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# SYNTHESIS OF A DI-OXYGEN BRIDGED [18]ANNULENE: A NEW EXAMPLE OF STRONGLY DIATROPIC [18]ANNULENE WITH A TWISTED PERIMETER

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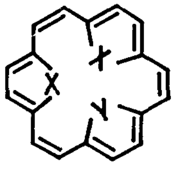
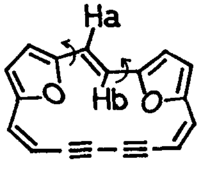
Abstract: The synthesis of 1,4:11,14-di-oxa-5,9,17-tri-*cis*-7,15-di-*trans*[18]annulene 4, whose periphery is forced to be twisted by two oxygen bridges is described.

Ever since [18]annulene tri-oxide 1a[1] was reported as the first example of tri-bridged [18]-annulene, consequences of the reduction of the number of bridges in the system have not been studied until 2[4] and 3[5] were reported recently. These studies indicated that the more interesting aspects of bridged annulene containing furan rings come from di-bridged annulene series rather than from tri-bridged ones: viz., 2 proved to be a "mobile dehydroannulene", in which exchange, coalescence, and freezing of the protons on the *trans* double bond (Ha and Hb) are quite temperature-dependent. On the contrary 3 proved to be a rigid annulene, and it displayed the most prominent diatropism ever recorded, — far beyond the diatropism of [18]annulene itself —, indicating the significance of equivalent Kekulé structures of 3a and 3b as for benzene.

In order to get further knowledges on di-bridged annulenes in this series we addressed ourselves to prepare 4, a position isomer of 3 made up of same building blocks (i.e., ten sp$^2$ carbons and two furan rings). While 3 provides a snag-fitted inner space for two oxygens and two hydrogens in the pseudohexagonal frame, 4 provides only a poor accommodation for these atoms due to the unsymmetrically arranged cavity. Thus, it is clear that coplanar sp$^2$ carbon arrangement is not met in 4. Model considerations indicate that twisting occurs at both the diene and triene parts. Especially, an extensive twisting arises in the C-9 carbon atom as the consequence of steric interaction between the H-7 and the oxygen bridge linked at the C-11 and 14 positions (dihedral angle of C-8 and C-9 is ca. 45° from model). Another torsional strain which exists in the diene moiety expels the H-16 from the inside to the outside positon of the annulene ring. Therefore,



1a: X=Y=O
1b:[2] X=O, Y=S
1c:[3] X=S, Y=O



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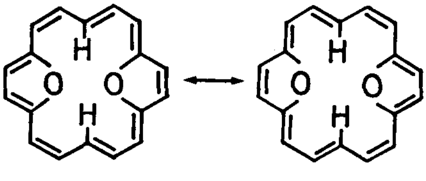
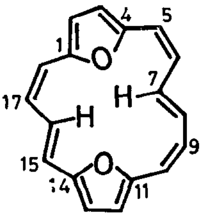


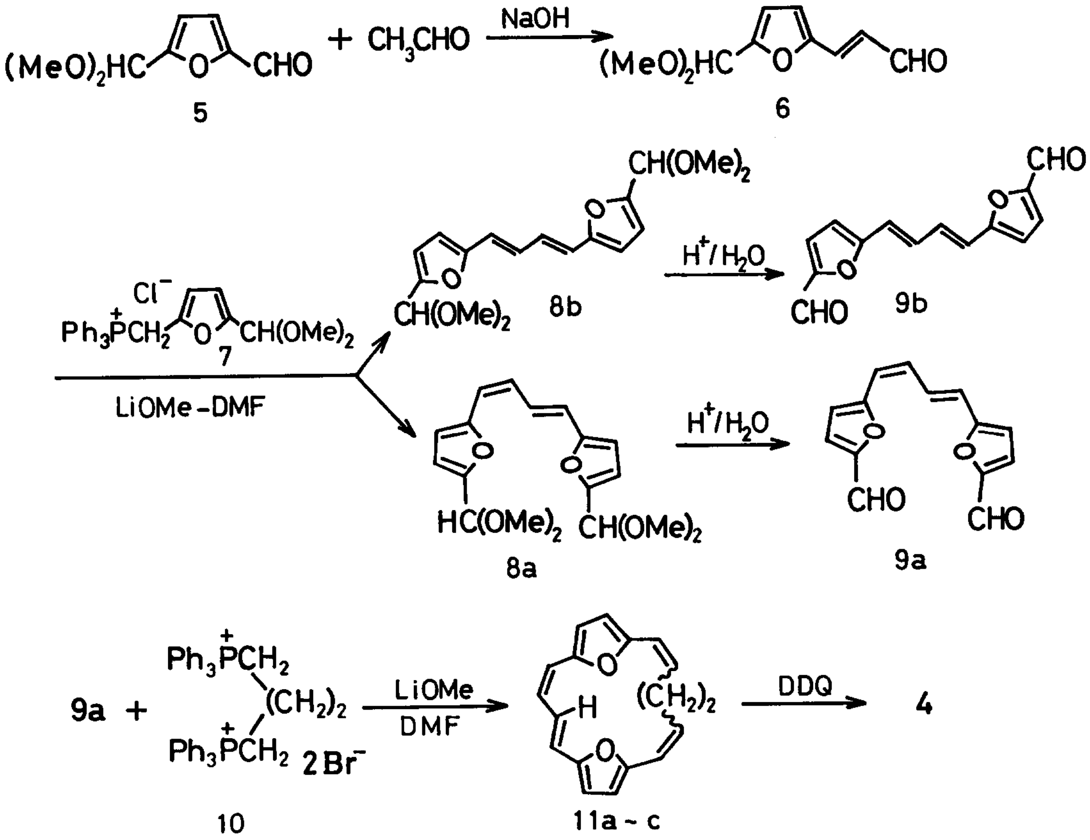
3a 3b



4

the geometrical requirements should lead to a considerable barrier in 4 for the peripheral conjugation, and 4 is a suitable model whose diatropicity is to be examined by synthesis.

*cis*-Dialdehyde 9a, a key intermediate for 4, was prepared from 5-dimethoxymethyl-2-furfural 5 *via* three steps. 3-[5-(Dimethoxymethyl)-2-furanyl]propenal 6 [bp$_1$ 110 - 113°C] was obtained by the aldol condensation of 5 and acetaldehyde [NaOH, aq. EtOH, 0°C]. The Wittig reaction of 6 with 5-(dimethoxymethyl)-2-furyl-triphenylphosphonium chloride 7[6] in DMF at 60°C using LiOMe as base afforded a mixture of acetals 8a and 8b (total yield, 90%). Hydrolysis of the mixture (p-TsOH, EtOH/$H_2O$ at 50°C) followed by the chromatographic separation ($SiO_2$, benzene) gave isomeric dialdehyde 9a (mp 100 - 102°C) and 9b (mp 176 - 177°C) in a ratio of ca. 1 : 1. The double Wittig reaction of *cis*-dialdehyde 9a and bisphosphonium salt 10[7] in DMF at 70°C by employing LiOMe as base afforded a mixture of isomeric dihydroannulenes 11a, 11b, and 11c in an approximate ratio of 8:1:4 in the order of chromatographic elution ($SiO_2$, n-hexane). These isomers about the newly formed double bonds exhibit the corresponding inside proton (each 1H) at considerably lowered field at $\delta$ 9.0, 8.0, and 7.5, respectively, due to the different proximity to the oxygen bridge. Dehydroganation of major dihydroannulene 11a with DDQ in benzene at room temperature for 1 nr gave [18]annulene 4 as a sole product [yield, 20%, greenish-brown prisms (n-hexane), m.p. 200 °C (decomp.), *m/e* 262 ($M^+$)]. 4 was also formed from other minor isomers 11b and 11c without forming other stereoisomers. Thus, it emerges that 4 exists as a thermodynamical sink. 4 is stable in



both solid state and solution towards air, even after prolonged standing.

The $^1$H-nmr spectrum of 4 [essentially temperature independent in the range of 25° - 150°C in DMF-$d_7$] supports the structure. Spin decoupling experiments afforded the assignment of each annulene proton (Fig. 1 and footnote 9). Although two regio-orientations of the central trans double bond on the triene moiety are possible, the H-7 inside conformation is considered more likely than the alternative one (H-8 inside conformation) since the magnetic equivalence of the H-2 and H-3 protons [appeared at δ 8.36 (2H singlet)] is only explainable in this conformation.

High field resonances of the inner protons [δ -1.85 (H-16) and -2.06 (H-7)] and the low field resonances of the outer protons [δ 8.05 - 9.28] confirmed strong diatropism of 4. Interestingly, the H-16 proton is shifted to lowered field by 0.21 ppm than the H-7 proton, and the H-9 proton is shifted to higher field by 0.98 ppm than the average chemical shift of the H-6, H-8, and H-16 protons. These opposite shifts indicate that 4 has a twisted conformation, in accordance with the model mentioned above. Indeed, the diamagnetic shifts became less effective in those protons, indicating that they are attached on twisted carbon centers. Further indirect support that 4 has a twisted conformation is also obtained from a comparison of the electronic spectrum of 4 with that of a planar model 3. As shown in Fig. 2, spectra of these two annulenes are remarkably similar in shape, but, in 4, most of the bands are shifted to the shorter wavelength side and reduced in intensities [electronic spectrum (n-hexane): λmax [nm] (log ε): 278 (4.63), 336 (4.86), 345 (4.85), 382 (3.53), 403 (3.73), 423 (4.11), 442 (3.35), 480 (2.14), 489 (2.10), 498 (2.01), 522 (2.32), 533 (2.18), 544 (2.05), 564sh (2.10), 573 (2.46), 587 (2.15), 602 (1.95), and 632 (2.53)].

Table 1 indicates that furan protons of 4 resonate almost identical positions with those of

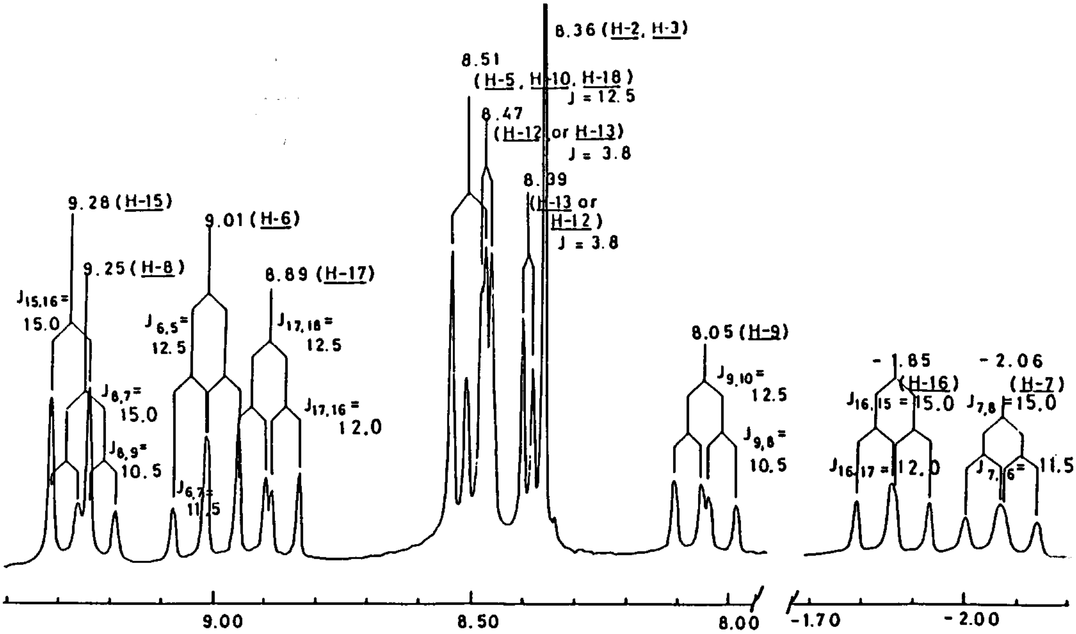


Fig. 1 200 MHz $^1$H-n.m.r. spectrum of di-oxa[18]annulene 4 in $CDCl_3$ at room temperature tri-bridged [18]annulenes, 1a and 1b, both of which were reported as planar.[1,3] Therefore, it seems likely that 1a, 1b, and 1c might have excessive bridging effects — intrinsic for tri-bridged [18]-annulene systems, although differing in extents according to the bulkiness of X and Y. In accordance with this implication the diatropicity of tri-bridged [18]annulenes is completely quenched passing from 1b to 1c (X=O,Y=S→X=S,Y=O), while 4 could sustain strong diatropicity counterbalancing its unfavorable nonplanar twisted conformation with its reduced number of bridges.

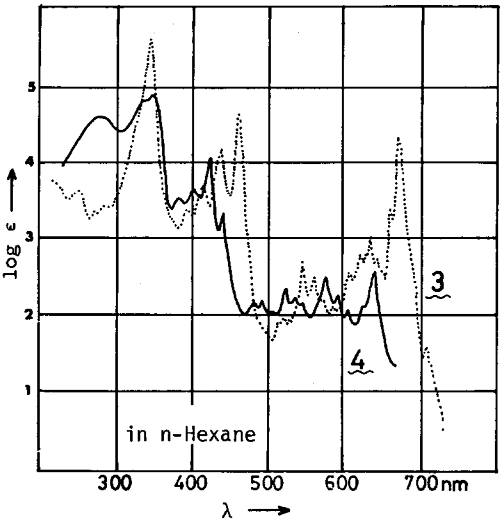


Fig. 2 Electronic Spectra of 3 and 4

Table 1. Chemical Shifts of Furan Ring Protons in $CDCl_3$ (δ values)

| 1a[1] | 1b[2] | 1c[3] | 3[5] | 4 |
|---|---|---|---|---|
| 8.68<br>or<br>8.66 | 8.39<br>or<br>8.29 | 6.73<br>or<br>6.67 | 9.20<br>or<br>9.13 | 8.47 (1H)<br>8.39 (1H)<br>8.36 (2H) |

## Reference and Notes

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8 Similar down field shifts of inside protons are reported in some cyclic systems, see T.M. Cresp and M.V. Sargent, J. Chem. Soc. Perkin I, 1974, 2145.

9 Decoupling experiments of 4 : Irradiation of high field proton at δ -1.85 induces the doublet at δ 9.28 into a singlet, and the doublet of doublets at δ 8.89 into a doublet ($J_{cis}$ 12.5 Hz). Irradiation of δ -2.05 collapses the doublet of doublets at δ 9.01 into a doublet ($J_{cis}$ 12.5 Hz), and the signal of multiplets of δ 9.25 is simplified. Either irradiation at δ -1.85 or -2.06 does not affect the doublet of doublets at δ 8.05, but irradiation of the doublet of doublets at δ 9.25 changes the signal into a doublet ($J_{cis}$ 12.5 Hz). Thus, it is now clear that the inner proton at δ -1.85 belongs to the diene system, and the proton at δ -2.05 to the triene system. Reciprocal irradiation of δ 8.05 results in the multiplet of δ 9.25 into a doublet ($J_{trans}$ 15.0 Hz), together with a partial simplification of overlapped 3H multiplet at δ 8.51. This indicates that proton appearing at δ 8.05 is placed at the adjacent position to the proton appearing at δ 9.25. Thus, all the protons adjacent to furan rings (H-5, H-10, H-18) resonate at the same position (δ 8.51) except for the one attached to the trans double bond in the diene system (δ 9.28).

10 For the reported diatropicity of a bent [18]annulene, see W. Wagemann, M. Iyoda, H.M. Deger, J. Sombroek, and E. Vogel, Angew. Chem. Int. Ed. Engl., 1978, 17, 956.

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