Tetrahedron Letters No. 5, pp 361 - 364, 1973. Pergamon Press. Printed in Great Britain.

SYNTHESIS OF [16]ANNULENE 1,4:7,10-DIOXIDE AND THE VERIFICATION OF AN INDUCED PARAMAGNETIC RING CURRENT

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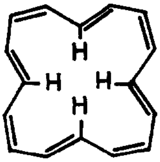
(Received in Japan 24 November 1972; received in UK for publication 2 January 1973)

[16]ANNULENE 1[1,2] does not comply with Hückel rule and has been shown to be antiaromatic. Even in the most thermodynamically stable configuration, 1 is not stable and exists as a dynamic equilibrium mixture[2a] between two interchangeable configurations by a consequence of a low temperature cis-trans isomerization (-140°), which is not expected to occur at such a very low temperature in ordinary olefins.[2] It appeared of interest to synthesize another 16π electron system, whose geometry is not only planar, but also fixed by the insertion of appropriate bridges, which may remove comlexities due to the intrinsic valence[2b] and configurational interconversions[2c], occurred in [16]annulene. If the bridges are introduced coplanar with the plane of the periphery so as to prevent the interchange of the hydrogens bounded to a *trans* double bond, the inner and outer hydrogens of the *trans* double bond do not coalesced, and the nmr spectrum of this model is expected to become temperature-independent exhibiting the internal proton(s) at low fields and the external protons at high fields by a paramagnetic ring current.[3]



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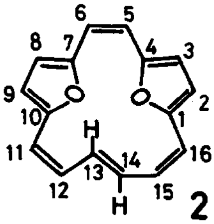

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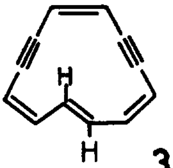

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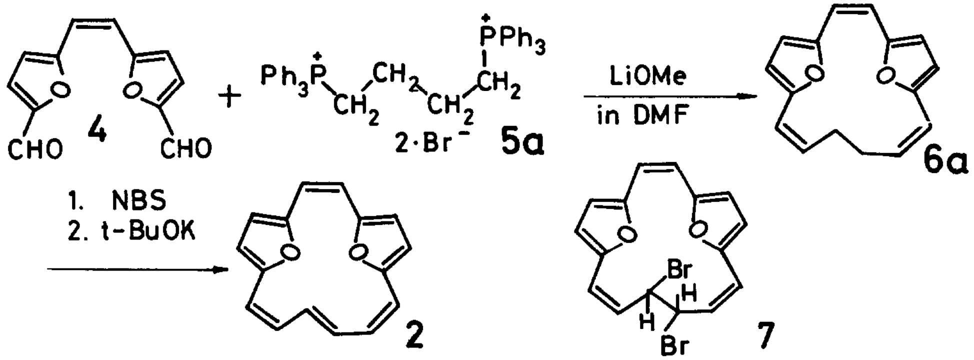
Inspection of the molecular models indicates that [16]annulene 1,4:7,10-dioxide 2 is an essentially planar 16π system and the close proximity of the oxygen atom to the inner hydrogen may fulfil the above requisite. We now report this



expectation was realized by the nmr measurements of 2. The structure of 2 seems to have a similar geometry to that of 1,9-bisdehydro[12]annulene 3,[4] whose acetylenic bonds are replaced by furan rings.

The double Wittig reaction of cis-α,β-bis(5-formyl-2-furyl)ethylene 4[5] with 1,4-tetramethylene triphenylphosphonium dibromide 5a[6] with lithium methoxide at 70° in DMF led to a mixture of products, which was separated by chromatography on silica gel with cyclohexane to give 13,14-dihydro[16]annulene 1,4:7,10-dioxide 6a as greenish yellow prisms, mp 145° (25%); molecular ion peak at m/e 238. The assignment of the di-cis stereochemistry is based upon the spin decoupling experiments. Irradiation at τ 7.96 (methylene protons) caused the collapse of the complex multiplets due to the olefinic protons adjacent to the methylene protons to a doublet centered at τ 3.80 (J = 12 Hz), which composed of an AB quartet with another doublet centered at τ 3.32 (J = 12 Hz), while irradiation of the τ 3.6-4.0 band at the position of the olefinic protons caused the collapse of the triplet at τ 8.00 to a singlet due to the methylene protons. The other signals of 6a confirmed its structure. The electronic spectrum in cyclohexane (Figure 2) showed maxima at 222 sh (ε 28,500), 227 (32,900), 277 (40,300), 286 (62,700), 365 (8,840), 375 (9,750), 387 (14,300), 400 (9,870) and 412 nm (12,400) It is of interest to note that a series of the characteristic fine structures appeared at 365-410 nm is in good accordance with the longer wavelength bands of [18]annulene 1,4:7,10:13,16-trioxide[7], and that the above characteristic bands were commonly observed in the spectra of the other seventeen and eighteen membered homologues (6b, and 6c), which were prepared analogously by the double Wittig reactions of 4 with 1,5-pentamethylene- and 1,6-hexamethylene triphenylphosphonium bromide (5b and 5c[8]), respectively [6b: mp 94-96, 1.1%; 6c: mp 146-148, 3%]**.

The monobromination of the dihydro[16]annulene 6a was carried out under several conditions. The best results were obtained by refluxing equimolar amounts of 6a and N-bromosuccinimide in CCl_4 under illumination of a uv lamp. After 6 hr, analysis of the reaction mixture (by gas chromatography) indicates almost conversion of the starting materials into the monobromo-dihydroannulene, accompanying some crystalline dibromo-product 7, mp 138, in less than 5% yield [molecular ion peak at m/e 396 ($C_{16}H_{12}Br_2$)].

Treatment of the monobrominated product, without isolation[8], with a saturated solution of t-BuOK in t-BuOH / THF (1:1) for 20 minute at 80° yielded a mixture of products (five products were detected by gas chromatography), besides unchanged 6a. Chromatography of the reaction mixture on silica gel (CCl_4) gave mainly a well separated violet band, as was recognized in the preparation of [16]annulene itself.[1] Collection and evaporation of the violet fractions afforded 2 as a dark brown solid, mp 167-70° (ca. 30% based on 6a). The structure of 2 was confirmed on the basis of the spectral and analytical data. The mass spectrum exhibited the expected molecular ion at m/e 236 (100%). The infrared spectrum (KBr) exhibited absorption at 790 cm^{-1} due to the *cis*-double bonds. The electronic spectrum in cyclohexane exhibited a doubly splitted maxima at 280 (ε 77,700) and 287 nm (81,700), along with a long tailing band at

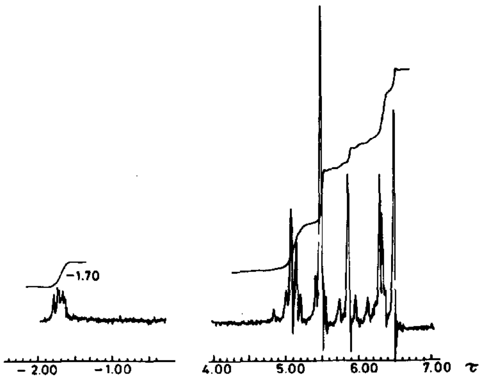


Figure 1. Nmr spectrum at 25° of 2, measured in CCl_4 at 60 MHz.

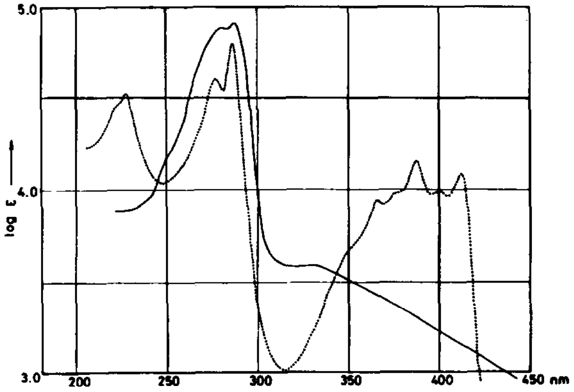


Figure 2. Electronic spectra of 2 (———) and of 6a (·····) in cyclohexane.

515-555 nm (ε 270), showing a complete accordance with the reported data of **1** and dehydro[16]annulenes.[1]

The nmr spectrum of **2** (25° in CCl_4) showed low field signals at τ - 1.70, assigned to the inner proton, and a series of unassignable multiplets at the relatively high field (τ 5.2- 6.5) due to the remaining outer protons of **2**, with relative intensities of ca. 1:11, clearly indicating the presence of a paramagnetic ring current. It was found that the separation of the inner and outer proton resonances of **2** is considerably wide-ranged as compared with that of [16]annulene itself, which resonated inner protons at τ - 0.43 and outer protons at τ 4.60 at - 120°.[2a] The nmr spectrum of **2** measured at 25° is not the average one due to the rapid interchange of the inner and outer hydrogens of the *trans* double bonds, because the spectrum does not essentially change on cooling to - 78° (in perdeuterio acetone).

The conversion of **2** into the corresponding anion radical and the dianion is our next synthetic challenge.

REFERENCES AND FOOTNOTES

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** Satisfactory elemental analytical data were obtained for all new compounds.

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