

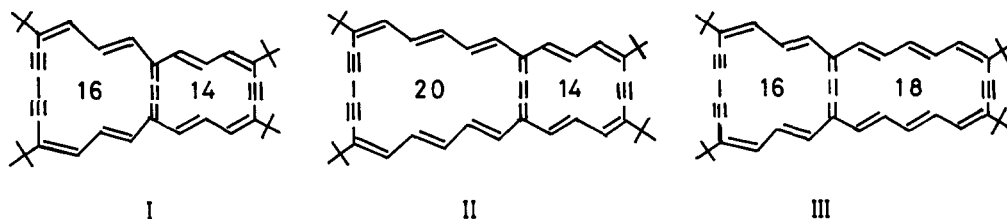
TETRAKISDEHYDRO[16]ANNULENO[18]ANNULENE

Koichi Sakano, Tsutomu Nakagawa, Masahiko Iyoda, and Masazumi Nakagawa*

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

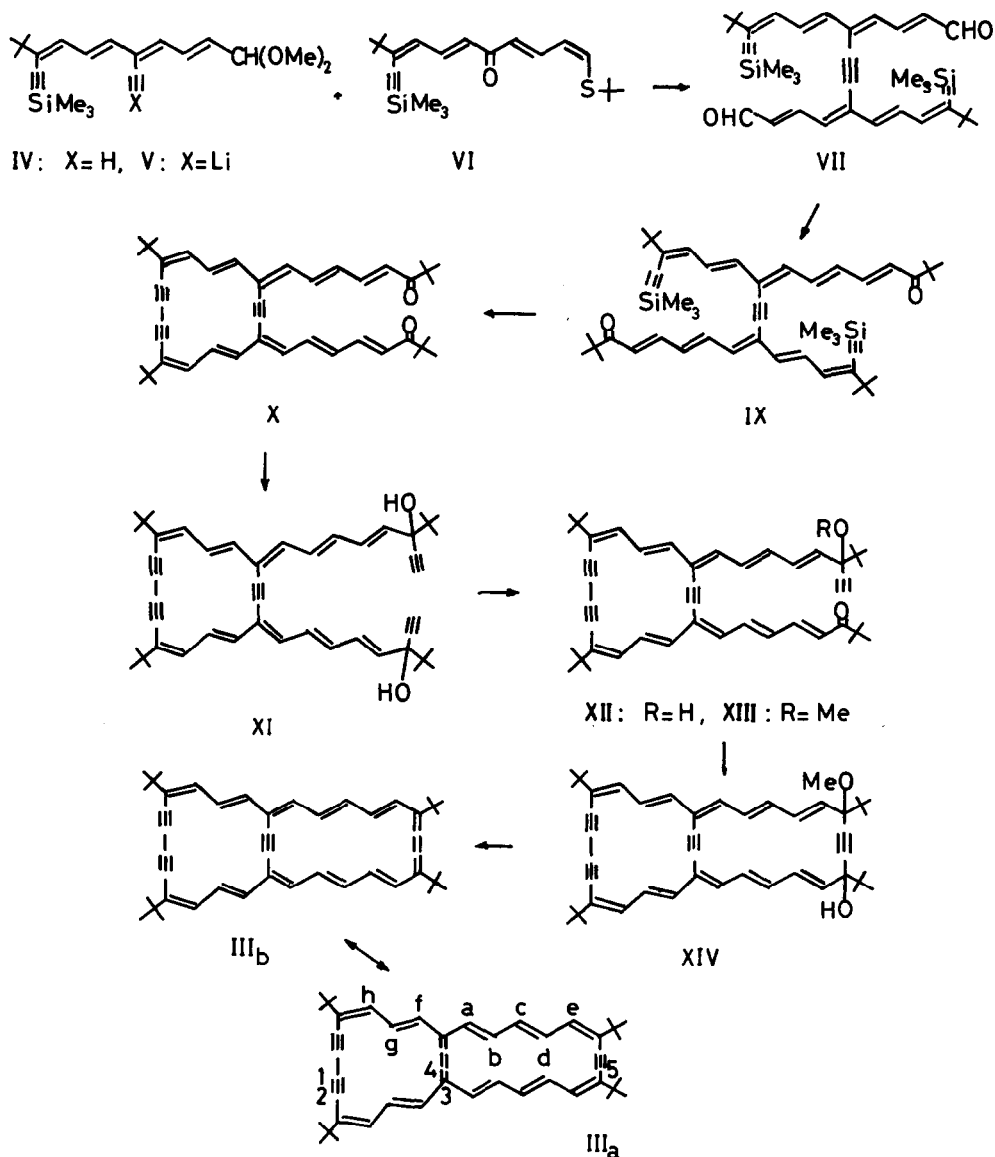
Summary: Tetrakisdehydro[16]annuleno[18]annulene consisting of trisdehydro[16]annulene and bisdehydro[18]annulene has been synthesized. Induction of para- and diamagnetic ring currents in 16- and 18-membered rings, respectively, was clearly recognized by the ^1H NMR spectroscopy. A marked suppression of the diatropicity in the 18π moiety was observed in the same trend as observed in tetrakisdehydro[14]annuleno[16]annulene.

In previous papers, we reported the synthesis and properties of tetrakisdehydro[14]annuleno[4n]annulenes (I)¹, n=4 and (II)², n=5 consisting of an aromatic bisdehydro[14]annulene and an antiaromatic trisdehydro[4n]annulene. It was found that the suppression of the ring currents caused by the fusion of two π -electron systems is larger in the 14π -electron system than in the $4n\pi$ -electron systems. We undertook the synthesis of tetrakisdehydro[16]annuleno[18]annulene (III), because it seemed of considerable interest to compare the magnitude of the diamagnetic ring current in the 18π -electron system with that in 14π -electron system in [16]annuleno[4n+2]annulenes.



The synthesis of tetrakisdehydro[14.12.2][16]annuleno[18]annulene (III) was carried out by the reaction sequence outlined in Scheme. The dimethyl acetal (IV)³ was treated with butyllithium to give the lithio derivative (V). Reaction of V with trimethylsilylethynylketone (VI)³, followed by hydrolysis with diluted sulfuric acid, yielded dialdehyde (VII, orange crystals, mp 153.2-154.0°C, 63%)⁴. The Wittig-Horner-Emmons reaction of the dialdehyde (VII) with the carbanion derived from diethyl 3,3-dimethyl-2-oxobutane-phosphonate (VIII, $t\text{-BuCOCH}_2\text{P}(\text{O})(\text{OEt})_2$)⁵ gave diketone (IX, orange crystals, mp 179.8-180.0°C, 92%). Oxidative coupling of the bis-trimethylsilyl diketone (IX) with copper(II) acetate in pyridine-methanol at 90°C afforded cyclic triyne diketone (X, carmine red crystals, mp ca. 220°C (dec.), 82%). Bisethynylation of the diketone (X) with lithium acetylide in THF⁶ yielded diol (XI, orange fine crystals, mp 155.1-156.0°C, 93%). One molar solution of potassium *t*-butoxide in *t*-butanol was added to a solution of the diol (XI) in benzene, and the mixture was stirred for 30 min. at 25°C to give the ketoalcohol (XII, deep red crystals, mp 163.5-164.5°C, 82%). Treatment of XII in THF with dimethyl sulfate in the presence of powdered potassium hydroxide gave methoxy derivative (XIII,

orange needles, mp 177.2-178.0°C, 68%). Cyclization of XIII could be achieved on treatment with lithium amide in liquid ammonia at -78°C for 2 hrs. The diastereomers of bicyclic glycol mono-methyl ether (XIV_a, reddish orange fine crystals, mp *ca.* 180°C (dec.), 17% based on consumed XIII; XIV_b, reddish orange plates, mp *ca.* 220°C (dec.), 44% based on consumed XIII) could be obtained together with recovered XIII by chromatography on alumina. The cyclic glycol mono-methyl ether (XIV_a) yielded the tetrakisdehydro[16]annuleno[18]annulene (III, 72%) on treatment with tin(II) chloride and ether saturated with hydrogen chloride at -40°C. Similarly, XIV_b afforded III in 77% yield under the same reaction conditions.



Scheme

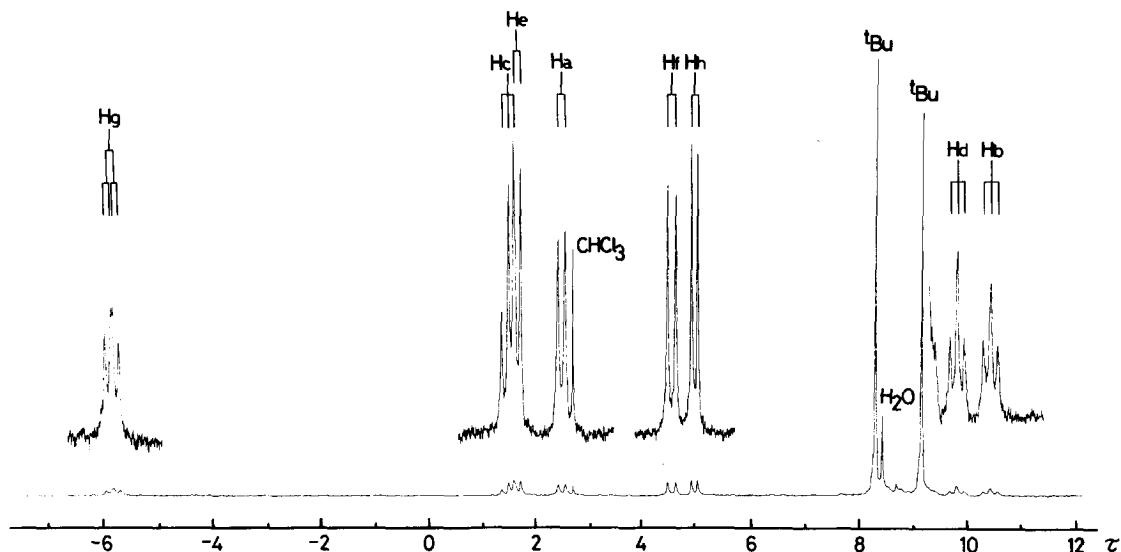
The tetrakisdehydro[16]annuleno[18]annulene (III) was obtained as blue violet plates with metallic luster, mp 180°C (dec.), Mass(m/e): 604(M⁺); IR(KBr-disk): 2192w, 1475s, 1458s, 1216s, 978vs, 958vs; ES: $\lambda_{\text{max}}^{\text{THF}}$ (ϵ) 250(17500), 281sh(13100), 293sh(14100), 304(15600), 324sh(21800), 339(36500), 377(51400), 430(154000), 457(161000), 725(3780), 792(3380), 881(2360) nm. The ¹H NMR spectrum of III is shown in Figure, and the ¹H and ¹³C NMR parameters are summarized in Table.

Table. ¹H and ¹³C NMR Parameters of III (CDCl₃ at room temperature)

¹ H NMR Parameters (τ -values)					
18-membered ring	H _a	2.53	d, J=13.3	H _b	10.46 t, J=13.3
	H _c	1.54	t, J=13.3	H _d	9.85 dd, J=13.0, 13.3
	H _e	1.71	d, J=13.0	<i>t</i> -Bu	8.35 s
16-membered ring	H _f	4.58	d, J=15.5	H _g	-5.80 dd, J=11.5, 15.5
	H _h	5.01	d, J=11.5	<i>t</i> -Bu	9.20 s

¹³ C NMR Parameters (δ -values)	
140.2, 139.6, 137.0, 136.4, 135.6, 134.3, 133.0, 132.4, 129.6 (<i>sp</i> ₂ -hybridized carbons)	
121.7 (C ₃ or C ₄), 118.3 (C ₃ or C ₄), 109.7 (C ₅), 89.6, 86.3 (C ₁ , C ₂), 37.6, 34.1, 31.6	
28.1 (<i>t</i> -Bu)	

Figure. The 100 MHz ¹H NMR Spectrum of III in CDCl₃ at 35°C.



The ¹H NMR spectrum and the parameters of III exhibit the induction of fairly strong para- and diamagnetic ring currents in each ring. The signals of both inner and outer protons in the 18-membered ring move to lower field as increasing distance from the 16 π moiety except H_e which seems to suffer a shielding effect of the formal acetylenic bond. This trend clearly indicates

that the shielding effect of paramagnetic ring current diminishes along with the increase of distance from the center of ring current induced in the 16π moiety to the particular proton. Inversely, the relatively high field shift of outer protons in the 16-membered ring indicates that the deshielding effect of diamagnetic ring current of the 18π moiety also diminishes with the increase of distance. Comparison of the vicinal coupling constants of the 18π moiety indicates that the 18π -electron system exists in the delocalized form⁷⁾, whereas the 16π -electron system shows marked bond alternation like trisdehydro[16]annulene⁸⁾. The small difference in the coupling constants between J_{ab} and J_{de} (*i.e.*, 13.3 and 13.0, respectively) suggests the structure III_a containing the central butatriene bond to be slightly dominant as compared with III_b containing the peripheral butatriene bond in the 18π -electron system. The ¹³C chemical shifts (δ 86.3, 89.6, 109.7, and 118.3 or 121.7 ppm) of the *sp*-hybridized carbon atoms are consistent with the structure described above. The same trend has been observed in I²⁾ and II²⁾. In agreement with the observation in other [4n]annuleno[4n'+2]annulenes (I and II), the 16π moiety in III shows a tendency to preserve the inherent paratropicity suppressing diatropicity of the 18π moiety (see Table). It is to be noted that the extent of suppression of diatropicity in the 18π moiety is the same as that in the 14π moiety in I. It has been recognized that the resonance energy in cyclic conjugated system decreases with increase of ring size⁹⁻¹²⁾, and fusion with a more strongly diatropic, *i.e.*, more strongly resonance stabilized system causes more strong suppression of [4n+2]annulene moiety in annelated annulenes and [4n+2]annuleno-[4n'+2]annulenes¹³⁾. Therefore, the fact that every 16π -electron system in both I and III shows induction of almost the same paramagnetic ring current, although this is fused with different size rings, seems to reflect characteristic difference between aromatic and antiaromatic π -electron systems.

References and Note

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