

Synthesis and Diatropicity of *trans*-10b-Methyl-10c-undecyl- and *trans*-10b-Methyl-10c-pentadecyl-10b,10c-dihydropyrene. An Empirical Approach to a Semiquantitative Assessment of the Diamagnetic Ring Current in a [14]Annulene

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Received July 1, 1996 (Revised Manuscript Received December 3, 1996[®])

trans-10b-Methyl-10c-undecyl- and *trans*-10b-methyl-10c-pentadecyl-10b,10c-dihydropyrene, **3b** and **3c**, were obtained from the valence isomerization of their corresponding [2.2]cyclophanedienes **28a** and **28b**. The long internal alkyl chain in each case was previously introduced via a Wittig reaction followed by reduction. The cyclophanedienes were synthesized from their corresponding dithia-[3.3]cyclophanes via a Wittig rearrangement–Hofmann elimination sequence. Proton chemical shifts of H1' to H9' of the alkyl chains in **3b** and **3c**, respectively, are identical, suggesting that the C1'–C9' section of the long alkyl chain in **3b** or **3c** has similar averaged conformational movement. Application of the Johnson–Bovey (J–B) model to **3b** does not give a satisfactory correlation between the proton ring current shift and the out-of-plane distance. A direct empirical plot of the out-of-plane distance, *D*, against the proton ring current shifts, $\Delta\delta$, however, gives a curve similar to that obtained from the J–B model of benzene. This curve in fact corresponds to a linear relationship between *D* and $\log |\Delta\delta|$. Calculated ring current shifts of several derivatives of 10b,10c-dihydropyrene based on the above empirical correlation agree well with the reported experimental values. Our model shows that the experimental detectable limit for the diatropicity of 10b,10c-dihydropyrene is about 14 Å from the mean molecular plane. A similar empirical treatment based on the carbon chemical shifts of the *n*-undecyl chain in **3b** gives unsatisfactory results. Our model does not support the prediction that the magnitude of ring current effect on proton and carbon chemical shifts is essentially the same at the sample position in space relative to the mean plane of delocalization of an aromatic π -electron cloud.

Introduction

The deshielding of aromatic protons relative to olefinic protons has occupied the attention of NMR spectroscopists and theoreticians for almost 30 years.¹ Following the initial ideas of Pauling,² the ring current concept was applied to benzene by Pople,³ who treated the system as possessing a point dipole located at the center of the ring and showed that this would account for the downfield shift of benzene protons relative to the protons of ethylene. One of the most widely used approaches today to explain the ring current shifts is perhaps the classical current loop model of Johnson and Bovey (the J–B model).⁴ This is partly due to an easy access to their tabulated shielding–deshielding contributions of the benzene ring.⁵ Waugh and Fessenden⁶ later developed their “Free Electron Model” in which the π -electrons were regarded as being analogous to a simple current loop, and using the well-established methods of classical electrodynamics,⁷ they were able to evaluate the induced field at any point whether in or out of the plane of the ring.

Their approach separated the π -current into two loops, one above and one below the ring plane. Following a quantum mechanical treatment, Haigh and Mallion have also presented a similar tabulation.⁸ Both the Johnson–Bovey and Haigh–Mallion approaches allow the evaluation of chemical shifts for out-of-plane protons.

10b,10c-Dimethyl-10b,10c-dihydropyrene (**1a**) and its derivatives have been shown to be good models for diatropicity studies.⁹ The J–B model was applied¹⁰ with some modifications by Boekelheide to rationalize the observed proton and carbon chemical shifts of the alkyl chains in the dihydropyrenes **1a–c** using the nonaromatic compounds **2a–c** as the corresponding references. Although the plot of $\Delta\delta$ (the observed shift difference) versus *Z* (distance perpendicular to the plane of the molecule) showed a curve similar to that of benzene, there are large deviations between the predicted and observed values. Thus, a direct application of the J–B model to an annulene does not seem appropriate. Before our work, the dihydropyrene with the longest internal alkyl chain was the *n*-butyl derivative **3a**.¹¹ A challenge to verify the general applicability of the J–B model would be to

[®] Abstract published in *Advance ACS Abstracts*, January 15, 1997.

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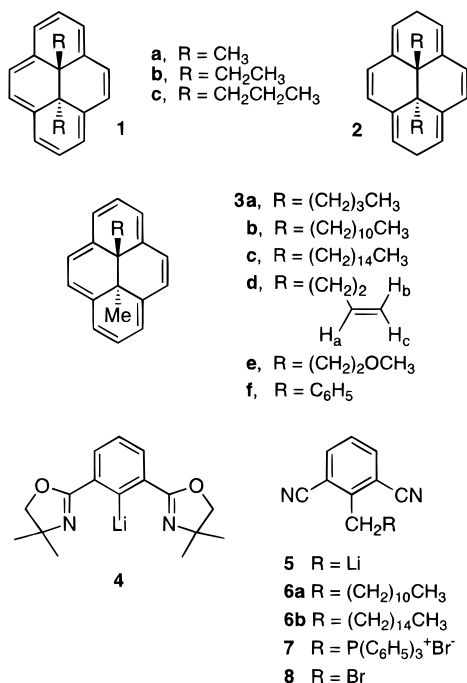
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investigate the diatropicity of dihydropyrene derivatives **3** with longer alkyl chains, which would provide more reference proton or carbon shifts to cover a larger range of Z values. These molecules may also serve as models to indicate the limit of the ring current shielding effect of 10b,10c-dihydropyrene and models to explore alternative empirical methods for ring current mapping of annulenes in general. In this paper, we wish to report the synthesis and ring current mapping study of *trans*-10b-methyl-10c-undecyl-10b,10c-dihydropyrene (**3b**) and *trans*-10b-methyl-10c-pentadecyl-10b,10c-dihydropyrene (**3c**).

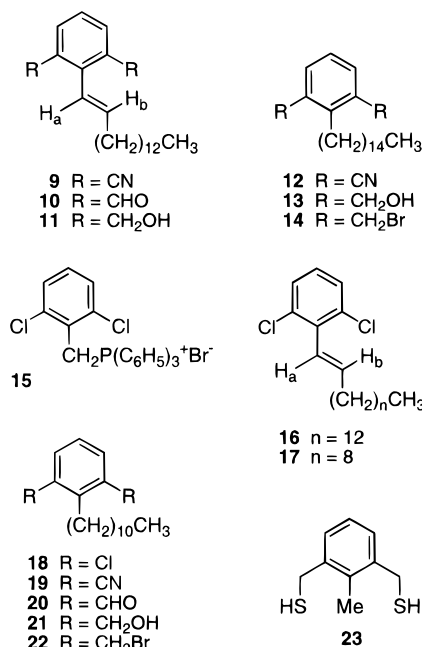


Results and Discussion

Synthesis. A general route¹² using dithiacyclophanes, followed by ring contraction reactions to give cyclophane-dienes and, hence, dihydropyrenes, has proved to be very useful in the synthesis of dihydropyrene derivatives. The alkyl groups in **1b,c** and **3a** were introduced by alkylation of the organolithium compounds **4**¹¹ and **5**,¹³ respectively. We have, however, failed to obtain **6a,b** by alkylation reactions of **5**. The Wittig reaction¹⁴ is in general an effective route to carbon-carbon bond formation, and thus, the reaction of the Wittig salt **7** was investigated. Treating the bromide **8**¹⁵ with triphenylphosphine readily afforded the salt **7**. The Wittig reaction between **7** and tetradecanal, however, gave only a 20% yield of the desired alkene **9**. An attempt to convert **9** to compound **12** under general hydrogenation conditions also failed. This could be attributed to the electron-withdrawing effect of the two *ortho*-cyano groups. The reaction of **9** with diisobutylaluminum hydride readily afforded com-

pound **10**, which upon treatment with sodium borohydride gave a 95% yield of the diol **11**. Hydrogenation of **11** went smoothly to yield quantitatively the desired compound **13**. A reaction between **13** and phosphorus tribromide readily afforded the dibromide **14** in a 90% yield.

The main drawback of the above synthesis is the low yield of the Wittig product **9**. The electron-withdrawing cyano groups, via a resonance effect, could stabilize the Wittig salt **7**, thus decreasing its reactivity. By using the dichloro analog **15**, its Wittig reactions with tetradecanal and decanal gave the desired products **16** and **17**, respectively, in 60% and 53% yield. Hydrogenation of **17** gave a quantitative yield of **18**. Conversion of **18** to the dicyano compound **19** could be achieved in an 89% yield. A series of functional group transformation reactions similar to those reported¹⁶ earlier gave the desired dibromide **22**.



With the dibromide **22** now available, a coupling reaction with compound **23**¹² under high dilution conditions¹⁷ gave an 85% yield of a product mixture of *anti*- and *syn*-dithiacyclophanes **24a** and **25a**, respectively, in a >95:5 ratio on the basis of the ¹H NMR spectrum. Only *anti*-**24a**, mp 85–88 °C, could be isolated pure after chromatography. A similar cyclization reaction between **14** and **23** afforded only *anti*-**24b**. The ArCH₃ protons in **24a** and **24b** have an identical chemical shift at δ 1.32 very similar to that of the parent *anti*-**24c** ($\delta\text{CH}_3 = 1.30$),¹² thus confirming their *anti* stereochemistry. The Wittig rearrangements¹⁸ of dithiacyclophanes **24a** and **24b** gave the ring-contracted [2₂]cyclophanes **26a** and **26b**, respectively. Remethylation of **26a** and **26b** with

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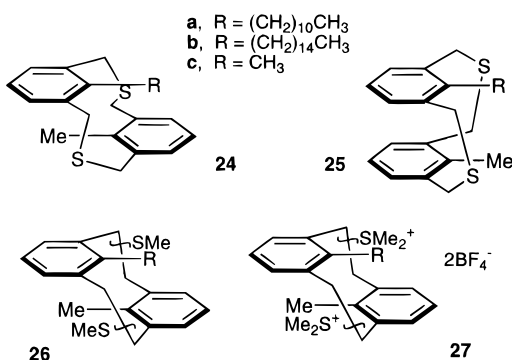
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Table 1. Proton and Carbon Chemical Shifts for the *n*-Undecyl and *n*-Pentadecyl Chains in Dihydropyrenes **3b and **3c**, Respectively**

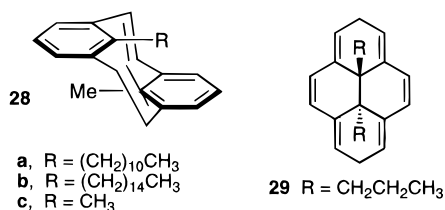
compd	H-1'	H-2'	H-3'	H-4'	H-5'	H-6'	H-7'	H-8'	H-9'	H-10'	H-11'	H-12'	H-13'	H-14'	H-15'
3b	-4.02	-1.68	-0.41	0.27	0.61	0.84	0.97	1.09	1.12	1.20	0.82 ^a				
3c	-4.01	-1.68	-0.43	0.27	0.61	0.83	0.97	1.06	←-----			1.11-1.28 ^b	-----→		0.97 ^a
compd	C-1'	C-2'	C-3'	C-4'	C-5'	C-6'	C-7'	C-8'	C-9'	C-10'	C-11'	C-12'	C-13'	C-14'	C-15'
3b	26.92	20.91	28.90	28.68	29.09	29.35	29.38	29.17	31.81	22.62	14.09 ^c				
3c	26.93	20.92	28.90	28.68	29.10	29.26	29.43	29.53	←-----			31.92 ^b	-----→		22.68 14.10

^a Methyl protons. ^b Signals unresolved. ^c Methyl carbon.

dimethoxycarbonium fluoroborate¹⁹ afforded the respective bis(sulfonium) salts **27a** and **27b**.



The Hofmann elimination of **27a** carried out with potassium *tert*-butoxide in tetrahydrofuran at room temperature gave an initial mixture of dihydropyrene **3b** (major) and cyclophanediene **28a** (minor). The presence of the latter was supported by an AB quartet (δ_A 6.35, δ_B 6.32; J 11.3 Hz; *cis* olefinic protons) and a shielded singlet at δ 1.53 for the ArCH₃ protons (δ_{CH_3} of **28c** = 1.52)¹² in the ¹H NMR spectrum of the crude mixture. The purified product mixture after chromatography indicated a ratio of >95:5 for **3b** and **28a**, but we failed to obtain a pure sample of the cyclophanediene **28a** due to its ready conversion to **3b** on standing even in the solid state. A similar Hofmann elimination of **27b** led to isolation of only the dihydropyrene **3c** in a 41% yield.



Both the dihydropyrenes **3b** and **3c** were isolated as a thick green oil. Their electronic spectra (see Experimental Section) are very similar to that of the parent dihydropyrene **1a**.²⁰ In general, their mass spectra show a weak molecular ion with the [M - (CH₂)_{*n*}CH₃]⁺ signal as the base peak. The ¹H NMR signal of the internal methyl protons of both **3b** and **3c** appears at δ -4.26, a value almost identical to that (δ -4.25)¹² of the parent **3a**. This is a good indication that despite the introduction of a long *n*-alkyl chain, the diatropicity of the 14 π system in **3a** is fully retained in **3b** and **3c**. Thus, the ring current mapping studies of **3b** and **3c** (see later

discussion) are expected to reflect in general the ring current effect of the dihydropyrene periphery.

Ring Current Mapping. All methylene protons in the internal *n*-undecyl chain of **3b** are resolved as presented in Table 1. Qualitatively, a proportional decrease in the shielding effect with an increase in distance from the plane of the macroring is confirmed by the assignment of the methylene protons in a ¹H COSY spectrum. A comparison of the ¹H NMR spectra data of **3b** and **3c** (Table 1) shows that the chemical shifts of the methylene protons are identical from C1' to C8' (perhaps even C9'), respectively. Variable-temperature ¹H NMR studies indicated no appreciable changes in the proton chemical shifts in the range of -60 to +100 °C. The above observation suggests that the C1'-C9' section of the long alkyl chain in **3b** or **3c** has similar averaged conformational movement. As the proton signals of the *n*-undecyl chain in **3b** are relatively better resolved, it is thus selected as the model compound for the following ring current mapping studies.

The averaged chemical shifts for the methylene protons and methyl protons, respectively, in decane,^{21,22} dodecane,^{23,24} ^a and pentadecane^{24b} are δ 1.28 and 0.89. Thus, the ring current shielding on the methylene and methyl protons in **3b** is estimated by $\Delta\delta = \delta_{CH_2} - 1.28$ and $\Delta\delta = \delta_{CH_3} - 0.89$, respectively. As the crystallographic structure of **3b** is not available, a Dreiding molecular model was used as an approximation of the molecular geometry of **3b**. The X-ray crystallographic structure of **1a** reported^{9c} recently shows negligible bond alternation at the periphery of the molecule with bond lengths in the range of 1.38-1.40 Å. These values agree well with the bond length of 1.39 Å for benzene,²⁵ and thus, the Dreiding molecular model of **3b** should serve as a reasonable approximation for our studies.

An initial approach was to apply the J-B model as described for **1a-c**.¹⁰ The out-of-plane distance, *d*, is the estimated averaged distance, in Å, of a proton from the molecular plane of the dihydropyrene moiety. The ring radius, *a*, of benzene is 1.39 Å, and a value of 2.23 Å is used for a [14]annulene.²⁶ The parameters *x*, *Z*, and ρ are those described in the J-B Model.^{4,10} From the data analysis, there is no satisfactory correlation between the experimental and calculated values. In fact, the J-B model is not applicable beyond H6' of the long chain. Thus our results confirm that the J-B model is definitely not appropriate for investigation of the diatropicity of

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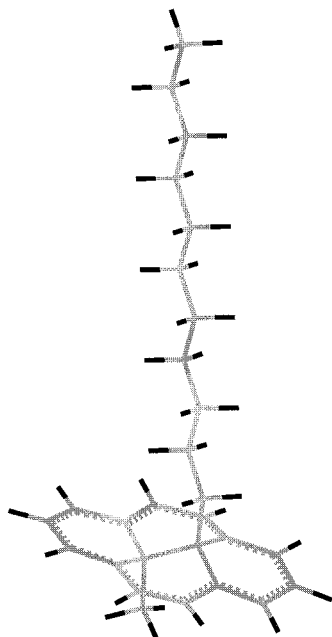
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Table 2. Estimated Out-of-Plane Distance D and Ring Current Shielding $\Delta\delta$ of Protons in the n -Undecyl Chain of **3b**

	H-1'	H-2'	H-3'	H-4'	H-5'	H-6'	H-7'	H-8'	H-9'	H-10'	H-11'
D^a (Å)	2.17	3.10	4.39	5.52	6.82	8.00	9.29	10.49	11.78	12.99	14.31
$\Delta\delta$	-5.30	-2.96	-1.69	-1.01	-0.67	-0.44	-0.31	-0.21	-0.16	-0.08	-0.07
$\log \Delta\delta $	0.724	0.471	0.228	0.004	-0.174	-0.356	-0.507	-0.678	-0.796	-1.097	-1.155

^a Data were derived from PM3-optimized structure.

**Figure 1.** Optimized conformation of compound **3b** derived from semiempirical molecular orbital calculations.

dihydroindene **1a** and its derivatives. This is likely to be due to significant differences in molecular geometry and ring current distribution pattern between benzene and 10b,10c-dihydroindene. The J–B model of separated current loops method⁴ is in fact known to be inappropriate for the evaluation of the chemical shift of out-of-plane protons.²⁷

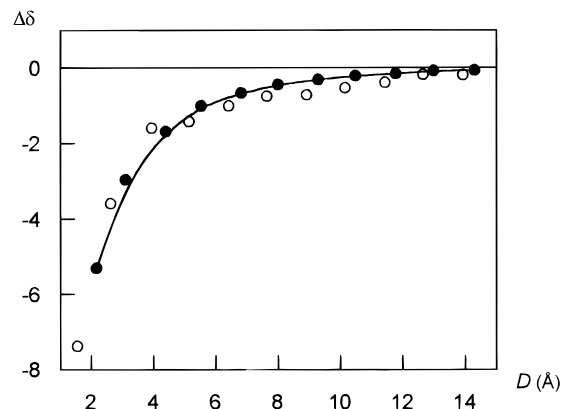
Since **1a** and its derivatives with different internal substituents are expected to have a common peripheral skeleton and thus almost identical ring currents (supported by very similar chemical shifts of the internal methyl protons for **1a**,¹² **3a**,^{11,13} **3b**, **3c**, **3d**,¹³ **3e**,¹³ and **3f**²⁸), it would be very useful to formulate a more direct and reliable relationship between ring current shifts and the out-of-plane distance, thus allowing a simple mapping of the ring current effect over a range of positions in space. An attempt was then made to derive an empirical correlation between D , the averaged distance of a proton from C10c, and $\Delta\delta$, the ring current shielding effect.

Our semiempirical molecular orbital PM3²⁹ calculations show that the conformer (Figure 1) with a “linear, all trans” hydrocarbon chain corresponds to an energy minimum. Calculated results for several other randomly selected conformers indicate that the “linear, all trans” (Figure 1) is relatively the most stable. This structure is thus taken as the averaged conformational representation of compound **3b**. The averaged distance, D , for each pair of methylene protons at a particular carbon in the optimized structure shown in Figure 1 is estimated

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**Figure 2.** Plot (●) of D against proton $\Delta\delta$ for compound **3b** (see Table 2) [data points (○) for D and carbon $\Delta\delta$ from Table 4 are not used in the graph].

(Table 2) from three positions with the α carbon arbitrarily replaced by a proton.

From the estimated $\Delta\delta$ values (≤ 0.08) for H10' and H11', the limit of the ring current shielding effect of 10b, 10c-dihydroindene is likely to be at H11', *i.e.*, about 14 Å from C10c. On the basis of the crystal structure of **1c**,³⁰ the angle between the internal n -propyl chain and the molecular plane is 83.5° with C10b located only at 0.4 Å from the mean plane.¹⁰ The above observation would collectively indicate that the experimental detectable limit for the diatropicity of 10b,10b-dihydroindene is about 14 Å from the mean molecular plane. Within this limit, a plot of D against $\Delta\delta$ (Figure 2; graph based on ●) results in an empirical correlation represented by the following equation:

$$\Delta\delta = 8.6922D - 1.8806D^2 + 0.2049D^3 - 0.0110D^4 + 0.0002D^5 - 17.1192 \quad (1)$$

This curve is in fact similar to that of benzene based on the J–B model.⁴ Equation 1 could be transformed into a linear relationship (Figure 3; graph based on ●) between D and $\log |\Delta\delta|$ with a correlation coefficient of >0.991 governed by the following equation:

$$\log |\Delta\delta| = 0.9184 - 0.1512D \quad (2)$$

The potential application of the above empirical correlation was examined using **3a** and **3d–3f** as examples (Table 3). The respective optimized structures of **3a** and **3e** were determined by PM3 calculations as described for **3b**. The averaged distance, D , for protons in **3d** and **3f** were estimated from their respective Drieding molecular models assuming free rotation about carbon–carbon single bonds. The proton chemical shifts for 1-hexene,³¹ a 1-methoxybutane,^{31b} and benzene ($\delta\text{H} = 7.15$) are used as references, respectively, to derive the experimental $\Delta\delta$ values. In general, the calculated $\Delta\delta$ value for H1'

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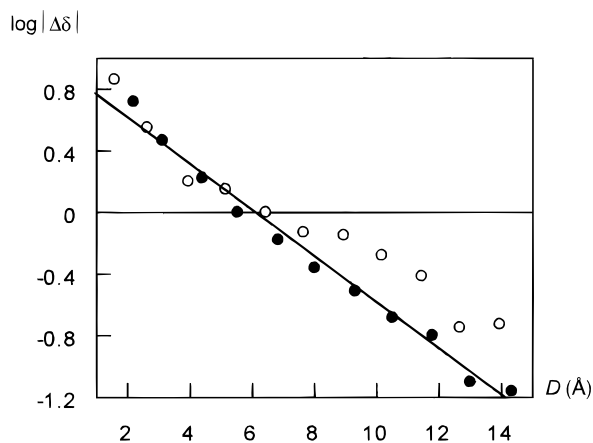


Figure 3. Plot (●) of D against proton $\log |\Delta\delta|$ for compound **3b** (see Table 2) [data points (○) for D and carbon $\log |\Delta\delta|$ from Table 4 are not used in the graph].

Table 3. Experimental and Calculated Values for Proton Ring Current Shielding in Selected Dihydropyrene Derivatives

compd	proton	D^a (Å)	$\Delta\delta$			$ \Delta\Delta\delta ^b$	$ \Delta\Delta\delta ^c$
			expt	calcd ^b	calcd ^c		
3a	H1'	2.18	-5.42	-5.23	-3.83	0.17	1.53
	H2'	3.10	-2.99	-3.09	-2.82	0.10	0.17
	H3'	4.39	-1.69	-1.62	-1.80	0.07	0.11
	H4'	5.55	-0.99	-1.16	-1.20	0.17	0.21
3d	H1'	2.1	-5.52	-5.48	-3.99	0.04	1.53
	H2'	3.1	-1.69	-3.09	-2.82	1.40	1.13
	H _a	4.4	-1.94	-1.62	-1.79	0.32	0.15
	H _b	4.5	-1.49	-1.56	-1.73	0.07	0.24
3e	H1'	2.16	-5.10	-5.25	-3.91	0.15	1.19
	H2'	3.10	-2.83	-3.09	-2.82	0.26	0.01
3f	OCH ₃	5.39	-0.94	-1.22	-1.27	0.28	0.33
	H1'	2.6	-4.61	-4.11	-3.35	0.50	1.26
	H2'	4.7	-1.56	-1.45	-1.61	0.11	0.05
	H3'	5.4	-1.16	-1.20	-1.27	0.04	0.11

^a Data for **3a** and **3e** were derived from PM3-optimized structures; data for **3d** and **3f** were estimated from Drieding molecular models. ^b Based on eq 1. ^c Based on eq 2.

derived from eq 2 deviates significantly from the corresponding experimental value. Results derived from eq 1, however, provide a good agreement between the calculated and experimental values. For some unknown reasons, the calculated chemical shift for H2' in **3d** is very different from that observed experimentally. A significant deviation is also observed for H1' of **3f**. This is likely to be due to a "mismatched" D value in this particular case using C10c as the reference center. H1' in **3f** is located very close to the center of the molecular plane (and thus more strongly shielded than expected) since the benzene ring is expected to enjoy unrestricted rotation.²⁸ This observation seems to indicate that a prediction for the proton chemical shift from eq 1 is satisfactory only if the proton concerned is somewhat confined to an averaged "linear" conformational zone similar to that in Figure 1. Unfortunately, there is no known derivative of **1a** with an internal substituent of intermediate chain length available for our study.

The ring current effect on heavier elements like carbon and fluorine is relatively less well established. There are

varied opinions^{10,32} on whether carbon chemical shifts would serve as a good probe for the ring current effect of an annulene. Predictions from the theory of NMR, however, suggest that the magnitude of the ring current effect for different nuclei should be similar if the nuclei are located at the same position in space relative to the aromatic π -cloud.³² It would thus be interesting to examine whether the carbon chemical shifts of the n -undecyl chain of **3b** would further support the above argument.

The carbon signals of the n -undecyl chain of **3b** are well resolved in its ¹³C NMR spectrum (Table 1). Their assignments were readily achieved by a ¹H-¹³C HETERO-COSY spectrum. The difference in chemical shifts between two adjacent carbon atoms seems somewhat "random", which is to a certain extent complicated by the α , β , and/or γ effects.³⁴ Mapping of the ring current effect on carbon chemical shifts of **3b** would require reference values for a similar n -undecyl chain (Table 4). Chemical shifts of C1-C5 of decane³⁴ could be correlated to C11'-C7' of the n -undecyl chain of **3b**, respectively. Applying the equation³⁴ $\delta(k) = -2.1 + \sum N_k A_i$ where $\delta(k)$ is the chemical shift of a paraffin carbon k , N_k is the number of carbon atoms at i th position, and A_i is the term to be added for each carbon at i th position ($A_1 = +9.1$ ppm for an α carbon; $A_2 = +9.4$ ppm for a β carbon; $A_3 = -2.5$ ppm for a γ carbon), a common value of 30.1 ppm would apply to C4'-C6'. Using the reported chemical shifts¹⁰ for the n -propyl chain of **29** (36.8, 17.6 and 14.5 ppm, respectively) with a similar molecular geometry as **1c**, and thus **3b**, and adding the corresponding α , β , and γ effects, reference chemical shifts for C1'-C3' of the n -undecyl chain in **3b** are calculated to be 34.3, 24.5, and 30.5 ppm, respectively. The ring current shielding, $\Delta\delta$, of the carbon atoms in the n -undecyl chain of **3b** are thus tabulated accordingly (Table 4). The out-of-plane distance from C10c, D , of each carbon is measured from the optimized structure of **3b** (Figure 1).

When the values of carbon $\Delta\delta$ (Table 4) are included in Figure 2 (represented by ○), they do not seem to fit well into the graph based on proton $\Delta\delta$ (represented by ●). The general deviation is more obvious in Figure 3. Thus, our model does not support the prediction that the magnitude of ring current effect on proton and carbon chemical shifts is essentially the same at the sample position in space relative to the mean plane of delocalization of an aromatic π -electron cloud.

Conclusion. Results from our work clearly confirm that the J-B model is insufficient to allow mapping of the ring current effect in an annulene. We, however, believe that proton chemical shifts of the n -undecyl chain in **3b** have provided sufficient experimental data points for a satisfactory empirical correlation between the ring current effect ($\Delta\delta$) and out-of-plane distance (D). This has been shown, albeit with only a small set of available examples, to be potentially useful for the prediction of chemical shift of protons on a somewhat "linear" substituent within the π -electron cloud of 10b,10c-dihydropyrene. The detectable limit for the diatropicity of 10b,10c-dihydropyrene is in fact estimated to be about 14 Å from the mean molecular plane. Interestingly, a recently reported³⁵ dihydropyrene **30** showed only one

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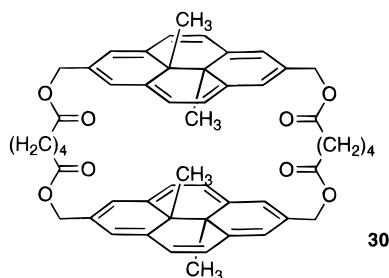
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Table 4. Ring Current Shielding of Carbons in the *n*-Undecyl Chain of **3b**

	C-1'	C-2'	C-3'	C-4'	C-5'	C-6'	C-7'	C-8'	C-9'	C-10'	C-11'
D^a (Å)	1.56	2.62	3.94	5.13	6.42	7.64	8.92	10.15	11.43	12.66	13.93
Ref δ	34.3	24.5	30.5	30.1	30.1	30.1	30.1	29.7	32.2	22.8	13.9
$\Delta\delta$	-7.38	-3.59	-1.60	-1.42	-1.01	-0.75	-0.72	-0.53	-0.39	-0.18	-0.19
$\log \Delta\delta $	0.868	0.555	0.204	0.152	0.004	-0.125	-0.143	-0.276	-0.409	-0.745	-0.721

^a Data were derived from PM3-optimized structure.



singlet at δ -4.31 for its methyl protons (δCH_3 of **1a** at -4.25) consistent with unrestricted rotation of the two dihydrodropyrene units. Our results also indirectly support this observation. If the two dihydrodropyrene units are arranged face to face, the methyl protons on one dihydrodropyrene unit within the cavity is estimated to be <7.5 Å (from Drieding molecular models) from the mean molecular plane of another dihydrodropyrene unit. This would have resulted in a $\Delta\delta$ value of about -0.8.

Experimental Section

Melting points are uncorrected. ^1H NMR spectra were recorded in CDCl_3 on 300 or 500 MHz spectrometer with Me_4Si as internal standard. Mass spectra were obtained using EI ionization at 70 eV. Microanalyses were performed by the Microanalytical Laboratory of the Department of Chemistry, National University of Singapore.

trans-2-(1-Pentadecenyl)benzene-1,3-dicarbonitrile (9). Compound **8**¹⁵ (1.1 g, 5 mmol) was added to a solution of triphenylphosphine (1.3 g, 5 mmol) in benzene (50 mL). The mixture was heated at solvent refluxing temperature for 18 h. The salt **7** formed was filtered, washed with benzene, and dried under vacuum. The salt **7** obtained was used directly for the following reaction.

A solution of lithium diisopropylamide (4.5 mmol) in dry THF was prepared from *n*-butyllithium and diisopropylamine and maintained at 0 °C. The salt **7** (2.0 g, 4.1 mmol) was added, and the mixture was stirred at 0 °C for 1 h, warmed to room temperature, and stirred until all solids dissolved. To the yellow solution was added a solution of tetradecanal (0.9 g, 4.1 mmol) in THF. The mixture was stirred at room temperature for 20 min and heated at solvent refluxing temperature for 18 h. The solvent was removed under reduced pressure, and the residue was extracted with dichloromethane. The organic layer was washed with water, dried, and evaporated. The crude product was chromatographed on silica gel using hexane/dichloromethane (1:1) as eluent to afford the compound **9** (0.3 g, 20%): mp 60–62 °C; ^1H NMR (500 MHz) δ 7.84 (d, J = 7.8 Hz, 2H), 7.40 (t, J = 7.8 Hz, 1H), 6.84 (dt, J = 16.1, 6.7 Hz, 1H), 6.70 (d, J = 16.1 Hz, 1H), 2.36 (q, J = 6.7 Hz, 2H), 1.10–1.26 (m, 22H), 0.88 (t, J = 6.4 Hz); IR (KBr) 2220 cm^{-1} ; MS m/z 336 (M^+ , 30), 308 (12), 293 (17), 279 (19), 265 (20), 251 (22), 223 (42), 209 (70), 195 (50), 181 (30). Anal. Calcd for $\text{C}_{23}\text{H}_{32}\text{N}_2$: C, 82.07; H, 9.60; N, 8.33. Found: C, 82.25; H, 9.69; N, 8.33.

trans-2-(1-Pentadecenyl)benzene-1,3-dicarbonyl (10).¹⁶ This was obtained, after chromatography, as a thick liquid (62%): ^1H NMR (300 MHz) δ 10.29 (s, 2H), 8.11 (d, J = 7.7 Hz, 2H), 7.54 (t, J = 7.7 Hz), 7.13 (d, J = 15.7 Hz, 1H), 5.80 (dt, J = 15.7, 6.8 Hz, 1H), 2.38 (m, 2H), 1.52–1.21 (m, 20H), 0.88 (t, J = 6.3 Hz, 3H); IR (neat) 1680 cm^{-1} ; MS m/z 342 (M^+ , 40), 174 (17), 159 (100); M_r calcd for $\text{C}_{23}\text{H}_{34}\text{O}_2$ 342.2559, found (MS) 342.2555.

trans-2,6-Bis(hydroxymethyl)-1-(1-pentadecenyl)benzene (11).¹⁶ This was obtained, after recrystallization from benzene, as colorless needles (95%): mp 107–107.5 °C; ^1H NMR (300 MHz) δ 7.40 (d, J = 7.6 Hz, 2H), 7.29 (t, J = 7.6 Hz, 1H), 6.50 (d, J = 16.1 Hz, 1H), 5.83 (dt, J = 16.1, 6.9 Hz, 1H), 4.70 (d, J = 5.9 Hz, 4H), 2.26 (q, J = 6.9 Hz), 1.62 (t, J = 5.9 Hz, 2H), 1.49–1.47 (m, 2H), 1.27 (m, 20H), 0.88 (t, J = 6.5 Hz, 3H); IR (KBr) 3320, 1454 cm^{-1} ; MS m/z 344 (M^+ - 2H, 5), 328 (22), 310 (20), 213 (30), 196 (25), 159 (50), 141 (100). Anal. Calcd for $\text{C}_{23}\text{H}_{38}\text{O}_2$: C, 79.69; H, 11.07. Found: C, 79.41; H, 11.06.

2,6-Bis(hydroxymethyl)-1-(1-pentadecenyl)benzene (13). To a solution of compound **11** (0.20 g, 0.58 mmol) in a mixture of THF and ethanol (1:1; 20 mL) was added 10% Pt/C (10 mg). The mixture was kept under a positive pressure of hydrogen gas and stirred until there was no further consumption of hydrogen gas. The catalyst was filtered and the solvent evaporated to give compound **13** (0.02 g, quant). Recrystallization from benzene–hexane gave colorless needles of **13**: mp 106–107 °C; ^1H NMR (300 MHz) δ 7.37 (d, J = 7.6 Hz), 7.24 (t, J = 7.6 Hz, 1H), 4.75 (d, J = 5.8 Hz, 4H), 2.73 (t, J = 7.2 Hz), 1.51 (t, J = 5.8 Hz, 2H), 1.46–1.26 (m, 26H), 0.88 (t, J = 6.4 Hz); IR (KBr) 3350 cm^{-1} ; MS m/z 348 (M^+ , 5), 330 (10), 312 (42), 213 (20), 196 (15), 143 (100). Anal. Calcd for $\text{C}_{23}\text{H}_{40}\text{O}_2$: C, 79.32; H, 11.48. Found: C, 79.62; H, 11.05.

2,6-Bis(bromomethyl)-1-(1-pentadecenyl)benzene (14).¹⁶ This was obtained, after chromatography, as colorless crystals (90%): mp 83–85 °C; ^1H -NMR (300 MHz) δ 7.32 (d, J = 7.6 Hz, 2H), 7.17 (t, J = 7.6 Hz, 1H), 4.54 (s, 4H), 2.87–2.82 (m, 2H), 1.69–1.60 (m, 2H), 1.51–1.47 (m, 2H), 1.50–1.26 (m, 24H), 0.88 (t, J = 6.5 Hz, 3H); MS m/z 474 (M^+ , 25), 393 (10), 313 (42), 197 (90), 145 (75), 119 (100). Anal. Calcd for $\text{C}_{23}\text{H}_{38}\text{Br}_2$: C, 58.23; H, 8.09; Br, 33.68. Found: C, 58.43; H, 8.01; Br, 33.24.

trans-2,6-Dichloro-1-(1-pentadecenyl)benzene (16). This was prepared from the salt **15** and tetradecanal according to a similar procedure described for the preparation of **9**. Compound **16** was obtained as a colorless liquid (60%): ^1H NMR (300 MHz) δ 7.28 (d, J = 8.0 Hz, 2H), 7.04 (t, J = 8.0 Hz, 1H), 6.33 (d, J = 16.2 Hz, 1H), 6.20 (dt, J = 16.2, 6.8 Hz, 1H), 2.25–2.47 (m, 2H), 1.64–1.68 (m, 2H), 1.48–1.54 (m, 2H), 1.38 (br m, 4H), 1.25–1.26 (m, 14H), 0.88 (t, J = 6.5 Hz); MS m/z 354 (M^+ , 18), 172 (100), 124 (90); M_r calcd for $\text{C}_{17}\text{H}_{24}\text{Cl}_2$ 353.9378, found (MS) 353.9381.

trans-2,6-Dichloro-1-(1-undecenyl)benzene (17). This was prepared from the salt **22** and undecanal according to a similar procedure described for the preparation of **9**. Compound **17** was obtained as a colorless liquid (53%): ^1H NMR (300 MHz) δ 7.28 (d, J = 8.1 Hz, 2H), 7.03 (t, J = 8.1 Hz, 1H), 6.33 (d, J = 16.2 Hz, 1H), 6.19 (dt, J = 16.2, 6.5 Hz, 1H), 2.27 (dt, J = 7.3, 6.5 Hz), 1.51 (m, 2H), 1.40–1.21 (m, 12H), 0.88 (t, J = 6.5 Hz); MS m/z 298 (M^+ , 20), 185 (10), 172 (100), 159 (20); M_r calcd for $\text{C}_{17}\text{H}_{24}\text{Cl}_2$ 298.1255, found (MS) 298.1251.

2,6-Dichloro-1-(1-undecyl)benzene (18). This was prepared from hydrogenation of **17** according to a similar procedure described for the preparation of **13**. Compound **24** was obtained as a colorless oil (quant): ^1H NMR (300 MHz) δ 7.25 (d, J = 7.9 Hz, 2H), 7.02 (t, J = 7.9 Hz, 1H), 2.89 (m, 2H), 1.59–1.51 (m, 2H), 1.44–1.26 (m, 16H), 0.88 (t, J = 6.5 Hz, 3H); MS m/z 300 (M^+ , 30), 159 (60), 125 (30); M_r calcd for $\text{C}_{17}\text{H}_{28}\text{Cl}_2$ 300.1412, found (MS) 300.1426.

2-(1-Undecyl)benzene-1,3-dicarbonitrile (19).¹⁶ This was obtained, after chromatography, as a colorless oil (89%): ^1H NMR (300 MHz) δ 7.83 (d, J = 7.9 Hz, 2H), 7.43 (t, J = 7.9 Hz, 1H), 3.07 (t, J = 7.8 Hz, 2H), 1.75–1.67 (m, 2H), 1.47–1.42 (m, 2H), 1.40–1.26 (m, 14H), 0.88 (t, J = 6.5 Hz, 3H); IR (neat) 2220 cm^{-1} ; MS m/z 282 (M^+ , 4), 253 (9), 239 (24), 225

(30), 211 (60), 197 (60), 183 (50), 169 (80); M_r calcd for $C_{29}H_{26}N_2$ 282.2096, found (MS) 282.2103.

2-(1-Undecyl)benzene-1,3-dicarbaldehyde (20).¹⁶ This was obtained, after chromatography, as a yellow oil (91%): 1H NMR (300 MHz) δ 10.42 (s, 2H), 8.09 (d, $J = 7.7$ Hz, 2H), 7.53 (t, $J = 7.7$ Hz, 1H), 3.46 (t, $J = 7.8$ Hz, 2H), 1.70–1.62 (m, 2H), 1.59–1.42 (m, 2H), 1.26 (m, 14H), 0.88 (t, $J = 6.4$ Hz, 3H); IR (neat) 1691 cm^{-1} ; MS m/z 288 (M^+ , 90), 259 (10), 161 (100), 144 (40); M_r calcd for $C_{19}H_{28}O_2$ 288.2089, found (MS) 288.2091.

2,6-Bis(hydroxymethyl)-1-(1-undecyl)benzene (21).¹⁶ This was obtained, after recrystallization from benzene–hexane, as colorless needles (quant): mp 84–86 °C; 1H NMR (300 MHz) δ 7.37 (d, $J = 7.6$ Hz, 2H), 7.24 (t, $J = 7.6$ Hz, 1H), 4.75 (s, 4H), 2.73 (m, 2H), 1.55–1.43 (m, 6H), 1.25–1.27 (m, 14H), 0.88 (t, 6.5 Hz, 3H); IR (KBr) 3350 cm^{-1} ; MS m/z 292 (M^+ , 15), 274 (20), 256 (55), 157 (45), 143 (100). Anal. Calcd for $C_{19}H_{32}O_2$: C, 78.02; H, 10.95. Found: C, 77.92; H, 11.01.

2,6-Bis(bromomethyl)-1-(1-undecyl)benzene (22).¹⁶ This was obtained, after chromatography, as colorless crystals (97%): mp 69–70 °C; 1H NMR (300 MHz) δ 7.32 (d, $J = 7.6$ Hz, 2H), 7.17 (t, $J = 7.6$ Hz, 1H), 4.54 (s, 4H), 2.84 (m, 2H), 1.60–1.68 (m, 2H), 1.52–1.45 (m, 2H), 1.33–1.28 (m, 14H), 0.89 (t, $J = 6.9$ Hz, 3H); MS m/z 416 (M^+ , 5), 337 (5), 257 (20), 197 (60), 119 (100). Anal. Calcd for $C_{19}H_{30}Br_2$: C, 54.81; H, 7.21; Br, 37.98. Found: C, 54.78; H, 7.03; Br, 38.10.

anti-9-Methyl-2,11-dithia-18-undecyl[3.3]metacyclophane (24a). A solution of **22** (0.19 g, 0.45 mmol) and **23** (84 mg, 0.45 mmol) in benzene (200 mL) was added dropwise over a period of 8 h to a vigorously stirred solution of potassium hydroxide (0.4 g) in 95% ethanol (500 mL) at room temperature under nitrogen. After being stirred for an additional 18 h, the bulk of the solvent was removed under reduced pressure. The residue was mixed with dichloromethane, washed with water, dried, and evaporated. The crude product was chromatographed on silica gel using hexane–dichloromethane (1:1) as eluent. Eluted first was a mixture of *anti-24a* and *syn-25a* followed by pure *anti-24a* (total 0.17 g, 85%): mp 85–88 °C; 1H NMR (500 MHz) δ 7.29 (d, $J = 7.6$ Hz, 2H), 7.28 (d, $J = 7.6$ Hz, 2H), 7.09 (t, $J = 7.6$ Hz, 1H), 7.07 (t, $J = 7.6$ Hz, 1H), 3.70 (s, 4H), 3.67 (s, 4H), 1.63 (t, $J = 7.9$ Hz, 2H), 1.32 (3H, s), 1.30–1.05 (m, 16H), 0.97–0.92 (m, 2H), 0.88 (t, $J = 6.9$ Hz, 3H); MS m/z 440 (M^+ , 30), 405 (5), 289 (100); M_r calcd for $C_{28}H_{40}S_2$ 440.2571, found (MS) 440.2570.

anti-9-Methyl-18-pentadecyl-2,11-dithia[3.3]metacyclophane (24b). This was prepared by a cyclization reaction of **14** and **23** according to a similar procedure described for the preparation of **24a**. Only the *anti* isomer **24b** was isolated as colorless crystals (82%): mp 88–90 °C; 1H NMR (500 MHz) δ 7.29 (d, $J = 7.6$ Hz, 2H), 7.28 (d, $J = 7.6$ Hz, 2H), 7.09 (t, $J = 7.6$ Hz, 1H), 7.07 (t, $J = 7.6$ Hz, 1H), 3.70 (s, 4H), 3.67 (s, 4H), 1.63 (t, $J = 7.8$ Hz, 2H), 1.32 (s, 3H), 1.30–0.93 (m, 26H), 0.88 (t, $J = 6.5$ Hz); MS m/z 496 (M^+ , 21), 462 (10), 345 (100), 313 (15), 299 (18), 265 (10), 149 (60). Anal. Calcd for $C_{32}H_{48}S_2$: C, 77.34; H, 9.75; S, 12.91. Found: C, 77.50; H, 9.82; S, 12.67.

Wittig Rearrangement of Dithiacyclophane 24a To Form 26a. To a solution of dithiacyclophane **24a** (100 mg, 0.23 mmol) in dry THF (20 mL) was added a solution of *n*-BuLi (2 mmol) in hexane under nitrogen at 0 °C. After 15 min, the dark solution was quenched with methyl iodide. Water was added, and the resulting mixture was extracted with dichloromethane. The organic phase was washed with water, dried, and evaporated. The residue was chromatographed on silica gel using hexane–dichloromethane (1:1) as eluent to give a mixture of isomers of **26a** (96 mg, 90%) as a yellow oil: 1H NMR (300 MHz) δ 7.87–7.69 (m, 2H), 7.27–6.83 (m, 4H), 4.14–3.98 (m, 2H), 3.24–3.16 (m, 2H), 2.75–2.53 (m, 2H), 2.30–2.14 (m, 6H), 1.25–0.57 (m, 26H); MS m/z 468 (M^+ , 100), 453 (30), 421 (30), 405 (50), 373 (20); M_r calcd for $C_{30}H_{44}S_2$ 468.2884, found (MS) 468.2884.

Wittig Rearrangement of Dithiacyclophane 24b To Form 26b. This was carried out with dithiacyclophane **24b** according to a similar procedure described for **24a**. A mixture of isomers of **26b** was obtained as a yellow oil (88%): 1H NMR (300 MHz) δ 7.79–7.76 (m, 2H), 7.21–6.96 (m, 4H), 4.03–3.99

(m, 2H), 3.24–2.57 (m, 4H), 2.30–2.14 (m, 6H), 1.25–0.73 (m, 29H), 0.64–0.57 (m, 5H); MS m/z 524 (M^+ , 51), 509 (20), 476 (41), 461 (39), 202 (100); M_r calcd for $C_{34}H_{52}S_2$ 524.3510, found (MS) 524.3528.

trans-10b-Methyl-10c-undecyl-10b,10c-dihydropyrene (3b). A solution of **26a** (96 mg, 0.21 mmol) in dry dichloromethane (5 mL) was added dropwise with stirring to a suspension of an excess of dimethoxycarbonium fluoroborate in dichloromethane (3 mL) at –30 °C under nitrogen. The mixture was stirred for an additional 6 h at room temperature. Ethyl acetate (10 mL) was then added, and the mixture was stirred for 2 h. The supernatant liquid was decanted. The bis(sulfonium) salt **27a** was collected by filtration and dried. It was then suspended in THF (10 mL), and potassium *tert*-butoxide (1.0 g) was added. After the mixture was stirred at room temperature for 10 min, benzene (10 mL), water (2 mL), and 3 N aqueous HCl (3 mL) were successively added. The organic layer was separated, washed with water, dried, and evaporated. The residue was then chromatographed on silica gel using hexane as eluent. The dihydropyrene **3b** was obtained as a thick green oil (46 mg, 59%): 1H NMR (500 MHz) δ 8.66 (d, $J = 7.7$ Hz, 4H, H-1,3,4,10), 8.58 (d, $J = 7.7$ Hz, 2H, H-5,9), 8.55 (d, $J = 7.7$ Hz, H-6,8), 8.08 (t, $J = 7.7$ Hz, 1H, H-2), 7.95 (t, $J = 7.7$ Hz, 1H, H-7), –4.26 (s, 3H, C10bCH₃); for chemical shifts of protons in the aliphatic chain, refer to Table 1; ^{13}C NMR δ 136.98 and 134.92 (C-3a,5a,10a,10d), 125.65 (C-1,3), 124.27 (C-6,8), 123.30 (C-4,10), 123.26 (C-5,9), 123.03 (C-2,7), 33.56 (C-10c), 31.33 (C-10b), 14.59 (C-C10b); for chemical shifts of carbon atoms in the aliphatic chain, refer to Table 1; MS m/z 372 (M^+ , 2), 357 (8), 217 (100), 202 (65); UV/vis (cyclohexane) 656 (ϵ 620), 480 (ϵ 6640), 382 (ϵ 36 700), 360 (ϵ 19 700), 340 (ϵ 69 000) nm; M_r calcd for $C_{28}H_{36}$ 372.2817, found (MS) 372.2817.

trans-10b-Methyl-10c-pentadecyl-10b,10c-dihydropyrene (3c). This was prepared from **26b** (21 mg, 0.04 mmol) via the salt **27b** according to a similar procedure described for the preparation of **3b**. The dihydropyrene **3c** was obtained as thick green oil (7 mg, 41%): 1H NMR (500 MHz) δ 8.67 (d, $J = 7.7$ Hz, 4H, H-1,3,4,10), 8.58 (d, $J = 7.7$ Hz, 2H, H-5,9), 8.55 (d, $J = 7.7$ Hz, 2H, H-6,8), 8.08 (t, $J = 7.7$ Hz, 1H, H-2), 7.96 (t, $J = 7.7$ Hz, 1H, H-7), –4.26 (s, 3H, C10bCH₃); for chemical shifts of protons in the aliphatic chain, refer to Table 1; ^{13}C NMR δ 136.99 and 134.93 (C-3a,5a,10a,10d), 125.66 (C-1,3), 124.27 (C-6,8), 123.31 (C-4,10), 123.26 (C-5,9), 123.03 (C-2,7), 33.57 (C-10c), 31.33 (C-10b), 14.59 (C-C10b); for chemical shifts of carbon atoms in the aliphatic chain, refer to Table 1; MS m/z 428 (M^+ , 7), 413 (12), 217 (100), 202 (50); UV/vis (cyclohexane) 654 (ϵ 370), 480 (ϵ 3650), 382 (ϵ 21 770), 342 (ϵ 45 280) nm; M_r calcd for $C_{32}H_{44}$ 428.3443, found (MS): 428.3445.

Computational Details. The initial geometries were generated using the MMX³⁶ force field with PCMODEL v4.0.³⁷ The semiempirical PM3²⁹ calculations were carried out with the MOPAC system (v6.0)³⁸ on a personal IRIS computer.

Acknowledgment. This work was supported by the National University of Singapore (NUS), Grant No. RP860606. Z.-L.Z. thanks the NUS for the Research Studentship (1991–94). Assistance from the technical staff of the Department of Chemistry, NUS, is gratefully acknowledged. The PM3 calculations were performed with assistance from Dr. Hway-Chuan Kang, Department of Chemistry, NUS.

Supporting Information Available: Table of calculated results for compound **3b** using the J–B model. 1H COSY spectrum (CDCl₃; 500 MHz) of compound **3b** (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9612382

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