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Extreme Projection of a Proton into the π-Cloud of an Aromatic Ring: Record Shielding of an Aromatic Proton in *trans*-10*b*-Methyl-10*c*-(1-naphthyl)-10*b*,10*c*-dihydropyrene

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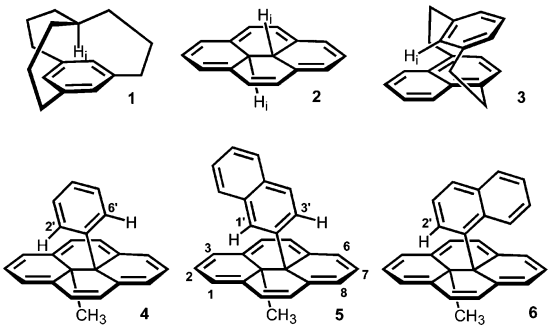
Abstract: A synthetic sequence involving dithiametacyclophane → metacyclophanediene → dihydropyrene was employed to prepare *trans*-10*b*-methyl-10*c*-(2-naphthyl)- and *trans*-10*b*-methyl-10*c*-(1-naphthyl)-10*b*,10*c*-dihydropyrene **5** and **6**, respectively. Both exhibit a strong diamagnetic ring current despite the introduction of an internal bulky substituent within the π-electron cloud. Their electronic spectra suggest interaction between the two near-perpendicular naphthyl and dihydropyrenyl π systems, resulting in red shift and band broadening. All naphthyl protons are well resolved in their ^{1}H NMR spectra due to a strong shielding effect of the dihydropyrene ring. The most shielded protons in **5** and **6** are H1′ and H2′ at δ 2.47 and 1.42, respectively, being 5.25 and 5.95 ppm shifted from those of reference protons. There is evidence for free rotation on the NMR time scale of the 2-naphthyl ring in **5** with a preference for a particular conformer, whereas the 1-naphthyl ring in **6** is conformationally rigid with its H2′ projecting deeply into the π-cloud, thus accounting for the most shielded aromatic proton (H2′ in **6**) reported to date.

Introduction

One of the strongest shielding effects of a benzene ring was observed on the methine proton (δ −4.03)[1] of metacyclophane **1** exhibiting a 6 ppm upfield shift from the methine resonance (δ 1.87)[2] in adamantane. Placing a methine proton within the π-cloud of the dihydropyrene **2** ($\delta H_i = -5.49$)[3] results in an even more significant shielding effect. The conformationally rigid naphthalenophane **3** has its aromatic H_i located directly above the shielding zone of one of its naphthalene rings. Its chemical shift ($\delta H_i = 3.95$)[4] is 4 ppm upfield compared to that of H2 (δ 6.95)[2] of *m*-xylene. Again a more substantial shift was observed going from H2,6 (δ 7.40)[2] of *tert*-butylbenzene to the H2′,6′ in **4** ($\delta H_i = 2.55$)[5] where the phenyl ring, despite the fact that it is likely to be freely rotating, is enclosed within the ring current of the dihyropyrene unit.

The 14π aromatic system in 10*b*,10*c*-dihydropyrene has been shown to be strongly diatropic, and the ring current is sensitive to geometric changes, annelation, and conjugation effect.[6] Replacing the phenyl ring in **4** with a sterically more demanding aromatic substituent was expected to restrict its conformational mobility, thus compelling one or more aromatic protons of the internal substituent to intrude more deeply into the π-cloud of the dihydropyrene moiety. An interesting question remains whether there is a limit to the proximity of a proton projecting into an aromatic π-cloud. We report the synthesis of the two naphthyldihydropyrenes **5** and **6** and a study of their diatropicity and shielding effect. The H2′ in **6** was in fact found to be shifted 6 ppm upfield—a record shielding of an aromatic proton—using the corresponding proton in 1,5-di-*tert*-butyl-naphthalene as a reference.



Results and Discussion

Synthetic Routes to 10*b*-Methyl-10*c*-naphthyl-10*b*,10*c*-dihydropyrenes. The organonickel-catalyzed[7] coupling reactions of the Grignard reagent of 2-bromo-*m*-xylene with 2-bromonaphthalene and 1-bromonaphthalene yielded **7a** and **7b**, respectively. Compound **7a** was obtained as a colorless oil, whereas **7b** was isolated as colorless crystals. Separate free radical bromination reactions of **7a** and **7b** with 2 equiv of NBS gave dibromides **8a** and **8b**, respectively, in about 40% yield.

(1) Pascal, R. A., Jr.; Grossman, R. B.; Van Engen, D. *J. Am. Chem. Soc.* **1987**, *109*, 6878.
(2) *ACD/Labs software: Aldrich FT-NMR Library Pro 4.5*; Advanced Chemistry Development, Inc.: Toronto, c1994−2000.
(3) Mitchell, R. H.; Boekelheide, V. *J. Am. Chem. Soc.* **1974**, *96*, 1547.
(4) Lai, Y.-H.; Lim, T.-H. *J. Org. Chem.* **1989**, *54*, 5991.
(5) Mitchell, R. H.; Anker, W. *Tetrahedron Lett.* **1981**, *22*, 5139.
(6) (a) Mitchell, R. H. *Chem. Rev.* **2001**, *101*, 1301. (b) Mitchell, R. H. *Adv. Theor. Interesting Mol.* **1989**, *1*, 135.
(7) Clough, R. L.; Mison, P.; Roberts, J. D. *J. Org. Chem.* **1976**, *41*, 2252.

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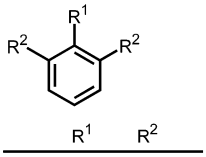
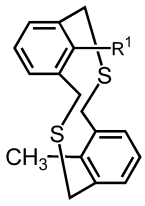
The ^{1}H NMR spectrum of **8a** shows an AB system at δ 4.26 and 4.21 for the two pairs of bromomethyl protons. The corresponding AB quartet for **8b** appears at δ 4.18 and 3.94. The above observation was consistent with restricted rotation of the benzene ring in each case, with the methylene protons in each bromomethyl group being diastereotopic and thus magnetically nonequivalent. These AB systems remained invariant at temperatures up to 150 °C, indicating high rotational energy barriers.[8] Treatment of dibromides **8a** and **8b** in separate reactions with thiourea in refluxing THF followed by hydrolysis in refluxing aqueous KOH solution afforded quantitatively the dithiols **9a** and **9b**, respectively, as colorless oils.

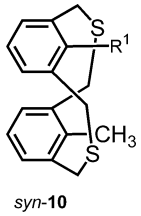
The coupling reaction of **9a** with 2,6-bis(bromomethyl)-toluene[3] under high dilution conditions[3] in refluxing ethanol in the presence of KOH yielded 68% of dithiacyclophane **10a** as a mixture of anti and syn isomers in a 3:1 ratio. All attempts to separate these isomers failed, but a satisfactory elemental analysis was obtained for a mixture of *anti*- and *syn*-**10a**. In the ^{1}H NMR spectrum of the mixture the internal methyl protons of *anti*-**10a** are significantly shielded by the opposite aryl ring at δ 1.59 similar to related examples reported earlier.[3,5] On the contrary the internal methyl protons of *syn*-**10a** appear at δ 2.52, being slightly deshielded by the opposite naphthyl ring compared to those in reported examples.[3,5]



	R^1	R^2
7a	2-naphtyl	CH_3
7b	1-naphtyl	CH_3
8a	2-naphtyl	CH_2Br
8b	1-naphtyl	CH_2Br
9a	2-naphtyl	CH_2SH
9b	1-naphtyl	CH_2SH



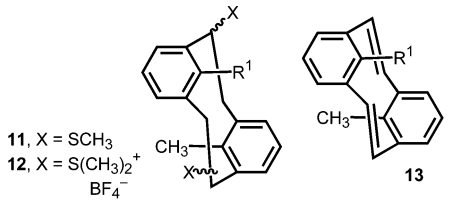
anti-**10**



syn-**10**

a, R^1= 2-naphthyl; **b**, R^1= 1-naphthyl

A similar coupling reaction between either 2,6-bis-(mercaptomethyl)toluene[3] with dibromide **8b** or dimercaptan **9b** with 2,6-bis(bromomethyl)toluene failed to give either isomer of dithiacyclophane **10b**. This could be attributed to unfavorable steric interaction caused by the 1-naphthyl group in the cyclization step. Cesium carbonate has been employed in the successful synthesis of many thia- and dithiacyclophanes that are otherwise difficultly accessible.[9] By employing the cesium effect[10] we could successfully prepare **10b**. It was, however, only obtained in about 10% optimum yield as a mixture of anti and syn isomers (5:1) by carrying out the coupling reaction in DMF in the presence of cesium carbonate at 70 °C. The decreased syn:anti ratio in going from **10a** to **10b** is also consistent with an increase in unfavorable steric interaction going from a 2-naphthyl to a 1-naphthyl moiety. Recrystallization and chromatography failed to yield pure samples of either anti or syn isomer of **10b**. Satisfactory elemental analysis was, however, obtained for the mixture of **10b**. Assignment of the stereochemistry of each isomer in the mixture could again be readily made on the basis of the chemical shift of the methyl protons. The methyl protons of *anti*-**10b** appear at δ 1.61, being strongly shielded by the opposite benzene ring while those of *syn*-**10b** were observed within the expected range at δ 2.62.



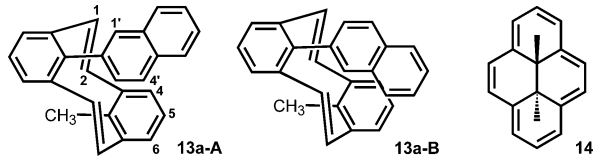
a, R^1= 2-naphthyl; **b**, R^1= 1-naphthyl

Separate Wittig rearrangements[11] of **10a** and **10b** occurred smoothly when they were treated with *n*-BuLi. Quenching with MeI yielded **11a** and **11b**, respectively, each as a mixture of isomers in near quantitative yield.[12] The general structures of **11a** and **11b** were supported on the basis of their respective mass and ^{1}H NMR spectra. In each case a molecular ion was observed at *m*/*z* 440, and singlets at δ 0.8−0.9 and δ 2.1−2.2 characteristic of the methylthio and anti methyl protons were present.[12] Treatment of compounds **11a** and **11b** separately with $(CH_3)_3CHBF_4$[13] afforded the corresponding bissulfonium salts **12a** and **12b**, respectively. Hofmann elimination[11] of the salt **12a** in the presence of *t*-BuOK at room temperature gave a mixture of the dihydropyrene **5** and the diene **13a** in a total yield of ca. 20%.[14] The observed ratio of **5** to **13a** in freshly isolated mixtures, based on integrations of the respective methyl signals, ranged from 1:1 to 2:1. Diene **13a** was found to undergo valence isomerization readily to **5** and thus could not be separated pure by chromatography. A pure sample of **5** could be obtained on prolonged standing of a solution of the mixture of **5** and **13a**. A similar elimination reaction of the salt **12b** at room temperature, however, did not result in the formation of either **6** or **13b**. Carrying out the reaction in THF at reflux gave, after chromatography, only the dihydropyrene **6** in 10% yield. Diene **13b**, the valence isomer of **6**, was not observed, presumably because the severe steric interaction caused by the 1-naphthyl group accelerated the isomerization of the initially formed diene **13b** to dihydropyrene **6**. The relatively more sterically demanding 1-naphthyl group in **13b** may then explain why the Hofmann elimination of **12b** to form **13b** was slower than that of **12a** to **13a** but the subsequent valence isomerization of **13b** to **6** is faster than that of **13a** to **5**. Carrying out the Hofmann elimination of salt **12a** in refluxing THF also resulted in direct isolation of only **5** without the presence of **13a** in the product. Thermally, **5** was found to be relatively more stable than **6**. In fact, **6** readily decomposed, particularly in solution, on prolonged standing.

The spatial demand of the 2-naphthyl group in **13a** was expected to restrict rotation about the aryl−aryl bond similar to that observed for the phenyl analogue reported earlier.[5] Two of its possible conformations are illustrated in **13a**-**A** and **13a**-

(8) (a) Clough, R. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1976**, *98*, 1018. (b) Wolf, C.; Mei, X. *J. Am. Chem. Soc.* **2003**, *125*, 10651.
(9) Rossa, L.; Vögtle, F. *Top. Curr. Chem.* **1983**, *113*, 12.
(10) (a) Buter, J.; Kellogg, R. M. *J. Org. Chem.* **1982**, *46*, 4481. (b) Vögtle, F.; Klieser, B. *Synthesis* **1982**, 249. (c) Klieser, B.; Vögtle, F. *Angew. Chem. Suppl.* **1982**, 1392. (d) Kato, N.; Matsunaga, H.; Oeda, S.; Fukazawa, Y.; Ito, S. *Tetrahedron Lett.* **1979**, *20*, 2419.
(11) Mitchell, R. H.; Otsubo, T.; Boekelheide, V. *Tetrahedron Lett.* **1975**, *16*, 319.
(12) A syn-to-anti isomerization is known to occur in such Wittig rearrangements although the extent of isomerization may vary from one system to another. Signals of methyl protons of the corresponding syn isomers, if present, would be masked by those of the SCH_3 protons.
(13) Borch, R. F. *J. Org. Chem.* **1969**, *32*, 627.
(14) Mixture of the bissulfonium salts might contain the corresponding syn isomers of anti **12**. There was, however, no indication of the presence of *syn*-cyclophandiene or *cis*-dihydropyrene in the product mixture after Hofmann elimination.

B. The appreciable shielding of H4′ (δ 7.46) compared to chemical shifts of other protons on the naphthyl ring indicates a preference for conformer **13a-A**. Conformer **13a-B** is also expected to be sterically unfavorable with the naphthyl ring in close proximity to the opposite phenyl ring. The upfield shift of H4,6 (δ 6.14) and H5 (δ 6.22) in **13a-A** no doubt derives from shielding by the naphthyl ring.



Diatropicity and Spectral Properties. The internal methyl protons of **5** and **6** appear at δ −4.25 and −4.32, respectively, indicating that their ring currents are very similar to that of the parent dihydropyrene **14** (δCH_3 −4.25).[3] Although the spatially more demanding 1-naphthyl group may result in certain degree of geometric deviation from planarity of the peripheral ring in **6** (see later discussion), the seemingly identical ring currents of **6** and **14** suggests that such deformation, if any, does not affect significantly the diatropicity of the macro ring. The ^{1}H NMR spectra of **5** and **6** are shown in Figure 1 and Figure 2, respectively. Proton assignments of **5** and **6** were made on the basis of their ^{1}H NMR, 2D COSY, and HMBC spectra and a series of NOE experiments.

Interestingly, all the ring protons in the dihyropyrene unit in **5** and **6** have essentially identical coupling constants (7.7−7.8 Hz). This clearly suggests that there is little bond alternation in the 14π peripheral ring consistent with the strong diatropicity observed in **5** and **6**.[15] In fact, their aromatic protons of the internal naphthyl ring were well resolved within a wide range

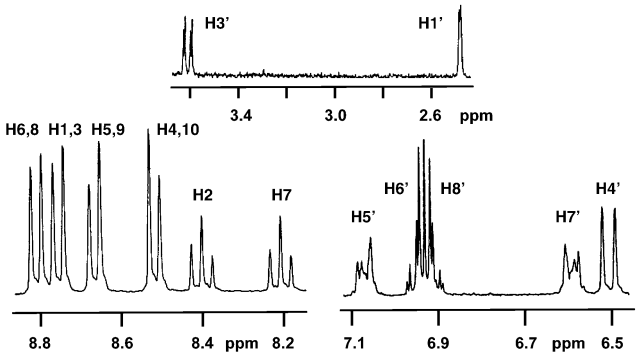


Figure 1. ^{1}H NMR (300 MHz) spectrum of the aromatic protons in dihydropyrene **5**.

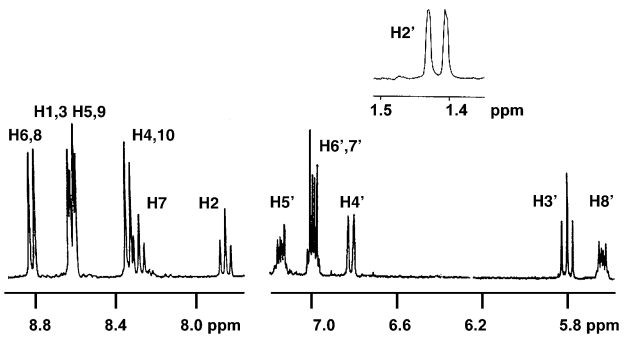


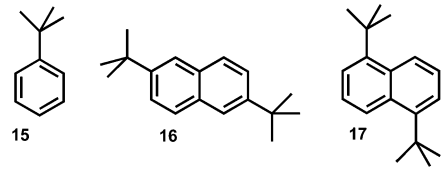
Figure 2. ^{1}H NMR (300 MHz) spectrum of the aromatic protons in dihydropyrene **6**.

Table 1. Shielding Effect on Selected Aromatic Protons of **4**−**6** in Comparison to Reference Protons in **15**−**17**

	ortho-H[a]		meta-H[b]		para-H[c]	
compd	δ	$\lvert\Delta\delta\rvert$	δ	$\lvert\Delta\delta\rvert$	δ	$\lvert\Delta\delta\rvert$
4	2.55	4.85	5.6	1.69	6.0	1.16
15	7.40		7.29		7.16	
5	2.47		6.50			
	3.62	5.25		1.25		
16	7.72	3.93	7.75			
	7.55					
6	1.42	5.95	5.80	1.42	6.82	1.45
17	7.37		7.22		8.27	

[a] H2′,6′ of **4**; H1′ and H3′ of **5**, respectively; H2′ of **6**; H2,6 of **15**; H1 and H3 of **16**, respectively; H2,6 of **17**. [b] H3′,5′ of **4**; H4′ of **5**; H3′ of **6**; H3,5 of **15**; H4 of **16**; H3,7 of **17**. [c] H4′ of **4**; H4′ of **6**; H4 of **15**; H4,8 of **17**.

of 5−6 ppm due to the extensive shielding effect of the dihydropyrene ring (Figures 1 and 2). The most shielded proton in **5** is H1′ appearing at δ 2.47. There is no reported series of reference compounds with similar steric, conformational, and/or strain effects found in **4**, **5**, and **6**, although such effects could affect proton chemical shift. In comparison to the strong shielding effect in **4**−**6**, the steric, strain, and/or conformational effect, if any, will, however, be expected to be relatively small. For example, from the optimized structures of **5** and **6** derived from B3LYP/6-31G* (DFT) method (refer to Figures 5a and 7a), the distances between H1′ (in **5**) or H2′ (in **6**) and the peripheral carbons C10b, C1, and C2 are between 2.6 and 2.9 Å. These are only slightly smaller than the sum of their van der Waals radii (2.9 Å),[16] and thus the steric effect is not expected to induce very significant changes in the proton chemical shift of H1′ or H2′. The series of compounds **15**, **16**, and **17** may not approximate the steric, conformational, and/or strain effects found in **4**, **5**, and **6**, respectively, but their structural features are consistent in the series for a reasonable comparative study. Using *tert*-butylbenzene **15**[2] and 2,6-di-*tert*-butylnaphthalene **16**[17] as the corresponding reference compounds, the shielding of H1′ in **5** is similar (ca. 5 ppm) to that[5] observed for the H2′,6′ in **4** (Table 1). Going from **5** to **6** leads to a more shielded aromatic proton in H2′ of **6**, being shifted upfield to δ 1.42—a shielding of about 6 ppm compared to the chemical shift of H2,6 of the reference 1,5-di-*tert*-butylnaphthalene **17**.[18] This appears to be one of the largest shieldings of an aromatic proton and may, in fact, be a record. The above observation may suggest a conformationally rigid naphthyl ring in **6** with its H2′ projecting deeply toward the center of its diamagnetic ring current (see later discussion on conformational studies).



Close promixity between the π orbitals in the benzenoid and the dihydropyrene in **4**−**6** held near-perpendicular to each other

(15) (a) Cremer, D.; Günther, H. *Liebigs Ann. Chem.* **1972**, *763*, 87. (b) Lai, Y.-H.; Chen, P.; Dingle, T. W. *J. Org. Chem.* **1997**, *62*, 916. (c) Mitchell, R. H.; Chen, Y. S.; Khalifa, N. *J. Am. Chem. Soc.* **1998**, *120*, 1785. (d) Andres, W.; Günther, H.; Günther, M.-E.; Hausmann, H.; Günther, J.; von Puttkamer, H.; Schmickler, H.; Niu-Schwarz, J.; Schwarz, W. H. E. *Helv. Chim. Acta* **2001**, *84*, 1737.
(16) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

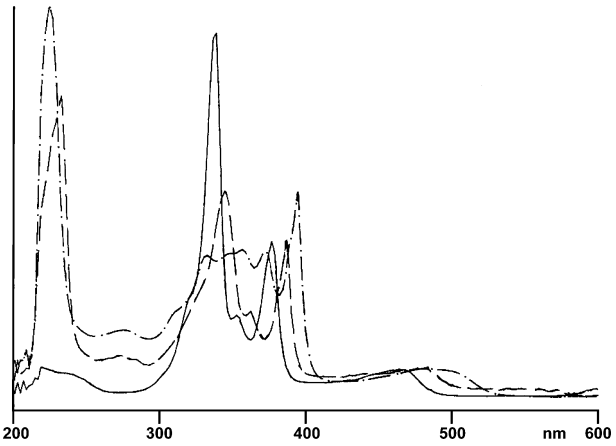


Figure 3. Electronic spectra of aryldihydropyrenes **4** (—), **5** (-- -) and **6** (— • — • —).

represents a unique type of $\pi-\pi$ interaction. Although this effect was not clearly evident in the study of **4**,[5] such interaction between two aromatic rings is expected to lead to a splitting of the molecular orbitals in the excited-state, thus resulting in a red shift and/or broadening of the absorption bands in their electronic spectra.[19] The electronic spectra of **4**,[5] **5**, and **6** are illustrated in Figure 3. It is interesting to note that the spectrum of **5** in the range of 300−600 nm is similar to that of **4** but the λ_{max} are red-shifted. The spectrum of **6** in the same wavelength range, however, exhibits significant broadening of the absorption bands in addition to a small red shift. This again supports a relatively rigid conformation of the 1-naphthyl ring in **6**, thus maximizing the novel through-space interaction between the two near-perpendicular aromatic π systems.

Conformational Studies. A conformational study of **4** did not confirm whether the phenyl ring in it undergoes free rotation on the NMR time scale.[5] It is interesting to note that the shielding of the two "ortho" protons H-1′ and H3′ of **5** is significantly different by >1 ppm (Table 1). This may suggest that the 2-naphthyl ring in **5** is not freely rotating on the NMR time scale or it favors a certain conformation at equilibrium. Observation from appropriate molecular models suggests several possible conformations as indicated in Figure 4. Geometries of these conformers of **5** were optimized using the B3LYP/6-31G* (DFT) method with the Gaussian 98 suite of programs.[20] Such programs have been employed successfully in optimizing structural geometries of macrocyclic annulenes that correlated satisfactorily with their experimentally observed physical properties.[21] Results derived from our calculations showed that

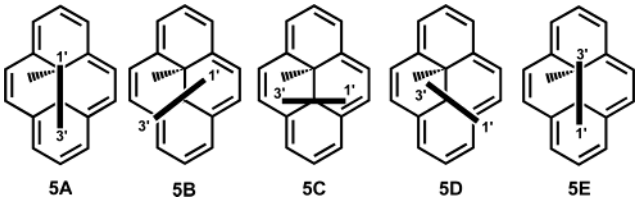


Figure 4. Possible conformations for naphthyldihydropyrene **5**.

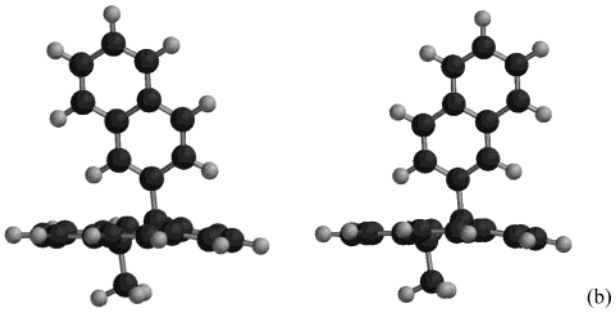


Figure 5. Optimized structures of (a) **5A** and (b) **5E** derived from B3LYP/6-31G* (DFT) method.

conformers **5A**, **5D**, and **5E** are energy minima, and their relative Gibb's free energy at 298 K was found to be 0:9.3:3.0 kJ mol^{-1}. The optimized structures of **5A** and **5E** are shown in Figure 5. The dihydropyrene moiety remains essentially planar in **5A** and **5E** with a relatively larger deviation observed for C7 in **5E**. Conformer **5C** was a random point on the potential energy surface, and full optimization of **5C** led to conformer **5D**. A full optimization of **5C** with the transition search keyword, however, resulted in conformer **5B**. Optimization of a structure whose starting geometry is very similar to that of **5B** led to **5D**. The above observation indicates that **5B** is a transition state, and its Gibb's free energy at 298 K was estimated to be 18.2 kJ mol^{-1} at 298 K. The differences in relative free energy of **5A**, **5B**, **5D**, and **5E** are reasonably low to suggest possible rotation of the naphthyl ring about the C10*b*−C2′ bond. A piece of evidence came from the following NOE experiments. Irradiation of either H1′ or H3′ of **5** resulted in enhancement of signals of all the peripheral ring protons H1−H10. Thus, it is likely that the naphthyl ring in **5** undergoes rotation with **5A** being the major conformer, and hence there is a significant difference in the shielding of H1′ and H3′. This is similar to a related phenomenon in the conformational study of 9-H-9-ethyl-10-methyl-anthracenium ion.[22] A dynamic ^{1}H NMR study of **5** ranging from −80 to 80 °C indicated a significant change ($\Delta\delta$ = 0.6 ppm) in the chemical shift of H1′. This was expected since the chemical shift of H1′ should be most sensitive to a change in the relative population of rapidly interconverting conformers as the temperature was varied. A much smaller change was observed for H3′, and the chemical shifts of the other protons remained practically invariant within the temperature range studied.

In the 14π system of 10*b*,10*c*-dihydropyrene the shielding effect is expected to be the most significant along the central *z*-axis given a distance *d* from the molecular plane.[23] In **6**, H8′

(17) (a) Koch, K.-H.; Müllen, K. *Chem. Ber.* **1991**, *124*, 2091. (b) Smith, K.; Roberts, S. D. *Catal. Today* **2000**, *60*, 227.
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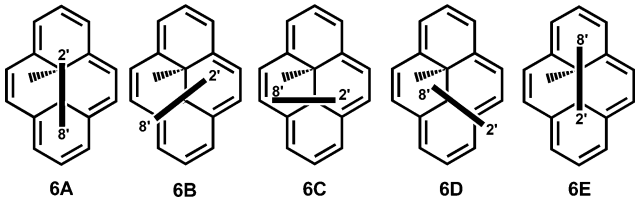

Figure 6. Possible conformations for naphthyldihydropyrene **6**.

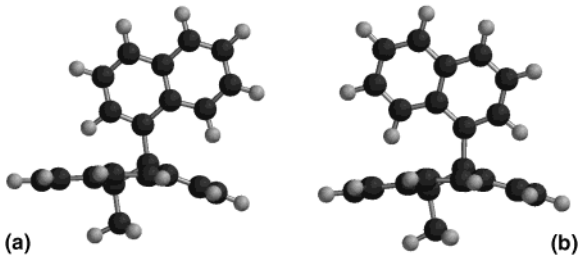

Figure 7. Optimized structures for (a) **6A** and (b) **6E** derived from B3LYP/6-31G* (DFT) method.

appears at δ 5.63, while H2′ is significantly more shielded at δ 1.41. This suggests a preference for a conformation where H2′ is located along the central axis of the dihydropyrene ring and projecting deeply into the center of the π-electron cloud such as **6A** or **6B** (Figure 6). Geometries of conformers of **6** (Figure 6) were also optimized using the B3LYP/6-31G* (DFT) method with the Gaussian 98 suite of programs.[20] Results from these calculations only indicated conformers **6A** and **6E** as energy minima, and their optimized structures are shown in Figure 7. It is apparent that the dihydropyrene moiety in **6A** and **6E** is significantly deviated from planarity compared to that in **5A** and **5E** (Figure 5) due to a larger steric demand of the 1-naphthyl substituent. Conformers **6B**, **6C**, and **6D** are random points on the potential energy surface. A transition state **6C′** was, however, found to have a structure similar to that of **6C** with a relatively larger dihedral angle of 42° for its C2′−C1′−C10*c*−C10*d* (that of **6C** is 30°). The relative Gibb's free energy of **6A**:**6C′**:**6E** was calculated to be 0:42.7:16.4 kJ mol^{-1} at 298 K.

The difference in relative stability between **6A** and **6E** was estimated to be 16.4 kJ mol^{-1}, and on this basis alone an interconversion between them might seem possible. It is, however, considered unlikely having to go through a transition state **6C′** with an energy barrier estimated to be 42.7 kJ mol^{-1}. Thus, we believe that **6** adopts a rigid conformation **6A** or **6E** at room temperature. Restricted rotation of the naphthyl ring and a preference for **6A** was indicated by results from a series of NOE experiments. Irradiation of the H8′ signal of **6** showed only selective enhancement of H6−8, unlike the comprehensive enhancement observed for H1−10 in similar experiments of **5** described earlier. This is the first example of confirmed restricted rotation of an internal substituent within the π-cloud of the 10*b*,10*c*-dihydropyrene system. Molecular rigidity in **6** was further supported by a dynamic ^{1}H NMR study. The results showed only a small change (0.25 ppm) in the chemical shift of H2′ in the temperature range of −90 to 90 °C. Chemical shifts of all other protons remained almost invariant.

Experimental Section

General Procedures. All reactions were carried out under nitrogen. Commercially available reagents and solvents were used without further purification. ^{1}H NMR spectra were obtained at 300 MHz using $CDCl_3$ as the solvent. Chemical shifts are reported in ppm relative to TMS. Elemental analysis was performed at the Chemical and Molecular Analysis Center, Department of Chemistry, National University of Singapore. Mass spectra were determined by electron impact ionization. Relative intensities are given in parentheses.

2-(2-Naphthyl)-*m*-xylene, 7a. A solution of 2-bromo-*m*-xylene (5.0 g, 27 mmol) in THF (20 mL) was added dropwise to a suspension of magnesium (0.65 g, 27 mmol) in THF (5 mL). The reaction was initiated by addition of 1,2-dibromoethane, and the mixture was maintained at gentle reflux until all magnesium reacted. The solution was transferred to a dropping funnel and added slowly to a solution of 2-bromonaphthalene (3.11 g, 15 mmol) and $Ni(acac)_2$ (30 mg, 3.24 mmol) at room temperature. The mixture was warmed to 40 °C and maintained at that temperature for 16 h. Water was added, and the mixture was extracted with CH_2Cl_2 (150 mL), washed, dried, and evaporated. The residue was preadsorbed on silica gel and chromatographed on silica gel with petroleum ether (40−60 °C) to give **7a** (66%) as colorless oil. ^{1}H NMR δ 7.90 (d, J = 8.4 Hz, 1H), 7.80−7.91 (m, 2H), 7.62 (br s, 1H), 7.47−7.52 (m, 2H), 7.29 (dd, J = 1.6 Hz, J = 8.4 Hz, 1H), 7.12−7.23 (m, 3H), 2.04 (s, 6H). MS *m*/*z* 232 (100, M$^+$), 217 (80), 202 (20). Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.82; H, 7.14.

2-(1-Naphthyl)-*m*-xylene, 7b. This was prepared by a procedure similar to that described for **7a**. Compound **7b** was isolated as colorless crystals (60%): mp 67−68 °C. ^{1}H NMR δ 7.90 (d, J = 8.2 Hz, 1H), 7.86 (d, J = 8.2 Hz, 1H), 7.56 (d, J = 7.0 Hz, 1H), 7.53 (d, J = 7.0 Hz, 1H), 7.16−7.46 (m, 6H), 1.90 (s, 6H). MS *m*/*z* 232 (100, M$^+$), 217 (90), 202 (30). Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.12; H, 6.94.

1,3-Bis(bromomethyl)-2-(2-naphthyl)benzene, 8a. NBS (3.38 g, 19.0 mmol) was added to a solution of **7a** (2.20 g, 9.48 mmol) in CCl_4. The reaction mixture was heated with a 200-W lamp at solvent refluxing temperature for 2 h. After filtration, the filtrate was washed with water, dried, and evaporated. The residue was chromatographed on silica gel with hexane as eluant to give the dibromide **8a** (37%) as colorless crystals: mp 108−109 °C. ^{1}H NMR δ 7.85−7.97 (m, 4H), 7.38−7.57 (m, 6H), 4.26, 4.21 (ABq, J = 10.0 Hz, 4H). MS *m*/*z* 388 (10, M$^+$), 229 (100). Anal. Calcd for $C_{18}H_{14}Br_2$: C, 55.42; H, 3.62. Found: C, 55.61; H, 3.54.

1,3-Bis(bromomethyl)-2-(1-naphthyl)benzene, 8b. This was prepared by a procedure similar to that described for **8a**. Compound **8b** was isolated as colorless crystals (40%): mp 72−73 °C. ^{1}H NMR δ 7.94 (t, J = 7.9 Hz, 2H), 7.2−7.6 (m, 8H), 4.18. 3.94 (ABq, J = 10.1 Hz, 4H). MS *m*/*z* 388 (10, M$^+$), 299 (100). Anal. Calcd for $C_{18}H_{14}Br_2$: C, 55.42; H, 3.62. Found: C, 55.51; H, 3.61.

1,3-Bis(mercaptomethyl)-2-(2-naphthyl)benzene, 9a. A solution of dibromide 8a (1.20 g, 3.07 mmol) and thiourea (0.47 g, 6.15 mmol) in THF (40 mL) was heated at reflux for 5 h. After removal of THF under reduced pressure, the residue was treated with 0.36 M KOH solution (50 mL), and the mixture was heated at reflux for 5 h. The solution was acidified with dilute HCl at 0−5 °C and then extracted with CH_2Cl_2 (150 mL). The organic layer was washed with water, dried, and evaporated. The residue was chromatographed on silica gel to give the dithiol **9a** (95%) as yellow oil. ^{1}H NMR δ 7.94 (d, J = 8.4 Hz, 1H), 7.85−7.91 (m, 2H), 7.78 (s, 1H), 7.52−7.65 (m, 2H), 742 (dd, J = 1.7 Hz, J = 8.4 Hz, 1H), 7.36 (br s, 3H), 3.48, 3.40 (dq, J = 7.6 Hz, J = 13.2 Hz, 4H), 1.60 (t, J = 7.6 Hz, 2H). MS *m*/*z* 296 (30, M$^+$), 229 (100). Anal. Calcd for $C_{18}H_{16}S_2$: C, 72.93; H, 5.44. Found: C, 73.11; H, 5.64.

1,3-Bis(mercaptomethyl)-2-(2-naphthyl)benzene, 9b. This was prepared by a procedure similar to that described for **9a**. Compound **9b** was isolated as yellow oil (90%). ^{1}H NMR δ 7.93 (d, J = 8.3 Hz, 2H), 7.2−7.6 (m, 8H), 3.38, 3.18 (dq, J = 7.9 Hz, J = 13.5 Hz, 4H), 1.49 (t, J = 7.6 Hz, 2H). MS *m*/*z* 296 (40, M$^+$), 229 (100). M_r Calcd for $C_{18}H_{16}S_2$: 296.0693; found (MS) 296.0691. This was used for the subsequent reaction without further purification.

***anti*- and *syn*-2,11-Dithia-18-methyl-9-(2-naphthyl)[3.3]metacyclophanes, 10a.** A solution of KOH (0.94 g, 16.8 mmol) in 95% EtOH (1 L) was heated to gentle reflux. A solution of 2,6-bis(bromomethyl)-toluene (1.46 g, 5.25 mmol) and dithiol **9a** (1.56 g, 5.25 mmol) in benzene (200 mL) was added dropwise over a period of 6 h to the warm KOH solution. After the addition, the mixture was stirred for 15 h while maintaining at near solvent refluxing temperatures. The solution was then cooled and the bulk of the solvent removed under reduced pressure. The residue was extracted with CH_2Cl_2. The organic layer was dried, concentrated, and chromatographed on silica gel using a 1:1 mixture of CH_2Cl_2/hexane as eluant. A mixture of *anti*- and *syn* **10a** in a 3:1 ratio was isolated (68%). Recrystallization from EtOH/CH_2Cl_2 gave colorless crystals of **10a**: mp 162−165 °C. ^{1}H NMR δ 6.8−7.8 (m), 4.25 (d, J = 15.2 Hz, syn), 4.01 (d, J = 14.3 Hz, syn), 3.82, 3.69 (AB, J = 14.3 Hz, anti), 3.76 (d, J = 15.2 Hz, syn), 3.74, 3.59 (AB, J = 13.7 Hz, anti), 3.69 (*d*, J = 14.3 Hz, syn), 2.52 (s, syn), 1.59 (s, anti). MS *m*/*z* 412 (40, M^+), 262 (75), 229 (100). Anal. Calcd for $C_{27}H_{24}S_2$: C, 78.59; H, 5.86; S, 15.54. Found: C, 78.43; H, 5.83; S, 15.74.

***anti*- and *syn*-2,11-Dithia-18-methyl-9-(1-naphthyl)[3.3]metacyclophanes, 10b.** A solution of 2,6-bis(bromomethyl)toluene (0.90 g, 3.2 mmol) and dithiol **9b** (0.95 g, 3.2 mmol) in DMF (400 mL) was added dropwise to stirred suspension of $Cs(CO_3)_2$ (3.13 g, 9.6 mmol) in DMF (1 L) maintained at 60−70 °C over a period of 12 h. After the addition, the reaction mixture was stirred at this temperature range for an additional 12 h. After removal of DMF under vacuum, the resulting residue was dissolved in CH_2Cl_2, washed with water, dried, and evaporated. The crude mixture was chromatographed on silica gel using CH_2Cl_2/hexane (1:1) as eluant to give **10b** (8%) as a mixture of anti and syn isomers in a 5:1 ratio. Recrystallization from EtOH/CH_2Cl_2 gave colorless crystals of 10b: mp 174−178 °C. ^{1}H NMR δ 8.48 (d, J = 8.4 Hz, syn), 6.9−7.9 (m), 6.52 (d, J = 8.5 Hz, anti), 6.26 (dd, J = 1.0 Hz, J = 7.2 Hz, anti), 4.22 (d, J = 15.2 Hz, syn), 3.84, 3.68 (AB, J = 14.3 Hz, anti), 3.78 (d, J = 15.2 Hz, syn), 3.57, 3.53 (AB, J = 11.4 Hz, syn), 3.52, 3.23 (AB, J = 13.6 Hz, anti), 2.62 (s, syn), 1.61 (s, anti). MS *m*/*z* 412 (40, M^+), 262 (55), 229 (100). Anal. Calcd for $C_{27}H_{24}S_2$: C, 78.59; H, 5.86; S, 15.54. Found: C, 78.65; H, 5.79; S, 15.57.

Wittig Rearrangement of 10a to Give 11a. To a solution of **10a** (0.11 g, 0.27 mmol) in THF (15 mL) maintained at 0−5 °C was added *n*-BuLi (0.27 mmol). The dark-brown solution was kept at this temperature for 20 min. CH_3I (0.5 mL) was added and the mixture stirred for 1 h. The mixture was then extracted with CH_2Cl_2 (100 mL). The organic layer was washed with water, dried, and evaporated. The residue was chromatographed on silica gel using CH_2Cl_2 as eluant to give a mixture of isomers of **11a** as yellow oil (91%). ^{1}H NMR δ 6.9−8.0 (m), 3.9−4.3 (m), 2.3−3.3 (m), 2.1−2.2 (m), 0.8−0.9 (m). MS *m*/*z* 440 (<10, M^+), 275 (70), 165 (100). M_r Calcd for $C_{29}H_{28}S_2$: 440.1632; found (MS) 440.1639. This was used for the subsequent reaction without further purification.

Wittig Rearrangement of 10b To Give 11b. This was prepared by a procedure similar to that described for **11a**. A mixture of the isomers of **11b** was isolated as yellow oil (90%). ^{1}H NMR δ 6.6−8.1 (m), 4.0−4.3 (m), 2.6−3.2 (m), 2.0−2.2 (m), 0.8−0.9 (m). MS *m*/*z* 440 (<10, M^+), 275 (70), 165 (100). M_r Calcd for $C_{29}H_{28}S_2$: 440.1632; found (MS) 440.1637. This was used for the subsequent reaction without further purification.

***trans*-10*b*-Methyl-10*c*-(2-naphthyl)-10*b*,10*c*-dihydropyrene, 5.** To a solution of an isomeric mixture of **11a** (g, 0.81 mmol) in CH_2Cl_2 (10 mL) was added $(CH_3)_3CHBF_4$ (0.48 g, 3.23 mmol) at −30 °C. The mixture was stirred at this temperature for 0.5 h and then at room temperature for 5 h. Ethyl acetate (15 mL) was added, and the mixture was stirred until fine precipitate was obtained. After removal of the clear supernatant liquor, the residual solid was washed with ethyl acetate and dried under vacuum to give the salt **12a**. This was treated with *t*-BuOK (2.0 mmol) in refluxing THF for 0.5 h. After removal of THF under reduced pressure, the residue was extracted with cyclohexane. The organic layer was washed with water, dried, and evaporated. The dark-blue residue was chromatographed on silica gel using hexane as eluant to give **5** (18%). Careful recrystallization from hexane/EtOH gave dark-green crystals of **5**: mp 160−161 °C. ^{1}H NMR δ 8.81 (d, J = 7.8 Hz, 2H), 8.75 (d, J = 7.8 Hz, 2H), 8.67 (d, J = 7.7 Hz, 2H), 8.52 (d, J = 7.7 Hz, 2H), 8.40 (t, J = 7.8 Hz, 1H), 8.21 (t, J = 7.8 Hz, 1H), 7.06−7.24 (m, 1H), 6.89−6.97 (m, 2H), 6.57−6.60 (m, 1H), 6.50 (d, J = 8.8 Hz, 1H), 3.62 (dd, J = 2.0 Hz, J = 8.8 Hz, 1H), 2.47 (d, J = 2.0 Hz, 1H), −4.24 (s, 3H). MS *m*/*z* 344 (28, M^+), 329 (100), 202 (74). UV−vis λ_{max} (cyclohexane) 232 (ϵ 84 060), 272 (11 800), 282 (10 670), 344 (57 720), 362 (23 970), 386 (43 590), 484 (8570) nm. Anal. Calcd for $C_{27}H_{20}$: C, 94.14; H, 5.86. Found: C, 94.24; H, 5.76.

***trans*-10*b*-Methyl-10*c*-(1-naphthyl)-10*b*,10*c*-dihydropyrene, 6.** This was prepared by a procedure similar to that described for **5**. Careful recrystallization of from hexane/EtOH gave dark-blue crystals of **6**: mp 154−156 °C. ^{1}H NMR δ 8.81 (d, J = 7.8 Hz, 2H), 8.62 (d, J = 7.8 Hz, 2H), 8.60 (d, J = 7.8 Hz, 2H), 8.34 (d, J = 7.8 Hz, 2H), 8.28 (t, J = 7.8 Hz, 1H), 7.86 (t, J = 7.8 Hz, 1H), 7.13−7.16 (m, 1H), 6.98−7.02 (m, 2H), 6.82 (d, J = 8.0 Hz, 1H), 5.80 (t, J = 8.0 Hz, 1H), 5.62−5.65 (m, 1H), 1.42 (br d, J = 8.0 Hz, 1H), −4.32 (s, 3H). MS *m*/*z* 344 (14, M^+), 329 (60), 217 (65), 202 (100). UV−vis λ_{max} (cyclohexane) 224 (ϵ 58 200), 274 (10 000), 332 (21 260), 356 (22 140), 372 (22 000), 394 (30 650), 480 (4360), 504 (3750) nm. Anal. Calcd for $C_{27}H_{20}$: C, 94.14; H, 5.86. Found: C, 93.78; H, 6.16.

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