

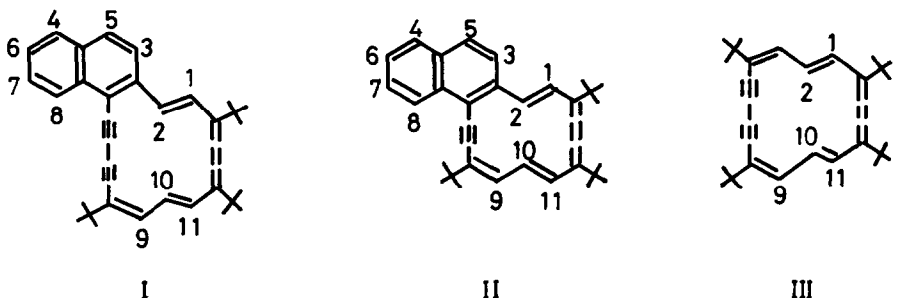
A NAPHTHO-TRI-*t*-BUTYLTRISDEHYDRO[16]ANNULENE

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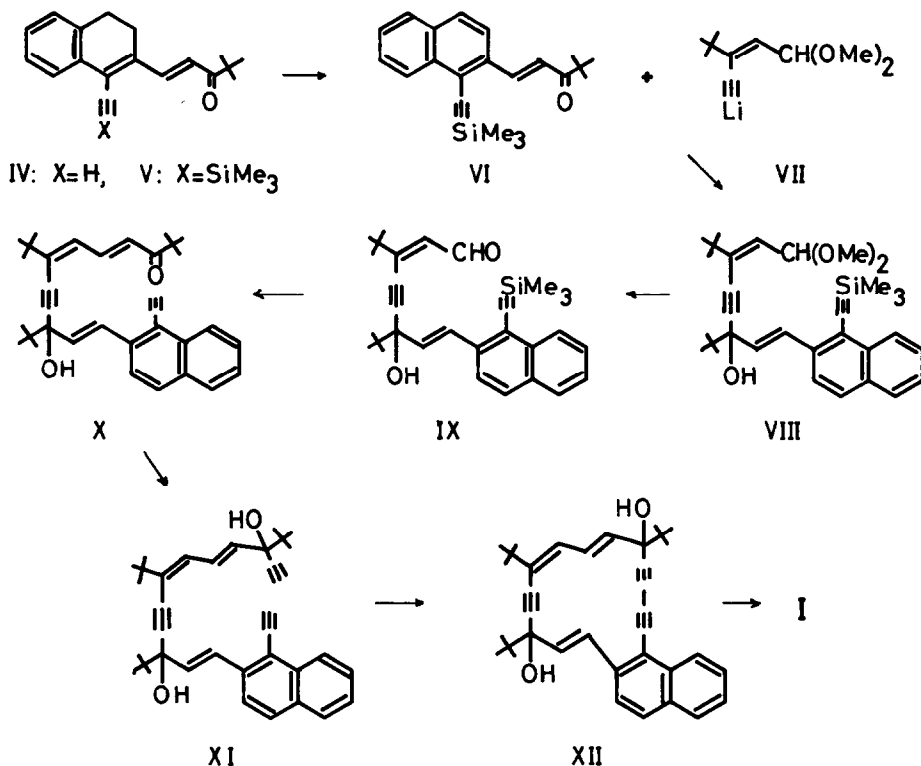
Summary: Synthesis of a naphtho-tri-*t*-butyltrisdehydro[16]annulene has been described. Suppression of paratropicity of the 16-membered ring was observed. Comparison of  $^1\text{H}$  NMR spectrum of the [16]annulene with that of naphtho-tri-*t*-butylbisdehydro[14]annulene suggests that the *trans* double bond adjacent to naphthalene in the [16]annulene is twisted out of the mean molecular plane.

In contrast to rather extensive studies on annelated  $[4n+2]$ annulenes, few was explored in the field of annelated  $[4n]$ annulenes, and only the synthesis and properties of dimethylmonodehydro[12]annulenes annelated with benzene, furan and thiophene have been reported by Sondheimer.<sup>1)</sup> Our recent observation of strong paratropicity of  $4n\pi$ -electron moiety in tetrakisdehydro[4n]-annuleno[4n+2]annulenes<sup>2)</sup> prompted us for the synthesis of naphtho-tri-*t*-butyltrisdehydro[16]-annulene (I). An analogous naphtho-tri-*t*-butylbisdehydro[14]annulene (II) was also prepared for comparison. Tetra-*t*-butyltrisdehydro[16]annulene (III)<sup>3)</sup> was used as a reference compound.



Synthesis.

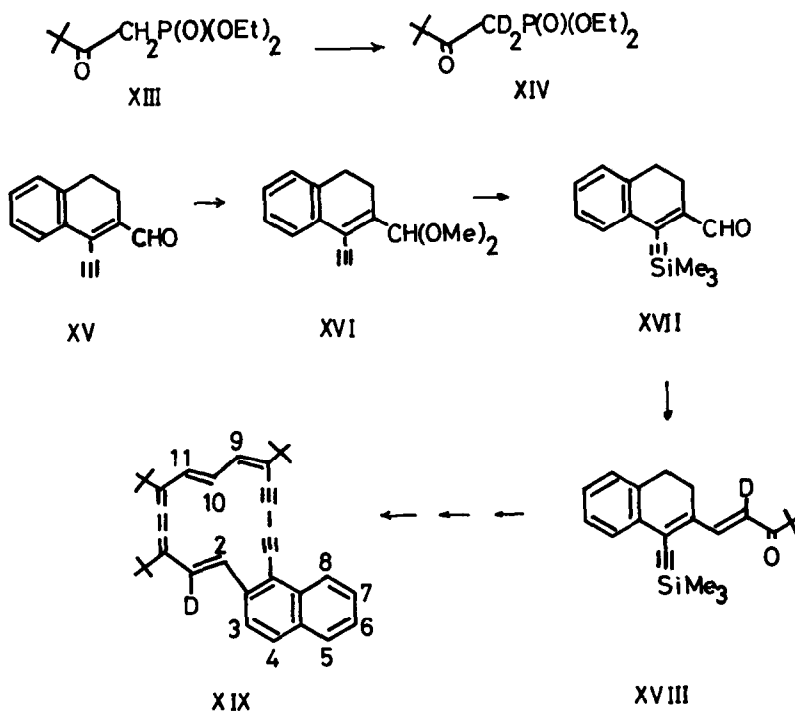
Ethynyl ketone (IV)<sup>4)</sup> was converted into trimethylsilyl derivative (V, pale yellow needles, mp 101.5-103.5°C (dec.), 74%)<sup>5)</sup> on successive treatment with lithium di-*i*-propyl amide and trimethylchlorosilane.<sup>6)</sup> Dehydrogenation of V in benzene with DDQ at 76-78°C yielded VI (colorless needles, mp 87.8-89.5°C, 67%). Reaction of lithio derivative of 3-*t*-butylpentenynal dimethyl acetal (VII)<sup>7)</sup> with VI gave hydroxy acetal (VIII), which was hydrolyzed without purification with aqueous acetic acid to give hydroxy aldehyde (IX, colorless fine needles, mp 89.1-90.0°C, 83% based on VI). The condensation of pinacolone with IX afforded hydroxy ketone (X, colorless needles, mp 103.0-104.3°C, 95%). Ethynylation of X with lithium acetylide in THF gave ethynyl glycol (XI, colorless rods, mp 122.3-123.3°C, 91%). Oxidation of XI with copper(II) acetate in



pyridine, methanol and ether under high dilution conditions at 63°C yielded cyclic glycol (XII). Chromatography of XII on alumina resulted in separation of diastereomers (XII<sub>a</sub>, colorless rods, mp 119-129°C, recrystallized from ether-hexane and contained 1 mole of ether of crystallization; XII<sub>b</sub>, pale yellow rods, mp 211.2-212.4°C, recrystallized from ether-pentane. XII<sub>a</sub>:XII<sub>b</sub> = 1 : 2.3). A solution of XII in ether was mixed at -40°C under nitrogen atmosphere with tin(II) chloride dihydrate and the same solvent saturated with hydrogen chloride. After being stirred for 15 min. at -15°C, the product dissolved in dichloromethane was chromatographed on alumina at -60°C. Elution with dichloromethane-pentane (1:9) gave I as deep blue crystalline solid (84%). Owing to the instability, elemental analysis of I could not be performed. As examination of molecular model of I indicates highly strained nature and possibility of inversion of C<sub>1</sub>-C<sub>2</sub> *trans* double bond, we have carried out the synthesis of deuterated derivative of I (XIX), in which H<sup>1</sup> is replaced by D. 3,3-Dimethyl-2-oxobutanephosphonate (XIII)<sup>8)</sup> was treated with sodium ethoxide in ethanol-0-*d*, and the reaction mixture was neutralized with acetic acid-0-*d* to give XIV (bp 111-112°C/2.5 mmHg, 90%, deuterium conversion 60%). Dimethyl acetal (XVI) derived from XV<sup>4)</sup> was treated successively with ethylmagnesium bromide and trimethylchlorosilane. Chromatography of the product on silica gel yielded XVII. The reaction of carbanion obtained from XIV<sup>8)</sup> with XVII gave XVIII (mono-deuterated V), which could be converted into XIX (monodeuterated I, deuterium content, *ca.* 50%) by analogous reaction sequence.

Naphtho-tri-*t*-butylbisdehydro[14]annulene (II, reddish brown violet cryst., mp 201-202°C (dec.)) could be prepared<sup>9)</sup> by similar reaction steps used in the synthesis of naphtho-dihydro-

naphtho-di-*t*-butyl-<sup>4)</sup> and benzo-tri-*t*-butylbisdehydro[14]annulenes.<sup>10)</sup>



#### Properties.

The naphtho-tri-*t*-butyltrisdehydro[16]annulene (I) was found to be unstable and gradually decomposed on standing at room temperature. The FT <sup>1</sup>H NMR spectrum of I [ $\tau$ -values at 0°C in THF-*d*<sub>6</sub>: -3.81 (dd,  $J=15.5, 11.5$ , H<sup>10</sup>), -2.32 (d,  $J=16.5$ , H<sup>2</sup>), 2.32 (d,  $J=16.5$ , H<sup>1</sup>), 2.30 ~ 2.78 (m, H<sup>4,5,6,7,8</sup>), 3.20 (d,  $J=9.0$ , H<sup>3</sup>), 4.64 (d,  $J=15.5$ , H<sup>11</sup>), 4.66 (d,  $J=11.0$ , H<sup>9</sup>), 9.04 s, 9.14 s, 9.17 s (*t*-Bu)] indicates induction of strong paramagnetic ring current in the 16-membered ring. Essentially temperature independent <sup>1</sup>H NMR spectra of I in the range of -30°C to +30°C was observed. The chemical shifts of outer and inner protons and the difference of chemical shifts between them ( $\tau_i - \tau_o$ ) are recorded in Table together with those for XIX, III<sup>10)</sup> and II. The fact that the doublet signal at  $\tau$  -2.35 changed to a singlet at  $\tau$  -2.43 on replacement of H<sup>1</sup> by deuterium confirms the assignment of H<sup>1</sup> and H<sup>2</sup> excluding the possibility of conformational change of C<sub>1</sub>-C<sub>2</sub> *trans* double bond. Comparison of the <sup>1</sup>H NMR parameters and ( $\tau_i - \tau_o$ )-values of I with those of non-annulated parent annulene (III)<sup>10)</sup> revealed a marked suppression of paratropicity in the 16 $\pi$ -electron system in I. The same trend has been observed in the decrease of diatropicity of annulated [4*n*+2]annulenes.<sup>3)</sup> The most remarkable characteristic of <sup>1</sup>H NMR spectrum of I is high- and low-field shifts of H<sup>2</sup> and H<sup>1</sup> signals, respectively. The anomaly could not be attributed solely to the deshielding effect of diamagnetic ring current induced in the fused naphthalene ring, because the difference in chemical shifts between H<sup>10</sup> and H<sup>2</sup>, and H<sup>11</sup> and H<sup>1</sup> in the naphtho[14]annulene (II) were found to be 0.12 and 0.68 ppm, respectively, being

significantly smaller than those of corresponding difference in I (1.51 and 2.32 ppm, respectively). The anomalous chemical shifts of H<sup>2</sup> and H<sup>1</sup> seemed to suggest that the C<sub>1</sub>-C<sub>2</sub> *trans* double bond is twisted out of the molecular plane due to an enhanced ring strain introduced by the fusion of naphthalene ring. Comparison of <sup>1</sup>H NMR spectrum of I with that of XIX revealed a slight increase of paratropicity of XIX. Because the steric requirement of deuterium has been demonstrated to be less than that of hydrogen,<sup>11)</sup> the increase of paratropicity of XIX seems to be a reflection of an increased planarity of the annulene perimeter caused by replacement of the most crowded proton in I (H<sup>1</sup>) by deuterium.

Table. <sup>1</sup>H NMR Parameters in THF-d<sub>8</sub> at -30°C. τ-values

	Inner-H		Outer-H			
	H <sup>10</sup>	H <sup>2</sup>	H <sup>9</sup>	H <sup>11</sup>	H <sup>1</sup>	τ <sub>i</sub> - τ <sub>o</sub>
I	-3.86 dd J=15.5, 11.0	-2.35 d J=16.5	4.71 d J=11.0	4.69 d J=15.5	2.37 d J=16.5	-8.52 -8.55 -4.72
XIX	-3.89 dd J=15.5, 11.0	-2.43 s (-2.35 d, J=16.5)	4.70 d J=11.0	4.72 d J=15.5	(2.37 d, J=16.5)	-8.59 -8.61 -4.72
III		-7.01 dd J=15.0, 11.0	5.60 d J=11.0		5.47 d J=15.0	-12.75 -12.61
II	11.71 dd J=14.5, 12.5	11.59 d J=15.5	1.15 d J=12.5	1.17 d J=14.5	0.49 d J=15.5	11.10 10.56 10.54

The parameters in parentheses indicate signals due to unchanged <sup>1</sup>H in XIX.

The electronic spectrum of I [ $\lambda_{\text{max}}^{\text{cyclohexane}}$  nm (ε): 235 (28400), 292 (32000), 324 (70300), 362 (36200), 408 sh(29000), 600 (1410), 480 ~ 840 (broad band)] showed characteristic feature of antiaromatic [4n]annulenes exhibiting a very broad absorption band in long wavelength region.

## References and Notes

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- 2) The preceding paper.
- 3) S. Nakatsuji, M. Morigaki, S. Akiyama, and M. Nakagawa, *Tetrahedron Lett.*, 1233 (1975).
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- 5) All new compounds reported in this paper gave mass, IR and NMR spectra consistent with the assigned structures, and all crystalline materials gave satisfactory elemental analyses, unless otherwise stated.
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(Received in Japan 21 July 1979)