Synthesis of New Soluble Triphenodithiazines and Investigation of Their Donor Properties

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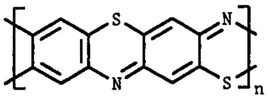
The syntheses of **6** and **7**, starting from 3,6-dichloro-2,5-bis(2-thioanisido)-1,4-benzoquinone (**4**), are reported. The solid-state conformations of **6** and **7** are elucidated by X-ray structure analysis, and the cyclovoltammetric investigation of **6** and **7** in solution shows low and reversible oxidation half-waves for both compounds. The relatively high oxidation potentials of **7** compared to **6** are related to their conformational features. EPR measurements on the radical cations derived from **6** and **7** both suggest a planarized conformation of these species. Oxidation of **6** with strong oxidants leads quantitatively to the quinoid triphenodithiazine **8**, whereas the charge-transfer complex formed between **7** and DDQ exhibits semiconducting properties.

Triphenodithiazine **2** has recently attracted attention as a model compound for poly(phenothiazine) (**1**)[1-3]. This ladder polymer is supposed to possess high intrinsic conductivity and shows non-linear optical activity[4-7]. The two most important features of this system are the rigid ladder structure that allows for extended π-conjugation and the presence of heteroatoms, which should give rise to low oxidation potentials and high donor ability. **1** is a hetero analog of a ladder-type arylenemethide[8]. The parent compound 7,14-dihydrotriphenodithiazine (**3**) has been synthesized by starting from N,N′-diphenyl-*p*-phenylenediamine which is thionated with elemental sulfur and a trace of iodine at elevated temperatures in a high-boiling solvent[2]. Unfortunately, the product shows a very low solubility, which seriously inhibits a full spectroscopic characterization and further chemical transformations. In order to obtain detailed information on the chemical and electrochemical properties of 7,14-dihydrotriphenodithiazine and triphenodithiazine, we have worked out a straightforward synthesis of a soluble derivative.



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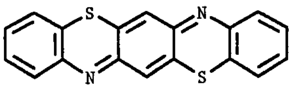

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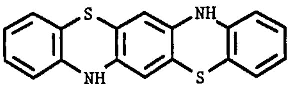

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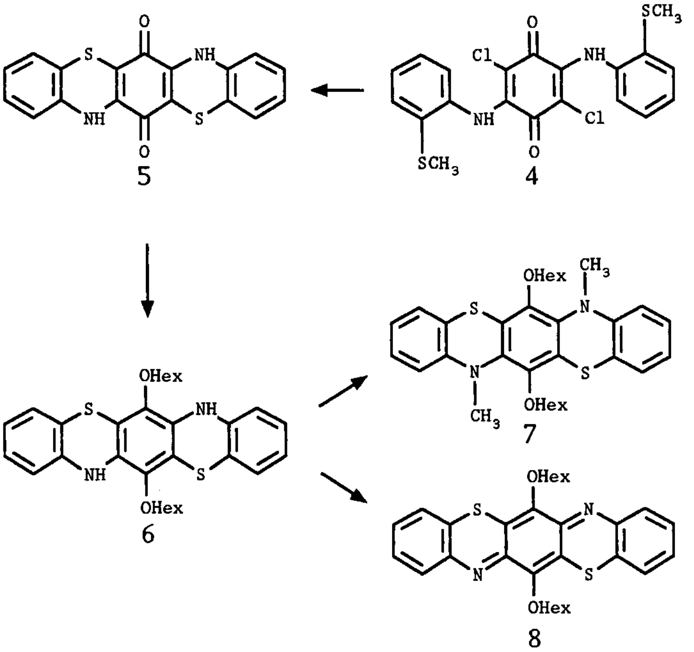
Results and Discussion

Synthesis

The starting material for the synthesis of a soluble triphenodithiazine is triphenodithiazinequinone **5**, which is prepared by an improved method based on the procedure suggested by Nishi et al.[10].



3,6-Dichloro-2,5-bis(2-thioanisido)-1,4-benzoquinone (**4**) is heated with aluminum chloride in *N*-methylpyrrolidone (NMP) to give **5** in 61% yield. **5** is reductively etherified with 1-bromohexane at the central quinoid unit in a phase-transfer-catalyzed reaction. The target molecule **6** is obtained in 79% yield and is soluble in common organic solvents. When treated with oxidants such as lead dioxide, a complete conversion to the stable deep red triphenodithiazine **8** takes place. It was impossible to obtain stable charge-transfer complexes from **6** with common acceptors such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), because of the immediate formation of the quinoid structure **8**. In order to overcome this problem, the *N*-methylated derivative **7** was synthesized by successive treatment of **6** with *n*-butyllithium and methyl iodide in tetrahydrofuran at −78°C. The *N*-methylated triphenodithiazine **7** was obtained in 60% yield. A solution of **7** in benzene treated with DDQ leads to a dark green charge-transfer complex. Elemental analysis indicates a 1:2 donor/acceptor stoichiometry. The powder conductivity is low ($\approx 10^{-7}$ S/cm) and crystalline complexes have not yet been obtained.

X-ray Structures of 6 and 7

The donor properties of phenothiazines are known to depend on their molecular conformations[11]. The solid-state structures of **6** and **7** were determined to study the folding angle between the central and terminal benzene units and to obtain some information regarding the position of the nonbonding electron pair on the nitrogen. These two structural features qualitatively describe the extent of the π-conjugation between the benzene units within the molecule. A maximal conjugation is expected for a folding angle of 180° between two adjacent benzene units and the spatial arrangement of the nonbonding electron pair on the nitrogen parallel to the p_z-orbitals of the benzene π-systems. It will be shown below, that crystal structures of **6** and **7** are relevant for understanding their electrochemical behavior. A single crystal of **6** was subjected to crystal structure analysis (Figure 1a). The molecule is located at a center of inversion. For the sake of clarity, the *O*-hexyl substituents are omitted in the side view of **6** (Figure 1b). **6** exhibits a dihedral angle of 156.6° between the central and a terminal benzene ring. This is similar to the corresponding angle for the monoclinic modification of phenothiazine (153.3°)[12], whereas substituted phenothiazines, especially those with a substituent adjacent to the nitrogen center, have smaller angles due to nonbonding interactions of the substituent with the proton at nitrogen[13]. The position of 7-H was located by difference Fourier synthesis. The characteristic torsion angle C11a−C7a−N7−(7-H) is 168°, which allows the nitrogen lone pair to overlap with the π-orbitals of the benzene moieties. A single crystal of **7** was also investigated by X-ray analysis (Figure 2a). The crystal was found to have two different conformers (**7a**, **7b**) within the unit cell, both located at a center of inversion. The two isomers differ not only in the conformation of the *O*-hexyl group, but also in the dihedral angles between the central and the terminal benzene units and in the relative position of the methyl group attached to nitrogen (Figure 2b). The dihedral angle for **7a** and **7b** is 139.6° and 146.1°, respectively, which is similar to the corresponding angle in *N*-methylphenothiazine (143.7°)[14]. The position of the *N*-methyl group in **7a** and **7b** differs significantly from the position of the corresponding hydrogen atom in **6**. The torsion angles C11a−C7a−N7−C1''' for the two isomers **7a** and **7b** are 146.3° and 139.8°, respectively. This finding readily explains that there is less overlap possible between the nitrogen lone pair and the π-systems of the benzene units for **7a** and **7b** than in **6**.

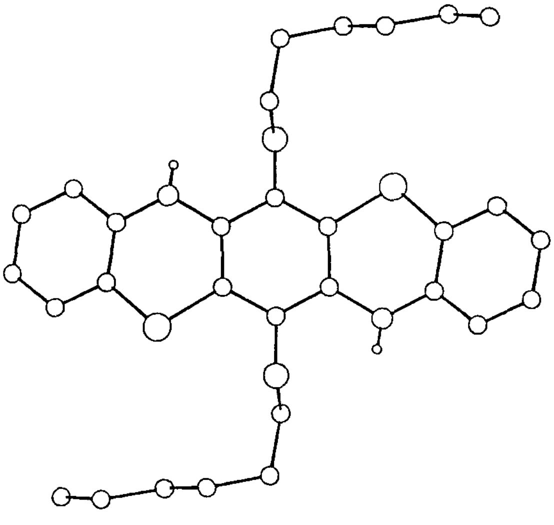


Figure 1a. Crystal structure of **6**

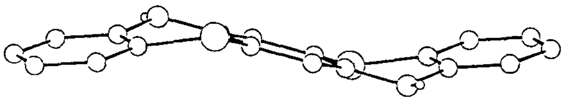


Figure 1b. Side view of **6**. The *O*-hexyl substituents are omitted

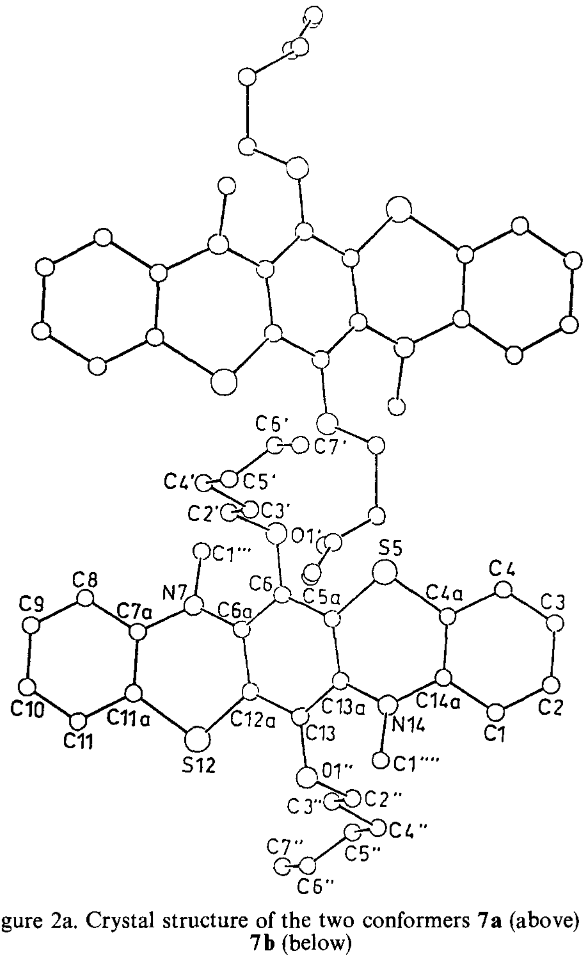


Figure 2a. Crystal structure of the two conformers **7a** (above) and **7b** (below)

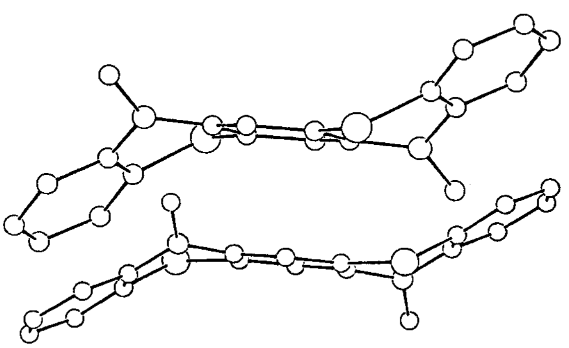


Figure 2b. Side view of **7a** (above) and **7b** (below). The *O*-hexyl substituents are omitted

Cyclovoltammetric Oxidation of Compounds 6 and 7

Compound **6** shows two reversible one-electron oxidations at 0.22 V and 0.69 V (vs. Standard Calomel Electrode, SCE, ferrocene calibration). These oxidation potentials are greatly shifted toward less positive values in **6** as compared to phenothiazine, that shows oxidation half-waves at 0.48 V and 1.14 V under the same experimental conditions. The positive charge is better stabilized by **6**, because the central benzene unit carries six electron-donating substituents. After a few redox-cycles the color of the solution changes from yellow to deep red. The intermediate dication is deprotonated irreversibly to the quinoid structure **8**. The cyclovoltammogram of **7** shows two reversible one-electron oxidations at 0.34 V and 0.76 V. The shift to more positive potentials with respect to **6** is in accordance with the structural data which point to the bent conformation of **7**.

EPR and ENDOR Spectroscopy

The low oxidation potential and the large difference between the first and second oxidative half-wave potential of compounds **6** and **7** allow the facile generation of the corresponding radical cations. The EPR spectra show highest resolutions when the radicals $6^{+\bullet}$ and $7^{+\bullet}$ are generated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in a mixture of toluene and trifluoroacetic acid. The spectral features did not change in the temperature range from 220 to 300 K. The EPR spectrum of $6^{+\bullet}$ is dominated by a septet splitting with an average spacing of 0.42 mT. The smaller hyperfine (hf) couplings can be resolved only partly in the EPR spectra. Therefore, highly resolved ENDOR spectra were recorded, which show four pairs of proton hf lines (Table 1), although five symmetrically unequivalent protons are present. From the intensity of the ENDOR signals and the multiplicity of the equivalent protons in the computer simulation of the EPR spectrum it is concluded that the smallest hyperfine coupling stems from two pairs of protons. A good agreement between the experimental and simulated EPR spectrum could be achieved by using the hf coupling constants deduced from the ENDOR spectra, where the nitrogen hf splitting is adjusted to 0.41 mT (Figure 3). The assignment of the ^{1}H hf couplings to the molecular positions of $6^{+\bullet}$ is based on a comparison with the well-characterized radical cation of phenothiazine (Table 1)[15]. The measured hf couplings for $6^{+\bullet}$ are generally reduced by a factor of roughly 0.6 compared to those of the phenothiazine radical cation[15], which is expected for a delocalized electron spin density taking into account the number of six membered rings. The largest proton coupling has to be assigned to the protons at the nitrogen ($a(\mathrm{H})_{7,14} = 0.44$ mT), which is the position of highest spin density. The good correlation of the hf couplings of $6^{+\bullet}$ with those of the phenothiazine radical cation allows the assignment of the other three couplings to the molecular positions by decreasing hyperfine couplings in the order: $a(\mathrm{H})_{3,10} > a(\mathrm{H})_{1,8} > a(\mathrm{H})_{2,9} \approx a(\mathrm{H})_{4,11}$ (Table 1). The EPR spectum of the *N*-methylated triphenodithiazine radical cation $7^{+\bullet}$ is somewhat better resolved than for $6^{+\bullet}$, but the ENDOR technique has again to be applied to the elucidation of small proton couplings. This enabled the detection of three pairs of proton couplings and one nitrogen hf coupling. The methyl groups in $7^{+\bullet}$ lead to small changes in the spin density compared to $6^{+\bullet}$. This may explain why only two hf splittings for four different sets of protons are detected. The experimental and simulated EPR spectra (Figure 4) are in good agreement. The largest proton coupling is assigned to the methyl group attached to nitrogen

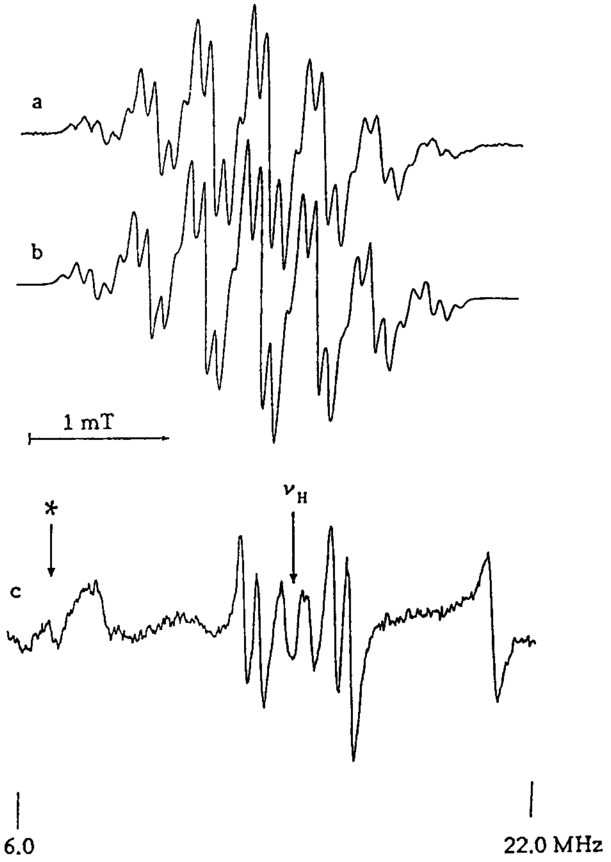


Figure 3. a) Experimental EPR spectrum (260 K) of the radical cation of triphenodithiazine $6^{+\bullet}$. b) Simulation of the EPR spectrum using the hyperfine coupling constants determined by ENDOR spectroscopy as given in Table 1. c) ENDOR spectrum recorded at 260 K. The asterisk denotes the high-frequency nitrogen transition

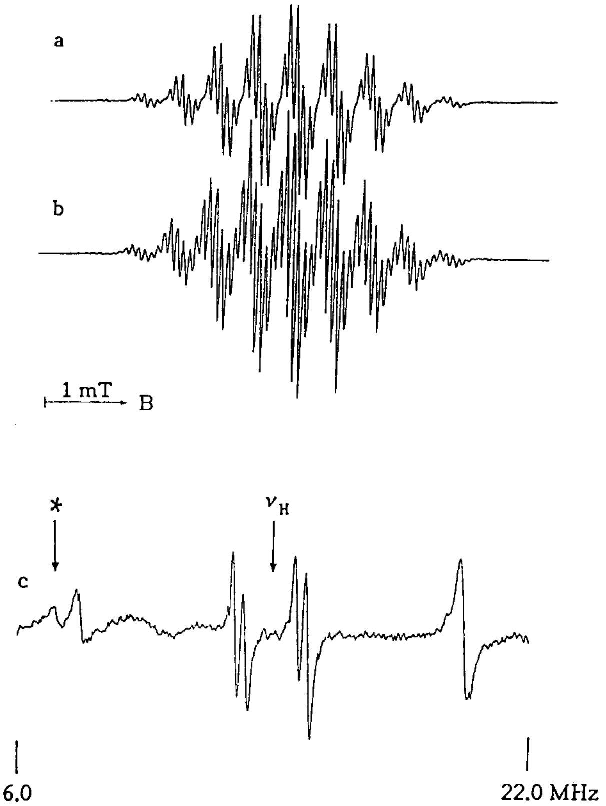


Figure 4. a) Experimental EPR spectrum (260 K) of the radical cation of triphenodithiazine $7^{+\bullet}$. b) Simulation of the EPR spectrum using the hyperfine coupling constants determined by ENDOR spectroscopy as given in Table 1. c) ENDOR spectrum recorded at 260 K. The asterisk denotes the high-frequency nitrogen transition

Table 1. ^{1}H and ^{14}N hyperfine coupling constants [mT] of the cation radicals $6^{+\bullet}$ and $7^{+\bullet}$. For comparison the values and the signs of the hyperfine couplings for the corresponding radicals of phenothiazine and *N*-methylphenothiazine are given from the literature reference[15]. The signs of the hyperfine coupling constants for $6^{+\bullet}$ and $7^{+\bullet}$ are assumed to be the same as for the phenothiazines given in this table

$6^{+\bullet}$	Phenothiazine$^{+\bullet}$
0.410 $a(N)_{7,14}$	0.667 $a(N)$
0.439 $a(H)_{7,14}$	0.745 $a(H)_{NH}$
0.085 $a(H)_{1,8}$	-0.124 $a(H)_{1,9}$
0.028 $a(H)_{2,9}$	-0.033 $a(H)_{2,8}$
0.120 $a(H)_{3,10}$	-0.257 $a(H)_{3,7}$
0.028 $a(H)_{4,11}$	+0.053 $a(H)_{4,6}$
$7^{+\bullet}$	N-Methyl-phenothiazine$^{+\bullet}$
0.450 $a(N)_{7,14}$	0.746 $a(N)$
0.452 $a(H)_{\beta\text{-}H}$	+0.672 $a(H)_{\beta\text{-}H}$
0.085 $a(H)_{1,8}$	-0.095 $a(H)_{1,9}$
0.065 $a(H)_{2,9}$	-0.072 $a(H)_{2,8}$
0.085 $a(H)_{3,10}$	-0.212 $a(H)_{3,7}$
0.065 $a(H)_{4,11}$	+0.019 $a(H)_{4,6}$

[$a(H)_{\beta\text{-}H}$ = 0.452 mT]. The smaller coupling constants for the protons in the positions 1,8 and 3,10 (0.085 mT) and positions 2,9 and 4,11 (0.065 mT) show an accidental degeneracy and are again assigned by referring to the data of the *N*-methylphenothiazine radical cation[15]. The observed delocalization of the unpaired electron requires an efficient delocalization of the unpaired electron between the adjacent benzene units. This suggests that the radical cations tend to planarize. As it is known from the literature, the solid-state conformation of the radical cation salt phenothiazine/hexachloroantimonate is nearly planar, exhibiting a folding angle of 175.8°[16].

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Experimental

Commercial solvents: Purified according to standard procedures. – Melting points uncorrected. – ^{1}H and ^{13}C NMR: Varian Gemini 200 (200 MHz and 50 MHz). – X-Band EPR/ENDOR: Bruker ESP 300 (9.5 GHz). – MS: VG-TRIO 2000.

Starting Materials: Except for 3,6-dichloro-2,5-bis(thioanisido)-1,4-benzoquinone (**4**), which has been prepared according to the literature procedure[17], all chemicals are commercially available.

Triphenodithiazinequinone (**5**): A suspension of **4** (2 g, 4.78 mmol)[17] and aluminium chloride (0.4 g, 3.00 mmol) in *N*-methylpyrrolidine is heated for 4 h at 160°C. The microcrystalline product formed is removed by filtration of the hot solution. Washing of the product with hot aqueous 2 M NaOH (150 ml) followed by hot water (200 ml) and acetone (200 ml) affords 1.02 g (61%) of **5** as dark blue microcrystals; m.p. >320°C. – No NMR data have been obtained because of the insolubility of **5** in common organic solvents. – IR (KBr): $\tilde{\nu}$ = 3240 cm^{-1} (NH), 3100 (CH), 1590 (CO). – UV (H_2SO_4): λ_{max} (lgε) = 337 nm (4.862), 713 (4.864). – MS (70 eV): *m/z* (%) = 350 (100) [M$^+$].

$C_{18}H_{10}N_2O_2S_2$ (350.4)
Calcd. C 61.7 H 2.88 N 7.99 S 18.3
Found C 61.9 H 2.85 N 7.74 S 18.3

7,14-Dihydro-6,13-bis(hexyloxy)triphenodithiazine (**6**): Triphenodithiazinequinone (**5**) (1.00 g, 2.85 mmol), sodium hydroxide (7.3 g, 130 mmol) and sodium dithionite $Na_2S_2O_4$ (5 g, 28.7 mmol) are suspended in water (20 ml). This mixture is stirred vigorously and heated under reflux in an argon atmosphere, until a clear, yellow solution is formed. Then 1-bromohexane (19.4 g, 117 mmol) is added via a syringe while refluxing. After 5 min tetrabutylammonium hydrogen sulfate (0.13 g, 0.38 mmol) dissolved in water (3 ml) and subsequently toluene (20 ml) are added. Refluxing is continued for 3 h. After the reaction is complete, the lower layer is colorless, whereas the upper one is deep red. Then toluene (50 ml) is added, the organic layer is separated and dried. After evaporation of the solvent a brown, oily residue is obtained. Treatment with *n*-hexane and filtration of the crystalline material afford **6** in a yield of 1.17 g (79%); m.p. 135°C. – IR (KBr): $\tilde{\nu}$ = 3350 cm^{-1} (NH), 3050 (CH arom.), 2950 (CH aliphat.). – UV (CH_2Cl_2): λ_{max} (lgε) = 277 nm (4.983), 326 (3.904). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.94–7.01 (m, 4H, 2-, 4-, 9-, 11-H), 6.75–6.83 (m, 2H, 2-, 10-H), 6.52 (d, *J* = 8.2 Hz, 2H, 1-, 8-H), 6.01 (s, 2H, NH), 3.92 (t, *J* = 6.6 Hz, 4H, OCH_2), 1.81–1.88 (m, 4H, 3′-, 3″-H), 1.36–1.59 (m, 12H, 4′-, 4″-, 5′-, 5″-, 6′-, 6″-H), 0.95 (t, *J* = 6.9 Hz, 6H, 7′-, 7″-H). – ^{13}C NMR (50 MHz, CD_2Cl_2): δ = 141.49 (q), 137.73 (q), 129.71 (q), 127.97 (t), 127.22 (t), 122.56 (t), 117.02 (q), 115.00 (t), 111.27 (q), 73.99 (s), 32.07 (s), 30.58 (s), 26.17 (s), 23.05 (s), 14.26 (p). – MS (70 eV): m/z (%) = 520 (100) [M$^+$], 435 (30) [M$^+$ – C_6H_{13}], 419 (7) [M$^+$ – OC_6H_{13}], 350 (18) [M$^+$ – 2 C_6H_{13}].

$C_{30}H_{36}N_2O_2S_2$ (520.8)
Calcd. C 69.2 H 6.97 N 5.38 S 12.3
Found C 69.3 H 6.93 H 5.32 S 12.4

6,13-Bis(hexyloxy)triphenodithiazine (**8**): PbO_2 (0.5 g, 2.1 mmol) is added to a solution of **6** (0.5 g, 0.96 mmol) in dichloromethane (25 ml). This mixture is stirred at room temperature for 48 h. The deep violet solution is filtered over silica gel with dichloromethane as eluent. After evaporation of the solvent 0.48 g (96%) of dark green needles of **8** is obtained. m.p. 137°C. – IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1} (CH arom.), 2950 (CH aliph.). – UV (CH_2Cl_2): λ_{max} (lg ε) = 294 nm (4.647), 370 (3.565), 514 (4.504), 550 (4.57). – ^1H NMR ($CDCl_3$): δ = 7.52 (d, J = 8.1 Hz, 2H), 7.12–7.24 (m, 6H), 4.21 (t, J = 6.7 Hz, 4H, OCH_2), 1.86–1.93 (m, 4H, 3′-, 3″-H), 1.35–1.59 (m, 12H, 4′-, 4″-, 5′-, 5″-, 6′-, 6″-H), 0.94 (t, J = 6.8 Hz, 6H, 7′-, 7″-H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 144.11 (q), 144.08 (q), 141.24 (q), 132.46 (t), 128.54 (t), 127.80 (t), 125.70 (t), 123.77 (q), 121.30 (q), 73.66 (s), 32.15 (s), 30.79 (s), 26.20 (s), 23.14 (s), 14.57 (p). – MS (70 eV): m/z (%) = 518 (54) [M$^+$], 446 (62) [M$^+$ – C_5H_{11}], 433 (28) [M$^+$ – C_6H_{13}], 417 (8) [M$^+$ – OC_6H_{13}].

$C_{30}H_{34}N_2O_2S_2$ (518.7)
Calcd. C 69.5 H 6.60 N 5.40 S 12.4
Found C 69.2 H 7.16 N 5.67 S 11.7

6,13-Bis(hexyloxy)-7,14-dimethyltriphenodithiazine (**7**): A solution of **6** (3 g, 5.76 mmol) in dry THF (50 ml) is degassed several times by the freeze-pump-thaw method and flushed with argon. The solution is cooled down to −78°C and a 2.5 M n-butyllithium (5.7 ml, 14.3 mmol) is added with stirring. The red solution is stirred further for 5 min at −78°C, then methyl iodide (3.4 g, 23.9 mmol) is added. The mixture is slowly heated to room temperature and stirred for 15 min. Aqueous NaOH solution (0.2 M, 50 ml) and ethyl acetate are added, the organic layer is separated, dried and the solvent evaporated. The dark solid residue is dissolved in a small amount of dichloromethane and then precipitated with methanol. This procedure is repeated several times to yield 2.02 g (64%) of **7** as a white crystalline powder with m.p. 128°C. – IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1} (CH arom.), 2950 (CH aliph.), 2790 (N-CH_3). – UV (CH_2Cl_2): λ_{max} (lg ε) = 278 nm (4.834), 326 (3.838). – ^1H NMR (200 MHz, CD_2Cl_2): δ = 7.06–7.16 (m, 4H), 6.84–6.91 (m, 4H), 3.67 (t, J = 6.6 Hz, 4H, OCH_2), 3.44 (s, 6H, N-CH_3), 1.78–1.85 (m, 4H, 3′-, 3″-H), 1.33–1.55 (m, 12H, 4′-, 4″-, 5′-, 5″-, 6′-, 6″-H), 0.94 (t, J = 6.2 Hz, 6H, 7′-, 7″-H). – ^{13}C-NMR (50 MHz, CD_2Cl_2): δ = 148.5 (q), 142.0 (q), 133.9 (q), 128.1 (t), 127.3 (t), 126.3 (q), 124.5 (q), 123.0 (t), 116.9 (t), 74.46 (s), 40.87 (s), 32.48 (s), 30.61 (s), 26.56 (s), 23.42 (s), 14.63 (p). – MS (70 eV), m/z (%) = 548 (100) [M$^+$], 533 (4) [M$^+$ – CH_3], 463 (9) [M$^+$ – C_6H_{13}], 378 (10) [M$^+$ – 2 C_6H_{13}].

$C_{32}H_{40}N_2O_2S_2$ (548.8)
Calcd. C 70.0 H 7.35 N 5.11 S 11.7
Found C 70.1 H 7.27 N 4.83 S 11.4

X-ray Structural Analysis: Single crystals of **6** and **7** (grown from ethyl acetate) have been measured on an Enraf-Nonius CAD-4 diffractometer using graphite – monochromized Cu-K_α radiation, ω/2Θ technique, lattice parameters have been derived by least-squares refinement of the scattering angles of 25 reflections. During the measurement, three standard reflections have been measured every 8000 s. Both structures have been solved with direct methods (MULTAN). H atoms, except for N–H in **6** have been placed into their computed positions by using known bonding geometry (C–H distance: 0.95 Å) and have been refined in the riding mode with isotropic temperature coefficients. Empirical absorption correction has been applied. During the last full matrix least-squares refinement, anisotropic temperature coefficients have been calculated for all non-hydrogen atoms.

X-ray Structure of **6**[18]: Crystal size: 0.4 × 0.2 × 0.25 mm^3, $C_{30}H_{36}N_2O_2S_2$, M = 520.8 g, monoclinic, a = 15.1822(7) Å, b = 5.9102(7) Å, c = 15.2211(7) Å, β = 92.516(4)°, V = 1364.5 Å^3, Z = 2, d_x = 1.27 g · cm^{-3}, space group: $P2_1/n$ (14), $1° < \Theta < 60°$, $0 < h < 17$, $0 < k < 6$, $-17 < l < 17$, 2360 reflections [1561 with $I > 3\sigma(I)$, 2170 unique], μ = 19.5 cm^{-1}, 166 variables, R = 0.041, R_w = 0.041 (w = 1).

X-ray Structure of **7**[18]: Crystal size: 0.55 × 0.25 × 0.25 mm^3, $C_{32}H_{40}N_2O_2S_2$, M = 548.8 g, triclinic, a = 12.856(1) Å, b = 13.387(2) Å, c = 9.658(1) Å, α = 104.30°, β = 91.56(1)°, γ = 111.75(1)°, V = 1483 Å^3, Z = 2, d_x = 1.23 g · cm^{-3}, space group: $P\bar{1}$ (2), $1° < \Theta < 60°$, $0 < h < 16$, $-14 < k < 14$, $-20 < l < 20$ (measured as a B-centered cell), 3056 reflections [2696 with $I > 3\sigma(I)$, 3054 unique], μ = 18.2 cm^{-1}, 343 variables, R = 0.060, R_w = 0.061 (w = 1).

Charge-Transfer Complex of (**7**) *with DDQ:* A solution of **7** (0.274 g, 0.5 mmol) in benzene (10 ml) is combined with a solution of DDQ (0.227 g, 1.0 mmol) in benzene (10 ml) with vigorous stirring. The color changes immediately to dark green. The mixture is cooled in a refrigerator. After 2 d the formed charge-transfer complex is filtered off and washed extensively with benzene. This procedure affords 120 mg (25%) of a dark green powder. – UV (CH_2Cl_2): λ_{max} (lg ε) = 275 nm (4.113), 328 (4.118), 454 (3.422), 605 (3.627), 703 (3.784), 791 (3.649).

$C_{48}H_{40}Cl_4N_6O_6S_2$ (1002.8)
Calcd. C 57.5 H 4.02 Cl 14.1 N 8.38 S 6.39
Found C 57.3 H 3.92 Cl 14.3 N 8.23 S 6.24

Preparation of Radical Cations for EPR/ENDOR Spectroscopy: The samples have been prepared by reaction of 10^{-3} M trifluoroacetic acid/toluene solutions of the parent triphenodithiazine with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). In principle, the radical cation can also be generated by using iodine (I_2) or silver(I) oxide (Ag_2O) as oxidants. The solutions have carefully been deoxygenated by flushing with purified argon and then degassed by the freeze-pump-thaw technique. The half-life periods of the radicals in sealed tubes are in the order of several days and may conveniently be determined by EPR and ENDOR spectroscopy.

Cyclic Voltammetry Experiments: The cyclic voltammograms have been obtained under strictly inert conditions in CH_2Cl_2 as solvent and with tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as conducting salt ($c = 5 \cdot 10^{-2}$ mol/l). The solution has been degassed with nitrogen and dried with an internal alumina column at 0°C. The substances were added in a nitrogen counterflow to yield a 10^{-4} to 10^{-5} M solution. The half-wave potentials are given vs. standard calomel electrode (SCE). They were obtained with a scan rate of 100 mV/s at a temperature of 0°C. A platinum disc has been used as working electrode and a platinum wire as counter electrode. A silver wire has been employed as a quasi reference and for calibration Cp_2Fe/Cp_2Fe^+ (Cp: cyclopentadienyl) as an internal standard (310 mV vs. SCE).

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[1] C. W. Spangler, M. L. Saindon, E. G. Nickel, L. S. Sapochak, D. W. Polis, L. R. Dalton, R. A. Norwood, *Nonlinear Optic and Materials (SPIE)* **1991**, *1497*, 408.

[2] C. Della Casa, F. Andreani, P. Costa Bizzarri, M. Fiorini, E. Salatelli, L. Grossi, W. Porzio, *Synth. Met.* **1989**, *29*, E477.

[3] F. Andreani, P. Costa Bizzarri, C. Della Casa, M. Fiorini, E. Salatelli, *J. Heterocycl. Chem.* **1991**, *28*, 295.

[4] L. Yu, M. Chen, L. R. Dalton, *Chem. Mater,* **1990**, *2*, 649.

[5] H. S. Nalwa, *J. Mater. Sci. Lett.* **1990**, *9*, 1296.

[6] O.-K. Kim, *J. Polym. Sci. Polym. Lett.* **1985**, *23*, 137.

[7] O.-K. Kim, *Mol. Cryst. Liq. Cryst.* **1984**, *105*, 161.

[8] U. Scherf, K. Müllen, *Polym. Commun.*, in press.

[9] C. Della Casa, P. Costa Bizzarri, F. Andreani, *Synth. Met.* **1987**, *18*, 381.

[10] H. Nishi, S. Minami, K. Kitahara, *J. Heterocycl. Chem.* **1989**, *26*, 875.

[11] R. R. Gupta, M. Kumar in *Phenothiazines and 1,4-Benzothiazines* (Ed.: R. R. Gupta), Elsevier, Amsterdam, **1988**, chapter 1.

[12] J. D. Bell, J. F. Blount, O. V. Briscoe, H. C. Freeman, *Chem. Commun.* **1968**, 1656.

[13] S. S. C. Chu, V. Napoleone, A. L. Ternay, S. Chang, *Acta Crystallogr. Sect. B.* **1982**, *38*, 2508.

[14] S. S. Chu, D. van der Helm, *Acta Crystallogr. Sect. B.* **1974**, *30*, 2489.

[15] N. Helle, H. Kurreck, M. Bock, W. Kieslich, *Magn. Reson. Chem.* **1985**, *23*, 964.

[16] T. Uchida, M. Ito, K. Kozawa, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 557.

[17] H. Nishi, Y. Hatada, K. Kitahara, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1482.

[18] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-56091, the names of the authors and the journal citation.

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