Articles

Oligomerization of the Thiophene-Based *p*-Quinodimethanes 2,5-Dimethylene-2,5-dihydrothiophene and 2-Ethylidene-5-methylene-2,5-dihydrothiophene

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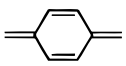
Flash vacuum pyrolysis (FVP) of (5-methyl-2-thiophene-yl)methyl benzoate (**8**) produces in *ca.* 75% yield 2,5-dimethylene-2,3-dihydrothiophene, S-monomer (**3**). S-Monomer **3** is relatively stable dissolved in carbon disulfide−chloroform at −78 °C. The structure of **3** is confirmed by its spectral properties. When a 0.17 M solution of *S*-monomer **3** was allowed to warm to room temperature, SS-dimer **5** ([2,2](2,5)thiophenophane, 14.7%), SSS-trimer **7** ([2,2,2](2,5)thiophenophane, 44.3%), and polymer were produced. A small amount (<1%) of an SSSS-tetramer was detected by GC/MS. The mechanism proposed for the formation of these oligomers involves the combination of two molecules of **3** to give an intermediate diradical (**11**) that can close to form dimer **5** or react with additional molecules of **3** to form the higher oligomers. Evidence for the trapping of diradical **11** by 2,5-dimethylene-2,5-dihydrofuran (O-monomer **2**) was obtained. Co-oligomerization of S-monomer **3** and O-monomer **2** gave four compounds containing the thiophene moiety: OS-dimer **16**, SS-dimer **5**, OSS-trimer **17**, and SSS-trimer **7**. Some OO-dimer **4** was produced but no OOO-trimer **6** was observed and only a trace of OOS-trimer **18** was detected. Additional support for the diradical mechanism was obtained from the study of the oligomerization of the methyl derivatives of **3**, 2-ethylidene-5-methylene-2,5-dihydrothiophene (**10**, *E* and *Z* isomers), prepared by the FVP of (5-ethyl-2-thiophene-yl)methyl benzoate (**9**). Oligomerization of **10** gave several dimers and trimers including two acyclic dimers that are accounted for by intramolecular disproportionation.

Introduction

During the past 50 years, considerable attention has been focused on *p*-quinodimethanes (*p*-QDMs), a large and important class of reactive molecules. In 1947 Szwarc reported for the first time that the pyrolysis of *p*-xylene at low pressure leads to the formation of a white polymeric material, and he proposed that this material was formed by polymerization of the reactive intermediate *p*-xylylene (**1**), the benzene-based *p*-QDM.[1] Ten years later Errede and co-workers showed that solutions of *p*-xylylene (**1**) could be prepared at low temperatures (−78 °C).[2]



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p-Xylylene (**1**), substituted *p*-xylylenes, and *p*-QDMs based on other benzenoid aromatic systems including naphthalene and anthracene have been prepared by a number of different methods. These *p*-QDMs have been fully characterized by NMR, IR, and UV−visible spectroscopic techniques, and their reactions have been studied in detail.[3]

The heterocyclic *p*-QDMs based on furan (O-monomer **2**) and thiophene (S-monomer **3**) have also been prepared by several different methods. Each has been fully characterized and is known to give the cyclic dimer (**4**, **5**), the cyclic trimer (**6**, **7**), and polymer at moderate temperatures.[4−17]

The S-monomer **3** can be prepared in good yield by the flash vacuum pyrolysis (FVP) of (5-methyl-2-thiophene-yl)methyl benzoate (**8**).[13b,16] We have prepared **3** by the FVP of **8** and studied its oligomerization. Also, in an attempt to more fully understand the mechanism of the dimerization and trimerization of **3**, the oligomerization

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(2) (a) Errede, L. A.; Landrum, B. F. *J. Am. Chem. Soc.* **1957**, *79*, 4952−4955. (b) Errede, L. A.; Hoyt, J. M. *J. Am. Chem. Soc.* **1960**, *82*, 436−439.

(3) (a) Williams, D. J.; Pearson, J. M.; Levy, M. *J. Am. Chem. Soc.* **1970**, *92*, 1436−1438. (b) Pearson, J. M.; Six, H. A.; Williams, D. J.; Levy, M. *J. Am. Chem. Soc.* **1971**, *93*, 5034−5036.

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(16) Huang, C.-S.; Peng, C.-C.; Chou, C.-H. *Tetrahedron Lett.* **1994**, *35*, 4175.

(17) Shiea, J.; Wang, W.-S.; Wang, C.-H.; Chen, P.-S.; Chou, C.-H. *Anal. Chem.* **1996**, *68*, 1062

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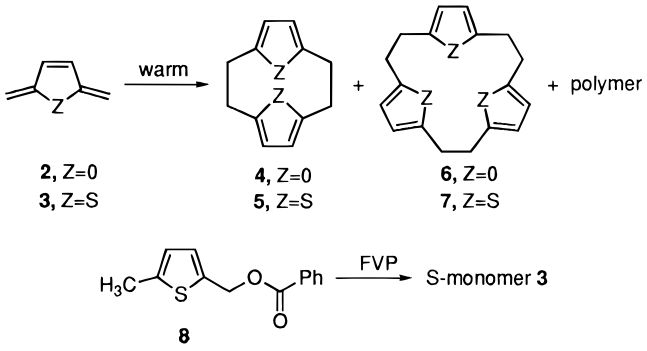
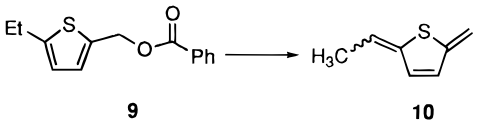


of the methyl derivative of **3**, 2-ethylidene-5-methylene-2,5-dihydrothiophene (**10**), prepared as a mixture of the *E* and *Z* isomers by FVP of (5-ethyl-2-thiophene-yl)methyl benzoate (**9**), was also studied. The results of this work are reported herein.



Results and Discussion

(5-Methyl-2-thiophene-yl)methyl benzoate (**8**) was prepared in high yield by the reduction of 5-methyl-2-thiophenecarboxaldehyde with lithium aluminum hydride followed by the esterification of the resulting alcohol with benzoyl chloride in the presence of triethylamine.

FVP of benzoate **8** at 650 °C and *ca.* 10^{-5} Torr produced in *ca.* 75% yield S-monomer **3**, which appeared as a yellow band in the cold trap at −196 °C. Benzoic acid and a small amount of a white polymer were also produced. Carbon disulfide−chloroform was added to the trap, and the mixture was then warmed to −78 °C. This provided a solution of **3** which was relatively stable.

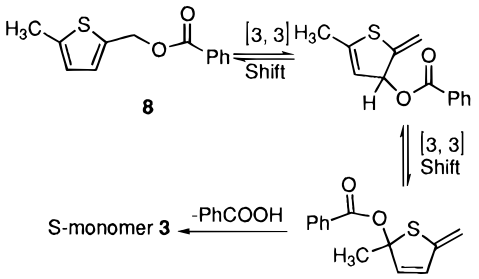
The structure of **3** was confirmed by its spectral properties. The ^{1}H and ^{13}C NMR spectra agree with those reported,[16] and the IR and mass spectra, obtained by GC/IR and GC/MS, are also consistent with structure **3**.

When a 0.17 M solution of S-monomer **3** (0.323 mmol) was allowed to warm to room temperature, SS-dimer **5** (0.0259 mmol, 14.7%), SSS-trimer **7** (0.0477 mmol, 44.3%), and polymer were produced. The structures of products **5** and **7** are indicated by their spectral properties, which agree well with the available literature data.[5,12]

Evidence for formation of an SSSS-tetramer with a molecular weight of 440 was obtained by GC-MS. Quantitative GC showed 0.0042 mmol (0.68%, based on amount of initial monomer) of the SSSS-tetramer.

A high-dilution experiment was carried out to explore the possibility of obtaining a greater yield of SS-dimer **5**. A preparative-scale pyrolysis (2.0 g) of benzoate **8** was carried out with S-monomer **3** being dissolved in 1.025 L of carbon disulfide, which resulted in a 0.0066 M solution of the S-monomer. After 5 days at room temperature, the solution contained SS-dimer **5** and SSS-trimer **7** in a mol ratio of 8.8:1.

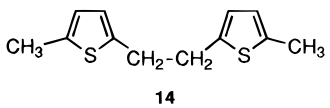
The formation of S-monomer **3** by FVP of the thiophene benzoate **8** is explained by a mechanism proposed for the furan analog, two [3,3] sigmatropic shifts followed by β elimination of benzoic acid.[9,13a]



Concerted or two-step diradical mechanisms could be proposed for conversion of S-monomer **3** to its corresponding SS-dimer **5**. However, a thermal concerted [π^6s + π^6s] cycloaddition is not allowed by the Woodward−Hoffmann rules[18] and is thus unlikely. Moreover, formation of a large amount of SSS-trimer **7** is easily explained by a diradical mechanism. We propose, therefore, the mechanism presented in Scheme 1. In this mechanism two molecules of S-monomer **3** combine to give diradical **11** which can close to give SS-dimer **5** or react with another molecule of S-monomer **3** to give diradical **12**, the precursor of SSS-trimer **7**. The production of a small amount of SSSS-tetramer is consistent with diradical **12** reacting with a molecule of S-monomer **3** to give diradical **13** which can close to give an SSSS-tetramer. Each diradical could either close to give an oligomer or react with a molecule of S-monomer **3** to give the next higher diradical. As the diradical becomes larger, closure to give an oligomer should be less likely since it should be more difficult for the two radical sites to encounter each other. Apparently diradical **13** and the larger diradicals lead primarily to polymer.

Attempted Trapping of Diradical Intermediate 11 or 12. Conventional Trapping Agents. In an attempt to obtain evidence for a diradical mechanism for dimerization and trimerization of S-monomer **3**, a series of trapping experiments was carried out. No evidence for trapping of an intermediate diradical was obtained with 1,4-cyclohexadiene, 9,10-dihydroanthracene, dimethyl maleate, phenylsilane, or styrene. In these cases the normal oligomerization products were obtained.

Several agents interfered with the oligomerization reactions but still provided no evidence for an intermediate diradical. Thiophenol gave the 1:1 addition product of thiophenol to S-monomer **3**, and tri-*n*-butyltin hydride gave several tin compounds. Neither thiophenol nor tri-*n*-butyltin hydride, both good hydrogen atom donors, gave **14**, the product expected from the addition of two hydrogen atoms to diradical **11**. Use of the stable nitroxyl radical 2,2,6,6-tetramethylpiperidinyl-l-oxyl (TEMPO)[19] gave products which we were unable to identify.

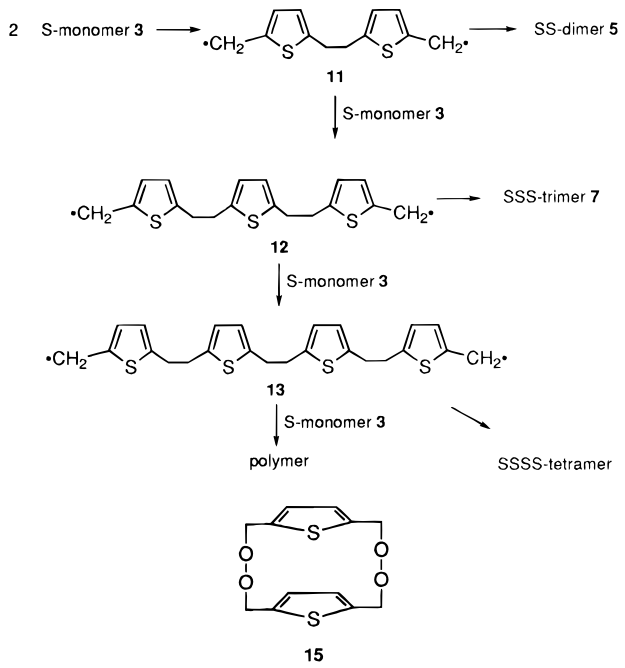


When molecular oxygen, an excellent carbon radical trap,[20] was bubbled through solutions of S-monomer **3**, compound **15** was formed. This is a 2:2 O_2:**3** adduct which has been characterized by C.-H. Chou[16] and our

(18) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic Press: New York, 1970.

(19) Ingold, K. U.; Walton, J. C. In *Landolt-Bornstein: Reactical Reaction Rates in Liquids*; Fischer, M., Ed.; Springer-Verlag: New York, 1994; Vol. 18c, pp 350−352.

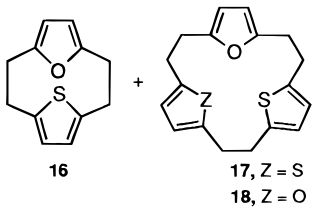
Scheme 1



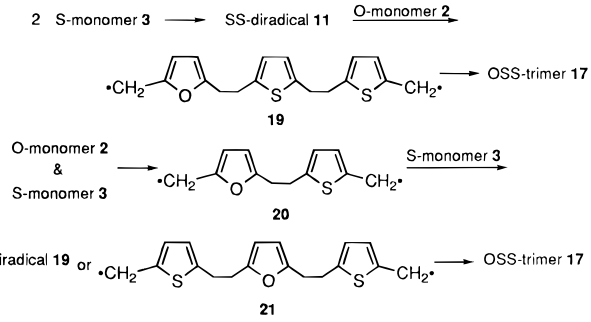
^{1}H NMR data match those reported. Separation of **15** was attempted, but it rearranged to other compounds which we were unable to identify. Compound **15** comes from the direct reaction of O_2 and S-monomer **3** and gives no evidence for the existence of diradical **11**.

Trapping by 2,5-Dimethylene-2,5-dihydrofuran (2). Although the above radical trapping reactions failed, trapping by O-monomer **2** was successful. O-Monomer **2** was selected as a potential trap of diradical intermediate **11** because it is similar both in size and reactivity to S-monomer **3.** O-Monomer **2** was prepared by FVP of 5-methylfurfuryl benzoate at 560 °C and *ca.* 10^{-5} Torr,[9,13a,15] and the solution in CS_2 was stored at −78 °C overnight. The following day S-monomer **3** was prepared, the solutions were mixed, and the relative concentrations of the monomers in the mixture were determined by ^{1}H NMR spectroscopy. The mixture was allowed to react at room temperature overnight until none of S-monomer **3** remained. However, due to the differences in reactivity, much of O-monomer **2** remained after all S-monomer **3** was gone. The excess O-monomer **2** was selectively destroyed by the addition of acetic acid. The excess acid was easily removed by basic workup without damage to the oligomerization products. Four compounds containing the thiophene moiety were produced: OS-dimer **16**,[21] SS-dimer **5**, OSS-trimer **17**, and SSS-trimer **7**. Relative yields of each depended on the ratio of monomers used and are summarized in Table 1. Some OO-dimer **4** was also produced, but amounts varied due to the variation in the length of time the solution of monomers was allowed to stand before the acetic acid treatment to destroy the excess O-monomer **2**. It should be noted that only a trace of OOS-trimer **18** was observed (by GC-MS) and no OOO-trimer **6**[16] was observed. The products were separated by careful column chromatography on silica gel with hexanes. OSS-Trimer **17** has not been previously reported, and its structure is indicated by its spectral properties.

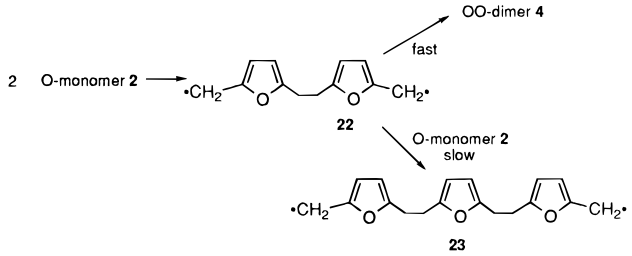
Formation of OSS-trimer **17** provides strong support for the diradical mechanism. Thus the following sequence involving the trapping of SS-diradical **11** accounts for the formation of OSS-trimer **17**. OSS-Trimer **17** could



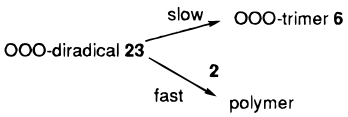
also result from OS-diradical **20**, which could react with



S-monomer **3** to form either OSS-diradical **19** or **21**, both of which could close to give OSS-trimer **17**. Because O-monomer **2** is in higher concentration, one might expect a comparable amount of OOS-trimer **18** to be produced instead of just a trace. OS-Diradical **20** is probably formed, but the rate of closure to give OS-dimer **16** must be faster than the rate of addition to another monomer. This agrees with the results of the oligomerization of O-monomer **2** alone which produces no or only small amounts[16] of OOO-trimer **6** in addition to OO-dimer **4** and polymer. An explanation for the low yields of OOO-trimer **6** is that once OO-diradical **22** is formed, it rapidly closes to OO-dimer **4** rather than picking up a third O-monomer **2** molecule. The polymer produced in this reaction could be formed by an independent route such as free radical polymerization. Another explanation is that if OO-diradical **22** picks up a third O-monomer **2**



molecule, the resulting OOO-diradical **23** reacts with another molecule of O-monomer **2** to form polymer faster than closing to OOO-trimer **6**.



Intramolecular Disproportionation Products from Oligomerization of 2-Ethylidene-5-methylene-2,5-dihydrothiophene (10) As Evidence for a Diradical Intermediate. In an attempt to provide direct evidence for the diradical mechanism for the oligomerization of

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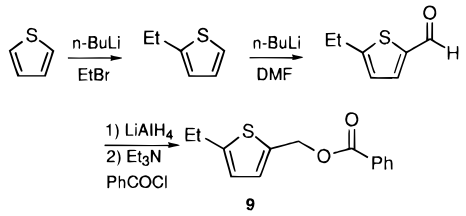
(21) Lee, A. W.; Keehn, P. M.; Ramos, S. M.; Rosenfeld, S. M. *Heterocycles* **1977**, *7*, 81−104.

Table 1. Summary of Yields of Products in the Co-oligomerization of O-Monomer 2 and S-Monomer 3

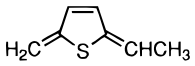
product	run 1 1:1 ratio[a] rel yield, mol %[b]	run 2 3:1 ratio[a] rel yield, mol %[b]	run 3 6:1 ratio[a] abs yield, mg[c]	run 3 6:1 ratio[a] abs yield, %[d]	run 3 6:1 ratio[a] rel yield, mol %[b]
OS-dimer **16**	34.2	56.6	44.1	18.1	58.3
SS-dimer **5**	24.1	12.6	25.6	19.5	31.3
OSS-trimer **17**	10.4	12.6	7.2	3.8	6.2
SSS-trimer **7**	31.3	18.2	5.1	3.8	4.2

[a] Ratio of O-monomer **2** to S-monomer **3**. [b] Relative yields are moles per 100 moles of products based on only the OS, SS, OSS, and SSS products and were determined by GC analysis (response factors proportional to weight were assumed). [c] Absolute yields in run 3 were determined by GC using biphenyl as an internal standard. [d] Absolute yield based on moles of S-monomer **3** available (this assumes a 75% yield from benzoate **8**).

Scheme 2



thiophene-based *p*-QDMs, we focused attention on the trapping of diradical intermediate **11**. Of the trapping agents we used, only O-monomer **2** trapped the diradical. The other trapping agents failed probably because (a) the diradical intermediate is too reactive to be trapped by the trapping agent or (b) some of the trapping agents, such as oxygen and thiophenol, react directly with the very reactive S-monomer **3**. In an attempt to gain more evidence for an intermediate diradical in the oligomerization of thiophene-based *p*-QDMs, it was decided to study **10**. Other studies have shown that diradicals with



α-methyl groups can give rise to intramolecular disproportionation products.[20,22] Observation of such a product from **10** would be good evidence for the existence of a diradical intermediate.

Compound **10** was prepared by FVP of (5-ethyl-2-thiophene-yl)methyl benzoate (**9**) which was obtained in high yield as shown in Scheme 2.

About 40% of **10** was obtained by FVP of **9** at 680 °C and *ca.* 10^{-5}. Product **10** appeared as a dark yellow band in the liquid nitrogen trap at −196 °C. Benzoic acid and white polymer were also produced.

The ^{1}H NMR spectrum of compound **10** shows that it exists as two isomers, the *E* and *Z* isomers, in a ratio of *ca.* 3:1 (stereochemistry not assigned). When a *ca.* 0.05 M solution (1:1 CS_2:$CDCl_3$) of S-monomer **10** was allowed to warm to room temperature, SS-cyclic dimers **24a** and **24b**, acyclic dimers **25a** and **25b**, and SSS-cyclic trimers **26a** and **26b** were produced. SSS-Acyclic trimers were not observed. The results are summarized in Table 2.

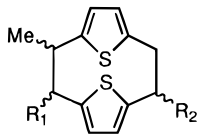
Formation of acyclic dimers **25a** and **25b** strongly support the proposed diradical mechanism.[20,22] Scheme 3 accounts for the formation of **24a**, **24b**, **25a** and **25b**, and Scheme 4 accounts for the formation of **26a**, **26b**.

In an attempt to further understand the composition of the mixture of dimers **24a** and **25b**, a quantitative ^{13}C NMR experiment[23] using $Cr(acac)_3$ in $CDCl_3$ was performed on the mixture. Analysis of these data showed 16 singlets in the thiophene carbon region (δ 159.8−147.9). This is consistent with the conclusion that each constitutional isomer exists in three stereoisomeric forms, one cis and two trans isomers. The parent dimer **5** has been shown to exist in the stepped anti conformation.[6,11] The ^{1}H NMR signal for the ethano bridge of **5** is an AA′BB′ pattern. Analysis of the temperature dependence of these ^{1}H NMR spectra of **5** shows that the barrier to interconversion of these forms is larger than 27 kcal/mol.[11] Thus, a mixture of **24a** and **24b** should consist of the six isomers shown in Chart 1.

Table 2. Summary of Oligomerization Products of 2-Ethylidene-5-methylene-2,5-dihydrothiophene (10)[a]

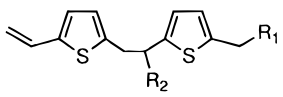
product	rel yield,[b] %
SS-cyclic dimers **24a** (*cis*, *trans*-A, *trans*-B)[c]	37
SS-cyclic dimers **24b** (*cis*, *trans*-A, *trans*-B)[c]	
SS-acyclic dimers **25a**[d]	20
SS-acyclic dimers **25b**[d]	
SSS-cyclic trimers **26a** (six possible stereoisomers)[e]	43
SSS-cyclic trimers **26b** (two possible stereoisomers)[e]	

[a] A 0.05 M of **10** (a 3:1 mixture of *E* and *Z* or *Z* and *E* isomers in a 1:1 mixture of CS_2:$CDCl_3$ as solvent was oligomerized. [b] Isolated yields after flash chromatography. [c] The mixture of isomers was isolated and identified by ^{1}H NMR, ^{13}C NMR, and GC/MS. [d] The mixture of isomers was isolated and identified by ^{1}H NMR, COSY, ^{13}C NMR, and GC/MS. The ratio of two acyclic dimers, **25a** and **25b**, is *ca.* 2.2:1 on the basis of ^{1}H NMR analysis. [e] The mixture of isomers was isolated and identified by ^{1}H NMR and GC/MS.



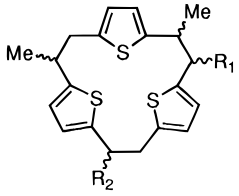
24a, R_1 = Me, R_2 = H

24b, R_1 = H, R_2 = Me



25a, R_1 = Me, R_2 = H

25b` R_1 = H, R_2 = Me



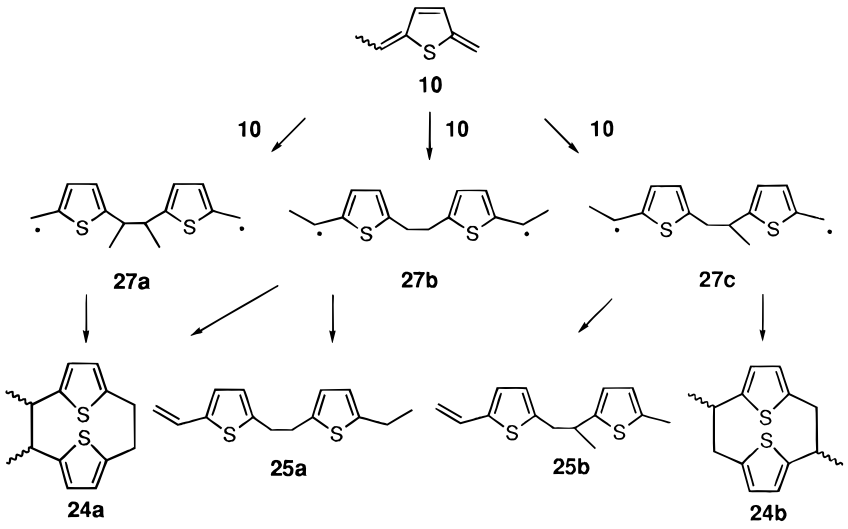
26a, R_1 = Me, R_2 = H

26b, R_1 = H, R_2 = Me

(22) (a) Bergman, R. G. In *Free Radicals*; Kochi, Jay K., Ed.; John Wiley and Sons: New York, 1973; Vol. I, p 231. (b) Leung, M.-k.; Trahanovsky, W. S. *J. Am. Chem. Soc.* **1995**, *117*, 841.

(23) Wehrli, F. W.; Marchand, A. P.; Wehrli, S. *Interpretation of Carbon-13 NMR Spectra*, 2nd ed.; John Wiley & Sons: New York, 1988.

Scheme 3



Scheme 4

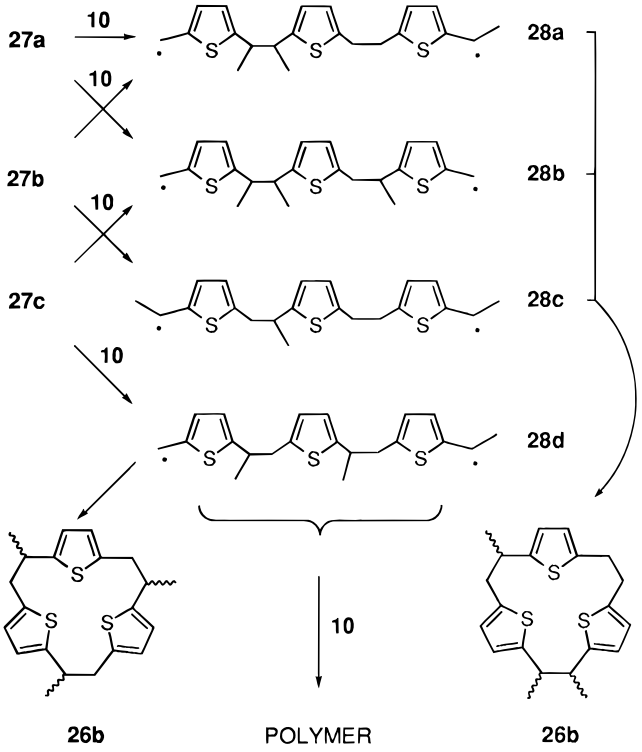
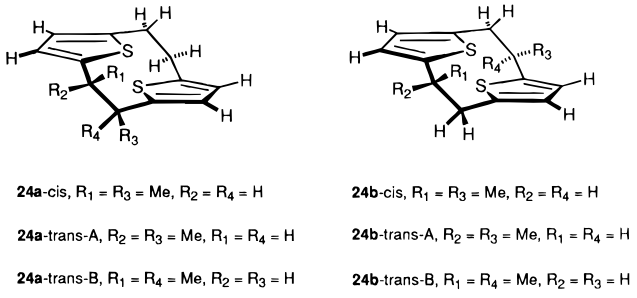


Chart 1



Conclusion

It is concluded that the mechanism of the oligomerization of thiophene-based *p*-quinodimethane 2,5-dimethylene-2,5-dihydrothiophene (**3**) involves the initial combination of two molecules of the monomer to give an intermediate diradical (**11**) that can close to form dimer **5** or react with additional molecules of **3** to produce higher oligomers. This mechanism is supported by successful trapping of **11** by 2,5-dimethyl-2,5-dihydrofuran (**2**) and the formation of intramolecular disproportionation products in the oligomerization of the methyl derivative of **3**, 2-ethylidene-5-methylene-2,5-dihydrothiophene (**10**).

Experimental Section

Methods and Materials. The pyrolysis apparatus[24] and some general methods[25] have been described previously. Elemental analyses were carried out by Spang Microanalytical Laboratory, Eagle Harbor, MI, and Galbraith laboratories, Knoxville, TN. Thiophene, ethyl bromine, *n*-butyllithium (*n*-BuLi), *N*,*N*-dimethylformamide (DMF), lithium aluminum hydride ($LiAlH_4$), triethylamine, 5-methyl-2-thiophenecarboxaldehyde, and benzoyl chloride (BzCl) were purchased from Aldrich Chemical Co.

(5-Methyl-2-thiophene-yl)methyl Benzoate (8). To a stirred slurry of 1.774 g (0.0467 mol) of $LiAlH_4$ in 150 mL of dry ether at 0 °C was slowly added a solution of 11.77 g (0.0933 mol) of 5-methyl-2-thiophenecarboxaldehyde in 50 mL of dry ether. The mixture was stirred at room temperature for 30 min. A standard workup[26] gave 10.86 g (0.0847 mol, 92%) of 5-methyl-2-thiophenemethanol: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.68 (d, J = 3 Hz, 1 H), 6.50 (m, 1 H), 4.64 (s, 2 H), 2.46 (s, 3 H) [lit.[27] ^{1}H NMR δ 6.65 (2 H), 4.52 (s, 2 H), 2.18 (s, 3 H)].

A solution of 12 mL (0.103 mol) of BzCl in 60 mL of dry ether was added dropwise over a 50-min period to a stirred solution of 10.86 g (0.086 mol) of 5-methyl-2-thiophenemethanol and 12 mL of distilled triethylamine in 150 mL of dry ether. After the solution was stirred at room temperature overnight (*ca.* 20 h), 100 mL of distilled water was added and the layers were separated. The aqueous layer was extracted with ether (4 × 25 mL). The combined ether layers was washed successively with 1 M hydrochloric acid (HCl) (3 × 50 mL), saturated sodium bicarbonate ($NaHCO_3$) (3 × 50 mL), and saturated sodium chloride (NaCl) (3 × 50 mL). After drying ($MgSO_4$) and concentrating, 18.7 g (0.081 mol) of **8** was recovered (95%) (bp 124 °C, 0.45 mmHg): IR (thin film) 3080, 2960, 2930, 1725,

(24) (a) Trahanovsky, W. S.; Ong, C. C.; Pataky, J. G.; Weitl, F. J.; Mullen, P. W.; Clardy, J. C.; Hansen, R. S. *J. Org. Chem.* **1971**, *36*, 3575. Commercial apparatus is available from Kontes Scientific Glassware, Vineland, NJ. (b) For review, see: Brown, R. C. F. *Pyrolysis Methods in Organic Chemistry*; Academic: New York, 1980; Chapter 2.

(25) Chou, C.-H.; Trahanovsky, W. S. *J. Org. Chem.* **1986**, *51*, 4208.

(26) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; John Wiley and Sons: New York, 1967; Vol. I, p 584.

(27) Lozanova, A. V.; Moiseenkov, A. M.; Semenovskii, A. V. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1981**, *30*, 619−623.

1610, 1455, 1270, 1100, 800, 710 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.08 (m, 2 H), 7.40 (m, 3 H), 6.90 (d, $J = 3.6$ Hz, 1 H), 6.56 (m, 1 H), 5.37 (s, 2 H), 2.44 (s, 3 H); HRMS calcd for $C_{13}H_{12}O_2S$ 232.05630, found 232.05581. Anal. Calcd: C, 67.22; H, 5.21; S, 13.80. Found: C, 67.22; H, 5.25; S, 13.68.

(5-Ethyl-2-thiophene-yl)methyl Benzoate (9). To a stirred solution of 5.26 g (0.0625 mol) of thiophene in 9:1 THF and HMPA (100 mL) at −78 °C was slowly added 1.98 M (35 mL) *n*-BuLi. After the solution was stirred for 2 h, 4.7 mL of distilled ethyl bromide was added to the same flask. The reaction mixture was stirred at room temperature overnight. After the reaction was complete, HCl (0 °C) was added to the reaction mixture until the solution turned yellow. The solution was transferred to a separatory funnel, and the organic layer was extracted with saturate $NaHCO_3$ (2 × 50 mL) and saturated NaCl (2 × 50 mL). After drying ($MgSO_4$) and concentrating, 5.66 g (0.051 mol) of 2-ethylthiophene was recovered (81%). The bp[28] and ^1H NMR[29] spectrum are in accord with published data.

To 4.0 g (0.0357 mol) of distilled 2-ethylthiophene in 9:1 THF and HMPA (100 mL) at −78 °C was slowly 1.9 M (23 mL) of *n*-BuLi added. After the solution was stirred for about 45 min, 28 mL of DMF was added to the solution. The reaction mixture was allowed to slowly warm to room temperature and stirred overnight. A standard workup gave 4.0 g (0.0285 mol) of 5-ethyl-2-thiophenecarboxaldhyde (80%). Pure aldehyde was obtained by vacuum distillation; bp and ^1H NMR spectrum match literature[30] values. IR (thin film) cm^{-1}: 2966, 1663, 1464, 1452, 1227, 812.

As described above for the preparation of 5-methyl-2-thiophenemethanol, 2.78 g (0.0198 mol) of 5-ethyl-2-thiophenecarboxaldehyde was reduced with 0.3760 g (0.0099 mol) of $LiAlH_4$ to 2.512 g (0.0177 mol) of 5-ethyl-2-thiophenemethanol (89%): ^1H NMR ($CDCl_3$, 300 MHz) δ 6.818 (d, $J = 3.3$ Hz, 1H), 6.648 (d, $J = 3.6$ Hz,, 1H), 4.746 (s, 2H), 2.861 (q, $J = 7.2$ Hz, $J = 7.8$ Hz, 2H), 1.648 (broad, 1H); IR (thin film) cm^{-1} 3333, 2966, 2930, 1456, 1207, 1005, 804.

As described above for the preparation of **8**, 2.512 g (0.0177 mol) of 5-ethyl-2-thiophenemethanol was converted to **9** (82%). Pure **9** was obtained by column chromatography (silica gel, 1:100 ethyl acetate to hexane as eluent) (bp 145 °C, 1.2 mmHg): ^1H NMR ($CDCl_3$, 300 MHz) δ 8.072 (m, 2H), 7.451 (m, 3H), 6.909 (d, $J = 3.3$ Hz, 1H), 6.683 (d, $J = 3.6$ Hz, 1H), 5.435 (s, 2H), 2.848 (q, $J = 7.5$ Hz, 2H), 1.307 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 166.10, 149.22, 135.05, 132.89, 129.87, 129.57, 128.18, 128.05, 122.88, 61.29, 23.44, 15.76; IR (thin film) cm^{-1} 3063, 2964, 1718, 1267, 1096, 712; HRMS calcd for $C_{14}H_{14}O_25$ 246.0715, found 246.0720. Anal. Calcd: C, 68.3; H, 5.73. Found: C, 68.4; H, 6.06.

Pyrolysis of (5-Methyl-2-thiophene-yl)methyl Benzoate (8). A 0.3360 g (0.0136 mol) of **8** was pyrolyzed at 640 °C in the normal manner.[24] Upon completion, 5 mL of a 1:1 mixture of CS_2 and $CDCl_3$ was distilled into the trap, which resulted in a 0.10 M solution of 2,5-dimethylene-2,5-dihydrothiophene (**3**). A quantitative low-temperature ^1H NMR analysis of the pyrolysate using dibromoethane as a standard showed the presence of **3** in 74.4% yield. After the pyrolysate was allowed to stand at room temperature overnight, substantial amounts of [2.2](2,5)thiophenophane (SS-dimer **5**, 14.7 mol %) and [2.2.2](2,5)thiophenophane (SSS-trimer **7**, 44.3 mol %) were formed. The products were separated by column chromatography on silica gel (1:100 ethyl acetate to hexanes).

2,5-Dimethylene-2,5-dihydrothiophene (3): ^1H and ^{13}C NMR data are in good accord with published values;[16] GC-IR 3101, 3001, 1589, 1192, 837 cm^{-1} [lit.[14] IR (Ar 15 K) 1586.6, 1187.4, 840.8, 831.2, 801.6 cm^{-1}]; GC-MS *m/e* (relative intensity) 112 (4.94), 111 (8.51), 110 (100.00), 109 (40.59), 95 (5.4), 84 (23.36), 77 (14.31), 74 (4.26), 71 (12.90), 69 (14.92), 66 (54.29), 65 (13.86), 63 (6.49), 58 (25.78), 55 (10.33), 51 (30.51), 50 (24.22), 47 (2.09).

13,14-Dithiatricyclo[8.2.1.1^{3,6}]tetradeca-4,6,10,12-tetraene ([2.2](2,5)thiophenophane, SS-dimer 5): mp and ^1H NMR spectrum are in accord with published data;[12] ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 151.2, 126.8, 32.2; GC-MS *m/e* (relative intensity) 222 (0.58), 221 (2), 220 (15), 112 (5), 111 (8), 110 (100.00), 109 (9), 84 (5), 77 (5), 66 (15), 58 (5) [lit.[12] mass spectrum *m/e* (relative intensity) 220 (24), 110 (100)]; HRMS calcd for $C_{12}H_{12}S_2$ 220.0380, found 220.03818.

19,20,21-Trithiatetracyclo[14.2.1.1^{3,6}.1^{9,12}]heneicosa-4,6,10,12,16,18-hexaene ([2.2.2](2,5)thiophenophane, SSS-trimer 7): mp and ^1H NMR spectrum are in accord with published data;[12] ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 140.3, 124.4, 31.2; GC-MS *m/e* (relative intensity) 332 (0.83), 331 (1), 330 (9), 222 (0.5), 221 (2), 220 (9), 112 (5), 111 (8), 110 (100), 84 (5), 77 (3), 66 (13) [lit.[12] mass spectrum *m/e* (relative intensity) 330 (100), 220 (36), 110 (61)]; HRMS calcd for $C_{18}H_{18}S_3$ 330.05707, found 330.05712.

SSSS-Tetramer. A 0.781 g (0.00336 mol) quantity of **8** was pyrolyzed at 680 °C in the normal manner. Upon completion, 10 mL of CS_2 was distilled into the trap. After being warmed to −78 °C, the solution was transferred to a flask containing 0.112 g (0.000724 mol) of biphenyl. A GC trace of the cold solution was obtained, and multiple ion detection GC-MS showed the expected SS-dimer **5** and SSS-trimer **7**, as well as 1.88 mg (0.677 mol %, based on amount of initial monomer) of a compound having a molecular weight of 440 and fragments at *m/e* 330 and 220.

Preparation of SS-Dimer 5 by High Dilution. A 2.10 g (0.00902 mol) quantity of **8** was pyrolyzed at 625 °C in the normal manner. Upon completion, 25 mL of CS_2 was distilled into the trap. After the solution was warmed to −78 °C, it was added to 1 L of CS_2, which resulted in a 0.00660 M solution of S-monomer **3**. After the solution was held at room temperature for 5 days, the mol ratio of S-monomer **3** to SS-dimer **5** to SSS-trimer **7** was 1.00:32.89:5.58 as determined by GC.

Trapping Experiments. To a 0.5 mL of S-monomer **3** solution (0.1 M) were added 0.3615 g of purified 9,10-dihydroanthracene and 4.5 mL of CCl_4. This results in a 1:40 monomer:9,10-dihydroanthracene ratio. To a 0.5 mL of S-monomer **3** solution (0.1 M) was added 0.3606 g of anthracene in 4.5 mL of CCl_4. Both reactions were allowed to stand at room temperature overnight. GC, GCMS, and NMR were used to analyze the final products. The same procedure was used for the rest of the conventional trapping agents.

Oxygen Used as Trapping Agent. To each of six NMR tubes was added 0.5 mL of an S-monomer **3** (0.1 M) solution. Oxygen then was bubbled through the monomer solution at different time periods: 5, 10, 20, 50, 60, and 180 s. To each of six NMR tubes was added 0.5 mL of an S-monomer **3** (0.1 M) solution. Nitrogen was bubbled to each tube at different times: 5, 10, 20, 50, 60, and 180 s. ^1H NMR was used to follow both reactions. After standing at room temperature for 2 days, the solution was analyzed by GC.

Co-Oligomerization of O-Monomer 2 and S-Monomer 3. Preparation of O-monomer 2.[9,13a] A 1.77 g (0.00819 mol) quantity of 5-methyl-2-furfuryl benzoate was pyrolyzed at 560 °C in the normal manner. Upon completion, 17 mL of CS_2 was distilled into the trap. After warming to −78 °C, the solution containing O-monomer **2** was stored at −78 °C.

A 0.370 g (0.00159 mol) quantity of **8** was pyrolyzed at 680 °C in the normal manner. Upon completion, 10 mL of CS_2 was distilled into the trap. After warming to −78 °C, the solution containing S-monomer **3** was combined with the O-monomer **2** solution and allowed to stand at room temperature overnight. Integration of the ^1H NMR obtained just before warming showed the ratio of O-monomer **2** to S-monomer **3** to be 5.6:1.

Oligomerization Products. After standing at room temperature overnight, a number of dimers and trimers derived from S-monomer **3** were formed, as well as OO-dimer **4** (identified by GC/MS) and polymer. Yields were determined by GC analysis using biphenyl as an internal standard. The compounds and yields are summarized in Table 1.

It should be noted that using a 1:1 ratio of O-monomer **2** to S-monomer **3** gave the highest relative yield of trimers but

(28) King, W. J.; Nord, F. F. *J. Org. Chem.* **1949**, *14*, 638−42.
(29) *The Aldrich Library of NMR spectra*, Vol. 2, p 466; Pouchert, Ed. II, Aldrich Chemical Co., Milwaukee, 1983.
(30) Lantz, R.; Hörnfeldt, A.-B. *Chem. Scr.* **1972**, *2*, 9−15.

that using a 3:1 ratio gave a greater OSS-trimer **17** to SSS-trimer **7** ratio.

Because excess O-monomer **2** remained for several days after all of the S-monomer **3** had reacted, the excess O-monomer **2** was destroyed by addition of an equal volume of glacial acetic acid to the reaction mixture. This mixture was allowed to stand for 30−90 min. Excess acetic acid was removed by first adding ethyl ether and then extracting with water (2 × 50 mL) followed by saturated $NaHCO_3$ until the ether solution was basic. After drying ($MgSO_4$) and concentrating, the products were dissolved in a minimum amount of hexanes. Separation by careful column chromatography on silica gel (hexanes) yielded pure samples of all five products.

13-Oxa-14-thiatricyclo[8.2.1.1^{3,6}]tetradeca-4,6,10,12-tetraene (OS-dimer 16): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.93 (s, 2 H), 5.96 (s, 2 H), 2.90 (m, 8 H) [lit.[13a] ^{1}H NMR ($CDCl_3$) δ 6.92 (s, 2 H), 5.94 (s, 2 H), 2.88 (m, 8 H)]; ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 154.9, 151.6, 128.3, 108.5, 33.1, 31.0; GC-MS *m/e* (relative intensity) 206 (1.28), 205 (3.17), 204 (24.40), 112 (4.69), 111 (7.48), 110 (100.00), 94 (29.94), 84 (3.70), 77 (7.36), 66 (22.20), 51 (17.82) [lit.[21] mass spectrum *m/e* 110, 94].

19-Oxa-20,21-dithiatetracyclo[14.2.1.1^{3,6}.1^{9,12}]heneicosa-4,6,10,12,-16,18-hexaene (OSS-trimer 17): mp 79.5−84 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.58 (q, AB, 2 H), 5.98 (s, 4 H), 2.96 (m, 12 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 152.4, 141.4, 140.5, 124.2, 123.9, 106.7, 32.0, 29.7, 29.2; HRMS calcd for $C_{18}H_{18}OS_2$ 314.07991, found 314.07872.

Pyrolysis of (5-Ethyl-2-thiophene-yl)methyl Benzoate (9). A 0.1439 g (0.000 584 5 mol) of quantity of **9** was pyrolyzed at 680 °C in the normal manner. Upon completion, 4.4 mL of 1:1 mixture of CS_2 and $CDCl_3$ was distilled into the trap, which resulted in a 0.05 M solution of **10**.

A quantitative low-temperature ^{1}H NMR analysis of the pyrolysate using diphenylmethane as a standard showed the presence of **10a** in 34% yield and **10b** in 9% yield. After the pyrolysate was allowed to stand at room temperature under argon for *ca.* 3 days, substantial amounts of SS-dimers **24**, acyclic dimers **25**, and SSS-trimers **26** were formed. The products were separated by flash column chromatography (silica gel; ethyl acetate and hexane (1:200) was used as eluent).

2-Ethylidene-5-methylene-2,5-dihydrothiophene (mixture of two isomers) (major isomer 10a): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.435 (d, J = 6 Hz, 1H), 6.399 (d, J = 5.7 Hz, 1H), 5.635 (q, J = 7.2 Hz, 1H), 5.147 (s, 1H), 4.979 (s, 1H), 1.803 (d, J = 7.2 Hz, 3H).

2-Ethylidene-5-methylene-2,5-dihydrothiopene (minor isomer 10b): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.49−6.4 (d, J = 6.6 Hz, 2H), 5.4 (q, J = 6.9 Hz, 1H), 5.1 (s, 1H), 4.9 (s, 1H), 1.9 (d, J = 7.5 Hz, 3H).

2,3-Dimethyl-13,14-dithiatricyclo[8.2.1.1^{3,6}]tetradeca-4,6,10,12-tetraene (SS-dimer 24a, three isomers; *cis, trans*-A, and *trans*-B) and 2,8-dimethyl-13,14-dithiatricyclo[8.2.1.1^{3,6}]tetradeca-4,6,10,12-tetraene (SS-dimer 24b, three isomers; *cis, trans*-A, and *trans*-B): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.8−6.6 (m, 8H), 3.7−2.3 (m, 12H), 1.6−1.2 (several d, J = 6.9 Hz, 12H); GC/MS: *m/e* (relative intensity) 248 (M^+, 4), 124 (100), 97.1 (6.02), 65.0 (2.82), 39.1 (5.17); ^{13}C NMR ($CDCl_3$, 75.5 MHz, 7 mg of $Cr(acac)_3$ was added) δ 159.78, 158.07, 157.26, 157.16, 156.73, 156.19, 155.94, 154.12, 150.54, 150.46, 150.23, 149.59, 149.55, 148.80, 148.39, 147.93 (16 quaternary carbons), 126.94,126.26, 125.87, 125.82, 125.32, 125.26, 124.57, 124.38, 122.82, 122.48, 122.26 (11 signals), 47.02, 44.96, 43.64, 41.69, 41.47, 39.77, 39.57 (7 signals), 36.98, 32.37, 32.31, 31.68, 31.11 (5 signals), 19.49, 19.30, 18.56, 17.19, 16.17, 12.46 (6 signals).

5-Ethyl-5′-vinyl-2,2′-ethylenedithiophene (acyclic dimer 25a) and 5-methyl-5′-vinyl-2,2′-(α-methylethylene)dithiophene (acyclic dimer 25b): ^{1}H NMR ($CDCl_3$, 300 MHz) for **25a** δ 6.7 (m, 2H), 6.5 (m, 2H), 6.7 (q, J = 17.1 Hz, J = 10.8 Hz, 1H), 5.48 (d, J = 17.1 Hz, 1H), 5.08 (d, J = 10.8 Hz, 1H), 3.1 (s, 4H), 2.8 (q, J = 7.5 Hz, 2H), 1.3 (t, J = 7.2 Hz, 3H); for **25b** δ 6.7 (m, 2H), 6.5 (m, 2H), 6.7 (q, J = 17.4 Hz, 1H), 5.48 (d, J = 17.4 Hz, 1H), 5.08 (d, J = 10.8 Hz, 1H), 3.25−2.9 (m, 3H), 2.4 (s, 3H), 1.3 (d, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) for both **25a** and **25b** δ 145.6, 143.3, 141.2, 140.96, 130.2, 125.8, 124.8, 124.2, 122.8, 112.2, 40.1, 37.6, 32.5, 32.2, 29.8, 23.5, 22.2, 16.0; GC/MS *m/e* (relative intensity) 248.2 (8), 125.1 (100), 123 (35).

2,3,14-Trimethyl-19,20,21-trithiatetracyclo[14.2.1.1^{3,6}.1^{9,12}]-heneicosa-4,6,10,12,16,18-hexaene (SSS-trimer 26a, possibly six stereoisomers) and (3,9,15-trimethyl)-19,20,21-trithiatetracyclo[14.2.1.1^{3,6}.1^{9,12}]heneicosa-4,6,10,12,16,18-hexaene (SSS-trimer 26b, possibly two stereoisomers): GC/MS *m/e* (relative intensity) 372.5 (M^+, 0.3), 234.1 (11), 123.0 (54), 111 (100); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.63−6.55 (m, 12H), 3.47 (s, 4H), 3.0−3.2 (m, 14H), 1.37−1.27 (m, 18H).

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Supporting Information Available: ^{1}H NMR spectra for compounds **3**, **5**, **7**−**10**, **15**−**17**, **24a**/**b**, **25a**/**b**, **26a**/**b**, and several synthetic intermediates; ^{1}H NMR COSY for compunds **25a**/**b**; ^{13}C NMR spectra for compounds **3**, **17**, **24a**/**b**, and **25a**/**b**; IR spectra for compounds **3**, **9**, and several intermediates; MS for compounds **3**, **24a**/**b**, **25a**/**b**, and **26a**/**b** (31 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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