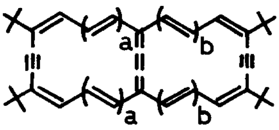
Tetrahedron Letters No. 17, pp 1483 - 1486, 1978. Pergamon Press. Printed in Great Britain.

SYNTHESIS AND PROPERTIES OF A TRISDEHYDRO[18.10.2][14]ANNULENO[22]ANNULENE

Shin'ichi Nakatsuji, Shuzo Akiyama, and Masazumi Nakagawa*
Department of Chemistry, Faculty of Science, Osaka University
Toyonaka, Osaka 560, Japan

(Received in Japan 10 February 1978; received in UK for publication 7 March 1978)

The interesting NMR spectral behavior of trisdehydro[4n+2]annuleno[4n'+2]-annulenes (I_a: n=n'=3 (1); I_b: n=n'=4 (2) and I_c: n=3, n'=4 (3)) inspired us to prepare a higher analogue of this series of annulenoannulenes, the trisdehydro-[18.10.2][14]annuleno[22]annulene (I_d: n=3, n'=5) in order to get further information on the induction of ring current in bicyclic system.

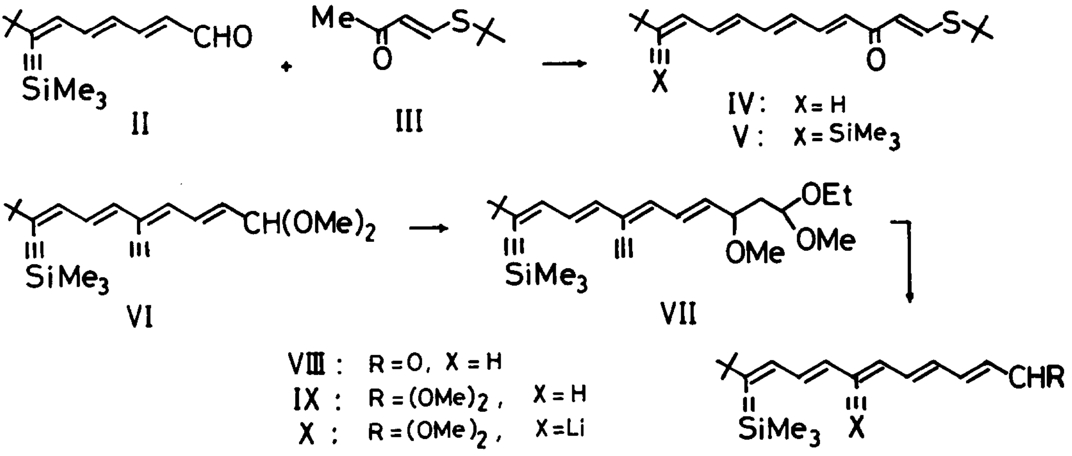


I_a : a = b = 1, I_c : a=1, b=2

I_b: a = b = 2, I_d : a=1, b=3

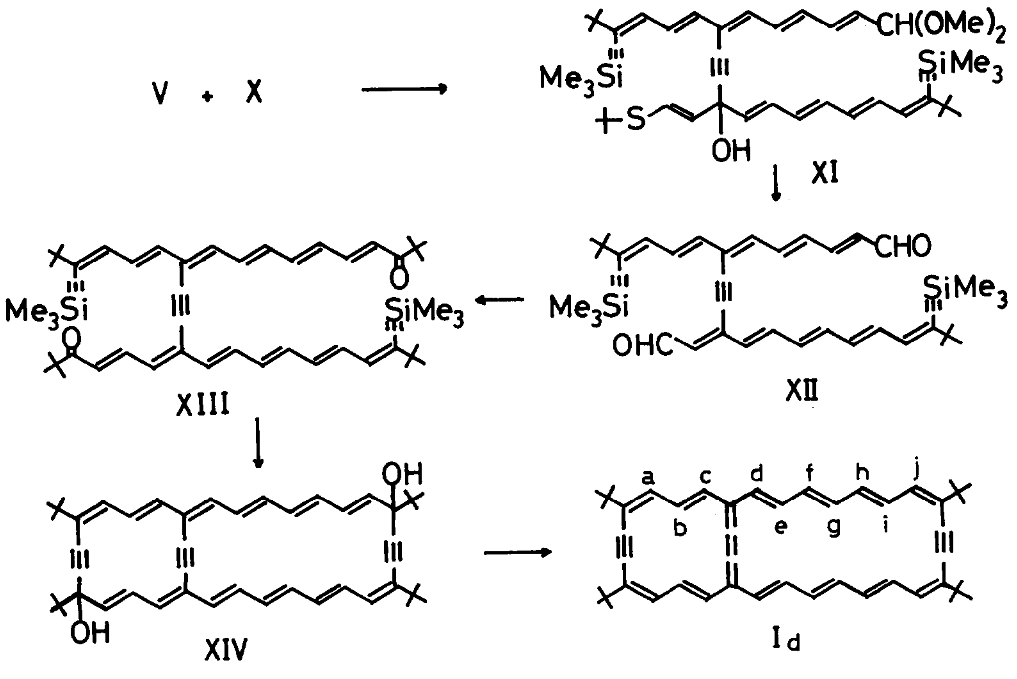
The trimethylsilyl derivative of trienyne aldehyde (II) (4) was condensed with *t*-butylthiovinyl methyl ketone (III) (1) in an aqueous ethanol in the presence of sodium hydroxide to give the pentaenyne ketone (IV, yellow cryst., mp 87-88°C, 46%) (5). The ethynyl ketone (IV) was converted into the trimethylsilyl derivative (V) on successive treatment with lithium diethylamide and trimethylchlorosilane.

The condensation of ethyl vinyl ether with the tetraendiyne aldehyde dimethyl acetal (VI) (3) in the presence of borontrifluoride afforded a diastereo-



meric mixture of the methoxy acetal (VII), which was treated without purification with an aqueous acetic acid containing sodium acetate to yield the pentaendiyne aldehyde (VIII, orange liquid, 29% based on VI; 2,4-dinitrophenylhydrazone, mp >280°C, brownish red cryst.). The aldehyde (VIII) was converted into the dimethyl acetal (IX, reddish orange liquid), which was found to be highly sensitive to hydrolysis. The lithio derivative (X) was obtained on treatment of IX with butyllithium.

The product (XI) of the reaction of X with the pentaene ketone (V) was treated with an aqueous sulphuric acid to give the dialdehyde (XII, orange yellow cryst., mp 142-142.5°C, 78%). The reaction of carbanion derived from diethyl 3,3-dimethyl-2-oxobutanephosphonate (t-BuCOCH$_2$(O)P(OEt)$_2$) (1,6) with the dialdehyde (XII) yielded the diketone (XIII, red cryst., mp 202-202.5°C, 63%) with the desired skeleton of carbon atoms. A solution of the diketone (XIII) in tetrahydrofuran was added to a suspension of finely powdered potassium hydroxide in liquid ammonia. The reaction mixture was worked up in the usual manner to give brownish yellow crystals. The crude crystals in ether were chromatographed on alumina to give a diastereomeric mixture of the bicyclic glycol (XIV, brownish yellow cryst., mp >280°C, 80%). Ether saturated with hydrogen chloride was added at -55°C to a mixture of the bicyclic glycol (XIV), powdered tin(II) chloride dihydrate and ether. Deep green crystals obtained on working up the reaction mixture were chromatographed on alumina (Merck II-III) to give the trisdehydro[18.10.2][14]annuleno[22]annulene (I_d, greenish deep blue cryst., mp *ca.* 290°C (dec.), 92%, UV: λ_{max}^{THF} (ε) nm, 267.0(23400), 292.0 sh(33100), 302.5



(39700), 325.5(10400), 368.0 sh(24300), 427.0 sh(102000), 446.0(203000), 465.5(391000), 566.5 sh(11200), 603.5(21300), 653.0(21100), 740(900), 825(800), 945(490)). The electronic spectra of I_d and I_b showed close similarity. However, an appreciable hypochromism was observed in the spectrum of the [14][22]-system, although the both annulenoannulenes (I_d and I_b) contain the same number of π-electrons and the perimeters are also the same 30π-electron system.

The ^{1}H NMR parameters of I_d are recorded in Table 1. The signals of some inner protons (H^e or H^g) are submerged under the tail of strong signal of *t*-butyl protons and could not be located simultaneously at a temperature. The ^{1}H chemical shifts of the [14]annuleno[22]annulene (I_d) are compared in Fig. 1 with those of I_a (1), I_b (2), I_c (3) and the related monocyclic systems, *i.e.*, bisdehydro[14]-(XV) (7) and bisdehydro[22]annulenes (XVI) (4).

Table 1. 100 MHz NMR parameters of the [14]annuleno[22]annulene (I_d)
τ-Values in $CDCl_3$. Me_4Si as an internal standard.

	36°C	-60°C
Outer-H	H^c 0.22 d J=14, H^f 1.23 dd J=13,14 H^a 0.51 d J=13, H^h 1.35 dd J=13,14 H^d 0.95 d J=14, H^j 1.77 d J=12.5	H^c 0.11 d J=14, H^f 1.09 dd J=13,15 H^a 0.45 d J=13, H^h 1.21 dd J=13,14 H^d 0.81 d J=14, H^j 1.67 d J=12.5
Inner-H	H^e 7.53 dd J=13,14 H^i 8.64 dd J=12.5,13.5 H^b 13.10 dd J=13,14	H^g 8.93 dd J=13,14 H^i 9.12 dd J=12.5,13.5 H^b 13.37 dd J=13,14
t-Bu-H	8.03 s, 8.30 s	8.03 s, 8.29 s

The characteristic feature found in the [14]annuleno[18]annulene (I_c) was also observed in the spectrum of the [14][22]-system (I_d), *i.e.*, the signals of both of the inner and outer protons in the 22-membered ring in I_d moved to higher field as the distance from the common bond is increased. The NMR trend observed in I_c and I_d can be explained in terms of independent ring current induced in each ring as is assumed in polycondensed benzenoid systems, such as anthracene and perylene (8), namely the ring current induced in the 14-membered ring in I_d exerts deshielding effect on the all protons in the 22-membered ring causing low field shift of all of them. The gradual high field shift can be attributed to the diminishing deshielding effect along with the increase of the distance from the 14-membered ring. In spite of a marked low field shift of the inner proton (H^b) in the 14-membered ring of I_d, the outer protons (H^a and H^c) gave signals at lower field than the corresponding protons in the parent bisdehydro[14]annulene (XV). This fact can also be ascribed to the deshielding effect of ring current of the 22-membered ring on the 14-membered moiety.

As shown in Fig. 1, the annulenoannulenes consisting of two identical rings (I_a and I_b) exhibit quite similar ^{1}H NMR spectral properties as that of the unsymmetrical analogues (I_c and I_d). Also the much stronger diatropicity of I_a

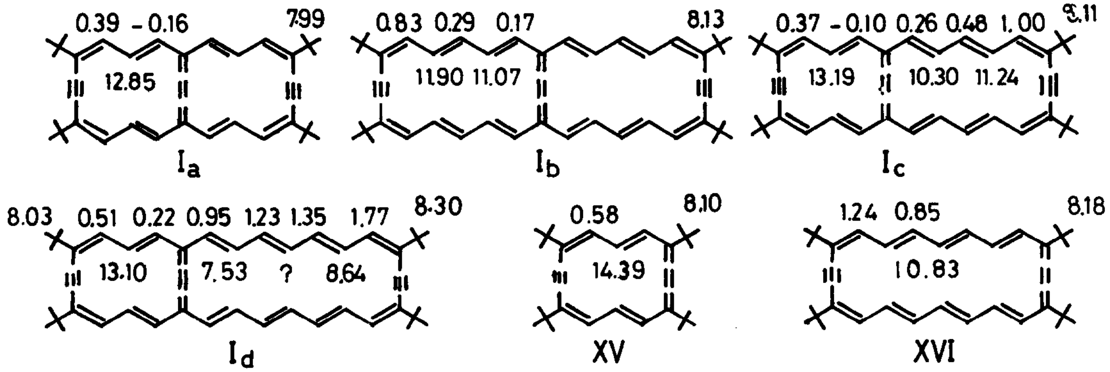


Fig. 1. ^1H Chemical shifts of annulenoannulenes and related bisdehydroannulenes

and I_b as compared with corresponding bisdehydro[4n+2]annulenes, *e.g.*, I_a *vs.* XVI, suggests that the symmetrical annulenoannulenes (I_a, I_b and hexakisdehydro-[12.12.4][18]annuleno[18]annulene (9)) can not be regarded as bridged bisdehydro-[4n+2]annulenes. Furthermore, the X-ray structure analysis (10) and the ^{13}C NMR spectrum (11) of the [14]annuleno[14]annulene (I_a) revealed that the three sp-sp bonds in I_a should have an almost identical hybrid nature of acetylene and cumulene. These facts seem to indicate that an independent ring current is induced in each ring even in the symmetrical annulenoannulenes, such as I_a and I_b, although the ring current of naphthalene has been considered to confine to the 10π periphery.

References and Note

1) S. Akiyama, M. Iyoda, and M. Nakagawa, *J. Am. Chem. Soc.*, 98, 6410 (1976).

2) M. Osuka, Y. Yoshikawa, S. Akiyama, and M. Nakagawa, *Tetrahedron Lett.*, 1977, 3719.

3) S. Nakatsuji, S. Akiyama, and M. Nakagawa, *Tetrahedron Lett.*, 1972, 3723.

4) M. Iyoda and M. Nakagawa, *J. Chem. Soc., Chem. Commun.*, 1977, 1003.

5) All the new compounds reported in this communication gave NMR, mass and IR spectra consistent with the assigned structures and the crystalline compounds gave satisfactory elemental analyses.

6) G. Sturz, *Bull. Soc. Chim. France*, 1964, 2349.

7) K. Fukui, T. Nomoto, S. Nakatsuji, and M. Nakagawa, *Tetrahedron Lett.*, 1972, 3157; K. Fukui, T. Nomoto, S. Nakatsuji, S. Akiyama, and M. Nakagawa, *Bull. Chem. Soc. Jpn.*, 50, 2758 (1977).

8) *Inter al.*, N. Jonathan, S. Gordon, and B. P. Dailey, *J. Chem. Phys.*, 36, 2443 (1962); J. D. Memory, *J. Chem. Phys.*, 38, 1341 (1964); H. P. Figeys, *Tetrahedron Lett.*, 1966, 4625.

9) T. Kashitani, S. Akiyama, M. Iyoda, and M. Nakagawa, *J. Am. Chem. Soc.*, 97, 4424 (1975).

10) N. Kasai, Y. Kai, N. Yasuda, S. Akiyama, and M. Nakagawa, to be published.

11) H. Nakanishi, S. Akiyama, and M. Nakagawa, *Chem. Lett.*, 1977, 1515.