Journal of Sulfur Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926081

A new synthesis of highly functionalized thiophene-1,1-dioxide derivatives

Gunther Buehrdel[a]; Rainer Beckert[a]; Dietrich Raabe[a]; Helmar Goerls[b]
[a] Institute of Organic and Macromolecular Chemistry, Friedrich Schiller University, Jena, Germany [b] Institute of Inorganic and Analytical Chemistry, Friedrich Schiller University, Jena, Germany

To cite this Article Buehrdel, Gunther , Beckert, Rainer , Raabe, Dietrich and Goerls, Helmar(2006) 'A new synthesis of highly functionalized thiophene-1,1-dioxide derivatives', Journal of Sulfur Chemistry, 27: 5, 401 — 407
To link to this Article: DOI: 10.1080/17415990600926609
URL: http://dx.doi.org/10.1080/17415990600926609

Journal of Sulfur Chemistry
Vol. 27, No. 5, October 2006, 401–407

Taylor & Francis
Taylor & Francis Group

RESEARCH ARTICLE

A new synthesis of highly functionalized thiophene-1,1-dioxide derivatives

GUNTHER BUEHRDEL†, RAINER BECKERT*†, DIETRICH RAABE† and HELMAR GOERLS‡

†Institute of Organic and Macromolecular Chemistry, Friedrich Schiller University D-07743 Jena, Humboldtstr. 10, Germany
‡Institute of Inorganic and Analytical Chemistry, Friedrich Schiller University D-07743 Jena, August-Bebelstr. 2, Germany

(Received 20 June 2006; in final form 24 July 2006)

The reaction of *bis*-imidoylchlorides derived from oxalic acid with dibenzyl sulfones, afforded novel highly substituted thiophene-1,1-dioxide derivatives.

Keywords: Thiophenes; Sulfones; *Bis*-Imidoyl chlorides

1. Introduction

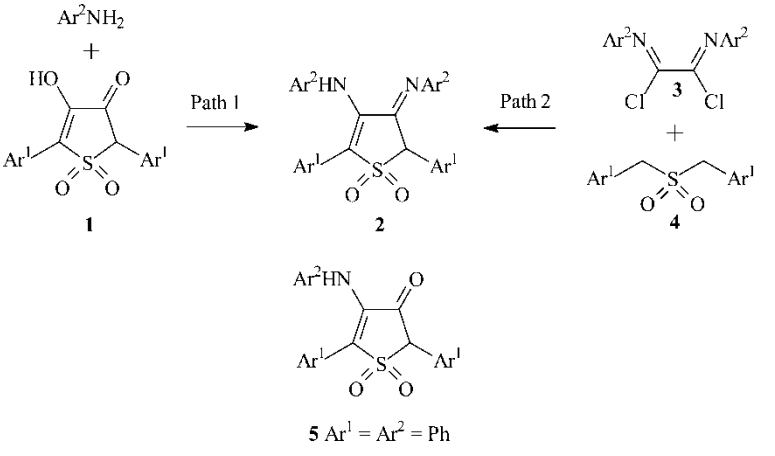
The first synthesis of 2,5-diphenyl-4-hydroxy-3-oxo-2,3-dihydrothiophene-1,1-dioxide **1** was reported by the cyclization reaction of ethyl oxalate with dibenzyl sulfone **4a** [1, 2]. The predominate tautomer, consisting of an α-hydroxy ketone, was confirmed by IR spectra and NMR experiments in solid state and in solution [3]. Starting from **1**, the same authors reported the syntheses of enaminoketones as well as ring-fused pyrazines and quinoxalines by simple condensation reactions. Since the work of Steglich [4, 5] derivatives of **1** are useful starting materials for the preparation of activated esters. Due to their significance, they are commercially available in the meantime.

The replacement of oxygen by nitrogen at C3 and C4 should lead to amino-substituted thiophene-1,1-dioxides, which are interesting building blocks for further ring-fusion reactions. They also might show biological activity because the analogous hydroxy substituted derivatives are described as inhibitors of lipoxygenase [6, 7].

The synthesis of **2** should be possible by condensation reactions of **1** with arylamines (scheme 1; path 1). An alternative is the cyclization reaction of dibenzyl sulfone **4** with *bis*-imidoylchlorides **3** (scheme 1; path 2).

*Corresponding author. Email: C6bera@uni-jena.de

Journal of Sulfur Chemistry
ISSN 1741-5993 print/ISSN 1741-6000 online © 2006 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/17415990600926609



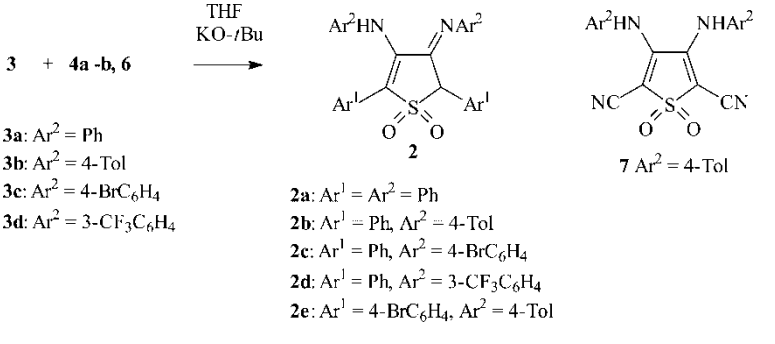
SCHEME 1

2. Results and discussion

First, the condensation reaction of **1** with aniline was studied. Despite broad variation of the reaction conditions, only replacement of the OH-group by PhNH occurred in compound **1** ($Ar^1 = Ar^2 = Ph$). Thus, upon treatment of **1** with boiling aniline for 1 h, the appropriate enaminoketone **5** was isolated in high yield.

Due to these experimental findings, we focussed our further studies on a different synthetic entry according to path 2. The *bis*-imidoylchlorides of type **3** are easily accessible [8] and in addition, they are versatile building blocks for numerous heterocyclic compounds [9]. Their well tuned selectivity should make them promising candidates for cyclization reactions with bifunctional carbon building blocks.

The reaction between **3a–d** and dibenzyl sulfone **4a** in the presence of KO-*t*Bu resulted in the formation of dark yellow cyclization products (scheme 2). The new derivatives were obtained in high yields and analytically pure. The ^{1}H- and ^{13}C-NMR spectra of derivatives **2** illustrated double sets of signals showing an unsymmetrical structure. The NH proton absorbs in the ^{1}H-NMR spectra at 7.7 ppm, whereas the cyclic CH proton could be detected as singlet at about 5.3 ppm. A single crystal X-ray analysis of **2b** allowed an unambiguous structural assignment of these compounds, as shown in figure 1. Hence, the cyclization products **2a–e** have the structure of 4-arylamino-3-arylimino-2,3-dihydro-thiophene-1,1-dioxides.



SCHEME 2

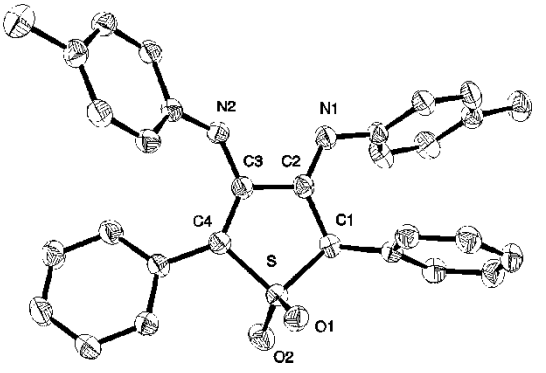


Figure 1. ORTEP-Plot of the molecular structure of **2b** (50% probability ellipsoids) with the atom numbering scheme. Selected bond lengths [Å]: S-C1 1.8150(17), S-C4 1.7660(16), C1-C2 1.516(2), C2-C3 1.492(2), C3-C4 1.365(2), N1-C2 1.271(2), N2-C3 1.366(2).

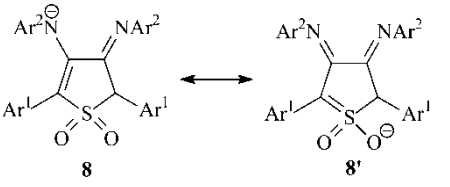
The observed bond lengths and angles confirmed the expectations of a partially saturated thiophene structure. Although the bond between N2 and C3 is a single bond, it is a little shorter than might have been expected for a normal C-N single bond.

Derivatives **2a–e** show a strong absorption at 360 nm in their UV/vis spectra. Interestingly, they can be deprotonated to form dark red solutions, which reversibly faded upon treatment with acids. This pH-switch can be explained by the formation of delocalized oxonole-like anions **8** or **8'** (scheme 3).

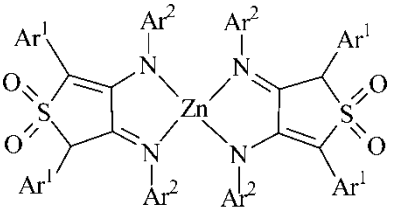
Due to the low solubility of the *bis*-(4-bromobenzyl)-sulfone **4b**, the cyclization reaction was carried out in N-methylpyrrolidone and only low yields of **2e** were obtained. Finally, sulfonyldiacetonitrile **6** was tested as binucleophilic reaction partner. In contrast to derivatives **2** in the ^{1}H-NMR spectrum of the yellow cyclization product **7**, only one set of signals could be detected. The high symmetry of the molecule was indicated by the broad signal at 9.29 ppm for two NH protons, two doublets for the aromatic protons at about 7.56 ppm and 7.21 ppm and an additional signal for the aromatic methyl group at 2.36 ppm. Most likely, the presence of the strong electron withdrawing cyano groups causes this shift of prototropism in favour of the symmetric structure of a 3,4-*bis*(arylamino)-2,5-dicyano-thiophene-1,1-dioxide **7**. The cyclization reactions of *bis*-imidoylchlorides of type **3** with other bifunctional building blocks such as sulfides or ketones will be the subject of a forthcoming publication.

When the cyclization products **2** in aqueous THF are heated, they easily undergo a hydrolysis reaction. Enaminoketones of type **5** and hydroxyketones of type **1** could be detected as products by TLC. This hydrolysis reaction confirms that small amounts of derivative **5** were formed and isolated during aqueous work-up procedures of **2a**.

Due to their chelating substructures, derivatives **2** offer good requirements for the construction of metal complexes. Upon treatment of **2b** with diethylzinc, the yellow zinc complex **9** was isolated in nearly quantitative yield whereby the species ZnL_2 could be detected by MS (scheme 4).



SCHEME 3



9

SCHEME 4

3. Experimental

3.1 *General*

The reagents described in the following section were purchased from commercial sources and were used directly unless otherwise stated in the text. The *bis*-imidoylchlorides **3a–d** were synthesized according to literature [8]. The sulfones **4a** [2], **4b** [10] and **6** [11] were synthesized according to literature. All solvents were of reagent grade and were dried according to common practice and were distilled prior to use. Reactions were monitored by TLC, carried out on 0.2 mm Merck silica gel plates (60 F_{254}) or Merck aluminium sheets aluminium oxide (150 F_{254}) using uv light. ^{1}H- and ^{13}C-NMR spectra were recorded on Bruker DRX 400 (400 MHz) and Bruker AC 250 (250 MHz) spectrometers, shifts are relative to the signals of the solvent. Melting points were measured with a Galen III apparatus (Böetius system) and are uncorrected. Uv/vis spectra were recorded on a UNICAM UV 500 spectrophotometer. IR: Digital Division FTS 25 from BioRad. MS spectra were taken from measurements on a Finnigan MAT SAQ 710 mass spectrometer or TRIO 2000 from FISONS. Elemental analyses were carried out in-house with an automatic analyzer LECO CHNS 932.

3.2 *Crystal structure determination*

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects, and not for absorption effects [12, 13].

The structure was solved by direct methods (SHELXS [14]) and refined by full-matrix least squares techniques against Fo^2 (SHELXL-97 [15]). For the N2 of compound **2b** the hydrogen atom was located by difference Fourier synthesis and refined isotropically. The other hydrogen atoms were included at calculated positions with fixed thermal parameters. All nonhydrogen atoms were refined anisotropically [15].

XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data for **2b** [16]: $C_{30}H_{26}N_2O_2S$, $Mr = 478.59\,\mathrm{gmol^{-1}}$, yellow prism, size $0.04 \times 0.04 \times 0.03\,\mathrm{mm^3}$, monoclinic, space group $P2_1/n$, $a = 12.7260(6)$, $b = 10.8617(5)$, $c = 17.7779(5)$Å, $\beta = 95.302(3)^\circ$, $V = 2446.85(18)$Å^3, $T = -90\,^\circ$C, $Z = 4$, $\rho_{calcd.} = 1.299\,\mathrm{gcm^{-3}}$, μ(Mo-K_α) $= 1.63\,\mathrm{cm^{-1}}$, $F(000) = 1008$, 16084 reflections in $h(-13/16)$, $k(-14/11)$, $l(-23/19)$, measured in the range $2.20^\circ \leq \Theta \leq 27.47^\circ$, completeness $\Theta_{\max} = 97.8\%$, 5483 independent reflections, $R_{int} = 0.036$, 4117 reflections with $F_o > 4\sigma(F_o)$, 322

parameters, 0 restraints, $R1_{obs} = 0.042$, $wR^2_{obs} = 0.099$, $R1_{all} = 0.0642$, $wR^2_{all} = 0.111$, GOOF = 1.010, largest difference peak and hole: $0.252/-0.378$ e Å^{-3}.

3.3 *General procedure for the preparation of 4-arylamino-3-arylimino-2,3-dihydrothiophene-1,1-dioxides of type 2*

To a solution of 3.00 g (12.2 mmol) of dibenzyl sulfone **4a** in 200 mL of dry THF was added 6.00 g (54 mmol) KO-*t*Bu and stirred for 5 minutes. The slight yellow solution was cooled down to −10 °C and 12.5 mmol of the corresponding *bis*-imidoylchloride **3a–d** was added. The deep red reaction mixture was stirred at 20 °C for 1 h. The mixture was acidified by addition of hydrochloric acid to pH 5. The mixture was concentrated *in vacuo* to dryness and the residue was washed with water. The remaining solid was dissolved in ethyl acetate and the organic extract was dried over Na_2SO_4. Upon removal of the solvent *in vacuo*, the product was recrystallised from ethyl acetate/n-heptane to yield **2a–d** as yellow crystals.

3.3.1 4-Phenylamino-3-phenylimino-2,5-diphenyl-2,3-dihydrothiophene-1,1-dioxide (2a). Yellow crystals, yield: 4.5 g (83%), mp 203 °C. ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.79 (s, 1H, NH), 7.36–6.82 (m, 16H), 6.82–6.79 (m, 2H), 6.61–6.58 (m, 2H), 5.36 (s, 1H, ring-CH) ppm. ^{13}C-NMR (63 MHz, $CDCl_3$): δ 158.5 (C-3), 148.2 (C-4), 138.0, 137.0, 129.6, 129.3, 129.0, 128.8, 128.7, 128.6, 128.3, 128.0, 126.9, 125.0, 124.1, 121.8, 121.1, 119.8 (C-5), 119.0, 65.3 (C-2), ppm. Elemental analysis calculated for $C_{28}H_{22}N_2SO_2$ (450.56) C 74.64, H 4.92, N 6.22, S 7.12, found C 74.57, H 5.07, N 6.36, S 6.67%. UV/vis ($CHCl_3$): λ_{max} (lg ε) 363 nm (3.8).

3.3.2 4-(4-Tolylamino)-3-(4-tolylimino)-2,5-diphenyl-2,3-dihydrothiophene-1,1-dioxide (2b). Yellow crystals, yield: 4.9 g (85%), mp 165 °C. ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.74 (s, 1H, NH), 7.40–6.94 (m, 10H, CH_{Ar}), 6.92 (d, 2H, J = 10 Hz, CH_{Ar}), 6.79 (d, 2H, J = 10 Hz, CH_{Ar}), 6.67 (d, 2H, J =10 Hz, CH_{Ar}), 6.50 (d, 2H, J = 10 Hz, CH_{Ar}), 5.34 (s, 1H, ring-CH), 2.27 (s, 3H, CH_3), 2.21 (s, 3H, CH_3) ppm. ^{13}C-NMR (63 MHz, $CDCl_3$): δ157.9 (C-4), 145.5 (C-3), 138.5, 134.8, 134.6, 133.9, 130.8, 130.4, 129.5, 129.3, 129.0, 128.7, 128.6, 127.9, 127.5, 127.0, 121.8, 119.8 (C-5), 119.2, 65.3 (C-2), 20.8, 20.7 ppm. MS(EI) m/z: 478 (20) [M^+], 413 (20) [M^+ -HSO_2], 323 (30), 207 (70), 91 [$C_7H_7^+$] (100). Elemental analysis calculated for $C_{30}H_{26}N_2SO_2$ (478.61) C 75.29, H 5.48, N 5.85, S 6.70, found C 75.11, H 5.40, N 5.91, S 6.91. IR(ATR): ν 3289 (NH), 3028, 2980, 2921, 1732, 1606, 1519, 1287 (SO_2), 1122 (SO_2), 692 cm^{-1}. UV/vis ($CHCl_3$): λ_{max} (lg ε) = 362 nm (4.5).

3.3.3 4-(4-Bromophenylamino)-3-(4-bromophenylimino)-2,5-diphenyl-2,3-dihydrothiophene-1,1-dioxide (2c). Yellow crystals, yield: 5.3 g (72%), mp 219–221 °C. ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.65 (s, 1H, NH), 7.34–7.18 (m, 10H, CH_{Ar}), 7.11 (d, 2H, J = 8 Hz, CH_{Ar}), 6.97 (d, 2H, J = 8 Hz, CH_{Ar}), 6.65 (d, 2H, J = 8 Hz, CH_{Ar}), 6.44 (d, 2H, J = 8 Hz, CH_{Ar}), 5.28 (s, 1H, ring-CH) ppm. ^{13}C-NMR (63 MHz, $CDCl_3$): δ 158.9 (C-3), 146.9 (C-4), 137.4, 136.1, 131.9, 131.2, 129.7, 129.6, 129.4, 129.1, 129.0, 128.8, 128.3, 126.5, 123.1, 122.2, 120.8, 118.4, 117.0, 65.3 (C-2) ppm. Elemental analysis calculated for $C_{28}H_{20}Br_2N_2SO_2$ (608.35) C 55.28, H 3.31, N 4.60, S 5.27, Br 26.27, found C 55.14, H 3.49, N 4.55, S 5.10, Br 26.52%.

3.3.4 4-(3-Trifluoromethylphenylamino)-3-(3-trifluoromethyphenylimino)-2,5-diphenyl-2,3-dihydrothiophene-1,1-dioxide (2d). Yellow crystals, yield 5.7 g (80%), mp 152 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.78 (s, 1H, NH), 7.36–7.17 (m, 12H, CH_{Ar}), 7.00–6.96 (m, 4H, CH_{Ar}), 6.82–6.77 (m, 2H, CH_{Ar}), 5.31 (s, 1H, ring-CH) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.8 (C-3), 148.4 (C-4), 137.5, 137.0, 131.3 (q, $J = 32$ Hz, C-CF_3), 130.9 (q, $J = 34$ Hz, C-CF_3), 129.7, 129.6, 129.5, 129.4, 129.2, 128.9, 128.8, 128.4, 127.9, 126.3, 124.6, 123.5 (q, $J = 270$ Hz, CF_3), 123.4 (q, $J = 270$ Hz, CF_3), 123.4, 122.2, 121.7 (q, $J = 4$ Hz), 120.8 (q, $J = 4$ Hz), 118.4 (q, $J = 4$ Hz), 116.2 (q, $J = 4$ Hz), 65.6 (C-2) ppm. MS (EI) m/z: 586 (4) [M^+], 521 (6) [M^+ -HSO_2], 350 (10), 261 (30), 191 (30), 145 (80), 91 (100) [$C_7H_7^+$]. Elemental analysis calculated for $C_{30}H_{20}F_6N_2SO_2$ (586.56) C 61.43, H 3.44, N 4.78, S 5.47, found C 61.39, H 3.53, N 4.43, S 5.72%. IR (ATR): ν 3340 (NH), 3078, 3054, 2913, 1704, 1609, 1529, 1451, 1325 (CF_3),1298 (SO_2), 1124 (SO_2), 694 cm^{-1}. UV/vis ($CHCl_3$): λ_{max} (lg ε) 353 nm(4.0).

3.4 *4-(4-Tolylamino)-3-(4-tolylimino)-2,5-(4-bromophenyl)-2,3-dihydrothiophene-1,1-dioxide (2e)*

To a solution of 3.00 g (7.4 mmol) of *bis*-(4-bromobenzyl)-sulfone **4b** in 200 mL of dry N-methylpyrrolidone was added 3.40 g (30 mmol) of KO-*t*Bu and the mixture was stirred for 5 minutes. The slight yellow solution was cooled down to −10 °C and 2.40 g (7.8 mmol) *bis*-imidoylchloride **3b** was added. The reaction mixture was stirred at 20 °C for 6 h. The dark brown mixture was acidified by addition of hydrochloric acid to pH 5. The mixture was then poured in water and the brown solid was filtered off. The residue was dissolved in ethyl acetate and the organic extract was dried over Na_2SO_4. Upon removal of the solvent *in vacuo*, the product was recrystallised three times from ethyl acetate to isolate **2e** as yellow crystals. Yield 0.42 g (10%), mp 183–185 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.76 (s, 1H, NH), 7.57 (d, 2H, $J = 8$ Hz, CH_{Ar}), 7.34 (d, 2H, $J = 8$ Hz, CH_{Ar}), 7.27 (d, 2H, $J = 8$ Hz, CH_{Ar}), 7.21 (d, 2H, $J = 8$ Hz, CH_{Ar}), 7.14 (d, 2H, $J = 8$ Hz, CH_{Ar}), 6.99 (d, 2H, $J = 8$ Hz, CH_{Ar}), 6.70 (d, 2H, $J = 8Hz$, CH_{Ar}), 6.56 (d, 2H, $J = 8$ Hz, CH_{Ar}), 5.32 (s, 1H, ring-CH), 2.37 (s, 3H, CH_3). 2.26 (s, 3H, CH_3) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ 157.9 (C-3), 145.3 (C-4), 138.9, 135.4, 135.3, 134.7, 134.2, 133.7, 132.0, 131.5, 131.2, 130.5, 129.8, 129.0, 125.8, 122.2, 119.8, 119.3, 118.4, 64.8 (C-2), 21.0, 20.8 ppm. MS (EI) m/z: 478 (20) [M^+], 413 (20) [$M^+ - HSO_2$], 323 (30), 207 (70), 91 (100) [$C_7H_7^+$].

3.5 *Synthesis of 4-phenylamino-3-oxo-2,5-diphenyl-2,3-dihydrothiophene-1, 1-dioxide (5)*

1.00 g (3.3 mmol) of **1** were heated in freshly distilled aniline for about 1 h and then the aniline was removed by distillation. The orange residue was recrystallised from acetone to yield **5** as yellow crystals. Yield 1.24 g (83%), mp 228 °C. ^{1}H-NMR (250 MHz, DMSO-d_6): δ 9.24 (s, 1H, NH), 7.49–7.17 (m, 10H, CH_{Ph}), 6.99–6.73 (m, 5H, CH_{Ph}), 6.07 (s, 1H, ring-CH) ppm. ^{13}C-NMR (63 MHz, DMSO-d_6): δ 189.7 (C-3), 138.1, 137.5, 131.1, 129.2, 129.1, 128.8, 128.6, 128.3, 127.9, 127.7, 126.7, 125.6, 123.2, 121.3, 68.8 (C-2) ppm. MS(EI) m/z: 375 (15) [M^+], 310 (5) [M^+-HSO_2], 206 (15), 193 (100), 165 (50). Elemental analysis calculated for $C_{22}H_{17}N_2SO_3$ (375.45) C 70.38, H 4.56, N 3.73, S 8.54, found C 70.21, H 4.51, N 3.82, S 8.59%.

The same product was obtained as by-product during the isolation of derivative **2a**.

3.6 *Synthesis of 2,5-dicyano-3,4-bis(4-tolylamino)-thiophene-1,1-dioxide 7*

To a solution of 1.00 g (6.9 mmol) of sulfonyldiacetonitrile **6** in 200 mL of dry THF 3.90 g (35 mmol) KO-*t*Bu was added and stirred for 5 minutes. To the solution 2.30 g (7.5 mmol) of *bis*-imidoylchloride **3b** was added. The reaction mixture was stirred at 20 °C for 4 h whereby the colour changed from yellow to dark brown. The mixture was acidified by addition of hydrochloric acid to pH 5 and then was concentrated *in vacuo* to dryness. The residue was treated with water and the solid was dissolved in ethyl acetate. Upon drying with Na_2SO_4 the solvent was removed *in vacuo* and the residue was recrystallised from ethyl acetate. Yellow crystals, yield 1.12 g (43%), mp 295 °C. ^{1}H-NMR (250 MHz, $CDCl_3$): δ 9.29 (s, 2H, NH), 7.56 (d, 4H, $J = 7.5$ Hz, CH_{Ar}), 7.21 (d, 4H, $J = 7.5$ Hz, CH_{Ar}), 2.36 (s, 6H, CH_3) ppm. ^{13}C-NMR (63 MHz, DMSO-d_6): δ 147.7 (C-3), 137.8 (C-1'), 133.4 (C-4'), 129.7 (C-3'), 125.2 (C-2'), 109.2 (CN), 81.3 (C-2), 20.7 (CH_3) ppm. Elemental analysis calculated for $C_{20}H_{16}N_4SO_2$ (376.44) C 63.81, H 4.28, N 14.88, S 8.52, found C 63.46, H 4.49, N 14.77, S 8.24%. IR(ATR): ν 3313 (NH), 3120, 3040, 2925, 2201 (CN), 1684, 1573, 1264 (SO_2), 1115 (SO_2), 812 cm^{-1}. UV/vis ($CHCl_3$): λ_{max}(lg ε) 311 nm (3.6).

3.7 *Preparation of Zinc-complex 9*

0.50 g (1.0 mmol) of **2b** were dissolved in 5 mL of dry THF and 5 mL of dry diethyl ether and at RT 0.5 mL of an 1 M diethyl zinc solution in n-hexane were added. After 5 min an yellow precipitate separated. The precipitate was washed with ether and was dried *in vacuo*. The Zinc-complex **9** was obtained (0.47 g, 93%) as yellow powder.

MS (EI) m/z: 1020 (100) [M^+], 1018 (90) [M^+], 478 [**2b**$^+$]

Acknowledgements

We thank Clariant GmbH and Degussa AG for their support by chemicals.

References

[1] R.H. Eastman, R.M. Wagner. *J. Am. Chem. Soc.*, **71**, 4089 (1949).
[2] C.G. Overberger, J.P. Lighthelm, E.A. Swire. *J. Am. Chem. Soc.*, **72**, 2856 (1950).
[3] W. Ried, O. Bellinger, G. Oremek. *Chem. Ber.*, **113**, 750 (1980).
[4] O. Hollitzer, A. Seewald, W. Steglich. *Angew. Chem.*, **88**, 480 (1976).
[5] W. Steglich, H. Schmidt, O. Hollitzer. *Synthesis*, **8**, 622 (1978).
[6] B. Witzel, D. Allison, C. Caldwell, K. Rupprecht. US Patent 4999436.
[7] F. Gadient, A. Stoll, R. Suess. US Patent 3832354.
[8] D. Lindauer, R. Beckert, H. Görls, P. Fehling, M. Döring. *J. prakt. Chem./Chemiker- Ztg.*, **337**, 143 (1995).
[9] P. Langer, M. Döring. *Eur. J. Org. Chem.*, 221 (2002).
[10] C.G. Overberger, R.A. Gagea, J.A. Smith, I.C. Kogon. *J. Am. Chem. Soc.*, **75**, 2075 (1953).
[11] E. McCormick, R.S. McElhinne. *J. C. S. Perkin I*, 1335 (1972).
[12] COLLECT, Data Collection Software, Nonius B.V., Netherlands (1998).
[13] Z. Otwinowski, W. Minor. In *Methods in Enzymology, Vol. 276, Macromolecular Crystallography, Part A*, C.W. Carter, R.M. Sweet (Eds.), pp. 307–326, Academic Press, London (1997).
[14] G.M. Sheldrick. *Acta Crystallogr. Sect. A*, **46**, 467 (1990).
[15] G.M. Sheldrick. *SHELXL-97 (Release 97-2)*, University of Göttingen, Germany (1997).
[16] CCDC 606653 (**2b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, fax: (+44) 1223-336-033, or deposit@ccdc.cam.ac.uk).