5, 8, 17, 20-Tetrakis(3, 5-di-*t*-butylphenyl)-6, 7, 18, 19-tetradehydrotetrathia[24]annulene-(4. 0. 4. 0) and Its Dianion: New Thiophene-Derived Paratropic and Diatropic Annulenes

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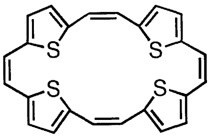
5, 8, 17, 20-Tetrakis(3, 5-di-*t*-butylphenyl)-6, 7, 18, 19-tetradehydrotetrathia[24]annulene (4. 0. 4. 0) shows clear paratropicity (antiaromaticity) and highly amphoteric redox properties, whereas the dianion obtained by its alkali metal reduction strong diatropicity (aromaticity) as a novel 26π-electron system.

Recently, conjugated macrocycles containing thiophene rings have attracted considerable attention in relation to the novel chemistry of porphyrinoids and annulenes.[1-3] There have been reported two kind of [24]annulenes containing four thiophene rings: tetrathia[24]annulene (2.2.2.2) **1** by Wennerström[4] and Cava[3] and its tetradehydro derivative **2** by us.[5] While coformationally mobile **1** was reported to show weak antiaromatic (paratropic) properties at low temperature, **2** hardly show effects of peripheral conjugation in spite of the planar X-ray structure. As a part of our studies toward the construction of novel extended π-electron systems composed of butatrienes and thiophenes, we have synthesized the titled compound **3**, namely 5, 8, 17, 20-tetrakis(3, 5-di-*t*-butylphenyl)-6, 7, 18, 19-tetradehydrotetrathia-[24]annulene (4. 0. 4. 0), which is the first example of tetrathia[24]annulene having tetradehydro (4. 0. 4. 0) skeleton. Here we wish to report the synthesis and properties of **3** and its dianion **8** which show clear paratropic and diatropic properties, respectively.



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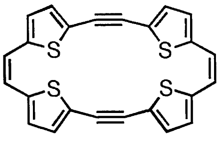

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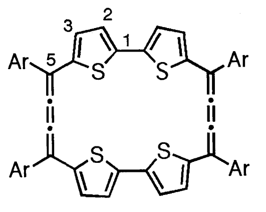

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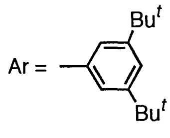
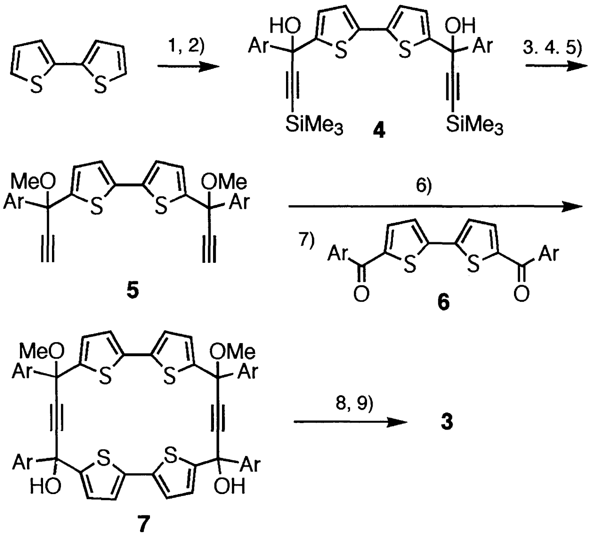


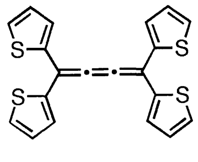
Reaction of diacetylide of **5**, obtained from 2,2-bithiophene via **4**, with diketone **6** at -78 °C gave a complex mixture containing desired cyclic diol **7** (Scheme 1). Without purification, the mixture was subject to reductive dehydroxylation by treatment with tin(II) chloride in ethereal hydrogen chloride[6,7] followed by neutralization with triethylamine to afford **3** in 4% yield (from **5**) after chromatographic purification on alumina.

Annulene **3** is dark green crystalline substance and stable enough for chromatography on alumina, although sensitive to acids and silica gel. ^{1}H-NMR spectrum of **3** exhibits the thiophene protons (5.39 ppm) and ortho-protons of the aryl groups (6.70 ppm; Table 1) at considerably high field compared to those of acyclic precursor **5** (thiophene protons: 6.88 ppm; aryl ortho-protons: 7.50 ppm) and (2.2.2.2) annulene **2** (thiophene protons: 7.01 and 6.84 ppm[5]), indicating induction of considerable paramagnetic ring current around the 24π-electron periphery. The ^{13}C-chemical shift of cumulenic sp carbons of **3** (134.48 ppm) is appreciably higher than those of tetraphenylbutatriene (152.03 ppm[8]) and tetrakis(2-thienyl)butatriene **8** (140.53 ppm[9]) to suggest increase of acetylenic character of the central double bonds owing to resonance contribution of **3'**.



Scheme 1.

Reagents and conditions: 1) 2.2 eq. *n*-BuLi/THF, -78 °C; 2) 2.2 eq. ArCOC≡CSiMe$_3$ (81%); 3) 2.0 eq. NaH/THF, rt; 4) 3.0 eq. MeI; 5) K$_2$CO$_3$/MeOH (90% from **4**); 6) 4.0 eq. *n*-BuLi/THF, -78 °C; 7) 1.0 eq. **6**, -78 °C; 8) SnCl$_2$•2H$_2$O / HCl / ether, 0 °C; 9) Et$_3$N (4% from **5**).



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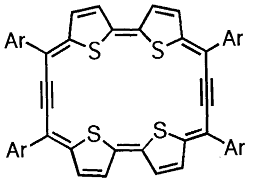

3'

Upon cyclic voltammetry, **3** displays amphoteric redox properties better than **8**, showing two reversible waves for each oxidation and reduction at lower potentials (Table 2); thus, the numerical sums of E_{ox} and E_{red},[10] $^1E_{sum}$ (1.47 V) and $^2E_{sum}$ (1.80 V) are considerably smaller than those of **8** (2.13 and 2.62 V, respectively). The E_{sum} values of **3** are among the lowest ones observed for butatriene derivatives.[9,11] The highly amphoteric properties may be due to aromatic stabilization of its dication (a

Table 1. Selected spectral data of **3**, **5** and **9**

3: MS(FAB): m/z 1181 ([M+H]$^+$); ^{1}H-NMR (270 MHz / CDCl$_3$): δ = 7.14 (t, J = 1.7 Hz, 4H), 6.70 (d, J = 1.7 MHz, 8H), 5.39 (br.s, 4H, thiophene), 1.14 (s, 72H); ^{13}C-NMR (67.8 MHz / CDCl$_3$): δ = 149.81, 148.55, 147.08 141.67, 134.48 (cumulenic), 129.12, 123.86, 121.99, 120.50, 117.16, 34.05, 30.67; UV-Vis (CH$_2$Cl$_2$): λ_{max}/nm (log ε) = 597 sh (3.79), 436 (4.67), 377 (4.74); Raman: ν = 2021 cm^{-1}.

5: MS(FAB): m/z 678 (M$^+$); ^{1}H-NMR (270 MHz/CDCl$_3$) d = 7.50 (d, J = 2.0 Hz, 4H), 7.35 (t, J = 2.0 Hz, 2H), 6.88 (br.s, 4H, thiophene), 3.40 (s, 6H), 2.90 (s, 2H), 1.31 (s, 36H).

9: ^{1}H-NMR (270 MHz/THF-d$_8$): δ = 11.17 (d, J = 4.3 Hz, 4H)[a], 10.52 (d, J = 4.3 Hz, 4H)[a], 9.17 (d, J = 1.7 Hz, 8H), 7.59 (t, J = 1.7 Hz, 4H), 1.71 (s, 72H).

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[a] Ref. 12.

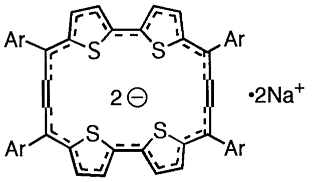
Table 2. Redox potentials[a] of **3** in comparison with **8**

	^{2}Eox	^{1}Eox	^{1}Ered	^{2}Ered	^{1}Esum	^{2}Esum
3	+0.54	+0.34	-1.13	-1.26	1.47	1.80
8[b]		+0.94[c,d]	-1.19	-1.68	2.13	2.62

[a] V vs. Ag/AgCl (ferrocene = +0.40 V) in 0.1 M n-Bu$_4$NClO$_4$/DMF at 25 ℃. [b] Ref. 9. [c] Peak potential. [d] Two-electron wave.

22π-electron system) and dianion (a 26π-electron system).

Indeed, reduction of **3** with 3% sodium-amalgam in THF gave dianion **9** in a deep purple solution which regenerated **3** upon exposure to air. ^{1}H-NMR spectrum of **9** (Fig. 1) exhibits the thiophene protons at remarkably low field of 11.17 and 10.52 ppm,[12] despite its dianionic nature, comparable to those of **10** (10.86 and 10.84 ppm[3]), a thiophene-derived 22π aromatic annulene. The ortho protons and *t*-butyl groups of the aryl groups are also observed at appreciably lower field (9.17 and 1.71 ppm, respectively) than those of **3** and **5**. Dianion **9** is thus a new, distnct, thiophene-derived 26π-electron aromatic species.



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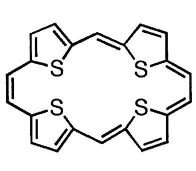

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The semiempirical calculations (AM1 and PM3[13]) of **3** predict an almost planar structure with only slight bending in the butatriene moieties (177-178°), whereas the triple bonds of **2** are more severely bent (165-166°) in the X-ray structure. Degree of the strain energy in the minor resonance structures, e.g. **3'** for **3**, would be primarily responsible for the remarkable difference in the tropicity between **2** and **3**.

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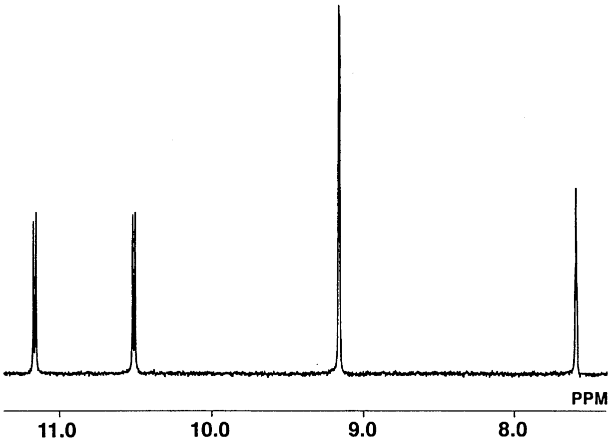

Figure 1. ^{1}H-NMR spectrum of **9** (aromatic region; 270 MHz, THF-d$_8$, 30 °C).

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