

Characterization of Cyclo-Polyphenacenes

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Cyclo-polyphenacenes belt-type compounds are considered here in terms of some simple chemico-graph-theoretic invariants. First the compounds of this group are neatly encoded in an unambiguous way. Then all the isomers in this system are categorized with respect to their “combinatorial curvature”, and for the case of the 52 cyclo-hexaphenacenes it is found to correlate with steric stresses. A systematic effort is made to correlate the reactivity (via additive oxidation) of the various isomers with their Kekule-structure counts.

I. INTRODUCTION

The class of polyphenacene compounds with a chain of fused phenyl rings are of long interest. Recently this interest has further mounted in consideration of cyclocized polyphenacenes, so that the strip of rings binds into the form of a belt (or bracelet). Indeed, consideration has been made not only to the possibility of regular belts^{1–3} but also of Möbius twisted ones,^{4–7} such as are most reasonable when the number of phenyl rings is not too small.⁶ Most of these works focus on the aceneic case where fusion occurs solely on opposite sides of each ring.^{1–5,7} But Dobrowolski⁶ considers the general case where the fusions may be either on opposite sides or “alternate” sides. The most trivial belt-type compound of cyclo-hexaphenacene, that is, coronene, is already well-known, and also the correspondingly simplest pentacenic^{8–11} and heptacenic^{12,13} belts are known. But coronene has six phenyl rings all fused in a very special unstrained fashion, though many other cyclo-hexaphenacenes may also be imagined. Efforts to synthesize different belt-type compounds have also been reported.^{14–16} Recently, Dobrowolski has carried out an extensive theoretical study on belt-type and möbius-type cyclo-hexaphenacenes and reported the number of distinct isomers possible for this system.⁶ He also computed the energy of these cyclo-hexaphenacenes at different levels of quantum-chemical theory and proposed a nomenclature for these compounds.

The objective of the present work is to investigate different aspects of belt-type polyphenacene compounds theoretically in terms of simple chemico-graph-theoretic invariants. We follow the technique of encoding of structures described in the next section to discuss a curvature characteristic of polyhexacene belts. Next we indicate a “combinatorial curvature” characteristic and consider its plausible relation to structural stresses, as manifested in thermodynamic stability. Then we describe a general method for the enumeration of Kekule structures of cyclo-polyphenacenes and consider a plausible relation between the number of Kekule structure and the reactivities of such systems.

II. ISOMER CODING

The general formula for an open polyphenacene chain is $C_{4n+2}H_{2n+4}$. However, when they cyclocize to form belt-type compounds the two ends are fused, and a compound of general formula $C_{4n}H_{2n}$ results. Once this hypothetical fusion takes place, which pair was fused together is no longer identifiable. So, any enumeration should also have this feature, that is, the effective enumeration should incorporate this cyclo-symmetry.

We first mark any arbitrary point of fusion and then in tracing along one boundary of the ring locate how many carbon atoms before the next fusion, as indicated in Figure 1. Obviously, this can be either 0, 1 or 2, whereas if traced along the other boundary of the same ring the respective number of carbon atoms would be 2, 1, or 0. With a_i this number of carbon atoms for the i th ring, the sequence (a_1, a_2, \dots, a_N) then specifies the particular cyclo-polyphenacene. But since any one of the rings might be chosen as the first, and since counts might be either to the right or to the left, and since one side of the belt or the other might be identified as the one to be traced along, it is seen that (up to) $4N$ codes are conceivable.

Now each of these $4N$ (sometimes redundant) strings of digits may be viewed as a ternary number, whence from all these numbers we choose the smallest to correspond to the canonical code. This lexicographically ordered n -tuple code is a distinct identification for a particular belt-type n -phenacene compound. Thus, coronene, the “trivial” cyclo-hexaphenacene has the code 000000. A few examples of such codes are given in Figure 2 along with a correspondent “chemical” name for each example. This name views each ring along the phenacene strip to be one of three kinds: *meta*-fused if $a_i = 0$; *para*-fused if $a_i = 1$; and *meta**-fused if $a_i = 2$. The sequence $a_1 a_2 \dots a_n$ then is identified to a correspondent sequence of m, p, m^* labels (which in verbally pronouncing a name are expressed as *meta*, *para*, *meta*-star). The numerical codes lend themselves to the generation of comprehensive listings of isomers for a given number N of benzene rings. One cycles through the N -digit ternary numbers, generating up to $4N$ equivalent codes for each such number to select the lowest one out of each set. Thence we

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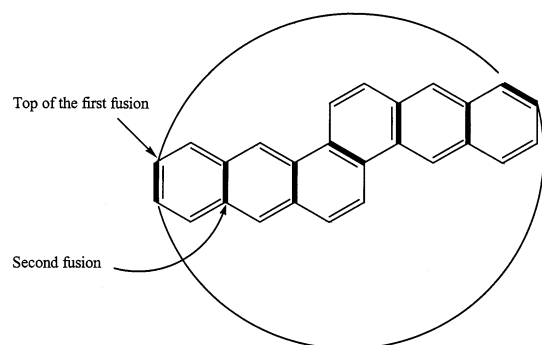


Figure 1. A typical cyclohexaphenacene for which the numbers of carbon atoms between successive fusions (along the “top” boundary) are 1 1 0 2 1 1. The canonical code is 0 1 1 1 1 2, and a corresponding “chemical” name would be *m,p,p,p,p,m**-cyclohexaphenacene.

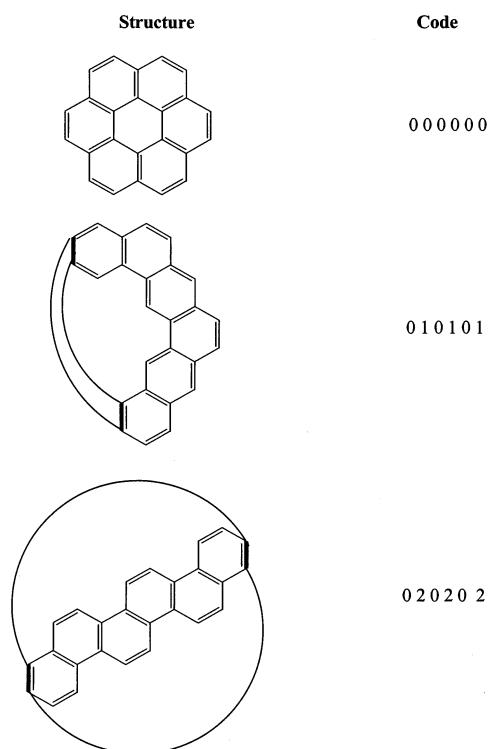


Figure 2. Examples of belt-type cyclohexaphenacenes with their canonical codes. These would be *mmmmmm*-, *mpmpmp*-, *mm*mm*mm**-cyclohexaphenacene.

have a code which besides efficient description and implementation to generate comprehensive isomer lists also lends itself to an amenable chemical nomenclature.

III. CURVATURE CHARACTERISTIC

Oftentimes in the fusion of two ends of a polyphenacenic strip together there may be some stress, with some distortion to the consequent of geometrically nonplanar structure. One way to approach this is to imagine that the cyclo-polyphenacenic strip is further embedded in a network of hexagons. Such a network is a “graphitic” cone, for which stresses and strains have already been considered in a very simple manner.¹⁷ This stress should correlate with the Gaussian curvature at the apex of the cone, and this is further correlated with a “combinatorial curvature” associated to the cone.

Table 1. Combinatorial Curvature (κ), Number of Kekule Structures, Relative Stability, the Index of Reactivity R_{Max} and $K_{\text{prod}}^{1/6}$ of All 52 Isomers with Their Codes in Cyclo-Hexaphenacene Belts

code	$\kappa(\text{G})$	no. of Kekule structures K(G)	ΔE (kcal/mol) [ref 6]	$K_{\text{prod}}^{1/6}$	R_{Max}
000000	0	20	000.0	1.648	-0.155
000001	$\pi/3$	13	160.9	1.533	-0.090
001001	$2\pi/3$	16	227.0	1.587	-0.125
000101	$2\pi/3$	17	233.7	1.604	-0.084
000002	$2\pi/3$	20	235.9	1.648	-0.155
000011	$2\pi/3$	15	256.0	1.570	-0.062
010101	π	14	257.0	1.552	-0.067
001011	π	12	260.3	1.513	0.000
001002	π	16	263.6	1.587	-0.090
000102	π	16	267.4	1.587	-0.090
000111	π	10	279.4	1.468	0.114
000012	π	16	281.6	1.587	-0.090
010102	$4\pi/3$	17	271.8	1.604	-0.084
010111	$4\pi/3$	12	278.1	1.513	0.000
011011	$4\pi/3$	13	278.2	1.533	-0.073
001012	$4\pi/3$	17	279.3	1.604	-0.084
001021	$4\pi/3$	16	281.1	1.587	-0.125
001102	$4\pi/3$	15	282.7	1.570	-0.062
002002	$4\pi/3$	20	286.5	1.648	-0.155
000202	$4\pi/3$	20	294.4	1.648	-0.155
000121	$4\pi/3$	17	299.7	1.604	-0.084
001111	$4\pi/3$	9	300.3	1.442	0.087
000112	$4\pi/3$	15	302.4	1.570	-0.062
000022	$4\pi/3$	20	318.9	1.648	-0.155
010202	$5\pi/3$	16	279.2	1.587	-0.090
010121	$5\pi/3$	14	283.8	1.552	-0.067
001202	$5\pi/3$	16	286.5	1.587	-0.090
011012	$5\pi/3$	12	287.0	1.513	-0.038
002012	$5\pi/3$	16	288.5	1.587	-0.090
010112	$5\pi/3$	12	289.1	1.513	0.000
011102	$5\pi/3$	10	295.4	1.468	0.114
001121	$5\pi/3$	12	296.4	1.513	-0.038
001022	$5\pi/3$	16	308.3	1.587	-0.090
001112	$5\pi/3$	10	308.4	1.468	0.114
011111	$5\pi/3$	6	308.9	1.348	0.222
000122	$5\pi/3$	16	316.5	1.587	-0.090
000212	$5\pi/3$	16	326.2	1.587	-0.090
020202	2π	20	279.2	1.648	-0.155
012012	2π	16	291.2	1.587	-0.125
012021	2π	17	291.7	1.604	-0.084
011202	2π	15	295.7	1.570	-0.062
011211	2π	13	300.4	1.533	-0.073
010212	2π	16	305.2	1.587	-0.125
011121	2π	12	307.6	1.513	0.000
001212	2π	17	308.4	1.604	-0.084
002112	2π	15	314.2	1.570	-0.062
001122	2π	15	316.7	1.570	-0.062
001221	2π	16	317.3	1.587	-0.125
011112	2π	9	321.2	1.442	0.087
002022	2π	20	330.5	1.648	-0.155
000222	2π	20	344.9	1.648	-0.155
111111	2π	4	359.4	1.260	0.176

Within our present context the combinatorial-curvature of belt-type compounds may be defined as

$$\kappa = 2\pi\{1 - \frac{1}{6}|\#(m) - \#(m^*)|\} \quad (1)$$

where $\#(m)$ is the number of *meta*-fused benzene rings in a cycle and $\#(m^*)$ is the number of *meta**-fused benzene rings. Thence from the codes of the previous section, the combinatorial curvature for each is readily obtained.

For a hexaphenacene belt-type system it is seen that the 52 distinct structural isomers can be categorized with seven different κ values, namely, 0, $\pi/3$, $2\pi/3$, π , $4\pi/3$, $5\pi/3$ and 2π . In Table 1, all the 52 isomers are classified with their κ

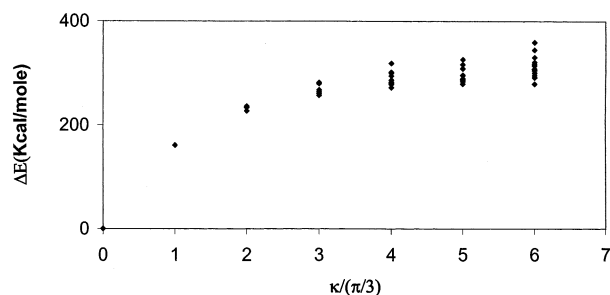


Figure 3. Plot of (rescaled) combinatorial curvature vs energy difference from coronene.

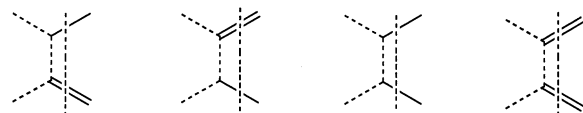


Figure 4. Different possible arrangements of double bonds at a cell boundary, with the cell boundary marked by the longer vertical dashed line.

values (and with Kekule-structure counts as considered in the next section). For cyclo-*N*-phenacenes with $N > 6$, negative combinatorial curvatures would also be possible.

If we plot Dobrowolski's⁶ Hartree–Fock energy for each belt against the combinatorial curvature, then an interesting trend is noted. But rather than plotting the total Hartree–Fock energies, their values as referenced to coronene are more “reasonable” numbers, as appear in the plot of Figure 3. It is seen that the energy difference between the most stable isomer of a particular κ value and the same of the next higher κ value decreases gradually and becomes zero at $\kappa = 2\pi$. That is, κ evidently provides a lower bound to the amount of stress due to the curving of the phenacenic structure into a cyclic three-dimensional structure.

IV. KEKULE-STRUCTURE ENUMERATION

The number $K(G)$ of Kekule structures is generally accepted as a relevant measure of the stability of an aromatic system G . For instance, Cyvin and Gutman¹⁸ give an extensive review. For belt-type polyphenacene systems $K(G)$ can be defined in terms of “transfer” matrices, one of which is associated to each ring of the belt. Granted a pattern ξ of double bond assignments in a Kekule structure just after the fusion at the i th ring one lets $(T_i)_{\xi\zeta}$ denote the number of consistent ways to assign a pattern ζ at the corresponding position in the subsequent $(i+1)$ th ring. The various patterns referred to are conveniently associated with a division of the polyphenacene into “cells” whose boundaries we choose to be just to the “right” of the fusion bonds in each ring. Then the patterns for each ring are specified by the different ways in which double bonds might occur at each cell boundary. That is, with two connections (i.e., σ -bonds) in a ring just after a fusion a local pattern ξ takes four different “values” as each of these two connections forms either a single or double bond, as indicated in Figure 4. Thence a sequence of so-called transfer matrices T_i is obtained¹⁹ with there being just three types of such matrices depending on whether the ring is m , p , or m^* , and the number of Kekule structures for the π -network belt G is

$$K(G) = \text{Tr}(T_N T_{N-1} \dots T_1) \quad (2)$$

Generally these T_i are block diagonal, in one of three forms

$$T_{(m)} = \begin{pmatrix} \tau_{(m)} & \mathbf{0} \\ \mathbf{0} & \tau'_{(m)} \end{pmatrix}, T_{(p)} = \begin{pmatrix} \tau_{(p)} & \mathbf{0} \\ \mathbf{0} & \tau'_{(p)} \end{pmatrix},$$

$$T_{(m^*)} = \begin{pmatrix} \tau_{(m^*)} & \mathbf{0} \\ \mathbf{0} & \tau'_{(m^*)} \end{pmatrix} \quad (3)$$

depending on the type (m, p, m^*) of the ring. Here the rows and columns are identified with the local patterns ordered as in Figure 4, and

$$\tau_{(m)} = \tau_{(m^*)} = \begin{pmatrix} 0 & 1 \\ 1 & 1 \end{pmatrix}, \tau_{(p)} = \begin{pmatrix} 1 & 1 \\ 0 & 1 \end{pmatrix}$$

and

$$\tau'_{(m)} = \tau'_{(m^*)} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \tau'_{(p)} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (4)$$

Then we obtain the number of Kekule structures as

$$K(G) = \text{Tr}(\tau_N \tau_{N-1} \dots \tau_1) + \text{Tr}(\tau'_N \tau'_{N-1} \dots \tau'_1) \quad (5)$$

In the work of Cyvin et al.,²⁰ a different type of enumeration formula for the regular cyclophenacenes is also found. The numbers of Kekule structures corresponding to the various isomers in belt-type cyclo-hexaphenacenes are reported in Table 1. In a simple approximation the resonance energy of each structure G should^{21–23} be directly proportional to $\ln K(G)$, although these are seen in Table 1 to be of little correspondence to the Hartree–Fock energies. This may be surmised to be because the strain energies associated to the embedding of the structure into three-dimensional space are so important. Still they should be of use in gauging reactivities, as in the next section.

For Möbius twisted cyclo-hexaphenacenes the Kekule structure count can be written as

$$K(G) = \text{Tr}(T_N T_{N-1} \dots T_1 M) \quad (6)$$

where M indicating the presence of a Möbius twist is

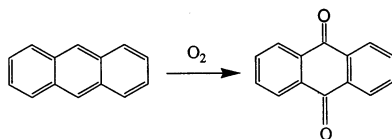
$$M = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \quad (7)$$

Here M may be placed in eq 6 between any neighboring pair of transfer matrices, with an open chain structure or even another type of interconnection between the ends of the phenacenic strip; all that results is a different type of matrix in place of M .

V. REACTIVITY ESTIMATES

The ab initio Hartree–Fock-SCF computations of Dobrowolski on the cyclohexaphenacenes reveal that each classical structural isomer typically associates with a well-established minimum in the potential-energy hypersurface.⁶ This however does not necessarily say much about the depth of the minima, nor does it say much about the reactivity of the species, perhaps even about the reactivity of the molecule with itself. Now the per-ring Kekule-structure count is an

index which has been found to be relevant in gauging reactivity and indeed in gauging a whole range of properties associated with “aromaticity”. Of relevance in this regard in the present context is the observation that the higher linear (noncyclic) polyacenes are well-known to evince ever higher reactivity as the length of the chain grows ever larger, though it seems likely each corresponds to a minimum in the (single-molecule) potential energy hypersurface. This behavior can be rationalized in terms of the ever smaller number of Kekule structures “per ring” (with increasing aceneic chain length), especially in comparison to the reacted forms. Of course this last description depends on what is viewed to be the reacted forms, as in turn depends on what there is around to react with. The linear polyacenes become ever more susceptible to oxidation, e.g., by O_2 in the air. For anthracene



and one sees that there are four Kekule structures for both the reactant and product. But for ever longer polyacenes the balance shifts ever farther in favor of the (quinoid oxidation) product: one finds $K_{\text{react}} = 2(n+1)$ vs $K_{\text{prod}} = (n+1)^2$ for $N = 2n+1$. That is, for increasing chain lengths the relative resonance stabilization of the products becomes ever greater in comparison with that of the reactants. For cyclopolyacenes $K_{\text{react}} = 4$ independent of N , while the reactant with a quinoid oxidation product in one ring now leaves a resonance network of just $N-1$ acenic rings in an open chain, so that $K_{\text{prod}} = N$, and one imagines a similar increasing reactivity for ever higher N .

The situation is somewhat different for angularly (*meta* or *anti-meta*) fused rings: removal of two nonfusion centers in a ring from the resonance network often does not increase the number of Kekule structures. And further the total initial (i.e., reactant) number of Kekule structures increases exponentially with the number of rings. Now the understanding that Kekule-structure counts are roughly multiplicative (in terms of component substructures), while energies are roughly additive (in terms of component structures), it is reasonable to take a reactivity index to be

$$R \equiv \log K_{\text{prod}} - \log K_{\text{react}} \quad (8)$$

Then one sees that the predicted reactivities for ever longer linear polyacenes ever increases. Indeed this seems to be in agreement with experiment, as we illustratively test in Figure 5 for the open-chain phenacenes, where some experimental data is available.²⁴

For our cyclo-phenacenes we choose this same reactivity index. We need only specify what the imagined product is, and this we imagine simply involves the removal of two nonfusion sites of one ring from the resonance network. Of course not all the rings are equivalent, so what is relevant to report is the maximum such R -value. This R_{Max} should indicate the maximum reactivity, such as would associate to the most ready reaction. This then is also reported in Table 1, where we see that R_{Max} takes quite different values for different structures. Here those with positive R_{Max} should be quite reactive, those with $R_{\text{Max}} \sim 0$ should be similar in

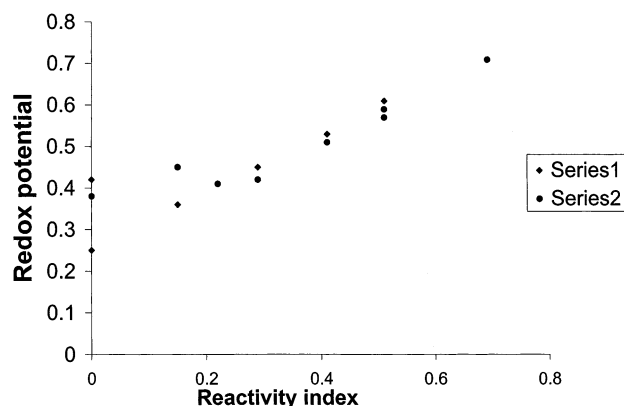


Figure 5. Plot of reactivity index vs redox potentials for reaction of quinones to hydroquinones. Series 1 for *para* quinones and series 2 for *ortho* quinones.

reactivity to anthracene, and those with negative R_{Max} should be quite stable.

VI. CONCLUSIONS

The coding technique described here is unambiguous and can be extended to all kinds of polyphenacenes. This technique helps us to determine all the possible topological isomers in any polyphenacene system. Following the canonical code generation process any isomer can readily be drawn for a given code. Combinatorial curvature κ evidently is a lower-bounding indicator of stress present in each isomer of a given code. Coronene is globally flat with 0 combinatorial curvature and is also the most stable among all 52 isomers of belt-type hexaphenacenes. In coronene the central ring is modestly aromatic unlike the other isomers,²⁵ although in Clar's picture the central ring is less aromatic than the peripheral rings.²⁶ The number of Kekule structures of the reactant and that of a possible product helps us to compare the reactivity of different isomers. It is clear from Table 1 that the presence of consecutive *p*-fused rings increases the reactivity of a particular isomer, while the presence of *m*-fused or *m**-fused rings makes them comparatively inert. The quantity $K_{\text{prod}}^{1/6}$ is a kind of average Kekule structure count per ring, and it is also clear from Table 1 that the value of $K_{\text{prod}}^{1/6}$ is substantially less when the isomer is more reactive, i.e., when R_{Max} is positive.

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