Syntheses and Properties of S$_2$-Bridged Benzidines

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The syntheses of 1,2-benzodithiino[5,4,3-*cde*][1,2]benzodithiin-2,7-diamine (**1**) and dithio-bridged benzidine **2** have been achieved. The starting material for the synthesis of **1** was 1,3-diiodo-5-nitrobenzene (**15**) which was transformed by conventional means into 1,2-bis[3,5-bis(ethylthio)phenyl]-diazane (**19**). The benzidine rearrangement of **19** in the presence of HBF$_4$ at –30 °C yielded 4,4′-diamino-2,2′,6,6′-tetraethylthiobiphenyl (**20**) in 50 % yield. Treatment of **20** with sodium in ammonia and work-up in the presence of air yielded **1**. The latter compound could be reduced with LiAlH$_4$ to the tetrathiol **20a**. The starting material for the preparation of **2** was 3-chloro-1-iodo-5-nitrobenzene (**23**), a side product of the preparation of **15**. It was transformed analogously to the preparation of **1** into 1,2-bis(3-ethylthiophenyl)diazane (**28**). The benzidine rearrangement of **28** in presence of HBF$_4$ at –30 °C afforded 4,4′-diamino-2,2′-bis(ethylthio)biphenyl (**29**) in 49 % yield. Treatment of **29** with sodium in ammonia and work-up under aerobic conditions yielded **2**. Quantitative reduction of **2** to the thiol **29a** could be achieved with LiAlH$_4$. The reversible electrochemical reduction of **1** on unmodified glassy carbon electrodes leads to a product to which the structure of **3** was assigned.

The search for materials with new properties has influenced synthetic inorganic and organic chemistry considerably. Organic compounds that are conductors,[1] have high spin,[2] or possess novel optical properties,[3] have all been of main interest. As part of a study of substances which may change conformational and conducting properties as a function of the redox state we focused on disulfides. Our interest in these compounds was attracted by the finding that enzymes from the Calvin cycle can be modulated by the reversible reduction of an S–S bond by means of a special mediator, thioredoxin.[4][5] Very simple systems whose structures should change dramatically upon reduction are benzidines that are bridged by two (**1**) or one (**2**) sulfur bridges.

Both compounds should undergo large conformational changes when reduced to **3** and **4**, respectively. Amino groups were chosen as substituents for the 4,4′-positions of the biphenyl systems in **1**–**4** because they can be connected with other functional groups or even solid surfaces by condensation reactions or incorporated into a pyrrole ring, to name only two possibilities. In addition these functional groups can be manipulated easily by procedures known from the chemistry of aromatic amines. In this paper we report on the syntheses of 1,2-benzodithiino[5,4,3-*cde*][1,2]-benzodithiin-2,7-diamine (**1**) and dibenzo[*ce*][1,2]dithiin-2,7-diamine (**2**).

Synthesis of Compound 1

The parent system of **1**, 1,2-benzodithiino[5,4,3-*cde*][1,2]-benzodithiin (**8**) has been synthesized by De Lucchi et al.[6] Starting from 2,2′,6,6′-tetrahydroxybiphenyl (**5**)[7], **8** was prepared by this route in four steps which involved the rearrangement of the 2,2′,6,6′-tetrakis[(dimethylamino)thiocarbonyloxy]biphenyl (**6**) to the 2,2′,6,6′-tetrakis[(dimethylamino)carbonylthio]biphenyl (**7**) and subsequent hydrolysis and air oxidation of **7** to **8**. The synthetic bottle neck in this route was the reaction of **5** with dimethylthiocarbamoyl chloride which gave **6** in only 18 % yield.

We first tried to adapt this route and attempted to couple 5-phthalimidoresorcin (**9**)[8] to **10**. However, oxidation of **9**, using FeCl$_3$ or Pd(acac)$_2$ as oxidant, was unsuccessful. Therefore, we tried a different approach in which we used
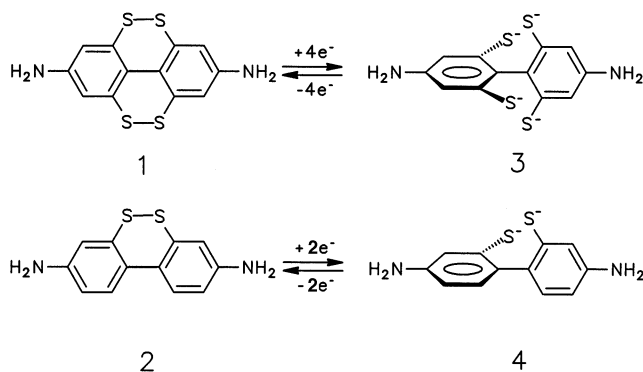
Scheme 1
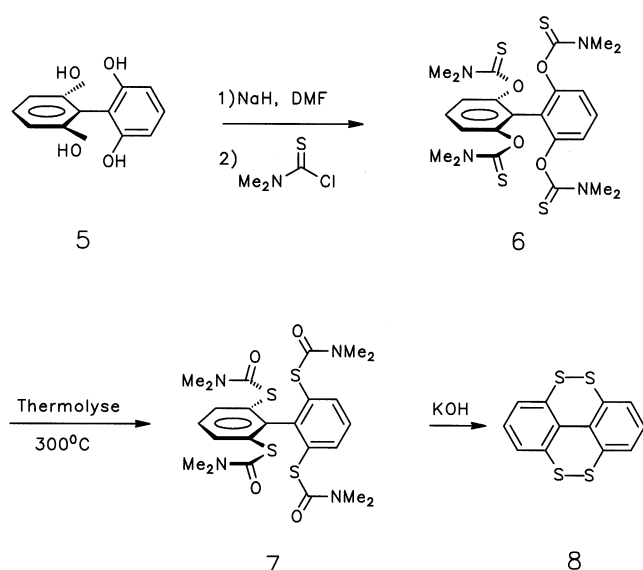
Scheme 2


the benzidine rearrangement[9][10] to couple the two aromatic rings and to place the amino groups in the *p* position in one step. The starting point of this sequence (Scheme 2) was 1,2-bis[(3,5-dimethoxy)phenyl] diazane (**11**), which was available from 3,5-dimethoxyaniline in two steps.[11] The yield of the desired 4,4′-diamino-2,2′,6,6′-tetramethoxybiphenyl (**12**) was very much dependent on the reaction conditions. We found that in aqueous solution at room temperature the product was mostly 6,6′-diamino-2,2′,4,4′-tetramethoxybiphenyl (**13**), but, when dry ethanol, saturated with HCl was used and when the reaction was carried out at low temperature (−30 °C), we could obtain **12** in 44% yield. In addition, **13** (44%) and 4,6′-diamino-2,2′,4′,6-tetramethoxybiphenyl (**14**, 12%) were isolated. This promising route was abandoned when we were unable to remove the methyl groups in **12**, by treating it with HI or BBr$_3$ or AlCl$_3$.

Since the benzidine rearrangement worked rather well, we modified the route shown in Scheme 2 in order to avoid the necessity of ether cleavage. Success was realized by starting with 1,3-diiodo-5-nitrobenzene (**15**)[12] which could be transferred to the corresponding bis(ethylthio) derivative **16**.[13] Reduction of the nitro group in **16** to the amino group in **17** could be accomplished by using Sn^{II}.[14] Treatment of **17** with CuCl[15] and subsequent reduction[11] of the azobenzene moiety yielded the desired hydrazine derivative **19**. The overall yield of these four steps was 50%.

The key step in our synthesis of **1** was the benzidine rearrangement of **19** into 4,4′-diamino-2,2′,6,6′-tetraethylthiobiphenyl (**20**). Our first attempt, using dry ethanol saturated with HCl at −75 °C was not very encouraging. We obtained a mixture of **20** and the isomers **21** and **22** of which only 12% was **20**. However, variation of the solvent, temperature and acid increased the yield of **20** to 56%, when a 0.0078 M concentration of **19** in dry diethyl ether with 54% HBF$_4$ at −30 °C was used. The step from **20** to **1** was straightforward by treating **20** with sodium in liquid
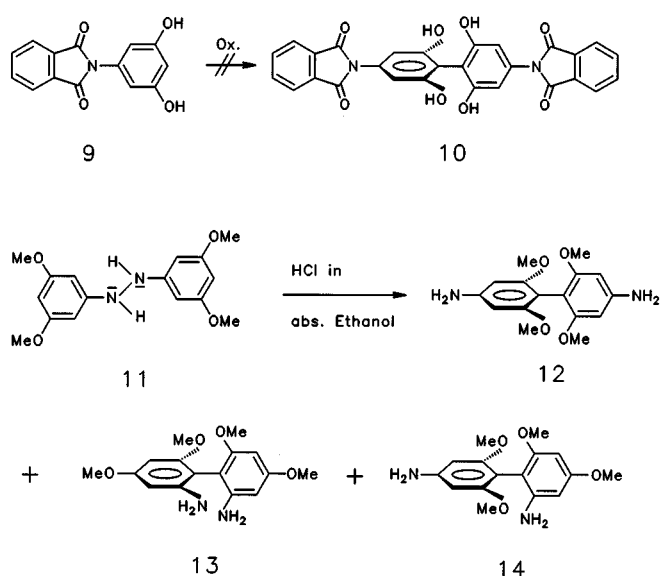
ammonia and subsequent work-up in presence of air yielded **1** almost quantitatively. The parent system **1** could be reduced quantitatively with LiAlH$_4$ to yield the tetrathiol **20a**. The latter reverts back to **1** when exposed to air.

Scheme 3 (**20a** = **20** with H instead of Et)
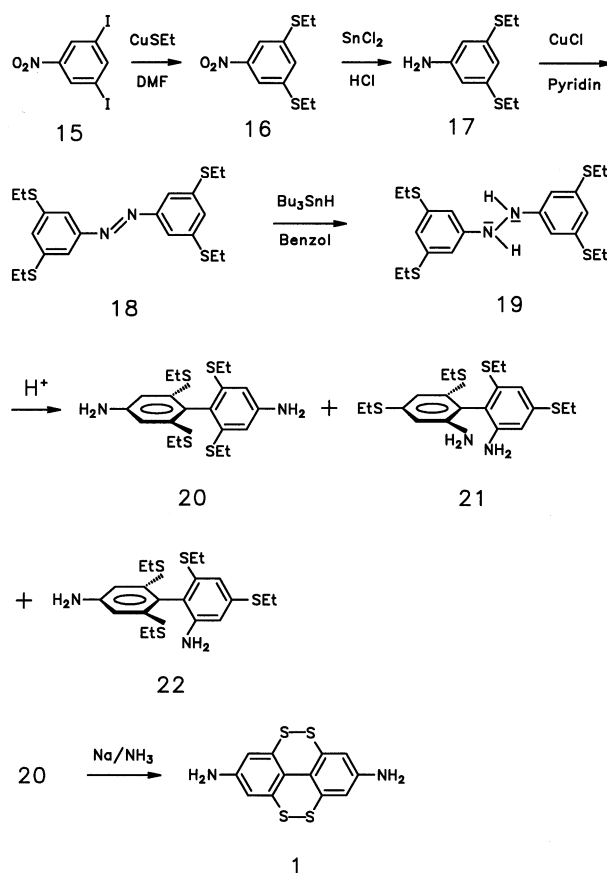
Synthesis of Compound 2

The preparation of **15** involved the reaction of *p*-nitro-aniline with iodine chloride followed by the removal of the amino group.[12] As a side-product of the iodination we isolated 3-chloro-1-iodo-5-nitrobenzene (**23**), which proved to be a good starting material for the preparation of **2** (Scheme 4).

Scheme 4 (**29a** = **29** with H instead of Et)
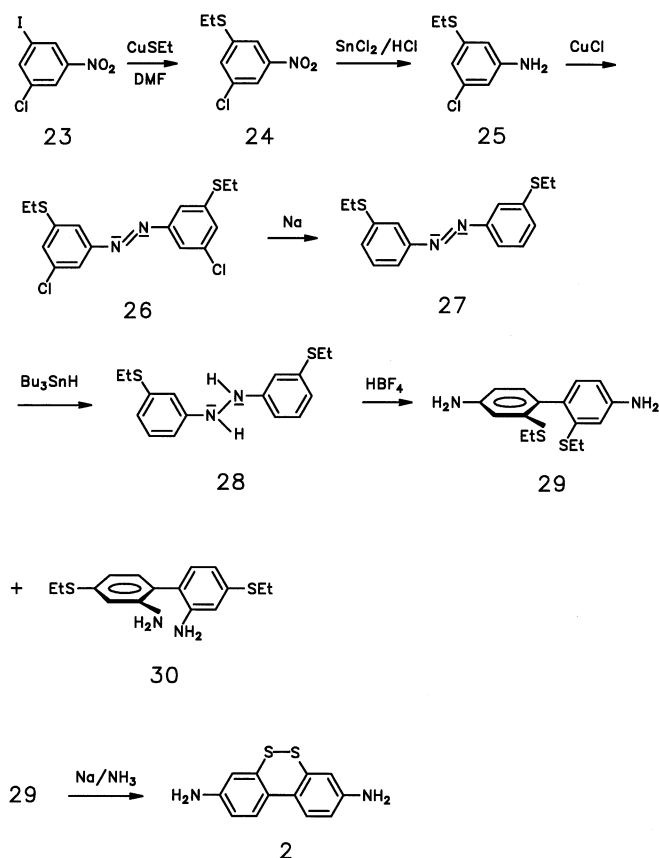
In this protocol we made use of the fact that iodine bound to the benzene nucleus reacts faster than chlorine. This allowed **23** to be transformed into **24** in reasonable yield. The succeeding steps were analogous to those shown in Scheme 3. The nitro group in **24** was reduced to the amino group in **25**, and the azobenzene derivative **26** was obtained by reaction of **25** with CuCl/pyridine. The chlorine in **26** was reductively removed with sodium to yield the azobenzene derivative **27**.[16] Subsequent reduction of the azo linkage in **27** with Bu$_3$SnH yielded hydrazine **28**. The benzidine rearrangement of **28** with HBF$_4$ in diethyl ether at −30 °C yielded mainly two products, the 4,4′-diamino (**29**) and the 2,2′-diamino (**30**) isomers in about 50% yield each. Treatment of **29** with sodium in liquid ammonia and subsequent work-up in presence of air afforded **2** in almost quantitative yield. The latter could be reduced quantitatively with LiAlH$_4$ to the dithiol **29a**. **29a** reverts to **2** when exposed to air.

Properties of Compounds 1 and 2

X-ray Investigations

We were able to grow single crystals of **1**, **2**, **20**, and **20a** which allowed us to study the molecular structure of these species in a crystalline environment. Figure 1 shows the molecular structure of **1** in a view along the crystallographic C_2 axis. The most relevant bond lengths and angles are given in the legend of Figure 1.

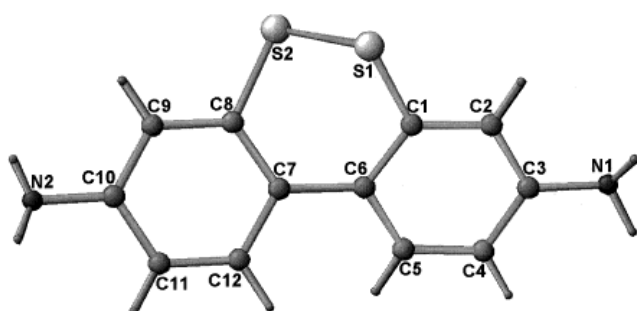Figure 1. Molecular structure of **1** viewed along the crystallographic C_2 axis (a)
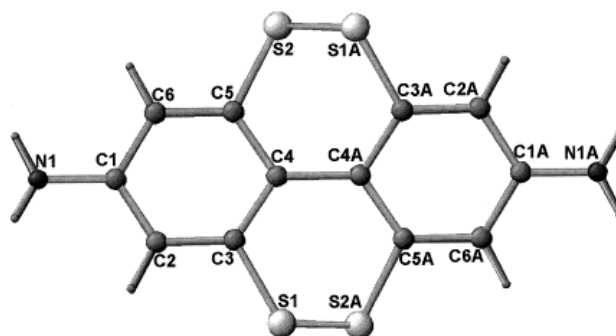
[a] Selected bond lengths [Å] and angles [°]: N1−C1 1.374(3), C1−C2 1.394(3), C3−S1 1.783(2), S1−S2A 2.0547(8), C4−C4A 1.483(4), C5−S2 1.773 (2), S2−S1A 2.0546(8); N1−C1−C2 121.6(2), C2−C1−C6 117.7(2), C2−C3−C4 123.9(2), C2−C3−S1 116.9(2), C4−C3−S1 119.2(2), C3−S1−S2A 96.66(7), C3−C4−C5 114.2(2), C3−C4−C4A 123.2(2), C5−S2−S1A 96.89(7).

The dihedral angle between the planes of the phenyl rings is 29°. The C−N bond lengths [1.374(3) Å] are somewhat longer than those in aniline (1.34 Å).[17] This finding is consistent with the slight pyramidalization at the nitrogen atoms [sum of the angles at the nitrogen atom 357(6)°].

The crystal packing in **2** is rather complex. It shows 16 molecules in the unit cell. The amino groups of **2** form via hydrogen bridges two associates, giving rise to two independent molecules in the unit cell. In Figure 2 a view of **2** from the top is shown. The dihedral angles between the biphenyl units are 28.4° and 30.4°, respectively. The NH$_2$ groups are pyramidalized, as seen from the sum of the angles at the nitrogen centers which were found to be 343(6)° and 337(6)° for the first molecule and 338(6)° and 340(6)° for the second one. The HNH plane is bent towards the plane of the adjacent phenyl ring by 39(2)° and 49(2)° for one and 46(2)° and 44(2)° for the other molecule in the unit cell. A comparison with **1** shows a considerably stronger bending of the NH$_2$ group in **2**. In line with this fact is the longer C−N bond in **2** [1.400(3) Å] as compared to that in **1** [1.374(3) Å].

Figure 3 shows the molecular structure of **20** viewed along the crystallographic S_4 axis. The dihedral angle between the two phenyl rings in the molecule is 90° due to crystal symmetry.

The HNH plane is twisted by 18(2)° towards the plane of the adjacent phenyl ring. The NH$_2$ group in **20** is planar (due to crystal symmetry). The ethyl groups are disordered in such a way that the terminal methyl groups are randomly

Figure 2. Molecular structure of one selected molecule of **2**[a]

[a] Selected bond lengths [Å] and angles [°] of one molecule of the unit cell: S1−C1 1.772(2), S1−S2 2.0534(8), S2−C8 1.774(2), N1−C3 1.400(3), N2−C10 1.399(3), C1−C2 1.386(3), C6−C7 1.484(3); C1−S1−S2 98.17(7), C8−S2−S1 98.27(7), C2−C1−C6 122.2(2), C2−C1−S1 118.2(2), C6−C1−S1 119.4(2), C4−C3−C2 118.3(2), C4−C3−N1 121.4(2), C2−C3−N1 120.1(2), C1−C6−C7 123.4(2), C8−C7−C12 115.4(2).

Figure 3. Molecular structure of **20** viewed along the crystallographic S_4 axis
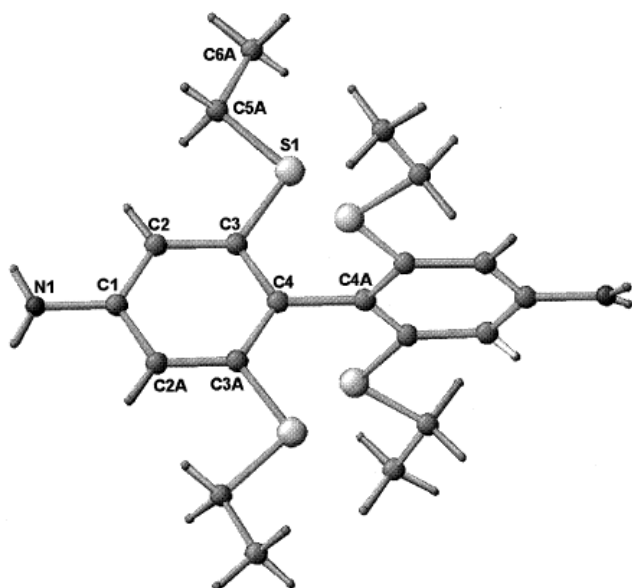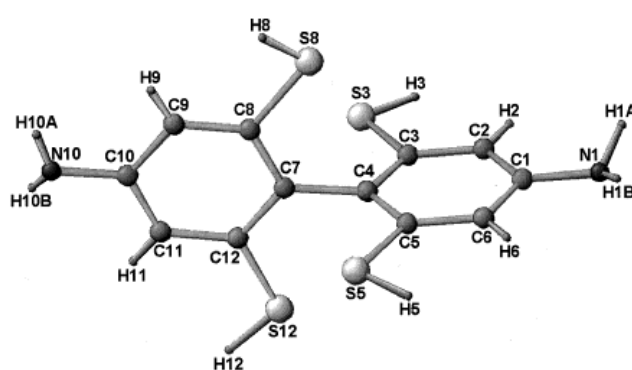

[a] Selected bond lengths [Å] and angles [°]: N1−C1 1.397(3), C1−C2 1.388(2), C3−C4 1.402(2), C3−S1 1.770(2), C4−C4A 1.505(4); C2−C1−C2A 120.0(2), C2−C1−N1 120.00(10), C2−C3−S1 122.27(12), C4−C3−S1 116.61(11), C3A−C4−C3 117.8(2), C3A−C4−C4A 121.08(9).

distributed over two positions (only the main component is shown in Figure 3).

Although **20a** is quite sensitive towards air we were able to grow single crystals for X-ray investigations. Similar to **20** we found for **20a** (Figure 4) a dihedral angle of 90° between both phenyl rings. Both HNH planes are bent towards the planes of the adjacent phenyl rings by 44.8(2)° and 39.0(2)°, respectively.

Electrochemical Properties of Compounds 1 and 3

Dichloromethane was used as the solvent for the cyclovoltammetric investigations of the redox behavior of **1** and

Figure 4. Molecular structure of **20a**[a]

[a] Selected bond lengths [Å] and angles [°]: C1−C6 1.384(4), C1−C2 1.390(4), C1−N1 1.399(4), N1−H1A 1.03(4), N1−H1B 0.80(4), C3−S3 1.763(3), S3−H3 1.21(3), C4−C7 1.495(4), C5−S5 1.781(3), C10−N10 1.377(4); C6−C1−C2 118.9(3), C6−C1−N1 122.0(3), C2−C1−N1 119.1(3), C1−N1−H1A 117(2), C1−N1−H1B 113(3), H1A−N1−H1B 109(4), C2−C3−S3 119.2(2), C4−C3−S3 119.6(2), C3−S3−H3 99(2), C3−C4−C5 117.2(3), C3−C4−C7 121.3(3), C10−N10−H10A 117(3), C10−N10−H10B 112(3), H10A−N10−H10B 116(4).

its tetrathiolate anion **3** because of solubility reasons. Dichloromethane also permitted to extend the electrochemical window to the range of −1.9 to 1.6 V vs. SCE. As disulfides are irreversibly chemisorbed on Au surfaces,[21] thiols on both Au[22] and Pt surfaces,[23][24][25] glassy carbon electrodes were used. The voltammograms of compounds **1** and **3** (Figure 5) were obtained in two independent measurements, applying 0 to −1.9 V vs. SCE and 0 to 1.4 V vs. SCE, respectively. The response for both ranges is shown in Figure 5.

Figure 5. Cyclic voltammograms taken in reference electrolyte (·····) in the presence of 138 μg/ml of compound **1** (—) and in the presence of 118 μg/ml of compound **3** (− − −) with glassy carbon electrode; the third cycles are shown; scan rate 100 mV/s
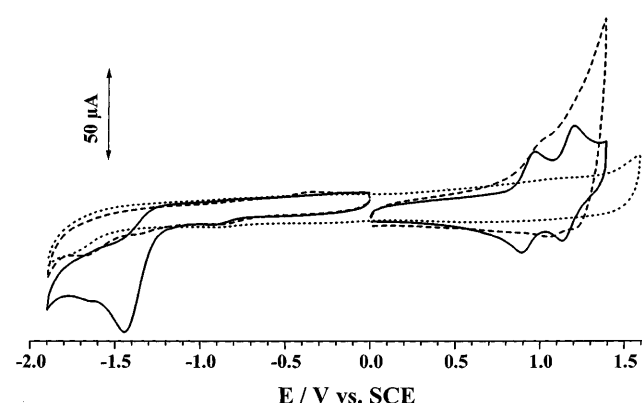
Compound **1** showed a rather large reduction peak at −1.443 V vs. SCE. As the substance contains no other electrochemically reducable functional groups in addition to the disulfide groups, we assume that this reduction peak corresponds to the reductive cleavage of one or both disulfide bridges. However, as it is not possible to determine the total

charge per molecule transferred, quantitative information cannot be drawn. The electrode reaction is completely irreversible. At unmodified electrodes unusual reduction potentials of ≤ -1 V vs. SCE, have already been observed for other disulfides. They are probably caused by overpotentials. For example, under corresponding conditions, cystine was not reducible below a potential sufficient for hydrogen evolution.[26] On the other hand it has been observed that tetrasulfonated phthalocyaninemetal compounds substantially decrease these overpotentials on graphite,[27] and with a correspondingly modified electrode, cystine ($E^0 = -0.5812$ V vs. SCE) became reducible at about -1 V vs. SCE. With compound **3**, the chemically reduced form of **1**, no electron transfer was observed in the cathodic range, indicating that this compound cannot electrochemically be further reduced in the potential range ≥ -1.9 V vs. SCE.

In the anodic range, a stepwise oxidation of substance **1** is recorded with two waves at $E^{01} = +0.932$ V, $E^{02} = +1.170$ V vs. SCE and $\Delta E_{P1} = 79$ mV, $\Delta E_{P2} = 71$ mV. This indicates the existence of two quasi-reversible redox pairs. Benzidine showed two redox pairs at nearly the same redox potentials.[28] Diphenyl disulfide is oxidized at a significantly higher potential.[29] We suggest that the stepwise oxidation of compound **1** yields analogous to benzidines the corresponding quinone imines.

Surprisingly, **3** is stable in air. Possibly, this thiolate anion is stabilized by inter- or intramolecular salt bridges. The voltammogram of compound **3** shows a quite enhanced oxidation current with a small shoulder at 1 V vs. SCE in the anodic range. There is no indication that the voltammogram shifts into the typical quasi-reversible redox waves of compound **1**. Therefore, the chemical reduction is obviously not reversible by electrochemical oxidation, and probably the expected intramolecular disulfide bonds cannot be reformed by this process. Repeated cycling in the range between 0 and 1.6 V vs. SCE leads to an increase of the above mentioned shoulder, indicating the adsorption of an unknown compound. Probably the voltammogram indicates the formation of intermolecular disulfide bonds to yield dimer or polymer products.

When compound **1** was analyzed over the whole range from -1.9 to 1.4 V vs. SCE, a voltammogram is observed which is in the anodic part similar to that of compound **1**, but which, after some cycles, shifts to that of compound **3**.

In summary, we believe that the electroreduction of compound **1** results in the formation of compound **3** but that the product **3** is electrochemically not oxidable.

Experimental Section

General: All reactions were carried out under Ar with magnetic stirring (except for the synthesis of **18** and **26**). The solvents were purified and dried using standard procedures. CuSEt was prepared from Cu₂O (Fluka, powder < 5μ) and EtSH in diethyl ether. − The ¹H- and ¹³C-NMR spectra were recorded at 200 and 50 MHz,

respectively, in CDCl₃ if not otherwise noted. − Elemental analyses were performed at the Mikroanalytisches Laboratorium der Universität Heidelberg, Germany.

Benzidine Rearrangement of 1,2-Bis[(3,5-dimethoxy)phenyl]diazane (**11**): To a suspension of 500 mg (1.6 mmol) of 1,2-bis[(3,5-dimethoxy)phenyl] diazane (**11**) in 200 ml of dry ethanol was added dropwise at $-30\,°C$ 30 ml of ethanol, which was satured with HCl gas. Within a few minutes no starting material could be detected (TLC), but three products were observed. The mixture was allowed to slowly warm up to 0 °C. A 10% aqueous solution of NaOH was added until a pH > 11 was attained, then the aqueous layer was extracted with CH₂Cl₂. After drying with MgSO₄ and removal of the solvent under reduced pressure, the raw material was purified by silica-gel chromatography (ethyl acetate) to yield 220 mg (44%) of 4,4′-diamino-2,2′,6,6′-tetramethoxybiphenyl (**12**), 220 mg (44%) of 6,6′-diamino-2,2′,4,4′-tetramethoxybiphenyl (**13**) and 60 mg (1 2%) of 4,6′-diamino-2,2′,4′,6-tetramethoxybiphenyl (**14**). − **12**: M.p. 179°C. − ¹H NMR: δ = 6.00 (s, 4 H), 3.70 (s, 12 H). − ¹³C NMR: δ = 159.2, 146.9, 103.0, 92.5, 55.8. − IR (KBr): ṽ = 3364 cm⁻¹, 2936, 1608, 1581, 1465, 1423, 1232, 1201, 1174, 1127. − UV/Vis (CHCl₃): λ_{max} (log ε) = 232 nm (4.19), 256 (3.0), 332 (2.02). − C₁₆H₂₀N₂O₄ (304.3): calcd. C 63.14, H 6.62, N 9.21; found C 62.93, H 6.65, N 9.14. − **13**: M.p. 148−150°C. − ¹H NMR: δ = 6.03 (dd, $^4J_{H,H}$ = 2.32, $^4J_{H,H}$ = 4.59, 4 H), 3.80 (s, 6 H), 3.70 (s, 6 H), 3.60 (s, 4 H). − ¹³C NMR: δ = 160.9, 159.6, 146.8, 101.0, 92.9, 89.7, 55.9, 55.1. − IR (KBr): ṽ = 3454 cm⁻¹, 3432, 3361, 2938, 2838, 1617, 1598, 1486, 1468, 1450, 1427, 1342, 1237, 1204, 1186, 1159, 1131, 1086, 1065. − UV/Vis (CHCl₃): λ_{max} (log ε) = 234 nm (4.51), 280 (3.61). − C₁₆H₂₀N₂O₄ (304.3): calcd. C 63.14, H 6.62, N 9.21; found C 62.97, H 6.59, N 9.16. − **14**: M.p. 175−176°C. − ¹H NMR: δ = 6.01 (m, 4 H), 3.78 (s, 3 H), 3.68 (s, 6 H), 3.67 (s, 3 H). − ¹³C NMR: δ = 160.3, 159.5, 147.8, 146.5, 102.3, 102.1, 93.0, 92.4, 89.9, 56.0, 55.9, 55.0. − IR (KBr): ṽ = 3450 cm⁻¹, 3411, 3336, 1606, 1583, 1487, 1466, 1451, 1423, 1236, 1202, 1171, 1150, 1115, 1086, 1056. − UV/Vis (CHCl₃): λ_{max} (log ε) = 234 nm (4.30). − C₁₆H₂₀N₂O₄ (304.3): calcd. C 63.14, H 6.62, N 9.21; found C 62.86, H 6.64, N 9.06.

1,3-Bis(ethylthio)-5-nitrobenzene (**16**): A solution of 1,3-diiodo-5-nitrobenzene (**15**, 87.7 g, 234 mmol), and of CuSEt (117.0 g, 936 mmol) in 3 l of anhydrous DMF was stirred at 100°C for 60 h. The mixture was cooled, diluted with diethyl ether and filtered through Celite. Subsequently, the organic layer was separated, washed three times with brine, dried with MgSO₄, and concentrated. Purification of the residue by silica-gel chromatography (hexane/diethyl ether, 30:1) yielded 45.5 g of **16** (80%) as a yellow oil. − ¹H NMR: δ = 7.82 (d, $^4J_{H,H}$ = 1.64, 2 H), 7.40 (t, $^4J_{H,H}$ = 1.64, 1 H), 3.01 (q, $^3J_{H,H}$ = 7.36, 4 H), 1.35 (t, $^3J_{H,H}$ = 7.37, 6 H). − ¹³C NMR: δ = 148.7, 140.5, 131.7, 118.6, 26.9, 13.8. − IR (film): ṽ = 3073 cm⁻¹, 2973, 2929, 2871, 1596, 1529, 1449, 1377, 1345, 1303, 1266. − UV/Vis (CHCl₃): λ_{max} (log ε) = 248 nm (4.24), 266 (4.30), 354 (3.22). − HRMS (EI): *m/z*: calcd. 243.0388; found 243.0379.

3,5-Bis(ethylthio)aniline (**17**): To a refluxing solution of 34.2 g (140 mmol) of 1,3-bis(ethylthio)-5-nitrobenzene (**16**) in 800 ml of anhydrous ethanol was added dropwise over 2 h a suspension of 126.6 g (560 mmol) of SnCl₂ · 2 H₂O in 450 ml of concd. HCl. The color changed from orange to green. After cooling the reaction mixture with ice, concd. NaOH solution was added dropwise until a pH > 11 was maintained. The white precipitate that formed was filtered and washed with diethyl ether. The combined organic layers were washed twice with brine, dried with MgSO₄ and concentrated. Purification of the residue by silica-gel chromatography (hexane/diethyl ether, 1:1) yielded 28.5 g (95%) of **17** as a red-brown-colored

oil. − ^{1}H NMR (300 MHz): δ = 6.64 (s, 1 H), 6.41 (s, 2 H), 2.88 (q, $^3J_{H,H}$ = 7.35, 4 H), 1.28 (t, $^3J_{H,H}$ = 7.36, 6 H). − ^{13}C NMR (75 MHz): δ = 147.1, 138.3, 118.5, 112.7, 27.3, 14.4. − IR (film): ṽ = 3443 cm^{-1}, 3349, 3202, 2968, 2927, 2866, 1617, 1560, 1440, 1376, 1311, 1287, 1262, 1109, 1053. − UV/Vis (CHCl$_3$): λ$_{max}$ (log ε) = 242 nm (4.30), 314 (3.42). − HRMS (EI); m/z: calcd. 213.0646; obsd. 213.0646. − C$_{10}$H$_{15}$NS$_2$ (213.4): calcd. C 56.30, H 7.09, N 6.56; found C 55.83, H 7.19, N 6.46.

1,2-Bis[3,5-bis(ethylthio)phenyl]diazene (**18**): A mixture of 26.2 g (123 mmol) of 3,5-bis(ethylthio)aniline (**17**), 6.09 g (61.5 mmol) of CuCl and 1 l of pyridine was stirred for 48 h at ambient temperature. 5 N HCl solution was then added until a pH < 2 was attained, and the mixture was extracted three times with diethyl ether. The combined organic layers were dried with MgSO$_4$ and concentrated. Purification of the residue by silica-gel chromatography (diethyl ether) yielded 20.8 g (80%) of **18** as an orange-colored oil, which solidified in the refrigerator, m.p. 72°C. − ^{1}H NMR: δ = 7.62 (d, $^4J_{H,H}$ = 1.65, 4 H), 7.32 (t, $^4J_{H,H}$ = 1.59, 2 H), 3.02 (q, $^3J_{H,H}$ = 7.34, 8 H), 1.36 (t, $^3J_{H,H}$ = 7.37, 12 H). − ^{13}C NMR: δ = 152.7, 139.0, 130.0, 119.7, 27.2, 14.1.− IR (KBr): ṽ = 3440 cm^{-1}, 2964, 2929, 2868, 1570, 1552, 1460, 1432, 1378, 1310, 1257, 1209, 1108. − UV/Vis (CHCl$_3$): λ$_{max}$ (log ε) = 254 nm (4.40), 276 (4.47), 352 (3.96). − HRMS (EI); m/z: calcd. 422.0979; obsd. 422.0985 − C$_{20}$H$_{26}$N$_2$S$_4$ (422.7): calcd. C 56.83, H 6.20, N 6.63; found C 56.80, H 6.34, N 6.40.

1,2-Bis[3,5-bis(ethylthio)phenyl]diazane (**19**): To a solution of 26.2 g (62 mmol) of **18** in 750 ml of benzene was added 57.3 g (197 mmol) of tributyltin hydride, and the solution was refluxed for 18 h. After removal of the solvent, purification was accomplished by silica-gel chromatography (hexane/diethyl ether, 1:1) to yield 24 g (91%) of **19** as a brown oil. − ^{1}H NMR (300 MHz): δ = 6.71 (t, $^4J_{H,H}$ = 1.51, 2 H), 6.55 (d, $^4J_{H,H}$ = 1.49, 4 H), 5.55 (s, 2 H), 2.88 (q, $^3J_{H,H}$ = 7.35, 8 H), 1.28 (t, $^3J_{H,H}$ = 7.35,12 H). − ^{13}C NMR (75 MHz): δ = 149.2, 138.7, 119.5, 109.7, 27.2, 14.2. − IR (film): ṽ = 3325 cm^{-1}, 2968, 2925, 2868, 1566, 1478, 1427, 1375, 1307, 1264, 1111, 1053. − UV/Vis (CHCl$_3$): λ$_{max}$ (log ε) = 236 nm (4.56), 254 (4.67), 308 (3.73), 316 (3.76). − HRMS (EI); m/z: calcd. 424.1135; obsd. 424.1130. − C$_{20}$H$_{28}$N$_2$S$_4$ (424.7): calcd. C 56.56, H 6.65, N 6.60; found C 56.65, H 6.73, N 6.52.

4,4′-Diamino-2,2′,6,6′-tetraethylthiobiphenyl (**20**), *6,6′-Diamino-2,2′,4,4′-tetraethylthiobiphenyl* (**21**), *and 4,6′-Diamino-2,2′,4′,6-tetraethylthiobiphenyl* (**22**): 3.6 ml of a solution of HBF$_4$ in diethyl ether (54%) was added dropwise at −30°C to a solution of 3 g (7 mmol) of **19** in 300 ml of anhydrous diethyl ether in a Schlenk tube. The color changed from orange to brown and green. After warming up to 0°C in an ice bath, the suspension was diluted slowly with 100 ml of water and brought with concd. NaOH solution to pH > 11. The organic layer was separated, the aqueous layer was extracted four times with CH$_2$Cl$_2$ and the combined organic layers were dried with MgSO$_4$. After removal of the solvent, the brown residue was purified by silica-gel chromatography (hexane/diethyl ether, 1:1) to yield 1.7 g of **20** (56%) as white crystals, 1.2 g (40%) of **21** as red-brown crystals and 0.1 g (3%) of **22** as light-brown crystals. − **20**: M.p. 219°C. − ^{1}H NMR ([D$_8$]THF): δ = 6.36 (s, 4 H), 4.47 (s, 4 H), 2.72 (q, $^3J_{H,H}$ = 7.37, 8 H), 1.18 (t, $^3J_{H,H}$ = 7.36, 12 H). − ^{13}C NMR ([D$_8$]THF): δ = 151.3, 143.0, 129.5, 113.1, 29.5, 16.9. − IR (film): ṽ = 3310 cm^{-1}, 3134, 3061, 2958, 2877, 1771, 1594, 1502, 1438, 1373, 1342, 1300, 1255, 1190, 1138, 1119, 1038. − UV/Vis (CHCl$_3$): λ$_{max}$ (log ε) = 250 nm (3.84), 318 (3.07). − HRMS (EI); m/z: calcd. 424.1135; found 424.1114. − C$_{20}$H$_{28}$N$_2$S$_4$ (424.7): calcd. C 56.56, H 6.65, N 6.60; found C 56.33, H 6.74, N 6.52. − **21**: M.p. 85°C. − ^{1}H NMR: δ = 6.60 (d, $^4J_{H,H}$ =

1.44, 2 H), 6.49 (d, $^4J_{H,H}$ = 1.50, 2 H), 3.52 (s, 4 H), 2.86 (m, 8 H), 1.27 (m, 12 H). − ^{13}C NMR: δ = 145.4, 139.8, 138.4, 116.4, 115.0, 111.5, 27.2, 25.9, 14.5, 13.8. − IR (KBr): ṽ = 3455 cm^{-1}, 3361, 2967, 2926, 2867, 1606, 1567, 1544, 1439, 1409, 1375, 1260, 1121. − UV/Vis (CHCl$_3$): λ$_{max}$ (log ε) = 246 nm (4.6), 318 (3.8). − HRMS (EI); m/z: calcd. 424.1135; found 424.1146. − C$_{20}$H$_{28}$N$_2$S$_4$ (424.7): calcd. C 56.56, H 6.65, N 6.60; found C 56.47, H 6.79, N 6.43. − **22**: M.p. 124°C. − ^{1}H NMR (300 MHz): δ = 6.66 (d, $^4J_{H,H}$ = 1.44, 1 H), 6.52 (d, $^4J_{H,H}$ = 1.51, 1 H), 6.40 (s, 2 H), 3.48 (s, b, 4 H), 2.88 (m, 8 H), 1.30 (m, 12 H). − ^{13}C NMR: δ = 146.9, 144.9, 139.9, 139.6, 137.5, 121.7, 119.4, 115.4, 111.4, 108.5, 27.0, 26.1, 25.5, 14.2, 13.6, 13.5. − IR (KBr): ṽ = 3442 cm^{-1}, 3412, 3345, 3332, 2964, 2925, 2869, 1621, 1606, 1584, 1573, 1548, 1451, 1423, 1407, 1374, 1291, 1262, 1200. − UV/Vis (CHCl$_3$): λ$_{max}$ (log ε) = 248 nm (4.6), 318 (3.7). − HRMS (EI); m/z: calcd. 424.1135; found 424.1148. −C$_{20}$H$_{28}$N$_2$S$_4$ (424.7): calcd. C 56.56, H 6.65, N 6.60; found C 56.73, H 6.75, N 6.49.

1,2-Benzodithiino[5,4,3-cde][1,2]benzodithiin-2,7-diamine (**1**): About 200 ml of dry NH$_3$ was condensed into 109 mg (0.26 mmol) of **20** at −75°C. To this mixture, 179 mg (7.8 mmol) of sodium in small pieces was added under stirring and reflux (−33°C). After 3 h of stirring, the mixture was allowed to warm to room temperature and the residue was quenched firstly with 25 ml of methanol followed by 125 ml of water. The aqueous layer was extracted several times with diethyl ether, the combined organic layers were washed with water and dried with MgSO$_4$. After removal of the solvent, the purification was achieved by chromatography on Alox III (hexane/diethyl ether, 1:1), which yielded 75 mg (95%) of **1** as yellow crystals, m.p. 219°C (decomposition). − ^{1}H NMR ([D$_8$]THF): δ = 6.63 (s, 4 H), 5.03 (s, 4 H). − ^{13}C NMR ([D$_8$]THF): δ = 147.5, 135.7, 126.1, 115.6. − IR (KBr): ṽ = 3435 cm^{-1}, 3413, 3354, 3338, 1626, 1591, 1527, 1486, 1431, 1279, 1191, 1168, 1141, 1111, 1064, 1035. − UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ (log ε) = 222 nm (4.60), 238 (4.39), 284 (4.20), 402 (3.70). − HRMS (EI); m/z: calcd. 307.9570; found 307.9579. − C$_{12}$H$_8$N$_2$S$_4$ (308.4): calcd. C 46.73, H 2.61, N 9.08, S 41.58; found C 46.87, H 2.79, N 8.87, S 41.30.

4,4′-Diamino-2,2′,6,6′-tetramercaptobiphenyl (**20a**): To a cooled (0°C) suspension of 247 mg (6.5 mmol) of LiAlH$_4$ in 20 ml of anhydrous THF was added slowly a solution of 50 mg (0.16 mmol) of **1** in 10 ml of anhydrous THF. After reflux (5 h) and cooling to room temp., the mixture was hydrolyzed slowly with degassed water under Ar, neutralized with aq. HCl to pH = 6−7. Extraction with diethyl ether, drying with MgSO$_4$, and evaporating of the solvent in vacuo led to a quantitative yield of **20a** as yellow crystals, m.p. 199°C. − ^{1}H NMR (300 MHz, [D$_8$]THF): δ = 6.44 (s, 4 H), 4.02 (s, 4 H), 3.39 (s, 4 H). − ^{13}C NMR (75 MHz, [D$_8$]THF): δ = 149.4, 136.6, 123.8, 112.0. − IR (KBr): ṽ = 3424 cm^{-1}, 3340, 2545, 1618, 1584, 1542, 1434, 1414, 1261, 1097, 1022, 801. − UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ (log ε) = 242 nm (4.59), 266 (4.21), 314 (3.44). − HRMS (EI); m/z: calcd. 311.9883; found 311.9880.

1,2-Bis[(3-chloro-5-ethylthio)phenyl]diazene (**26**): The synthesis of **26** was carried out analogously to that of **18**, using 1 g (5.3 mmol) of **25**, 0.26 g (2.6 mmol) of CuCl and 200 ml of anhydrous pyridine. We isolated 787 mg (80%) of **26**, m.p. 78−82°C. − ^{1}H NMR: δ = 7.73 (t, $^4J_{H,H}$ = 1.65, 2 H), 7.65 (t, $^4J_{H,H}$ = 1.77, 2 H), 7.37 (t, $^4J_{H,H}$ = 1.79, 2 H), 3.04 (q, $^3J_{H,H}$ = 7.36, 4 H), 1.38 (t, $^3J_{H,H}$ = 7.35, 6 H). − ^{13}C NMR: δ = 153.0, 140.5, 135.5, 130.0, 121.6, 119.3, 27.2, 14.1. − IR (KBr): ṽ = 3444 cm^{-1}, 2964, 2921, 2851, 1582, 1555, 1451, 1424, 1373, 1202. − UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ (log ε) = 221 nm (4.35), 274 (4.38), 328 (4.24). − HRMS (EI); m/z: calcd. 370.0132; found 370.0142.

1,2-Bis[(3-ethylthio)phenyl]diazene (**27**): To a solution of 2 g (5.4 mmol) of **26** and 3.1 g (41.9 mmol) of *tert*-butyl alcohol in 100

ml of anhydrous THF was added under reflux 0.8 g (34.8 mmol) of sodium in small pieces. After completion of the addition, the mixture was refluxed for 12 h. 100 ml of diethyl ether was then added to the cooled solution, and the mixture was poured onto ice. The aqueous phase was extracted with diethyl ether. The organic phase was washed with water, dried with MgSO$_4$, and concentrated under vacuum. Purification of the residue by silica-gel chromatography (diethyl ether) yielded 1.1 g of **27** (67%) as orange-colored crystals, m.p. 47−48°C. − ^{1}H NMR: δ = 7.87 (s, 2 H), 7.71 (m, 2 H), 7.42 (m, 4 H), 3.04 (q, $^3J_{\text{H,H}}$ = 7.34, 4 H), 1.37 (t, $^3J_{\text{H,H}}$ = 7.36, 6 H). − ^{13}C NMR: δ = 152.7, 138.2, 130.9, 129.2, 122.2, 120.5, 27.3, 14.1. − IR (KBr): ν̃ = 3446 cm^{-1}, 2967, 2924, 1631, 1575, 1460, 1441, 1308, 1261, 1200, 1073. − UV/Vis (CH$_2$Cl$_2$): λ$_{\text{max}}$ (log ε) = 220 nm (4.39), 266 (4.43), 316 (4.28), 370 (3.77). − HRMS (EI); *m/z*: calcd. 302.0912; found 302.0908. − C$_{16}$H$_{18}$N$_2$S$_2$ (302.5): calcd. C 63.54, H 6.00, N 9.26; found C 63.56, H 6.13, N 9.19.

1,2-Bis[(3-ethylthio)phenyl]diazane (**28**): The synthesis of **28** was carried out analogously to that of **19** using 1 g (3.3 mmol) of **27** in 150 ml of benzene and 5.8 g (19.9 mmol) of tributyltin hydride. 955 mg (95%) of **28** was isolated as yellow crystals, m.p. 58−60°C. − ^{1}H NMR: δ = 7.13 (t, $^3J_{\text{H,H}}$ = 8.14, 2 H), 6.79 (d, $^3J_{\text{H,H}}$ = 7.82, 2 H), 6.78 (s, 2 H), 6.62 (d, $^3J_{\text{H,H}}$ = 7.92, 2 H), 5.59 (s, 2 H), 2.91 (q, $^3J_{\text{H,H}}$ = 7.36, 4 H), 1.30 (t, $^3J_{\text{H,H}}$ = 7.35, 6 H). − ^{13}C NMR: δ = 149.0, 137.7, 129.5, 119.6, 111.9, 109.7, 27.0, 14.1. − IR (KBr): ν̃ = 3349 cm^{-1}, 2971, 2927, 1590, 1476, 1458, 1300, 1266. − UV/Vis (CH$_2$Cl$_2$): λ$_{\text{max}}$ (log ε) = 244 nm (4.44), 304 (3.69). − HRMS (EI); *m/z*: calcd. 304.1068; found 304.1074. − C$_{16}$H$_{20}$N$_2$S$_2$ (304.5): calcd. C 63.12, H 6.62, N 9.20; found C 63.29, H 6.77, N 9.05.

4,4′-Diamino-2,2′-bis(ethylthio)biphenyl (**29**) *and 2,2′-Diamino-4,4′-bis(ethylthio)biphenyl* (**30**): The syntheses of **29** and **30** were carried out analogously to that of **20**, **21**, and **22**, using 900 mg (2.96 mmol) of **28**, 1.8 ml of a solution of HBF$_4$ in diethyl ether (54%), and 150 ml of anhydrous diethyl ether. We isolated 445 mg (49%) of **29** as a clear viscous oil, which solidified in the refrigerator and 445 mg (49%) of **30** as white crystals. − **29**: M.p. 64−66°C. − ^{1}H NMR (300 MHz): δ = 6.95 (d, $^3J_{\text{H,H}}$ = 8.04, 2 H), 6.66 (d, $^4J_{\text{H,H}}$ = 2.29, 2 H), 6.51 (dd, $^3J_{\text{H,H}}$ = 8.03, $^4J_{\text{H,H}}$ = 2.33, 2 H), 3.68 (s, 4 H), 2.79 (q, $^3J_{\text{H,H}}$ = 7.38, 4 H), 1.24 (t, $^3J_{\text{H,H}}$ = 7.37, 6 H). − ^{13}C NMR (75 MHz): δ = 146.5, 138.3, 132.2, 131.0, 113.8, 112.4, 27.2, 14.4. − IR (film): ν̃ = 3347 cm^{-1}, 3214, 2968, 2925, 2868, 1596, 1560, 1473, 1295, 1263, 1243, 1083, 1059. − UV/Vis (CH$_2$Cl$_2$): λ$_{\text{max}}$ (log ε) = 234 nm (4.55), 308 (3.84). − HRMS (EI); *m/z*: calcd. 304.1068; found 304.1072. − C$_{16}$H$_{20}$N$_2$S$_2$ (304.5): calcd. C 63.12, H 6.62, N 9.20; found C 62.99, H 6.71, N 9.04. − **30**: M.p. 74°C. − ^{1}H NMR (300 MHz, [D$_8$]THF): δ = 6.89 (d, $^3J_{\text{H,H}}$ = 7.85, 2 H), 6.69 (d, $^4J_{\text{H,H}}$ = 1.73, 2 H), 6.61 (dd, $^3J_{\text{H,H}}$ = 7.88, $^4J_{\text{H,H}}$ = 1.81, 2 H), 4.33 (s, 4 H), 2.90 (q, $^3J_{\text{H,H}}$ = 7.33, 4 H), 1.29 (t, $^3J_{\text{H,H}}$ = 7.34, 6 H). − ^{13}C NMR (75 MHz, [D$_8$]THF): δ = 146.3, 136.9, 131.4, 122.0, 117.6, 115.1, 27.2, 14.4. − IR (KBr): ν̃ = 3398 cm^{-1}, 3379, 3280, 3172, 2969, 2924, 2866, 1629, 1586, 1535, 1480, 1449, 1408, 1288, 1260, 1095. − UV/Vis (CH$_2$Cl$_2$): λ$_{\text{max}}$ (log ε) = 236 nm (4.56), 274 (4.05), 312 (4.08). − HRMS (EI); *m/z*: calcd. 304.1068; found 304.1075. − C$_{16}$H$_{20}$N$_2$S$_2$ (304.5): calcd. C 63.12, H 6.62, N 9.20; found C 63.13, H 6.60, N 9.24.

Dibenzo[ce][1,2]dithiin-2,7-diamine (**2**): The synthesis of **2** was carried out analogously to that of **1**, using 200 mg (0.66 mmol) of **29**, 100 ml of NH$_3$ and 1.5 g (65 mmol) of sodium. Purification by chromatography on Alox III (hexane/diethyl ether, 1:1) yielded 160 mg (99%) of **2** as orange crystals, m.p. 158°C. − ^{1}H NMR (300 MHz, [D$_8$]THF): δ = 7.29 (d, $^3J_{\text{H,H}}$ = 8.40, 2 H), 6.61 (d, $^4J_{\text{H,H}}$ = 2.35, 2 H), 6.52 (dd, $^3J_{\text{H,H}}$ = 8.40, $^4J_{\text{H,H}}$ = 2.39, 2 H), 4.66 (s, 4 H). − ^{13}C NMR (75 MHz, [D$_8$]THF): δ = 147.5, 134.5, 127.8, 127.4, 114.6, 114.1. − IR (KBr): ν̃ = 3412 cm^{-1}, 3335, 3195, 1594, 1474, 1293, 1246. − UV/Vis (CH$_2$Cl$_2$): λ$_{\text{max}}$ (log ε) = 226 nm (4.35), 262 (3.95), 312 (4.15), 366 (3.10). − HRMS (EI); *m/z*: calcd. 246.0286; found 246.0283. − C$_{12}$H$_{10}$N$_2$S$_2$ (246.3): calcd. C 58.51, H 4.09, N 11.37; found C 57.45, H 4.09, N 11.04.

4,4′-Diamino-2,2′-dimercaptobiphenyl (**29a**): The synthesis was carried out analogously to that of **20a**. Starting materials: 20 mg

Table 1. Crystallographic data of compounds **1**, **2**, **20**, and **20a**, wavelength 0.71073 Å, temperature 200(2) K, absorption correction semi-empirical from ψ scans, refinement method full-matrix least squares on F^2

compound	1	2	20	20a
empirical formula	C$_{18}$H$_{20}$N$_2$O$_2$S$_4$	C$_{12}$H$_{10}$N$_2$S$_2$	C$_{20}$H$_{28}$N$_2$S$_4$	C$_{12}$H$_{12}$N$_2$S$_4$
formular weight [g/mol]	424.6	246.3	424.7	312.5
crystal size [mm]	0.50 × 0.46 × 0.03	0.28 × 0.24 × 0.22	0.54 × 0.34 × 0.34	0.40 × 0.14 × 0.09
crystal system	orthorhombic	tetragonal	tetragonal	orthorhombic
space group	Fdd2	P4̄/n	I4$_1$/a	Pbca
a [Å]	13.7443(3)	20.2110(1)	10.4286(1)	12.6213(4)
b [Å]	39.5056(2)	20.2110(1)	10.4286(1)	14.7026(5)
c [Å]	7.3315(1)	11.1207(1)	20.0086(1)	14.7177(5)
V [Å^3]	3980.83(10)	4542.63(5)	2176.05(3)	2731.1(2)
D$_{\text{calcd.}}$ [Mg/m^3]	1.42	1.44	1.296	1.52
Z	8	16	4	8
absorption coefficient [mm^{-1}]	0.49	0.44	0.44	0.68
h$_{\text{min}}$/h$_{\text{max}}$	−8/16	−24/24	−12/7	−15/14
k$_{\text{min}}$/k$_{\text{max}}$	−42/45	−24/23	−12/9	−17/17
l$_{\text{min}}$/l$_{\text{max}}$	−8/8	−12/12	−20/22	−17/17
refl. collected	4544	32545	4947	18882
refl. uniqe	1626	4026	951	2457
refl. observed	1557	3444	873	1758
final R indices	R1 = 0.023, wR2 = 0.053	R1 = 0.029, wR2 = 0.074	R1 = 0.027, wR2 = 0.075	R1 = 0.037, wR2 = 0.082
goodness-of-fit on F^2	1.11	1.07	1.07	1.10
largest diff. peak and hole [eÅ^{-3}]	0.21 and −0.17	0.44 and −0.22	0.23 and −0.15	0.32 and −0.25
Θ range for data collection [°]	2.1−25.5	1.42−25.64	2.2−25.6	2.5−25.6
max. and min. transmission	0.93 and 0.80	0.98 and 0.68	0.89 and 0.78	0.93 and 0.76
data/restraints/parameters	4026/0/369	1626/1/158	951/9/85	2451/30/217

(0.08 mmol) of **2**, 100 mg of LiAlH$_4$ (2.6 mmol), and 35 ml of dry THF. The product was obtained quantitatively as yellow crystals. $-$ ^{1}H NMR (300 MHz, [D$_8$]THF): δ = 6.75 (d, $^3J_{H,H}$ = 8.15, 2 H), 6.57 (d, $^4J_{H,H}$ = 2.27, 2 H), 6.36 (dd, $^3J_{H,H}$ = 8.13, $^4J_{H,H}$ = 2.25, 2 H), 3.81 (s, 4 H), 3.39 (s, 2 H). $-$ ^{13}C NMR (75 MHz, [D$_8$]THF): δ = 149.0, 134.0, 132.2, 128.5, 114.3, 112.2. $-$ HRMS (EI); *m/z:* calcd. 248.0442; found 248.0441.

X-ray Structural Analyses of **1**, **2**, **20**, *and* **20a**: Suitable crystals were mounted on a glass fiber in random orientation. Preliminary examination and data collection were performed at 200 K with a Siemens X-ray diffractometer, equipped with a SMART CCD detector system using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) from a sealed-tube X-ray source (50 kV/30 mA). Several unique sets of data were collected in each case at a crystal-to-detector distance of 6.0 cm. The SMART[18] software package was used for data collection as well as frame integration. An empirical absorption correction was applied using SADABS,[19] based on the Laue symmetry of the reciprocal space. Structure solution and refinement were carried out using the SHELXTL-PLUS software package.[20] The structures were solved by direct methods. Full-matrix least-squares refinement was carried out against F^2. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically, except those of the ethyl group (C5, C6) in **20**, which is randomly disordered over two positions. The treatment of the disordered atoms was done by refining site occupation factors and using suitable geometrical restraints. The crystallographic data and details of the refinement procedure are shown in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-103077 (**1**), -103078 (**2**), -103079 (**20**) and -103080 (**20a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336−033; E-mail: deposit@ccdc.cam.ac.uk].

Cyclovoltammetry: The cyclovoltammetric measurements were carried out by means of a three-electrode electrochemical cell connected to a Solartron 1286 electrochemical interface (Schlumberger, UK). A platinum wire counter electrode and a KCl-saturated calomel reference electrode (E = 241.2 mV vs. NHE) were used in combination with the glassy carbon electrode (Sigradur, Sigri, Meitingen, Germany, area 0.385 cm^2). Prior to use, this working electrode was mechanically polished with alumina powder (0.3 μm). Compound solutions were prepared in dichloromethane (Merck, Darmstadt, Germany) containing 100 mmol/l of supporting electrolyte tetrabutylammonium hexafluorophosphate (Fluka, Buchs, Switzerland). Ar bubbling was used to remove oxygen and molecular sieves (Union Carbide Type 4 Å, Fluka, Buchs, Switzerland) to remove water from the solution in the electrochemical cell. Measurements were made at ambient temperatures between 23 and 25 °C.

[1] J. M. Williams, J. R. Ferraro, R. J. Thorn, K. Douglas Carlson, U. Geiser, H. H. Wang, A. M. Kini, M.-H. Whangbo, *Organic Superconductors*, Prentice-Hall, Inc., **1992** and references therein.

[2] H. Iwamura, *Adv. Phys. Org. Chem.* **1990**, *26*, 179 and references therein.

[3] J. J. Wolff, R. Wortmann, *J. Prakt. Chem.* **1998**, *340*, 99.

[4] R. Scheibe, *Physiol. Plant.* **1987**, *71*, 393; X. H. Yuan, L. E. Anderson, *Plant Physiol.* **1987**, *85*, 598.

[5] H. Huck, A. Schelter-Graf, J. Danzer, P. Kirch, H.-L. Schmidt, *Analyst* **1984**, *109*, 147; W. Schuhmann. J. Huber, H. Wohlschläger, B. Strehlitz, B. Gründig, *J. Biotechnol.* **1993**, *27*, 149.

[6] S. Cossu, O. De Lucchi, E. Piga, G. Valle, *Phosphorus, Sulfur, Silicon* **1991**, *63*, 31.

[7] M. Frantisi, G. Lindsten, O. Wennerström, *Acta Chem. Scand.* **1982**, 135.

[8] M. A. Thorn, G. H. Denny, R. D. Babson, *J. Org. Chem.* **1975**, *40*, 1556.

[9] H. J. Shine, H. Zmunda, K. H. Park, H. Kwart, A. G. Horgan, M. Brechbiel, *J. Am. Chem. Soc.* **1982**, *104*, 2501.

[10] G. A. Olah, K. Dunne, D. P. Kelly, Y. K. Mo, *J. Am. Chem. Soc.* **1972**, *94*, 7438.

[11] A. Alberti, N. Bedogni, M. Benaglia, R. Leardini, D. Nanni, A. F. Pedulli, A. Tundo, G. Zanadi, *J. Org. Chem.* **1992**, *57*, 607.

[12] M. P. Doyle, B. Siegfried, J. F. Dellaria, Jr. *J. Org. Chem.* **1977**, *42*, 2426.

[13] R. Adams, W. Reifschneider, M. D. Nair, *Croat. Chem. Acta* **1957**, *29*, 277; J. J. Wolff, unpublished results.

[14] R. Schöfer in *Methoden Org. Chem. (Houben Weyl)* **1957** , vol. XI/1, 422 and references therein.

[15] K. Kinoshita, *Bull. Chem. Soc. Jpn.* **1959**, *32*, 777.

[16] J. P. Melder, H. Prinzbach, *Chem. Ber.* **1991**, *124*, 1271.

[17] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans. 2* **1987**, 1.

[18] Siemens (Bruker) Analytical X-ray Division, Madison, WI, **1996**.

[19] G. M. Sheldrick, **1996**. Unpublished work based on the method described in: R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33.

[20] G. M. Sheldrick, Siemens Analytical X-ray Division, Madison, WI, **1996**.

[21] R. G. Nuzzo, F. A. Fusco, D. L. Allara, *J. Am. Chem. Soc.* **1987**, *109*, 2358.

[22] See for recent summary: P. E. Laibinis, G. M. Whitesides, D. L. Allara, Y. Tao, A. N. Parikh, R. G. Nuzzo, *J. Am. Chem. Soc.* **1991**, *113*, 7125 and references cited therein.

[23] B. G. Bravo, T. Mebrahtu, M. P. Soriaga, D. C. Zapien, A. T. Hubbard, J. L. Stickney, *Langmuir* **1987**, *3*, 595.

[24] A. Stern, E. Wellner, G. N. Salaita, L. Laguren-Davidson, F. Lu, N. Batina, D. G. Frank, D. C. Zapien, N. Walton, A. T. Hubbard, *J. Am. Chem. Soc.* **1988**, *110*, 4885.

[25] J. J. Hickman, P. E. Laibinis, D. I. Auerbach, C. Zou, T. J. Gardner, G. M. Whitesides, M. S. Wrighton, *Langmuir* **1992**, *8*, 357.

[26] J. H. Zagal, C. Fierro, R. Rozas, *J. Electroanal. Chem.* **1981**, *119*, 403.

[27] J. H. Zagal, P. Herrera, *Electrochim. Acta* **1985**, *30*, 449.

[28] E. Córdova, R. A. Bissel, A. E. Kaifer, *J. Org. Chem.* **1995**, *60*, 1033.

[29] S. Töteberg-Kaulen, E. Steckhan, *Tetrahedron* **1988**, *44*, 4389.

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