CHEMISTRY LETTERS, pp. 815-818, 1975. Published by the Chemical Society of Japan

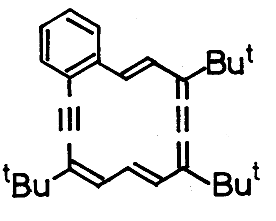
DINAPHTHO[2,1-h:1',2'-n]-5,18-DI-*t*-BUTYL-1,3,10,12-TETRADEHYDRO[18]ANNULENE AND RELATED COMPOUNDS.
THE EFFECT OF POSITION OF ANNELATION ON THE DIATROPICITY OF ANNULENE RING

Masahiko IYODA and Masazumi NAKAGAWA
Department of Chemistry, Faculty of Science, Osaka University
Toyonaka, Osaka 560

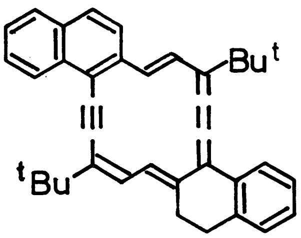
Dinaphtho-di-*t*-butyltetradehydro[18]annulene (X) was prepared in order to clarify the effect of annelation on the diatropicity of dehydroannulenes containing formal acetylene and cumulene in the cyclic system. It was found that the diatropicity of X is strongly suppressed by fusion with two naphthalene nuclei in contrast to strongly diatropic dinaphtho-di-*t*-butyldidehydro[14]annulene (III). The result indicates that equivalent Kekulé structures exert prominent effect on the delocalization of π-electrons in annelated annulene. The preparation of bis(dihydronaphtho)- (VIII) and naphtho-dihydronaphtho- (XII) analogues as reference compounds was also described.

As reported in previous papers, the diatropicity of benzo- and naphtho-1,8-didehydro[14]annulenes (I and II) was found to be less than that of parent tetra-*t*-butyldidehydro[14]annulene,1,2) whereas dinaphtho-1,8-didehydro[14]annulene (III) showed a strong diamagnetic ring current comparable to the parent didehydroannulene.3) The strong diatropicity found in III is of considerable interest, because it has been shown recently that the ring current of annulenones and their protonated species are strongly suppressed by annelation with two benzene rings.4,5)

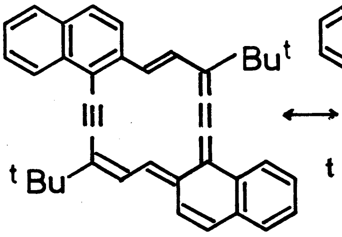
A structural characteristic of III seems to be the presence of equivalent Kekulé structures (III_a and III_b) in contrast to I and II, in which no such type of equivalent structures can be written. Consequently, it was desired to study the properties of the same type of dehydroannulene fused with two benzenoid rings at the positions which exclude the contribution of equivalent Kekulé structures.



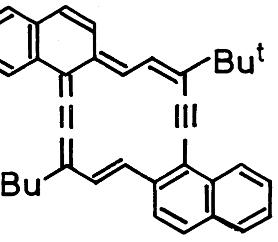
I



II



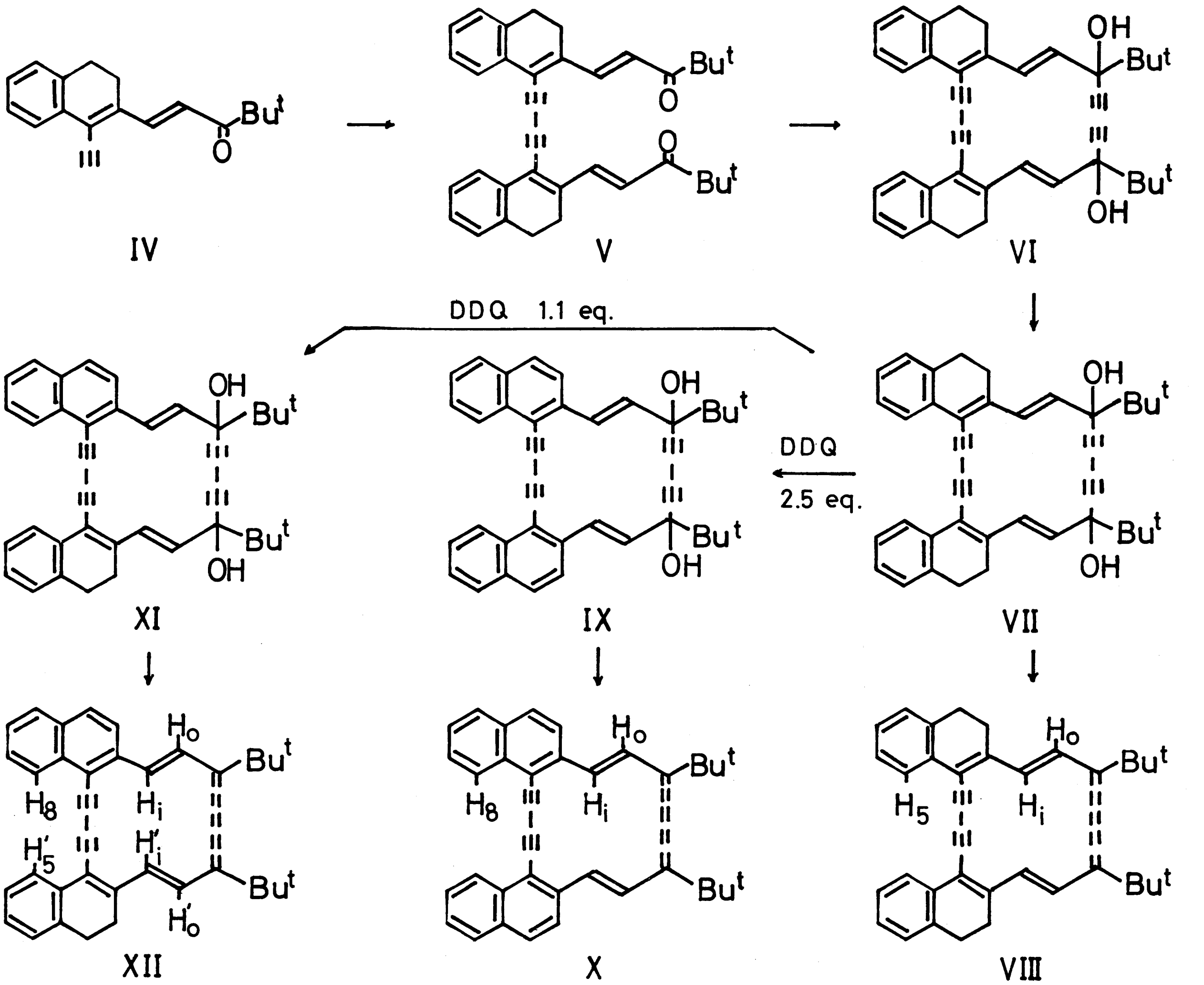
III_a



III_b

We wish now to report the synthesis and properties of di-*t*-butyl-1,3,10,12-tetradehydro[18]annulenes annelated with naphthalene(s) (X and XII) and a reference non-annelated bis(dihydronaphtho)-analogue (VIII).

The oxidative coupling of ethynyl ketone (IV)1) by cupric acetate monohydrate in pyridine-methanol yielded diketone (V, bright yellow crystals, mp 208.5-209.5°C, 92%).6) The diketone (V) in tetrahydrofuran was added to a suspension of lithium acetylide-ethylenediamine complex7) in the same solvent saturated with acetylene. The product was chromatographed on alumina to give bis-ethynyl alcohol (VI, pale yellow crystals, mp 104.0-104.5°C, 93%, m/e 578 (M^+)). Oxidative coupling of VI was performed by cupric acetate monohydrate in pyridine-ether-methanol under high dilution conditions. The reaction mixture was worked up in the usual manner, and the product was chromatographed on alumina. Elution with benzene and ether-benzene (5:95) yielded high melting isomer of cyclic glycol (VII$_a$, lemon yellow prisms, mp ca. 270°C (dec.), 54%, m/e 576 (M^+)). Low melting isomer (VII$_b$, lemon yellow prisms, mp ca. 245°C (dec.), 27%, m/e 576 (M^+)) was obtained from the following ether-benzene eluates (3:7~5:5). Ether saturated with hydrogen chloride and powdered stannous chloride dihydrate were added at -40~-50°C to a stirred suspension of VII$_b$ in ether. After 15 min, the reaction mixture was treated in the usual way to give bis(dihydronaphtho)-di-t-butyltetradehydro[18]annulene (VIII, black violet needles,



mp ca. 160°C (dec.), 61%).

The cyclic glycol (VII_a) in benzene was mixed at 60°C with a solution of DDQ (2.5 eq.) in the same solvent. After being stirred for 30 min at the same temperature, the reaction mixture was chromatographed on alumina (Merck, Act. II-III). Elution with ether-benzene (2:8~3:7) yielded IX (pale yellow prisms, decom. ca. 290°C, 47%, m/e 572 (M^+)). Ether saturated with hydrogen chloride and powdered stannous chloride dihydrate were added under argon atmosphere at -30°C to a solution of IX in the same solvent. After 20 min, dichloromethane chilled to -70°C was added to the reaction mixture and worked up carefully below -15°C. The product dissolved in n-pentane-dichloromethane (1:1) at -15~-20°C was passed through a column of alumina (Merck, Act. II-III) at -70°C. Concentration of the filtrate below -15°C under reduced pressure yielded dinaphtho-di-t-butyltetradehydro[18]-annulene (X) as unstable black violet crystals. Elemental analysis of X could not be performed owing to the instability. A solution of X in tetrahydrofuran could be kept without decomposition at -20°C.

A solution of the cyclic glycol (VII_a) and DDQ (1.1 eq.) in benzene was kept at 55°C for 2 hr under stirring. Chromatography of the reaction mixture on alumina (Merck, Act. II-III) followed by elution with ether-benzene (2:8) gave yellow crystals. N.m.r. spectroscopy reveals that the crystals are a mixture of VII_a (25%), IX (17%) and XI (58%). Because the separation was found to be difficult, the crystals in THF-d_8 were treated at -50°C under argon atmosphere with stannous chloride dihydrate and the same solvent saturated with deuterium chloride. The resulting deep blue solution containing naphtho-dihydronaphtho-di-t-butyltetradehydro[18]annulene (XII) was used directly for the measurement of n.m.r. spectrum. The signals ascribable to XII could be clearly discriminated from the signals of VIII and X. A qualitative electronic spectrum of XII could be obtained using XI purified by preparative TLC [λ_{max} (ether, -78°C): 401, 417.5, 556, 596, 735 sh, 755 nm].

The electronic spectra of VIII and X are illustrated in Fig. 1. The n.m.r. spectrum of X is shown in Fig. 2, and the n.m.r. parameters of VIII, XII and X are summarized in Table 1.

The difference in chemical shifts between inner (τ_i) and outer (τ_o) protons, $\Delta\tau = \tau_i - \tau_o$, can be regarded as an approximate measure of magnitude of ring current. As shown in Table 1, an appreciable decrease of $\Delta\tau$ -value for dinaphthoannulene (X) as compared with that of mononaphtho derivative (XII) was observed being in contrast to the strongly diatropic dinaphtho-di-t-butyldidehydro[14]annulene (III).2) However, the fact that the dinaphtho derivative (X) showed still an appreciable diatropicity ($\Delta\tau$ =7.08) seems to reflect the highly aromatic nature of the parent tetradehydro[18]annulene system. The present results suggest that the diatropicity of annelated dehydroannulene containing formal acetylenic and cumulenic linkages is further suppressed by fusion with an additional benzenoid ring, unless the mode of fusion of the two benzenoid nuclei allows the contribution of equivalent Kekulé structures. The tendency is in accord with the observation on the other type of annulenes,4,5,8) in which the dia- or paratropicity is suppressed with an increase in the number of fused benzenoid rings resulting finally in atropic species.

Table 1. The 100 MHz n.m.r. parameters (τ -values)

	H_o, H_o'	H_8,H_5,H_5'	t-Bu	H_i, H_i'	$\Delta\tau$	Solvent (°C)
VIII	H_o: 0.23 d, J=14.0	H_5: 0.87 d, J=8.0	7.95 s	H_i: 13.98 d, J=14.0	13.75	$CDCl_3$ (-50°C)
XII	H_o': 0.73 d, J=15	H_5': 0.51 d, J=8	8.08 s	H_i': 11.26 d, J=15	10.53	THF-d_8 (-50°C)
	H_o: 0.11 d, J=15	H_8: 0.31 d, J=8	8.14 s	H_i: 11.03 d, J=15	10.92	
X	H_o: 1.11 d, J=16.0	H_8: 0.56 d, J=8.0	8.25 s	H_i: 8.19 d, J=16.0	7.08	$CDCl_3$ (-40°C)

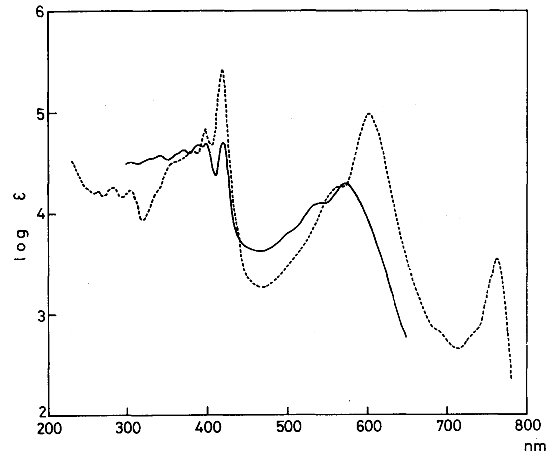


Fig. 1. The UV spectra of VIII (------, in THF) and X (———, in ether, -78°C).

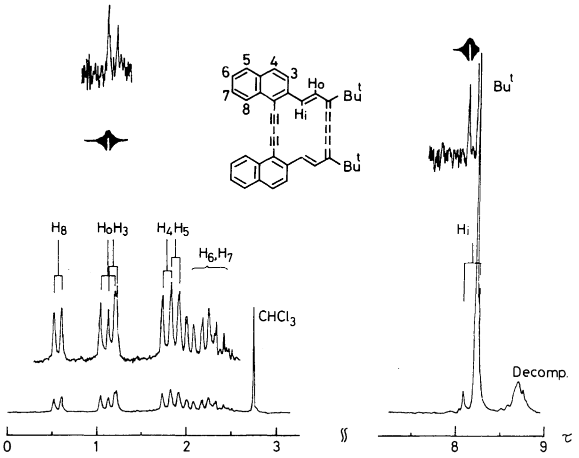


Fig. 2. The 100 MHz n.m.r. spectrum of X ($CDCl_3$, -40°C).

References and Note

1) M. Iyoda, M. Morigaki, and M. Nakagawa, Tetrahedron Lett., 3677 (1974).
2) A. Yasuhara, T. Satake, M. Iyoda, and M. Nakagawa, Tetrahedron Lett., 895 (1975).
3) M. Iyoda, M. Morigaki, and M. Nakagawa, Tetrahedron Lett., 817 (1974).
4) J. Ojima, Y. Yokoyama, and T. Yokoyama, Chem. Lett., 1261 (1974); J. Ojima, A. Kimura, and T. Yokoyama, ibid., 207 (1975); J. Ojima, Y. Yokoyama, and T. Yokoyama, ibid., 487 (1975).
5) R. T. Weavers, R. R. Jones, and F. Sondheimer, Tetrahedron Lett., 1043 (1975).
6) All new compounds described in this paper gave IR, n.m.r. and mass spectral data consistent with the assigned structures and satisfactory elemental analyses were obtained on crystalline compounds, unless otherwise stated.
7) D. F. Beumel, Jr. and R. F. Harries, J. Org. Chem., 28, 2775 (1963); 29, 1872 (1964).
8) K. Endo, Y. Sakata, and S. Misumi, Tetrahedron Lett., 2557 (1970).

(Received June 6, 1975)