Synthesis of 2-Aryl-10b,10c-dimethyl-10b,10c-dihydropyrenes and a Study of Their Conjugation Behavior: Linear Relationship between the Degree of Conjugation and the Electronic Nature of Substituents

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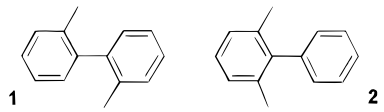
A new Gomberg−Bachmann reaction between 10b,10c-dimethyl-10b,10c-dihydropyrene (**3**) and an arenediazonium salt under acidic conditions afforded a mixture of mono- and diarylated derivatives of **3**. The major product was 2-aryl-10b,10c-dimethyl-10b,10c-dihydropyrene **6**. The desired products were obtained only from diazonium salts prepared from anilines with at least one strongly electron-withdrawing substituent. The combined conjugation and electronic effects of the arene substituent on the diatropicity of the dihydropyrene moiety in the monoarylated product is insignificant. The conjugation effect in **6** is, however, readily observed by the color appearance of **6** in the solid state and the significant red shift in the absorption bands between 300 and 520 nm in its electronic spectrum. A linear relationship was in fact obtained when the degree of conjugation (ρ band λ_{max} values) is correlated with the electronic nature (σ^+ values) of the corresponding substituents.

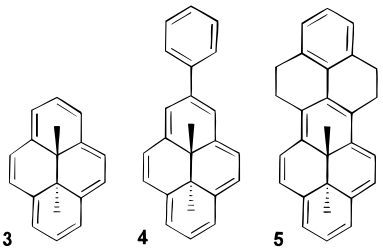
The stereochemistry and the conjugation effect are areas of special interests in the chemistry of biaryls. The dependence of the conjugation effect on coplanarity of the two aryl rings in a biaryl was evident from the studies of the electronic spectra of simple biaryls, *e.g.*, **1** and **2**.[1]



1 **2**

Two of the most common classical methods for the synthesis of unsymmetrical biaryls are the Gomberg−Bachmann reaction[2] between a diazonium salt and an arene in an alkaline medium and the Ullmann[3] reaction involving a coupling of two aryl halides in the presence of finely powdered copper. More recently a versatile synthetic approach to the preparation of biaryls is the transition metal-catalyzed cross-coupling of electrophilic and nucleophilic aromatic partners.[4] For example, the palladium-catalyzed couplings of aryl halides or sulfonates with arylstannanes (the Stille reaction)[5] or arylboronic acids or esters (the Suzuki reaction).[6] Most of these methods are, however, mainly restricted to benzenoid compounds.

10b,10c-Dimethyl-10b,10c-dihydropyrene (**3**) and its derivatives have been shown to be good models for the investigation of the effect of conjugation[7] on the diatropicity of the 14π annulene. Mitchell *et al.* reported the isolation[4d] of 2-phenyl-10b,10c-dimethyl-10b,10c-dihydropyrene (**4**) in low yield from a very slow coupling reaction using zero valent nickel complex.[8] Reduction in the ring current of **4** relative to the parent **3** is minimal, whereas significant conjugation between the two rings was indicated by electronic spectroscopy. A bridged derivative of **4**, namely, compound **5**,[9] however shows a further decrease in diatropicity. In order to confirm whether the conjugation effect in **4** is responsible for the small decrease in its observed diatropicity, our efforts were directed toward finding a correlation, if any, of the conjugation and diatropicity in a series of 2-aryl-10b,10c-dimethyl-10b,10c-dihydropyrenes **6**. We wish to describe a simple and general synthesis of **6**.



3 **4** **5**

δCH_3 = -4.25 -4.00, -4.03 -3.81, -3.89

Results and Discussion

Synthesis. The Gomberg−Bachmann reaction was first investigated based on the fact that various aryldiazonium salts are readily accessible and that dihydropy-

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(1) (a) Mills, W. H. *Chem. Ind. (London)* **1926**, *45*, 884, 905. (b) Stoughton, R. W.; Adams, R. *J. Am. Chem. Soc.* **1932**, *54*, 4426. (c) Stanley, W. M.; Adams, R. *J. Am. Chem. Soc.* **1930**, *52*, 1200. (d) Beaven, G. H.; Hall, D. M.; Lesslie, M. S.; Turner, E. E.; Bird, G. R. *J. Chem. Soc.* **1954**, 131. (e) Braude, E. A.; Forbes, W. F. *J. Chem. Soc.* **1955**, 3776. (f) Murrell, J. N. *J. Chem. Soc.* **1956**, 3779.

(2) (a) Gomberg, M.; Bachmann, W. E. *J. Am. Chem. Soc.* **1924**, *42*, 2339. (b) Campbell, N.; Barclay, B. M. *Chem. Rev.* **1947**, *40*, 359. (c) Dermer, O. C.; Edmison, M. T. *Chem. Rev.* **1957**, *57*, 77.

(3) (a) Ullmann, F. *Chem. Ber.* **1903**, *36*, 2382. (b) Bunnell, J. F.; Zahler, R. E. *Chem. Rev.* **1951**, *49*, 392. (c) Schulenberg, J. W.; Archer, S. *Org. React.* **1965**, *14*, 19. (d) Yamamoto, T.; Kurata, Y. *Can. J. Chem.* **1983**, *61*, 86. (e) Renger, B. *Synthesis* **1985**, 856.

(4) (a) Hayashi, T.; Hayashizaki, K.; Kiyo, T.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 8153. (b) Saa, J. M.; Martorell, G. *J. Org. Chem.* **1993**, *58*, 1963. (c) Anderson, J. C.; Namli, H. *Synlett* **1995**, 765. (d) Mitchell, R. H.; Chaudhary, M.; Dingle, T. W.; Williams, R. V. *J. Am. Chem. Soc.* **1984**, *106*, 7776 and references cited therein.

(5) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.

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(7) Lai, Y.-H.; Chen, P.; Peck, T.-G. *Pure Appl. Chem.* **1993**, *65*, 81.

(8) Kende, A. S.; Liebeskind, L. S.; Braitsch, D. *Tetrahedron Lett.* **1975**, 3375.

(9) (a) Mitchell, R. H.; Mahadevan, R. *Tetrahedron Lett.* **1981**, *22*, 5131. (b) Mitchell, R. H.; Iyer, V. S.; Khalifa, N.; Mahadevan, R.; Venugopalan, S.; Weerawarna, S. A.; Zhou, P. *J. Am. Chem. Soc.* **1995**, *117*, 1514.

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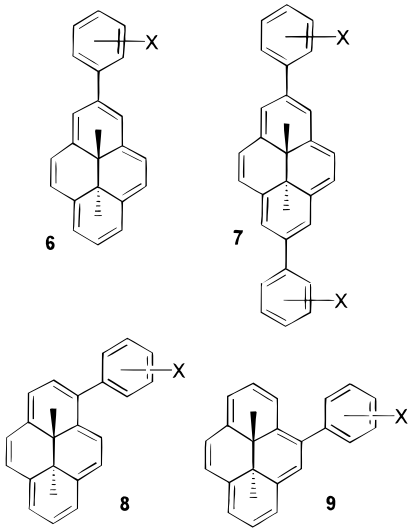
rene **3** undergoes electrophilic substitution reactions under mild conditions.[10] Our attempts in treating **3** with the diazonium tetrafluoroborate derived from 4-nitroaniline under basic conditions reported for Gomberg–Bachmann reactions,[11] however, failed to afford the unsymmetrical biaryl **6a**. There were several reports on examples which did not follow the homolytic Gomberg–Bachmann pathway.[12,13] The choice of a solvent suitable for both the diazonium salt and the substrate seemed to be an important factor.[13]

In our work, glacial acetic acid was chosen as an alternative solvent as it is only weakly nucleophilic and both the arenediazonium salt and compound **3** are soluble in it. An aqueous acidic solution of the diazonium salt formed *in situ* at 0 °C was then added dropwise to a solution of **3** in glacial acetic acid at room temperature. Surprisingly, the reactions studied (Table 1) were completed in about 20 min to afford a fair to good yield of the desired biaryls and teraryls.

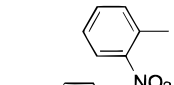
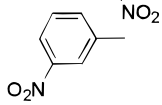
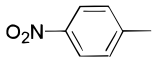
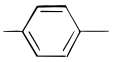
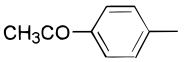
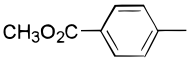
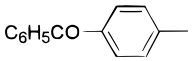
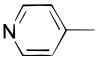
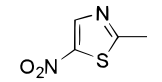
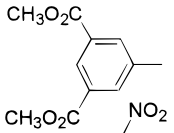
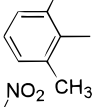
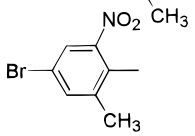
Results from mass spectral analyses of the product mixtures always suggested the presence of monoaryl and diaryl derivatives of **3**. The optimum yield of the major product, namely, 2-aryldihydropyrene **6**, was obtained when the ratio of the diazonium salt to **3** was about 1.5:1. Increasing the ratio would result in a higher yield of the 2,7-diaryldihydropyrene **7** (and in some cases its structural isomer(s), see Table 1) at the expense of compound **6**. The substituent's position, namely, *ortho*, *meta*, or *para*, of the monosubstituted examples did not seem to affect the product yield significantly. The use of diazonium salts prepared from 2,6-disubstituted anilines, however, led to low yields of **6m**,**n** presumably due to the unfavorable steric interactions in the transition state. A similar steric factor due the presence of an *ortho* substituent should also account for the fact that 1-aryldihydropyrene **8** was only isolated mainly from reactions involving 4-substituted anilines.



Spectroscopic identification of the structures of **6** and **7** was straightforward based on their high symmetry. The structure of compound **8** was confirmed by a ^{1}H NMR analysis indicating the AB and AB_2 splitting patterns of the $H_{2,3}$ and $H_{6,7,8}$ systems, respectively. All proton signals in compounds **6**–**8** were assigned on the basis of their 2D-^{1}H COSY NMR spectra and the results from a series of NOE experiments.

Pure samples of 1-aryldihydropyrenes **8f**,**8g** were obtained in our work (Table 1). In other examples, a mixture of **8** and perhaps 4-aryldihydropyrene **9** was observed by ^{1}H NMR analyses. It was reported that the relative preference for electrophilic substitution in **3** was C2 > C4 > C1 based on the relative heats of formation of the intermediate cations.[14] The relative strain energies

Table 1. Isolated Yields of Mono- and Diarylated Products from the Reactions of 3 with the Respective Diazonium Salts

Cpd	Ar	Isolated Yield (%)		
		6	**7**	**8**
a		48	20	0
b		47	23	0
c		49	(21)[a]	(8)[b]
d		65	15	0
e		35	(13)[a]	(9)[b]
f		41	(13)[a]	7
g		43	(11)[a]	9
h		50	27	(6)[b]
i		32	34	(5)[b]
j		34	0	0
k		45	(17)[a]	0
l		34	0	0
m		27	17	0
n		16	0	0

[a] Mixture of **7** and other bisarylated isomers. [b] Mixture of monoarylated **8** and **9**.

(10) Phillips, J. B.; Molyneux, R. J.; Sturm, E.; Boekelheide, V. *J. Am. Chem. Soc.* **1967**, *89*, 1704.

(11) (a) Rosenberg, D. E.; Beadle, J. R. *Tetrahedron Lett.* **1980**, *21*, 4141. (b) Beadle, J. R.; Korzeniowski, H.; Rosenberg, D. E.; Garcia-Slanga, B. J.; Gokel, G. W. *J. Org. Chem.* **1984**, *49*, 1594.

(12) (a) Abramovitch, R. A.; Gadallah, F. F. *J. Chem. Soc. B* **1968**, 497. (b) Kobayashi, M.; Minato, H.; Yamada, E.; Kobori, N. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 215. (c) Kaul, B. L.; Zollinger, H. *Helv. Chim. Acta* **1968**, *51*, 2132.

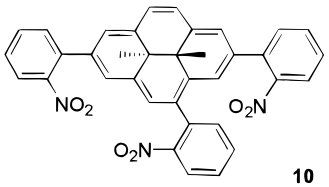
(13) Burri, P.; Zollinger, H. *Helv. Chim. Acta* **1973**, *56*, 232.

(14) Mitchell, R. H.; Iyer, V. S.; Mahadevan, R.; Venugopalan, S.; Zhou, P. *J. Org. Chem.* **1996**, *61*, 5116.

of the cationic intermediates may, however, follow a reverse order. Thus a predication on which of **8** and **9** is preferred would be rather impossible.

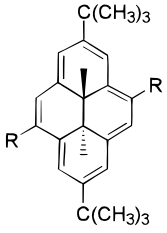
2,7-Diaryldihydropyrene **7** was isolated as the only bisarylated product in several reactions (Table 1). The other examples, however, were found to be a mixture of two or more bisarylated products. This is not surprising as the second arylation on **6** could in principle occur at C1, C4, C5, or C6.

In a separate attempt when the ratio of the diazonium salt of 4-nitroaniline to compound **3** was increased to 2.5:1, a small quantity of a trisarylated derivative of **3** was isolated in addition to compounds **6a** and **7a**. On the basis of a detailed ^{1}H NMR analysis, the third product was shown to be 2,4,7-triaryldihydropyrene **10**. The steric factor would again discourage the third aryl substitution to take place at C1 of **7a**. Our result is also consistent with the report that bromination of dihydropyrene **11a** gave the dibromo derivative **11b**.[15]

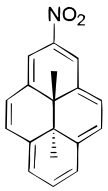


10

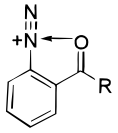
Two significant substituent effects were observed in our work. Firstly, only diazonium salts with electron-withdrawing substituents led to formation of the desired biaryls. An example with a weak "electron-withdrawing" group (*i.e.*, pyridine) gave only a low yield of the product **6j**. No biaryl product was formed in separate attempts by treating **2** with the diazonium salts derived from 4-methoxyaniline, 4-chloroaniline, and 4-toluidine, respectively. A reaction between nitrodihydropyrene **12** with the diazonium salt derived from 4-nitroaniline did not afford any biaryl product either. Another interesting observation was that the desired reaction did not occur when a carbonyl group was *ortho* to the diazo function (refer to **13**), whereas compounds **6f**,**g** could be isolated in fair yields. An intramolecular stabilization[16] of the diazonium salt **13** could account for a significant decrease in its reactivity.



11a R = H
11b R = Br



12



13a R = CH_3
13b R = OCH_3

Atropisomerism. The teraryl system **7a** could in principle exhibit atropisomerism and exist as two conformational isomers. The ^{1}H NMR spectrum of **7a** at room temperature shows only a sharp singlet at δ −3.83 for the "internal" methyl protons suggesting a rapid interconversion between its two conformers. The "internal" methyl protons in compound **10** appear, however, as four singlets at δ −3.55, −3.59, −3.63, and −3.67 in a 2:1:1:2 ratio. This is consistent with free rotation about the aryl−aryl single bonds of aryl rings at C2 and C7 and restricted rotation of the aryl ring at C4 resulting in two rigid conformational isomers in a 2:1 ratio at room temperature. A variable-temperature ^{1}H NMR study indicated no coalescence of the methyl signals up to a temperature of 90 °C above which a gradual decomposition of the sample was observed. Using the coalescence temperature method,[17] the conformational energy barrier ($\Delta G^{\ddagger}_c$) for rotation of the aryl ring at C4 in **10** was estimated to be larger than 77 kJ mol^{-1}.

Table 2. Proton Chemical Shift of the Internal Methyl Protons and Principal Electronic Absorption Maxima of 6

		absorption bands (λ_{max})		
compd	δ of internal CH_3	ρ	β	β'
6a	−4.01, −4.07	484	382	340
6b	−3.99, −4.02	496	386	342
6c	−3.96, −3.99	514	396	338
6d	−4.02, −4.06	490	386	344
6e	−3.98, −4.00	506	394	350
6f	−3.97, −4.00	502	390	346
6g	−3.98, −4.01	498	382	348
6h	−3.95, −3.99	502	390	344
6i	−4.06, −4.10	472	378	338
6j	−3.99, −4.02	496	386	346
6k	−3.77, −3.81	562	420	336
6l	−3.99, −4.03	492	384	344
6m	−4.00, −4.02, −4.05, −4.08	476	380	342
6n	−4.03, −4.04, −4.07, −4.09	482	382	344

The ^{1}H NMR spectra of compounds **6m**,**n** suggest a restricted rotation of the aryl rings about the aryl−aryl single bond. Protons of the two "internal" methyl groups in **6m** appear as two pairs of singlets in a 3:2 ratio. In a dynamic ^{1}H NMR spectroscopic study of a solution of **6m** in deuterated chloroform, the coalescence of the two pairs of singlets was observed at 38 and 40 °C, respectively, corresponding to $\Delta G^{\ddagger}_c$ values of 69.5 and 68.9 kJ mol^{-1}. The energy barrier (about 69 kJ mol^{-1}) for free rotation of the aryl rings in **6m** was thus significantly lower than that (>77 kJ mol^{-1}) for the rotation of the aryl ring at C4 in **10**, although **6m** has bulky groups at both *ortho* positions of the benzene ring.

Diatropicity and Conjugation. The chemical shifts of the internal methyl protons in the *para*-substituted series of **6c,e**−**h** do not change significantly (Table 2). Thus the conjugation effect of the substituent X in **6** on the diatropicity of the dihydropyrene moiety, if any, is not readily observable by employing the proton chemical shift as a probe. A similar observation was made when chemical shifts of the internal methyl protons of **6a**−**c** were compared. Although unrestricted rotation about the aryl−aryl single bond is expected in the above series of biaryl systems, a planar conformation for the maximum conjugation effect would be unfavorable due to steric interactions among the *ortho* protons. This is supported by the fact that the most appreciable shift was observed for compound **6k**. With the two spatially less demanding heteroatoms at the "*ortho*" positions of the 5-membered ring, the biaryl system in **6k** could achieve planarity to result in a stronger conjugation effect leading to a more appreciable change in the diatropicity of the dihydropyrene system. Compounds **6a**−**c** appear in the solid state

(15) Mitchell, R. H.; Chen, Y. *Tetrahedron Lett.* **1996**, *37*, 5239.
(16) Wallis, J. D.; Easton, R. J. C.; Dunitz, J. D. *Helv. Chim. Acta* **1993**, *76*, 1411.
(17) (a) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228. (b) Oki, M. *Applications of Dynamic NMR Spectroscopy to Organic Chemistry;* VCH Publishers: Deerfield Beach, FL, 1985.

as yellow-green, yellow-brown, and purple crystals, respectively, seemingly corresponding to an increase in conjugation. This is clearly reflected by a continuous red shift (Table 2) in the absorptions between 300 and 520 nm in their electronic spectra. This spectral range corresponds to Clar's ρ, β, and β' bands[4d,18] (the weak α bands are, however, not detectable) and is chiefly responsible for the observed chromatic colors of these compounds. Thus the dependence of the conjugation effect on the coplanarity of the two aryl rings in **6** could be monitored satisfactorily. Our semiempirical molecular orbital PM3[19] calculations show that in isolation, the dihedral angle between the two aryl rings in the optimized structure of **6a** is about 64° compared to that of about 37° in **6c**. Thus the most significant conjugation effect is, as expected, observed in the *para*-substituted **6c**. Coplanarity is unfavorable in **6a**, and the *meta* substituent in **6b** does not have a direct resonance interaction with the dihydroyprene moiety.

Most examples of **6** prepared in our work have bright colors ranging from green to purple in the solid state. Their solutions in organic solvents, however, exhibit very different colors. For example, solutions of **6a**,**b** in dichloromethane are yellow-green, while that of **6c** is red. The most significant solvent effect on the color appearance was observed for compound **6k**. It forms dark purple needles in the solid state and has the strongest α band λ_{max} at 676 nm (ϵ_{max} 2700) among all examples of **6**. A solution of **6k** in dichloromethane is blue, but a red solution is obtained in hexane.

The electronic influence that substituents exert on the rate and course of a reaction has been described effectively by the Hammett and related approaches.[20,21] A correlation between the electronic influence that substituents exert on the conjugation effect in a molecule has, however, not been directly mentioned. In the series of compounds **6c**,**e**−**g**, the electron-rich dihydropyrene is in direct resonance interaction with an electron-deficient substituent held in a *para* position. Thus it would be interesting to observe whether the σ^+ values[22] of the substituents could be correlated with the degree of conjugation in the biaryls. Using σ^+ values[23] of 0.740, 0.674, 0.567, and 0.472 for *p*-NO_2, *p*-CN, *p*-$COCH_3$, and *p*-$COOCH_3$, respectively, a linear relationship with a correlation coefficient of 0.9622 is indeed obtained when these are plotted against the corresponding ρ band λ_{max} values of compounds **6c**,**e**−**g** (Figure 1). Our results have thus shown that the electron-withdrawing nature of a substituent may be directly and quantitatively reflected in the electronic absorption band of a molecule.

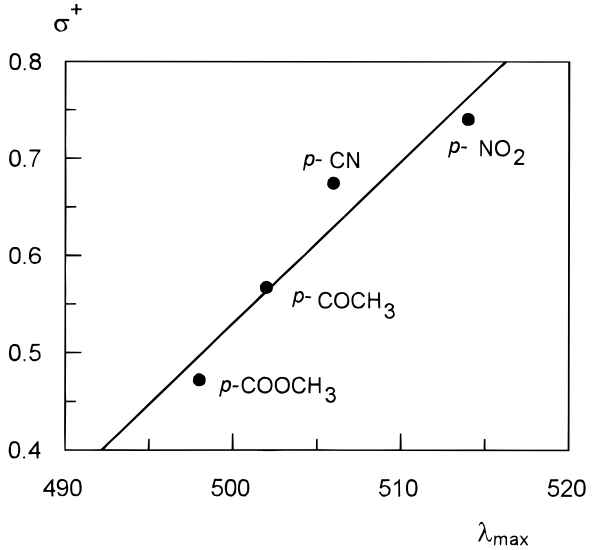


Figure 1. Correlation between ρ band λ_{max} values of compounds **6c**,**e**−**g** and σ^+ values of *p*-NO_2, *p*-CN, *p*-$COCH_3$, and *p*-$COOCH_3$.

Conclusion

The reaction between dihydropyrene **3** (a [14]annulene) and a diazonium salt under acidic conditions provides a convenient route to selected 2-aryldihydropyrene **6**. This reaction may be useful for arylation of other annulenes which undergo electrophilic substitution reactions under similar conditions. Although the effect of conjugation on the diatropicity of the dihydropyrene moiety in **6** was not significant, the electronic influence that substituents exert on the conjugation effect in the biaryl system could be readily observed. A linear relationship was in fact obtained when the degree of conjugation (ρ band λ_{max} values) is correlated with the electronic nature (σ^+ values) of the corresponding substituents.

Experimental Section

Melting points are uncorrected. ^{1}H NMR spectra were recorded in $CDCl_3$ on 300 or 500 MHz spectrometer with Me_4-Si as internal standard. All *J* values are given in hertz (Hz). 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.

General Procedure for the Preparation of *trans*-2-Aryl-10b,10c-dimethyl-10b,10c-dihydropyrenes 6, *trans*-2,7-Diaryl-10b,10c-dimethyl-10b,10c-dihydropyrenes 7, and/or *trans*-1-Aryl-10b,10c-dimethyl-10b,10c-dihydropyrenes 8. To a mixture of concd H_2SO_4 (2 mL) and water (2 mL) in a 25 mL round bottom flask was added the aniline derivative (0.65 mmol). The solution was cooled to about 0 °C with an ice bath. A solution of $NaNO_2$ (0.78 mmol) in the minimum amount of water was added dropwise over a period of 10 min while maintaining the temperature of the reaction mixture near 0 °C. After the addition of the $NaNO_2$ solution was completed, the reaction mixture was stirred for an additional 10 min near 0 °C. Urea (0.25 mmol) was then added to react with the excess $NaNO_2$, and the solution was stirred for another 10 min. The resulting solution of the diazonium salt was then added dropwise to a solution of dimethyldihydropyrene **3** (100 mg, 0.43 mmol) in glacial acetic acid (20 mL) at room temperature. After 10 min, the solution was poured into ice water (200 mL). The mixture was extracted successively with three portions (30 mL each) of dichloromethane. The organic layers were combined and washed successively with water, 10% aqueous $NaHCO_3$ solution, and water. The organic solution was dried and the solvent removed under

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reduced pressure. The residue was chromatographed on silica gel using CH_2Cl_2−hexane (1:1) as an eluant. Eluted first was compound **6** followed by **8** or a mixture of **8** and **9**. The last component eluted was compound **7** or a mixture of **7** and its structural isomers.

***trans*-2-(2-Nitrophenyl)-10b,10c-dimethyl-10b,10c-dihydropyrene (6a).** Recrystallization (*n*-hexane) gave **6a** (48%) as yellow-green needles: mp 180−182 °C; ^{1}H NMR (500 MHz) 8.65, 8.64 (AB q, J = 7.9, 4H), 8.60 (d, J = 7.7, 2H), 8.56 (s, 2H), 8.12 (t, J = 7.7, 1H), 8.04 (dd, J = 7.7, 1.3, 1H), 7.88 (dd, J = 7.7, 1.3, 1H), 7.76 (dt, J = 7.7, 1.3, 1H), 7.59 (dt, J = 7.7, 1.3, 1H), −4.01, −4.07 (s, ratio 1:1, total 6H); UV (*n*-hexane) λ_{max} 484 (ϵ 13 300), 382 (31 300), 340 (100 000); MS m/z 353 (M^+, 23), 338 (32), 323 (20), 305 (72), 291 (100), 276 (28), 145 (37), 138 (22). Anal. Calcd for $C_{24}H_{19}NO_2$: C, 81.57; H, 5.42; N, 3.96. Found: C, 81.18; H, 5.53; N, 3.95.

***trans*-2,7-Bis(2-nitrophenyl)-10b,10c-dimethyl-10b,10c-dihydropyrene (7a).** Recrystallization (*n*-hexane−CH_2Cl_2) gave **7a** (20%) as brown crystals: mp 226−228 °C; ^{1}H NMR (300 MHz) 8.64 (s, 4H), 8.54 (s, 4H), 8.05 (dd, J = 7.7, 1.1, 2H), 7.88 (dd, J = 7.7, 1.1, 2H), 7.79 (dt, J = 7.7, 1.1, 2H), 7.60 (dt, J = 7.7, 1.1, 2H), −3.83 (s, 6H); UV (*n*-hexane) λ_{max} 484 (ϵ 11 600), 376 (29 000), 342 (93 300); MS m/z 474 (M^+, 40), 459 (100), 444 (33), 425 (67), 379 (50), 350 (49), 175 (39). Anal. Calcd for $C_{30}H_{22}N_2O_4$: C, 75.94; H, 4.67; N, 5.90. Found: C, 75.76; H, 4.74; N, 5.80.

***trans*-2,4,7-Tris(2-nitrophenyl)-10b,10c-dimethyl-10b,10c-dihydropyrene (10).** When the ratio of the diazonium salt derived from 2-nitroaniline to compound **3** was increased to 2.5:1, a mixture of conformational isomers of compound **10** (7%) was isolated (in addition to **6a** and **7a**) as a red solid: mp 180−200 °C; ^{1}H NMR (500 MHz) 8.63−8.66 (m), 8.58, 8.50 (AB q, J = 10.3), 8.53 (s), 8.06−8.18 (m), 7.96 (d, J = 8.1), 7.53−7.88 (m), −3.55, −3.59, −3.63, −3.67 (s, ratio 2:1:1:2); UV (*n*-hexane) λ_{max} 498 (ϵ 12 800), 394 (28 300), 348 (70 900); MS m/z 595 (M^+, 12), 580 (55), 565 (18), 546 (20), 366 (42), 276 (30), 57 (100). Anal. Calcd for $C_{36}H_{25}N_3O_6$: C, 72.60; H, 4.27; N, 7.06. Found: C, 72.23; H, 4.71; N, 6.65.

***trans*-2-(3-Nitrophenyl)-10b,10c-dimethyl-10b,10c-dihydropyrene (6b).** Recrystallization (*n*-hexane) gave **6b** (47%) as yellow-brown needles: mp 140−142 °C; ^{1}H NMR (500 MHz) 8.98 (t, J = 1.9, 1H), 8.92 (s, 2H), 8.74, 8.65 (AB q, J = 7.7, 4H), 8.59 (d, J = 7.7, 2H), 8.45 (br d, J = 7.8, 1H), 8.28 (br d, J = 7.8, 1H), 8.12 (t, J = 7.7, 1H), 7.76 (t, J = 7.8, 1H), −3.99, −4.02 (s, ratio 1:1, total 6H); UV (*n*-hexane) λ_{max} 496 (ϵ 18 000), 386 (36 100), 342 (92 800); MS m/z 353 (M^+, 24), 338 (100), 323 (73), 276 (62), 216 (22),138 (60). Anal. Calcd for $C_{24}H_{19}NO_2$: C, 81.57; H, 5.42; N, 3.96. Found: C, 81.50; H, 5.37; N, 3.80.

***trans*-2,7-Bis(3-nitrophenyl)-10b,10c-dimethyl-10b,10c-dihydropyrene (7b).** Chromatography (*n*-hexane−CH_2Cl_2 (1:1)) on silica gel gave **7b** (23%) as a red solid: mp 246−248 °C; ^{1}H NMR (300 MHz) 8.98 (t, J = 1.9, 2H), 8.91 (s, 4H), 8.74 (s, 4H), 8.45 (br d, J = 8.3, 2H), 8.29 (dd, J = 8.3, 1.9, 2H), 7.78 (t, J = 8.3, 2H), −3.76 (s, 6H); UV (*n*-hexane) λ_{max} 492 (ϵ 16 800), 390 (47 500), 350 (96 900); MS m/z 474 (M^+, 30), 459 (100), 444 (85), 349 (45), 337 (31), 276 (26), 175 (64); M_r calcd for $C_{30}H_{22}N_2O_4$ 474.1580, found (MS) 474.1588.

***trans*-2-(4-Nitrophenyl)-10b,10c-dimethyl-10b,10c-dihydropyrene (6c).** Recrystallization (*n*-hexane) gave **6c** (49%) as purple needles: mp 175−177 °C; ^{1}H NMR (500 MHz) 8.93 (s, 2H), 8.74, 8.64 (AB q, J = 7.8, 4H), 8.59 (d, J = 7.7, 2H), 8.45, 8.28 (AB q, J = 7.1, 4H), 8.13 (t, J = 7.7, 1H), −3.96, −3.99 (s, ratio 1:1, total 6H); UV (*n*-hexane) λ_{max} 514 (ϵ 22 400), 396 (27 500), 338 (66 000); MS m/z 353 (M^+, 21), 338 (100), 323 (51), 292 (12), 276 (48), 138 (43). Anal. Calcd for $C_{24}H_{19}NO_2$: C, 81.57; H, 5.42; N, 3.96. Found: C, 81.04; H, 5.09; N, 3.68.

***trans*-2-(2-Cyanophenyl)-10b,10c-dimethyl-10b,10c-dihydropyrene (6d).** Recrystallization (*n*-hexane) gave **6d** (65%) as brown needles: mp 168−170 °C; ^{1}H NMR (500 MHz) 8.82 (s, 2H), 8.74, 8.67 (AB q, J = 7.7, 4H), 8.62 (d, J = 7.7, 2H), 8.14 (t, J = 7.7, 1H), 7.97 (br d, J = 7.8, 2H), 7.92 (dd, J = 7.8, 1.1, 1H), 7.79 (dt, J = 7.8, 1.1, 1H), 7.54 (dt, J = 7.8, 1.1, 1H), −4.02, −4.06 (s, ratio 1:1, total 6H); UV (*n*-hexane) λ_{max} 490 (ϵ 12 600), 386 (33 900), 344 (76 400); MS m/z 333 (M^+, 25), 318 (100), 303 (75), 276 (13), 158 (35), 137 (35). Anal. Calcd for $C_{25}H_{19}N$: C, 90.06; H, 5.74; N, 4.20. Found: C, 89.54; H, 5.76; N, 4.43.

***trans*-2,7-Bis(2-cyanophenyl)-10b,10c-dimethyl-10b,10c-dihydropyrene (7d).** Chromatography (*n*-hexane−CH_2Cl_2 (1:1)) on silica gel gave **7d** (15%) as a red solid: mp 258−260 °C; ^{1}H NMR δ (300 MHz) 8.82 (s, 4H), 8.76 (s, 4H), 7.96 (br d, J = 7.7, 2H), 7.93 (dd, J = 7.7, 1.1, 2H), 7.81 (dt, J = 7.7, 1.1, 2H), 7.55 (dt, J = 7.7, 1.1, 2H), −3.83 (s, 6H); UV (hexane) λ_{max} 490 (ϵ 20 600), 390 (30 400), 350 (79 500); MS m/z 434 (M^+, 8), 419 (100), 404 (25), 209 (15); M_r calcd for $C_{32}H_{22}N_2$ 434.1783, found (MS) 434.1783.

***trans*-2-(4-Cyanophenyl)-10b,10c-dimethyl-10b,10c-dihydropyrene (6e).** Recrystallization (*n*-hexane) gave **6e** (35%) as brown needles: mp 202−204 °C; ^{1}H NMR δ (500 MHz) 8.88 (s, 2H), 8.71, 8.63 (AB q, J = 7.7, 4H), 8.57 (d, J = 7.7, 2H), 8.22, 7.87 (AB q, J = 8.5, 4H), 8.11 (t, J = 7.7, 1H), −3.98, −4.00 (s, ratio 1:1, total 6H); UV (hexane) λ_{max} 506 (ϵ 18 800), 394 (29 000), 350 (73 400); MS m/z 333 (M^+, 15), 318 (100), 303 (90). Anal. Calcd for $C_{25}H_{19}N$: C, 90.06; H, 5.74; N, 4.20. Found: C, 89.60; H, 5.62; N, 3.90.

***trans*-2-(4-Acetylphenyl)-10b,10c-dimethyl-10b,10c-dihydropyrene (6f).** Recrystallization (*n*-hexane) gave **6f** (41%) as red needles: mp 156−158 °C; ^{1}H NMR δ (500 MHz) 8.94 (s, 2H), 8.71, 8.63 (AB q, J = 7.7, 4H), 8.57 (d, J = 7.7, 2H), 8.23, 8.19 (AB q, J = 8.6, 4H), 8.10 (t, J = 7.7, 1H), 2.72 (s, 3H), −3.97, −4.00 (s, ratio 1:1, total 6H); UV (hexane) λ_{max} 502 (ϵ 21 100), 390 (30 500), 346 (69 100); MS m/z 350 (M^+, 20), 335 (100), 320 (50), 276 (47), 138 (62). Anal. Calcd for $C_{26}H_{22}O$: C, 89.11; H, 6.33. Found: C, 88.83; H, 6.34.

***trans*-1-(4-Acetylphenyl)-10b,10c-dimethyl-10b,10c-dihydropyrene (8f).** Chromatography (*n*-hexane−CH_2Cl_2 (1:1)) on silica gel gave **8f** (7%) as a green solid: mp 121−123 °C; ^{1}H NMR δ (500 MHz) 8.68 (s, 2H), 8.66 (d, J = 7.8, 1H), 8.64 (d, J = 8.4, 1H), 8.62 (d, J = 8.4, 1H), 8.59 (d, J = 7.7, 2H), 8.20, 7.90 (AB q, J = 8.5, 4H), 8.13 (t, J = 7.7, 1H), 8.11 (d, J = 7.8, 1H), 2.76 (s, 3H), −4.08 (s, 6H); UV (hexane) λ_{max} 468 (ϵ 21 100), 382 (30 500), 344 (152 200); MS m/z 350 (M^+, 24), 335 (100), 320 (60), 292 (27), 276 (66), 138 (58); M_r calcd for $C_{26}H_{22}O$ 350.1671, found (MS) 350.1665.

***trans*-Methyl 2-(10b,10c-Dimethyl-10b,10c-dihydropyrenyl)benzene-4-carboxylate (6g).** Recrystallization (*n*-hexane) gave **6g** (43%) as brown crystals: mp 152−154 °C; ^{1}H NMR δ (500 MHz) 8.94 (s, 2H), 8.71, 8.63 (AB q, J = 7.7, 4H), 8.57 (d, J = 7.7, 2H), 8.26, 8.21 (AB q, J = 8.6, 4H), 8.10 (t, J = 7.7, 1H), 4.00 (s, 3H), −3.98, −4.01 (s, ratio 1:1, total 6H); UV (hexane) λ_{max} 498 (ϵ 15 100), 382 (50 600), 348 (112 900); MS m/z 366 (M^+, 15), 351 (100), 336 (70), 276 (47), 138 (62). Anal. Calcd for $C_{26}H_{22}O_2$: C, 85.22; H, 6.05. Found: C, 85.26; H, 6.16.

***trans*-Methyl 1-(10b,10c-Dimethyl-10b,10c-dihydropyrenyl)benzene-4-carboxylate (8g).** Chromatography (*n*-hexane−CH_2Cl_2 (1:1)) on silica gel gave **8g** (9%) as a green solid: mp 120−122 °C; ^{1}H NMR δ (500 MHz) 8.68 (s, 2H), 8.61−8.67 (m, 3H), 8.59 (d, J = 7.7, 2H), 8.27, 7.87 (AB q, J = 8.5, 4H), 8.13 (t, J = 7.7, 1H), 8.11 (d, J = 7.8, 1H), 4.02 (s, 3H), −4.08 (s, 6H); UV (hexane) λ_{max} 468 (ϵ 20 700), 382 (123 700), 346 (155 800); MS m/z 366 (M^+, 18), 351 (100), 336 (70), 292 (27), 276 (35), 138 (52); M_r calcd for $C_{26}H_{22}O_2$ 366.1620, found (MS) 366.1618.

***trans*-4-[2-(10b,10c-Dimethyl-10b,10c-dihydropyrenyl)]-benzophenone (6h).** Recrystallization (*n*-hexane) gave **6h** (50%) as brown needles: mp195−196 °C; ^{1}H NMR δ (500 MHz) 8.96 (s, 2H), 8.72, 8.63 (AB q, J = 7.7, 4H), 8.57 (d, J = 7.7, 2H), 8.25, 8.06 (AB q, J = 8.4, 4H), 8.10 (t, J = 7.7, 1H), 7.91 (br d, J = 7.5, 2H), 7.64 (br t, J = 7.5, 1H), 7.55 (br t, J = 7.5, 2H), −3.95, −3.99 (s, ratio 1:1, total 6H); UV (hexane) λ_{max} 502 (ϵ 17 400), 390 (27 200), 370 (30 100), 346 (60 300); MS m/z 412 (M^+, 13), 397 (100), 382 (47), 276 (33), 105 (75), 77 (32). Anal. Calcd for $C_{31}H_{24}O$: C, 90.26; H, 5.86. Found: C, 89.82; H, 5.86.

***trans*-4,4′-[2,7-(10b,10c-Dimethyl-10b,10c-dihydropyreno)]dibenzophenone (7h).** Chromatography (*n*-hexane−CH_2Cl_2 (1:1)) on silica gel gave **7h** (27%) as a red solid: mp 250−252 °C; ^{1}H NMR δ (500 MHz) 8.93 (s, 4H), 8.71 (s, 4H), 8.25, 8.06 (AB q, J = 8.4, 8H), 7.91 (br d, J = 7.5, 4H), 7.64

(br t, $J = 7.5$, 2H), 7.55 (br t, $J = 7.5$, 4H), −3.71 (s, 6H); UV (hexane) λ_{max} 504 (ϵ 19 000), 406 (27 000), 386 (35 400), 358 (81 100); MS m/z 592 (M^+, 7), 577 (80), 562 (35), 350 (7), 276 (6), 105 (100), 77 (45). Anal. Calcd for $C_{44}H_{32}O_2$: C, 89.16; H, 5.44. Found: C, 89.56; H, 5.68.

***trans*-2-[2-(Trifluoromethyl)phenyl]-10b,10c-dimethyl-10b,10c-dihydropyrene (6i).** Recrystallization (*n*-hexane) gave **6i** (32%) as green needles: mp 104−106 °C; ^{1}H NMR δ (300 MHz) 8.65 (br s, 4H), 8.60 (d, $J = 7.6$, 2H), 8.59 (s, 2H), 8.11 (t, $J = 7.6$, 1H), 7.88 (br d, $J = 7.8$, 1H), 7.68−7.71 (m, 2H), 7.58 (br t, $J = 7.8$, 1H), −4.06, −4.10 (s, ratio 1:1, total 6H); UV (hexane) λ_{max} 472 (ϵ 9 100), 378 (29 600), 338 (75 400); MS m/z 376 (M^+, 30), 361 (100), 346 (88), 326 (41), 276 (18). Anal. Calcd for $C_{25}H_{19}F_3$: C, 79.77; H, 5.09; F, 15.14. Found: C, 79.72; H, 5.04; F, 15.32.

***trans*-2,7-Bis[2-(trifluoromethyl)phenyl]-10b,10c-dimethyl-10b,10c-dihydropyrene (7i).** Recrystallization (*n*-hexane) gave **7i** (34%) as green needles: mp 218−219 °C; ^{1}H NMR δ (500 MHz) 8.66 (s, 4H), 8.58 (s, 4H), 7.89 (br d, $J =$ 7.9, 2H), 7.68−7.72 (m, 4H), 7.59 (br t, $J = 7.9$, 2H), −3.92 (s, 6H); UV (hexane) λ_{max} 482 (ϵ 16 500), 384 (35 200), 346 (105 800); MS m/z 520 (M^+, 13), 505 (100), 490 (71), 400 (20), 215 (32), 149 (68). Anal. Calcd for $C_{32}H_{22}F_6$: C, 73.84; H, 4.26; F, 21.90. Found: C, 73.26; H, 4.22; F, 22.53.

***trans*-2-(4-Pyridyl)-10b,10c-dimethyl-10b,10c-dihydropyrene (6j).** Chromatography (*n*-hexane−CH_2Cl_2 (1:1)) on silica gel gave **6j** (34%) as a green solid: mp 166−167 °C; ^{1}H NMR δ (500 MHz) 8.94 (s, 2H), 8.80 (dd, $J = 6.2$, 1.6, 2H), 8.74, 8.64 (AB q, $J = 7.7$, 4H), 8.59 (d, $J = 7.7$, 2H), 8.13 (t, $J =$ 7.7, 1H), 8.04 (dd, $J = 6.2$, 1.6, 2H), −3.99, −4.02 (s, ratio 1:1, total 6H); UV (hexane) λ_{max} 496 (ϵ 12 400), 386 (25 000), 344 (68 800); MS m/z 309 (M^+, 15), 294 (93), 279 (100). Anal. Calcd for $C_{23}H_{19}N$: C, 89.28; H, 6.19; N, 4.53. Found: C, 89.08; H, 5.98; N, 4.02.

***trans*-2-(5-Nitrothiazole-2-yl)-10b,10c-dimethyl-10b,10c-dihydropyrene (6k).** Recrystallization (*n*-hexane) gave **6k** (45%) as purple needles: mp 254−256 °C; ^{1}H NMR δ (300 MHz) 9.20 (s, 2H), 8.78, 8.60 (AB q, $J = 7.9$, 4H), 8.73 (s, 1H), 8.55 (d, $J = 7.7$, 2H), 8.17 (t, $J = 7.7$, 1H), −3.77, −3.81 (s, ratio 1:1, total 6H); UV (hexane) λ_{max} 676 (ϵ 2700), 562 (27 000), 420 (53 600), 336 (86 800); MS m/z 360 (M^+, 25), 345 (100), 242 (53), 227 (67). Anal. Calcd for $C_{21}H_{16}N_2O_2S$: C, 69.98; H, 4.47; N, 7.77; S, 8.90. Found: C, 69.64; H, 4.55; N, 7.93; S, 8.59.

***trans*-Dimethyl 5-[2-(10b,10c-Dimethyl-10b,10c-dihydropyrenyl)]benzene-1,3-dicarboxylate (6l).** Recrystallization (*n*-hexane) gave **6l** (34%) as yellow-green crystals: mp 177−178 °C; ^{1}H NMR δ (500 MHz) 8.99 (d, $J = 1.6$, 2H), 8.96 (s, 2H), 8.73, 8.65 (AB q, $J = 7.7$, 4H), 8.72 (t, $J = 1.6$, 1H), 8.59 (d, $J = 7.7$, 2H), 8.11 (t, $J = 7.7$, 1H), 4.06 (s, 6H), −3.99, −4.03 (s, ratio 1:1, total 6H); UV (hexane) λ_{max} 492 (ϵ 17 000), 384 (30 400), 344 (76 600); MS m/z 424 (M^+, 23), 409 (100), 394 (75), 350 (29), 276 (31), 189 (37); M_r calcd for $C_{28}H_{24}O_4$: 424.4936, found (MS) 424.4932.

***trans*-2-(2-Methyl-6-nitrophenyl)-10b,10c-dimethyl-10b,10c-dihydropyrene (6m).** Recrystallization (*n*-hexane) gave a mixture of conformational isomers of **6m** (27%) as green needles: mp 135−150 °C; ^{1}H NMR δ (300 MHz) 8.66−8.59 (m, 6H), 8.41 (s, 2H), 8.11 (t, $J = 7.7$, 1H), 7.88, 7.85 (d, $J = 7.9$, total 1H), 7.63 (br d, $J = 7.9$, 1H), 7.52 (t, $J = 7.9$, 1H), 2.33, 2.14 (s, total 3H), −4.00, −4.02, −4.05, −4.08 (s, ratio 2:1:1:2, total 6H); UV (hexane) λ_{max} 476 (ϵ 8400), 380 (25 000), 342 (67 600); MS m/z 367 (M^+, 40), 352 (78), 337 (62), 320 (100), 289 (75), 145 (70). Anal. Calcd for $C_{25}H_{21}NO_2$: C, 81.72; H, 5.76; N, 3.81. Found: C, 81.85; H, 5.65; N, 3.64.

***trans*-2,7-Bis(2-methyl-6-nitrophenyl)-10b,10c-dimethyl-10b,10c-dihydropyrene (7m).** Chromatography (*n*-hexane−CH_2Cl_2 (1:1)) on silica gel gave a mixture of isomers of **7m** (17%) as a green solid: mp 226−240 °C; ^{1}H NMR δ (300 MHz) 8.61 (s, 4H), 8.40 (s, 4H), 7.85−7.92 (m, 2H), 7.64 (d, $J = 7.7$, 2H), 7.52 (t, $J = 7.7$, 2H), 2.34, 2.16 (s, total 6H), −3.81, −3.84, −3.85, −3.87 (s, total 6H); UV (hexane) λ_{max} 486 (ϵ 13 500), 382 (27 800), 346 (77 900); MS m/z 502 (M^+, 20), 487 (100), 472 (30), 455 (70), 408 (40), 182 (73); M_r calcd for $C_{32}H_{26}N_2O_4$ 502.1893, found (MS) 502.1888.

***trans*-2-(4-Bromo-2-methyl-6-nitrophenyl)-10b,10c-dimethyl-10b,10c-dihydropyrene (6n).** Recrystallization (*n*-hexane) gave a mixture of isomers of **6n** (16%) as brown needles: mp 160−182 °C; ^{1}H NMR δ (300 MHz) 8.59−8.67 (m, 6H), 8.37 (s, 2H), 8.13 (t, $J = 7.7$, 1H), 8.03, 7.99 (br s, total 1H), 7.78 (br s, 1H), 2.32, 2.13 (s, total 3H), −4.03, −4.04, −4.07, −4.09 (s, ratio 2:1:1:2, total 6H); UV (hexane) λ_{max} 482 (ϵ 9200), 382 (25 600), 344 (72 400); MS m/z 445 (M^+, 22), 430 (50), 398 (100), 289 (69), 145 (86). Anal. Calcd for $C_{25}H_{20}BrNO_2$: C, 67.27; H, 4.52; N, 3.14; Br, 17.90. Found: C, 67.29; H, 4.41; N, 2.90; Br, 17.67.

Computational Details. The initial geometries were generated using the MMX[24] force field with PCMODEL v4.0.[25] The semiempirical PM3[26] calculations were carried out with the MOPAC system (v6.0)[27] on a personal IRIS computer.

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(24) Based on the MM2(87) force field with expanded parameter sets; See: Bays, J. P. *J. Chem. Educ.* **1992**, *62*, 209.

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