Tetrahedron Letters No. 11, pp 895 - 898, 1975. Pergamon Press. Printed in Great Britain.

SYNTHESIS AND PROPERTIES OF BENZO[c]-7,10,14-TRI-t-BUTYL-1,8-DIDEHYDRO[14]ANNULENE

Akio Yasuhara, Takeshi Satake, Masahiko Iyoda and Masazumi Nakagawa*
Department of Chemistry, Faculty of Science, Osaka University
Toyonaka, Osaka 560, Japan

(Received in Japan 21 December 1974; received in UK for publication 5 February 1975)

Observation of strong diamagnetic ring current in the 14π-electron system in dinaphtho-di-t-butyl- and naphtho-dihydronaphtho-di-t-butyl-1,8-didehydro[14]-annulenes (VIII and IX) (1,2) prompted us to synthesize a benzo-annelated annulene to get further insight into the role of fused benzenoid system on π-electron delocalization in annulene system. The present paper deals with the synthesis and properties of benzo-tri-t-butyldidehydro[14]annulene (VII).

2-Ethynylbenzaldehyde diethyl acetal (bp 87-88°C/2 mmHg, 81%) obtained from 2-ethynylbenzaldehyde (3) in the usual way was converted into lithio derivative (I) on treatment with n-butyllithium in ether. Crude hydroxy-acetal (III, yellow liquid) obtained by the reaction of I with diene ketone (II) (4) was hydrolyzed with an aqueous acetic acid, and the product was chromatographed on silica gel to afford hydroxy-aldehyde (IV, colorless plates, mp 76.5-77.0°C, 43% based on I). The aldol condensation of the hydroxy-aldehyde (IV) with pinacolone yielded ethynyl ketone (V, colorless crystals, mp 55.7-57.8°C, 83.7%). A solution of the ethynyl ketone (V) in tetrahydrofuran was added to a suspension of powdered potassium hydroxide in liquid ammonia. Chromatography of the product on silica gel followed by elution with benzene containing 3%, 5% and 10% ether afforded a small amount of a diastereomer of cyclic glycol (VI_a, colorless crystals, M^+ 430), recovered ethynyl ketone (V) and another diastereomer of cyclic glycol

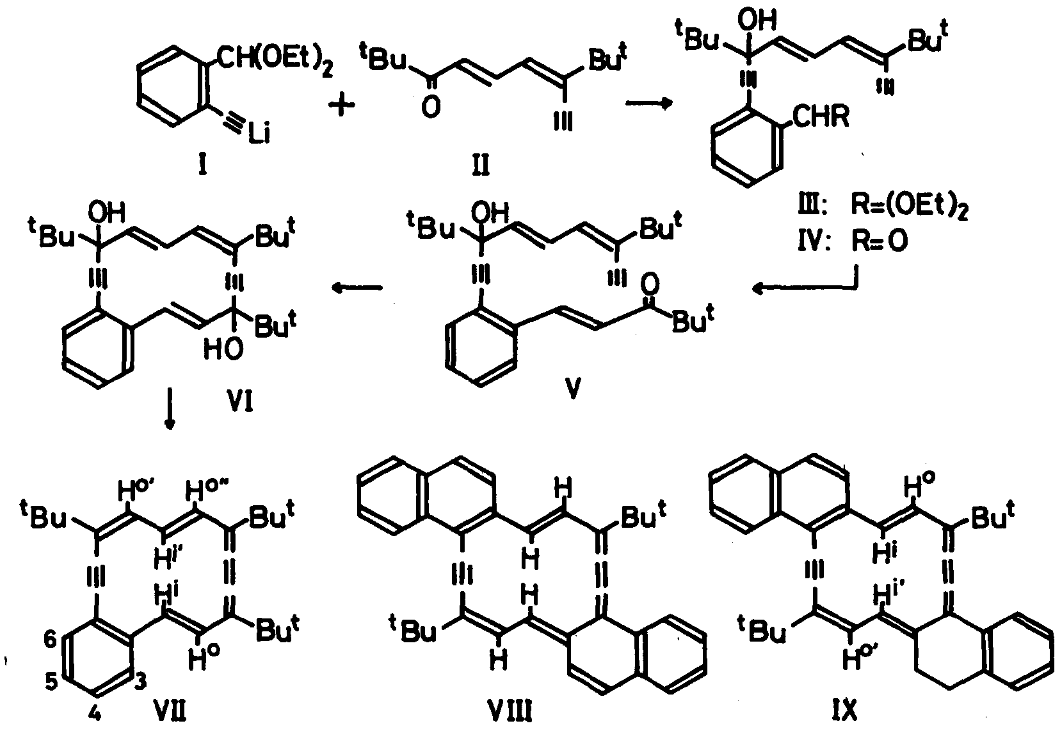
---

* Author to whom correspondence should be addressed.

(VI_b, colorless crystals, mp 84.0-84.5°C, M^+ 430), respectively. Owing to the minor amount, VI_a could not be purified. But the IR and mass spectra were consistent with the assigned structure.

Crude cyclic glycol (VI) dissolved in ether was mixed at -60°C with ether saturated with hydrogen chloride and powdered stannous chloride dihydrate, and the mixture was stirred for 30 min. at the same temperature. After the reaction mixture had been worked up in the usual manner, the product was chromatographed on alumina to give benzo-tri-t-butyldidehydro[14]annulene (VII, scarlet crystals, 44% based on V, mp ca. 160°C (dec.), M^+ 396, Found: C, 90.69; H, 9.18%. Calcd. for $C_{30}H_{36}$: C, 90.85; H, 9.15%). The annulene (VII) gave 1:1 CT-complex with trinitrofluorenone, dark reddish violet crystals, mp ca. 255°C (dec.).

As illustrated in Fig. 1, the benzoannulene (VII) exhibits rather similar electronic spectrum to that of 3,7,10,14-tetra-t-butyl-1,8-didehydro[14]annulene (5). The n.m.r. spectrum of the benzoannulene (VII) is shown in Fig. 2 and the parameters are summarized in Table 1. The n.m.r. spectra clearly show that the



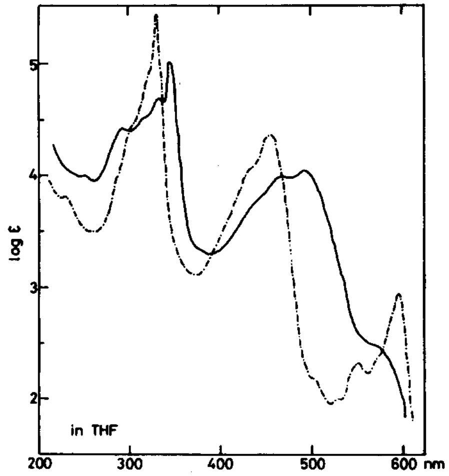


Fig. 1. Electronic spectra of VII (———) and tetra-t-butyl-didehydro[14]annulene (-·-·-·-).

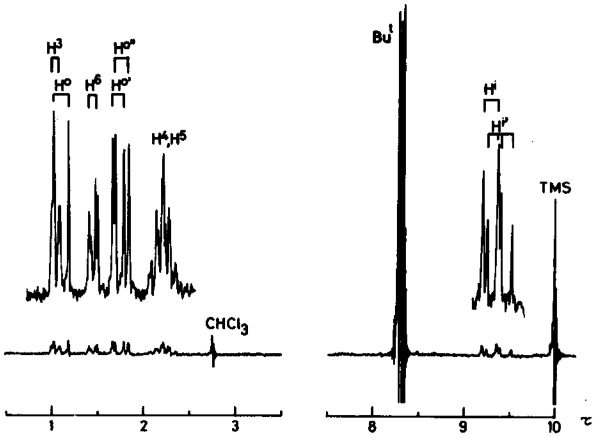


Fig. 2. 100 MHz n.m.r. spectrum of VII in $CDCl_3$ at 35°C.

Table 1. 100 MHz n.m.r. spectra of benzoannulene (VII). τ-values

	THF-d_8 35°C	THF-d_8 -50°C	$CDCl_3$ 35°C
H^3	0.98 m	0.80 m	1.06 m
H^o	1.03 d	0.88 d	1.12 d
	J=15.5	J=16.0	J=16.0
H^6	1.48 m	1.41 m	1.47 m
$H^{o'}$	1.67 d	1.59 d	1.74 d
	J=12.0	J=12.0	J=12.0
$H^{o''}$	1.70 d	1.56 d	1.78 d
	J=14.5	J=14.5	J=14.5
H^4, H^5	2.26 m	2.17 m	2.21 m
<u>t</u>-Bu	8.30 s	8.28 s	8.30 s
	8.32 s	8.31 s	8.34 s
	8.36 s	8.35 s	8.36 s
H^i	9.19 d	9.30 d	9.30 d
	J=15.5	J=16.0	J=16.0
$H^{i'}$	9.29 dd	9.40 dd	9.40 dd
	J=14.5; 12.0	J=14.5; 12.0	J=14.5; 12.0

14π-electron system in the benzo-annelated annulene (VII) sustains fairly large diamagnetic ring current. The difference of chemical shifts between inner and outer protons can be regarded as a measure of magnitude of ring current. The values observed in the benzoannulene (VII, $\tau_i - \tau_o$=8.42, $\tau_{i'} - \tau_{o'}$=7.81 in THF-d_8 at -50°C) are found to be much less than those of naphtho-dihydronaphtho-analogue (IX, $\tau_i - \tau_o$=10.02, $\tau_{i'} - \tau_{o'}$=10.70 in THF-d_8 at -52°C) (2). This fact indicates that the extent of π-electron delocalization in annulene ring fused with a benzene is less than that in the annulene annelated with a naphthalene (IX). As shown in the formula, one of the naphthalene nuclei in dinaphtho-didehydro[14]annulene (VIII) is forced to take 1,2-naphthoquinone type structure. Similarly, *o*-benzoquinone and 1,2-naphthoquinone type structures are contained in resonance structures of VII and IX, respectively. If we ignore the resonance energy of *o*-benzoquinoid structure, and if we assume that the resonance energy of 1,2-naphthoquinone type structure is the same with that of 1,2-dihydronaphthalene (6), the energy required to transform naphthalene into 1,2-naphthoquinone type structure [61(naphthalene)-40(1,2-dihydronaphthalene)=21 Kcal/mole] is estimated to be smaller than that of transformation of benzene into *o*-quinoid structure [36 Kcal/mole]. Difference in the energy seems to be reflected in the enhanced delocalization of π-electrons in the 14-membered ring in the naphtho-annelated annulene (IX), *i.e.*, the extent of delocalization of π-electrons in annulene ring annelated with benzenoid system seems to be governed by the magnitude of energy required to transform benzenoid structure into *o*-quinone type structure.

References

1) M. Iyoda, M. Morigaki ans M. Nakagawa, *Tetrahedron Lett.*, **1974**, 817.

2) M. Iyoda, M. Morigaki and M. Nakagawa, *ibid.*, **1974**, 3677.

3) J. Ojima, T. Yokomachi and T. Yokoyama, *Chemistry Lett.*, **1972**, 633.

4) T. Katakami, S. Tomita, K. Fukui and M. Nakagawa, *ibid.*, **1972**, 225.

5) K. Fukui, T. Nomoto, S. Nakatsuji and M. Nakagawa, *Tetrahedron Lett.*, **1972**, 3157.

6) G. W. Wheland, " Resonance in Organic Chemistry ", John Wiley and Sons, Inc., New York (1955), p. 80, p. 132.