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Clar and sextet polynomials of boron-nitrogen fullerenes

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Abstract

Clar sextet theory is well known for its role in the research of molecule stability and resonance energy. The count of Clar structures of C_{60} and the associated Clar polynomial and sextet polynomial were already given by W.C. Shiu et al. For boron-nitrogen fullerenes, the corresponding problems have not been solved. In this paper we consider three BN-fullerenes ($B_{12}N_{12}$,$B_{16}N_{16}$ and $B_{28}N_{28}$) which are anomalously stable and one type of capped boron-nitride nanotubes. By combinatorial enumeration we obtain the Clar polynomials and the sextet polynomials of $B_{12}N_{12}$ and $B_{16}N_{16}$. Furthermore, the results of $B_{28}N_{28}$ is also enumerated by the usage of computer.

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1 Introduction

Many researchers (see [1-7]) considered the possible existence of the inorganic analogues of the fullerene cages which have the same number of boron and nitrogen atoms. As pointed out in [7], a boron-nitrogen polyhedron $(BN)_x$ forms a planar bipartite graph with four- and six- membered rings as its faces. By a systematic density functional tight-binding study, the magic clusters $B_{12}N_{12}$, $B_{16}N_{16}$ and $B_{28}N_{28}$ were determined in [7]. Clearly $B_{12}N_{12}$ is the smallest boron-nitrogen polyhedron with isolate squares and it plays a similar role as C_{60} in fullerenes. Similar to the isolated-pentagon rule for fullerenes, it was found in [7] that the stablest isomer corresponding to a boron-nitrogen polyhedron has isolated squares.

Note that $B_{12}N_{12}$ and C_{60} can be considered as truncated octahedron and icosahedron respectively. The Clar polynomial and the sextet polynomial of C_{60} were obtained recently in [8,9]. A natural question is to calculate these two polynomials for $B_{12}N_{12}$ and the other BN-fullerenes and BN-nanotubes. In this paper we deal with $B_{12}N_{12}$ and $B_{16}N_{16}$ by using some combinatorial techniques. As for the case of larger BN-fullerenes, we find it necessary to use computers. So we design a program for enumeration of such cases. As an illustration, the Clar polynomial and the sextet polynomial of $B_{28}N_{28}$ are given.

A Kekulé structure of a molecule G is a chemical notion which coincides with what is known in graph theory under the name "*perfect matching*", i.e., a set of pairwise disjoint edges of G that cover all vertices of G. For example, the double bonds in Fig.1 show a Kekulé structure of $B_{12}N_{12}$.

The notion of Clar structure was first defined by Clar [10] for hexagonal systems, and it has been extended to fullerenes [9,11-13] and nanotubes [14]. We recall it as follows: a *Clar structure* of G is obtained by drawing circles in some hexagons of G and these circles represent the so-called "*aromatic sextets*". The three rules of drawing circles are as follows:

(a) circles are not allowed to be drawn in adjacent hexagons;

(b) circles can be drawn in hexagons if the rest of G either has at least one Kekulé structure or is empty;

(c) a Clar structure contains the maximum number of circles which can be drawn using (a) and (b).

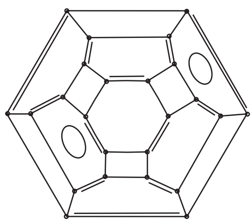

Figure 1: One type of Clar strutures of $B_{12}N_{12}$

The number of *aromatic sextets* in a Clar structure of G is called the Clar number of G and denoted as $CL(G)$. It is clear that the Clar number of a benzenoid molecule is unique no matter which circles are drawn. The main chemical implication of the Clar number is the following empirically established regularity: If G_a and G_b are two isomeric benzenoid hydrocarbons and CL(G_a)>CL(G_a), then the compound G_a is more stable both chemically and thermodynamically.

A set of circles is said to be a *sextet pattern* if only the rules (a) and (b) are obeyed. It is not necessary for two sextet patterns to own the same number of circles. Hosoya and Yamaguchi defined *sextet polynomial* for a benzenoid system G [16] as follows:

$$B_G(x) = \sum_{i=0}^{m} \sigma(G,i)x^i$$

where $m = CL(G)$ and $\sigma(G,i)$ denotes the number of sextet patterns of G with i hexagons.

The sextet polynomial was used to define and discuss resonance energies (RE). For some large benzenoid systems, however, the corresponding sextet polynomial may have no acceptable physical meaning[19,20]. So Herndon and Hosoya [13] gave an alternative extension of Clar structure by replacing rule (c) by (d) the set of circles is maximal, i.e. no new circle can be drawn using (a) and (b). In this paper we will follow this definition for a Clar structure, and rename the original definition by Clar as *proper Clar structure*. So, the circles in Fig.1 give a Clar structure, but not a proper Clar structure of $B_{12}N_{12}$.

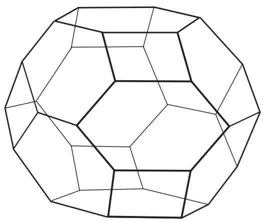

Figure 2: $B_{16}N_{16}$

The count polynomial of Clar structures, referred to as *Clar polynomial*, was defined by El-Basil[11] for a benzenoid system G:

$$\xi(G;x) = \sum_{i=0}^{m} \rho(G,i)x^i$$

where $\rho(G,i)$ is the number of Clar structures of G with i circles and m is the number of circles of a proper Clar structure of G.

In this paper, we always use $\mid I \mid$ for the cardinality of I; $N(u)$ for the set of vertices adjacent to u; $N(I)$ for the set of vertices adjacent to at least one vertex of I. In a graph G, we say some hexagons are independent if and only if any two of them have no common vertex. Two hexagons in G are said to be adjacent if they have at least one common edge.

2 Clar polynomial and sextet polynomial of $B_{12}N_{12}$

For convenience of calculation, we will employ a concept called the hexagon-dual, which was introduced by W.C. Shiu et al. [9]. Let G be a graph containing at least one induced subgraph as a hexagon. The *hexagon – dual* of G is a graph G^* defined as follows: corresponding to each hexagon of G there is a vertex of G^*; two vertices of G^* are joined by an edge if and only if the corresponding hexagons share an edge. Note that the definition of hexagon-dual is simply the reverse of Fowler's leapfrog transform [15] in the study of fullerenes. It is easily seen that the hexagon-dual of $B_{12}N_{12}$ is the 3-cube Q_3(see Fig.3).

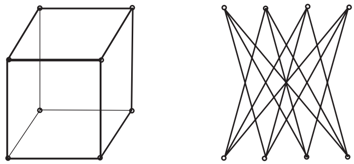

Figure 3: Two diagrams of the 3-cube Q_3

It should be noticed that $B_{12}N_{12}$ has a nice property: any set S of independent hexagons in $B_{12}N_{12}$ is a sextet pattern. This can be easily shown as follows. Set $M = \{e \mid e \text{ is a common edge of two hexagons in } B_{12}N_{12})\ \}$. It is easy to see from Fig. 1 that M is a perfect matching of $B_{12}N_{12}$. Then the property follows from the fact that the restriction of M on $B_{12}N_{12} - S$ is a perfect matching of $B_{12}N_{12} - S$. Note that, in general, this property is not valid for $B_{16}N_{16}$ and other BN-fullerences. By this property of $B_{12}N_{12}$, there is a natural bijection between the sextet patterns (the Clar structures, resp.) of $B_{12}N_{12}$ and the independent sets (the maximal independent sets, resp.) of Q_3. Therefore, the sextet polynomial and the Clar polynomial of $B_{12}N_{12}$ are the same as the independent set polynomial and the maximal independent set polynomial of Q_3, respectively. Recall that the *independent set polynomial* of G was defined [17,18] as:

$$I(G,x) = \sum_{k=0}^{\alpha} b(G,k)x^k$$

where α is the maximum of cardinalities of the independent sets of G, $b(G,k)$ is the number of independent sets of G each of which has exactly k vertices.

The *maximal independent set polynomial* of a graph G was defined in [9] as:

$$I_m(G,x) = \sum_T x^{|T|} = \sum_k \beta(G,k)x^k$$

where T is taken over all maximal independent sets of G, $\beta(G,k)$ is the number of maximal independent sets of G each of which has exactly k vertices.

Thus, we get the following result:

Proposition 1.

(a) $\xi(B_{12}N_{12};x) = I_m(Q_3,x)$

(b) $B_{B_{12}N_{12}}(x) = I(Q_3, x)$

Now we can get $\xi(B_{12}N_{12}; x)$ and $B_{B_{12}N_{12}}(x)$ as follows.

Note that Q_3 is a bipartite graph. Let (X, Y) be the bipartition of Q_3. Obviously $|X| = |Y| = 4$. Let T be a maximal independent set of Q_3. There are two possibilities of T as follows:

(1) $T = X$ or $T = Y$. Then $|T| = 4$;

(2) None of $T \cap X$ and $T \cap Y$ is empty. Note that Q_3 is 3-regular and it has 4 vertices in each of X and Y. It is easy to see that if T contains two vertices of X then T can not contain any vertex of Y. So $|T \cap X| = 1$. For a vertex x in $T \cap X$, there is a unique vertex of Y that is not adjacent to x. So, there are exactly 4 such maximal independent sets T of Q_3 since $|X| = 4$.

Thus we have $I_m(Q_3, x) = 2x^4 + 4x^2$, and so:

$$\xi(B_{12}N_{12}; x) = 2x^4 + 4x^2$$

Let I be an independent set of Q_3. Then it is clear that $|I| \leq 4$. So, according to the number of vertices in I, there are four possibilities:

(1) $|I| = 4$. Then there are two cases: $I = X$ or $I = Y$;

(2) $|I| = 3$. Then all vertices of I must belong to X (or Y). Otherwise, at least two of them are adjacent. Any three vertices of X (or Y) make up such an independent set. So there are 8 $(= 2 \times \binom{4}{3})$ cases;

(3) $|I| = 2$. If one vertex of I belongs to X and the other belongs to Y, then as we explained before, I is a maximal independent set of Q_3, and there are exactly 4 such cases. If both vertices of I belong to X (or Y), there are 12 $(= 2 \times \binom{4}{2})$ such cases;

(4) $|I| = 1$. Each vertex of Q_3 makes up such an independent set and so there are 8 cases.

Thus we have $I(Q_3, x) = 2x^4 + 8x^3 + 16x^2 + 8x + 1$, and so

$$B_{B_{12}N_{12}}(x) = 2x^4 + 8x^3 + 16x^2 + 8x + 1$$

3 Clar polynomial and sextet polynomial of $B_{16}N_{16}$ and $B_{28}N_{28}$

The graph $B_{16}N_{16}$ contains 32 vertices, and 18 faces which are 12 hexagons and 6 squares. As a 3-regular graph without cut edges, $B_{16}N_{16}$ has a Kekulé structure. In the planar embedding of $B_{16}N_{16}$ (see Fig.4), we use h_i (i=1, 2,$\cdots$, 12) to represent its hexagons. In the hexagon-dual C_{12} of $B_{16}N_{16}$ (see Fig.5), we use v_i to represent the vertex corresponding to h_i.

From the 3-dimensional figure of $B_{16}N_{16}$ (Fig.2), we can easily see that $B_{16}N_{16}$ can be positioned such that any chosen hexagonal face lies at the bottom with the whole figure left unchanged. This means that for any two hexagons h_i and h_j, there is an element g in

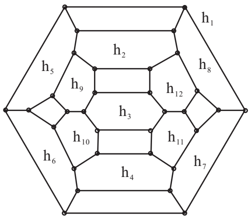

Figure 4: A planar embedding of $B_{16}N_{16}$

Aut($B_{16}N_{16}$), the automorphism group of $B_{16}N_{16}$, such that $g(h_i)$=h_j. That is, the action of Aut($B_{16}N_{16}$) on the set of twelve hexagons of $B_{16}N_{16}$ is transitive. It follows that the hexagon-dual C_{12} is vertex-transitive.

Proposition 2. Let I be a maximal independentset of C_{12}, then $3 \leq\mid I \mid\leq 4$

Proof. Let T be a set of any two non-adjacent vertices of C_{12}. Since C_{12} is a 4-regular graph, then

$$\mid T \cup N(T) \mid\leq 2 + 2 \times 4 = 10 < 12 =\mid V(C_{12}) \mid .$$

So there is at least one vertex of C_{12} that is not adjacent to any vertex in T. It follows that $\mid I \mid\geq 3$.

On the other hand, note that the twelve vertices of C_{12} belong to the four pairwise disjoint triangles: $\triangle v_1v_5v_6$, $\triangle v_3v_9v_{10}$, $\triangle v_4v_7v_{11}$, $\triangle v_2v_8v_{12}$. Since any two vertices in a triangle are adjacent, I has at most one vertex in each triangle. It follows that $\mid I \mid\leq 4$. This completes the proof. □

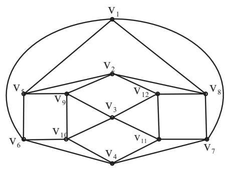

Figure 5: C_{12}

From Proposition 2, we see that if I is an independent set of C_{12} with $\mid I \mid= 4$, then I is a maximal independent set. Let S denote the set of hexagons in $B_{16}N_{16}$ corresponding to I. Then S is a maximal set of independent hexagons with $\mid S \mid= 4$.

Proposition 3. Let S be a maximal set of independent hexagons in $B_{16}N_{16}$ with $\mid S \mid= 4$, then $B_{16}N_{16} - S$ has a perfect matching.

Proof. The action of Aut($B_{16}N_{16}$) on the set of twelve hexagons in $B_{16}N_{16}$ is transitive. So, without loss of generality, we can assume that $h_1 \in S$. Then the four hexagons which are adjacent to h_1 do not belong to S. Let I denote the vertex set in C_{12} corresponding to

S, and G_1 denote the hexagon-dual of $B_{16}N_{16} - h_1$ (see Fig.6). Then the restriction of I on G_1 is an independent set of G_1 which has exactly three vertices. Obviously, it has three possible cases: $\{v_2, v_3, v_4\}$, $\{v_2, v_{10}, v_{11}\}$, $\{v_4, v_9, v_{12}\}$. In the first case, $B_{16}N_{16} - S$ consists of two independent squares. In the other two cases, $B_{16}N_{16} - S$ consists of four edges in which no two are adjacent. So, $B_{16}N_{16} - S$ has a perfect matching in all cases. □

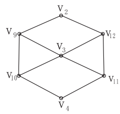

Figure 6: G_1

Proposition 4. Let I_0=$\{u, v\}$ be an independent set of C_{12}. Then there is a maximal independent set I containg I_0 with $| I |= 4$.

Proof. Without loss of generality, we may assume $u = v_1$ since C_{12} is vertex-transitive (see Fig. 5). It is easy to see that $v \in \{v_2, v_3, v_4, v_9, v_{10}, v_{11}, v_{12}\}$. Then by direct verification, we see that I_0 can always be extended to a maximal independent set I with $| I |= 4$. □

Proposition 5. Let I be a maximal independent set of C_{12} with $| I |= 3$, and let S be the set of hexagons of $B_{16}N_{16}$ corresponding to I. Then $B_{16}N_{16} - S$ has no perfect matching.

Proof. Without loss of generality, we may assume that $v_1 \in I$. Then the restriction of I on G_1 is a maximal independent set of G_1 with two vertices, which is clearly seen from Fig.6 to be either $\{v_9, v_{11}\}$ or $\{v_{10}, v_{12}\}$. So S must be either $\{h_1, h_9, h_{11}\}$ or $\{h_1, h_{10}, h_{12}\}$. Then it is easy to see that $B_{16}N_{16} - S$ consists of two connected components each of which is a tree with seven vertices. Therefore, $B_{16}N_{16} - S$ has no perfect matching. □

Theorem 6. Let S be a set of independent hexagons of $B_{16}N_{16}$. Then S is a Clar structure of $B_{16}N_{16}$ if and only if $| S |= 4$.

Proof. It is clear that $| S |\leq 4$. We discuss all possible cases as follows:

If $| S |= 1$ or $| S |= 2$, by Proposition 4, there is S_0 with $| S_0 |= 4$ such that $S \subset S_0$. By Proposition 3 $B_{16}N_{16} - S_0$ has a perfect matching. So S is not a Clar structure of $B_{16}N_{16}$.

If $| S |= 3$ and S is not a maximal set of independent hexagons, we can obtain the same conclusion as above by analogous discussion.

If $| S |= 3$ and S is maximal, then by Proposition 5, $B_{16}N_{16} - S$ has no perfect matching.

If $| S |= 4$, we know S is maximal by Proposition 2. Then by Proposition 3, $B_{16}N_{16} - S$ has a perfect matching. So S is a Clar structure of $B_{16}N_{16}$. □

Proposition 7. Let S be a set of independent hexagons of $B_{16}N_{16}$ with $| S |= 3$. Then S is a sextet pattern if and only if S is not maximal.

Proof. Suppose that S is a sextet pattern. If S is maximal, then by Proposition 5, $B_{16}N_{16} - S$ has no perfect matching. It follows that S is not a sextet pattern, a contradiction.

Conversely, suppose that S is not maximal, then there is a maximal set S_0 of four independent hexagons such that $S \subset S_0$. By Theorem 6, $B_{16}N_{16} - S_0$ has a perfect matching.

Since a hexagon itself always has a perfect matching, $B_{16}N_{16} - S$ has a perfect matching and S is a sextet pattern. □

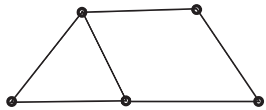

Figure 7: $C_{12} - T - N(T)$

Proposition 8. Let I_1, I_2 be two distinct maximal independent sets of C_{12}. Then $\mid I_1 \cap I_2 \mid \leq 2$

Proof. By Proposition 2, $\mid I_1 \cap I_2 \mid \leq 3$. We prove $\mid I_1 \cap I_2 \mid \neq 3$ as follow:

Suppose that $\mid I_1 \cap I_2 \mid = 3$. Set $\{u\} = I_1 - I_2$ and $\{v\} = I_2 - I_1$. Then u and v are adjacent in C_{12}. Otherwise $I_1 \cup \{v\}$ is an independent set of C_{12}, contradicting the choice of I_1.

Let $T = \{u, v\}$. Then $I_1 \cap I_2$ is an independent set of $C_{12} - T - N(T)$ (see Fig.7). On the other hand, it is obvious that $C_{12} - T - N(T)$ has no independent set of three vertices, a contradiction. Then the result follows. □

Now we focus on the count of Clar structures with four hexagons in $B_{16}N_{16}$. Since there are three independent sets with three vertices in G_1, by Proposition 3 there are three such Clar structures containing a given hexagon h. Furthermore, the action of $\mathrm{Aut}(B_{16}N_{16})$ on the set of twelve hexagons in $B_{16}N_{16}$ is transitive. So the number of times that each hexagon appears in these Clar structures must be the same. Thus we get the number of Clar structures with four hexagons in $B_{16}N_{16}$:

$$\rho(B_{16}N_{16}, 4) = \frac{3 \times \binom{12}{1}}{4} = 9$$

By Theorem 6 we know a Clar structure of $B_{16}N_{16}$ always has four hexagons. Therefore, the Clar polynomial of $B_{16}N_{16}$ is

$$\xi(B_{16}N_{16}; x) = 9x^4 \tag{1}$$

Now we compute the number of sextet patterns S consisting of three independent hexagons in $B_{16}N_{16}$. By Proposition 7, each S is not maximal and it is contained in a maximal set S_0 with $\mid S_0 \mid = 4$. By Proposition 8, all these S are distinct from each other. So

$$\sigma(B_{16}N_{16}, 3) = \binom{4}{3} \times \rho(B_{16}N_{16}, 4) = 36 \tag{2}$$

From the proof of Theorem 6, we can see that any two independent hexagons in $B_{16}N_{16}$ make up a sextet pattern. When one hexagon is fixed, the other has seven choices. Then

$$\sigma(B_{16}N_{16}, 2) = \frac{\binom{12}{1} \times 7}{2} = 42 \tag{3}$$

Notice that every sextet pattern with four independent hexagons is a Clar structure and the number of sextet patterns with exactly one hexagon is the number of hexagons in $B_{16}N_{16}$. Then by (1),(2) and (3), we finally arrive at the sextet polynomial of $B_{16}N_{16}$:

$$B_{B_{16}N_{16}}(x) = 9x^4 + 36x^3 + 42x^2 + 12x + 1$$

For larger BN-fullerenes, it is difficult to compute these polynomials only using pen and paper. We design a program for enumeration of such cases. For $B_{28}N_{28}$, the program gives the following result:

$$\xi(B_{28}N_{28}; x) = 3x^8 + 48x^7 + 156x^6 + 96x^5 + 9x^4$$

$$B_{B_{28}N_{28}}(x) = 3x^8 + 72x^7 + 522x^6 + 1434x^5 + 1719x^4 + 894x^3 + 216x^2 + 24x + 1$$

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