Tetrahedron Letters No. 51, pp 4859 - 4862, 1971. Pergamon Press. Printed in Great Britain.

THE DEMONSTRATION OF A DIAMAGNETIC AND PARAMAGNETIC RING CURRENT IN FULLY UNSATURATED 15-MEMBERED CYCLIC SYSTEMS

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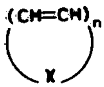
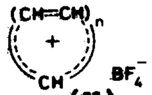
(**Received in Japan 6 November 1971; received in UK for publication 16 November 1971**)

IF planarity can be affirmed in the fully unsaturated cycles of the type (I) and (II), pmr spectra measured in these groups of compounds are expected to show a striking contrast[1], since (I) would be aromatic, exhibiting a diamagnetic ring current, provided n is 2, 4, 6···, and antiaromatic, if n is 3, 5, 7,··· , exhibiting a paramagnetic ring current[2]. Conversely, in (II), the feature is quite opposite, being these groups of compounds should be aromatic, when n is 3, 5, 7,···.

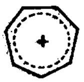


(I)

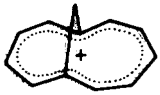
Ia : X=O, n=7



(II)



(III)



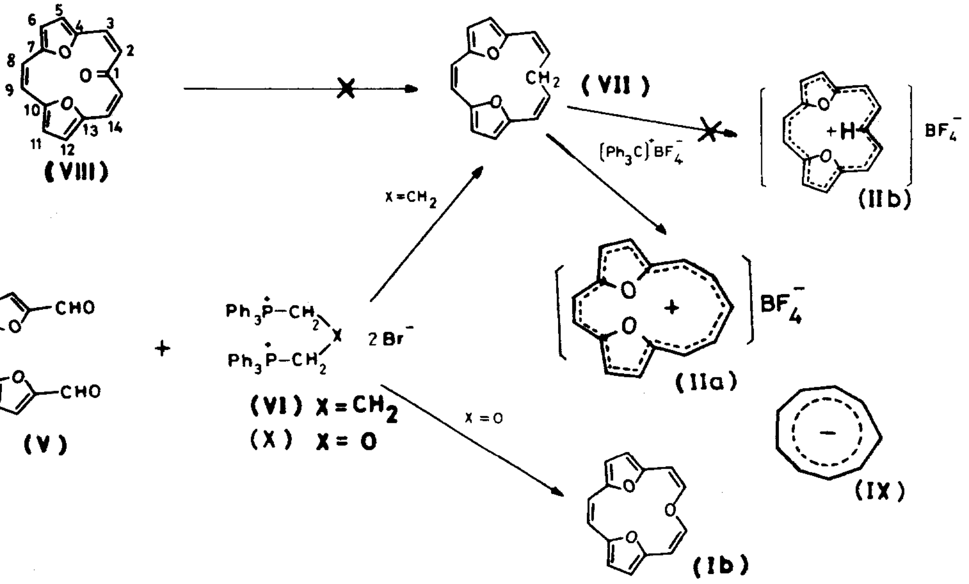
(IV)

The tropylium cation (III) [3,4] is a well-known member (n = 3), and bicyclo[5.4.1]dodecapentaenylium cation (IV)[5] is the next higher member (n = 5) representing (II). However, no higher cyclic members exhibiting ring current than the fully unsaturated 11-membered ring have been prepared[6]. Therefore, it is of interest to prepare the 15-membered fully unsaturated oxygen heterocycle (Ia) as well as the pentadecaheptaenylium cation (II, n = 7) to determine whether they would also show the corresponding ring current to their electron systems, keeping geometry of the 15-membered skeletons unchanged. We prepared 1-oxa-4:7,10:13-dioxido-cyclotetradecaheptaene (Ib) and 4:7,10:13-dioxido-cyclopentadecaheptaenylium salt (IIa), and realized our object, since the pmr spectrum of (Ib) indeed exhibited a paramagnetic, and that of (IIa) a diamagnetic ring current, respectively.

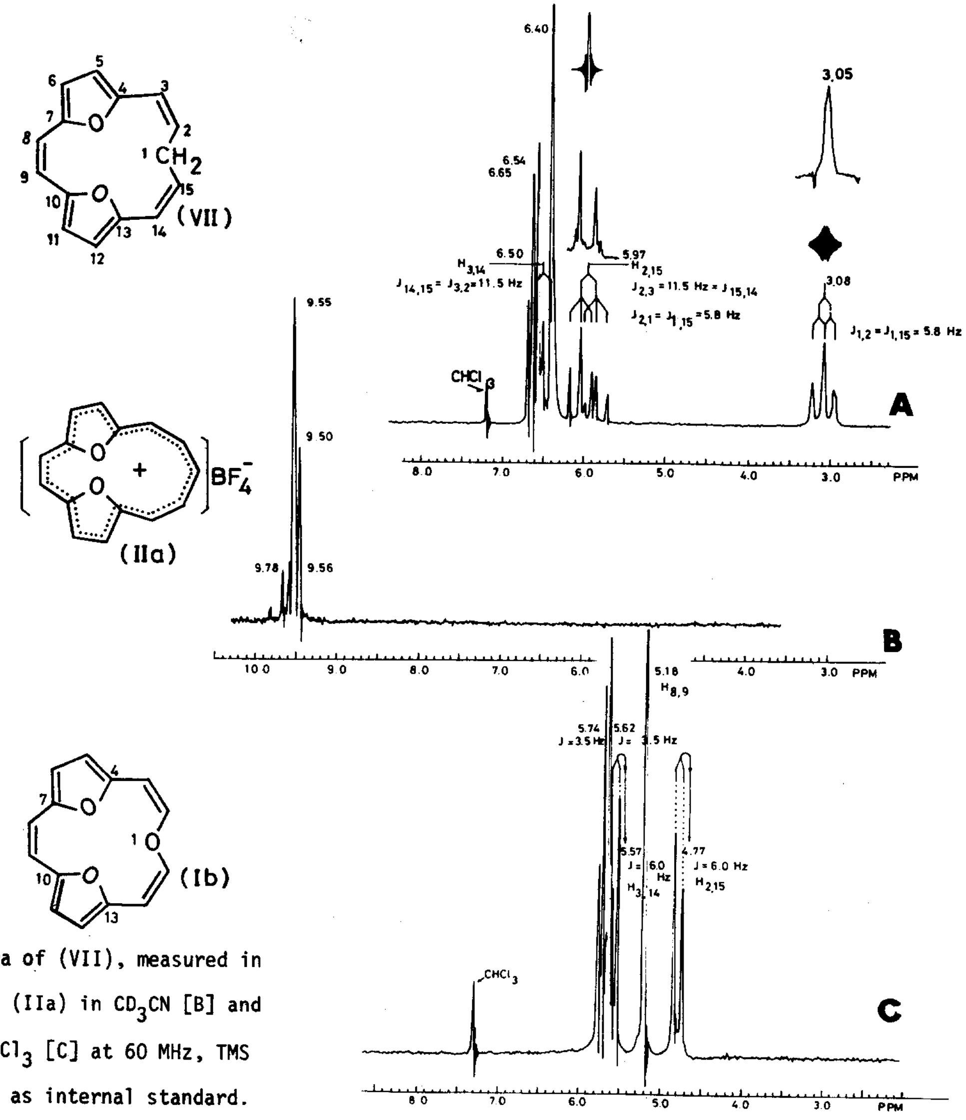
The Wittig reaction of cis-α,β-di(5-formyl-2-furyl)ethylene (V)[7] and trimethylene-1,3-(triphenylphosphonium)bromide[8] (VI) in DMF with methanolic lithium methoxide at 90° under N_2 gave a mixture of products, which were separated by chromatography on silica gel. Substance (VII) was isolated in 11.2 % yield, yellow leaflets (from EtOH), mp 110°; mass spectrum, molecular ion at m/e 224; uv max (EtOH) 227 (ϵ 40,200), 272 sh (41,800), 280 (55,200) and 383 nm (10,300); ir (KBr) 1176, 1023, 800 cm^{-1}. The pmr spectrum of (VII) confirmed the assigned structure (see FIG. A). An irradiation at δ 3.08 ppm transformed the olefinic protons into an AB system made up of 4 sharp lines (J = 11.5 Hz), supporting the cis configuration, and an alternate irradiation at δ 5.95 ppm transformed the methylene protons into a somewhat broadend singlet at δ 3.05 ppm. There are two possible conformations of (VII), one with methylene group tilted away from the adjacent double bonds, and the another completely in the plane. We predicate the latter is more preferable on the basis of the magnetic equivalence of the methylene protons. In addition, the spectrum effectively eliminates the existence of a homoaromatic ring current[9].

Another attempt obtaining (VII) by the Wolff-Kishner reduction of 2,8,14-cis,cis,cis-4:7,-10:13-dioxido[15]annulenone[10] (VIII) was unsuccessful.

Substance (IIa) was produced in good yield by treating the pure (VII) with equimolar $[Ph_3C]^+ BF_4^-$ in acetic anhydride, beautiful orange red crystals, mp 260° (from AcOH). The ionic structure was assigned on the basis of the following spectral evidence; uv max (30% H_2SO_4) 230 (21,500), 290 (12,500), 331 (110,000), 345.5 (108,000), 481 (8,200) and 503 nm (8,420), showing a



quite similar spectrum with that of 1-hydroxy-2,8,14-cis,cis,cis-4:7,10:13-dioxido-[15]-annulenyl cation, which is produced by dissolving (VIII) in H_2SO_4. The pmr spectrum of (IIa) in CD_3CN was surprisingly simple and the dramatic down field shifts of all the outer protons confirmed the existence of an induced diamagnetic ring current (see FIG. B). Since, apparently, we could not observe a high-field resonance due to an inner proton in the spectrum, it follows that the structure must be the all-cis one (IIa), and not be (IIb) [see formula]. There is no



Pmr spectra of (VII), measured in $CDCl_3$ [A], (IIa) in CD_3CN [B] and (Ib) in $CDCl_3$ [C] at 60 MHz, TMS being used as internal standard.

reason why the structure (IIa) should not be planar, since (IIa) has a very similar geometry to the all-cis cyclononatetraene anion (IX), and the angle strain in (IIa) is expected to be less severe than the steric overcrowding, due to the inner proton in the structure of (IIb)[11].

The Wittig reaction of the dialdehyde (V) and dimethylether-α,α'-bis(triphenylphosphonium-bromide) (X)[12] with lithium methoxide under the previously mentioned conditions, followed by separation as before, gave (Ib) in 15.3 % yield, mp 255° (decomp); mass spectrum, molecular ion at *m/e* 226; uv max (EtOH) 227.5 (24,300), 254 (49,800), 277.5 (38,800) and 465 nm (1,900). As expected, the chemical shift of the H_8,H_9 protons is ca. 1.20 ppm to the higher field relative to that of the corresponding protons of (VII), a suitable cyclic model in which no ring current can occur (see FIG. C). An effect that caused such a shielding is best explained by a paramagnetic ring current. A smaller coupling constant of H_2,H_3 and $H_{14,15}$ protons ($J_{2,3} = J_{14,15} = 6.0$ Hz) is obtained as compared with that of the corresponding protons of (VII) ($J_{2,3} = J_{14,15} = 11.5$ Hz). This serves to emphasize that (Ib) is not polyolefinic but antiaromatic as the consequence of the possible overlap of the oxygen lone pair with the heptaene system, although the overlap leads to an increase in the energy of the system.

Acknowledgement The authors are deeply grateful to Professor Franz Sondheimer, University College London, for reading this manuscript and offering valuable discussions.

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