

Dihydropyrenes: Further insight into effects of annulenoannellation, benzannelation, conjugation and isoannellation

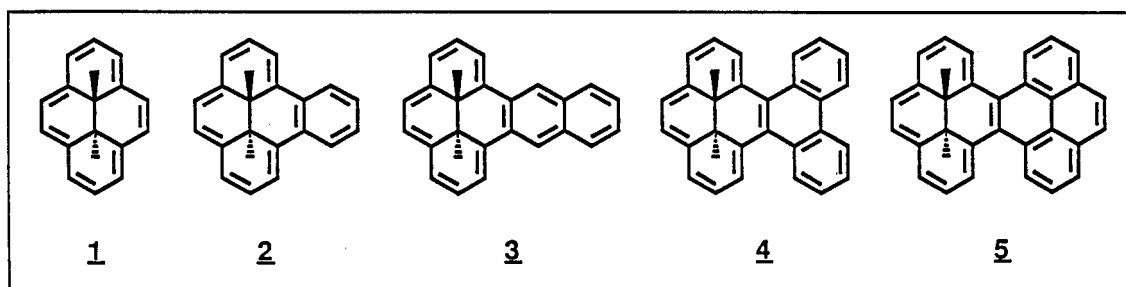
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Abstract - A series of [e]-annulated derivatives of dimethyldihydropyrene 1 have been synthesized and their relative diatropicities studied. The high π -bond orders of the annulated bonds in 4 and 5 clearly result in relatively smaller effects on the diatropicities of the respective [14]annulenes compared to benzoannulation in 2. The derivative 11 shows a strong effect of conjugation on the diatropiicity of the [14]annulene. A linear relationship between the diatropiicity of dihydropyrene and the resonance energy of the annulated benzenoid system is observed based on a discussion of either the effect of benzannelation or the effect of conjugation. The first example of an isoannulated aza[18]annulene, namely 14, unambiguously indicates a more effective participation of nitrogen compared with oxygen in sustaining a ring current. Adverse steric interactions in 22 and 23 result in a deviation from planarity of the dihydropyrene periphery leading to a further decrease in diatropiicity in addition to the effect of benzannelation. The anthroannulated system 24 is the first derivative of 1 which apparently shows no appreciable ring current. A comparison of the relative diatropiities of 23 and 26 suggests that the effective aromaticities of isoquinoline and pyridine are very similar to those of naphthalene and benzene respectively.

INTRODUCTION

The change in chemical shift of the "internal" methyl protons in dimethyldihydropyrene 1 (ref. 1) has been shown to be an excellent probe (ref. 2) for studies of the effects on the diatropiicity of 1 resulting from annellation to other aromatic systems. A series of [a]-annulated derivatives of 1 have been reported by Mitchell *et al.* (ref. 2-6); only two [e]-annulated derivatives, namely 2 and 3, were studied by these workers (ref. 7,8). The effect of annellation commonly results in a decrease in diatropiicity of the macrocyclic ring as indicated, for example, in the significant downfield shifts of δCH_3 (Table 1) in 2 and 3 compared with that of 1. This is believed to be a result of bond localization caused by annellation. It is thus interesting to study the effects of benzannelation of higher benzenoids, particularly those with bonds known to exhibit high π -bond order such as the 9,10-bond and 4,5-bond in phenanthrene and pyrene respectively. Such annellation would be expected to result in a much smaller effect on the diatropiicity of the annulene with the π -bond concerned participating more freely in the macrocyclic ring current.



PHENANTHROANNELATION AND PYRENOANNELATION

The syntheses of 4 (ref. 9) and 5 have been successfully achieved in our laboratory. Qualitatively a comparison to the non-aromatic system 6 ($\delta\text{CH}_3 = 0.97$; ref. 10) with methyl protons in a similar environment and the assumption that shielding is proportional to ring current would give an estimate of the relative diatropicity (Table 1) of a benzannelated derivative compared with that of the parent [14]annulene 1. Such a comparison clearly indicates a decreasing bond localization effect going from naphtho-, benzo-, pyreno- to phenanthro-annelation. This seems to be consistent with an increase in π -bond order going from the 2,3-, 1,2-, 4,5- to 9,10-bond of naphthalene, benzene, pyrene and phenanthrene respectively. The above results also serve as simple experimental evidence for the prediction that the effects of benzannelation on the magnetic ring current of an annulene are reduced as the aromatic character of the annelated benzene ring is reduced.

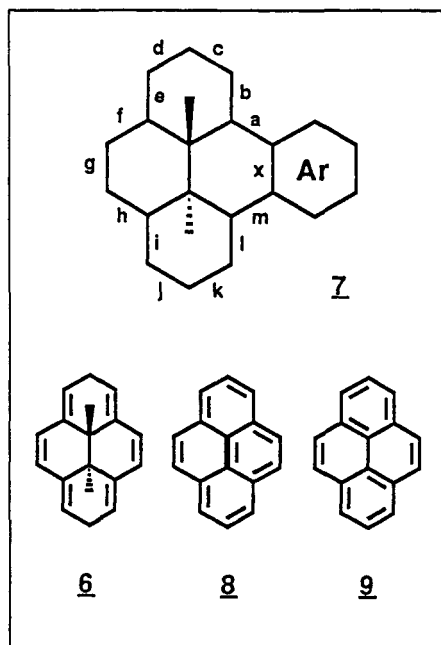
TABLE 1. Comparison of the diatropicities in several dimethyldihydropyrenes.

Compd	δCH_3	$\Delta\delta\text{CH}_3^a$	% ring current	Compd	δCH_3	$\Delta\delta\text{CH}_3^a$	% ring current
<u>1</u> (ref. 1)	-4.25	5.22	100	<u>14</u>	-0.42	1.39	27
<u>2</u> (ref. 7)	-1.85	2.82	54	<u>22</u>	-0.78	1.75	34
<u>3</u> (ref. 8)	-0.74	1.71	33	<u>23</u>	0.72	0.25	5
<u>4</u>	-3.32	4.22	82	<u>24</u>	1.22	(-0.25)	0
<u>5</u>	-2.94	3.91	75	<u>25</u>	0.05	0.92	18
<u>11</u>	-3.48	4.45	85	<u>26</u>	0.69	0.28	5
<u>13</u>	0.63	0.34	7	<u>10</u> (ref. 16)	-3.81, -3.89	4.81, 4.89	92-93

^aThe shielding (in ppm) of the internal methyl protons relative to those in the nonaromatic model 6.

TABLE 2. Calculated bond orders and chemical shifts of methyl protons in several dimethyldihydropyrenes.

Bond (refer to <u>7</u>)	The	π -SCF	Bond	Order
	<u>2</u>	<u>4</u>	<u>5</u>	<u>11</u>
x	0.537	0.415	0.571	0.587
a, m	0.477	0.560	0.567	0.555
b, l	0.748	0.686	0.680	0.691
c, k	0.550	0.608	0.614	0.604
d, j	0.729	0.680	0.674	0.684
e, i	0.553	0.605	0.611	0.601
f, h	0.713	0.667	0.661	0.671
g	0.567	0.618	0.624	0.614
Δr	0.100	0.042	0.036	0.046
calcd $\Delta\delta$	2.77	4.38	4.54	4.27
calcd δCH_3	-1.80	-3.41	-3.57	-3.30
observed δCH_3	-1.85	-3.32	-2.94	-3.48



A simple correlation (ref. 11) of the diatropicity of benzannelated dihydropyrenes in terms of bond order deviations has been employed successfully to predict the chemical shift of the methyl protons in derivatives of 1. From the data obtained for 2, 4 and 5 (Table 2; refer to formula 7), the predicted and observed values of δCH_3 for 2 and 4 agree well ($<\pm 0.1$ ppm). A much larger deviation (>0.6 ppm) of

the observed δCH_3 value from that predicted is however obtained for 5. Recently it was reported (ref. 4) that the change in δCH_3 of 1 on [a]-annulation with various benzenoid systems is proportional to the resonance energy of the original annelating benzenoid less any resonance energy of a residual benzenoid in the Kekulé structure which has the 14π system of 1 delocalized (ΔRE). Our results on the [e]-annulated series are summarized in Table 3 and a plot of $\Delta\delta\text{CH}_3$ vs ΔRE (Fig. 1) clearly indicates that the correlation is linear among 1 - 4 with data of 5 again significantly deviated from expected values using this empirical treatment. Theoretically the aromaticity of pyrene could be considered by either the peripheral model (ref. 12,13) considering a Hückel-type 14π perimeter perturbed by an inner double bond as seen in formula 8 or the partial contributions of the components as indicated by formula 9 (ref. 14,15), the second model being more commonly accepted. Contribution of 8 to the properties of 5 however would result in an effect of annulenoannulation. The parameters used for the empirical treatments mentioned above may not have fully taken into account the 14π peripheral character of pyrene in 5, thus leading to more significant deviations from the expected values in the correlations.

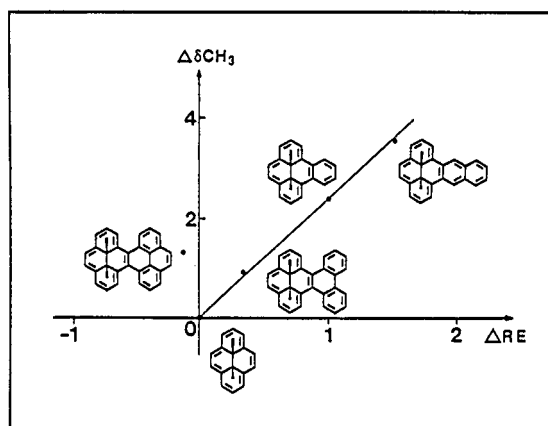
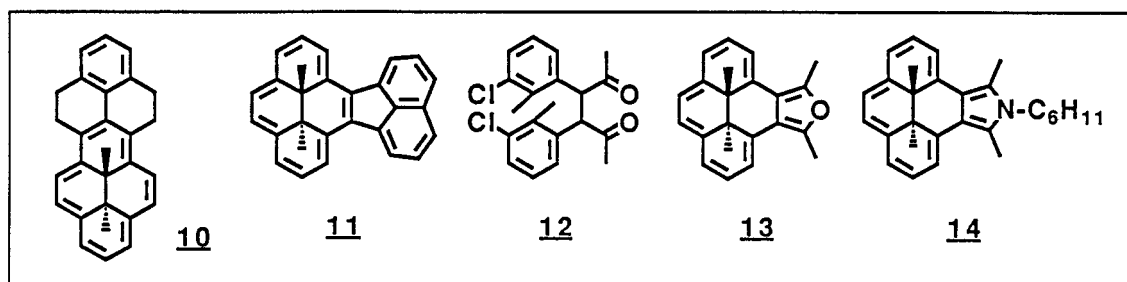


Fig. 1. A plot of $\Delta\delta\text{CH}_3$ vs ΔRE for 1 - 5 based on data presented in Table 1.

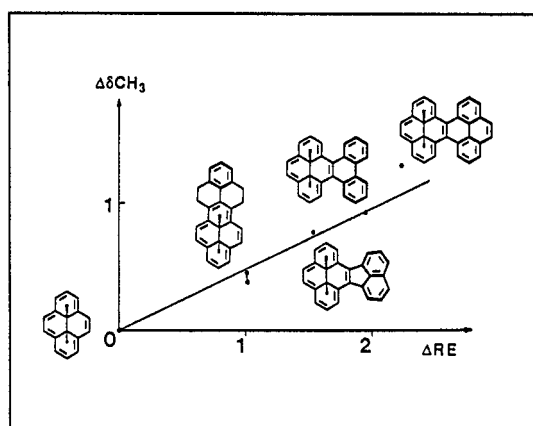


Fig. 2. A plot of $\Delta\delta\text{CH}_3$ vs ΔRE for 1, 4, 5, 10 and 11 based on data presented in Table 2.

EFFECT OF CONJUGATION

An alternative factor to be considered for the reduced diatropicities in 4 and 5 is the effect of conjugation assuming that the 9,10- and 4,5-bonds of the phenanthrene and pyrene moieties respectively participate to a large extent in the ring currents of the macrorings. Conjugation between two rings would, in principle, be expected to reduce the delocalization within any of the rings. The effect of conjugation on the diatropicity of an annulene however has yet to receive as extensive a consideration as the effect of annelation. A decrease of about 10% in the ring current is observed (Table 1) going from 1 to 10 (ref. 16) which represents 1 in conjugation with one benzene ring. An ideal model to study the effect of conjugation on the diatropicity of 1 due to naphthalene is 11 the synthesis of which was accomplished in our laboratory. The observed chemical shift (δ -3.48) of the methyl protons of 11 agrees quite well with that predicted based on the bond order-chemical shift correlation (Table 2).

The comparison in Table 1 shows that 11 sustains about 85% of the ring current of 1, a value similar to that of the diatropicity observed for 4. This serves as clear evidence for a significant reduction in the magnetic ring current of an annulene due to an effect of conjugation. Assuming that the annelated π -bond participates freely in the macrocoring, the change in chemical shift of the internal methyl protons and the corresponding Dewar resonance energy associated with the benzenoid system in conjugation with the parent [14]annulene 1 could be correlated empirically (Table 4). An ideal linear relationship (Fig. 2) is observed among 1, 4, 10 and 11 with the exception of 5 which again results in a significant deviation. Nevertheless the above correlation (Table 4; Fig. 2) based on the effect of conjugation on diatropicity may serve as a complementary method to that based on the effect of benzannelation on diatropicity (ref. 5 and Fig. 1) in the estimate of resonance energies of aromatic systems relative to that of benzene.

TABLE 3. Correlation between chemical shift and resonance energy based on effect of benzannelation in several dimethyldihydropyrenes.

Compd	Dewar RE of the Benzenoids				Δ RE		δCH_3	$\Delta\delta\text{CH}_3^c$
	Original ^a	eV	Residual ^b	eV	eV	ϕH units		
<u>1</u>	absent	0.000	absent	0.000	0.000	0	-4.25	0.00
<u>2</u>	benzene	0.869	absent	0.000	0.869	1	-1.85	2.40
<u>3</u>	naphthalene	1.323	absent	0.000	1.323	1.52	-0.74	3.51
<u>4</u>	phenanthrene	1.933	biphenyl	1.699	0.234	0.27	-3.32	0.93
<u>5</u>	pyrene	1.822	phenanthrene	1.933	-0.111	-0.13	-2.94	1.31
<u>21</u>	benzene	0.869	absent	0.000	0.869	1	-0.78	3.47
<u>22</u>	naphthalene	1.323	absent	0.000	1.323	1.52	0.72	4.97
<u>23</u>	anthracene	1.600	absent	0.000	1.600	1.84	1.22	5.47
<u>24</u>	phenanthrene	1.933	benzene	0.869	1.064	1.22	0.05	4.30

^aThe annelating benzenoid system.

^bThe residual benzenoid system in the Kekulé structure which has the 14π system of 1 delocalized.

^cThe shielding (in ppm) of the internal methyl protons relative to those in dihydropyrene 1.

TABLE 4. Correlation between chemical shift and resonance energy based on effect of conjugation in several dimethyldihydropyrenes.

Compd	Dewar RE of Benzenoids		δCH_3	$\Delta\delta\text{CH}_3$
	Benzenoids	ϕH units (eV)		
<u>1</u>	absent	0 (0.000)	-4.25	0.00
<u>9</u>	benzene	1 (0.869)	-3.81, -3.89	0.36-0.44
<u>4</u>	biphenyl	1.92 (1.699)	-3.32	0.93
<u>6</u>	naphthalene	1.52 (1.323)	-3.48	0.77
<u>5</u>	phenanthrene	2.22 (1.933)	-2.94	1.31

^aThe shielding (in ppm) of the internal methyl protons relative to those in dihydropyrene 1.

The effect of conjugation undoubtedly involves both the resonance and inductive effects which are not readily differentiated experimentally. The resonance effect is however expected to result in bond localization which is reflected in the observed coupling constants of adjacent bonds. Based on the calculated bond orders for 2 and 11 (Table 2) the respective coupling constants (Table 5) for bonds c (k) and d (j) (refer to formula 7) are calculated (ref. 17) and corrected for steric compression (ref. 18).

The estimated and experimental values for 11 (Table 5) agree well and suggest that bond localization in the macroring of 11 is not very significant as indicated by a difference of only about 0.3 Hz between the two coupling constants compared to a corresponding value of >2 Hz for 2. 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.

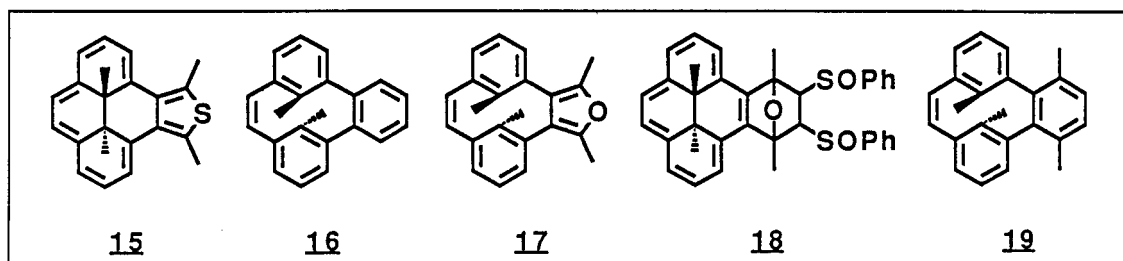
TABLE 5. Calculated bond orders, calculated and experimental coupling constants for dimethyldihydropyrenes 2 and 6.

Bond	Bond Order $P_{\mu,\nu}$		$^3J_{\mu,\nu}$ (calcd), ^a Hz		$^3J_{\mu,\nu}$ (corr.), ^b Hz		$^3J_{\mu,\nu}$ (expt), ^c Hz	
	<u>2</u>	<u>6</u>	<u>2</u>	<u>6</u>	<u>2</u>	<u>6</u>	<u>2</u>	<u>6</u>
c, k	0.550	0.604	6.44	6.96	6.74	>7.26	6.84	7.56
d, j	0.729	0.684	8.16	7.73	8.24	7.81	8.97	7.84

^aCalculated coupling constants (ref. 17) based on calculated bond orders (Table 2).

^bEstimated coupling constants corrected for steric compression (ref. 18).

^cExperimental coupling constants based on ¹H NMR spectra.



EFFECT OF ISOANNELATION

The order of decreasing aromaticity is widely accepted as thiophene > pyrrole > furan among these heteroaromatic systems. Based on theoretical calculations of topological resonance energy, it has however been reported (ref. 19) that the aromatic character follows the order of isobenzopyrrole > isobenzothiophene > isobenzofuran. With the success in using 1 as a diatropicity probe, it would be interesting to study the relative diatropcities in the related series of isoannelated derivatives of 1. Using the diketone 12 (ref. 20) as a common precursor, isoannulenofuran 13 and isoannulenopyrrole 14 have been synthesized. All attempts to prepare the isoannulenothiophene 15 however failed.

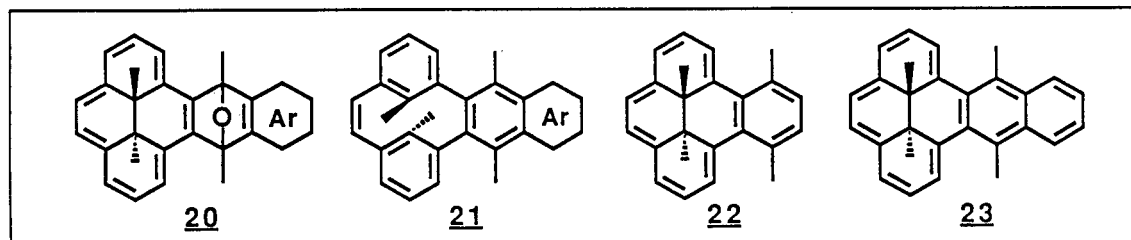
The isoannulenofuran 13 sustains only a weak ring current, relatively about 7% of that observed for 1 (Table 1). This is not unexpected as related examples in other annulene systems (ref. 21,22) exhibit similar results. The nitrogen derivative 14, perhaps the first example of an isoannelated aza[18]annulene, however undoubtedly shows a significantly higher diatropicity (ca. 20%; Table 1) than that of 13. This clearly provides experimental evidence for a significantly more effective participation of nitrogen than oxygen in sustaining a ring current in the macroring of an isoannelated annulene.

In the synthesis of 2 (ref. 7), the cyclophanediene 16 isomerized readily to 2. The facile partial disruption of three benzene rings in 16 to form the macrocyclic system 2 points to the exceptional aromatic character of the dihydropyrene system. The isoannulenofuran 13 is shown to exhibit a much lower diatropicity compared to that of 2. The cyclophanene 17 obtained as a precursor in the synthetic route could however still be thermally converted, although exceptionally slow, to afford 13. Rate constants of 2.2×10^{-5} , 7.9×10^{-5} and $3.1 \times 10^{-4} \text{ min}^{-1}$ were obtained at 39, 49 and 59°C respectively which give an estimate of ca. 112 kJ mol⁻¹ as the energy of activation for 17 → 13 compared with a value of 105 kJ mol⁻¹ for 16 → 2 (ref. 7). The above results are clearly consistent with a less favorable conversion in 17 → 13 due to a simultaneous decrease in diatropicity and an increase in steric strains between the external methyl groups and H_{3,6} on the macroring in 13.

EFFECT OF BENZANNELATION

The synthetic routes to 4, 5, 11, 13 and 14 mentioned earlier involved separate and long sequences of reactions. The novel isoannuleno-furan 13 is however expected to behave chemically like isobenzofuran (ref. 23) which is a reactive diene undergoing facile Diels-Alder reactions with dienophiles. Reaction of 13 and cis-1,2-bis(phenylsulfonyl)ethylene in fact readily gave the adduct 18 which after deoxygenation/reduction afforded the cyclophanediene 19. Similar treatment of 13 with benzynes prepared from 1-bromobenzene, 2,3-dibromonaphthalene, 1-bromonaphthalene, 9-bromophenanthrene and 3-bromopyridine led to the respective Diels-Alder adducts 20. Photochemical deoxygenation in the presence of $\text{Fe}_2(\text{CO})_9$ afforded the series of cyclophanedienes 21. Thermal or photochemical (210 nm) isomerization of 19 and 21 led to partial conversion of these cyclophanedienes to the dimethyldihydropyrenes 22 - 26 respectively. The above behavior is in great contrast to the facile isomerization of 16 to 2. The adverse steric interactions between the external methyl groups and H3,6 on the dihydropyrene moiety in the near-planar structures of 22 - 26 should account for the less favorable valence isomerization of the cyclophanedienes to the respective dihydropyrene systems.

A comparison of the relative diatropcities (Table 1) surprisingly indicates a large decrease of 20-30% of ring current going from 2 to 22 and 3 to 23. The exceptional diatropcity of 1 is to a large extent attributed to its molecular rigidity resulting in a planar periphery of a 14π system. Deviation from this planarity however would lead to a significant decrease in diatropcity as indicated by the chemical shift (δ -2.06) of the saucer-shaped cis-dihydropyrene 27 (ref. 24). The steric compressions between the external methyl groups and H3,6 on the dihydropyrene moieties in 22 and 23 must be very unfavorable resulting in severe deviation from planarity of the dihydropyrene peripheries and thus lead to significantly weaker ring currents than those observed for 2 and 3.



Among the linear acene-annulated derivatives 22 - 24 (Table 1), a gradual decrease in diatropcity is observed in that order inversely proportional to an increase in the loss of resonance energy (Table 3) of the benzenoid system exhibiting total bond localization when the 14π system in dihydropyrene is fully delocalized. The combined effects of the above factor and the unfavorable steric strains mentioned earlier in fact result in the first example of a derivative of 1, namely the anthroannulated 24 ($\delta\text{CH}_3 = 1.22$), which no longer sustains an appreciable ring current. In the related angular-annulated derivative 25, more adverse steric compression is experienced but there is less severe bond localization (loss of resonance energy; Table 3) in the benzenoid system if full delocalization occurs in the dihydropyrene. The resulting net effect is, going from 24 to 25, an increase of about 18% of the ring current (Table 1).

Among the dihydropyrenes 22 - 25, a correlation (Table 3) between the chemical shift of the internal methyl protons and the resonance energy of the benzenoid system indicates a non-linear relationship although a smooth graph could be empirically obtained (Fig. 3). This is in contrast to results obtained for 1 - 4 (Fig. 1). Evidently steric effects resulting from the presence of the external methyl groups in 22 - 25, which account partly for the decrease in diatropcities of the macrorings, vary among these derivatives of 1 particularly in 25.

Delocalization of the 14π systems in 23 and 26, both of which are shown to sustain about 5% of the ring current of 1, will lead to bond localization (loss of resonance energy) in the naphthalene and isoquinoline moieties respectively. Steric effects in 23 and 26 are however expected to be almost identical. Based on the successful correlation (ref. 5 and Fig. 1) of diatropcity (of dihydropyrene) and resonance energy (of annulated aromatic system), our results clearly indicate that resonance energies of naphthalene and isoquinoline are very similar. As the central dimethyl substituted ring is a common "buffer" in 23 and 26, the above argument also indirectly suggests that delocalization in the respective dihydropyrenes is accompanied by loss of almost identical resonance energies in the terminal benzene and pyridine rings. The effective aromatic character of isoquinoline and pyridine are thus shown to be very similar to that of naphthalene and benzene respectively.

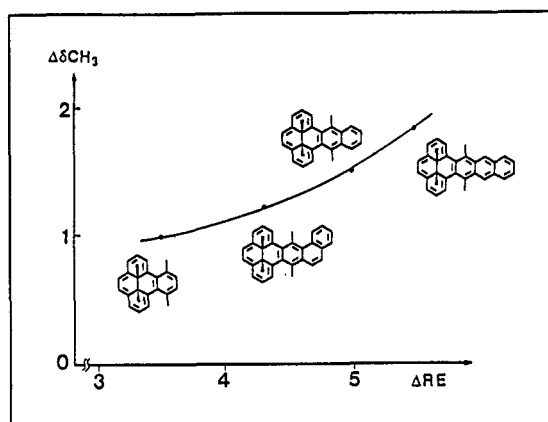
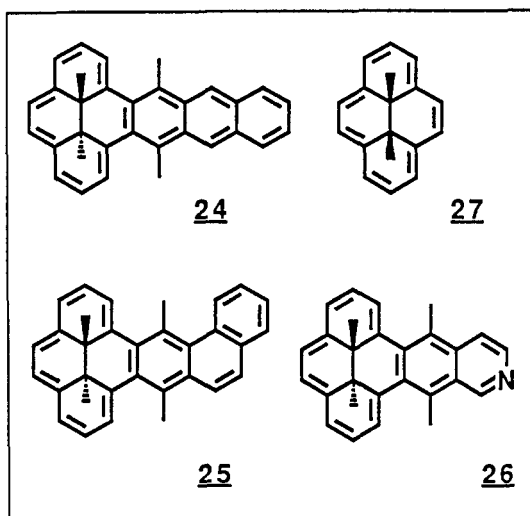


Fig. 3. A plot of $\Delta\delta\text{CH}_3$ vs ΔRE for 22 - 25 based on data presented in Table 1.



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