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Aromaticity of 15,16-dimethyldihydropyrene relative to benzene and strain energies of elusive [e]-fused bis-dimethyldihydropyrenes

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ABSTRACT

Density functional theory calculations have been performed to quantify the aromaticity of 15,16-dimethyldihydropyrene relative to benzene through the dimethyldihydropyrene probe. Moreover, the strain energies in [e]-fused bis dihydropyrenes **6a–d** are also calculated by comparison with a suitable reference system. The geometric analysis reveals that all isomers of the bis dihydropyrene **6** (**6a–d**) are strained, and the strain energies range from 5.87–11.31 kcal mol^{-1}. The dihydropyrenes **6b** and **6d** show only splitting type distortion (S-) whereas **6a** and **6c** have additional arching type distortion (A-) which results in higher strain energies for **6a** and **6c**. A planar non-strained analog **7** has been proposed, and investigated to elucidate the aromaticity of dimethyldihydropyrene relative to benzene, through magnetic (^{1}H NMR and NICS) and geometric (bond fixation) criteria. The aromaticity of the dimethyldihydropyrene is estimated comparable to benzene. Moreover, magnetic and geometric parameters of **6a–d** are also discussed within the context of their inability to estimate the aromaticity of dimethyldihydropyrene.

1. Introduction

Numerous criteria or definitions have been presented to estimate aromaticity since 1865 when Kekulé [1] proposed the cyclic structure of benzene, with alternating single and double bonds. Therefore, the concept "aromaticity" has grown as a general, commonly used, but a highly controversial concept in chemistry. Qualitative description of a compound as aromatic, non-aromatic and anti-aromatic is generally less contentious; however, quantitative estimation of aromaticity is not trivial, and generally leads to controversies, primarily due to the quantification methods applied [2]. Therefore, no single method has got universal acceptance. The difference in estimates of aromaticities by different methods is generally compromised in terms of multidimensional nature of aromaticity. Three major categories to quantify aromaticity are energetic, structural and magnetic, essentially all theoretical!

Hess–Schaad resonance energy [3–8], Schleyer isomerization stabilization energies [9], Dewar resonance energy [10–13] and topological resonance energies [14–16] are a few important energetic criteria. The Harmonic Oscillator Model of Aromaticity (HOMA) [17–19], Bird's aromaticity index [20–24], Julg aromaticity index [25], and Fringuelli structural index [26,27] are a few important structural methods for the quantification of aromaticity.

The more common magnetic criteria include; magnetic susceptibility exaltation [28–36], NMR [31,37–43] and nucleus independent chemical shifts (NICS) [44]. In NMR based methods, chemical shift analysis of ^{3}He and ^{7}Li nuclei placed above the aromatic nucleus, [31,37–43] ^{1}H chemical shift [45,46] analysis of probe protons usually in the center of the nucleus under consideration, and coupling constants [47,48] analysis in ^{1}H NMR (Gunther Q-values) are more common.

In NMR based methods, an arene under consideration may be fused with a probe molecule; however the choice of a suitable probe to quantify aromaticity is very important. A probe of high accuracy based on ^{1}H NMR chemical shift is 15,16-dimethyldihydropyrene **1**. An arene under investigation of aromaticity is fused with the dimethyldihydropyrene and the change in the ring current of the dihydropryene is taken as a measure of the aromaticity.

The internal methyl protons in 15,16-dimethyldihydropyrene **1** (Fig. 1) appear at δ-4.25, and their comparison with the chemical

Abbreviations: DHP, 15,16-dimethyldihydropyrene; CPD, *meta* cyclophanediene.

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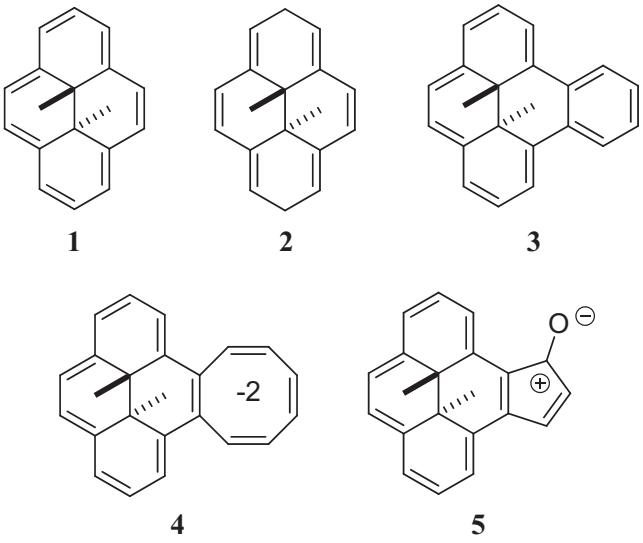

Fig. 1. Dimethyldihydropyrene **1**, non-aromatic model **2** and arenes fused dimethyldihydropyrenes **3**–**5**.

shift of the non-conjugated model **2** (δ 0.97) indicates large shielding of ~5.2 ppm due to a strong ring current in **1** [45]. When an aromatic ring is [a]- or [e]- fused to the dimethyldihydropyrene, the ring current in the latter is reduced. The internal protons of [e]- fused benzodihydropyrene [49] **3** appear at −1.85 ppm (experimentally observed) which means that the internal methyl protons in **3** are shielded by 2.82 ppm. Comparison of the shielding of ~5.2 ppm for **1** with 2.82 for **3** leads to experimental estimate of 52% aromaticity of **3** relative to **1** [50]. The greater the aromaticity of the fused ring, the greater is the reduction in the ring current. This concept can be used to compare the relative aromaticities of any two molecules provided the following two conditions are met; (i) effect of fusion on the geometry of the probe molecules is negligible, and the ring current around the probe molecule is only affected by the new delocalization, (ii) through space anisotropic effects are not significant enough to affect the chemical shifts of the probe protons. Dimethyldihydropyrene is an excellent probe to fulfill these requirements and has successfully been used to compare aromaticities of a large number of molecules and ions. The latter includes both aromatic tropylium [51] and antiaromatic cyclopentadienone [52] systems through molecules **4** and **5**, respectively. The aromaticity of dimethyldihdyropyrene (**1**) probe itself relative to benzene is not well investigated. The only report of the comparison of the relative aromaticities of benzene and 15,16-dimethyldihydropyrene is by Haddon where he applied Biot–Savart law to ring current analysis of Benzene and 15,16-dimethyldihydropyrene (and other annulenes), and found that both benzene and dimethyldihydropyrene are equally aromatic [53,54]. Aromatic character of the annulenes was calculated by expressing the fraction of maximum ring current that each molecule displays. Since the dimethyldihydropyrene is an excellent probe, therefore, quantifying the aromaticity of 15,16-dimethyldihydropyrene itself relative to benzene through the dimethyldihydropyrene probe is a topic of significant interest. A molecule of choice, in this regard, is [e]-fused bis-dihydropyrene **6**. Several strides had been made to synthesize this compound to quantify the aromaticity of the dimethyldihydropyrene; however, all of them met with failure. The failure in synthesis may be attributed to the associated strain (vide infra), and due to limited synthetic strategies available for this class of compounds [55,56]. Computational chemistry is quite helpful in cases where experimental chemistry fails to deliver the information. The computational study of the aromaticity of **6** and related molecules is an excellent way to determine aromaticity of the dimethyldihydropyrene. In this manuscript aromaticity of dimethyldihydropyrene relative to benzene is described through magnetic (^{1}H NMR and NICS) and geometric analysis by suitable bisdihydropyrene molecules. Moreover the strain in [e] fused Bis-dihydropyrene and its open cyclophanediene isomer is also discussed.

2. Computational methods

All calculations were performed with the Gaussian 09 suite of programs [57]. Geometries of the structures were optimized without any symmetry constraints at hybrid B3LYP method using 6-31G* basis set [58]. The B3LYP method, which consists of parameter hybrid functional of Becke [59] three in conjunction with the correlation functional of Lee, Yang, and Parr [60], 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. Each optimized structure was confirmed by frequency analysis at the same level (B3LYP/6-31G*) as a true minimum (no imaginary frequency). Predictions based on the B3LYP method for the dihydropyrene nucleus have previously led to the development of robust photoswitches [61] as well. ^{1}H NMR chemical shifts were calculated by Hartree–Fock (HF) Gauge Independent Atomic Orbital (GIAO) method at 6-31G* basis set on the B3LYP/6-31G* optimized geometries (GIAO-HF/6-31G*//B3LYP/6-31G*). GIAO-HF/6-31G* was chosen because the predicted aromaticities of a number of dihydropyrenes through this method correlate very well with the experiment [51].

3. Results and discussions

3.1. Geometries of [e] fused bisdihydropyrenes

First of all, the geometry of **6** is analyzed to investigate the strain energy. A first glance analysis of the molecule indicates that the hydrogens (shown in Fig. 2) have strong steric interactions with one another, provided that the molecule is perfectly planar. To avoid these steric interactions, both dihydropyrene fragments need to loose co-planarity, a splitting (S-) type distortion [62]. The lack of co-planarity combined with the relative orientations of the internal methyl groups yields four isomers for **6** i.e., **6a**–**d**. Isomers **6a** and **6c** show arching type distortions (A-), in addition to splitting type distortions. For **6a**, front and side views are shown in Fig. 3a and b, respectively. The dihedral angle between two DHP fragments (1′–10a′–10–10a, See Fig. 4 for numbering) is taken as a measure for deformation from planarity, and is found 28.8° for **6a** and 18.4° for **6c**.

The larger twist from planarity in **6a** causes more loss in delocalization which is reflected in higher energy of **6a** relative to **6c**. **6a** is unstable relative to **6c** by 1.15 kcal mol^{-1}. Steric interactions between methyl groups on one DHP fragment with the methyl groups on the 2nd DHP unit are similar in **6a** and **6c,** because of similar interatomic distances. For example, in **6a**, a hydrogen on C12 is close to a hydrogen on C12′ at a distance of 3.24 Å whereas in **6c**, the same hydrogen on C12 is close in space to C11′ at a distance of 3.27 Å.

In **6a** and **6c**, each DHP fragment has arching type distortion whereas the parent dimethyldihydropyrene is a planar structure. Since the internal carbons 10b and 10c are displaced above and below the plane of the DHP ring due to their sp3 nature, therefore, to analyze the planarity of the DHP skeleton, a dummy atom is placed at the center of the DHP fragment (between C_{10b} and C_{10c}) and the angle H_2–G–H_7 (where G is a ghost or dummy atom) is taken as a measure of the planarity. The calculated bond angle