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INTERRELATIONSHIPS AMONGST *PERI*-CONDENSED THIOPHENES AND SOME POLYCYCLIC AROMATIC HYDROCARBONS

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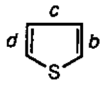
Abstract—In the laboratory a *peri*-condensed thiophene (I) is commonly synthesized by inserting a sulfur bridging atom (from hydrogen sulfide or elemental sulfur) across the bay region of a polycyclic aromatic hydrocarbon precursor (II). This transformation may simulate the geochemical process whereby I forms in fossil fuels. Electrophilic substitution into I occurs *ortho* and/or *para* to the sulfur bridge and to the analogous positions in the isosteric hydrocarbon (III). The ultraviolet absorption spectra of I and III show similar shapes and characteristics. These interrelationships amongst I, II, and III are discussed.

CONTENTS

1. DEFINITIONS AND SCOPE

Peri-condensed thiophenes are compounds which contain other rings fused to all three of the carbon-carbon bonded sides *b*, *c*, and *d* of the thiophene ring (1). We are concerned here only with cases where the fused rings are benzenoid in nature. Thus, the simplest *peri*-condensed thiophene is phenanthro[4,5-*bcd*]thiophene (2), a compound first synthesized in our laboratory two decades ago[1] by passing phenanthrene (3), designated the "arene precursor", and hydrogen sulfide gas over a sulfided chromia or molybdena catalyst at 430-630 °C (32-

39% yield).[2,3] In this process, called "sulfur bridging", a sulfur atom is inserted into the bay region of the arene precursor with the loss of two hydrogen atoms from the arene.



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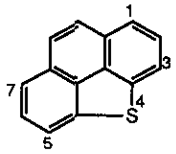

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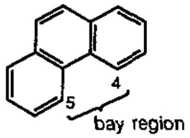

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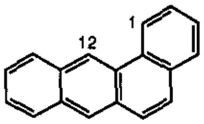
If one has a list of all possible condensed aromatic hydrocarbons with n rings, it is easy to select those molecules with a bay region whereby insertion of a sulfur bridge would form a *peri*-condensed thiophene of $(n + 1)$ rings. Thus, one can systematically write structural formulas for all possible *peri*-condensed thiophenes. Of the six tetracyclic arenes[4] only benz[*a*]anthracene (4), chrysene (5), and triphenylene (6) qualify as arene precursors



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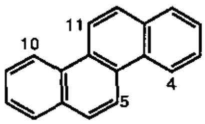

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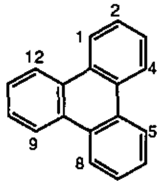

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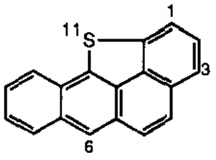

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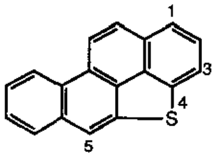

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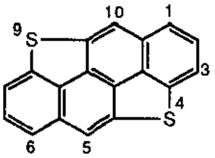

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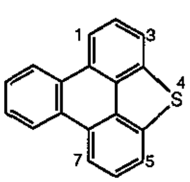

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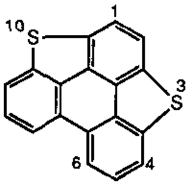

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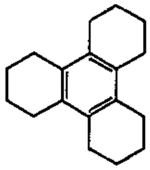

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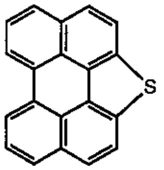
in this sense, with one, two, and three available bay regions, respectively. Our hydrogen sulfide method served to convert 6 into 10 (18%)[5] or, with a faster flow of hydrogen sulfide, into the dibridged $(n + 2)$ product 11 (0.8%).[6] More conveniently, dodecahydrotriphenylene (12) was used as the starting material to effect both catalyzed dehydrogenation and sulfur bridging to produce a mixture of 6 (45%) and 10 (44%)[7] or a mixture of 6, 10, and 11 (2.5%).[6] Colmsjö *et al.* also accomplished conversion of the commercially available 12 into a mixture of 6, 10, and 11 (0.5%) by reaction with elemental sulfur in a sealed tube at a temperature above 400 °C.[8] The possible tribridged triphenylene was not detected in these studies and remains unknown.[6] The Swedish workers[8] also prepared 7-9, as well as the hexacyclic condensed thiophenes 13-15, by a two-step procedure wherein they first hydrogenated the corresponding arene precursor and then treated the hydroarene by their sealed tube method.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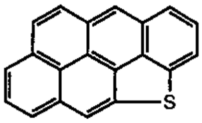
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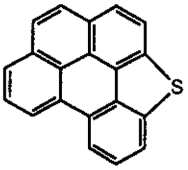
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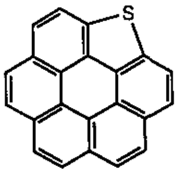
There are fifteen pentacyclic condensed arenes[4] of which ten bear one or more bay regions and could potentially lead to sixteen monobridged, nine dibridged, and two tribridged *peri*-condensed thiophenes. Only three of these twenty-seven possibilities (i.e. 13-15) appear in the Ring Index of *Chemical Abstracts* for volumes 66-109, inclusive (1967-1988). Additionally, thirteen *peri*-condensed thiophenes with 7-9 total rings (and one sulfur bridge per molecule) are reported. *Of these, the symmetrical molecules* 16 *and* 17 *are of special*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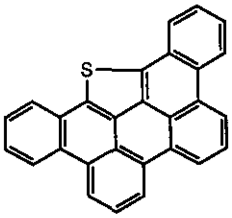
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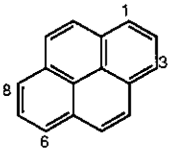
interest since they have been synthesized (by various procedures) and characterized.[9-12] The other eleven were only tentatively identified in fossil fuels[13] or carbon black.[14] Colmsjö and Östman have recently suggested structures for two more.[15]

It should be noted that Castle and coworkers have used multi-step syntheses to prepare reference samples of 2, 7, and 8 as well as the four methyl derivatives of 2 and a group of eight methyl derivatives of 7.[16-18] Others have also synthesized 13.[19,20]

2. THEMES OF INTEREST

Discussion in this paper will be directed toward three proposed correlations between *peri*-condensed thiophenes and (a) their arene precursors with respect to occurrence in natural products, i.e. fossil fuels, hydrogenated coal, coal tar, shale oil, or carbon black, and (b) their benzologs with respect to (1) chemical reactions and (2) ultraviolet absorption spectra. As previously defined by this author[21] the benzolog of a condensed thiophene is the arene which results from replacing the sulfur atom of the former compound by a -CH=CH- portion of a benzene ring. In earlier parlance the thiophene compound (thienolog) and its benzolog have been called "isosteres".[22] Illustrative of thienolog-benzolog pairs are 2 and pyrene (18), 7 or 8 and benzo[*a*]pyrene (19), and 10 and benzo[*e*]pyrene (20).



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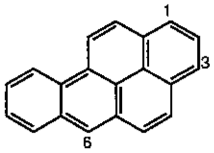

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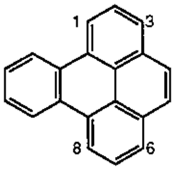

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3. NATURAL OCCURRENCE AND *S*-BRIDGING

A number of people have proposed that the thiophene compounds present in fossil fuels have arisen from secondary reactions between hydrocarbons and hydrogen sulfide, sulfur, or the mineral pyrite.[23-26] In particular, the sulfur bridging reactions described in part 1 could serve as models for the geochemical processes, albeit with the laboratory conversions probably conducted under higher reaction temperatures, lower pressures, and shorter reaction times than occurred in nature. If the concept is correct, then one ought to find evidence for the presence of both arene precursors and their *S*-bridged products in analyzed samples of fossil fuels and carbon blacks. Some examples where such a coexistence has been reported are presented here.

The most extensive coexistence was reported by Nishioka *et al.* who identified 2, 7, 8, 10, and 13-15 as well as their arene precursors in coal tar and a coal liquid vacuum residue.[27] Listing only the numbers for the condensed thiophenes, one notes that these compounds plus their arene precursors were also reported: 2 and 10 in lubricating oils,[28] 2 and 8 in a distillate from gasified coal,[29] 2 and 10 in coal tar,[30,31] 2 and 7 in used crankcase oil,[32] 2 and **10** in the emission from combustion of hard coal,[33] 2 and probably 13 and **16** in carbon black,[34] and very tentatively, five *peri*-condensed thiophenes of eight and nine rings in another carbon black.[14] Additionally, some methyl and dimethyl (or ethyl) condensed thiophenes of uncertain structures were identified in a number of instances. Positively identified in heavy oils and tars was 2-methyl-2.[35] Both 2 and two of its methyl derivatives were found in solvent-refined coal.[36]

We consider the preceding associations as strongly supportive evidence that sulfur bridging, as discussed in Part 1, is the main source of parent thiophene structures in fossil fuels. However, a shortcoming of the laboratory bridging experiments is the fact that they do not normally produce methyl (or ethyl) derivatives. Thus, use of 3-methylphenanthrene as a substrate in catalyzed bridging gave only 2, devoid of a methyl group.[37] Alkyl groups may or may not survive bridging by heating with elemental sulfur or they may change considerably in structure.[21] White *et al.* reported a recent attempt to effect sulfur bridging by heating phenanthrene, 1-methylphenanthrene, triphenylene, and chrysene with elemental sulfur and/or pyrite in sealed tubes at a low temperature (115-118 °C) for six months.[26] Various other chemicals were added to some tubes. Results were variable and somewhat dubious, but they did obtain high resolution mass spectral data consistent with the formation of **8**, 10, and possibly a methyl-2 (but not 2 itself).

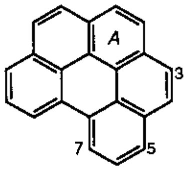
Alkyl groups identified in fossil fuels may arise as artifacts of the treatment of the sample. An extreme case was found by Lee and coworkers who analyzed a catalytically cracked *petroleum vacuum residue for tri-, tetra-, and pentacyclic condensed* thiophenes.[38] They found C_2-C_5 derivatives of 2 and C_1-C_4 derivatives of **8**. These alkyl groups appeared to be predominantly linear and to average three carbons in length.

4. SUBSTITUTION AND OTHER REACTIONS

In an ongoing investigation of substitution reactions of *peri*-condensed thiophenes Klemm *et al.* have subjected phenanthro[4,5-*bcd*]thiophene *(2) and triphenyleno[1,12-bcd]thiophene* (**10**) to nitration by means of nitric acid in acetic anhydride and to Friedel-Crafts acetylation by means of aluminum chloride and acetyl chloride in nitrobenzene. These electrophilic substitutions occur only *ortho* and/or *para* to the heteroatomic sulfur, when the sulfur is viewed as a substituent on the arene precursor. Thus, compound 2 yields varying ratios (1.2 ± 0.6)/1 of 1-nitro (or *para* substitution) to 3-nitro (or *ortho* substitution) derivatives, dependent on reaction conditions.[3] On monoacetylation position 1 is preferred over position 3, while on diacetylation the 1,5-diacetyl product predominates, though there is tentative evidence for the presence of both 1,7- and 3,5-diacetyl compounds also.[39] These substitution patterns of **2** are completely analogous to those of its benzolog, pyrene (**18**), which undergoes mononitration and acetylation at position 1 and even gives a 1,3,6,8-tetranitro derivative.[40a]

Compound **10** produces 1-nitro, 3-nitro, and 1,7-dinitro derivatives with an overall ratio of *ortho*-substitution:*para*-substitution of *ca.* 1:1.[7] However, steric hindrance to reaction at the 1 and 7 positions was apparent on acetylation of **10** which formed only 3-acetyl and 3,5-diacetyl derivatives.[41] Analogous results have been reported for triphenylene (**6**) where nitration produces nearly equal amounts of the 1- and 2-nitro isomers[7,42] while acetylation occurs only at the sterically less-hindered 2-position.[43] More pertinent to this discussion are the results of electrophilic substitution into benzo[*e*]pyrene (**20**), the benzolog of **10**. Nitration of **20** with nitric acid-acetic anhydride gives a mixture of 1-nitro and 3-nitro derivatives in a ratio of (1.4 ± 0.4)/1.[44] Although no study of acetylation of **20** has been found in the literature, Lang and Zander[45] and Harvey and coworkers[46] have investigated direct bromination and chlorination of this arene. Bromination yields 3-bromo and/or 3,6-dibromo derivatives, while chlorination proceeds to the 1,3,6,8-tetrachloro stage. Efforts to substitute more than two bromine atoms into **20** failed, but the 3,6-dibromo derivative was still susceptible to chlorination to give 3,6-dibromo-1,8-dichloro-**20**. As noted by Lang and Zander positions 1 and 8 of **20** may be too sterically hindered to undergo substitution by bromine but not so hindered as to be attacked by the smaller chlorine electrophilic entity.

At this time substitution reactions into other *peri*-condensed thiophenes have not been reported. However, it seems likely that the foregoing correlations on substitutions into analogous positions in thienolog-benzolog pairs will be retained, as based on the following two cases. From the simple rule of *ortho-para* orientation by heteroatomic sulfur one would expect dibridged compound **11** to give electrophilic monosubstitution at position 1, 4, or 6, with position 6 unlikely for acetylation because of steric hindrance. This prediction can



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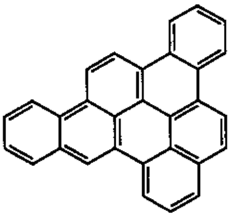

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be further limited by means of molecular orbital reactivity indices for **11** which show that positions 4 and 6 are preferred to 1.[6] In benzo[*ghi*]perylene (**21**), the benzolog of **11**, the analogous preferred positions would be 5 and 7. In fact, Swedish workers observed that nitration of **21** in acetic anhydride forms both 5- and 7-nitro derivatives, with the 5-isomer predominant.[44] The reader may note that **21** is also the benzolog of **13**, with ring *A* of **21** corresponding to the thiophene ring in **13**. On this basis one might expect **21** to undergo substitution at the 3-position as well.

A second example is provided by the pair **7** and **8** plus the benzolog **19**. From *ortho-para* orientation rules only, one would expect **19** to undergo electrophilic monosubstitution at position 1, 3, or 6. Again the Swedes have corroborated this prediction by finding that benzo[*a*]pyrene (**19**) gives a mixture of these three nitro isomers in a ratio of 0.14:0.05:1, respectively.[44]

Meanwhile, it should be noted that our acetyl derivatives of **10** have been reduced under Wolff-Kishner conditions to 3-ethyl and 3,5-diethyl derivatives[41] and that sulfoxides and sulfones of various *peri*-condensed thiophenes have been prepared. In fact oxidation of mixtures of arenes and thiaarenes was used on a number of occasions in order to permit separation of the thiaarene sulfoxides or sulfones from the arenes (or arene oxidation products) by chromatography on silica gel.[3,5-7,29,36,47] The sulfoxides and sulfones were then reduced back to the parent thiaarenes.

5. ULTRAVIOLET ABSORPTION SPECTRA

In 1956 Badger and Christie[48] noted that the ultraviolet absorption spectra of *cata*-condensed thienolog-benzolog pairs with 1-3 rings resemble one another in general shape. In particular, both exhibit (in the Clar terminology[49]) β, p, and α bands in order of increasing wavelength. These chemists generalized that (a) the β bands of the thienolog are shifted to shorter wavelengths from those in the benzolog and (b) the α bands in the thienolog are more intense. Badger and Christie overlooked the fact that the α bands in their thienolog examples were also shifted hypsochromically from those in the benzologs so that the enhanced intensity stated in (b) could result from greater overlap of the α bands with the p bands, which do not shift in unison. As noted by Clar for arenes, α bands become "gradually hidden behind the p bands" in the phene (i.e. angularly catenated) series and "disappear completely" in the arene (i.e. linearly catenated) molecules anthracene and naphthacene. Taking this situation into account, it seems more appropriate to revise the Badger-Christie generalizations to state that "both the β and α bands of a thienolog are shifted to shorter wavelengths from those of the benzolog". This coordinated, unidirectional shift of β and α bands has been described for arenes,[49] and would also be expected to occur in thiaarenes.

Does the revised Badger-Christie rule apply to *peri*-condensed thiophenes? Klemm and coworkers have plotted ultraviolet spectra of the thienolog-benzolog pairs 2 plus **18**,[1] 10 plus 20,[5] and 11 plus benzo[*ghi*]perylene (21)[6] on the same graphs in order to check the Badger-Christie concept. In all cases (1) β, *p*, and α bands are present, (2) corresponding β and α bands generally fall at shorter wavelengths in the thienologs, and (3) the thienologs show less fine structure than the benzologs, especially in the *p* bands. For compound **2**, as a limiting case, the β (and β') bands occur at essentially the same wavelenths as in **18**. In another case, Depaus isolated both **7** and **8** from a commercial sample of benzo[*a*]pyrene (**19**) and plotted their ultraviolet spectra together.[50] Expected shifts in the α ($\Delta\lambda$ 19 nm) and β bands ($\Delta\lambda$ 32 nm) are observed for the pair **8** and **19**, but not for the pair 7 and 19. Thus, no α band is shown for 7, its *p* bands almost coincide with those of 19, and its β bands are shifted bathochromically by 4-6 nm from those of 19. In the pair 17 and 22 the most intense β band for the thienolog appears to be shifted as expected but its α band is either not reported or has been shifted under the *p* band.[12,40b] It seems clear that considerably more data on ultraviolet spectra of benzolog-thienolog pairs will be necessary if one is to obtain a reliable, revised Badger-Christie rule for correlations involving *peri*-condensed thiophenes. However, the generalization that the spectra of such pairs resemble one another (sometimes very closely) still seems appropriate and useful for corroborating structures.

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