Ring-Opening Cycloaddition of 4-Thiadispiro[2.1.2.2]non-8-ene with Tetracyanoquinodimethane via Zwitterion. Formation of (2,5)Thiophenophanes and a Specific Effect of Ethereal Solvent

Takashi Tsuji,* Takaya Ishihara, and Shinya Nishida

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

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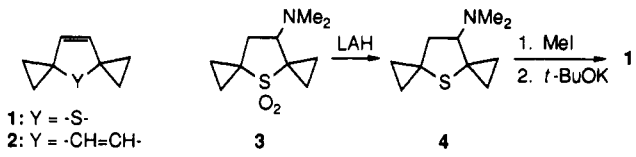
Ring-opening cycloadditions of dispiro[2.2.2.2]deca-4,9-diene (**2**) with unsaturated compounds provide a variety of paracyclophane derivatives.[1] In those reactions, the aromatization of the central six-membered ring of **2** is presumed to play a critical role in stimulating the cleavage of the cyclopropane rings. A reasonable extention to this versatile substrate is the substitution of one of the vinylene moieties with a divalent sulfur atom to give **1** which generates a thiophene ring upon cleavage of both the cyclopropane rings. In this note we report a simple synthesis of **1** and its ring-opening cycloaddition with tetracyanoquinodimethane (TCNQ) via zwitterions in ethereal solvents to afford (2,5)thiophenophanes. These solvents were found to play a specific role in the reaction.

The preparation of **1** was achieved by successively treating readily accessible **3**,[2] (1) with $LiAlH_4$ to give the sulfide **4**, (2) with methyl iodide to quarternize the amine moiety of **4**, and finally (3) with *t*-BuOK in DMF to accomplish the elimination reaction (Scheme I). Compound **1** was obtained as colorless, readily sublimable crystals in 44% overall yield from **3**. It is noteworthy that **1**, as compared with 2,5-dihydrothiophene, has UV absorption bands in the region of substantially longer wavelengths. Thus **1** exhibits an intense band at 238 nm with a shoulder around 280 nm while a band with λ_{max} at 211 nm and an inflection around 230 nm has been reported for 2,5-dihydrothiophene.[3] The observed bathochromic effect of the spiro-linked cyclopropyl groups suggests their significant electronic interaction with the π bond and the sulfur.[4] The interaction also renders the oxidation potential (E_p^{ox}) of **1** unusually low, 1.07 V vs SCE in acetonitrile,[5] and thus **1** highly electron-donating for an isolated alkene or sulfide.[6] Accordingly, the cycloaddition of **1** with electron-deficient TCNQ was examined in several

Scheme I

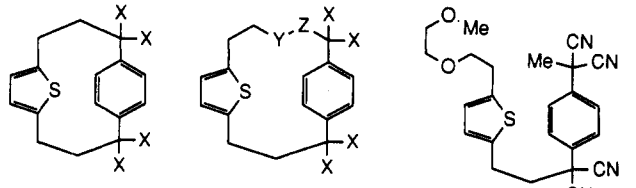


1: Y = -S-
2: Y = -CH=CH-

3 4

solvents and the use of cyclic ethers was found to be essential to achieve the reaction.

The reaction in refluxing dioxane was complete within 10 h, affording **5a** in 24% yield together with **6a** in 48% yield in which a molecule of dioxane was cleaved and incorporated. When the reaction was run in THF at 60 °C for 36 h, the sole product isolated from the resultant mixture was **7a** (64%), a 1:1:1 cycloadduct of **1**, TCNQ, and THF. The incorporation of an ethereal solvent molecule in the adduct was also observed when acyclic DME was employed as the solvent: namely, the single isolable product obtained in 44% yield was **8**, resulting



5 6: Y - Z = -(OCH2CH2)2- 7: Y - Z = -O(CH2)4- 8

a: X = CN, b: X = H

from the selective cleavage of the *O*-methyl but not *O*-methylene bond of DME. In contrast, the reaction of **1** with TCNQ in a nonethereal solvent such as acetonitrile, nitromethane, or 1,2-dichloroethane led only to an intractable complex mixture. The cycloadducts **5a**, **6a**, and **7a** were readily reductively decyanated by treatment with sodium in liquid ammonia[9] to afford **5b**, **6b**, and **7b** in 66%, 59%, and 53% yields, respectively. Thus the present reactions provide a convenient synthetic route to some novel thiophenophanes.[10]

Particularly interesting are the role of the ethereal solvents in rendering the cycloaddition of **1** with TCNQ successful and their incorporation into the adducts. These observations seem to be best accommodated by postulating the formation of a cationic intermediate which is led to an oxonium ion in an ethereal solvent. According to the Weller equation,[11] the endothermicity of electron transfer (ET) from **1** to TCNQ is only 20.3 kcal/mol in acetonitrile. Accordingly, it is not unreasonable to assume the ET process as the initial step of the reaction,[12] though the thermicity of the process in the ethers might differ from that value to some extent. Cleavage of one of the cyclopropane rings followed by coupling within the resultant radical ion pair generates zwitterion **9** which would

(1) (a) Tsuji, T.; Shibata, T.; Hienuki, Y.; Nishida, S. *J. Am. Chem. Soc.* **1978**, *100*, 1806. (b) Shibata, T.; Tsuji, T.; Nishida, S. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2039. (c) Hienuki, Y.; Tsuji, T.; Nishida, S. *Tetrahedron Lett.* **1981**, *22*, 863.

(2) Tsuji, T.; Kikuchi, R.; Nishida, S. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1603.

(3) Procházka, M.; Palecek, M. *Collect. Czech. Chem. Commun.* **1967**, *32*, 3149.

(4) It should be noted that the cyclopropyl rings are fixed in the bisected conformation by virtue of the spiro union where the electronic interaction with the π bond and possibly also with the sulfur will be maximized. Tidwell, T. T. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; John Wiley & Sons: Chichester, 1987; p 565.

(5) The oxidation peak potential (E_p^{ox}) of **1** was measured using cyclic voltammetry at a sweep rate of 200 mV/s in acetonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte. The anodic oxidation of **1** was irreversible.

(6) The E_p^{ox}s of dialkyl sulfides are in a range of 1.75–1.85 V[7] and that of 1,2-dicyclopropylethene is 1.5 V vs SCE[8] in acetonitrile. Thus the E_p^{ox} of **1** is substantially lower than those values. The one-electron oxidation of **1** would therefore produce an extensively delocalized radical cation rather than one in which charge and spin were largely localized on the sulfur or the unsaturated carbons.

(7) Siegerman, H. In *Technique of Electroorganic Synthesis*, Part II; Weinberg, N. L., Ed.; John Wiley & Sons: New York, 1975; p 667.

(8) Nishida, S.; Masui, M.; Murakami, M.; Imai, T.; Tsuji, T. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1454.

(9) Arapakos, P. G.; Scott, M. K.; Huber, F. E., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 2059.

(10) For the preparation of related heterophanes, see: (a) Paudler, W. W.; Bezoari, M. D. In *Cyclophanes*; Keehn, P. M., Rosenfeld, S. M., Eds.; Academic Press: New York, 1983; p 359. (b) Shinmyozu, T.; Hirai, Y.; Inazu, T. *J. Org. Chem.* **1986**, *51*, 1551 and references cited therein. (c) Takeshita, M.; Tashiro, M. *J. Org. Chem.* **1991**, *56*, 2837; **1992**, *57*, 746.

(11) Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 834; *Isr. J. Chem.* **1970**, *8*, 259.

(12) Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79; *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag: Berlin, 1987.

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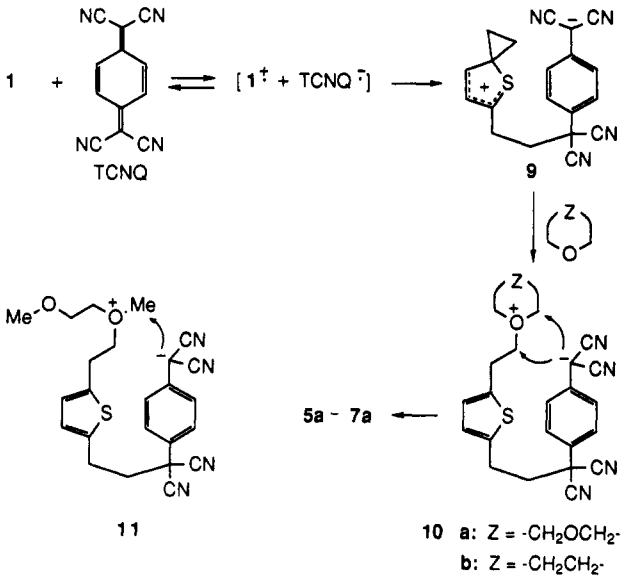
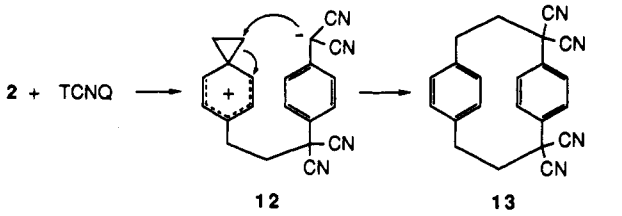
Scheme II

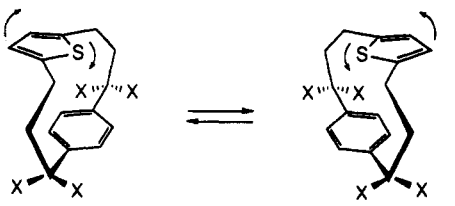


Scheme III



undergo further rearrangement in the ethereal solvents to produce oxonium ions **10**. The subsequent intramolecular displacement of the oxygen by the carbanionic center completes the reaction. Thus the concurrent formation of **5a** and **6a** in dioxane is readily rationalized as a result of competing substitution at the alternative reaction sites (Scheme II). The preferential nucleophilic substitution at the less crowded methyl carbon in the formation of **8** is also in good accord with this mechanism (see **11**). de Meijere and his co-workers have reported similar participation of cyclic ethers in a reaction presumed to proceed via zwitterions and their incorporation in products.[13] Previously we reported the formation of [3.3]paracyclophane **13** from **2** and TCNQ in *o*-dichlorobenzene.[1a] The production of **13** was confirmed in the repetition of the reaction in 1,2-dichloroethane. In addition, the reaction of **2** with TCNQ in THF was now found to give a 1:1:1 cycloadduct of **2**, TCNQ, and THF corresponding to **7a** in 74% yield, together with **13** (4%). These reactions also seem to proceed via ET followed by zwitterion formation[14] in a manner similar to that of **1** with TCNQ. The use of ethereal solvent is thus not requisite to achieve the ring-opening cycloaddition of cyclopropyl compound via zwitterion. The production of **13** in the nonethereal solvents probably results from the direct attack on one of the cyclopropyl methylene carbons by the carbanionic center in the zwitterion **12** (Scheme III). Such a process would require the adequate activation of the cyclopropyl moiety[15] toward the nucleophilic attack and also the proper arrangement of relevant bonds and reaction centers in the transition state.[16] Those requirements would not be met in **9**. Hindered from undergoing the cleavage of the cyclopropane ring which leads to an unstable primary carbonium ion or from collapsing directly to **5a**, **9** would decompose only to give a complex mixture in the nonethereal solvents.[18]

Scheme IV



5a (X = CN); **5b** (X = H)

In the ^{1}H NMR spectra of **5a** and **5b**, the benzene ring protons appear as two singlets of equal intensity at or below room temperature. This indicates that two pairs of neighboring protons are located in different magnetic environments. When the temperature of a solution of **5b** in C_6D_6 was raised from 10 °C to 100 °C, the two singlets at δ 6.41 and 6.96 coalesced at 50 °C ultimately to give a single narrow line, while the thiophene ring proton signal at δ 6.17 remained a sharp singlet throughout. The spectrum of **5a** exhibited a similar temperature dependence and the two singlets coalesced at 98 °C (in DMSO-d_6). The observed spectral change probably arises from the flipping of the thiophene ring in the manner shown in Scheme IV.[20] The calculated free energy barrier for the process was 18.3 kcal/mol for **5a** and 15.9 kcal/mol for **5b**.[21]

Experimental Section

^{1}H NMR spectra were measured at 100 MHz in $CDCl_3$ unless otherwise indicated. Mass spectra were recorded at an ionizing voltage of 70 eV. Elemental analyses were performed by the Center for Instrumental Analysis of Hokkaido University. TCNQ was purchased (Tokyo Kasei) and purified by sublimation under vacuum before use. Dioxane, THF, and DME were freshly distilled from Na under N_2 before use.

Preparation of 4. To a suspension of $LiAlH_4$ (2.0 g, 53 mmol) in 60 mL of THF was added a solution of **3** (2.30 g, 10.7 mmol) in 30 mL of THF. The resultant mixture was refluxed for 3 h,

(13) Kaufmann, D.; de Meijere, A.; Hingerty, B.; Saenger, W. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 816. König, B.; Kaufmann, D.; Näder, R.; de Meijere, A. *J. Chem. Soc., Chem. Commun.* **1983**, 771.

(14) The E_p^{ox} of **2** is 1.14 V vs SCE in acetonitrile.

(15) The cationic center of **9** may be stabilized more efficiently than that of **12**, and hence the cyclopropyl moiety of the former may be somewhat less susceptible toward nucleophilic attack than that of the latter.

(16) The direct collapse of **12** to give **13** may be viewed as an example of nucleophilic ring-opening reactions of activated cyclopropanes which are generally controlled by powerful stereoelectronic effects.[17] The cyclopropyl moiety of **12** may be disposed more favorably toward the intramolecular nucleophilic attack by the carbanionic center than that of **9**.

(17) (a) Danishefsky, S. *Acc. Chem. Res.* **1979**, *12*, 66. (b) Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon Press: Oxford, England, 1983.

(18) $E_T(30)$ values of dioxane, THF, DMF, 1,2-dichloroethane, acetonitrile, and nitromethane are 36.0, 37.4, 38.2, 41.9, 46.0, and 46.3, respectively.[19] Therefore, the ET from **1** to TCNQ and the subsequent zwitterion formation would be easier in the latter three solvents than in the former three ethereal solvents. The reaction of **1** with TCNQ, in fact, appeared to proceed slightly more rapidly in the latter than in the former. The scrutiny of resultant reaction mixtures in the latter three solvents, however, did not provide evidence for the production of any low-molecular-weight adduct including **5** in a significant yield (>2%).

(19) Dimroth, K.; Reichardt, C.; Siepmann, T.; Bohlmann, F. *Ann.* **1963**, *661*, 1.

(20) Force field calculations indicate that the two aromatic rings in **5b** are nearly parallel to each other in the ground state. The calculations were performed with Chem3D Plus, Ver. 3.0; Cambridge Scientific Computing, Cambridge, MA, 1990.

(21) For the energetics of conformational changes in cyclophanes, see: (a) Förster, H.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 429. (b) Mitchell, R. H. In *Cyclophanes*; Keehn, P. M., Rosenfeld, S. M., Eds.; Academic Press: New York, 1983; p 240.

cooled in an ice bath, and treated successively with 2 mL of water, 2 mL of 15% aqueous NaOH, and 6 mL of water.[22] The mixture was filtered and the precipitate was washed with ether (3 × 50 mL). The filtrate and the washings were combined, dried ($MgSO_4$), and concentrated to give a light brown oil, which was distilled in vacuo to afford 1.18 g of **4** (60%): bp 88–90 °C/1.2 mmHg; ^{1}H NMR δ 0.65–0.90 (m, 7 H), 1.05–1.23 (m, 1 H), 1.72 (dd, J = 12.5, 6.5 Hz, 1 H), 2.20 (dd, J = 12.5, 6.5 Hz, 1 H), 2.23 (s, 6 H), 3.08 (t, J = 6.5 Hz, 1 H); IR (neat) 3010, 2785, 1054, 1042, 1018 cm^{-1}. Anal. Calcd for $C_{10}H_{17}NS$: C, 65.52; H, 9.35; N, 7.64; S, 17.49. Found: C, 65.40; H, 9.29; N, 7.47; S, 17.55.

Preparation of 1. To a solution of **4** (430 mg, 2.3 mmol) in 5 mL of acetone was added 220 μL of methyl iodide (500 mg, 3.5 mmol) at room temperature. The mixture was stirred for 5 h, diluted with ether (30 mL), and filtered. The colorless precipitate was washed with ether and dried in vacuo to afford 716 mg of ammonium iodide (94%): IR (KBr) 1486, 1476, 1418, 1405, 958 cm^{-1}.

To a suspension of the salt (716 mg, 2.2 mmol) in 32 mL of DMF–pentane (3:5) was added a solution of *t*-BuOK (360 mg, 3.2 mmol) in 5 mL of DMF at 0 °C. After being stirred for 1 h at the same temperature, the mixture was diluted with water (40 mL) and extracted with pentane (3 × 50 mL). The extracts were combined, washed with water (2 × 50 mL), and dried ($MgSO_4$). After removal of the solvent through a Vigreux column, the crystalline residue was sublimed at 50 °C to give 237 mg of **1** (78%): mp 66–67 °C (in a sealed tube); ^{1}H NMR δ 0.80–1.15 (AA′BB′ m, 8 H), 5.08 (s, 2 H); IR (CCl_3) 3000, 1620, 1195, 935, 910, 860 cm^{-1}; UV (EtOH) λ_{max} (ε) 238 (6900), 280 nm (sh, 350); MS m/z 138 (M, 100), 137 (93), 123 (80), 111 (21), 97 (15), 91 (12), 77 (17). Anal. Calcd for $C_8H_{10}S$: C, 69.51; H, 7.29; S, 23.20. Found: C, 69.44; H, 7.22; S, 23.42.

Reaction of 1 with TCNQ. (1) In Dioxane. A suspension of TCNQ (401 mg, 1.97 mmol) in 100 mL of dioxane was heated to 60 °C under Ar to give a homogeneous solution, in which **1** (279 mg, 2.02 mmol) was dissolved. The mixture was refluxed for 10 h while the TCNQ was nearly consumed. After removal of the solvent, the residual deep green solid was subjected to continuous extraction by benzene (Soxhlet extractor, 16 h). The extract was chromatographed on silica gel (CH_2Cl_2) to afford 163 mg of **5a** (24%) and 404 mg of **6a** (48%), which were further purified respectively by crystallization from AcOEt. **5a**: mp 264–265 °C; ^{1}H NMR (C_6D_6) δ 1.06–1.71 (m, 4 H), 1.89–2.40 (m, 2 H), 2.40–3.00 (m, 2 H), 5.74 (s, 2 H), 6.35 (br s, 2 H), 6.82 (br s, 2 H); IR (KBr) 2225, 1514, 1000, 818, 802 cm^{-1}; UV (CH_3CN) λ_{max} (ε) 210 (sh, 15 000), 237 (8600), 275 nm (sh, 860); MS m/z 342 (M, 82), 138 (55), 125 (37), 124 (75), 123 (100), 111 (32). Anal. Calcd for $C_{20}H_{14}N_4S$: C, 70.15; H, 4.12; N, 16.32; S, 9.36. Found: C, 70.34; H, 4.17; N, 16.29; S, 9.20. **6a**: mp 149–150 °C; ^{1}H NMR (C_6D_6) δ 1.87–2.03 (m, 4 H), 2.30–2.52 (m, 4 H), 2.92–3.17 (m, 4 H), 3.17–3.38 (m, 4 H), 5.80 (d, J = 3.4 Hz, 1 H), 6.13 (d, J = 3.4 Hz, 1 H), 6.89–7.14 (AA′BB′ m, 4 H); IR (KBr) 2260, 1136, 1112, 1018, 848, 800 cm^{-1}; UV (CH_3CN) λ_{max} (ε) 205 (sh, 12 500), 239 (8700), 271 nm (sh, 1000); MS m/z 430 (M, 12), 342 (13), 137 (100), 124 (31), 123 (46). Anal. Calcd for $C_{24}H_{22}N_4O_2S$: C, 66.96; H, 5.15; N, 13.01; S, 7.45. Found: C, 67.03; H, 5.24; N, 13.03; S, 7.69.

(2) In THF. To a solution of TCNQ (413 mg, 2.02 mmol) in 80 mL of THF was added **1** (306 mg, 2.22 mmol) under Ar, and the mixture was heated at 60 °C for 36 h. After removal of the solvent, the residual solid was extracted with benzene (Soxhlet, 15 h) and the extract was chromatographed on silica gel (20:1 benzene–AcOEt) to afford 535 mg of **7a** (64%), which was recrystallized from benzene: mp 187–188 °C; ^{1}H NMR δ 1.26–1.83 (m, 4 H), 2.32–2.47 (m, 2 H), 2.76–2.93 (m, 6 H), 3.38–3.53 (m, 4 H), 6.37 (AB q, J = 3.5 Hz, 2 H), 7.60–7.79 (AA′BB′ m, 4 H); IR (KBr) 2260, 1518, 1122, 829 cm^{-1}; UV (CH_3CN) λ_{max} (ε) 239 (7800), 271 nm (sh, 890); MS m/z 414 (M, 68), 316 (16), 137 (60), 125 (47), 124 (100), 123 (96), 111 (48). Anal. Calcd for $C_{24}H_{22}N_4OS$: C, 69.54; H, 5.37; N, 13.52; S, 7.73. Found: C, 69.54; H, 5.29; N, 13.33; S, 7.78.

(3) In DME. A suspension of TCNQ (305 mg, 1.50 mmol) in 90 mL of DME was heated to 40 °C under N_2 to give a homogeneous solution, in which **1** (226 mg, 1.64 mmol) was dissolved. After 48 h at 60 °C, the reaction was worked up as described for **7a** and the crude product was chromatographed on silica gel (20:3 benzene–AcOEt) to afford 282 mg of **8** (44%), which was recrystallized from ether: mp 69–70 °C; ^{1}H NMR (C_6D_6) δ 1.12 (s, 3 H), 1.86–2.03 (m, 2 H), 2.72–2.90 (m, 4 H), 3.10 (s, 3 H), 3.25–3.54 (m, 6 H), 6.29 (d, J = 3.4 Hz, 1 H), 6.49 (d, J = 3.4 Hz, 1 H), 6.91 (s, 4 H); IR (KBr) 2260, 1420, 1100, 815 cm^{-1}; UV (CH_3CN) λ_{max} (ε) 210 (sh, 11 000), 240 (9800), 270 nm (sh, 550); MS m/z 356 (57), 137 (26), 123 (50), 89 (40), 59 (100); FDMS m/z 432 (M, 100), 356 (32). Anal. Calcd for $C_{24}H_{24}N_4O_2S$: C, 66.64; H, 5.59; N, 12.95; S, 7.40. Found: C, 66.60; H, 5.59; N, 12.90; S, 7.16.

Reaction of 2 with TCNQ. (1) In 1,2-Dichloroethane. A suspension of TCNQ (151 mg, 0.74 mmol) in 30 mL of 1,2-dichloroethane was heated at 60 °C under Ar to give a homogeneous solution, to which a solution of **1** (114 mg, 0.86 mmol) in 3 mL of the solvent was added. After 3 h at 60 °C, the mixture was freed from the solvent in vacuo and the residue was chromatographed on silica gel (CH_2Cl_2) to afford 163 mg of **13** (65%).[1a]

(2) In THF. To a solution of TCNQ (151 mg, 0.74 mmol) in 25 mL of THF was added a solution of **2** (112 mg, 0.85) in 3 mL of THF under Ar, and the mixture was heated at 60 °C for 5 h. After removal of the solvent, the residue was chromatographed on silica gel (CH_2Cl_2) to afford 10 mg of **13** (4%) and 224 mg of a 1:1:1 cycloadduct of **2**, TCNQ, and THF: mp 156–157 °C; ^{1}H NMR δ 1.57–1.73 (m, 4 H), 2.02–2.17 (m, 2 H), 2.67 (t, J = 5.3 Hz, 2 H), 2.97 (s, 4 H), 3.45–3.64 (m, 4 H), 6.61 (d, J = 8.3 Hz, 2 H), 6.85 (d, J = 8.3 Hz, 2 H), 7.33–7.57 (AA′BB′, 4 H); IR (KBr) 2260, 1520, 1110, 825 cm^{-1}; UV (CH_3CN) λ_{max} (ε) 212 (sh, 17 000), 259 (530), 266 (560), 273 nm (410); MS m/z 408 (M, 32), 133 (40), 131 (51), 119 (100), 118 (58), 117 (91). Anal. Calcd for $C_{26}H_{24}N_4O$: C, 76.45; H, 5.92; N, 13.72. Found: C, 76.58; H, 5.91; N, 13.79.

Reductive Decyanation of 5a. To 15 mL of liquid NH_3 were added a solution of **5a** (80 mg, 0.23 mmol) in 4 mL of THF and then Na metal (53 mg, 2.3 mmol) at ca. −60 °C. After the solution was stirred for 10 min, solid NH_4Cl was added until the mixture discharged a deep blue color. The NH_3 was allowed to evaporate to give a residue, which was dissolved in 50 mL of water and extracted with ether (3 × 50 mL). The extracts were combined, washed with water, dried ($MgSO_4$), and concentrated to give a crystalline solid, which was subjected to sublimation (80–95 °C/20 mmHg) to afford 37 mg of **5b** (66%): mp 113–116 °C; ^{1}H NMR (C_6D_6) δ 1.67–1.86 (m, 4 H), 2.45–2.74 (m, 8 H), 6.16 (s, 2 H), 6.41 (br s, 2 H), 6.95 (br s, 2 H); IR (KBr) 2920, 1435, 810, 790 cm^{-1}; UV (CH_3CN) λ_{max} (ε) 235 (sh, 7600), 270 nm (1700); MS m/z 242 (M, 100), 136 (28), 124 (76), 123 (47), 117 (36), 112 (80), 111 (36). Anal. Calcd for $C_{16}H_{18}S$: C, 79.29; H, 7.49; S, 13.23. Found: C, 79.12; H, 7.61; S, 13.08.

Reductive Decyanation of 6a. Compound **6a** (151 mg, 0.35 mmol) in 27 mL of THF–NH_3 (2:25) was treated with Na (252 mg, 11 mmol) as described above for **5a**. The crude product was chromatographed on silica gel (5:1 benzene–AcOEt) to afford 97 mg of crystalline product, which was recrystallized from MeOH to give 68 mg of analytically pure **6b** (59%): mp 54–55 °C; ^{1}H NMR δ 1.75–2.17 (m, 4 H), 2.58–2.92 (m, 8 H), 3.32–3.73 (m, 8 H), 6.26 (d, J = 3.4 Hz, 1 H), 6.40 (d, J = 3.4 Hz, 1 H), 6.99 (s, 4 H); IR (KBr) 1515, 1140, 1105, 1055, 810, 795 cm^{-1}; UV (CH_3CN) λ_{max} (ε) 222 (13 200), 242 (7900), 274 (470); MS m/z 330 (M, 31), 255 (11), 137 (100), 126 (31), 124 (49), 123 (30), 117 (26). Anal. Calcd for $C_{20}H_{26}O_2S$: C, 72.69; H, 7.93; S, 9.70. Found: C, 72.56; H, 7.92; S, 9.78.

Reductive Decyanation of 7a. Compound **7a** (103 mg, 0.25 mmol) in 20 mL of THF–NH_3 (1:9) was treated with Na (182 mg, 7.9 mmol) as described above for **5a**. The crude crystalline product (87 mg) was recrystallized twice from MeOH to afford 41 mg of analytically pure **7b** (53%): mp 56–58 °C; ^{1}H NMR δ 1.10–1.86 (m, 4 H), 1.92–2.14 (m, 2 H), 2.59–2.91 (m, 8 H), 3.33–3.52 (m, 4 H), 6.36 (AB q, J = 3.4 Hz, 2 H), 7.05 (s, 4 H); IR (KBr) 1112, 792 cm^{-1}; UV (CH_3CN) λ_{max} (ε) 218 (11 500), 241 (6900), 273 (sh, 410); MS m/z 314 (M, 100), 142 (40), 137 (82), 124 (63), 117 (58), 111 (51). Anal. Calcd for $C_{20}H_{26}OS$: C, 76.38; H, 8.33; S, 10.20. Found: C, 76.31; H, 8.47; S, 10.22. The prolonged reaction of **7a** with Na (1 h at −60 °C) in THF–NH_3 led to the production of a secondary product (33%) resulting from the reductive cleavage of one of the C–O bonds in **7b**.

(22) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; John Wiley & Sons: New York, 1967; p 584.