Identifying Molecular Structural Aromaticity for Hydrocarbon Classification

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ABSTRACT: Determination of aromaticity in hydrocarbons may be as simple as determining the average bond length for the molecule of interest. This would greatly assist in classifying the nature of hydrocarbon chemistry, especially for large molecules such as polycyclic aromatic hydrocarbons (PAHs) where today’s aromatic classification methods are prohibitively expensive. The average C–C bond lengths for a test set of known aromatic, antiaromatic, and aliphatic cyclic hydrocarbons are computed here, and they show strong delineating patterns for the structural discernment of these aromaticity classifications. Aromatic molecules have average C–C bond lengths of 1.41 Å or less with the largest molecules, PAHs, having the longest average C–C bond lengths; aliphatic species have such lengths of 1.50 Å or more; and antiaromatic species fall between the two. Consequently, a first-order guess as to the aromaticity of a system may simply arise from its geometry. Although this prediction will likely have exceptions, such simple screening can easily classify most cases, and more advanced techniques can be brought to bear on the cases that lie in the boundaries. Benchmarks for hydrocarbons are provided here, but other classes of molecular structural aromaticity likely will have to be defined on an ad hoc basis.

INTRODUCTION

The simple average C–C bond length in a cyclic, planar molecule is promoted in this work as a correlating predictor of aromaticity or antiaromaticity, but no attempt is made to define either term. The definition of aromaticity has ranged across various forms since the inception of this chemical term in the mid-19th century. Modern definitions of aromaticity include delocalization of electrons leading to stabilization in the bonding energy. Such is a long way from simply invoking the chemist’s nose to discern some odor. One of the most successful, and certainly longest lasting, definitions of aromaticity is Hückel’s 4n + 2 rule for the number of electrons in planar, cyclic molecules. Although this equation applies well to π electrons in sp² hybridized systems, σ and δ aromaticities are also typically defined utilizing this same approach. H₃⁺ is a classic example of σ aromaticity with n = 0.5–3. Although the 4n + 2 rule works well in monocylic systems, it starts to break down as the ring size grows. Consequently, more concrete definitions of aromaticity, especially π aromaticity, have been a major thrust of research over recent decades. Some include various methods put forth by late Paul v. R. Schleyer such as block-localized wave function-extra cyclic resonance energy (BLW-ECRE), energy decomposition analysis-aromatic stabilization energy, and nucleus-independent chemical shift. Others include the multicenter index (MCI), the para-delocalization index, and the aromatic fluctuation index (FLU), among many others. Each of these methods involves computing energies for different portions of the molecule and constructing a schema to physically interpret the results as aromaticity and its subsequent molecular energy stabilization. These methods are powerful and provide excellent insights into the geometry of cyclic systems even beyond hydrocarbons.

However, simpler metrics such as the average C–C bond length may be available to predict aromaticity even without defining or expressly quantifying it. Although this molecular observable is used as one of the conditional constraints in some quantifications of aromaticity, such as the harmonic oscillator stabilization energy (HOSE) method, this simpler approach in averaging the C–C bond lengths may be useful for roughly approximating aromaticity in cyclic hydrocarbons with notable application to polycyclic aromatic hydrocarbons (PAHs). PAHs are believed to make up as much as 20% of the carbon in the universe and can grow to immense sizes.

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Table 1. Average C–C Bond Lengths (Å), Average C–C Bond Energies (kcal/mol), and Isodesmic Energies (kcal/mol)

|                 | CCSD(T)/apVTZ |             | MP2-F12/apVTZ |             | Experimental |
|-----------------|---------------|-------------|---------------|-------------|--------------|
|                 | bond length   | bond energy | isodesmic energy | bond length | bond energy | isodesmic energy | bond length |
| c-C3H2          | 1.385         | 110.0       | −0.8          | 1.388       | 126.3        | −6.3           | 1.390       |
| c-C3H4          | 1.368         | 139.0       | 30.4          | 1.363       | 150.3        | 29.9           |
| c-C4H4−         | 1.418         | 138.6       | −85.6         | 1.414       | 150.9        | −96.6          |
| benzene         | 1.398         | 140.5       | −59.6         | 1.393       | 151.9        | −69.3          | 1.397       |
| anthracene      | 1.406         | 131.2       | −110.9        | 1.402       | 145.4        | −128.8         | 1.400       |
| pyrene          | 1.405         |             | 142.7         | 1.407       |             | 141.0          |
| coronene        | 1.405         | 133.5       |               |             | 133.5        |               |
| c-C5H6          | 1.511         | 101.3       | 24.6          | 1.520       | 110.4        | 23.6           | 1.501       |
| c-C5H5          | 1.502         | 86.8        | 26.6          | 1.419       | 135.9        | −33.7          |
| c-C6H6          | 1.553         | 104.4       | 20.0          | 1.544       | 113.4        | 19.5           | 1.555       |
| c-C6H10         | 1.535         | 119.0       | −3.5          | 1.535       | 119.0        | −3.5           | 1.546       |
| c-C4H4          | 1.525         | 120.3       | −12.4         | 1.404       | 145.4        | −40.5          | 1.404       |
| c-C8H8 (planar) | 1.407         | 143.6       | −26.1         | 1.398       | 143.8        | 58.9           |
| c-C10H10 (planar) | 1.418      | 108.0       | 41.8          |             | 108.0        | 41.8           |

aCoronene’s values are computed with cc-pVDZ instead of aug-cc-pVDZ because of linear dependencies in the basis set for this large D5h molecule. bRef 11. cRef 12. dRef 13. eRef 14. fRef 15. gRef 16. hRef 17.

including hundreds of atoms. Small changes in the PAH geometry are also common with an internal carbon easily removed from the system due to collisions with energetic particles and cosmic rays. As a result, the aromaticity of such systems can change, leading to new chemistry as the PAH attempts a return to aromatic planarity or even antiaromatic (in the 4n + 2 definition) spheres creating species such as buckyballs. 20–23 FLU, MCI, ECRE, and HOSE computations of PAHs and buckyballs are intractable from a practical sense. Certain PAHs of interest could be computed, but the number of PAHs and closely related hydrocarbon derivatives could become immense, especially for dynamics and chemical reaction studies. There can be hundreds of resulting species where accurate but costly methods are not capable of treating each system of interest. Structure may help in the aromaticity predictor of aromaticity, quantum chemical computations are utilized to compute the geometries of a set of known aromatic, antiaromatic, and aliphatic species. Coupled cluster theory,26,27 at the single, double, and perturbative triple level [CCSD(T)],28 with the aug-cc-pVTZ basis set,29,30 as well as explicitly correlated MP2-F12,31,32 with the aug-cc-pVDZ basis set, is utilized to treat larger systems like PAHs for this assessment. The methods are chosen because CCSD(T) is considered to be the “gold standard” of quantum chemistry33 but sometimes it is too costly. Reducing down to MP2 can provide robust geometric information for the larger systems, and the explicit correlation will further improve the accuracy.

Table 1 presents the average bond lengths for the systems analyzed as well as the average C–C bond energies and the isodesmic energies. The average bond energies are computed by breaking down each of the molecules into its 3P, 1Σ+, CH, and 1A1 CH2 fragments. For instance, the average bond energy for c-C6H6 is defined as

$$E(c-C_6H_6) = E(C) + E(CH_2)$$

$$n_b$$

where $$n_b$$ represents the number of C–C bonds present in the molecule. For c-C6H6, $$n_b = 3$$. CCSD(T)/apVTZ (utilizing an abbreviation for aug-cc-pVTZ) produces a value of 110.0 kcal/mol with MP2-F12/apVDZ similar at 126.3 kcal/mol.
The isodesmic energy is often utilized to compute ring strain in a cyclic system and is defined as a reaction energy scheme where the number and type of bonds are conserved. The lowest energy spin states for each system are utilized, making most of the computed fragments closed-shell singlets. The isodesmic scheme for $c$-$C_3H_2$ is defined as

$$[E(c-C_3H_2) + E(CH_4) + 2E(CH_4)]\]
$$

- $[E(C(CH_3)_2) + 2E(HCCCH_2)]$ (2)

The isodesmic energies are $–0.8$ and $–6.3$ kcal/mol for CCSD(T)/apVTZ and MP2-F12/apVDZ, respectively, for $c$-$C_3H_2$. The isodesmic energies are reported here to avoid interpretations of destabilization in the average bond energy resulting from ring strain.

At first glance of Table 1, one interpretation would be that $c$-$C_3H_2$ is not highly strained. However, similar cyclic geometries are known to be highly strained. Cyclopropane is a notable example. The present computations put the strain energy of that system right at 24.6 and 23.6 kcal/mol again for CCSD(T) and MP2-F12, respectively. These are quite close to the generally accepted 27 kcal/mol ring strain in $c$-$C_3H_2$. Removing two of the hydrogens to create a lone pair on the new terminal carbon in cyclopropyldiene ($c$-$C_3H_4$), a less stable isomer of allene, actually raises the strain energy by roughly 2 kcal/mol. Consequently, the difference in the isodesmic energies between the $c$-$C_3H_2\pi$ molecule and either of the non-$\pi$ bonded systems could be a measure of aromaticity.

Additionally, the average bond energies are notably different between $c$-$C_3H_2$ and the other cyclic propyl alkanes. The dissociation of cyclopropanylidene by way of eq 1, again requires 110.0 kcal/mol from CCSD(T). Similar reactions for cyclopropane and cyclopropyldiene require less at 101.3 and 86.8 kcal/mol, respectively. The MP2-F12 values are higher but present the same qualitative relative energies. In any case, the energies have a clear bright line between a traditionally interpreted aromatic system and traditionally interpreted aliphatic systems. This correlates with the average bond lengths: 1.385 Å for $c$-$C_3H_2$ compared to 1.511 and 1.502 Å for $c$-$C_3H_4$ and $c$-$C_3H_6$, respectively. Hence, the average bond length corresponds to aromaticity in this first example.

Taking the values of Table 1 on the whole, traditional aromatic geometries have MP2-F12/apVDZ bond lengths of roughly 1.41 Å and lower. This is similar for CCSD(T)/apVTZ for those systems suited for study with this more costly level of theory. Because aromaticity is a cyclic property, an average bond length approaching that of a double bond is irrelevant (or isoelectronic at worst) for the present analysis as continuous double bonds in cyclic molecules are most often highly strained and unstable. Aliphatic geometries have bond lengths of 1.50 Å and greater. This is not surprising because C–C single bonds are typically in this same range. Comparison of experimental bond lengths to the computed values is within 0.01 Å for both levels of the theory employed here. $c$-$C_3H_4^+$ extends slightly beyond the trend for aromatic species; however, the additional electron delocalizes the system slightly, thereby extending the bond lengths.

All of the $C_3H_4$ geometries for $c$-$C_3H_4^+$ have notable amounts of strain in them as evidenced by both the average bond energies and the isodesmic energies in Table 1. $c$-$C_3H_4$ is known to be unstable, and work on $c$-$C_3H_4$ has shown that even the single hydrogen is not enough to stabilize the ring such that a large-amplitude motion is present in the ring-deformation vibrational modes. The outlier in $c$-$C_3H_4^+$ is resonantly stabilized, lowering the isodesmic energy below the other cyclopropenyl family members.

An interesting result is that the traditionally interpreted antiaromatic geometries, those cyclic systems with even numbers of $\pi$ electrons that do not follow Hückel’s $4n + 2$ rule, have average bond lengths and average bond energies that fall in between those from the aromatic and aliphatic groups. Although any amount of bond order greater than 1.0 will decrease the average bond length, the fact that antiaromatic species are more stable than pure aliphatics is not initially obvious, especially to students. Two quintessential antiaromatic species include $C_2H$ cyclobutadiene ($c$-$C_4H_4$) and the $D_{1h}$ cyclopentadienyl cation ($c$-$C_5H_5^+$). As shown in the middle of Table 1, they exhibit average bond lengths between 1.50 and 1.41 Å with average bond energies that also fall in this middle range for both CCSD(T) and MP2-F12. The cyclopentadienyl cation has an average bond energy nearly in the range of that expected for aromatic geometries but the empty $p$ orbital on one of the carbon atoms in the ring leads to this stabilization. Additionally, the bicyclic $c$-$C_4H_4$ pentalen geometry is also antiaromatic for $n = 8$ with an average bond length of 1.419 Å and an average bond energy of 135.9 kcal/mol, both falling in this middle region. In each case, the C–C bonds share additional electrons, creating bonds that are shorter than C–C single bonds but longer than average C–C bonds exhibited in aromatic geometries. As a result, antiaromatic bonding falls between that of aromatic and aliphatic.

Larger PAH geometries exhibit convergent behavior for both bond lengths and average bond energies. Excluding coronene, which required use of cc-pVDZ instead of aug-cc-pVDZ, the average MP2-F12/apVDZ bond length is converging to close to 1.410 Å and the average MP2-F12/apVDZ bond energy to 140.0 kcal/mol. Such convergent behavior has been shown for various PAH properties as functions of increasing numbers of benzene rings. Quick AM1 computations put the average C–C bond lengths in our four PAHs converging to slightly longer values at 1.413 Å as compared to the MP2-F12/apVDZ bond length. Consequently, generic and large PAHs will have bond lengths that are slightly longer than that of benzene (1.397 Å) and will be close to 1.410 Å. Including coronene in the analysis lends qualitative evidence that the trend holds. As a side note, specifically pyrene but also many other PAHs actually fail the 4$n + 2$ test. However, each of the rings taken individually in each PAH passes the test. Again, this has been known for over half of a century. Additionally, pyrene is experimentally aromatic in behavior, and the trend for aromaticity based on its bond lengths and energies is also present in our computations.

To examine if the nonaromatic or antiaromatic behavior in molecules of force planarity that optimize as nonplanar can also be predicted by this method, cyclooctatetraene ($C_8H_8$) is investigated. This molecule is experimentally known to be of $D_{2h}$ symmetry and has two classes of four bond lengths, 1.470 and 1.337 Å, giving an average of 1.404 Å and is exactly what the MP2-F12/apVDZ results predict. Cyclooctatetraene is nonplanar, meaning that it will be aliphatic even though it is cyclic. The stabilization brought about by the out-of-plane bends renders any prediction of aromaticity from the average bond length moot. However, forcing planarity in a $D_{4h}$ geometry is antiaromatic by Hückel’s rule, but our
computations put the average bond length of planar C₆H₆ at 1.407 Å with an average bond energy of 143.6 kcal/mol. This is at the outer edge of the antiaromatic range and is encroaching upon the PAH average bond length range. However, the strain energy for this molecule is negative, indicating that although it prefers to bend out of plane, the reduced interior angle of an octagon is enough to provide stability in the system. Furthermore, C₆H₆ is large enough to delocalize without moving into true antiaromaticity, as indicated by the 1.407 Å bond length existing on the border between aromaticity and antiaromaticity. This is further evidenced by C₁₀H₁₀ in Table 1, which, if planar, meets the 4n + 2 requirement. Its average bond length of 1.398 Å fits well into the aromatic criterion but it also bends out of plane in its lowest energy form, rendering comments of aromaticity for the C₂ minimum geometry moot, as well.

For prediction purposes, the cyclic c-(C)C₃H₂, cyclopropenylidene with an additional carbon atom bonded to the apical carbon and shown in Figure 1, can be classified in two ways. Relying only on the bonds in the ring (neglecting the apical C=CC bond), the average bond length for nₛ = 3 falls into the antiaromatic range, as shown in Table 1. The 4n + 2 rule fails here because there are four electrons in the ring, assuming that the central carbon possesses both π electrons at a given instant. Even so, the 1.424 CCSD(T) average bond length is approaching the aromatic region of the continuum. Consequently, removing the carbon atom from c-(C)C₃H₂ to create c-C₃H₂ clearly affects the aromaticity in notable ways. Such results corroborate the conclusions from ref 6 that substituents can greatly influence aromaticity in cyclopropenyl geometries even when merely replacing a carbon atom with a carbide group.

**CONCLUSIONS**

In conclusion, planar, aromatic molecules defined in the traditional sense have average C–C bond lengths of 1.41 Å or less. PAHs, apparently large molecules, represent the upper bound to this average bond length. Planar, cyclic antiaromatic species have average bond lengths of between 1.41 and 1.50 Å. Cyclic geometries with bond lengths of greater than 1.50 Å are in line with C–C single bond definitions of ~1.54 Å. Consequently, the average C–C bond length can be a good first-order predictor as to whether a cyclic hydrocarbon is aromatic or antiaromatic. We are not advocating a robust prediction for the aromatic classification, but this simple metric appears to correlate well as an initial guess. Although most quantum chemical determinations of aromaticity are far too costly for molecules of astrophysical importance like PAHs, effectively determining the nature of the chemical species can be easily achieved through the structural aromatic metric described herein.

It has yet to be seen how side groups and other substituents affect the average bond length for aromaticity (see c-(C)C₃H₂ for example). However, such analysis will be left for future work. A similar approach can likely be utilized for other classes of molecules beyond hydrocarbons such as nitrogenated PAH molecules (PANHs) and three-dimensional geometries such as fullerenes. However, benchmarks for average bond lengths in such systems deemed aromatic or antiaromatic must be established first.

**COMPUTATIONAL DETAILS**

The CCSD(T)/apVTZ computations utilize the PSi4 program, the MP2-F12/apVDZ computations are from MOLPRO 2015.1, and the AM1 computations are from Gaussian. The two former computational approaches utilize the frozen core electron approximation. Zero-point vibrational energies (ZPVEs) are not included in the energy computations due to the complexity in computing these for the PAHs with current, standard approaches. However, the absolute bonding and isodesmic energies themselves are not as important to this study as the relative values are, and ZPVE inclusions are known to affect relative energies slightly for PAHs due to their regularity.

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**Notes**

The authors declare no competing financial interest.

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