DOI: 10.1002/ejoc.200700539

A Simple One-Pot Synthesis of Solvatofluorescent Push-Pull Thiophenes

Gunther Buehrdel,[a] Rainer Beckert,*[a] Eckhard Birckner,[b] Ulrich-Walter Grummt,[b] Beatrice Beyer,[a] Stefan Kluge,[a] Jamie Weston,[a] and Helmar Goerls[c]

Dedicated to Prof. Dr. Waldemar Adam on the occasion of his 70th birthday

Keywords: Thiophene / Fluorescence / Bis-imidoyl chlorides / Cyclization reaction / Rearrangement

Depending on the substitution patterns in the sulfanes **1**, two different types of thiophenes **3** and **4** can be obtained upon cyclization with a bis-imidoyl chloride **2**. Whereas thiodiglycolic acid diester yielded a thiophene derivative with the expected symmetrical structure, thiodiacetonitrile gives a derivative with an asymmetrical substitution pattern (2,3-arylamino/4,5-dicyano). This unexpected finding was confirmed by single-crystal X-ray analysis and possibly originates from a 1,2-rearrangement of a thietanium salt intermediate. These new push-pull thiophenes are easily accessible in a single step from simple starting materials. Unlike in the case of the derivatives **3**, the substitution pattern in **4** was not previously known. A simple hydrolysis of compounds **4** offers a new and efficient route to derivatives of thiomaleic acid anhydrides **6**. The 2,3-dicyano-4,5-bis(arylamino)thiophenes **4** exhibit strong solvatofluorescence with unusually large Stokes shifts. Quantum chemical calculations explain the large Stokes shifts as most probably being due to strong structural relaxation upon excitation to the S_1 state.

Introduction

Thiophene-based heterocycles are invaluable building blocks in organic chemistry, with widespread applications in both materials science and pharmaceutical chemistry. With regard to functional materials, thiophenes are rapidly gaining importance as electroluminescence materials in display devices such as OLEDs, OTETs, wearable displays, and organic solar cells.[1] It is quite interesting that thiophenes display unusually large solvatochromic shifts, which extend almost over the whole visible range.

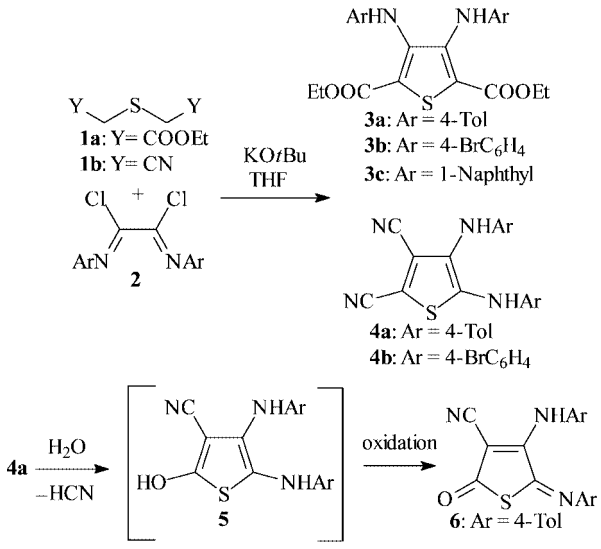
Synthetic routes, inspired by donor-acceptor substituted polyenes, have been developed for several push-pull thiophenes.[2,3] At the beginning of the last century, Hinsberg discovered that derivatives of thiodiglycol provide good building blocks for obtaining thiophenes.[4a] More recently, it was found that thiodiacetonitrile **1b** and its S,S-dioxide can be employed as starting materials for sulfur heterocycles.[5–7] Current work performed by us in this field includes a new approach to highly functionalized thiophene S,S-dioxides by cycloacylation of selected CH-acidic sulfones with oxalic acid-derived bis-imidoyl chlorides **2**.[7] Our current goal is to employ bis-electrophiles **2** as building blocks for thiophenes. We have recently extended our studies to include sulfanes, which we now demonstrate are capable of reacting with bis-electrophiles **2**. These electrophiles are easily accessible[8] and, in addition, their well tuned selectivity makes them useful starting materials for obtaining numerous heterocyclic compounds.[9]

Results and Discussion

Diethyl thiodiglycolate (**1a**, Y = COOEt) reacts readily with bis-electrophiles **2**. Under quite mild conditions (THF in the presence of *t*BuOK at –78 °C), single products (TLC) were formed and could be isolated in high yields in the form of large yellow crystals. Elemental analyses and MS data confirmed the presence of 1:1 cyclization products **3**. Evidence for a symmetric substitution pattern in these novel tetrasubstituted thiophenes **3** (Scheme 1) was provided by single sets of signals in the ^1H and ^{13}C NMR spectra. The NH protons of derivative **3a** resonate at δ = 7.26 ppm. Due to the presence of donor-acceptor substituents, solutions of compounds **3** are dark yellow (**3a** in $CHCl_3$: λ_{max} = 411 nm, log ε = 4.1). In addition, they display a yellow fluorescence with a large Stokes shift (**3a** in $CHCl_3$: λ_{Em} = 550 nm). Thiophenes of type **3** can easily be deprotonated with a

[a] Institute of Organic and Macromolecular Chemistry, Friedrich Schiller University,
Humboldtstrasse 10, 07743 Jena, Germany
Fax: +49-3641-948212
E-mail: c6bera@uni-jena.de
[b] Institute of Physical Chemistry, Friedrich Schiller University,
Lessingstrasse 10, 07743 Jena, Germany
[c] Institute of Inorganic and Analytical Chemistry, Friedrich Schiller University,
August-Bebelstrasse 2, 07743 Jena, Germany

strong base such as *t*BuOK or *n*BuLi; a red anion is generated, with the neutral thiophene **3** being regenerated upon treatment with acid.



Scheme 1.

The bis-nitrile **1b** (Y = CN) also reacts with the bis-electrophiles **2**. Under the same conditions as used for the preparation of compounds **3**, yellow crystalline products were obtained. Elemental analysis and MS data also confirmed the presence of 1:1 cyclization products. However, ^{1}H and ^{13}C NMR spectra, due to the presence of double signal sets, suggested an unusual symmetrical structure **4** originating from a cyclization reaction. The NH protons absorb at δ = 9.28 ppm and 7.43 ppm. The signals for the nitrile groups were detected as singlets at 112 and 94 ppm in the ^{13}C NMR spectrum. A single-crystal X-ray analysis of **4a** allowed an unambiguous structural assignment for these compounds (Figure 1). The cyclization products **4a** and **4b** can be described as 2,3-bis(arylamino)-4,5-dicyanothiophenes (Scheme 1).

Thiophenes of type **4** can easily be deprotonated by using a strong base such as *t*BuOK or *n*BuLi. A red anion is generated, forming a blue dianion upon addition of a second equivalent of base. Upon treatment with acid, the neutral thiophene **4** can be regenerated. Compound **4** is electrochemically active and can be quasi-reversibly oxidized at a potential of E_{OX} = 1.216 V.

When thiophene **4a** was heated in a H_2O/acetone mixture, it hydrolyzed to yield a yellow crystalline product. Elemental analysis, MS data, and $^{1}H/^{13}C$ NMR spectra all indicate that a cyano group had been replaced by OH (possibly via intermediate **5**), followed by oxidation. A single-crystal X-ray analysis showed **6** to be a monomer in the solid state (Figure 2). The bond lengths and angles are in the expected range; only the bond between N2–C3 is somewhat shortened. Derivative **6** can be regarded as a highly substituted derivative of thiomaleic acid anhydride. Substitution reactions in which a cyano group is replaced by OH

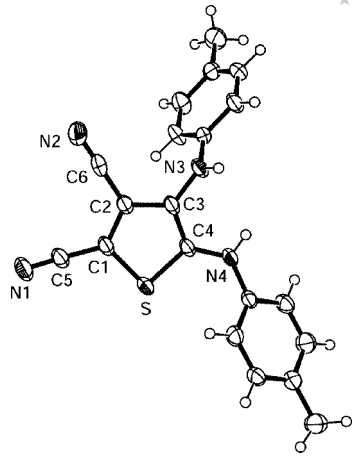


Figure 1.ORTEP plot (50% probability ellipsoids) of the solid-state molecular structure of **4a**.

by simple hydrolysis are still unknown in the thiophene series and may, in this case, be caused by the unusual substitution pattern in **4**.

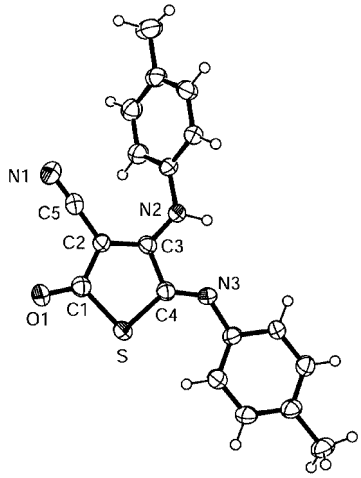
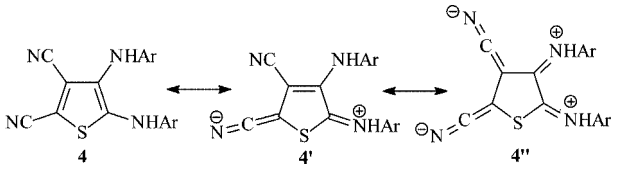


Figure 2.ORTEP plot (50% probability ellipsoids) of the solid-state molecular structure of **6**. Selected bond lengths in Å: S–C(1) 1.801(3), S–C(4) 1.762(3), O(1)–C(1) 1.223(4), N(1)–C(5) 1.156(4), N(2)–C(3) 1.324(4), N(3)–C(4) 1.276(4), C(2)–C(5) 1.410(5), C(1)–C(2) 1.441(5), C(2)–C(3) 1.384(4), C(3)–C(4) 1.492(4).

Several resonance structures for **4** are possible (Scheme 2). The pattern of donor/acceptor substituents favors a large contribution from the mesomeric form **4′**, as evidenced by the bond lengths observed in the solid-state structure of **4a** and supported by quantum chemical calculations (Table 1). The C1–C5 and N4–C4 bond lengths are shortened in relation to the C2–C6 and N3–C3 distances. DFT, TDDFT and HF calculations were performed on derivative **4a**. The B3LYP/6–31+g(d) calculation level were used for full geometry optimization. In addition, the ground state structure was optimized at the RHF/6-31+g(d) level for subsequent comparison with the excited state cal-

culations at the CIS/6-31+g(d) level of theory. All calculated bond lengths compare well with the solid state structural data (Table 1).



Scheme 2.

Table 1. Comparison of experimentally determined and calculated bond distances (Å) in thiophene **4a**.

Bond	X-ray	B3LYP/6-31+g(d)
N3–C3	1.408(3)	1.412
N4–C4	1.363(3)	1.364
C1–C2	1.383(3)	1.389
C1–C5	1.421(3)	1.409
C2–C3	1.412(3)	1.427
C2–C6	1.430(4)	1.426
C3–C4	1.390(3)	1.395

Compound **4a** exhibits interesting fluorescence properties, with moderate solvatochromism being observed. The absorption maximum at 385 nm in cyclohexane is bathochromically shifted to 401 nm in ethanol. In spite of the shorter conjugated system, **4** displays behavior analogous to that of 5-dimethylamino-5′-nitro-2,2′-bithiophene.[2] In addition, compound **4** exhibits strong solvatofluorescence with an unusually large Stokes shift. The compound fluoresces blue in cyclohexane, green in toluene, yellow in chloroform, and orange in ethanol.

The UV/Vis absorption/fluorescence spectra of **4a** are illustrated in Figure 3. Table 2 contains the spectroscopic data, including quantum yields measured in dilute solutions. The long-wavelength absorption band (ε = 11200 $M^{-1}cm^{-1}$; $CHCl_3$) as well as the fluorescence spectra are broad and without structure. The fluorescence spectra, in contrast to the absorption spectra, show strong solvatofluorescence. The large bathochromic shift observed is remarkable, even in the nonpolar solvent cyclohexane. We attribute this to different geometries in the S_0 and the S_1 state (see quantum-chemical calculations discussed below).

An enhanced red shift of the fluorescence spectra is observed in solvents of increasing polarity, which indicates a large difference between the dipole moments in the ground (S_o) and excited electronic (S_1) states. Complex deactivation behavior of the S_1 state can be assumed from the solvent dependence of the fluorescence quantum yield (Table 2). First results from fluorescence kinetic measurements yielded biexponential decay curves with average excited state lifetimes between 5 ns (diethyl ether) and 0.6 ns (ethanol). Initial experiments show that the thiophene **4b** exhibits behavior similar to that of **4a**.

Calculation of the stationary dipole moment in the ground (S_o) [9.16 D; RHF/6–31+G(d)] and excited (S_1) states [8.64 D; CIS/6–31+g(d)] allowed us to interpret the solvatofluorescence properties of derivative **4a**. These dipole moments possess roughly opposite directions, which can explain the large Stokes shift, the solvatochromism, and the solvatofluorescence. Upon excitation, the resonance structure **4′** gains in importance, as can be seen from the molecular diagram showing bond lengths in Å for the S_1 (printed in *italics*) and the S_0 states (Figure 4). These changes in the bond lengths suggest that another mesomeric structure **4′′** (Scheme 2) also contributes to the S_1 state.

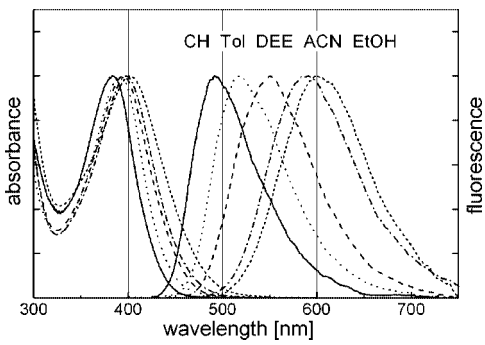


Figure 3. Absorption and fluorescence spectra of **4a** in solvents of differing polarity at 293 K.

Table 2. Solvatochromism data for compound **4a** in selected solvents.

Solvent	λ_a [nm]	λ_f [nm]	$\Delta\nu_{af}$ [cm^{-1}]	Φ_f
Cyclohexane (CH)	385	492	5650	0.043
Toluene (Tol)	391	517	6230	0.20
Chloroform	398	547	6780	0.20
Diethyl ether (DEE)	394	550	7200	0.14
Acetonitrile (ACN)	398	588	8120	0.027
Ethanol (EtOH)	401	600	8270	0.01

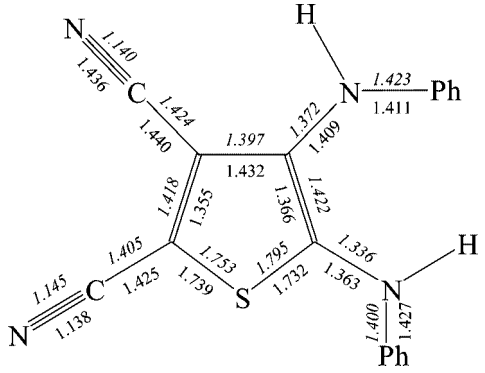


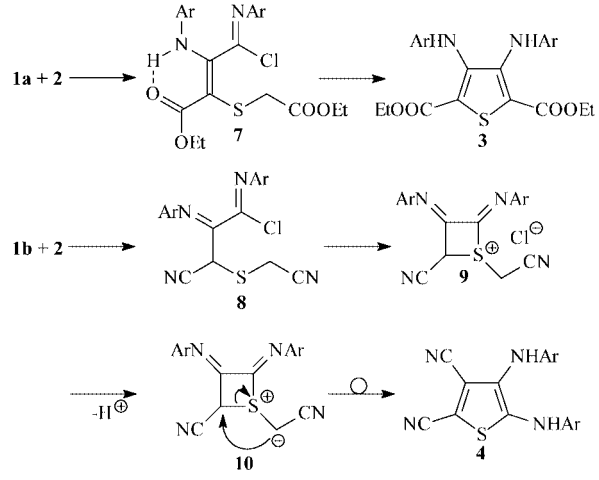
Figure 4. Molecular diagram of **4** showing the calculated bond lengths [Å] for the S_1 state [CIS/6-31G+(d); italics] and the S_0 state [RHF/6-31G+(d) level of theory].

A TDDFT B3LYP/6-31+g(d) calculation yields λ_{max} = 405 nm for derivative **4** (geometry optimized at the same level of theory). Emission at 544 nm is predicted (structure from CIS optimization), resulting in a calculated anomalous Stokes shift of 6310 cm^{-1}, which corresponds satisfac-

torily to the experimentally observed shifts of 5650 cm^{-1} and 6230 cm^{-1} in the nonpolar solvents cyclohexane and toluene, respectively.

Analysis of the calculated structures delivers a reasonable explanation for this large Stokes shift. In the ground state (S_o), the π-systems of the two phenyl rings are nearly perpendicular with respect to the thiophene functionality. The lone pair of N4 has considerable π character and interacts strongly with the thiophene ring, whereas the lone pair of N3 is oriented perpendicular to the thiophene and interacts strongly with the π-system of the attached phenyl group. Upon excitation, the calculations indicate a strong structural relaxation such that *both* phenylamino substituents become π-conjugated with the central thiophene ring. This comparatively large geometric relaxation in the S_1 state is probably the primary reason for the large observed Stokes shift.

We postulate the following mechanism (Scheme 3) for the unexpected formation of these push-pull thiophenes **4**. "Normal" acylation probably takes place first, resulting in the formation of intermediate **8**. Instead of a further *C*-acylation, attack at sulfur then leads to the formation of a cyclic sulfonium (thietanium) salt **9**. Deprotonation of this CH-acidic species then results in the sulfur ylide **10**. Finally, a 1,2-shift (coupled with prototropism) takes place to yield **4**. Support for this mechanism, in which thietanes are key intermediates, is as follows: a) thietanes have already been isolated and characterized in the courses of cyclization reactions of bis-electrophiles **2** with organosulfur compounds[10] (and furthermore, thietanium ions comparable to **9** have been described as intermediates in other reactions and have also been isolated[11]), and b) sulfur ylides are important intermediates in reactions of sulfur-containing derivatives. In this context, the 1,2-shift (Stevens rearrangement) of a carbon atom from sulfur to the next α-carbon atom with the formation of a sulfane is well known. This reaction is often used as a synthetic pathway.[12,13]



Scheme 3.

It is noteworthy that attempts to rearrange derivatives **3** to give thiophenes possessing the same pattern as in **4** (Y = COOEt) failed under both basic and acidic conditions and on irradiation.[14] To the best of our knowledge, the thietanium system **9** should be the key intermediate, which might explain the formation of asymmetric products **4**. We suggest that during the formation of **3**, a strong hydrogen bond is formed between the amino group and the carboxy group in intermediate **7**.[15] This prior fixation inhibits the formation of a thietanium intermediate and finally an asymmetric thiophene possessing the same pattern as in **4** (Y = COOEt).

Conclusions

Surprisingly, the reactions between the two sulfanes **1** and bis-imidoyl chlorides, under the same reaction conditions, result in the formation of two different types of thiophenes **3** and **4**. These new push-pull thiophenes are easily accessible in a one-step synthesis starting from simple starting materials. Unlike in the case of derivatives **3**, the substitution pattern in **4** was not previously known. A simple hydrolysis reaction of compounds **4** offers a new and efficient route to thiomaleic acid anhydride derivatives **6**. The thiophenes **4** exhibit strong solvatofluorescence with unusually large Stokes shifts. Quantum chemical calculations have explained the large Stokes shifts as most probably being due to strong structural relaxation upon excitation to the S_1 state.

Experimental Section

General: The reagents described in the following section were purchased from commercial sources and used directly unless otherwise stated in the text. The bis-imidoyl chlorides **2**,[8] diethyl thiodiglycolate (**1a**),[4b] and thiodiacetonitrile (**1b**)[5] were synthesized by literature procedures. All solvents were reagent grade, were dried by standard practices, and were distilled prior to use. Reactions were monitored by TLC (0.2 mm Merck silica gel plates; 60 F_{254}). ^1H and ^{13}C NMR spectra were recorded on Bruker AVANCE 250 and 400 spectrometers; shifts are given relative to solvent signals. Melting points were measured on a Galen III apparatus (Boëtius system) and are uncorrected.

General Procedure for the Preparation of Diethyl 3,4-Bis(arylamino)-thiophene-2,5-dicarboxylates: A solution of diethyl thiodiglycolate **1a** (1.00 g, 4.9 mmol) in dry THF (40 mL) was cooled to –78 °C and *t*BuOK (1.70 g, 15 mmol) was added. The corresponding bis-imidoyl chloride **2a**–**c** (5.1 mmol) was added to the solution. The reaction mixture was stirred at –78 °C for 30 min and then acidified (HCl/propan-2-ol) to pH 7. The mixture was concentrated to dryness in vacuo. The remaining solid was dissolved in $CHCl_3$/*n*-heptane and dried with Na_2SO_4. Upon removal of the solvent in vacuo, the residue was either purified by column chromatography on silica gel ($CHCl_3$/*n*-heptane, 1:3) or the crude product was purified by recrystallization from $CHCl_3$/*n*-heptane to yield **3a**–**c** as yellow crystals.

Diethyl 3,4-Bis(4-tolylamino)thiophene-2,5-dicarboxylate (3a): Yellow crystals, yield 1.80 g (84%), m.p. 148 °C ($CHCl_3$/*n*-heptane). ^1H NMR (250 MHz, $CDCl_3$): δ = 7.26 (s, 2 H, NH), 6.75 (d, ^3J = 8 Hz, 4 H, CH-Ar), 6.34 (d, ^3J = 8 Hz, 4 H, CH-Ar), 4.33 (q, ^3J = 7.1 Hz, 4 H, CH_2), 2.27 (s, 6 H, CH-Tol), 1.37 (t, ^3J = 7.1 Hz, 6 H, CH_3) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 164.2 (COOEt),

141.6 (C-2), 137.3, 131.6, 128.2, 120.5, 111.8 (C-3), 61.1, 20.7, 14.3 ppm. IR (ATR): $\tilde{\nu}_{max}$ = 3320 (NH), 3028, 2982, 2867, 1669, 1577, 1514, 1360, 1318, 808, 700 cm^{-1}. MS (EI): *m/z* (%) = 438 (50) $[M]^+$, 346 (60), 319 (100), 91 (10) $[C_7H_7]^+$. $C_{24}H_{26}N_2O_4S$ (438.54): calcd. C 65.73, H 5.98, N 6.39, S 7.31; found C 65.76, H 6.03, N 6.32, S 7.27.

Diethyl 3,4-Bis(4-bromophenylamino)thiophene-2,5-dicarboxylate (3b): Yellow crystals, yield 2.08 g (76%), m.p. 172 °C ($CHCl_3$/*n*-heptane). ^1H NMR (250 MHz, $CDCl_3$): δ = 8.13 (s, 2 H, NH), 7.08 (d, ^3J = 8 Hz, 4 H, CH-Ar), 6.34 (d, ^3J = 8 Hz, 4 H, CH-Ar), 4.35 (q, ^3J = 7.1 Hz, 4 H, CH_2), 1.39 (t, ^3J = 7.1 Hz, 6 H, CH_3) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 164.1 (COOEt), 140.1 (C-2), 138.4, 130.6, 122.0, 114.9, 113.0 (C-3), 61.4, 14.3 ppm. MS (EI): *m/z* (%) = 570 (10), 568 (20) and 566 (10) $[M]^+$, 362 (20), 316 (50), 29 (100). $C_{22}H_{20}Br_2N_2O_4S$ (568.29): calcd. C 46.50, H 3.55, N 4.93, Br 28.12, S 5.64; found C 46.53, H 3.55, N 4.71, Br 29.01, S 5.43.

Diethyl 3,4-Bis(1-naphthylamino)thiophene-2,5-dicarboxylate (3c): Yellow crystals, yield 1.82 g (73%), m.p. 185 °C ($CHCl_3$/*n*-heptane), ^1H NMR (250 MHz, $CDCl_3$): δ = 8.71 (s, 2 H, NH), 7.7–6.6 (m, 14 H), 4.39 (q, ^3J = 7.1 Hz, 4 H, CH_2), 1.41 (t, ^3J = 7.1 Hz, 6 H, CH_3) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 164.6 (COOEt), 141.6 (C-3), 134.7, 133.3, 127.4, 126.6, 125.0, 124.9, 124.6, 122.7, 122.0, 116.6, 111.9 (C-2), 61.2, 14.3 ppm. MS (EI): *m/z* (%) = 510 (50) $[M]^+$, 418 (60), 195 (40), 127 (100). $C_{30}H_{26}N_2O_4S$ (510.62): calcd. C 70.57, H 5.13, N 5.49, S 6.28; found C 70.52, H 4.90, N 5.61, S 5.96.

General Procedure for the Preparation of 2,3-Bis(arylamino)thiophene-4,5-dicarbonitriles: A solution of thiodiacetonitrile **1b** (1.00 g, 8.9 mmol) in dry THF (50 mL) was cooled to –78 °C, and *t*BuOK (2.00 g, 17.8 mmol) was added. The corresponding bis-imidoyl chloride (**2a/b**, 8.2 mmol) was added to the solution. The reaction mixture was stirred at –78 °C for 10 min and then acidified (diluted aqueous HCl) to pH 5. The mixture was concentrated to dryness in vacuo, and the remaining black solid was dissolved in ethyl acetate and dried with Na_2SO_4. Upon removal of the solvent in vacuo, the product was dissolved in ethyl acetate (50 mL). The solution was treated with *n*-heptane (60 mL) and was then filtered to remove polymeric byproducts. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (ethyl acetate/*n*-heptane, 2:3). The crude product was purified by recrystallization from $CHCl_3$/*n*-heptane to yield **4a** or **4b** as yellow crystals.

4,5-Bis(4-tolylamino)thiophene-2,3-dicarbonitrile (4a): Yellow crystals, yield 0.90 g (32%), m.p. 200 °C ($CHCl_3$). ^1H NMR (250 MHz, [D$_6$]DMSO): δ = 9.28 (s, 1 H, NH), 7.43 (s, 1 H, NH), 7.14 (s, 4 H, CH-Tol), 6.95 (d, ^3J = 8 Hz, 2 H, CH-Tol), 6.55 (d, ^3J = 8 Hz, 2 H, CH-Tol), 2.24 (s, 3 H, CH-Tol), 2.16 (s, 3 H, CH-Tol) ppm. ^{13}C NMR (63 MHz, [D$_6$]DMSO): δ = 150.2, 143.0, 138.7, 132.7, 133.0, 129.4, 127.0, 123.4, 118.6, 118.5, 113.7, 113.3, 112.3, 94.1, 20.3, 20.1 ppm. IR (ATR): $\tilde{\nu}_{max}$ = 3391 (NH), 3241 (NH), 3035, 2921, 2862, 2203 (CN), 1612, 1544, 1511, 1488, 1409, 1315, 1225, 815, 801 cm^{-1}. MS (EI): *m/z* (%) = 344 (100) $[M]^+$, 329 (25), 237 (40), 91 (50) $[C_7H_7]^+$. HRMS: calcd. for $C_{20}H_{16}N_4SNa$: 367.099; found 367.100. $C_{20}H_{16}N_4S$ (344.44): calcd. C 69.74, H 4.68, N 16.27, S 9.31; found C 69.68, H 4.68, N 16.18, S 9.19. CV in dry CH_2Cl_2/0.1 M $Bu_4N^+PF_6^-$: E_{Ox} = 1.216 V, $\Delta E_{Red,Ox}$ = 0.1 V cm^{-1}.

2,3-Bis(4-bromophenylamino)thiophene-4,5-dicarbonitrile (4b): Yellow crystals, yield 1.48 g (35%), m.p. 212 °C ($CHCl_3$). ^1H NMR (250 MHz, [D$_6$]DMSO): δ = 9.45 (s, 1 H, NH), 8.30 (s, 1 H, NH), 7.44 (d, ^3J = 8 Hz, 2 H, CH-Ar), 7.26 (d, ^3J = 8 Hz, 2 H, CH-Ar), 7.13 (d, ^3J = 8 Hz, 2 H, CH-Ar), (d, ^3J = 8 Hz, 2 H, CH-Ar) ppm. ^{13}C NMR (63 MHz, [D$_6$]DMSO): δ = 147.5, 144.2, 140.7, 132.0, 131.4, 124.6, 119.6, 118.3, 115.8, 114.0, 112.8, 112.1, 109.5, 97.8 ppm. IR (ATR): $\tilde{\nu}_{max}$ = 3336 (NH), 3241 (NH), 2198 (CN), 1585, 1550, 1484, 1410, 1316, 1233, 812 cm^{-1}. MS (EI): *m/z* (%) = 476 (30), 474 (70) and 472 (30) $[M]^+$, 314 (60), 237 (100), 156 (60), 76 (60). $C_{18}H_{10}N_4S$ (474.18): calcd. C 45.59, H 2.13, N 11.82, S 6.76, Br 33.70; found C 45.49, H 2.26, N 11.72, S 6.31, Br 34.48.

Preparation of 3-Cyano-4-(4-tolylamino)-5-(4-tolylimino)-2(5*H*)-thiophenone: A solution of 2,3-dicyano-4,5-bis(4-tolylamino)thiophene (**4a**, 0.50 g, 1.5 mmol) in acetone (50 mL) and water (40 mL) was acidified (dilute HCl) to pH 5 before being heated to reflux. The reaction was monitored by TLC and when starting material was no longer detected (after 1 h), the solvent was removed under reduced pressure. The crude product was purified by recrystallization from $CHCl_3$/*n*-heptane to yield **6** as yellow crystals. Yield 0.39 g (78%), m.p. 224 °C ($CHCl_3$/*n*-heptane). ^1H NMR (250 MHz, [D$_6$]DMSO): δ = 11.24 (s, 1 H, NH), 7.33–7.23 (m, 6 H, CH-Tol), 7.13 (d, ^3J = 8 Hz, 2 H, CH-Tol), 2.34 (s, 6 H, CH-Tol) ppm. ^{13}C NMR (63 MHz, [D$_6$]DMSO): δ = 184.8 (C-2), 160.6 (C-5), 154.6, 146.3, 138.2, 137.5, 134.4, 130.6, 129.6, 126.6, 121.0, 112.2, 82.6, 21.2, 21.1 ppm. IR (ATR): $\tilde{\nu}_{max}$ = 3229 (NH), 3035, 2919, 2211 (CN), 1678, 1617, 1581, 1522, 1443, 1194, 840, 794, 700 cm^{-1}. MS (EI): *m/z* (%) = 333 (80) $[M]^+$, 318 (60), 155 (30), 91 (100) $[C_7H_7]^+$. $C_{19}H_{15}N_3OS$ (333.41): calcd. C 68.45, H 4.53, N 12.66, S 9.62; found C 68.25, H 4.70, N 12.62, S 9.59.

Crystal Structure Determination for 4a and 6: The intensity data for each compound were collected on a Nonius Kappa CCD diffractometer, using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects, but not for absorption effects.[16]

The structure was solved by direct methods (SHELXS)[17] and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97).[18] For the amine groups N3, N4 (for **4a**), and N2 (for **6**) the hydrogen atoms were located by difference Fourier synthesis and refined isotropically. The other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[18] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

CCDC-634187 (for **4a**) and -650037 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Data for 4a: $C_{20}H_{16}N_4S$, M = 344.4 gmol^{-1}, yellow prism, size 0.04 × 0.04 × 0.03 mm^3, monoclinic, space group $P2_1/c$, a = 4.4502(2), b = 22.6110(13), c = 16.9969(8) Å, β = 95.875(3)°, V = 1701.30(15) $Å^3$, T = –90 °C, Z = 4, $\rho_{calcd.}$ = 1.345 gcm^{-3}, μ (Mo-K_α) = 2 cm^{-1}, F(000) = 720, 11196 reflections in h(–5/5), k(–25/29), l(–21/19), measured in the range 2.96° ≤ Θ ≤ 27.45°, completeness Θ_{max} = 99.5%, 3867 independent reflections, R_{int} = 0.0580, 2452 reflections with $F_o > 4\sigma(F_o)$, 235 parameters, 0 restraints, $R1_{obs}$ = 0.0549, wR^2_{obs} = 0.1250, $R1_{all}$ = 0.1031, wR^2_{all} = 0.1467, GOOF = 1.015, largest difference peak and hole: 0.341/–0.320 e $Å^{-3}$.

Crystal Data for 6: $C_{19}H_{15}N_3OS$, M = 333.4 gmol^{-1}, yellow prism, size 0.05 × 0.05 × 0.03 mm^3, monoclinic, space group $P2_1/n$, a = 4.8471(6), b = 15.1454(18), c = 22.417(3) Å, β = 93.115(8)°, V = 1643.2(4) $Å^3$, T = –90 °C, Z = 4, $\rho_{calcd.}$ = 1.348 gcm^{-3}, μ (Mo-K_α) = 2 cm^{-1}, F(000) = 696, 9504 reflections in h(–6/6), k(–18/19), l(–27/29), measured in the range 2.26° ≤ Θ ≤ 27.48°, completeness Θ_{max} = 98.6%, 3720 independent reflections, R_{int} = 0.0983, 1951 reflections with $F_o > 4\sigma(F_o)$, 221 parameters, 0 restraints, $R1_{obs}$ = 0.0705, wR^2_{obs} = 0.1343, $R1_{all}$ = 0.1614, wR^2_{all} = 0.1673, GOOF = 1.015, largest difference peak and hole: 0.286/–0.301 e $Å^{-3}$.

Calculations: DFT, TDDFT, and HF calculations were performed on derivative **4**. The ground state was optimized at the B3LYP/6-31+G(d)[19,20] and additionally at the RHF/6-31+G(d) levels of theory for subsequent comparison with the excited state structure calculated at the CIS/6-31+G(d)[21] level of theory utilizing the Gaussian03 program package.[22]

Acknowledgments

We are grateful to the Friedrich Schiller University Jena for financial support of the work of G. B. through a stipend.

[1] G. Barbarella, M. Melucci, G. Sotigiu, *Adv. Mater.* **2005**, *17*, 1581–1593; M. M. Oliva, J. Casado, M. M. Raposo, A. M. Fonseca, H. Hartmann, V. Hernandez, J. L. Navarrete, *J. Org. Chem.* **2006**, *71*, 7509–7520.
[2] F. Effenberger, F. Würthner, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 719–721.
[3] A. S. Karpov, F. Rominger, J. T. T. Müller, *J. Org. Chem.* **2003**, *68*, 1503–1511.
[4] a) O. Hinsberg, *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 901–906; b) C. G. Overberger, H. J. Mallon, R. Fine, *J. Am. Chem. Soc.* **1950**, *72*, 4958–4961.
[5] J. E. McCormick, R. S. McElhinne, *J. Chem. Soc. Perkin Trans. 1* **1972**, 1335–1342.
[6] D. A. Crombie, J. R. Kiely, C. J. Ryan, *J. Heterocycl. Chem.* **1979**, *16*, 381–382.
[7] G. Buehrdel, R. Beckert, D. Raabe, H. Goerls, *J. Sulfur Chem.* **2006**, *27*, 401–407.
[8] D. Lindauer, R. Beckert, H. Görls, P. Fehling, M. Döring, *J. Prakt. Chem./Chem.-Ztg.* **1995**, *337*, 143–152.
[9] P. Langer, M. Döring, *Eur. J. Org. Chem.* **2002**, 221–234.
[10] E. Bellur, H. Goerls, P. Langer, *J. Org. Chem.* **2006**, *71*, 2332–2338.
[11] R. Destro, E. Ortoleva, G. Modena, L. Pasquato, V. Lucchini, *Helv. Chim. Acta* **2001**, *84*, 860–866.
[12] *Houben-Weyl, Methods of Organic Chemistry*, Vol. E 11/part 2, pp. 1410–1419.
[13] M. Ioannou, M. J. Porter, F. Saez, *Chem. Commun.* **2002**, 346–347.
[14] R. M. Kellogg, J. K. Dik, H. van Driel, H. Wynberg, *J. Org. Chem.* **1970**, *35*, 2737–2741; H. Wynberg, R. M. Kellogg, H. van Driel, G. H. Beekhuls, *J. Am. Chem. Soc.* **1967**, *89*, 3501–3505; R. M. Kellogg, *Tetrahedron Lett.* **1972**, *15*, 1429–1432.
[15] S. Saito, H. Yamamoto, *Acc. Chem. Res.* **2004**, *37*, 570–579.
[16] *COLLECT*, Data Collection Software, Nonius B. V., Netherlands, **1998**; Z. Otwinowski, W. Minor, "*Processing of X-ray Diffraction Data Collected in Oscillation Mode*", in *Methods in Enzymology*, vol. 276, *Macromolecular Crystallography, Part A* (Eds.: C. W. Carter, R. M. Sweet), pp. 307–326, Academic Press, **1997**.
[17] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.
[18] G. M. Sheldrick, *SHELXL-97* (Release 97-2), University of Göttingen, Germany, **1997**.
[19] A. D. Becke, *Phys. Rev. A: At. Mol. Opt. Phys.* **1988**, *38*, 3098–3100; C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B: Condens. Matter* **1988**, *37*, 785–789; A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.
[20] P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213–222; M. M. Francl, W. J. Petro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFree, J. A. Pople, *J. Chem. Phys.* **1982**, *77*, 3654–3665.
[21] J. B. Foresman, M. Head-Gordon, J. A. Pople, M. J. Frisch, *J. Phys. Chem.* **1992**, *96*, 135–149.
[22] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03*, Revision C.02, Gaussian, Inc., Wallingford, CT, **2004**.

Received: June 12, 2007
Published Online: August 31, 2007

