

The Effect of Benzo-fusion on Tricyclic [10]Annulenes: Synthesis, Properties, and X-Ray Structure of 9c-Methyl-9cH-cyclopenta[*jk*]fluorene

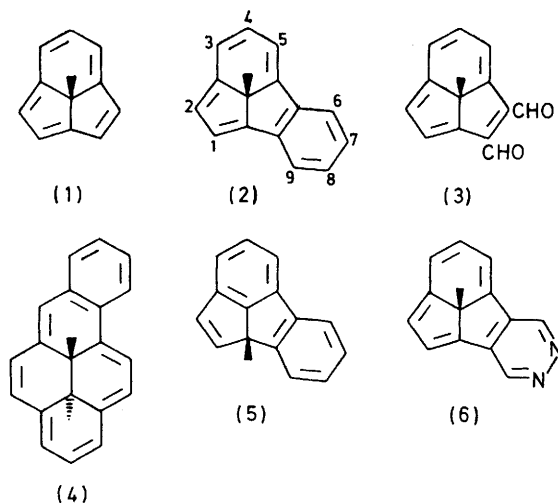
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The benzo-fused [10]annulene (**2**) has been synthesised; n.m.r. spectroscopy establishes that the compound retains about two-thirds of the ring current of the unperturbed annulene (**1**), and an accurate X-ray structure determination demonstrates the presence of some [14]annulene character.

We have recently reported the synthesis and properties of 7b-methyl-7bH-cyclopent[*cd*]indene (**1**), a tricyclic [10]annulene.^{1,2} Annulene (**1**) exhibits typical aromatic properties in that it undergoes substitution rather than addition reactions with electrophiles, and supports a diamagnetic ring current in an applied magnetic field. Thus, in the n.m.r. spectrum, the central methyl group resonates upfield of tetramethylsilane at $\delta -1.67$. The chemical shift of the central methyl group acts as a sensitive probe for the induced ring current, and hence the effects of substituents are easily monitored. The fusion of a benzene ring to an aromatic system markedly affects the properties of that system. We now report that 9c-methyl-9cH-cyclopenta[*jk*]fluorene (**2**), a benzo-fused derivative of (**1**), retains a substantial proportion of the ring current of (**1**).

The benzo-fused annulene (**2**) was prepared by reaction of the annulene dialdehyde (**3**),¹ with thiodimethylenedi(tri-phenylphosphonium bromide), $\text{Ph}_3\text{P}^+\text{CH}_2\text{SCH}_2\text{P}^+\text{Ph}_3\text{2Br}^-$, in the presence of lithium methoxide in dimethylformamide at room temperature.³ After chromatography, and crystallisation from petrol (b.p. 40–60 °C), annulene (**2**) was obtained (14%) as yellow crystals, m.p. 74–76 °C, λ_{max} (EtOH) 311 (log ϵ 4.43), 400 br. (3.34), and 464 sh (2.82) nm. In the n.m.r. spectrum, the central methyl group resonates at δ (CDCl₃) –0.79, and the peripheral protons at δ 7.30–7.58 (1-H to 5-H) and 7.67–8.40 (6-H to 9-H). Thus, the effect of benzo-fusion is to shift the central methyl group signal downfield relative to (**1**), implying a reduction in ring current. A calculation based on the relative chemical shifts of the methyl



groups in (1) and (2) suggests that the benzo-fused annulene (2) retains 67% of the ring current in (1).†

Further information on electron delocalisation in (2) can be gained from the coupling constants of the peripheral protons, which were obtained to within ± 0.04 Hz from the 400 MHz n.m.r. spectrum ($J_{1,2}$ 2.42, $J_{3,4}$ 8.26, $J_{4,5}$ 5.97, $J_{6,7}$ 8.03, $J_{7,8}$ 7.05, and $J_{8,9}$ 8.05 Hz). The coupling constants between 3-H and 4-H, 4-H and 5-H, and around the benzo-ring are comparable to those observed for the benzo-fused [14]annulene (4)⁴ suggesting a similar degree of imposed bond fixation. Benzo-fusion in the [14]annulene (4) reduces the ring current by 50%.⁴ Since resonance energy is inversely proportional to the size of the annulene,⁵ the [10]annulene should have greater resonance energy than the [14]annulene and therefore be less perturbed by benzo-fusion. However, the resonance energy in the tricyclic [10]annulene is reduced by torsional strain in the periphery more than in the dihydro-pyrenes.

In order to obtain further insight into the bonding in (2), and in particular the bond lengths, a single crystal X-ray analysis was undertaken.

Crystal data: (2), C₁₆H₁₂, orthorhombic, $a = 6.887(1)$, $b = 9.297(2)$, $c = 17.673(3)$ Å, $U = 1132$ Å³, space group $P2_12_12_1$, $Z = 4$, $D_c = 1.20$ g cm⁻³. This space group contains molecules of one chirality only; the compound, being a racemate in solution, thus exhibits spontaneous resolution on crystallisation. Data for a spherically ground crystal were measured on a diffractometer with Cu-K α radiation. A total of 917 independent reflections were measured ($\theta \leq 58^\circ$) and of these 21 had $|F_o| < 3\sigma(|F_o|)$ and were classed as unobserved. The structure was solved by direct methods and refined anisotropically to $R = 0.032$.‡

† Calculated on the basis of equation (1) where 1.01 is the chemical shift of the central methyl group in the model compound, 2a-methoxy-7b-methyl-4a,7b-dihydro-2aH-cyclopent[cd]indene (ref. 2), where there can be no ring current, and -0.79 and -1.67 are the chemical shifts of the methyl group in (2) and (1) respectively (cf. ref. 4).

$$\text{Residual ring current} = \frac{1.01 - (-0.79)/1.01 - (-1.67)}{0.67} \quad (1)$$

‡ The atomic co-ordinates for this work are available on request from the Director of Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

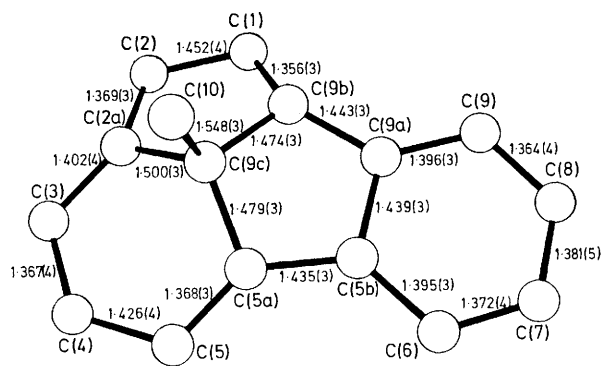


Figure 1. The crystal structure of (2) showing the bond lengths with e.s.d.'s in parentheses. A librational analysis has indicated that all the lengths shown should be increased by between 0.005 and 0.007 Å. Torsion angles about the peripheral bonds: C(1)-C(2)-C(2a) -3.0(3); C(2)-C(2a)-C(3) 146.1(3); C(3)-C(4)-C(5) 11.9(4); C(5)-C(5a)-C(5b) -19.9(5); C(5b)-C(6)-C(7) 175.2(3); C(6)-C(7)-C(8) 1.6(5); C(8)-C(9)-C(9a) -174.9(2); C(9a)-C(9b)-C(1) 143.4(3)°.

The results (Figure 1) show that benzo-fusion causes a distinct alternation in bond lengths around the periphery of the tricyclic [10]annulene portion. The bond common to the [10]annulene and the benzo-ring (C-5b-C-9a) is longer than expected, thus relieving strain in the five-membered ring. The result of this increased single bond character in an internal bond is that the compound has some [14]annulene character involving the entire periphery, and hence a higher ring current than might be expected, since ring current is proportional to the size of the annulene.⁵

The chemistry of (2) contrasts with that of the annulene (1). Nitration with copper(II) nitrate in acetic anhydride² was unsuccessful, and whereas reaction of (1) with 4-phenyl-1,2,4-triazole-3,5-dione at 80 °C cleanly gave a 1:2 adduct,¹ the corresponding reaction of (2) at 0 °C gave a complex mixture. On heating in solution, (2) rearranged by a [1,5]methyl shift to the known 9bH-isomer (5)⁶ in a first-order reaction with $t_{1/2}$ (138 °C, decalin) = 8.3 min. The corresponding rearrangement of (1) has $t_{1/2}$ = 12 h under similar conditions. This rate difference, which reflects the difference in activation energies for the rearrangement of (1) (33 kcal mol⁻¹) and (2) (30 kcal mol⁻¹)§ again illustrates that benzo-fusion has reduced the resonance energy in (1).

The dialdehyde (3) is a versatile precursor to other annelated [10]annulenes. Reaction with hydrazine hydrate in ethanol at 0 °C gave the pyridazino-fused annulene (6) (90%). This heteroaromatic fused annulene has properties intermediate between those of (1) and (2). The central methyl group resonates at δ (CDCl₃) -1.06, and on heating the compound rearranges by a similar [1,5]methyl shift with $t_{1/2}$ = 38 min at 138 °C.

Thus the effect of benzannulation on the [10]annulene (1) is to reduce the ring current, although the effect is moderated by an increase in the 5b-9a bond length which confers some [14]annulene character on the system.

§ The activation energies were obtained from rate measurements at four different temperatures in the range 138–190 °C for (1) and 109–138 °C for (2). 1 kcal = 4.18 kJ.

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