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THE SYNTHESIS OF THE FIRST BENZANNELATED <u>TRANS</u>-15,16-DIHYDROPYRENE: AN EXAMPLE OF THE REDUCTION OF THE DIATROPICITY OF A 14π-ELECTRON SYSTEM BY BENZANNELATION

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The recent surge of interest[1] on the effect on the ring current of macrocyclic conjugated systems produced by annelation of one or more benzene rings is of considerable note, especially in light of the fact that many tri and higher benzannelated annulenes have been known for a considerable number of years.[2] This was probably prompted in part to a growing interest by theoretical chemists in these systems, for example the work of Günther,[3] and a realization that only when one or two benzene rings annelate the macrocyclic system, is the diatropicity of the large ring still likely to be observable.

One of the more interesting compounds on which to study this effect is <u>trans</u>-15,16-dihydropyrene[4] (**1**), since (a) the macrocyclic ring is conformationally fixed by the bridge and (b) the internal protons are strongly shielded (τ 15.49) by being buried so deeply within the cavity of the π-electron cloud. Progressive benzannelation of **1** should reduce the diatropicity of the macrocyclic ring[1a,d,e] and this should be readily apparent by pmr spectroscopy from the position of the internal protons.

This paper reports the synthesis and properties of **2**, the monobenzannelated[5] derivative of <u>trans</u>-15,16-dihydropyrene (**1**).

Coupling of 1,3-bis(bromomethyl)naphthalene[6,8](**3**) with <u>meta</u>-xylylene thiol (**4**) under high dilution conditions,[9] gave the benzo-dithiacyclophane **5**, m.p. 126-127° in 82% yield. Wittig rearrangement[9] of **5** using n-butyl lithium in THF followed by alkylation of the bis-thiolate anion with methyl iodide gave the ring contracted [2,2]metacyclophane **6** in 92%

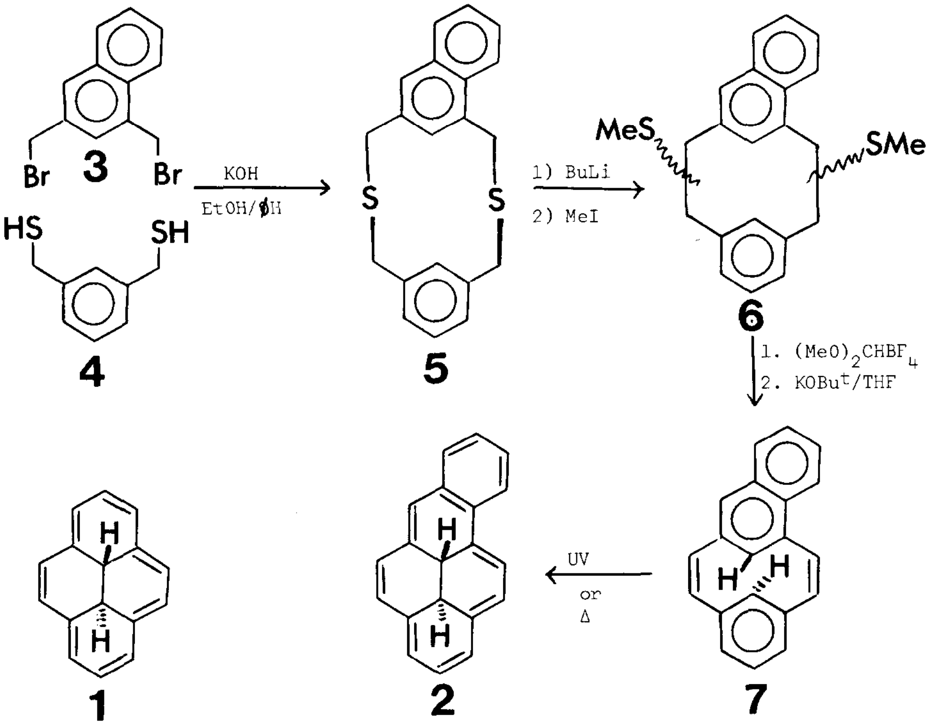
yield as a mixture of stereoisomers.[4] This mixture was directly methylated with dimethoxycarbonium fluoroborate,[10] and the resulting bis sulphonium salt was treated with anhydrous potassium tert-butoxide in THF at 0°C to effect the Hofmann elimination to give after chromatography on silica gel the benzannelated [2,2]metacyclophanediene **7**, as orange crystals,[11] m.p. ca. 120° (dec)[12]. As evidenced by thin layer chromatography and pmr spectroscopy this contains some benz(a)pyrene **8**. Further chromatography or crystallization results in the formation[4] of more benz(a)pyrene. Fortunately the pmr spectrum[13] of benz(a)pyrene (τ 0.8-2.4) does not overlap with that of the cyclophane diene **7**, at τ 2.5-3.6 (all protons, multiplet). When a degassed solution of **7** in THF-d_8 sealed under vacuum in an nmr tube is irradiated[7] for 4 hours with 2537A° light, valence tautomerization to the red benzo-dihydropyrene **2** occurs, together with formation of benz(a)pyrene. The pmr spectrum of **2** shows a multiplet at τ 2.2-2.8 (external protons) and a broad singlet at τ 11.35 (internal protons). As observed this is superimposed on a low intensity spectrum of **7** and **8**.

If the radiation is continued, the peaks due to **7** completely disappear, those of **2** reduce and those of benz(a)pyrene **8** increase.

The remarkably large downfield shift of 4.14 ppm for the internal protons of **2** relative to those of **1** is convincing evidence for the large reduction of diatropicity when a macrocyclic ring is benzannelated. This is also apparent from the position of the external protons, however the effect is not as marked (approximate 0.8 ppm upfield shift of **2** relative to **1**).

At present no theory exists which relates quantitatively the magnitude of the ring current to the position of protons; the compounds **1** and **2** however would make good starting points for such a theory, since they must have almost identical geometry.

We are currently extending this work to other derivatives of **1** and **2** such that data for such a theory becomes available, and a better understanding of change of properties with benzannelation is developed.



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