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Synthesis of the Elusive Dibenzannelated Dihydropyrene Dibenzo[e,l]dimethyldihydropyrene, a Molecular Photo-switch.

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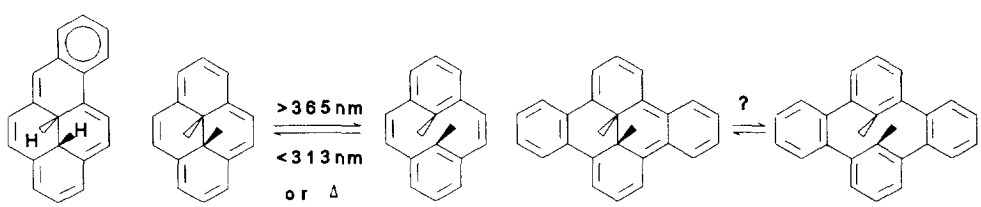
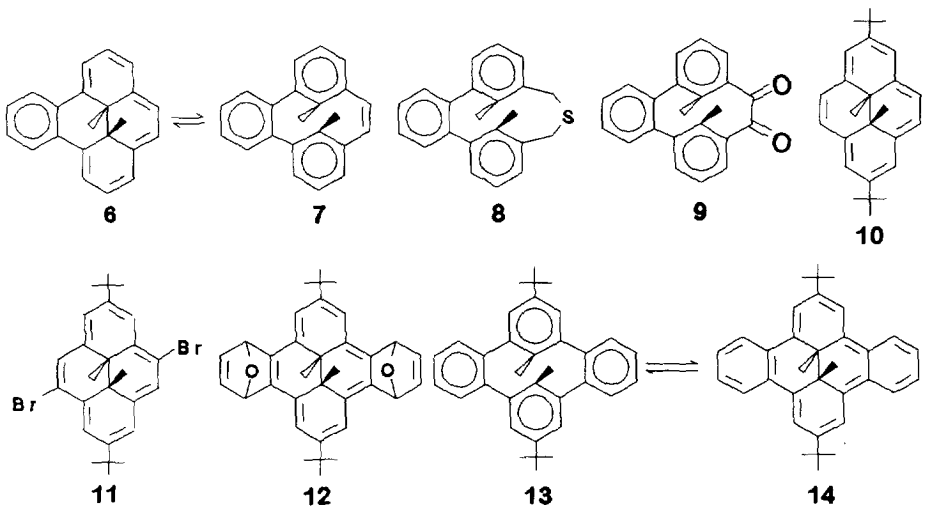
Abstract: Synthesis of the unknown *o-m-o-m*-cyclophane derivative **13** is achieved by deoxygenation of the adduct **12**, derived from a bis-Diels-Alder addition of furan to the intermediate bis-aryne generated by bis-dehydrobromination of dibromide **11**. The colorless photochromic cyclophanediene **13** switches to the green dibenzannulene **14** on uv irradiation, and **14** thermally or photochemically reverts to **13**, with E_{act} = 20 kcal/mole.

In 1975 we reported[1] the synthesis of the first benzannelated dihydropyrene, **1**, in which benzene was fused to the [a] position of dihydropyrene. Most of our subsequent work has used dimethyldihydropyrene, **2**, as the bridged annulene, since unlike the internal hydrogen atoms of **1**, the internal methyl groups are stable to oxygen.[2] Over the intervening two decades, we have synthesised many other annelated dihydropyrenes and have discussed their relative aromaticities.[3] So far however, the example **4** which has benzene rings fused symmetrically in the [e] and [l] positions of **2**, has evaded us. This compound is especially interesting because of the valence isomerization that normally occurs between the dihydropyrenes, **2**, and the metacyclophanedienes, **3**.[4] In the case of **2**⇔**3** , the pyrene **2** is the thermodynamically more stable isomer. Irradiation of **2** with visible light partially converts it to **3**, while allowing **3** to stand in the dark or heating it or irradiating it with uv light converts it back to **2**.[5] The site of annelation and the number of annelating rings however, dramatically changes the position and reversibility of this equilibrium.[4] Whether the dibenzannelated dihydropyrene **4** would show the photoswitchable valence isomerization with the cyclophanediene **5** (which contains four benzenoid rings), and which of **4** or **5** would be the thermodynamically preferred isomer is an interesting question, which this paper answers.



Synthesis: Most annelated dihydropyrenes have been synthesised through the thiacyclophanes,[3,4] for example the pair **6**⇌**7** was accessed through **8**. However, we[6] were unable to convert the C-S-C bridge in **8** to the benzene ring of **5**. We also attempted synthesis of **5** through the bridge diketone **9**, but again failed.[7] Our recently described[3,8] "aryne" route to several [a] annelated dihydropyrenes opened up a possible route to **4**. Bromination of the di-*t*-butyldihydropyrene[9] **10** using 2.1 equivalents of NBS[10] in DMF : CCl_4 (7:1) at 20°C gave an essentially quantitative yield of dibromides, from which the pure dibromide **11**, mp 220-222°C, was easily isolated by recrystallization in 88% yield.[11] Reaction of **11** with a large excess of $NaNH_2$ containing catalytic *t*-BuOK in furan-THF (10:1) gave furan adducts of the intermediate arynes as a mixture of mono-adduct (about 5%) and bis-adduct **12** (60%) as a 1:1 mixture of two isomers.[12] Reaction of the bis-adduct **12** with $Fe_2(CO)_9$ in benzene at 60°C gave 68% of the colorless cyclophane **13**, mp 231-232°C.



6 **7** **8** **9** **10**

11 **12** **13** **14**

The structure of **13** was readily apparent from its mass spectrum, MH^+=445, and CH analysis, together with its ^1H NMR spectrum[13] which showed the internal methyl protons shielded at δ 1.07, consistent with those of other cyclophanedienes.[14] Moreover the compound only exhibited weak uv absorption beyond λ_{max} (cyclohexane) 287 nm (12,000), unlike the precursor dihydropyrenes which are all intensely colored. The cyclophanediene form, **13** was thus the thermodynamically stable isomer in this case. This is consistent with an AM1 calculation[4], which suggests that **5** has an enthalpy of formation about 18 kcal/mole lower than that of **4**.

Valence isomerization: a sample of **13** (3 mg) was dissolved in d_8-THF (0.8 mL) and was irradiated at -90°C with 300nm light for 10 minutes and formed about 35% of the green[15] dihydropyrene **14**. Removal from the cold bath rapidly isomerized **14** back to **13**. This process could be repeated many times. To obtain NMR data for **14**, the irradiated sample at -90°C was immediately transferred to a cold nmr probe and the spectra were recorded at -80°C. The internal methyl protons appeared at δ -3.41, consistent with that found for the

dibenzo[a,i]isomer[16] at δ -3.68. As well both the singlet for the benzene protons adjacent to the *t*-butyl groups and the AA'XX' multiplet for the other aryl hydrogens of **14** are strongly deshielded from those in **13**, to δ 9.45 from δ 6.91, and to δ 9.37 and 7.59 from δ 7.69 and 7.39 respectively, consistent with the much stronger ring current present in the fully delocalized dihydropyrene ring of **14**, and collectively leave no doubt that **14** had indeed formed. The *t*-Bu protons also are likewise deshielded to δ 1.79 from δ 1.29.

Thermodynamics: In the case of the monobenzannelated dihydropyrene **6**, this is the thermodynamically more stable isomer, and the cyclophanediene **7** reverts thermally to this with E_{act} = 25 kcal/mole.[4c] The thermal reversion of **14** to **13** is much faster and was measured by integrating the methyl and *t*-butyl signals at various times at the temperatures 233K, 243K, 253K and 263K, and then using an Arrhenius ln k vs 1/T plot to determine E_{act} = 20 (±1) kcal/mole. Using a standard transition state plot of ln (k/T) vs 1/T, yields $\Delta H^{\ddagger}$ = 20 (±1) kcal/mole and $\Delta S^{\ddagger}$ = 53 (±3) cal/K. The half-life of the dihydropyrene at various temperatures is interesting, 400 mins at -40°C, 53 mins at -30°C, 12 mins at -20°C and 3 mins at -10°C, suggesting that at 20°C, reversion of **14** to **13** is very fast, 1-2 seconds! When cyclophanediene **7** reverts to dihydropyrene **6**, a new sp^3-sp^3 bond is formed, at the expense of a π-bond, and as well at a cost of some loss of resonance energy (three benzene rings less a benzo[14]annulene), while at the same time strain energy is reduced as the internal methyls are moved away from the opposite benzene rings; in the conversion of dihydropyrene **14** to cyclophanediene **13**, the sum total of these energetics must be reversed, where the sp^3-sp^3 bond is now broken and a π-bond is reformed; probably the factor that most changes the total is that now the resonance energies of four benzene rings are pitted against that of one benzo[18]annulene ring, making the cyclophanediene the preferred isomer. Irradiation of dihydropyrene **14** at -90°C with visible light also causes reversion back to the cyclophanediene isomer **13.**

The equilibrium between **13** and **14** has been demonstrated, and as such this switch is quite different in character from that of **6**↔**7**. Irradiation of purple **6** with visible light completely converts it to colorless **7**, however the reversion is quite slow. In contrast, **13**↔**14** is a uv switch, in which irradiation of colorless **13** switches it partially to colored **14**, which can revert fast thermally or photochemically to **13**. The conversion of **13** to **14** can probably be improved by a suitable low temperature light pipe, and we will continue to explore how change in structure of the two components of this valence isomerization can affect the switching between the two isomers.

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11. Major isomer **11**: ^{1}H NMR (360 MHz) δ 8.81 (d, J = 1.2 Hz, H-3,8), 8.64 (s, H-1,6), 8.49 (s, H-5,10), 1.68 (s, 18H, *t*-Bu), -3.83 (s, 6H, -CH_3); ^{13}C NMR (90.6 MHz) δ 148.2, 137.2, 132.4, 126.9, 121.9, 121.5, 116.5, 36.3, 32.2, 31.9, 14.3; CI MS, MH^+ = 503; Satisfactory CH analysis. Minor isomer: 4,10-dibromo-**10**: showed internal methyl protons at δ -3.81 and -3.84. Use of Br_2 in CCl_4 was not so successful, see: Miyazawa, A.; Yamato, T.; Tashiro, M. *J. Org. Chem.* **1991**, *56*, 1334-1337.
12. *Procedure:* $NaNH_2$ (400 mg, 10 mmol) and *t*-BuOK (2 mg) were added to a stirred solution of bromide **11** (430 mg, 0.86 mmol) in dried furan (5 mL) and THF (0.5 mL), and then the mixture was stirred at 55°C for 4 days. Methanol (0.5 mL) and silica gel were added and the solvent was evaporated, and the residue was chromatographed over silica gel using petroleum ether - ethyl acetate (9:1) as eluant. After about 5% of the mono-adduct was eluted, the second fraction contained the bis-adduct, 241 mg (59%) as a 1:1 mixture of two isomers. Satisfactory CH analysis; CI MS, MH^+ = 477; Fractional recrystallisation from hexane gave the less soluble isomer where the oxygen bridges were anti to each other, mp 236-238°C. ^{1}H NMR (360 MHz) δ 8.34 and 8.31 (bs, 4H, ArH), 7.29 and 7.19 (dd, J = 5.5, 1.9 Hz, 4H, -CH=CH-), 6.67 and 6.65(m, 4H, OCH), 1.67 (s, 18H, *t*-Bu) and -3.99 (s, 6H, -CH_3); ^{13}C NMR (90.6 MHz) δ 145.1, 141.7, 139.2, 138.9, 128.4, 128.3, 115.8, 115.7, 115.2, 82.0, 81.7, 36.0, 31.9, 31.3, 14.2; uv ($CHCl_3$) λ_{max} nm (ϵ_{max}) 377 (53,000), 391 (36,100), 446 (6,900), 665 (800). The more soluble isomer, two syn oxygen bridges, showed internal methyl protons at δ -3.70 and -4.30.
13. ^{1}H NMR (360MHz) δ 7.69 and 7.39 (AA'XX', 8H), 6.95 (s, 4H), 1.29 (s, 18H, *t*-Bu), 1.07 (s, 6H, -CH_3); ^{13}C NMR (90.6 MHz) δ 150.9, 144.6, 140.6, 138.9, 129.4, 129.2, 129.0, 34.7, 31.6, 18.7.
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15. The uv spectrum of **14** was estimated from the mixture: λ_{max} (THF) nm (ϵ_{max}) 301 (63,000), 327 (80,000), 340 (79,000), 407 (67,000), 431 (154,000), 625 (ca 8,000), 680 (ca 8,000) 730 (ca 4,000).
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