been prepared.

A similar reaction sequence can be used for the synthesis of the heterocyclic compounds **38–41**. As starting materials, besides the bromo compounds **13-15**, the *N*,*N*'-diphenyl-substituted diamines **28** and **29** were used which are commercially available. They were allowed to react first with pivaloylisothiocyanate (**16**) or with acetyl chlorides **17**. From the expected compounds **30–33** the bis-(*N*-pivaloyl)-substituted bis-thiourea **30** as well as the bis-aceta-mides **32** and **33** were obtained only (see Table 1). The bis-(*N*-pivaloyl)-substituted bis-thiourea **31** was not formed, however, so that the corresponding consecutive products **35** and **39** could not be obtained until now. Prob-

ably, the low solubility of the N,N'-diphenylbenzidine (29) in the solvents used prevents the reaction with pivaloylisothiocyanate (16).

From the compounds **30**, **32**, and **33** the bis-thioureas **34** (Scheme 3) as well as the bis-thioacetamide derivatives **36** and **37** were obtained in the same way as described above. Their transformation into the bis-thiazoles **38** and the bis-thiophenes **40** and **41** was performed by reaction with the bromoketones **13** in DMF at reflux temperature.

Due to the *N*-bound aryl groups the solubility of the products obtained is high enough in most polar organic solvents that, in general, the synthesis can be performed without difficulties.

The structure of the compounds prepared was confirmed by means of elemental analyses and spectroscopic data. Thus, in the mass spectra all compounds exhibit an intense peak for the molecular ion  $M^+$  or for the  $MH^+$  ion. Although in the <sup>1</sup>H and <sup>13</sup>C NMR spectra, as seen from the data collected in Table 1, only less characteristic signals can be detected, their positions and intensities are in agreement with the predicted structure.



Scheme 3

 Table 1
 NMR Spectroscopic Data of the Heteroaromatic Compounds Prepared

Com- pound	Ar <sup>1</sup>	Ar <sup>2</sup>	R <sup>3</sup>	$\mathbb{R}^4$	<b>R</b> <sup>5</sup>	<sup>1</sup> H NMR (CDCl <sub>3</sub> ), $\delta$ [ppm]	<sup>13</sup> C NMR (CDCl <sub>3</sub> ), $\delta$ [ppm]		
22a	Phenyl	Phenyl	-	Phenyl	Н	6.86 (s, 1 H, hetarom.), 7.20–7.28 (m, 4 H, arom.), 7.33–7.45 (m, 9 H, arom.), 7.81 (d, 2 H, arom.)	126.7, 126.8, 127.2, 128.8, 129.6, 130.6, 134.5, 135.9, 146.3, 152.8, 169.7		
22b	Phenyl	Phenyl	-	Phenyl	Phenyl	7.19–7.28 (m, 10 H, arom.), 7.37 (t, 4 H, arom.), 7.43–7.47 (m, 4 H, arom.), 7.50 (dd, 2 H, arom.)	124.2, 125.6, 127.7, 127.3, 127.4, 128.0, 128.5, 128.9, 129.4, 129.5, 132.5, 135.2, 145.0, 145.9, 166.1		
23	Phenyl	Phenyl	-	Phenyl	-	7.21 (d, 8 H, arom.), 7.32–7.42 (m, 18 H, arom.), 7.68 (m, 4 H, arom.)	113.8, 126.9, 128.8, 129.2, 129.3, 129.4, 130.6, 135.6, 141.7, 145.8 150.8		
24	Phenyl	Phenyl	-	-	Phenyl	6.86 (s, 2 H, arom.), 7.22 (t, 4 H, arom.), 7.36–7.45 (m, 16 H, arom.), 7.82 (s, 4 H, arom.)	105.4, 126.8, 126.9, 127.3, 130.6, 135.2, 146.3, 152.6, 169.7		

Com- pound	Ar <sup>1</sup>	Ar <sup>2</sup>	<b>R</b> <sup>3</sup>	$\mathbb{R}^4$	<b>R</b> <sup>5</sup>	<sup>1</sup> H NMR (CDCl <sub>3</sub> ), δ [ppm]	<sup>13</sup> C NMR (CDCl <sub>3</sub> ), δ [ppm]		
25	Phenyl	Phenyl	Phenyl	-	Н	6.83–6.90 (m, 8 H, arom.), 6.92 (s, 2 H, hetarom.), 6.91–7.04 (m, 16 H, arom.), 7.08–7.13 (m, 10 H, arom.)	119.4, 121.5, 122.1, 126.7, 127.7, 128.3, 128.7, 129.7, 134.7, 135.1, 137.1, 141.0, 146.0, 147.3		
26	Phenyl	Phenyl	Phenyl	Phenyl	-	6.78 (d, 4 H, arom.), 6.84–6.96 (m, 18 H, arom.), 7.02–7.15 (m, 16 H, arom.), 7.24 (t, 2 H, arom.)	121.5, 122.1, 126.5, 126.6, 127.4, 127.8, 128.7, 128.8, 129.7, 130.6, 134.7, 135.4, 137.9, 140.9, 145.7, 147.0		
27a	Phenyl	Phenyl	Phenyl	Phenyl	Н	6.92 (s, 1 H, hetarom.), 6.90–6.94 (m, 4 H, arom.), 6.98–7.08 (m, 6 H, arom.), 7.15–7.21 (m, 10 H, arom.)	120.8, 122.7, 123.3, 127.9, 127.8, 128.9, 129.1, 129.8, 130.0, 130.9, 136.0, 138.0, 138.4, 142.6, 147.3, 148.6		
27b	Phenyl	Phenyl	Phenyl	Phenyl	Phenyl	6.83 (d, 2 H, arom.), 6.89–7.00 (m, 6 H, arom.), 7.03–7.10 (m, 6 H, arom.), 7.13–7.24 (m, 9 H, arom.), 7.30–7.37 (m, 4 H, arom.), 7.60 (t, 2 H, arom.), 7.69 (d, 1 H, arom.)	122.5, 123.0, 127.2, 127.3, 127.8, 128.1, 128.5, 129.1, 129.5, 130.0, 130.5, 131.6, 135.1, 135.8, 136.4, 136.9, 137.9, 140.1, 145.1, 148.1		
27c	Phenyl	1-Naphthyl	Phenyl	Phenyl	Н	6.77 (d, 2 H, arom.), 6.83 (t, 1 H, arom.), 6.87–6.99 (m, 4 H, arom.; 1 H, hetarom.), 7.06–7.16 (m, 10 H, arom.), 7.28–7.35 (m, 2 H, arom.), 7.54 (d, 1 H, arom.), 7.62 (d, 1 H, arom.), 7.73 (d, 1 H, arom.)	118.9, 120.1, 121.3, 125.5, 126.6, 126.7, 126.8, 127.0, 127.5, 127.6, 127.8, 128.9, 129.0, 129.1, 129.8, 129.9, 131.1, 131.2, 135.9, 136.3, 137.8, 138.0, 142.6, 143,8, 148.4, 151.3		
27d	Phenyl	2-Naphthyl	Phenyl	Phenyl	Phenyl	6.88–7.00 (m, 2 H, arom.), 7.03–7.14 (m, 8 H, arom.), 7.18–7.27 (m, 9 H, arom.), 7.29–7.43 (m, 4 H, arom.), 7.64 (t, 2 H, arom.), 7.73 (d, 2 H, arom.)	118.6, 122.7, 122.9, 123.2, 125.0, 126.9, 127.2, 127.4, 127.7, 127.9, 128.1, 128.2, 128.6, 128.9, 129.2, 129.6, 130.0, 130.4, 130.5, 131.6, 134.9, 135.1, 135.8, 136.5, 136.8, 138.0, 140.2, 145.0, 145.8, 148.0		
38	-	-	-	Phenyl	Phenyl	7.23 (d, 4 H, arom.), 7.27–7.31 (m, 6 H, arom.), 7.32–7.42 (m, 8 H, arom.), 7.45– 7.48 (m, 4 H, arom.), 7.55 (d, 4 H, arom.), 7.60 (s, 4 H, arom.), 7.61 (t, 4 H, arom.) <sup>a</sup>	124.0, 125.6, 126.8, 127.3, 128.0, 128.4, 128.8, 129.4, 129.5, 130.6, 132.3, 135.3,141.7, 144.6, 145.9, 162.3, 165.7 <sup>a</sup>		
40a	-	-	Phenyl	Phenyl	Н	6.66 (s, 4 H, arom.), 6.83–6.90 (m, 8 H, arom.; 2 H, hetarom.), 6.98–7.06 (m, 6 H, arom.), 7.09–7.19 (m, 16 H, arom.)	119.3, 120.0, 121.3, 123.8, 126.8, 126.9, 127.9, 128.1, 128.8, 130.0, 135.1, 136.8, 136.9, 141.6, 142.1, 146.8, 148.2		
40b	-	-	Phenyl	Phenyl	Phenyl	6.73 (s, 4 arom. H), 6.81 (d, 4 arom. H), 6.86 (t, 2 arom. H), 6.93–7.00 (m, 12 arom. H), 7.04–7.19, (m, 22 arom. H)	120.1, 121.3, 123.8, 126.5, 126.9, 127.2,127.5, 127.7, 128.2, 128.8, 129.4, 129.8, 130.9, 134.5, 135.3, 136.1, 137.1, 138.8, 142.0, 144.5, 148.0		
41a	-	-	Phenyl	Phenyl	Н	6.85–6.98 (m, 12 H, arom.; 2 H, hetarom.), 7.02–7.12 (m, 10 H, arom.), 7.14–7.26 (m, 14 H, arom.), 7.19 (t, 2 H, arom.)	120.4, 124.6, 128.3, 129.4, 136.0, 138.9, 146.1, 151.3		
41b	-	-	Phenyl	Phenyl	Phenyl	6.83 (d, 4 H, arom.), 6.90 (t, 4 H, arom.) 6.94–6.98 (m, 8 H, arom.), 7.01 (t, 2 H, arom.), 7.03–7.10 (m, 12 H, arom.), 7.12– 7.21 (m, 14 H, arom.), 7.32 (d, 4 H, arom.)	121.8. 122.0, 122.5, 126.6, 126.7, 127.0, 127.2, 127.6, 127.9, 128.3, 128.9, 129.4, 129.9, 131.0, 134.5, 134.6, 135.2, 135.8, 136.3, 137.3, 139.6, 144.3, 146.5, 147.3		

 Table 1
 NMR Spectroscopic Data of the Heteroaromatic Compounds Prepared (continued)

<sup>a</sup> In HMPT- $d_{18}$ .

DSC was used to investigate the tendency of the new materials to form the amorphous state. These data are compiled in Table 2. The glass transition temperatures  $T_g$ s, the

melting temperatures  $T_{\rm ms}$ , and the decomposition temperatures  $T_d$ s were measured under nitrogen atmosphere with a heating rate of 5 K min<sup>-1</sup>.

Table 2 Characteristic Substance Data of Some of the Compounds Prepared

Com- pound	Ar <sup>1</sup>	Ar <sup>2</sup>	<b>R</b> <sup>3</sup>	$\mathbb{R}^4$	<b>R</b> <sup>5</sup>	$T_{\rm m}^{\ a}$	$T_{\rm d}{}^{\rm a}$	$T_{\rm g}{}^{\rm a}$	Type <sup>b</sup>	E <sub>ox</sub> [V] <sup>c</sup>	Molecular Formula	EIMS [ <i>m</i> / <i>z</i> (%)]
22b	Phenyl	Phenyl	-	Phenyl	Phenyl	223	268	-	А	1.14 (ir)	$C_{27}H_{20}N_2S$	405.4 (MH+, 100)
23	Phenyl	Phenyl	-	Phenyl	-	232	391	72	В	0.95 (qr), 1.00 (qr)	$C_{42}H_{30}N_{4}S_{2}$	655.4 (MH+, 100)
24	Phenyl	Phenyl	-	-	Phenyl	279	386	65	В	1.03 (qr)	$C_{36}H_{26}N_4S_2$	579.4 (MH+, 100)
25	Phenyl	Phenyl	Phenyl	-	Phenyl	241	384	82	В	1.05 (qr)	$C_{50}H_{36}N_2S_2$	728.5 (M <sup>+</sup> , 100)
26	Phenyl	Phenyl	Phenyl	Phenyl	-	262	368	87	В	0.64 (r)	$C_{56}H_{40}N_2S_2$	804.5 (M <sup>+</sup> , 100)
27a	Phenyl	Phenyl	Phenyl	Phenyl	Н	102	230	20	С	1.00 (ir)	$C_{26}H_{21}NS$	404.3 (MH+, 100)
27b	Phenyl	Phenyl	Phenyl	Phenyl	Phenyl	120	434	57	В	0.95 (r)	C <sub>34</sub> H <sub>25</sub> NS	479.3 (MH+, 100)
27c	Phenyl	1-Naphthyl	Phenyl	Phenyl	Н	64	252	51	С	1.10 (ir)	C <sub>32</sub> H <sub>23</sub> NS	454.4 (MH+, 100)
27d	Phenyl	2-Naphthyl	Phenyl	Phenyl	Phenyl	198	330	61	В	0.73 (r)	C <sub>38</sub> H <sub>27</sub> NS	529.4 (MH+, 100)
38	-	-	-	Phenyl	Phenyl	302	418	91	В	1.01(r), 1.23 (qr)	$C_{48}H_{34}N_{4}S_{2} \\$	731.4 (MH+, 100)
40a	-	-	Phenyl	Phenyl	Н	263	283	83	В	0.75(qr), 1.13 (qr))	$C_{50}H_{36}N_2S_2$	728.3 (M <sup>+</sup> , 100)
40b	-	-	Phenyl	Phenyl	Phenyl	317	410	118	В	0.75 (r), 1.07 (r)	$C_{62}H_{44}N_2S_2$	880.5 (M <sup>+</sup> , 100)
41b	-	-	Phenyl	Phenyl	phenyl	276	431	114	В	0.94 (qr)	$C_{68}H_{48}N_2S_2$	956.5 (M <sup>+</sup> , 100)

<sup>a</sup>  $T_{\rm m}$ : melting point,  $T_{\rm d}$ : decomposition point,  $T_{\rm g}$ : glass transition point, all data in °C.

<sup>b</sup> Type A: recrystallization at cooling, type B: no crystallization at cooling, recrystallization above Tg, type C: no crystallization at cooling, no crystallization above  $T_g$ .

<sup>c</sup> ir: irreversible potential; pr: quasi-reversible potential; r: reversible potential.

In order to prove that the observed  $T_g$ s are real glass transition temperatures and not originating from other relaxation processes, the measurements were repeated several times and corresponding transition energies were estimated. They were generally in the range of 0.2-0.3 J g<sup>-1</sup> K<sup>-1</sup>.

As it can be seen from Table 2, melting temperatures  $T_{\rm m}$  and decomposition temperatures  $T_{\rm d}$  depend, similarly as the decomposition temperatures  $T_{\rm g}$ , significantly on the substitution pattern at the heterocyclic moiety. Besides compound **22b**, all other compounds studied are able to attain the amorphous state after cooling the melt. In some cases, the obtained glasses are rather stable and do not recrystallize even after repeated heating beyond glass transition temperature (Type B). In some cases, however, some glasses recrystallize during the heating procedure (Type C). Compounds of type B are expected to be good candidates for electrical conducting materials.

All the compounds studied exhibit, as measured by cyclic voltammetry and exemplified with to compounds in Figure 2, low oxidation potentials, but not all potentials are reversible. This means, that under the conditions applied the radical cations formed are not very stable. As demonstrated in a forthcoming paper in detail, such radical ions give rise to the formation of the corresponding dimers.



Figure 2 Cyclic voltammograms of compound 27b (a) and 26a (b), measured in acetonitrile/ $Bu_4PF_6/Pt$  versus SCE

Synthesis 2002, No. 9, 1268-1276 ISSN 0039-7881 © Thieme Stuttgart · New York

The compounds, which exhibit reversible oxidation potentials, were investigated as hole transport materials in organic luminescence diodes. Such compounds are, in general, aryl substituted at their thiophene 5-position.

The diodes were manufactured by vacuum-evaporation on an ITO-coated glass substrate. The effectiveness of the hole transport ability of the compounds studied was estimated by measuring the luminescence quantum yield of Alq<sub>3</sub> as function of the voltage applied. The results obtained were compared to OLEDs manufactured with standard transport materials such as 1-Naphdata or  $\alpha$ -NPD.<sup>16</sup> The data which will be published in detail in a forthcoming paper,<sup>17</sup> demonstrate that an OLED in which both the standard materials were substituted by, e.g., the compounds **40b** and **41b** exhibit nearly the same or a slight better luminance efficiency as an OLED manufactured with standard materials.

Hence, the *N*-perarylated 2-aminothiophenes and 2-aminothiazoles of the structure **23–26** and **38–41**, easily available by a Hantzsch-type reaction from mono- or bifunctional *N*,*N*-diarylsubstituted thioureas or thioacetamides and  $\alpha$ -haloketones, represent a new class of easily oxidizable compounds with a high tendency to form amorphous glasses in which the charged species formed by electrochemical oxidation exhibit a high mobility giving rise to high quantum yields of the Alq<sub>3</sub> luminescence.

The following apparatus and analytical techniques were used: Melting points: Boetius hot-stage microscope, corrected, IR: Philips FTIR spectrometer PU 9624 (in potassium bromide pellets), NMR: Varian 300 MHz spectrometer Gemini 300 or JEOL 200 MHz spectrometer JNM FX 200, Elemental analysis data: LECO analyzer CHNS 932, MS: AMO spectrometer 402 (70 eV, EI), Cyclic voltammetry: Autolab instrument PGSTAT 20, The measurements were performed under argon in MeCN containing 0.1 M Bu<sub>4</sub>PF<sub>6</sub> as supporting electrolyte with a scan rate of 0.1 V s<sup>-1</sup> using a platinum working electrode, a platinum counter electrode and, a sat. Calomel reference electrode, Mass spectra: ESI, LCQ, Finnigan MAT, DTA/TGA: STA 1500, Polymer Laboratories, U.S.A, DSC: Netzsch DSC 200.

#### 1,2-Dibenzoyl-1,2-dibromoethane (14)

To a 10 °C cooled soln of 1,2-dibenzoylethene (0.01 mol, 23.6 g) in HOAc (150 mL), bromine (0.01 mol, 18 g) was added dropwise with stirring. After 30 min, the mixture was poured into ice-water, the precipitated product was isolated by suction and recrystallized from EtOH.

Yield 25.8 g (65%).

Mp 178 °C (Lit.18 178 °C).

#### 1,4-Bis-(bromoacetyl)benzene (15)

By analogy to the previous procedure 1,4-diacetylbenzene (0.01 mol, 16.2 g) was allowed to react with  $Br_2$  (0.02 mol, 32.0 g). The product was obtained in a yield of 21.8 g (68%).

Mp 168 °C (Lit.19 173 °C).

#### 2,N,N-Triaryl-substituted Acetamides 19; General Procedure

To a stirred soln of a diarylamine 2 (0.1 mol) in anhyd dioxane (200 mL), in a three-necked flask fitted with dropping-funnel, refluxcondenser and an inlet for nitrogen, phenacetylchloride [(17), (0.2 mol, 30.8 g)] was added dropwise at r.t. Then, the mixture was refluxed until the generation of HCl decreased. After cooling, the mixture was poured in ice-water (1 L), the product precipitated was isolated by suction and recrystallized from EtOH. The following products were obtained:

## 2,N,N-Triphenylacetamide (19a)

Compound **19a** has been synthesized according to the general procedure from diphenylamine (**2a**) and phenacetylchloride (**17a**) in a yield of 44.8 g (78%).

Mp 71–72 °C (Lit.<sup>20</sup> 72 °C).

 $^1H$  NMR (CDCl\_3):  $\delta$  = 3.55 (s, 2 H, CH\_2), 7.09 (d, 2 H, CH), 7.17–7.42 (m, 13 H, CH).

## N-Phenyl-N-phenacetyl-1-naphthylamine (19b)

Compound **19b** has been synthesized according to the general procedure from 1-(*N*-phenyl)naphthylamine (**2b**) and phenacetylchloride (**17a**) in a yield of 28.0 g (83%).

Mp 85-88 °C.

 $^1H$  NMR (CDCl\_3):  $\delta$  = 3.50 (s, 2 H, CH\_2), 6.96 (m, 2 H, CH), 7.11– 7.35 (m, 9 H, CH), 7.43- 5.53 (m, 3 H, CH), 7.80-7.87 (m, 3 H, CH).

## *N*-Phenyl-*N*-phenacetyl-2-naphthylamine (19c)

Compound **19c** has been synthesized according to the general procedure from 2-(*N*-phenyl)naphthylamine (**2c**) and phenacetylchloride (**17a**) in a yield of 28.0 g (83%).

Mp 129-130 °C.

<sup>1</sup>H NMR (CD<sub>3</sub>CN): δ = 3.68 (s, 2 H, CH<sub>2</sub>), 7.13–7.16 (m, 2 ArH), 7.22-7.31 (m, 4 ArH), 7.35–7.44 (m, 5 ArH), 7.31 (q, 2 ArH), 7.78–7.83 (m, 2 ArH), 7.86-7.89 (m, 2 ArH).

# $N,\!N'\text{-}\mathsf{Diphenyl-}N,\!N'\text{-}\mathsf{bis}(2\text{-}\mathsf{phenacetyl})\mathsf{phenylene-}1,\!4\text{-}\mathsf{diamine}$ (32)

By analogy to the previous procedure N,N'-(diphenyl)phenylene-1,4-diamine **28** (0.1 mol, 26.0 g) was allowed to react with phenacetylchloride (**17a**, 0.2 mol, 30.8 g). The product was obtained in a yield of 30.3 g (61%).

Mp 190 °C.

<sup>1</sup>H NMR (DMSO- $d_6$ ), δ = 3.75 (s, 4 H, CH<sub>2</sub>), 7.05 (d, 4 H, CH), 7.15–745 (m, 20 H, CH).

Anal. Calcd for  $C_{34}H_{28}N_2O_2$  (496.6): C, 82.3; H, 5.6; N, 5.6. Found: C, 82.1; H, 5.6; N, 5.5.

#### N,N'-Diphenyl-N,N'-bis(2-phenacetyl)benzidine (33)

By analogy to the previous procedure N,N'-(diphenyl)benzidine (**29**, 0.1 mol, 33.6 g) was allowed to react with phenacetylchloride (**17a**, 0.2 mol, 30.8 g). The product was obtained in a yield of 33.7 g (59%).

#### Mp 155 °C.

 $^1\text{H}$  NMR (CDCl\_3):  $\delta$  = 3.60 (s, 4 H, CH\_2), 7.11 (d, 4 H, CH), 7.19 (t, 4 H, CH), 7.26 (t, 4 H, CH), 7.30–7.44 (m, 12 H, CH), 7.62–7.69 (m, 4 H, CH).

Anal. Calcd for  $C_{40}H_{32}N_2O_2$  (572.7): C, 83.9; H, 5.6; N, 4.9. Found: C, 82.8; H, 5.7; N, 4.7.

# N,N-Diphenylthiourea (20)

To a refluxing mixture of potassium thiocyanate (0.31 mol, 30.1 g) in acetone (200 mL) pivaloylic chloride (0.3 mol, 36.0 g), followed by a soln of a diarylamine **2** (0.3 mol) in acetone (150 mL) was added under stirring. After cooling to r.t. the mixture was diluted with  $H_2O$  (600 mL), containing concd HCl (50 mL). The solid formed was decanted and mixed with concd HCl (100 mL). The resulting mixture was refluxed for 15 min and poured in ice-water (2 L). The product precipitated was grinded with EtOH, isolated by suction,

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and purified by twofold recrystallization from EtOH. The product was obtained in a yield of 50.7 g (64%).

Mp 212 °C. (Lit.21 212 °C).

#### *N*,*N*'-Bis-(thiocarbamido)-*N*,*N*'-(diphenyl)phenylene-1,4-diamine (34)

By analogy to the previous procedure N,N'-(diphenyl)phenylene-1,4-diamine (**28**, 39.0 g, 0.15 mol) was allowed to react with pivaloylisothiocyanate (0.15 mol) prepared in situ from potassium thiocyanate and pivaloylchloride in acetone. The product was obtained in a yield of 31.0 g (55%).

Mp 177 °C.

Anal. Calcd for  $C_{30}H_{34}N_4O_2S_2$  (546.7): C, 65.9; H, 6.3; N, 10.3; S, 11.7. Found: C, 64.2; H, 6.3; N, 10.8; S, 10.9.

#### N,N-Diarylthioacetamides 21; General Procedure

A mixture of a *N*,*N*-disubstituted acetamide (**19**, 0.1 mol), Lawesson's reagent (0.06 mol, 24.4 g), and 1,2-dimethoxyethane (200 mL) was stirred at 100 °C for 5 h. The product, precipitated after cooling, was isolated by suction followed by washing with a mixture of  $Et_2O-CH_2Cl_2$  (1:1). The following products were obtained:

#### 2,N,N-triphenylthioacetamide (21a)

From **19a** in a yield of 27.3 g (90%).

Mp 142-144 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 4.30 (s. 2 H. CH<sub>2</sub>), 7.05–7.10 (m, 4 ArH), 7.17–7.21 (m, 3 ArH), 7.23–7.32 (m, 6 ArH), 7.37 (t, 2 ArH).

Anal. Calcd for  $C_{20}H_{17}NS$  (303.4): C, 79.2; H, 5.6; N, 4.6; S, 10.6. Found: C, 79.0; H, 5.8; N, 4.6; S, 10.4.

## N-Phenyl-N-(phenylthioacetyl)1-naphthylamine (21b)

From **19b** in a yield of 27.9 g (79%).

Mp 100-103 °C.

<sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  = 3.87 (s, 1 H, CH<sub>2</sub>), 4.18 (s, 1 H, CH<sub>2</sub>), 6.93 (t, 2 Ar H), 7.08–7.17 (m, 4 ArH), 7.30–7.38 (m, 3 ArH), 7.42 (t, 1 ArH), 7.58 (dd, 2 ArH), 7.76–7.84 (m, 3 ArH), 7.91 (d, 1 ArH), 8.10 (d 1 ArH).

Anal. Calcd for  $C_{24}H_{19}NS$  (353.5): C, 81.6; H, 5.4; N, 4.0; S, 9.1. Found: C, 81.5; H, 5.4; N, 4.3; S, 9.1.

#### N-Phenyl-N-(phenylthioacetyl)2-naphthylamine (21c)

From **19c** in a yield of 14.0 g (40%).

Mp 112–113 °C.

<sup>1</sup>H NMR (MeCN):  $\delta$  = 4.24 (s, 2 H, CH<sub>2</sub>), 7.13–7.16 (m, 2 ArH), 7.22–7.30 (m, 4 Ar H), 7.35–7.44 (m, 5 ArH), 7.50 (q, 2 ArH), 7.78–7.80 (m, 2 ArH), 7.8–7.88 (m, 2 ArH).

Anal. Calcd for  $C_{24}H_{19}NS$  (353.5): C, 81.6; H, 5.4; N, 4.0; S, 9.1. Found: C, 81.0; H, 5.5 N; 4.3, S, 9.4.

# *N*,*N*′-Bis-(phenylthioacetyl)-*N*,*N*′-(diphenyl)phenylene-1,4-diamine (36)

By analogy to the previous procedure N,N'-bis(phenacetyl)-N,N'-(diphenyl)phenylene-1,4-diamine (**32**, 24.8 g, 0.05 mol) was allowed to react with Lawesson's reagent (0.06 mol, 24.4 g) in 1,2-dimethoxyethane (200 mL). The product was obtained in a yield of 16.9 g (79%).

#### Mp 223-227 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 4.25 (s, 4 H, CH<sub>2</sub>), 6.97–7.10 (m, 8 ArH), 7.14–7.20 (m, 4 ArH), 7.22 (s, 4 ArH), 7.25–7.35 (m, 8 ArH).

Anal. Calcd for  $C_{34}H_{28}N_2S_2$  (528.7): C, 77.3; H, 5.3; N, 5.3; S, 12.1. Found: C, 77.7; H, 5.2; N, 4.9; S, 11.5.

#### *N*,*N*'-diphenyl-*N*,*N*'-bis-(phenylthioacetyl)benzidine (37)

By analogy to the previous procedure N,N'-diphenyl-N,N'-bis-(phenylthioacetyl)benzidine (**33**, 28.6 g, 0.05 mol) was allowed to react with Lawesson's reagent (0.06 mol, 24.4g) in 1,2-dimethoxyethane (200 mL). The product was obtained in a yield of 21.1 g (70%).

Mp 190-194 °C.

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ = 4.12 (s, 4 H, CH<sub>2</sub>), 7.08 (d, 4 ArH), 7.16–7.50 (m, 20 ArH), 7.66 (t, 4 ArH).

Anal. Calcd for  $C_{40}H_{32}N_2O_2$  (604.8): C, 79.5; H, 5.3; N, 4.6; S, 10.6. Found: C, 78.7; H, 5.4; N, 4.4; S, 10.4.

#### 2-(N,N-Diarylamino)thiazoles 22; General Procedure

A soln of *N*,*N*-diphenylthiourea (**20**, 0.01 mol, 2.28 g) and of the corresponding bromoketone **13** (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 formed was isolated by filtration, followed by recrystallization from EtOH. The following products were obtained:

#### 2-(N,N-diphenylamino)-3-phenylthiazole (22a)

From *N*,*N*-diphenylthiourea (**20**) and phenacylbromide (**13a**) in a yield of 2.5 g (76%).

Mp 120 °C (Lit.<sup>22</sup> 120 °C).

Anal. Calcd for  $C_{21}H_{16}N_2S$  (328.4): C, 76.8; H, 4.9; N, 8.5; S, 9.8. Found: C, 77.1; H, 5.2; N, 8.7; S, 9.8.

#### 2-(*N*,*N*-diphenylamino)-3,4-diphenylthiazole (22b)

From *N*,*N*-diphenylthiourea (**20**) and 2-bromo-1,2-diphenylethanone (**13b**) in a yield of 3.3 g (82%).

Mp 223 °C.

Anal. Calcd for  $C_{27}H_{20}N_2S$  (404.5): C, 80.2; H, 5.0; N, 6.9; S, 7.9. Found: C, 79.8; H, 5.0; N, 7.1; S, 7.4.

#### 2,2'-Bis(*N*,*N*-diphenylamino)-4,4'-diphenyl-5,5'-bithiazole (23)

By analogy to the previous procedure *N*,*N*-diphenylthiourea (**20**, 0.02 mol, 4.6 g) was allowed to react with 1,2-dibenzoyl-1,2-dibromoethane (**14**, 0.01 mol, 4.0 g). The product was obtained after recrystallization from DMF in a yield of 4.3 g (63%).

Mp 232 °C.

Anal. Calcd for  $C_{42}H_{30}N_4S_2\,(654.8)\colon C,\,77.1;\,H,\,4.6;\,N,\,8.6;\,S,\,9.8.$  Found: C, 76.8; H, 5.2; N, 8.5; S, 9.3.

# 1,4-Bis{[2-(*N*,*N*'-diphenylamino)-1,3-thiazol]-4-yl}benzene (24)

By analogy to the previous procedure N,N-diphenylthiourea (**20**, 0.02 mol, 4.6 g) was allowed to react with 1,4-bis-(bro-moacetyl)benzene (**15**, 0.01 mol, 3.2 g). The product was obtained after recrystallization from DMF in a yield of 3.3 g (57%).

#### Mp 279 °C.

Anal. Calcd for  $C_{36}H_{26}N_4S_2\,(578.8)\colon C,\,74.7;\,H,\,4.5;\,N,\,9.7,\,S,\,11.1.$  Found: C, 74.4; H, 4.6; N, 9.7; S, 10.9.

# 1,4-Bis{[2-(N,N-diphenylamino)-3-phenyl]-4-thienyl}benzene (25)

By analogy to the previous procedure N,N,2-triphenylthioacetamide (**21a**, 0.02 mol, 6.06 g) was allowed to react with 1,4-bis(bro-moacetyl)benzene (**15**, 0.01 mol, 3.2 g). The product was obtained after recrystallization from DMF in a yield of 3.8 g (52%).

### Mp 241 °C.

Anal. Calcd for  $C_{50}H_{36}N_2S_2$  (728.5): C, 82.4; H, 4.9; N, 3.8; S, 8.8. Found: C, 81.7; H, 5.2; N, 3.9; S, 9.4.

#### 2,2'-Bis(*N*,*N*-diphenylamino)-3,3',4,4'-tetraphenyl-5,5'bithiophene (26)

By analogy to the previous procedure *N*,*N*,2-triphenylthioacetamide (**21a**, 0.02 mol, 6.1 g) was allowed to react with 1,2-dibenzoyl-1,2-dibromoethane (**14**, 0.01 mol, 4.0 g)] in DMF (100 mL). The product was obtained by pouring the reaction mixture into H<sub>2</sub>O–EtOH (1:1) (200 mL) and recrystallization from DMF in a yield of 3.0 g (37%).

Mp 262 °C.

Anal. Calcd for  $C_{56}H_{40}N_2S_2$  (805.1): C, 83.6; H, 5.0; N, 3.5; S, 8.0. Found: C, 82.3; H, 5.3; N, 3.2; S, 7.9.

## 2-(N,N-Diarylamino)thiophenes 27; General Procedure

Equivalent amounts of a thioacetamide **21** (0.01 mol) and a bromoketone **13** (0.01 mol, 2.0 g) in EtOH (100 mL) were refluxed for 8 h. After cooling the mixture was diluted with ice-water (300 mL) and the precipitated product was isolated by filtration or, when obtained as oil, titruated with EtOH (20 mL) and recrystallized from EtOH. The following products were obtained:

# *N*,*N*,**3**,**4**-Tetraphenyl-2-aminothiophene (27a)

From N,N,2-triphenylacetamide (**21a**) and phenacylbromide (**13a**) in a yield of 2.7 g (67%).

Mp 102 °C.

Anal. Calcd for C<sub>28</sub>H<sub>21</sub>NS (403.5): C, 83.4; H, 5.2; N, 3.5; S, 7.9. Found: C, 83.4; H, 5.8; N, 3.2; S, 8.2.

# N,N,3,4,5-Pentaphenyl-2-aminothiophene (27b)

From N,N,2-triphenylacetamide (**21a**) and 2-bromo-1,2-diphenylethanone (**13b**) in a yield of 3.2 g (67%).

Mp 120 °C.

Anal. Calcd for  $C_{34}H_{25}NS$  (479.5): C, 85.1; H, 5.2; N, 2.9; S, 6.7. Found: C, 85.2; H, 5.0; N, 3.0; S, 6.8.

# N-(1-Naphthyl)-N,3,4-triphenyl-2-aminothiophene (27c)

From N-(1-naphthyl)-N,2-diphenyl-acetamide (**21b**) and phenacylbromide (**13a**) in a yield of 2.3 g (51%).

Mp 64 °C.

Anal. Calcd for  $C_{32}H_{23}NS$  (453.6): C, 84.8; H, 5.1; N, 3.1; S, 7.1. Found: C, 83.6; H, 5.3; N, 3.0; S, 7.5.

# *N*-(2-Naphthyl)-*N*,3,4,5-tetraphenyl-2-aminothiophene (27d)

From N-(1-naphthyl)-N,2-diphenyl-acetamide (**21b**) and 2-bromo-1,2-diphenylethanone (**13b**) in a yield of 1.2 g (25%).

# Mp 198 °C.

Anal. Calcd for C<sub>38</sub>H<sub>27</sub>NS (529.7): C, 86.2; H, 5.1; N, 2.6; S, 6.1. Found: C, 86.28; H, 5.4; N, 2.3; S, 6.0.

# $N,\!N'\text{-}Diphenyl-N,\!N'\text{-}bis(4,5\text{-}diphenyl-2\text{-}thiazolyl)phenylene-1,4\text{-}diamine~(38)$

A mixture of N,N'-diphenyl-N,N'-bis(thiocarbamido)phenylene-1,4-diamine (**34**, 0.01 mol, 3.78 g) and 2-bromo-1,2-diphenylethanone (**13b**, 0.02 mol, 5.5 g) in DMF (100 mL) was stirred for 8 h at 100 °C. After cooling, the mixture was diluted with ice-water (250 mL) and the precipitate formed was isolated by filtration, followed by recrystallization from DMF. The product was obtained in a yield of 3.9 g (53%).

Mp 302 °C.

Anal. Calcd for  $C_{48}H_{34}N_4S_2$  (730.9): C, 78.9; H, 4.7; N, 7.7; S, 8.8. Found: C, 78.9; H, 5.0; N, 7.5; S, 8.3.

# *N,N'*-Diphenyl-*N,N'*-bis(3,4-diphenyl-2-thienyl)-phenylene-1,4-diamine (40a)

A mixture of *N*,*N*'-diphenyl-*N*,*N*'-bis(phenylthioacetyl)phenylene-1,4-diamine (**36**, 0.01 mol, 5.28 g) and phenacylbromide (**13a**, 0.02 mol, 4.0 g) in DMF (100 mL) was stirred for 10 h at 100 °C. After cooling, the mixture was diluted with ice-water (250 mL) and the precipitate formed was isolated by filtration, followed by recrystallization from DMF. The product was obtained in a yield of 3.3 g (45%).

# Mp 263 °C.

Anal. Calcd for  $C_{50}H_{36}N_2S_2\,(729.0)\colon C,\,82.4;\,H,\,4.9;\,N,\,3.8;\,S,\,8.8.$  Found: C, 81.9; H, 5.1; N, 3.8; S, 8.4.

#### *N,N'*-Diphenyl-*N,N'*-bis(3,4,5-triphenyl-2-thienyl)phenylene-1,4-diamine (40b)

By analogy to the previous procedure N,N'-diphenyl-N,N'-bis(phenylthioacetyl)phenylene-1,4-diamine (**36**, 0.01 mol, 5.28 g) and 2-bromo-1,2-diphenylethanone (**13b**, 0.02 mol, 5.5 g) in acetic anhydride (100 mL) was stirred for 10 h at 100 °C. After cooling, the mixture was poured into ice-water (250 mL) and stirred for 4 h. The precipitate formed was isolated by filtration and recrystallizied from DMF. The product was obtained in a yield of 5.7 g (65%).

## Mp 317 °C.

Anal. Calcd for  $C_{62}H_{44}N_2S_2$  (881.2): C, 84.5; H, 5.0; N, 3.2; S, 7.3. Found: C, 84.7; H, 5.2; N, 2.7; S, 7.4.

# *N*,*N*′-Diphenyl-*N*,*N*′-bis(3,4-diphenyl-2-thienyl)benzidine (41a)

A mixture of N,N'-diphenyl-N,N'-bis(phenylthioacetyl)benzidine (**37**, 0.01 mol, 6.04 g) and phenacylbromide (**13a**, 0.02 mol, 4.0 g) in DMF (100 mL) was stirred for 10 h at 100 °C. After cooling, the mixture was diluted with ice-water (250 mL). The precipitate formed was isolated by filtration and recrystallized from DMF. The product was obtained in a yield of 4.4 g (55%).

## Mp 183-185 °C.

Anal. Calcd for  $C_{56}H_{40}N_2S_2$  (805.0): C, 83.6; H, 5.0; N, 3.5; S, 8.0. Found: C, 82.9; H, 5.2; N, 3.1; S, 7.9.

# *N,N'*-Diphenyl-*N,N'*-bis[(3,4,5-triphenyl-2-thienyl]benzidine (41b)

In analogy to the previous procedure N,N'-diphenyl-N,N'-bis(phenylthioacetyl)benzidine (**37**, 0.01 mol, 6.04 g) and 2-bromo-1,2-diphenylethanone (**13b**, 0.02 mol, 5.5 g) in acetic anhydride (100 mL) was stirred for 10 h at 100 °C. After cooling, the mixture was poured into ice-water (250 mL) and stirred for 4 h. The precipitate formed was isolated by filtration and recrystallized from DMF. The product was obtained in a yield of 6.8 g (71%).

# Mp 276 °C.

Anal. Calcd for  $C_{40}H_{32}N_2S_2(957.3);$  C, 85.4; H, 5.0; N, 2.9; S, 6.7. Found: C, 84.6; H, 5.2; N, 2.8; S, 6.8.

# Acknowledgement

The authors are grateful to the Bundesministerium für Bildung und Forschung (BMBF) for financial support and to Dr. D. Rohde for recording the thermal and electrochemical data.

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