

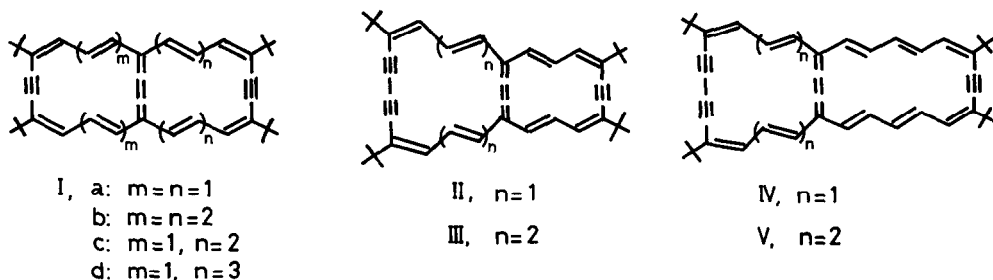
### TETRAKISDEHYDRO[18]ANNULENO[20]ANNULENE

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**Summary:** Tetrakisdehydro[18]annuleno[20]annulene has been synthesized. The  $^1\text{H}$  NMR spectra clearly indicate the induction of dia- and paramagnetic ring currents in 18- and 20-rings, respectively. A marked suppression of the diatropicity in the  $18\pi$  moiety was observed being in the same trend as observed in other tetrakisdehydro[4n]annuleno[4n'+2]annulenes. The  $^1\text{H}$  NMR spectroscopic behavior of the annulenoannulenes is consistent with theoretical conclusion.

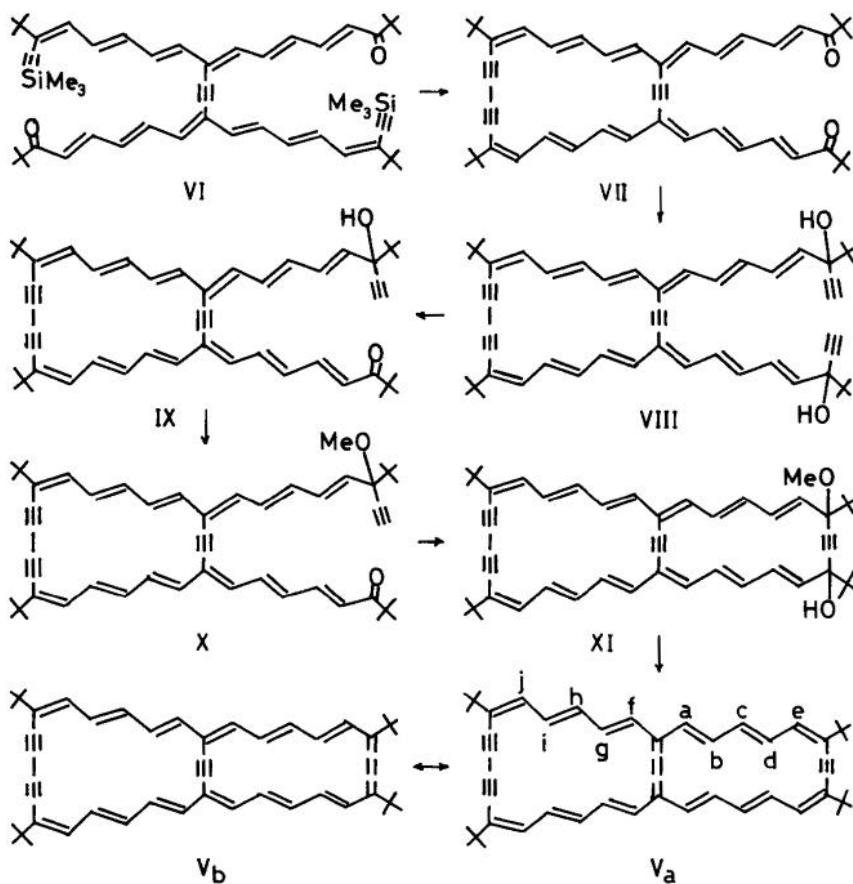
Our recent systematic studies on [4n+2]annuleno[4n'+2]annulenes such as  $\text{I}_{\text{and}}$  corresponding to naphthalene showed that they can be regarded as fused system consisting of two essentially independent diatropic moieties<sup>1)</sup>. Inspired by the interesting behavior of  $\pi$ -electrons in these bicyclic systems, we have carried out the studies on [4n]annuleno[4n'+2]annulenes similar to benzocyclobutadiene, and reported the syntheses of three tetrakisdehydro[4n]annuleno[4n'+2]-annulenes ( $\text{II}^{2)}$ ,  $\text{III}^{3)}$ , and  $\text{IV}^{4)}$ ). It has been revealed on the basis of  $^1\text{H}$  NMR spectroscopy that they also consist of essentially independent antiaromatic and aromatic moieties. In this paper we wish to report the synthesis and properties of tetrakisdehydro[18]annuleno[20]annulene ( $\text{V}$ ) in order to add further information on the fused system of antiaromatic and aromatic rings.



Diketone (VI), which has been prepared as an intermediate of the synthesis of trisdehydro[18]annuleno[18]annulene ( $\text{I}_D$ )<sup>5)</sup>, was treated with copper(II) acetate in pyridine and methanol at  $90^\circ\text{C}$  to give monocyclic diketone (VII, reddish brown fine crystals, mp  $193.7$ - $195.4^\circ\text{C}$  (dec.), 47%)<sup>6)</sup>. Bisethynylation of VII with lithium acetylide in THF yielded acyclic glycol (VIII, reddish orange fine crystals, mp *ca.*  $200^\circ\text{C}$  (dec.), 80%). Retro-ethynylation of VII with potassium *t*-butoxide in benzene-THF afforded ketoalcohol (IX, deep violet plates, mp  $> 250^\circ\text{C}$  (dec.), 79.5%). Treatment of IX with dimethyl sulfate and potassium hydroxide in THF gave methoxy ketone (X, reddish brown crystals, mp  $> 250^\circ\text{C}$  (dec.), 53.5%). Treatment of X with lithium amide in liquid ammonia at  $-65^\circ\text{C}$  gave a mixture of recovered X and diastereomers of the bicyclic glycol monomethyl ether, which were separated by chromatography ( $\text{XI}_a$ , reddish orange crystalline powder, mp  $> 250^\circ\text{C}$  (dec.), 14% based on consumed X;  $\text{XI}_b$ , reddish orange crystalline

powder, mp > 250°C (dec.), 32% based on consumed X). A solution of XI in ether or THF was treated with tin(II) chloride-hydrogen chloride under nitrogen atmosphere at -20°C resulting in a deep green solution. The deeply colored solution was found to be rather unstable and evaporation to dryness of the solution led to fade the observed color. However, a solution of the annulenoannulene (V) with high purity could be obtained by chromatography on alumina at -30°C. The  $^1\text{H}$  NMR and qualitative electronic spectrum were obtained by replacement of elution solvent with  $\text{CDCl}_3$  and cyclohexane, respectively.

As illustrated in Figure, the absorption curve indicates clearly the formation of tetrakis-dehydro[18]annuleno[20]annulene (V) being closely related with those of II, III, and IV. The  $^1\text{H}$  NMR and electronic spectral parameters of V are summarized in Table 1. The  $^1\text{H}$  NMR parameters of V indicate the induction of dia- and paramagnetic ring currents in 18- and 20-rings, respectively.



Scheme

The difference in chemical shifts between the inner and outer protons ( $\tau_i - \tau_o$ ), which can be regarded as an approximate measure of tropicity, of this series of  $[4n]$ annuleno $[4n'+2]$ -annulenes (II, III, IV, and V) are summarized in Table 2. Because the annulenoannulenes (II-V)

Table 1. Spectral Parameters of V.

$^1\text{H}$ NMR in $\text{CDCl}_3$ . $\tau$ -values at $-10^\circ\text{C}$ .					
18-membered ring	$\text{H}_a$	2.28	d, $J=13.5$	$\text{H}_b$	11.15 t, $J=13.5$
	$\text{H}_c$	1.34	t, $J=13.5$	$\text{H}_d$	10.61 t, $J=13.5$
	$\text{H}_e$	1.56	d, $J=13.5$	<i>t</i> -Bu	8.37 s
20-membered ring	$\text{H}_f$	4.40	d, $J=15.0$	$\text{H}_g$	-3.31 dd, $J=11.0, 15.0$
	$\text{H}_h$	5.14	dd, $J=11.0, 15.0$	$\text{H}_i$	-2.87 dd, $J=11.0, 15.0$
	$\text{H}_j$	4.91	d, $J=11.0$	<i>t</i> -Bu	9.26 s
Electronic Spectrum in Cyclohexane. $\lambda_{\text{max}}$ nm.					
440, 467, 623, 715, 776, 863					

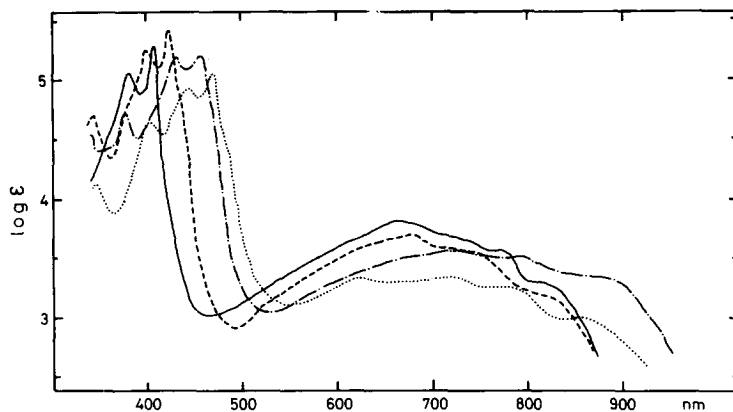


Figure. Electronic Spectra of Tetrakisdehydro[4n]annuleno[4n'+2]annulenes (I, II, III, and IV).

- I (THF).  
 - - - II (cyclohexane).  
 - · - · III (THF).  
 ····· IV (cyclohexane).

Table 2. The  $^1\text{H}$  NMR Chemical Shifts of Tetrakisdehydro[4n]annuleno[4n'+2]annulenes in  $\text{CDCl}_3$  ( $\tau$ -values).

		inner H ( $\tau_i$ )	outer H ( $\tau_o$ )	$\tau_i - \tau_o$
[14]-[16] (II) <sup>a</sup>	[14]	10.24	1.98, 2.68	7.56, 8.26
	[16]	-6.10	4.83, 5.13	-10.93, -11.23
[14]-[20] (III) <sup>a</sup>	[14]	10.76	1.79, 2.39	8.37, 8.97
	[20]	-2.74, -3.14	4.46, 4.84, 5.09	-7.58 ~ -8.23
[16]-[18] (IV) <sup>a</sup>	[18]	9.85, 10.46	1.54, 1.71, 2.53	7.93 ~ 8.92
	[16]	-5.80	4.58, 5.01	-10.38, -10.81
[18]-[20] (V) <sup>b</sup>	[18]	10.61, 11.15	1.34, 1.56, 2.28	8.87 ~ 9.81
	[20]	-2.87, -3.31	4.40, 4.91, 5.14	-7.71 ~ -8.45

a) At  $35^\circ\text{C}$ .b) At  $-10^\circ\text{C}$ .

should have similar geometry and planarity, the  $\tau_i - \tau_o$  values can be reasonably compared. The values for the parent annulenes of V, *i.e.*, bisdehydro[18]- and trisdehydro[20]annulenes<sup>7)</sup>, have been found to be 13.29 and  $-9.08 \sim -9.69$ , respectively. The corresponding values for V ( $8.87 \sim 9.81$  for the  $18\pi$  moiety and  $-7.71 \sim -8.45$  for the  $20\pi$  system) indicate that the extent of suppression of tropicity caused by annelation is much larger in the aromatic  $18\pi$ -electron system than in the  $20\pi$  antiaromatic system. The same trend has been observed in the other members of this series (II  $\sim$  IV)<sup>2)-4)</sup>. It has been suggested that a fairly strong paramagnetic ring current can be observed in an antiaromatic system even when the relatively small resonance energy per  $\pi$ -electron (REPE) is calculated (*e.g.*, for trisdehydro[24]annulene:  $\tau_i - \tau_o = -6.79$ ; the REPE =  $-0.0020$ <sup>8)</sup>). Therefore, the fact that the  $[4n]$  moiety in  $[4n]$ annuleno $[4n'+2]$ annulenes shows the tendency to preserve its paratropicity suppressing strongly the diatropicity of the  $[4n'+2]$  congener seems to be reasonable.

Comparison of the  $\tau_i - \tau_o$  values for  $[4n]$  moiety between II ([14]-[16]) and IV ([18]-[16]) and between III([14]-[20]) and V ([18]-[20]) (Table 2) indicates that the change in magnitude of diatropicity exerts a minor effect on the paratropicity of antiaromatic moiety of  $[4n]$ annuleno- $[4n'+2]$ annulenes. On the contrary, comparison of the diatropicity of aromatic moiety between II and III and between IV and V reveals that the more strongly paratropic moiety causes a larger suppression of the diatropicity of the aromatic portion of  $[4n]$ annuleno $[4n'+2]$ annulenes. The same trend has been observed in annelated annulenes and  $[4n+2]$ annuleno $[4n'+2]$ annulenes, *i.e.*, fusion of a ring with stronger aromaticity suppresses more strongly the diatropicity of  $[4n+2]$ -annulene moiety<sup>7)</sup>.

The results of these investigations indicate independent nature of the antiaromatic and the aromatic rings in  $[4n]$ annuleno $[4n'+2]$ annulenes (II, III, IV and V) suggesting a minor contribution of peripheral  $4n\pi$  antiaromatic system. The observation that both of  $[4n+2]$ -annuleno $[4n'+2]$ annulenes ( $I_{a \sim d}$ ) and  $[4n]$ annuleno $[4n'+2]$ annulenes (II $\sim$ V) exert additive characteristics of comprising two nuclei is consistent with the theoretical conclusion of B. A. Hess, Jr., L. J. Schaad and I. Agranat<sup>9)</sup>.

#### References and Note

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