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SYNTHESIS OF TWO ANNELATED 1,7,13-TRIDEHYDRO[18]ANNULENES*

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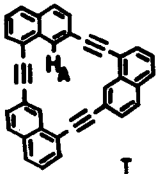
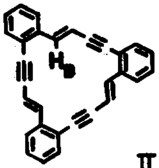
Since the chemistry of annulenes was extensively studied by Sondheimer and his co-workers1), some planar and non-planar annelated annulenes have been recently synthesized for the examination of peripheral conjugation or aromatic character on the central ring systems containing (4n + 2) out-of-plane π-electrons2).

We wish to report the synthesis and properties of two planar annelated derivatives of aromatic 1,7,13-tridehydro[18]annulene3), i.e., trinaphtho[1,9,8,7-abc:1',9',8',7'-ghi:1'',9'',8'',7''-mno]- and tribenzo[a,g,m]-5,11,17-tridehydro[18]annulene (I and II), for which Kekulé type structure of the inner eighteen membered ring systems can be written and diamagnetic ring current in the ring can be confirmed by the chemical shift of the inner protons (H_A and H_B) on NMR spectra.



I



II

1-Acetyl-7-iodonaphthalene (III) which was prepared according to Harnik4) was treated with phosphorus pentachloride in phosphorus oxychloride, followed by dehydrochlorination of the resulting chloride mixture with alcoholic potassium hydroxide to give a 49% yield of 1-ethynyl-7-iodonaphthalene [IV, pale yellow oil. Hg salt: colorless fine needles, m.p. 263.5~264.7°(decomp.), Found: C, 38.20; H, 1.63. Calcd. for $C_{24}H_{12}I_2Hg$: C, 38.19; H, 1.60%]. Well dried cuprous salt of IV was subjected to the Castro reaction in pyridine under nitrogen. Chromatography on

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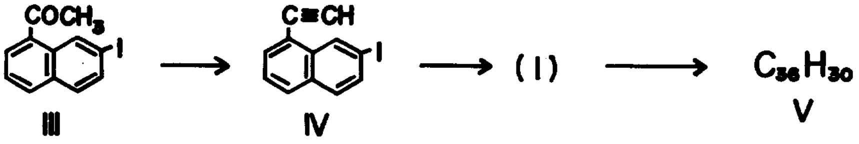
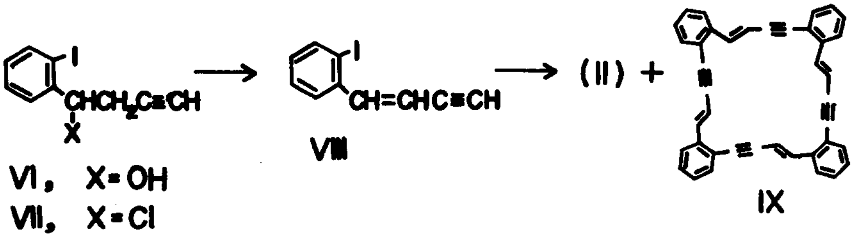
* **This paper is dedicated to Emeritus Professor Munio Kotake in commemoration of his 75th birthday, Oct. 24, 1970.**

alumina and recrystallization from benzene of the reaction product afforded 8% yield of a cyclic trimer [I, pale yellow needles, decomp. over 360°. Anal. Found: C, 95.72; H, 4.08. Calcd. for $C_{36}H_{18}$: C, 95.97; H, 4.03%]. The hydrogenated product [V, m.p. 286~286.5°. Anal. Found: C, 92.92; H, 6.54, mol. wt. 477 (vapor pressure osmometry). Calcd. for $C_{36}H_{30}$: C, 93.46; H, 6.54%, mol. wt. 462.6], which is easily soluble in usual solvents for molecular weight determination in contrast with I, confirmed trimolecular cyclisation of IV in the Castro reaction.





An acetylenic alcohol (VI) was prepared by Reformatsky-type reaction of o-iodobenzaldehyde with propargyl bromide using aluminum in a good yield (79%), although the normal Reformatsky as well as the Grignard reactions afforded lower yields of VI. The chloride VII, obtained by treatment of VI with phosphorus oxychloride, was dehydrochlorinated with methanolic potassium hydroxide. Chromatography on alumina of the reaction product gave pale yellow oil of 4-o-iodophenyl-3-buten-1-yne [VIII, NMR in $CDCl_3$: 2.1~3.4 (m, 4H, arom.), 2.84 (d, 1H, olef., J = 15.6 Hz), 4.10 (dd, 1H, olef., J = 15.6 Hz), 6.94 τ (d, 1H, ethyn.). Hg salt: colorless needles, m.p. 227~232°(decomp.). Anal. Found: C, 34.06; H, 1.75. Calcd. for $C_{20}H\ {}_{2}I_{2}Hg$: C, 33.99; H, 1.71%] in overall yield of 30% based on VI. The Castro reaction of well dried cuprous salt of VIII afforded fairly stable cyclic trimer II [14.3% yield, bright yellow needles, decomp. over 275°. Anal. Found: C, 95.37; H, 4.59, mol. wt. 372 (vapor pressure osmometry). Calcd. for $C_{30}H_{18}$: C, 95.21; H, 4.79%, mol. wt. 378.5] and cyclic tetramer IX [2.4% yield, colorless prisms, decomp. over 260°. Anal. Found: C, 95.00; H, 4.93, mol. wt. 509 (vapor pressure osmometry). Calcd. for $C_{40}H_{24}$: C, 95.21; H, 4.79%, mol. wt. 504.6. UV (THF): λmax (ε), 252 (36,200), 292.5 (71,700), 312.5 mμ (70,900)].

The electronic spectra of I and II as well as those of 1,4-diphenylbutenyne (X) and 1,7,13-tridehydro[18]annulene (XI) as reference substances are shown in Fig. 1. The spectra of I and

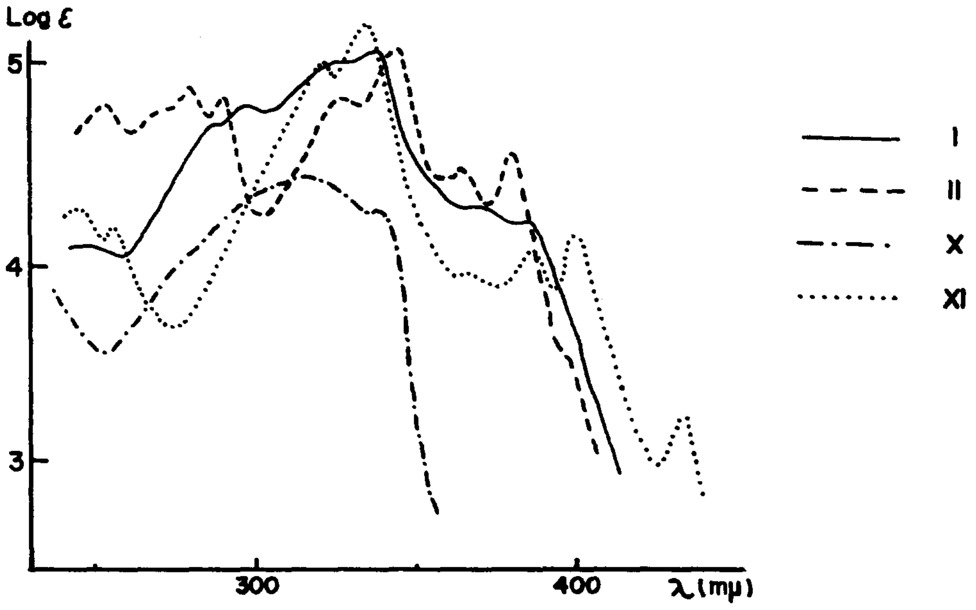


Fig. 1. The electronic spectra of I, II, X (in THF) and XI (in iso-octane).

II are similar to that of XI except the lack of the maximum at near 430 mμ. While the spectrum of a cyclic trimer[5] of phenanthrene shows the maximum at nearly same wavelength as those of biphenanthryl and terphenanthryl, the maxima at longer wavelength of I and II exhibit distinct red shift as compared with IX and X. The comparison of these spectra, therefore, indicates the presence of considerable delocalization of π-electrons over the inner eighteen membered ring I and II.

Table 1 records the chemical shifts of the inner protons in I, II, IX and XI as well as the shifts of olefinic protons in X. The shift of the inner protons toward higher field due to induced diamagnetic ring current is not observed on the spectra of I and II in contrast with

Table 1. Chemical shifts (δ) and coupling constants (J) of inner proton of I as well as those of olefinic protons of II, IX, X and XI in $CDCl_3$

I	II	IX	X	XI[3]
δ 8.49*	6.64 7.13	6.49 7.44	6.31 6.96	7.56 1.74 ppm
J —	16.2	16.2	16.2	15.6 Hz

* in $AsCl_3$ solution.

that of XI. These inner protons are found to resonate at rather lower field owing to shielding effect of other unsaturated bonds and aromatic nuclei. The anisotropic effect of such unsaturated groups, estimated using McConnell equation and Johnson-Bovey table[6], was found to be in good agreement with observed values [H_A to α-proton of naphthalene (δ 7.81)[7]: Calcd. Δδ, -0.91; Observed one, -0.76 ppm. H_B to the corresponding olefinic proton of X: Calcd. Δδ, -0.50; Observed one, -0.17 ppm]. Table 1 also shows equal coupling constant of olefinic protons in II, IX and X. Consequently, it is concluded that these spectral data on NMR suggest to involve significant bond alternation in the inner eighteen membered rings of I and II.

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