

SYNTHESIS OF 1,14-DI-*t*-BUTYL-5,10-DIPHENYL-6,8,15,17-TETRADEHYDRO-[18]ANNULENE.
CHEMICAL EVIDENCE FOR THE IDENTITY OF ACETYLENIC AND CUMULENIC LINKAGES
IN THE AROMATIC SYSTEM

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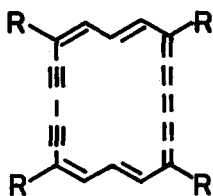
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The diacetylene and hexapentaene units in the aromatic tetrasubstituted-tetradecahydro-[18]annulenes (I_a , I_b and I_c) have been proved to be identical in the 18π electron system on the basis of ^1H nmr spectroscopy (1,2,3), *i.e.*, the acetylenic and cumulenenic carbon atoms equally offer their p -electrons in the orbitals perpendicular to the molecular plane for the formation of continuous π -molecular orbital.

We have carried out the synthesis of 1,14-di-*t*-butyl-5,10-diphenyl-6,8,15,17-tetradecahydro-[18]annulene (II and III) according to two different routes to get chemical evidence for the identity of diacetylenic and cumulenenic linkages in the annulene system. Dienyne ketone (V, yellow rods, mp $82.1-83.4^\circ$, 62%) was obtained by the condensation of acetophenone with *t*-butyl-enyne aldehyde (IV) (3)

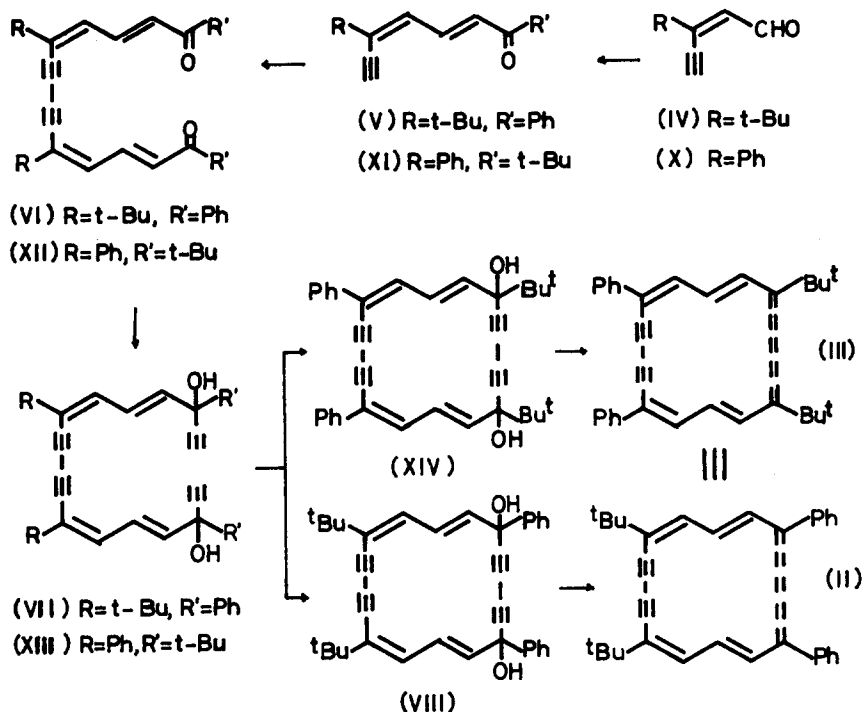


I_a : $R = \text{Me}$

I_b : $R = \text{Ph}$

I_c : $R = t\text{-Bu}$

under an alkaline condition. Similarly, condensation of pinacolone with phenyl-enyne aldehyde (X) (2) afforded isomeric dienyne ketone (XI, pale yellow leaflets, mp $75.5-76.2^\circ$, 42%). The Eglinton's oxidative coupling (4) of the dienyne ketone (V or XI) gave diketone (VI, yellow leaflets, mp $144-146^\circ$, 98% or XII, yellow needles, mp $154-156^\circ$, 98%). The product obtained by the reaction of lithium acetylide-ethylene diamine complex (5) with the diketone (VI or XII) in tetrahydrofuran was chromatographed on silica gel to give diethynyl glycol (VII,



yellow viscous liquid, ca. 90% or XIII, pale yellow fine crystals, mp 145.5–148.5 °, 97%). Oxidative coupling of the diethynyl glycol (VII or XIII) by means of cupric acetate in pyridine under a high dilution condition (entraining solvent: ether) resulted in 18-membered cyclic glycol (VIII, colorless fine leaflets, mp ca. 160° (dec.), 85% or XIV, pale yellow needles, mp 156–158° (dec.), 71%[†]).

A solution of stannous chloride dihydrate in concentrated hydrochloric acid was added to a solution of VIII in ether under nitrogen atmosphere at -10°~ -12°. The resulting deep blue violet solution was worked up by the usual way. The product dissolved in n-hexane-ether (10:1) was chromatographed on alumina to yield reddish violet crystals. Recrystallization of the crystals from the same solvent afforded pure di-t-butyl-diphenyltetradehydro-[18]annulene (II, reddish violet leaflets, mp 189–191° (turned to colorless without fusion), 80%. Found: C, 92.77; H, 7.05%, M⁺ 490. Calc. for C₃₈H₃₄: C, 93.02; H, 6.98%, Mol. wt., 490.7).

[†] XIV recrystallized from carbon tetrachloride or carbon tetrachloride-n-hexane contained tenaciously a small amount of the chloride and gave unsatisfactory elemental analysis.

Similar treatment of a solution of cyclic glycol (XIV) in ether with stannous chloride-hydrochloric acid gave reddish violet crystals which were recrystallized from n-hexane-ether (3:1) to yield pure III (reddish violet leaflets, mp 189-191° (turned to colorless without fusion), 67%, M^+ 490. Found: C, 92.60; H, 7.04%. Calc. for $C_{38}H_{34}$: C, 93.02; H, 6.98%).

As illustrated in Fig. 1, the 1H nmr spectrum of II exhibited doublets at

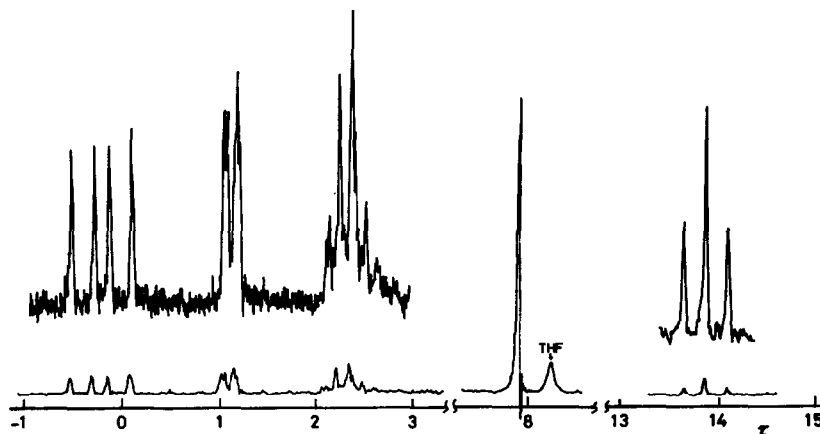


Fig. 1. 1H Nmr Spectrum of Di-*t*-butyl-diphenyltetra-dehydro-[18]annulene (II), measured at 60MHz in $THF-d_6$.

low-field (τ -0.40 and -0.01) and a triplet at fairly high-field (τ 13.90), due to the outer and inner protons, respectively. The nmr spectral pattern clearly demonstrates the existence of diamagnetic induced ring-current, indicating the aromatic nature of II. Down-field shift of signals of protons of the *t*-butyl groups (τ 7.93) and those of *o*-position of the phenyl groups (τ 1.13) also reflects the deshielding effect of induced ring-current in the annulene system.

The di-*t*-butyl-diphenyltetra-dehydro-[18]annulenes (II and III), thus prepared, were found to be identical in every respect. They gave superimposable IR spectra, and as summarized in Tables 1 and 2, their electronic and 1H nmr spectra were found to be identical within the experimental error. These facts are regarded as a confirmative chemical evidence for the identity of the diacetylene and hexapentaene units incorporated in the aromatic dehydroannulene system.

The compounds described in this paper gave satisfactory elemental analyses.

Table 1. Electronic Spectra of II and III. λ_{\max} in $\text{\AA} \times 10^{-2}$ in THF

II	231* (288), 245* (160), 256.5 (179), 270* (153), 277.5 (176), 299 (142), 325* (152), 347* (303), 368* (373), 386* (616), 402 (2,200), 544* (164), 587 (875), 670* (4.80), 740 (21.7)
III	231* (285), 245* (162), 256.5 (177), 270* (152), 277.7 (175), 299 (142), 325* (151), 347* (303), 368* (374), 386* (614), 402 (2,190), 544* (164), 587 (873), 670* (4.72), 740 (21.6)

A Hitachi EPS-3T spectrophotometer was used. * indicates shoulder.

Table 2. ^1H Nmr Spectra of II and III in THF- d_6 (60 MHz)

Protons	II		III	
Outer protons adjacent to phenyl	τ -0.40 d (J=14 Hz)	1H	-0.40 d (J=14 Hz)	1H
Outer protons adjacent to <i>t</i> -butyl	-0.01 d (J=14 Hz)	1H	0.01 d (J=14 Hz)	1H
<i>o</i> -Protons of phenyl	1.13 m	2H	1.15 m	2H
<i>m,p</i> -Protons of phenyl	2.37 m	3H	2.39 m	3H
Protons of <i>t</i> -butyl	7.93 s	9H	7.93 s	9H
Inner protons	13.90 t (J=14 Hz)	1H	13.90 t (J=14 Hz)	1H

A Varian A-60 spectrometer was used employing TMS as an internal standard.

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