Synthesis and Characterization of Hepta[5][5]circulene as a Subunit of C_{70} Fullerene

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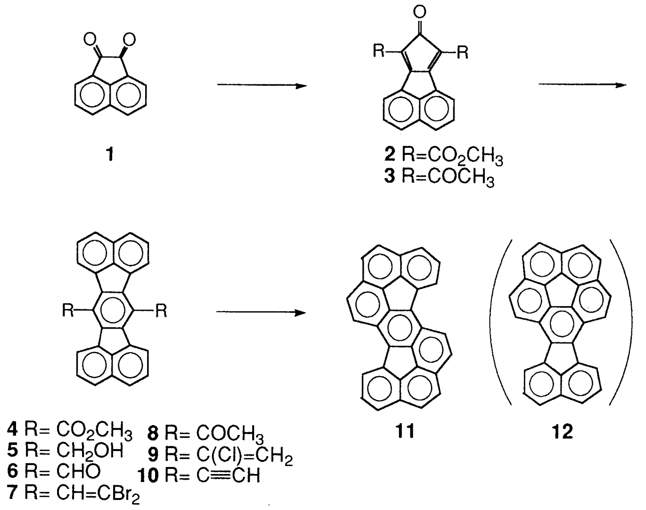
The polycyclic aromatic compound with a S-shaped circular arrangement of seven benzene rings, hepta[5][5]circulene **11**, was prepared by FVP of bis(1-chlorovinyl)acenaphthofluoranthene **9**. The structure and electrochemical properties were also reported.

Recent advances in carbon cluster chemistry (fullerenes) have aroused a large interest in the field of nonplanar polycyclic aromatic compounds with circular arrangement of benzene rings known as circulene.[1] We have been interested in the synthetic studies of nonplanar polycyclic aromatic systems and previous papers described the syntheses of [7]circulene[2] (plaiadannulene[3]) and [7.7]circulene[4] with saddle-shaped structure. An obvious extension of our interests in these studies let us to investigate the preparation of hepta[5][5]circulene whose carbon framework represents a subunit of spheroidal C_{70} fullerene.[5]



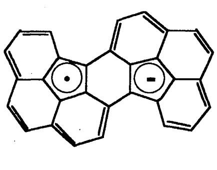
First, we carried out an attempted preparation of **11** and **12** from bis(dibromovinyl)acenaphthofluoranthene precursor **7** to complete the synthesis according to the Scott procedure.[6] Condensation of acenaphthenequinone **1** with dimethyl 1,3-acetonedicarboxylate by a double Knoevenagel reaction[7] afforded acecyclone derivative **2** [8] (mp 245-247 °C, 74% yield) whose Diels-Alder condensation with acenaphthylene at 250 °C gave acenaphthofluoranthene dimethyl ester **4** (mp >300 °C, 52% yield)[9] with evolution of carbon monoxide and hydrogen.[10] Lithium aluminum hydride reduction of **4** in tetrahydrofuran yielded diol **5** (mp 255-257 °C, 76% yield) whose oxidation using pyridinium chlorocromate gave dialdehyde **6** (mp 266-268 °C, 5%) in low yield, because of the low solubility of **5**, and we have so far been unable to lead **7** . In the next approach, we selected as a key compound diacetylacenaphthofluoranthene **8** which was easily convertible into the precursor bis(1-chlorovinyl)-acenaphthofuloranthene **9** with a suitable substituent for ring closure to give the final hepta[5][5]circulene by flash vacuum pyrolysis developed by Rabideau et al.[11] Diacetylacenaphthofluoranthene **8** (mp 226-228 °C, 40% from 1),[12] provided by the condensation of **1** with 2,4,6-heptanetrione followed by Diels-Alder reaction with acenaphthylene at 250 °C, was treated with phosphorous pentachloride in refluxing benzene for 3 days to afford vinyl chloride **9** (mp >300 °C, 26% yield). Flash vacuum pyrolysis of **9** at 900 °C / 10^{-3} Torr. was found to give diethynylacenaphthofluoranthene **10** (mp 283-285 °C, orange needles, 7% yield) and hepta[5][5]circulene **11** (mp >350 °C, red plates, 6% yield), respectively. These two compounds were separated by preparative TLC (silica gel / hexane-benzene) and recrystallization and characterized by ^{1}H NMR, MASS and UV/VIS spectroscopy. Comparison of their electrical spectra with that of ZINDO calculations[13,14] added strong support for their structures. The diethynyl compound **10** also gave hepta[5][5]circulene under FVP condition at 1000 °C / 10^{-3} Torr. in 20% yield. MM3 calculations[15] predict a strain energy about 9.2 kcal/mol for **11**, which shows it more than 28 kcal/mol stable than acenaphthocorannulene **12** (SE 37.2 kcal/mol).

Finally, the redox properties of the newly obtained planar hepta[5][5]circulene **11** with that of non-planar [7]circulene[2] were examined by use of cyclic voltammetry. The results are shown in Table 1. The voltammograms of **11** exhibited one irreversible oxidation peak and two reversible reduction waves. The differences between the reduction potentials of **11** and [7]circulene indicate it is easier to add electrons to **11** compared with [7]circulene. The remarkable decrease in the reduction potentials of **11** may be explained not only by a S-shaped planar extension of π-conjugation but also by large contribution of structure of radical anion such as **13** to its resonance hybrid.[16] On the other hand, the oxidation potential of [7]circulene relative to **11** shows that it is easier to remove an electron from [7]circulene compared with **11**, reflecting the contribution of structure such as **14** to its resonance hybrid.

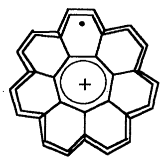
Table 1. Results of cyclic voltammetry

compound	oxidation^a	reduction^b			
	$E_{ox}{}^c$	$E_{pc}1$	$E_{pa}1$	$E_{pc}2$	$E_{pa}2$
11	+0.80	-1.06	-0.99	-1.58	-1.52
[7]Circulene	+0.73	-1.94	-1.84	-2.29^d	-----

^{a}Potential in volts vs. Ag/Ag$^+$ with a glassy carbon working electrode in methylene chloride using tetraethylammonium tetrafluoroborate (0.05 mol dm^{-3}) as a supporting electrolyte, scan rate 0.05 V s^{-1}. ^{b}Potential in volts vs. SCE with a hanging mercury drop working electrode in DMF using tetrabutylammonium perchlorate (0.2 mol dm^{-3}) as a supporting electrolyte, scan rate 0.05 V s^{-1} for **11**, 0.3 V s^{-1} for [7]circulene. ^{c}Irreversible oxidation. ^{d}Irreversible reduction.



13



14

We are at present investigating the synthesis of its parent compound with 8-shaped circular arrangement of nine benzene rings, [5][5]circulene, as a half-unit of C_{70} fullerene.

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12 Selected data for **8**: ^{1}H NMR(500 Mz, $CDCl_3$) δ 2.98(6H, s, CH_3), 7.68(4H, t, J=7.6 Hz, ArH), 7.85(4H, d, J=7.0 Hz, ArH), 7.93(4H, d, J=8.2 Hz, ArH); IR(KBr) vmax/cm^{-1} 1680(C=O); MS(EI, 75 eV) m/z 410(M^+). For **9**: ^{1}H NMR(500 Mz, $CDCl_3$) δ 5.95(2H, s, CH_2), 6.21(2H, s, CH_2), 7.71(4H, t, J=7.6 Hz, ArH), 7.93(4H, d, J=8.2 Hz, ArH), 8.39(4H, d, J=7.3 Hz, ArH); FABMS m/z 447($[M+H]^+$). For **10**: ^{1}H NMR(500 Mz, $CDCl_3$) δ 4.11(2H, s, $C\equiv CH$), 7.74(4H, t, J=8.0 Hz, ArH), 7.95(4H, d, J=8.0 Hz, ArH), 8.79(4H, d, J=7.0 Hz, ArH); UV/VIS(1,4-dioxane) λmax/nm 244(23530), 290(10500), 332(29940), 347(39880), 417(7780), 442(9760); IR(KBr) vmax/cm^{-1} 3280($H-C\equiv C$); FABMS m/z 374(M^+). For **11**: ^{1}H NMR(500 Mz, $CDCl_3$) δ 7.76(2H, t, J=7.5 Hz, ArH), 7.99(2H, d, J=8.2 Hz, ArH), 8.00(2H, d, J=8.2 Hz, ArH), 8.04(2H, d, J=8.5 Hz, ArH), 8.12(2H, d, J=8.5 Hz, ArH), 8.50(2H, d, J=7.9 Hz, ArH), 8.60(2H, d, J=8.5 Hz, ArH); UV/VIS(1,4-dioxane) λmax/nm 244(144560), 285(117840), 303(61870), 335(80640), 350(81120), 424(510530), 448(60580); FABMS m/z 374(M^+).

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