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TRISDEHYDRO[14]ANNULENO[16]ANNULENE

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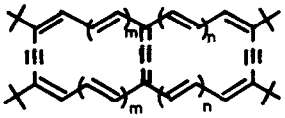
Summary: Trisdehydro[14]annuleno[16]annulene consisting of an aromatic bisdehydro[14]annulene and an antiaromatic bisdehydro[16]annulene has been synthesized. The strong paratropicity was observed in the [16]annulene moiety being comparable with that of extremely unstable parent bisdehydro[16]annulene.

Preparation of both series of trisdehydro[4n+2]annuleno[4n'+2]annulenes (1 ∿ 4)1) and tetrakisdehydro[4n]annuleno[4n'+2]annulenes (5 ∿ 8)2) revealed essentially independent nature of aromatic or antiaromatic ring in the annulenoannulenes, *i,e.*, their ^{1}H NMR spectra clearly indicate induction of diamagnetic or paramagnetic ring current in each ring. This paper is concerned with the synthesis and properties of another type of [4n]annuleno[4n'+2]annulene, trisdehydro[14]annuleno[16]annulene (9).



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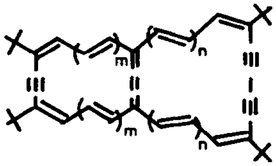

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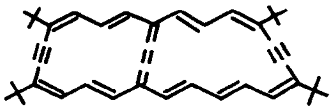
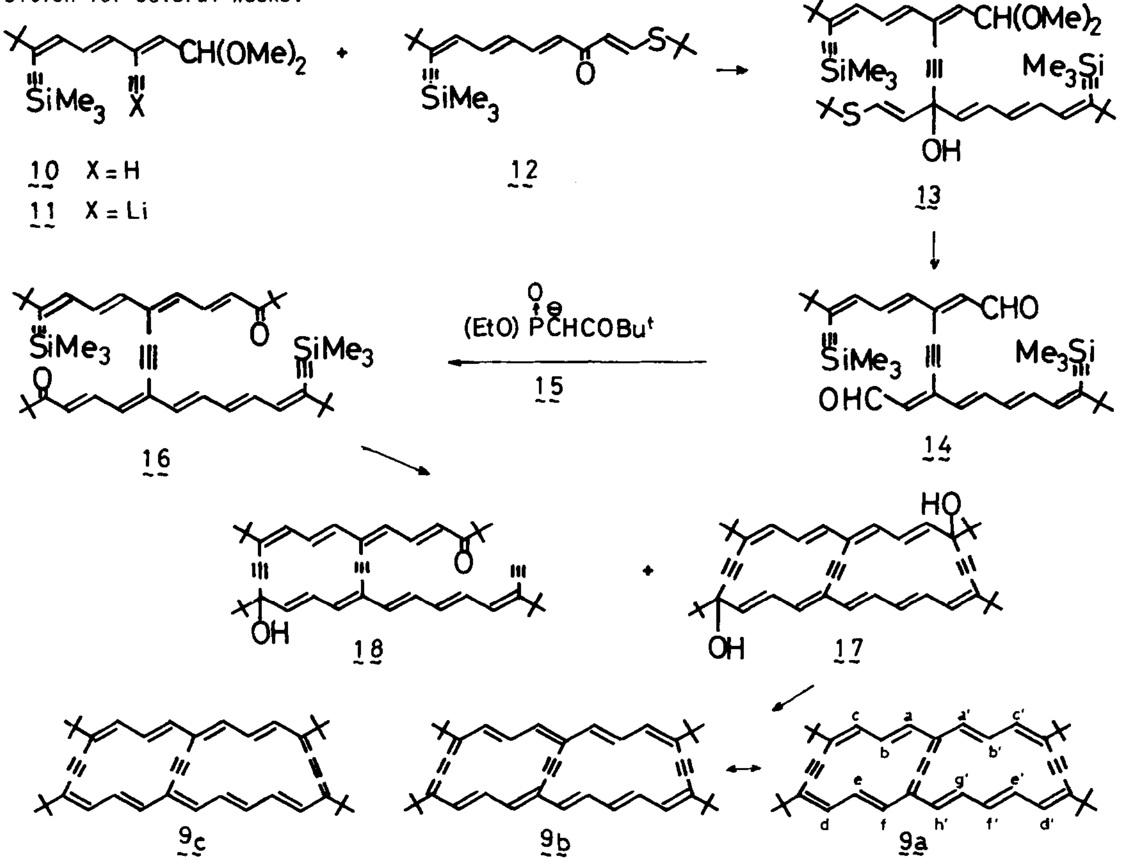


9

The lithium derivative (11) of the triene aldehyde dimethyl acetal (10)3) was allowed to react with the tetraene ketone (12)4) and the product (13) was treated with dilute sulfuric acid to give the dialdehyde (14, yellow crystals, mp 106.9-108.4°C (dec.), 24%)5). The dialdehyde (14) was found to be rather unstable and gradual decomposition was observed during the purification. Therefore, 14 was chromatographed on silica gel and the resulting viscous oil was used without further purification. Reaction of the crude dialdehyde (14) with the ketophosphonate carbanion (15)$^{3)}$ yielded diketone (16, yellow crystals, mp 181.0-182.0°C(dec.), 32% based on 12, Mass(m/e): 732 (M$^+$), 675). The cyclization of 16 could be realized on a slow addition of a solution of 16 in THF into a suspension of finely powdered KOH in liquid ammonia. A mixture of diastereomers of the cyclic glycol (17) and monocyclic alcohol (18) was obtained (17a, brownish yellow crystals, mp 204-209°C (dec.), 23%, Mass(m/e): 588 (M$^+$); 17b, yellow crystals, mp *ca.*200°C (dec.), 29%, Mass(m/e): 588 (M$^+$)). Unsuccessful attempts to convert 18 into 17 on treatment with KOH in liquid ammonia seem to indicate the participation of ethynyl anion generated by the cleavage of trimethylsilyl groups with KOH in the cyclization reaction. The cyclic glycol (17b) yielded the trisdehydro[14]annuleno[16]annulene (9, 68%) on treatment with tin(II) chloride and ether saturated with hydrogen chloride at -60 ∿ -30°C. Similarly, 17a afforded 9 under the same reaction conditions. In contrast with extremely unstable bisdehydro[16]annulene (19)$^{6)}$(decomposed at -20°C), 9 could be stored at -20°C without decomposition for several weeks.



Scheme

The trisdehydro[14]annuleno[16]annulene (9) was obtained as dark green crystals, mp *ca.* 190°C (dec.), Mass(m/e): 554 (M$^+$); IR(KBr-disk): 2147vw, 991s, 967s cm^{-1}; ES: $\lambda_{max}^{cyclohexane}$ (ε) 225sh (14300), 239sh (18100), 245 (19700), 265 (14600), 277 (14200), 299sh (22000), 311sh (42300), 323 (57600), 334sh (33600), 371sh (55500), 388 (126000), 409 (20600), 581sh (1630), 676 (2630), 750sh (1840), 840sh (760) nm. The ^{1}H and ^{13}C NMR parameters are summarized in Table.

Table. ^{1}H and ^{13}C NMR Parameters of 9.

^{1}H NMR Parameters (CD_2Cl_2, 0°C, τ-values).

14-membered ring	H_a/H_f	2.74 d, J=13.7 2.78 d, J=13.7	H_b/H_e	9.71 dd, J=13.3, 13.7 9.85 dd, J=13.3, 13.7
	H_c/H_d	2.20 d, J=13.3 2.06 d, J=13.3	*t*-Bu	8.39 s
16-membered ring	$H_{a'}$	4.94 d, J=15.0	$H_{b'}$	-5.92 dd, J=11.5, 15.0
	$H_{c'}$	5.42 d, J=11.5	$H_{e'}$	-6.22 dd, J=12.0, 14.0
	$H_{d'}$	5.21 d, J=12.0	$H_{g'}$	-6.82 dd, J=11.5, 15.5
	$H_{f'}$	5.46 dd, J=11.5, 14.0	*t*-Bu	9.22 s
	$H_{h'}$	4.91 d, J=15.5		

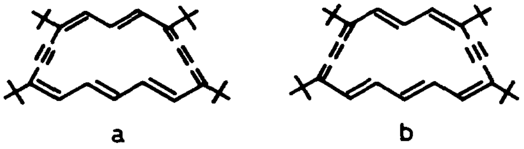
^{13}C NMR Parameters ($CDCl_3$, -30°C, δ-values).

148.5, 146.3, 142.0, 140.5, 135.9, 135.5, 135.3, 134.9, 134.4, 133.3, 132.7, 131.9, 131.4, 130.7, 130.1, 128.8, 127.5, 126.8 (*sp*^{2}-hybridized carbons), 122.0, 121.0, 112.20, 112.15, 102.2, 99.5 (*sp*-hybridized carbons), 37.2, 36.0, 34.9, 31.4, 28.1, 28.0 (*t*-Bu)

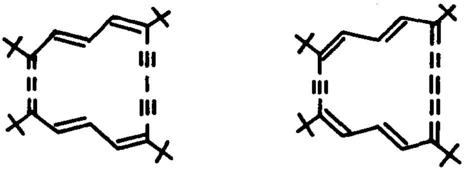
The most characteristic feature of the properties of the trisdehydro[14]annuleno[16]-annulene (9) is the strong paratropicity observed in the bisdehydro[16]annulene moiety being comparable with that of extremely unstable parent bisdehydro[16]annulene (19)$^{6)}$. A marked suppression of the diatropicity in the 14π moiety in 9 was observed being in the same trend as observed in the series of tetrakisdehydro[4n]annuleno[4n'+2]annulenes (5 ∿ 8). However, it is to be noted that the magnitude of diatropicity is more reduced in the case of 9 as compared with that observed in 5.

The small difference in the coupling constants between J_{ab}/J_{ef} and J_{bc}/J_{de} (*i.e.*, 13.7 and 13.3, respectively) suggests that the structure 9a is slightly dominant as compared with 9b, whereas a significant contribution of cannonical form 9c containing nonaromatic 14π-electron system can be excluded. The ^{13}C chemical shifts (δ 99.5, 102.2, 112.15, 112.20, 121.0 and 122.0 ppm) of *sp*-hybridized carbon atoms are consistent with the structure described above. The same trend has been observed in 5 ∿ 8.

The bisdehydro[16]annulene (19) can be regarded as a resonance hybrid of the equivalent structures 19a ↔ 19b, and the difference in the chemical shifts between inner protons (τ_i) and outer protons (τ_o)$^{7)}$ was found to be $\Delta\tau$= -11.90 ∿ -12.39 (-50°C), which is smaller than the values for the trisdehydro[16]annulene (20) ($\Delta\tau$ = -12.61 ∿ -12.75 at -30°C)$^{8)}$. The bisdehydro[16]annulene moiety of 9 shows a strong paratropicity comparable with that of 19, whereas the paratropicity of trisdehydro[16]annulene moiety of 5 was found to be smaller than that of parent 20. Because suppression of diatropicity of aromatic moiety in [4n]annuleno-[4n'+2]annulene should be smaller on fusion with a less paratropic ring, the fact that the diatropicity of the bisdehydro[14]annulene moiety in 9 is smaller than that in 5 may be attributed to the contribution of peripheral 24π-electron system.



19 $\tau_i - \tau_o$ = -11.90 ~ -12.39
(-50 °C)



20 $\tau_i - \tau_o$ = -12.61 ~ -12.75
(-30 °C)

Acknowledgement

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References and Notes

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