

Quantifying energetics of topological frustration in carbon nanostructures

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We develop a graph theoretical formalism to account for the fact that sp^2 carbon can become spin ordered or generate free radicals for purely topological reasons. While this phenomenon has been previously considered a binary operator, we here show a quantification in discrete units of *frustrations*. The graph theory method is combined with open density functional theory calculations to establish the existence of an energy of frustration that is shown to greatly improve the description of carbon nanostructure energetics using classical force fields. The methodology is illustrated for a number of systems and, owing to the small computational overhead associated with its evaluation, is expected to be easily integrable into any modeling approach based on a structure's adjacency matrix.

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I. INTRODUCTION

The hybridization of one s orbital and two p orbitals of carbon results in intriguing structures such as fullerenes, graphite, graphene, and nanotubes [1–4] with many attractive properties. These properties are consequences of the intrinsic rules of sp^2 hybridization, which impose that each carbon atom must be σ bonded to precisely three neighbors, exactly one of these necessarily possessing an additional π bond. This relatively simple idea of drawing organic structures in terms of one double and two single bonds per carbon is named after August Kekulé, who proposed the concept in the 1800s [5].

The Kekulé structure, as a model, became outdated with the development of quantum mechanics, which established a more complex picture where knowledge of the localization of an electron is expressed as a probability distribution. However, the original model remains a valuable concept, but its intrinsically quantum mechanical origins often make it hard to incorporate into broadly used classical descriptions of carbon physics. Due to its inherent power as a metric for structural characterization, the Kekulé model's untapped potential can be brought to light using modern techniques such as those provided by graph theory, the study of nodes and connections. It follows that mathematical rigor can be combined with well-established classical molecular dynamics (MD) such that significant improvement can be reached by incorporating Kekulé's prescriptions. As a consequence, this refined approach avoids unstable structures that classical force fields cannot detect. Furthermore, the systematic inclusion of these rules has the power to significantly accelerate the virtual design of stable multifunctional structures.

The focus of this paper is to demonstrate the existence of a formal link between quantum mechanics, Kekulé structure, and graph theory, and to provide a means to identify and assess the energetics of topological frustration. Topological frustration, when viewed by quantum mechanics with regards to sp^2 carbon, refers to open and localized π orbital shells leading to a nonsinglet state having the lowest ground-state energy [6]. In reference to chemistry, a frustration corresponds

to a sp^2 carbon atom being unable to link to any double bond under any possible Kekulé structure (without creating additional unlinked atoms). In the graph theory sense, starting from a network made up of a structure's adjacency matrix (i.e., a listing of all neighboring atoms), a frustration appears when the maximal matching of a graph leaves unmatched nodes. In addition, topologically frustrated structures have also been known as *concealed* structures and non-Kekuléan structures [7]. An example of this phenomenon viewed from different disciplines is illustrated in Fig. 1, using the smallest triangular zigzag graphene nanoflake (TZ GNF) as a demonstration structure.

The general approach presented here aims at classifying these structures and moving beyond the current paradigm, which is based on considering the presence of topological frustrations as a binary operator: Either the structure is frustrated or not [8]. Our method instead measures the number of topological frustrations in quantized units by an original application of the concept of maximal matching borrowed from graph theory. We define the number of frustrations of any given structure as n_f and the energy penalty per frustration as u_f .

Empirically, topological frustrations are relatively seldom observed in stable products, but they are generally needed to account for transition states during structure formation and chemical reactions in general. Further, a single frustration corresponds to a doublet state. Finding stable multiplet states is the bane of experimentalists working in many fields, such as in the search for undoped, ferromagnetic carbon. One of the most famous examples in this category is that of TZ GNFs, of which triangulene is a notable member. TZ GNFs exhibit ferromagnetism (FM) ordering with a magnetic moment that scales with increasing flake size, a consequence of Lieb's theorem [9,10]. While purely hydrocarbon ferromagnets would have many applications in device fabrication, they have not been brought to practical fruition. Early pioneers such as Clar had difficulty synthesizing any such structure at all [11], and modern attempts have only been partially successful at creating metastable structures due to characteristic decay at ambient

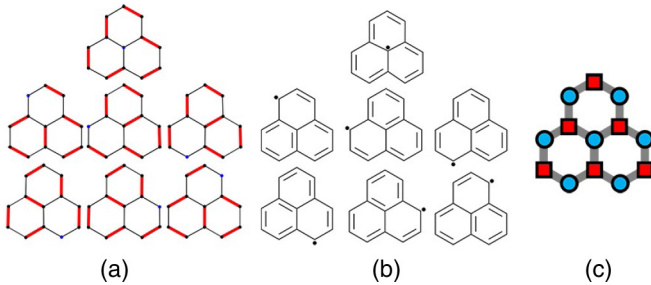


FIG. 1. (Color online) (a) Maximal matchings (red) enumerating all the unique positions of the unmatched node (blue), or frustration, in the graph of the smallest TZ GNF. Note that more maximal matchings are possible, but have symmetry equivalent unmatched node locations. (b) Kekulé representations of the matchings in (a). The unmatched node corresponds to an unbound π orbital electron, or free radical. (c) After graph theoretical enumeration, some nodes can be unmatched (blue circles) and others always matched (red squares). We call the former “frustration resonant” and the latter “frustration forbidden.”

conditions, destroying the desired properties [12]. Magnetism and stability are intimately related in hydrocarbon structures through topology of the adjacency matrix, and indeed in this study we will demonstrate that hydrocarbon structures possessing a FM character are frustrated.

Here we show, using large-scale quantum chemistry methods for high-multiplet structures, that each quantized unit of frustration is characterized by a constant energy u_f . The ease of identifying frustration and the uniformity of the corresponding energy penalty enable the straightforward integration of frustration energy into existing MD codes based on classical force fields. This advance can facilitate rapid quantification of the energetics for topologically frustrated carbon nanostructures and thus promote high-throughput materials discovery.

II. COMPUTATIONAL METHODS

We employ two distinct theoretical and computational methods to address the energetics of frustrations, ranging from first-principles (density functional theory, or DFT) to classical (the Tersoff-Brenner parametrized reactive bond-order, or REBO, model) computational approaches.

The higher fidelity calculations are based on all-electron quantum DFT calculations and were performed using the NWCHEM package [13]. The B3LYP exchange-correlation functional was used with Dunning’s correlation consistent basis set, cc-pVDZ [14], during the calculation of the open-shell self-consistent solution (ODFT). The initial starting geometries for the different all-carbon systems were based on the structures obtained using REBO. Full ODFT geometry optimization was performed to obtain the total energy of each possible spin state in order to determine the lowest energy spin configuration. In all cases, spin contamination was carefully monitored ($\langle S^2 \rangle$) for these open-shell calculations. In addition, corroboration of the lowest energy spin state was obtained using restricted open-shell Hartree-Fock (ROHF) calculations.

A hybrid approach was also used since standard DFT methods for conjugated systems can fail due to significant electronic delocalization [15]. At the heart of this failure is

the description of electron exchange, which is particularly important at describing magnetic properties. ROHF, while accurate for exchange does not include important correlation effects. We therefore have also checked the presented results using Perdew-Zunger correlation with 100% exact exchange.

The classical method employed to calculate energy is a custom implementation of a MD function set for hydrocarbons. Specifically, it is the second-generation reactive empirical bond order (REBO) potential originally developed by Brenner *et al.* [16]. Minor modifications were made to the original potential in the interest of computational efficiency, taken from an earlier paper on the same potential [17]. The potential itself accounts for basic bond length and bond angle preferences, changes in hybridization from bond formation or removal, and π -bond conjugation effects up to the second-nearest neighbor. However, in contrast to ODFT, it completely ignores the energy contribution related to frustration, as it is a purely quantum mechanical property.

III. MAXIMAL MATCHING AND ENERGY OF FRUSTRATION

A. Graph theory, application

Graph theory is the mathematical study of networks, applicable to many disciplines in science and technology. A graph G is defined as a set of nodes V connected by a set of edges E . A *matching* is any set of edges that do not share the same node, i.e., do not overlap. If all the nodes can be matched by an edge once and exactly once, the graph is said to have *perfect* matching. If we correlate nodes to sp^2 carbon atoms (and not hydrogen or sp^3 atoms) and matched edges to double bonds, then we clearly see that the Kekulé structure is topologically synonymous to the aforementioned perfect matching.

However, what if all nodes cannot be matched exactly once, for purely topological reasons? We can still attempt to match as many nodes as possible without overlap: This set of edges is known as the *maximal* matching. By taking the total number of nodes in the graph and subtracting the number of nodes in the maximal matching, we analogously arrive at the number of atoms that do not have their π bonds satisfied, consequentially raising the energy of formation. Thus, we arrive at a way to measure the severity of topological frustration, by counting the number of unmatched nodes, which we will simply call *frustrations*. The number of topological frustrations in an sp^2 carbon structure will produce an exactly equal number of free radicals, by definition of unbound π electrons.

The application of maximal matching to large-scale simulation is fairly straightforward. Many fast algorithms have been developed to compute the maximal matching in a number of areas of network theory. Current algorithms are based on variations of Edmond’s blossoming algorithm, which has a runtime proportional to $O[VE \log(V)]$ [18]. This scaling is valid for an arbitrary graph and even faster algorithms exist for bipartite graphs, which can be applied to all benzoid structures (note that in this case the A and B sublattices are their own partitions). For bipartite graphs, run times can reach $O(E\sqrt{V})$ [19]. However, we want to insist on the fact that the structures do not have to be benzoid for the concept of maximal matching to be applied. These computational times

are much faster than many other operations performed in electronic structure and MD calculations. Thus, calculating the number of frustrations, and their contribution to the formation energy, adds negligible processing time, provided an estimate of an energy penalty can be made.

To calculate n_f , Edmund's blossoming algorithm is sufficient, as it will quickly find a maximal matching. However, to find and enumerate over *all* possible maximal matchings to find frustration-resonant and -forbidden nodes (as shown in Fig. 1), algorithms such as those developed by Uno are required [20,21]. Uno's enumeration algorithms have runtimes of $O(|V|N)$ or $O(|V| + |E| + \Delta N)$ (where V , E , and N are the numbers of vertices, edges, and maximal matchings, respectively, and Δ is the degree of the graph), depending on if the graph is bipartite or not, respectively [20,21]. For more discussion on enumeration of matchings and the relation between frustrations and Pauling bond order, see the Supplemental Material [22].

B. Locating free radicals and resonances

We have established a number of rules that allow us to calculate the Kekuléan nature of a structure from its base building blocks and some elementary transformations, which we call *the rules of frustration annihilation*. Using TZ GNFs as an example, we observe that in no enumeration of the maximal matching does a free radical ever exist at any of the three extreme tips (Fig. 1). This remains true for all sizes of TZ GNFs, for purely topological reasons, i.e., there is an imbalance in the A and B sublattices of the bipartite network, and the frustration will exist on the surplus sublattice. Thus, TZ GNF side atoms can be considered as nodes with frustration resonance, and the tip atoms can be considered as nodes that are frustration forbidden.

If two TZ GNFs are connected at their tips (or a tip to a side), the combined structure merely has the sum of their frustrations, leaving the total number of free radicals unchanged. However, if two side nodes are connected by one edge, two frustrations can annihilate and leave a matching on the added edge. It follows that this effect is equivalent to two free radicals recombining into a π bond. A simple demonstration of these rules in action is illustrated in Fig. 2 by observing how the number of frustrations, n_f , changes by simply choosing different locations of the connecting edge.

There are more ways to control n_f than just connecting subunits. Bringing two resonant nodes into contact via a Stone-Thrower-Wales (STW) defect will have a similar effect (see Fig. 3). STW defects also destroy the bipartite nature of benzenoid structures. Our methodology is unaffected by this loss of ordering, displaying a significant advantage over other models that only work for bipartite graphs, such as Lieb's theorem [9].

It is important to mention that simply bringing frustration-resonant nodes into contact with each other is not sufficient for annihilation: At least two frustrations must exist in the structure to annihilate. This is a consequence of the fact that two neighboring unmatched nodes are required to match an edge by definition; a single frustration, however resonant, will not be able to find another to pair up. Physically, this can be thought of as two electrons being required to form a bond, a lone free radical is not enough.

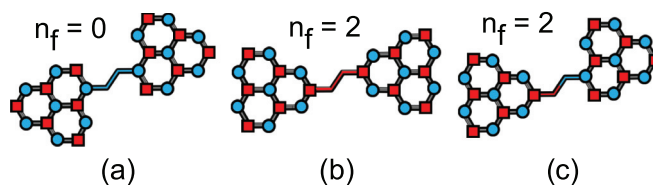


FIG. 2. (Color online) All combinations of frustration-resonant and -forbidden node connections between two of the smallest TZ GNFs. Each TZ GNF subunit has number of frustrations, n_f , equal to one when unconnected. The subunits are connected by dimers to avoid regions of high hydrogen-hydrogen repulsion [22], but this has no effect on topological properties such as frustration resonance or Kekuléan nature. (a) Two resonant nodes are connected, allowing the free radicals (unmatched nodes) to combine (match), reducing the total system n_f to zero. (b) With two forbidden nodes connected, the free radicals cannot be satisfied, and $n_f = 2$. (c) Even when connecting a forbidden and a resonant node, two radicals are required to recombine; thus, the total number of frustrations remains $n_f = 2$.

In summary, bringing nodes with frustration resonance to connect with one another will lower the total number of frustrations by two if there are two frustrations available. This can be considered frustration annihilation, or free radical combination. In contrast, edges between frustration-forbidden nodes, or a frustration-forbidden and a resonant node, will not result in any change in number of frustrations. In total, these can be considered the rules of frustration annihilation.

In addition to having charted frustration resonance locations, the number of frustrations can be easily deduced for TZ GNFs as well. The smallest flake has exactly one topological frustration, and every additional row adds exactly one more frustration. For instance, a TZ GNF with a side length of 2 benzene rings has one frustration (Fig. 1), a TZ GNF with a side of 3 rings has two frustrations [triangulene, Fig. 4, row (b), leftmost panel], and a TZ GNF with a side of 100 rings

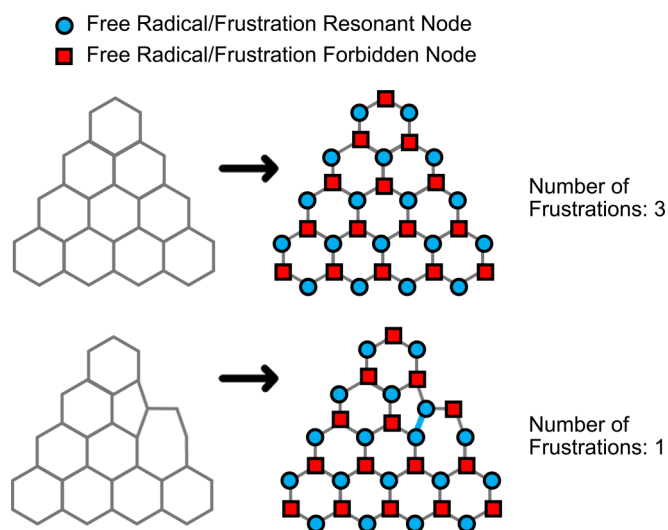


FIG. 3. (Color online) Annihilation of free radicals (matching of previously unmatched nodes) via STW defect. The bond rotation forces two resonant nodes into contact, reducing the number of frustrations from three to one (the lattice is also no longer bipartite). However, if another STW defect is introduced elsewhere, n_f will remain 1, as frustrations annihilate in pairs.

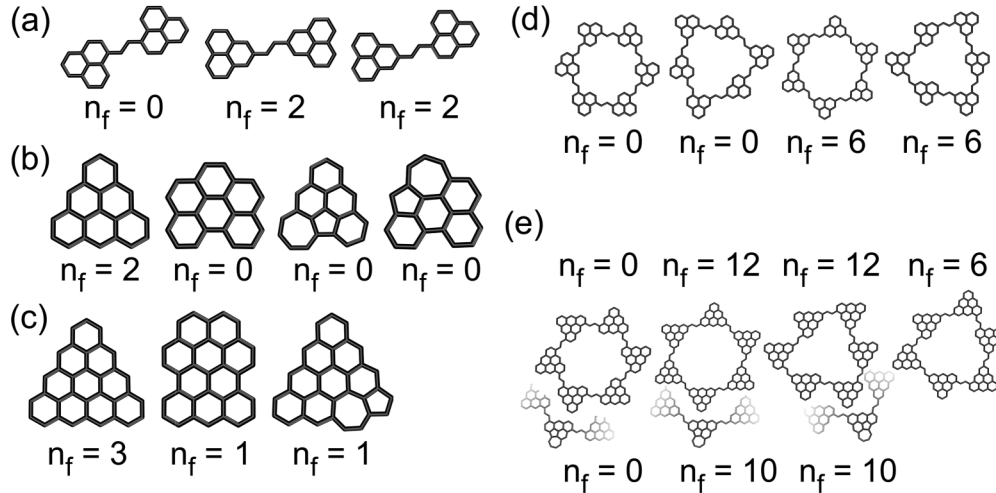


FIG. 4. Collection of all structures presented for analysis in this study. Edge carbon atoms are saturated with hydrogen atoms (not shown). n_f is the number of frustrations in each system. Every structure in a given row has the exact same number of interior and edge atoms. Row (a): The simplest structures demonstrating the rules of frustration annihilation. By connecting the TZ GNF subunits with a dimer, we avoid strong hydrogen-hydrogen repulsion from “coves.” Many more variants can be created by connecting TZ GNFs of various sizes in differing ways. Rows (b) and (c): A comparison of GNFs having zigzag and armchair edge types. Rows (d) and (e): Similar to row (a), but linking in a wheel- or gearlike fashion. The n_f values below row (e) are for the wheel structures that have a single STW defect on a single tip (as the subimage shows) while the values above are for the pristine structures.

has 99 frustrations. Clearly, from these simple rules and their predictable topological behavior, TZ GNFs make for great building blocks for constructing Kekuléan and non-Kekuléan allotropes. It must be stressed that all the concepts discussed in this paper, from frustration resonance nodes to the rules of frustration annihilation, can be applied to any arbitrary sp^2 hybridized hydrocarbon, not just those cut from graphene.

The established rules of frustration annihilation allow us to manipulate the number of frustrations in a structure while preserving the number of bonds and atoms. Thus, a non-Kekuléan structure can become Kekuléan with the appropriate topological changes. In the rest of this study we only present molecular structures, but the rules of frustration annihilation can be used to create one-dimensional (1D), 2D, and 3D analogs as well.

C. Quantifying frustration: u_f

Moving beyond the simple TZ-GNF family, we now present a methodology that will allow us to quantify the energetics of frustration in a predictive manner. To this end, we have employed open-shell DFT, which, in principle, includes frustration and other quantum mechanical properties, and the well-tested Tersoff-Brenner parametrized REBO classical force field for hydrocarbons which faithfully reproduces most structural properties while ignoring quantum mechanical effects beyond the possibility of bonding. The number of frustrations is calculated using the maximal matching technique presented above. By carefully constructing sterically similar but topologically different structures and comparing DFT to REBO energies, we can isolate the structural effects from the Kekuléan ones. This is done by contrasting allotropes with the same number and type of bonds. For instance, structures in every row in Fig. 4 have the same number of interior and edge carbons, preserving the number of carbon-carbon and carbon-hydrogen bonds. Careful consideration of edge

and aromatic effects must be made, but we posit that the majority of the energy difference within each row must be attributed to the Kekuléan character, and is therefore a measure of frustration.

As to be expected, raw REBO and DFT results have mediocre agreement, unless the structures to be compared have the same number of frustrations as the reference structure

TABLE I. Table that correlates the structures from Fig. 4 to the energies (in eV) of Fig. 5. The labels used in the first column correspond to a structure in Fig. 4. Every structure in a row has the same number of bonds, as well as interior and exterior sp^2 carbon atoms. All energies are shifted to a baseline structure in each row, and the baseline structure energies are not shown, as they would lie on the origin of Fig. 5. Δn_f is the number of frustrations in surplus of the base line’s Δn_f , E_{DFT} is the formation energy acquired from DFT, and E_{REBO} is the formation energy from REBO. E_{REBO}^* is the frustration corrected REBO energy and is expressed as $E_{\text{REBO}}^* = E_{\text{REBO}} + \Delta n_f \times u_f$.

Structure	Δn_f	E_{DFT}	E_{REBO}	E_{REBO}^*
(a) 2	2	0.316	0	0.3
(a) 3	2	0.279	-0.01	0.29
(b) 1	2	-1.18	-1.928	-1.628
(c) 1	2	-1.34	-1.71	-1.41
(d) 2	0	-0.297	-0.0587	-0.0587
(d) 3	6	0.685	-0.117	0.783
(d) 4	6	0.497	-0.059	0.31
(e) 2, top	12	1.67	-0.13	1.67
(e) 3, top	12	1.32	-0.07	1.73
(e) 4, top	6	0.792	-0.065	0.835
(e) 1, bottom	0	1.57	1.71	1.71
(e) 2, bottom	10	3.03	1.65	3.15
(e) 3, bottom	10	2.73	1.68	3.18

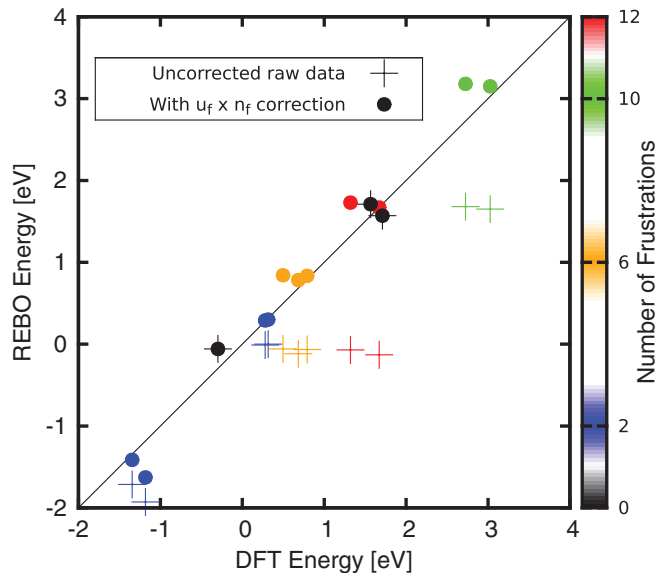


FIG. 5. (Color online) Plot of ODFT versus Tersoff-Brenner parametrized REBO energies with and without correction for frustration added to REBO. Crosses represent the uncorrected energies for all structures shown in Fig. 4. Explicit values are listed in Table I. A perfect correlation between the structures would yield a coefficient of determination (CD) of 1.0 (i.e., all the data points would fall on the bisector of the plot). Without correction, the CD is found to be 0.64. The dots represent the REBO energies corrected by $n_f \times u_f$, where n_f is provided on by the color of each data point and $u_f = 150$ meV is a fitting constant. n_f is the number of frustrations present in surplus of those of the reference structure (usually the reference has zero frustrations). The resulting CD is found to be 0.98, thereby highlighting a strong correlation. Note that the structures with $n_f = 0$ (Kekuléan) have overlapping crosses and dots, and lie very close to the bisector, confirming the known validity of REBO to accurately model Kekuléan structures.

(black dots and crosses on Fig. 5). While REBO predicts very similar energies between allotropes, ODFT detects deviations that grow as a function of the difference of n_f . By parametrizing a single value of energy of frustration u_f and multiplying it by n_f for each individual structure we see that the corrected REBO energy allows an excellent alignment with the DFT energy values, thereby validating our initial hypothesis for the cross-structural nature of the energy of frustration. A perfect fit would place all the points of Fig. 5 on the bisector (coefficient of determination $CD = 1.0$). Explicit values for the data presented in Fig. 5 are presented in Table I. Here, the linear fit for the actual data for all structures in Fig. 2 corresponds to $CD = 0.98$, with $u_f = 150$ meV. This fitting constant was derived for planar sp^2 hydrocarbons; while the energy of frustration will certainly penalize 3D structures as it is a topological and electronic effect, some variation in u_f should be expected.

This is a remarkable improvement in accuracy, considering that the learning set of structures is mediated by a broad array of Kekuléan and non-Kekuléan transition methods, namely, by benzene arrangements, dimer links, and STW defects. An example of a benzene arrangement-mediated Kekuléan transition is found in Fig. 4, row (b): The first two structures

are constructed completely with benzenes, and yet one is non-Kekuléan ($n_f = 1$) and the other is not ($n_f = 0$). Notably, the edge nature transitions from zigzag to partially armchair. A demonstration of a dimer link-mediated Kekuléan transition is found across row (a) of Fig. 4; n_f is being controlled across substructures connected by dimer links via the rules of frustration annihilation (as explicitly discussed in Fig. 2). Finally, the STW defect-mediated Kekuléan transition is seen in Fig. 4, row (b), between the first and third structures. The STW creates a nonbenzoid structure, but the rules of frustration annihilation are still valid, and there is a predicted reduction of n_f by two. By comparing the structures in each row of Fig. 4, combinations of these transitions can be seen, and thus u_f provides for a robust correction despite many independent topological variables.

u_f takes into account all aspects of the creation of the free radical, including having a nonsinglet state as the ground state and related spin effects. For instance, for the frustrated wheel structures of Fig. 4, row (e), $n_f = 12$, the ground-state energy state is a tredecuplet. This is important to note, as while a little energy is recouped compared to the paramagnetic state, overall the energy of frustration overpowers and destabilizes any beneficial effect from spin ordering. Additionally, theoretical calculations beyond the triplet states are often difficult to execute, but neglecting them would lead to incorrect ground-state energies in highly frustrated structures.

Graph theory has been used previously to calculate energy in the form of aromaticity, such as the method of conjugated circuits by Randić [23]. However, aromatic energy is ill-defined for non-Kekuléan structures [23], and we can consider these effects built into u_f . We should also note the rare cases where maximizing Clar sextets can lead to the formation of free radicals where normally there would be a perfect matching Kekulé configuration [24]. In that case, free radicals are created due to the favorable aromatic energy associated with the single and double bond arrangements. An additional benefit of graph theory is that while many methods (such as Clar's sextant) require benzoid structures, the concept of topological frustration is versatile enough to be applied to arbitrary nonbenzoid hydrocarbons, including, but not limited to, those with a STW defect.

IV. APPLICATIONS

A. Spintronics

At this point, we are ready to make an important statement about spintronics in hydrocarbons as a direct consequence of the duality between graph theory and frustration: The prospect of FM hydrocarbons is untenable without additional chemical variations such as doping.

Graphene-type structures (also known as benzoid structures) can be seen as having two hexagonal sublattices of nearest neighbors, often denoted by A and B [25]. Structures with unequal sublattices can exhibit spin ordering, as posited by Lieb's theorem [9]. For a bipartite system, this theorem can generally be stated as

$$S = \frac{1}{2}|N_A - N_B|, \quad (1)$$

where S is the total spin, and N_A and N_B are the number of atoms on the A and B sublattices. The connection between S and the number of frustrations is straightforward: Mismatched

bipartite structures with a net total spin are also guaranteed to have topological frustration, with the number of frustrations equaling $2S$ at the very least. This relation can be seen as the consequence that every sublattice atom in excess of its opposing sublattice will be missing a nearest neighbor for matching, by definition. Thus, when $S > 0$, an FM state will ensue with at least $2S$ frustrations (as seen in TZ GNFs). When $S = 0$, either a paramagnetic (PM) or antiferromagnetic (AFM) state will ensue, and the number of frustrations is entirely dependent on topology.

To differentiate between structures that have an FM or AFM ground state, Wang *et al.* proposed labeling structures that have $S > 0$ as class I GNFs, while structures that have $S = 0$ in total but have $S > 0$ for arbitrarily delineated substructures are called class II GNFs [26]. Class I GNFs are FM, with TZ GNFs as paragons. Class II GNFs have an AFM ground state, for example Clar's goblet (Fig. 6). However, in this classification scheme the differentiation of substructures for class II GNFs can be ambiguous; while it is obvious that the substructures for Clar's goblet are TZ GNFs, the division line placement is still a qualitative matter, and claims of AFM or PM properties must be supported by additional spin-ordering considerations.

More all-hydrocarbon AFM structure variants exist than are presented here, such as graphene nanoislands [27]. Spintronic structures provide for exciting avenues of research; Clar's goblet, and modifications of it, have been proposed for usage in various spin-based devices, such as logic gates [26].

B. Possible zigzag carbon nanotube growth suppression

The applications of assisting the design of carbon spintronics and increasing MD accuracy are immediate and obvious. However, keeping tabs of topological frustrations can lead to



FIG. 6. Clar's goblet. This pure hydrocarbon exhibits antiferromagnetism, which can be seen as arising from topological reasons. However, it is also destabilized by topological frustration [26]. Using a quantified approach, this presented structure has two topological frustrations.

other surprising discoveries as well, since the Kekuléan nature of graphs is often not obvious, especially in large structures.

In the course of applying the prescriptions of graph theory to many carbon structures, zigzag carbon nanotubes (CNTs) of odd chirality [such as (7,0), (9,0), etc.] were built with a single capped end and a single open end [28] and analyzed. We serendipitously discovered that structures of these specifications possess exactly one topological frustration. This observation can have key consequences in the understanding of root growth mechanism of CNTs. Note that in the experimental synthesis of CNTs using methods like metal-assisted arc-discharge and laser irradiation, it is observed that the formation of armchair CNTs is preferred over others, and that zigzag CNTs (ZZ CNTs) are somewhat scarce [29,30]. While these growth processes are more complex and have more interactions than a single-capped CNT in a vacuum, the principle still stands that the intermediate growth structures of odd chiral ZZ CNTs are at an energetic disadvantage from frustration, perhaps biasing them to not be formed.

V. CONCLUSIONS

By providing an unambiguous connection to link structure and configuration of double bonds using the concept of maximal matching, we managed to isolate the energy of frustration from other energy terms. With the use of maximal matching, structure manipulation, and the rules of frustration annihilation, it has been demonstrated that each individual topological frustration increases a sp^2 carbon system's energy of formation by approximately 150 meV, as obtained by ODFT (B3LYP). This trend holds true over multiple size scales and allotropes.

Variations in this energy can be seen as a consequence of edge-edge interactions and aromatic energies. While it remains difficult to completely isolate the effects of topological frustration from all other quantum mechanical phenomena, the magnitude of the energy shift suggests that the change in energy of such structures mainly arises from frustration. It should be noted that because classical MD does not detect any quantum mechanical-based topological effect, it ignores topological frustration altogether. However, the findings presented herein provide a simple and numerically tractable way to add energy penalties related to the frustration to the overall energy function. This approach allows an important improvement of quantitative validity for classical MD systems.

By measuring discrete frustrations, not only can the stability be measured in terms of Kekuléan vs non-Kekuléan, but also within non-Kekuléan vs non-Kekuléan by comparing number of frustrations. With this tool, the feasibility of virtual design of nanostructures and transformation pathways can be quickly gauged, and the accuracy of MD simulations improved. Even if an arbitrary structure is non-Kekuléan, careful consideration of graph theory can yield alternate, yet similar, structures that greatly reduce the number of frustrations. Applications to many fields are possible, especially when modeling structure growth and reactivity.

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