

## Synthesis, Stability, and Reactivity

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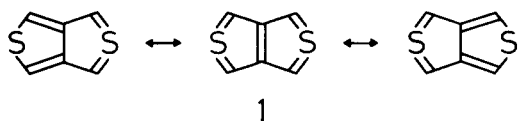
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The synthesis of tetrakis(alkylthio)thieno[3,4-*c*]thiophenes **1a-e** by the dimerization reaction of bis(alkylthio)cyclopropenethiones is described. The remarkable thermodynamic and kinetic stability suggests the significant electron-accepting conjugation of the alkylthio substituents to the carbanionic 1, 3, 4, and 6 carbons in the framework. The isopropylthio- and ethylthio-substituted thienothiophenes **1d** and **1e** undergo cycloaddition reactions with dienophiles such as *N*-phenylmaleimide and dimethyl acetylenedicarboxylate to give the cycloadducts in moderate yields.

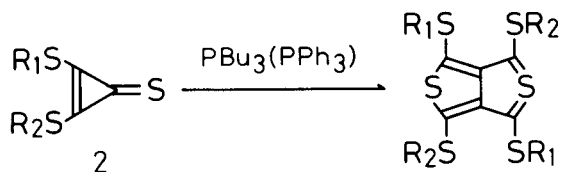
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The thieno[3,4-*c*]thiophene system **1** is of interest, since the uncharged resonance contributors are nonclassical structures containing hypervalent sulfur. However, until recently, the study [1] on the chemistry of the system **1** was



1

restricted almost exclusively to the isolable derivative [2] having four pheny substituents at the 1, 3, 4, and 6 positions. In a preliminary communication [3], we reported the synthesis of tetrakis(alkylthio)thieno[3,4-*c*]thiophenes **1a-d** by the dimerization reaction of bis(alkylthio)cyclopropenethiones **2a-d**. In this paper, we detail our studies on the 1,3,4,6-tetrasubstituted derivatives **1a-d** as well as the ethylthio derivative **1e** newly synthesized.



- a,  $R_1 = R_2 = t\text{-Bu}$   
 b,  $R_1 = t\text{-Bu}; R_2 = \text{Et}$   
 c,  $R_1 = t\text{-Bu}; R_2 = \text{Me}$   
 d,  $R_1 = R_2 = i\text{-Pr}$   
 e,  $R_1 = R_2 = \text{Et}$

The dimerization reaction of **2a** in the presence of tri-n-butylphosphine in refluxing benzene afforded **1a** as the main product in the form of red needles (mp 199.5-200.0° dec) in 40% yield. Similarly, thieno[3,4-*c*]thiophenes, **1b**, **1c**, **1d**, and **1e** were prepared from cyclopropenethiones, **2b**, **2c**, **2d**, and **2e** in 26%, 24%, 68%, and 53% yields, re-

spectively. All the derivatives **1a-e** are stable enough for long periods *in vacuo*. This thermodynamic stability is surprising in view of the theoretical predictions [1a,b] that the thieno[3,4-*c*]thiophene framework is highly unstable. Gimarc [4] very recently proposed the rule of topological charge stabilization, which implies that the introduction of electron-withdrawing groups at the 1, 3, 4, and 6 positions could stabilize the thieno[3,4-*c*]thiophene. Accordingly, the remarkable stability of the derivatives **1a-e** can be rationalized by the electron-accepting conjugation [5] of the alkylthio substituents.

The relatively high stability of **1a-e** to atmospheric oxygen was also unexpected results, because the ready addition of oxygen to 1,3,4,6-tetraphenylthieno[3,4-*c*]thiophene was reported by Potts *et al.* [1e] to occur either in solution or more slowly at the crystal surface. Compound **1a** is stable to air at room temperature for several months, **1b,d** for several weeks, and **1c** for several days. Tetrakis(ethyl-

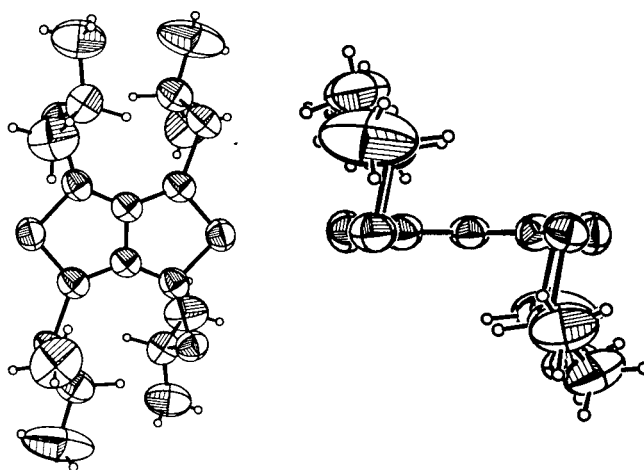
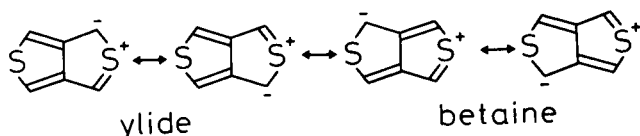
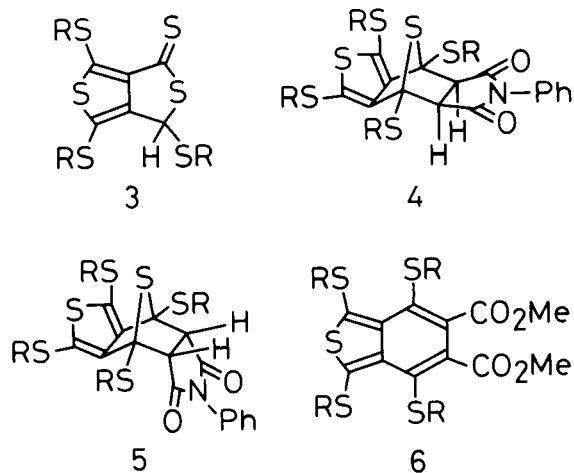


Figure 1. ORTEP drawing of **1d** viewed perpendicular (left) and parallel (right) to the thieno[3,4-*c*]thiophene.

thio)thieno[3,4-*c*]thiophene **1e** gradually decomposed in the air, and accordingly **1e** was handled in degassed solvents or under nitrogen atmosphere. The considerable kinetic stability of **1a-e** to oxygen seems to depend not only on the steric hindrance of the alkylthio groups, but on the electromeric effect. The X-ray structure of **1d** is shown in Figure 1. The side-view clearly exhibits that the carbons at 1, 3, 4, and 6 positions are open to the outside. The difference between the ionization potential of **1d** (6.72 eV) [6] and that of the tetraphenyl derivative (6.19 eV) [1c,d] indicates that the alkylthio substituents more stabilize the highest occupied MO energy level than the phenyl substituents. The alkylthio groups are considered to markedly serve to stabilize the 1, 3, 4, and 6 carbanionic centers through electron-accepting conjugations. This is consistent with the C-SP<sup>+</sup> bond (average 1.738 Å) is much shorter than the normal C-S single bond (1.802 Å) [7]. These results suggest that the thieno[3,4-*c*]thiophene inherently possesses the polar electronic structure represented by contributions from many ylide and betaine resonance structures.



The reactions of **1** with dienophiles such as *N*-phenylmaleimide (NPM) and dimethyl acetylenedicarboxylate (DMAC) were carried out. The reaction of **1a** with *N*-phenylmaleimide in refluxing xylene gave the exo cycloadduct **4a** in 8% yield along with 18% yield of the thiophene derivative **3**. The similar reaction of **1d** in refluxing benzene afforded the exo and endo cycloadducts **4d** and **5d** in 77% and 12% yields, respectively. The structures of **4d** and **5d** were assigned on the basis of their <sup>1</sup>H nmr spectra, by analogy with the case of the tetraphenylthieno[3,4-*c*]thiophene-NPM adducts [8]. In the similar reaction of **1e** in degassed benzene at room temperature, the exo and endo



cycloadducts **4e** and **5e** were obtained in 47% and 13% yields, respectively. The reaction of **1d** with dimethyl acetylenedicarboxylate in xylene at 100° afforded 1,3,4,7-tetrakis(isopropylthio)-5,6-dicarbomethoxybenzo[*c*]thiophene **6d** in 49% yield, which formed by the loss of atomic sulfur from the initial 1:1 cycloadduct. The similar reaction of **1e** in degassed benzene at room temperature afforded the corresponding benzo[*c*]thiophene derivative **6e** in 53% yield. The results are summarized in Table I.

Table I  
Cycloaddition Reactions of **1** with Dienophiles

Compound	Dienophile	temp, °C	time, hours	Product, %		
				4	5	6
<b>1a</b>	NPM	140	10	8	—	
<b>1d</b>	NPM	80	3	77	12	
<b>1e</b>	NPM	rt	7	47	13	
<b>1a</b>	DMAC	100	24			trace
<b>1d</b>	DMAC	100	10			49
<b>1e</b>	DMAC	rt	27			53

Table II  
Fractional Atomic Coordinates

Atom	x	y	z	Beq(Å <sup>2</sup> )
S(1)	0.3142(1)	0.51284(9)	0.7455(2)	5.32(2)
S(2)	0.4357(1)	0.74534(9)	0.8516(2)	5.49(2)
S(3)	0.2870(1)	0.27235(9)	0.5217(2)	5.23(2)
C(1)	0.4805(4)	0.4415(3)	0.4601(7)	4.31(8)
C(2)	0.4332(4)	0.6088(3)	0.7035(8)	4.81(9)
C(3)	0.3700(4)	0.4036(3)	0.5600(8)	4.68(9)
C(4)	0.3614(5)	0.8307(4)	0.5728(9)	6.0(1)
C(5)	0.2228(6)	0.7896(6)	0.429(1)	9.8(2)
C(6)	0.366(1)	0.9519(5)	0.685(2)	14.5(3)
C(7)	0.1843(4)	0.2741(4)	0.1869(9)	5.6(1)
C(8)	0.0732(5)	0.3637(5)	0.160(1)	8.3(2)
C(9)	0.1264(6)	0.1565(5)	0.114(1)	8.6(2)
H(4)	0.566(5)	0.178(4)	0.560(9)	6.0
H(5A)	0.183(5)	0.806(4)	0.607(9)	6.0
H(5B)	0.168(5)	0.831(4)	0.338(9)	6.0
H(5C)	0.224(5)	0.723(4)	0.362(9)	6.0
H(6A)	0.356(5)	0.998(4)	0.58(1)	6.0
H(6B)	0.294(5)	0.933(4)	0.77(1)	6.0
H(6C)	0.442(5)	0.982(4)	0.830(9)	6.0
H(7)	0.254(5)	0.295(4)	0.08(1)	6.0
H(8A)	0.001(5)	0.348(4)	0.25(1)	6.0
H(8B)	0.025(5)	0.346(4)	−0.017(9)	6.0
H(8C)	0.110(5)	0.436(4)	0.238(9)	6.0
H(9A)	0.086(5)	0.136(4)	0.24(1)	6.0
H(9B)	0.185(5)	0.101(4)	0.143(9)	6.0
H(9C)	0.070(5)	0.153(4)	−0.054(9)	6.0

Table III  
Bond Distances (Å)

S(1)-C(2)	1.691(3)	C(1)-C(2)	1.419(4)
S(1)-C(3)	1.712(3)	C(1)-C(3)	1.386(4)
S(2)-C(2)	1.737(3)	C(4)-C(5)	1.488(7)
S(2)-C(4)	1.837(4)	C(4)-C(6)	1.504(8)
S(3)-C(3)	1.738(3)	C(7)-C(8)	1.504(5)
S(3)-C(7)	1.828(3)	C(7)-C(9)	1.500(6)
C(1)-C(1)	1.447(6)		
C(4)-H(4)	1.09(4)	C(7)-H(7)	1.02(5)
C(5)-H(5A)	1.08(5)	C(8)-H(8A)	0.96(4)
C(5)-H(5B)	0.82(4)	C(8)-H(8B)	0.95(4)
C(5)-H(5C)	0.84(5)	C(8)-H(8C)	0.96(5)
C(6)-H(6A)	0.79(5)	C(9)-H(9A)	0.86(5)
C(6)-H(6B)	0.95(5)	C(9)-H(9B)	0.86(4)
C(6)-H(6C)	1.01(5)	C(9)-H(9C)	0.93(4)

Table IV  
Bond Angles (deg)

C(2)-S(1)-C(3)	96.0(2)	S(1)-C(3)-S(3)	119.9(2)
C(2)-S(2)-C(4)	102.4(2)	S(1)-C(3)-C(1)	109.0(2)
C(3)-S(3)-C(7)	102.1(2)	S(3)-C(3)-C(1)	131.2(2)
C(1)-C(1)-C(2)	111.4(3)	S(2)-C(4)-C(5)	113.2(3)
C(1)-C(1)-C(3)	114.0(3)	S(2)-C(4)-C(6)	105.5(4)
C(2)-C(1)-C(3)	134.6(3)	C(5)-C(4)-C(6)	115.3(6)
S(1)-C(2)-S(2)	120.3(2)	S(3)-C(7)-C(8)	112.9(3)
S(1)-C(2)-C(1)	109.7(2)	S(3)-C(7)-C(9)	106.8(3)
S(2)-C(2)-C(1)	130.0(3)	C(8)-C(7)-C(9)	112.3(4)
S(2)-C(4)-H(4)	105(2)	C(4)-C(6)-H(6C)	123(3)
C(5)-C(4)-H(4)	109(2)	H(6A)-C(6)-H(6B)	122(6)
C(6)-C(4)-H(4)	108(2)	H(6A)-C(6)-H(6C)	106(6)
H(8B)-C(8)-H(8C)	128(5)	H(6B)-C(6)-H(6C)	105(5)
C(7)-C(9)-H(9A)	110(4)	S(3)-C(7)-H(7)	104(2)
C(7)-C(9)-H(9B)	116(3)	C(8)-C(7)-H(7)	108(2)
C(7)-C(9)-H(9C)	111(3)	C(9)-C(7)-H(7)	113(2)
C(4)-C(5)-H(5A)	89(2)	C(7)-C(8)-H(8A)	113(3)
C(4)-C(5)-H(5B)	122(3)	C(7)-C(8)-H(8B)	101(3)
C(4)-C(5)-H(5C)	113(4)	C(7)-C(8)-H(8C)	111(3)
H(5A)-C(5)-H(5B)	96(4)	H(8A)-C(8)-H(8B)	101(4)
H(5A)-C(5)-H(5C)	121(5)	H(8A)-C(8)-H(8C)	104(4)
H(5B)-C(5)-H(5C)	113(5)	H(9A)-C(9)-H(9B)	92(5)
C(4)-C(6)-H(6A)	115(5)	H(9A)-C(9)-H(9C)	114(5)
C(4)-C(6)-H(6B)	88(4)	H(9B)-C(9)-H(9C)	114(4)

The difficult formations of the cycloadducts in the reaction of **1a** with dienophiles are apparently ascribed to the steric interference of the bulky *t*-butylthio groups, while the isopropylthio and ethylthio derivatives **1d** and **1e** seem to be much less subject to the steric inhibition (see Figure 1).

Further work will be required to elucidate the reaction mechanism for the formation of **1**, and to prepare and characterize the charge-transfer complexes of the electron-donating **1** with electron acceptors.

## EXPERIMENTAL

All melting points were determined on a Yanaco MP-S3 melting point apparatus and are uncorrected. Infrared spectra were recorded on a Hitachi 215 spectrometer. Nuclear magnetic resonance spectra were recorded on a JEOL JNM-GX270 spectrometer, and the chemical shifts are reported in  $\delta$  values relative to tetramethylsilane as an internal standard. Ultraviolet spectra were recorded on a Hitachi EPS-3T spectrometer. Mass spectra were taken at 70 eV on a Shimadzu LKB-9000 spectrometer.

### 1,3,4,6-Tetrakis(*t*-butylthio)thieno[3,4-*c*]thiophene (**1a**).

To a stirred solution of 3.92 g (16.0 mmoles) of 2,3-bis(*t*-butylthio)cyclopropenethione (**2a**) in 200 ml of benzene under nitrogen was added a solution of 4.21 g (20.8 mmoles, 1.3 equivalents) of tributylphosphine in 80 ml of benzene, and the reaction mixture was refluxed for 4 hours. Most of the solvent was evaporated under reduced pressure and methanol was added. The resulting solid was separated by filtration, washed with methanol. The crude product was recrystallized from benzene-hexane (1:3) to give 1.57 g (40%) of **1a** as red needles, mp 199.5-200.0° dec; ir (potassium bromide): 2950, 1460, 1370, 1160  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.34 (s, 36H);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  30.8, 50.1, 117.4, 153.0; uv (hexane):  $\lambda$  max 255 nm (log  $\epsilon$  4.29), 305 (4.07), 506 (4.23); ms:  $m/e$  492 ( $\text{M}^+$ ).

Anal. Calcd. for  $\text{C}_{22}\text{H}_{30}\text{S}_6$ : C, 53.61; H, 7.36. Found: C, 53.53; H, 7.62.

### 1,4-Bis(*t*-butylthio)-3,6-bis(ethylthio)thieno[3,4-*c*]thiophene (**1b**).

To a solution of 0.63 g (2.88 mmoles) of 2-*t*-butylthio-3-ethylthiocyclopropenethione (**2b**) in 60 ml of benzene under nitrogen was added a solution of 0.98 g (3.75 mmoles, 1.3 equivalents) of triphenylphosphine in 20 ml of benzene. After the reaction mixture was stirred for 44 hours at room temperature, the procedure as above provided the crude product. Recrystallization from ethanol afforded 0.16 g (26%) of **1b** as reddish purple needles, mp 110.0-110.5° dec; ir (potassium bromide): 2950, 1455, 1363, 1240, 1160  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.32 (t,  $J$  = 7.4 Hz, 6H), 1.35 (s, 18H), 3.00 (q,  $J$  = 7.4 Hz, 4H);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  14.0, 30.6, 32.4, 49.7, 111.9, 120.9, 150.7; uv (hexane):  $\lambda$  max 258 nm (log  $\epsilon$  4.26), 303 (3.96), 515 (4.11); ms:  $m/e$  436 ( $\text{M}^+$ ).

Anal. Calcd. for  $\text{C}_{18}\text{H}_{26}\text{S}_6$ : C, 49.50; H, 6.46. Found: C, 49.69; H, 6.73.

### 1,4-Bis(*t*-butylthio)-3,6-bis(methylthio)thieno[3,4-*c*]thiophene (**1c**).

To a solution of 2.20 g (10.8 mmoles) of 2-*t*-butylthio-3-methylthiocyclopropenethione (**2c**) in 160 ml of degassed benzene under nitrogen was added a solution of 2.82 g (10.8 mmoles, 1.0 equivalent) of triphenylphosphine in 40 ml of degassed benzene. After the reaction mixture was stirred for 15 hours at room temperature, the above procedure provided the crude product. Recrystallization from degassed ethanol-methanol (1:1) afforded 0.53 g (24%) of **1c** as reddish purple needles, mp 158.0-158.5° dec; ir (potassium bromide): 2950, 1370, 1245, 1160  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.35 (s, 18H), 2.58 (s, 6H);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  21.2, 30.5, 49.6, 110.2, 123.8, 149.9; uv (hexane):  $\lambda$  max 259 nm (log  $\epsilon$  4.24), 304 (3.91), 534 (4.03); ms:  $m/e$  408 ( $\text{M}^+$ ).

Anal. Calcd. for  $\text{C}_{16}\text{H}_{24}\text{S}_6$ : C, 47.02; H, 5.92. Found: C, 46.87; H, 5.89.

### 1,3,4,6-Tetrakis(isopropylthio)thieno[3,4-*c*]thiophene (**1d**).

To a solution of 0.48 g (2.18 mmoles) of 2,3-bis(isopropylthio)cyclopropenethione (**2d**) in 30 ml of benzene under nitrogen was added a solution of 0.58 g (2.18 mmoles, 1.0 equivalent) of triphenylphosphine in 20 ml of benzene. After the reaction mixture was stirred for 3 hours at 60°, the above procedure provided the crude product. Recrystallization from

Table V  
Anisotropic Thermal Parameters [a]

Name	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
S(1)	0.0706(5)	0.0694(6)	0.0671(5)	0.0098(5)	0.0252(4)	0.0074(5)
S(2)	0.0794(6)	0.0670(6)	0.0579(5)	0.0149(5)	0.0068(5)	−0.0042(5)
S(3)	0.0732(6)	0.0630(5)	0.0626(5)	0.0011(5)	0.0110(5)	0.0137(5)
C(1)	0.057(2)	0.055(2)	0.049(2)	0.010(2)	0.005(2)	0.009(2)
C(2)	0.064(2)	0.060(2)	0.057(2)	0.011(2)	0.007(2)	0.007(2)
C(3)	0.060(2)	0.062(2)	0.055(2)	0.012(2)	0.010(2)	0.004(2)
C(4)	0.076(3)	0.070(3)	0.079(3)	0.018(2)	0.006(2)	0.008(2)
C(5)	0.096(4)	0.146(5)	0.118(4)	0.007(4)	−0.017(3)	0.042(4)
C(6)	0.29(1)	0.072(4)	0.157(7)	0.044(5)	−0.036(7)	0.006(4)
C(7)	0.059(2)	0.081(3)	0.068(2)	0.002(2)	0.004(2)	0.015(2)
C(8)	0.076(3)	0.094(3)	0.133(5)	0.015(3)	−0.009(3)	0.022(3)
C(9)	0.112(4)	0.084(3)	0.113(4)	0.001(3)	−0.016(4)	−0.001(3)

[a] The form of the anisotropic thermal parameter is:  $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$  where  $a^*, b^*,$  and  $c^*$  are reciprocal lattice constants.

methanol afforded 0.33 g (68%) of **1d** as red needles, mp 116.5–117.0° dec; ir (potassium bromide): 2950, 1460, 1375, 1360, 1230, 1150, 1045  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.29 (d,  $J = 6.7$  Hz, 24H), 3.44 (sep,  $J = 6.7$  Hz, 4H);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  22.6, 43.6, 116.4, 151.2; uv (hexane):  $\lambda$  max 258 nm ( $\log \epsilon$  4.30), 301 (3.95), 505 (4.13); ms:  $m/e$  436 ( $M^+$ ).

Anal. Calcd. for  $\text{C}_{18}\text{H}_{28}\text{S}_6$ : C, 49.50; H, 6.46. Found: C, 49.26; H, 6.62.

#### 1,3,4,6-Tetrakis(ethylthio)thieno[3,4-*c*]thiophene (**1e**).

To a solution of 0.45 g (2.35 mmoles) of 2,3-bis(ethylthio)cyclopropenethione (**2e**) in 30 ml of degassed benzene under nitrogen was added a solution of 0.62 g (2.35 mmoles, 1.0 equivalent) of triphenylphosphine in 15 ml of degassed benzene. After the reaction mixture was stirred for 2.5 hours at room temperature, the above procedure provided the crude product. Recrystallization from degassed methanol afforded 0.24 g (53%) of **1e** as red needles, mp 50.5–51.0° dec; ir (methylene chloride): 2920, 1445, 1375, 1240  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.29 (t,  $J = 7.3$  Hz, 12H), 2.95 (q,  $J = 7.3$  Hz, 8H);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  14.2, 34.2, 115.9, 150.4; uv (hexane):  $\lambda$  max 259 nm ( $\log \epsilon$  4.29), 301 (3.94), 507 (4.07); ms:  $m/e$  380 ( $M^+$ ).

#### Crystallographic Structural Determination of **1d**.

A red needles-shaped crystal of  $\text{C}_{18}\text{H}_{28}\text{S}_6$ ; **1d**, belonged to the triclinic space group  $P\bar{1}$ :  $a = 9.860(2)$ ,  $b = 11.765(2)$ ,  $c = 5.195(1)$  Å,  $\alpha = 93.50(1)$ ,  $\beta = 101.65(1)$ ,  $\gamma = 89.41(1)^\circ$ ,  $V = 589.1$  Å<sup>3</sup>,  $Z = 1$ , and  $D_x = 1.23$   $\text{g/cm}^3$ . Of 2237 reflections collected at 23° (Enraf-Nonius CAD 4,  $\text{CuK}\alpha$  ( $\lambda = 1.5418$  Å,  $2^\circ < 2\theta < 140^\circ$ ), 1425 with  $I > 3\sigma(I)$  were used in the solution and refinement of the structure. All atoms including hydrogen atoms were located by direct methods and subsequent difference Fourier syntheses. Refinement of all non-hydrogen atoms with anisotropic thermal parameters (hydrogen atoms fixed at  $6$  Å<sup>2</sup>) led to convergence at  $R = 0.049$ ,  $R_w = 0.064$ ,  $\text{GOF} = 1.87$ , with the highest peak on the final difference map of  $0.40$  e Å<sup>−3</sup>. Tables of the experimental data for the crystallographic structural determination are available as supplementary material.

#### Reaction of **1a** with *N*-Phenylmaleimide.

A mixture of 0.20 g (0.41 mmole) of **1a** and 0.11 g (0.61 mmole, 1.5 equivalents) of *N*-phenylmaleimide in 7 ml of xylene was refluxed for 10 hours under nitrogen. The solvent was evaporated under reduced pressure and the residue subjected to chromatography on silica gel using

mixtures of methylene chloride and hexane to afford the thiophene derivative **3** and the exo adduct **4a**. Recrystallization from methanol-ethanol (1:1) afforded 0.03 g (18%) of **3** as reddish purple solid, and from hexane afforded 0.02 g (8%) of **4a** as pale yellow solid.

Compound **3** had mp 129.5–130.0° dec; ir (potassium bromide): 2950, 1415, 1365, 1205, 1160, 960  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.42 (s, 9H), 1.45 (s, 9H), 1.57 (s, 9H), 5.67 (s, 1H); uv (hexane):  $\lambda$  max 266 nm (sh,  $\log \epsilon$  4.14), 284 (4.25), 301 (sh, 4.03), 321 (sh, 3.92), 361 (3.92), 398 (sh, 3.77); ms:  $m/e$  436 ( $M^+$ ).

Anal. Calcd. for  $\text{C}_{18}\text{H}_{28}\text{S}_6$ : C, 49.50; H, 6.46. Found: C, 49.26; H, 6.76.

Compound **4a** had dec pt 200°; ir (potassium bromide): 2960, 1720, 1380, 1370, 1200, 1165  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.44 (s, 18H), 1.50 (s, 18H), 3.47 (s, 2H), 7.31–7.47 (m, 5H); ms:  $m/e$  665 ( $M^+$ ).

Anal. Calcd. for  $\text{C}_{32}\text{H}_{43}\text{NO}_2\text{S}_6$ : C, 57.71; H, 6.51; N, 2.10. Found: C, 57.58; H, 6.62; N, 2.09.

#### Reaction of **1d** with *N*-Phenylmaleimide.

To a stirred solution of 0.05 g (0.12 mmole) of **1d** in 4 ml of benzene under nitrogen was added a solution of 0.03 g (0.17 mmole, 1.5 equivalents) of *N*-phenylmaleimide in 3 ml of benzene. After the reaction mixture was refluxed for 3 hours, the above procedure provided the exo and endo adducts **4d** and **5d**. Recrystallization from benzene-hexane (1:3) afforded 0.05 g (77%) of **4d** as pale yellow crystals, and from hexane afforded 0.01 g (12%) of **5d** as colorless solid.

Compound **4d** had mp 178.0–179.0° dec; ir (potassium bromide): 2950, 1715, 1380, 1200  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.33 (d,  $J = 6.7$  Hz, 6H), 1.36 (d,  $J = 6.7$  Hz, 6H), 1.42 (d,  $J = 6.7$  Hz, 6H), 1.46 (d,  $J = 6.7$  Hz, 6H), 3.30 (qq,  $J = 6.7, 6.7$  Hz, 2H), 3.42 (qq,  $J = 6.7, 6.7$  Hz, 2H), 3.45 (s, 2H), 7.30–7.48 (m, 5H); ms:  $m/e$  609 ( $M^+$ ).

Anal. Calcd. for  $\text{C}_{28}\text{H}_{35}\text{NO}_2\text{S}_6$ : C, 55.14; H, 5.78; N, 2.30. Found: C, 55.10; H, 5.67; N, 2.22.

Compound **5d** had mp 165.5–166.5° dec; ir (potassium bromide): 2950, 1705, 1360, 1175  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.19 (d,  $J = 6.7$  Hz, 6H), 1.26 (d,  $J = 6.7$  Hz, 6H), 1.44 (d,  $J = 6.7$  Hz, 6H), 1.48 (d,  $J = 6.7$  Hz, 6H), 3.29 (qq,  $J = 6.7, 6.7$  Hz, 2H), 3.32 (qq,  $J = 6.7, 6.7$  Hz, 2H), 4.22 (s, 2H), 6.95–6.99 (m, 2H), 7.28–7.38 (m, 3H); ms:  $m/e$  609 ( $M^+$ ).

Anal. Calcd. for  $\text{C}_{28}\text{H}_{35}\text{NO}_2\text{S}_6$ : C, 55.14; H, 5.78; N, 2.30. Found: C, 55.23; H, 6.00; N, 2.33.

#### Reaction of **1e** with *N*-Phenylmaleimide.

To a solution of 0.09 g (0.24 mmole) of **1e** in 9 ml of degassed benzene

under nitrogen was added a solution of 0.06 g (0.35 mmole, 1.5 equivalents) of *N*-phenylmaleimide in 5 ml of degassed benzene. After the reaction mixture was stirred for 7 hours at room temperature, the above procedure provided the exo and endo adducts **4e** and **5e**. Recrystallization from ethanol afforded 0.06 g (47%) of **4e** as colorless needles, and from hexane afforded 0.02 g (13%) of **5e** as pale yellow solid.

Compound **4e** had mp 197.5-198.5° dec; ir (potassium bromide): 2960, 1717, 1390, 1200  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.33 (X part of  $\text{ABX}_3$  spectrum, dd,  $J = 7.5, 7.5$  Hz, 6H), 1.36 (t,  $J = 7.5$  Hz, 6H), 2.78 and 2.97 (AB part of  $\text{ABX}_3$  spectrum, dq,  $J = 7.5, 11.3$  Hz, 4H), 2.96 (q,  $J = 7.5$  Hz, 4H), 3.54 (s, 2H), 7.31-7.45 (m, 5H); ms:  $m/e$  553 ( $\text{M}^+$ ).

Anal. Calcd. for  $\text{C}_{24}\text{H}_{27}\text{NO}_2\text{S}_6$ : C, 52.05; H, 4.91; N, 2.53. Found: C, 51.93; H, 4.96; N, 2.45.

Compound **5e** had mp 68.0-69.0°; ir (potassium bromide): 2930, 1717, 1385, 1200  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.21 (t,  $J = 7.5$  Hz, 6H), 1.37 (X part of  $\text{ABX}_3$  spectrum, dd,  $J = 7.5, 7.5$  Hz, 6H), 2.84 (q,  $J = 7.5$  Hz, 4H), 2.86 and 2.93 (AB part of  $\text{ABX}_3$  spectrum, dq,  $J = 7.5, 11.5$  Hz, 4H), 4.27 (s, 2H), 6.90-6.93 (m, 2H), 7.31-7.39 (m, 3H); ms:  $m/e$  553 ( $\text{M}^+$ ).

Anal. Calcd. for  $\text{C}_{24}\text{H}_{27}\text{NO}_2\text{S}_6$ : C, 52.05; H, 4.91; N, 2.53. Found: C, 51.85; H, 4.79; N, 2.48.

#### Reaction of **1d** with Dimethyl Acetylenedicarboxylate.

To a solution of 0.17 g (0.40 mmole) of **1d** in 20 ml of xylene under nitrogen was added 0.06 ml (0.52 mmole, 1.3 equivalents) of dimethyl acetylenedicarboxylate. After the reaction mixture was stirred for 10 hours at 100°, the above procedure provided 1,3,4,7-tetrakis(isopropylthio)-5,6-dicarbomethoxybenzo[*c*]thiophene (**6d**). Recrystallization from acetonitrile afforded 0.11 g (49%) of **6d** as orange plates, mp 95.5-96.0°; ir (potassium bromide): 2960, 1740, 1440, 1380, 1280, 1245, 1200, 1165  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.20 (d,  $J = 6.7$  Hz, 12H), 1.30 (d,  $J = 6.7$  Hz, 12H), 3.36 (sep,  $J = 6.7$  Hz, 2H), 3.47 (sep,  $J = 6.7$  Hz, 2H), 3.90 (s, 6H); uv (hexane):  $\lambda$  max 266 nm ( $\log \epsilon$  4.41), 389 (3.68), 446 (3.72); ms:  $m/e$  546 ( $\text{M}^+$ ).

Anal. Calcd. for  $\text{C}_{24}\text{H}_{34}\text{O}_4\text{S}_4$ : C, 52.72; H, 6.27. Found: C, 52.59; H, 6.45.

#### Reaction of **1e** with Dimethyl Acetylenedicarboxylate.

To a solution of 0.10 g (0.27 mmole) of **1e** in 8 ml of degassed benzene under nitrogen was added a solution of 0.05 ml (0.41 mmole, 1.5 equiv-

alents) of dimethyl acetylenedicarboxylate in 4 ml of degassed benzene. After the reaction mixture was stirred for 27 hours at room temperature, the above procedure provided 1,3,4,7-tetrakis(ethylthio)-5,6-dicarbomethoxybenzo[*c*]thiophene (**6e**). Recrystallization from acetonitrile afforded 0.07 g (53%) of **6e** as reddish brown plates, mp 108.5-109.0°; ir (potassium bromide): 2960, 1755, 1440, 1390, 1295, 1260, 1200, 1165  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.22 (t,  $J = 7.5$  Hz, 6H), 1.34 (t,  $J = 7.5$  Hz, 6H), 2.91 (q,  $J = 7.5$  Hz, 4H), 3.03 (q,  $J = 7.5$  Hz, 4H), 3.91 (s, 6H); uv (hexane):  $\lambda$  max 269 nm ( $\log \epsilon$  4.46), 402 (sh, 3.49), 450 (3.83); ms:  $m/e$  490 ( $\text{M}^+$ ).

Anal. Calcd. for  $\text{C}_{20}\text{H}_{26}\text{O}_4\text{S}_4$ : C, 48.95; H, 5.34. Found: C, 48.68; H, 5.39.

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