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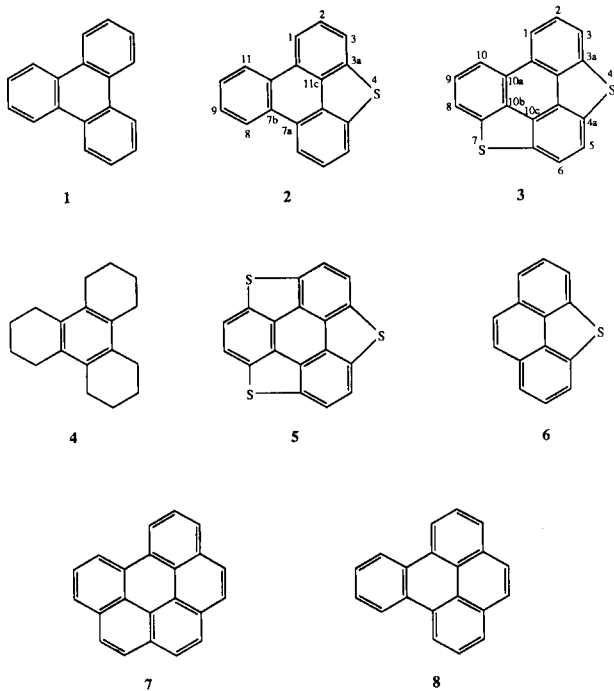
Triphenyleno[1,12-*bcd*:4,5-*b'c'd'*]dithiophene (**3**) is synthesized in low yield (2.5% maximum) from a mixture of triphenylene (**1**) and triphenyleno[4,5-*bcd*]thiophene or from **1** alone by means of heterogeneously catalyzed sulfur bridging by hydrogen sulfide at 500-550°. Compound **3** is characterized by spectral and other properties. Hückel molecular orbital calculations for the formation and reaction of **3** are presented.

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Several previous publications in this series have been concerned with the insertion of a sulfur bridge into the bay region of phenanthrene or triphenylene (**1**) by means of hydrogen sulfide and a heterogeneous catalyst at $530 \pm 100^\circ$ [4-8]. Triphenylene is of special interest as a substrate since it offers the potentiality of also undergoing di- or tribridging in bay regions of the molecule to form **3** and **5**, respectively [9]. We now report the formation of **3** in low yield, 0.8% from **1** directly or 2.5% from a mixture of **1** and **2** (1.3:1), by the same procedure as used previously but at an increased flowrate of hydrogen sulfide gas. Meanwhile, Swedish workers reported the formation of **1**, **2**, and **3** (*ca.* 0.5%) from dodecahydrotriphenylene (**4**) and elemental sulfur at a temperature above 400° [10].

trum; *viz.* a downfield doublet at δ 8.52 for the two bay-region protons H-1 and H-10, a singlet for H-5 and H-6, a doublet at 8.14 for H-3 and H-8, and a doublet of doublets for H-2 and H-9. In accordance with the concept of Badger and Christie [11], the ultraviolet absorption spectrum of **3** shows similarities (albeit not close ones) to that of its benzolog [12] benzo[*ghi*]perylene (**7**) [13] (Figure 1). In particular, analogous prominent structural features in the spectrum of **3** fall at shorter wavelengths than in that of **7** as follows (λ for **3** and $\Delta\lambda$ for the difference): 297 and 6 nm for the most intense β band, 352 and 35 nm for the *para* band of longest wavelength, and 372 and 35 nm for the α band. The *para* bands are well resolved in **7**; but poorly, in **3**. In fact, **7** is pale yellow-green [13], while **3** is colorless. The phenomena of hypsochromic displacements of maxima and poor resolution of *para* bands in the sulfur analog also occurs in the ultraviolet spectrum of **2**, as compared to that of its benzolog, benzo[*e*]pyrene (**8**) [6]. The fluorescence and phosphorescence spectra of **3** have been reported and interpreted previously [14].

Table I gives simple HMO reactivity indices for electrophilic and nucleophilic attack on **3** and its cation radical as based on the relationship $\alpha_s = \alpha_c + 0.2 \beta_{c-c}$ and $\beta_{c-s} = 0.9 \beta_{c-c}$. While the poor yield of **3** from sulfur bridging makes an experimental study of electrophilic substitution (S_E) into **3** unattractive at this point, one notes that highest reactivity for S_E is indicated for positions 1 and 3, *i.e.* for substitution *para* or *ortho* to one of the sulfur atoms. This prediction is consistent with experimental observations on regioselectivity in nitration and Friedel-Crafts acetylation of the analogous *peri*-condensed thiophenes **2** and **6** and with HMO calculations for them [7,8,15]. However, in calculations for **2** and **6** α_s was taken as equal to α_c and no correction was made (*i.e.* was taken as zero in the relationship $\alpha_s = \alpha_c + h\beta_{c-c}$) for a difference in electro-negativities of an aromatic carbon and an aromatic sulfur atom. With $h = 0$ for **3**, superdelocalizability values for electrophilic attack become infinite for all positions *r* and this same result ensues for nucleophilic attack on the cation radical **3**⁺. As noted in Table I, with $h = 0.2$ this problem is circumvented. Moreover, these parameters ($h = 0.2$, $k =$



Compound **3** was characterized by means of elemental analysis and spectra. Because of symmetry in the molecule there are only four separate signals in the ¹H nmr spec-

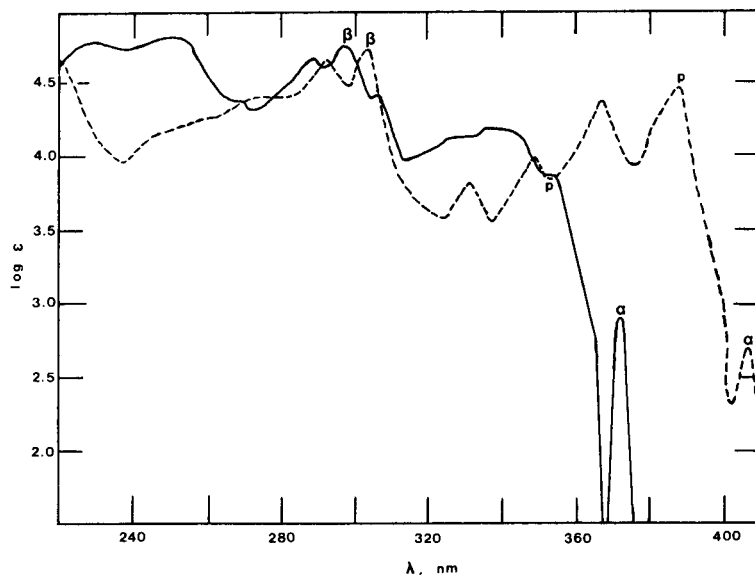


Figure 1. Ultraviolet absorption spectra for triphenyleno[1,12-*bcd*:4,5-*b'c'd'*]dithiophene (**3**) (continuous line) in absolute ethanol and for benzo[*ghi*]perylene (**7**) (broken line) in 95% ethanol for the wavelength range of 220-280 nm and in benzene for wavelengths > 280 nm [13].

0.9) give reasonable values of reactivity indices for **2**, **5**, and **6** [17].

Table I

Calculated Reactivity Indices for Compound 3 and Its Cation Radical [a]				
Position	S_r^{elec}	S_r^{nucl}	S_r^{elec}	S_r^{nucl}
	for 3	for 3	for 3⁺	for 3⁺
r				
1	2.75	0.78	1.84	-0.13
2	1.24	0.78	1.05	0.58
3	2.81	0.84	1.83	-0.14
3a	1.12	0.66	0.98	0.52
4(S)	6.48	0.39	4.01	-2.08
4a	1.60	0.62	1.26	0.27
5	1.78	0.79	1.48	0.50
10a	1.23	0.77	0.97	0.50
10b	1.35	0.63	1.19	0.47
10c	2.44	0.60	1.60	-0.24

[a] S_r is given in units of β_c^{-1} and represents superdelocalizability toward electrophilic or nucleophilic attack, as based on simple HMO theory with $\alpha_s = \alpha_c + 0.2 \beta_{c-c}$ and $\beta_{c-s} = 0.9 \beta_{c-c}$ [16].

Specific data for electrophilic attack on **2** and nucleophilic attack on **2⁺** are presented in Table II. Comparison of the data in this table with those previously reported for electrophilic attack on **2** shows that S_F reaction is still predicted to be fostered at C-1 and C-3 [17].

Table II

Calculated Reactivity Indices for Compound **2** and Its Cation Radical [a]

Position	S_r^{elec}	S_r^{nucl}
	for 2	for 2⁺
r		
1	1.70	0.29
2	0.94	0.77
3	1.74	0.28
3a	0.83	0.69
4 (S)	3.96	-1.31
7a	0.92	0.67
7b	0.82	0.74
8	0.95	0.90
9	0.91	0.84
11c	1.21	0.46

[a] See footnote in Table I.

In the mechanism which we proposed for heterogeneously catalyzed sulfur bridging by means of hydrogen sulfide, an adsorbed aromatic substrate first loses an electron to the catalyst surface to yield a cation radical, which is then attacked by an adsorbed sulfide (or bisulfide) ion at a reactive position [9]. It is now appropriate to note from Table II that cation radical **2⁺** should be attacked most readily by an anion at C-8 (or C-11), with subsequent cyclization across the bay region to produce **3**. Likewise from Table I one sees that **3⁺** would be unlikely to undergo at-

tack by an anion at C-1, as would be needed in order to convert **3** into **5**. Neither we nor the Swedish workers have found clear evidence for the formation of **5** in our reaction mixtures.

Nishioka *et al.* noted that many polycyclic aromatic hydrocarbons and their thienologs [12] bearing a single sulfur atom occur in coal tars and coal liquids [18]. Thus, **2** and benzo[*e*]pyrene (**8**) were found in the same sample. It seems likely that thienologs bearing two or more sulfur atoms should also be present, but few components with more than a single thiophene ring per molecule have yet been identified [18-21]. Since **7** is a significant component of coal-derived products [13], it would not be surprising to find **3** (C₁₈H_{2n-28}S₂) also present in such samples. In fact, Coleman *et al.* suggest that a high-boiling distillate from crude oil bears a component having the molecular formula of **3** [21].

EXPERIMENTAL [22]

Triphenyleno[1,12-*bcd*:4,5-*b'c'd'*]dithiophene (**3**). (a) In Two Steps from Dodecahydrotriphenylene (**4**) and Hydrogen Sulfide.

A powdered mixture of **1** and **2** (3.5 g, 14.5 total mmoles, molar ratio 1:3:1 by ¹H nmr, mp 135-180°) from sulfur bridging of dodecahydrotriphenylene (**4**) [8] was added in 5 equal portions at 30-minute intervals to a reactor tube containing 150 g of pre-conditioned Harshaw Cr-0101 T catalyst (topped with a 2-cm zone of glass beads) held at 550° in a stream of hydrogen sulfide gas at a flowrate of 0.04 mole/minute by a general procedure previously described [8]. The reaction was stopped after 4 hours and a chloroform extract of the effluent was washed successively with 5% aqueous sodium hydroxide and water, dried (sodium sulfate), and evaporated to leave 1.57 g of solid product, mp 112-178°, molar ratio of 1:2:3 = 0.08:2.92:1 by ¹H nmr. A chloroform solution of this solid was rotoevaporated onto 16 g of alumina which was placed atop a 2.5-cm column of plain alumina (350 g) and the column was eluted with petroleum ether (35-60°) to give 0.49 g of sulfur (R_f 0.84 with alumina/benzene-petroleum ether, 1:1) in 900 ml of effluent. Changing to an eluent of benzene-petroleum ether (1:1) gave 845 ml of effluent containing 0.84 g of a mixture of **1**, **2**, and **3** and then 105 mg (2.5%) of **3** only, R_f 0.4, in the next 635 ml. Recrystallization of the last fraction from benzene gave **3** as fine, matted needles, mp 297.5-298.5°; ¹H nmr: δ 8.52 (d, J_{1,2} = J_{9,10} = 7.8 Hz, 2H, H-1 and H-10), 8.17 (s, 2H, H-5 and H-6), 8.14 (d, J_{2,3} = J_{8,9} = 7.8 Hz, 2H, H-3 and H-8), 7.92 (dd, 2H, H-2 and H-9); ir: 1410-1420, 1160, 785, 735 cm⁻¹; ms: (70 V) m/e 290 (13), 289 (26), 288 (M⁺, 100), 243 (M⁺ - CHS, 16), 144 (M⁺, 36), 121.5 (M⁺ - CHS, 11) [23]; uv (absolute ethanol): λ max (log ε) 232 (4.80), 252 (4.82), 267 shoulder (4.38), 288 (4.69), 297 (4.76), 307 (4.42), 330 shoulder (4.14), 339 (4.18), 352 shoulder (3.89), 372 (2.90).

Anal. Calcd. for C₁₈H₈S₂: C, 74.97; H, 2.80; S, 22.23. Found: C, 74.88; H, 2.59; S, 22.41.

(b) From Triphenylene (**1**) and Hydrogen Sulfide.

In a modification of method (a), a solution of 5 g (21.9 mmoles) of **1** in 400 ml of benzene was added dropwise to 200 g of catalyst at 500° and with a flowrate of 0.03 mole/minute of hydrogen sulfide. The solid effluent was recrystallized from minimal benzene

to remove biphenyl and dibenzothiophene byproducts and yield 219 mg of a mixture of **1**, **2** and **3** plus elemental sulfur. This solid was dissolved in a warm mixture of 3 ml of pyridine, 3 ml of water, and 20 ml of tetrahydrofuran and stirred with 0.25 g (excess) of iodobenzene dichloride. Reaction was monitored by tlc (silica gel/chloroform) until spots for **2** and **3** had disappeared.

The mixture was acidified with 10% hydrochloric acid and extracted with chloroform. Column chromatography (silica gel/chloroform) of the dried (sodium sulfate), concentrated organic extract removed components with R_f > 0 and gave 116 mg of mixed sulfoxides, mp 222-240°. A stirred solution of this solid in 100 ml of dry, peroxide-free tetrahydrofuran (nitrogen atmosphere) was treated (with care!) with 60 mg of lithium aluminum hydride (fizzing). After 5 hours the solution was refluxed for 30 minutes until a tlc spot at R_f = 0 disappeared. Processing of the solution produced a mixture of **2** and **3**. Two recrystallizations from chloroform yielded 48 mg (0.8% from **1**) of **3**, mp 258-261°, converted to a cream powder, mp 269-272°, after further recrystallizations plus sublimation at 180° (0.025 mm), identified by ir, ¹H nmr, and mass spectra.

Anal. Calcd. for C₁₈H₈S₂: C, 74.97; H, 2.80; exact mass, 288.006. Found: C, 75.14; H, 3.05; exact mass, 288.006.

REFERENCES AND NOTES

- [1] For the previous paper in this series see L. H. Klemm, M. P. Stevens, L. K. Tran, and J. Sheley, *J. Heterocyclic Chem.*, **25**, 1111 (1988).
- [2] Undergraduate and postbaccalaureate research assistant, 1985-1987.
- [3] Undergraduate research assistant, 1983.
- [4] L. H. Klemm, D. R. McCoy, and D. R. Olson, *J. Heterocyclic Chem.*, **7**, 1347 (1970).
- [5] L. H. Klemm and W. Hsin, *ibid.*, **13**, 1245 (1976).
- [6] L. H. Klemm and R. F. Lawrence, *ibid.*, **16**, 599 (1979).
- [7] L. H. Klemm, R. Tsuchiya, E. K. L. Wong, M. P. Stevens, J. J. Lu, and C. E. Klopfenstein, *ibid.*, **24**, 357 (1987).
- [8] L. H. Klemm, E. Hall, L. Cousins, and C. E. Klopfenstein, *ibid.*, **24**, 1749 (1987).
- [9] L. H. Klemm, J. J. Karchesy, and D. R. McCoy, *Phosphorus Sulfur*, **7**, 9 (1979).
- [10] A. L. Colmsjö, Y. U. Zebühr, and C. E. Östman, in press. Paper presented at the Tenth International Symposium on Hydrocarbons, Columbus, Ohio, October, 1985.
- [11] G. M. Badger and B. J. Christie, *J. Chem. Soc.*, 3438 (1956).
- [12] For definition of this term see L. H. Klemm, in "Advances in Heterocyclic Chemistry," Vol **32**, A. R. Katritzky, ed, Academic Press, New York, NY, 1982, p 154.
- [13] E. Clar, "Polycyclic Hydrocarbons," Vol **2**, Academic Press, New York, NY, 1964, p 62.
- [14] A. L. Colmsjö, Y. U. Zebühr, and C. Östman, *Anal. Chem.*, **54**, 1673 (1982); *Chem. Scripta*, **24**, 95 (1984).
- [15] Unpublished observations from this laboratory.
- [16] A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, NY, 1961, Chapter 5.
- [17] Superdelocalizability calculations are used here because they provide data consistent with observed positions of substitution in the individual molecules and ions. The data are not meant to represent relative rates of reactions as might be determined in competitive experiments, e.g. for mixtures of **2** and **3**.
- [18] M. Nishioka, M. L. Lee, and R. N. Castle, *Prepr. Am. Chem. Soc., Div. Pet. Chem.*, **31**, 827 (1986).
- [19] M. Nishioka, D. G. Whiting, R. M. Campbell, and M. L. Lee, *Anal. Chem.*, **58**, 2251 (1986).
- [20] H. V. Drushel and A. L. Sommers, *ibid.*, **39**, 1819 (1967).

[21] H. J. Coleman, J. E. Dooley, D. E. Hirsch, and C. J. Thompson, *ibid.*, **45**, 1724 (1973).

[22] Unless otherwise indicated, infrared spectra were determined on potassium bromide wafers by means of a Nicolet 5-DXB FTIR instrument; ^1H nmr spectra, on solutions in deuteriochloroform by means of a General Electric QE-300 instrument; and uv spectra (by Sandip K. Sur)

by means of a Beckman DU-7 spectrophotometer. Mass spectra were obtained by Dr. Richard Wielesek with a VG 12-250 instrument. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

[23] Colmsjö *et al.* indicate that various *peri*-condensed thiophenes are characterized by $(M + 2)$ and $(M - 45)$ peaks in their mass spectra [14].