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Kekulénoid Addition Patterns for Fullerenes and Some Lower Homologs

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The challenging problem of the enumeration and generation of addition patterns for fullerenes such that the remnant π-network has a Kekulé structure (i.e., a nearest neighbor pairing pattern) is studied. A methodology to generate (and thence also to enumerate) these Kekulénoid addition patterns is described, and applied to several fullerenes of up to 36 carbons. Pólya-theoretic (coloring) pattern counts which ignore Kekulé structures are found to be much larger than the Kekulénoid-restricted counts. Evidence is marshaled for simple yet general approximate "asymptotic-flavored" formulas for the various counts. As a consequence, the number of Kekulénoid addition patterns C_NH_{2m} for buckminsterfullerene C_{60} is estimated. Overall, this is but $\approx$0.1% of the Pólya-theoretic addition pattern counts for all numbers of addition sites.

Since the 1985 article of Kroto et al.[1] fullerenes have received much attention, and compounds formed from them as well. There was some theoretical consideration of the possibility of C_{60}-buckminsterfullerene even before Kroto's seminal paper, with one of the least noted works (which though dated 1986 must have been completed earlier) being that of Professor Haruo Hosoya,[2] who determined C_{60}'s so-called "acyclic" polynomial. Indeed, this incidentally determines the number of Kekulé structures for C_{60}, though a later work[3] (that focused further on "conjugated-circuits" counts) is sometimes credited as the first one to make this enumeration. With the advent of fullerenes, compounds formed from them naturally become of interest. Now, hydrogen, halogens, and numerous other moieties have been experimentally added to fullerenes, thereby eliminating some of the π-network conjugation from the system. For a review of these addition compounds see, e.g., Refs. 4–7. On the theoretical side too, there has been much work on such species, starting perhaps first with H. Hosoya's enumeration[8] of hypothetically conceivable addition patterns to C_{60}–$\mathcal{I}_h$. Thereafter, Fujita[9] amended this enumeration, accounting for various subsymmetries for the resultant addition products, and there followed many further related treatments[10–19] of fullereneic structures. Indeed, all these enumerative efforts were carried out with the use of the fundamental Pólya-theoretic counting methods, as are described in Pólya's original paper,[20] which has also been translated into English[21] along with an up-dating chemically focused review. In addition, descriptions of Pólya's theory are found in numerous mathematical combinatorics texts, often with little or no chemical connection, though one exception in this regard is the comprehensive text of Kerber.[22] A chemically oriented text is that of Knop et al.,[23] while Fujita[24] and El-Basil[25] provide chemically focused reviews of a refinement of Pólya's theory to enumerate isomers of different symmetries of the final substitution (or addition) patterns. Still, all this formal "Pólya" theory has some short-comings—particularly in the present context, since radicaloid addition patterns are included in the counts. That is, the addition patterns counted by standard combinatorial methods are simply the symmetry inequivalent ways to color the vertices of a fullerene polyhedron, with a set of colors taken in correspondence with the different types of addends. In such an approach all colorings are presumed independent of whether the remnant π-network of sites (where there are no addends) admits a Kekulé structure (here viewed as a classical π-bonding pattern with π-bonds solely between neighbor sites). Indeed classically, if a conjugated π-network does not admit a Kekulé structure, it then is viewed very likely to be a reactive radical, and typically is not observed (unless there is some novel circumstance, say with the radical site "shielded", as in Gomberg's[26] classical *tris*-biphenyl-methyl). Because of the importance of *Kekulé structures* (also more formally a partitioning of sites into neighbor pairs) for π-network graphs, such graphs with at least one Kekulé structure are termed *Kekulénoid*. In the case of acyclic polyenes, the problem of identifying the Kekulénoid subset for enumeration (and further treatment) can be neatly resolved[27] within the context of Pólya theory (if properly formulated), though in this case there also was earlier work[28–31] which disregarded the radicality problem associated with the absence of Kekulé structures. But the resolution found for acyclics does not seem to carry neatly over to the case of fullerenes.

At the same time it should be emphasized that the Pólya-theoretic counts do in themselves give chemically relevant information, say for substitution patterns at aliphatic polyhedral structures. In particular, for dodecahedrane $C_{20}H_{20}$, as dramatically synthesized[32,33] by Paquette's group, there are a number of ways to substitute the H atoms, by say F, and these patterns in classical chemistry would be precisely as counted by

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Pólya's enumeration. Thus several earlier enumerations, rather than counting fullerene addition patterns, really are better viewed as counting substitution patterns for fully hydrogenated aliphatic fullereneic analogues. Overall Pólya's theory offers a powerful technique for combinatorial enumeration, with extensions to identify subsymmetries, as reviewed by Fujita[24] and by El-Basil,[25] and also with extensions to property estimation, as discussed in Refs. 34 and 35, and a few further references therein. Yet further for a fixed skeleton, isomer enumeration may be considered just a first step of a more comprehensive study of the substitution-reaction network, which may be viewed[36] as a partially ordered set. Evidently there are a number of combinatoric enumerative problems[37] in chemistry which seem to be refractive to Pólya-theoretic methods, and one of them seems to be the present problem of the enumeration of Kekulénoid addition patterns to fullerenes (or other cycle-containing conjugated π-networks).

Here, as a step in the development of a general theoretical combinatoric chemistry, we turn attention to the identification and enumeration of fullereneic addition patterns. Special attention is directed to the case of Kekulénoid addition patterns, first using a brute force approach which explicitly generates each addition pattern. Section 1 describes this approach, and section 2 gives numerical counts for C_{20}–$\mathcal{I}_h$, C_{24}–$\mathcal{D}_{6d}$, C_{26}–$\mathcal{D}_{3h}$, C_{28}–$\mathcal{T}_d$, C_{30}–$\mathcal{D}_{5h}$, C_{32}–$\mathcal{D}_3$, C_{36}–$\mathcal{D}_{6h}$, and a few other related smaller polyhedral (non-fullereneic) structures. The enormous numbers of possibilities presently tend to limit this approach from proceeding beyond C_{36} (where there turn out to be around 40 million Kekulénoid addition patterns). Though the numbers (of Kekulénoid addition patterns) are large, the numbers of addition patterns as counted by Pólya enumeration theory are greater, so that a simple manner of quantitative estimation is developed in section 3. The ratio of the Kekulénoid to the Pólya-theoretic counts seems to decrease exponentially as a function of the total number N of π-centers in the parent fullerene, so that by the time one reaches buckminsterfullerene C_{60}–$\mathcal{I}_h$ our asymptotic formulas predict that around 0.1% of the Pólya-theoretic coloring patterns correspond to Kekulénoid addition patterns. Some study is made of the manner of variation of the probability of Kekulénoidicity as a function of the fraction of fullerene π-centers to which an addend is attached. Finally, some partial results for C_{60}–$\mathcal{I}_h$ are obtained, and some concluding discussion is presented.

1. Generation of Kekulénoid Addition Patterns

Two different independent schemes are used to identify Kekulénoid addition patterns on N-site Kekulénoid π-networks C_N. Both schemes generate lists

$$S_m = \{S_m(1), S_m(2), \ldots, S_m(n_m)\} \tag{1}$$

of inequivalent Kekulénoid addition patterns $S_m(i)$ with $2m$ addends (which for simplicity we assume are H atoms). That is, these lists identify the different classically non-radicaloid addition patterns. Each $S_m(i)$ may be viewed as a fullereneic subgraph comprised from the sites without addends. The fully hydrogenated C_NH_N fullerene is understood to be non-radicaloid, so that it is counted as Kekulénoid. The remnant π-network graphs at various partial degrees of hydrogenation may be treated by different chemical graph-theoretic methods, e.g., computing their Hückel eigenvalue spectrum or the number $K(S_m(i))$ of their Kekulé structures. In fact, one of these schemes generates the counts $K(S_m(i))$ integral to the generation, with different methods of computation possible, say either that of Heilbronner[38] or that of Kasteleyn.[39,40] The algorithm of Kasteleyn offers some advantages, e.g., with slight modification[41] it can efficiently compute conjugated-circuits resonance energies. The two schemes in fact are applicable beyond fullerenes (to ordinary benzenoids, and, for the Heilbronner method, to bucky-tori).

In the first *additive* scheme, one starts at the 0th stage with the unadded π-network C_N, and at the mth stage proceeds to add pairs of addends to all possible Kekulénoid C_NH_{2m} patterns in all possible ways eliminating duplicate addition patterns and checking to see whether each is Kekulénoid. This scheme is summarized in Fig. 1. With $N - 2m + 2$ unadded sites at stage m, there evidently are $(N - 2m + 2)(N - 2m + 1)/2$ ways to delete pairs of sites in step A, and in the next step duplicate occurrences of equivalent patterns so generated are to be eliminated, by a means equivalent to that used for our second scheme and explained after the next paragraph. In step C, Kekulé structures are to be counted or at least their existence is to be checked.

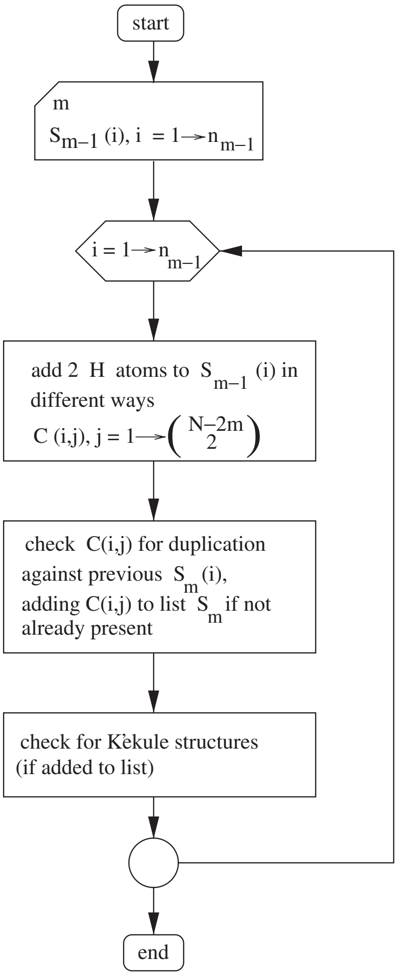

Fig. 1. Flow chart for the additive scheme generating S_m from S_{m-1}.

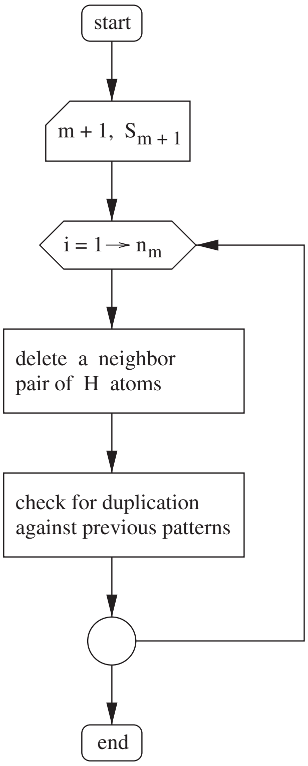

Fig. 2. Flow chart for the subtractive scheme generating S_m from S_{m+1}.

In the second *subtractive* scheme, one starts at the 0th stage with the completely hydrogenated network C_NH_N, and at the mth stage proceeds to delete neighbor pairs of H atoms in all possible Kekulénoid C_NH_{N-2m+2} patterns, with the scheme as indicated in Fig. 2. In deleting only neighbor pairs of H atoms one guarantees that the resultant C_NH_{N-2m} pattern must be Kekulénoid—because there is a Kekulé structure for C_NH_{N-2m} with one double bond at the position of the two deleted H atoms and $m-1$ double bonds in the positions of those of the parent Kekulénoid C_NH_{N-2m}. Moreover, no Kekulénoid C_NH_{N-2m} patterns are missed by this procedure—because each Kekulénoid C_NH_{N-2m} pattern would be obtained from C_NH_N through the deletion of a sequence of neighbor H-atom pairs corresponding to the (neighbor) paired atoms in any Kekulé structure of C_NH_{N-2m}. Of course, one again generally obtains each addition pattern more than once, so that duplicates need to be eliminated at each stage. This subtractive scheme has an advantage over the additive scheme in that one never generates non-Kekulénoid addition patterns, and one need not expend effort on checking for Kekulénoidicity. But sometimes there are so many addition patterns (as for C_{60}–$\mathcal{I}_h$) that neither scheme has been able to be completed for all m.

In the elimination of duplicate addition patterns, we presume the parent C_N graph and its associated symmetry group $\mathcal{A}(C_N) = \mathcal{A}$. The sites are labeled with integers $1 \to N$ and the elements of $\mathcal{A}$ are viewed as permutations on these labels. It is convenient to introduce a code for each $S_m(i)$: to each $S_m(i)$ identify an increasing sequence of the numbers $n_1, n_2, \ldots, n_{2m}$ of the sites of C_N which are occupied by an H atom in $S_m(i)$. Now one sees that given any code (i.e., an $S_m(i)$) an application of any $P \in \mathcal{A}$ to the site labels of the code yields back another code (if the labels are arranged to be in increasing order) for a symmetry equivalent pattern—and in fact this yields all symmetry equivalent patterns. From amongst all these symmetry-equivalent codes we specify one as *canonical*, namely the one which is lexicographically earliest. That is, the code $n_1, n_2, \ldots, n_{2m}$ is earlier than the code $n'_1, n'_2, \ldots, n'_{2m}$ if and only if when read as a base-N number $n_1, n_2, \ldots, n_{2m}$ is smaller than $n'_1, n'_2, \ldots, n'_{2m}$. Thus from each pattern $S_m(i)$ one can readily generate all the equivalent patterns and keep only the canonically coded one in a list of canonical codes, each corresponding to a symmetry inequivalent addition pattern.

2. Exact Numerical Results

One or both of the generation schemes have been applied to yield complete lists for several fullerenes: C_{20}–$\mathcal{I}_h$, C_{24}–$\mathcal{D}_{6d}$, C_{26}–$\mathcal{D}_{3h}$, C_{28}–$\mathcal{T}_d$, C_{30}–$\mathcal{D}_{5h}$, C_{32}–$\mathcal{D}_3$, and C_{36}–$\mathcal{D}_{6h}$. Schlegel diagrams for the six of these seven fullerenes that were used in fitting are indicated in Fig. 3. Overall total addition-pattern counts for both Kekulénoid and non-Kekulénoid patterns are given in Table 1. Counts as a function of the number $2m$ of additions are reported in Table 2. Results for all Pólya-theoretic coloring patterns are also either already available[12,13] for C_{20}–$\mathcal{I}_h$ (as well as some other fullerenes) or obtainable[20–23] via the standard Pólya-theoretic enumeration procedure. Further, the resultant isomers for C_{20}–$\mathcal{I}_h$ have been categorized[13,16] according to the symmetry of the substitution pattern. Here for C_{20}–$\mathcal{I}_h$ the computer time we used was negligable (i.e., a few minutes), whereas for C_{36}–$\mathcal{D}_{6h}$ we needed 3 days of time, so that complete generation for larger fullerenes was deemed to require excessive time.

The C_{20} species is the smallest possible fullerene and has been subject of several ab initio quantum chemical computations. Even at the Hückel level C_{20} has an open-shell ground state, so that it should undergo a distortion to a lower symme-

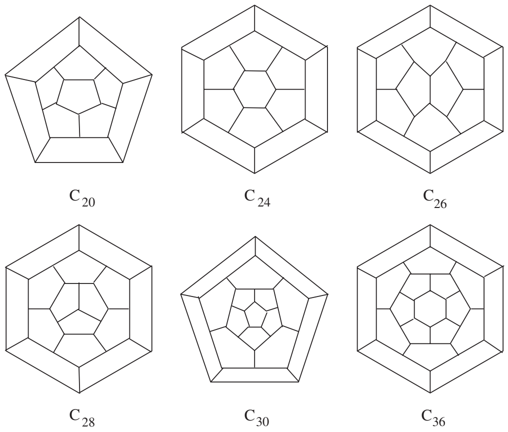

Fig. 3. Fullereneic Schlegel diagrams such as to manifest a high rotational symmetry about an axis normal to the plane and through the center ring. For C_{20}–$\mathcal{I}_h$ there are similar 5-fold symmetry axes through every opposite pair of pentagons; for C_{28}–$\mathcal{T}_d$ there are similar 3-fold axes through the centers of each of the four hexagons; and for C_{24}–$\mathcal{D}_{6d}$, C_{26}–$\mathcal{D}_{3h}$, C_{30}–$\mathcal{D}_{5h}$, and C_{36}–$\mathcal{D}_{6h}$ there is only one high-symmetry axis through the central polygon.

try, say $\mathcal{T}_d$. But for our isomer enumerations we still consider an $\mathcal{I}_h$ symmetry, which is to say that we presume that any distortion is realized in a fluxional manner. The C_{28} structure is believed[44] to have been observed in a doped form, and there is a considerable experimental work[45] on the C_{36} structure. That the parent fullerene is Kekulénoid is a general result[42,43] which in fact applies to all polyhedral graphs with all vertices of degree 3. It is clear that, for any hydrogenated species with an odd number of H atoms, there can be no Kekulé structure. On the other hand, it has been proved[43] that every di-hydrogen fullerene C_NH_2 (for an arbitrary fullerene parent C_N) is Kekulénoid, and this is bourne out for the examples in the table. It is generally true that at C_NH_4 there must be at least one non-Kekulénoid structure: e.g., one where H occurs at the three neighbors of a non-H-added site. This occurrence of non-Kekulénoid patterns is also seen from the table, and it is also seen that the Kekulénoid addition patterns are ever smaller fractions of the total Pólya-theoretic possibilities, as the number of H atoms increases up through $2m \approx 7N/10$. This is in fact rather plausible, since with increasing numbers of H atoms the probability of the occurrence of some locally non-Kekulénoid substructure may be imagined to increase, at least for a while. Further, for a given fullerene, the overall fraction over all numbers of H-atoms diminishes as the number N of

Table 1. Number of Kekulénoid and Non-Kekulénoid Addition Patterns for Various Polyhedral Skeletons

N	$\mathcal{A}(C_N)$	$\lvert\mathcal{A}(C_N)\rvert$	$\#^{(K)}(C_N)$	$\#^{(0)}(C_N)$
4	$\mathcal{T}_d$	24	3	3
8	$\mathcal{O}_h$	48	9	15
12	$\mathcal{D}_{3d}$	12	101	226
16	$\mathcal{D}_{4d}$	16	623	2259
20	$\mathcal{I}_h$	120	929	4788
24	$\mathcal{D}_{6d}$	24	40675	352786
26	$\mathcal{D}_{3h}$	12	253640	2805168
28	$\mathcal{T}_d$	24	401173	5611040
30	$\mathcal{D}_{5h}$	20	1516791	26886152
32	$\mathcal{D}_3$	6	15999770	357947392
36	$\mathcal{D}_{6h}$	24	40068232	1810294952

Table 2. Number of Kekulénoid and Non-Kekulénoid Addition Patterns for Fullerenes from Table 1 as a Function of the Extent of Hydrogenation

m	$\frac{\#^{(K)}(C_{20})}{\#^{(0)}(C_{20})}$	$\frac{\#^{(K)}(C_{24})}{\#^{(0)}(C_{24})}$	$\frac{\#^{(K)}(C_{26})}{\#^{(0)}(C_{26})}$	$\frac{\#^{(K)}(C_{28})}{\#^{(0)}(C_{28})}$	$\frac{\#^{(K)}(C_{30})}{\#^{(0)}(C_{30})}$	$\frac{\#^{(K)}(C_{32})}{\#^{(0)}(C_{32})}$	$\frac{\#^{(K)}(C_{36})}{\#^{(0)}(C_{36})}$
0	$\frac{1}{1}$	$\frac{1}{1}$	$\frac{1}{1}$	$\frac{1}{1}$	$\frac{1}{1}$	$\frac{1}{1}$	$\frac{1}{1}$
2	$\frac{5}{5}$	$\frac{19}{19}$	$\frac{37}{37}$	$\frac{24}{24}$	$\frac{33}{33}$	$\frac{91}{91}$	$\frac{41}{41}$
4	$\frac{53}{58}$	$\frac{462}{489}$	$\frac{1208}{1316}$	$\frac{868}{928}$	$\frac{1414}{1467}$	$\frac{5888}{6060}$	$\frac{2544}{2608}$
6	$\frac{200}{371}$	$\frac{3772}{5775}$	$\frac{13239}{19468}$	$\frac{11413}{16044}$	$\frac{22803}{30173}$	$\frac{117999}{151327}$	$\frac{69468}{82123}$
8	$\frac{303}{1135}$	$\frac{9843}{31034}$	$\frac{45839}{130942}$	$\frac{50397}{130545}$	$\frac{124829}{294255}$	$\frac{812992}{1753975}$	$\frac{686228}{1264902}$
10	$\frac{225}{1648}$	$\frac{12355}{82358}$	$\frac{73042}{444074}$	$\frac{100156}{549060}$	$\frac{304749}{1506051}$	$\frac{2434734}{10754304}$	$\frac{2963198}{10603572}$
12	$\frac{103}{1135}$	$\frac{8883}{113434}$	$\frac{65625}{806746}$	$\frac{111202}{1271126}$	$\frac{412384}{4331275}$	$\frac{3975455}{37636214}$	$\frac{6841827}{52182175}$
14	$\frac{30}{371}$	$\frac{3961}{82358}$	$\frac{36964}{806746}$	$\frac{77276}{1675584}$	$\frac{349480}{7279821}$	$\frac{4036818}{78578390}$	$\frac{9707059}{158230972}$
16	$\frac{7}{58}$	$\frac{1168}{31034}$	$\frac{13644}{444074}$	$\frac{35711}{1271126}$	$\frac{197618}{7279821}$	$\frac{2745327}{100186668}$	$\frac{9219821}{304568066}$
18	$\frac{1}{5}$	$\frac{224}{5775}$	$\frac{3403}{130942}$	$\frac{11254}{549060}$	$\frac{77451}{4331275}$	$\frac{1302438}{78578390}$	$\frac{6163678}{378213016}$
20	$\frac{1}{1}$	$\frac{33}{489}$	$\frac{565}{19468}$	$\frac{2457}{130545}$	$\frac{21263}{1506051}$	$\frac{440475}{37636214}$	$\frac{2992436}{304568066}$
22		$\frac{3}{19}$	$\frac{67}{1316}$	$\frac{370}{16044}$	$\frac{4146}{294255}$	$\frac{106695}{10754304}$	$\frac{1071252}{158230972}$
24		$\frac{1}{1}$	$\frac{5}{37}$	$\frac{40}{928}$	$\frac{557}{30173}$	$\frac{18449}{1753975}$	$\frac{285376}{52182175}$
26			$\frac{1}{1}$	$\frac{3}{24}$	$\frac{58}{1467}$	$\frac{2214}{151327}$	$\frac{56173}{10603572}$
28				$\frac{1}{1}$	$\frac{4}{33}$	$\frac{184}{6060}$	$\frac{8201}{1264902}$
30					$\frac{1}{1}$	$\frac{9}{91}$	$\frac{851}{82123}$
32						$\frac{1}{1}$	$\frac{73}{2608}$
34							$\frac{4}{41}$
36							$\frac{1}{1}$

sites increases. Again this seems plausible, since with increasing N one can again imagine that with more localities there would be more possibilities for occurrences of locally non-Kekulénoid substructures. At $m = N - 2$, it is clear that there generally must be some non-Kekulénoid addition patterns—i.e., whenever the two unadded sites are not nearest neighbors.

Generally one can understand some bounds on the enumerations. For the Pólya-theoretic counts $\#_M^{(0)}(\mathrm{C}_N)$ for adding M hydrogens, one readily sees that the number of ways of placing M (indistinguishable) objects at N (distinguishable) sites must be an upper bound to $\#_M^{(0)}(\mathrm{C}_N)$ as various sites and that sets of sites are equivalent because of the group symmetry of C_N. Notably, in terms of the order $|\mathcal{A}|$ of the symmetry group $\mathcal{A}$ of C_N, one may further identify rigorous upper and lower bounds, thusly

$$\binom{N}{M} \geq \#_M^{(0)}(\mathrm{C}_N) \geq \binom{N}{M}/|\mathcal{A}|. \tag{2}$$

Here the upper bound is simply the number of substitution patterns in the absence of any symmetry, while for the lower bound we note that the symmetry group can induce no more than $|\mathcal{A}|$ equivalences amongst structures which would otherwise be distinguishable. Somewhat similar but less confining rigorous bounds can be argued for the counts $\#_M^{(K)}(\mathrm{C}_N)$ of Kekulénoid addition patterns with an even number $M = 2m$ of H atoms:

$$\#_{2m}^{(0)}(\mathrm{C}_N) \geq \#_{2m}^{(K)}(\mathrm{C}_N) \geq \binom{N/2}{m}/|\mathcal{A}| \tag{3}$$

(while of course $\#_M^{(K)}(\mathrm{C}_N) = 0$ if M is odd). Here the lower bound is understood upon considering a Kekulé structure of C_N and noting that: if at the positions of m of the $N/2$ different π-bonds of this Kekulé structure one adds m pairs of H atoms, then one must obtain a Kekulénoid addition pattern $\mathrm{C}_N\mathrm{H}_{2m}$. As already noted such a parent Kekulé structure of the C_N always exists, and in fact there are[46] at least $[3(N+2)/4]$ Kekulé structures. These additional Kekulé structures generally indicate that the lower bound in Eq. 3 is not expected to be very tight. These various bounds are all satisfied in Table 2.

Finally, several other fullerenes with the same number of carbons as those already noted were also treated. This includes one other (of $\mathcal{D}_2$ symmetry) at $N = 28$, two others (both of $\mathcal{C}_{2v}$ symmetry) at $N = 30$, and five others (of symmetries $\mathcal{C}_2$, $\mathcal{C}_2$, $\mathcal{D}_2$, $\mathcal{D}_{3h}$, and $\mathcal{D}_{3d}$) at $N = 32$. These additional results seem fully consistent with our already noted modest regularities. Overall, our results support the contention that for any fullerene the fraction of Kekulénoid addition species diminishes rapidly with system size. Further, one can attempt to quantify some of the qualitative rationalizations of the behavior observed in the tables, as is done in the next two sections.

3. Asymptotics for All Addition Isomers of a Fullerene

Empirical approximations might be sought so as to enable extrapolations to larger fullerenes, such as C_{60}, C_{70}, and beyond. Firstly, one might attempt to approximate relative total counts $\#^{(K)}(\mathrm{C}_N)$ of addition patterns for Kekulénoids, as gauged against the total Pólya-theoretic counts $\#^{(0)}(\mathrm{C}_N)$ for the different fullerenes C_N. Both counts are seen to increase rapidly with N, even exponentially fast as is implied by the lower bounds of Eqs. 2 and 3. But we do not imagine that the exponential growth factor is the same for both. Thus we might guess

$$\frac{\#^{(K)}(\mathrm{C}_N)}{\#^{(0)}(\mathrm{C}_N)} = A \cdot \kappa^N. \tag{4}$$

A test is made of this for the 6 fullerenes and 4 additional polyhedral structures with all sites of degree 3. Schlegel diagrams for these additional hypothetical "sub-fullereneic" polyhedral structures with degree-3 vertices and $N = 4$, 8, 12, and 16 are shown in Fig. 4. The C_{12} and C_{16} species fit very neatly into a sequence C_{4p} of which the C_{20} and C_{24} members are our already included fullerenes: in this sequence there is a p-fold axis contained in two p-sided polygons surrounded by a double row of $2p$ pentagons. To determine whether the relation of (4) is followed, one might make a plot of

$$\ln \frac{\#^{(K)}(\mathrm{C}_N)}{\#^{(0)}(\mathrm{C}_N)} \quad \text{vs} \quad N \tag{5}$$

whence, if the hypothesized relation holds, a linear plot is anticipated. Thus in Fig. 5 such a plot is made, and it is evidently roughly linear, with the displayed straight line chosen to fit the larger-cage data ($N \geq 12$) with the idea that there is a sort of asymptotic ($N \to \infty$) behavior. This straight line corresponds to

$$\kappa \approx 0.885 \quad \text{and} \quad A \approx 2.075. \tag{6}$$

Thence (as anticipated) the liklihood of Kekulénoidicity evidently diminishes exponentially fast, with N. The fitting is made without the use of the C_{32} cage, which instead we use as a check on the accuracy of our surmised and fitted asymptotic form. The above values of A and κ were used to predict

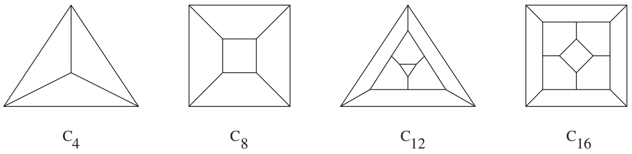

Fig. 4. Schlegel diagrams for four additional polyhedral structures considered: the tetrahedron C_4; the cube C_8; a C_{12} structure; and a C_{16} structure. The respective symmetry groups are $\mathcal{T}_d$, $\mathcal{O}_h$, $\mathcal{D}_{3d}$, and $\mathcal{D}_{4d}$.

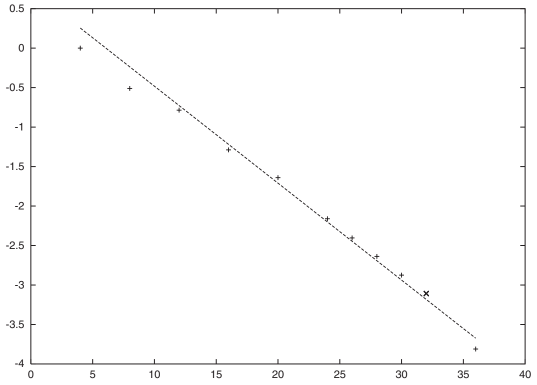

Fig. 5. Logarithmic plot for the relative total numbers of Kekulénoid addition patterns for various polyhedral skeletons.

the value of $\#^{(K)}(C_{32})/\#^{(0)}(C_{32})$ for all six isomers of C_{32}, and the results were compared with the exact enumerations; the relative error was found not to exceed 7%.

A test can be made of an even stronger assumption: that of exponential growth rates for the total number of addition patterns $\#^{(0)}(C_N)$ and $\#^{(K)}(C_N)$ individually. Here, one may anticipate that the overall exponential N-dependence might be modified by the fullerene skeleton (automorphism) symmetry group, say $\mathcal{A}(C_N) = \mathcal{A}$. That is, in comparing two fullerenes of the same number of sites, the one with a larger group should have more equivalences amongst addition patterns, and thence fewer (inequivalent) addition patterns. Thus, anticipating that the number of such equivalences should scale as the order $|\mathcal{A}|$ of $\mathcal{A}(C_N)$, we consider the possibility that

$$\#^{(*)}(C_N) \approx B_* \cdot \kappa_*^N \cdot |\mathcal{A}|, \quad * = 0 \quad \text{or} \quad K. \tag{7}$$

Clearly this is a stronger assumption than of Eq. 3, and as already indicated in Eq. 2 the exponential aspect must be asymptotically correct for the Pólya-theoretic counts ($* = 0$). A test can be made with plots of

$$\ln\{\#^{(*)}(C_N) \cdot |\mathcal{A}|\} \quad \text{vs} \quad N \tag{8}$$

whence linearity occurs if the anticipated relation of Eq. 7 applies. Such a plot is made in Fig. 6, from which it is seen that either with Kekulénoidicity ($* = K$) or without ($* = 0$) there is reasonable linearity. Making a linear least-squares fit, we obtain

$$\begin{aligned} \kappa_0 &\approx 1.9921, \quad & B_0 &\approx 0.6017, \\ \kappa_K &\approx 1.763, \quad & B_K &\approx 1.2485. \end{aligned} \tag{9}$$

This is the same fitting scheme as used for the results of Eq. 6, with which the present results compare favorably: κ_K/κ_0 is equal to $\kappa \approx 0.885$ of Eq. 6, and even the more sensitive ratio B_K/B_0 is equal to $A \approx 2.075$ of Eq. 6. The fitted result of $\kappa_0 \approx 1.9921$ is reasonably close to what Eq. 2 implies must be the exact result of $\kappa_0 = 2$, and thereby also gives us an estimate of the error in κ_K say of 0.4%. Again, the above values of κ_0, B_0, κ_K, and B_K were used to predict $\#^{(0)}(C_{32})$ and $\#^{(K)}(C_{32})$ for all isomers of C_{32}, and the relative errors were found to be below 5% for $\#^{(0)}(C_{32})$ and around 2% for $\#^{(K)}(C_{32})$.

Finally [Fig. 6], utilization of our results for the several other fullerenes C_N with the same number of carbons as one of those already indicated would likely make little difference. The values for their entries on the plots of Figs. 5 and 6 lie very nearly on top of the data points already recorded there for our already displayed structures.

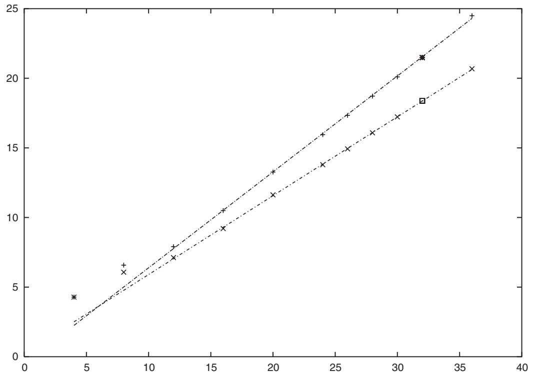

Fig. 6. Logarithmic plot for the symmetry-modified total counts of addition patterns.

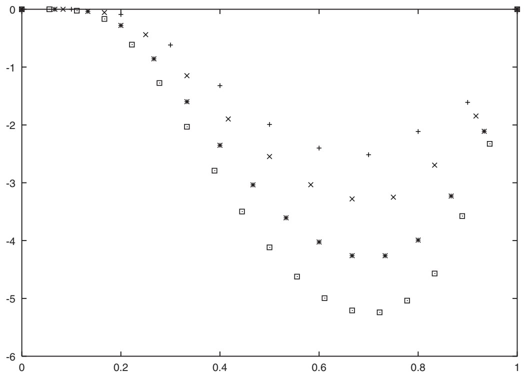

Fig. 7. Logarithmic plot for the relative numbers of Kekulénoid addition patterns as a function of the extent of hydrogenation, for the fullerenes of $N = 20$, 24, 30, and 36 sites, from top to bottom respectively.

4. Asymptotics as a Function of the Extent of Hydrogenation

We seek to extend our asymptotic forms to estimate the counts $\#_M^{(*)}(C_N)$ of the numbers of isomers with a given number M of H atoms. In Fig. 7 is shown the logarithm of the relative abundance of Kekulénoid patterns among all addition patterns as a function of the extent of hydrogenation. That is, we plot $\ln\{\#_M^{(K)}(C_N)/\#_M^{(0)}(C_N)\}$ vs M/N. One can see that the minimum is consistently achieved when ~70% of sites are hydrogenated. From this plot, one perceives what seems to be a sort of general dependence for the fraction $F(M,N)$ of Kekulénoid addition patterns at a given M and N:

$$F(M,N) \equiv [a + b\ln(N) + cN] \cdot f(M/N) \tag{10}$$

with all the M-dependence accounted for in the presumed universal function $f(x)$. We here use the form

$$f(x) = (1 - d\,\mathrm{e}^{hx})^2(x-1). \tag{11}$$

Least-squares fitting for the parameters a, b, c, d, and h in this expression gives

$$\begin{aligned} &a \approx -19.6021, \quad b \approx -19.033, \quad c \approx 12.8094, \\ &d \approx 0.98106, \quad h \approx 0.311742 \end{aligned} \tag{12}$$

with the resultant fitted $F(M,N)$ vs M/N plots given in Fig. 8. A reasonable agreement is found between the data and the fitted curves. As a consequence, predictive estimates may be made for numbers of Kekulénoid addition patterns for fullerenes too big to count the patterns exactly.

5. Buckminsterfullerene C_{60}–$\mathcal{I}_h$

As already noted,it is currently beyond our abilities to generate a comprehensive listing of the Kekulénoid addition patterns in the case of buckminsterfullerene. However, with either only a few H atoms (say $M \leq 12$) or a few non-H-added sites (say $N - M \leq 24$) the generative techniques of section 1 may be applied. This we have done with results reported in Table 3.

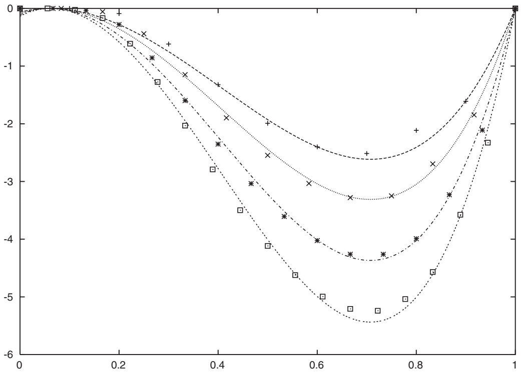

Fig. 8. Logarithms of relative numbers of Kekulénoid addition patterns together with fitted functions $f(M/N)$ for fullerenes of $N = 20$, 24, 30, and 36 sites, from top to bottom, respectively.

Table 3. Number of Computed ($\#^{(K)}(C_{60}H_M)$) and Predicted ($\#^{(K)}_{pred}(C_{60}H_M)$) Kekulénoid Addition Patterns and the Number of All Addition Patterns for Various Degrees of Hydrogenation of Buckminsterfullerene

M	$\#^{(K)}(C_{60}H_M)$	$\#^{(K)}_{pred}(C_{60}H_M)$	$\#^{(0)}(C_{60}H_M)$
0	1	1	1
2	23	22	23
4	4158	4183	4190
6	400626	382914	418470
8	18483084	15808184	21330558
10	432151597	336966585	628330629
12	5177219075	4090763022	11661527055
14		30348930076	144549869700
16		145193416843	1246738569480
18		467691095556	7708584971055
20		1051598504341	34932048763560
22		1702691118887	117952355252550
24		2040614783626	300436595453640
26		1855562553278	582384767014701
28		1309433785171	864332935668892
30		732151275418	985538239868528
32		330633379486	864332935668892
34		122738145417	582384767014701
36	57674928381	38061063007	300436595453640
38	17285102219	10001933176	117952355252550
40	4316429758	2254940925	34932048763560
42	895876888	440419451	7708584971055
44	153799119	74995820	1246738569480
46	21670333	11152488	144549869700
48	2479248	1440990	11661527055
50	226574	159315	628330629
52	16324	14602	21330558
54	908	1046	418470
56	46	53	4190
58	2	2	23
60	1	1	1

Further, with the asymptotic results of the preceding section, we can make estimates for arbitrary numbers $2m$ of added H atoms. And these results, along with the Pólya-theoretic counts, are also reported in Table 3. The comparison between the exact and predicted results is seen to be modestly reasonable, at least for those cases $C_{60}H_{2m}$ ($0 \le m \le 6$ and $18 \le m \le 30$) which we managed to exactly treat. Presumably then the estimated counts for $C_{60}H_{2m}$ isomers with $7 \le m \le 17$ are fairly accurate. Our arguments and data clearly indicate that the Pólya enumeration greatly overestimates the realizable (Kekulénoid) addition patterns. Overall, for C_{60} we might anticipate but a small fraction $\approx A \bullet \kappa^{60} \approx 1.4 \times 10^{-3}$ of the Pólya counted even-M addition patterns to be non-radicaloid. This amounts to about 0.7% of all (even and odd M) addition patterns. This fraction can also be estimated by summing predicted values for $\#^{(K)}_{2m}(C_{60})$ over all $0 \le m \le 30$ and then dividing the sum by total number of all addition patterns $\#^{(0)}(C_{60})$. This procedure yields the value of $\approx 2 \times 10^{-3}$ for even-M non-radicaloid species. This is reasonably close to our first estimate.

It may be pointed out that with regard to a different aspect of the problem that the current approach greatly underestimates the "realizable" number of substitution patterns—in particular with regard to the potential for H atoms occurring either outside or inside the fullerene cage. This can be relevant especially at higher extents of addition M so as to relieve curvature strain, as suggested in Refs. 47–49. In terms of some simple ideas,[50] consider the perfect bond angles (of $\phi = 109.5°$) at ideal tetrahedral bonding that would give rise to a Cartesian angle defect of $\delta \equiv 2\pi - 3\phi \approx 31.5°$ at each hydrogenated vertex of a cage. Since (for a planar-faced polyhedral structure) the sum of such actual angle defects must sum to 4π, it is seen that there is an "ideal" number of H atoms: $4\pi/\delta \approx 23$. That is, for a number $M < 23$ of H-atoms appended to the surface of a cage, there is a net angular strain $\sim(4\pi - M\delta)$ to angles smaller than the ideal, while for $M > 23$ H-atoms there is a net angular strain $\sim(M\delta - 4\pi)$ to angles larger than the ideal. Thence, beyond $M = 23$, one might imagine that strain could be relieved through the device of introducing negative (Gaussian) curvature sites with the H atom directed to the inside of the cage rather than the outside. A minimum in the angle strain then is imagined with roughly half the H atoms in excess of 23 being directed to the inside (so that the + and − curvatures for sp^3 carbons in excess of 23 would cancel). In terms of the present enumerations, one would then simply entertain the possibility of addition of two types: outside H atoms, and inside H atoms. However, we do not pursue these possibilities here.

6. Conclusion

The numbers of Kekulénoid hydrogenation addition patterns to fullerenes have been explicitly enumerated, at least for several smaller fullerenes. These classically non-radicaloid structures are found to be but a small fraction of the total number of Pólya-theoretic colorings, with the fraction becoming smaller exponentially fast for larger fullerenes. Simple approximate counting formulas have been found (in sections 3 and 4) for enumerations both with and without the imposition of the condition of Kekulénoidicity. This then provides (at least approximate) answers to questions now raised several times, especially in the case of buckminsterfullerene, as illustrated in section 5.

It has been further emphasized that the "fullereneic" Pólya-theoretic counts of addition patterns previously reported in the literature[8–19] are better viewed as substitution patterns on corresponding fully hydrogenated aliphatic molecular polyhedral hydrocarbons. Alternatively, following our discussion in the last paragraph of section 5, these counts could be viewed as isomer counts for placing H-atoms on the inside or outside of the cage of a fully hydrogenated fullerene—though here only those counts where the stress is more nearly completely removed are the more meaningful ones. The refractory nature of the exact enumerations for the Kekulénoid addition patterns exhibits a circumstance where the classical Pólya-theoretic methods as currently formulated seem not to apply. Previously, several other such counting problems have been noted[37] also to be similarly refractory. That is, despite much mathematical combinatorics research, there seem to be a number of chemically interesting circumstances ill-treated by current methods. Further powerful techniques would seem a worthy mathematical challenge.

The utility of explicit generation of Kekulénoid structures (as in section 1) can of course be used as a starting point for quantum computations on the different structures. But, in as much as the number of addition patterns C_NH_m increases exponentially fast with N, more over-arching schemes may be sought. As earlier noted within suitably simple approximations such over-arching schemes have been illustrated, for some cases[27,34,35] susceptible to Pólya-theoretic enumeration. For the present less tractable circumstance, some modest degree of further simple theory may be imparted through the consideration of addition-reaction-diagrams viewable as "posets",[36] as we hope to consider in a future work.

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