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Synthesis and Rotational Barrier of an Unsymmetrical Bi-annulenyl Derived from a Bridged [14]annulene, A Model for 1,2'-Binaphthyl.

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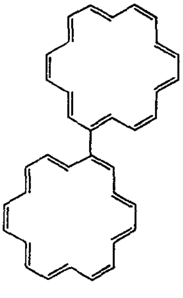
Abstract: Nickel(0) catalysed coupling of a 1:1 mixture of 2-bromo- and 4-bromo-*trans*-10b,10c-dimethyldihydropyrene yields 28% of the first unsymmetrically connected bi-annulenyl **4**, with 33% of **2**. Unlike **2**, the bi-annulenyl **4** has a significant barrier to rotation which is estimated at 11.0 kcal/mole from T_c measurement, compared to an MM2+PI calculated barrier of 12 kcal/mole. This is the first measurement of the barrier to rotation in a 1,2'-binaphthyl type system.

The dynamic stereochemistry of organic molecules containing rotating aryl rings has provoked much research.[1] However, examples in which both aryl rings are *annulenes* are rare, only three are known, **1**,[2a] **2**,[2b] and **3**,[2c] and all of these are symmetrical. Because annulenes and bridged annulenes are less planar[3] than their polycyclic benzenoid analogs, the barriers to rotation for bi-annulenyls are not necessarily the same as for the corresponding bi-aryls, and can have greater complexity.

We here report the synthesis and rotational barrier of the first unsymmetrically connected bi-annulenyl, **4**.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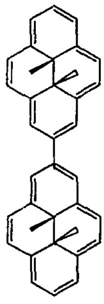
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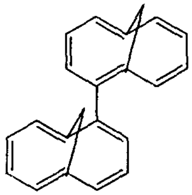
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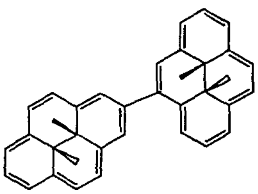
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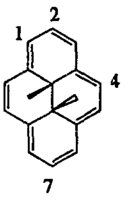

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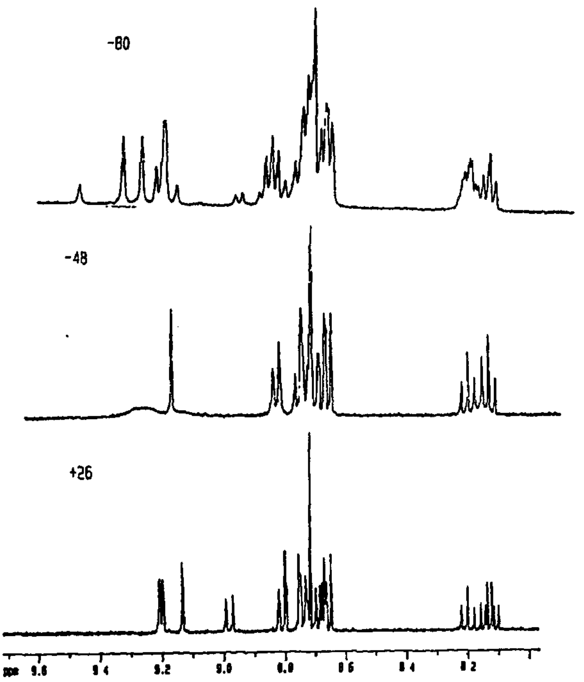
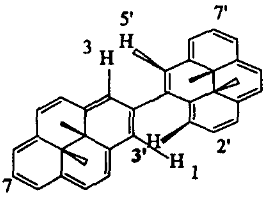
When dimethyldihydropyrene, **5**, is brominated with NBS/DMF[4] the 2-bromo derivative is the major product, however recently we have discovered that when NBS/$CHCl_3$[5] is used at room temperature, a 1:1 mixture of the 2- and 4-bromo derivatives is formed. Coupling[6] of this mixture using bis(triphenylphosphine)nickel (II) chloride, triphenylphosphine, zinc powder and $Et_4N^+I^-$ conditions,[2c,7] gave 33% of dimer **2** and 28% yield of the new dimer **4**. These could be separated by careful chromatography several times on silica gel and recrystallization from methanol. The structure of **4** was evident from its mass spectrum which indicated the molecular formula to be $C_{36}H_{30}$, supported by an elemental analysis, and its proton spectrum which showed the required three triplets for the 7-, 2'- and 7'- protons, and the four singlets for the internal methyl protons. Of greater interest are the variable temperature proton spectra, shown in Figure 1.

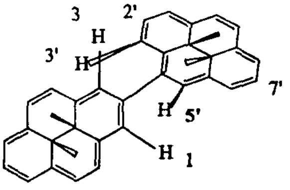
Figure 1: VT ^{1}H NMR spectra of **4** at +26°C, -48°C and -80°C.



The most deshielded peaks of **4** are the singlets corresponding to H-1 and H-3, which in d_8-THF are separated from each other at δ 9.21 and 9.20.[8] These singlets collapse at low temperature, T_c = -48°C, and re-emerge as two peaks each at -80°C, in unequal amounts corresponding to the two conformers **4A** and **4B**. The separation between H-1 and H-3 for the major conformer is 0.06 ppm, while for the minor conformer is 0.29 ppm. Molecular mechanics calculations[9] indicate that H-1 is about 0.5Å closer to the centre of the ring current of the other dihydropyrene ring than is H-3, and presumably is thus slightly more deshielded. This difference grows to about 1Å during the rotation, and hence the greater separation in chemical shift of the minor isomer. The steric interaction with H-3' on rotation about the aryl-aryl bond is the principal cause of the energy barrier. The singlet for H-5' at δ 9.14 is much slower to collapse, T_c < -70°C, and all of the other signals have T_c values too low to accurately determine.



4A



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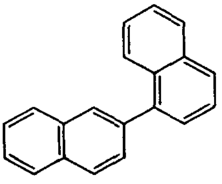

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Determination of rotational barriers by VT NMR in the simple *unsubstituted* bi-aryls is not easy[10] because of the overlapping of the aromatic signals[11] and the generally rather small barriers, and values that are known have usually been determined by other methods.[12] However, the exceptionally large ring currents of the dihydropyrenes make the task possible in a system such as **4**, which can be considered equivalent for rotational study purposes, to an unsubstituted 1,2'-binaphthyl, since only the 1,3 and 3',5' protons of **4** are involved in the rotational barrier. Interestingly, the energy barrier to rotation in 1,2'-binaphthyl, **6**, appears not to have been reported, either the experimental barrier or a calculated one, even though this system has been well studied at a high level of calculation,[13] the emphasis was on the energies and the twist angles of the two minima. PCMODEL[9] calculation of the barrier for **6** yields a value of 11.7 kcal/mole. The barrier calculated for the slightly less planar **4**, is 12.0 kcal/mole. There are two energy maxima with the 5'-4'-2-3 dihedral angle being about 25° and 195° at the two maxima, with relatively flat minima between 60-120° and 240-300°. The 195° conformer is about 1.5 kcal/mole higher in energy than the 25° conformer. The closest approach for H-3/H-3' in the higher energy 195° conformer is calculated to be 1.94Å, while in the 25° conformer H-1/H-3' is 2.04Å. Thus it is harder for H-3' to pass H-3 than H-1. The experimental barrier for **4** can be estimated[14] from $T_c = -48\,^\circ C$ and the low temperature average shift difference for H-1 or H-3, $\Delta\nu = 45$ Hz, as 11.0 kcal/mole, in excellent agreement with the PCMODEL calculation of 12.0 kcal/mole. PCMODEL suggests that the difference between the maxima (0° and 200° dihedral angle) for the two conformers of the binaphthyl **6** (3.4 kcal/mole) is slightly greater than for the bi-annulenyl **4** (1.5 kcal/mole). This larger energy difference between the maxima for **6** is consistent with the greater difference in calculated closest approach distances of 1.76Å (H-3'/H-8 0° conformer) and 1.99Å (H-1'/H-8 200° conformer) than those for **4** above.

A further comparison between a bi-annulenyl and a bi-aryl can be made: The barrier for rotation of the bi-[10]annulenyl **3** has been measured[2c] as 15 kcal/mole, and that for 1,1'-binaphthyl as 23 kcal/mole.[12] Our PCMODEL calculations suggest barriers of 17.5 and 27.2 kcal/mole respectively, again in reasonably good agreement with the experimental results. Clearly the much greater curvature of the [10]annulene skeleton in **3** relative to the more planar [14]annulene skeleton in **4**, reduces the barrier of **3** relative to 1,1'-binaphthyl more than of **4** relative to **6**. It thus turns out that the relatively planar **5**, makes the bi-annulenyl **4** a relatively good model for **6**, which is less true for the more curved annulene skeleton present in **3**.

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6. **Procedure**: a mixture of bis(triphenylphosphine)nickel(II) chloride (9.7 mg, 0.015 mmol), triphenylphosphine (50 mg, 0.19 mmol), zinc powder (15 mg, 0.23 mmol), tetraethylammonium iodide (39 mg, 0.15 mmol) and dry THF (10 mL) was stirred at 50°C under argon for about 1 hour, when the colour changed from green-blue to reddish-brown. A 1:1 mixture[5] of the 2- and 4-bromo derivatives of **5** (46 mg, 0.15 mmol) in THF (10 mL) was then added, and the reaction mixture was stirred at 50°C for 24h. After cooling, the reaction mixture was filtered through a short column of neutral aluminum oxide using petroleum ether (bp 40-60°C) as eluant. The product was then chromatographed three or four times over silica gel using petroleum ether as eluant to remove any triphenylphosphine and separate dimer **2** from **4**. Eluted first was the dimer **4** as 13 mg (28%) of red crystals from methanol, mp 185-186°C; HRMS calcd for $C_{36}H_{30}$: 462.2348. Found: 462.2337; ^{1}H NMR (360 MHz, $CDCl_3$) δ 9.16 (s, 2, H-1,3), 9.10 (s, 1, H-5'), 8.94 (d, J = 8.0 Hz, 1, H-3'), 8.90-8.62 (m, 11), 8.18, 8.12, 8.10 (t, 1 each, H-7,2',7'), -3.81, -3.82, -3.87, -3.94 (s, 3 each, $-CH_3$); ^{13}C NMR (90.6 MHz, d_8-THF) δ 138.46, 138.09, 138.02, 137.98, 137.80, 137.56, 135.02, 127.64, 127.56, 127.53, 125.00, 124.87, 124.85, 124.80, 124.70(x2), 124.61, 124.54, 124.40, 124.34, 123.97, 123.95, 31.77, 31.30, 31.26, 30.95, 15.18, 14.71 (in $CDCl_3$ also two methyl peaks at 14.83 and 14.33); UV (THF) λ_{max} (ε_{max}) 337 (13,000), 396 (11,500), 470 (4,600), 513 (4,700), 646 (460). Eluted second was 15 mg (33%) of purple dimer **2**, identical to an authentic sample.[2b] ^{1}H NMR spectrum (300 MHz, d_8-THF) δ 9.56 (s, 4, H-1,3), 8.81 (d, J = 7.8 Hz, 4, H-4,10), 8.63 (d, J = 7.7 Hz, 4, H-5,9), 8.54 (d, J = 7.6 Hz, H-6,8). 8.03 (t, 2, H-7), -3.68 and -3.77 (s, 6 each, $-CH_3$); ^{13}C NMR (90.6 MHz, $CDCl_3$) δ 137.6, 135.2, 124.5, 124.3, 123.9, 123.4, 123.3, 31.1, 30.9, 30.3, 29.7, 15.1, 14.7; HRMS calcd for $C_{36}H_{30}$: 462.2348. Found: 462.2343.
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8. The ^{1}H NMR spectrum of **4** in d_8-THF is slightly different than in $CDCl_3$ (above[6]) (360 MHz) δ 9.21 (s, 1, H-1), 9.20 (s, 1, H-3), 9.14 (s, 1, H-5'), 8.98 (d, J = 8.0 Hz), 1, H-3'), 8.82-8.65 (m, 11), 8.20, 8.14, 8.12 (t, 1 each, H-7,2',7'), -3.81, -3.82, -3.87, -3.94 (s, 3 each, $-CH_3$).
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