

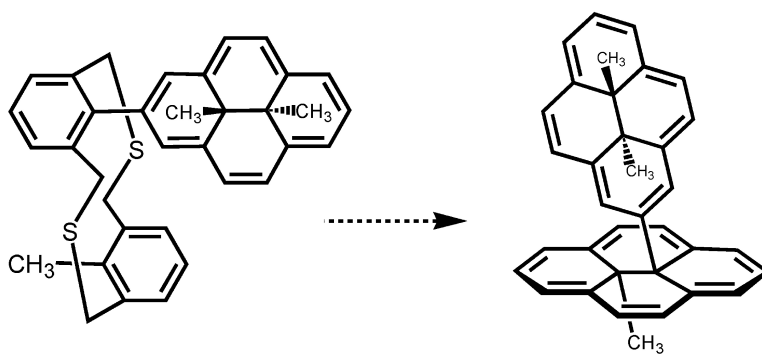
Communication

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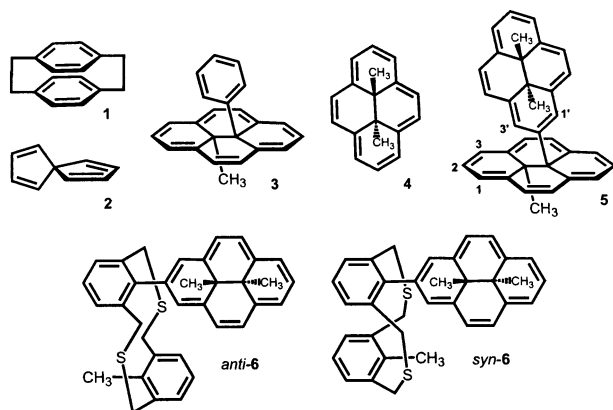
Evidence for Homo-Conjugation between Two Revolving 14 π -Electron Systems in 10b-Methyl-10c-[2-(10b,10c-dimethyl-10b,10c-dihydropyrenyl)]-10b,10c-dihydropyrene

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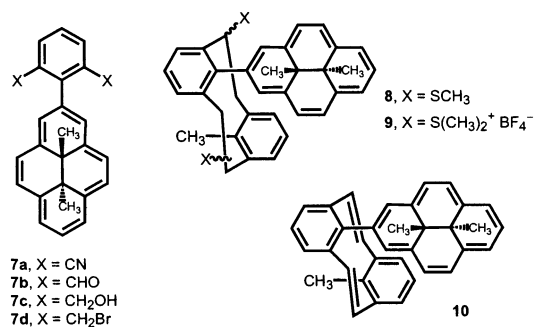
Two commonly encountered transannular π - π interactions are represented by the face-to-face interactions¹ in paracyclophane **1** and spiro(homo)-conjugation² in spiro-tetraene **2**. The first involves two parallel π systems, while the second has two perpendicular π systems. The spiro-interactions in particular have been employed recently in the design of organic materials.³ Spectroscopic studies of **3**, however, indicated that its benzene ring is freely rotating and there is little or no interaction between the two π systems in **3**. It is known that there is a correlation between spiro(homo)-conjugation and HOMO-LUMO of the molecule.⁴ Results from theoretical calculations⁵ indicate a large decrease in the HOMO-LUMO separation going from benzene to 10,10c-dimethyl-10b,10c-dihydropyrene **4**. We thus wish to report the synthesis of dihydropyrenyldihydropyrene **5** and spectroscopic evidence for a homo-conjugation effect between the two π systems in **5**.



The dithiacyclophane route to a cyclophanediene, and hence the dihydropyrene, is considered the most efficient.⁶ Thus, the dithiacyclophane **6** is an appropriate precursor to **5**. We reported earlier an arylation⁷ reaction of dihydropyrene which proved to be a successful route to **6**. A coupling reaction⁷ of dihydropyrene **4**^{6,8} with the diazonium salt derived from 2,6-dicyanoaniline⁹ gave 2-aryldihydropyrene **7a** in 32% yield after chromatography.¹⁰ Reduction of **7a** with DIBAL at room temperature afforded the dialdehyde **7b**. Reduction of **7b** with NaBH₄ gave a 98% yield of diol **7c**. Treatment of **7c** with PBr₃ at room temperature afforded the desired dibromide **7d**. It was evident from their ¹H NMR spectra that atropisomers of **7b**–**7d** existed in solution.⁷ Surprisingly, a dynamic ¹H NMR study of **7d** indicated no coalescence of its pair of methylene proton signals up to a temperature of 110 °C, corresponding to a conformational energy barrier (ΔG^\ddagger_c)¹¹ of >77 kJ mol⁻¹ for unrestricted rotation about the aryl-aryl single bond in **7d**.

A coupling reaction between 2,6-bis(mercaptomethyl)toluene^{6b} and the dibromide **7d** under high-dilution conditions¹² gave an 18%

yield of a mixture of *anti*-**6** and *syn*-**6**. These were obtained in a ratio of 95:5 based on ¹H NMR spectral analysis. Isolation of *anti*-**6** could be achieved by either chromatography or fractional recrystallization. Its anti stereochemistry was assigned on the basis of its low-temperature (–40 °C) ¹H NMR spectrum where the internal methyl protons in the cyclophane moiety were significantly shielded and appeared as a singlet at δ 1.64. A dynamic ¹H NMR study¹¹ was carried out by probing H1' and H3' (δ 7.90 and 8.75, respectively at –40 °C) of the dihydropyrene moiety. The free energy of activation (ΔG^\ddagger_c)¹¹ for rotation about the aryl-aryl bond in *anti*-**6** was thus estimated to be 53.5 kJ mol⁻¹.

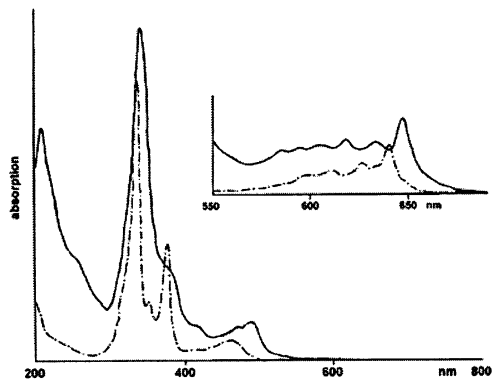


Treatment of *anti*-**6** with LDA followed by quenching the intermediates with methyl iodide resulted in a mixture of isomers of *m*-cyclophane **8**. Remethylation¹³ of **8** with (CH₃O)₂CHBF₄ afforded the salt **9** isolated as a brown solid in about 95% yield. A Hofmann elimination of **9** carried out with *t*-BuOK in THF gave the cyclophanediene **10** which underwent valence tautomerization to afford the desired product **5** in a 31% yield.

Compound **5** was isolated as thick, yellow-green oil, and its structure was supported by a molecular ion observed at *m/z* 448 and a base peak at *m/z* 202 (corresponding to pyrene) in its mass spectrum. The chemical shift (δ –4.14) of the methyl protons at C10b in **5** is very similar to that (δ –4.25)^{6b} of the parent **4** thus indicating that **5** sustains a ring current essentially identical to that in **4**. The diatropicity of the dihydropyrene ring is sensitive to geometric deviation from planarity of the macro-ring.¹⁴ The above observation suggests that despite the introduction of a spatially demanding 2-dihydropyrenyl group at C10c, the molecular structure of **5** is expected to show no appreciable changes in its overall geometry of its dihydropyrene moieties. The aromatic protons in **5** (Table 1) could be readily assigned by its ¹H NMR (Figure 1) and COSY spectra. It is evident that the “internal” dihydropyrenyl ring is freely rotating. There is appreciable downfield shift of H1,3, being in the deshielding zone of the internal dihydropyrenyl ring. On the other hand, the series of protons H1'–H10' are strongly shielded,¹⁵ even for H7' being furthest from the molecular plane of the opposite dihydropyrene. The ring current of each dihydropyrene ring in **5**

Table 1. Chemical Shifts of Protons in **5**

CH ₃ at C10b	H1,3	H2	H4,10	H5,9	H6,8	H7
-4.14	9.01	8.42	8.75	8.61	8.97	8.63
CH ₃ at C10b',10c'	H1',3'	H2'	H4',10'	H5',9'	H6',8'	H7'
-5.16, -4.86	4.05	-	7.48	8.12	8.23	7.79

**Figure 1.** ¹H NMR spectrum of the aromatic protons in **5**.**Figure 2.** Electronic spectra of **4** (---) and **5** (—).**Table 2.** Principal Absorption Spectral Bands [λ_{\max} (log ϵ_{\max})] for **3**, **4**, **5**, **11**, and **12**

compd	α	p	β	β'
3 ¹⁷	645.5 (2.51)	481 (3.81)	383 (4.66)	341 (4.93)
4 ¹⁸	641 (2.52)	463 (3.78)	377 (4.57)	337.5 (4.96)
5	648 (2.78)	488 (4.06)	416 (4.04)	341 (5.02)
11 ¹⁸	648 (2.51)	493 (4.18)	390 (4.52)	348 (5.15)
12 ¹⁸	(tail to 700)	577 (4.20)	400 (4.12)	368 (4.72)

clearly extends to an appreciable distance with respect to each molecular plane.

Transannular π - π electronic interactions could best be studied by electronic spectroscopy. The electronic spectra of **4** and **5** are illustrated in Figure 2. Bathochromic shift and peak broadening of absorption bands are generally observed going from **4** to **5**. This is consistent with appreciable π - π interaction between the two 14π systems in **5**.

Using the Clar's α , p , β , and β' notation,¹⁶ the λ_{\max} of the principal bands of **5** could be compared to those of the phenyl-substituted analogue **3** and the biphenyl-type conjugation in **11** and **12** (Table 2). Comparing to the spectrum of **4**, the most significant shifts of 25 and 39 nm were observed for the p and β bands of **5**, respectively, with relatively smaller shifts for the α and β' bands. The bathochromic shifts of the p and β bands of **5** are similar to

those going from **4** to **11** and **12** involving linear conjugation. The fine structures at 580–650 nm (Figure 2) are also collectively shifted by about 8 nm to the longer wavelength going from **4** to **5**. A comparison with the electronic spectral data of **3**¹⁷ further adds evidence that the dihydropyrene unit in **5** interacts with greater effect than the benzene in **3**, validating our prediction that the relatively small HOMO–LUMO gap of the two identical dihydropyrene moieties in **5** optimizes the opportunity for observing homoconjugation that earlier reported systems failed to reveal.

The above observations strongly suggest through-space homoconjugation between the two macrocyclic 14π systems in **5**. The behavior of a spiro(homo)-conjugation effect in an electronic spectrum could be a shift of the absorption maxima to longer or shorter wavelength.¹⁹ Thus, the homo-conjugation effect in **5** observed in our work corresponds to a class I spiro(homo)-conjugation¹⁹ with its absorption maxima shifted to longer wavelength compared to those of the reference compound **4**.

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Supporting Information Available: Experimental details and analytical data for compounds **5**–**8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (a) Keehn, P.; Resenfeld, S. *Cyclophanes*; Academic Press: New York, 1983. (b) Vögtle, F. *Cyclophanes*; Springer-Verlag: Heidelberg, 1983. (c) Vögtle, F. *Supramolecular Chemistry*; Wiley: Chichester, 1989. (d) Vögtle, F. *Cyclophane Chemistry*; Wiley, Chichester, 1989. (e) Diederich, F. *Cyclophanes*; The Royal Society of Chemistry: Cambridge, 1991.
- (a) Semmelhack, M. E.; Foos, J. S.; Katz, S. *J. Am. Chem. Soc.* **1973**, *95*, 7325. (b) Batich, C.; Heibronner, E.; Rommel, E.; Semmelhack, M. F.; Foos, J. S. *J. Am. Chem. Soc.* **1974**, *96*, 7662.
- (a) Maslak, P. *Adv. Mater.* **1994**, *6*, 405. (b) Fu, W.; Feng, J. K.; Pan, G. B. *J. Mol. Struct. (THEOCHEM)* **2001**, *545*, 157. (c) Kim, S. Y.; Lee, M.; Boo, B. H. *J. Chem. Phys.* **1998**, *109*, 2593. (d) Feng, J. K.; Sun, X. Y.; Ren, A. H.; Yu, K. Q.; Sun, C. C. *J. Mol. Struct. (THEOCHEM)* **1999**, *489*, 247.
- (a) Durr, H.; Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 559. (b) Raman, J. V.; Nielsen, K. E.; Randall, L. H.; Burke, L. A.; Dmitrienko, G. I. *Tetrahedron Lett.* **1994**, *35*, 5973. (c) Dodziuk, H.; Leszczynski, J.; Jackowski, K. *Tetrahedron* **2001**, *57*, 5509.
- Bock, H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 613.
- (a) Mitchell, R. H.; Otsubo, T.; Boekelheide, V. *Tetrahedron Lett.* **1975**, *16*, 219. (b) Mitchell, R. H.; Boekelheide, V. *J. Am. Chem. Soc.* **1974**, *96*, 1547.
- Lai, Y.-H.; Jiang, J. *J. Org. Chem.* **1997**, *62*, 4412.
- Phillips, J. B.; Molyneux, R. J.; Sturm, E.; Boekelheide, V. *J. Am. Chem. Soc.* **1967**, *89*, 1704.
- Prepared from a reaction between commercially available 2,6-dichloroaniline and CuCN. See Supporting Information.
- The corresponding 2,7-diaryldihydropyrene was isolated in 28%.
- Oki, M. *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*; VCH Publishers: New York, 1985.
- (a) Rossa, L.; Vögtle, F. *Top. Curr. Chem.* **1983**, *113*, 1. (b) Knops, P.; Sendhoff, N.; Mekelburger, H. B.; Vögtle, F. *Top. Curr. Chem.* **1991**, *161*, 1. (c) Ostrowicki, A.; Koepf, E.; Vögtle, F. *Top. Curr. Chem.* **1991**, *161*, 37.
- Borch, R. F. *J. Org. Chem.* **1969**, *34*, 627.
- (a) Mitchell, R. H. *Adv. Theor. Interesting Mol.* **1989**, *1*, 135. (b) Mitchell, R. H. *Chem. Rev.* **2001**, *101*, 1301.
- Lai, Y.-H.; Zhou, Z. L. *J. Org. Chem.* **1997**, *62*, 925.
- Clar, E. *Polycyclic Hydrocarbons*; Academic Press-Springer-Verlag: London, 1964; Vol. 2, p 116.
- Anker, W. PhD Thesis, University of Victoria, 1982.
- Mitchell, R. H.; Chaudhary, M.; Dingle, T. W.; Williams, R. V. *J. Am. Chem. Soc.* **1984**, *106*, 7776.
- (a) Simmons, H. E.; Fukunage, T. *J. Am. Chem. Soc.* **1967**, *89*, 5208. (b) Hoffmann, R.; Iwamura, A.; Zeiss, G. D. *J. Am. Chem. Soc.* **1967**, *89*, 5215.

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