

3,9,14,20-TETRA-t-BUTYL-1,10,12-TRISDEHYDRO[20]ANNULENE.  
A PARATROPIC 20 $\pi$ -ELECTRON SYSTEM

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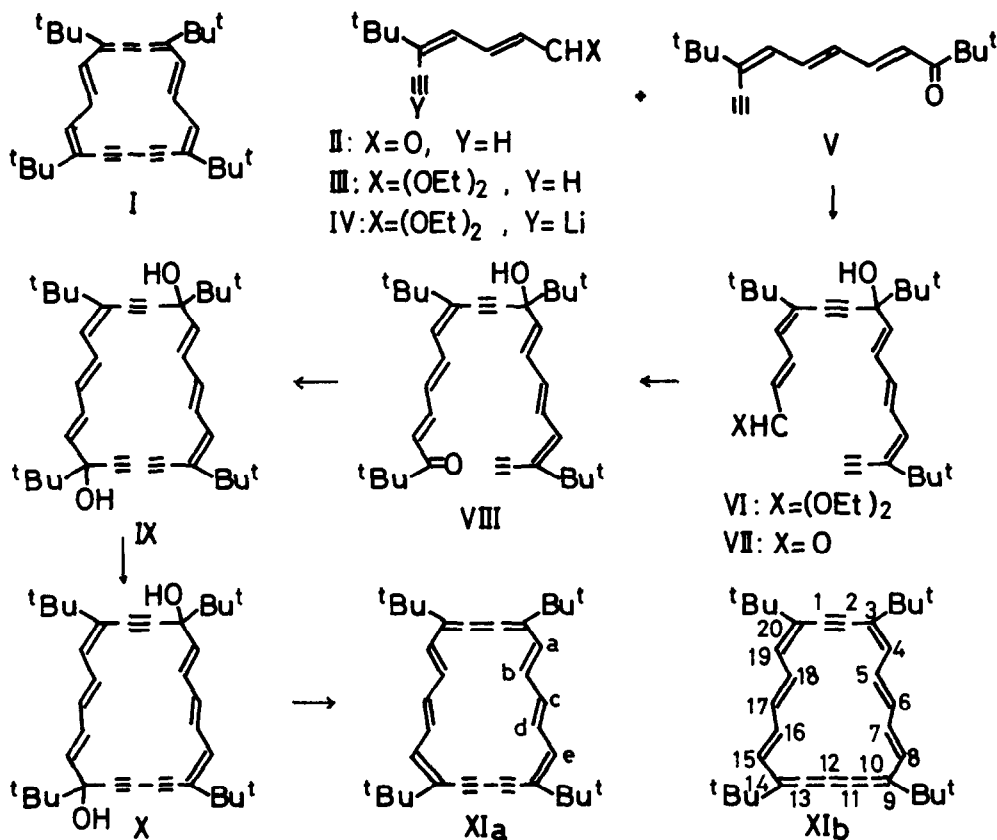
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Inspired from the fact that conformationally stable 3,7,12,16-tetra-t-butyl-1,8,10-trisdehydro[16]annulene (I) is strongly paratropic (1), we have carried out the synthesis of 3,9,14,20-tetra-t-butyl-1,10,12-trisdehydro[20]-annulene (XI), a higher vinylogue of the trisdehydro[16]annulene (I), to clarify the effect of ring size on paramagnetic ring current.

4-t-Butyl-2,4-heptadien-4-ynal (II) (2) was converted into acetal (III), yellow liquid, bp 105°C/2 mmHg, in the usual way (3). Lithio derivative (IV) obtained by the reaction of III with *n*-butyllithium was allowed to react with triene ketone (V) (2). Resulting hydroxy acetal (VI), orange yellow liquid, was directly hydrolyzed with aqueous tartaric acid at room temperature to give hydroxy-aldehyde (VII), pale yellow solid, mp 41.0-41.5°C, 75%,  $M^+$  406 (4), 2,4-dinitrophenylhydrazone, orange red needles, mp 138.5-140.0°C. Product of the aldol condensation of VII with pinacolone in ethanol in the presence of sodium hydroxide was chromatographed on silica gel (Merck) to give ethynyl ketone (VIII), pale yellow solid, mp 59.5-60.5°C, 62%,  $M^+$  488 (4). Ethynylation of VIII with lithium acetylide-ethylenediamine complex (5) in tetrahydrofuran saturated with acetylene yielded glycol (IX), pale yellow solid, mp 43.0-45.0°C, 93%,  $M^+$  514, PMR (CCl<sub>4</sub>):  $\tau$  2.93-4.28 (m, 10H, olefinic H), 6.67 (s, 1H, C $\equiv$ CH), 5.77 (s, 1H, C $\equiv$ CH), 8.00 (broad s, 2H, OH), 8.82, 8.84, 8.93, 9.00 (each s, 36H, t-Bu). Oxidative coupling of IX by cupric acetate in pyridine-methanol-ether under high dilution conditions gave diastereomeric mixture of cyclic glycol (X), which upon chromatography on silica gel (Merck), yielded a low melting isomer (X<sub>a</sub>), pale yellow crystals, mp 210.5-212.0°C (dec.), 27%,  $M^+$  512, PMR (CDCl<sub>3</sub>):  $\tau$  2.88-4.14 (m, 10H, olefinic H), 7.95 (broad s, 2H, OH), 8.80, 8.83, 8.92, 8.93 (each s, 36H, t-Bu), and a high melting isomer (X<sub>b</sub>), pale yellow crystals, mp 213.0-214.0°C (dec.), 38%,  $M^+$  512, PMR (CDCl<sub>3</sub>):  $\tau$  2.88-4.21 (m, 10H, olefinic H), 7.95 (broad s, 2H, OH), 8.79, 8.83, 8.92, 8.93 (each s, 36H, t-Bu). The fact that the 20-membered cyclic glycol (X) could be obtained in a much higher yield (65%) than the corresponding 16-membered cyclic glycol (35%) (1) seems to reflect a diminished ring

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strain in the larger ring.

Treatment of  $X_a$  in ether under nitrogen atmosphere with stannous chloride dihydrate in the same solvent saturated with hydrogen chloride at  $-55^\circ\text{C}$  for 5 min. resulted in a deep blue solution. After quenching with water, the solution was worked up in the usual manner, and the product was purified by chromatography on alumina (Merck, Act. II-III) to give tetra-*t*-butyltrisdehydro[20]annulene (XI) in 90% yield. Similar treatment of  $X_b$  also gave XI in a yield of 85%. The trisdehydro[20]annulene (XI), deep blue crystals, mp  $174.0\text{--}175.0^\circ\text{C}$  (dec.),  $M^+$  478, was found moderately stable in crystalline state, but the color of solution gradually changed from deep blue to reddish brown on standing.

As illustrated in Fig. 1, the electronic spectrum of XI showed characteristic feature of  $[4n]$ annulene showing bathochromic shift as compared with that of  $16\pi$ -analogue (I) (1). Induction of remarkable paramagnetic ring current in the trisdehydro[20]annulene (XI) is evidenced by low field signals of the inner protons and by high field shifts of the signals of outer and *t*-butyl protons (Fig. 2 and Table 1). The PMR spectrum of XI was essentially temperature independent ( $+36^\circ\text{C}$  and  $-42^\circ\text{C}$ ) indicating high conformational stability of XI.

Attempted measurement of the PMR spectrum at +70°C resulted in decomposition of XI.

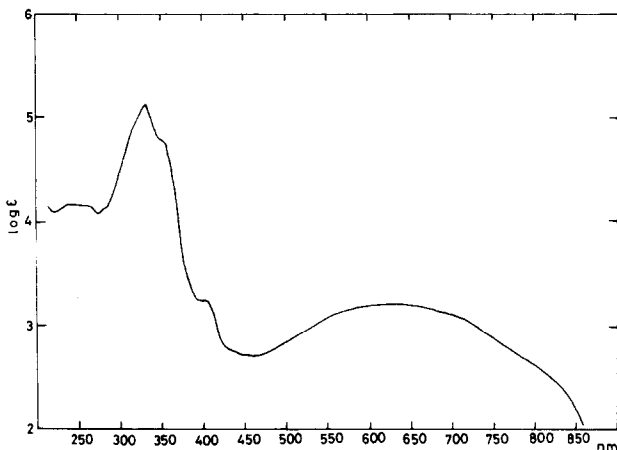


Fig. 1. Electronic spectrum of XI in cyclohexane.

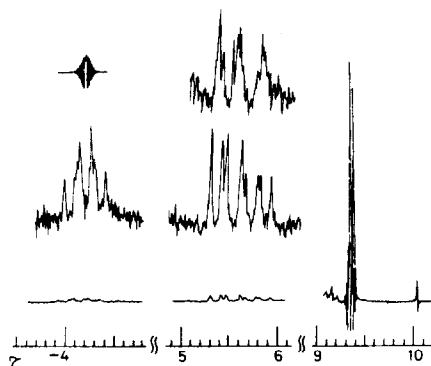


Fig. 2. 100 MHz PMR spectrum of XI in  $\text{CDCl}_3$  at 36°C.

Table 1. 100 MHz PMR Spectra of XI in  $\text{CDCl}_3$  ( $\tau$ -value)

	-42°C	+36°C
$\text{H}^b, \text{H}^d$	-4.02 dd, J=11, 15 Hz	-3.86 dd, J=11, 15 Hz
	-3.85 dd, J=11, 15	-3.69 dd, J=11, 15
$\text{H}^a, \text{H}^e$	5.44 d, J=11	5.39 d, J=11
	5.64 d, J=15	5.57 d, J=15
$\text{H}^c$	5.86 dd, J=11, 15	5.83 dd, J=11, 15
$\text{t-Bu}$	9.38 s	9.32 s
	9.41 s	9.35 s

$^{13}\text{C}$ -NMR spectra of paratropic trisdehydro[16]- (I), [20]- (XI) and diatropic tetra-t-butylbisdehydro[14]- (6) and [18]annulenes (7) afforded interesting information on the nature of  $\text{sp}$ -hybridized carbons in dehydroannulenes. As summa-

Table 2. Carbon-13 Chemical Shifts of  $\text{sp}$ -Hybridized Carbons in  $\text{CDCl}_3$

Trisdehydro[4n]annulene	-20°C	Bisdehydro[4n+2]annulene	36°C
[16]-	86.6, 90.5, 153.3	[14]-	116.7
[20]-	85.2, 86.5, 148.3	[18]-	115.7

Varian XL-100-15 FT NMR spectrometer operated at 25.2 MHz.  $^1\text{H}$  noise decoupling. TMS as an internal standard.

ri- zed in Table 2, the bisdehydro[4n+2]annulenes gave signals ascribable to  $\text{sp}$ -hybridized carbons at intermediate field between the region of acetylenic (65-90 ppm) (8,9) and cumulen- ic carbons (ca. 150 ppm) (9) indicating highly de-

localized  $[4n+2]\pi$ -electron system, whereas the trisdehydro $[4n]$ annulenes (I and XI) exhibit two groups of signals, which are attributable to acetylenic and cumulenenic carbons. Appearance of two signals in acetylenic carbon region seems to be ascribable to the terminal and central carbons in diacetylene bond, thus suggesting that  $[4n]$ annulenes hold alternate bond structures containing a butatriene and a diacetylene units (I and XI<sub>a</sub>). The observed coupling constants in PMR spectra of I and XI ( $J=11$  and  $15$  Hz) are consistent with alternate bond structures.

The difference in chemical shifts between inner and outer protons of the trisdehydro $[20]$ annulene (XI,  $\Delta\tau = 5.57 - (-3.86) = 9.43$ ) was found to be smaller than that of the trisdehydro $[16]$ annulene (I,  $\Delta\tau = 5.89 - (-7.17) = 13.06$ ) (1). In view of their conformational stability, XI and I certainly have similar geometries, and the  $\Delta\tau$  -values can be regarded as an approximate measure of intensity of paramagnetic ring current. Therefore, the observed  $\Delta\tau$  -value for XI seems to indicate that paramagnetic ring current in  $[4n]$ annulenes is reduced by an increase in the ring size just as the case of  $[4n+2]$ annulenes (10) being consistent with the theoretically predicted decrease of resonance energy along with the increase in ring size.

#### References and Note

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