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A NAPHTHO-TRI-*t*-BUTYLTRISDEHYDRO[16]ANNULENE AND RELATED COMPOUNDS

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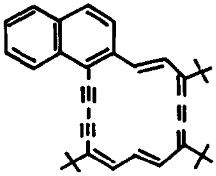
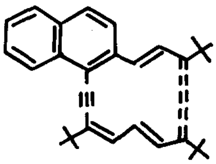
Summary: Synthesis of naphtho-tri-*t*-butyltrisdehydro[16]annulene containing a hexapentaene and an acetylene units has been described. It was found that the [16]annulene is less stable and the paratropicity is much stronger as compared with previously reported isomeric naphtho[16]-annulene containing a diacetylene and a butatriene linkage.

In contrast to rather extensive studies on annelated [4n+2]annulenes[1], few was explored in the field of annelated [4n]annulenes[2]. Our recent observation of strong paratropicity of 4nπ-electron system in tetrakisdehydro[4n]annuleno[4n'+2]annulenes[3] prompted us for the synthesis of two isomeric naphthotrisdehydro[16]annulenes (I and II). As reported in a previous paper[2b], paratropicity of 16π-electron moiety in the naphthotrisdehydro[16]annulene (I) having a butatriene and a diacetylene units is suppressed markedly by annelation with a naphthalene nucleus. Because structure (III_a) containing a diacetylene and a butatriene units has been found to be favorable in trisdehydro[16]annulene (III)[4], it seemed to be of considerable interest to reveal the property of trisdehydro[16]annulene, which is forced to have unfavored bond structure containing a hexapentaene and an acetylene. We wish now to report the synthesis and properties of naphthotrisdehydro[16]annulene (II) having bond structure of III_b, and a reference non-annelated bis(dihydronaphtho)-analogue (IV).

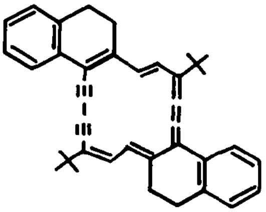


$\tau_o - \tau_i$
4.72 ~ 8.57
(-30 °C)

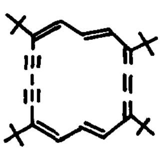
(I)



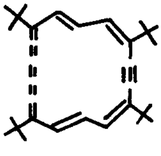
(II)



(IV)



(III_a)

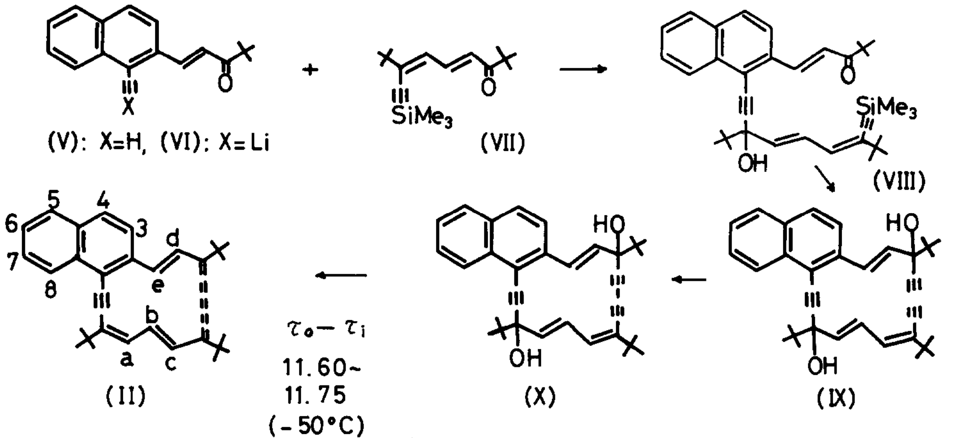


(III_b)

$\tau_o - \tau_i$
12.61, 12.75
(- 30 °C)

The synthesis of the naphthotrisdehydro[16]annulene (II) was carried out by the reaction sequence outlined in Scheme 1. The ethynyl ketone (V)[5] was treated with lithium diethylamide at -80 ∿ -90°C to give the lithio derivative (VI). The reaction of VI with VII[6] gave the keto alcohol (VIII, pale yellow amorphous solid, 54%)[7]. Ethynylation of VIII with lithium acetylide in THF gave ethynyl glycol, which was converted into diethynyl glycol (IX, pale yellow amorphous solid, 72%). The diethynyl glycol (IX) in pyridine-methanol-ether was oxidized by copper(II) acetate under high dilution conditions. After being worked up, chromatography of the product on silica gel resulted in separation of diastereomers of cyclic glycol (X_a, pale yellow fine needles, mp 217.0-221.5°C (dec.), 27%; X_b, pale yellow amorphous solid, 22.5%).

A solution of X in THF was treated with tin(II) chloride-hydrogen chloride under argon atmosphere at a low temperature resulting in a deep green solution. The deep colored solution was found to be unstable and gradual decomposition was observed even at -30°C. Electronic spectrum could be obtained using a dilute solution prepared by a similar procedure. The absorption curve is closely related with those of I and III, indicating the formation of naphthotrisdehydro[16]annulene (II). The solution obtained using THF-d_8 and deuterium chloride was directly subjected to measurement of ^1H NMR spectrum at low temperature. The ^1H NMR and electronic spectral parameters of II are summarized in Table 1.



Scheme 1

The route of synthesis of the non-annelated bis(dihydronaphtho)trisdehydro[16]annulene (IV) was shown in Scheme 2. We also attempted the synthesis of dinaphthotrisdehydro[16]annulene (XVI). Since it has been found that the presence of equivalent Kekulé structures in dinaphthobisdehydro-[4n+2]annulenes[5),8)] and other annelated annulenes[9)] exerts prominent enhancement of delocalization of the (4n+2)π-electron systems, whether the dinaphthotrisdehydro[16]annulene (XVI), for which nearly equivalent Kekulé structures (XVI_a and XVI_b) can be written, shows strong paratropicity or not is an interesting problem.

Dimerization of the ethynyl ketone (XI)[10)] with lithium diethylamide in THF gave the ethynyl alcohol (XII, pale yellow amorphous solid, 72%). Ethynylation of XII with lithium acetylide in THF afforded the ethynyl glycol (XIII, pale yellow amorphous solid, 67%). Oxidative coupling of XIII was carried out by copper(II) acetate in pyridine-methanol-ether under high dilution conditions. The reaction mixture was worked up, and the product was chromatographed on silica gel to result in separation of diastereomers of cyclic glycol (XIV_a, pale yellow prisms, mp 215.3-217.5°C (dec.), 12%; XIV_b, pale yellow prisms, mp 148-157°C (dec.), 51%). The cyclic glycol (XIV) was converted into the bis(dihydronaphtho)trisdehydro[16]annulene (IV) with tin(II) cloride-hydrogen chloride. The annulene (IV) was obtained as unstable deep green crystals and gradually decomposed at 0°C. The ^{1}H NMR parameters of IV are summarized in Table 2.

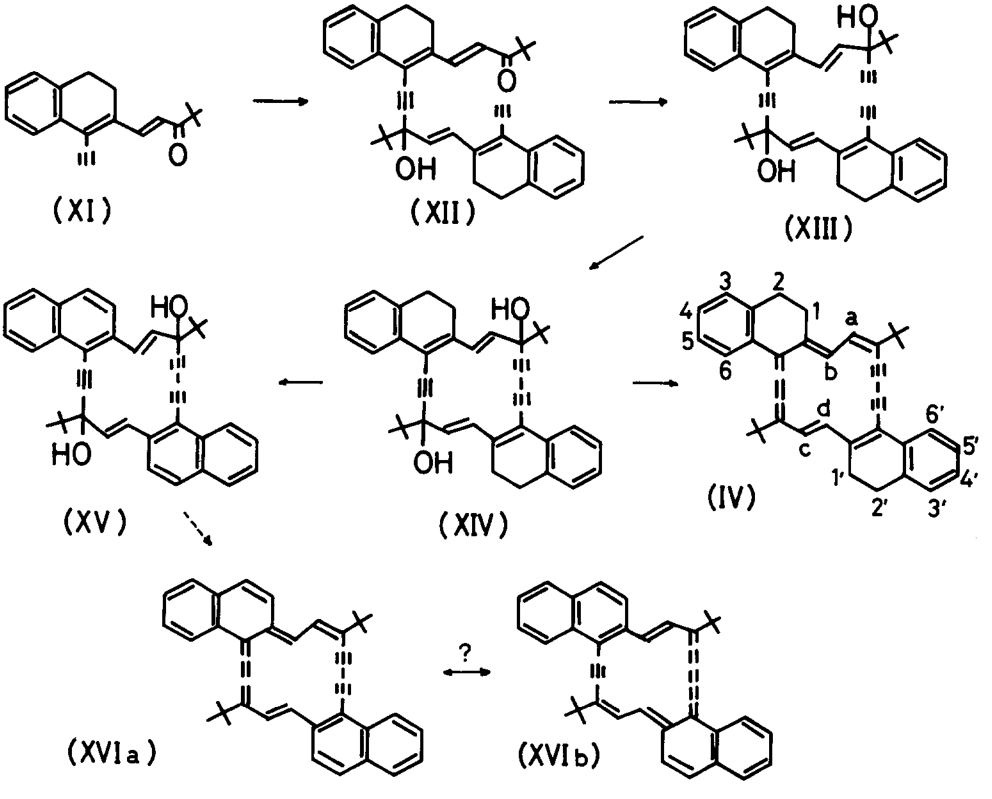
Table 1. Spectral Parameters of II.

^{1}H NMR in THF-d_8. τ-values at -50°C.								
H_e	-6.79	d, J=16.0	H_b	-6.26	dd, J=12.5, 14.0	$H_4 \sim H_8$	1.9 ∿ 3.0	m
H_3	3.50	d, J=9.0	H_d	4.81	d, J=16.0	H_c	5.35	d, J=14.0
H_a	5.48	d, J=12.5	*t*-Bu	9.17 s, 9.24 s, 9.28 s				

Electronic Spectrum in THF. λmax nm (ε)
300(45300), 359(24400), 676(530), 760sh(410), 825sh(240)

Table 2. ^{1}H NMR Parameters of IV ($CDCl_3$, τ-values at -30°C)

H_b	-7.76	d, J=11.5	H_d	-7.47	d, J=16.0	$H_3 \sim H_5$ $H_{3'} \sim H_{5'}$	2.1 ∿ 3.2	m
H_6 $H_{6'}$	3.49	br. d, J=5.0	H_c	4.83	d, J=16.0	H_a	5.25	d, J=11.5
$H_{1,2}$ $H_{1',2'}$	7.52 ∿ 7.86	m	*t*-Bu	9.33 s, 9.38 s				



Scheme 2

A solution of the cyclic glycol (XIVa) and DDQ (12eq) in benzene-THF[11] was kept at 60-70°C for 1 hr to yield the naphthalene derivative (XV, pale yellow crystals, mp 248-253°C (dec.), 22%). Attempted conversion of XV into dinaphthotrisdehydro[16]annulene (XVI) under various conditions using tin(II) chloride-hydrogen chloride or diphosphorous tetraiodide gave unidentifiable product presumably owing to instability of XVI.

Because I, II, III and IV should hold essentially similar geometry, the difference in chemical shifts between outer and inner protons (τ_o - τ_i), which can be regarded as an approximate measure of intensity of ring current, can be reasonably compared. The values of (τ_o - τ_i) of the non-annelated bis(dihydronaphtho)trisdehydro[16]annulene (IV) was found to be almost the same as those of the parent trisdehydro[16]annulene (III) suggesting that the fusion of naphthalene nuclei causes no appreciable change of planarity of the 16π-electron system. However, IV was found to be less stable than III. Fusion of naphthalene nucleus caused an appreciable suppression of paratropicity of both I and II being consistent with the fact that annelation of an aromatic or an annulene ring with an annulene always causes a decrease of tropicity of the parent annulene system[1),4b)]. The magnitude of suppression was found to be much smaller in II. The ^{1}H NMR spectrum of I suggests that the *trans* double bond adjacent to naphthalene ring is twisted out of the molecular plane[2b)]. On the contrary, almost the same planarity of II and III was revealed by their ^{1}H NMR spectra. Consequently, the marked suppression of paratropicity of I could be ascribed to the combined effect of annelation and low planarity of the molecule. The effects of annelation and unfavored bond structure containing a hexapentaene unit can be regarded as the cause of suppression of paratropicity in II. We have observed that the paratropicity of antiaromatic moiety in [4n]annuleno[4n+2]annulenes suffers much less effect by annelation with [4n+2]annulene ring in contrast to a large suppression of diatropicity in the [4n+2]-ring. The rather large paratropicity observed in II is consistent with the results obtained on [4n]annuleno[4n+2]annulenes.

References and Notes

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11) V could be also converted into XV (overall yield 28%) by the similar reaction sequence shown in Scheme 2.

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