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# 2,5b,10b,11-TETRAMETHYLDIHYDROPYRENO[5,6-c]FURAN: THE FIRST FURAN-ISOANNELATED [14]ANNULENE THAT SUSTAINS AS STRONG A DIAMAGNETIC RING CURRENT AS THE PARENT SYSTEM

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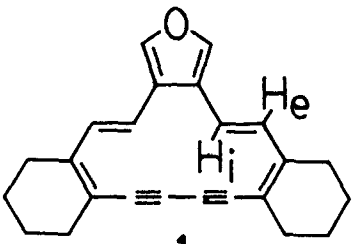
Summary - Relative chemical shifts of internal methyl protons of trans-furanodimethyldihydropyrene 4 and its parent 3 provide the first evidence that such an isoannelation does not lead to a significant decrease in diatropicity.

The effect of benzannelation on diatropicity has been an area of special interest in annulene chemistry.[1] The decrease in diatropicity observed in the annulene is conveniently indicated by the chemical shifts of selected reference protons or substituents.[1,2] The effect of isoannelation, e.g. fusion of furan at the 3,4-positions to an annulene, has also received much attention.[3] The first example of such a [14]annulenofuran, 1, was reported by Sondheimer.[3] The difference in chemical shifts between the internal ($H_i$) and external ($H_e$) protons, $\Delta\delta = \delta H_e - \delta H_i$, could be regarded as an approximate measure of magnitude of the ring current. It is then obvious that there is hardly a detectable diamagnetic ring current ($\Delta\delta$ = 0.33 ppm) in 1, having both the $H_i$ and $H_e$ protons appeared in the olefin region at $\delta$6.46 and 6.79 respectively.[3] Another bisdehydro[14]annuleno[c]furan 2 however seemed to show an observable diatropicity,[4] with the internal and external protons separated at $\delta$4.35-4.69 and $\delta$7.34-7.87 respectively ( $\Delta\delta$ = 2.7-3.5 ppm). The internal protons of 2 are however likely to be affected by anisotropy effects.[2] A bridged [14]annulene, dimethyldihydropyrene 3, has been shown to be an ideal model for studies of the effects of benzannelation[5,6] and strained-ring annelation.[7]



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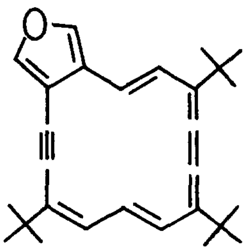

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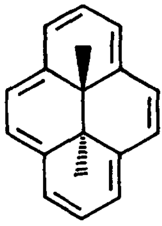

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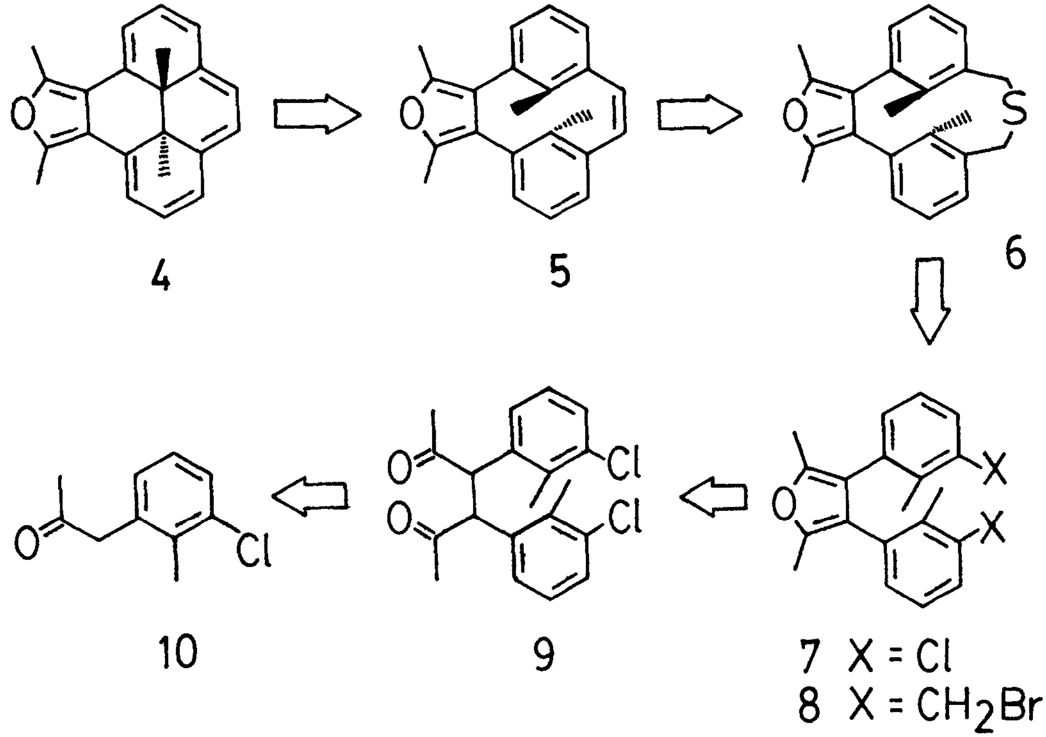

However, no heterocyclic isoannelated derivative of 3 has yet been reported. We now wish to communicate the synthesis and diatropicity of the dihydropyreno[c]-furan 4.

The retrosynthetic scheme suggests the benzylmethyl ketone derivative 10 as an appropriate precursor. Treatment of the mono-Grignard[8] from 2,6-dichloro-toluene with 3-bromo-2-methoxy-1-propene[9] afforded the desired ketone 10. The 1,4-dicarbonyl compound 9 was prepared via oxidative coupling of 10 with activated manganese dioxide in acetic acid.[10] This reaction in fact yielded a mixture of the diketone 9 and the furan 7 which could be separated readily by column chromatography. The latter was clearly formed from the acid-catalysed dehydration of the former. In fact dehydration[11] of 9 with phosphorus pentoxide in ethanol also readily yielded the desired 3,4-diarylfuran 7. Conversion of 7 to 8 was achieved via a similar sequence of reactions reported for the syntheses[6,12] of other annelated derivatives of 3. Cyclization of 8 to the thiacyclophane 6 was readily effected with sodium sulfide. The anti isomer 6, mp 208-211°C, could be obtained in 66% yield after column chromatography. Surprisingly, no detectable amount of the corresponding syn isomer could be isolated. The anti stereochemistry of anti 6 was confirmed when its internal methyl protons were observed significantly shielded at $\delta 0.87$. A Wittig rearrangement-Hofmann elimination sequence on anti 6 then led to a 61% overall yield of the cyclophanediene 5. Although a solution of 5 appeared pale violet in color, its $^1$H NMR spectrum did not indicate a detectable amount of the dimethyldihydropyrene 4. The internal methyl protons of 5 was clearly observed as a sharp singlet at δ1.13. Irradiation of a solution of 5 with light at 254 nm led to a dark violet solution with apparent decomposition. The $^1$H NMR spectrum of the product mixture however clearly showed a new sharp singlet at δ-3.97 in addition to the methyl signal of 5, indicating the conversion of 5 to 4. This was further supported by the conversion of 4 back to 5 when the solution was irradiated with visible light. This phenomenon of interconversion has been observed for most derivatives of dimethyldihydropyrene 3.

A qualitative measure of the effect of isoannelation on the diatropicity of the macroring should be reflected by the relative chemical shifts of shielded internal protons of the parent [14]annulene and those of the annelated derivative. Such a comparison clearly reveals that the diatropicity in 2 (internal protons at δ4.35, 4.69) is drastically reduced compared with that observed in the parent [14]annulene 11 (internal protons at δ-4.39).[14] In addition, 2 may not be a good model to indicate the effect of isoannelation as the macroring is not perfectly rigid and the chemical shifts of the internal protons are subject to anisotropic effects. On the contrary, the central bridge in 4 allows no flexibility in the macroring with the methyl protons three bonds away from the π-periphery and thus their chemical shift mainly depends on the strength of the diamagnetic ring current. The chemical shift of the internal methyl protons of 4 (δ-3.97) in fact indicates that it sustains a comparable degree of delocalization of the π-electrons (diatropicity) as the parent [14]annulene 3 (δ-4.25).[15] This we believe is the first piece of experimental evidence to indicate that such an isoannelation of a rigid, highly stabilized [4n+2]π-electron system would not result in significant π-bond localization in the parent annulene. Synthesis of the related [14]annuleno[c]pyrrole 12 and -[c]thiophene 13 via the common precursor 9 are in progress. They should collectively serve as a series of ideal models for the understanding of effects of isoannelation by the respective heterocyclic rings.

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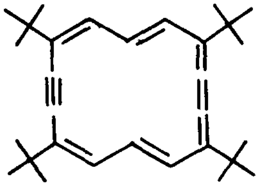

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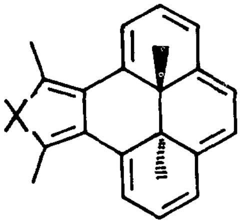

12 X = NH
13 X = S

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