Synthesis and Diatropicity of *trans*-10b,10c-Dimethylacenaphthyleno[1,2:*e*]-10b,10c-dihydropyrene: A Model Aromatic Molecule To Verify the Effect of Conjugation on the Diatropicity of an Annulene

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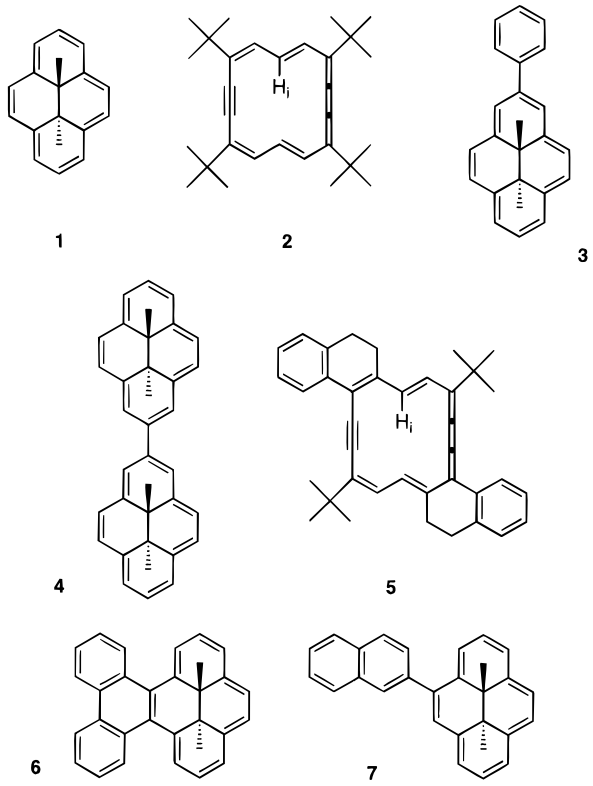
The title compound **11** was synthesized from acenaphthenequinone in 11 steps with an overall yield of *ca.* 1.3%. Photochemical desulfurization of the thiacyclophanene **24** afforded the cyclophanene **28**. Photochemical isomerization of **28** to the tetrahydropyrene derivative **32** followed by DDQ oxidation gave the desired dihydropyrene **11**. Compound **11** is found to sustain only about 85% of the ring current of the parent dihydropyrene **1**. On the basis of our results, a significant effect on the diatropicity of the 14π annulene in **11** due to its conjugation with a naphthalene moiety is verified. A correlation between theoretically calculated bond orders and experimentally observed coupling constants for selected bonds in **11** indicates that the inductive effect, relative to the resonance effect, plays a major role in the net effect of conjugation observed in **11**. Among several derivatives of dihydropyrene **1**, a linear relationship is observed for an empirical correlation between the methyl chemical shifts and the corresponding Dewar resonance energies associated with the benzenoid systems in conjugation with **1**. This may serve as a method to estimate the resonance energies of other aromatic systems relative to that of benzene. Compound **11** underwent electrophilic nitration, acetylation, and bromination readily under mild conditions. The electrophiles reacted selectively with the dihydropyrene system in **11** and not the acenaphthylene moiety in conjugation.

Introduction

In the discussion of many aspects of the chemistry of aromatic compounds, benzene undoubtedly is still commonly being termed as "the reference aromatic molecule". The advances in the chemistry of [4*n* + 2]annulenes,[1] however, have contributed significantly to the understanding of other aspects of aromaticity not exhibited by nor readily observed experimentally from the studies of benzenoids. One such example is the effect of annelation on the diatropicity of an aromatic molecule. Among the [14]annulenes, the relative effect of benzannelation due to a series of annelating rings has been extensively studied,[1,2] mainly by probing the change in diatropicity in the annelated derivatives compared with that of the corresponding parent [14]annulene **1** and dehydro[14]-annulene **2**, respectively.

The effect of conjugation on the diatropicity of an annulene, contrary to the effect of annelation, has yet to receive an extensive investigation. A recent UV spectroscopic study[3] clearly indicated a substantial inter-ring interaction going from the [14]annulene **1** to its conjugated derivatives **3** and **4**. Reduction in ring current of **3** and **4** relative to **1** is, however, minimal. On the other



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

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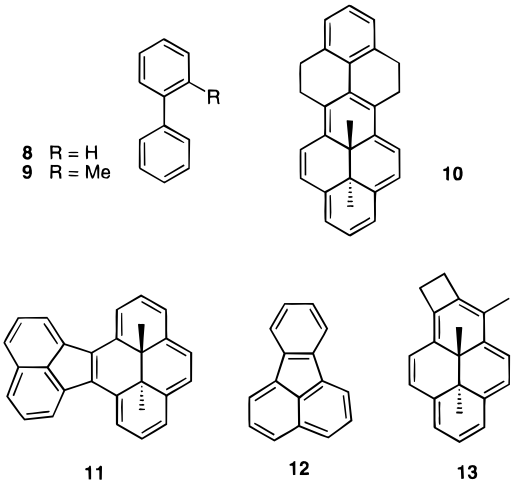
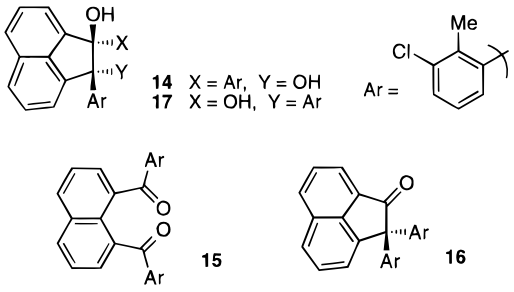
hand, the chemical shift of the H_i protons (δ −3.47)[4] in **5** (a [14]annulene in conjugation with two benzene rings) is significantly shifted from that (δ −4.39)[5] of the parent **2**. There was, however, no mention on whether such a shift is a result of the effect of conjugation. In the study of the diatropicity of **6**,[6] it was pointed out that the effect of conjugation (assuming that the 9,10-bond of the phenanthrene moiety in **6** participates to a large extent in the ring current of the macroring, which is then in conjugation with a biphenyl moiety) could perhaps be monitored by the decrease in diatropicity in the [14]-annulene using ^{1}H NMR spectroscopy. After all, conjugation between two rings would in principle be expected to reduce delocalization within any of the rings. An interesting challenge to verify this idea would require a model of the [14]annulene in conjugation with a naphthalene ring. A molecule such as **7** is, however, not suitable as the two π-systems are not expected to be coplanar. A dependence of the conjugation effect on the coplanarity of the two aryl rings in biphenyl systems such as **8** and **9** is clearly evident from studies of their electronic spectra.[7] The ^{1}H NMR signal of the internal methyl protons also shifts downfield, going from **3** (δ −4.00, −4.03)[3] to **10** (δ −3.81, −3.89).[8] A more ideal model in our work would then be the acenaphthylene-annelated dimethyldihydropyrene **11**, whose molecular models show a rigid and almost planar periphery. In addition, the macroring is in conjugation directly with both rings of the naphthalene moiety. A crystallographic study[9] of fluoranthene **12** has revealed slight angle strains and bond fixation in the molecule. The diatropicity observed in cyclobutane-annelated **13**, however, indicates[10] clearly the absence of a Mills−Nixon effect in the model [14]annulene. A recent experimental study[11] on strained benzocycloalkenes also revealed no evidence for sterically induced bond fixation. This suggests that the five-membered ring in **11** is not expected to affect the diatropicity significantly in another manner. The change in diatropicity, if any, observed for the [14]-annulene in **11** compared with that of the parent **1** would then be expected to be a result of basically a true conjugation effect due to naphthalene.



Results and Discussion

Synthesis. The synthesis of 1,2-diarylacenaphthylenes from acenaphthoquinone has been reported.[12] A similar synthetic approach would allow the preparation of the 1,2-diarylacenaphthylene **18**,[13] a precursor to the thiacyclophanene **24**. An initial attempt in treating acenaphthoquinone with the mono-Grignard reagent from 2,6-dichlorotoluene unexpectedly gave a mixture of 1,8-diacylnaphthalene **15** and acenaphthenone **16** instead of the diol **14**. Oxidative cleavage of 1,2-acenaphthene-



diol and its derivatives to 1,2-diacylnaphthalenes is, however, known.[14] The use of concd H_2SO_4 in the hydrolysis of the reaction mixture might have caused a similar cleavage of **14** formed initially to yield **15**. The strong acidic conditions would also encourage a pinacol rearrangement of **14** to give **16**. Thus, hydrolysis under milder conditions did lead to the isolation of **14** as the major product. The identity of **15** was confirmed when it afforded **18** directly when treated with hydrazine hydrate.[15] In a separate attempt, acid-catalyzed rearrangement of **14** afforded **16** cleanly. Reduction of the latter to give **17** followed by another acid-catalyzed rearrangement also led to the desired 1,2-diarylacenaphthylene **18**.

The diol **14** is believed to be the *trans* isomer on the basis of steric considerations. Both diol **14** and ketone **16**, due to the steric demand of the *ortho* methyl groups, exhibit a propelling process and/or free rotation of the aryl rings as reported for their respective parent systems.[13]

The functional group transformation sequences, namely **18** → **19** → **21** → **22** → **23** and **18** → **19** → **20** → **22** → **23**, respectively, were achieved with minor modifications on those reported for the corresponding 1,2-diarylbenzenes[16] and 9,10-diarylphenanthrenes.[6] The series of 1,2-diarylacenaphthylenes **18**−**23** have been found to exist in *anti* and *syn* conformers. A study of their rotational barriers, which depend on the buttressing effects of the 3′,3″-substituents, was reported earlier.[13]

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(14) See, for example: Stille, J. K.; Foster, R. T. *J. Org. Chem.* **1963**, *28*, 2703.
(15) (a) Bergmann, E. D.; Agranat, I. *Tetrahedron Suppl.* **1966**, No. 8, Part 1, 135. (b) Agosta, W. C. *J. Am. Chem. Soc.* **1967**, *89*, 3505. (c) Mitchell, R. H.; Fyles, T.; Ralph, L. M. *Can. J. Chem.* **1977**, *55*, 1480.
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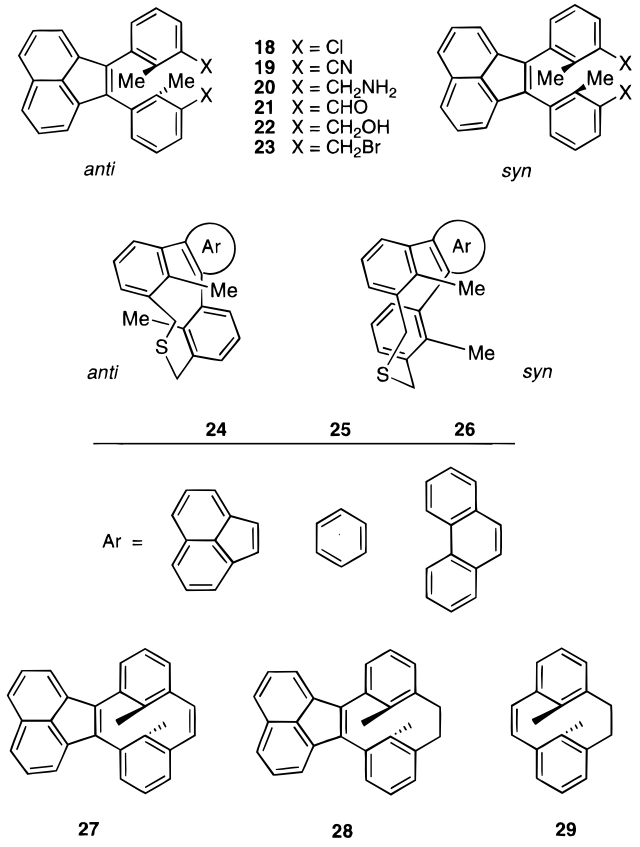
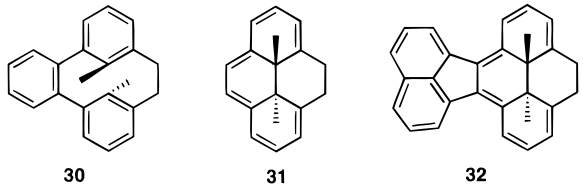
Our approach to the synthesis of **11** was to prepare the *anti* thiacyclophanene **24** as a precursor. This was obtained as bright orange crystals, mp 276−278 °C, in *ca.* 70% yield by a cyclization reaction of **23** with sodium sulfide under high dilution conditions.[17] Only one isomer of **24** was observed, and its stereochemistry was assigned the *anti* conformation on the basis of its ^{1}H NMR spectrum. The internal methyl protons of **24** appear shielded by the opposite aryl rings at δ 1.10 comparable to the corresponding methyl protons of cyclophanenes *anti*-**25** (δ 0.94)[18b] and *anti*-**26** (δ1.10),[6] respectively. Isolation of only *anti*-**25** was attributed[18b] mainly to severe steric crowding of the methyl groups in *syn*-**25**. Appropriate molecular models of *syn*-**24** indicate in addition to the above steric interaction a significantly unfavorable geometric strain in the annelated bridge due to the five-membered ring. This is consistent with the isolation of only *anti*-**24** in our work. In the preparation of the phenanthro derivative, where a 1:2 ratio of *syn*:*anti* isomers of **26** was obtained,[6] the result is believed to be due to a compromise between the steric interaction of the methyl groups in *syn*-**26** and that of H7-H1′/H13-H8′ aryl protons in *anti*-**26**.



A general synthetic approach to the parent dimethyldihydropyrene **1**[19] and its derivatives[6,10,18] involves a Stevens rearrangement−Hofmann elimination or a Wittig rearrangement−Hofmann elimination sequence on a thia- or dithia[3.3]metacyclophane to afford the corresponding [2.2]metacyclophanediene. The later undergoes a valence isomerization to afford the dihydropyrene system. We had, however, attempted to prepare the cyclophanediene **27** (and thus **11**) via the cyclophanene **28** on the basis of a report that oxidation[20] of cyclophanene **29** to afford the parent system **1** could be achieved. Thus, a photochemical extrusion of sulfur[21] was carried out by irradiation of *anti*-**24** in the presence of triethyl (or trimethyl) phosphite. The cyclophanene **28** was obtained as bright red crystals, mp 234−236 °C, in *ca.* 55% yield. The *anti* stereochemistry of **28** was again confirmed by the chemical shift of the methyl protons observed at δ 0.80 comparable to values reported for **29** (δ 0.79)[20] and **30** (δ 0.67).[18b] Treatment of **28** with 2,3-dichloro-4,5-dicyanoquinone (DDQ) in refluxing toluene, conditions known to convert **29** to **1**,[20] however, failed to yield the desired product **11**. As **29** is known to undergo photochemical isomerization to the tetrahydropyrene **31**,[22] an attempt was made to irradiate **28** in the presence of DDQ. Initial formation of the tetrahydropyrene derivative **32** should encourage further oxidation by DDQ to afford **11**. In fact, the latter was obtained as dark green crystals, mp 198.5−200 °C, in *ca.* 40% yield. Unexpectedly, a monochloro derivative of **11** was also isolated from the reaction (see later discussion). It is noted that **30** failed to yield **33** under similar conditions.[23] This is, however, consistent with the fact that dihydrotriphenylene could only be prepared from *o*-terphenyl under more drastic conditions.[24a]



The structure of **11** was supported by its mass spectrum with a molecular ion at *m*/*z* 356, with the base peak at *m*/*z* 326 corresponding to the loss of two methyl groups and formation of the acenaphthylenopyrene **34**.[24b] An attempt was made to convert **11** to **27** by irradiating the former with visible light, a condition known to result in a valence isomerization of **1** and **33** to the cyclophanedienes **35**[25] and **36**,[18b] respectively. There was, however, no evidence for **11** to undergo a similar reverse photochemical conversion to afford **27**. No significant decomposition was observed either in each attempt, and **11** could be recovered almost quantitatively. A possible explanation is a result of unfavorable geometic strain in the latter due to bridge annelation of an acenaphthylene unit. The dihydropyrene in general is also known to be the thermodynamically more stable valence isomer.

Diatropicity. The internal methyl protons of **11** appear highly shielded at δ −3.49 in its ^{1}H NMR

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Table 1. Chemical Shifts (δ) of Aromatic Protons in Selected Dihydropyrenes

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
1[26]	8.63	8.11	8.63	8.62	8.62	8.63	8.11	8.63	8.62	8.62				
33[18b]	8.30	7.25	7.59	7.36	7.36	7.59	7.25	8.30	8.81	7.62	7.62	8.81		
11	9.38	8.11	8.45	8.47	8.47	8.45	8.11	9.38	8.66	7.73	7.81	7.81	7.73	8.66
42	9.31		8.43	8.45	8.40	8.36	8.08	9.36	8.66	7.75	7.82	7.82	7.72	8.63
43	10.34		9.33	(8.52)[a]		8.75	8.29	9.44	8.71		(7.7−8.0)[b]			8.89
44	10.06		9.02	(8.84)[a]		8.65	8.12	9.36	8.67		(7.4−7.8)[b]			8.83

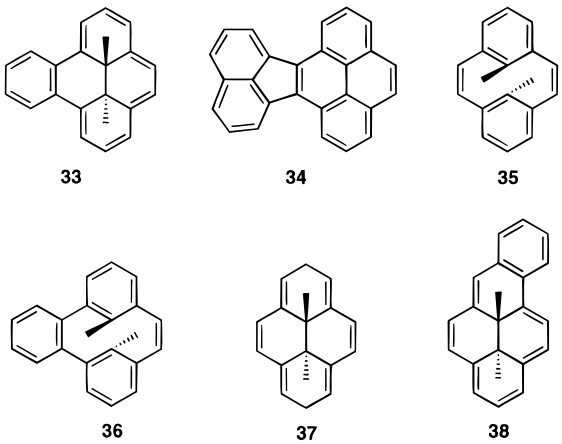
[a] H-4 and H-5 are not fully resolved. [b] H-10, H-11, H-12, and H-13 are not fully resolved.

Table 2. Comparison of the Diatropicities in Selected Dihydropyrenes

compd	δMe	$\Delta\delta$Me[a]	% ring current
1[26]	−4.25	5.22	100
33[18b]	−1.85	2.82	54
10[8]	−3.81, −3.89	4.81, 4.89	92−93
11	−3.49	4.46	85
6[6]	−3.32	4.22	82

[a] $\Delta\delta$Me is the shielding (in ppm) of the internal methyl protons relative to those in the nonaromatic model **37**.[26]

spectrum, indicating that **11** still sustains a strong ring current despite the annelation of an acenaphthylene moiety on the macroring. The aromatic protons of **11** could be readily assigned (Table 1) by decoupling experiments and a comparison with data reported for the parent **1** and the benzo derivative **33**. It is noted that H-1,8 of **11** are shifted signficantly downfield due to an additional deshielding effect by the adjacent naphthalene moiety. H-3 and H-4 of **11** appear at slightly higher fields than those of **1** but are significantly deshielded compared with those of **33**. This is qualitatively consistent with a decreasing order in diatropicity going from **1** to **11** to **33**.



Qualitatively, a comparison to the non-aromatic system **37** (δ, Me = 0.97)[26] with methyl protons in a similar geometric environment, and the assumption that shielding is proportional to ring current,[2e] would give an estimate of the relative diatropicity (Table 2) of a conjugated derivative compared with that of the parent system **1**. Such a comparison indicates that a decrease in the diatropicity of the macroring is clearly observed in going from **1** to any of its conjugated derivatives. The degree of the effect of conjugation, however, depends largely on the benzenoid in conjugation with the dihydropyrene, but in any case is relatively less significant than the effect of benzannelation observed in **33**.

The comparison in Table 2 indicates that **11** (**1** in conjugation with a naphthalene) sustains about 85% of the ring current of **1**. Its diatropicity is thus in between those of **10** (92−93%; **1** in conjugation with one benzene) and **6** (82%; **1** in conjugation with a biphenyl). Qualitatively, there are three other factors that might lead to a downfield shift of the methyl signals going from **1** to **11**. These are bond fixation (thus a decrease in diatropicity) in the macroring due to a Mills−Nixon effect of the annelating five-membered ring, a through-space anisotropic deshielding effect of the naphthalene moiety, and a deviation from planarity (thus, a decrease in diatropicity) of the macroring due to "bay region" steric interactions in **11**. The first factor was considered insignificant as discussed in the Introduction. The diamagnetic deshielding of the internal methyl protons by the benzene ring in benzo[*a*]-**38** (δMe = −1.60) was estimated to be only 0.05 ppm.[18a] The benzo[*e*]-**33**, with a change in the points of ring fusion at different positions on the noncircular current loop, seems to exhibit a relatively higher diatropicity (δMe = −1.85).[18b] Thus, the diamagnetic deshielding of the internal methyl protons by the benzene ring in **33** or the naphthelene moiety (which is relatively further away from the internal methyl protons) in **11** is also expected to be very small.

Steric interactions in the "bay regions" of polycyclic aromatic compounds may result in deviation from peripheral planarity and thus a decrease in diatropicity. The structure of benzo[*j*]fluoranthene (**39**) was, however, found to be coplanar from completely-optimized molecular geometry calculations,[28] indicating that the "bay region" interactions in this molecule are perhaps insignificant. Similar interactions in **11** are expected to be slightly more severe. The optimized structure of **11** derived from our semiempirical molecular orbital PM3[29] calculations show that the periphery of each of the acenaphthalene and dihydropyrene moieties is essentially planar, although the two planes are tilted at about 12° to each other. The distance between H1 and H14 (H8 and H9) is 1.8 Å. Dihedral angles measured for the respective pairs of "opposite" bonds in the periphery of the dihydropyrene unit are <5° except one at 5.1° for C4,5 and C14b,14c. Thus, there is no severe deviation from peripheral planarity of the dihydropyrene macroring. It is thus believed that the effect of conjugation is the major factor responsible for the reduction in the diatropicity of the [14]annulene going from **1** to **11**.

Effect of Conjugation. A simple correlation[30] of the diatropicity of benzannelated dihydropyrenes in terms of bond order deviation has been employed successfully to predict the chemical shift of the methyl protons in derivatives of **1**. Similar calculations on **6** and **11** in our

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Table 3. Calculated Bond Orders and Chemical Shifts of Internal Methyl Protons in Selected Dihydropyrenes

	π-SCF bond order, $P_\mu \times 10^3$		
bond[a] (μ)	**6**	**11**	**33**[30]
x	415	587	537
a, m	560	555	477
b, l	686	691	748
c, k	608	604	550
d, j	680	684	729
e, i	605	601	553
f, h	667	671	713
g	618	614	567
Q value[b]	1.118	1.132	1.818
Δr[c]	41.85	46.15	100.23
δMe$_{calcd}$[d]	−3.41	−3.29	−1.80
δMe$_{found}$	−3.32	−3.49	−1.85

[a] Refer to structure **40**. [b] Ratio of bond orders for bonds d(j) and c(k). [c] Average deviation of bond order (excluding bond x). [d] δMe $= 0.97 - (5.533 - 0.02752\Delta r)$.[30]

Table 4. Calculated Bond Orders (P_μ) and Calculated and Experimental Coupling Constants ($^3J_\mu$) for Dihydropyrenes 11 and 33

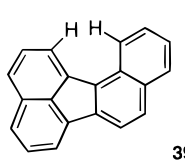
			$^3J_\mu$ calcd		corrected[b]		exptl	
bond[a] (μ)	P_μ **11**	**33**	**11**	**33**	**11**	**33**	**11**	**33**
c(k)	0.604	0.550	6.96	6.44	>7.26	6.74	7.56	6.84
d(j)	0.684	0.729	7.73	8.16	7.81	8.24	7.84	8.97

[a] Refer to structure **40**. [b] Corrected for steric effect; refer to text.

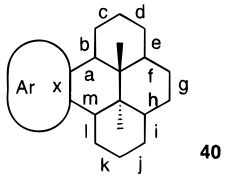
work afforded the results summarized in Table 3. It was surprising to find that the predicted (δ −3.29) and observed (δ −3.49) values for the chemical shift of the internal methyl protons of **11** agree very well. This is the first example of such a correlation for a dihydropyrene derivative involving the effect of conjugation. The initial approach[30] for these calculations was based entirely on benzannelated systems. With the above positive results, the bond orders (Table 3) obtained for **11** could then be used more convincingly in the following discussion on the effect of conjugation.

The alternance parameter Q (the quotient of the bond orders of two adjacent bonds)[31] has been used to reflect the extent of π-bond localization ($Q = P_{3,2}/P_{2,1}$) in **33**[18b] and other benzannelated derivatives of **1**.[2h,18] From our calculations (Table 3), the corresponding Q value for **11** is slightly larger than that of its parent **1** ($Q = 1.000$), similar to that of **6** but much smaller than that of **33**. This is consistent with a small appreciable bond alternation in **11** due to an effect of conjugation. It is, however, much less significant than the bond alternation in **33** resulting from an effect of benzannelation.

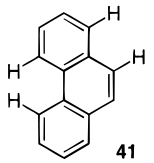
The net effect of conjugation in **11** should involve both the resonance and inductive effects that are not readily differentiable experimentally. Several methods of separation have been attempted[32] that are based on empirical grounds and classical chemical concepts. The resonance effect is, however, expected to result in bond localization, which should be reflected in the observed coupling constants of adjacent bonds. On the basis of the calculated bond orders for **11** and **33** (Table 4), the respective coupling constant, $^3J_{\mu,\nu}$, for bonds *c*(k) and *d*(j) (refer to **40**) are calculated.[31a] A correlation for steric compression has, however, to be estimated for the interaction between H-1 and H-14 (H-8 and H-9) in **11** for a more accurate predication of the coupling constant, $^3J_{\mu,\nu}$. Correlation factors of 0.08 and 0.30 Hz were reported[33] for 1,8-naphthalene- and 4,5-phenanthrene-type interactions, respectively, as represented in **41**. Qualitatively, the steric interaction between H-6 and H-7 in benzofluoranthene **39** is expected to be larger than that between H-4 and H-5 in phenanthrene **41**. Thus, the corresponding correction factor for the coupling constant in bond c due to the interaction between H-1 and H-14 (H-8 and H-9) in **11** is expected to be >0.30 Hz.



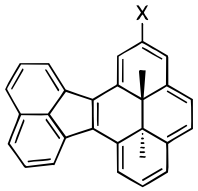
39



40



41



42 X = Cl
43 X = NO_2
44 X = $COCH_3$

The estimated and experimental values of the coupling constants for **11** (Table 4) agree well and suggest that bond localization (due to resonance effect) in the macroring of **11** is not very significant as indicated by a difference of only *ca.* 0.3 Hz between the coupling constants of adjacent bonds c and d (refer to **40**) compared to a corresponding value of >2 Hz for **33**. On the other hand, although no quantitative treatment is possible, it is evident that the inductive effect of the naphthalene moiety plays a major role in the decrease in diatropicity going from **1** to **11**.

The resulting effect of conjugation (resonance and inductive) is likely to depend on the aromaticity, which could be described in terms of delocalization energy or resonance energy, of the benzenoid system. Assuming that the annelated π-bond participates freely in the macroring in each of **6** and **11**, an attempt was made to correlate empirically the change in chemical shift of the internal methyl protons and the corresponding Dewar resonance energy[34] associated with the benzenoid system in conjugation with the parent dihydropyrene **1** (Table 5). The diatropic properties of **1** and **2**, and their respective derivatives, have been found[2e,30] to correlate well with other physical parameters collectively. Thus, the annulene **2** and its derivative **5** are also included (Table 5) in the correlation. A satisfactory linear relationship (Figure 1), governed by the equation $\Delta\delta$Me-($\Delta\delta H_i$) $= 0.4826\phi$H with a correlation coefficient of 0.994, is clearly observed among the systems studied in our work. This correlation, based on the effect of conjugation on diatropicity, could serve as a complementary method to that based on the effect of benzannelation on diatropicity[35] in the estimate of resonance energies of aromatic systems relative to that of benzene. Although both are empirical methods, the results obtained are, however, based on experimental evidence.

(31) (a) Cremer, D.; Günther, H. *Ann.* **1972**, *763*, 87. (b) Günther, H.; Shyoukh, A.; Cremer, D.; Risch, K. *Ibid.* **1978**, 150. (c) Günther, H.; Günther, M.; Mondeshka, D.; Schmickler, H. *Ibid.* **1978**, 165; (d) *Chem. Ber.* **1979**, *112*, 71.

(32) See, for example: Robert, P. *Collect. Czech. Chem. Commun.* **1983**, *48*, 1564.

(33) Cooper, M. A.; Manatt, S. L. *J. Am. Chem. Soc.* **1969**, *91*, 6352.

(34) Dewar, M. J. S.; De Llano, C. *J. Am. Chem. Soc.* **1969**, *91*, 789.

(35) Mitchell, R. H.; Venugopalan, S.; Zhou, P.; Dingle, T. W. *Tetrahedron Lett.* **1990**, *31*, 5281.

Table 5. Correlation between Chemical Shift and Resonance Energy Based on the Effect of Conjugation in Selected Dihydropyrenes

	Dewar RE of benzenoids in conjugation[34]			
dihydropyrene	benzenoids	ϕH units (eV)	δMe(δH$_i$)	$\Delta\delta$Me($\Delta\delta$H$_i$)
1	absent	0 (0.000)	−4.25	0.00[a]
2	absent	0 (0.000)	−4.39	0.00[b]
10	benzene	1 (0.869)	−3.81, −3.89	0.36−0.44[a]
5	benzene	2 (1.738)	−3.47	0.92[b]
6	biphenyl	1.92 (1.699)	−3.32	0.93[a]
11	naphthalene	1.52 (1.323)	−3.49	0.76[a]

[a] The shielding (in ppm) of the internal methyl protons relative to those in **1**. [b] The shielding (in ppm) of the internal proton (H$_i$) relative to those in **2**.

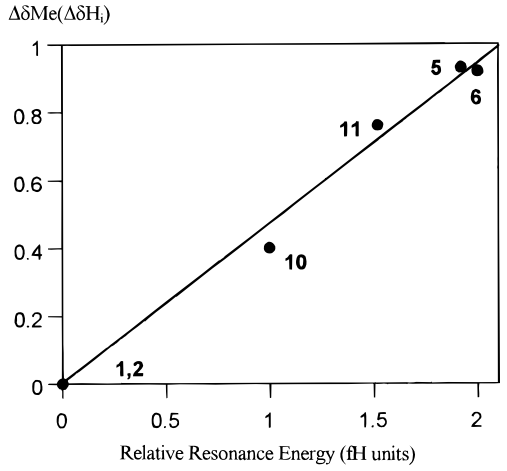


Figure 1. Plot of $\Delta\delta$Me($\Delta\delta$H$_i$) versus the relative resonance energy on the basis of the data presented in Table 5.

Electrophilic Substitutions. It was mentioned earlier that a monochlorinated derivative was also isolated in the conversion of **28** to **11** under photochemical conditions in the presence of DDQ. The formation of the chloro derivative was likely to involve an electrophilic substitution reaction of **11**. This we believe is the first example that suggests that DDQ could act as a source, though minor, of chlorine radicals (or less likely chlorine cations) under photolytic conditions. Electrophilic substitutions of several annulene systems have been reported.[1,36] Similar reactions on benzannelated annulenes are, however, less well known.[18b] It is thus of interest to study whether **11**, which in addition to the dihydropyrene system contains another reactive acenaphthene unit in conjugation, will undergo selective electrophilic substitution reactions in either the annulene or the benzenoid moiety.

In the ^{1}H NMR spectrum of the monochloro derivative (Table 1), the presence of a strongly deshielded singlet at δ 9.31 (H-1) confirms that the position of substitution is at C-2. H-8 appears at δ 9.36 as a doublet similar to that of **11**. The loss of symmetry going from **11** to **42** results in the resolution of most protons. A set of decoupling experiments and a comparison with the spectrum of **11** allows the assignments of all aromatic protons of **42** (Table 1). The chemical shifts of these protons, including H-1 and H-3, which are in close proximity to the chlorine atom, are very similar to those observed for **11**.

Attempts were then made to study several electrophilic substitutions of **11** using electrophiles generated under mild conditions for reactive aromatic compounds.[36b,37] Thus, the nitration of **11** was carried out with cupric nitrate. Only the mononitro derivative **43** was isolated in a 30% yield. The structure of **43** is supported by a molecular ion at m/z 401 in its mass spectrum. The $-NO_2$ absorptions at 1500 and 1285 cm^{-1} are observed in its IR spectrum. The unique features in its ^{1}H NMR spectrum (Table 1) are the highly deshielded H-1 (δ 10.34) and H-3 (δ 9.33) due to strong anisotropic and inductive effects of the 2-nitro group. The other aromatic protons of **43** are in general shifted slightly downfield relative to the corresponding protons in **11**, probably due to the electron-withdrawing inductive effect of the nitro group. Assignments of some of these protons (Table 1) are achieved with decoupling experiments.

The acetylation of **11** was carried out with acetic anhydride in the presence of boron trifluoride etherate as a catalyst. A monoacetyl derivative isolated was supported by the molecular ion at m/z 398 in its mass spectrum. In its IR spectrum, the C=O absorption at 1655 cm^{-1} also confirmed the presence of the acetyl group. A comparison of its ^{1}H NMR spectrum with those of **11** and **43** (Table 1) confirms that it is the 2-acetyl derivative **44**. The H-1 (δ 10.06) and H-3 (δ 9.02) protons are again significantly deshielded, although to a lesser extent than those in **43**, by the anisotropic effect of the carbonyl group at C-2.

The chemical shift of the methyl protons of **42** (δ −3.41) is very similar to that (δ −3.49) of **11**. The identical methyl proton chemical shift (δ −3.30) for both **43** and **44** also indicates that the substituents do not affect the diatropicity of the dihydropyrene signficiantly. The mononitration and monoacylation of **11** were thus found to occur preferentially in the dihydropyrene moiety at C-2. These results were similar to those observed for reactions of **33**.[18b] However, in the two electrophilic substitutions of **11** described above, no appreciable di- or polysubstituted derivatives could be isolated even when 2 equiv of reagents were used. A di- and a trinitro derivative have been reported in the nitration of **33** under different conditions.[18b] Bromination of the parent **1** was also found to give di- and/or polybrominated derivatives.[36b,38]

Treatment of **11** with 2 equiv of *N*-bromosuccinimide in dry DMF did result in a mixture of brominated products. Chromatographic purification afforded only

(36) See, for example: (a) Calder, L. C.; Garratt, P. J.; Longuet-Higgins, H. C.; Sondheimer, F. *J. Chem. Soc. C* **1967**, 1041. (b) Philips, J. B.; Molyneux, R. J.; Sturm, E.; Boekelheide, V. *J. Am. Chem. Soc.* **1967**, *89*, 1704. (c) Vogel, E.; Boll, W. A. *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 642. (d) Vogel, E.; Boll, W. A.; Biskup, M. *Tetrahedron Lett.* **1966**, 1569. (e) Gaoni, Y.; Sondheimer, F. *J. Am. Chem. Soc.* **1964**, *86*, 521.

(37) Anderson, A. G., Jr.; Nelson, J. A.; Tazuma, J. J. *J. Am. Chem. Soc.* **1953**, *75*, 4980.

(38) Mitchell, R. H.; Lai, Y.-H.; Williams, R. V. *J. Org. Chem.* **1979**, *44*, 4733.

one major fraction whose mass spectrum indicates a molecular ion at *m/z* 592 with a correct isotope pattern for three bromine atoms. There was, however, no evidence for the presence of a monobromo or dibromo derivative. The ^{1}H NMR spectrum, however, shows four singlets in the range of δ −3.0 to −3.3 in a peak height ratio of 1:8:8:3, clearly indicating the presence of several tribrominated derivatives of **11** in the mixture. The spectrum of the aromatic protons is too complicated to allow any reasonable proton assignment.

Conclusions

The synthesis of the desired compound **11** from acenaphthenequinone was achieved in 11 steps with an overall yield of *ca.* 1.3%. There is a significant decrease in diatropicity going from the parent dihydropyrene **1** to its derivative **11**. From our analysis, we have provided perhaps the first piece of experimental verification for a significant effect on the diatropicity of an annulene due to its conjugation with another aromatic (diatropic) system. On the basis of a correlation between theoretically calculated bond orders and experimentally observed coupling constants, it is clearly evident that the inductive effect, relative to the resonance effect, plays a major role in the net effect of conjugation observed in **11**. The dihydropyrene system in **11** has also been shown to be a more reactive site for electrophiles compared to the acenaphthylene moiety in conjugation.

Experimental Section

Melting points are uncorrected. ^{1}H NMR spectra were recorded in $CDCl_3$ on a 90 or 250 MHz spectrometer with Me_4-Si as internal standard. Mass spectra were obtained using EI ionization at 70 eV. UV photolysis was carried out in a Rayonet photochemical reactor (254 nm, 400W). Microanalyses were performed by the Microanalytical Laboratory of the Department of Chemistry, National University of Singapore.

1,8-Bis(3-chloro-2-methylbenzoyl)naphthalene (15) and 2,2-Bis(3-chloro-2-methylphenyl)acenaphthen-1-one (16). The Grignard reagent was prepared by reacting 2,6-dichlorotoluene (128.17 g, 0.796 mol) with magnesium (19.35 g, 0.796 mol) in dry THF (400 mL) using 1,2-dibromoethane as an initiator. The reaction mixture was heated at reflux under nitrogen until all magnesium was consumed. A solution of acenaphthenequinone (48.28 g, 0.265 mol) in dry THF (400 mL) was then added slowly and the mixture heated at reflux for 20 h. The reaction mixture was cooled to room temperature, and concd H_2SO_4 was added until all solids dissolved. Ether was used to extract the product. The organic layer was separated, washed, dried, and evaporated. The product mixture was preadsorbed and chromatographed on silica gel using dichloromethane/hexane (1:1) as eluant.

Eluting first was the ketone **16**: 30.25 g (27%). Recrystallization from cyclohexane gave colorless crystals of **16**: mp 176−178 °C; ^{1}H NMR (90 MHz) δ 6.5−8.2 (m, 12H), 1.94, 2.26 (ratio 1:1, s, total 6H); IR (KBr) 1715, 1555, 1450, 1425, 1375, 1355, 1330, 1250, 1210, 1100, 1010, 980, 830, 770 cm^{-1}; MS *m/z* 416 (M^+, 100), 401 (30), 400 (53), 399 (25), 398 (81), 381 (17), 373 (22), 363 (23), 322 (21), 303 (22), 302 (31), 301 (16), 300 (24), 277 (43), 263 (37), 262 (17), 226 (20), 153 (28), 152 (50), 151 (23), 150 (85), 139 (20). Anal. Calcd for $C_{26}H_{18}Cl_2O$: C, 74.83; H, 4.35. Found: C, 74.64; H, 4.31.

Eluting next was the dione **15**: 8.20 g (7%). Recrystallization from cyclohexane gave colorless crystals of **15**: mp 218−219.5 °C; ^{1}H NMR (90 MHz) δ 7.1−8.1 (m, 12H), 2.47 (s, 6H); IR (KBr) 1700, 1560, 1490, 1430, 1375, 1265, 1190, 1140, 1040, 995, 915, 900, 830, 795, 770, 710, 690, 660 cm^{-1}; MS *m/z* 432 (M^+, 21), 282 (13), 281 (61), 280 (40), 279 (100), 215 (23), 155 (27), 153 (82), 125 (28). Anal. Calcd for $C_{26}H_{18}Cl_2O_2$: C, 72.07; H, 4.19. Found: C, 72.05; H, 3.95.

1,2-Bis(3-chloro-2-methylphenyl)acenaphthene-1,2-diol (14). The Grignard reagent was prepared by reacting 2,6-dichlorotoluene (34.30 g, 0.213 mol) with magnesium (5.18 g, 0.213 mol) in dry THF (150 mL) as described above. Dry benzene (150 mL) was added and the reaction mixture cooled to *ca.* 50 °C. Acenaphthenequinone (13.00 g, 0.071 mol) was then added in batches and the mixture heated at reflux for 24 h. After being cooled in an ice bath, the reaction mixture was slowly hydrolyzed with H_2SO_4/H_2O (1:1) and stirred until all solids dissolved. The mixture was then extracted with dichloromethane. The organic layer was washed with water and aqueous $NaHCO_3$ solution, dried, and evaporated. The crude product was chromatographed on silica gel using hexane/dichloromethane (1:1) as eluent to give an isomeric mixture of the diol **14**: 11.25 g (36%); ^{1}H NMR (90 MHz) δ 6.7−8.0 (m, 12H), 2.07, 2.15 and 2.48 (ratio 1:2:1, s, total 2H), 1.52, 1.66 and 2.22 (ratio 1:2:1, s, total 6H); IR (KBr) 3700, 1420, 1280, 1245, 1175, 1130, 1105, 1050, 1005, 980, 925, 820, 765, 715, 685 cm^{-1}; MS *m/z* 432 (M^+, 12), 416 (30), 400 (36) 398 (22), 279 (100), 153 (49), 150 (15), 125 (15). A sample recrystallized from benzene gave colorless crystals of **14**, mp 163.5−164.5 °C. Anal. Calcd for $C_{26}H_{20}Cl_2O_2$: C, 71.73; H, 4.63. Found: C, 71.84; H, 4.42.

2,2-Bis(3-chloro-2-methylphenyl)acenaphthen-1-one (16). To a solution of the diol **14** (2.00 g, 4.59 mmol) in acetic acid (30 mL) was added concd H_2SO_4 (0.7 mL), and the mixture was heated at reflux for 45 min. The reaction mixture was cooled to room temperature and poured into water. The white solid was collected by filtration, washed thoroughly with water, dried, and chromatographed on silica gel using dichloromethane/hexane (1:1) as eluant to give the ketone **16**: 1.70 g (89%), identical (mp, ^{1}H NMR, IR, MS) to the previously obtained sample.

2,2-Bis(3-chloro-2-methylphenyl)acenaphthen-1-ol (17). A solution of the ketone **16** (2.00 g, 4.8 mmol) in dry THF (50 mL) was added slowly to a suspension of $LiAlH_4$ (0.32 g, 8.5 mmol) in dry THF at room temperature under nitrogen. The reaction mixture was heated at reflux for an additional 1.5 h. After being cooled to room temperature, the mixture was decomposed by ethyl acetate followed by addition of 1 N HCl. The product was extracted into dichloromethane, washed, dried, and evaporated. The crude product was chromatographed on silica gel using dichloromethane/hexane (1:1) as eluant to yield the alcohol **17**: 2.00 g (quant). Recrystallization from benzene gave colorless crystals of **17**: mp 193−194 °C; ^{1}H NMR (90 MHz) δ 6.3−7.9 (m, 12H), 6.20 (s, 1H), 2.06, 2.04 (s, total 6H), 1.74 (s, 1H); IR (KBr) 3300, 1575, 1550, 1450, 1410, 1350, 1300, 1165, 1120, 1095, 1080, 1040, 1000, 880, 825, 775, 750, 720, 680 cm^{-1}; MS *m/z* 418 (M^+, 23), 403 (16), 402 (33), 400 (41), 280 (19), 279 (100) 273 (19), 240 (21), 239 (42), 229 (18), 228 (15), 157 (16), 155 (15), 131 (91). Anal. Calcd for $C_{26}H_{20}Cl_2O$: C, 74.47; H, 4.81. Found: C, 74.76; H, 4.66.

1,2-Bis(3-chloro-2-methylphenyl)acenaphthylene (18). (a) The dione **15** (1.92 g, 4.4 mmol), KOH (21.18 g), and 99% hydrazine monohydrate (41 mL) were added to a mixture of ethylene glycol (225 mL) and water (55 mL). The mixture was heated for 8 h under nitrogen in an oil bath maintained at 110 °C. The mixture was then cooled and diluted with water. The product was extracted into dichloromethane, washed, dried, and evaporated. The crude product was chromatographed on silica gel using dichloromethane/cyclohexane (1:2) as eluant to give **18**: 529 mg (30%). Recrystallization from benzene/ethanol gave bright yellow crystals of **18**: mp 147−149 °C; ^{1}H NMR (90 MHz) δ 7.0−8.0 (m, 12H), 2.17, 2.20 (ratio 1.0:1.3, s, total 6H); IR (KBr) 1555, 1480, 1450, 1425, 1210, 1130, 1105, 1070, 1030, 1015, 1000, 820, 755, 680 cm^{-1}; MS *m/z* 400 (M^+, 100), 313 (16), 273 (20), 240 (18), 239 (400, 165 (19), 157 (18), 156 (30). Anal. Calcd for $C_{26}H_{18}Cl_2$: C, 77.81; H, 4.52. Found: C, 77.83; H, 4.43.

(b) The alcohol **17** (2.00 g, 4.78 mmol) was added to a 0.3% iodine solution in acetic acid (70 mL), and the mixture was heated at reflux for 1.5 h. The reaction mixture was then cooled and decomposed by sodium thiosulfate solution until the color of iodine was discharged. The yellow solid was filtered and redissolved in chloroform. The organic layer was washed with $NaHCO_3$ solution and water, dried, and evapo-

rated. The product mixture was chromatographed on silica gel using dichloromethane/cyclohexane (1:2) as eluant to give **18**: 1.65 g (86%), identical (mp, ^{1}H NMR, IR, MS) to the previously obtained sample.

Conversion of 18 to 23. Reaction conditions for the series of functional group transformations going from **18** to **23** were similar to those reported for the benzo[16] and/or phenanthro[6] series.

1,2-Bis(3-cyano-2-methylphenyl)acenaphthylene (19). This was obtained, after recrystallization from cyclohexane, as bright yellow crystals (2.7 g, 55%): mp 178−180 °C; ^{1}H NMR (90 MHz) δ 7.4−8.0 (m, 12H), 2.33, 2.41 (ratio 1.0:1.2, s, total 6H); IR (KBr) 2220, 1425, 1210, 1030, 820, 750, 665 cm^{-1}; MS *m*/*z* 382 (M$^+$, 100), 380 (34), 367 (21), 266 (28), 265 (26), 264 (59), 184 (15). Anal. Calcd for $C_{28}H_{18}N_2$: C, 87.93; H, 4.74; N,7.32. Found: C, 87.98; H, 4.66; N, 7.30.

1,2-Bis[3-(aminomethyl)-2-methylphenyl]acenaphthylene (20). This was obtained, after recrystallization from benzene, as bright yellow crystals (2.13 g, 86%): mp 70−78 °C dec; ^{1}H NMR (90 MHz) δ 7.1−8.0 (m, 12H), 3.84 (br s, 4H), 3.81 (br s, 4H), 2.01, 2.15 (ratio 1.0:1.4, s, total 6H); IR (KBr) 3370, 1620, 1580, 1450, 1370, 1060, 1025, 905, 820, 770 cm^{-1}; MS *m*/*z* 390 (M$^+$, 47), 375 (36), 373 (35), 356 (97), 344 (44), 341 (57), 328 (22), 326 (28), 313 (21), 252 (23), 251 (26), 239 (25), 187 (22), 179 (18), 178 (22); M_r calcd for $C_{28}H_{26}N_2$ 390.2095, found (MS) 390.2118.

1,2-Bis(3-formyl-2-methylphenyl)acenaphthylene (21). This was obtained, after chromatography on silica gel, as bright yellow crystals (0.86 g, 84%): mp 174−178 °C; ^{1}H NMR (90 MHz) δ 10.27, 10.30 (ratio 1.0:1.2, s, total 2H), 7.4−8.1 (m, 12H), 2.53, 2.58 (ratio 1.0:1.2, s, total 6H); IR (KBr) 1760, 1540, 1420, 1370, 1235, 1200, 1170, 1150, 1105, 1075, 970, 905, 880, 820, 790, 765, 720, 670, 630 cm^{-1}; MS *m*/*z* 388 (M$^+$, 100), 373 (22), 317 (20), 240 (27), 239 (75), 156 (15), 150 (11). Anal. Calcd for $C_{28}H_{20}O_2$: C, 86.57; H, 5.19. Found: C, 86.42; H, 5.18.

1,2-Bis[3-(hydroxymethyl)-2-methylphenyl]acenaphthylene (22). This was obtained, after recrystallization from methanol/chloroform, as bright yellow crystals [(a) 1.34 g (53%) from the diamine **20**; (b) 5.51g (99%) from the dialdehyde **21**]: mp 188−190 °C; ^{1}H NMR (90 MHz) δ 7.1−7.9 (m, 12H), 4.63, 4.68 (ratio 1.0:1.2, s, total 4H), 1.98, 2.17 (ratio 1.0:1.2, s, total 6H); IR (KBr) 3280, 1610, 1425, 1370, 1300, 1250, 1215, 1170, 1125, 1080, 1025, 990, 910, 865, 820, 790, 760, 730, 630 cm^{-1}; MS *m*/*z* 392 (M$^+$, 100), 329 (57), 316 (18), 314 (30), 253 (36), 252 (44), 242 (25), 241 (19), 239 (63), 163 (22), 158 (24), 157 (18), 156 (22). Anal. Calcd for $C_{28}H_{24}O_2$: C, 85.68; H, 6.16. Found: C, 85.21; H, 6.22.

1,2-Bis[3-(bromomethyl)-2-methylphenyl]acenaphthylene (23). This was obtained, after recrystallization from benzene, as bright yellow crystals (0.65 g, 69%): mp 148−150 °C; ^{1}H NMR (90 MHz) δ 7.1−7.9 (m, 12H), 4.48, 4.52 (ratio 1.0:1.1, s, total 4H), 2.04, 2.24 (ratio 1.0:1.1, s, total 6H); IR (KBr) 1475, 1420, 1370, 1210, 1165, 1120, 1025, 810, 775, 750, 720 cm^{-1}; MS *m*/*z* 516 (M$^+$, 50), 494 (21), 475 (15), 438 (25), 437 (42), 425 (17), 375 (22), 357 (15), 328 (43), 327 (27), 326 (32), 291 (28), 287 (21), 253 (54), 220 (26), 218 (23), 194 (26), 157 (32), 137 (15). Anal. Calcd for $C_{28}H_{22}Br_2$: C, 64.89; H, 4.29. Found: C, 65.14; H, 4.17.

***anti*-8,17-Dimethylacenaphthyleno[1,2-*a*]-10-thia[2.3]-metacyclophan-1-ene (24).** A solution of **23** (1.26 g, 2.43 mmol) in benzene (200 mL) and a solution of sodium sulfide nonahydrate (0.61 g, 2.43 mmol) in 95% ethanol/water (9:1; 200 mL) were added, in separate rotaflow dropping funnels, dropwise at the same rate into vigorously stirred 95% ethanol (1 L) under nitrogen over a period of 6 h. After the addition, the mixture was stirred for another 14 h, and the bulk of the solvent was then removed under reduced pressure. The residue was extracted with dichloromethane. The organic layer was washed, dried, and evaporated. The crude product was preadsorbed on silica gel and chromatographed using hexane/dichloromethane (2:1) as eluant to give *anti*-**24**: 0.65 g (68%). Recrystallization from benzene/cyclohexane gave bright orange crystals of *anti*-**24**: mp 276−278 °C; ^{1}H NMR (90 MHz) δ 7.3−8.0 (m, 12H), 3.89, 3.75 (ABq, J = 13.3 Hz, 4H), 1.10 (s, 6H); IR (KBr) 1470, 1440, 1420, 1370, 1210, 1160, 1120, 1060, 1040, 1020, 810, 765, 750, 720 cm^{-1}; MS *m*/*z* 390 (M$^+$, 100), 356 (32), 343 (27), 341 (18), 327 (17), 326 (19), 252 (14), 163 (10). Anal. Calcd for $C_{28}H_{22}S$: C, 86.11; H, 5.68. Found: C, 86.23; H, 5.69.

***anti*-8,16-Dimethylacenaphthyleno[1,2-*a*][2.3]-metacyclophan-1-ene (28).** Triethyl phosphite (40 mL) was added to a solution of **24** (0.20 g, 0.56 mmol) in cyclohexane (80 mL) in a quartz cell. The mixture was irradiated with light at 254 nm using a Rayonet photochemical reactor (Model RPR-100) under nitrogen at room temperature for 15 h. The reaction mixture was poured into 1 N HCl (200 mL) and mixed thoroughly with stirring for 1 h. The organic layer was separated, dried, and evaporated. The crude product was chromatographed on silica gel using cyclohexane as eluant to yield **28**: 0.10 g (55%). Recrystallization from cyclohexane/methanol gave bright red crystals of **28**: mp 234−236 °C; ^{1}H NMR (90 MHz) δ 7.0−8.0 (m, 12H), 2.5−3.0 (m, 4H), 0.80 (s, 6H); IR (KBr) 1470, 1425, 1180, 1140, 1125, 1110, 1025, 900, 815, 760, 750, 710 cm^{-1}; MS *m*/*z* 358 (M$^+$, 17), 344 (41), 343 (100), 328 (97), 326 (64), 162 (55), 156 (21). Anal. Calcd for $C_{28}H_{22}$: C, 93.81; H, 6.19. Found: C, 93.65; H, 6.06.

***trans*-10b,10c-Dimethylacenaphthyleno[1,2-*e*]-10b,10c-dihydropyrene (11) and *trans*-2-Chloro-10b,10c-dimethylacenaphthyleno[1,2-*e*]-10b,10c-dihydropyrene (42).** DDQ (0.27 g, 1.20 mmol) was added to a solution of **28** (0.20 g, 0.59 mmol) in cyclohexane (100 mL). The mixture was irradiated with light at 254 nm using a Rayonet photochemical reactor (Model RPR-100) for 10 h under nitrogen. The solvent was then removed under reduced pressure and the residue chromatographed on silica gel using cyclohexane as eluant.

Eluting first was the hydrocarbon **11**: 80 mg (40%). Recrystallization from cyclohexane/ethanol gave dark green crystals of **11**: mp 198.5−200 °C; ^{1}H NMR (250 MHz) δ 9.38 (d, J = 7.6 Hz, 2H), 8.66 (d, J = 7.0 Hz, 2H), 8.47 (s, 2H), 8.45 (d, J = 7.8 Hz, 2H), 8.11 (dd, J = 7.8, 7.6 Hz, 2H), 7.81 (d, J = 7.1 Hz, 2H), 7.73, (dd, J = 7.1, 7.0 Hz, 2H), −3.49 (s, 6H); IR (KBr) 1440, 1370, 1310, 1195, 905, 825, 760, 715, 665 cm^{-1}; MS *m*/*z* 356 (M$^+$, 12), 343 (15), 342 (18), 341 (53), 327 (32), 326 (100), 324 (17), 163 (29), 162 (20). Anal. Calcd for $C_{28}H_{20}$: C, 94.35; H, 5.65. Found: C, 94.32; H, 5.67.

Eluting next was the chloro derivative **42**: 5 mg (2%). Recrystallization from hexane gave dark green crystals of **42**: mp 214−216 °C; ^{1}H NMR (250 MHz) δ 9.36 (d, J = 8.2 Hz, 1H), 9.31 (s, 1H), 8.66 (d, J = 7.0 Hz, 1H), 8.63 (d, J = 7.0 Hz, 1H), 8.45 (d, J = 5.7 Hz, 1H), 8.43 (s, 1H), 8.40 (d, J = 5.7 Hz, 1H), 8.36 (d, J = 8.2 hz, 1H), 8.08 (t, J = 8.2 Hz, 1H), 7.82 (d, J = 8.1 Hz, 2H), 7.75 (dd, J = 8.1, 7.0 Hz, 1H), 7.72 (dd, J = 8.1, 7.0 Hz, 1H), −3.39, −3.41 (s, 6H); IR (KBr) 1360, 1300, 1150, 905, 870, 840, 815, 800, 765, 755, 665, 650 cm^{-1}; MS *m*/*z* 390 (M$^+$, 21), 375 (56), 360 (100), 340 (93), 324 (42), 322 (15), 180 (23), 170 (38), 162 (52), 161 (23); M_r calcd for $C_{28}H_{19}Cl$ 390.1175, found (MS) 390.1188.

***trans*-10a,10b-Dimethyl-2-nitroacenaphthyleno[1,2-*e*]-10b,10c-dihydropyrene (43).** To a solution of **11** (20 mg, 0.056 mmol) in acetic anhydride (5 mL) at 0 °C under nitrogen was added $Cu(NO_3)_2 \cdot 3H_2O$ (15 mg, 0.062 mmol). The mixture was stirred for 45 min, and water/ether (1:1; 50 mL) was added. The organic layer was separated, washed thoroughly, dried, and evaporated. The residue was chromatographed on silica gel using hexane/dichloromethane (1:1) as eluant to give **43**: 7 mg (30%). Recrystallization from hexane gave dark green crystals of **43**: mp 224−226 °C; ^{1}H NMR (90 MHz) δ 10.34 (br s, 1H), 9.44 (d, J = 7.9 Hz, 1H), 9.33 (s, 1H), 8.89 (d, J = 6.5 Hz, 1H), 8.75 (d, J = 8.0 Hz, 1H), 8.71 (d, J = 6.5 Hz, 1H), 8.52 (br d, J = 8.2 Hz, 2H), 8.29 (br dd, J = 7.9 Hz, 1H), 7.7−8.0 (m, 4H), −3.30 (s, 6H); IR (KBr) 1530, 1500, 1455, 1430, 1365, 1285, 1085, 880, 860, 820, 760, 750, 665, 650 cm^{-1}; MS *m*/*z* 401 (M$^+$, 36), 386 (100), 371 (92), 369 (26), 340 (67), 324 (59), 322 (11), 313 (11), 170 (28), 163 (26); M_r calcd for $C_{28}H_{19}NO_2$ 401.1416, found (MS) 401.1423.

***trans*-2-Acetyl-10b,10c-dimethylacenaphthyleno[1,2-*e*]-10b,10c-dihydropyrene (44).** Acetic anhydride (2 mL) and boron trifluoride etherate (0.5 mL) were added to a solution of **11** (20 mg, 0.056 mmol) in dichloromethane (10 mL) at room temperature under nitrogen. The color of the reaction mixture changed from dark green to reddish brown. After 2

min, ether (40 mL) and a saturated solution of $NaHCO_3$ were added. The organic layer was separated, washed, dried, and evaporated. The residue was chromatographed on silica gel using hexane as eluant to yield **44**: 8 mg (36%). Recrystallization from hexane/methanol gave bright red crystals of **44**: mp 197−199 °C; ^{1}H NMR (90 MHz) δ 10.06 (s, 1H), 9.36 (br d, J = 8.4 Hz, 1H), 9.02 (s, 1H), 8.83 (d, J = 6.2 Hz, 1H), 8.67 (d, J = 6.4 Hz, 1H), 8.65 (d, J = 8.5 Hz, 1H), 8.84 (br d, J = 8.1 Hz, 2H), 8.12 (br dd, J = 8.5 Hz, 1H), 7.4−7.8 (m, 4H), 3.10 (s, 3H), −3.30 (s, 6H); IR (KBr) 1655, 1420, 1350, 1235, 1205, 820, 765 cm^{-1}; MS m/z 398 (M^+, 23), 383 (48), 368 (62), 342 (23), 341 (81), 340 (100), 325 (46), 324 (40), 162 (39), 161 (22); M_r calcd for $C_{30}H_{22}O$ 398.1671, found (MS) 398.1665.

Computational Details. The initial geometries were generated using the MMX[39] force field with PCMODEL v4.0.[40] The semiempirical PM3[29] calculations were carried out with the MOPAC system (v6.0)[41] on a personal IRIS computer.

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