Facile Synthesis of Functionalized Oligophenothiazines via One-Pot Bromine–Lithium Exchange–Borylation–Suzuki Coupling (BLEBS)

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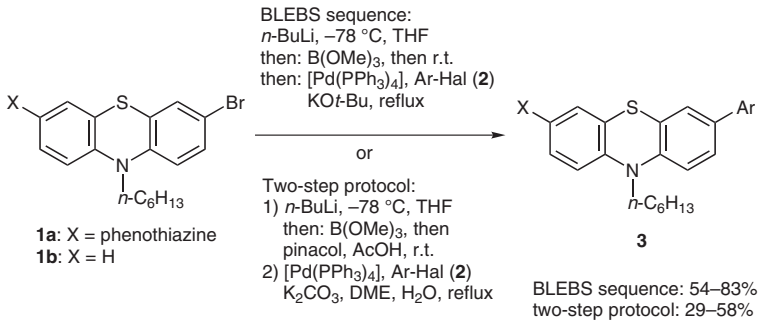
Received 26 October 2007; revised 18 December 2007

Abstract: The bromine–lithium exchange in bromophenothiazines followed by transmetalation with trimethyl borate and addition of palladium catalyst, 1.2 equivalents of a base, and an aryl halide yields the cross-coupling products in moderate to very good yields.

Key words: borylations, cross-coupling, heterocycles, metalation, oligomers, one-pot reactions

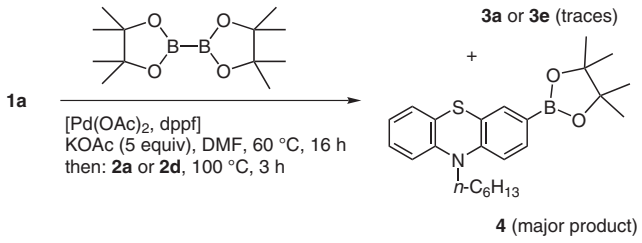
Phenothiazines constitute a pharmaceutically important class of heterocycles[1] with a broad spectrum of pharmacological activity.[2] Most interestingly, phenothiazines are also able to cleave DNA upon photochemical induction.[3] As a consequence of the low oxidation potential, these tricyclic nitrogen–sulfur heterocycles readily form stable radical cations and their physiological activities can also be attributed to this circumstance.[4] Furthermore, the first reversible oxidations[1,5] are accompanied by characteristic, deep colored radical cation absorptions. Thus, phenothiazine derivatives have become valuable spectroscopic probes in molecular and supramolecular arrangements for photoinduced electron transfer (PET) studies[6] and as functional motifs in materials science.[7] The prospect of incorporating highly redox active fragments like phenothiazines into conjugated chains could constitute a so far unknown class of redox addressable molecular wires, and in particular, for redox manipulation of single molecules with nanoscopic scanning techniques.[8,9] Recently, as part of our program to synthesize and investigate wire-like oligophenothiazines,[10] we communicated the syntheses, structures, and first cyclic voltammetry measurements of directly linked phenothiazinyl dyads and triads[11] that can be regarded as models for polymers with electronically coupled electrophores. Retrosynthetic analysis with fragmentations based upon Suzuki arylations[12] suggested the use of boronates. Although several one-pot procedures with Negishi, Stille, and Kumada cross-coupling reactions have been reported,[13] practical one-pot preparations of boronates from electron-rich heterocycles by halogen–lithium exchange followed by subsequent Suzuki–Miyaura cross-coupling have remained largely unexplored. Here, we report a straightforward access to functionalized arylated phenothiazines, phenothiazinyl dyads and triads by a one-pot bromine–lithium exchange–borylation–Suzuki (BLEBS) sequence.

In contrast to stepwise protocols which inevitably lead to reduced yields during workup or chromatography, we set out to develop a one-pot synthesis of arylphenothiazines and oligophenothiazines by a BLEBS sequence. Therefore, in the BLEBS reaction, a THF solution of a bromophenothiazine **1** was cooled to –78 °C (dry ice/acetone bath) and treated with *n*-butyllithium. Then, trimethyl borate was added and the reaction mixture was allowed to come to room temperature. Finally, an aryl halide **2**, catalytic amounts of $[Pd(PPh_3)_3]_4$, and 1.2 equivalents of potassium *tert*-butoxide were added and the mixture was heated overnight affording the corresponding cross-coupling products **3** in moderate to good yields (Scheme 1, Table 1).



Scheme 1 One-pot BLEBS sequence

SYNTHESIS 2008, No. 7, pp 1121–1125
Advanced online publication: 06.03.2008
DOI: 10.1055/s-2008-1032118; Art ID: T16907SS



Scheme 2 Attempted one-pot palladium-catalyzed borylation–Suzuki coupling using bis(pinacolato)diboron

The conventional two step synthesis of the desired arylphenothiazines and oligophenothiazines **3** requires the preparation and isolation of the phenothiazine pinacolyl boronate or boronic acid.[14] Either the rather expensive tetramethyl dioxoborolane is coupled by palladium catalysis according to Masuda's procedure[15] with a suitable bromophenothiazine **1**, or, by bromine–lithium exchange of **1** followed by trapping with trialkyl borate and subsequent transesterification with pinacol, the corresponding pinacolyl boronate is obtained in moderate yield.[14] After purification, Suzuki–Miyaura cross-coupling of borylated phenothiazines works in many cases in very good yields in a DME–H_2O mixture and in the presence of an excess of potassium carbonate.[16] Yet, following the two-step protocol, with workup and chromatography after each step, several days are required for the preparation of the desired products **3** and the maximum yield is always limited by the synthesis of the boronate. Most advantageously, the BLEBS sequence circumvents the isolation of the boronate and simultaneously reduces the amounts of added base for the Suzuki step. Furthermore, THF can be successfully used as the sole and common solvent in the reaction mixture under water-free conditions. Only one equivalent of base is finally needed since an ate-complex is already formed by electrophilic trapping of the lithiophenothiazine. This makes the BLEBS protocol most suitable for aryl and heteroaryl halides bearing base-sensitive functional groups (Table 1, entries 3 and 4). Even aldehyde functionalities are carried through the sequence without formation of undesired side products (entries 5 and 6). The overall equimolarity of all reagents and substrates used render the BLEBS protocol very economical and practical. Therefore, functionalized (oligo)phenothiazines can be easily obtained in a one-pot reaction.

All products **3** were fully characterized by ^1H, ^{13}C NMR, UV/Vis, and IR spectroscopy, mass spectrometry, and correct combustion analysis. The obtained phenothiazines and oligophenothiazines from the BLEBS sequence are favorable building blocks in oligomer syntheses,[16,17] and starting materials for the design of phenothiazine-fullerene dyads[18] and phenothiazine functionalized surfaces.[19] Therefore, an inexpensive and straightforward preparation is highly desirable. An alternative could be the Miyaura reaction using the rather expensive bis(pinacolato)diboron.[20] However, in our hands attempts to apply a similar one-pot procedure[21] to the coupling of **1a** and **2a** or **2d** only gave trace amounts of the desired products **3a** or **3e**, respectively (Scheme 2). The major product in either case was the pinacolyl boronate **4**. Hence, the BLEBS sequence appears to be superior with respect of efficiency and practicability.

In conclusion, we have developed a one-pot approach to functionalized (oligo)phenothiazines, starting from bromophenothiazines. In comparison to the conventional two-step protocol with intermediate workup and purification, or even in comparison to a one-pot protocol with bis(pinacolato)diboron as borylation source, the BLEBS sequence always gives higher yields in shorter time. Furthermore, THF is used as the sole solvent, which allows maintaining water-free conditions. Finally, only one equivalent of the base is needed. This makes the BLEBS protocol generally suitable for coupling with base sensitive aryl halides. Further studies with other heterocyclic substrates and the extension of this one-pot methodology are currently underway.

All reactions involving water-sensitive compounds were carried out in flame-dried Schlenk glassware under N_2 or argon. Reagents and catalysts were purchased reagent grade and used without further purification. Solvents were dried and distilled according to standard procedures.[22] The phenothiazine compounds **1a**, **1b**, **2a**, and **2d** were synthesized according to literature procedures.[11,16c] Flash column chromatography: silica gel 60, mesh 230–400, Merck. TLC: silica gel plates (60 F_{254} Merck, Darmstadt). ^1H, ^{13}C, and DEPT spectra were recorded on Bruker ARX 250, Bruker DRX 300 or Bruker DRX 500 spectrometer in CD_2Cl_2 or acetone-d_6 as solvent, unless otherwise stated. The assignments of quaternary C, CH, CH_2 and CH_3 were made on the basis of DEPT spectra. Mass spectra were recorded with JEOL JMS-700 und Finnigan TSQ 700 spectrometers. Elemental analyses were carried out in the microanalytical laboratory of the Organisch-Chemisches Institut, Universität Heidelberg.

BLEBS Sequences on Bromophenothiazines 1; General Procedure (GP)

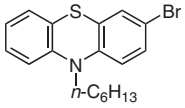
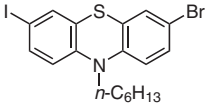
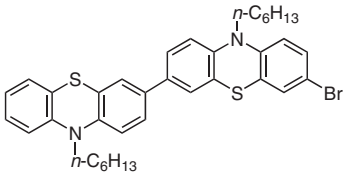
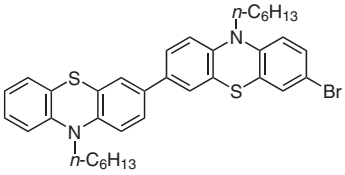
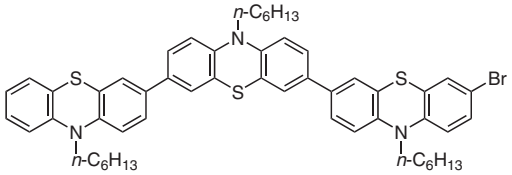
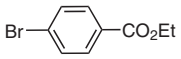
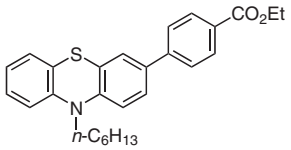
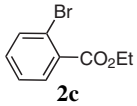
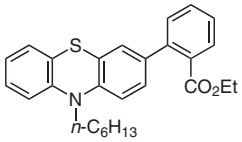
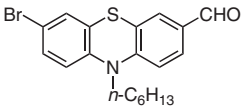
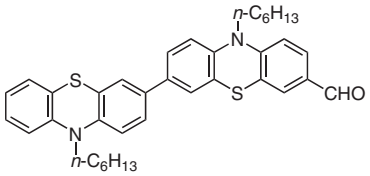
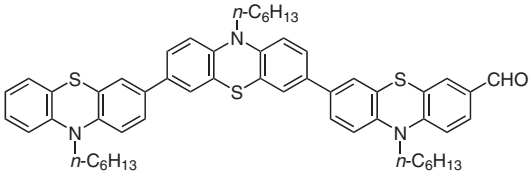
To a well-stirred mixture of bromophenothiazine **1** (1 equiv) dissolved in anhyd THF and cooled down to –78 °C, was added dropwise a 1.6 M hexane solution of *n*-BuLi (1.1 equiv) via a syringe. After stirring for 5 min at –78 °C, trimethyl borate (1.2 equiv) was dropped slowly into the mixture and it was allowed to come to r.t. Then, aryl halide **2** (1.2 equiv), $Pd(PPh_3)_4$ (4 mol%), and *t*-BuOK (1.2 equiv) were added and the solution was stirred for 14 h at 67 °C. After cooling down to r.t., the mixture was diluted with CH_2Cl_2 (150 mL) and aq sat. Na_2SO_3 (100 mL). The organic phase was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried ($MgSO_4$) and the solvents were removed under vacuum. The residue was purified with flash chromatography yielding in the phenothiazines **3a–f** as yellow or orange oils or resins.

7-Bromo-10,10′-dihexyl-10*H*,10′*H*-3,3′-biphenothiazine (3a)

Prepared according to the GP and purified by flash chromatography (hexane–acetone, 25:1); yield: 2.70 g (83%); yellow resin.

IR (KBr): 2952, 2925, 2853, 1600, 1575, 1457, 1250 cm^{-1}.

Table 1 One-Pot BLEBS Reactions

Entry	Bromophenothiazine **1**	Aryl halide **2**	Coupling product **3** (yield of BLEBS protocol, %)	Yield (%) of the conventional two-step protocol
1	 **1a**	 **2a**	 **3a** (83)	40[16c]
2	 **1b**	**2a**	 **3b** (77)	53[17]
3	**1a**	 **2b**	 **3c** (72)	42
4	**1a**	 **2c**	 **3d** (54)	29
5	**1a**	 **2d**	 **3e** (69)	46
6	**1b**	**2d**	 **3f** (62)	58[18a]

^{1}H NMR (300 MHz, acetone-d_6): δ = 0.82–0.87 (m, 6 H), 1.27–1.29 (m, 8 H), 1.43–1.45 (m, 4 H), 1.71–1.83 (m, 4 H), 3.89 (t, J = 6.8 Hz, 2 H), 3.92 (t, J = 7.0 Hz, 2 H), 6.90–7.03 (m, 5 H), 7.13–7.22 (m, 2 H), 7.26–7.32 (m, 2 H), 7.35 (d, J = 2.2 Hz, 2 H), 7.39–7.44 (m, 2 H).

^{13}C NMR (75 MHz, acetone-d_6): δ = 14.2 (CH_3), 23.2 (CH_2), 27.1 (CH_2), 27.1 (CH_2), 27.4 (CH_2), 27.5 (CH_2), 32.1 (CH_2), 32.2 (CH_2), 47.8 (CH_2), 47.9 (CH_2), 114.7 (C_q), 116.6 (CH), 116.7 (CH), 117.0 (CH), 118.0 (CH), 123.2 (CH), 125.0 (C_q), 125.6 (CH), 126.0 (C_q), 126.1 (CH), 126.3 (CH), 127.6 (C_q) 128.0 (CH), 128.3 (CH), 130.0 (CH), 130.9 (CH), 134.7 (C_q), 135.3 (C_q), 144.7 (C_q), 145.3 (C_q), 145.4 (C_q), 146.0 (C_q).

MS (FAB$^+$): m/z (%) = 644.2 (M^+, 100), 599.1 ($M^+ - C_6H_{13}$, 40), 474.0 ($M^+ - 2\ C_6H_{13}$, 35).

UV/Vis (CH_2Cl_2): λ_{max} (ε) = 268 (44000), 284 (320000), 326 (16400), 362 nm (11800).

Anal. Calcd for $C_{36}H_{39}BrN_2S_2$ (643.8): C, 67.17; H, 6.11; Br, 12.41; N, 4.35; S, 9.96. Found: C, 67.13; H, 6.20; Br, 12.23; N, 4.35; S, 9.89.

7-Bromo-10,10′-dihexyl-7′-(10-hexyl-10*H*-phenothiazin-3-yl)-10*H*,10′*H*-3,3′-biphenothiazine (3b)

Prepared according to the GP and purified by flash chromatography (hexane–acetone, 25:1); yield: 1.11 g (77%); yellow resin.

IR (KBr): 2953, 2928, 2868, 2854, 1630, 1458, 1378, 1332, 1252, 1241, 807 cm^{-1}.

^{1}H NMR (300 MHz, CD_2Cl_2): δ = 0.85 (m, 9 H), 1.29 (m, 12 H), 1.46 (m, 6 H), 1.81 (m, 6 H), 3.95 (m, 6 H), 6.94 (m, 2 H), 7.04 (m, 4 H), 7.21 (m, 3 H), 7.33 (m, 2 H), 7.48 (m, 8 H), 7.39–7.44 (m, 2 H).

^{13}C NMR (75 MHz, CD_2Cl_2): δ = 14.2 (CH_3), 23.0 (CH_2), 23.0 (CH_2), 26.9 (CH_2), 27.0 (CH_2), 27.1 (CH_2), 27.2 (CH_2), 27.2 (CH_2), 31.8 (CH_2), 31.9 (CH_2), 47.9 (CH_2), 47.9 (CH_2), 48.0 (CH_2), 114.6 (C_q), 115.8 (CH), 115.9 (CH), 116.0 (CH), 116.1 (CH), 117.0 (CH), 122.7 (CH), 124.7 (C_q), 124.8 (C_q), 125.0 (C_q), 125.0 (C_q), 125.2 (CH), 125.3 (CH), 125.3 (CH), 125.5 (CH), 125.5 (C_q), 125.6 (CH), 125.8 (CH), 127.1 (C_q), 127.7 (CH), 127.7 (CH), 129.8 (CH), 130.3 (CH), 134.3 (C_q), 134.4 (C_q), 134.5 (C_q), 134.8 (C_q), 144.2 (C_q), 144.4 (C_q), 144.5 (C_q), 144.7 (C_q), 144.8 (C_q), 145.5 (C_q).

MS (FAB$^+$): *m*/*z* (%) = 925 (M^+, 100), 840 ($M^+ - C_6H_{13}$, 26), 755 ($M^+ - 2\ C_6H_{13}$, 10), 640 ($M^+ - 3\ C_6H_{13}$, 12).

UV/Vis (CH_2Cl_2): λ_{max} (ε) = 240 (4300), 272 (6600), 326 (2900), 364 nm (2300).

Anal. Calcd for $C_{54}H_{58}BrN_3S_3$ (925.2): C, 70.11; H, 6.32; Br, 8.64; N, 4.54; S, 10.40. Found: C, 70.29; H, 6.32; Br, 8.37; N, 4.67; S, 10.57.

Ethyl 4-(10-Hexyl-10*H*-phenothiazin-3-yl)benzoate (3c)

Prepared according to the GP and purified by flash chromatography (hexane–acetone, 25:1); yield: 0.311 g (72%); yellow oil.

IR (film): 2956, 2928, 2855, 1713, 1605, 1575, 1463, 1366, 1334, 1273, 1182, 1106, 1019, 856, 772, 748, 485 cm^{-1}.

^{1}H NMR (300 MHz, acetone-d_6): δ = 0.85 (t, *J* = 7.1 Hz, 3 H), 1.30 (m, 4 H), 1.37 (t, *J* = 7.1 Hz, 3 H), 1.47 (m, 2 H), 1.81 (m, 2 H), 3.97 (t, *J* = 6.9 Hz, 2 H), 4.35 (q, *J* = 7.2 Hz, 2 H), 6.95 (dt, *J* = 1.2, 7.5 Hz, 1 H), 7.04 (d, *J* = 8.1 Hz, 1 H), 7.11 (d, *J* = 8.4 Hz, 1 H), 7.16 (m, 1 H), 7.21 (m, 1 H), 7.49 (d, *J* = 2.1 Hz, 1 H), 7.55 (dd, *J* = 2.1, *J* = 8.7 Hz, 1 H), 7.74 (d, *J* = 8.7 Hz, 2 H), 8.04 (d, *J* = 8.7 Hz, 2 H).

^{13}C NMR (75 MHz, acetone-d_6): δ = 14.2 (CH_3), 14.6 (CH_3), 23.3 (CH_2), 27.1 (CH_2), 27.5 (CH_2), 32.1 (CH_2), 47.9 (CH_2), 61.4 (CH_2), 116.7 (CH), 116.9 (CH), 123.5 (CH), 124.9 (C_q), 126.2 (C_q), 126.3 (CH), 127.0 (CH), 127.1 (CH), 128.0 (CH), 128.4 (CH), 129.8 (C_q), 130.7 (CH), 134.6 (C_q), 144.9 (C_q), 145.8 (C_q), 146.4 (C_q), 166.5 (C_q).

MS (FAB$^+$): *m*/*z* (%) = 431.3 (M^+, 100), 386.3 ($M^+ - OCH_2CH_3$, 11), 346.2 ($M^+ - C_6H_{13}$, 14), 300.2 ($M^+ - C_6H_{13} - OCH_2CH_3$, 4), 273.2 ($M^+ - C_6H_{13} - CO_2CH_2CH_3$, 3).

UV/Vis (CH_2Cl_2): λ_{max} (ε) = 264 (31500), 320 nm (8200).

Anal. Calcd for $C_{27}H_{29}NO_2S$ (431.7): C, 75.14; H, 6.77; N, 3.25; S, 7.43. Found: C, 74.95; H, 6.91; N, 3.15; S, 7.33.

Ethyl 2-(10-Hexyl-10*H*-phenothiazin-3-yl)benzoate (3d)

Prepared according to the GP and purified by flash chromatography (hexane–acetone 25:1); yield: 0.231 g (54%); yellow oil.

IR (film): 2955, 2928, 2856, 1716, 1601, 1577, 1463, 1444, 1395, 1365, 1333, 1288, 1246, 1194, 1163, 1128, 1089, 762, 465 cm^{-1}.

^{1}H NMR (300 MHz, acetone-d_6): δ = 0.86 (t, *J* = 7.2 Hz, 3 H), 1.04 (t, *J* = 7.1 Hz, 3 H), 1.31 (m, 4 H), 1.48 (m, 2 H), 1.81 (m, 2 H), 3.97 (t, *J* = 7.1 Hz, 2 H), 4.10 (q, *J* = 7.2 Hz, 2 H), 6.94 (dt, *J* = 1.2, 7.5 Hz, 1 H), 7.05 (m, 2 H), 7.09 (m, 1 H), 7.12 (m, 1 H), 7.15 (m, 1 H), 7.21 (m, 1 H), 7.41 (m, 1 H), 7.45 (m, 1 H), 7.57 (dt, *J* = 1.5, 7.5 Hz, 1 H), 7.74 (dd, *J* = 1.8, 7.2 Hz, 1 H).

^{13}C NMR (75 MHz, acetone-d_6): δ = 14.2 (CH_3), 14.3 (CH_3), 23.3 (CH_2), 27.2 (CH_2), 27.6 (CH_2), 32.2 (CH_2), 47.8 (CH_2), 61.4 (CH_2), 116.2 (CH), 116.7 (CH), 123.3 (CH), 125.2 (C_q), 125.3 (C_q), 127.8 (CH), 127.9 (CH), 128.1 (CH), 128.4 (CH), 128.5 (CH), 130.3 (CH), 131.1 (CH), 132.0 (CH), 132.6 (C_q), 136.4 (C_q), 141.7 (C_q), 145.5 (C_q), 146.2 (C_q), 169.2 (C_q).

MS (FAB$^+$): *m*/*z* (%) = 431.3 (M^+, 100), 386.3 ($M^+ - OCH_2CH_3$, 14), 346.2 ($M^+ - C_6H_{13}$, 15), 300.2 ($M^+ - C_6H_{13} - OCH_2CH_3$, 5), 273.2 ($M^+ - C_6H_{13} - CO_2CH_2CH_3$, 2).

UV/Vis (CH_2Cl_2): λ_{max} (ε) = 246 (28700), 274 (35900), 304 (14400), 352 nm (10800).

Anal. Calcd for $C_{27}H_{29}NO_2S$ (431.6): C, 75.14; H, 6.77; N, 3.25; S, 7.43. Found: C, 75.02; H, 6.83; N, 3.44; S, 7.45.

10,10′-Dihexyl-10*H*,10′*H*-3,3′-biphenothiazine-7-carbaldehyde (3e)

Prepared according to the GP and purified by flash chromatography (hexane–acetone, 20:1); yield: 0.41 g (69%); orange oil.

IR (KBr): 2953, 2926, 2854, 1685, 1602, 1579, 1461, 1415, 1377, 1335, 1310, 1279, 1244, 1198, 1144, 1104, 807, 747 cm^{-1}.

^{1}H NMR (300 MHz, CD_2Cl_2): δ = 0.86–0.90 (m, 6 H), 1.28–1.35 (m, 8 H), 1.40–1.47 (m, 4 H), 1.75–1.86 (m, 4 H), 3.84 (t, *J* = 7.3 Hz, 2 H), 3.88 (t, *J* = 7.3 Hz, 2 H), 6.87–6.94 (m, 5 H), 7.13 (dd, *J* = 7.8, 1.2 Hz, 1 H), 7.16–7.19 (m, 1 H), 7.28 (dd, *J* = 5.7, 2.1 Hz, 2 H), 7.31 (t, *J* = 2.3 Hz, 1 H), 7.34 (t, *J* = 2.3 Hz, 1 H), 7.56 (d, *J* = 2.0 Hz, 1 H), 7.63 (dd, *J* = 8.4, 2.0 Hz, 1 H), 9.77 (s, 1 H).

^{13}C NMR (75 MHz, CD_2Cl_2): δ = 14.32 (CH_3), 14.33 (CH_3), 23.17 (CH_2), 23.19 (CH_2), 27.0 (CH_2), 27.1 (CH_2), 27.2 (CH_2), 27.4 (CH_2), 32.0 (CH_2), 32.1 (CH_2), 48.0 (CH_2), 48.6 (CH_2), 115.4 (CH), 116.0 (CH), 116.2 (CH), 116.8 (CH), 122.9 (CH), 124.6 (C_q), 124.8 (C_q), 125.0 (C_q), 125.4 (CH), 125.5 (CH), 125.7 (CH), 125.8 (C_q), 125.9 (CH), 127.8 (CH), 127.9 (CH), 128.5 (CH), 130.7 (CH), 131.7 (C_q), 134.2 (C_q), 135.8 (C_q), 142.9 (C_q), 145.1 (C_q), 145.6 (C_q), 150.9 (C_q), 190.3 (CH).

EI MS (70 eV): *m*/*z* (%) = 594 (18), 593 (43), 592 (M^+, 100), 507 ($M^+ - C_6H_{13}$, 24), 422 ($M^+ - 2\ C_6H_{13}$, 25).

UV/Vis (CH_2Cl_2): λ_{max} (ε) = 270 (39400), 290 (57300), 326 (17800), 396 nm (14100).

Anal. Calcd for $C_{37}H_{40}N_2OS_2$ (592.9): C, 74.96; H, 6.80; N, 4.73; S, 10.82. Found: C, 75.12; H, 6.81; N, 4.85; S, 10.66.

10,10′-Dihexyl-7′-(10-hexyl-10*H*-phenothiazin-3-yl)-10*H*,10′*H*-3,3'-biphenothiazine-7-carbaldehyde (3f)

Prepared according to the GP and purified by flash chromatography (hexane–acetone, 20:1); yield: 0.37 g (62%); orange resin.

IR (KBr): 2954, 2927, 2855, 1684, 1603, 1579, 1459, 1416, 1379, 1336, 1243, 1199, 1148, 1106, 1006, 874, 807, 747 cm^{-1}.

^{1}H NMR (300 MHz, CD_2Cl_2): δ = 0.86–0.91 (m, 9 H), 1.28–1.35 (m, 12 H), 1.39–1.49 (m, 6 H), 1.75–1.86 (m, 6 H), 3.82–3.91 (m, 6 H), 6.87–6.94 (m, 7 H), 7.11–7.19 (m, 2 H), 7.28–7.36 (m, 8 H), 7.56 (d, *J* = 1.9 Hz, 1 H), 7.63 (dd, *J* = 8.4, 1.9 Hz, 1 H), 9.71 (s, 1 H).

^{13}C NMR (75 MHz, CD_2Cl_2): δ = 14.32 (CH_3), 14.34 (CH_3), 14.35 (CH_3), 23.17 (CH_2), 23.20 (CH_2), 23.21 (CH_2), 27.0 (CH_2), 27.20 (CH_2), 27.22 (CH_2), 27.36 (CH_2), 27.37 (CH_2), 27.4 (CH_2), 32.0 (CH_2), 32.1 (CH_2), 48.0 (CH_2), 48.1 (CH_2), 48.6 (CH_2), 115.3 (CH), 116.0 (CH), 116.09 (CH), 116.10 (CH), 116.14 (CH), 116.8 (CH), 122.9 (CH), 124.6 (C_q), 124.8 (C_q), 125.0 (C_q), 125.1 (C_q), 125.2 (C_q), 125.4 (CH), 125.42 (CH), 125.44 (CH), 125.47 (CH), 125.67 (C_q), 125.69 (CH), 125.76 (CH), 125.78 (CH), 125.9 (CH), 127.8 (CH), 127.9 (CH), 128.5 (CH), 130.7 (CH), 131.7 (C_q), 134.2 (C_q), 134.6 (C_q), 134.7 (C_q), 135.8 (C_q), 142.9 (C_q), 144.5 (C_q), 144.8 (C_q), 144.9 (C_q), 145.7 (C_q), 150.9 (C_q), 190.3 (CH).

MS (FAB$^+$): *m*/*z* (%) = 876 (19), 875 (44), 874 (M + H^+, 78), 873 (M^+, 100), 872 (31), 802 ($M^+ - C_5H_{11}$, 14), 790 (20), 789 ($M^+ + H - C_6H_{13}$, 32), 788 ($M^+ - C_6H_{13}$, 24), 704 ($M^+ + H - C_{12}H_{26}$, 12), 703 ($M^+ - C_{12}H_{26}$, 9), 620 (12), 619 ($M^+ + H - C_{18}H_{39}$, 19), 618 ($M^+ - C_{18}H_{39}$, 20).

UV/Vis (CH_2Cl_2): λ_{max} (ε) = 264 (66300), 288 (101300), 368 nm (26800).

Anal. Calcd for $C_{55}H_{59}N_3OS_3$ (874.3): C, 75.56; H, 6.80; N, 4.81; S, 11.00. Found: C, 75.56; H, 6.83; N, 4.88; S, 11.10.

Acknowledgment

The support of this work by the Deutsche Forschungsgemeinschaft (Graduate College 850, stipend for A.W.F.; SPP 1181) and by the Fonds der Chemischen Industrie is gratefully acknowledged. The authors also cordially thank Dr. Markus Sailer for valuable discussions and the BASF AG for the generous donation of chemicals.

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