Tetrahedron Letters, Vol.22, No.21, pp 1989 - 1992, 1981
Printed in Great Britain

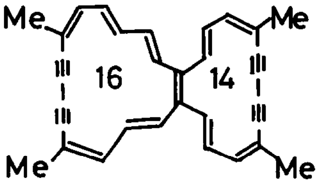
0040-4039/81/211989-04$02.00/0

TETRAKISDEHYDRO[14]ANNULENO[20]ANNULENE

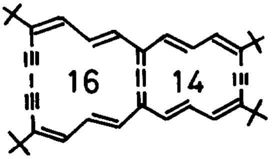
Yukihiro Yoshikawa, Masahiko Iyoda, and Masazumi Nakagawa*
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

Summary: Tetrakisdehydro[14]annuleno[20]annulene consisting of an aromatic bisdehydro[14]annulene and an antiaromatic trisdehydro[20]annulene has been synthesized. The ^1H NMR spectra clearly indicate the induction of para- and diamagnetic ring currents in each of the [4n]- and [4n+2]-rings, respectively.

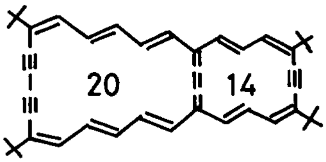
Recently several kinds of [4n+2]annuleno[4n'+2]annulenes have been synthesized$^{1)}$ affording interesting information on the nature of π-electron delocalization in bicyclic system. However, little was known on [4n]annuleno[4n'+2]annulenes, and only two tetrakisdehydro[14]annuleno[16]-annulenes (I and II) have been reported by Sondheimer's$^{2)}$ and by our groups$^{3)}$, respectively. In order to obtain further insights into the nature of [4n]annuleno[4n'+2]annulene systems, we have prepared conformationally stable and planar tetra-*t*-butyltetrakisdehydro[16.10.2][14]-annuleno[20]annulene (III).



(I)

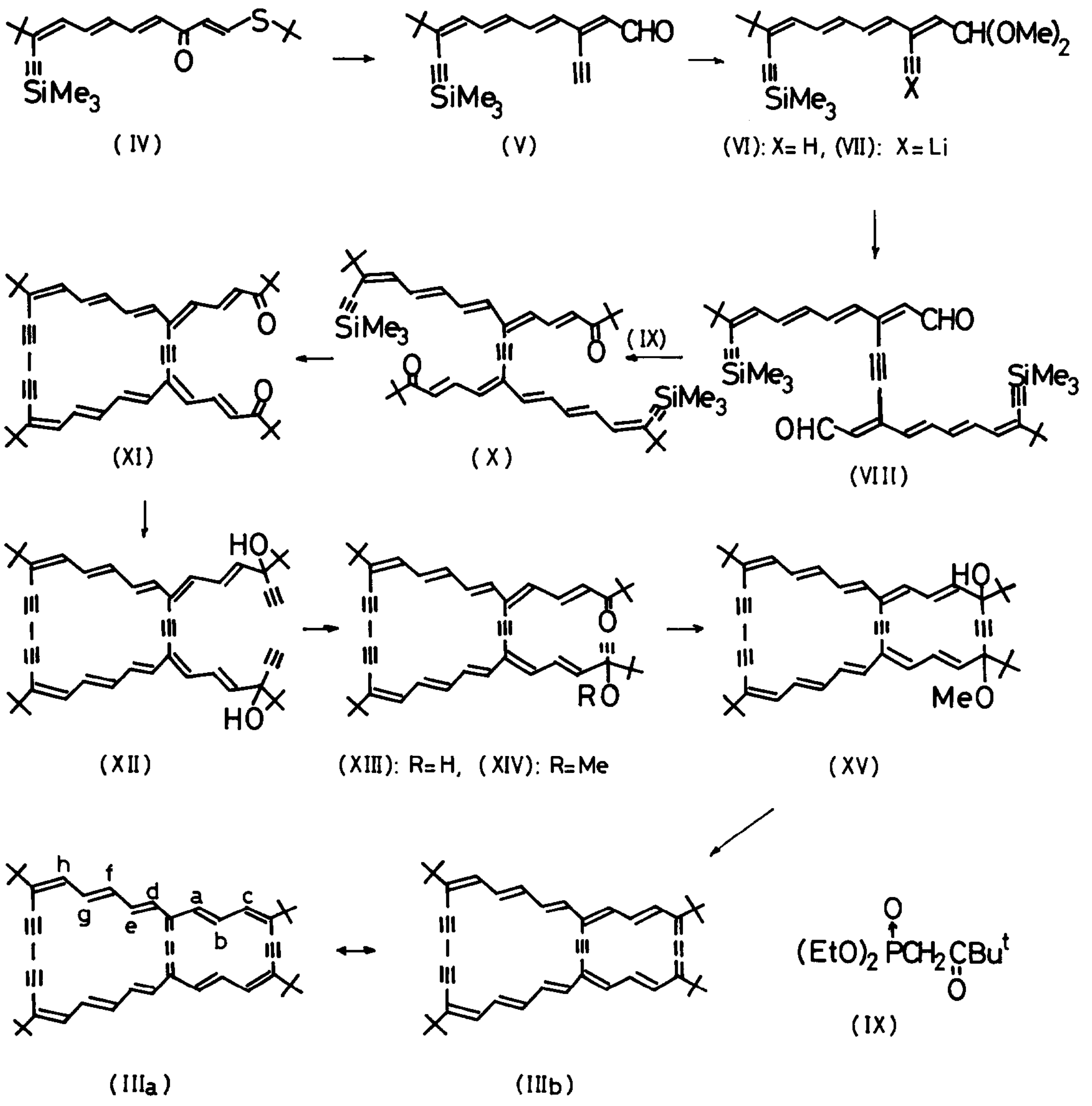


(II)



(III)

Trimethylsilylethynyl ketone (IV)$^{4)}$ was ethynylated with lithium acetylide in THF$^{5)}$ and the product was treated without isolation with a dilute sulfuric acid to give tetraene aldehyde$^{6)}$ (V, yellow needles, mp 77.5-79.2°C, 86%). The aldehyde (V) was converted into dimethyl acetal (VI) in the usual way and treated with butyllithium to give lithium derivative (VII). Reaction of VII with the trimethylsilyl ketone (IV) followed by hydrolysis with an acid yielded dialdehyde (VIII, yellow needles, mp 153.8-154.4°C (dec.), 43% based on IV). The Wittig-Horner-Emmoms reaction of the dialdehyde (VIII) with the carbanion derived from diethyl 3,3-dimethyl-2-oxo-butanephosphonate (IX)$^{7)}$ gave diketone (X, yellow needles, mp 178.9-179.6°C (dec.), 71%). Oxidative coupling of the bis(trimethylsilyl)diketone (X) with copper(II) acetate in pyridine-methanol at 90°C afforded cyclic triyne diketone (XI, bright reddish brown crystals, mp *ca.* 220°C (dec.), 48%). Bisethynylation of the diketone (XI) with lithium acetylide in THF$^{5)}$ yielded monocyclic diol (XII, vermilion prisms, mp 236.0-240.3°C (dec.), 96%). One molar solution of potassium *t*-butoxide in *t*-butanol was added to a solution of XII in benzene-THF (5:1), and the mixture was stirred for 20 min. at 10°C to give keto alcohol[3] (XIII, reddish brown prisms, mp 250°C (dec.), 75%). Treatment of XIII in THF with dimethyl sulfate in the presence of powdered potassium hydroxide gave methoxy derivative (XIV, reddish brown crystals, mp > 220°C (dec.), 62%). The cyclization of XIV could be realized with lithium amide in liquid ammonia at -65 ∿ -70°C for 6 hrs., and chromatography of the product on alumina resulted in separation of recovered XIV (13%) and diastereomers of cyclic glycol monomethyl ether (XV_a, orange crystals, mp *ca.* 260°C (dec.), 22%, and XV_b, deep orange crystals, mp *ca.* 255°C (dec.), 18%). The cyclic glycol monomethyl ether (XV_b) yielded desired annulenoannulene (III, 61%) on treatment with tin(II) chloride and ether saturated with hydrogen chloride at -40°C. Similarly, another diastereomer (XV_a) afforded III under the same reaction conditions.



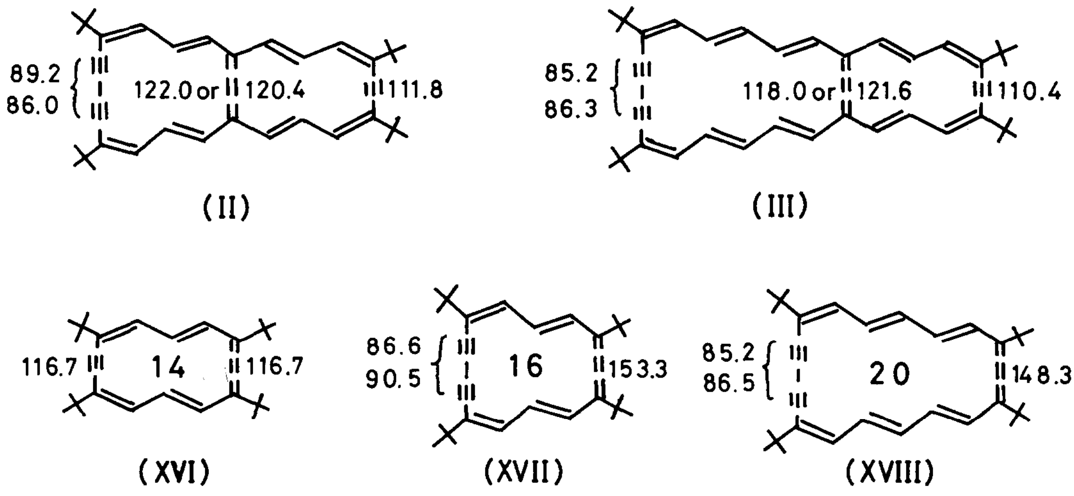
The tetrakisdehydro[14]annuleno[20]annulene (III) was obtained as deep green needles with metallic lustre (mp *ca.* 220°C (dec.), Mass(m/e): 604 (M^+); IR(KBr-disk): 2180 w, 987 s, 959 m cm^{-1}; ES: $\lambda_{max}^{cyclohexane}$ nm(ε) 247 sh (17200), 254 sh (21000), 258 sh (22600), 264.5 (24500), 299 (21500), 330 (40600), 343.5 (49300), 386 sh (74900), 399.5 (174000), 423.5 (262000), 435 sh (77100), 600 sh (3040), 648 sh (4400), 680 (4980), 734 sh (3780), 812 sh (1630)). The annulenoannulene (III) gave 1:1 CT complex with 2,4,7-trinitrofluorenone (deep green fine crystals, mp > 220°C (dec.)). The ^1H NMR parameters of III are summarized in Table.

Table. ^1H NMR Parameters of III ($CDCl_3$, τ-values at 35°C)

14-membered ring	H^a	2.39 d, J=13.8	H^b	10.76 dd, J=13.2, 13.8
	H^c	1.79 d, J=13.2	*t*-Bu	8.42 s
20-membered ring	H^d	4.46 d, J=15.0	H^e	-3.14 dd, J=11.5, 15.0
	H^f	5.09 dd, J=11.5, 15.0	H^g	-2.74 dd, J=11.5, 15.0
	H^h	4.84 d, J=11.5	*t*-Bu	9.19 s

The ^1H NMR parameters clearly indicate that the 20-membered ring sustains a strong paramagnetic ring current, whereas the 14-membered ring shows strong diamagnetic ring current. The difference of the coupling constants in each ring exhibits that the 14π-electron system exists in a highly delocalized form ($J_{ab} \simeq J_{bc}$). On the other hand, the 20π-electron system shows marked difference in the coupling constants indicating an appreciable bond alternation in the antiaromatic system like trisdehydro[4n]annulenes. The ^{13}C chemical shifts of *sp*-hybridized carbon atoms in the trisdehydro[4n]annuleno[4n'+2]annulenes (II and III) are shown in Figure together with those of bisdehydro[14]annulene (XVI) and the related trisdehydro[4n]annulenes (XVII and XVIII)[8].

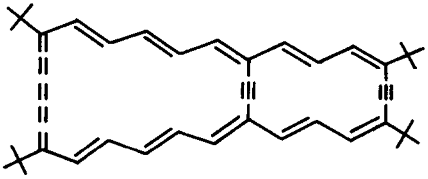
Figure. ^{13}C Chemical Shifts (δ-values) of *sp*-Hybridized Carbon Atoms



(II) (III)

(XVI) (XVII) (XVIII)

The observed ^1H and ^{13}C NMR data suggest that the [14]annuleno[20]annulene (III) can be regarded as a resonance hybrid of two canonical forms containing aromatic π-electron structure in the [4n'+2]-moiety (III_a and III_b) and a significant contribution of canonical form III_c which contains non-aromatic 14π-electron system can be excluded. This trend is consistent with the NMR behavior of the [14]annuleno[16]annulene (II) (*cf.*, the Figure and reference 3) and with the reported diminished bond alternation in the 6-membered ring in an alkyl substituted benzocyclobutadiene$^{9)}$. Among the two canonical forms (III_a and III_b), the structure containing the central butatriene bond (III_a) seems to be dominant as compared with III_b in view of the slight difference between the coupling constants J_{ab} and J_{bc} and the ^{13}C chemical shifts of *sp*-hybridized carbon atoms.



(III_c)

It is to be noted that the apparent suppression of each ring current in [4n]annuleno-[4n'+2]annulene is larger in the aromatic (4n'+2)π-electron system than in the antiaromatic 4n congener.

References and Note

1) For a review, see, M. Nakagawa, *Angew. Chem.*, 91, 215 (1979); *Angew. Chem. Int. Ed. Engl.*, 18, 202 (1979).
2) T. M. Cresp and F. Sondheimer, *J. Am. Chem. Soc.*, 99, 194 (1977).
3) M. Iyoda, S. Akiyama, and M. Nakagawa, *Tetrahedron Lett.*, 4213 (1979).
4) S. Nakatsuji, S. Akiyama, and M. Nakagawa, *Tetrahedron Lett.*, 3723 (1977).
5) M. M. Midland, *J. Org. Chem.*, 40, 2250 (1975).
6) All new crystalline compounds described in this communication gave IR, NMR, and mass spectral data consistent with the assigned structures and satisfactory elemental analyses were obtained.
7) S. Akiyama, M. Iyoda, and M. Nakagawa, *J. Am. Chem. Soc.*, 98, 6410 (1976).
8) M. Nakagawa, Chapter 15 in "The Chemistry of Carbon Carbon Triple Bond, Part II", ed. by S. Patai, John Wiley (1978).
9) W. Winter and H. Straub, *Angew. Chem.*, 90, 142 (1978).

(Received in Japan 6 February 1981)