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Resonance in elemental benzenoids

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Abstract

The phenomenon of resonance amongst a set of different classical chemical structures entails at an elementary level the enumeration of these resonance structures, corresponding (in benzenoid molecules) to perfect matchings of the underlying molecular (π -network) graph. This enumeration is analytically performed here for the finite-sized elemental benzenoid graphs corresponding to hexagonal coverings on suitable closed surfaces, namely the torus and the Klein bottle. Relevance is also indicated for a class of benzenoid structures corresponding to cylinders with polyhex coverings on the sides (but not the “ends”).

1. Introduction

Classically, chemical bonding structures were identified to certain types of graphs: with partial labellings of vertices corresponding to atom types; with degree restrictions dictated by chemical valency; and with allowance made for double or triple bonds. For this history see, e.g., [36]. With the development of the chemical bond idea in the 1860s it was imagined that to each chemical compound there corresponds a unique chemical structure, and subsequently the whole field of stereochemistry was built up to a large extent around exceptions to the converse correspondence. Moreover, it gradually came to be realized that sometimes a single molecular species corresponds to more than one classical chemical-bonding structure. The prototypical class of chemical species exhibiting this feature is that of the polyhex-structured benzenoids [10, 12] wherein multiple ways to place double bonds occur giving rise to *resonance* [45] and novel “aromatic” modifications to properties. A simple “resonance” or “aromaticity” index is the number of possible double-bond placements, each called a *Kekulé structure*. Indeed, general formulas have been sought for such enumerations for numerous “homologous” sequences of benzenoids, such as reviewed in [10]. The most general such enumerations [26, 27] discern different “long-range-ordered” types

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of Kekulé structures for general classes of benzenoid species (i.e., of polyhex graphs) with variable lengths and widths.

Here we illustrate such enumerations for “typed” Kekulé structures of a new novel class of benzenoids: the finite *elemental benzenoids*, with graphs corresponding to hexagonal coverings (or tilings) of finite closed surfaces, these having no boundaries (with lower-valent sites) where hydrogen atoms would occur. There are [25] exactly two possibilities for such surfaces: the torus in Fig. 1 and the Klein bottle (named after Felix Klein [30]) in Fig. 2. In addition to these two surfaces the enumeration results here bear relevance for cylinders, especially if long, as indeed have recently been experimentally realized [20].

The enumeration problem stated more mathematically entails a *graph* G corresponding to the (polyhex) molecular network embedded on one of the surfaces of the preceding paragraph. The Kekulé structure enumeration then is essentially just the enumeration of spanning degree-one subgraphs (also called *perfect matchings*) of G . In statistical mechanics such perfect matchings are called *dimer coverings* and are of use in describing absorption [9] of dimer molecules on structured surfaces, usually

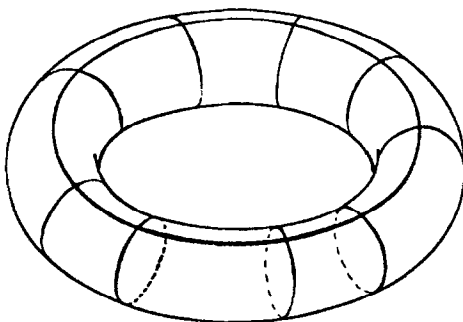


Fig. 1

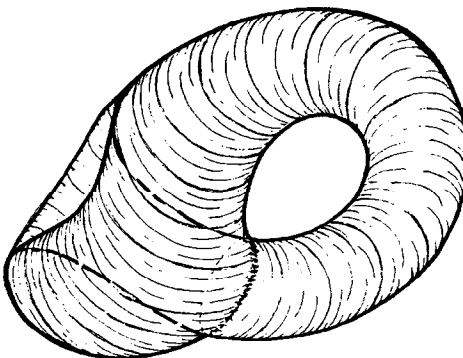


Fig. 2

represented by translationally symmetric planar graphs G . Indeed in such a context, Kasteleyn [23] has already treated a polyhex covered torus with special focus on the infinite size limit. Moreover, Kasteleyn's approach (really best applicable to planar G) is different than the transfer-matrix scheme used here. In fact, the transfer-matrix scheme is of rather general use for many subgraph enumeration problems on translationally symmetric (polymer) graphs G , as indicated in several texts [5, 7, 43]. In particular, this scheme has been used several times for perfect matching enumerations, most frequently for the simple case of quasi-one-dimensional polymers (e.g., as in [1, 4, 13, 15, 18], or [19], and also occasionally for extended two-dimensional lattices, as in [26, 28, 33]. In fact, of all the transfer-matrix solutions so far described for any subgraph generating functions on extended two-dimensional lattices, the current solution provides a candidate for the "simplest" nontrivial one.

2. Elemental benzenoid graphs

The graphs G to be considered here may be constructed by starting from a suitable rectangular section cut from the honeycomb lattice. An example of such a fragment of length $L = 10$ and width $w = 8$ is shown in Fig. 3. Further examples may be generated by adding (or subtracting) rows of hexagons at the top (to change w) or columns of hexagons at the right (to change L). We constrain w to be even but L may be either odd or even. Next each dangling bond at the bottom (at $y = 0$) is joined to the corresponding (equal- x) dangling bond at the top (at $y = L$). The final graph G is obtained by joining dangling bonds at the left ($x = 0$) and right ($x = L$) ends of the fragment. The graph G is denoted by $T_m(L, w)$ if we join the dangling bond on the left at $y = i$ to the dangling bond on the right at $y = i + m$. Evidently, this corresponds to a polyhex embeddable on a torus, and evidently the parity of m and L must be the same. In an alternative construction the graph G is denoted by $K_m(L, w)$ if we join the dangling bond on the left at $y = i$ to the dangling bond on the right at $y = w - i + m + 2$. This corresponds to the polyhex embeddable on a Klein bottle, and again the parities of L and m are to match.

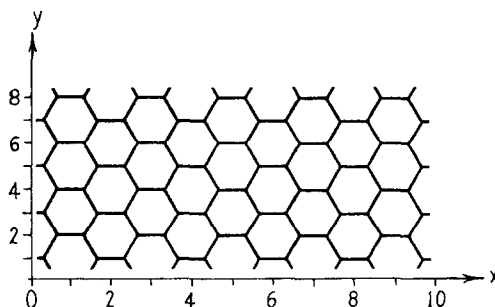


Fig. 3

In either the case of a torus (T) or a Klein bottle (K) the polyhex embedding may also be viewed in terms of L equivalent cyclic strips of $h \equiv w/2$ hexagons. The different cyclic bracelets are simply fused to one another, the last fusion between the first and last (L th) bracelet characterizing the twist parameter m as well as whether the overall structure is of class T or K .

There are [25] additional manners of polyhex embeddings (both for the torus and for the Klein bottle) which evidently fall into different topological *isotopy* equivalence classes. But at least for the torus the circumstance with respect to homotopy equivalence is much better, and in particular all [2] embeddable polyhex coverings (up to graph isomorphism) are included in the $T_m(L, w)$.

3. Cylindrical near-benzenoid graphs

In addition to the graphs embedded on tori and Klein bottles, some of the results here carry over to graphs embedded on a closed cylinder. Thence caps say A and B are required at the $x = 0$ and $x = L$ ends of what is otherwise a long open tube. That is, corresponding dangling bonds at the top and bottom of a rectangular strip as in Fig. 3 are joined and then suitable graphical caps A and B are added to the left and right ends. A set of caps for tubes with $2 < h \leq 7$ are shown in Fig. 4, and clearly such caps based on h -sided polygons may be extended to arbitrarily large w . Significantly rings of sizes other than 6 are involved, so that these do not give rise to benzenoids (as defined here in terms of polyhex coverings). In fact, this must be true for any choice of caps (embeddable as a 3-valent connected planar graph on a disc, with the $h = w/2$

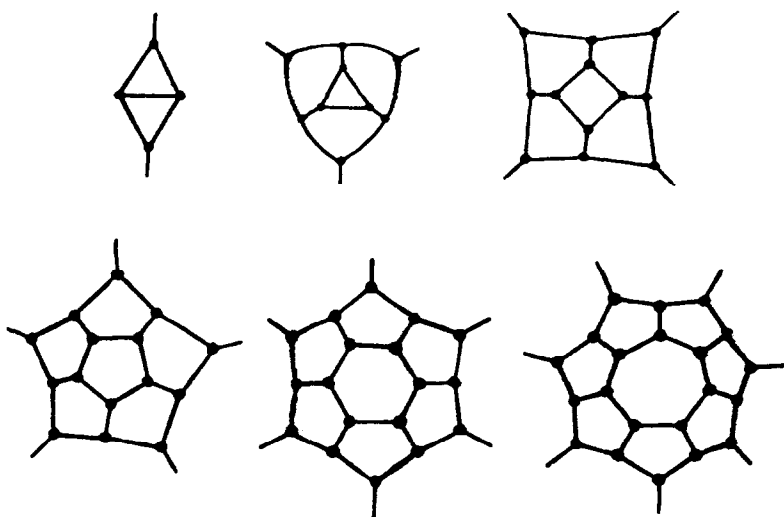


Fig. 4

dangling bonds at the disc boundary): the overall capped cylinder is on a surface homeomorphic to a sphere, so that a simple (and presumably well-known) application of Euler's theorem implies some faces of 5 or fewer sides, e.g., much as in [16] or [38]. In fact, if we let $f_n(X)$ denote the number of n -sided faces on cap X , this result leads to

$$\sum_n (6 - n)f_n(X) = 6, \quad X = A, B. \quad (3.1)$$

As it turns out there are qualitative chemical arguments [38] that indicate maximal (resonance) stabilization occurs for structures as “near” benzenoid as possible, namely the only nonhexagonal faces are pentagonal ones, here 6 in number for each cap. Such so-called *fullerenic* caps can be achieved only for $h \geq 5$. These $h = 5$ and 6 caps are shown in Fig. 4, while examples of fullerenic caps for $7 \leq h \leq 12$ are shown in Fig. 5. In fact, a general method of constructing such larger- h fullerenic caps is hinted at in Fig. 5: One takes a common benzenoid polyhex constrained to be “convex”, as indicated in the shaded regions of Fig. 5, and then circumscribes around it a cyclic band of hexagons and pentagons such that the pentagons occur at the (6) positions where the direction of this band bends (60° off from straight ahead). Taking this core benzenoid to be two rows of $r \geq 1$ hexagons (situated as closely as possible one on top of the other) yields caps for $h = 2r + 6$, while taking two rows of $r \geq 2$ and $r - 1$ hexagons (again situated as closely as possible one on top of the other) yields caps for $h = 2r + 5$. In general, of course there are many other possible choices for convex core benzenoids, e.g., as found in Dias' [12] “periodic table of benzenoids”. More generally,

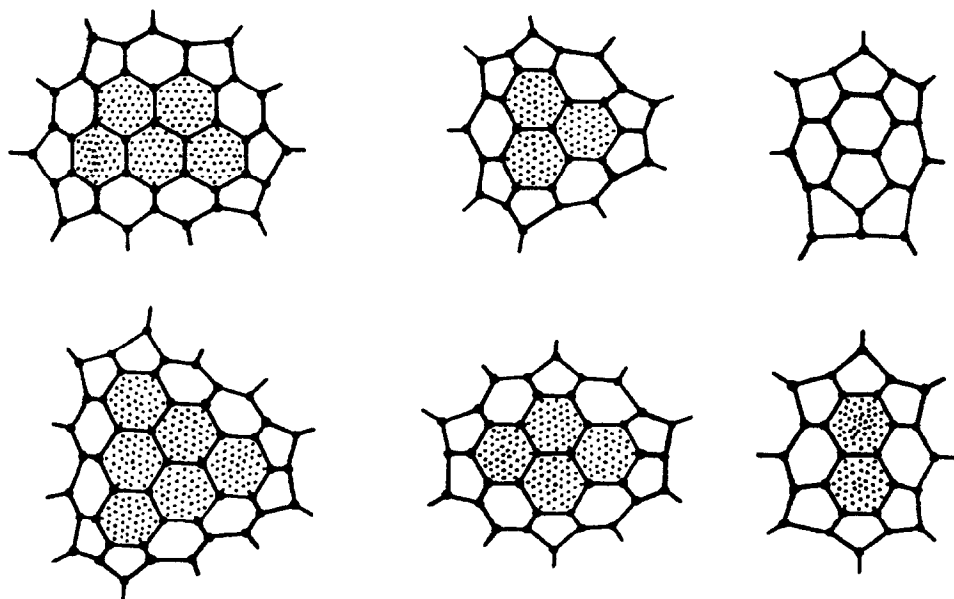


Fig. 5

one might imagine open-ended cylinders with degree-2 sites, whereas hydrogens would then occur, and the species would not be elemental. In any case the consequent cylinders generated by caps A and B could be denoted $C_{A,B}(L, w)$.

4. Perfect matching correspondence

The enumeration problem is conveniently carried out by way of a correspondence. Each Kekulé structure on a toroidal network $T_m(L, w)$ corresponds to a (directed) *self-avoiding walk system* (SAWS) around the torus. One such SAWS and the corresponding Kekulé structure is indicated in Fig. 6. A second is indicated in Fig. 7. In general, a SAWS with steps alternating in horizontal and diagonal directions includes all the diagonal double bonds and none of the horizontal double bonds of the corresponding Kekulé structure. This is essentially the same correspondence as that of Gordon and Davison [14] and many others [6, 8, 21–23, 28, 34, 37] as applied to (planar) polyhex structures. For the present case of toroidal structures there are $h + 1$ different *classes* of SAWSs, each one of the R th class having R passages of (directed) self-avoiding walk(s) through any cross-sectional position x along the torus. That is, each member of the R th class consists of R disjoint cycles. The $R = 0$ class is understood to contain a sole SAWS (the “empty” one).

The SAWSs are given a more complete mathematical representation by specifying positions of each successive horizontal bond passed through by each “cyclic walk” in a SAWS. More particularly the label for an R -walker SAWS at a given horizontal

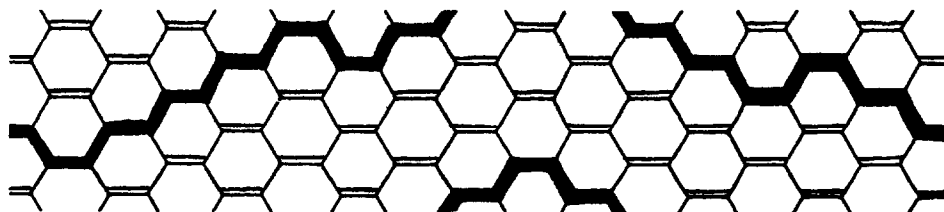


Fig. 6

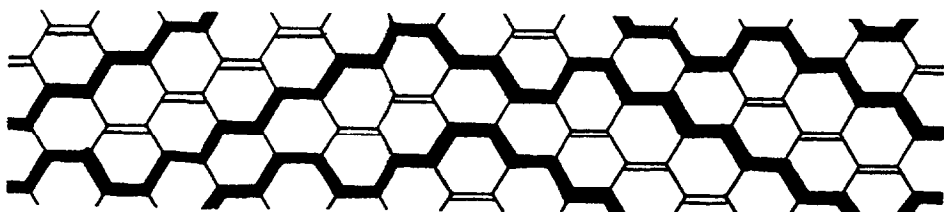


Fig. 7

position x is given as a numerically ordered sequence i_1, i_2, \dots, i_R of R integers identifying the vertical positions of the different walked-on (horizontal) bonds at the given x . Then, e.g., the walk of Fig. 6 is specified (starting from $x = 0$) by a sequence of single-member sequences: 3,2,3,4,5,6,5,6,1,2,1,6,5,4,5,4. When $R \geq 2$ there will of course be more than one bond label at a single x -value in specifying a whole SAWS. Thus, for a SAWS at a single x -value we have *local-state* labels

$$i(R) = i_1, i_2, \dots, i_R \tag{4.1}$$

with $0 < i_1 < i_2 < \dots < i_R < w + 1$ where in addition the i_j of $i(R)$ are all of the same parity (odd or even) as x . A SAWS is then characterized by its sequence of local state labels. For example, for Fig. 7: (1,3), (2,4), (1,5), (2,6), (1,3), (2,4), (1,5), (2,6), etc.

The *local states* may be viewed as column vectors, the $i(R)$ th identified by $|i(R)\rangle$ having a 1 in the $i(R)$ th position and 0 elsewhere. That the i_m in a label $i(R)$ are all distinct and ordered with the i_m falling in a range (from 1 to w , if we relax the parity constraint following Eq. (4.1)) is like the natural basis for an R -fold antisymmetric product of a w -dimensional space. So let us view such $|i(R)\rangle$ as the antisymmetric component of an R -fold Kronecker product

$$|i(R)\rangle = A \{ |i_1\rangle \times |i_2\rangle \times \dots \times |i_R\rangle \}, \tag{4.2}$$

where A is the antisymmetrization operator. That is,

$$|i(R)\rangle = \frac{1}{\sqrt{R!}} \sum_{\pi} (-1)^{\pi} |i_{\pi 1}\rangle \times |i_{\pi 2}\rangle \times \dots \times |i_{\pi R}\rangle \tag{4.3}$$

where the sum is over all permutations of $\{1, 2, \dots, R\}$, πn , is the integer which the permutation π carries n to, and $(-1)^{\pi}$ is the parity of π . This then suggests the relaxation of the ordering constraint in (4.1), so that $|i'(r)\rangle$ has meaning regardless of whether the i'_n are ordered (just so long as $1 \leq i'_n \leq w$). That is, $|i'(R)\rangle$ is as in (3.3) with $i'(R)$ replacing $i(R)$, whence the result is 0 if any i'_n are repeated. Then $|i'(R)\rangle \neq 0$ must involve a sequence $i'(R)$ which differs from an ordered one $i(R)$ only by some permutation π ; thus, $i'_n = i_{\pi n}$ $n = 1$ to R , and from (4.3) one has

$$|i'(R)\rangle = (-1)^{\pi} |i(R)\rangle. \tag{4.4}$$

This representation via (what also are called) Grassmann products seems natural and is utilized in the next section.

5. Transfer matrix

A *transfer matrix* T_R is introduced to keep count of the number of ways in which one local state may follow another in a SAWS. That is, the element $(j(R)|T_R|i(R))$ is simply to be the number of ways that the local state $j(R)$ may immediately follow $i(R)$. Then the number of ways that $k(R)$ may follow $i(R)$ one horizontal step yet farther

along is given by

$$\sum_{j(R)} (k(R)|T_R|j(R)) (j(R)|T_R|i(R)) = (k(R)|T_R^2|i(R)), \tag{5.1}$$

so that repeated multiplication of T_R leads us towards the desired counts of SAWs (and thence too of Kekulé structures). The only problem concerns our allowance of nonrealizable states $|i(R)\rangle$ with i_m of different parities. If $|i(R)\rangle$ in (5.1) is realizable (with all i_m in $i(R)$ of the same parity, corresponding to that of the particular x position under consideration), then T_R is to be constructed maintaining this realizability for $|j(R)\rangle$ and $|k(R)\rangle$. Then the total count of SAWs in the R th class for untwisted tori $T_0(L, w)$ is

$$\#_{0,R}(L, w) = \sum_{i(R)}^{\text{odd}} (i(R)|T_R^L|i(R)) = \text{tr } T_R^L P_o, \quad L = \text{even}, \tag{5.2}$$

where P_o is the (involutory Hermitian) projection matrix onto the subspace of $|i(R)\rangle$ with all i_m in $i(R)$ being odd.

Consider the $R = 1$ case now, since it turns out that the $R \geq 2$ cases may be developed from it. Rather clearly the (w by w) matrix τ_+ with elements

$$(j|\tau_+|i) = \delta(i - j, 1) + \delta(j - i, 1) \tag{5.3}$$

is in fact T_1 (where the Kronecker-delta functions have arguments using modulo w arithmetic).

Next consider the restriction of the R -fold Kronecker product of τ_+ to the antisymmetric subspace

$$(\tau_+)^{\wedge R} \equiv A(\tau_{+1} \times \tau_{+2} \times \dots \times \tau_{+R})A. \tag{5.4}$$

This acts on a local-state vector, thusly,

$$\begin{aligned} (\tau_+)^{\wedge R}|i(R)\rangle &= \frac{1}{R!} A\{\tau_+|i_1\rangle \times \tau_+|i_2\rangle \times \dots \times \tau_+|i_R\rangle\} \\ &= \sum_{j(R)} \left\{ \prod_{n=1}^R (j_n|\tau_+|i_n) \right\} |j(R)\rangle, \end{aligned} \tag{5.5}$$

where the sum here entails $j(R)$ not necessarily constrained as in (5.1). If any j_n are repeated then $|j(R)\rangle = 0$, and one sees that each nonvanishing term in (5.5) corresponds to a pattern by which for any physically realizable $i(R)$ in a SAWS the immediately following $j(R)$ must also be physically realizable. That is, if all i_n of $i(R)$ are the same parity, then so too are the j_n of any following $j(R)$ giving a nonvanishing term. We nearly have T_R then except (possibly) for some sign problems. The simplest circumstance occurs if there is no transition between bonds 1 and w . Then the $j(R)$ of (5.5) are in the correct order. Thus, if there is no transition between bonds 1 and w , then $(j(R)|T_R|i(R))$ and $(j(R)|(\tau_+)^{\wedge R}|i(R))$ are the same. If, however, there is a transition between 1 and w , then $|j(R)\rangle$ has all elements in order except either the first or last, which needs to be moved to the other end to effect the proper order, this

permutation providing an additional factor of $(-1)^{R-1}$. Thus, sometimes we need an extra factor of -1 if there is a transition between 1 and w . But this can be provided by the $(1, w)$ th and $(w, 1)$ th elements of a matrix τ_- which is the same as τ_+ except in these two corner positions where τ_- has a -1 (instead of $+1$). Thus, we write

$$T_R = \begin{cases} 1, & R = 0, \\ (\tau_+)^R, & R = \text{odd}, \\ (\tau_-)^R, & R = \text{even} \neq 0, \end{cases} \tag{5.6}$$

our desired representation of the transfer matrix. Sometimes matrices such as $(\tau_\sigma)^R$ are found in the mathematical literature [41] with a rather different nomenclature, calling this matrix the R th compound of τ_σ .

6. Twisted tori

The tori $T_m(L, w)$ even with $m \neq 0$ may also be treated. The same transfer matrices T_R are relevant. But in place of Eq. (5.2) the desired counting expression has local state labels at the left and right which are shifted from one another by m positions. That is, the count of SWASs in the R th class is for tori $T_m(L, w)$ given by

$$\begin{aligned} \#_{m,R}(L, w) &= \sum_{i(R)}^{\text{odd}} \sum_{j(R)} (i(R)|T_R^L|j(R))(j(R)|C_R^m|i(R)), \\ &= \text{tr } T_R^L C_R^m P_0 \end{aligned} \tag{6.1}$$

where the sums are over properly ordered local-state labels (with the first restricted to odd sites) and where the *connection* matrix C_R^m shifts each index i_n to $j_n \equiv i_n + m$ and possibly also introduces a phase to allow proper reordering of the j_n . Each factor of T_R switches the realizable local-state parities, while C_R^m does or does not as m is odd or even, so that the parities of L and m must be the same.

The first step in a further characterization of C_R^m is to note that it is the m th power of another matrix C_R that makes a minimal twist. We introduce $(w$ by $w)$ matrices γ_+ and γ_- with elements

$$(j|\gamma_\pm|i) = \begin{cases} +1, & i + 1 = j = 1 \text{ to } w - 1, \\ \pm 1, & i = w, j = 1, \\ 0, & \text{otherwise.} \end{cases} \tag{6.2}$$

Then via an argument like that of the preceding section we find

$$C_R = \begin{cases} 1, & R = 0, \\ (\gamma_+)^R, & R = \text{odd}, \\ (\gamma_-)^R, & R = \text{even} \neq 0, \end{cases} \tag{6.3}$$

the present desired expression.

7. Klein bottles

An analysis similar to that of the preceding section applies for Klein bottles $K_m(L, w)$. The general enumeration formula for SAWs of the R th class is

$$\#_{m,R}^K(L, w) = \text{tr } T_R^L C_R^m \omega_R P_o, \tag{7.1}$$

where ω_R is a suitable “inversion” matrix taking $|i(R)\rangle$ to $|j(R)\rangle$ with $j_n = w - i_n + 2$. Generally (for $R \geq 2$), these j_n are out of the order specified in (4.1), and restoration of this order implicates a phase. This involves moving j_1 through j_n , $n = 2$ to R , to place it in the last position $j'_R = j_1$, then j_2 through j_n , $n = 3$ to $R - 1$, to the next to last position $j'_{R-1} = j_2$, etc., each transposition giving rise to a factor of -1 in the overall phase

$$(-1)^{R-1} (-1)^{R-2} \dots (-1)^1 = (-1)^{R(R-1)/2}. \tag{7.2}$$

By arguments similar to those of the preceding section we obtain

$$\omega_R = (-1)^{R(R-1)/2} (\omega)^{\wedge R} \tag{7.3}$$

where $\omega = \omega_1$ is a $w \times w$ matrix with elements

$$(j|\omega|i) = \begin{cases} 1, & i + j = w + 1, \\ 0, & \text{otherwise.} \end{cases} \tag{7.4}$$

Thence we have achieved the presently desired result.

8. Long cylinders

Analyses as in the preceding three sections may also be extended to (long) cylindrical structures $C_{A,B}(L, w)$. The caps A and B at the ends of the cylinder allow only certain possibilities for Kekulé structures within the cap, so that only certain (suitable weighted) local states may occur at the boundary, and propagate along the cylinder. What may occur on a cap X may be encoded in vectors $|X, R\rangle$ with weights $(i(R)|X, R)$ being the numbers of perfect-matching structures for X such that exactly the bonds at positions $i(R)$ on the cap boundary are not included. Then the enumeration formula for SAWs of the R th class is

$$\#_{A,B,R}^C(L, w) = (A, R | T_R^L | B, R), \tag{8.1}$$

Thence, the overall L -dependence is accounted for in the now standard transfer matrix. For a cap X based on an h -sided polygon,

$$|X, R\rangle = \sum_{i(R)}^{\wedge \text{even}} |i(R)\rangle, \tag{8.2}$$

where the sum is over all $i(R)$ such that the i_n of $i(R)$ are all of the same parity in all $i(R)$ and the maximal subsequences of i_m differing by 2 are all of even length.

In general, the end vectors $|X, R\rangle$ depend upon the structural details of the cap X . Still there are some restrictions arising from the fact that aside from the h - R cap sites paired in double bonds across the boundary of a cap, there must be an even number of remaining sites paired in double bonds internally within the cap. Thus, in general, if we denote the number of vertices within a cap X by $v(X)$, then in order for $|X, R\rangle$ to be nonzero it must be that $v(X) - h + R$ is even. Conceivably for more general caps (as “open-ended” tubes), there can be even more severe constraints such that R values from the two end caps A and B do not match and there are no Kekulé structures. However, so long as the caps are graph structures as presumed here (trivalent and embeddable on a disc with the h dangling bonds at the disc boundary) the overall cylinder structure corresponds to a trivalent polyhedron and has [27] at least 3 Kekulé structures.

9. Eigenanalysis

The counting expressions of Sections 5–8 may be refined in terms of the eigenproblem for the transfer matrices. The eigenproblems for τ_+ and τ_- , then arise

$$\tau_\sigma |\lambda^\sigma\rangle = \lambda^\sigma |\lambda^\sigma\rangle, \quad \sigma = + \text{ or } - . \quad (9.1)$$

The eigenvectors to $(\tau_\sigma)^{\wedge R}$ then are just a subset of those to the Kronecker power $(\tau_\sigma)^{\times R}$, namely those which are the antisymmetric component of an R -fold Kronecker product of R distinct eigenvectors to τ_σ .

Thence, the solution of the whole eigenproblem for T_R rests on that for τ_σ . It is evident that

$$\tau_\sigma = \gamma_\sigma + \tilde{\gamma}_\sigma \quad (9.2)$$

where $\tilde{\gamma}_\sigma$ is the transpose (and inverse) of γ_σ . Now $\gamma_+ + \tilde{\gamma}_+$ and $\gamma_- + \tilde{\gamma}_-$ may be recognized to be the adjacency matrices (i.e., in chemistry the $\alpha = 0$ and $\beta = 1$ Hückel MO matrices) for so-called *regular* and *Möbius* cycles of w sites. Thus, the eigensolutions are already known [11, 17], but a novel elegant approach of special utility here is possible. To implement this approach note that τ_σ and γ_σ commute, while γ_σ is the generator of a cyclic group C_σ , of order $|C_\sigma| = w$ when $\sigma = +$ and order $|C_\sigma| = 2w$ when $\sigma = -$. Thence, τ_σ and γ_σ have simultaneous eigenvectors which may be identified to symmetries of C_σ . These symmetries or irreducible representations are identified to the $|C_\sigma|$ roots of unity

$$\Gamma^k(\gamma_\sigma^p) = e^{ink}, \quad k = \frac{2\pi p}{|C_\sigma|}, \quad p = 0 \text{ to } |C_\sigma| - 1. \quad (9.3)$$

With our present w by w matrices γ_σ it is readily seen that, there occur only w symmetries each once:

$$\Gamma^k \text{ with } p = \begin{cases} 0, 1, 2, \dots, w-1, & \sigma = +, \\ 1, 3, 5, \dots, 2w-1, & \sigma = -. \end{cases} \quad (9.4)$$

As a consequence, we find

$$\begin{aligned} \lambda_k^\sigma &= 2 \cos k, \\ (j|\lambda_k^\sigma) &= \frac{1}{\sqrt{w}} e^{ikj} \end{aligned} \tag{9.5}$$

for both cases $\sigma = +$ and $-$. An advantage of the present approach is that now the $|\lambda_k^\sigma\rangle$ are also recognized as eigenvectors to γ_σ :

$$\gamma_\sigma |\lambda_k^\sigma\rangle = e^{ik} |\lambda_k^\sigma\rangle. \tag{9.6}$$

For the “inversion” ω one finds

$$\omega |\lambda_k^\sigma\rangle = |\lambda_{-k}^\sigma\rangle, \tag{9.7}$$

where $-k$ represents (in 2π -modular arithmetic) $2\pi-k$. Here (9.6) and (9.7) are of aid in dealing with the connection matrices C_R^m and ω_R .

Thus, the antisymmetrized R -fold products

$$|\lambda_{k(R)}^\sigma\rangle \equiv A \{ |\lambda_{k_1}^\sigma\rangle \times |\lambda_{k_2}^\sigma\rangle \times \dots \times |\lambda_{k_R}^\sigma\rangle \} \tag{9.8}$$

are acted on quite simply by T_R , C_R^m , ω_R ,

$$\begin{aligned} T_R |\lambda_{k(R)}^\sigma\rangle &= \left\{ \prod_{j=1}^R \lambda_{k_j}^\sigma \right\} |\lambda_{k(R)}^\sigma\rangle, \\ C_R |\lambda_{k(R)}^\sigma\rangle &= \left\{ \prod_{j=1}^R e^{ik_j m} \right\} |\lambda_{k(R)}^\sigma\rangle, \\ \omega_R |\lambda_{k(R)}^\sigma\rangle &= (-1)^{R(R-1)/2} |\lambda_{-k(R)}^\sigma\rangle. \end{aligned} \tag{9.9}$$

Of course, $\sigma = +$ or $-$ as R is odd or even, and the k_j of $k(R)$ are all distinct and given by (9.3) and (9.4).

10. Solution

A fairly explicit general solution is obtained if the trace of the enumeration formula (6.1) is developed on the eigenbasis of (9.7). That is, we first rewrite (6.1) as

$$\#_{m,R}(L, w) = \sum_{k(R)} (\lambda_{k(R)}^\sigma | T_R^L | \lambda_{k(R)}^\sigma) (\lambda_{k(R)}^\sigma | C_R^m P_0 | \lambda_{k(R)}^\sigma) \tag{10.1}$$

and then use (9.7) and (9.8),

$$\#_{m,R}(L, w) = \sum_{k(R)} \prod_{j=1}^R (2 \cos k_j)^L e^{ik_j m}, \tag{10.2}$$

where the $k(R)$ sum is restricted with

$$k(R) = k_1, k_2, \dots, k_R \quad \text{with } 0 \leq k_1 < k_2 < \dots < k_R < 2\pi, \quad k_j = 2\pi \frac{p_j}{|C_\sigma|}, \tag{10.3}$$

and p_j is odd or even as R is even or odd. The overall Kekulé-structure count is, of course,

$$\#_m(L, w) = \sum_{R=0}^w \#_{m,R}(L, w). \quad (10.4)$$

Eqs (10.2), (10.3), and (10.4) then constitute our general solution for the Kekulé-structure count on a toroidal graph $T_m(L, w)$. The partitioning of this count according to R has some chemico-physical relevance, as discussed elsewhere [29] – of course, as noted in Section 8 for cylinders only certain R values survive.

The counts may be made more explicit for special cases here done for smaller-width tori. First

$$\begin{aligned} \#_{m,0}(L, 2h) &= 1, \\ \#_{m,h-1}(L, 2h) &= h^L, \\ \#_{m,h}(L, 2h) &= 2^L. \end{aligned} \quad (10.5)$$

Then for h up to 6 we find the remaining counts to be as given in Table 1. Here counts at any m are the same as those at twists of $-m$ and $m + 2h$, so that we have reported results just for m values from 0 to h . Further, the restriction of L and m to be the same parity is presumed, so that in listing results at particular m values the $(-1)^L$ factors associated with negative eigenvalues to T_R are explicitly evaluated. Of course, higher hexagon widths h could be treated analytically, though the expressions rapidly become cumbersome. Eventually (for $h \geq 11$) too, the eigenvalues of τ_σ become identified to roots of fifth or higher degree secular polynomials evidently without analytical expressions in Galois' sense. For the Klein bottle, results similar to that of Table 1 could be constructed, involving the same L th powers but with different coefficients. Similar comments apply for each type of cylinder some of which have already been experimentally realized starting with Iijima's report [20]. (Indeed a few special types of cylinders have already been considered, even before Iijima, mostly within an alternative so-called "molecular-orbital" framework. Much of such molecular-orbital-based work has also been done for the limit of infinitely long tubes.)

11. Conclusion

Kekulé structures (or perfect matchings) have been analytically enumerated for a variety of polyhex covering graphs on closed surfaces. The basic surface considered is the torus, though extension is made to Klein bottles, as well as capped (and infinite) tubes. Further, the lateral and longitudinal extents of the covering graph are allowed to vary along with a "twist" parameter. Yet further the counts are obtained in a partitioned form for different long-range-ordered subclasses of Kekulé structures. Notably the $(w, L \rightarrow \infty)$ graphite limit for the number of Kekulé structures per site often is approached from above, especially for the untwisted ($m = 0$) tori. Since further

graphite seems to give the maximum such per-site counts for all ordinary planar benzenoids, the toroidal benzenoids evidently are those benzenoids displaying a maximum resonance, thereby enhancing their chemical interest. The Kekulé structure (or perfect matching) counts for the novel classes of chemical structures as reported here presumably will find application in describing resonance effects in these species.

Table 1
Enumeration for twisted tori $T_m(L, 2h)$

| h | m | R | $\#_{m,R}(L, 2h)$ |
|--|--|---|---|
| 3 | $\left. \begin{matrix} 0 \\ 1, 5 \\ 2, 4 \\ 3 \end{matrix} \right\} 1$ | | $2^L + 2$ |
| | | | $2^L + 1$ |
| | | | $2^L - 1$ |
| | | | $2^L - 2$ |
| 4 | $\left. \begin{matrix} 0 \\ 1, 7 \\ 2, 6 \\ 3, 5 \\ 4 \end{matrix} \right\} 1$ | | $2^L + 2(\sqrt{2})^L$ |
| | | | $2^L + \sqrt{2}(\sqrt{2})^L$ |
| | | | 2^L |
| | | | $2^L - \sqrt{2}(\sqrt{2})^L$ |
| | $\left. \begin{matrix} 0 \\ 1, 7 \\ 2, 6 \\ 3, 5 \\ 4 \end{matrix} \right\} 2$ | | $2^L - 2(\sqrt{2})^L$ |
| | | | $(2 + \sqrt{2})^L + 4(\sqrt{2})^L + (2 - \sqrt{2})^L$ |
| | | | $(2 + \sqrt{2})^L + \sqrt{2}(\sqrt{2})^L + (2 - \sqrt{2})^L$ |
| | | | $(2 + \sqrt{2})^L - 2(\sqrt{2})^L + (2 - \sqrt{2})^L$ |
| | | | $(2 + \sqrt{2})^L - \sqrt{2}(\sqrt{2})^L + (2 - \sqrt{2})^L$ |
| | | | $(2 + \sqrt{2})^L + (2 - \sqrt{2})^L$ |
| 5 | $\left. \begin{matrix} 0 \\ 1, 9 \\ 2, 8 \\ 3, 7 \\ 4, 6 \\ 5 \end{matrix} \right\} 1$ | | $2^L + 2((\sqrt{5} + 1)/2)^L + 2((\sqrt{5} - 1)/2)^L$ |
| | | | $2^L + ((\sqrt{5} + 1)/2)((\sqrt{5} + 1)/2)^L + ((\sqrt{5} - 1)/2)((\sqrt{5} - 1)/2)^L$ |
| | | | $2^L + ((\sqrt{5} - 1)/2)((\sqrt{5} + 1)/2)^L - ((\sqrt{5} + 1)/2)((\sqrt{5} - 1)/2)^L$ |
| | | | $2^L - ((\sqrt{5} - 1)/2)((\sqrt{5} + 1)/2)^L - ((\sqrt{5} + 1)/2)((\sqrt{5} - 1)/2)^L$ |
| | | | $2^L - ((\sqrt{5} + 1)/2)((\sqrt{5} + 1)/2)^L + ((\sqrt{5} - 1)/2)((\sqrt{5} - 1)/2)^L$ |
| | $\left. \begin{matrix} 0 \\ 1, 9 \\ 2, 4, 6, 8 \\ 3, 7 \\ 5 \end{matrix} \right\} 2$ | | $2^L - 2((\sqrt{5} + 1)/2)^L + 2((\sqrt{5} - 1)/2)^L$ |
| | | | $((5 + \sqrt{5})/2)^L + 4(\sqrt{5})^L + ((5 - \sqrt{5})/2)^L$ |
| | | | $((5 + \sqrt{5})/2)^L + \sqrt{5}(\sqrt{5})^L + ((5 - \sqrt{5})/2)^L$ |
| | | | $((5 + \sqrt{5})/2)^L - (\sqrt{5})^L + ((5 - \sqrt{5})/2)^L$ |
| | | | $((5 + \sqrt{5})/2)^L - \sqrt{5}(\sqrt{5})^L + ((5 - \sqrt{5})/2)^L$ |
| $\left. \begin{matrix} 0 \\ 1, 9 \\ 2, 8 \\ 3, 7 \\ 4, 6 \\ 5 \end{matrix} \right\} 3$ | | $((5 + \sqrt{5})/2)^L + ((5 - \sqrt{5})/2)^L$ | |
| | | $(3 + \sqrt{5})^L + 4(2)^L + 2((\sqrt{5} + 1)/2)^L + (3 - \sqrt{5})^L + 2((\sqrt{5} - 1)/2)^L$ | |
| | | $(3 + \sqrt{5})^L + 2^L + ((\sqrt{5} - 1)/2)((\sqrt{5} + 1)/2)^L + (3 - \sqrt{5})^L + ((\sqrt{5} + 1)/2)((\sqrt{5} - 1)/2)^L$ | |
| | | $(3 + \sqrt{5})^L - 2^L - ((\sqrt{5} + 1)/2)((\sqrt{5} + 1)/2)^L + (3 - \sqrt{5})^L + ((\sqrt{5} - 1)/2)((\sqrt{5} - 1)/2)^L$ | |
| | | $(3 + \sqrt{5})^L + 2^L - ((\sqrt{5} + 1)/2)((\sqrt{5} + 1)/2)^L + (3 - \sqrt{5})^L - ((\sqrt{5} - 1)/2)((\sqrt{5} - 1)/2)^L$ | |
| | | $(3 + \sqrt{5})^L - 2^L + ((\sqrt{5} - 1)/2)((\sqrt{5} + 1)/2)^L + (3 - \sqrt{5})^L - ((\sqrt{5} + 1)/2)((\sqrt{5} - 1)/2)^L$ | |

Table 1 (continued)

| h | m | R | $\#_{m,R}(L, 2h)$ |
|-----|-------|---|---|
| 6 | 0 | 1 | $2^L + 2(\sqrt{3})^L + 2$ |
| | 1, 11 | | $2^L + \sqrt{3}(\sqrt{3})^L + 1$ |
| | 2, 10 | | $2^L + (\sqrt{3})^L - 1$ |
| | 3, 9 | | $2^L - 2$ |
| | 4, 8 | | $2^L - (\sqrt{3})^L - 1$ |
| | 5, 7 | | $2^L - \sqrt{3}(\sqrt{3})^L + 1$ |
| 6 | | $2^L - 2(\sqrt{3})^L + 2$ | |
| 6 | 0 | 2 | $(2 + \sqrt{3})^L + 4(\sqrt{3} + 1)^L + 2^L + 4(\sqrt{3} - 1)^L + (2 - \sqrt{3})^L + 4$ |
| | 1, 11 | | $(2 + \sqrt{3})^L + (\sqrt{3} + 1)(\sqrt{3} + 1)^L + 2^L + (\sqrt{3} - 1)(\sqrt{3} - 1)^L + (2 - \sqrt{3})^L + 1$ |
| | 2, 10 | | $(2 + \sqrt{3})^L + 2^L + (2 - \sqrt{3})^L - 3$ |
| | 3, 9 | | $(2 + \sqrt{3})^L - 2(\sqrt{3} + 1)^L + 2^L + 2(\sqrt{3} - 1)^L + (2 - \sqrt{3})^L - 2$ |
| | 4, 8 | | $(2 + \sqrt{3})^L - 2(\sqrt{3} + 1)^L - 2(\sqrt{3} - 1)^L + (2 - \sqrt{3})^L + 1$ |
| | 5, 7 | | $(2 + \sqrt{3})^L - (\sqrt{3} - 1)(\sqrt{3} + 1)^L + 2^L - (\sqrt{3} + 1)(\sqrt{3} - 1)^L + (2 - \sqrt{3})^L + 1$ |
| 6 | | $(2 + \sqrt{3})^L + 2^L + (2 - \sqrt{3})^L$ | |
| 6 | 0 | 3 | $6^L + 4(\sqrt{12})^L + 2(3)^L + 2^L + 2(\sqrt{3})^L$ |
| | 1, 11 | | $6^L + \sqrt{3}(\sqrt{12})^L + 3^L + 2^L + \sqrt{3}(\sqrt{3})^L$ |
| | 2, 10 | | $6^L - (\sqrt{12})^L - 3^L + 2^L + (\sqrt{3})^L$ |
| | 3, 9 | | $6^L - 2(3)^L + 2^L$ |
| | 4, 8 | | $6^L + (\sqrt{12})^L - 3^L + 2^L - (\sqrt{3})^L$ |
| | 5, 7 | | $6^L - \sqrt{3}(\sqrt{12})^L + 3^L + 2^L - \sqrt{3}(\sqrt{3})^L$ |
| 6 | | $6^L - 4(\sqrt{12})^L + 2(3)^L + 2^L - 2(\sqrt{3})^L$ | |
| 6 | 0 | 4 | $(\sqrt{3} + 1)^{2L} + 4(\sqrt{3} + 1)^L + 4(2)^L + 4(\sqrt{3} - 1)^L + (\sqrt{3} - 1)^{2L} + 1$ |
| | 1, 11 | | $(\sqrt{3} + 1)^{2L} + (\sqrt{3} - 1)(\sqrt{3} + 1)^L + 2^L + (\sqrt{3} + 1)(\sqrt{3} - 1)^L + (\sqrt{3} - 1)^{2L} + 1$ |
| | 2, 10 | | $(\sqrt{3} + 1)^{2L} - 3(2)^L + (\sqrt{3} - 1)^{2L} + 1$ |
| | 3, 9 | | $(\sqrt{3} + 1)^{2L} + 2(\sqrt{3} + 1)^L - 2(2)^L - (\sqrt{3} - 1)^L + (\sqrt{3} - 1)^{2L} + 1$ |
| | 4, 8 | | $(\sqrt{3} + 1)^{2L} - 2(\sqrt{3} + 1)^L + 2^L - 2(\sqrt{3} - 1)^L + (\sqrt{3} - 1)^{2L} + 1$ |
| | 5, 7 | | $(\sqrt{3} - 1)^{2L} - (\sqrt{3} + 1)(\sqrt{3} + 1)^L + 2^L - (\sqrt{3} - 1)(\sqrt{3} - 1)^L + (\sqrt{3} - 1)^{2L} + 1$ |
| 6 | | $(\sqrt{3} - 1)^{2L} + (\sqrt{3} - 1)^L + 1$ | |

Questions remain concerning curvature strain (since often benzenoids have a preference towards planarity); concerning correspondences to molecular-orbital approaches; and (even more so) concerning the synthetic challenge posed by the considered structures.

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