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ANNELATED 1,5-DI-*TRANS*-[10]ANNULENES

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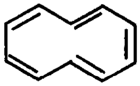
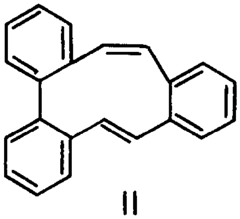
Evidence has recently been presented which established the transitory existence of cyclodecapentaene or [10]annulene (I) in solution at -190°(1). Destabilisation of (I) has been attributed to steric or strain effects (1,2). However two annelated derivatives of this intriguing hydrocarbon, namely mono-*trans*-1,2:3,4:7,8-tribenz[10]annulene (II) (3) and dinaphtho[10]annulene (III), (4) have been shown to be relatively stable. We now report the synthesis of two stable conformational isomers of di-*trans*-1,2:3,4-dibenzo[7,8-c]furo[10] annulene (IV) (5), the first annelated derivatives of di-*trans*-[10]annulene.



I



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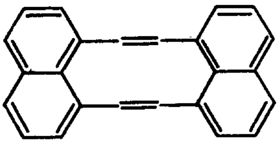

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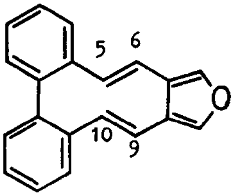

IV

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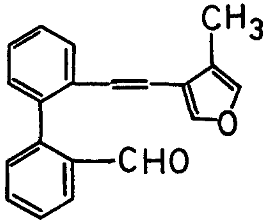
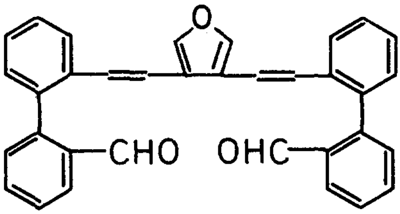
The synthesis of of (IV) was accomplished by the Wittig reaction of biphenyl-2,2'-dialdehyde and 3,4-furanbis(methylenetriphenylphosphonium chloride)(6) with lithium methoxide in dimethylformamide at 90°. Byproducts from this cyclisation including the aldehydes (V) and (VI), and the diolefins (VII) and (VIII), were separated by preparative thin layer chromatography on silica gel.



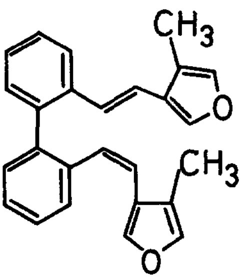
mixture of cis and trans

V

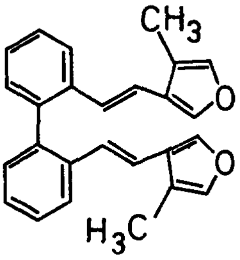


mixture of isomers

VI



VII



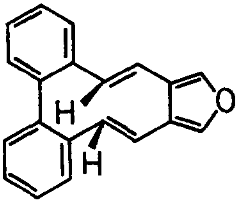
VIII

The major conformer of di-trans-1,2:3,4-dibenzo[7,8-c]furo[10]annulene (IVA, higher R_F) was obtained in 10% yield and crystallised from aqueous ethanol in colourless prisms, m.p. 113°: mass spectrum molecular ion at m/e 270.1036 (calcd for $C_{20}H_{14}O$: 270.1044); λ_{max}^{EtOH} 243 mμ log ε 4.41; $\nu_{max}^{CHCl_3}$ 965(s) cm⁻¹. The n.m.r. spectrum (60 Mcps, CCl_4) showed an 8H multiplet at τ 2.50 - 3.20 (benzenoid protons), a 2H singlet at 3.57 (furan protons) and a 4H double doublet centred at 3.70 and 4.90 (J = 16 cps, olefinic protons 5,6,9 and 10). The assignment of the di-trans configuration to (IVA) follows from the above infrared and n.m.r. data (and is further substantiated by comparison with spectra of II, III, VII and VIII).

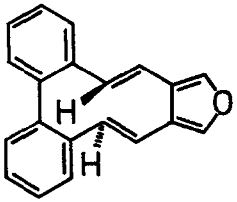
The minor conformer of di-trans-1,2:3,4-dibenzo[7,8-c]furo[10]annulene (IV_B, lower R_F) was isolated in 3% yield, and crystallised from aqueous ethanol as colourless needles, m.p. [illegible]°; λ_{max}^{EtOH} 243 mμ, log ε 4.23. The infrared and n.m.r. spectra of this conformer showed only minor differences to those of (IVA). Conformer (IVB) slowly reverted to the more stable conformation (IVA), on standing in the solid state. This change was accompanied by an increase in m.p. and intensity of ultraviolet absorption.

The fact that the annulene (IV) can exist in two relatively stable conformations must be a result of the steric interference of the internal, 5 and 10, hydrogen atoms. The two conformers can be represented as E (eclipsed 5 and 10H) and S (staggered 5 and 10H).

A similar phenomenon has been observed with [14]annulene (7), where two conformational isomers arise from overcrowding of the internal hydrogen atoms.



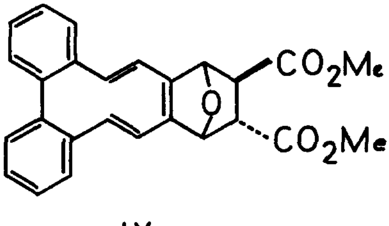
E



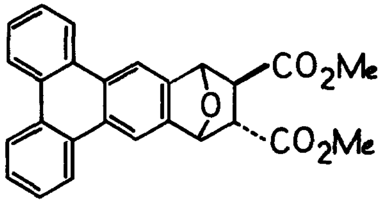
S

In marked contrast to the behaviour of the annelated [10]annulenes II (3) and III (4), (IV) did not undergo smooth transannular isomerisation of heating. Instead polymerisation was observed, the only recognisable product being phenanthrene (in low yield).

Compound (IV) (mixture of conformers) underwent a Diels-Alder reaction with dimethyl fumarate to give 48% of di-<u>trans</u>-1,2:3,4-dibenzo-7,8(3',6'-epoxy-4',5'-dicarbomethoxy) cyclohexeno[10]annulene (IX), a [10]annulene annelated by only two aromatic nuclei.



IX



X

The diester (IX) was obtained as colourless crystals, m.p. 96-98°: λ^{EtOH}_{max} 262, 278(sh), 300(sh) mμ; log ε 4.17, 4.08, 3.70: $\nu^{CHCl_3}_{max}$ 975 cm^{-1}. The n.m.r. spectrum (CCl_4) showed a 10H multiplet at τ 2.20-2.90 (benzenoid plus two olefinic protons), a 2H doublet centred at

3.75 (J = 12 cps, olefinic protons), a 2H broad singlet at 4.85 (protons 3', 6'), overlapping a 1H doublet (methine proton) and a further 1H doublet at 6.75 (J = 5 cps, methine proton). The diester (IX) was only isolated as one conformer (presumably the more stable) and underwent facile transannular rearrangement (50% rearrangement after 2 weeks at 0°) followed by autoxidation to give the substituted triphenylene (X); m.p. 233-234°: λ_{max}^{EtOH} 253, 262, and shoulders at 278, 288, and 310 mμ; logε5.09, 5.27, 4.31, 4.25, and 3.70 respectively: n.m.r. ($CDCl_3$)τ 1.10 - 1.50 (m,6 aromatic H), 2.20-2.40 (m,4 aromatic H), 4.05 (broad s,2 bridgehead H), 5.90, 6.80 (d.d., J=4 cps, 2 methine H) and 6.15, 6.50 (s,6 methoxyl H).

The structure of the di-*trans*-1,2:3,4-dibenzo[7,8-c]furo[10]annulenes (IV_A, IV_B) follow unequivocally from the properties and reactions described above. It is also apparent from the above data that the ten membered ring in compounds (IV_A),(IV_B) and (IX) is non-planar and does not represent a delocalised ten-π-electron system.

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