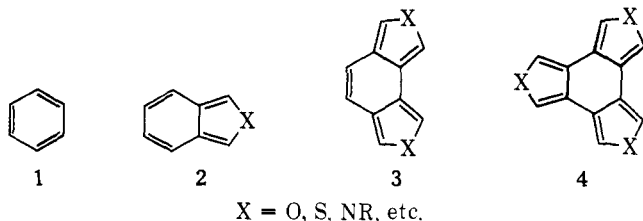


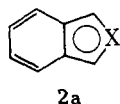
Exocyclic Benzenes. Synthesis and Properties of Benzo[1,2-*c*:3,4-*c'*:5,6-*c''*]trithiophene, a Tristhiahexaradialene

Sir:

In the series 1-4 a benzene ring is converted in a formal sense from having six overlapping p orbitals associated with endocyclic "double bonds" to having those orbitals associated with exocyclic carbon-carbon "double bonds". Orthoquinoidal

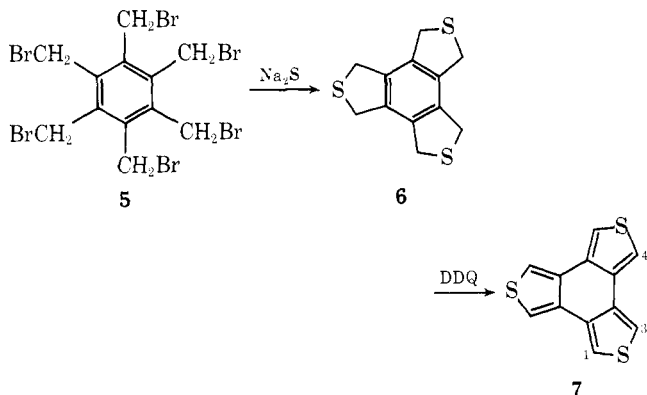


heterocycles of the type 2 show extreme chemical reactivity, particularly in cycloadditions which restore the endocyclic aromaticity of the six-membered ring.¹ The most recent view of their electronic structure suggests an aromatic heterocyclic ring with a relatively noninteracting butadiene moiety (2a).²



It seemed likely that, if the number of exocyclic double bonds were increased (as in 3 or 4), the additional heteroaromatic rings would diminish reactivity and restore overall aromaticity to the structure. We describe here the synthesis and some chemistry of 4 (X = S), the first example and a prototype of such molecules.³

Treatment of hexakis(bromomethyl)benzene 5⁴ (10 mmol) with 15 g of Na₂S·9H₂O in a mixture of ethanol (800 mL), THF (400 mL), and water (40 mL) at reflux for 19 h gave (80-90%) the tris sulfide 6, a pale yellow solid which, owing to its difficult solubility properties, was not purified.⁵ Crude



6 (2 mmol) and either DDQ or *o*-chloranil (6.5 mmol) in 250 mL of chlorobenzene at reflux for 4 h gave 7 (40-45%). Chromatography on alumina (benzene eluent) and recrystallization (CHCl₃) gave pure 7, mp 236-238 °C.⁶ It showed a singlet at δ 7.52 (CDCl₃), somewhat downfield from that of the C-2 proton in thiophene (δ 7.19),⁷ possibly owing to deshielding by the adjacent thiophene rings.⁸ The ¹³C NMR spectrum of 7 consisted of two peaks, at δ 117.4 and 132.4 corresponding to C-1- and C-3a-type carbons respectively. These shifts may be compared with those of thiophene (C-2, 124.9; C-3, 126.7)⁹ and triphenylene (C-1, 123.7; C-2, 127.6; C-4a, 130.2).¹⁰

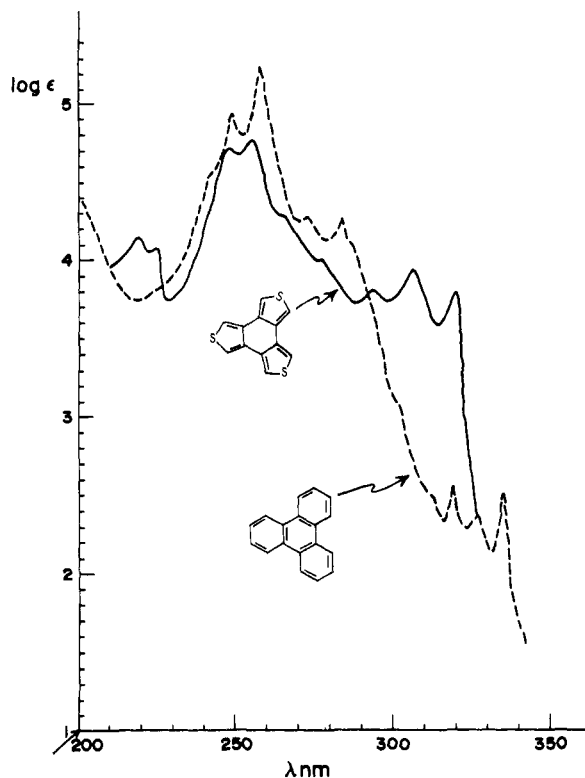
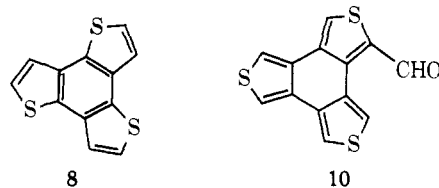


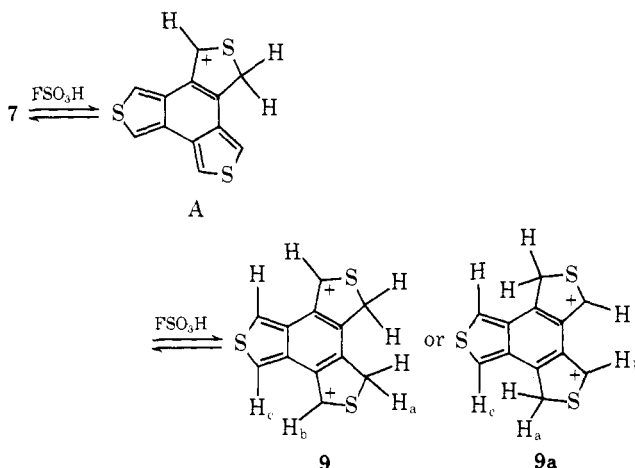
Figure 1. UV spectra of 7 (—) and triphenylene (---).

The ultraviolet spectrum of 7 is similar to that of triphenylene (Figure 1).¹¹ The longest wavelength absorption (320 nm) occurs at appreciably lower energy than that of the tris benzo[*b*] isomer 8 (286 nm).¹²



In contrast to 2, 7 does not readily add dienophiles (i.e., dimethyl acetylenedicarboxylate, benzyne). It does form intensely colored, air- and moisture-stable crystalline 1:1 charge-transfer (CT) complexes with TCNE, DDQ, TCNQ (all dark blue, CT band near 610 nm), and chloranil (dark red, CT band at 527 nm).¹³ Oxidation of 7 with SbCl₅ in methylene chloride gives a rather stable blue radical cation.¹⁴

Compound 7 exhibits unusual protonation behavior; in FSO₃H-SO₂ClF at -20 to -78 °C it gives a single species,

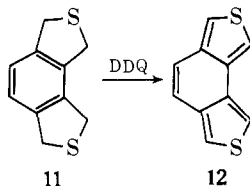


considered to be either **9** or **9a**.¹⁵ The ¹H NMR spectrum (−20 °C) had peaks at δ 5.90 (d, 4 H, *J* = 1.5 Hz, H_a), 9.34 (s, 2 H, H_c), 11.45 (t, 2 H, *J* = 1.5 Hz, H_b). With FSO₃D, exchange was rapid at H_a (δ 5.90 peak nearly absent in 5 min, δ 11.45 peak a singlet; quench gave 7-*d*₂) but extensive at all positions after 8 h (quench gave mainly 7-*d*₅ and 7-*d*₆). Although the monoprotonated species A could not be detected, rapid exchange of two protons and slow exchange of the remaining protons can best be rationalized by assuming a rapid equilibrium between **9** or **9a** and A but slow deprotonation of A in the strongly acidic medium.

Treatment of **7** with Br₂ in CCl₄ at room temperature (30 min) gave mono-, di-, or tribromo derivatives, depending on the Br₂/7 mole ratio. Isomer separation was difficult, but NMR analysis showed that three dibromo and two tribromo compounds were formed, these being the isomers possible without having two sterically interfering bromines in the same "wedge" of the structure. The isomer ratios were statistical.

Metalation of **7** was also possible. For example, treatment with butyllithium (2 equiv) in ether at −25 °C for 1 h followed by addition of DMF gave (60%) the yellow aldehyde **10**, mp 170–173 °C.¹⁶

The same mild dehydrogenation used to synthesize **7** was successful for the preparation of **12** (3, X = S)¹⁷ from **11**,¹⁸ in 35% yield, mp 111–112 °C (lit.¹⁷ mp 112–113 °C).



It is clear that, although exocyclic benzenes of type **2** are highly reactive toward cycloaddition, those of type **3** and **4** are much more aromatic in their reactivity. Extensions of the synthetic route described here to analogues of **7** and **12**¹⁹ (including those in which the remaining "wedges" in **7** are closed) and further studies of the chemistry of these exocyclic benzenes are in progress.

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- (3) Compound **4** can be regarded as a tris(hexamethylene)adialene. Its only classic valence bond structure (excluding dipolar forms or forms which use d orbitals of X) has all "double bonds" exocyclic to the central ring. The parent hydrocarbon, hexaradialene, was recently obtained in solution (A. J. Barkovich, E. S. Strauss, and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, **99**, 8321 (1977)), and two crystalline hexaalkyl derivatives have been known for some years (H. Hopff and A. K. Wick, *Helv. Chim. Acta*, **44**, 380 (1961); H. Hopff and A. Gati, *ibid.*, **48**, 1289 (1965)). NOTE ADDED IN PROOF. A synthesis of **4** (X = NCH₃) has recently been proposed but not yet realized: J. Ciric, S. L. Lawton, G. T. Kokotailo, and G. W. Griffin, *J. Am. Chem. Soc.*, **100**, 2173 (1978).
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- (5) NMR (Me₂SO-*d*₆) δ 4.17 (s); mass spectrum, calculated for C₁₂H₁₂S₃ 252.01013, observed 252.01065; mp 250–256 °C dec. Oxidation of **6** with 40% peracetic acid at room temperature for 14 h gave the corresponding tris sulfone: NMR (Me₂SO-*d*₆) δ 4.55 (s); mass spectrum, *m/e* (rel intensity) 348 (M⁺, trivial), 284 (M⁺ − SO₂, 25), 220 (M⁺ − 2SO₂, 42), 156 (M⁺ − 3SO₂, 85), 64 (SO₂⁺, 100). The mass spectrum of the sulfone suggests that it may serve, under appropriate conditions, as a precursor of hexaradialene or its cyclobutane isomers (E. Giovannini and H. Vuilleumier, *Helv. Chim. Acta*, **60**, 1452 (1977); R. S. Givens, *Tetrahedron Lett.*, 865 (1978)). NOTE ADDED IN PROOF. This prediction was recently verified: L. G. Harruff, M. Brown, and V. Boekelheide, *J. Am. Chem. Soc.*, **100**, 2894 (1978).
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- (15) A unique choice is not yet possible, but the dication obtained by "meta" diprotonation can be excluded on symmetry grounds. The chemical shifts of H_a and H_b agree well with those obtained on protonation of thiophene with HF–BF₃ at C-2 (δ 5.40 (H₂) and 11.27 (H₅); H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, **85**, 1072 (1966)).
- (16) NMR (CDCl₃) δ 7.58 (m, 3 H, C-4, -6, -7 protons), 7.97 (s, 1-H, C-3 proton), 8.72 (d, 1 H, *J* = 2.5 Hz, C-9 proton), 10.13 (s, 1 H, aldehyde); IR ν_{C=O} 1645 cm^{−1}.
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- (18) Improvements in literature procedures⁵ gave **11** in two steps (46%) from prehnitene.
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