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TRISDEHYDRO[16]ANNULENO[18]ANNULENE

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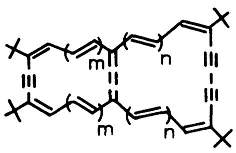
Trisdehydro[16]annuleno[18]annulene has been synthesized. A strong paratropicity was observed in the [16]annulene moiety. The observed diatropicity of the 18π moiety indicates that the ^{1}H NMR behavior of the annulenoannulene can be regarded as a superposition of the nature of individual rings and the peripheral $4n\pi$-system.

Recently we have synthesized several kinds of [4n]annuleno[4n'+2]annulenes, *i.e.*, tetrakisdehydro[4n]annuleno[4n'+2]annulenes (1 ∿ 4),1) pentakisdehydro[16]annuleno[18]annulene (5),2) and trisdehydro[14]annuleno[16]annulene (6).3) Because the 14π-electron system in 6 shows weaker diatropicity than the 14π-electron system in 1, it is contemplated that the contribution of peripheral 24π-electron system may exist in these systems, paticularly in the case of 6. In order to clarify the contribution of peripheral $4n\pi$-electron system in [4n]annuleno[4n'+2]annulenes, we have prepared tetra-*t*-butyltrisdehydro[16]annuleno[18]annulene (7), a higher homologue of 6. We might expect to observe the contribution of peripheral 24π-electron system in 6 as compared with the diatropicity and paratropicity of 7.



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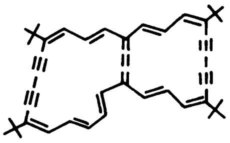
2: m=1, n = 2
3: m=2, n = 1
4: m = n = 2



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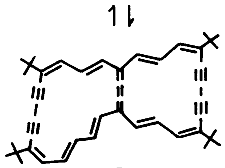

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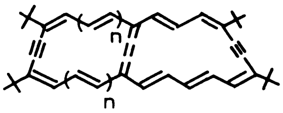

6 : n = 1
7 : n = 2

Product of the reaction of thiovinyl ketone (9)4) with 81b) was treated with a dilute sulfuric acid to give unstable dialdehyde (10). The Wittig-Horner-Emmons reaction of 10 with 115) yielded diketone (12,6) 59% based on 9). A diastereomeric mixture of cyclic glycol (13) obtained on treatment of 12 with KOH in liquid ammonia was chromatographed on alumina to give pure 13a7) (36%) and 13b7) (18%). Treatment of 13 with tin(II) chloride and hydrogen chloride in THF gave the tris-

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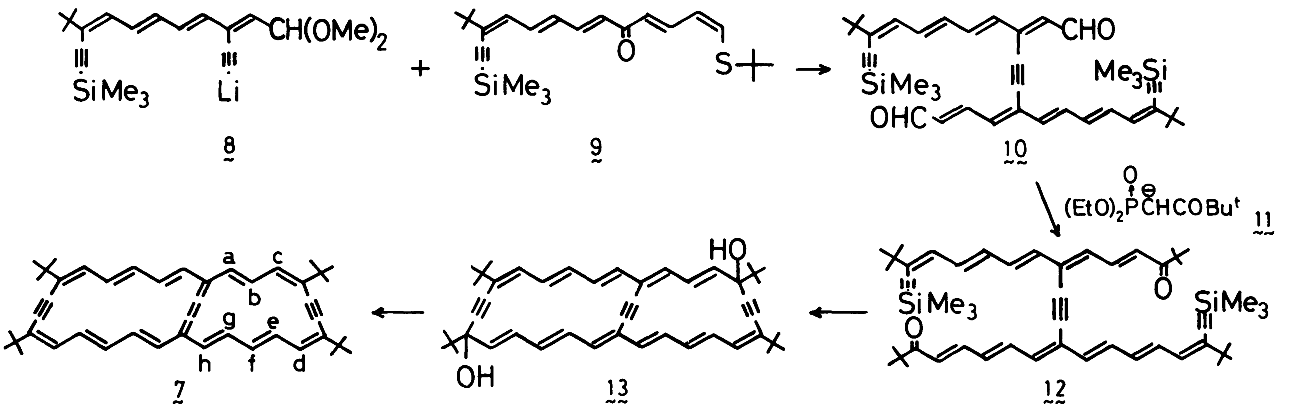
dehydro[16]annuleno[18]annulene (7) which was found to be unstable.8) Therefore, deep green solution obtained by $SnCl_2$ and DCl (HCl) in THF-d_8 (THF) was directly subjected to the measurement of the ^{1}H NMR and electronic spectra.



Scheme

Table. Electronic Spectrum of Tetra-*t*-butyltrisdehydro[16]annuleno-[18]annulene (7) in THF. λ_{max} (ε)9) nm.

345 (40,600), 349 sh (45,000), 358 (41,800), 378 (56,800), 431 (130,000),
456 (133,000), 680 sh (2,730), 733 (2,780), 805 sh (2,210), 910 sh (1,120).

The electronic spectral maxima are summarized in Table. The ^{1}H NMR parameters (chemical shifts in τ-values) of 7 are denoted on the formula in Figure together with those of 6 and related monocyclic dehydroannulenes (14 ∿ 16).10) The difference of chemical shifts ($\Delta\tau$) between adjacent inner and outer protons (*e.g.*, $\tau_b - \tau_a$, $\tau_b - \tau_c$, $\tau_e - \tau_d$, etc.,) is also given under the formulas.

The electronic spectrum of 7 was closely related to those of [14]annuleno-[16]annulenes (1 and 6) except for a bathochromic shift, and almost superimposable on tetrakisdehydro[16]annuleno[18]annulene (3).

The ^{1}H NMR spectrum of 7 clearly indicates induction of para- and diamagnetic ring currents in the 16- and 18-membered rings, respectively. A marked suppression of diamagnetic ring current in the 18π moiety in 7 was observed being in the same trend as observed in the other [4n]annuleno[4n'+2]annulenes (1 ∿ 6). On the contrary, magnitude of paramagnetic ring current in the 16π moiety in 7 was found to be comparable with that of extremely unstable parent bisdehydro[16]annulene (16).

The non-alternating coupling constants of vicinal hydrogen in the 18-membered ring (J = *ca.* 13.5 Hz, which is the same value observed for delocalized 'acetylene-cumulene' dehydroannulenes11)) indicate highly delocalized structure of the 18π-system. On the other hand, the 16π moiety shows marked bond alternation (*i.e.*, $J_{ab} = J_{gh} = 15.0$, $J_{ef} = 14.5$, $J_{de} = 12.0$, and $J_{bc} = J_{fg} = 11.5$ Hz), thus indicating the structure with the peripheral acetylenic and central cumulenic linkages. These results are compatible with the structural information obtained from the trisdehydro[14]annuleno[16]annulene (6).

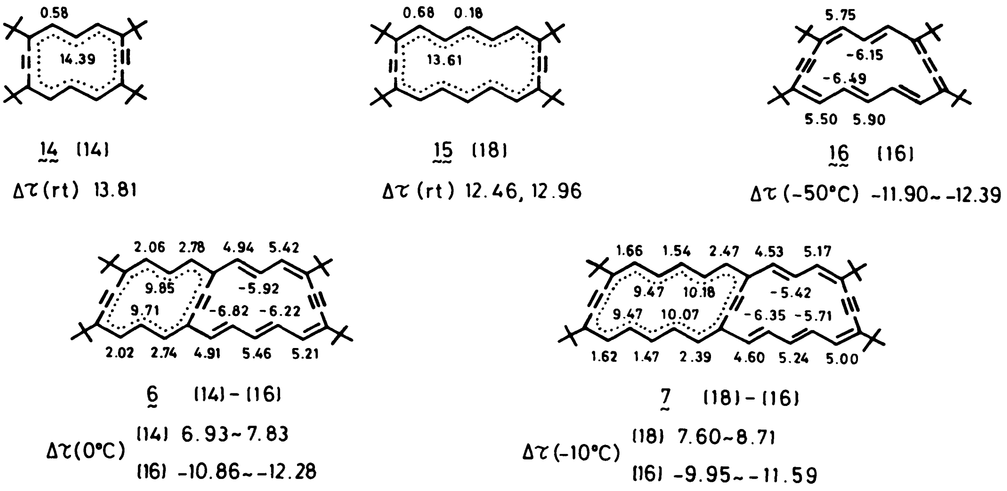


Figure. ^{1}H NMR Parameters of Annulenoannulenes and Related Annulenes.

The difference in chemical shifts between the inner and outer protons ($\tau_i - \tau_o$) can be regarded as an approximate measure of tropicity. The 18π-electron system in 7 shows stronger diatropicity ($\Delta\tau = \tau_i - \tau_o = 7.60 \sim 8.71$) than the 14π-electron system in 6 ($\Delta\tau = 6.93 \sim 7.83$), whereas the magnitude of paratropicity of the 16π-electron system is more distinct in the case of 6 ($\Delta\tau = -10.86 \sim -12.28$) as compared with that observed in 7 ($\Delta\tau = -9.95 \sim -11.59$). A similar trend has been observed in the Δτ-values of [4n'+2] moiety of two pairs of tetrakisdehydro[4n]annuleno-[4n'+2]annulenes, *i.e.*, 1 and 3, and 2 and 4. Experimental evidence[12] and theoretical treatment[13] have suggested that the diatropicity and the resonance energy per π-electron (REPE) in [4n+2]annulenes should decrease along with the increase of n. Also a linear correlation was found between the observed Δτ-values of bisdehydro[4n+2]annulenes and REPE.[14] The above-mentioned larger Δτ-value of 7 as compared with that of the lower member (6) is inconsistent with the results obtained on monocyclic bisdehydro[4n+2]annulenes. Although the fundamental nature of annulenoannulenes can be regarded as superposition of individual rings consisting of the bicyclic system,[15] the observed diatropicity of [4n'+2] moiety in [4n]-annuleno[4n'+2]annulenes seems to indicate that a contribution of peripheral system cannot be ignored. Consequently, the resonance energy of the system is of interest in connection with the appreciable contribution of peripheral 4nπ-system.[16]

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6) **12**: reddish orange needles, mp 127.0-127.5°C, Mass(m/e): 784 (M$^+$), 699; IR(KBr-disk) 2138 m, 1677 s, 1585 s, 1071 vs, 1003 s, 987 s, 880 vs, 843 vs cm^{-1}; ^{1}H NMR (CDCl$_3$) τ 1.96 ∿ 3.72 m (18H, olefinic H), 8.82 s (9H, *t*-Bu), 8.84 s (9H, *t*-Bu), 8.86 s (18H, *t*-Bu), 9.83 s, 9.84 s (18H, SiMe$_3$).

7) **13a**: orange yellow needles, dp *ca.* 280°C, Mass(m/e): 640 (M$^+$); IR(KBr-disk) 3570 m, 3450 m, 2190 w, 1615 w, 988 vs cm^{-1}; ^{1}H NMR (CDCl$_3$) τ 2.31 ∿ 4.06 m (18H, olefinic H), 7.86 br. s, 8.01 br. s (2H, -OH), 8.79 s, 8.80 s, 8.89 s, 8.90 s (36H, *t*-Bu). **13b**: yellow fine crystals, dp *ca.* 220°C, Mass(m/e): 640 (M$^+$); IR(KBr-disk) 3555 m, 3450 m, 2190 w, 1620 w, 985 s cm^{-1}; ^{1}H NMR (CDCl$_3$) τ 2.32 ∿ 4.10 m (18H, olefinic H), 7.78 br. s, 7.93 br. s (2H, -OH), 8.79 s (9H, *t*-Bu), 8.80 s (9H, *t*-Bu), 8.91 s (18H, *t*-Bu).

8) The annulenoannulene (**7**) decomposed gradually during the evaporation of the solvent at -10°C *in vacuo*. In contrast to the stability of tetrakisdehydro-[16]annuleno[18]annulene (**3**), **7** is unstable presumably owing to the ring strain of the 16-membered ring.

9) The ε-values were calculated assuming quantitative conversion of **13** into **7**.

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