Novel Donor 1,4-Benzothiazino[2,3-*b*]phenothiazine

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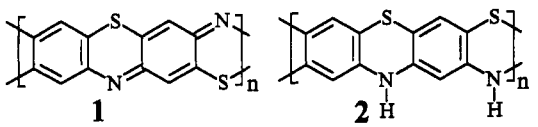
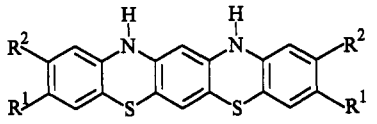
The synthesis of the novel organic donor 1,4-benzothiazino[2,3-*b*]phenothiazine (**3**) via a double Cadogan-type ring closure is reported. The target molecule is characterized by a ^{1}H-NOE spectrum and by X-ray analysis, thus confirming the "migration" of the lateral alkyl groups involved in this rearrangement. Surprisingly, the solid-state structure of neutral **3** shows that one phenothiazine subunit exists in a nearly planar conformation, a feature hitherto only known from crystalline radical ion salts of phenothiazine and from phenothiazines with strong electron-withdrawing substituents. **3** undergoes electrochemical oxidation at an extremely low potential as shown by cyclic voltammetry. EPR and ENDOR spectroscopic investigations of the radical cation of **3** demonstrate the delocalization of the unpaired electron over the whole pentacene perimeter, whereas in the neutral monoradical the spin is localized on one phenothiazine subunit.

Introduction

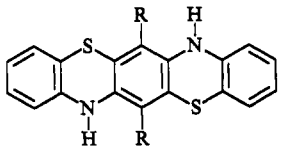
In our continuing efforts toward model compounds of poly(phenothiazine) **1** and **2** we report here the novel heterocycle 1,4-benzothiazino[2,3-*b*]phenothiazine (**3**). For symmetry reasons, **3** (mirror symmetry) is expected to possess a different electronic behavior as compared to its isomer 1,4-benzothiazino[3,2-*b*]phenothiazine (**4**) (inversion symmetry), which has been previously described.[1] **3** represents a promising new organic donor for charge-transfer complexes and radical ion salts with interesting electrical and magnetic properties.



1 **2**

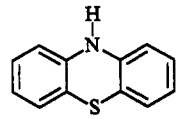


3 $R^1 = C(CH_3)_2(CH_2)_3CH_3$, $R^2 = H$



4 $R = O(CH_2)_5CH_3$

Whereas phenothiazine (**5**) is known to be easily oxidized to the phenothiazinyl neutral radical,[2] the oxidation of **4** immediately led to the stable iminoquinone **6**.[1] In contrast, if two hydrogen atoms are formally removed from the nitrogen centers in **3**, no neutral Kekulé-structure can be drawn. The question thus arises whether it is possible to generate the hypothetical diradical **7** by an oxidation of **3**. In relation to the open-chain *m*-phenylene nitroxides,[3] which exhibit triplet and quartet ground states, **7** would serve as a prototype of a sulfur-bridged *m*-phenylenediamine biradical.



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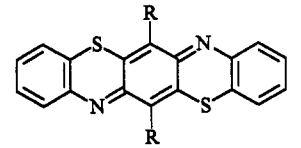
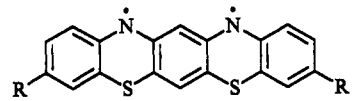
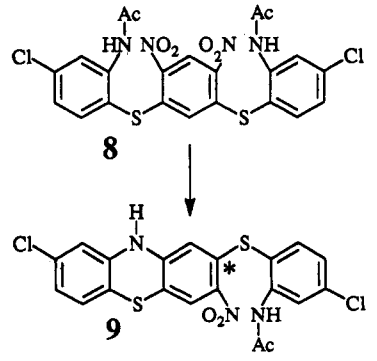


6 $R = O(CH_2)_5CH_3$



7 $R = C(CH_3)_2(CH_2)_3CH_3$

The synthesis of a chlorine substituted derivative of **3** (R1 = H, R2 = Cl) was first attempted by W. K. Warburton et al.[4] As a starting compound was used 4,6-bis[(2-acetamido-4-chlorophenyl)thio]-1,3-dinitrobenzene (**8**), which, via a two-fold Smiles rearrangement, was expected to transform into **3**. The only isolated product, however, was **9**, which was formed by a single Smiles rearrangement from **8**. A second Smiles rearrangement was not observed, which was probably due to the decreased electrophilicity of the starred carbon atom of structure **9**, thus preventing a nucleophilic attack of the acetylamido-anion.[5]



8 → **9**

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(3) Ishida, T.; Iwamura, H. *J. Am. Chem. Soc.* **1991**, *113*, 4238. Calder, A.; Forrester, A. R.; James, P. G.; Luckhurst, G. R. *J. Am. Chem. Soc.* **1969**, *91*, 3724.

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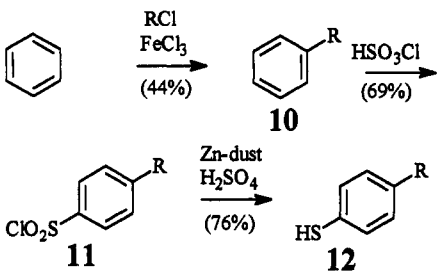
Results and Discussion

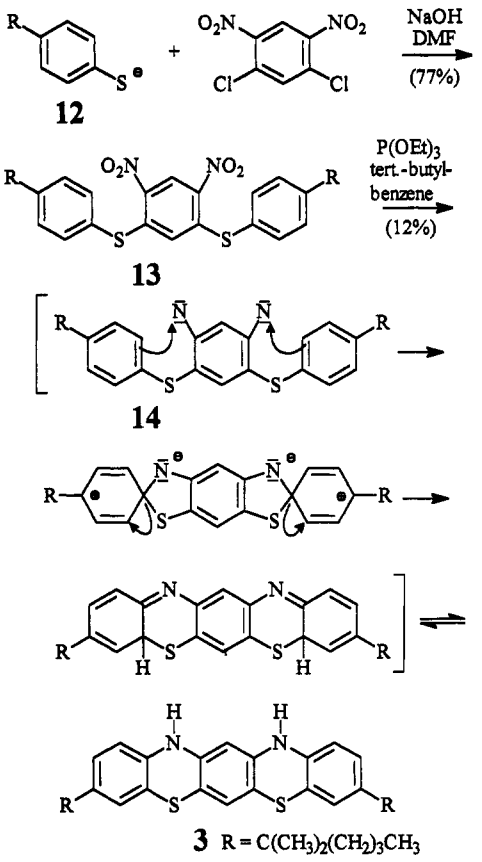
Synthesis. The structure of the target molecule **3** was chosen in order to satisfy the requirements of good solubility in organic solvents and of maximal stabilization of the aminyl radicals to be formed. To enhance the poor solubility usually found for rigid-rod units, **3** was prepared having solubilizing pendant alkyl chains. The goal was to locate these alkyl groups in a position para to the nitrogen atoms, because for the aminyl radical **7** these positions with high spin density were expected to be extremely sensitive to oxidation if unsubstituted. In order to avoid the target molecule from having reactive benzylic protons, alkyl chains were attached to the pentacene core yielding quarternary carbon atoms. Our synthetic route toward structure **3**, taking into consideration these requirements, is somewhat similar to the one by Warburton et al., as described above.[4] 4-(1,1-dimethylpentyl)thiophenol (**12**) was first prepared from 2-methyl-2-phenylhexane (**10**), which, upon chlorosulfonation yields 4-(1,1-dimethylpentyl)benzenesulfonyl chloride (**11**). **11** was subsequently reduced with zinc dust in sulfuric acid to yield 4-(1,1-dimethylpentyl)thiophenol (**12**).[6-8] The thiophenolate



generated from the reaction of **12** with sodium hydroxide in dimethylformamide was then reacted with 1,3-dichloro-4,6-dinitrobenzene to yield 1,3-bis[[4-(1,1-dimethylpentyl)phenyl]thio]-4,6-dinitrobenzene (**13**). To achieve the ring closure via the nitro groups, the nitrene-induced cyclization previously described by Cadogan[9] was used. A similar double reductive ring closure was recently reported in a new synthetic approach toward indolocarbazoles.[10] The mechanism as suggested by Cadogan is shown in Scheme 1. In the first step, the nitro groups are reduced to the dinitrene-intermediate **14**,[11] followed by an electrophilic ipso-attack of the nitrene moiety on the sulfur-bearing aromatic carbon atom of the terminal benzene unit. The rearrangement proceeds with a 1,2-shift of the sulfur–carbon bond as indicated by an arrow leading to the target structure **3**.

A ^{1}H-NMR NOE-experiment was performed to confirm the rearrangement-induced "migration" of the alkyl substituents to the 3 and 9 positions (500 MHz, DMSO-d_6). In agreement with the expected molecular structure, the doublet signal at $\delta = 6.62$ and the singlet at $\delta = 6.12$ showed a positive NOE enhancement when saturating the resonance of the amino proton ($\delta = 8.45$) and were therefore assigned to the protons H-1(11) and H-13, respectively.

Scheme 1



Crystal structure of 3. Single crystals of **3**, grown from deoxygenated tetrahydrofuran, were found to contain two hydrogen-bonded solvent molecules per donor molecule, which slowly evaporated if the crystals were stored at room temperature. Therefore, crystal structure analysis was carried out at 165 K with the crystal mounted in a sealed glass capillary. As expected from the difference of the C–S (1.76–1.77 Å) and C–N bond lengths (1.39–1.41 Å), the pentacene core is slightly bent (Figure 1). With regard to the conformation of the alkyl side chains, two crystallographically different molecules were found in the single crystal.

Analysis of the molecular structure of **3** revealed some surprising features (Figure 2). One of the phenothiazine subunits is nearly planar, with a folding angle of 176°(3°) between the central and the terminal benzene unit, whereas the other subunit shows a folding angle of 148.5°(0.4°). This latter angle is typical for substituted neutral phenothiazines, which are usually found in the range of 146–158°.[14] A planar conformation has not been reported previously, except for phenothiazines with strong electron-withdrawing substituents[14] and crystalline radical ion salts of phenothiazine and triphenodithiazines.[15] The peculiar solid-state geometry of **3** suggests that π-electronic conjugation is confined to one phenothiazine subunit, while

(6) Inatome, M.; Grennlee, K. W.; Derfer, J. M.; Boord, C. E. *J. Am. Chem. Soc.* **1952**, *74*, 292.
(7) Shirley, D. A.; Lehto, E. A. *J. Am. Chem. Soc.* **1957**, *79*, 3481.
(8) Adams, R.; Marvel, C. S. *Org. Synth.* **1921**, *1*, 71.
(9) Cadogan, J. I. G. *Synthesis* **1969**, *1*, 11.
(10) Kistenmacher, A.; Müllen, K. *J. Heterocycl. Chem.* **1992**, *29*, 1237.
(11) The dinitrene intermediate **14** was assumed for the sake of simplicity. Whether such a species really exists or the reaction proceeds in a consecutive manner was not investigated.
(12) MOPAC 6.0. Stewart, J. J. S.; Frank J. Seiler Research Laboratory, United States Air Force Academy, Colorado Springs, CO 80840 (1989).
(13) Structure **3** was calculated with R = $C(CH_3)_3$ and structure **4** with R = OCH_3.
(14) Chu, S. S. C. In *Phenothiazines and 1,4-Benzothiazines*; Gupta, R. R., Ed.; Elsevier: Amsterdam, 1988; pp 475–480.
(15) Kistenmacher, A.; Adam, M.; Baumgarten, M.; Pawlik, J.; Shen, Y.-J.; Müllen, K. *Synth. Met.* **1993**, *55–57*, 2034.

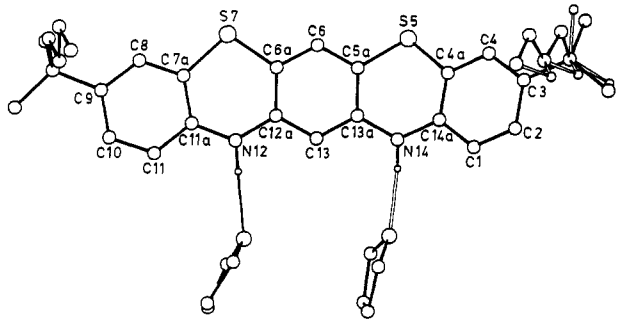


Figure 1. Top view of **3** with hydrogen bondings to tetrahydrofuran indicated by broken bonds.

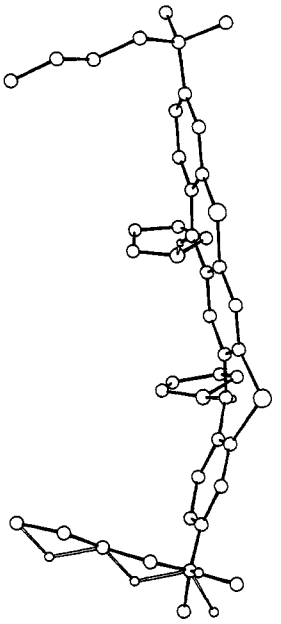


Figure 2. Side view of **3**. Two crystallographically different alkyl chains (solid/broken bonds) are observed.

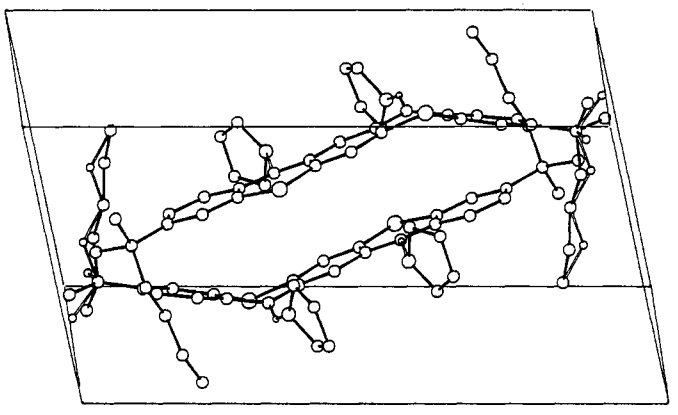


Figure 3. View onto the bc-plane of the unit cell.

the third benzene unit is electronically decoupled. The donor molecules have a parallel orientation in the unit cell. They are not arranged in a face-to-face arrangement, but are separated from each other by the two bulky alkyl chains and two solvent molecules (Figure 3).

Chemical and Electrochemical Oxidation of 1,4-Benzothiazino[2,3-*b*]phenothiazine (3). The radical cation of **3** is readily formed after storage of **3** in a chloroform solution for several hours. The solution changes to light green color. The UV/vis spectrum of this cationic species exhibits a broad absorption band with

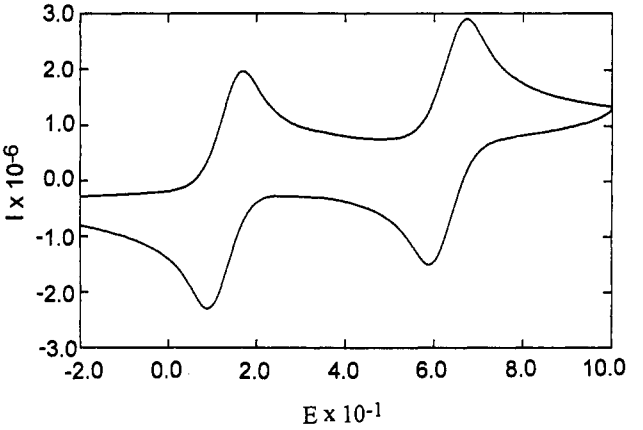


Figure 4. Cyclic voltammogram of **3** in CH_2Cl_2 (0 °C) with tetrabutylammonium hexafluorophosphate as conducting salt ($c = 5 \times 10^{-2}$ mol/L) and scan rate 100 mV/s (vs SCE).

maximum at 1223 nm (log ϵ = 4.320) and a shoulder at 1050 nm (log ϵ = 3.936). Several organic acceptors including 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), 7,7,8,8-tetracyanoquinodimethane (TCNQ), and tetracyanoethylene (TCNE) were evaluated for the formation of charge-transfer complexes with **3** as the donor. Amongst these, only DDQ gives rise to a color change when added to the donor solution. The UV/vis spectrum of the resulting complex formed between **3** and DDQ in dichloromethane shows a broad charge-transfer band in the range from 750 to 1100 nm with a maximum at 934 nm (log ϵ = 3.960). The cyclic voltammogram of 1,4-benzothiazino-[2,3-*b*]phenothiazine (**3**) measured in dichloromethane shows two separate and reversible single-electron oxidations at $E^1_{1/2}$ = 0.14 V and $E^2_{1/2}$ = 0.63 V (vs standard calomel electrode (SCE), ferrocene calibration) (Figure 4). Remarkably enough, the dication 3^{2+} is stable under the prevailing experimental conditions and does not act as proton donor. Under the same experimental conditions the parent phenothiazine (**5**) exhibits the first and second oxidative half-wave at 0.48 and 1.14 V, respectively. This dramatic shift of 340 and 510 mV to more negative potentials of the oxidation half-waves of **3** as compared to those of **5** emphasizes gain in donor strength when fusing a benzothiazine unit with phenothiazine (**5**). In comparison with the "para"-substituted 6,13-bis(hexyloxy) triphenodithiazine **4** ($E^1_{1/2}$ = 0.22 V, $E^2_{1/2}$ = 0.69 V) the first oxidation potential of **3** is shifted by 80 mV to negative potential, although **4** possesses two extra donating *O*-hexyl substituents on the central benzene unit.

MNDO-PM3 calculations[12] performed for structures **3** and **4**[13] predict adiabatic ionization potentials of 7.34 and 7.54 eV, respectively. These results are in qualitative agreement with the experimental findings. The low potential of the first one-electron oxidation indicates that even mild oxidants should be able to transform **3** into the corresponding radical cation.

EPR/ENDOR Results. The spin density distribution of the radicals derived from **3** were studied by EPR/ENDOR spectroscopy. The radical cation formed in solution in the presence of oxidants such as DDQ and iodine is characterized by a dominant septet splitting (Figure 5) comparable to that of the para isomer **4**.[1] This septet stems from the two nitrogens and their adjacent protons which possess the highest spin density (I_N = 1, I_H = 0.5; I_{tot} = 3). With highly resolved ENDOR measurements, five different proton couplings and the high-field

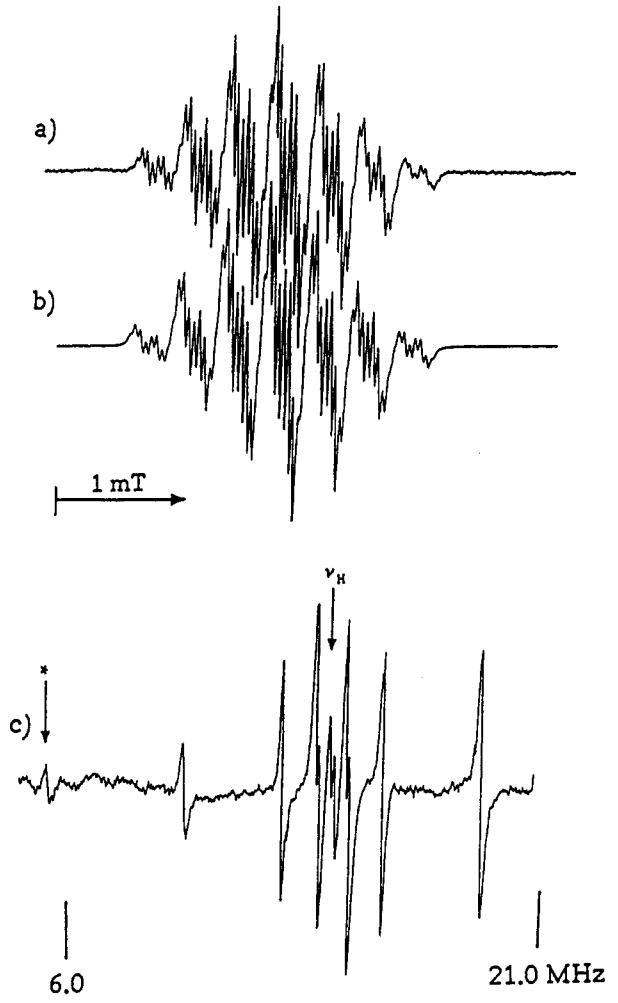


Figure 5. (a) Experimental EPR spectrum (260 K) of the radical cation $3^{\bullet+}$. (b) Simulation of the EPR spectrum using the hfc's determined by ENDOR spectroscopy as given in Table 1. (c) ENDOR spectrum recorded at 260 K. The high frequency nitrogen transition is denoted.

Table 1. Hyperfine Couplings Determined by EPR/ENDOR Measurements

radical cation $3^{\bullet+}$			neutral radical $3^{\bullet}$		
hfc [mT]		multiplet	hfc [mT]		multiplet
0.34	a(H)NH	2	0.226		1
0.116		1	0.204		1
0.040		2	0.119		1
0.032		2	0.081		1
0.0056		3	0.0223		–
0.301	a(N)	2	0.00957		–
			0.052		1
			0.64	a(N)	1

line of the pair of nitrogen signals could be detected. The hyperfine coupling constants (hfc's) for the nitrogens and the NH protons are reduced by 50% (Table 1) when compared to the cation radical of phenothiazine (**5**)[2] which clearly indicates that the unpaired electron is completely delocalized over the whole molecule. A considerable high spin-density ρ at C-6 (a_H = 0.12 mT, i.e. $\rho \sim 0.05$) of the central benzene unit reflects the different symmetry of **3** when compared to **4**.

When oxidizing agents such as lead tetraacetate or lead dioxide were added to a solution of **3**, a neutral radical was obtained yielding a three-line EPR spectrum with additional proton couplings. Thus, the neutral radical shows spin localization with only one nitrogen hfc. The ENDOR spectrum allows the resolution of the different proton couplings as shown in Figure 6. The assignment, however, is ambigous since in the localized form the multiplicity can no longer be used to differentiate between the protons of the terminal benzene units and those of the central benzene units. The formation of a biradical can be excluded due to the fact that no zero-field splitting in the frozen state could be observed under any conditions.

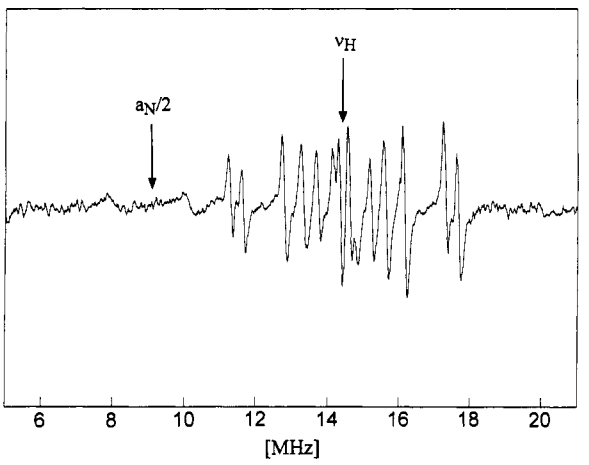


Figure 6. ENDOR spectrum of the neutral radical $3^{\bullet}$ recorded at 260 K. The high frequency nitrogen transition is denoted.

As another method for the preparation of the bisaminyl radical **7** from **3** we investigated the N–H homolysis with the potent H-acceptor 2,2-diphenylpicrylhydrazyl (DPPH). The abstraction of hydrogen atoms from **3** by DPPH was indicated by a spontaneous bleaching, when a solution of DPPH in toluene was added to a solution of **3**. However, this solution exhibited the same three-line EPR spectrum as described before for the oxidation of **3** with lead tetraacetate and lead dioxide. The same EPR spectrum was detected in a solution of **3** and 2,2-azoisobutyronitrile (AIBN) upon irradiation with UV-light. These results indicate that treatment of **3** with hydrogen abstractors such as DPPH and AIBN, only produces the monoradical of **3**. The abstraction of the remaining second amino hydrogen was not feasible with the methods used.

Experimental Section

General. All commercial solvents were of p.A. grade quality and were used as received. Melting points are uncorrected. ^1H and ^{13}C NMR: Varian Gemini 200 (200 MHz), Bruker AMX 500 (500 MHz). X-Band EPR/ENDOR: Bruker ESP 300 (9.5 GHz). MS: VG-Fisons Trio 2000 Quadrupole.

2-Methyl-2-phenylhexane (10). This reaction follows the general procedure of Boord et al.[6] To a cooled mixture (10 °C) of benzene (68.2 g, 874 mmol) and anhydrous ferric chloride (7.38 g, 45.5 mmol) was added slowly 2-chloro-2-methylhexane[16] (23.5 g, 175 mmol). The mixture was then heated carefully to 25–30 °C. After 2–3 h the evolution of hydrogen chloride gas ceased and the reaction mixture was poured into a hydrochloric acid/ice–water mixture. The dark-colored organic layer was separated, dried, and filtered over a short silica gel column with low boiling petroleum ether as the solvent. After distillation of the solvent, the product was distilled at reduced pressure (bp 72 °C, 10^{-2} mbar): 13.6 g (44%) of **10** were obtained; IR (neat) ν = 3050, 2960 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ϵ) = 256 nm (2.411); ^1H NMR (200

(16) 2-Chlor-2-methylhexane was prepared in 95% yield from the reaction of the commercially available 2-methyl-2-hexanol with HCl. For an analogous reaction see: Norris, J. F.; Olmsted, A. W. In *Organic Syntheses*; Gilman, H., Ed.; J. Wiley; New York, 1964; Collect. Vol. I, p 144.

MHz, $CDCl_3$) δ = 7.31–7.45 (m, 4H), 7.19–7.3 (m, 1H), 1.68 (t, J = 8.2 Hz, 2H), 1.37 (s, 6H), 1.23–1.41 (m, 2H), 1.06–1.17 (m, 2H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 150.4, 128.7, 126.4, 126.0, 45.1, 38.3, 29.7, 27.7, 24.1, 14.7; MS (70 eV) m/z (%) = 176.2 (100) [M^+]. Anal. Calcd for $C_{13}H_{20}$ (176.3): C, 88.6; H, 11.4. Found: C, 88.6; H, 11.5.

4-(1,1-Dimethylpentyl)benzenesulfonyl Chloride (11). This preparation of 11 is based on the preparation method of *p-tert*-butylbenzenesulfonyl chloride previously described by Shirley and Lehto.[7] 2-Methyl-2-phenylhexane (**10**) (12.8 g, 72.6 mmol) was dissolved in chloroform (25 mL) and cooled to 0 °C. Chlorosulfonic acid (22.5 g, 219 mmol) was then added dropwise while a temperature of 0 °C was maintained. During 12 h the mixture was allowed to warm to room temperature. The reaction mixture was poured into ice generating a turbid suspension. The mixture separated into two layers upon addition of ethyl acetate (100 mL). The organic layer was dried, the solvent was removed by distillation, and the residue was distilled under reduced pressure (bp 137 °C, 10^{-2} mbar) to give 13.8 g (69%) of 11: IR (neat) ν = 3040, 2870 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ϵ) = 241 nm (3.637); ^1H NMR (200 MHz, $CDCl_3$) δ = 7.94 (d, J = 7.2 Hz, 2H), 7.55 (d, J = 7.2 Hz, 2H), 1.63 (t, J = 8.2 Hz, 2H), 1.33 (s, 6H), 1.15–1.28 (m, 2H), 0.94–1.12 (m, 2H), 0.82 (t, J = 7.1 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 159.2, 142.0, 127.7, 127.3, 44.5, 39.1, 29.1, 27.3, 23.7, 14.4; MS (70 eV) m/z (%) = 274.1 (40) [M^+], 239.3 (42) [M^+ – Cl], 217.1 (100) [$M^+ - C_4H_9$]. Anal. Calcd for $C_{13}H_{19}Cl\,O_2S$ (274.8): C, 56.8; H, 6.97; Cl, 12.9; S, 11.7. Found: C, 56.9; H, 7.04; Cl, 12.8; S, 11.9.

4-(1,1-Dimethylpentyl)thiophenol (12). The preparation of **12** follows a previously described method used for the preparation of thiophenol from benzenesulfonyl chloride given by Adams and Marvel.[8] 4-(1,1-Dimethylpentyl)benzenesulfonyl chloride (11) (10.7 g, 38.9 mmol) was slowly added to a mixture consisting of concentrated sulfuric acid (37 g) and cracked ice (110 g), while a temperature of ca. –5 °C was maintained. Zinc dust (18.7 g, 286 mmol) was then gradually added at the same temperature and the mixture was allowed to stir for 20 min. The mixture was slowly heated to boiling and refluxed for 4 h. To the turbid suspension was added ethyl acetate (200 mL), after which the organic layer was separated and dried. Ethyl acetate was evaporated and a subsequent distillation under reduced pressure (bp 90–91 °C, 10^{-2} mbar) afforded 6.2 g (76%) of pure **12**: IR (neat) ν = 3040, 2860, 2580 cm^{-1}, UV (CH_2Cl_2) λ_{max} (log ϵ) = 234 nm (3.224); ^1H NMR (200 MHz, $CDCl_3$) δ = 7.16–7.28 (m, 4H), 3.39 (s, 1H), 1.57 (t, J = 8.2 Hz, 2H), 1.26 (s, 6H), 1.14–1.27 (m, 2H), 0.95–1.12 (m, 2H), 0.82 (t, J = 7.0 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 148.1, 130.2, 127.9, 127.3, 44.9, 38.0, 29.6, 27.6, 24.1, 14.8; MS (70 eV) m/z (%) = 208.1 (100)[M^+]. Anal. Calcd for $C_{13}H_{20}S$ (208.4): C, 74.9; H, 9.68; S, 11.6. Found: C, 74.6; H, 9.57; S, 11.9.

1,3-Bis[[4-(1,1-dimethylpentyl)phenyl]thio]-4,6-dinitrobenzene (13). A solution of 1,3-dichloro-4,6-dinitrobenzene[17] (3.1 g, 13.1 mmol) in dimethylformamide (100 mL) was heated to gentle boiling. To this, a thiolate solution prepared from **12** (5.4 g, 25.9 mmol), sodium hydroxide (1.5 g, 26.7 mmol), and dimethylformamide (100 mL) was added slowly. The mixture was refluxed for 40 min and the dimethylformamide was removed by distillation at reduced pressure. The orange oily residue was dissolved in chloroform and washed twice with water to remove traces of dimethylformamide. The oily residue was concentrated and dissolved in a few milliliters of acetone. In a hot water bath methanol was added carefully to this solution until a faint cloudiness was observed. The flask was stored in a refrigerator for 2 days, and the precipitated solid was isolated, filtrated, and recrystallized three times from ethanol to yield 5.8 g (77%) of **13** as a bright yellow crystalline powder: mp 84 °C; IR (KBr) ν = 3050, 2900, 1560 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ϵ) = 338 nm (4.279); ^1H NMR (200 MHz, $CDCl_3$) δ = 8.99 (s, 1H), 7.26 (d, J = 8.5 Hz, 4H), 7.12 (d, J = 8.5 Hz, 4H), 6.83 (s, 1H), 1.66 (t, J = 8.2 Hz, 4H), 1.37 (s, 12H), 1.24–1.42 (m, 4H), 1.05–1.21 (m, 4H), 0.89 (t, J = 7.2 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 153.0, 146.1, 142.4, 135.2, 130.7, 128.3, 127.3, 123.1, 44.6, 38.4, 29.3, 27.5, 23.8, 14.5; MS (70 eV) m/z (%) = 580.2 (30) [M^+], 523.2 (100) [$M^+ - C_4H_9$]. Anal. Calcd for $C_{32}H_{40}N_2O_4S_2$ (580.8): C, 66.2; H, 6.94; N, 4.82; S, 11.0. Found: C, 66.0; H, 7.01; N, 4.96; S, 11.0.

12,14-Dihydro-3,9-bis(1,1-dimethylpentyl)-5,7-dithia-12,14-diazapentacene (3). A mixture of **13** (2 g, 3.44 mmol) and triethyl phosphite (7.8 g, 46.9 mmol) in *tert*-butylbenzene (30 mL) was heated under argon at reflux (oil-bath, 180 °C) for 12 h. *tert*-Butylbenzene was removed by distillation and the dark brown, oily residue was purified by column chromatography using silica gel (eluent: dichloromethane/petroleum ether, 1:1); 210 mg (12%) of a white amorphous solid was obtained: mp 190 °C (dec); IR (KBr) ν = 3350, 2940 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ϵ) = 264 nm (5.026), 360 (3.973); ^1H NMR (500 MHz, DMSO-d_6) δ = 8.45 (s, 2H), 6.92 (dd, J = 8.3, 2.1 Hz, 2H), 6.79 (d, J = 2.1 Hz, 2H), 6.62 (d, J = 8.3 Hz, 2H), 6.46 (s, 1H), 6.12 (s, 1H), 1.52 (t, J = 5.2 Hz, 4H), 1.17 (s, 12H), 1.10–1.18 (m, 4H), 0.88–0.97 (m, 4H), 0.80 (t, J = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, THF-d_8) δ = 145.0, 144.3, 141.7, 126.3, 125.7, 125.1, 119.8, 115.7, 111.2, 102.6, 46.4, 38.9, 30.6, 29.1, 24.5, 15.6; MS (70 eV) m/z (%) = 516.2 (100) [M^+], 459.2 (20) [$M^+ - C_4H_9$], 401.2 (10) [$M^+ - 2\,C_4H_9 - H$]. Anal. Calcd for $C_{32}H_{40}N_2S_2$ (516.8): C, 74.4; H, 7.80; N, 5.42; S, 12.4. Found: C, 73.9; H, 7.85; N, 5.40; S, 12.6.

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Supplementary Material Available: ^1H- and ^{13}C-NMR spectra of **3** and **10–13** (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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