1,2-Dithiins and Precursors, 18[◇]

3,6-Bis(*p*-dimethylaminophenyl)-1,2-dithiin versus 3,4-Bis(*p*-dimethylaminophenyl)-1,2-dithiete – A Mechanistic Probe for the Photoinduced Behavior of the 1,2-Dithiin System☆

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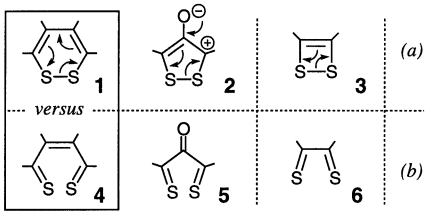
Whereas 3,4-bis(*p*-dimethylaminophenyl)-1,2-dithiete (**18**) is in equilibrium with its ring-opened valence isomer **19**/**19′**, which can also exist as a solid, the analogously disubstituted 1,2-dithiin **20** is stable when protected from light, but on exposure to light undergoes immediate ring transformation to 2,5-bis(*p*-dimethylaminophenyl)thiophene-3-thiol (**30**). To a lesser extent, it also undergoes sulfur extrusion to form 2,5-bis(*p*-dimethylaminophenyl)thiophene (**29**). The ring-opened valence isomer **21**/**21′** and dihydrothiophene episulfide **28** are suggested as key intermediates. X-ray crystallography of the disulfide **31** obtained from the main product **30** unequivocally confirms the structure. The synthesis of **20** is based on the nucleophilic addition of 1,1-dimethylethanethiol to 1,4-bis(*p*-dimethylaminophenyl)butadiyne (**23a**) with ensuing functional group conversion. An efficient variant of this method using ethoxycarbonylsulfenyl chloride as a deprotecting reagent is described, leading to the synthesis of 3,6-diphenyl-1,2-dithiin (**27**).

Since the discovery of the 1,2-dithiin system **1**[1], structural alternatives, especially the electrocyclically ring-opened valence isomer **4**, have repeatedly been discussed[1c][1d][2] with regard to the surprising red color[3][4] (Scheme 1). This property and other unusual features[5] (e.g. its facile photoinduced sulfur extrusion,[1] its occurrence as a plant constituent,[1c][1d][2a][2b][6] and its antibiotic activity[7][8]) have led to continued interest[9] in this unique 8π-electron sulfur system.

Scheme 1



Theoretical Background and Overview of Problems

In general terms, 1,2-dithiins **1**, together with 1,2-dithiolium-4-olates **2**[10] and 1,2-dithietes **3**[11], belong to a large family of cyclic-conjugated disulfides, which is considered alongside the series of ring-opened valence isomers **4**–**6**. According to quantum chemical calculations by Fabian et al.[3b][9g][10d][11h], the preferred structure depends largely on the substituents adjacent to the S atoms. Thus, H and organic substituents, especially electron-withdrawing groups, favour the cyclic structures **1**–**3**, whilst with π-donor substituents the ring-opened valence isomers **4**–**6** are preferred. The non-planar cyclic structure of the parent compound and the C–S–S–C dihedral angle of around 50–60°, found in various substituted and anellated derivatives, is now well established.[12]

However, the 1,4-dithioxo-2-butene valence isomer **4** plays a significant role as a reactive intermediate in the photoinduced sulfur extrusion from **1** to yield thiophenes (Scheme 2). In contrast, the dianellated analogues, e.g. the diborneno- and dithieno-anellated 1,2-dithiins **7**[12c][13a], **8**[3c][12d] and **9**[12b], are exceptional and are surprisingly resistant to sulfur extrusion. Hence, we rationalized the reaction[13b] in terms of an intramolecular $_{\pi}4+_{\pi}2$ cycloaddition[14] of the conformer **4′**[15], which is sterically hindered in the case of **7**–**9**. This course, which generally leads to the bicyclic thiirane **10**, parallels the behavior in the heteroanalogous hexatriene series,[14a] and sulfur removal to afford the thiophene **11** is a familiar process in episulfide chemistry.[16] Shortly afterwards, we learned that this ring transformation had been independently elucidated by Block

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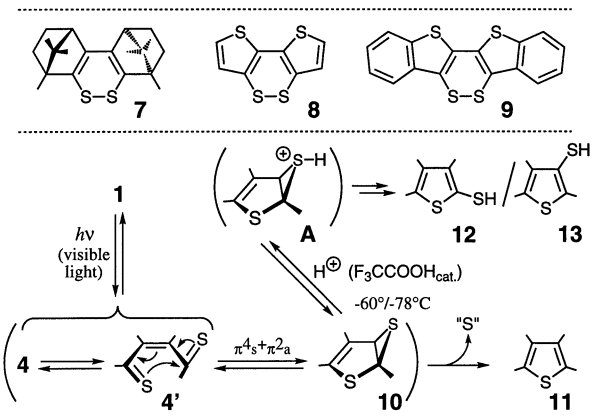
  1434–193X/98/1111–2365 $ 17.50+.50/0

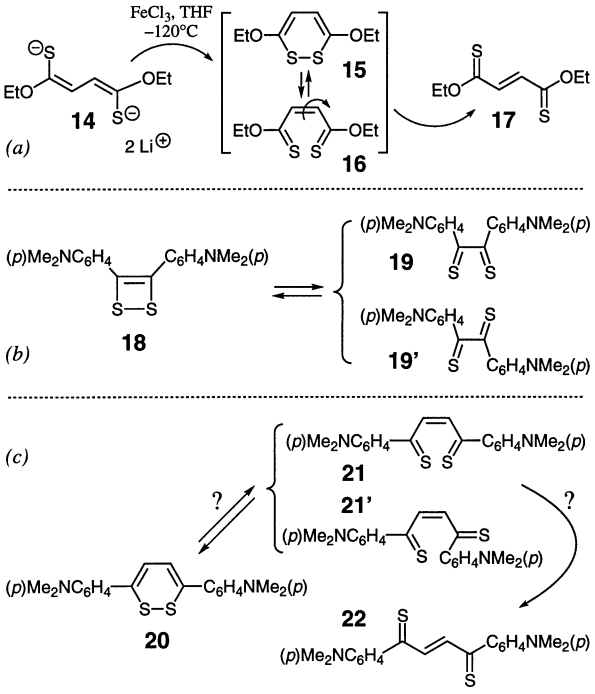
et al.[9i] following photochemical studies at low temperatures. Using Ar matrix isolation (at 25 K) and flash photolysis techniques, unequivocal spectroscopic evidence was obtained for the intermediacy of the 1,4-dithioxo-2-butene **4**/**4′**. The novel bicyclic thiirane of type **10** was spectroscopically characterized at −60 to −75°C and, after addition of an acid catalyst, formation of thiophenethiols of type **12** (from the parent compound) and of type **13** (from 3,6-diphenyl-1,2-dithiin), evidently via cation **A**, could be observed.

Scheme 2



However, two other experimental observations still suggested the existence of 2-butene-1,4-dithiones under "normal" conditions (e.g. at room temperature), depending upon the substituents (Scheme 3). Firstly, Hartke and Pfleging[17] [row *(a)*] found that the oxidation of dilithium 1,4-diethoxybutadiene-1,4-dithiolate (**14**) gave diethyl dithiofumarate (**17**) and not 3,6-diethoxy-1,2-dithiin (**15**), possibly by subsequent (*Z*) → (*E*) isomerization of the ring-opened valence isomer **16**. Thus, this represents an alternative to intramolecular cycloaddition involving **4′**. On the other hand [row *(b)*], Küsters and de Mayo[18] found that bis(*p*-dimethylaminophenyl)-1,2-dithiete (**18**) is in equilibrium with the acyclic valence isomer **19**/**19′**, which can also exist in the solid state. A phenylogous relationship with *N*,*N′*-tetramethyldithiooxalic amide appears obvious. We were therefore interested in the situation that exists in the analogously 3,6-disubstituted 1,2-dithiin **20** [row *(c)*], especially to what extent the ring-opened valence isomer **21**/**21′** or its (*E*) isomer **22** may be analogously stabilized by the donor effect of the *p*-dimethylaminophenyl group.

Scheme 3

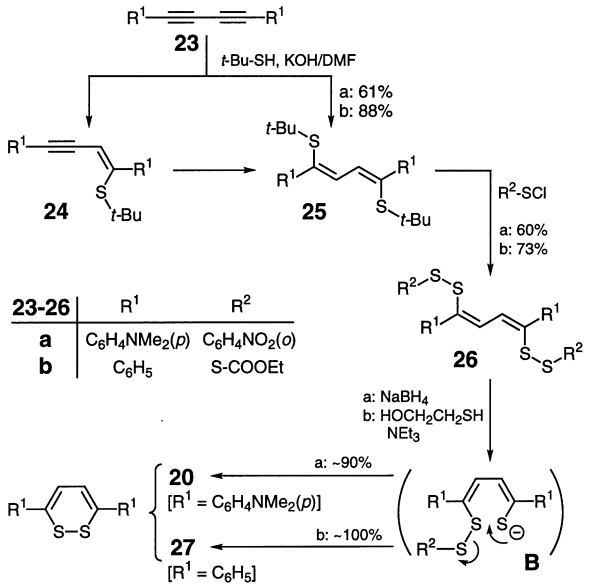


Preparation of 20 and Synthetic Variations

The synthesis of 3,6-bis(*p*-dimethylaminophenyl)-1,2-dithiin (**20**) was carried out according to our former methodology[12e] (Scheme 4). In the initial step, nucleophilic addition of 1,1-dimethylethanethiol to bis(dimethylaminophenyl)butadiyne[19] (**23a**), with the aid of KOH in DMF, yielded (*Z*,*Z*)-1,4-di(*tert*-butylthio)butadiene **25a**.[20] Due to the donor effect of the *p*-dimethylaminophenyl substituents, more vigorous conditions were required, e.g. elevated temperature (50°C), a longer reaction time (up to 70 h in total), and the supplementary addition of KOH (owing to the hydrolysis of DMF under the reaction conditions). Under milder conditions (e.g. room temperature), the monoadduct **24a** could be isolated without problems and transformed into the bis-adduct **25a** by a second treatment with 1,1-dimethylethanethiol. Both intermediates, **24a** and **25a**, show a strong UV fluorescence (λ = 254 nm). Subsequently, **25a** was treated with *o*-nitrobenzenesulfenyl chloride to yield the bis(disulfide) **26a**. In the mass spectrum (70 eV) of the latter, however, no molecular ion peak could be detected. Instead, we observed ion peaks due to the target product **20** and the derived thiophene (resulting from loss of S) with *m/z* 354 and 322, respectively. Finally, reductive S−S fission of **26a** by treatment with $NaBH_4$ at 60°C in benzene/EtOH/H_2O furnished 1,2-dithiin **20** in high yield. In this method, no subsequent oxidation is necessary, as would have been expected following reductive fission of both disulfide units to the corresponding dithiolate. We therefore assume that reductive fission occurs only at one disulfide unit and is followed by an intramolecular "thiol-disulfide interchange reaction"[21] according to **B**, and that the fast precipitation of product **20** prevents further reductive attack. Attempts to prepare **20** using 2-mercaptoethanol and triethylamine, a method which we have successfully employed in previous work,[12e] failed because of the extremely poor solubility of **26a**.

Some further remarks concerning this synthesis are merited. The comparable reaction of the diyne **23a** with phenylmethanethiol rather than 1,1-dimethylethanethiol, as originally used in our 1,2-dithiin synthesis,[1b][12e] gave poor results and only a highly complex product mixture, unsuitable for further transformations, was obtained. In the 1,1-dimethylethanethiol route,[12e] other sulfenyl chlorides can be

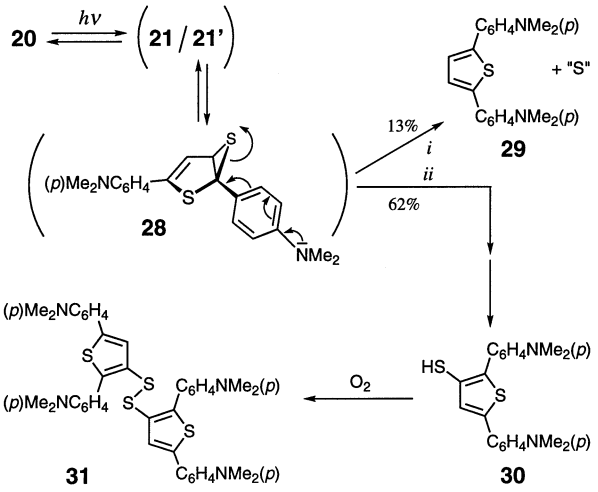
Scheme 4



used instead of *o*-nitrobenzenesulfenyl chloride for removal of the *tert*-butyl group. At this stage, the use of ethoxycarbonylsulfenyl chloride[22] permits an efficient synthesis of 3,6-diphenyl-1,2-dithiin (**27**), which leads to a facile separation of the product from the by-products compared to the situation using *o*-nitrobenzenesulfenyl chloride (Scheme 5). The 1,4-di(*tert*-butylthio)butadiene **25b**, obtained from 1,4-diphenylbutadiyne (**23b**) and 1,1-dimethylethanethiol in 88% yield, was smoothly transformed into the bis(disulfide) **26b**. Deprotection of the latter, performed with the aid of 2-mercaptoethanol and base, immediately afforded **27** in almost quantitative yield. In contrast to the *o*-nitrobenzenesulfenyl chloride variant, two molar equivalents, rather than catalytic amounts of 2-mercaptoethanol/base were required, owing to competitive attack at the ethoxycarbonyl groups.

3,6-Bis(*p*-dimethylaminophenyl)-1,2-dithiin (**20**) was isolated as madder-red crystals that were found to be poorly soluble in all common solvents. Its cyclic structure is in accord with several spectroscopic observations and contrasts with the behavior of dithiete **18**. There is no evidence for the presence of one of the ring-opened valence isomers **21**/**21′** and **22**. Thus, only one olefinic ^{1}H-NMR signal (δ = 6.80) is observed, whereas in the case of an equilibrium with the ring-opened valence isomers, distinct olefinic signals would be expected. The proton signals of the aromatic rings are seen at δ = 6.73 and δ = 7.56, in contrast to those expected for **21**/**21′** or **22**, where signals further downfield than δ = 8 would be observed due to thiocarbonyl anisotropy.[18][23] Finally, **20** displays a long-wave absorption at 493 nm with a relatively high extinction coefficient (ε = 13021), which is not sufficiently bathochromically shifted for **21**/**21′** or **22**. Conjugated thiobenzoyl compounds give absorptions at significantly longer wavelengths (n $\rightarrow$ π^* transitions) with considerably lower extinction coefficients as shown, e.g., by *p*-aminothiobenzophenone with λ_{max} = 595 nm and ε = 92.[24]

Scheme 5

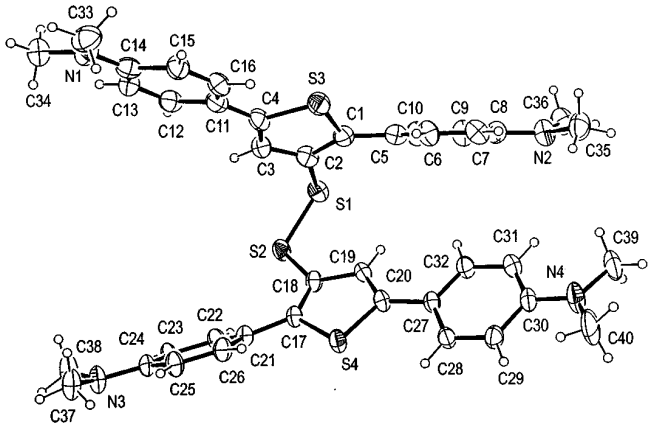


Photoinduced Ring Transformation of 20 and Conclusions

Surprisingly, **20** is very unstable towards daylight (Scheme 5). The cherry-red dichloromethane solution is decolorized significantly more rapidly than the 3,6-diphenyl analogue **27**, thus convincingly illustrating the accelerating effect of the dimethylamino group in *para* position.[25] After evaporation of the solvent, mass spectrometry indicated two independent molecular ion peaks, the first appearing at *m/z* 322 and the other at *m/z* 354. Correspondingly, 2,5-bis(*p*-dimethylaminophenyl)thiophene[26] (**29**) and 2,5-bis(*p*-dimethylaminophenyl)thiophene-3-thiol (**30**) were produced in a ratio of about 1:5, as estimated by ^{1}H-NMR spectroscopy. The first compound could only be obtained in an enriched form because of its extreme oxygen sensitivity (a deep-blue color developed during chromatography). The latter product, actually an isomer of the original 1,2-dithiin **20**, was oxidized to the crystalline dithienyl disulfide **31**, which could be isolated without any difficulties. Its structure has been unambiguously elucidated by X-ray crystallography[27] (Figure 1). The C−S−S−C dihedral angle is around 73.5(4)°, the aryl units are twisted towards the plane of the thiophene rings such that C5−C10 and C21−C26 adopt angles of 33.9(3)° and 36.5(3)° with respect to the thiophene planes S3/C1−C4 and S4/C17−C20, respectively. The two thiophene planes are at an angle of about 75° to one another. The mass spectrum (70 eV) of **31** features [M^+/2] as the base peak.

Two pathways are therefore possible involving the key intermediate episulfide **28**. In the minor route (*i*) "normal" sulfur extrusion occurs leading to the disubstituted thiophene 29. In the main path (*ii*), however, the π-donor effect of the *p*-(dimethylamino)phenyl group leads to heterolytic opening of the episulfide ring of **28**, resulting in the formation of thiophene-3-thiol **30**, and ultimately the disulfide **31**. Here, ring transformation of **20** has occurred by a formal migration of one of the sulfur atoms from a cyclic to an exocyclic position. This course parallels that of the acid-catalyzed process **10** $\rightarrow$ **A** $\rightarrow$ **12**/**13**[9i] in Scheme 2, but now takes place exclusively due to a substituent effect.

Figure 1. Molecular structure of **31** in the crystal; displacement ellipsoids are drawn at a 30% probability level and H atoms as small circles of arbitrary radius



In summary, the behavior of 1,2-dithiin **20** differs fundamentally from that of the analogously disubstituted 1,2-dithiete **18**. No valence-isomeric equilibrium could be observed in solution under conditions where **18** is in equilibrium with its valence isomers. In the 1,2-dithiin series, the *p*-dimethylaminophenyl group appears to be insufficiently donor-active to preserve the dithioxo state. Furthermore, it is obvious that in this series the existence of a ring-opened valence isomer of the general type **4**/**4′** under "normal" conditions is impeded by a highly favored intramolecular $_{\pi}4+_{\pi}2$-cycloaddition, unless a (*Z*) → (*E*) isomerization can successfully compete. Indeed, (*E*) isomers of type **4** are formed when NR_2 substituents are present, as will be reported in detail in our following paper.

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Experimental Section

Solvents and reagents were purified and dried according to standard procedures. − For TLC, Merck silica gel plates were used; detection was carried out by exposure to iodine vapour. − CC was performed with silica gel 60 Å, 32−63 μm (ICN Biomedicals). − Melting points were taken with a Boetius M hot-stage microscope and are uncorrected. − Elemental analyses (C, H, N, S) were obtained with an automatic microanalyzer (Carlo Erba). − NMR: Varian Unity 500 and Varian Gemini 200 spectrometers, using TMS as internal standard and wide-band decoupling of ^{13}C NMR. − EI-MS: Varian MAT CH6 and AMD Intectra 402 (70 eV). − IR: Perkin-Elmer FT-IR spectrometer 100. − UV/Vis: Perkin-Elmer Lambda 14 spectrophotometer.

(Z)-1-tert-Butylthio-1,4-bis(p-dimethylaminophenyl)but-1-en-3-yne (**24a**): A mixture of powdered KOH (120 mg, 2.14 mmol), 1,1-dimethylethanethiol (800 mg, 8.8 mmol) and absolute DMF (30 ml) was stirred under argon for 20 min. Then, 1,4-bis(*p*-dimethylaminophenyl)butadiyne (**23a**)[19] (1.16 g, 4 mmol) was added and stirring was continued at room temp. for 21 d (reaction monitored by TLC using CH_2Cl_2). The precipitated solid (mainly consisting of **25a**, ca. 30%) was filtered by suction and washed with a little DMF and EtOH. To the combined filtrates water (ca. 10 ml) was added dropwise with stirring. Isolation of the separated crude solid (670 mg) and purification by recrystallization from EtOH (× 3) and finally by dissolving the solids in CH_2Cl_2 and re-precipitating with EtOH afforded 0.31 g (21%) of **24a** as yellow rods, m.p. 150−151°C. − IR (KBr): $\tilde{\nu}$ = 1603 cm^{-1} (C=C), 2179 (C≡C). − UV/Vis (MeCN): λ_{max} (lg ε) = 239 nm (4.14), 258 (4.13, sh), 290 (4.09), 338 (4.26, sh), 388 (4.59). − ^1H NMR ($CDCl_3$): δ = 1.26 [s, 9 H, $C(CH_3)_3$], 2.96 [s, 12 H, 2 $N(CH_3)_2$], 6.39 (s, 1 H, =C−H), 6.64 (m_c, 4 H, aromatic H-3′, H-3′′), 7.36 (ps d, 2 H), 7.54 (ps d, 2 H, aromatic H-2′, H-2′′). − ^{13}C NMR ($CDCl_3$): δ = 31.9 [$C(CH_3)_3$], 40.2, 40.3 [s, $N(CH_3)_2$], 48.4 [$SC(CH_3)_3$], 88.3 (≡*C*−CH=), 96.8 (≡*C*−aryl), 111.1 (aromatic C-1′′), 111.7, 111.9 (aromatic C-3′, C-3′′), 115.6 (=CH), 128.6 (aromatic C-2′ or C-2′′), 130.6 (aromatic C-1′), 132.6 (aromatic C-2′ or C-2′′,), 143.9 (=C−S), 150.0, 150.4 (aromatic C-4′, C-4′′). − MS (70 eV); *m/z* (%): 378 (58) [M^+], 322 (100) [$M^+ - C_4H_8$], 307 (21) [$M^+ - C_4H_8 - CH_3$]. − $C_{24}H_{30}N_2S$ (378.6): calcd. C 76.14, H 7.99, N 7.40, S 8.47; found C 76.24, H 7.91, N 7.34, S 8.51.

(Z,Z)-1,4-Di(tert-butylthio)-1,4-bis(p-dimethylaminophenyl)-buta-1,3-diene (**25a**): The reaction mixture, prepared as described above from powdered KOH (150 mg, 2.67 mmol), 1,1-dimethylethanethiol (1.6 g, 17.8 mmol), **23a** (1.5 g, 5.6 mmol) and absolute DMF (40 ml), was heated in a sealed vessel for 14 h at 50°C. After the addition of further KOH (100 mg, 1.78 mmol), heating was continued for another 40 h. More KOH (100 mg) was then added and the mixture was heated for a further 16 h (reaction monitored by TLC using CH_2Cl_2). The separated solid was filtered by suction at room temp., washed with a little DMF, then with water, EtOH and diethyl ether, and finally recrystallized from DMF to afford 1.5 g (61%) of the bis-adduct **25a** as deep-yellow hexagonal prisms, m.p. 245−250°C (decomp.; after melting about 10 components are detectable by TLC). − UV/Vis (MeCN): λ_{max} (lg ε) = 255 nm (4.59), 331 (4.39), 405 (4.88). − ^1H NMR ($CDCl_3$): δ = 1.18 [s, 18 H, $C(CH_3)_3$], 2.97 [s, 12 H, $N(CH_3)_2$], 6.68 (ps d, 4 H, aromatic H-3′), 7.61 (ps d, 4 H, aromatic H-2′), 7.74 (s, 2 H, =CH−). − ^{13}C NMR ($CDCl_3$): δ = 31.8 [$C(CH_3)_3$], 40.5 [$N(CH_3)_2$], 47.8 [$C(CH_3)_3$], 111.8 (aromatic C-3′), 128.8 (aromatic C-2′), 132.1, 135.0, 150.0 ($C_{quat.}$). − MS (70 eV); *m/z* (%): 468 (31) [M^+], 322 (100) [$M^+ - C_4H_9 - SC_4H_9$], 307 (6) [$M^+ - C_4H_9 - SC_4H_9 - CH_3$]. − $C_{28}H_{40}N_2S_2$ (468.8): calcd. C 71.74, H 8.60, N 5.98, S 13.68; found C 71.73, H 8.41, N 6.28, S 13.54.

(Z,Z)-1,4-Bis(p-dimethylaminophenyl)-1,4-bis(2-nitrophenyldithio)buta-1,3-diene (**26a**): *o*-Nitrobenzenesulfenyl chloride (210 mg, 1.11 mmol) was added in four portions to a suspension of **25a** (260 mg, 0.554 mmol) in acetic acid (5 ml) and trichloroethene (5 ml). After heating at 50−55°C for 6 h and allowing to stand overnight, the mixture was concentrated under reduced pressure. The residue was treated with ethanol (5 ml), and the resulting solid was recrystallized from $CHCl_3$/EtOH (2:1) to afford 220 mg (60%) of **26** as orange-red prisms, m.p. 184−185°C (decomp.). − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 243 nm (4.65), 275 (4.63), 373 (4.47). − ^1H NMR ($CDCl_3$): δ = 3.12 [s, 12 H, $N(CH_3)_2$], 6.32 (s, 2 H, =CH−), 7.19 [m_c, 10 H, $(CH_3)_2N-ArH$], 7.49 (m_c, 2 H), 7.65 (m_c, 2 H), 7.88 (ps d, 2 H), 8.24 [ps d, 2 H, (*o*)-O_2N-Ar*H*]. −^{13}C NMR ($CDCl_3$): δ = 40.1 [$N(CH_3)_2$], 111.4 [aromatic C adjacent to $N(CH_3)_2$], 122.4, 122.6, 125.7, 125.9, 127.9, 130.3, 133.8 (aromatic C, olefinic C), 136.0, 137.1, 145.6 ($C_{quat.}$), 150.5 [*C*-$N(CH_3)_2$]. − MS (70 eV); *m/z* (%): [M^+] absent, 354 (1.4) [$M^+ - 2\,SC_6H_4NO_2$], 322 (100) [$M^+ - 2\,SC_6H_4NO_2 - S$], 307 (21) [$M^+ - 2\,SC_6H_4NO_2 - S - CH_3$]. − $C_{32}H_{30}N_4O_4S_4$ (662.9): calcd. C 57.98, H 4.56, N 8.45, S 19.35; found C 58.46, H 4.44, N 8.48, S 19.79.

3,6-Bis(p-dimethylaminophenyl)-1,2-dithiin (**20**): The preparation was carried out under the exclusion of daylight. Sodium tetrahydroborate (95 mg, 2.5 mmol) was added to a suspension of **26a** (160 mg, 0.25 mmol) in benzene (5 ml), ethanol (2.5 ml) and water (0.25 ml). The mixture was stirred at room temperature for 2 h and then at 60°C for 1 h. After cooling, the resulting deep-red solid was filtered by suction, washed with water and ethanol, and recrystallized from dichloromethane. The product, which was found to be extremely light-sensitive and poorly soluble, was obtained as madder-red needles (its red solution in CH_2Cl_2 or $CHCl_3$ was decolorized almost immediately upon exposure to daylight), m.p. 191−192°C (decomp. with brightening of color). − IR (KBr): $\tilde{\nu}$ = 1601 cm^{-1} [*no* significant band at 1200−1220 cm^{-1} (C=S)]. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 261 nm (4.15), 361 (4.31), 493 (4.11) [after 2 s in polychromatic daylight: λ_{max} = 233, 251, 369 nm]. − ^{1}H NMR (CD_2Cl_2): δ = 3.00 [s, 12 H, $N(CH_3)_2$], 6.73 (d, *J* = 9.0 Hz, 4 H, aromatic H-3′,), 6.80 (s, 2 H, dithiin-H), 7.56 (d, *J* = 9.0 Hz, 4 H, aromatic H-2′,). − ^{13}C NMR ($CDCl_3$): δ = 40.3 [$N(CH_3)_2$], 112.1 (aromatic C-3′/5′), 122.7 (C-4/5, dithiin), 124.9 (aromatic C-1′), 128.7 (aromatic C-2′/6′), 132.9 (C-3/6, dithiin), 150.6 [*C*-$N(CH_3)_2$]. − MS (70 eV); *m/z* (%): 354 (83) [M^+], 339 (6) [$M^+ - CH_3$], 322 (100) [$M^+ - S$], 307 (20) [$M^+ - S - CH_3$], 177 (9) [$M/2^+$], 161 (10) [$M/2^+ - CH_4$]. − $C_{20}H_{22}N_2S_2$ (354.5): calcd. C 67.76, H 6.25, N 7.90, S 18.09; found C 67.81, H 6.26, N 7.80, S 17.85.

(Z,Z)-1,4-Bis(ethoxycarbonyldithio)-1,4-diphenylbuta-1,3-diene (**26b**): Ethoxycarbonylsulfenyl chloride (420 mg, 3 mmol) was added dropwise to a suspension of butadiene **25b**[12e] (380 mg, 1 mmol) in acetic acid (10 ml) and trichloroethene (5 ml). On heating at 60°C for 3 h, **25b** dissolved and a solid separated. After concentration under reduced pressure, the residue was washed successively with hexane, water, and a little ethanol, and recrystallized from ethanol/benzene (3:1) to yield yellow, rhombic crystals, m.p. 148−149°C (thermally stable). − IR (KBr): $\tilde{\nu}$ = 1134 cm^{-1} (C−O−C), 1732 (C=O), 2974 (C−H, aliphatic), 3062 (C−H, aromatic H). − UV/Vis (MeCN): λ_{max} (lg ε) = 238 nm (4.08), 292 (3.99, sh), 355 (4.43). − ^{1}H NMR ($CDCl_3$): δ = 1.22 (t, 3 H, CH_3), 4.25 (q, 2 H, OCH_2), 7.38 (m_c, 6 H, aromatic H), 7.71 (m_c, 4 H, aromatic H), 7.71 (m_c, 4 H, aromatic H), 7.79 (s, 2 H, =CH). − ^{13}C NMR ($CDCl_3$): δ = 14.2 (CH_3), 65.2 (OCH_2), 128.46, 128.51, 128.9 (aromatic C_o, C_m, C_p), 132.9 (=CH−), 138.3, 140.6 ($C_{quat.}$), 168.0 (C=O). − MS (70 eV); *m/z* (%): 478 (2) [M^+], 373 (5) [$M^+ - C_2H_5OCOS$], 341 (2) [$M^+ - C_2H_5OCOS_2$], 268 (31) [$M^+ - 2\ C_2H_5OCOS$], 236 (100) [$M^+ - 2\ C_2H_5OCOS_2$] ("thiophene"), 121 (13) [$C_6H_5CS^+$]. − $C_{22}H_{22}O_4S_4$ (478.7): calcd. C 55.20, H 4.63, S 26.80; found C 55.55, H 4.52, S 26.60.

Conversion of **26b** *to 3,6-Diphenyl-1,2-dithiin* (**27**): A solution of triethylamine (101 mg, 1 mmol) and 2-mercaptoethanol (78 mg, 1 mmol) in absolute THF (5 ml) was added dropwise to a stirred solution of **26b** (240 mg, 0.5 mmol) in absolute THF (10 ml) at room temp. (red solution). Stirring was continued until completion of the reaction [about 20 min, monitored by TLC using benzene/hexane (1:1)]. The mixture was then concentrated under reduced pressure, the residue was washed with cold ethanol and recrystallized from ethyl acetate/ethanol (3:1) to afford 130 mg (97%) of **27** (for data see ref.[12e]).

Ring Transformation of **20** *to 2,5-Bis(p-dimethylaminophenyl)-thiophene* (**29**) *and 2,5-Bis(p-dimethylaminophenyl)thiophene-3-thiol* (**30**)*/3,3′-Dithiodi[2,5-bis(p-dimethylaminophenyl)thiophene]* (**31**): 1. A suspension of **20** (50 mg, 0.141 mmol) in dichloromethane (100 ml) was vigorously shaken at room temperature in sunlight for 1 min to give an almost colorless solution (slight blue fluorescence), which was then concentrated under reduced pressure. The residue was found to contain **29** and **30** in a ratio of 1:5 [as indicated by ^{1}H-NMR ([D_6]acetone) with δ = 7.14 (=CH−) for **29**, and δ = 4.07 (S−H) and 7.10 (=CH−) for **30**; by IR (KBr) with $\tilde{\nu}$ = 2553 cm^{-1} (S−H) for **30**; and by mass chromatography with the molecular ion peak *m/z* 322 for **29** observed before that for **30** at *m/z* 354]. − 2. The residue was then dissolved in acetone (15 ml) and the resulting solution was left open to air for 24 h. The precipitated solid was filtered by suction (40 mg) and purified by CC (silica gel 60, 32−63 μm; CH_2Cl_2, R_f = 0.15) and finally by recrystallization from toluene to yield **31**, 31 mg (62%), as orange-red hexagonal crystals, m.p. 227−228°C. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 265 nm (4.79), 361 (5.01). − ^{1}H NMR (CD_2Cl_2): δ = 2.90 [s, 12 H, 2 $N(CH_3)_2$], 2.98 [s, 12 H, 2 $N(CH_3)_2$], 6.62 [m_c, 4 H, aromatic H adjacent to $N(CH_3)_2$], 6.69 [m_c, 4 H, aromatic H adjacent to $N(CH_3)_2$], 7.15 (s, 2 H, thiophene-H), 7.32 (m_c, 4 H, aromatic H), 7.37 (m_c, 4 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 40.2, 40.4 [$N(CH_3)_2$], 111.9, 112.6 (aromatic C-3′/3′′), 121.5, 122.7 ($C_{quat.}$), 126.6, 126.7, 127.4, 130.3 (aromatic C, thiophene-C), 141.8, 143.9 ($C_{quat.}$), 150.1 (aromatic C-4′/4′′). − MS (70 eV); *m/z* (%): 706 (2) [M^+], 674 (15), [$M^+ - S$], 354 (100) [$M/2^+ + 1$], 340 (72). − MALDITOF-MS: Two intense peaks with *m/z* 706.2 [M^+] and 674.2 [$M^+ - S$]. − $C_{40}H_{42}N_4S_4$ (707.0): calcd. C 67.95, H 5.99, N 7.92, S 18.14; found C 68.23, H 6.10, N 7.81, S 18.18. − 3. The filtrate obtained after separation of the solid (40 mg, crude **31**) from the acetone solution as described above (2), was concentrated under reduced pressure. The resulting material (6.2 mg) was subjected to flash chromatography (silica gel/CH_2Cl_2 as above). After evaporation of the solvent from the appropriate fraction, the solid was crystallized from hot ethanol yielding 6.0 mg (13%) of **29** as yellow, flat, rod-like crystals, m.p. 256−270°C (decomp. with deep-brown coloration), showing intense blue fluorescence in solution (CH_2Cl_2). − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 301 nm (3.89), 377 (4.56). − ^{1}H NMR (CD_2Cl_2): δ = 2.98 [s, 12 H, 2 $N(CH_3)_2$], 6.77 [ps d, 4 H, aromatic H adjacent to $N(CH_3)_2$], 7.16 (s, 2 H, thiophene-H), 7.49 (ps d, 4 H, aromatic H). − MS (70 eV); *m/z* (%): 322 (100) [M^+], 307 (25) [$M^+ - CH_3$], 161 (14) [M^{2+}].

X-ray Crystallographic Study of **31**: Crystal data: $C_{40}H_{42}N_4S_4$, M_r = 707.02, monoclinic, $P2_1/c$. Unit cell dimensions: *a* = 15.833(11), *b* = 9.91(2), *c* = 23.41(2) Å; β = 100.97(7)°, *V* = 3608(8) $Å^3$, *Z* = 4, $D_{calcd.}$ = 1.302 $g \cdot cm^{-3}$, *F*(000) = 1496, *T* = 298(1) K. − Data collection: Stoe Stadi-4 four-circle diffractometer, graphite-monochromated Mo-K_α radiation (λ_0 = 0.71073 Å), orange-red crystal (0.40 × 0.40 × 0.20 mm), ω/2Θ scans, Θ range 1.77−22.52°, index ranges: $-17 \le h \le 17$, $0 \le k \le 8$, $-25 \le l \le 25$, 8436 reflections measured, 4323 symmetry independent reflections (R_{int} = 0.0808), 2827 observed reflections with $I > 2\sigma(I)$, μ = 0.299 m^{-1}. − Structural analysis and refinement: The structure was solved by direct methods (SHELXS-86[29]) and refined with full-matrix routines on F^2 (SHELXL-93[30]). All non-hydrogen atoms were refined anisotropically, the H atoms were placed in calculated positions and refined with free isotropic displacement parameters, data/restraints/parameters: 4313/0/475, *R*1 = 0.0725 and *wR*2 = 0.1787 for reflections with $I > 2\sigma(I)$. *R*1 = 0.1171 and *wR*2 = 0.2209 for all data. Maximum and minimum peak and hole in the final Fourier synthesis: 0.873 and −0.432 $eÅ^{-3}$. The drawing of the molecular structure was performed using the program ORTEPIII[31].

☆ This paper is dedicated to Professor *Ernst Schmitz* on the occasion of his 70th birthday.

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[25] It should be emphasized that under the same conditions **27** suffers exclusively sulfur extrusion yielding 2,5-diphenylthiophene; cf. also ref.[1b][12e].
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[27] Crystallographic data (excluding structure factors) for the structure of **31** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-101386. Copies of this data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk].
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