Tetrahedron Letters No. 49, pp 4929 - 4932.
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0040-4039/78/1201-4929$02.00/0

BRIDGING EFFECTS OF FURAN RING INCORPORATED IN THE PERIMETERS OF A BISDEHYDRO[16]ANNULENE AND A BISDEHYDRO[18]ANNULENE: SYNTHESES OF 1:14-EPOXY-6,8-BISDEHYDRO[16]ANNULENE AND 1:16,10:13-DIEPOXY-4,6-BISDEHYDRO[18]ANNULENE[†]

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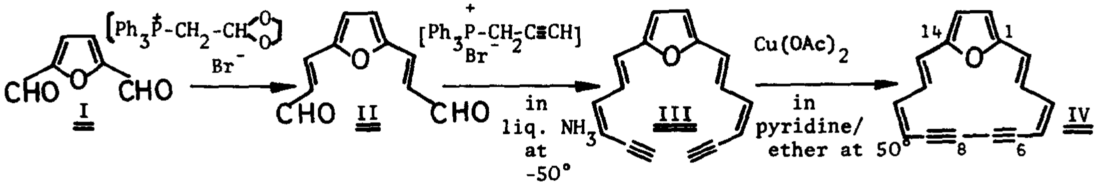
THE aim of this communication is to study the ring current effects of bisdehydro[4n]- and [4n+2]-annulenes (IV and X; n=4) in terms of the bridging effect of the incorporated furan ring(s). A wealth of data on ^{1}H nmr chemical shifts in both series of non-bridged counterparts (VIIa,b[4] and XIV[5]; n=4) and "acetylene-cumulene" dehydroannulenes (V[2], VI[3] and XIII[1]; n=4) makes it possible to estimate the bridging effect of furan ring in comparison with those dehydroannulenes, if such compounds as IV and X could be prepared. We now realized the preparation of IV and X, the first bridged bisdehydroannulenes. The comparison of our ^{1}H chemical shift data on IV and X, although they are limited only in n=4 series, revealed the fact that furan ring incorporation in IV and X gives stronger paramagnetic and diamagnetic ring currents, respectively, as compared with the respective non-bridged dehydroannulenes VIIa, VIIb and XIV, but weaker than those of the corresponding "acetylene-cumulene" dehydroannulenes V, VI and XIII, respectively.

Wittig reaction of 2,5-bis-(β-formyl vinyl)furan II[6)], prepared from 2,5-furandialdehyde I, with 2.2 mole equivalent of propargyl triphenylphosphonium bromide[7)] in MeCN at -50° with a large excess liq. NH_3 yielded a stereoisomeric mixture, from which di-cis isomer III was separated by chromatography [benzene, on silica gel]. Successive coupling of III with $Cu(OAc)_2$ in pyridine-ether (50°, 3.5 hr) followed by chromatography on silica gel [n-hexane]



afforded 1:14-epoxy-6,8-bisdehydro[16]annulene IV, as blue-violet needles, mp 300° (decomp), 15% based on III; *m/e* 218 (M$^+$); λ_{max}^{EtOH} nm (ε): 227.5 (12,900), 281 (83,300), 296 (49,000) and 535.5 (384); ir ν_{max}^{KBr} cm^{-1}: 2180w (ν c≡c), 1600 (ν c=c), and 972s (δ trans c=c). Examination of molecular model indicates that IV has a triangular geometry.** The nmr spectrum of IV (Fig. 1) confirmed its c_{2v}-symmetry and proved to be paratropic, being outer protons resonated at high-field and inner protons at low-field. The comparison of IV and V (see below) indicates that the furan ring exerts a similar effect as the cumulenic group of V. Paratropicity decreases in the order ["acetylene-cumulene" dehydroannulenes V and VI > IV > non-bridged dehydroannulenes VIIa, b].

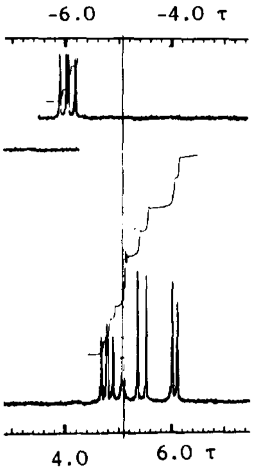
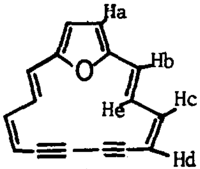
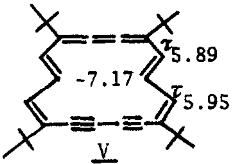


Figure 1. Nmr spectrum of IV in CDCl$_3$ at 27° (100 MHz)

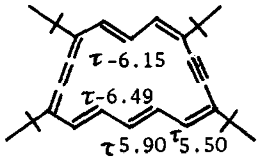


IV

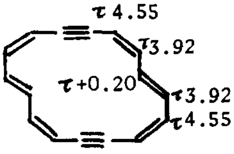
H^a τ5.08s
H^b 5.44d (J=16.0 Hz)
H^c 4.78dd(J=10.0, J=12.0)
H^d 6.06d (J=10.0)
H^e -5.96dd(J=16.0, J=12.0)



V
(ref. 2)

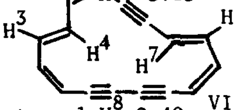


VI
(ref. 3)



VIIa (-80°)4)

internal H^3 τ-3.60
H^4 -2.00
H^7 +1.10
H^8 -3.05

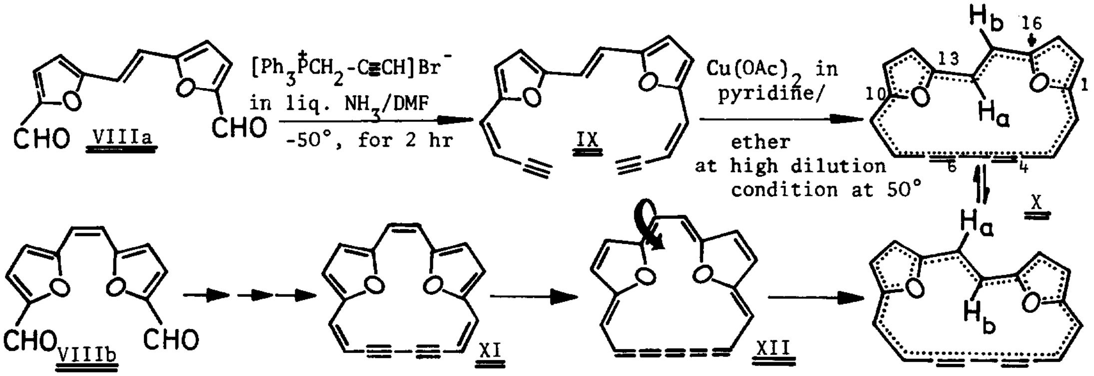


VIIb4)

external H^8 τ2.40
$H^{3,4,7}$ τ3.5~5.6

The second sample to be readily available by the above method is 1:16,10:13-diepoxy-4,6-bisdehydro[18]annulene X, a rectangular shaped molecule. Wittig reaction of trans-(2,2′-difurylethylene)-5,5′-dicarbaldehyde VIII$_a$ 8) with propargyl triphenylphosphonium bromide yielded a mixture of stereoisomers. The di-*cis* isomer IX was isolated by chromatography on silica gel (benzene), *ca.* 30% yield, as yellow needles, mp *ca.* 60° (decomp). Ring closure of IX with Cu(OAc)$_2$ in pyridine at 50° for 1 hr gave X, 17%, red prisms, mp 280-2°; *m/e* 258 (M$^+$); $\lambda_{max}^{CCl_4}$ nm (ε): 335 (47,200), 345 (72,700), 375sh (5,800), 398 (9,000), 408 (9,800), 432 (5,900), 459sh (3,000), 470 (3,100), 506 (980), 522 (490); ir ν_{max}^{KBr} cm^{-1}: 1013, 1000, 950 (δ trans c=c), and 690. Similar synthesis starting from the corresponding *cis*-dialdehyde VIIIb 8) led also to X in a less yield, and no formation of XI was observed, indicating that cis-trans isomerization *via* cumulene intermediate XII had occurred readily to give the exclusive formation of the most stable isomer X.

Unlike IV, bisdehydro[18]annulene X proved to be conformationally mobile. The nmr spectrum at 25° in THF-d_8 consists of only two AB systems, and the trans double bond protons



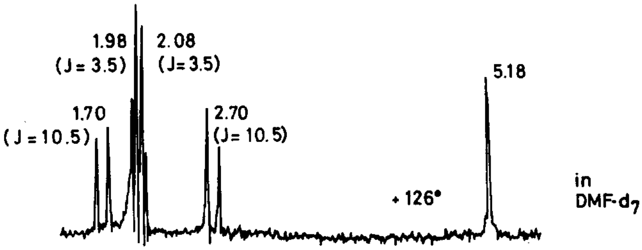


Figure 2a. Nmr spectra of X in DMF-d_7 (100 MHz)

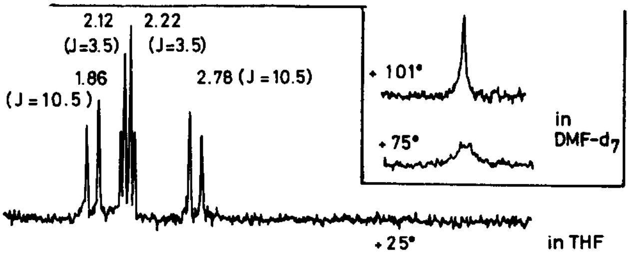


Figure 2b. Nmr spectrum of X in THF-d_8 at 25° (100 MHz)

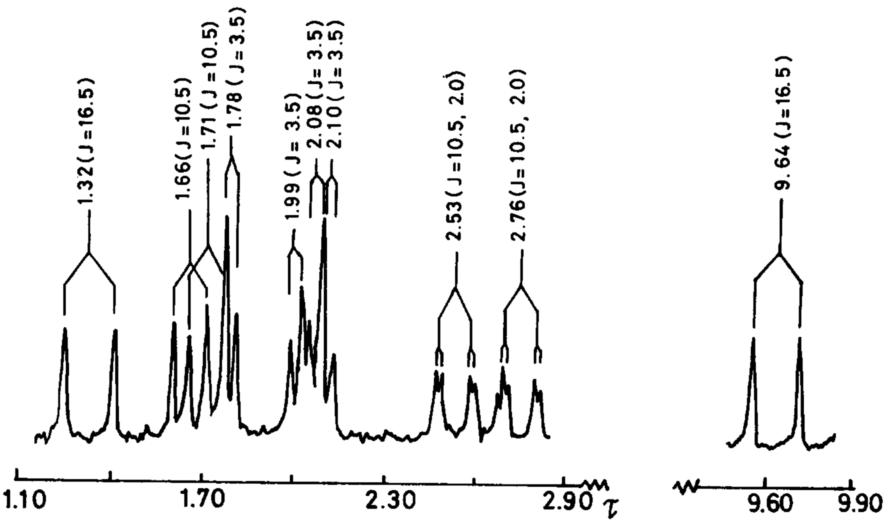
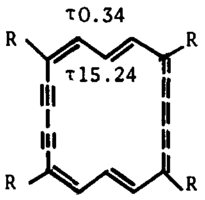


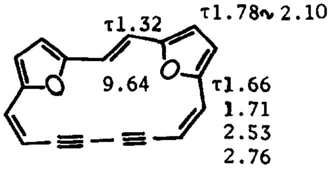
Figure 2c. Nmr spectrum of X at -53.5° in THF-d_8 (100 MHz)

became so difused that they can no longer detected (Fig. 2b). Above 60°, a new broad signal at *ca.* τ 5.2, which became sharper progressively to give a high-temperature singlet at 126° at τ 5.18 (Fig. 2a). The low temperature spectrum was transient between +10∼-30° due to the flipping of furan rings. The frozen spectrum of **X** in THF-d_8 was obtained, which exhibited a low-field doublet at τ 1.32 (J=16.5 Hz) and a high-field doublet at τ 9.64 (Fig. 2c). These signals are clearly ascribable to the outer and inner protons on the trans double bond. Obviously, diatropicity of [4n+2]dehydroannulenes decreases in the order ["acetylene-cumulene"dehydroannulene > **X** > nonbridged bisdehydroannulene]. The reported strong diatropicity of "acetylene-cumulene"dehydroannulenes **XIII** is due to, in part, the contribution from the equivalent Kekulé structures.1)

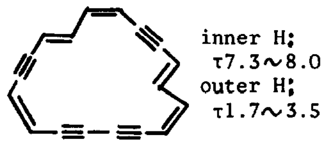
The observed conformational mobility of **X** has two advantages in the study of the rotational process, since (1) the equilibrium of **X**⇌**XI** is much favoured towards **X**, eliminating the usually occurred cis-trans isomerism, and (2) rotation of the central trans double bond does not yield nonequivalent conformers. Studies of the rate process by nmr line shape analysis are now in progress in our laboratories.



XIII1) R = Me



X



XIV5)

REFERENCES AND NOTES

† A part of this work was presented at the third International Symposium on Novel Aromatic Compounds, San Francisco, California, August, 1977.

** Attempted synthesis of 6,8-bisdehydro[16]annulene 1:14-sufide starting from trans-(2,2'-dithienyl ethylene)-5,5'-dicarbaldehyde was unsuccessful.

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(Received in Japan 7 September 1978)