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SYNTHESIS OF 3,11,16,24-TETRA-*t*-BUTYL-1,12,14-TRISDEHYDRO[24]ANNULENE. EFFECT OF RING SIZE ON INTENSITY OF PARAMAGNETIC RING CURRENT

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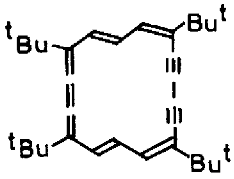
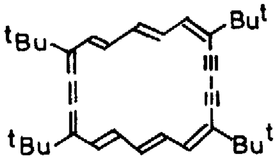
We have reported the synthesis of conformationally stable and strongly paratropic tetra-*t*-butyltridehydro[16]- (I) (1) and [20]annulenes (II) (2). In view of their high conformational stability, synthesis of 24π-electron congener (X) seemed to be of considerable interest with respect to the effect of ring size on the magnitude of paramagnetic ring current.



I



II

7-*t*-Butyl-2,4,6-nonatrien-8-ynal dimethyl acetal (III) (3) was converted into lithio derivative (IV) by the action of butyllithium. The reaction of IV with tetraenyne ketone (V) (4) followed by chromatography on silica gel (Merck, Kiesel Gel 60) yielded hydroxyaldehyde (VI: yellow crystalline solid; 79%; mp 60.5-62.5°C; 2,4-dinitrophenylhydrazone: dark reddish brown crystals; mp 96.0-96.5°C) (5). Non-crystalline hydroxy ketone (VII: orange yellow solid; 68%; mp 48-52°C) obtained by the aldol condensation of VI with pinacolone (EtOH-H_2O-NaOH; 0°C, 30 min; room temperature, 24 hr) was ethynylated by lithium acetylide-ethylenediamine complex (6) in THF saturated with acetylene to give acyclic glycol (VIII: yellow crystalline solid; 82%; mp 51-53°C). Attempts to crystallize VIII were failed. VIII in pyridine-methanol-ether was oxidized by copper(II) acetate under high dilution conditions. After being concentrated under reduced pressure, the reaction mixture was worked up in the usual manner. The product was chromatographed on silica gel (Merck, Kiesel Gel 60). Elution with benzene gave a diastereomer of cyclic glycol (IX_a: colorless crystals; mp 218.5-219.0°C (dec.); 36%). Another diastereomer (IX_b: pale yellow crystals; mp 220.0-220.5°C (dec.); 36%) was obtained on further elution with benzene-ether (99:1).

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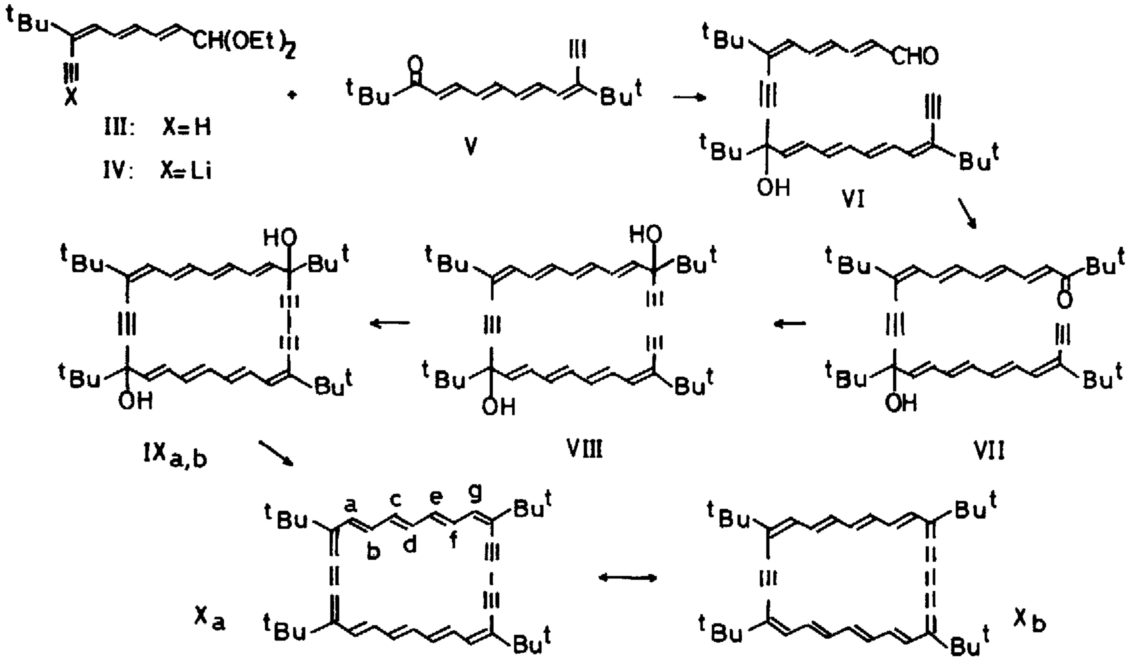

Ether saturated with hydrogen chloride was added under argon atmosphere at -55°C to a solution of IX_a in ether containing finely powdered tin(II) chloride dihydrate, and the mixture was stirred for 3 min at the same temperature. The resulting deep greenish blue solution was poured onto ice-water, and the mixture was worked up in the usual way. Concentrated solution was chromatographed on alumina (Merck, Act. II-III). X (bluish green crystals; 82%) was obtained on elution with hexane-ether (98:2). IX_b also gave X (86%) under the same reaction conditions. X was found to be a rather unstable compound. In crystalline state, X decomposed at room temperature in a few hours forming yellowish brown solid. The half-life period of X in a diluted solution (in cyclohexane, 2.325×10^{-5} mol/l, 15°C, under argon) was estimated to be *ca.* 48 hr by UV spectrophotometry. The thermal stability of solid state and of concentrated solution of trisdehydro-[4n]annulenes were found to be in the sequence of I > II > X (7). Interestingly, inversed sequence (I < II < X) was observed for the stability of diluted solutions (8) and for the qualitative sensitivity to oxygen. The same trend of sensitivity to oxygen has been found for bisdehydro[14]annulene derivatives annelated with one or two naphthalene nuclei, *i.e.*, the less paratropic trisdehydroannulene is less sensitive to oxygen, and similarly the strongly diatropic dinaphtho-di-*t*-butylbisdehydro[14]annulene (9) has been found to be much more sensitive than the less diatropic mononaphtho analogue (10).

Elemental analyses of X gave poor results presumably owing to the unstable nature (Found: C, 89.55; H, 9.54%. Calcd. for $C_{40}H_{50}$: C, 90.50; H, 9.50%). Electronic spectrum of X measured at -78°C (Fig. 1) was obtained with a solution prepared from fresh X obtained using accurately weighed IX. The ε-values were estimated assuming 100% conversion of IX into X. The electronic spectrum exhibits features characteristic of [4n]annulenes showing a very broad and structureless band at long wavelength region.

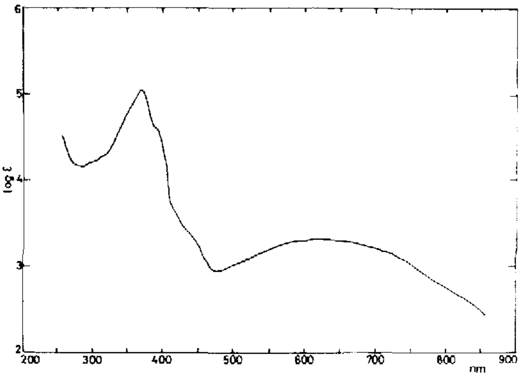

Fig. 1. The electronic spectrum of X in THF at -78°C.

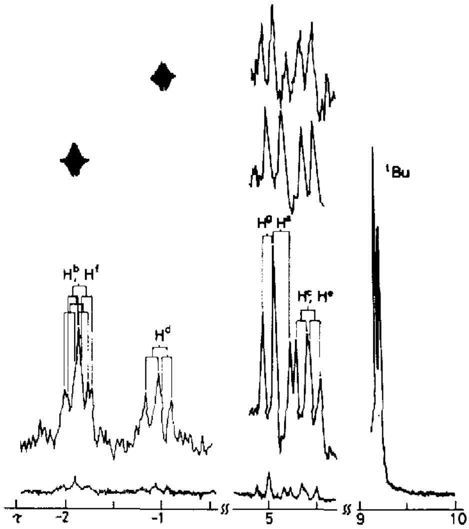

Fig. 2. The NMR spectrum of X in $CDCl_3$ at -50°C.

The H NMR spectrum is shown in Fig. 2 and the parameters are recorded in Table 1. Assignment of protons could be attained by double resonance technique.

Table 1. 100 MHz ^1H NMR Spectra of X in $CDCl_3$

	-50°C	-10°C	31°C
H^b, H^f	-1.91 dd, J=11, 15 -1.87 dd, J=11, 15	-1.87 dd, J=11, 15 -1.84 dd, J=11, 15	-1.80 dd, J=11, 15 -1.78 dd, J=11, 15
H^d	-1.05 dd, J=11, 15	-1.01 dd, J=11, 15	-0.95 dd, J=11, 15
H^g	4.91 d, J=11	4.89 d, J=11	4.86 d, J=11
H^a	5.05 d, J=15	5.03 d, J=15	5.00 d, J=15
H^c, H^e	5.33 dd, J=11, 15	5.31 dd, J=11, 15	5.30 dd, J=11, 15 5.29 dd, J=11, 15
t-Bu	9.22 s 9.26 s	9.20 s 9.24 s	9.19 s 9.22 s

The NMR spectrum clearly indicates that X is strongly paratropic, and the essentially temperature-independent spectra (Table 1) demonstrate that X has a high conformational stability as the lower analogues (I and II).

Because, I, II and X should have similar geometries and planarities, the difference in chemical shifts between outer and inner protons ($\tau_o - \tau_i$), which can be regarded as an approximate measure of intensity of ring current, can be reasonably compared. As recorded in Table 2, marked decrease in $\tau_o - \tau_i$-values were found along with increase in the ring size. It has been predicted theoretically that polyolefinic character both of [4n+2]- and [4n]annulenes should increase with increase in the size of ring (11). The results shown in Table 2 seem to be the first experimental verification of the prediction for [4n]-annulenes.

Table 2. $\tau_o - \tau_i$-Values for Trisdehydro[4n]annulenes

	[4n]	Outer-H (τ_o)	Inner-H (τ_i)	$\tau_o - \tau_i$
I	[16]	5.83	-7.10	12.93
II	[20]	5.61	-3.78	9.39
X	[24]	5.30	-1.80	7.10

References and Notes

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5) All new compounds described in this paper gave IR, mass and NMR spectra consistent with the assigned structures, and the crystalline compounds gave satisfactory elemental analyses, unless otherwise stated.
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7) Under inert atmosphere, crystals of I could be kept without decomposition at room temperature. II could be stored in solid state for several weeks in a refrigerator at *ca.* 0°C. The rate of decomposition of concentrated solution was determined by NMR spectroscopy.
8) The half-life period of diluted solutions were found to be 6 hr for I, and 16 hr for II by UV spectrophotometry.
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