Oxygen Bridged [19]- and [21]-Annulenones

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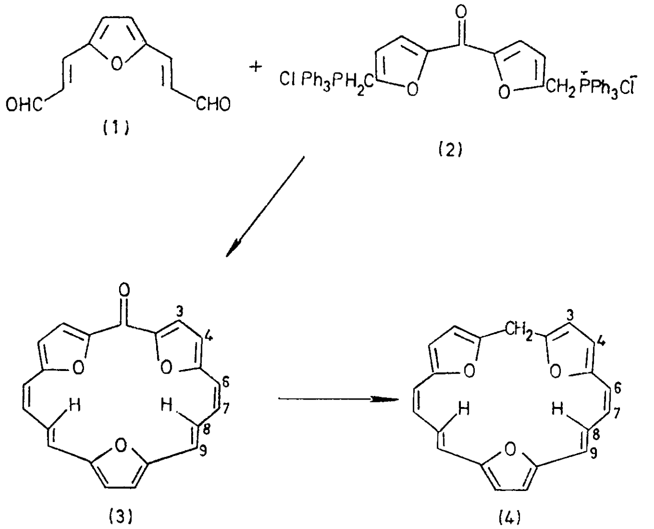
Summary The synthesis of two oxygen-bridged [21]-annulenones and an oxygen-bridged [19]annulenone is described; evidence is adduced to suggest that the former are atropic whilst the latter is diatropic.

Annulenones fall into two groups, those with a $(4n + 1)$-membered ring and $4n\pi$ electrons, which are potentially paratropic, and those with a $(4n + 3)$-membered ring and $(4n + 2)\pi$ electrons which are potentially diatropic. The largest known examples of the $(4n+1)$ series contain 17-membered rings,[1] and in the $(4n+3)$ series the largest known examples contain 15-membered rings.[2] It was predicted[3] that the limiting ring size for aromaticity in the $(4n+2)$ annulene series would be reached at [26]annulene although doubt has been cast on this prediction by the synthesis of a diatropic monodehydro[26]annulene.[4] Similarly, the question of limiting ring size for the paratropicity of $4n$ annulenes has yet to be resolved. Little theoretical work[5] has been reported on the ring size limitation of the diatropicity and paratropicity in annulenones.



We report the synthesis and n.m.r. spectroscopic properties of a potentially diatropic [19]annulenone and of two potentially paratropic [21]annulenones.

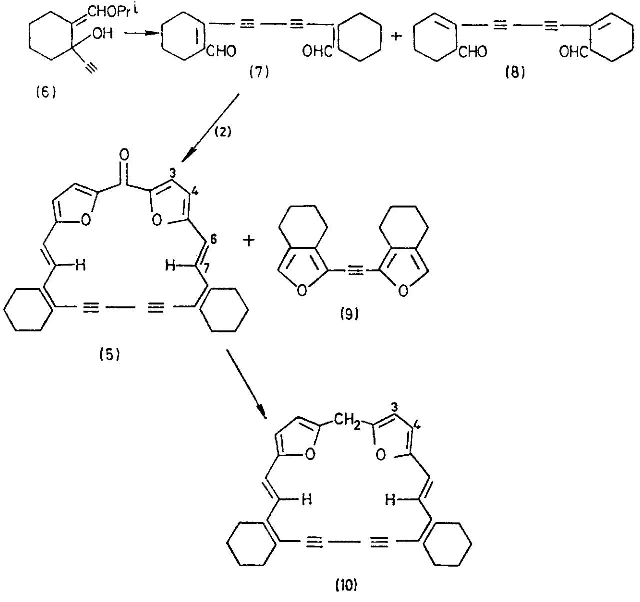
Wittig reaction of the diacrolein **(1)**[6] and the bis-phosphonium salt **(2)**[1c] by the usual method[1c] yielded 2,5: 10, 13:18, 21-triepoxy-6, 16-di-*cis*-8, 14-di-*trans*-[21]annulenone **(3)**† as a red gum (15%). Reduction of **(3)** with LiAlH$_4$/AlCl$_3$ afforded the homoannulene **(4)**† (*ca.* 95%) as orange needles, m.p. 142—144°.

Table. Chemical shifts (τ, CDCl$_3$, 90 MHz) for protons of macrocycles

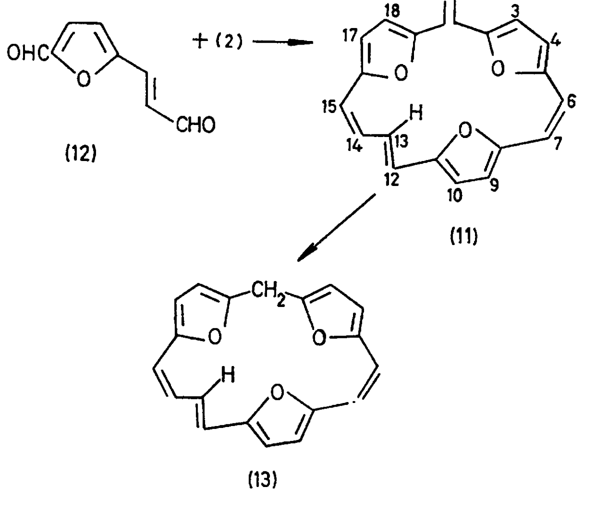
Compound	Protons						
	3	4	6	7	8	9	11
(3)[a]	2·60	3·44[b]	3·97[b]	3·77	1·95	3·96	3·95
(4)[c]	4·04	4·04	4·34	4·12	0·89	4·03	4·28
(5)	2·76	3·68	2·27[d]	2·33[d]	—	—	—
(10)	3·99	3·99	3·85	1·86	—	—	—

[a] These assignments were made by first-order analysis of the results of INDOR experiments monitoring at the frequencies of 3-, 4-, and 8-H. [b] The coupling constant $J_{4,6}$ 1·0 Hz confirms the *cis,trans* stereochemistry of the 6,7,8,9-diene system. [c] These assignments were made by double irradiation at the methylene protons and by INDOR experiments monitoring at the frequency of 8-H. [d] These assignments may be reversed.

In the n.m.r. spectrum of **(3)** (see Table) the internal protons (8-H) resonate at lower field than the external protons (6-, 7-, and 9-H). That this is not due to a paramagnetic ring current in **(3)** is apparent from the n.m.r. spectrum of the derived homoannulene **(4)** where the internal protons (8-H) resonate at even lower field than in **(3)**. The deshielding of the internal protons (8-H) in **(3)** and **(4)** is presumably due to two effects: the proximity of the inner protons to each other, and to some extent proximity of the inner protons to the furan oxygens.[7] Thus the [21]-annulenone **(3)** appears to be atropic.



To investigate the possible paratropicity of [21]annulenones we have synthesised the bisdehydro[21]annulenone **(5)**. Oxidative coupling of the acetylenic alcohol **(6)**[8]† gave **(7)**† (37%), m.p. 91—92·5°, as well as the isomeric dialdehyde **(8)**† (8%) m.p. 109—110°. Wittig reaction of **(7)** and **(2)** in DMF with 1,5-diazobicyclo[4,3,0]non-5-ene as base[9] gave **(5)** (12%) and **(9)** (6%).†



The annulenone **(5)**† formed maroon prisms, decomp. > 270° without melting. LiAlH$_4$/AlCl$_3$ reduction of **(5)** afforded the homoannulene **(10)**† (90%) as yellow prisms,

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† All new compounds gave satisfactory elemental analyses or high resolution mass spectral molecular weights. Where spectroscopic data are not quoted these were in agreement with the assigned structure.

m.p. 270—271° (decomp.). The atropicity of (**5**) follows from its n.m.r. spectrum and the lower field resonance of the inner protons (7-H) of homoannulene (**10**) compared with the inner protons (7-H) of (**5**).

From these results it appears that in the $(4n+1)$-membered ring annulenones the ring size becomes important at $n = 5$.

In order to investigate the properties of the higher $(4n + 3)$ annulenone series we have synthesised 2,5:8,11:16,19-triepoxy-6,14-di-*cis*-12-*trans*-[19]annulenone (**11**). Wittig reaction between the acrolein (**12**)[6] and the bisphosphonium salt (**2**) afforded the [19]annulenone (**11**)† (3%) as red prisms, m.p. 208—209°; τ($CDCl_3$, 90 MHz) 1·86, 2·87, and 2·07, 2·95 (2 × ABq, 3-, 4-, and 18-, 17-H), 2·61 (d, 12-H), 3·01 (dd, 14-H), 2·63—3·02 (m, 6-, 7-, 9-, 10-, and 15-H), and 4·88 (dd, 13-H).

$LiAlH_4/AlCl_3$ reduction of (**11**) gave the homoannulene (**13**)† (93%) as a gum. The highly complex n.m.r. spectrum of (**13**) was not amenable to analysis; τ 3·22—3·67 (m, furanoid and olefinic H) and 5·95 (s, CH_2).

That (**11**) is diatropic is demonstrated by the high field resonance of the internal proton (13-H) compared to the adjacent (12- and 14-H) external protons, and to all the olefinic protons of (**13**).

It is therefore concluded that the ring size limitation for diatropicity in $(4n + 3)$-membered ring annulenones lies beyond $n = 4$.

(*Received*, 6*th September* 1973; *Com.* 1253.)

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