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TETRATHIA[22]ANNULENE[2,1,2,1]. A NEW THIOPHENE-DERIVED AROMATIC MACROCYCLE

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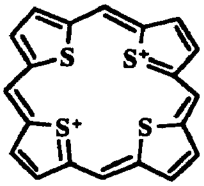
Abstract- Tetrathia[22]annulene[2,1,2,1] (4) has been synthesized in four steps from 2-bromothiophene. Compound 4 represents the first porphyrinoid containing only sulfur bridges which is a neutral aromatic annulene.

The synthesis and properties of expanded porphyrins and analogs containing furan or thiophene units has developed into an active area of research in recent years.[1] Thus, a number of new aromatic porphyrinoids are now known, including several (2 and 3) containing both pyrrole and thiophene subunits.[2] Among the known conjugated macrocycles derived only from thiophene, neither aromatic nor antiaromatic ring currents have been observed,[3] with the sole exception of the aromatic tetrathiaporphyrin dication 1.[4] We now report the synthesis of the first neutral aromatic annulene (4) derived only from thiophene and methine units.



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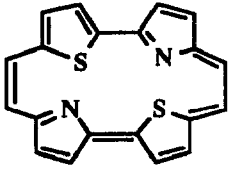

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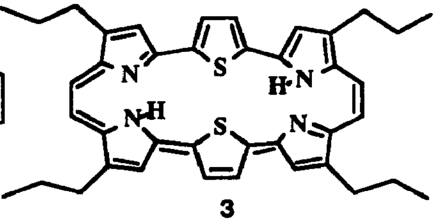

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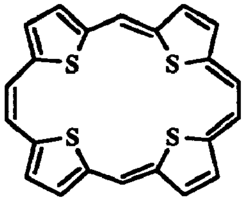
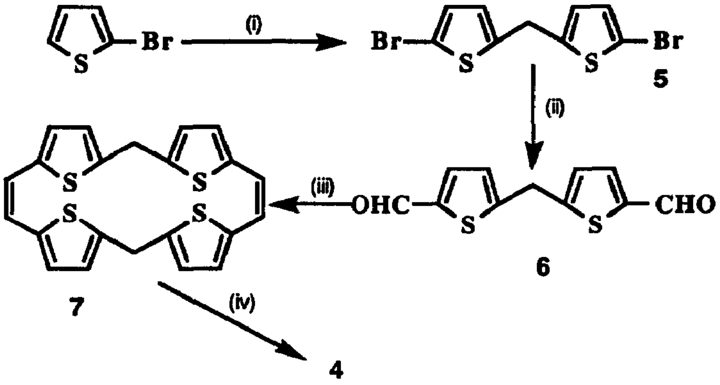


4

The acid catalysized condensation of 2-bromothiophene with dimethoxymethane afforded, in excellent yield, dibromide **5**. The unsubstituted dithienylmethane has been prepared in a similar manner from thiophene, along with considerable amounts of oligomeric materials.[5] Low temperature halogen-lithium exchange of **5**, followed by reaction with DMF and subsequent hydrolysis, yielded dialdehyde **6**. The preparation of **6** by direct lithiation of dithienylmethane was not practical, in view of the competing lithiation of the central methylene group.[6] The reductive McMurry coupling of dialdehyde **6** gave the macrocycle **7** in remarkably high yield (75%). The dehydrogenation of **7** by DDQ occurred immediately in methylene chloride solution to give an insoluble black complex, which was readily reduced by hydrazine to give the black annulene **4** in 82% yield.[7]



(i) $CH_2(OMe)_2$, $HOAc/H_2SO_4$, 85% (ii) BuLi, THF/-70°C;DMF. 63%
(iii) $TiCl_4/Zn$, pyridine, THF, reflux. 75% (iv) DDQ,then hydrazine 82%
Scheme I

The aromaticity of **4** was evidenced by its ^1H NMR and UV-visible absorption spectrum. In the ^1H NMR, there are two singlets at 12.34 and 11.36 ppm, corresponding to the protons on the methine carbon and the double bond, and an AB system of the protons on thiophene units at 10.86 and 10.84 ppm. All of the protons are obviously deshielded by the aromatic ring current. In contrast, no protons of the dihydro compound **7** appear below 6.8 ppm.[7] The mass spectrum showed a strong molecular peak (100%) and little fragmentation. In the UV-visible spectrum, there are sharp and strong maxima at 417 nm and several weaker absorptions at longer wavelength (503, 540, 579 and 771 nm). The first absorption (at 417 nm) is analogous to the typical Soret band of porphyrins and porphycenes, while absorptions at longer wavelengths are similar to Q-bands, but with a bathchromic shift with respect to porphycene. These spectra are clearly typical of an aromatic system. The aromaticity of **4** requires a planar structure. Compared to other solely thiophene derived annulenes, this macrocycle is less crowded enabling it to have a planer structure with its π-electrons fully conjugated around the periphery.

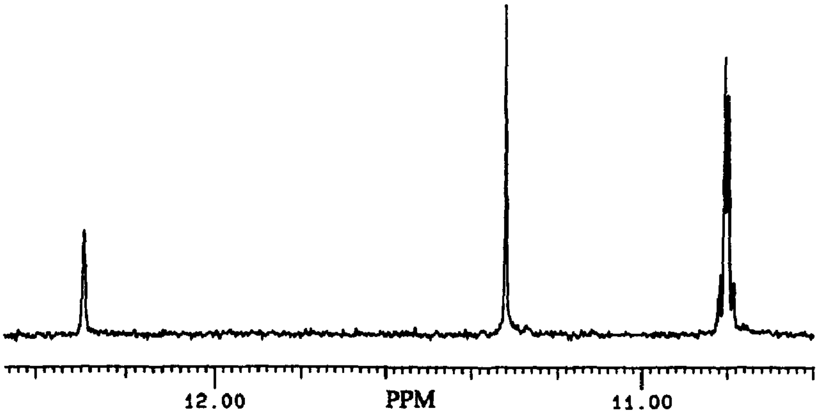


Figure 1. ^1H NMR spectrum of Aromatic 22π macrocycle 4 (360 MHz, in DMSO-d_6)

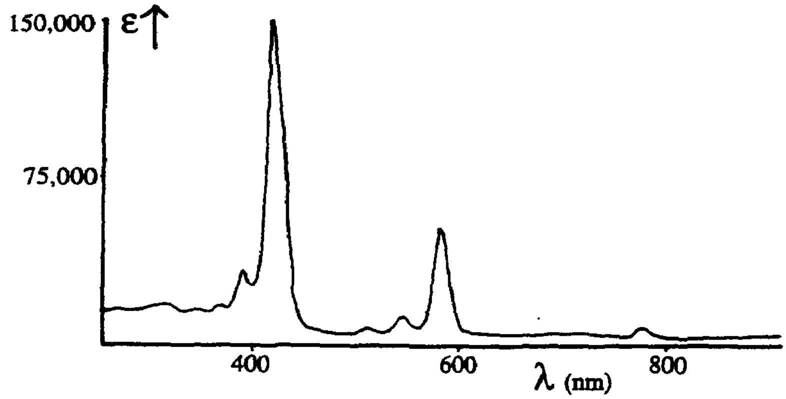


Figure 2. UV-Visible Absorption Spectrum of 4 (in methylene chloride)

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7. Compounds **4**, **5**, **6** and **7** exhibit satisfactory ^{1}H, ^{13}C NMR data and high resolution mass spectra in accord with the assigned structures.
   Compound **4**: ^{1}H NMR (DMSO-d_6): δ12.34 (2H, s), δ11.36(4H, s), δ10.86(4H, d, J=4.7 Hz), δ10.84(4H, d, J=4.7Hz);^{13}C NMR (DMSO-d_6)(ppm): 136.16(q-C), 135.50(q-C), 135.23, 131.12, 113.26, 111.57(q-C); UV-Visible: λnm(logε), 771(3.62), 579(4.71),540(4.01), 503(3.70), 417(5.18), 387(4.50), 311(4.23) MS(EI):(m/e, %), 406 (M$^+$, 100), 203(M^{++}, 22); HRMS: calcd. for $C_{22}H_{14}S_4$,405.9978, found 405.9977
   Compound **5**:^{1}H NMR(CDCl$_3$): δ 6.88(2H, d, J=3.7Hz), δ6.63(2H, d, J= 3.7Hz), δ4.18(2H, s); ^{13}C NMR (CDCl$_3$) 143.79, 129.62, 125.81, 110.73, 30.81; MS: 338(M$^+$, 78), 259(M-Br, 78), 176(M-2Br, 100), 134(75); HRMS: calcd for $C_9H_6S_2Br_2$, 335.8278, found 335.8279
   Compound **6**: ^{1}H NMR(CDCl$_3$) δ9.84(2H,s), δ7.64(2H, d, J=3.7Hz), δ7.02(2H, d, J=3.6Hz), δ4.43(2H, s); ^{13}C NMR (CDCl$_3$)(ppm): 182.63, 151.79, 143.15, 136.67, 127.30, 31.56; MS: 236(M+, 85), 207 (100), 179(33), 135(29); HRMS: calcd for $C_{11}H_8S_2O_2$, 235.9966, found 235.9958
   Compound **7**: ^{1}H NMR (CDCl$_3$): δ6.78(8H, s), δ6.52(4H, s), δ6.77(4H, s); ^{13}C NMR(CDCl$_3$): (ppm): 145.17(q-C), 138.48(q-C), 128.25(CH), 124.81(CH), 123.48(CH), 31.64(CH$_2$); UV-Visible: λnm(logε), 348(4.30), 259(4.29), 223(4.23); MS(EI):(m/e, %), 408 (M$^+$, 100), 300(16); HRMS: calcd. for $C_{22}H_{16}S_4$, 408.0135, found 408.0137

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