

## TETRAKISDEHYDRO[14]ANNULENO[16]ANNULENE

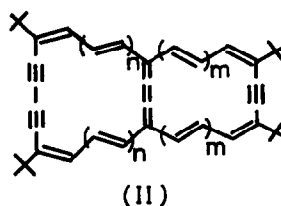
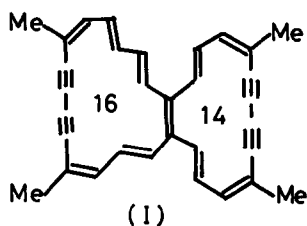
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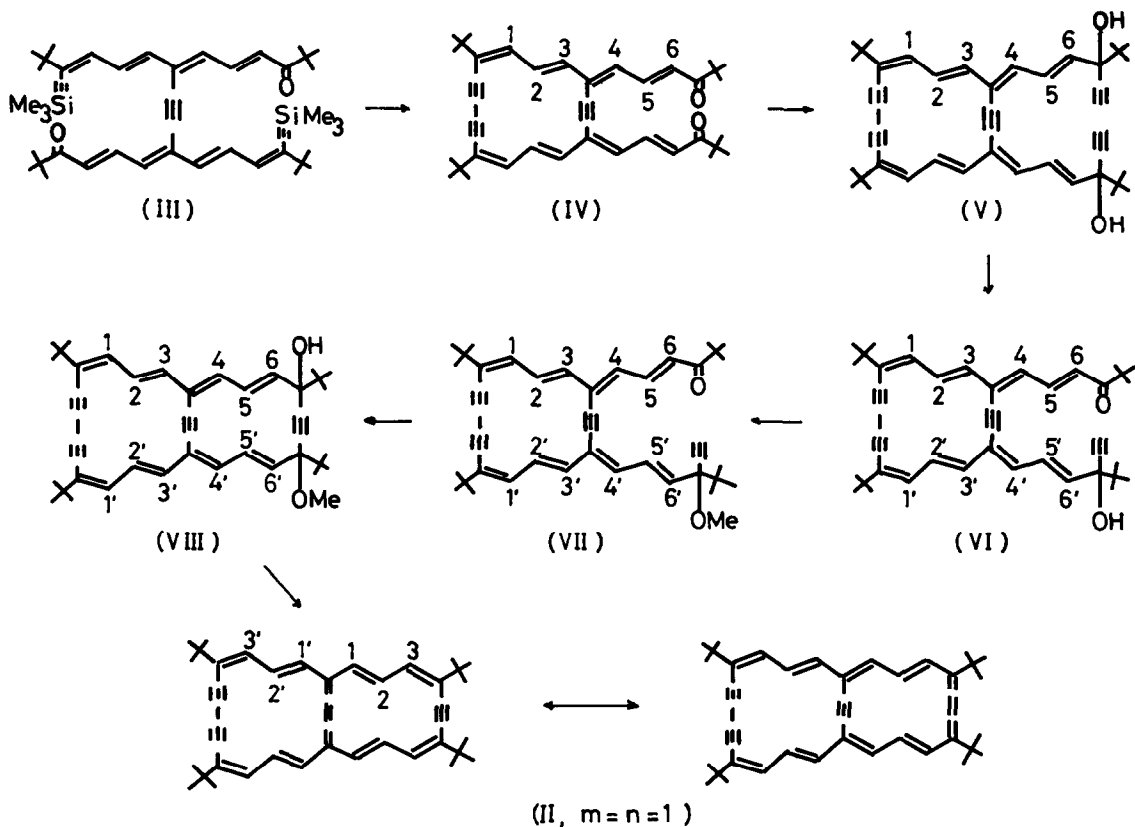
Summary: Tetrakisdehydro[14]annuleno[16]annulene consisting of an aromatic bisdehydro[14]-annulene and an antiaromatic trisdehydro[16]annulene has been synthesized. The <sup>1</sup>H NMR parameters clearly indicate the strong paratropicity and diatropicity of the 16-membered and 14-membered rings, respectively.

Recently rather independent behavior of each ring in [4n+2]annuleno[4n+2]annulenes has been observed.<sup>2)</sup> Also, the properties of [M]annuleno[N]annulenes have been examined theoretically.<sup>3)</sup> Therefore, studies on [4n]annuleno[4n+2]annulenes are of considerable interest. The sole instance of this class of annulenoannulene was *ortho*-fused tetrakisdehydro[14]annuleno[16]annulene (I) reported by Sondheimer.<sup>4)</sup>

We have carried out the syntheses of tetrakisdehydro[4n]annuleno[4n+2]annulenes (II) taking into account the strong tropicity of 'acetylene-cumulene'-bisdehydro[4n+2]-<sup>5)</sup> and trisdehydro[4n]annulenes.<sup>6)</sup> In this communication we wish to report the synthesis and properties of tetra-*t*-butyltetrakisdehydro[14]annuleno[16]annulene (II, m=n=1).



Diketone (III), which has been prepared as an intermediate of the synthesis of trisdehydro[14]annuleno[14]annulene,<sup>7)</sup> was treated with copper(II) acetate in pyridine and methanol at 90°C. Oxidative coupling accompanied with the cleavage of the trimethylsilyl groups gave monocyclic diketone<sup>8)</sup> [IV, red needles, mp 242-245°C (dec.), 87%, Mass(m/e): 560 (M<sup>+</sup>); IR(KBr-disk): 2180 w (C≡C), 1675 s (C=O), 1602 m (C=C), 987, 975 vs (*trans* -CH=CH-) cm<sup>-1</sup>; UV: λ<sub>max</sub><sup>THF</sup> nm (ε) 237 (14700), 281 (28400), 306 sh (17300), 380 (98600); <sup>1</sup>H NMR(CDCl<sub>3</sub>): τ 2.19 (2H, dd, J=15, 11, H<sup>5</sup>), 2.23 (2H, dd, J=11, 15, H<sup>2</sup>), 3.31 (2H, d, J=15, H<sup>3</sup>), 3.43 (2H, d, J=11, H<sup>1</sup>), 3.64 (2H, d, J=15, H<sup>6</sup>), 8.84 s, 8.85 s (36H, *t*-Bu); <sup>13</sup>C NMR(CDCl<sub>3</sub>): δ from TMS, 202.7 (C=O), 138.7, 136.5, 134.3, 133.8, 136.5, 131.1, 127.0 (olefinic), 94.7, 86.6 (acetylenic), 42.9, 35.4, 29.4, 26.3 (*t*-Bu)]. A solution of IV in THF was added to a suspension of lithium acetylide-ethylenediamine complex<sup>9)</sup> in the same solvent saturated with acetylene. The reaction mixture was worked up to give acyclic



glycol<sup>10</sup>) [V, orange yellow cryst., mp 151.5–152.2°C, 97%, Mass(m/e): 612 ( $M^+$ ); IR(KBr-disk): 3050 m, 3440 br.m (OH), 3290 m ( $\equiv C-H$ ), 2180 w ( $C\equiv C$ ), 970, 960 vs (*trans* -CH=CH-)  $cm^{-1}$ ; UV:  $\lambda_{max}^{THF}$  nm ( $\epsilon$ ) 268 (40800), 290 sh (13200), 350 sh (89300), 361 (100500), 431 (7890), 456 (430);  $^1H$  NMR ( $CDCl_3$ ):  $\tau$  2.46 (2H, dd,  $J=11, 15$ ,  $H^2$ ), 2.72 (2H, dd,  $J=11, 15$ ,  $H^5$ ), 3.44 (2H, d,  $J=11$ ,  $H^4$ ), 3.46 (2H, d,  $J=11$ ,  $H^1$ ), 3.70 (2H, d,  $J=15$ ,  $H^3$ ), 3.90 (2H, d,  $J=15$ ,  $H^6$ ), 6.76 (2H, s, OH), 7.45 (2H, s,  $-C\equiv C-H$ ), 8.84 (18H, s, *t*-Bu), 8.97 (18H, s, *t*-Bu);  $^{13}C$  NMR( $CDCl_3$ ):  $\delta$  from TMS, 139.4, 137.2, 136.5, 134.9, 130.8, 128.2, 124.1 (olefinic), 92.6, 86.4, 85.5, 84.1 (acetylenic), 76.3, 74.3 (C-OH or  $\equiv C-H$ ), 39.0, 35.2, 29.4, 25.1 (*t*-Bu)]. One molar solution of potassium *t*-butoxide in *t*-butanol (2.5 ml) was added to a solution of V (0.5 mmol) in benzene (25 ml), and the mixture was stirred for 20 min. at 20°C to result in retro-ethynylation reaction. Chromatography of the product on alumina yielded ketoalcohol [VI, reddish orange cryst., mp 227.5–229.0°C (dec.), 87%, Mass(m/e): 586 ( $M^+$ ), 529 ( $M^+-57$ ); IR(KBr-disk): 3440 m (OH), 3305 w ( $\equiv C-H$ ), 2175 w ( $C\equiv C$ ), 1662 s (C=O), 1598 m (C=C), 962 vs (*trans* -CH=CH-)  $cm^{-1}$ ;  $^1H$  NMR( $CD_2Cl_2$ ):  $\tau$  2.06 (1H, dd,  $J=12.0, 14.5$ ,  $H^5$ ), 2.21 (1H, dd,  $J=11.0, 15.0$ ,  $H^2$ ), 2.39 (1H, dd,  $J=11.0, 15.0$ ,  $H^{2'}$ ), 2.78 (1H, dd,  $J=11.0, 15.0$ ,  $H^{5'}$ ), 3.23 (1H, d,  $J=14.5$ ,  $H^6$ ), 3.30 (1H, d,  $J=11.0$ ,  $H^{4'}$ ), 3.30 (1H,  $J=12.0$ ,  $H^4$ ), 3.42 (2H, d,  $J=11.0$ ,  $H^1, H^{1'}$ ), 3.60 (1H, d,  $J=15.0$ ,  $H^3$ ), 3.63 (1H, d,  $J=15.0$ ,  $H^{3'}$ ), 3.68 (1H, d,  $J=15.0$ ,

H<sup>6'</sup>), 6.07 (1H, br.s, OH), 7.62 (1H, s, ≡CH), 8.83 s, 8.84 s, 8.85 s (27H, *t*-Bu), 8.97 (9H, s, *t*-Bu)]. Dimethyl sulfate was added to a mixture of VI and finely powdered potassium hydroxide in THF. After being stirred for 48 hrs. at 30°C under nitrogen atmosphere, the product was chromatographed on alumina to give methoxy ketone [VII, reddish orange cryst., mp 212-214°C (dec.), 71%, Mass(m/e): 600 (M<sup>+</sup>), 568 (M<sup>+</sup>-32), 543 (M<sup>+</sup>-57), 57 (base peak); IR(KBr-disk): 3310 w (≡C-H), 2185 w (C≡C), 1680 s (C=O), 1602 m (C=C), 968 vs (*trans* -CH=CH-) cm<sup>-1</sup>; <sup>1</sup>H NMR(CD<sub>2</sub>Cl<sub>2</sub>): τ 2.16 (1H, dd, J=12.0, 15.0, H<sup>5</sup>), 2.34 (1H, dd, J=11.0, 15.0, H<sup>2</sup>), 2.48 (1H, dd, J=11.0, 15.0, H<sup>2'</sup>), 2.81 (1H, dd, J=11.0, 15.0, H<sup>5'</sup>), 3.31 (1H, d, J=14.5, H<sup>6</sup>), 3.33 (1H, d, J=11.0, H<sup>4'</sup>), 3.33 (1H, d, J=12.0, H<sup>4</sup>), 3.38 (2H, d, J=11.0, H<sup>1</sup>, H<sup>1'</sup>), 3.58 (1H, d, J=15.0, H<sup>3</sup> or H<sup>3'</sup>), 4.09 (1H, d, J=15.0, H<sup>6'</sup>), 6.82 (3H, s, -OMe), 7.66 (1H, s, ≡CH), 8.83 (18H, s, *t*-Bu), 8.87 (9H, s, *t*-Bu), 9.03 (9H, s, *t*-Bu)]. Because treatment of a solution of VII in THF with a suspension of potassium hydroxide in liquid ammonia, which has been successfully applied for a wide variety of ethynyl ketones to give monocyclic<sup>4,5)</sup> and bicyclic glycols,<sup>2)</sup> resulted in a decomposition of VII, a solution of VII in THF was gradually added to a solution of lithium amide in dry liquid ammonia at -70°C. After the mixture had been stirred for 15 hrs. at the same temperature, the reaction mixture was worked up in the usual way, and extracted with ether. The residue obtained on evaporation of the solvent was chromatographed on alumina to result in separation of recovered VII (56%) and diastereomers of cyclic glycol monomethyl ether [VIII<sub>a</sub>, orange needles, mp 197.0-198.0°C, 24.5% based on consumed VII, Mass(m/e): 600 (M<sup>+</sup>), 543 (M<sup>+</sup>-57, base peak); IR(KBr-disk): 3360 m(OH), 2180 w (C≡C), 968 vs, 960 vs (*trans* -CH=CH-) cm<sup>-1</sup>; <sup>1</sup>H NMR(CDCl<sub>3</sub>): τ 2.43 (1H, dd, J=11.0, 15.0, H<sup>5</sup>), 2.45 (1H, dd, J=11.0, 15.0, H<sup>5'</sup>), 2.48 (2H, dd, J=11.0, 15.0, H<sup>3</sup>, H<sup>3'</sup>), 3.40 (2H, d, J=11.0, H<sup>4</sup>, H<sup>4'</sup>), 3.49 (2H, d, J=11.0, H<sup>1</sup>, H<sup>1'</sup>), 3.68 (2H, d, J=15.0, H<sup>3</sup>, H<sup>3'</sup>), 3.88 (1H, d, J=15.0, H<sup>6</sup>), 4.08 (1H, d, J=11.0, H<sup>6'</sup>), 6.73 (3H, s, OMe), 8.07 (1H, s, OH), 8.84 (18H, s, *t*-Bu), 8.91 (9H, s, *t*-Bu), 8.97 (9H, s, *t*-Bu); UV: λ<sub>max</sub><sup>THF</sup> nm (ε) 267.5 (50200), 277(40400), 349 sh(87800), 362.5 (103000), 436 (7300), 463 (4060),<sup>11)</sup> and VIII<sub>b</sub>, yellow fine cryst., mp >265°C (dec.), 31% based on consumed VII, Mass(m/e): 600 (M<sup>+</sup>), 543 (M<sup>+</sup>-57, base peak); IR(KBr-disk): 3440 m (OH), 2175 w (C≡C), 965 vs (*trans* -CH=CH-) cm<sup>-1</sup>; <sup>1</sup>H NMR(CD<sub>2</sub>Cl<sub>2</sub>): τ 2.39 (1H, dd, J=11.0, 15.0, H<sup>5</sup>), 2.41 (1H, dd, J=11.0, 15.0, H<sup>5'</sup>), 2.52 (2H, dd, J=11.0, 15.0, H<sup>2</sup>, H<sup>2'</sup>), 3.33 (2H, d, J=11.0, H<sup>4</sup>, H<sup>4'</sup>), 3.43 (2H, d, J=11.0, H<sup>1</sup>, H<sup>1'</sup>), 3.62 (2H, d, J=15.0, H<sup>3</sup>, H<sup>3'</sup>), 3.80 (1H, d, J=15.0, H<sup>6</sup>), 4.02 (1H, d, J=15.0, H<sup>6'</sup>), 6.78 (3H, s, OMe), 7.90 (1H, s, OH), 8.84 (18H, s, *t*-Bu), 8.91 (9H, s, *t*-Bu), 8.95 (9H, s, *t*-Bu); UV: λ<sub>max</sub><sup>THF</sup> nm (ε) 267 (49100), 276.5 (37800), 349 sh (85500), 362.5 (101000), 435 (7180), 464 sh(4020)]. The cyclic glycol monomethyl ether (VIII<sub>a</sub>) yielded II (m=n=1, 82%) on treatment with tin(II) chloride and ether saturated with hydrogen chloride at -35°C. Similarly, VIII<sub>b</sub> afforded II (m=n=1, 79%) under the same reaction conditions.

The tetrakisdehydro[14]annuleno[16]annulene (II, m=n=1) was obtained as deep violet crystals with metallic lustre [mp 182-183°C (dec.), Mass(m/e): 522 (M<sup>+</sup>, base peak), 495 (M<sup>+</sup>-57); IR(KBr-disk): 2190 vw, 1464 s, 1459 s, 1363 s, 1253 vs, 1052 m, 962 vs cm<sup>-1</sup>]. The annulenoannulene (II, m=n=1) gave 1:1 CT complex with 2,4,7-trinitrofluorenone [deep green fine cryst., mp ca. 240°C (dec.)]. The <sup>1</sup>H NMR and electronic spectral parameters of II (m=n=1) are summarized in Table. The NMR parameters clearly indicate that the 16-membered ring sustains strong paramagnetic ring current, and diatropicity of the 14-membered moiety is evidenced by the high-field signal of the

Table. Spectral Parameters of II ( $m=n=1$ )

$^1\text{H}$ NMR in $\text{CDCl}_3$ . $\tau$ -values at $35^\circ\text{C}$				
14-membered ring	$\text{H}^1$	2.68 d, $J=13.0$	$\text{H}^3$	1.98 d, $J=13.0$
	$\text{H}^2$	10.24 t, $J=13.0$	<i>t</i> -Bu	8.74 s
16-membered ring	$\text{H}^{1'}$	4.83 d, $J=15.5$	$\text{H}^{3'}$	5.13 d, $J=11.0$
	$\text{H}^{2'}$	-6.10 dd, $J=11.0, 15.0$	<i>t</i> -Bu	9.25 s
Electronic Spectrum in THF. $\lambda_{\text{max}}$ nm ( $\epsilon$ )				
233(16600), 240(17100), 265(14700), 278(14800), 304 sh(37300), 315.5(47700), 329 sh(41300), 384(124000), 407(196000), 676(4520), 750 sh(3120), 830 sh(1520)				

inner protons ( $\text{H}^2$ ). The high-field shift of  $\text{H}^1$  signal as compared with that of  $\text{H}^3$  indicates the shielding effect of paramagnetic ring current in the 16-membered ring. Inversely, the fact that  $\text{H}^{1'}$  resonated at a lower field than  $\text{H}^{3'}$  can be attributed to the deshielding effect of diamagnetic ring current induced in the  $14\pi$ -electron system. The  $^1\text{H}$  NMR parameters seem to indicate that the  $16\pi$ -electron system exerts tendency to preserve the inherent paratropicity of tris-dehydro[16]annulene<sup>6)</sup> suppressing the diatropicity of the 14-membered ring. Extremely broad absorption band in the long wavelength region of electronic spectrum exhibits characteristic feature of antiaromatic [4n]annulenes.<sup>6)</sup>

## References and Notes

- 1) Present address: *Faculty of Pharmaceutical Sciences, Nagasaki University, Bunkyo-machi, Nagasaki 852, Japan.*
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- 7) S. Akiyama, M. Iyoda, and M. Nakagawa, *J. Am. Chem. Soc.*, **98**, 6410 (1976).
- 8) All new crystalline compounds gave satisfactory elemental analyses.
- 9) D. F. Beumel, Jr. and R. F. Harries, *J. Org. Chem.*, **29**, 1872 (1964).
- 10) All attempts to mono-ethynylate IV gave V with a recovery of IV. This results seem to indicate that the second step of ethynylation ( $\text{VI} \rightarrow \text{V}$ ) is faster than the first step ( $\text{IV} \rightarrow \text{VI}$ ).
- 11) VIII<sub>a</sub> recrystallized from ether contained one mole of ether as solvent of crystallization.

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