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Synthesis of the First 3,6,9,12,15,18-Hexa-substituted-1,2,4,5,7,8,10,11,13,14,16,17-Dodecadehydro[18]annulenes with D_{6h}-Symmetry

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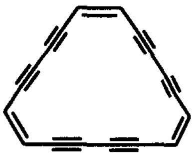
Abstract: 3,6,9,12,15,18-Hexaphenyl-1,2,4,5,7,8,10,11,13,14,16,17-dodecadehydro[18]annulene and related compounds have been synthesized. These compounds were found to be stable both in crystalline forms and chloroform solution at room temperature, to have aromatic character by the existance of a diamagnetic ring current on the basis of the nmr spectral data, and to conform to the D_{6h}-symmetry group.

1,3,7,9,13,15-Hexadehydro[18]annulene (**1**),[1] 6,8,15,17-tetrakisdehydro[18]annulene (**2**),[2] and 1,10-bis-dehydro[18]annulene (**3**)[3] have been synthesized by two groups. These systems contain (4n + 2) out-of-plane π electrons and the existence of a diamagnetic ring current has been shown.



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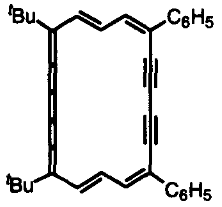

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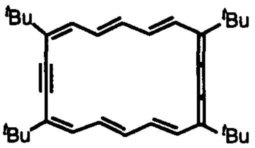

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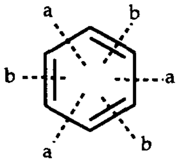

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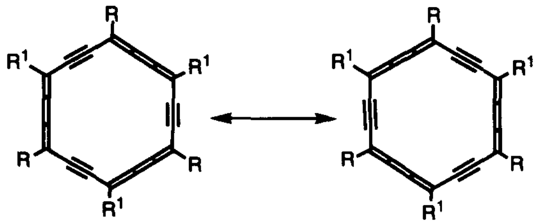


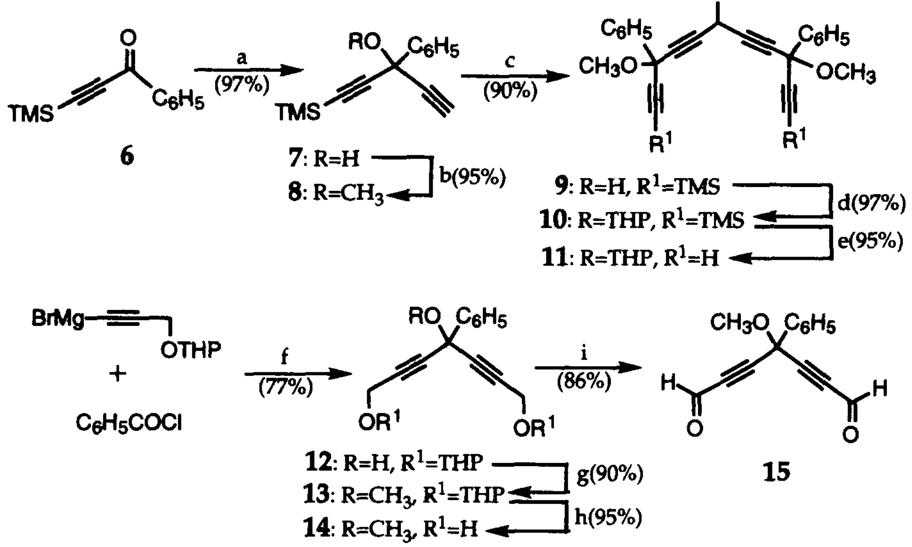
5a,b,c,d **5'a,b,c,d**

a: $R=R^1=H$, **c**: $R=C_6H_5$, $R^1=C_6H_4{}^tBu$-*p*,
b: $R=R^1=C_6H_5$, **d**: $R=C_6H_5$, $R^1={}^tBu$

1,2,4,5,7,8,10,11,13,14,16,17-dodecadehydro[18]annulene (**5a**) can be drived from **4** by the insertion of the linear acetylenic group (-C≡C-) at the position a and the linear cumulene group (=C=C=) at the position b.[4] The protons in this compound are in a similar environment to those in **4**. Compound **5a** contains (4n + 2) out-of-plane π electrons and is to conform to the D_{6h}-symmetry group. This symmetry implies that no bond length alternation (in the sense of successive 'single' and 'double' bonds) exists in this molecule. We now describe a synthesis of 3,6,9,12,15,18-hexa-substituted-1,2,4,5,7,8,10,11,13,14,16,17-dodecadehydro[18]annulenes (**5b**, **5c**, and **5d**), the nmr spectra of which provide strong evidence for the existence of a diamagnetic ring current.

Reaction of **6**, which was prepared by the method in the literature,[5] with ethynylmagnesium bromide gave **7**, which was converted into *O*-methyl derivative **8**. Compound **8** after treated with ethylmagnesium bromide was allowed to react with methyl formate to give alcohol **9**. After protection of the hydroxyl group of **9** with tetrahydropyranyl (THP) group, **10** obtained was treated with tetrabutylammonium fluoride (TBAF) to give an important key intermediate **11** in the over-all yield of 85% from **6**. Methylation of **12**, which was prepared from benzoyl chloride and tetrahydropyranyloxypropargylmagnesium bromide, gave **13**. To remove of THP moiety **13** was treated with pyridinium *p*-toluenesulfonate (PPTS) in MeOH. Compound **14** obtained was converted into dialdehyde **15** by Dess-Martin oxidation in the over-all yield of 57% from benzoyl chloride.

Scheme 1

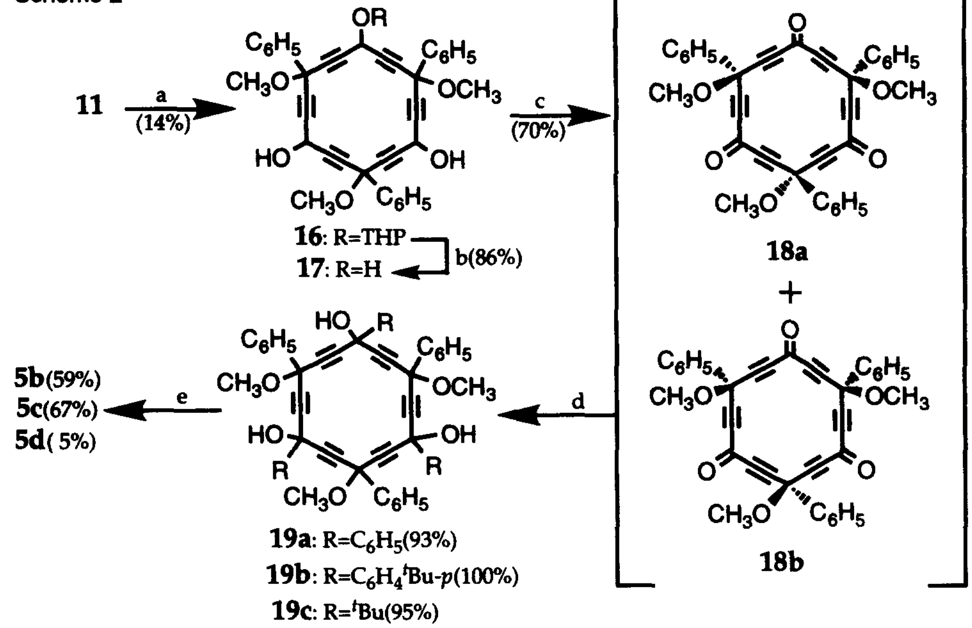


Reagents and conditions: a) HC≡CMgBr, THF, 0 °C, b) 1) *n*-BuLi, THF, -78 °C; 2) CH_3I, DMSO, -25 °C, c) 1) C_2H_5MgBr, THF, 0 °C; 2) $HCOOCH_3$, THF, 0 °C, d) DHP/PPTS, CH_2Cl_2, rt, e) TBAF, THF/H_2O, rt, f) THF, 0 °C, g) NaH, CH_3I, THF, rt, h) PPTS, MeOH, 55 °C, i) Dess-Martin oxidation, CH_2Cl_2, rt.

After many attempts we found a useful procedure for intermolcularcyclization of **11**with **15** (Scheme 2): acetylide derivative, which was prepared by reaction of **11** in the concentration of 0.2 mol/l with ethylmagnesium bromide in the presence of cerium chloride, was allowed to react with **15** (1.1 equiv) to give **16** in 14% yield. Removal of THP moiety of **16** gave **17**, which was converted by Dess-Martin oxidation into triketone derivatives (**18a** and **18b**) in a ratio of 7:1 in 70% yield. Relative configuration of **18a** and **18b** illustrated in Scheme 2 was assigned on the basis of ^{1}H-NMR spectral data. Reaction of a mixture of **18a** and **18b** with phenylmagnesium bromide (3 equiv) gave triol derivative **19a** in high yield. Reaction of **18** with corresponding Grignard reagents gave triols (**19b** and **19c**), respectively. Conversion of **19a** into **5b** was achieved with success as follows: **19a** was added to an ether solution saturated with hydrochloric acid in the presence of stannous chloride dihydrate (10 equiv). The mixture was stirred for 30 min at O °C and the reaction was quenched by pouring the reaction mixture into a (1:3) mixture of 10*N* aqueous sodium hydroxide and saturated aqueous sodium bicarbonate.

Purification by silicagel column chromatograhpy using chloroform as an eluent gave **5b**[6] in 59% yield. Similar treatments of **19b** and **19c** gave **5c** and **5d** in 67% and 5% yields, respectively. **5b** [mp 250°C (dec.); violet needles], **5c** [mp 220°C (dec.); violet needles], and **5d** [mp 235-237°C; red-orange needles] were stable in the crystalline forms and in chloroform solution at room temperature.

Scheme 2



Reagents and conditions: a) 1) $C_2H_5MgBr/CeCl_3$, THF, 0 °C; 2) Addition of **15**, THF, 0 °C, 0 °C, b) PPTS, MeOH, 55 °C, c) Dess-Martin oxidation, CH_2Cl_2, rt, d) RMgBr, THF, 0 °C, e) $HCl/SnCl_2$, Et_2O, 0 °C.

The ^{1}H-NMR spectrum ($CDCl_3$, 270.05 MHz) of **5b** consisted of three signals of δ 9.49 (d, *J*=7.5Hz, 12H) ppm for *ortho* protons, 8.01 (t, *J*=7.5Hz, 12H) ppm for *meta* protons, and 7.74 (t, *J*=7.5Hz, 6H) ppm for *para* protons. In the ^{13}C-NMR spectrum ($CDCl_3$, 67.80 MHz) of **5b**, six carbon signals of δ 140.3, 130.6, 129.9, 129.4, 118.5, and 104.5 ppm were observed. Of these signals, both signals of δ 118.5 and 104.5 ppm were determined to be sp- and sp^2-carbons of annulene skeleton. The ^{1}H-NMR spectra of **5c** and **5d** showed that the protons on benzene rings were in a similar environment to those of **5b**. The signals of δ 1.65 (s, 27H) and 2.56 (s, 27H) ppm were determined to be *t*-butyl groups of **5c** and **5d**, respectively. By the comparison of *t*-butyl group (δ 2.56 ppm) of **5d** with those of **19c** (δ 1.14 ppm) and **2** (δ 2.07 ppm) the downfield shift in the (4n + 2) π-electorn system **5d** is δ 1.42 ppm and δ 0.49 ppm, respectively.[2] These observations on the downfield shifts of protons of benzene and *t*-butyl groups provide strong evidence for the existence of a diamagnetic ring current in **5**.

Acknowledgments

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4) T. J. Sworski, *J. Chem. Phys.*, **1948**, *16*, 550.
5) H. Newman, *J. Org. Chem.*, **1973**, *38*, 2254.
6) All new compounds in this paper gave IR, NMR, and mass spectral data consistent with the assigned structures with elemental analyses. Selected physical data. **5b**: MS (FAB) m/z 678 (M^+), FT-IR (KBr) ν 2135 cm^{-1}, UV ($CHCl_3$) λ_{max} (log ε) 276 (4.60), 308s (4.17), 398s (3.89), 447s (4.86), 472 (5.56), 515 (4.99), 534 (4.80), 560s (4.18). *Anal.* Calcd for $C_{54}H_{30}{\bullet}CHCl_3$: C, 82.79; H, 3.92; Cl, 13.29%. Found: C, 82.81; H, 3.84; Cl, 13.19%. **5c**: MS (FAB) m/z 846 (M^+), ^{1}H-NMR (270.05 MHz, $CDCl_3$) δ 9.45 (d, *J*=7.4 Hz, 6H), 9.38 (d, *J*=8.4 Hz, 6H), 8.02 (d, *J*=8.4 Hz, 6H), 8.00 (t, *J*=7.4 Hz, 6H), 7.73 (t, *J*=7.4 Hz, 3H), 1.63 (s, 27H) ppm. ^{13}C-NMR (67.80 MHz, $CDCl_3$) δ 152.8, 140.3, 137.6, 130.5, 130.3, 129.8, 129.1, 126.9, 118.0, 117.7, 104.3, 103.3, 35.2, 31.5 ppm. FT-IR (KBr) ν 2135 cm^{-1}, UV ($CHCl_3$) λ_{max} (log ε) 278 (4.67), 316s (4.29), 403s (4.01), 454 (4.95), 479 (5.62), 521 (5.09), 540 (4.92), 568s (4.30), 735 (2.24), 786s (2.20), 844s (2.55), 871 (2.59). *Anal.* Calcd for $C_{66}H_{54}$: C, 93.57; H, 6.43%. Found: C, 93.29; H, 6.14%. **5d**: MS (FAB) m/z 618 (M^+), ^{1}H-NMR (270.05 MHz, $CDCl_3$) δ 9.52 (d, *J*=7.5 Hz, 6H), 7.94 (d, *J*=7.5 Hz, 6H), 7.67 (t, *J*=7.5 Hz, 3H), 2.56 (s, 27H) ppm. ^{13}C-NMR (67.80 MHz, $CDCl_3$) δ 140.4, 129.7, 129.4, 129.0, 120.7, 118.9, 117.3, 102.0, 41.8, 33.3 ppm. FT-IR (KBr) ν 2131 cm^{-1}. UV ($CHCl_3$), λ_{max} (log ε) 276 (3.62), 323 (3.09), 348 (4.29), 427 (5.66), 475 (4.97), 491 (4.79), 518(4.27), 653s (2.19), 673 (2.29), 720s (2.35), 758 (2.56), 789s (2.47).

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