

Research Article

Aromaticities of Five Membered Heterocycles through Dimethyldihydropyrenes Probe by Magnetic and Geometric Criteria

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Aromaticities of five membered heterocycles, containing up to three heteroatoms, are quantified through the dimethyldihydropyrene (DHP) probe. Bond fixation caused by the fusion of heterocycles to the dimethyldihydropyrene nucleus (DHPN) was measured by changes in the ¹H NMR chemical shifts (magnetic) and bond lengths alterations (structural criterion). Chemical shifts of dihydropyrenes were calculated at GIAO HF/6-31G(d)//B3LYP/6-31+G(d). For ¹H NMR chemical shift analysis, two nonaromatic reference models are studied. Among the studied heterocycles, pyrazole and triazole are about 80–85% aromatic relative to benzene, through both magnetic and geometric criteria. Thiazole and oxazoles are found least aromatic where quantitative estimates of aromaticities are about 34–42%, relative to benzene. These quantitative estimates of aromaticities of five membered heterocycles are also comparable to those from aromatic stabilization energies. The quantification of aromaticity through energetic, magnetic, and structural criteria can deliver the similar inferences provided that suitable reference systems are chosen.

1. Introduction

Aromaticity is a fundamental and commonly used concept in chemistry. Aromaticity is universally understood by convention because it is not a directly measurable quantity. Qualitatively, a compound can be easily categorized as aromatic, nonaromatic, or antiaromatic. However, quantifying the extent of aromaticity has become highly controversial. A number of methods have appeared in the literature for the quantification of aromaticity since the concept was first introduced by Kekulé [1]. However, no single method could get the universal acceptance. Our perception about the aromaticity of a compound may vary considerably depending on the method chosen for quantitative analysis [2]. Any method chosen for quantification of aromaticity generally relies on a single criterion [3], whereas the aromaticity is multidimensional in nature (composed of energetic, magnetic, and structural components).

The “aromaticity” imparts some “extra stability” to aromatic compounds compared to the nonaromatic reference model compound. Therefore, the aromatic stabilization energy (which is based on homodesmotic reaction [4, 5]) is often considered the principle criterion for the reactivity of aromatic compounds [6, 7]. A number of other stabilization energies reported in the literature to account for this “extra stability” are Hess-Schaad resonance energy [8–13], Huckel resonance energy [14–16], Schleyer isomerization stabilization energies [17], Dewar resonance energy [18–21], and topological resonance energies [22–24]. Among structural criteria, the Harmonic Oscillator Model of Aromaticity (HOMA) [25–27] is a common method for the estimation of aromaticities. A few other structure based criteria are also reported in the literature [28–35].

A third category of methods for the quantification of aromaticity is based on magnetic properties. Magnetic criterion of aromaticity quantification includes magnetic susceptibility

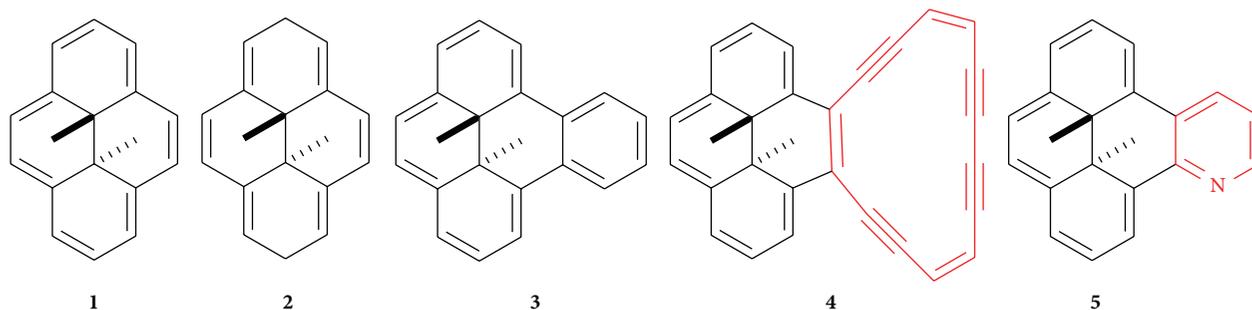


FIGURE 1: A few aromatic and nonaromatic compounds.

exaltation [36–47], anisotropy of magnetic susceptibility, NMR (chemical shifts and coupling constant analysis) [42, 48–54], and nucleus independent chemical shifts (NICS) [55]. In the chemical shift analysis, the atom of interest above the aromatic nucleus is either bonded covalently or placed artificially (through noncovalent interactions). The latter includes ^3He and ^9Li nuclei placed above the aromatic nucleus [42, 48–54], whereas the former involves ^1H chemical shift [56, 57] analysis of probe protons, usually in the center of the nucleus under consideration. A probe molecule for ^1H chemical shift analysis must meet the following two requirements: (i) ring current in the probe molecule is only affected by the delocalization of electrons and (ii) through space anisotropic effect should not affect the chemical shifts of the probe protons. 15,16-Dimethyldihydropyrene **1** (Figure 1) is an excellent probe molecule in this regard. The internal methyl protons in the dihydropyrene are highly shielded due to diatropic ring current (by 5.2 ppm), compared to the nonconjugated model **2**, and [a] or [e] fusion of an arene to the dihydropyrene nucleus results in the reduction of ring current of the dihydropyrene nucleus. This reduction in the ring current is proportional to the aromaticity of the arene fused. A highly aromatic arene will cause much larger reduction in the ring current, and vice versa. For example, fusion of benzene ring to the DHPN (**3**) causes 58% bond fixation whereas a less aromatic octadehydro[14]annulene (in **4**) causes 30% bond fixation [57]. Fusion of an arene to DHP not only causes change in the ring current of the DHPN (vide supra) but also affects the geometric parameters. Therefore, the results from magnetic (NMR) criterion can easily be correlated with the geometric parameters (bond fixation).

The dimethyldihydropyrene probe has successfully been applied to the quantification of aromaticities of a number of arenes including polycyclic aromatic hydrocarbons [56] and heteroarenes. Recently, we have successfully applied the chemical shift analysis of DHPN to quantify the aromaticities of six membered nitrogen containing heterocycles (azines) [58]. For example, the azine fused DHP **5** is used for the quantification of aromaticity of pyridine. In this work, we extend our recently developed approach to the quantification of aromaticities of five membered heterocycles. Two different nonaromatic reference models are tested for the quantification of aromaticities, and the results are compared with bond fixation values obtained from structural criterion. Moreover,

the results are compared to the HOMA and ASE for these heterocycles.

2. Results and Discussion

2.1. Choice of the Reference System. In our recent study on the quantification of aromaticity of azines [58], choice of a suitable reference model is shown to play very crucial role due to anisotropic effect [60], arising from heteroatoms. We had compared different nonaromatic models (shown below in Figure 3) and the best nonaromatic model for reliable estimate of quantification of aromaticity is the one with partial unsaturation of the azine (pyridine). Partially saturated nonaromatic reference model (**7**) is very similar to the azine under study except that it lacks the aromaticity of azine. Compound **8** was used as a nonconjugated reference model for the quantification of aromaticity; however, compound **2** can also be used with negligible effects on the results (Figure 2).

The importance of selecting a suitable reference model was also reported during the quantification of aromaticity of cyclopentadienone **9** [61]. The cyclopentadiene fused DHP (**10**) was more reliable reference model than the cyclopentanone DHP **11**.

2.2. Parent DHP as a Reference Model. Over the past three decades, dihydropyrene has emerged as an excellent probe for the quantification of aromaticity [56, 61]. Generally, change in the ring current of the DHPN by fusion with an arene is described by change in the chemical shift of the internal protons with reference to the parent DHP **1** (DHP **1** is the reference model). For example, change in ring current of the dihydropyrene nucleus (DHPN) on fusion with heterocycle (pyrrole) is follows:

$$\begin{aligned}
 &([\delta \text{ methyl protons of heterocycle fused DHP}] \\
 &- [\delta \text{ methyl protons of DHP}]) \\
 &\cdot ([\delta \text{ methyl protons of nonconjugated model}] \\
 &- [\delta \text{ methyl protons of DHP}])^{-1}
 \end{aligned} \quad (1)$$

$$\frac{[\delta 12] - [\delta 1]}{[\delta 2] - [\delta 1]}$$

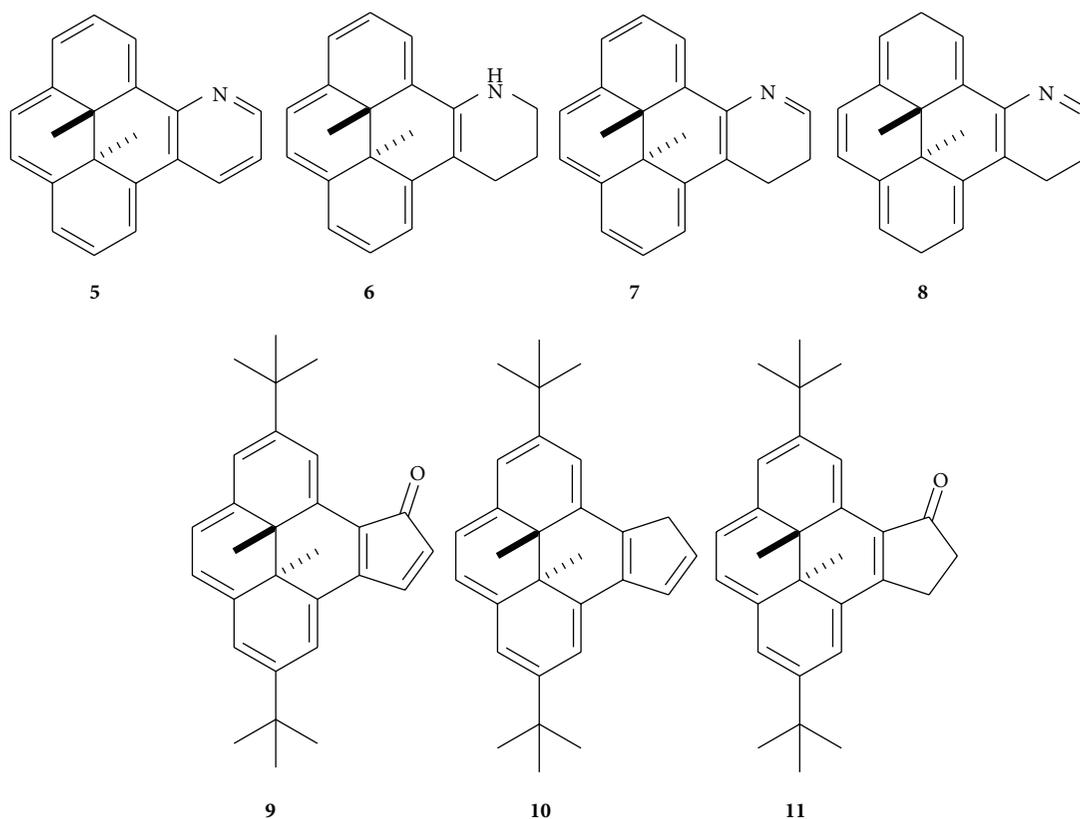


FIGURE 2: Pyridine and cyclopentadienone fused dihydroxyrenes and their nonaromatic and nonconjugated reference models, required for quantification of aromaticity through (2) and (5).

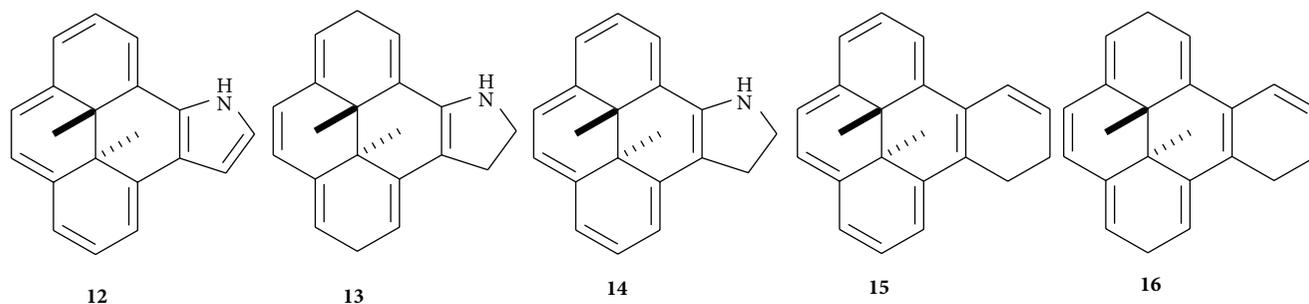


FIGURE 3: Nonaromatic and nonconjugated reference models required for quantification of aromaticity of pyrrole fused dihydroxyrene 12 through (2) and (5).

The equation above is actually a measure of bond fixation in the dimethyldihydroxyrene nucleus by fusion with an aromatic moiety. Based on the formula above, aromaticity of arene (pyrrole) relative to benzene can be estimated by

$$\begin{aligned}
 &([\delta \text{ methyl protons of heterocycle fused DHP}] \\
 &- [\delta \text{ methyl protons of DHP}]) \\
 &\cdot ([\delta \text{ methyl protons of benzo - DHP}]
 \end{aligned}$$

$$\begin{aligned}
 &- [\delta \text{ methyl protons of DHP}])^{-1} \\
 &\frac{[\delta 12] - [\delta 1]}{[\delta 3] - [\delta 1]}.
 \end{aligned}$$

(2)

This approach has been successful for the quantification of aromaticity of carbocycles such as benzene, naphthalene, anthracene [56], cyclopentadienone [61], and cyclooctatetraene [62] (vide supra). Heterocycles present additional

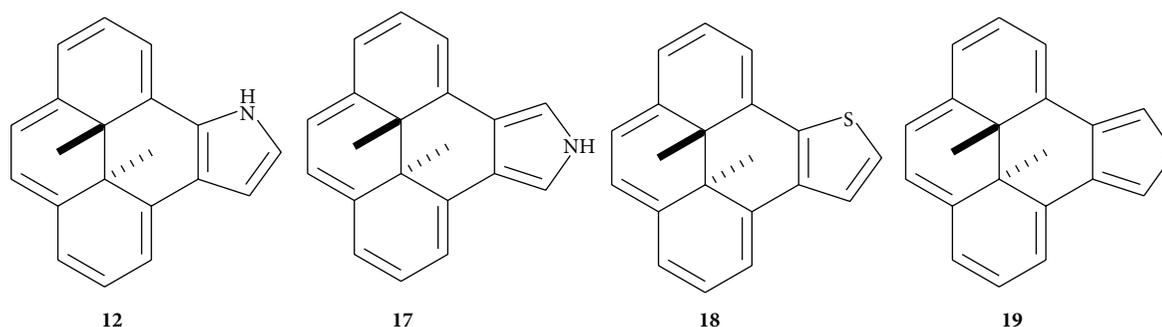


FIGURE 4: Pyrrole and thiophene fused dihydropyrenes.

anisotropy effects, as well as potential conjugation effects, therefore, have not been extensively studied for the quantification of aromaticity through DHP probe. For such instances, the parent DHP **1** cannot serve as a better reference model compound; therefore, the reference model and the equations to calculate the aromaticity are modified.

The decrease in the delocalization of pyrrole fused DHP **12** through reference model **14** can be calculated using

$$\begin{aligned} &([\delta \text{ methyl protons of heterocyclic fused DHP}] \\ &- [\delta \text{ methyl protons of sat. N hetero DHP}]) \\ &\cdot ([\delta \text{ methyl protons of nonaromatic model}] \\ &- [\delta \text{ methyl protons of sat. N hetero DHP}])^{-1} \end{aligned} \quad (3)$$

$$\frac{[\delta 12] - [\delta 14]}{[\delta 13] - [\delta 14]}$$

Aromaticity of pyrrole relative to benzene can be calculated by

$$\frac{([\delta 12] - [\delta 14]) / ([\delta 13] - [\delta 14])}{([\delta 3] - [\delta 15]) / ([\delta 16] - [\delta 15])}, \quad (4)$$

$$\frac{([\delta 12] - [\delta 14]) / ([\delta 2] - [\delta 14])}{([\delta 3] - [\delta 15]) / ([\delta 2] - [\delta 15])}. \quad (5)$$

The chemical shifts of the methyl protons in nonconjugated models (**5** and **16**) are not very different than the chemical shifts of similar protons in **2** [58], and it is expected that the chemical shifts of the internal protons of **13** will not be significantly different as well. Indeed, the internal methyl protons in **13** appear at δ 1.14 compared to δ 1.12 for **2**. With these approximations, (4) can be modified to (5). In this study, (2) and (5) are used for the quantification of aromaticity of five membered heterocycles.

2.3. Computational Methods. All calculations were performed with Gaussian 09 suite of programs [63]. Geometries of the structures were optimized without any symmetry constraints at hybrid B3LYP method using 6-31+G* basis set [64]. The B3LYP method consists of three parameter hybrid functional of Becke [65] in conjunction with the correlation functional of Lee et al. [66]. The B3LYP method provides

a nice balance between cost and accuracy, and it is known to perform very well for the prediction of geometries of a number of dihydropyrenes [67]. Each optimized structure was confirmed by frequency analysis at the same level (B3LYP/6-31+G(d)) as a true minimum (no imaginary frequency). ^1H NMR chemical shifts were calculated by Hartree-Fock (HF) gauge independent atomic orbital (GIAO) method at 6-31G* basis set on the B3LYP/6-31+G(d) optimized geometries (GIAO-HF/6-31G(d)//B3LYP/6-31+G*). GIAO-HF/6-31G* was chosen because the predicted aromaticities of a number of dihydropyrenes through this method correlate very well with the experiment [68]. The three hydrogens of the methyl group appeared different due to their fixed positions in magnetically different environment. The reported values are averaged chemical shifts.

2.3.1. Five Membered Heteroatomic Rings. Pyrrole can be fused to DHP in two different ways to deliver dihydropyrenes **12** and **17** (Figure 4). We had shown previously that isomeric fusion of heteroarenes (azines) to the DHPN can deliver somewhat different estimate of aromaticity even though when there is complete delocalization in each fragment. However, if the delocalization in one fragment is blocked by the other fragment, then the estimate of aromaticity is not reliable. Fusion of pyrrole to the DHP fragment in **12** allows equal chance of delocalization of π electron in each fragment; however, the situation is different in **17**. Fusion of pyrrole to DHPN in **17** causes almost complete loss of aromaticity of DHPN nucleus (vide infra) because the π electronic cloud is not available for delocalization on DHPN. Therefore, compound **12** is ideal for estimation of aromaticity of pyrrole.

The internal methyl protons in **12** appear at δ_{av} -3.31, for both methyl groups, which indicates that the anisotropic effect arising from nitrogen is either negligible or very similar for both methyl groups. The internal methyl protons in **2** are calculated at δ 1.12. Therefore, the internal protons in **12** are shielded by only 4.43 ppm, compared to 7.40 ppm for the parent DHP **1** (δ_{theor} -6.29). The DHPN in pyrrole DHP **12** retains about 59.8% of its aromaticity which means that the pyrrole ring causes 40.2% bond fixation in the DHPN. This bond fixation is relatively small compared to 58.9% bond fixation caused by the benzene ring (see Table 1 for details). The relative aromaticity of pyrrole to benzene, calculated through (2), is 68.2%. It is important to mention that the

TABLE 1: Comparison of ^1H NMR chemical shifts (calculated), % bond fixation of dihydropyrene nucleus, and % aromaticities of five membered heterocycles with benzene, calculated through (2).

Entry	Heterocycles	DHP	δ	% bond fixation	% aromaticity (relative to benzene)
1		1	-6.29		
2	Benzene	3	-1.91	59.1	100
3	Pyrrrole	12	-3.31	40.3	68.1
4	Thiophene	18	-4.16	28.8	48.9
5	Oxazole	20	-4.8	20.2	34.1
6	Isoxazole	21	-3.51	39.6	63.5
7	Thiazole	22	-4.59	23.0	38.9
8	Isothiazole	23	-3.99	33.8	59.1
9	Pyrazole	24	-2.52	50.9	86.1
10	Imidazole	25	-3.81	33.5	56.9
11	Oxadiazole	26	-3.59	36.8	62.2
12	Triazole	27	-2.91	48.4	81.8

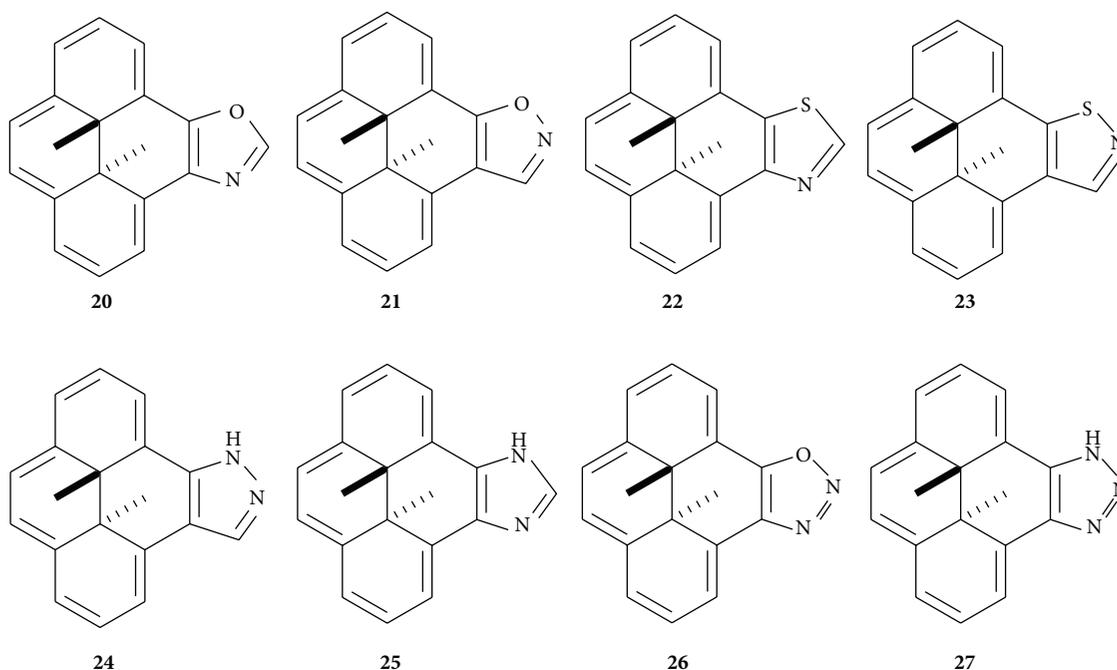


FIGURE 5: Five membered heterocycles fused dihydropyrenes **20**–**27**.

experimental chemical shifts are available for the benzo DHP **3**; however, to maintain consistency, theoretical values are used for bond fixation calculations in this study. The higher aromaticity of benzene can be rationalized by Clar rule [69].

The internal methyl protons in the isomeric **17** appear at δ -0.31 which indicates that the pyrrole ring in this fusion has caused almost complete loss of aromaticity of DHPN (as expected). A similar behavior is also observed in the thiophene fused dihydropyrenes **18** and **19**. The internal protons in **19** appear at δ 0.24 compared to δ -4.16 for **18**. The bond fixation caused by a thiophene ring in **18** is 28.9% which indicates that the thiophene ring is only 48.9% aromatic relative to benzene.

Among heterocycles bearing two heteroatoms, oxazole (**20**), isoxazole (**21**), thiazole (**22**), isothiazole (**23**), pyrazole (**24**), and imidazole (**25**) are studied for aromaticity quantification (Figure 5). The isoxazole causes more bond fixation in the DHPN than oxazole (Table 1, entries 5 and 6). The aromaticities of oxazole and isoxazole, relative to benzene, are 34 and 63.5%, respectively. A similar trend of aromaticities is observed in thiazole and isothiazole fused dihydropyrenes (**22** and **23**). The percent aromaticities of thiazole and isothiazole relative to benzene are 38.9 and 58.9%, respectively (Table 1, Entries 7 and 8). The aromaticity of thiazole is relatively high compared to oxazole whereas the aromaticity of isothiazole is less than isoxazole.

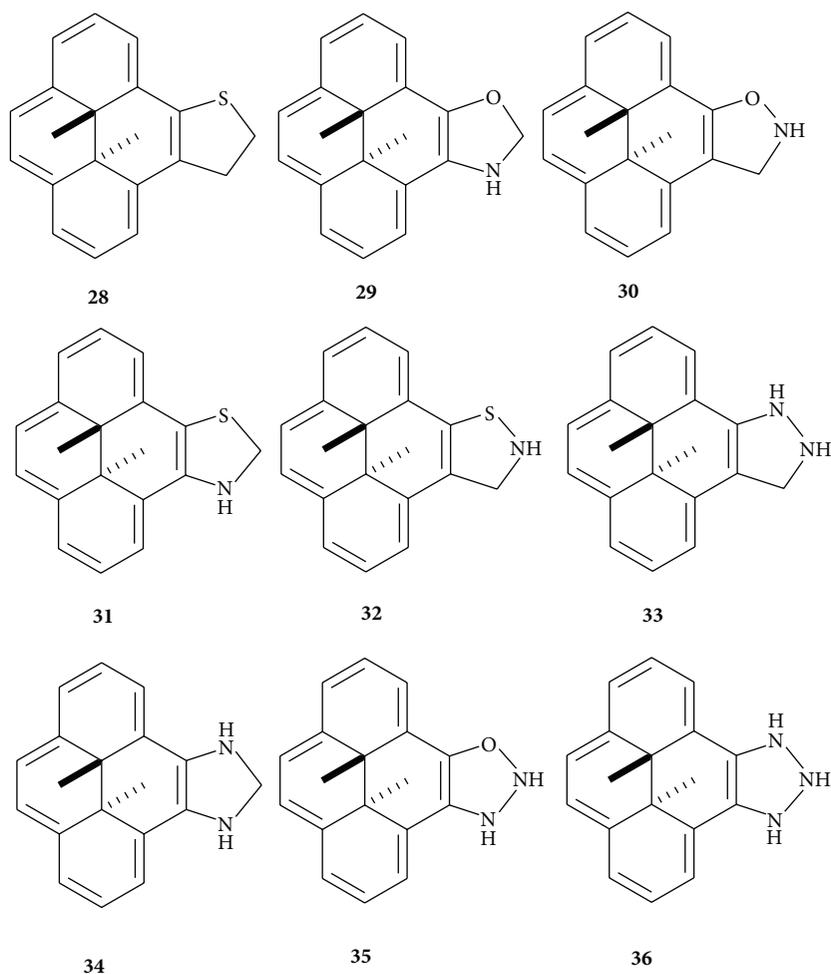


FIGURE 6: Nonaromatic model for heterocyclic arene fused dihydropyrene, for the quantification of aromaticity through (5).

The aromaticity of pyrazole **24** (86% relative to benzene) is higher than the isomeric imidazole **25**.

Among heterocycles bearing three heteroatoms, oxadiazole (**26**) and triazole (**27**) are studied. The latter causes more reduction in the ring current (48%) as expressed by downfield signal at $\delta -2.91$. The aromaticity of triazaole is 82% relative to benzene, and this is very comparable to pyrazole. The internal methyl protons in oxadiazole are simulated to appear at $\delta -3.59$ which indicates 62% aromaticity relative to benzene.

2.4. Nonaromatic Model with Heteroatom. Next, the relative aromaticities of these heterocycles are estimated using saturated reference model (**14**, **28–36**). The reference models are very similar to fused dihydropyrenes **12**, **17–27** except that the heterocycles lack aromaticities. For example, the reference models for pyrrole fused DHP **12** are pyrrolidine fused DHP **14**. Similarly, saturated reference model for **18** is **28**. Suitable saturated reference systems for other heterocycles fused DHP are shown in Figure 6, whereas the aromaticity estimates through these reference models using (5) are shown in Table 2.

The data in Table 2 reveal that the estimates of aromaticities using the nonaromatic reference models **14**,

28–38 (through (5), shown in Table 2) are very similar to those from (2) (Table 1, when parent DHP is used as the reference). For example, the aromaticity of pyrrole relative to benzene is 68% (through (2)) compared to 64% when (5) is used for the aromaticity quantification. For thiophene, the difference in aromaticities measured through two different methods is even smaller; 48.9% (2) compared to 49.5% (5). The difference in percent aromaticities relative to benzene is within 5% (for both methods) for most of the heterocycles except that imidazole fused DHP **25**, where 56.9% and 49.6% aromaticities are estimated relative to benzene through (2) and (5), respectively.

Although both methods deliver comparable estimates of aromaticities except imidazole and oxazole which reflects that the anisotropic effect of the heteroatom is very negligible on the chemical shifts of the internal methyl protons of DHPN. Moreover, it is also supported by the fact that both internal methyl protons in dihydropyrenes **12**, **17–25** show similar chemical shifts (within 0.02 ppm units). However, to further confirm which of the above-mentioned methods is more accurate regarding the estimates of aromaticities, geometric parameters have also been studied.

TABLE 2: ^1H NMR chemical shifts (calculated) of dihydropyrenes and nonaromatic reference models, % aromaticities of five membered heterocycles, calculated through (5).

Entry	Heterocycles	DHP	δ	Nonaromatic reference	δ	% bond fixation	% aromaticity
1		1	-6.29				
2	Benzene	3	-1.91		-5.45	53.9	100
3	Pyrrole	12	-3.31	14	-5.62	34.3	63.6
4	Thiophene	18	-4.16	28	-6.08	26.9	49.5
5	Oxazole	20	-4.8	29	-5.88	15.4	28.6
6	Isoxazole	21	-3.51	30	-5.65	31.6	58.9
7	Thiazole	22	-4.59	31	-5.98	19.6	36.3
8	Isothiazole	23	-3.99	32	-6.05	31.5	58.5
9	Pyrazole	24	-2.52	33	-5.89	48.1	89.2
10	Imidazole	25	-3.81	34	-5.51	25.6	49.6
11	Oxadiazole	26	-3.59	35	-5.63	30.5	56.6
12	Triazole	27	-2.91	36	-5.83	44.9	83.3

TABLE 3: Bond fixation in DHPN and % aromaticity of heteroarenes calculated through geometric parameters.

	3	12	18	20	21	22	23	24	25	26	27
C1-C2	1.396	1.384	1.388	1.391	1.385	1.39	1.386	1.381	1.389	1.386	1.382
C2-C3	1.419	1.412	1.408	1.406	1.412	1.409	1.41	1.416	1.411	1.416	1.416
C3-C4	1.382	1.388	1.391	1.394	1.389	1.393	1.39	1.385	1.39	1.39	1.386
C4-C5	1.419	1.415	1.41	1.409	1.413	1.409	1.412	1.4196	1.413	1.413	1.419
C5-C6	1.382	1.388	1.391	1.394	1.389	1.393	1.39	1.385	1.39	1.39	1.386
C6-C7	1.419	1.412	1.409	1.406	1.411	1.406	1.409	1.416	1.41	1.41	1.415
C7-C8	1.399	1.385	1.389	1.3923	1.388	1.391	1.388	1.382	1.389	1.3866	1.382
C8-C9	1.4296	1.42	1.414	1.413	1.419	1.413	1.419	1.425	1.419	1.418	1.4245
C9-C10	1.393	1.398	1.382	1.383	1.398	1.384	1.38	1.393	1.399	1.398	1.393
C10-C11	1.454	1.419	1.415	1.400	1.41	1.412	1.419	1.424	1.413	1.41	1.421
C11-C12	1.435	1.419	1.419	1.4	1.3986	1.416	1.413	1.414	1.412	1.4	1.4065
C12-C13	1.454	1.426	1.429	1.4124	1.423	1.42	1.428	1.429	1.419	1.419	1.425
C13-C14	1.393	1.396	1.38	1.38	1.396	1.381	1.399	1.393	1.399	1.395	1.391
C14-C1	1.428	1.421	1.419	1.415	1.421	1.415	1.419	1.425	1.419	1.421	1.425
A_{av} (bold italic)	1.431	1.4196	1.414	1.4088	1.4156	1.4119	1.416	1.4218	1.4149	1.4151	1.4205
B_{av} (italic)	1.385	1.3883	1.391	1.3906	1.3862	1.3926	1.3894	1.3848	1.3889	1.3865	1.3838
Bond fixation ($A_{av} - B_{av}$)	0.0454	0.0293	0.0229	0.0182	0.0294	0.0191	0.0266	0.039	0.0259	0.0286	0.0369
% arom.	100.0	64.5	50.3	40.1	64.6	42.2	58.5	81.6	59.1	62.9	80.9

The bond fixation in the DHPN also alters the bond lengths of the DHPN. Degree of change in bond lengths of the DHPN should also reflect the aromaticity of the arene fused. The results of the geometric analysis are given in Table 3 (for numbering scheme, see Figure 7). Analyses of the geometric data reveal that the aromaticity of imidazole relative to benzene is 59% which is very similar to the aromaticity values of 56.9% through (2) (magnetic criteria). Similarly, aromaticity value of oxadiazole through geometric criteria is 62.9% relative to benzene, which is again consistent with the value obtained through (2) (magnetic criteria). In general the results from the geometric criteria are very comparable to the results from (2) (when parent DHP 1 is the reference model).

The results here are contrary to our recent study where we have shown that these saturated reference models containing heteroatoms deliver better estimates of aromaticities. It may be possible that the anisotropic effect may be present in the saturated reference model which leads to unreliable estimates of aromaticities for these heterocycles.

Since both geometric and magnetic (NMR) based methods, in this study, deliver similar inferences about the aromaticities of five membered heterocycles; therefore, we are not only confident about the reliability of the results here but also illustrate that different criteria of aromaticity can deliver the same information if suitable model system is chosen. We also compared the results obtained here

TABLE 4: Comparison of our results (Geom. and NMR) with NICS, ASE's, and NMR shielding values [59] for five membered heterocyclic rings.

Molecule	$\Delta\sigma_{2.5}$ ppm	ASE's	NICS	HOMA	Geom.	NMR
Pyrrole	2.04	20.59	-10.60	0.493	64.5	68.1
Thiophene	2.39	18.59	-10.99	0.999	50.3	48.9
Oxazole	2.15	12.39	-9.45	0.08	40.1	34.1
Isoxazole	1.99	19.29	-10.58	0.261	64.6	63.5
Thiazole	2.54	19.43	-11.39	0.929	42.2	38.9
Isothiazole	2.63	20.18	-11.66	0.994	58.5	59.1
Pyrazole	2.29	23.9	-11.93	0.821	81.6	86.1
Imidazole	2.29	18.98	-10.83	0.811	59.1	56.9
1,2,3-Triazole	2.92	26.66	-13.61	0.819	80.9	81.8

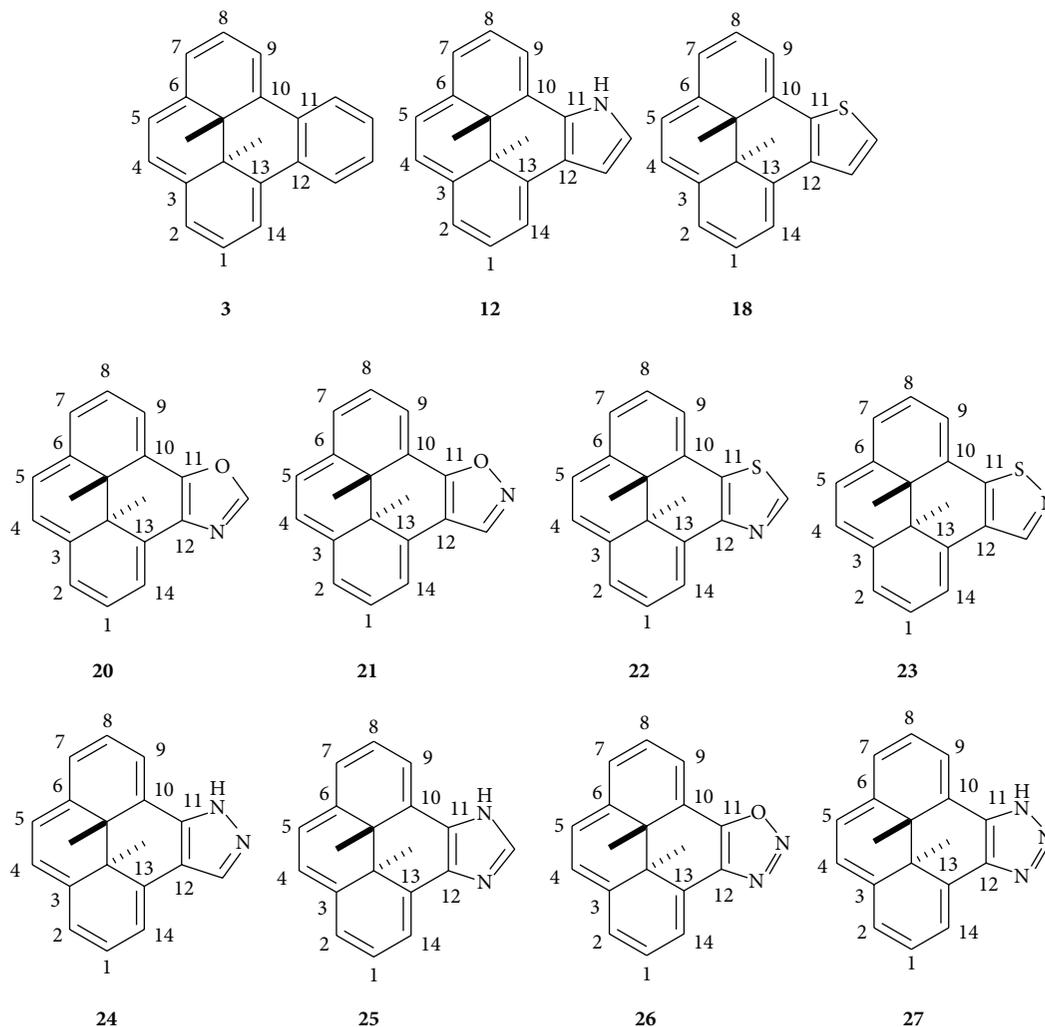


FIGURE 7: Numbering scheme of dihydropyrene skeleton for benzene and heterocycles fused dihydropyrenes.

with the literature aromaticity values for these heterocycles through other methods [70] (Table 4). The comparison of the results clearly illustrates that the results here are very comparable to the aromatic stabilization energy values. For example, ASE of pyrrole is higher than thiophene (20.59 versus 18.59) which indicates that the pyrrole ring is more

aromatic than the thiophene. This is consistent with our calculations that higher bond fixation is observed caused by pyrrole than thiophene. Moreover, oxazole (Table 4 Entry 3) has even lower ASE which is consistent with our results here that the bond fixation caused by oxazole is lower than both thiophene and pyrrole. Among these heterocycles,

the highest ASE is for 1,2,3 triazine (26.66) followed by pyrazole (23.9). It is interesting to note that triazole and pyrazole are the heterocycles which are shown to have the highest bond fixation in DHPN.

We have also compared our results to the HOMA values [71]. Trends in estimate of relative aromaticities are very similar in a series of heterocycles. For example, both HOMA and NMR deliver the same trends in aromaticities of azoles: aromaticity of pyrazole > triazole > imidazole. Some differences do exist when two different series of heterocycles are studied (thiophene and pyrrole). With this comparison, we have shown that geometric, magnetic (this work), and energetic (literature) criteria of aromaticity can deliver the same trend in aromaticities of arenes provided that a suitable system is chosen. This further validates the potential of DHPN in quantifying the aromaticity of heteroarenes.

3. Conclusions

Aromaticities of five membered heterocycles containing up to three heteroatoms are quantified through the dimethyldihydropyrene (DHP) probe. Bond fixation caused by fusion of heterocycle to the dimethyldihydropyrene nucleus (DHPN) was measured by changes in the ^1H NMR chemical shifts (magnetic) and bond lengths alterations (structural criterion). Chemical shift data for dihydropyrenes were calculated at GIAO HF/6-31G(d)//B3LYP/6-31+G(d). For ^1H NMR chemical shift analysis, two nonaromatic reference models are studied. The parent DHP serves a better reference model for the quantification of aromaticities. The aromaticities of these heterocycles are described relative to benzene. Among the studied heterocycles, pyrazole and triazole are the most aromatic which are about 80–85% aromatic relative to benzene, through both magnetic and geometric criteria. On the other hand, thiazole and oxazoles are found least aromatic where quantitative estimates of aromaticities are about 34–42% relative to benzene. The quantitative estimates of aromaticities through magnetic (2) and geometric parameters correlate nicely (within 5%). The maximum deviation between the two parameters is observed for pyrazole where 86.1% aromaticity is calculated through NMR, and 81.6% is calculated through geometric parameters. These quantitative estimates of aromaticities of five membered heterocycles are also comparable to those from aromatic stabilization energies. The quantification of aromaticity through energetic, magnetic, and structural criteria can deliver the same information provided that suitable systems are chosen.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References

- [1] A. Kekulé, "Sur la constitution des substances aromatiques," *Bulletin de la Societe Chimique de Paris*, vol. 3, no. 2, pp. 98–110, 1865.
- [2] A. T. Balaban, D. C. Oniciu, and A. R. Katritzky, "Aromaticity as a cornerstone of heterocyclic chemistry," *Chemical Reviews*, vol. 104, no. 5, pp. 2777–2812, 2004.
- [3] P. von Ragué Schleyer, "Aromaticity: introduction," *Chemical Reviews*, vol. 101, no. 5, pp. 1115–1117, 2001.
- [4] P. George, M. Trachtman, A. M. Brett, and C. W. Bock, "Comparison of various isodesmic and homodesmotic reaction heats with values derived from published *ab initio* molecular orbital calculations," *Journal of the Chemical Society, Perkin Transactions 2*, no. 8, pp. 1036–1047, 1977.
- [5] W. J. Hehre, R. T. McIver Jr., J. A. Pople, and P. V. R. Schleyer, "Alkyl substituent effects on the stability of protonated benzene," *Journal of the American Chemical Society*, vol. 96, no. 22, pp. 7162–7163, 1974.
- [6] A. R. Katritzky, M. Karelson, S. Sild, T. M. Krygowski, and K. Jug, "Aromaticity as a quantitative concept. 7. Aromaticity reaffirmed as a multidimensional characteristic," *The Journal of Organic Chemistry*, vol. 63, no. 15, pp. 5228–5231, 1998.
- [7] M. Hanif, T. Mahmood, R. Ludwig, and K. Ayub, "Aromaticity of azines through dyotropic double hydrogen transfer reaction," *Journal of Molecular Modeling*, vol. 20, no. 6, article 2304, 2014.
- [8] B. A. Hess Jr., L. J. Schaad, and C. W. Holyoke Jr., "On the aromaticity of heterocycles containing the amine nitrogen or the ether oxygen," *Tetrahedron*, vol. 28, no. 14, pp. 3657–3667, 1972.
- [9] B. A. Hess Jr. and L. J. Schaad, "Hückel molecular orbital π -resonance energies. Heterocycles containing divalent sulfur," *Journal of the American Chemical Society*, vol. 95, no. 12, pp. 3907–3912, 1973.
- [10] B. A. Hess Jr. and L. J. Schaad, "Hückel molecular orbital π resonance energies. The benzenoid hydrocarbons," *Journal of the American Chemical Society*, vol. 93, no. 10, pp. 2413–2416, 1971.
- [11] B. A. Hess Jr. and L. J. Schaad, "Hückel molecular orbital π resonance energies. A new approach," *Journal of the American Chemical Society*, vol. 93, no. 2, pp. 305–310, 1971.
- [12] B. A. Hess Jr. and L. J. Schaad, "Hückel molecular orbital π resonance energies. The nonalternant hydrocarbons," *Journal of Organic Chemistry*, vol. 36, no. 22, pp. 3418–3423, 1971.
- [13] L. J. Schaad and B. A. Hess Jr., "Hückel molecular orbital π resonance energies. The question of the σ structure," *Journal of the American Chemical Society*, vol. 94, no. 9, pp. 3068–3074, 1972.
- [14] B. A. Hess Jr., L. J. Schaad, and C. W. Holyoke Jr., "The aromaticity of heterocycles containing the imine nitrogen," *Tetrahedron*, vol. 31, no. 4, pp. 295–298, 1975.
- [15] M. Randić, "Aromaticity and conjugation," *Journal of the American Chemical Society*, vol. 99, no. 2, pp. 444–450, 1977.
- [16] L. J. Schaad and B. A. Hess Jr., "Hückel theory and aromaticity," *Journal of Chemical Education*, vol. 51, no. 10, pp. 640–643, 1974.

- [17] P. von Ragué Schleyer and F. Pühlhofer, "Recommendations for the evaluation of aromatic stabilization energies," *Organic Letters*, vol. 4, no. 17, pp. 2873–2876, 2002.
- [18] M. J. S. Dewar and C. De Llano, "Ground states of conjugated molecules. XI. Improved treatment of hydrocarbons," *Journal of the American Chemical Society*, vol. 91, no. 4, pp. 789–795, 1969.
- [19] M. J. S. Dewar and G. J. Gleicher, "Ground states of conjugated molecules. III. Classical polyenes," *Journal of the American Chemical Society*, vol. 87, no. 4, pp. 692–696, 1965.
- [20] M. J. S. Dewar and J. G. Gleicher, "Ground states of conjugated molecules. VII. Compounds containing nitrogen and oxygen," *The Journal of Chemical Physics*, vol. 44, no. 2, pp. 759–773, 1966.
- [21] L. J. Schaad and B. A. Hess Jr., "Dewar resonance energy," *Chemical Reviews*, vol. 101, no. 5, pp. 1465–1476, 2001.
- [22] J.-I. Aihara, "A new definition of Dewar-type resonance energies," *Journal of the American Chemical Society*, vol. 98, no. 10, pp. 2750–2758, 1976.
- [23] I. Gutman, M. Milun, and N. Trinajstić, "Graph theory and molecular orbitals. 19. Nonparametric resonance energies of arbitrary conjugated systems," *Journal of the American Chemical Society*, vol. 99, no. 6, pp. 1692–1704, 1977.
- [24] I. Gutman, M. Milun, and N. Trinajstić, "Topological definition of delocalization energy," *MATCH-Communications in Mathematical and in Computer Chemistry*, vol. 1, pp. 171–175, 1975.
- [25] J. Kruszewski and T. M. Krygowski, "Definition of aromaticity basing on the harmonic oscillator model," *Tetrahedron Letters*, vol. 13, no. 36, pp. 3839–3842, 1972.
- [26] T. M. Krygowski, "Crystallographic studies of inter- and intramolecular interactions reflected in aromatic character of π -electron systems," *Journal of Chemical Information and Computer Sciences*, vol. 33, no. 1, pp. 70–78, 1993.
- [27] T. M. Krygowski and M. Cyrański, "Separation of the energetic and geometric contributions to the aromaticity of π -electron carbocyclics," *Tetrahedron*, vol. 52, no. 5, pp. 1713–1722, 1996.
- [28] C. W. Bird, "The application of a new aromaticity index to six-membered ring heterocycles," *Tetrahedron*, vol. 42, no. 1, pp. 89–92, 1986.
- [29] C. W. Bird, "A new aromaticity index and its application to five-membered ring heterocycles," *Tetrahedron*, vol. 41, no. 7, pp. 1409–1414, 1985.
- [30] C. W. Bird, "The application of a new aromaticity index to some bicyclic heterocycles," *Tetrahedron*, vol. 43, no. 20, pp. 4725–4730, 1987.
- [31] C. W. Bird, "Heteroaromaticity. 4 The status of phosphorus and arsenic as heteroatoms," *Tetrahedron*, vol. 46, no. 16, pp. 5697–5702, 1990.
- [32] C. W. Bird, "Heteroaromaticity. 6. The effect of molecular distortion on aromaticity," *Tetrahedron*, vol. 48, no. 9, pp. 1675–1682, 1992.
- [33] A. Jug and P. François, "Recherches sur la géométrie de quelques hydrocarbures non-alternants: son influence sur les énergies de transition, une nouvelle définition de l'aromaticité," *Theoretical Chemistry Accounts*, vol. 8, no. 3, pp. 249–259, 1967.
- [34] F. Fringuelli, G. Marino, A. Taticchi, and G. Grandolini, "A comparative study of the aromatic character of furan, thiophen, selenophen, and tellurophen," *Journal of the Chemical Society, Perkin Transactions*, vol. 2, no. 4, pp. 332–337, 1974.
- [35] K. Jug, "A bond order approach to ring current and aromaticity," *Journal of Organic Chemistry*, vol. 48, no. 8, pp. 1344–1348, 1983.
- [36] H. J. Dauben Jr., J. D. Wilson, and J. L. Laity, "Diamagnetic susceptibility exaltation as a criterion of aromaticity," *Journal of the American Chemical Society*, vol. 90, no. 3, pp. 811–813, 1968.
- [37] H. J. Dauben Jr., J. D. Wilson, and J. L. Laity, "Diamagnetic susceptibility exaltation in hydrocarbons," *Journal of the American Chemical Society*, vol. 91, no. 8, pp. 1991–1998, 1969.
- [38] B. Goldfuss, P. von Ragué Schleyer, and F. Hampel, "Aromaticity in silole dianions: structural, energetic, and magnetic aspects," *Organometallics*, vol. 15, no. 7, pp. 1755–1757, 1996.
- [39] R. Herges, H. Jiao, and P. von Ragué Schleyer, "Magnetic properties of aromatic transition states: the Diels-Alder reactions," *Angewandte Chemie—International Edition in English*, vol. 33, no. 13, pp. 1376–1378, 1994.
- [40] H. Jiao and P. R. von Schleyer, "Is kekulene really superaromatic?" *Angewandte Chemie—International Edition in English*, vol. 35, no. 20, pp. 2383–2386, 1996.
- [41] H. Jiao and P. von Ragué Schleyer, "The cope rearrangement transition structure is not diradicaloid, but is it aromatic?" *Angewandte Chemie—International Edition in English*, vol. 34, no. 3, pp. 334–337, 1995.
- [42] H. Jiao and P. von Ragué Schleyer, "Elimination of the barrier to cope rearrangement in semibullvalene by Li^+ complexation," *Angewandte Chemie International Edition*, vol. 32, pp. 1760–1763, 1993.
- [43] H. Jiao and P. V. R. Schleyer, "Introductory lecture. Electrostatic acceleration of the 1,5-H shifts in cyclopentadiene and in penta-1,3-diene by Li^+ complexation: aromaticity of the transition structures," *Journal of the Chemical Society, Faraday Transactions*, vol. 90, no. 12, pp. 1559–1567, 1994.
- [44] P. V. R. Schleyer, H. Jiao, M. N. Glukhovtsev, J. Chandrasekhar, and E. Kraka, "Double aromaticity in the 3,5-dehydrophenyl cation and in cyclo[6] carbon," *Journal of the American Chemical Society*, vol. 116, no. 22, pp. 10129–10134, 1994.
- [45] P. V. R. Schleyer, H. Jiao, H. M. Sulzbach, and H. F. Schaefer III, "Highly aromatic planar all-cis-[10]annulene derivatives," *Journal of the American Chemical Society*, vol. 118, no. 8, pp. 2093–2094, 1996.
- [46] H. M. Sulzbach, P. Von Ragué Schleyer, H. Jiao, Y. Xie, and H. F. Schaefer III, "A [10]annulene isomer may be aromatic, after all!" *Journal of the American Chemical Society*, vol. 117, no. 4, pp. 1369–1373, 1995.
- [47] P. V. R. Schleyer, H. Jiao, B. Goldfuss, and P. K. Freeman, "Aromaticity and antiaromaticity in five-membered $\text{C}_4\text{H}_4\text{X}$ ring systems: 'Classical' and 'magnetic' concepts may not be 'orthogonal,'" *Angewandte Chemie—International Edition in English*, vol. 34, no. 3, pp. 337–340, 1995.
- [48] M. Bühl, W. Thiel, H. Jiao, P. Von Ragué Schleyer, M. Saunders, and F. A. L. Anet, "Helium and lithium NMR chemical shifts of endohedral fullerene compounds: an ab initio study," *Journal of the American Chemical Society*, vol. 116, no. 13, pp. 6005–6006, 1994.
- [49] M. Bühl and A. Hirsch, "Spherical aromaticity of fullerenes," *Chemical Reviews*, vol. 101, no. 5, pp. 1153–1183, 2001.
- [50] H. Jiao and P. V. R. Schleyer, "Electrostatic acceleration of electrolytic reactions by metal cation complexation: the cyclization of 1,3-cis-5-hexatriene into 1,3-cyclohexadiene and the 1,5-hydrogen shift in cyclopentadiene. The aromaticity of the transition structures," *Journal of the American Chemical Society*, vol. 117, no. 46, pp. 11529–11535, 1995.
- [51] L. A. Paquette, W. Bauer, M. R. Sivik, M. Bühl, M. Feigel, and P. V. R. Schleyer, "Structure of lithium isodicyclopentadienide and lithium cyclopentadienide in tetrahydrofuran solution. A combined NMR, IGLO, and MNDO study," *Journal of the American Chemical Society*, vol. 112, no. 24, pp. 8776–8789, 1990.

- [52] M. Saunders, R. J. Cross, H. A. Jiménez-Vázquez, R. Shimshi, and A. Khong, "Noble gas atoms inside fullerenes," *Science*, vol. 271, no. 5256, pp. 1693–1697, 1996.
- [53] M. Saunders, H. A. Jiménez-Vázquez, R. J. Cross et al., "Analysis of isomers of the higher fullerenes by ^3He NMR spectroscopy," *Journal of the American Chemical Society*, vol. 117, no. 36, pp. 9305–9308, 1995.
- [54] T. Siegrist, H. W. Zandbergen, R. J. Cava, J. J. Krajewski, and W. F. Peck Jr., "The crystal structure of superconducting $\text{LuNi}_2\text{B}_2\text{C}$ and the related phase LuNiBC ," *Nature*, vol. 367, no. 6460, pp. 254–256, 1994.
- [55] P. von Ragué Schleyer, C. Maerker, A. Dransfeld, H. Jiao, and N. J. R. van Eikema Hommes, "Nucleus-independent chemical shifts: A simple and efficient aromaticity probe," *Journal of the American Chemical Society*, vol. 118, no. 26, pp. 6317–6318, 1996.
- [56] R. H. Mitchell, "Measuring aromaticity by NMR," *Chemical Reviews*, vol. 101, no. 5, pp. 1301–1315, 2001.
- [57] D. B. Kimball, M. M. Haley, R. H. Mitchell et al., "Dimethylidihydropyrene-dehydrobenzoannulene hybrids: studies in aromaticity and photoisomerization," *Journal of Organic Chemistry*, vol. 67, no. 25, pp. 8798–8811, 2002.
- [58] Maria, R. U. Nisa, M. Hanif, A. Mahmood, and K. Ayub, "Aromaticities of azines relative to benzene; a theoretical approach through the dimethylidihydropyrene probe," *Journal of Physical Organic Chemistry*, vol. 27, no. 11, pp. 860–866, 2014.
- [59] N. H. Martin, J. E. Rowe, and E. L. Pittman, "Computed NMR shielding increments over unsaturated five-membered ring heterocyclic compounds as a measure of aromaticity," *Journal of Molecular Graphics and Modelling*, vol. 27, no. 8, pp. 853–859, 2009.
- [60] M. Baranac-Stojanović, "New insight into the anisotropic effects in solution-state NMR spectroscopy," *RSC Advances*, vol. 4, no. 1, pp. 308–321, 2014.
- [61] R. H. Mitchell, "Measuring aromaticity by NMR," *Chemical Reviews*, vol. 10, pp. 1301–1316, 2001.
- [62] R. H. Mitchell, P. Zhang, D. J. Berg, and R. V. Williams, "An experimental estimate of the relative aromaticity of the cyclooctatetraene dianion by fusion to dimethylidihydropyrene," *Chemical Communications*, vol. 48, no. 65, pp. 8144–8146, 2012.
- [63] M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., "G09a: GAUSSIAN 09, Revision B.01," Gaussian, Inc., Wallingford, Conn, USA, 2010.
- [64] P. C. Hariharan and J. A. Pople, "The influence of polarization functions on molecular orbital hydrogenation energies," *Theoretica Chimica Acta*, vol. 28, no. 3, pp. 213–222, 1973.
- [65] A. D. Becke, "Density-functional thermochemistry. III. The role of exact exchange," *The Journal of Chemical Physics*, vol. 98, no. 7, pp. 5648–5652, 1993.
- [66] C. Lee, W. Yang, and R. G. Parr, "Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density," *Physical Review B*, vol. 37, no. 2, pp. 785–789, 1988.
- [67] K. Ayub, R. Zhang, S. G. Robinson, B. Twamley, R. V. Williams, and R. H. Mitchell, "Suppressing the thermal metacyclopentadiene to dihydropyrene isomerization: Synthesis and rearrangement of 8,16-dicyano[2.2]metacyclopentane-1,9-diene and evidence supporting the proposed biradicaloid mechanism," *Journal of Organic Chemistry*, vol. 73, no. 2, pp. 451–456, 2008.
- [68] R. V. Williams, W. D. Edwards, P. Zhang, D. J. Berg, and R. H. Mitchell, "Experimental verification of the homoaromaticity of 1,3,5-cycloheptatriene and evaluation of the aromaticity of tropone and the tropylium cation by use of the dimethylidihydropyrene probe," *Journal of the American Chemical Society*, vol. 134, no. 40, pp. 16742–16752, 2012.
- [69] M. Solà, "Forty years of Clar's aromatic π -sextet rule," *Frontiers in Chemistry*, vol. 1, article 22, 2013.
- [70] I. Păușescu, M. Medeleanu, M. Ștefănescu, F. Peter, and R. Pop, "A DFT study on the stability and aromaticity of heterobenzenes containing group 15 elements," *Heteroatom Chemistry*, 2014.
- [71] A. Mrozek, J. Karolak-Wojciechowska, P. Amiel, and J. Barbe, "Five-membered heterocycles. Part I. Application of the HOMA index to 1,2,4-triazoles," *Journal of Molecular Structure*, vol. 524, no. 1–3, pp. 151–157, 2000.



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