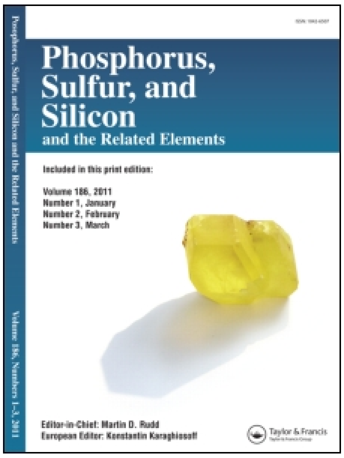

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# ON THE VARIOUS MODES OF INTERACTION OF SULFUR WITH PHENYLATED DIYNES

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# ON THE VARIOUS MODES OF INTERACTION OF SULFUR WITH PHENYLATED DIYNES

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*(Received January 26, 1993)*

The reaction of elemental sulfur and five diynes of general formula PhC≡C(G)$_n$C≡CR has been studied. While 1-(1-propynyl)-2-phenylethynylbenzene **1b** reacted at 120°C to give solely 6-methylbenz[*b*]indeno[2,1-*d*]-thiopyran **2b**, 1,1′-(1,2-phenylene)bis(3-phenyl-2-propyn-1-one) **4** and 1,8-bis(phenylethynyl)naphthalene **5** yielded the sulfides 11,11′-thiobis-(6-phenyl-5,12-naphthacenedione) **9** and 12,12′-thiobis(7-phenylbenzo[*k*]-fluoranthene) **13**, respectively, as the major products. Diyne **5** gave also a small amount of bis(7-phenylbenzo[*k*]fluoranthene-12-yl)disulfide **14**. 3,3′-Oxybis(1-phenyl-1-propyne) **6** did not react in the absence of a metallic additive, but yielded 4,6-diphenyl-1*H*,3*H*-thieno[3,4-*c*]furan **15** in the presence of equimolar quantities of $RhCl_3 \cdot 3H_2O$ and Aliquat-336. The reaction of the conjugated diyne 1,1′-(1,3-butadiyne-1,4-diyl)bisbenzene **7** with sulfur afforded 3,6-diphenyl[1,2]dithiolo[4,3-*c*]-1,2-dithiole **16**.

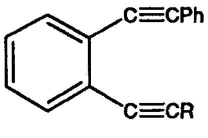
*Key words:* Sulfur addition to diynes; benz[*b*]indeno[2,1-*d*]thiopyran; [1,2]dithiolo[4,3-*c*]-1,2-dithiole; polycyclic sulfides; polycyclic disulfides.

## INTRODUCTION

Although a vast amount of work has been done in the field of organosulfur compounds, surprisingly little research has been published on the addition of elemental sulfur to carbon-carbon triple bonds.[1] Recently,[2] we have shown that sulfur adds to 1,2-bis(phenylethynyl)benzene **1a** in the presence of the $RhCl_3$-Aliquat-336 catalyst[3] to give compounds **2a** and **3a**. Since the reaction was found to take place also in the absence of the metallic catalyst, we find it interesting to investigate the interaction of the chalcogen also with some other diacetylenes of general formula RC≡C(G)$_n$C≡CR′. As representative diynes compounds **1b**, **4**, **5**, **6** and **7** were chosen.

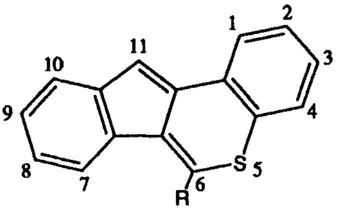
## RESULTS AND DISCUSSION

1-(1-Propynyl)-2-phenylethynylbenzene **1b**, obtained by CuI-$PdCl_2(PPh_3)_2$-catalyzed propynylation of 1-bromo-2-(phenylethynyl)benzene was found to react slowly

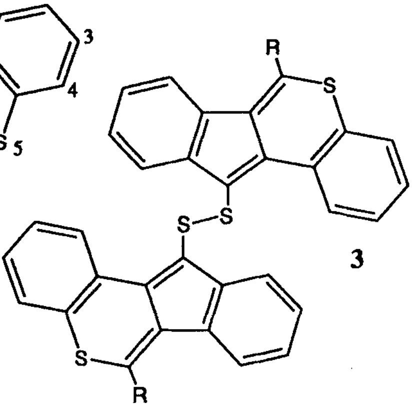


**1**

**a**, R = Ph
**b**, R = Me



**2**



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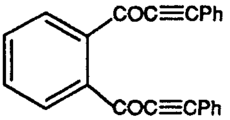
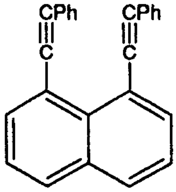


**4**



**5**

$O(CH_2C{\equiv}CPh)_2$

**6**

$(PhC{\equiv}C)_2$

**7**

with sulfur in a similar fashion to the diphenyl analog **1a** (though in a more selective manner), and to yield solely 6-methylbenz[*b*]indeno[2,1-*d*]thiopyran **2b**. The structure of the product was established by elemental analysis, by the NMR and mass spectra, as well as by the electronic spectrum (Table I), which resembles closely that of **1a** (for which X-ray diffraction analysis was carried out[2]), and that of the parent compound, benz[*b*]indeno[2,1-*d*]thiopyran.[4] It is notable that although **1a** forms **2a** only under exclusion of air and gives 3-benzoyl-2-phenyl-1*H*-inden-1-one in the presence of oxygen,[2] **2b** could be obtained from **1b** both in air and under argon atmosphere.

Since **2a** and **2b** can formally be regarded as the products of sulfur incorporation into the rearranged starting materials (i.e., 5-phenyl- and 5-methylindeno[2,1-*a*]indene, respectively[5]), a similar incorporation process was expected to occur also during the reaction of sulfur and 1,1′-(1,2-phenylene)bis(3-phenyl-2-propyn-1-one) **4** (which isomerizes under thermal conditions to 6-phenyl-5,12-naphthacenedione **8**[6]). In fact, no sulfur heterocyclic resulted but sulfide **9** was formed instead. The structure of **9** was deduced from the elemental analysis, the $^1$H- and $^{13}$C-NMR spectra and from the UV spectrum which resembles that of **8** (see Table I). Although **4** rearranges rapidly to **8** already at 50°C in the absence of sulfur, it is converted into **9** in the presence of the chalcogen even at 70–80°C (see Experimental Section). It should be recalled that when **4** was reacted with sulfur in the presence of an equimolar amount of $RhCl(PPh_3)_3$, 1,3-diphenyl-4,9-naphtho[2,3-*c*]thiophenedione **10** rather than a sulfur bridged dimer was obtained.[7]

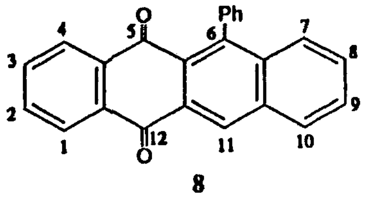
Also, 1,8-bis(phenylethynyl)naphthalene **5** (which rearranges thermally to 7-phenylbenzo[*k*]fluoranthene **11**[8]) failed to give any heterocyclic compounds, in spite of the fact that its complex with $RhCl(PPh_3)_3$ yielded 7,9-diphenylacenaphtho[1,2-

TABLE I

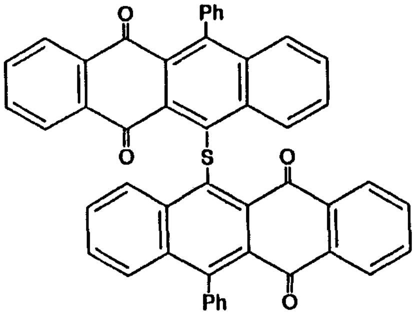
Electronic spectra of compounds **2a**, **2b**, **8**, **9**, **13** and **14**

| | Solvent | $\lambda_{max}$[nm][a] (log $\epsilon$) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **2a**[2] | *n*-heptane | 247 | 280(infl.) | 291 | 315 | 337 | 344 | 356 (infl.) | 365 | 436 |
| | | (4.41) | (4.34) | (4.62) | (4.20) | (4.14) | (4.15) | (4.04) | (3.98) | (3.73) |
| **2b** | *n*-heptane | 250 | 281(infl.) | 290 | 314 | | 344 | 358 | 363 | 428 |
| | | (4.32) | (4.55) | (4.72) | (4.14) | | (4.07) | (3.99) | (3.97) | (3.61) |
| **8** | EtOH | 240 | 273(infl.) | 284 | 292 | 339(infl.) | 391 | | | |
| | | (4.55) | (4.34) | (4.35) | (4.36) | (3.43) | (3.64) | | | |
| **9** | EtOH | 238(infl.) | 262 | 291(infl.) | 298 | 338(infl.) | 392 | | | |
| | | (4.32) | (4.48) | (4.18) | (4.21) | (3.61) | (3.54) | | | |
| **13** | cyclohexane | 272 | 303(infl.) | 312 | 340 | 360 | 372 | 394 | 418 | |
| | | (4.19) | (409) | (4.23) | (3.60) | (3.57) | (3.53) | 3.67 | (3.72) | |
| **14** | cyclohexane | 274 | 303(infl.) | 316 | | | 372 | 392 | 418 | |
| | | (4.88) | (4.42) | (4.49) | | | (3.93) | (3.95) | (3.90) | |

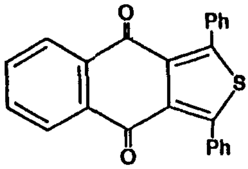
a) Infl.: inflection point.



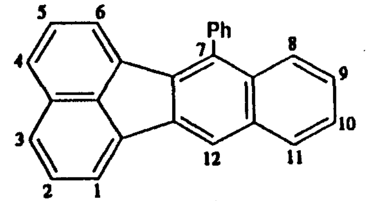
**8**



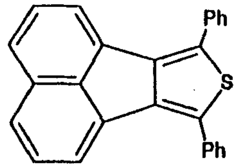
**9**



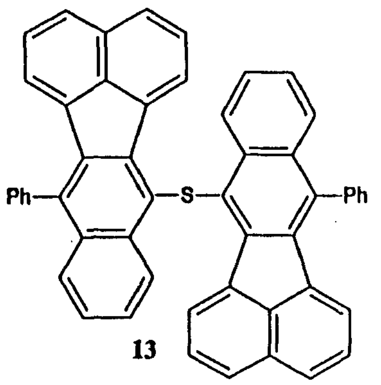
**10**



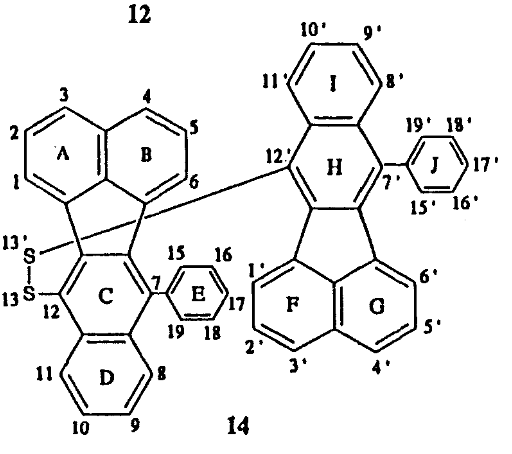
**11**



**12**



**13**



**14**

*c*]thiophene **12**.[7] Under our experimental conditions, **5** and $S_8$ formed 64% of the sulfide 12,12′-thiobis(7-phenylbenzo[*k*]fluoranthene) **13** accompanied by 9.5% of disulfide **14** and just <1% of **11**. The structure of compound **14** was unequivocally determined by X-ray diffraction analysis (see Figure 1).[9] The structure of **13** was deduced from the elemental analysis, from the mass spectrum, the NMR studies, and from the electronic spectrum which resembles that of **14** (see Table I).

Some interesting features of the X-ray structure of **14** are noteworthy. The stereoscopic view[9] shows that in the crystal the two benzo[*k*]fluoranthene moieties form two disulfide-bound non-parallel planes with a dihedral angle of 157° between the planes. The phenyl groups E and J that are connected to C7 and to C7′ are twisted, so that the dihedral angles between E and plane ABC, and between J and

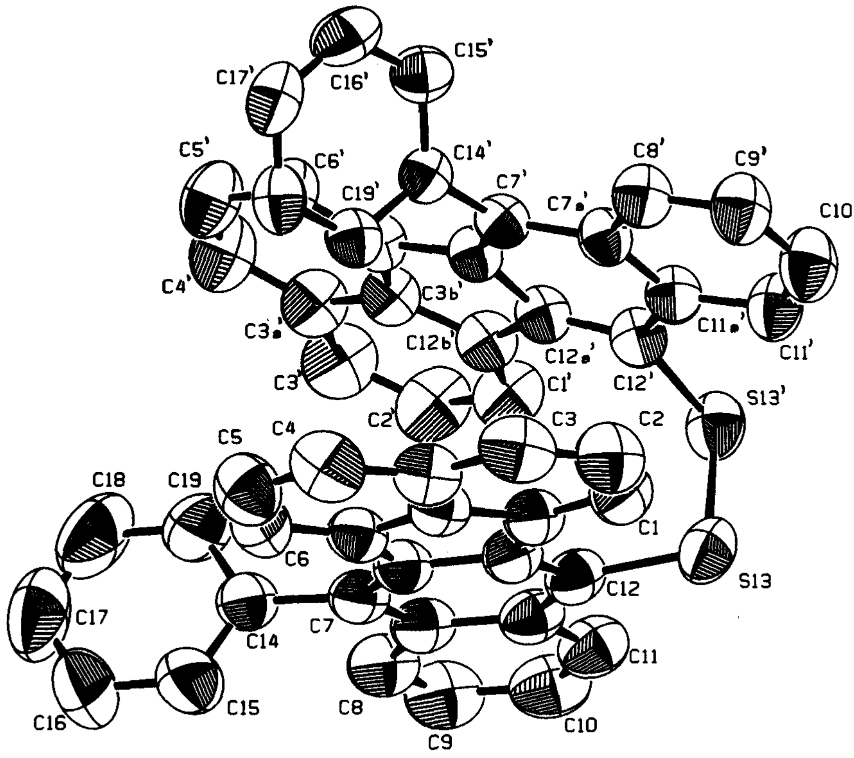
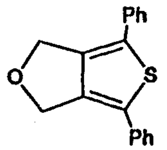


FIGURE 1 ORTEP drawing of **14**.

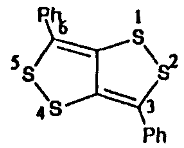
FGH are 76.5 and 75°, respectively. Ring E forms a right angle with plane FGHI and one of its sides is in close proximity to the atoms of ring F. The distances C19–C3a′ and C19–C4′ are 3.746(4) and 3.918(4) Å, respectively. Ring J forms an angle of 114° with plane ABC of the second benzo[*k*]fluoranthene moiety, and C19′ is even closer to ring A than C19 to ring F. The respective distances between C19′ and C3a, C3b, C4, C5, C6 and C6a are 3.648(3), 3.767(3), 3.686(3), 3.882(4), 3.989(3) and 3.972(3) Å, respectively. We assume that these structural features of **14** are exhibited also in solution, although the phenyl rings E and J can then rotate freely. It seems that due to the free rotation, several $^1$H-NMR peaks broaden. This broadening is particularly pronounced in the low field signals of the more hindered protons (see Experimental Section).

In contrast to the above diynes, 3,3′-oxybis(1-phenyl-1-propyne) **6**[10] did not react with elemental sulfur in the absence of a metallic additive. In the presence of a stoichiometric amount of the $RhCl_3$-Aliquat-336 ion pair, however, the diyne and sulfur reacted to give 4,6-diphenyl-1*H*,3*H*-thieno[3,4-*c*]furan **15**. Since **15** was reported to be formed also by interaction of eqimolar quantities of **6**, $S_8$ and $RhCl(PPh_3)_3$, it can be assumed that the diyne gives initially a complex of similar structure to that formed from **6** and the Wilkinson complex, and in a second step the rhodium atom is replaced by sulfur.[10]

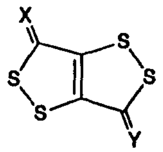
As an example for a conjugated phenylated diyne we chose 1,1′-(1,3-butadiyne-



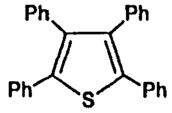
**15**



**16**



**17**



**18**

1,4-diyl)bisbenzene **7**.[11] Unlike the other acetylenes it reacted to give a compound with four sulfur atoms, i.e. 3,6-diphenyl[1,2]dithiolo[4,3-*c*]-1,2-dithiole **16**. Thus, the addition of sulfur to the conjugated diacetylenes is a most facile route to this bicyclic system. To the best of our knowledge the only stable [1,2]dithiolo[4,3-*c*]-1,2-dithiole derivatives that have been isolated so far, are of a higher oxidation state of general formula **17**.[12,13] Since **16** separates as large red crystals, its structure could readily be established by X-ray diffraction analysis.[9] The ORTEP drawing shown as Figure 2 reveals that **16** consists of two fused five-membered rings with an inversion center in the middle of bond C3a–C6a. The observed bond lengths of 1.439(8) Å for C3a–C6a and 1.362(5) Å for both C3–C3a and C6–C6a clearly indicate the locations of the single and double C—C bonds in the molecule.

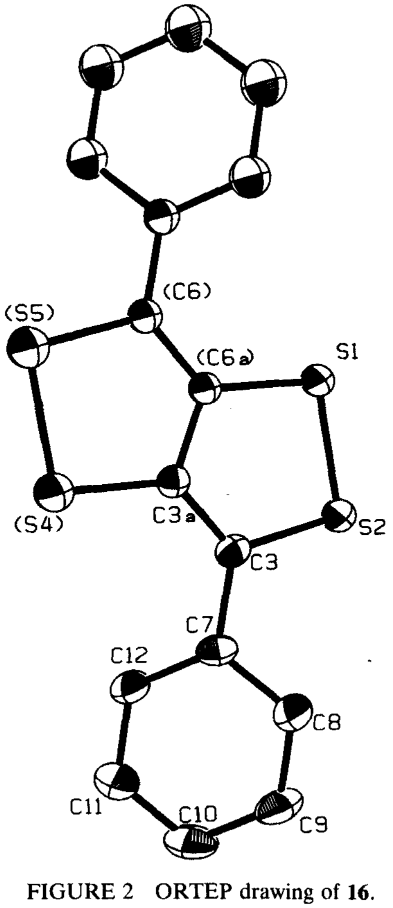


FIGURE 2 ORTEP drawing of **16**.

Finally, for comparison we examined the mode of interaction of $S_8$ with a monoalkyne. As a representative reagent we chose diphenylacetylene. Its reaction was slower than that of the diynes. The only isolable product was the well known tetraphenylthiophene **18**. It should be recalled that although **17** has not yet been prepared from PhC≡CPh, some other thiophenes have been synthesized from acetylenes and sulfur.[14]

The high selectivity in the interaction of sulfur with diynes is surprising since the addition of the chalcogen to C—C triple bonds is considered to give highly reactive thiirenes that may react with additional alkyne molecules to give thiophene derivatives,[15] but can equally well undergo fragmentation and form a variety of secondary products.[16]

## EXPERIMENTAL

*General Data.* Melting points (not corrected) were obtained on a Thomas-Hoover capillary melting point apparatus. IR and UV spectra were taken on a Perkin-Elmer Model 457 and a UVICON 860 instrument, respectively. $^1$H- and $^{13}$C-NMR were measured on Bruker WP 200 SY and AMX 400 spectrometers. MS were recorded on a Varian MAT-311 mass spectrometer.

*1-(1-Propynyl)-2-(phenylethynyl)benzene,* **1b**. A stream of propyne was bubbled through a solution of 7.71 g (30 mmol) of 1-bromo-2-phenylethynyl-benzene,[17] 0.42 g (0.6 mmol) of $PdCl_2(PPh_3)_2$ and 57 mg (0.3 meq) of $Cu_2I_2$ in 100 ml of dry $Et_3N$ at 60°C. After 6 h, when all the bromide reacted, the amine was evaporated and 200 ml of ether was added. The ammonium salt was filtered off and washed with ether. The filtrate was washed successively with 10% aq. HCl, water, 5% aq. $NaHCO_3$ and again with water. The dried etheral solution was evaporated to dryness and the residue was chromatographed on silica gel using a 1:19 ether-hexane mixture as eluent. Pale yellow oil; yield 4.20 g (65%). IR (neat): $\tilde{\upsilon}$ 2240, 2225 cm$^{-1}$ (C≡C). $^1$H-NMR ($CDCl_3$, 200 MHz): $\delta$ = 2.165 (s, 3H, $CH_3$), 7.229–7.594 (m, 9H, ArH). EI MS (70 eV, 25°C): m/z (%) 216 (100) [$M\cdot^+$], 215 (75) [$C_{17}H_{11}^+$], 213 (24) [$C_{17}H_9^+$], 189 (9) [$C_{15}H_9^+$].

$C_{17}H_{12}$(216.3). Calc.: C 94.40; H 5.59. Found: C 94.09; H 5.69%.

*General Procedure for the Reaction of Diynes with Sulfur.* A stirred mixture of 0.5 mmol of the diyne, 80 mg (2.5 mmol) of sulfur and 2 ml of an appropriate solvent was heated until the desired conversion was achieved. The crude product was separated by column chromatography using ether hexane mixtures as eluent.

*6-Methylbenz[b]indeno[2,1-d]thiopyran,* **2b**. Obtained in 22% yield by interaction of sulfur and **1b** in 1,1,2,2-tetrachloroethane at 120°C for 40 h. $R_f$ (ether/hexane 1:19) = 0.49; pale orange crystals, mp 120–122°C (from hexane). $^1$H-NMR ($CDCl_3$, 200 MHz): $\delta$ = 2.253 (s, 3H, $CH_3$), 7.345–7.759 (m, 7H), 8.111 (d, $J$ = 7.8 Hz, 1H), 8.303 (dd, $J_0$ = 8.1 Hz, $J_m$ = 1.3 Hz, 1H). $^{13}$C{$^1$H}-NMR ($CDCl_3$, 100 Hz): $\delta$ = 21.61, 114.49, 120,39, 122.99, 123.07, 125.35, 125.38, 126.24, 126.37, 127.25, 128.17, 129.14, 129.16, 131.19, 132.51, 138.10, 141.66. EI MS (70 eV, 80°C): m/z (%) = 248 (72) [$M\cdot^+$], 247 (14) [$C_{17}H_{11}S^+$], 223 (40) [$C_{15}H_{11}S^+$], 216 (100) [$C_{17}H_{12}\cdot^+$], 215 (83) [$C_{17}H_{11}^+$], 213 (25) [$C_{17}H_9^+$].

$C_{17}H_{12}S$ (248.3). Calc.: C 82.22; H 4.87; S 12.91. Found: C 82.01; H 4.60; S 12.73%.

*6-Phenyl-5,12-naphthacenedione,* **8**[7] *and 11,11'-thiobis(6-phenyl-5,12-naphthacenedione),* **9**. Obtained in 27 and 55% yield, respectively, when 1,1'-(1,2-phenylene)bis(3-phenyl-2-propyn-1-one), **4**[7] was allowed to react with sulfur for 48 h either in boiling chloroform or benzene. Separation of the products on silica gel was accomplished by a 2:8 mixture of ether/hexane followed by a 1:1 mixture of the same solvents ($R_f$ = 0.31 and 0.39, respectively). **9**: orange crystals. mp 170–172°C (dec.) (from $Et_2O$). $^1$H-NMR ($CDCl_3$, 200 MHz): $\delta$ = 7.086–7.110 (m, 4H, 3'-H, 5'-H), 7.361–7.647 (m, 16H), 7.816–7.839 (m, 2H), 7.910–7.931 (m, 2H), 8.713 (d, $J$ = 8.5 Hz, 2H, 1- or 4-H). $^{13}$C{$^1$H}-NMR ($CDCl_3$, 100 MHz): $\delta$ = 126.18, 126.79, 126.87, 127.26, 127.49, 128.28, 128.52, 128.99, 129.41, 129.42, 133.44, 133.49, 133.68, 134.21, 134.77, 135.02, 135.34, 139.51, 142.74, 143.30, 183.05, 184.73; EI MS (70 eV, 280°C): m/z (%) = 698 (34) [$M\cdot^+$], 697 (63) [$C_{48}H_{24}O_4S\cdot^+$], 366 (48) [$C_{24}H_{14}O_2S\cdot^+$], 365 (100) [$C_{24}H_{13}O_2S^+$], 334 (16) [$C_{24}H_{14}O_2\cdot^+$], 333 (29) [$C_{24}H_{13}O_2^+$].

$C_{48}H_{26}O_4S$ (698.8). Calc.: C 82.50; H 3.75; S 4.59. Found: C 82.26; H 4.04; S 4.14%.

*7-Phenylbenzo[k]fluoranthene*, **11**[8] *12,12'-thiobis(7-phenylbenzo[k]fluoranthene)*, **13** *and bis(7-phenylbenzo[k]fluoranthene-12-yl)disulfide*, **14**. Formed in <1, 64, and 9.5% yields, respectively by interaction of sulfur and 1,8-bis-phenylethynyl)naphthalene **5** in 1,1,2,2-tetrachloroethane at 120°C for 44 h. The products were separated by chromatography on silica gel with a 1:19 mixture of ether-hexane as eluent. The corresponding $R_f$ values for **11**, **13** and **14** were 0.52, 0.36 and 0.27.

**13**: Yellow crystals, mp 254–256°C (from $Et_2O$). $^1$H-NMR ($CDCl_3$, 200 MHz): $\delta$ = 6.596 (d, $J$ = 7.1 Hz, 2H), 6.964–7.967 (m, 24H), 8.578 (d, $J$ = 8.6 Hz, 2H), 9.562 (d, $J$ = 7.2 Hz, 2H). $^{13}$C{$^1$H}-NMR ($CDCl_3$, 100 MHz): $\delta$ = 122.28, 125.94, 126.11, 126.23, 126.29, 126.35, 126.58, 127.07, 127.26, 127.85, 128.06, 128.38, 128.97, 129.22, 130.30, 133.61, 134.71, 135.42, 135.85, 136.20, 136.42, 136.81, 138.53, 139.47. EI MS (70 eV, 280°C) m/z (%) 686 (16) $[M^{\cdot +}]$, 685 (41) $[C_{52}H_{29}S^+]$, 360 (100) $[C_{26}H_{16}S^{\cdot +}]$, 359 (60) $[C_{26}H_{15}S^+]$, 328 (17) $[C_{26}H_{16}^{\cdot +}]$, 327 (7) $[C_{26}H^+_{15}]$, 326 (39) $[C_{26}H_{14}^{\cdot +}]$.

$C_{52}H_{30}S$ (686.9). Calc.: C 90.93; H 4.40; S 4.67; Found: C 90.63; H 4.20; S 4.88%.

**14**: Yellow crystals, mp 231–233°C (from hexane). $^1$H-NMR ($CDCl_3$, 200 MHz): $\delta$ = 6.100 (d, $J$ = 7.7 Hz, 2H), 6.887 (dd, $J_1$ = 7.7 Hz, $J_2$ = 7.4 Hz, 2H), 7.145–7.642 (m, 22H), 8.316 (br s, 2H), 8.737 (br s, 2H). EI MS (70 eV, 265°C): m/z (%) 718 (38) $[M^{\cdot +}]$, 360 (67) $[C_{26}H_{16}S^{\cdot +}]$, 359 (100) $[C_{26}H_{15}S^+]$, 328 (56) $[C_{26}H_{16}S^{\cdot +}]$, 327 (8) $[C_{26}H^+_{15}]$, 326 (44) $[C_{26}H_{14}^{\cdot +}]$. A suitable crystal for X-ray diffraction analysis was obtained from a 1:19 mixture of ether and hexane (*vide infra*).

*4,6-Diphenyl-1H,3H-thieno[3,4-c]furan*, **15**. A mixture of 123 mg (0.5 mmol) of 3,3'-oxybis(1-phenyl-1-propyne) **6**,[10] 80 mg (2.5 mmol) of sulfur, 132 mg (0.5 mmol) of $RhCl_3 \cdot 3H_2O$, 202 mg (0.5 mmol) of Aliquat-336, 2 ml of 1,1,2,2-tetrachloroethane and 2 ml of $H_2O$ was stirred vigorously at 104°C for 24 h. The organic layer was separated, washed with water, dried and concentrated. The residue was chromatographed on silica gel using a 1:9 mixture of ether/hexane as eluent. The fraction with $R_f$ = 0.26 consisted of 70 mg (50%) of pure **15**; colorless needles, mp 150–151°C (from hexane). The compound was identical in every respect with a sample prepared according to Scheller *et al.*[10]

*3,6-Diphenyl[1,2]dithiolo[4,3-c]-1,2-dithiole*, **16**. Obtained in 24% yield when sulfur reacted with 1,1'-(1,3-butadiyne-1,4-diyl)bisbenzene **7** for 52 h in boiling 1,1,2,2-tetrachloroethane. The product was purified by chromatography on silica gel with hexane as eluent. $R_f$ = 0.20; red crystals, mp 142–144°C (from EtOH). $^1$H-NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.458 (m, 6H), 7.543 (m, 4H). $^{13}$C{$^1$H}-NMR ($CDCl_3$, 100 MHz): $\delta$ = 128.58, 129.18, 130.07, 132.60, 137.91, 148.39. EI MS (70 eV, 120°C): m/z (%) 330 (60) $[M^{\cdot +}]$, 298 (24) $[(M\text{-}S)^{\cdot +}]$, 297 (23) $[(M\text{-}SH)^+]$, 266 (24) $[(M\text{-}2S)^{\cdot +}]$, 145 (17) $[C_8H_5S^+]$, 121 (100) $[C_7H_5S^+]$, 77 (45) $[C_6H_5^+]$.

$C_{16}H_{10}S_4$ (330.5). Calc.: C 58.15; H 3.05; S 38.80. Found: C 58.35; H 3.21; S 38.53%.

A suitable crystal for X-ray diffraction analysis was obtained by slow recrystallization from dichloromethane (*vide infra*).

*Tetraphenylthiophene*, **18**. A stirred mixture of 178 mg (1 mmol) of diphenylacetylene, 160 mg (5 mmol) of sulfur and 2 ml of 1,1,2,2-tetrachloroethane was refluxed for 72 h. The product was chromatographed on silica gel with a 1:49 mixture of ether/hexane as eluent to give 65 mg (34%) of **18** which was identical with an authentic sample prepared from tetracyclone and sulfur.[17]

*X-ray crystal structure analysis of* **14** *and* **16**. Data were measured on an ENRAF-NONIUS-CAD-4 automatic diffractometer. Cu$K_\alpha$ ($\lambda$ = 1.54178 Å) radiation with a grphite crystal monochromator in the incident beam was used. The standard CAD-4 centering, indexing, and data collection programs were used. The unit cell dimensions were obtained by a least-squares fit of 24 centered reflections in the range of $24 \leqslant \theta \leqslant 28$ for **14** and in the range of $22 \leqslant \theta \leqslant 32°$ of **16**. Intensity data were collected using the $\omega$-$2\theta$ technique to a maximum $2\theta$ of 120° for **14** and of 110° for **16**. The scan width, $\Delta\omega$, for each reflection was $0.80 + 0.15 \cdot \tan \theta$. An aperture with a height of 4 mm and a variable width, calculated as ($2.0 + 0.5 \tan \theta$) mm, was located 173 mm from the crystal. Reflections were first measured with a scan of 4.12°/min. for **14** and of 8.24°/min for **16**. The rate of the final scan was calculated from the preliminary scan results so that the ratio $I/\sigma(I)$ would be at least 40 and the maximum scan time would not exceed 60 s. If in a preliminary scan $I/\sigma(I) \leqslant 2$, this measurement was used as the datum. Scan rates varied from 1.26 to 4.12°/min for **14** and from 1.26 to 8.24°/min for **16**. Of the 96 steps in the scan, the first and the last 16 steps were considered to be background. During data collection the intensities of three standard reflections were monitored after every hour of X-ray exposure. No decay was observed. In addition, three orientation standards were checked after 100 reflections to check the effects of crystal movement. If the standard deviation of the $h$, $k$, and $l$ values of any orientation reflection exceeded 0.06, a new orientation matrix was calculated on the basis of the recentering of the 24 reference reflections. Intensities were corrected for Lorentz and polarization effects. All non-hy-

TABLE II

Crystallographic data for **14** and **16**

| | **14** | **16** |
|---|---|---|
| Formula | $C_{52}H_{30}S_2$ | $C_{16}H_{10}S_4$ |
| Space group | $P2_1/n$ | $P2_1/c$ |
| $a$, Å | 17.299(5) | 13.776(3) |
| $b$, Å | 16.820(2) | 7.307(2) |
| $c$, Å | 12.416(2) | 7.120(2) |
| $\beta$, deg. | 98.34(2) | 74.79(2) |
| $V$, Å$^3$ | 3574(1) | 714.2(5) |
| $Z$ | 4 | 2 |
| $\delta$(calcd.), g cm$^{-3}$ | 1.34 | 1.54 |
| $\mu$(CuK$_\alpha$), cm$^{-1}$ | 15.94 | 58.96 |
| No. of unique reflections | 5443 | 1060 |
| No. of reflections with $I>3\sigma(I)$ | 4236 | 819 |
| $R$ | 0.038 | 0.074 |
| $R_w$ | 0.058 | 0.091 |

drogen atoms were found by using the results of the SHELXS-86 direct method analysis.[18] After several cycles of refinements[19] the positions of the hydrogen atoms were calculated, and added to the refinement process. Refinement proceeded to convergence by minimizing the function $\Sigma\, w(|F_0| - |F_c|)^2$. A final difference Fourier synthesis map showed several peaks less than 0.1 e/Å$^3$ scattered about the unit cell without a significant feature. The discrepancy indices, $R = \Sigma\, ||F_0| - |F_c||/\Sigma\, |F_0|$ and $R_w = [\Sigma\, w(|F_0| - |F_c|)^2]^{1/2}$ are presented with other pertinent crystallographic data in Table II.

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## REFERENCES AND NOTES

1. See e.g., A. Senning, "Sulfur in Organic and Inorganic Chemistry," Marcel Dekker, New York, 1971, Vol. 1.
2. Y. Badrieh, A. Greenwald, H. Schumann and J. Blum, *Chem. Ber.*, **125,** 667 (1992).
3. Y. Sasson, A. Zoran and J. Blum, *J. Mol. Catal.*, **22,** 293 (1981).

4. F. Kvis, E. Sv̂ateck, R. Zaharadník and M. Protiva, *Collect. Czech. Chem. Commun.*, **37,** 3803 (1972).
5. See Y. Badrieh, J. Blum, I. Amer and K. P. C. Vollhardt, *J. Mol. Catal.*, **66,** 295 (1991) and references cited therein.
6. H. A. Staab and B. Draeger, *Chem. Ber.*, **105,** 2320 (1972).
7. E. Müller, C. Beissner, H. Jakle, E. Langer, H. Muhm, G. Odenigbo, M. Sauerbier, A. Segnitz, D. Streichfuss and R. Thomas, *Justus Liebigs Ann. Chem.*, **754,** 64 (1971).
8. (a) B. Bossenbroek, D. C. Sanders, H. M. Curry and H. Shechter, *J. Am. Chem. Soc.*, **91,** 371 (1969); (b) H. A. Stabb, J. Ipaktschi, *Chem. Ber.* **104,** 1170 (1971).
9. Complete crystallographic data, including tables of the $F_0/F_c$ values, the positional and thermal parameters, bond lengths and bond angles and stereoscopic drawing are available on request from the Cambridge Crystallographic Data Centre (CCDC) U.K., on quoting the names of the authors, and the journal citation.
10. A. Scheller, W. Winter and E. Müller, *Justus Liebigs Ann. Chem.*, 1448 (1976).
11. I. D. Campbell and G. Eglinton, *Org. Synth. Coll.*, **5,** 517 (1973).
12. For a recent study on such compounds see e.g. B. Kordts, A. M. Richter and E. Fanghaenel, *Monatsh. Chem.*, **122,** 71 (1991).
13. Theoretical studies on this system were reported by G. Calzaferri and R. J. Gleiter, *J. Chem. Soc., Perkin Trans.*, **2,** 559 (1975).
14. For the few examples of transformation of monoalkynes and sulfur into substituted thiophenes see e.g. V. Jäger and H. G. Viehe, in "Methoden der Organische Chemie," ed., E. Müller, Thieme Vergag, Stuttgart, 1977, Vol. 5/2a, pp. 677–912.
15. O. P. Strausz, J. Font, L. F. Dedio, P. Kebarle and H. E. Gunning, *J. Am. Chem. Soc.*, **89,** 4805 (1967).
16. See e.g., R. Mayer, in "Organic Chemistry of Sulfur," ed., S. Oae, Plenum, New York, 1977, pp. 63–69.
17. T. Abraham, *J. Polym. Sci. Polym. Chem.*, **20,** 1953 (1982).
18. C. M. Sheldrick, "Crystallographic Computing 3," Oxford University Press, 1985, pp. 175–189.
19. All crystallographic computing was done on a CYBER 855 computer at the Hebrew University of Jerusalem, using the TEXAN Structure Analysis Software.
20. W. Dilthey, W. Schommer, W. Höschen and H. Dierichs, *Ber. Dtsch. Chem. Ges.*, **68,** 1959 (1935).