

SYNTHESIS AND PROPERTIES OF NAPHTHO[2,1-c]-9,12,18-TRI-t-BUTYL-
1,10-DIDEHYDRO[18]ANNULENE

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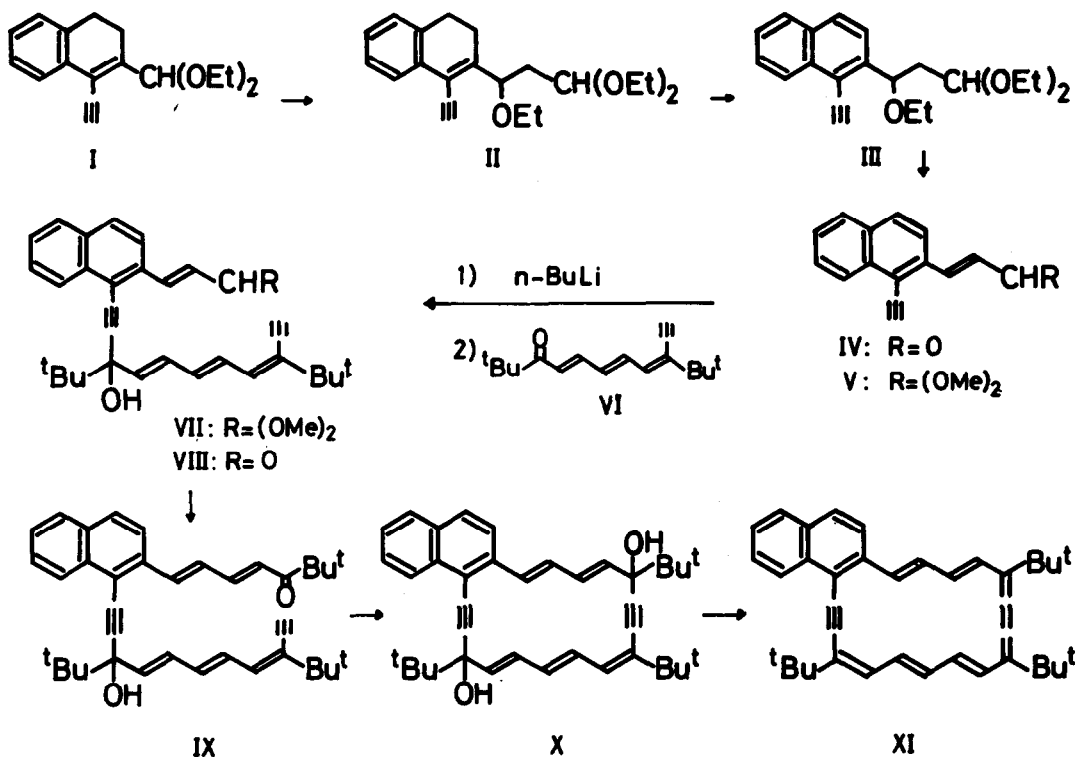
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In previous papers, we reported the synthesis and diatropicity of 1,8-didehydro[14]annulenes annelated with naphthalene (1,2) or benzene (3). It seemed of considerable interest to prepare 1,10-didehydro[18]annulene fused with benzenoid system to compare the ring current in the 18π -electron system with that in 14π -system.

Diethyl acetal (I) prepared from 1-ethynyl-3,4-dihydro-2-naphthaldehyde (2) was converted into ethoxy acetal (II, pale yellow liquid, 86%) by the Isler reaction (4). Dehydrogenation of II with DDQ in benzene yielded III (pale yellow liquid, 70%). Aldehyde (IV, pale yellow rods, mp 136.7-138.3°C (dec.), 65%) obtained on treatment of III with aqueous hydrochloric acid was converted into acetal (V, colorless crystals, mp 59.9-61.1°C (dec.), 98%) by the reaction with methyl orthoformate in the usual way. The reaction of triene ketone (VI) (5) with the lithio derivative obtained from V and *n*-butyllithium gave hydroxy acetal (VII) as an amorphous solid. Crude VII in ethanol was mixed with aqueous solution of tartaric acid to give hydroxyaldehyde (VIII, pale yellow crystals, mp 171.1-171.8°C (dec.), 46% based on V). The reaction of VIII with pinacolone in ethanol-tetrahydrofuran in the presence of sodium methoxide led to crude IX (amorphous solid, 80%). Crude IX in tetrahydrofuran was added to a suspension of potassium hydroxide in liquid ammonia. The product in dichloromethane was chromatographed on alumina and eluted with tetrahydrofuran-benzene (5:95) to give

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cyclic glycol (X). Slightly crude X, thus obtained, was mixed at -59°C with stannous chloride dihydrate and ether saturated with hydrogen chloride to give naphtho[2,1-c]-9,12,18-tri-t-butyl-1,10-didehydro[18]annulene (XI, dark reddish violet needles, mp $234.0\text{--}234.8^\circ\text{C}$ (dec.), 53% based on IX, m/e 498 (M^+), Anal. Found: C, 91.30; H, 8.61%. Calcd. for $\text{C}_{38}\text{H}_{42}$: C, 91.51; H, 8.49%). XI gave 1:1 CT-complex with 2,4,7-trinitrofluorenone [black crystals, mp $263.4\text{--}274.5^\circ\text{C}$ (dec.)]. The electronic spectrum of XI is shown in Fig. 1 together with that of non-annelated parent tetra-t-butyl-didehydro[18]annulene (5). XI shows clearly features characteristic of $[4n+2]$ annulenes, indicating the 18π -electron system in XI still retains "aromatic" nature in spite of the fusion with naphthalene. As illustrated in Fig. 2, XI gave rather complex ^1H -nmr spectrum. However, assignments of protons could be attained using double resonance technique (Table 1). The appearance of the outer proton signals at low field and the inner proton signals at high field clearly demonstrates the diatropicity of the

Table 1. ^1H -nmr parameters of XI
(τ -Values; J in Hz in parentheses)

	THF- d_8 , 36°C	THF- d_8 , -40°C	CDCl_3 , 36°C	CDCl_3 , -50°C
H_O^2	0.46 dd (15.0, 12.0)	0.30 dd (15.0, 12.0)	0.59 dd (15.0, 12.0)	0.49 dd (15.0, 12.0)
H_B	0.54 d (8.0)	0.52 d (8.0)	0.52 d (8.0)	0.50 d (8.0)
H_S	0.86 d (9.0)	0.74 d (9.0)	0.92 d (9.0)	0.89 d (9.0)
H_O^4	1.18 dd (15.0, 12.0)	1.09 dd (15.0, 12.0)	1.22 dd (15.0, 12.0)	1.13 dd (15.0, 12.0)
H_O^1	1.40 d (15.0)	1.28 d (15.0)	1.47 d (15.0)	1.40 d (15.0)
H_O^3	1.50 d (12.0)	1.42 d (12.0)	1.53 d (12.0)	1.47 d (12.0)
H_O^5	1.58 d (15.0)	1.46 d (15.0)	1.64 d (15.0)	1.55 d (15.0)
H_4	1.72 d (9.0)	1.62 d (9.0)	1.76 d (9.0)	1.72 d (9.0)
$\text{H}_5\text{-H}_7$	1.82-2.44 m	1.74-2.36 m	1.83-2.44 m	1.81-2.34 m
tBu_2	8.12 s	8.11 s	8.11 s	8.08 s
tBu_1	8.26 s	8.26 s	8.26 s	8.24 s
tBu_3	8.30 s	8.29 s	8.28 s	8.26 s
H_1^3	9.26 d (15.0)	9.43 d (15.0)	9.34 d (15.0)	9.56 d (15.0)
H_1^3	9.46 dd (15.0, 12.0)	9.61 dd (15.0, 12.0)	9.42 dd (15.0, 12.0)	9.72 dd (15.0, 12.0)
H_1^1	9.50 dd (15.0, 12.0)	9.64 dd (15.0, 12.0)	9.59 dd (15.0, 12.0)	9.77 dd (15.0, 12.0)
H_1^4	9.56 dd (15.0, 12.0)	9.73 dd (15.0, 12.0)	9.65 dd (15.0, 12.0)	9.84 dd (15.0, 12.0)

annulene ring in XI. But the magnitude of suppression of ring current in annulene ring caused by annelation with a naphthalene was found to be larger in XI than that in naphtho-dihydronaphtho-di-*t*-butyl-didehydro[14]annulene, a corresponding 14π -electron analogue of XI (2). This fact seems to correlate with the theoretically predicted decrease of delocalization energy per double bond with increasing ring size (6-8).

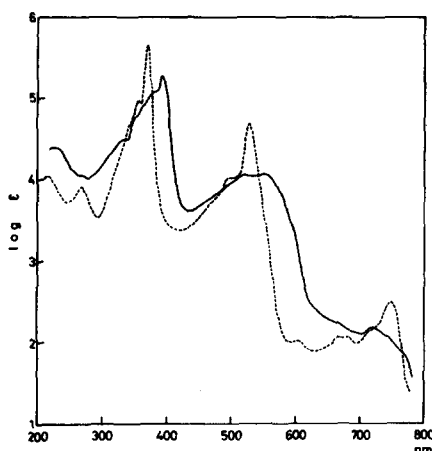


Fig. 1. The UV spectra of XI (—) and tetra-*t*-butyl-didehydro[18]annulene (-----) in THF.

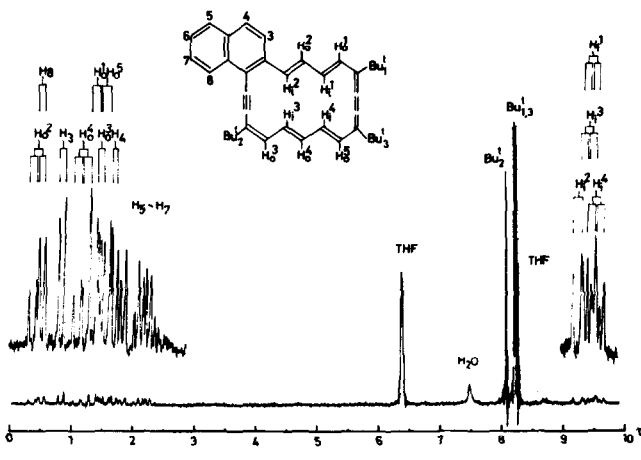


Fig. 2. The 100 MHz ^1H -NMR spectrum of XI in THF-d_8 at 36°C .

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