Synthesis and Reactivities of a Highly Strained Thiophene with Two Fused Four-Membered Rings, 1,2,4,5-Tetahydrodicyclobuta[*b*,*d*]thiophene

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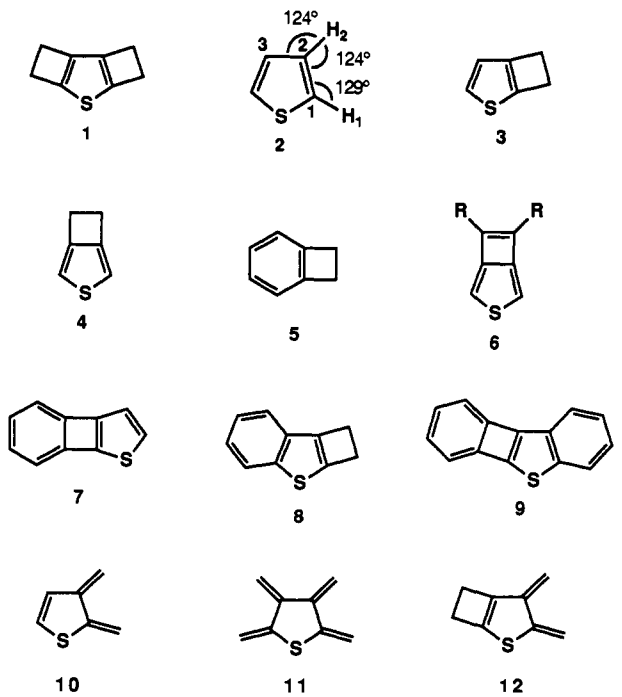
Abstract: The successful synthesis of 1,2,4,5-tetrahydrodicyclobuta[*b*,*d*]thiophene (**1**) and its ususually enhanced reactivities because of large ring strain are described. Thus, intramolecular pinacol coupling of diketo sulfide **14**, obtainable from 2-bromocyclobutanone and sodium sulfide, with a low-valent titanium reagent affords the thiolane-3,4-diol **15** in 36% yield based on the bromo ketone. After conversion of **15** to the bis-methanesulfonate **16** in 66% yield, the latter was treated with potassium *tert*-butoxide to give **1** nearly quantitatively as a rather thermally stable, colorless, highly sublimative, nicely crystalline compound. Bromine rapidly adds to **1** to give the tetrabromide **21**, revealing its olefinic character. Furthermore, **1** undergoes Diels–Alder reaction with tetracyanoethylene at room temperature to afford the adduct **22** in 83% yield. The Diels–Alder reaction with maleic anhydride at room temperature gives the adduct **23** in 87% yield in the endo–exo isomer ratio 5:1, whereas the reaction with excess maleic anhydride in refluxing benzene produces the bisadduct **24** in 84% yield with loss of sulfur. Similar behaviors of **1** toward *N*-phenylmaleimide were also observed. Flash vacuum pyrolysis of **1** gave benzo[*b*]thiophene in 16% yield but not the expected radialene **11** or its dimer, superthiophenophane. Other attempts to obtain **11** or to trap it with a dienophile were also unsuccessful.

Introduction

We have succeeded in the preparation of a highly strained thiophene with two fused four-membered rings, 1,2,4,5-tetrahydrodicyclobuta[*b*,*d*]thiophene (**1**).[1] We report here the synthesis



1 2 3 4 5 6 7 8 9 10 11 12

and reactivities of **1** in detail. In the parent thiophene (**2**), the H_1–C_1–C_2 bond angle is as large as 129° and the C_1–C_2–H_2 and H_2–C_2–C_3 bond angles are nearly equal (124°) but smaller than the former bond angle,[2] though they are still larger than the H–C–C bond angles of benzene (120°). Thus, among 1,2-dihydrocyclobuta[*b*]thiophene (**3**), 3,4-dihydrocyclobuta[*c*]-thiophene (**4**), and benzocyclobutene (**5**), angle strain must be the largest in compound **3** and should decrease in the order **3** > **4** > **5**. In accordance with this expectation, although many derivatives[3] of **4** including the parent compound[4] and unsaturated analogs **6**[3b,c,4,5] have been synthesized satisfactorily,[6] only a few derivatives of **3** are known. Thus, benzo[3,4]cyclobuta[1,2-*b*]-thiophene (**7**), the first compound of this class, was prepared in 1979 as an air- and heat-sensitive, yellow oil by flash vacuum pyrolysis of a cinnoline derivative.[7] Later, preparation of the benzo[*b*]thiophene derivative **8**[8] through [2 + 2] photocycloaddition of 2,3-dichlorobenzo[*b*]thiophene with vinyl bromide and that of **9**[9] by flash vacuum pyrolysis of a cinnoline derivative were reported. These papers report only their preparation, however, and do not give any information about chemical properties of these strained thiophenes except that **7** undergoes thermal dimerization.[7] Meanwhile, generation and trapping experiments of very reactive 2,3-dimethylene-2,3-dihydrothiophene (**10**), the valence tautomer of **3**, have been reported by several groups.[10] Although the interconversion of **10** and **3** in an argon matrix by photoirradiation was suggested,[11] no successful preparation of **3**

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(7) Barton, J. W.; Lapham, D. J. *Tetrahedron Lett.* **1979**, 3571–3572.

(8) Neckers, D. C.; Wagenaar, F. L. *J. Org. Chem.* **1981**, *46*, 3939–3940.

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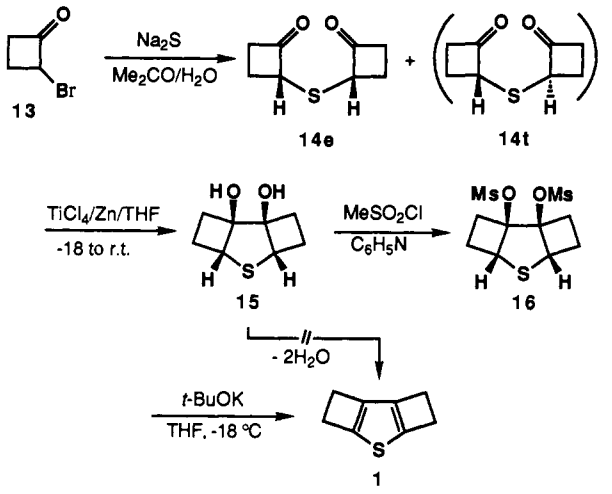
Scheme I

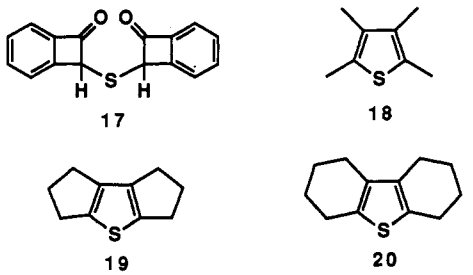


from **10** has been attained. It was also shown that the radialene **11**, generated by flash vacuum pyrolysis of 3,4-bis(chloromethyl)-2,5-dimethylthiophene, does not undergo thermal ring closure to the cyclobutathiophenes **1** or **12**.[12]

Results and Discussion

Preparation of 1,2,4,5-Tetrahydrodicyclobuta[*b,d*]thiophene (1). In 1984 we developed a new thiophene synthesis, which consists of intramolecular reductive coupling of diketo sulfides (3-thiapentane-1,5-diones) with a low-valent titanium reagent and acid-catalyzed dehydration of the resulting thiolane-3,4-diols.[13] The new method is very versatile and applicable to the preparation of a wide variety of thiophenes, including highly congested ones such as 3,4-di-*tert*-butyl- and 3,4-di-1-adamantylthiophenes.[14] We therefore applied this method to the preparation of **1**.

Treatment of 2-bromocyclobutanone (**13**)[15] with sodium sulfide nonahydrate in aqueous acetone affords the diketo sulfide **14** as a mixture of erythro (**14e**) and threo (**14t**) isomers in good yield (Scheme I). The sulfide **14** is rather sensitive to acid, base, and heat, and attempted isolation of isomers by column chromatography caused secondary reactions to give more impure **14** in low yield. Thus, this crude isomeric mixture was used immediately for the next step without further purification. Treatment of the crude **14** with a low-valent titanium reagent, prepared from titanium(IV) chloride and zinc powder in tetrahydrofuran (THF),[16] afforded the expected thiolane-3,4-diol **15** as a crystalline compound in 36% yield based on the bromide **13**. It is considered that two hydroxy groups of **15** are cis to each other and that two four-membered rings are fused to the central five-membered ring in the less strained cis orientation. It is known that the reductive coupling of a series of diketo sulfides with the foregoing low-valent titanium reagent affords the *cis*-thiolane-3,4-diols[14b,17] and that four-, five-, and six-membered ring-forming reductive coupling of diketones with low-valent titanium reagents generally produces *cis*-cycloalkanediols preferentially.[18] Among isomers **14e** and **14t**, only the erythro isomer **14e** has a correct geometry for giving **15** by intramolecular coupling. In fact, in the case of the diketo sulfide **17**, two isomers were isolated in pure form, and only the erythro isomer afforded the thiolane-3,4-diol in good yield, whereas the threo isomer gave a complex mixture from which no intramolecular reductive coupling product was isolated.[19]



Unfortunately, *p*-toluenesulfonic acid-catalyzed dehydration of **15** leading to the desired thiophene **1** did not take place, unlike other cases of thiolanediols.[13,14] Accordingly, **15** was converted to the bis-methanesulfonate **16** in 66% yield by treatment with methanesulfonyl chloride in pyridine. Formation of the bis-*p*-toluenesulfonate from **15** and *p*-toluenesulfonyl chloride was sluggish and suffered from low yield (11% yield after 2 weeks). Treatment of **16** with potassium *tert*-butoxide in THF at −18 °C cleanly gave the thiophene **1** nearly quantitatively. Treatment of **16** with other bases such as triethylamine did not bring about the conversion to **1**.

Properties of the Thiophene 1. The thiophene **1**, which is stabler than we expected, is a nicely crystalline, easily sublimed, colorless compound. Although **1** is easily soluble in common organic solvents and rather stable in dilute solution, keeping it in crystalline form in a refrigerator resulted in the formation of a thin film of polymeric materials on the surface of the crystals, which are no longer soluble in hydrocarbon solvents. In the ^{1}H NMR spectrum, hydrogens of two unequivalent methylenes appear at δ 3.06 and 3.21 ppm as multiplets. In the ^{13}C NMR spectrum two methylene carbons appear at δ 28.10 and 29.79 ppm and two thiophene ring carbons at δ 140.98 and 141.76 ppm. The latter two chemical shift values are about 8–9 ppm lower than those of the corresponding carbons of the six-membered analog **20** (δ 132.0 and 134.0 ppm).[20] A similar trend was also observed on going from benzocyclohexene (δ 137.0 ppm) to benzocyclobutene (δ 145.6 ppm).[21] The ring carbons of the open chain analog **18**[13] appear at δ 127.65 and 132.85. $J_{^{13}C-H}$ coupling constant values observed at two methylene carbons are 142.5 and 143.3 Hz. These values are larger than those observed with methylene carbons of benzocyclobutene (138 Hz) and cyclobutene (137.2 Hz), but smaller than that of cyclopropene (167.0 Hz).[22] The s character of the methylene C–H bonds of **1** is estimated to be about 29% (4% deviation from sp^3) from the coupling constant values.[23]

UV spectroscopic data of **1** and related compounds are summarized in Table I. The broad absorption maximum of **1**

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Table I. UV Data of 1 and Some Related Thiophenes Determined in Ethanol

	1[a]	18[a]	19[b]	20[b]
λ_{max} (nm)	235[c]	240[d]	241	239
ϵ_{max}	4850[c]	6860[d]	5650	6350

[a] This work. [b] Reference 24. [c] In hexane: λ_{max} 235 nm (ϵ 5100). [d] In hexane: λ_{max} 240 (ϵ 7330).

Table II. CV Data of 1 and Some Related Thiophenes[a,b]

	1	2	18	20
E^{ox} (V)	0.91	1.63	0.89	0.91

[a] Versus Ag/Ag^+; electrolyte $Bu_4N^+ClO_4^-$; solvent MeCN; scan rate 100 mV s^{-1}. [b] $E_{1/2}$ (ferrocene): 0.07 V vs Ag/Ag^+ in MeCN.

Table III. Calculated Energies of HOMO and LUMO and Heat of Formation of Thiophenes 1 and Its Ring-Opened Tautomers, 11 and 12, and Related Thiophenes 18 and 20

	1	11	12	18	20
HOMO (eV)	-8.90	-8.59	-8.20	-9.08	-9.01
LUMO (eV)	-0.26	-0.39	-0.56	-0.10	-0.06
ΔH_f (kcal/mol)	101.84	72.25	90.83	-2.21	-4.31

appears at 235 nm in ethanol, which is 4–6 nm shorter than those of the open chain analog **18** and of the five- and six-membered analogs **19** and **20**.[24] The molar absorptivity of **1** is also considerably smaller than those of **18–20**. These observations should be ascribed to the strained structure of **1**. The CV oxidation potential data of thiophenes **1**, **18**, and **20** and of the parent thiophene **2**, which were obtained with a platinum working electrode and 0.1 M electrolyte (tetrabutylammonium chloride) and are corrected by the redox potential of ferrocene, are summarized in Table II. All of the compounds show irreversible oxidation peaks probably because the radical cations formed are reactive and undergo radical polymerization.[25] Contrary to our expectation, no clear difference in oxidation potentials was observed between **1** and reference compounds **18** and **20**.

Molecular orbital calculations of thiophenes **1**, **18**, and **20** and of the radialene **11** and the half-radialene **12** by the PM3 method were performed with MOPAC Ver. 5.0.[26] These results are summarized in Table III.

Unfortunately, the highly sublimative nature of **1** made it impossible to perform X-ray single-crystal structure analysis.[27]

Reactivities of 1. *Bromine rapidly adds to 1 at room temperature in dichloromethane to give the tetrabromide 21*, which is a mixture of two stereoisomers. Both isomers can be isolated in pure form by column chromatography in 65% and 8% yields, although their stereochemical assignment could not be made. Tetramethylthiophene (**18**), when treated with 2 equiv of bromine under the same conditions for comparison, resulted in the quantitative formation of the side chain bromination product **28** but not the addition product.[28] Thus, easy addition of bromine to **1** should be attributable to its considerable olefinic character, which originates from large angle strain. A similar bromine addition was also observed with the strained thiophenes **4**[4b] and **6** (R,R = CH=CHCH=CH).[5c]

The olefinic properties of **1** are further manifested by its extremely enhanced reactivity to dienophiles, which leads to structurally interesting unique ring systems. Thiophenes do not undergo Diels–Alder reactions with usual dienophiles under conventional conditions.[29] On the contrary, *1 reacts with tetracyanoethylene (TCNE) at room temperature for 12 h to give the adduct 22 in 83% yield* (Scheme II). *It also reacts slowly with maleic anhydride in chloroform at room temperature to give the adduct 23 in 87% yield*, which is a mixture of endo and exo isomers (**23a** and **23b**) in the ratio 5:1. When a mixture of **23a** and **23b** was heated at 40 °C for 60 h in $CDCl_3$ in an NMR tube, it was converted into the endo–endo bisadduct **24**. This implies that the adduct **23** undergoes both sulfur extrusion to the cyclohexadiene **29** and the retro Diels–Alder reaction to **1** and maleic anhydride, and the maleic anhydride regenerated reacts with the diene **29** to produce **24**. Thus, heating **1** and excess maleic anhydride in refluxing benzene gave **24** exclusively in 84% yield. To our knowledge, the only thiophene that can undergo Diels–Alder reaction with maleic anhydride under conventional conditions is electronically activated 2,5-dimethoxythiophene.[30,31] The Diels–Alder reaction of the parent thiophene with maleic anhydride requires extremely forcing conditions (15 kbar, 100 °C) to give the adduct in moderate yield.[32] The stereochemical assignment of the adduct **23** was made by comparison of the chemical shift values of each isomer; the methine hydrogen signal of the exo isomer **23b** appears at δ 3.60 ppm as a singlet, while that of the endo isomer **23a** appears at a lower field δ 4.07 ppm due to a deshielding effect by the adjacent divalent sulfur.[32,33] The ^1H NMR spectrum of **24** shows only one singlet due to methine hydrogens in addition to multiplets due to methylene hydrogens, and the ^{13}C NMR spectrum shows signals for one olefinic carbon, two methylene carbons, one methine carbon, one bridgehead carbon, and one carbonyl carbon. These data are indicative of the symmetrical structure of **24**, thus eliminating the endo–exo structure. Although the exo–exo isomer is compatible with the NMR data, its formation is least favorable from the viewpoints of the endo addition mode of the Diels–Alder reaction and its unfavorable, highly congested structure (repulsion between two anhydride moieties).[14d] *N*-Phenylmaleimide also reacts with **1** at room temperature, but more slowly than does maleic anhydride, to give the adducts **25a** and **25b** in the ratio 5:1, but they are thermally unstable and slowly turned to the endo–endo bisadduct **26**. When **1** was heated with excess *N*-phenylmaleimide in refluxing benzene, **26** was obtained in 36% yield. Structural assignment of **25** and **26** was made on the basis of NMR data. Phenyl vinyl sulfone failed to react with **1** even at 140 °C in benzene in a sealed glass tube; no expected dicyclobutabenzene, which arises from the cycloaddition followed by elimination of sulfur and benzenesulfinic acid, was formed.[14d] Dimethyl acetylenedicarboxylate (DMAD) also fails to reacts with **1** even under forcing conditions.

To compare the Diels–Alder reactivities of **1** with those of thiophenes **18** and **20**, which have four alkyl substituents but should be free from ring strain, the latter two thiophenes were allowed to react with dienophiles. The reaction of **18** with TCNE in CH_2Cl_2 afforded only a charge-transfer complex (λ_{max} 490, 604 nm) instead of giving the cycloadduct. It is known that **18** does not react with maleic anhydride even under forcing conditions

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(27) We thank Professor T. Nishio of University of Tsukuba for an attempted X-ray analysis of **1**.

(28) Side chain bromination of **18** and related compounds will be reported by us in detail elsewhere. The present reaction probably proceeds in a mechanism similar to the one operative in the side chain chlorination of hexamethylbenzene: Baciocchi, E.; Ciana, A.; Illuminati, G.; Pasini, C. *J. Am. Chem. Soc.* **1965**, *87*, 3953–3957. Baciocchi, E.; Mandolini, L.; Patara, A. *Tetrahedron Lett.* **1975**, 2268–2270. Kochi, J. K. *Tetrahedron Lett.* **1974**, 4305–4308. For side chain bromination of alkyl thiophenes, see: Reinecke, M. G.; Pedaja, P. In *Chemistry of Heterocyclic Compounds, Thiophene and Its Derivatives*; Gronowitz, S., Ed.; Wiley: New York, 1985; Vol. 44, Part 2, Chapter 3.

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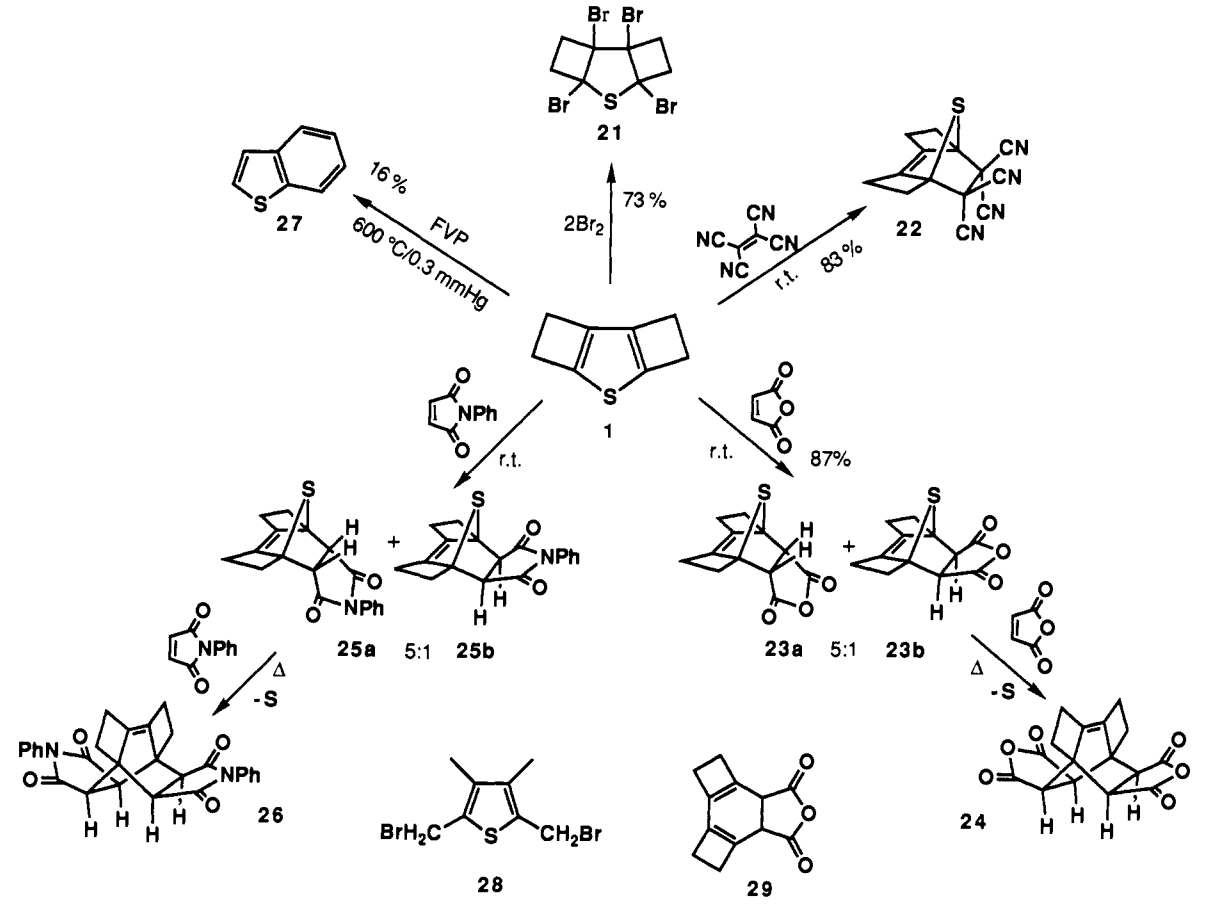
Scheme II



(refluxing for 2 days in benzene or refluxing for 4 h in nitrobenzene).[34] Thiophene **20** is also inert to maleic anhydride; heating **20** and maleic anhydride in refluxing benzene for 2 weeks or at 110 °C for 3 days in benzene in a sealed glass tube did not give any cycloadduct. It is therefore concluded that the enhanced reactivity of **1** is ascribed to an increase of the HOMO energy by ring strain but not to the electronic effect of substituents; the increase of the HOMO level decreases the energy difference between $HOMO_{diene}$ and $LUMO_{dienophile}$, thus making HOMO–LUMO interaction at the transition state favorable.[35] This is in line with the calculated HOMO levels of **1** (–8.90 eV), **18** (–9.08 eV), and **20** (–9.01 eV) (Table III).[36]

Thiophene **1** does not behave as a dienophile toward 2,3-dimethylbutadiene and furan; it failed to react with the former diene at 120 °C for 3 days and with the latter at 40 °C for 2 weeks in a sealed tube.

Oxidation of **1** with *m*-chloroperbenzoic acid and dimethyldioxirane[37] was attempted under a variety of conditions with expectation of obtaining the corresponding *S,S*-dioxide. The reaction gave complex mixtures from which no identifiable pure products were isolated. Photolysis of **1** in hexane with a 100-W low-pressure mercury lamp gave only polymeric products. Neither the expected radialene **11**,[11] half-radialene **12**, nor their dimers such as superthiophenophanes[38] were obtained, although formation of **11** or **12** is an enthalpically favorable process (Table III). Attempted trapping of **11** or **12** by cycloaddition with DMAD was also unsuccessful. Unexpectedly, flash vacuum pyrolysis of **1** at 600 °C/0.3 mmHg gave benzo[*b*]thiophene in 16% yield by a process whose mechanism is not apparent. Again, neither **11**, **12**, nor their dimerization products were obtained.

Experimental Section

Melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^1H NMR spectra (400 MHz) and ^{13}C NMR spectra (100.6 MHz) were determined on a Bruker AM400 spectrometer. Mass spectra were determined on a JEOL JMS-DX303 spectrometer operating at 70 eV in the EI mode. IR spectra were taken on a Hitachi 340 spectrometer. UV spectra were obtained on a Shimadzu UV-160A spectrometer. Elemental analyses were performed by the Chemical Analysis Center of Saitama University. Column chromatography was performed with Merck Kieselgel 60 F_{254}. All solvents were dried in appropriate ways prior to use. Titanium(IV) chloride, zinc powder, potassium *tert*-butoxide, tetracyanoethylene, maleic anhydride, *N*-phenylmaleimide, phenyl vinyl sulfone, and dimethyl acetylenedicarboxylate were used as purchased. Thiophenes **18**[14] and **20**[38] were prepared according to the literature methods.

Diketo Sulfide 14. A solution of bromine (48.4 g, 0.3 mol) in $CHCl_3$ (50 mL) was added to a solution of cyclobutanone[39] (21.2 g, 0.3 mol) in $CHCl_3$ (250 mL) at room temperature over a period of 8 h. After stirring for 1 h, the reaction was quenched by addition of ice–water. The organic layer was washed with water and then with aqueous $NaHCO_3$, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was distilled to give 27.5 g (61%) of 2-bromocyclobutanone (**13**),[15] bp 79–82 °C/20 mmHg. A solution of $Na_2S{\cdot}9H_2O$ (8.92 g, 37.1 mmol) in water (40 mL) was added to a stirred solution of **13** (11.07 g, 74.3 mmol) in acetone (150 mL) at 0 °C over a period of 0.5 h. The mixture was warmed to room temperature after 1 h, stirred for 6 h, and diluted with CH_2Cl_2 (150 mL) and water (150 mL). The organic layer was washed with water, dried over Na_2SO_4, and evaporated to give 6.31 g (100%) of crude **14** as yellow

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oil. The oil was used for the next step without further purification because attempted purification by column chromatography caused secondary reactions.

Thiolane-3,4-diol 15. To a stirred mixture of crude **14** (6.31 g, 37 mmol) and zinc powder (14.37 g, 223 mmol) in THF (200 mL) was added titanium(IV) chloride (12.2 mL, 111.5 mmol) over a period of 1 h at −18 °C under argon. The mixture was warmed to room temperature after 1 h and stirred for 20 h at that temperature. The reaction was quenched by adding crushed ice (ca. 100 g) and then saturated aqueous Na_2CO_3 until the pH of the mixture became 8–9. After addition of ether (300 mL), the mixture was stirred for 1 h and filtered through a pad of Celite. The organic layer of the filtrate was washed with water many times, dried over $MgSO_4$, and evaporated. The oily residue was chromatographed on a column of silica gel (200 g). Elution with CH_2Cl_2:ether (2:1) gave 2.27 g (36% based on the bromo ketone **13**) of **15** as colorless crystals: mp 66–67 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 1.73 (m, 2H), 2.18 (m, 2H), 2.53 (m, 4H), 3.73 (broad s, 2H, OH), 3.94 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 24.77 (t, CH_2), 29.28 (t, CH_2), 56.75 (d, CH), 87.70 (s, COH); IR (KBr) 3326, 2972, 2942, 1409, 1352, 1259, 1197, 1141, 1113, 1097, 1058, 929, 501 cm^{-1}. Anal. Calcd for $C_8H_{12}O_2S$: C, 55.78; H, 7.02. Found: C, 55.64; H, 6.84.

Bis-methanesulfonate 16. To a stirred solution of **15** (548 mg, 3.19 mmol) in pyridine (3 mL) was added methanesulfonyl chloride (1.82 g, 15.9 mmol) through a microsyringe over a period of 10 min at −18 °C. The mixture was slowly warmed to room temperature, allowed to stand at that temperature for 7 h, and diluted with ice–water (50 mL). The resulting crystalline precipitate was collected by filtration, washed with water, dried, and recrystallized from CCl_4 to give 689 mg (66%) of **16** as colorless crystals: mp 105–106 °C; ^{1}H NMR ($CDCl_3$) δ 1.87–1.91 (m, 2H), 2.70–2.73 (m, 2H), 2.82–2.90 (m, 4H), 3.18 (s, 6H), 4.57 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 24.98 (t, CH_2), 28.05 (t, CH_2), 40.71 (q, CH_3), 53.95 (d, CH), 96.79 (s, C–OMs); IR (KBr) 3032, 3016, 2938, 1338, 1320, 1188, 1171, 1162, 934, 904, 821, 524, 514 cm^{-1}; MS *m/z* 328 (M^+), 272, 249, 153, 125, 111, 97, 86 (100), 85, 79, 69. Anal. Calcd for $C_{10}H_{16}O_6S_3$: C, 36.57; H, 4.91. Found: C, 36.45; H, 4.93.

Dicyclobutathiophene 1. To a stirred solution of *t*-BuOK (310 mg, 2.76 mmol) in THF (5 mL) was added a solution of **16** (300 mg, 0.92 mmol) in THF (2 mL) over a period of 20 min at −18 °C under argon. Analysis of the mixture by TLC after 1 h shows that the reaction is complete and gives a single product. The reaction was quenched by adding ice–water (30 mL) and then pentane (50 mL). The organic layer was washed with water, dried over $MgSO_4$, concentrated to ca. 1 mL, and placed on a column of silica gel (15 g). The column was eluted with pentane, and the pentane was evaporated slowly under reduced pressure to give 107 mg (86%) of **1** as highly sublimative, colorless long needles, which have a characteristic penetrating odor, mp 47–48 °C after purification by sublimation at 20 °C/0.15 mmHg. The yield of **1** is nearly quantitative, and observed loss of the yield may occur during workup because of its highly sublimative nature. When the crystals of **1** were kept in a refrigerator for several days, their surface was covered by a thin film of polymeric materials, making the crystals no longer soluble in hydrocarbon solvents. ^{1}H NMR ($CDCl_3$) δ 3.06 (m, 4H), 3.21 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 28.10 (t, CH_2), 29.79 (t, CH_2), 140.98 (s, thiophene ring carbon), 141.76 (s, thiophene ring carbon); IR (KBr) 2930, 2914, 2830, 1418, 1394, 1228, 1171, 912, 820, 793, 587, 536, 494 cm^{-1}; MS *m/z* 136 (M^+, 100), 135 (69), 134 (21), 121 (25), 91 (49), 77 (13); UV (EtOH) nm (ϵ) 235 (4850); (hexane) 235 (5100); HRMS calcd for C_8H_8S 136.0347, found 136.0347.

Addition of Bromine to 1. A solution of bromine (138 mg, 0.86 mmol) in CH_2Cl_2 (2 mL) was added to a solution of **1** (58 mg, 0.43 mmol) in CH_2Cl_2 (5 mL) at −18 °C under argon. Bromine was immediately consumed to give a pale-yellow solution. The mixture was evaporated under reduced pressure, and the crystalline residue was chromatographed on a column of silica gel (30 g). Elution of the column with CCl_4 gave 126 mg (65%) of one of the isomers of **21** and 15 mg (8%) of the other isomer. Major isomer: mp 178–179 °C dec (from MeOH); ^{1}H NMR ($CDCl_3$) δ 2.41 (m, 2H), 2.72 (m, 2H), 3.03 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 33.13 (t), 39.69 (t), 70.98 (s), 80.91 (s); IR (KBr) 2994, 2944, 2854, 1443, 1427, 1239, 1229, 1128, 1108, 1076, 1044, 843, 824, 759, 655 cm^{-1}; MS *m/z* 378, 376, 374 (100), 372, 297, 295, 293, 217, 216, 215, 136, 135, 134. Anal. Calcd for $C_8H_8Br_4S$: C, 21.08; H, 1.77. Found: C, 21.76; H, 1.87. Minor isomer: mp 181–182 °C dec; ^{1}H NMR ($CDCl_3$) δ 2.76 (m, 4H), 3.07–3.23 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 36.66 (t), 38.84 (t), 76.24 (s), 80.79 (s); IR (KBr) 2990, 1438, 1235, 1187, 1119, 1031, 936, 908, 837, 803, 739, 716, 661, 369 cm^{-1}; MS *m/z* 458, 456 (M^+), 454, 379, 377, 375, 373, 297, 296, 295, 293, 217, 216, 215 (100), 214, 136, 135, 134; HRMS calcd for $C_8H_8{}^{79}Br_2{}^{81}Br_2S$ 455.7039, found 455.7018.

Reaction of 1 with TCNE. On addition of a solution of **1** (49 mg, 0.36 mmol) in benzene (1 mL) to a solution of TCNE (46 mg, 0.36 mmol) in benzene (2 mL), a dark blue color, which faded immediately, developed probably because of charge transfer complex formation. The mixture was kept at room temperature for 12 h, and the resulting yellow crystalline precipitate was collected by filtration and washed with a small amount of benzene to give 78 mg (83%) of the adduct **22**: mp 123–124 °C dec; ^{1}H NMR ($CDCl_3$) δ 2.91–3.32 (m); ^{13}C NMR δ 23.15 (t), 26.79 (t), 76.91 (s), 77.26 (s), 110.38 (s), 111.06 (s), 144.76 (s); IR (KBr) 2954, 2938, 2262 (C≡N), 2224 (C≡N), 1434, 1155, 1147, 1114, 1085, 961, 795, 559 cm^{-1}; MS *m/z* 264 (M^+), 237, 232, 210; UV (CH_2Cl_2) nm (ϵ) 224 (1750), 241 (2360), 278 (1080), 376 (550). Anal. Calcd for $C_{14}H_8N_4S$: C, 63.62; H, 3.05; N, 21.20. Found: C, 63.82; H, 3.21; N, 21.06.

Reaction of 1 with Maleic Anhydride. At Room Temperature. A mixture of **1** (35 mg, 0.26 mmol) and maleic anhydride (26 mg, 0.26 mmol) in $CDCl_3$ (2 mL) was allowed to stand at room temperature. The progress of the reaction was monitored by ^{1}H NMR, which revealed that the conversion to the adduct is about 20% after 24 h, and 2 weeks is required for 100% consumption of **1** to give **23** in the endo–exo isomer ratio 5:1. The $CDCl_3$ was removed under reduced pressure, and trace amounts of the volatile materials were removed from the residue to vacuo to give 53 mg (87%) of **23** as a yellow oil. No effort was made to separate the endo and exo isomers. The mixture gave the following spectroscopic properties: ^{1}H NMR ($CDCl_3$) δ 2.77–3.05 (m, four methylenes of the endo adduct, ca. 6.7H), 3.20 (m, four methylenes of the exo adduct, ca. 1.3H), 3.60 (s, two methines of the exo adduct, 0.33H), 4.07 (s, two methines of the endo adduct, 1.67H); ^{13}C NMR ($CDCl_3$) δ 23.18 (t), 23.95 (t), 24.68 (t), 26.12 (t), 46.32 (d), 53.15 (d), 71.65 (s), 71.81 (s), 144.26 (s), 144.94 (s), 169.07 (s), 169.53 (s); IR (film) 2930, 2840, 1855, 1779, 1418, 1226, 1214, 1082, 1058, 929, 915, 735 cm^{-1}; MS *m/z* 234 (M^+), 202, 200, 162, 136, 135, 130 (100), 129, 128, 115, 84; HRMS calcd for $C_{12}H_{10}O_3S$, 234.0351; found, 234.0369. When a solution of a mixture of the endo–exo isomers **23** in $CDCl_3$ was heated at 40 °C in an NMR tube, the signal intensities due to **23** slowly decreased, the signals due to the bisadduct **24** began to appear instead, and after 10 h the signals due to **23** disappeared nearly completely. During this period, no appreciable change of the endo–exo isomer ratio was observed, although the crystalline precipitate of **24** began to separate. In a separate experiment, when a mixture of **1** (37 mg, 0.27 mmol) and maleic anhydride (27 mg, 0.27 mmol) in $CDCl_3$ (2 mL) was heated at 40 °C for 29 h, 29 mg (46%) of **23** in the endo–exo isomer ratio 5:1 and 14 mg (12%) of **24** were obtained.

In Refluxing Benzene. A mixture of **1** (80 mg, 0.59 mmol) and maleic anhydride (230 mg, 2.35 mmol) in benzene (5 mL) was refluxed until **1** was completely consumed. The resulting crystalline precipitate was collected by filtration and washed with a small amount of benzene to give 149 mg (84%) of the endo–endo bisadduct **24** (formation of other stereoisomers was not detected by NMR): mp 337–338 °C (from ethanol); ^{1}H NMR (DMSO-d_6) δ 1.68 (m, 4H), 1.96 (m, 4H), 2.54 (s, 4H); ^{13}C NMR (DMSO-d_6) δ 21.49 (t, CH_2), 26.16 (t, CH_2), 45.74 (s, bridgehead), 46.18 (d, methine), 135.44 (s, olefinic), 170.99 (s, carbonyl); IR (KBr) 2992, 2940, 1861, 1841, 1784, 1448, 1419, 1315, 1259, 1222, 1138, 1124, 1079, 952, 932, 736, 406 cm^{-1}; MS *m/z* 300 (M^+), 273, 272, 156, 155, 141, 130 (100), 129, 128, 115, 104; HRMS calcd for $C_{16}H_{12}O_6$ 300.0634, found 300.0644.

Reaction with *N*-Phenylmaleimide. A mixture of **1** (22 mg, 0.16 mmol) and *N*-phenylmaleimide (28 mg, 0.16 mmol) in $CDCl_3$ was kept at room temperature. The progress of the reaction was monitored by ^{1}H NMR. The formation of both the endo and exo adducts **25** was observed after 4.5 h, and the endo–exo ratio determined after 3 days was 5:1. After 2 weeks most of the thiophene **1** was consumed to give **25** contaminated with the endo–endo bisadduct **26**. Evaporation of the mixture under reduced pressure gave 50 mg of **25** containing **26** as a yellow oil. The adduct **25** is thermally unstable and gradually turned to the bisadduct **26** by retro Diels–Alder reaction during workup and other analyses. The methine hydrogen of the endo isomer appears at δ 3.88 ppm and that of the exo isomer at δ 0.38 ppm. A mixture of **1** (50 mg, 0.37 mmol) and *N*-phenylmaleimide (191 mg, 1.10 mmol) in benzene (5 mL) was refluxed for 5 days. The mixture was evaporated, and the crystalline residue (230 mg) was recrystallized from CCl_4 to give 60 mg (36%) of the endo–endo bisadduct **26** (formation of other stereoisomers was not detected by NMR): mp 295–296 °C (dec); ^{1}H NMR ($CDCl_3$) δ 2.61 (m, 4H), 2.76

(s, 4H), 3.11 (m, 4H), 7.19–7.43 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 22.17 (t), 26.62 (t), 46.12 (d), 46.98 (s), 126.59 (d), 128.97 (d), 129.34 (d), 131.80 (s), 134.65 (s), 174.73 (s); IR (KBr) 3074, 2976, 2918, 1768, 1710, 1599, 1500, 1389, 1200, 1168, 745, 693, 454 cm^{-1}; MS *m/z* 450 (M^+), 303, 277, 174, 156, 130 (100), 129, 128, 115, 104. Anal. Calcd for $C_{28}H_{22}N_2O_4$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.24; H, 5.02; N, 5.92. HRMS: calcd 450.1579, found 450.1560.

Other Attempted Diels–Alder Reactions of 1. Heating a mixture of **1** with dimethyl acetylenedicarboxylate (3 equiv) or phenyl vinyl sulfone (1.1 equiv) in benzene at 140 °C for a prolonged time in a sealed glass tube did not bring about any reaction. Also, no Diels–Alder reaction of **1** with 2,3-dimethylbutadiene (3 equiv) took place at 120 °C for 3 days in a sealed glass tube. Furan also did not react with **1** at 40 °C for 2 weeks. In each case **1** remained unchanged.

Photolysis of 1. Photolysis of **1** in hexane with a 100-W low-pressure mercury lamp only resulted in the deposition of polymeric materials. The photolysis in the presence of dimethyl acetylene dicarboxylate also gave yellow polymeric materials.

Flash Vacuum Pyrolysis of 1. The thiophene **1** (94 mg) was pyrolyzed by using a quartz tube (25 mm × 50 cm) heated at 600 °C/0.3 mmHg. The pyrolysate was purified by column chromatography to give 15 mg (16%) of benzo[*b*]thiophene (**27**), which is identical with commercial product in every respect. Although pyrolysis was carried out under a variety of conditions varying temperature and pressure, neither expected radialene **11** nor its dimeric product, superthiophenophane, was obtained.

Attempted Oxidation of 1. Although oxidation of **1** with *m*-chloroperbenzoic acid was examined under a variety of conditions, complex mixtures formed and no expected *S,S*-dioxide was obtained. The oxidation with dimethyldioxirane[41] at room temperature also did not gave the *S,S*-dioxide, although **1** was consumed.

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