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SYNTHESIS AND PROPERTIES OF DIATROPIC NAPHTHO[2,1-f]-DIHYDRONAPHTHO[3',4'-m]-3,10-DI-t-BUTYL-1,8-DIDEHYDRO[14]ANNULENE AND A BIS-DIHYDRONAPHTHO ANALOGUE

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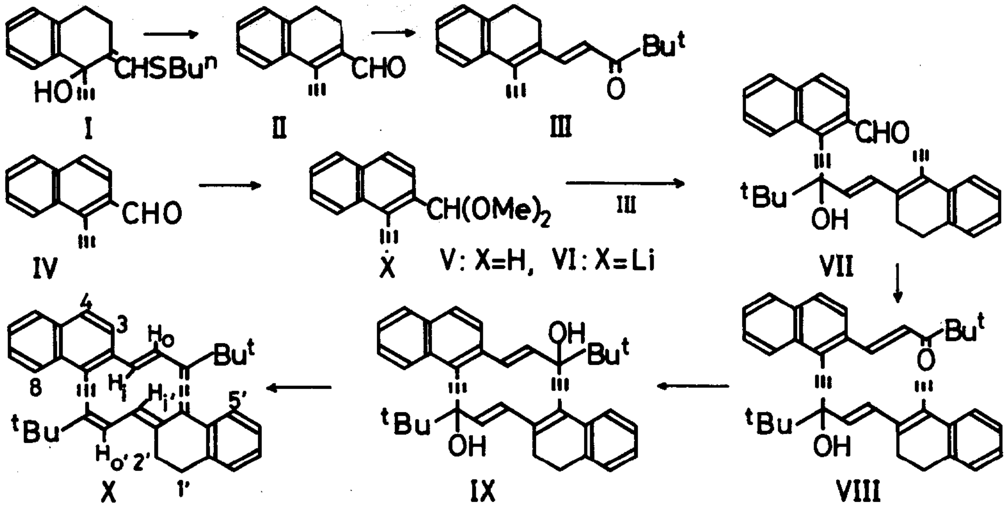
As reported in a previous paper (1), the 14π-electron system in dinaphtho-[2,1-f:2',1'-m]-3,10-di-t-butyl-1,8-didehydro[14]annulene (XIV) was found to be strongly diatropic. In this paper we wish to report the synthesis of naphtho-dihydronaphtho-di-t-butyldidehydro[14]annulene (X) and a non-annelated reference compound, bis(dihydronaphtho)-di-t-butyldidehydro[14]annulene (XII).

Ethynyl alcohol (I) derived from α-tetralone (1) was treated with an aqueous acetonitrile containing methyl iodide (2) to give aldehyde (II, pale yellow crystals, 77%, mp 71.6-72.2°C). The aldol condensation of II with pinacolone afforded ketone (III, yellow crystals, 68%, mp 92.0-93.0°C (dec.)).



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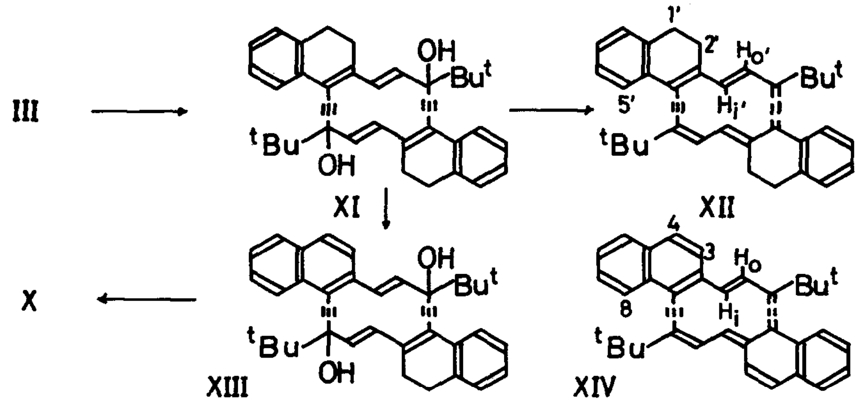
Dimethyl acetal (V, pale yellow crystals, 93.2%, mp 32.3-33.9°C) obtained from 1-ethynyl-2-naphthaldehyde (IV) (1) was treated with *n*-butyllithium to give lithio derivative (VI). A dioxane solution of the reaction product of the lithio derivative (VI) with III was treated with an aqueous acetic acid to yield ethynylaldehyde (VII, yellow amorphous solid, 39.5% based on V, M$^+$ 444). The aldol condensation of VII with pinacolone afforded ethynyl ketone (VIII, pale yellow crystals, 67.9%, mp 142.4-144.2°C (dec.)) which was treated with potassium hydroxide in liquid ammonia to give 14-membered cyclic glycol (IX, colorless crystals) (3). The cyclic glycol (IX) dissolved in tetrahydrofuran without further purification was treated with stannous chloride dihydrate and ether saturated with hydrogen chloride. A solution of the product in dichloromethane-*n*-hexane (1:9) was passed through a column of alumina. Elution with the same mixed solvent afforded naphtho-dihydronaphtho-di-*t*-butyldidehydro[14]annulene (X, dark reddish violet crystals, 37.8% based on VIII, mp 249°C (dec.), M$^+$ 492).

The ketone (III) dissolved in tetrahydrofuran was added to a suspension of potassium hydroxide in liquid ammonia to give cyclic glycol (XI, colorless crystals, 79%, mp 240.8-242.6°C (dec.), M$^+$ 528). Stannous chloride dihydrate was added at -60°C to a solution of XI in ether containing hydrogen chloride. Chromatographic purification of the product on alumina afforded bis(dihydronaphtho)-di-*t*-butyldidehydro[14]annulene (XII, dark reddish violet needles, 83%, mp 283.9-285.2°C (dec.), M$^+$ 494). The annulene (XII) gave 1:1 CT-complex with trinitrofluorenone, dark violet needles, mp 280.0-280.5°C.

A mixture of the cyclic glycol (XI, 0.199 mmol) and DDQ (0.264 mmol) in



benzene-tetrahydrofuran (14:1, 75 ml) was stirred for 11 hrs. at 55°C, and the product was chromatographed on alumina (Merck: activity II-III). Elution with tetrahydrofuran-benzene (1:9) yielded cyclic glycol containing a naphthalene nucleus (XIII, colorless crystals). The crude cyclic glycol (XIII) in tetrahydrofuran was treated at -15°C with stannous chloride dihydrate and ether saturated with hydrogen chloride. Chromatography of the product afforded mononaphtho-annulene (X, 17.1% based on XI) which was found to be identical in every respects with the naphtho-annulene derived from 1-ethynyl-2-naphthaldehyde (IV).

As illustrated in Fig. 1, electronic spectrum of the mononaphtho-monodihydronaphtho-annulene (X) resembles closely with that of non-annelated analogue (XII). The n.m.r. spectrum shown in Fig. 2 clearly indicates that the 14π-electron system in the mononaphtho-annulene (X) sustains fairly large diamagnetic ring current as evidenced by the low field signals of outer protons (τ_o 0.47 and $\tau_{o'}$ 0.95) and the high field signals of inner protons (τ_i 11.14 and $\tau_{i'}$ 11.44). The n.m.r. spectral parameters of X, XII and the dinaphtho-annulene (XIV) (1) obtained under nearly the same conditions are summarized in Table 1. The values of chemical shifts between inner and outer protons ($\tau_i - \tau_o$ or $\tau_{i'} - \tau_{o'}$) can be regarded as a measure of magnitude of diamagnetic ring current. The di-

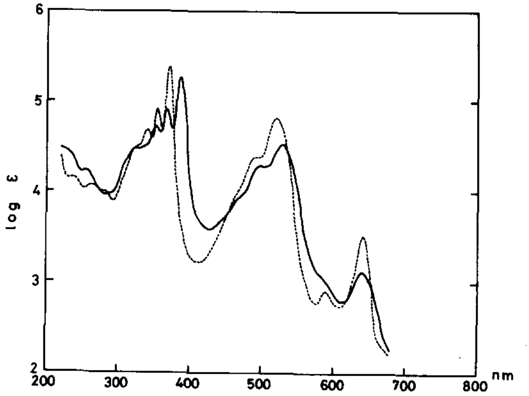


Fig. 1. Electronic spectra in THF.
X (———), XII (-----)

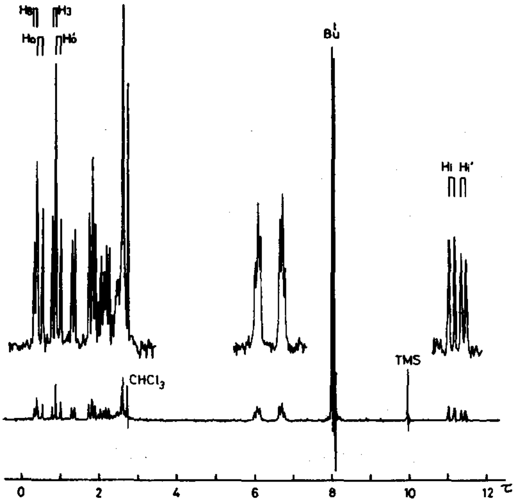


Fig. 2. 100 MHz n.m.r. spectrum of X in $CDCl_3$ at 35°C.

Table 1. 100 MHz n.m.r. spectra

Compound	XIV	X	XII
	THF-d_8, -54°C	THF-d_8, -52°C	THF-d_8, -55°C
H_o	-0.22 d, J=15.0	0.20 d, J=15.0	
$H_{o'}$		0.83 d, J=13.0	0.48 d, J=14.0
H_8	0.29 d, J=8.0	0.38 d, J=8.0	
H_3	0.46 d, J=10.0	0.54 d, J=9.0	
H_4	1.73 d, J=10.0	1.63 d, J=9.0	
$H_{5'}$		1.36 d, J=7.5	1.19 d, J=7.5
$H_{2'}$		6.08 m	5.88 m
$H_{1'}$		6.68 m	6.70 m
<u>t</u>-Bu	7.89 s	8.05 s, 8.09 s	8.01 s
H_i	13.45 d, J=15.0	11.22 d, J=15.0	
$H_{i'}$		11.53 d, J=13.0	13.47 d, J=14.0
$\tau_i - \tau_o$	13.67	11.02	
$\tau_{i'} - \tau_{o'}$		10.70	12.99

The assignments are based on double-resonance experiments.

naphtho-annulene (XIV) showed a large $\tau_i - \tau_o$-value comparable to that of non-annelated analogue (XII). However, the values of $\tau_o - \tau_i$ or $\tau_{i'} - \tau_{o'}$ of mononaphtho-annulene (X) were found to be much less than those of XIV and XII. The marked difference of properties between X and XIV is remarkable, i.e., as reported in a previous paper (1), the strongly diatropic dinaphtho-annulene (XIV) has been found to be highly air sensitive, whereas the less diatropic mononaphtho-annulene (X), was found to be stable just as the non-annelated analogue (XII). The fact that the mononaphtho-annulene (X) is less diatropic than the dinaphtho-annulene (XIV) seems to suggest the important role of equivalent Kekulé structures in π-electron delocalization of annulene ring annelated with benzenoid system.

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