

# The Reaction of Sulfur with Dilithio Compounds. The Syntheses and Structures of Phenanthro[1,10-cd]-1,2-dithiole and Phenanthro[4,5-cde][1,2]dithiin

Arthur J. Ashe, III,\* Jeff W. Kampf, and Paresh M. Savla

Department of Chemistry, The University of Michigan, Ann Arbor, MI 48109-1055

Received 4 November 1993; revised 13 December 1993

## ABSTRACT

The sequential reaction of selected polycyclic aromatic hydrocarbons with butyllithium/TMEDA/hexane and sulfur allows preparation of ring-fused dithiins, dithioles, and thiophenes. In this manner, phenanthrene has been converted to phenanthro[4,5-cde][1,2]dithiin and phenanthro[1,10cd]-1,2-dithiole. Yellow crystals of the dithiin form in  $C2/c$  (#15) space group with  $Z = 4$ ,  $a = 13.537(3)$  Å,  $b = 8.933(2)$  Å,  $c = 9.601(4)$  Å, and  $\beta = 116.19(2)^\circ$ ; while orange crystals of the dithiole form in  $P2_12_12_1$  (#19) space group with  $Z = 4$ ,  $a = 4.1507(5)$  Å,  $b = 14.436(3)$  Å, and  $c = 16.972(3)$  Å. Full structures have been determined for both compounds.

## INTRODUCTION

Dilithio compounds derived from polycyclic aromatic hydrocarbons (PAHs) are of considerable interest [1–3]. Calculations and experimental evidence indicate that both 1,3- and 1,4-dilithio compounds adopt highly favorable bridged geometries [2,5,6]. This thermodynamic favorability can provide the driving force for the formation of these dilithio species [1–4,6b]. Thus, the reaction of triphenylene (1) with butyllithium in TMEDA-hexane gives the 1,4-dilithio derivative 2 which affords thiophene 3 on reaction with  $SCl_2$  [1].

Although this reaction sequence represents an efficacious preparation of fused-ring thiophenes, the  $SCl_2$  reaction with 1,3-dilithio compounds is not

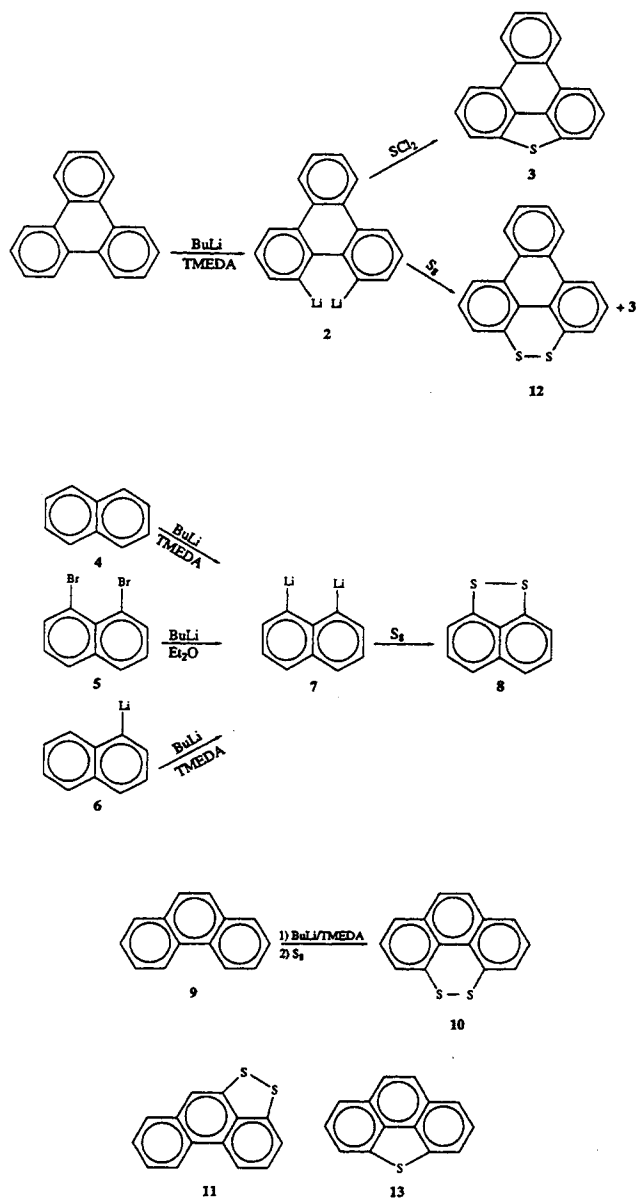
useful. However 1,3-dilithio compounds react with elemental sulfur to afford 1,2-dithioles [7 → 8] [7]. We report here on the direct dilithiation of PAHs followed by quenching with elemental sulfur. This sequence allows simultaneous detection of 1,3- and 1,4-dilithiation. In this manner, phenanthrene (9) has been converted to 10 and 11. The crystal and molecular structures of these novel heterocycles have been determined.

## RESULT AND DISCUSSION

Initially we chose to investigate polyolithiation of naphthalene (4), the simplest PAH. Prior work reports monolithiation of 4 followed by functionalization [3,8], while preformed 1-lithionaphthalene (6) has been converted to 1,8-dilithionaphthalene (7) with butyllithium/TMEDA [3,8]. We find the reaction of naphthalene with 4 equivalents of butyllithium in TMEDA at 60° followed by elemental sulfur affords 8 in 51% yield. This represents the simplest means of preparing 8 [7] and could probably be extended to the preparation of other 1,8-disubstituted naphthalenes. The conversion to 8 implies that naphthalene can be directly dilithiated to 8 in a minimum of 51% yield.

Since triphenylene is regioselectively dilithiated to the 1,4-dilithio derivative 2 [1], it was of interest to examine the subsequent reaction with sulfur. Under the same conditions as above, 1 gives a 1:2 mixture of thiophene 3 and triphenyleno-[1,12-cde][1,2]dithiin (12). The dithiin could be separated by chromatography (silica gel/hexane) as light yellow crystals, mp 138–140°C. The mass spectrum and the symmetrical  $^1H$  and  $^{13}C$  NMR

\*To whom correspondence should be addressed.



SCHEME 1

spectra are consistent with structure **12**. Thus, 1,4-dilithioarenes react with S<sub>8</sub> to give both thiophenes and dithiins.

Since phenanthrene (**9**) has both bay (C<sub>4</sub>, C<sub>5</sub>) and peri (C<sub>9</sub>, C<sub>10</sub>, C<sub>1</sub>, C<sub>8</sub>) positions, polyolithiation is potentially more complicated [1,2]. In fact, prior deuterium exchange experiments indicate that both regions are dilithiated [2,9]. Treatment of **9** with butyllithium/TMEDA followed by S<sub>8</sub> gives a mixture of 45% dithiin **10**, 30% thiophene **13**, and 25% dithiole **11**. Column chromatography (hexane/silica gel) allowed separation of the yellow crystalline **10** and **13** and the orange crystalline **11**. The structure of **10** and **11** were assigned initially on the basis of their spectra. The assignment was con-

firmed by an X-ray diffraction study discussed subsequently. These products require the intermediacy of both dilithio derivatives **14** and **15**.

We have also prepared **11** using the Schleyer peri-directed lithiation procedure [3,8]. Lithiation of 9-bromophenanthrene with 1 equivalent of butyllithium/TMEDA at -30°C affords 9-lithiophenanthrene (**17**). Further reaction with 3 equivalents of butyllithium/TMEDA at 60°C followed by reaction with sulfur gives 52% of the dithiole **11**. Clearly, this is the method of choice for preparing **11**.

The probable course of the dilithiation of phenanthrene shown in Scheme 2 involves monolithiation at both bay (C<sub>4</sub>) and peri (C<sub>9</sub> and C<sub>1</sub>) positions. It is likely that bay and peri positions are most acidic, since they are adjacent to the ring fusion [9]. The dilithio products are then formed by the selective lithium directed lithiation to the adjacent peri or bay position to give **14** or **15**.

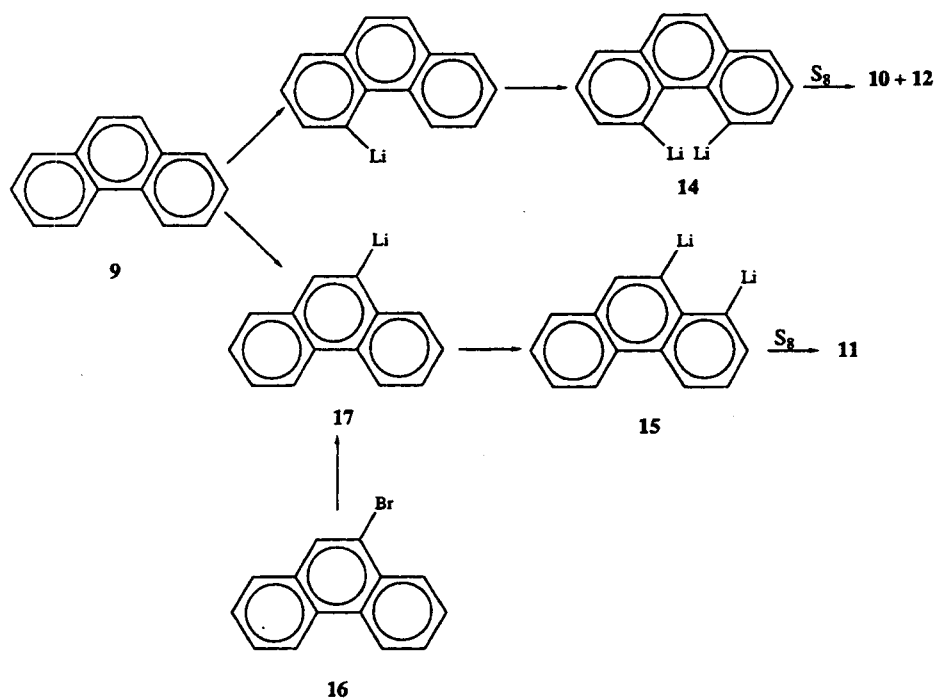
Dithiole **11** belongs to the class of peri-bridged naphthalene dichalcogenides which have interesting solid state structures [10]. Dithiin **10** contains an unusual 8π electron heterocycle [11] and is an example of a crowded 4,5-disubstituted phenanthrene [12]. Since it is of interest to examine their structures, we have determined crystal structures of **10** and **11** by X-ray diffraction [13].

## STRUCTURES

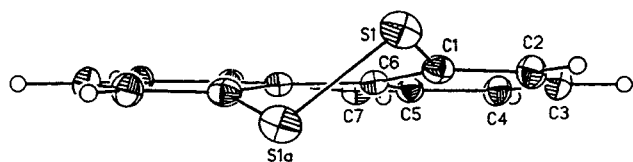
The molecular structure of dithiin **10** is illustrated in Figure 1, while Table 2 lists the final set of atomic coordinates. The molecule consists of a carbocyclic phenanthrene unit which is distorted from planarity by the 4,5-bridged disulfide group. The sulfur-substituted benzene rings are splayed away from each other so that the dihedral angle between their mean planes is 10.5(1)°. Interestingly, this distortion is nearly identical to that caused by the non-bonded F/F interaction found for 4,5-difluorophenanthrene [12].

The dithiin ring (C6C1S1S1aC1aC6a) is distinctly nonplanar, with a C<sub>2</sub> axis passing through the S1S1a and C6C6a bonds. However, the distortion from planarity is much greater in the disulfide than in the C<sub>4</sub> part of the ring. The torsional angle C1S1S1aC1a is 55.31(6)°, while the torsional angle C1C6C6aC1a is only 13.2(1)°. In comparison, the CSSC torsional angles in dithiins **18** (62°) [14] and **19** (50°) [15] are very similar, but the CCCC torsional angles of 54° for **18** [14] and 34° for **19** [15] are quite different. Consequently, the conformations of the three structurally characterized dithiins are quite different.

The bond distances and bond angles of **10** are similar to those found for analogous molecules. The C-C bond distances of **10** are insignificantly different from those of phenanthrene [16] (average difference ±0.011 Å). Similarly, the S-S bond of



SCHEME 2



**FIGURE 1** An ORTEP drawing of the molecular structure of phenanthro[4,5-cde][1,2]dithiin (**10**), showing the atom numbering scheme. Selected interatomic distances (Å) are angles (°) and as follows: S1-S1a, 2.0551(3); S1-C1, 1.768(1); C1-C6, 1.423(3); S1-C1-C6, 121.23(8); S1a-S1-C1, 98.98(3); and C1-C6-C6a, 124.2(1).

**10** (2.055 Å) compares with 2.056 Å for **18** [14] and 2.050 Å for **19** [15], while the CS bonds are 1.768 Å for **10**, 1.779 Å for **18** [14], and 1.757 Å for **19** [15].

The molecular structure of dithiole **11** is illustrated in Figure 2, while Table 3 lists the final positional values of the atoms. The molecule is completely planar within  $\pm 0.01$  Å. The bond lengths of the phenanthrene unit of **11** show no serious distortion from the corresponding bonds of phenanthrene [16] (average difference  $\pm 0.02$  Å). The S-C bond lengths (1.758, 1.768 Å) are somewhat shorter, while the S-S bond (2.088 Å) is somewhat longer than those of **10**. This is consistent with a greater electronic interaction of the S<sub>2</sub> unit in the dithiole.

The crystal packing diagram of **11**, shown in Figure 3, is of major interest. The molecules are inclined by 31.2° and are stacked along the *a* axis.

Parallel stacks form a herringbone pattern. The arrangement brings S1 of one molecule close (3.721(1) Å) to S2 of its neighbor in the stack so that there is a zig-zag chain of sulfur atoms: ...S2a-S1a...S2b-S1b...

The stacking arrangement of **11** is similar to that shown by many peri-bridged dichalcogeno naphthalenes, such as **20** [17], **21** [18], and **22** [19]. A number of compounds in this class form charge-transfer salts which show high electrical conductivity. Since molecular stacking of the type shown by **11** is necessary for conduction, further exploration of the chemistry of **11** seems warranted.

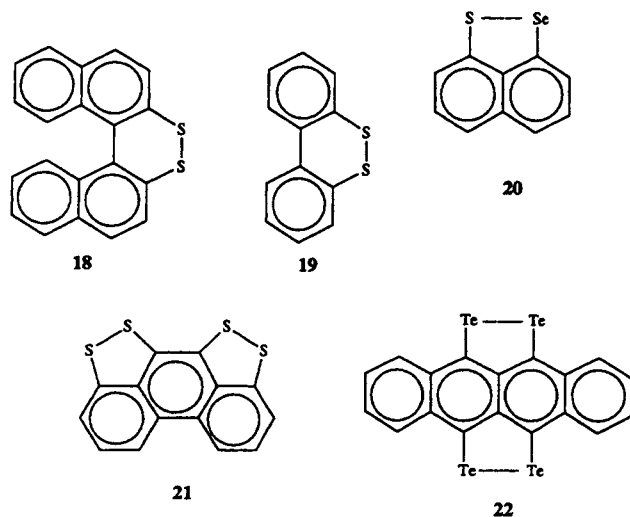


TABLE 1 Structure Determination Summary for 10 and 11

Crystal Data	10	11
Compound:	10	11
Empirical formula	C <sub>14</sub> H <sub>8</sub> S <sub>2</sub>	C <sub>14</sub> H <sub>8</sub> S <sub>2</sub>
Formula weight	240.340 amu	240.340 amu
Crystal color and habit	yellow rectangular blocks	orange rectangular needle
Crystal dimensions (mm)	0.20 × 0.30 × 0.32	0.42 × 0.20 × 0.22
Crystal system	monoclinic	orthorhombic
Space group	C2/c (#15)	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (#19)
Z	4	4
Unit cell dimensions from 25 reflections	(20.1° ≤ 2θ ≤ 32.0°)	(20° ≤ 2θ ≤ 35°)
a	13.537(3) Å	4.1507(5) Å
b	8.933(2) Å	14.436(3) Å
c	9.601(4) Å	16.972(3) Å
β	116.19(2)°	90.000°
Volume	1041.9(5) Å <sup>3</sup>	1017.0(2) Å <sup>3</sup>
Density (calcd.)	1.53 g cm <sup>-3</sup>	1.56 g cm <sup>-3</sup>
F(000)=	496 electrons	496 electrons
Linear absorption coefficient (μ)	4.52 cm <sup>-1</sup>	4.64 cm <sup>-1</sup>
<b>Data Collection</b>		
Diffractometer	Siemens R3 m/v, equipped with LT-2	same
Radiation type	Mo K <sub>α</sub> λ = 0.71073 Å, Lp corrected, graphite monochromator	same
Temperature	-95°C	-122°C
Scan type	θ/2θ scan	θ/2θ scan
2θ scan range	5-55°	5-55°
Octants used	+h, ±k, ±l (h: 0/18; k: -12/12; l: -13/13)	+h, +k, ±l (h: -1/6; k: -2/19; l: -23/23)
Scan rate	3.5-8.0° per minute, variable	3.5-7.0° per min., variable
Scan width	0.9° below K <sub>α1</sub> , to 0.9° above K <sub>α2</sub>	0.8° below K <sub>α1</sub> to 0.8° above K <sub>α2</sub>
Background/scan ratio	0.5	0.5
Standard reflections	3 measured every 97 reflections	3 measured every 97 reflections
	linear decay ~4%	random variation <4%
Number of data collected	5154	4074
Number of unique reflections	1214 R <sub>int.</sub> = 0.0223	2335, R <sub>int.</sub> = 0.0394
Absorption correction	none applied	empirical
R merge before/after correction		0.0423/0.0394
max./min. transmission		0.695/0.353
<b>Solution Refinement</b>		
System used	Siemens SHELXTL PLUS	same
	Vax Station 3500	same
Solution	direct methods	same
Refinement method	full-matrix least squares	same
Function minimized	Σw( F <sub>o</sub> - F <sub>c</sub>  ) <sup>2</sup>	same
Hydrogen atoms	individual isotropic refinement	same
Refined reflections	1197: (F <sub>o</sub> ) ≥ 2σ(F)	2141: (F <sub>o</sub> ) ≥ 3σ(F)
Number of parameters refined	89	179
Data/parameter ratio	13.4	12.0
R = Σ( F <sub>o</sub> - F <sub>c</sub>  )/Σ( F <sub>o</sub>  )	0.0299	0.0511
R <sub>w</sub> = [Σ(w F <sub>o</sub> - F <sub>c</sub> ) <sup>2</sup> /Σw(F <sub>o</sub> ) <sup>2</sup> ] <sup>1/2</sup>	0.0515(w <sup>-1</sup> = σ <sup>2</sup> (F <sub>o</sub> ) + 0.000666(F <sub>o</sub> ) <sup>2</sup> )	0.0622(w <sup>-1</sup> = σ <sup>2</sup> (F <sub>o</sub> ) + 0.001525(F <sub>o</sub> ) <sup>2</sup> )
GOF	1.75	1.18
Mean shift/error	<0.001	<0.001
Maximum shift/error	0.002	<0.001
Secondary extinction	no correction applied	6.5(6) × 10 <sup>-8</sup>
Residual electron density	+0.42/-0.27 e/Å <sup>3</sup>	+0.80/-0.71 e/Å <sup>3</sup>

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter, U(eq), defined as 1/3 Σ<sub>i</sub>Σ<sub>j</sub> · U<sub>ij</sub>a<sub>i</sub>\*a<sub>j</sub>\*a<sub>i</sub> · a<sub>j</sub>.

**TABLE 2** Positional Parameters and Isotropic Equivalent Thermal Parameters ( $\text{\AA}^2$ ) of **10**

Atom	X	Y	Z	U(eq)
S1	0.48583(3)	0.16073(3)	0.63575(4)	0.0242(2)
C1	0.4162(1)	0.3338(1)	0.5783(2)	0.0191(5)
C2	0.3299(1)	0.3408(1)	0.4306(2)	0.0241(5)
C3	0.2827(1)	0.4779(2)	0.3657(2)	0.0259(5)
C4	0.3234(1)	0.6074(2)	0.4483(2)	0.0224(5)
C5	0.41018(9)	0.6032(1)	0.6003(1)	0.0172(4)
C6	0.45650(9)	0.4644(1)	0.6709(1)	0.0157(4)
C7	0.4560(1)	0.7406(1)	0.6795(1)	0.0192(5)

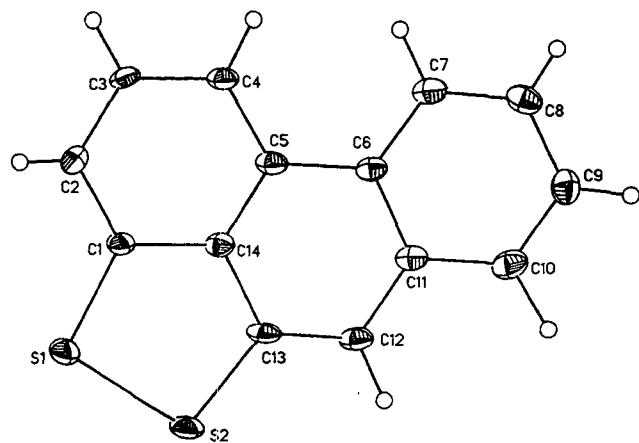
## EXPERIMENTAL

### General Remarks

All reactions were carried out under an atmosphere of nitrogen. Solvents were dried by using standard procedures. All starting materials are commercially available unless noted otherwise. The mass spectra were determined by using a VG-70-S spectrometer, while the NMR spectra were obtained using either a Bruker WH-360 or AM-300 spectrometer. These spectra were calibrated using signals from the solvents referenced to  $\text{Me}_4\text{Si}$ . The ultraviolet-visible spectra were recorded on a Shimadzu UV-2101 PC spectrophotometer. Melting points were taken on a Mel-Temp apparatus and are uncorrected.

### Naphtho[1,8-cd]-1,2-dithiole (**8**)

Naphthalene (0.77 g, 6 mmol) was stirred with 9.2 mL of hexane containing 24 mmol butyllithium and



**FIGURE 2** An ORTEP drawing of the molecular structure of phenanthro[1,10-cd]-1,2-dithiole (**11**), showing the atom numbering scheme. Selected interatomic distances ( $\text{\AA}$ ) and degrees ( $^\circ$ ) are as follows: S1-S2, 2.088(1); S1-C1, 1.758(3); S2-C13, 1.768(3); C1-C14, 1.405(4); C13-C14, 1.440(4); S1-S2-C13, 96.1(1); S1-C1-C14, 116.6(2); S2-S1-C1 95.1(1); S2-C13-C14, 114.4(2); and C1-C14-C13, 117.7(3).

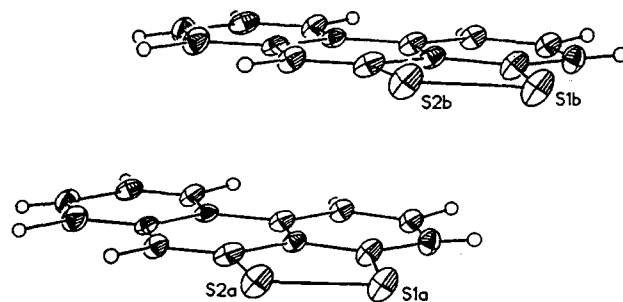
**TABLE 3** Positional Parameters and Isotropic Equivalent Thermal Parameters ( $\text{\AA}^2$ ) of **11**

Atom	X	Y	Z	U(eq)
S1	-0.1673(3)	0.42266(6)	0.03607(5)	0.0233(2)
S2	0.0574(3)	0.52445(6)	0.10407(5)	0.0223(2)
C1	-0.0885(9)	0.3318(2)	0.1023(2)	0.0187(9)
C2	-0.193(1)	0.2416(2)	0.0894(2)	0.0199(9)
C3	-0.1141(9)	0.1735(2)	0.1452(2)	0.0181(9)
C4	0.066(1)	0.1949(2)	0.2116(2)	0.0176(9)
C5	0.177(1)	0.2862(2)	0.2249(2)	0.0174(9)
C6	0.3721(9)	0.3135(2)	0.2921(2)	0.0155(8)
C7	0.470(1)	0.2508(2)	0.3511(2)	0.0204(9)
C8	0.658(1)	0.2786(3)	0.4127(2)	0.0216(9)
C9	0.7576(9)	0.3717(3)	0.4196(2)	0.022(1)
C10	0.664(1)	0.4345(2)	0.3635(2)	0.0233(9)
C11	0.4709(9)	0.4078(2)	0.2986(2)	0.0164(8)
C12	0.3778(9)	0.4745(2)	0.2402(2)	0.0193(9)
C13	0.197(1)	0.4487(2)	0.1786(2)	0.0182(9)
C14	0.0946(9)	0.3540(2)	0.1692(2)	0.0157(9)

3.6 mL (12 mmol) of TMEDA at  $60^\circ\text{C}$  for 3 hours. The resulting dark brown suspension of the lithio derivatives was allowed to cool to  $-78^\circ\text{C}$  and was diluted with 25 mL of THF. Resublimed sulfur (1.6 g, 50 mmol) was added to the suspension. The resulting orange mixture was warmed to  $25^\circ\text{C}$  and allowed to stir for 12 hours. It was then washed with water and the organic layer was separated and dried over anhydrous  $\text{MgSO}_4$ . Removal of the solvent left 1.0 g of dark brown oil. Purification by column chromatography (silica gel-hexane) gave 0.58 g (51%) red-brown crystals, mp  $114\text{--}5^\circ\text{C}$  (lit.  $116^\circ\text{C}$ ) [**7a**].

### Triphenyleno[1,12-cde][1,2]dithiin (**12**)

Triphenylene (0.46 g, 2 mmol) was stirred with 3.2 mL of hexane containing 8 mmol butyllithium and 1.2 mL (8 mmol) of TMEDA at  $60^\circ\text{C}$  for 3 hours. The brown suspension containing the lithio derivatives was cooled to  $-78^\circ\text{C}$  and diluted with 25 mL of THF. Resublimed sulfur (0.5 g, 16 mmol) was



**FIGURE 3** Drawing of 2 molecules of **11**, showing the close S1a-S2b distance (3.721(1)  $\text{\AA}$ ). The molecules of **11** are inclined by  $31.2^\circ$  to the  $a$  axis.

added to the suspension. The resulting orange mixture was warmed to 25°C and allowed to stir for 12 hours. It was added to water, and the organic layer was separated and dried over anhydrous MgSO<sub>4</sub>. Removal of the solvent left 0.5 g of a dark brown oil. It was found to be a 2:1 mixture of the dithiin **12** and triphenyleno[1,12-bcd]thiophene **3** [1] by <sup>1</sup>H NMR spectroscopy. The title compound was isolated by column chromatography (silica gel-hexane) as yellow crystals, mp 138–40°C. <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>): δ 7.57 (t, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 7.3 Hz, 2H), 7.66–7.70 (sym m, 2H), 8.56 (d, *J* = 8.2 Hz, 2H), 8.57–8.62 (sym m, 2H). <sup>13</sup>C NMR (90.6 MHz, CDCl<sub>3</sub>): δ 123.34, 123.38, 126.9, 127.3, 127.4, 127.8, 129.4, 130.1, 130.9. MS (EI) [*m/z* (intensity)]: 290 (100, M<sup>+</sup> for C<sub>18</sub>H<sub>10</sub>S<sub>2</sub>), 258 (69, M<sup>+</sup>-S), 226 (2, M<sup>+</sup>-2S). MS exact mass (EI): calcd for C<sub>18</sub>H<sub>10</sub>S<sub>2</sub>: 290.0224; found: 290.0234. UV(CH<sub>3</sub>CN) λ<sub>max</sub> nm (intensity): 208 (21,300), 225 (14,900), 267 (26,200), 299 (sh, 9000).

#### Phenanthro[4,5-cde][1,2]dithiin (**10**)

Phenanthrene (0.9 g, 5 mmol) was stirred with 5.8 mL of hexane containing 20 mmol butyllithium and 3.0 mL (20 mmol) of TMEDA at 60°C for 3 hours. The brown suspension containing the lithio derivatives was cooled to -78°C and diluted with 25 mL of THF. Sulfur (1.28 g, 40 mmol) was added to the suspension. The resulting orange mixture was warmed to 25°C and allowed to stir for 12 hours. It was added to water and the organic layer was separated and dried over anhydrous MgSO<sub>4</sub>. Removal of the solvent left 1.1 g of dark brown oil. It was found to be a mixture of 45% phenanthro[4,5-cde][1,2]dithiin (**10**), 30% phenanthro[4,5-bcd]thiophene (**13**), and 25% phenanthro[1,10-cd]-1,2-dithiole (**11**) by <sup>1</sup>H NMR spectroscopy. The products were separated by column chromatography (silica gel-hexane). The first pale yellow fraction was **13** [1], the second orange fraction was **11**, and the third pale yellow fraction was the title compound **10**. Removal of hexane from the third fraction gave 0.3 g (25%) of golden yellow needles, mp 128–129°C. <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>): δ 7.54 (t, *J* = 7.6 Hz, 2H), 7.61 (dd, *J* = 7.3, 1.4 Hz, 2H), 7.77 (s, 2H), 7.80 (dd, *J* = 7.9, 1.4 Hz, 2H). <sup>13</sup>C NMR (90.6 MHz, DMSO-d<sub>6</sub>): δ 126.7, 127.0, 127.6, 127.8, 128.0, 129.2, 132.5. MS (EI) [*m/z* (intensity)]: 240 (100, M<sup>+</sup> for C<sub>14</sub>H<sub>8</sub>S<sub>2</sub>), 208 (92, M<sup>+</sup>-S). MS exact mass (EI): calcd for C<sub>14</sub>H<sub>8</sub>S<sub>2</sub>: 240.0067; found: 240.0057. UV (CH<sub>3</sub>CN) λ<sub>max</sub> nm (intensity): 213 (45,100), 235 (32,000), 271 (26,000), 309 (14,300), 363 (2350), 382 (2250).

#### Phenanthro[1,10-cd]-1,2-dithiole (**11**)

A hexane solution (2.0 mL) containing 5 mmol *n*-BuLi and 0.75 mL (5 mmol) of TMEDA was added to a suspension of 9-bromophenanthrene (1.28 g, 5

mmol) in 25 mL hexane at -30°C. The yellow suspension was stirred for 1 hour at -30°C and then allowed to warm to 25°C. An aliquot was removed and added to rapidly stirred D<sub>2</sub>O. The organic layer was separated. Analysis by mass spectrometry showed *m/z* = 179 (100, M<sup>+</sup> for C<sub>14</sub>H<sub>9</sub>D). In the meantime, 15 mmol butyllithium in 6.0 mL of hexane and 2.25 mL (15 mmol) of TMEDA was added to the bulk of the material, and the resulting mixture was allowed to stir for 3 hours at 60°C. The resultant suspension containing the lithio derivatives was cooled to 25°C, diluted with 25 mL of THF, and cooled to -78°C. Resublimed sulfur (1.28 g, 40 mmol) was added to the reaction mixture and allowed to stir for 12 hours. It was added to an excess of water and the organic layer was separated and dried over anhydrous MgSO<sub>4</sub>. Removal of the solvent left 1.1 g of a dark brown oil. The product was isolated by flash chromatography (silica gel-hexane). On removal of the solvent, the relatively polar dark yellow fraction gave 0.6 g (52%) of the dithiole, which was recrystallized from CHCl<sub>3</sub> at -20°C to give bright orange needles, mp 129–131°C. <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>): δ 7.37 (d, *J* = 7.7 Hz, 1H), 7.42 (s, 1H), 7.49–7.54 (m, 3H), 7.65 (d, *J* = 7.0 Hz, 1H), 8.19 (d, *J* = 7.1 Hz, 1H), 8.44 (d, *J* = 7.0 Hz, 1H). <sup>13</sup>C NMR (90.6 MHz, CDCl<sub>3</sub>): δ 115.1, 118.0, 118.2, 122.8, 125.3, 127.0, 127.1, 127.7, 128.3, 132.6, 132.7, 133.5, 141.7, 143.6. MS (EI) [*m/z* (intensity)]: 240 (100, M<sup>+</sup> for C<sub>14</sub>H<sub>8</sub>S<sub>2</sub>), 208 (11, M<sup>+</sup>-S), 176 (7, M<sup>+</sup>-2S). MS exact mass (EI): calcd for C<sub>14</sub>H<sub>8</sub>S<sub>2</sub>: 240.0067; found: 240.0055. UV (CH<sub>3</sub>CN) λ<sub>max</sub> nm (intensity): 216 (36,000), 232 (sh, 22,300), 267 (25,500), 275 (sh, 25,000), 288 (sh, 18,500), 356 (12,600), 397 (sh 3120).

#### X-ray Structure Determination

Crystals of **10** and **11** suitable for X-ray diffraction were obtained by recrystallization from hexane and chloroform, respectively. Crystallographic data are collected in Table 1. Tables 2 and 3 give the positional values for **10** and **11**, respectively. Lists of observed and calculated structure factors are available from AJA on request.

#### ACKNOWLEDGMENT

We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society for partial support of this research.

#### REFERENCES

- [1] (a) A. J. Ashe, III, J. W. Kampf, P. M. Savla, *J. Org. Chem.*, **55**, 1990, 5558; (b) A. J. Ashe, III, P. M. Savla, *J. Organomet. Chem.*, **461**, 1993, 1.
- [2] W. Neugebauer, A. J. Kos, P. v. R. Schleyer, *J. Organomet. Chem.*, **228**, 1982, 107.
- [3] W. Neugebauer, T. Clark, P. v. R. Schleyer, *Chem.*

- Ber.*, 116, 1983, 3283; W. Bauer, T. Clark, P. v. R. Schleyer, *J. Am. Chem. Soc.*, 109, 1987, 970; W. Bauer, M. Feigel, G. Müller, P. v. R. Schleyer, *J. Am. Chem. Soc.*, 110, 1988, 6033.
- [4] (a) A. J. Kos, P. v. R. Schleyer, *J. Am. Chem. Soc.*, 102, 1980, 7928; (b) A. J. Ashe, III, L. L. Lohr, S. M. Al-Taweel, *Organometallics*, 10, 1991, 2424.
- [5] P. v. R. Schleyer, *Pure Appl. Chem.*, 55, 1983, 355; 56, 1984, 151.
- [6] (a) U. Schubert, W. Neugebauer, P. v. R. Schleyer, *J. Chem. Soc., Chem. Commun.*, 1982, 1184; (b) W. Bauer, M. Feigel, G. Müller, P. v. R. Schleyer, *J. Am. Chem. Soc.*, 110, 1988, 6033; (c) A. J. Ashe, III, J. W. Kampf, P. M. Savla, *Organometallics*, 12, 1993, 3350.
- [7] (a) J. Meinwald, D. Dauplaise, F. Wudl, J. J. Hauser, *J. Am. Chem. Soc.*, 99, 1977, 255. (b) R. L. Letsinger, J. H. Gilpin, W. J. Vullo, *J. Org. Chem.*, 27, 1962, 672.
- [8] L. Brandsma, H. Verkruisje: *Preparative Polar Organometallic Chemistry*, Springer Verlag, Berlin, vol. 1, p. 195 (1987).
- [9] (a) A. Streitweiser, Jr., G. R. Ziegler, P. C. Mowery, A. Lewis, R. G. Lawler, *J. Am. Chem. Soc.*, 90, 1968, 1357; (b) A. Streitweiser, Jr., R. G. Lawler, *J. Am. Chem. Soc.*, 87, 1965, 5388.
- [10] D. Dauplaise, J. Meinwald, J. C. Scott, H. Temkin, J. Clardy, *Ann. N.Y. Acad. Sci.*, 313, 1978, 382.
- [11] F. F. Freeman, D. S. H. L. Kim, E. Rodriguez, *Sulfur Rep.*, 9, 1989, 207.
- [12] R. Cosmo, T. W. Hambley, S. Sternhell, *J. Org. Chem.*, 52, 1987, 3119.
- [13] Full details of the crystallographic study of **10** and **11** have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB21EN, UK.
- [14] R. Kuroda, S. F. Mason, *Tetrahedron*, 37, 1981, 1995.
- [15] I. Bernal, J. Ricci, *Acta Crystallogr.*, 21, 1966, A104.
- [16] M. I. Kay, Y. Okaya, D. E. Cox, *Acta Crystallogr. Sect. B*, B27, 1971, 26.
- [17] J. Meinwald, D. Dauplaise, J. Clardy, *J. Am. Chem. Soc.*, 99, 1977, 7743.
- [18] K. Takimiya, T. Otsubo, A. Ohnishi, F. Ogura, Y. Aso, *J. Chem. Soc., Chem. Commun.*, 1992, 278.
- [19] D. J. Sandman, J. C. Stark, B. M. Foxman, *Organometallics*, 1, 1982, 739.