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HIGHER HOMOLOGUES OF CYCLOHEPTATRIENE, TROPYLIUM ION AND OXEPIN[1]

THE DEMONSTRATION OF A DIAMAGNETIC AND PARAMAGNETIC RING CURRENT IN NOVEL [15]ANNULENE SYSTEMS

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Abstract—Syntheses of 4,7:10,13-dioxido-cyclopentadecaheptaene (2.4.6.8.10.12.14) **8**, 4,7:10,13-dioxido-cyclopentadecaheptaenyl tetrafluoroborate **10**, and 1-oxa-4,7:10,13-dioxido-cyclopentadecaheptaene (2.4.6.8.10.12.14) **13** are described. As expected, the NMR spectrum of **10** exhibited a marked diamagnetic ring current, and that of **13** a paramagnetic ring current. These [15]annulenes **8**, **10**, and **13** are looked upon as the corresponding higher member of cycloheptatriene, tropylium ion, and oxepin, respectively.

Attempted preparation of sulphur containing 1-thia[15]annulene was unsuccessful, presumably because of its increased antiaromatic character.

An "odd" annulene can be characterized not only by the number of double bond *n*, but also by a grouping or heteroatom *X*, such as $>C{=}O$, $>CH_2$, O, S and NR. If planarity is affirmed both in heteroannulene **1a** (X = heteroatom) and annulenone **1a**[2,3] ($X{=}>C{=}O$), the properties of these systems are expected to show a striking contrast, since heteroannulene should be diatropic,[2a] when *n* is 2,4,6..., and paratropic,[2a] when *n* is 1,3,5..., while annulenone should be diatropic, when *n* is 1,3,5..., and paratropic when *n* is 2,4,6.... Completely delocalized aromatic annulenyl salt **1b** is also capable of existence, when *n* is an even integer with a certain limit.

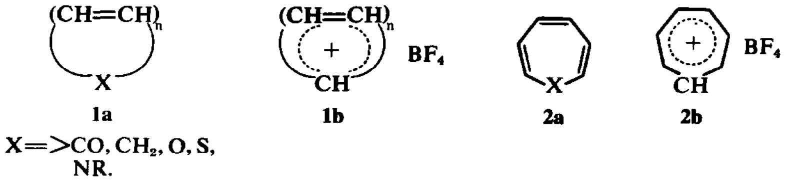
It is possible to line up all the representative "odd" annulenes belonging to 7-membered ring system, since tropone **2a**† ($X{=}>C{=}O$), tropylidene **2a**[5] ($X{=}>CH_2$), tropylium ion **2b**[5] and heterotropylidene[6] such as oxepin **2a** (X=O) are known.

Vogel[7] *et al.* have synthesised 11-membered annulene system, beginning with 4,9-methano[11]-annulenones **3a**[8,9] ($X{=}>C{=}O$, R=H or OH), bicyclo[5.4.1]dodecapentaene **3a**[10] (R=H, $X{=}CH_2$), bicyclo[5.4.1]dodecapentaenylium ion **3b**[11], and 4,9-methano-hetero[11]annulenes **3a**[12a] (R=H, X=O and S).

In view of our previous syntheses of 4,7:10,13-dioxido[15]annulenones **5a** and **5b**,[13] it appeared of interest to prepare the missing members of the [15]annulenes and to examine their properties. The only previously known [15]annulene derivatives are 4,5-tetramethylene-2,6,8,14-tetradehydro[15]-annulenone **4** and its aromatic cation.[14] In this paper, we describe the syntheses of 4,7:10,13-dioxido-cyclopentadecaheptaene(2.4.6.8.10.12.14) **8**, 4,7:10,13-dioxido-cyclopentadecaheptaenyl tetrafluoroborate **10** and 4,7:10,13-dioxido-1-oxa[15]-annulene **13**, and show that the NMR spectrum of **10** exhibits a diamagnetic ring current, and that of **13** a paramagnetic ring current.

RESULTS AND DISCUSSION

The double Wittig reaction of *cis*-α,β-di(5-formyl-2-furyl)ethylene **6**[15] with trimethylene-1,3-triphenylphosphonium bromide **7**[16] with lithium methoxide



1a **1b** **2a** **2b**

$X{=}>CO, CH_2$, O, S, NR.

SCHEME 1

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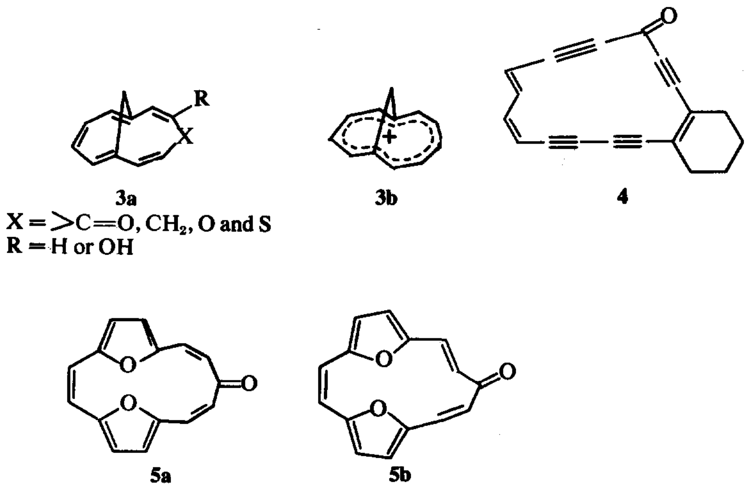
†The aromaticity of tropone has been questioned recently.[4]



3a
X = >C=O, CH$_2$, O and S
R = H or OH

3b

4

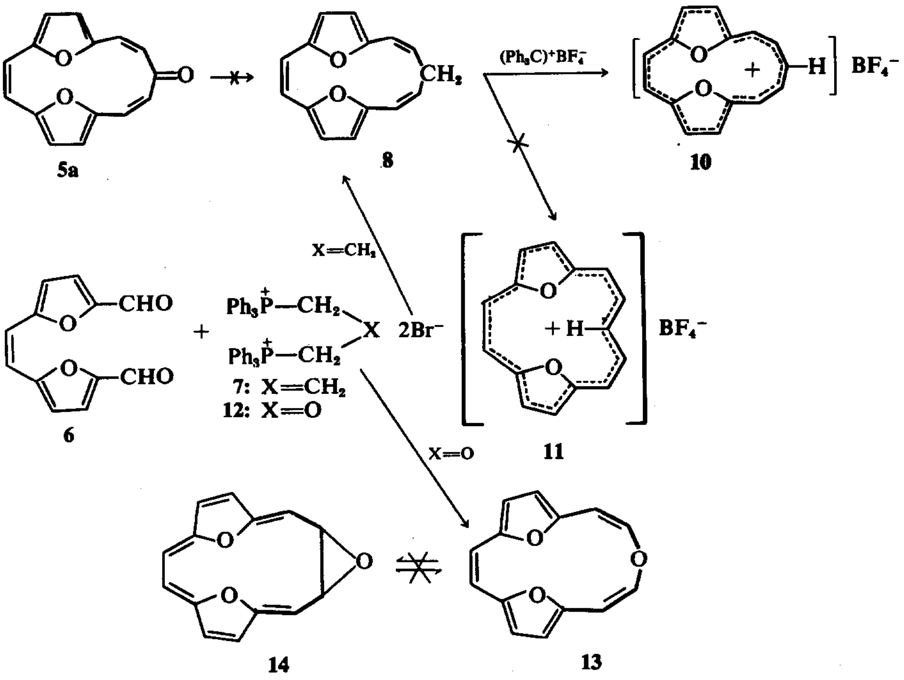
5a

5b

SCHEME 2

in DMF at 90° gave a mixture of products, which was separated by chromatography on silica gel. From the initial fraction compound **8** was isolated as yellow leaflets in 11% yield, mp 110°; M$^+$ *m/e* 224. The NMR spectrum (Fig 1a) exhibited 2H doublet centered at δ 5·97 ppm (H-2 and H-15 protons, $J_{1,2} = J_{1,15} = 5{\cdot}8$ Hz), 2H doublet centered at δ 6·50 ppm (H-3 and H-14 protons, $J_{2,3} = J_{14,15} = 11{\cdot}5$ Hz), 2H singlet at δ 6·40 ppm (H-8 and H-9 protons), two 2H AA′ systems each centered at δ 6·54 and 6·65 ppm (furan ring protons, J = 4 Hz), and 2H triplet centered at δ 3·08 ppm ($J_{1,2} = J_{1,15} = 5{\cdot}8$ Hz) due to the methylene protons.

The chemical shifts and coupling constant of the methylene protons of **8** were entirely analogous to those of the methylene protons of cyclononatetraene **9**[17] [triplet at δ 3·05 ppm with J = 5·5 Hz]. As depicted in Fig 1a, spin decoupling experiments revealed that **8** has the all *cis*-configuration, because an irradiation at δ 3·08 ppm transformed the



5a

8

10

6

11

14

13

SCHEME 3

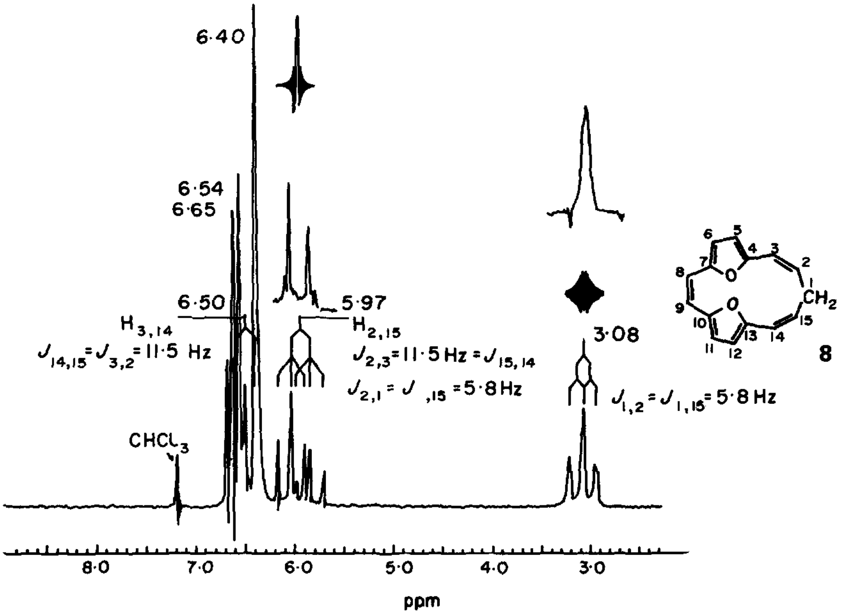


Fig 1a. NMR spectrum of **8**, in $CDCl_3$ at 60 MHz.

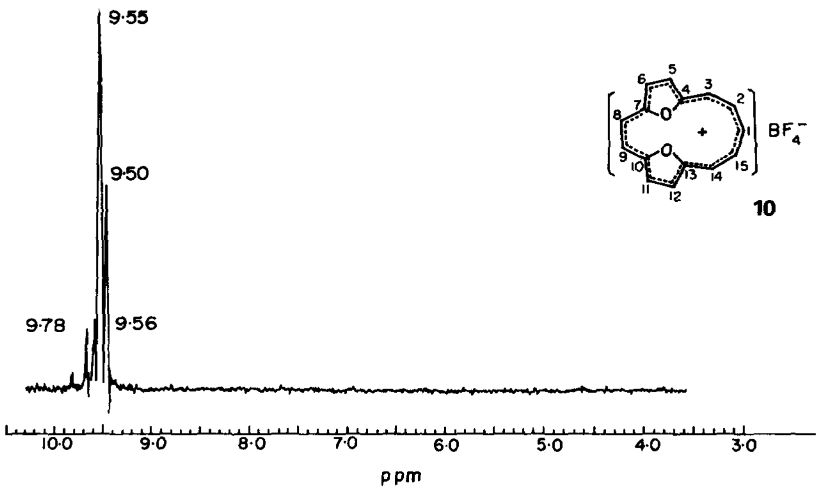
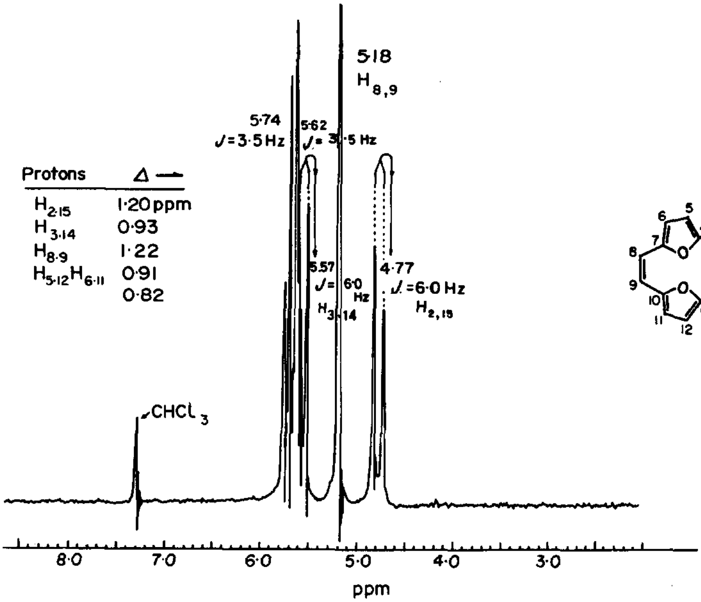
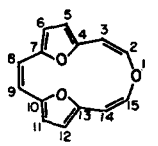


Fig 1b. NMR spectrum of **10**, in CH_3CN at 60 MHz.

olefinic double triplets into a doublet with *cis* coupling constant ($J = 11·5$ Hz). Although **8** has a very similar geometry, in part, to cyclononatetraene **9**[17] (Scheme 4), Dreiding and space-filling models indicate that **8** is considered to be a nonbuckled, strain-free homo[14]annulene dioxide, because **8** exhibits its highest wavelength maximum at 383 nm (in EtOH) (ϵ 10,300) together with the main absorptions at 227 nm (ϵ 40,200) and 280 (55,200), while **9** shows no appreciable absorption maxima corresponding to the conjugated tetraene chromophor [245 sh (ϵ 2,600)].[17]

Compound **8** is a potential precursor of aromatic [15]annulenyl salt **10**. The hydride ion abstraction of **8** by trityl fluoroborate in acetic anhydride *in situ technique*[18] afforded the corresponding tetrafluoroborate **10**, in an almost quantitative yield, orange red crystals, m.p. 260°, which were stable in air and light for a long time at room temperature. The ionic structure of **10** was confirmed on the basis of the spectral evidence, as well as the elemental analysis. The electronic spectrum in 30% H_2SO_4 was characterized by a pair of intense "Soret band"-like[23] absorptions at 331 (ϵ 110,000) and 345·5 nm (108,000) with other long tailing bathochromic bands at 481 (ϵ 8,260) and 503 nm





13

Fig 1c. NMR spectrum of 13, in $CDCl_3$ at 60 MHz.

(8,420) [Fig 2b]. The tetrafluoroborate **10** is a 14π-electron system, and should be aromatic. This could be confirmed by the dramatic downfield shifts of the outer protons, which appeared at δ 9·56–9·78 ppm [Fig 1b]. The diamagnetic ring current of **10** was found to be stronger than those of tropylium ion **2b**[19] [δ 9·09 ppm], bicyclo[5.4.1]dodecapentaenyl ion **3b**[11] [δ 9·6–8·3 ppm], and cyclononatetraenide anion **9a**[19] [δ 7·04 and 6·85 ppm].

Although methylene group inversion of **8** may admit to take another "caved-in" tetrafluoroborate **11** (Scheme 3), this structure proved not to be the case, because the NMR spectrum of **10** does not possess a highfield resonance due to the inner proton (Fig 1b). Therefore, we may conclude that the angle strain of **10** is smaller than that of **11**. After some experimentation, it was found that the [15]-annulenyl cation was generated most simply by the

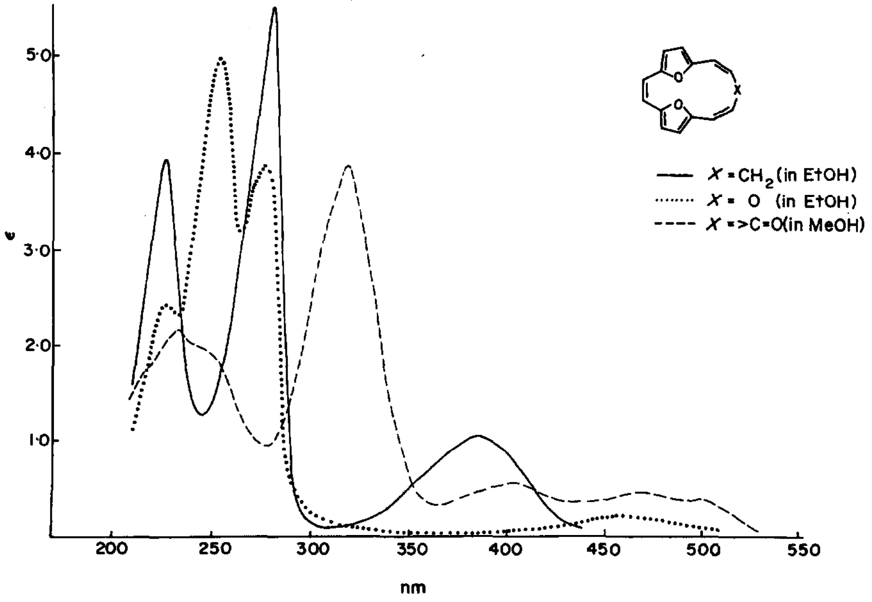


Fig 2a. The electronic spectra of **5a**, **8**, and **13**.

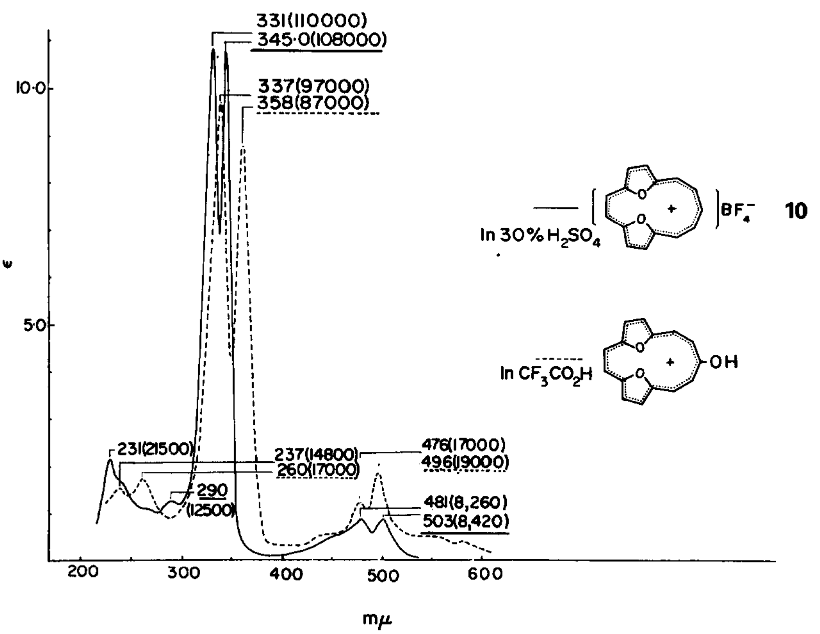
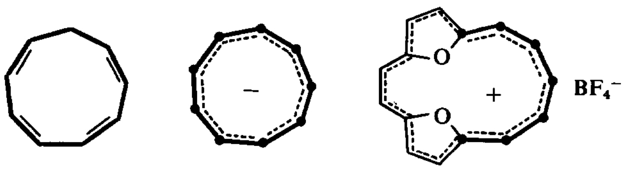


Fig 2b. Electronic spectra of 4,7:10,13-dioxido-cyclopentadecaheptaenyl tetrafluoroborate **10** (solid line, in 30% H_2SO_4) and 1-hydroxy-4,7:10,13-dioxido-cyclopentadecaheptaenylium cation (dotted line, in CF_3COOH).



9 **9a** **10**

SCHEME 4

reaction of **8** with conc H_2SO_4 in 31% yield (determined spectrophotometrically), indicating the easy formation of **10**.

In order to prepare yet unknown hetero[15]-annulenes, we investigated the Wittig reaction of the dialdehyde **6** and dimethylether-α,α′-bis(triphenylphosphonium bromide)[20] **12** with lithium methoxide under previously mentioned conditions. 1-Oxa-4,7:10,13-dioxido-cyclopentadecaheptaene (2.4.6.8.10.12.14) [1-oxa-[15]annulene-4,7:10,13-dioxide] **13** was obtained in 15·3% yield, m.p. 255° (dec), as reddish scales. The structure was established by mass spectrum and the elemental analysis, as well as by other spectral data. The mass spectrum exhibited molecular ion at *m/e* 226. The IR spectrum exhibited bands at 1220, 1110 cm^{-1} (enol ether). The NMR spectrum of **13** (in $CDCl_3$) consisted of a 4H AB system centered at δ 4·77 and 5·57 ppm (H-2, H-3 and H-14, H-15 protons, J = 6·0 Hz), a 2H singlet at δ 5·18 ppm (H-8, H-9 protons) and 4H AA′ system at δ 5·62 and 5·74 ppm (furan protons, J = 3·5 Hz), excluding the occurrence of valence tautomeric isomerism **13** $\rightleftarrows$ **14** [Scheme 3 and Fig 1c].

Apparently, 1-oxa[15]annulene **13** is looked upon as a higher homologue of oxepin. If the system is planar, and the oxygen lone pair contributes to make a π-excess system, **13** should be paratropic, sustaining a paramagnetic ring current. As expected, the NMR spectrum exhibited upfield shifts by δ 0·82–1·22 ppm as compared with that of **8** (Fig 1c), indicating the existence of a paramagnetic ring current. To the best of our knowledge, **13** is considered to be the first example of antiaromatic [15]heteroannulene containing one heteroatom.*

In order to obtain sulphur containing [15]annu-

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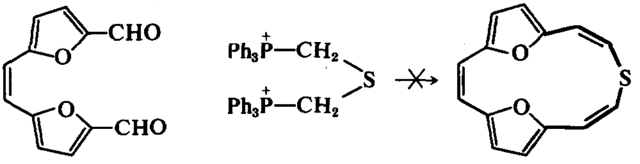
*Thieno[3,4-d]thiepin, prepared by J. S. Ponticello and R. H. Schlessinger [*J. Am. Chem. Soc.* **89**, 7138 (1967)], has been described as a completely delocalized antiaromatic 12π electron system, based upon its highfield resonance due to a paramagnetic ring current, as well as its X-ray determination.



6 **15** **16**

SCHEME 5

lene **16**, the Wittig reaction between the dialdehyde **6** and dimethylthioether-α,α′-triphenylphosphonium bromide **15**[21] was carried out.

Unfortunately, no detectable amount of **16** could be obtained, despite the fact that related Wittig reactions have been carried out successfully.[12a,b] In the course of chromatography, resinification occurred rapidly on silica gel, and earlier fractions of the eluant become cloudy and then deposited yellow polymeric material, which remained at the spotted place, when the TLC plate was developed with cyclohexane. The NMR spectrum of this polymeric material (in $CDCl_3$) showed complex broadened overlapping resonances at the ordinary olefinic region.* We consider, the elusiveness may be presumably due to the increased antiaromaticity of **16**, based on a decreased electronegativity of the S atom.†

EXPERIMENTAL

General procedures. M.ps were determined on a Yanagimoto hot-stage apparatus and are uncorrected. IR spectra: as KBr disc on a Koken 301 spectrophotometer. Electronic spectra: on a Hitachi-Perkin-Elmer 139 spectrophotometer. NMR spectra: on a Nihon Denshi H-60 spectrometer (TMS used as internal standard). Mass spectra: on a Nihon Denshi OISG spectrometer (70 eV, direct inlet system). All chromatography columns were prepared with cyclohexane using Mallinckrodt Silic-AR (100–200 Mesh).

4,7:10,13-*Dioxido-cyclopentadecaheptaene*(2.4.6.8.10.12.14) **8**. A mixture of **6**[15] (2·16 g, 10 mM) and **7**[16] (8·0 g, 11 mM) in absolute DMF (150 ml) was heated to 90°, and a soln of LiOMe (prepared from 280 mg Li) in abs MeOH (35 ml) was then added dropwise during 3 hr at 90° through a peristaltic pump with violent stirring in an atmosphere of dry N_2. The soln was stirred at 90° for further 1 hr and then evaporated the most of solvent *in vacuo*, and diluted with water. The mixture was extracted with benzene, and the combined extracts were washed several times with water, dried with Na_2SO_4, and evaporated. Ether (150 ml) was added to the residue to separate triphenylphosphineoxide, which was filtered off. The ethereal soln was evaporated, and the residue was dissolved in a minimum amount of cyclohexane, and chromatographed on a column of silica gel with cyclohexane, 25 ml fractions being collected. The first three fractions on evaporation gave **8** (250 mg, 11·2%), m.p. 110–111°, yellow needles; IR spectrum (KBr), bands at 1176, 1023, 961, 952, 901, and 800 cm^{-1}; electronic spectrum, λ_{max} (EtOH) 227 nm (ϵ 40,200), 272 sh (41,800), 280 (55,200) and 383 (10,300); PMR spectrum, see Discussion and Fig 1a; mass spectrum, molecular ion at *m/e* 224. (Found: C, 80·00; H, 5·31. Calcd for $C_{15}H_{12}O_2$: C, 80·33; H, 5·39%).

4,7:10,13-*Dioxido-cyclopentadecaheptaenyl tetrafluoroborate* **10**. To a soln of triphenylcarbinol (105 mg, 0·4 mM) and 40% hydrofluoroboric acid (0·5 ml) in Ac_2O (4 ml) was added to a soln of **8** (59 mg, 0·26 mM) in Ac_2O (0·5 ml) under cooling. After 10 min ether (5 ml) was added, and the separated crystals were collected, washed with ether, and recrystallized from AcOH, m.p. *ca* 270° (dec), 60 mg, as reddish orange prism; IR spectrum, bands at 1567, 1310, 1250, 1178, 1156, 1056, 940, 866 and 838 cm^{-1}; electronic spectrum, λ_{max} (30% H_2SO_4) 231 (ϵ 21,500), 290 (12,500), 331 (110,000), 345·5 (108,000), 481 (8,260) and 503 nm (8,240); NMR spectrum, see Discussion and Fig 1b. (Found: C, 57·79; H, 3·50. Calcd for $C_{15}H_{11}O_2BF_4$: C, 58·00; H, 3·54%).

1-*Oxa*-4,7:10,13-*dioxido-cyclopentadecaheptaene* (2.4.6.8.10.12.14.) **13**. A soln of **6** (2·16 g, 10 mM) and **12**[20] (8·0 g, 11 mM) in abs DMF (120 ml) was heated at 70°, and the product was isolated and chromatographed, as described above for the preparation of **8**. The crystalline solid, obtained from earlier fractions, was recrystallized

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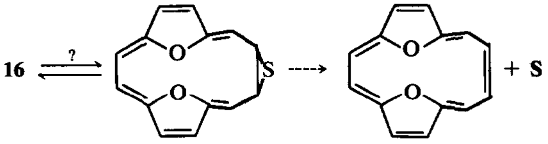
*Very recently, 1-thia[17]annulene-trioxide and 1-thia[17]annulene dioxide-sulphide have been prepared as other examples of bridged heteroannulene containing furan rings [T. M. Cresp and M. V. Sargent, *Chem. Comm.* 1458 (1971)]. Although these compounds are considered to be planner and isoelectronic with aromatic [18]annulene trioxide,[22] they were found to have no ring current, presumably because the expected delocalization energy of the 17-membered ring system is less than the sum of the delocalization energy of the incorporated furan rings.

†A referee kindly suggested another conceivable reason for the unsuccessful preparation of **16**. This involves a sulphur extrusion of valence isomeric compound **17** to give a 14π electron system **18**, which may be unstable by the loss of resonance energy of two furan nuclei.

We previously attempted the synthesis of **18** by hydrogen peroxide oxidation of **10** according to the procedure of Volpin *et al.* [M. E. Volpin, D. N. Kursanov, and V. G. Dulova, *Tetrahedron* **8**, 33 (1960)], but without success.



17 **18**

We cannot provide conclusive evidence of valence isomerism **16** ⇌ **17**, because we could not obtain any neat NMR spectrum of the reaction products prior to the chromatographic purification.

from cyclohexane to yield **13**, (346·8 mg, 15·3% yield), as deep-red scales, m.p. 255° (decomp); IR spectrum (KBr), 1621, 1220, 1110, 1025, 1015, 951, 788, 760 and 748 cm^{-1}; electronic spectrum (EtOH) 227·5 (ϵ 24,300), 254 (49,800), 277·5 (38,800) and 465 nm (1,900); NMR spectrum, see Discussion and Fig 1c; mass spectrum, molecular ion at *m/e* 226. (Found: C, 74·21; H, 4·40. Calcd for $C_{14}H_{10}O_3$: C, 74·33; H, 4·46%).

Wittig reaction between the dialdehyde **6** *and dimethylthioether-α,α′-bis-triphenylphosphonium bromide* **15**. A soln of **6** (2·16 g, 10 mM) and **15**[21] (prepared and purified by Dimroth's procedure) (8·2 g, 11 mM) in abs DMF was treated as described above for the preparation of **8** and **13**. However, no detectable amount of the sulphur-containing product could be obtained, despite the fact that the Wittig reaction has been carried out successfully (Discussion).

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