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The Synthesis of a [13][15]Fulvalene Derivative

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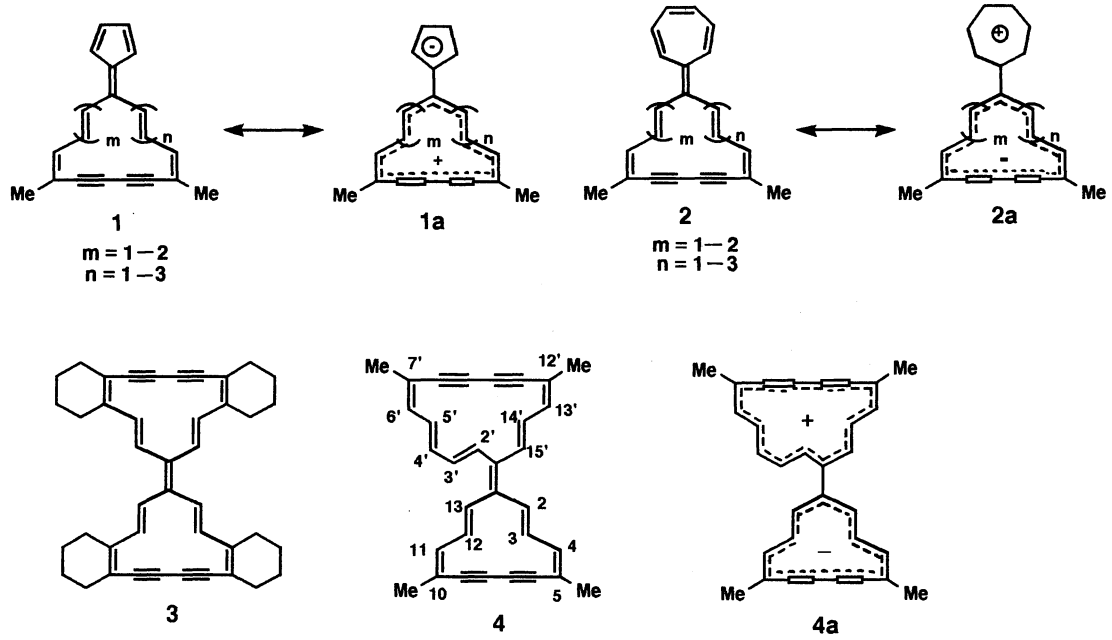
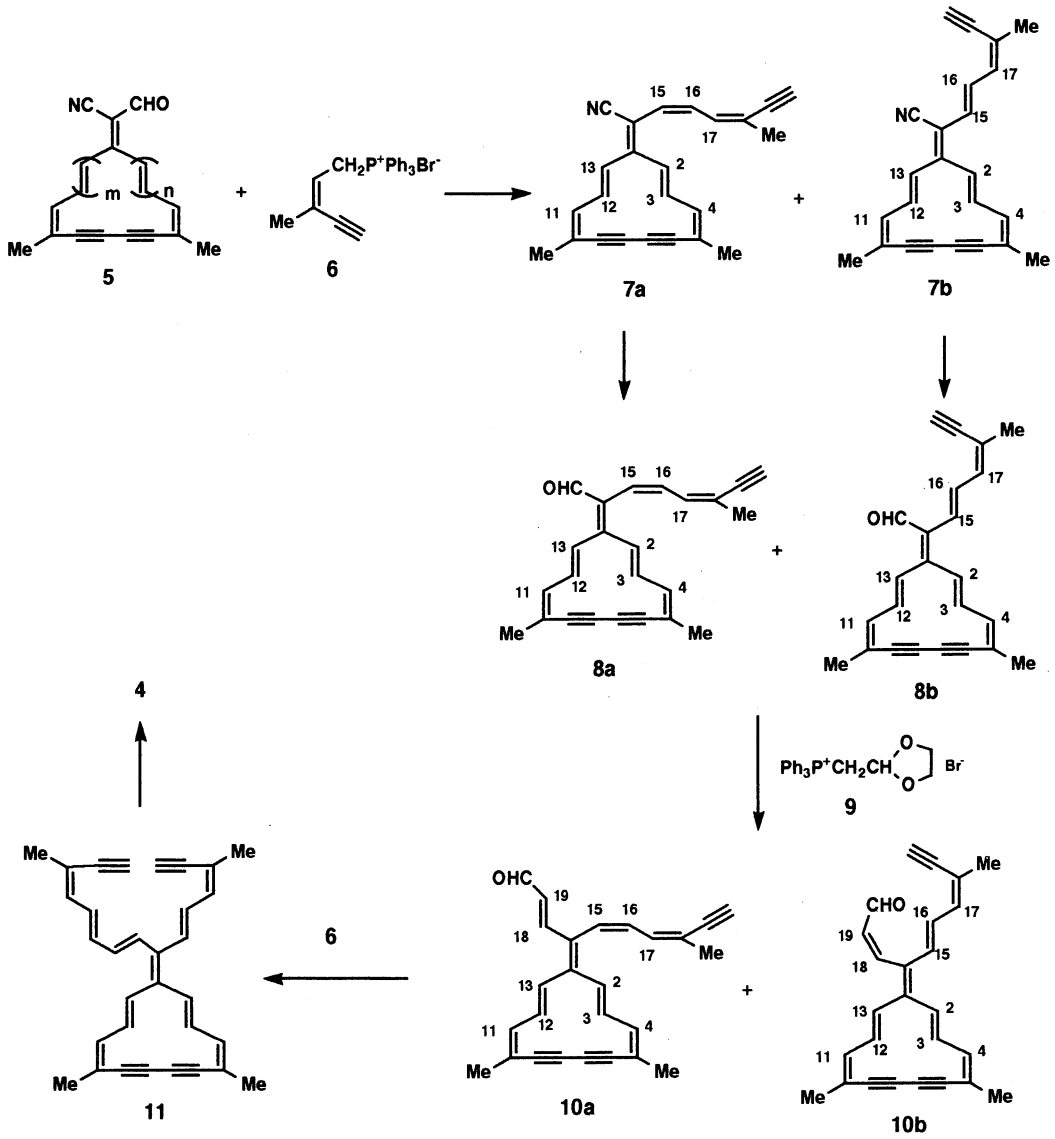
The first example of fuluvalene derivative containing two monocyclic large-membered rings, 1-(5,10-dimethyl-6,7,8,9-tetradehydrocyclotridecen-1-ylidene)-7,12-dimethyl-8,9,10,11-tetradehydrocyclopentadecene, has been synthesized. Examination of ^{1}H and ^{13}C NMR spectra indicates that the tridecapentadecafulvalene derivative shows no ring current effect but polyolefinic character.

We have been interested in the synthetic studies of the cyclic cross-conjugated π-electron systems, such as fulvenes[1] and fulvalenes containing monocyclic large-membered ring.[2] Of these, we have shown that a slight π-electron polarization occurs at the ground state from the large ring to the 5-membered ring in pentafulvalenes **1** and from the 7-membered ring to the large ring in heptafulvalenes **2**, as depicted in **1a** and **2a**, respectively. An obvious extension of our interests in these studies directed our efforts to the preparation of fulvalene derivatives composed of two large-membered rings. A precedent of this system is the tetrakis(cyclohexene)-annelated [13][13]fulvalene **3**, prepared by Howes and Sondheimer,[3] which was characterized only in a solution, and proved to be very unstable and to have highly polyolefinic character by ^{1}H NMR spectroscopy. The polyolefinic nature might be reasonable because the polarization of the pinch bond could render one ring 14π aromatic, but the other 12π antiaromatic. The result of the study on the [13][13]fulvalene **3** prompted us to investigate [13][15]fulvalene **4**, the higher homolog of sesquifulvalene,[4] which exhibits aromatic stabilization arising from possible contribution of a dipolar structure. We considered that compound **4** is potentially aromatic, because one ring is 13-membered and the other is 15-membered and polarization of the pinch bond will make both rings 14π-electron aromatic systems as shown in a dipolar structure **4a**.

The compound **4** was synthesized according to the procedure outlined in Scheme. Wittig condensation of the cyanoformyl derivative **5**[5] with the phosphonium salt **6**[6] with BuLi in THF afforded the Z-isomer **7a**[7] [red needles, mp 77-78 °C (dec); ^{1}H NMR[8] δ 8.46 (dd, J=16, 10 Hz, H^{12}), 8.14 (dd, J=16, 9 Hz, H^{3}), 7.24 (d, J=12 Hz, H^{15}), 6.75 (dd, J=12, 12 Hz, H^{16}), 6.63 (d, J=16 Hz, H^{13}), 6.56 (d, J=10 Hz, H^{11}), 6.41 (d, J=9 Hz, H^{4}), 6.29 (d, J=16 Hz, H^{2}), 6.20 (d, J=12 Hz, H^{17}), 3.43 (s, C≡CH), 2.03 (s, Me), 1.82 (br. s, Me)] and E-isomer **7b** [dark red needles, mp 74-76 °C (dec); δ 8.33 (dd, J=16, 10 Hz, H^{12}), 8.06 (dd, J=16, 10 Hz, H^{3}), 7.22 (d, J=15 Hz, H^{15}), 6.67 (d, J=16 Hz, H^{13}), 6.67 (dd, J=15, 8 Hz, H^{16}), 6.59 (d, J=10 Hz, H^{11}), 6.48 (d, J=10 Hz, H^{4}), 6.44 (d, J=8 Hz, H^{17}), 6.38 (d, J=16 Hz, H^{2}), 3.47 (s, C≡CH),



2.01 (s, Me), 1.84 (br. s, Me)] of the newly formed double bond in a total yield of 65%. Individual reduction of **7a** and **7b** with DIBAH in toluene afforded **8a** [red needles, mp 89-90 °C (dec); 30% yield; δ 10.10 (s, CHO), 8.09 (dd, J=16, 10 Hz, H^{12}), 7.21 (dd, J=16, 7 Hz, H^{3}), 6.88 (dd, J=12, 12 Hz, H^{16}), 6.77 (d, J=16 Hz, H^{13}), 6.58 (d, J=10 Hz, H^{11}), 6.45 (d, J=7 Hz, H^{4}), 6.24 (d, J=16 Hz, H^{2}), 6.22 (d, J=12 Hz, H^{15}), 6.04 (d, J=12 Hz, H^{17}), 3.37 (s, C≡CH), 1.90 (br. s. Me), 1.84 (s, Me)] and **8b** [brown needles, mp 115-117 °C (dec); 31% yield; δ 10.14 (s, CHO), 7.88 (dd, J=16, 10 Hz, H^{12}), 7.10 (dd, J=16, 10 Hz, H^{3}), 7.07 (dd, J=16, 8 Hz, H^{16}), 6.68 (d, J=16 Hz, H^{13}), 6.66 (d, J=10 Hz, H^{11}), 6.59 (d, 16 Hz, H^{2}), 6.52 (d, J=16 Hz, H^{15}), 6.46 (d, J=10 Hz, H^{4}), 6.45 (d, J=8 Hz, H^{17}), 3.34 (s, C≡CH), 2.00 (s, Me), 1.90 (s, Me), 1.87 (s, Me)], respectively. Wittig condensation of a mixture of **8a** and **8b** with 10 equivalents of the phosphonium salt **9**[6] afforded again a stereoisomeric mixture of the homologated aldehyde **10** in 30% yield. Among the four possible isomeric products the isomers **10a** [dark brown needles, mp 120 °C (dec); δ 9.67 (d, J=8 Hz, CHO), 7.87 (dd, J=16, 10 Hz, H^{12}), 7.78 (d, J=15 Hz, H^{18}), 7.48 (dd, J=16, 9 Hz, H^{3}), 6.88 (dd, J=12, 12 Hz, H^{16}), 6.58 (d, J=16 Hz, H^{13}), 6.57 (d, J=10 Hz, H^{11}), 6.56 (d, J=9 Hz, H^{4}), 6.31 (d, J=16 Hz, H^{2}), 6.23 (dd, J=15, 8 Hz, H^{19}), 6.10 (d, J=12 Hz, H^{15}), 6.04 (d, J=12 Hz, H^{17}), 3.36 (s, C≡CH), 1.90 (s, Me), 1.88 (s, Me), 1.84 (s, Me)] and **10b** [red brown needles, mp 80-82 °C (dec); δ 9.44 (d, J=8 Hz, CHO), 7.46—7.16 (m, H^{3}, H^{12}, H^{18}), 6.99 (d, J=15 Hz, H^{15}), 6.74—6.44 (m, H^{4}, H^{11}, H^{13}, H^{16}, H^{17}), 6.33 (dd, J=12, 8 Hz, H^{19}), 6.29 (d, J=16 Hz, H^{2}), 3.38 (s, C≡CH), 2.00 (s, Me), 1.91 (s, Me), 1.84 (s, Me)] could be characterized. Wittig reaction of an isomeric mixture of **10** with the salt **6** afforded the stereoisomeric mixture of **11** [δ 7.71—6.20 (m, 14 H, olefinic H), 3.36—3.30 (m, 2H, C≡CH), 2.01—1.86 (m, 12 H, Me)]. Since compound **11** proved to be very unstable, the following reaction was carried out without separation of these isomers. An intramolecular oxidative coupling of the mixture of the fulvene derivative **11** and its stereoisomers containing two terminal acetylene groups under high dilution conditions afforded the desired [13][15]fulvalene **4** in 22% yield as relatively unstable purple needles [mp 160 °C (dec)].



The ^{1}H NMR spectrum of **4** was thoroughly analyzed as follows, based on the homonuclear double resonance and nuclear Overhauser effect experiments. ^{1}H NMR (500 MHz, CDCl3) δ 7.36 (dd, J=15.4, 10.6 Hz, $H^{5'}$), 7.34 (dd, J=15.4, 11.3 Hz, $H^{14'}$), 7.22 (d, J=16.2 Hz, $H^{2'}$), 7.02 (dd, J=16.2 Hz, 10.4 Hz, H^{12}), 7.01 (d, J=15.4 Hz, $H^{15'}$), 6.97 (dd, J=16.3, 9.5 Hz, H^{3}), 6.77 (d, J=10.4 Hz, H^{11}), 6.70 (d, J=9.5 Hz, H^{4}), 6.67 (d, J=11.3 Hz, $H^{13'}$), 6.63 (d, J=10.6 Hz, $H^{6'}$), 6.50 (d, J=16.2 Hz, H^{13}), 6.45 (d, J=16.3 Hz, H^{2}), 6.43 (dd, J=15.4, 5.8 Hz, $H^{4'}$), 6.23 (dd, J=16.2, 5.8 Hz, $H^{3'}$), 1.93 (s, 5-Me), 1.92 (s, 12'-Me), 1.91 (s, 10-Me), 1.90 (s, 7'-Me). ^{13}C NMR (125 MHz, CDCl3) δ 19.7 (p), 20.3 (p), 20.5 (p), 20.9 (p), 83.0 (q), 83.3 (q), 84.6 (q), 86.3 (q), 90.1 (q), 91.3 (q), 100.4 (q), 101.1 (q), 119.8 (q), 120.4 (q), 121.7 (q), 121.7 (q), 124.6 (t), 127.7 (t), 131.8 (t), 132.1 (t), 132.5 (t), 132.7 (t), 133.4 (t), 133.5 (t), 136.6 (q, C^1 or $C^{1'}$), 138.9 (t), 141.0 (t), 141.6 (t), 141.6 (C^1 or $C^{1'}$), 142.2 (t), 142.8 (t). MS *m/z* 410 (M+, 18%) and 57 (100); mol wt 410.5.

Although thermally far more stable than **3**, compound **4** was considered to be an atropic molecule from the following observations. In the ^{1}H NMR spectrum the olefinic inner and outer protons of both rings of **4** resonate in a narrow region of the magnetic field and the four methyl groups have almost the same chemical shifts. This suggests that compound **4** shows no ring current effect. The small ^{13}C NMR chemical shift difference between the pinch bond carbon atoms (C^1 and $C^{1'}$) is also incompatible with the polarization of the bond.

The 5- and 10-methyl signals showed a slight exchange broadening at 110 °C in toluene-d_8 indicating that the energy barrier to rotation about pinch bond is at least 19 kcal mol^{-1} and that the bond has high double bond character.

The contribution of a dipolar structure in **4** seems even smaller than that of sesquifulvalene and compound **4** should be considered to be polyolefinic. This may be ascribed to the nonplanarity of either one or both of the two macrocyclic rings due to inherent strain of the rings and the inter-ring congestion.

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7) Satisfactory IR, mass spectral, and analytical data have been obtained for the compounds outlined in Scheme except for the extremely unstable compound **11**.
8) ^{1}H NMR spectra of the compounds described in this paper were taken in $CDCl_3$ solution at 270 MHz spectrometer unless otherwise stated.

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