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On Computing the Clar Number of a Fullerene Using Optimization Techniques

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Abstract

A fullerene graph is a cubic 3-connected plane graph with pentagonal and hexagonal faces. The Clar number of a fullerene is a parameter that is related to the stability of fullerene. In this paper we propose an effective mathematical model for determining the Clar number of a fullerene. The solution of the model was obtained by CPLEX 12.6 for many of large fullerene isomers and the results were very satisfactory. Moreover, the computation time ensures the efficiency and effectiveness of our proposed model for computing the Clar number of a fullerene graph.

1 Introduction

A fullerene graph F_n with n vertices is a cubic 3-connected plane graph which has exactly 12 pentagonal faces and $m := n/2 - 10$ hexagonal faces. The vertices represent carbon atoms and the edges represent the chemical bonds between them. Grünbaum and Motzkin [1] showed that fullerene graphs with n vertices exist for all even $n \geq 24$ and for $n = 20$. Fullerenes have wide application in various fields and have received a lot of recent mathematicians' attention [15, 16].

A fullerene is a molecule entirely composed of carbon. Carbon atoms form four chemical bonds. Three of these are strong bonds, and one is weak. In the graphical representation of a fullerene, we draw the three strong bonds by the edges in the graph. The fourth bond tends to occur as a double bond.

A perfect matching of a graph is a set of edges such that each vertex is incident with exactly one edge. Over a fullerene, the edges of a perfect matching correspond to double bonds. Papers written by Došlić [2,3] and Vukicevic et al. [4] are good references on structural properties of fullerene graphs.

The Clar and Fries numbers are two parameters that are related to the stability of fullerene. The Fries number of a fullerene is the maximum number of hexagons contain three double bonds over all possible perfect matchings of a fullerene graph. The perfect matchings of fullerene graphs have been well-studied (see [5–8]).

A set of hexagons contain three double bonds that attains the Fries number for a fullerene is called a Fries set. A set of *disjoint* hexagons of a perfect matching K of a fullerene graph is called a sextet pattern if every hexagon in this set contains three double bonds. The Clar set is any sextet pattern with the maximum number of hexagons over all perfect matching of fullerene graph. The Clar number of a fullerene graph is the cardinality of a Clar set, denote by $c(F_n)$.

In [10] authors introduced an integer linear program to compute the Fries number of a Fullerene. It is natural to ask whether a Clar set is always a subset of some Fries set, or equivalently, if there is a perfect matching that simultaneously gives a Fries set and a Clar set. It was generally assumed that this was true. Hartung showed that this assumption is false by constructing a family of fullerenes for which a Clar set is never a subset of a Fries set [10].

In the most published papers on the Clar number of a fullerene, authors provided some bounds for the Clar number [10-13, 19] and they did not offer a method to calculate the Clar number of a fullerene.

In [11], authors obtained an upper bound for the Clar number of fullerene graphs, which is described in the following theorem.

Theorem 1. ([11]). Let F_n be a fullerene with n vertices. Then $C(F_n) \leq \lfloor n/6 \rfloor - 2$.

The fullerene graphs whose Clar numbers attain this bound have been characterized in [10,13].

Yang Gao et al. [12] showed that there are no fullerenes with n ≡ 2 (mod 6) vertices attaining this bound. Thus Theorem 1 is refined as the following theorem.

Theorem 2. [12] Let F_n be a fullerene with n vertices. Then

$$C(F_n) \leq \begin{cases} \left\lfloor \frac{n}{6} \right\rfloor - 3, & n \equiv 2 \pmod 6, \\ \left\lfloor \frac{n}{6} \right\rfloor - 2, & \text{otherwise.} \end{cases}$$

A lower bound for the Clar number of fullerene graphs has been obtained in [14] as follows:

Theorem 3. ([14]). Let F_n be a fullerene graph with n vertices. Then

$$C(F_n) \geq (n - 380)/61.$$

Although a large number of literatures have studied the Clar number of fullerene graphs, to our knowledge, there has been no an effective method to compute the Clar number of a fullerene graph in general cases.

In this paper, we propose an integer linear programming model for determining a Clar set as well as the Clar number of a fullerene. Then we solve the model for many of fullerene isomers using Cplex 12.6.

2 A binary integer linear programming for computing the Clar number of a fullerene

In this section we formally define the problem considered in this paper. Here we denote by $A_{n\times n}$ the adjacency matrix describing the fullerene graph F_n. We denote by $H_{m\times 6}$ a node-hexagonal incident matrix and by $h_k, k = 1,2,\ldots,m$ its respective *k*th row, more precisely for each hexagonal face. Let $N(i), i = 1,2,\ldots,n$ denote the index set of the vertices adjacent to vertex i and let $Y(h), h = 1,2,\ldots,m$ denote the index set of the hexagonal faces adjacent to hexagon *h*. For each edge (i,j), joining the vertices i and j, a binary variable x_{ij} is associated. Given a perfect matching as a set of edges, the x_{ij} in which participated take the value 1 and otherwise 0. Similarly, for each hexagonal face, a binary variable $y_h, h = 1,2,\ldots,m$ takes the value 1 if its corresponding hexagonal face contains three double bonds and is separate from other hexagons in a given perfect matching and 0 otherwise.

With respect to the above parameters and variables definition, the binary integer linear programming problem (BILP) for finding the Clar number of a fullerene would be as follows:

$$\text{Maximize} \sum_{k=1}^{m} y_k$$

s.t.

$$\sum_{j\in N(i), j<i} x_{ij} + \sum_{j\in N(i), j>i} x_{ji} = 1 \qquad i = 1,2,\ldots,n; \qquad (1)$$

$$\sum_{i\in h_k} \sum_{j\in N(i)\cap h_k, j<i} x_{ij} - 3y_k \geq 0 \qquad k = 1,2,\ldots,m; \qquad (2)$$

$$y_i + y_j \leq 1 \qquad i = 1,2, \dots, m; j \in Y(i); \qquad (3)$$

$$x_{ij} \in \{0,1\} \qquad i = 1,2, \dots, n; j \in N(i), j < i \qquad (4)$$

$$y_k \in \{0,1\} \qquad k = 1,2, \dots, m; \qquad (5)$$

The feasible solution space of the above mathematical programming problem, is a set of all possible perfect matching of F_n. Objective function counts the number of disjoint hexagons with three double bonds in a given perfect matching. Constraint (1) ensures that each vertex is incident with exactly one double bound edge. In other words, double bound edges satisfying in this constraint form a perfect matching of F_n. Constraints (2) and (3) together guarantee that a hexagonal face in a perfect matching specified by constraint (1) is counted if and only if it has three double bound edges and separate from other hexagons in a given perfect matching.

The model proposed in this paper maximize the number of disjoint hexagons with three double bonds over all perfect matching of F_n. Considering the above stated, it is clear that the optimal value of the objective function of the model is the Clar number of a fullerene graph.

3 Computational experiments

To demonstrate the feasibility and efficiency of our proposed model, it has been implemented on many fullerene isomers. We obtained the Clar numbers for all isomers of fullerenes C24-C70 and 3500 isomers of each fullerenes C72-C300 from our model using CPLEX 12.6 under Matlab (R2013 a) on an Intel Pentium Core i2 CPU running at 2.2 GHz with 4 KB cache and 4 GB RAM under the Windows 7 operating system (64-bit). The results for C24-C70 are reported in table 1.

In table 1, column ‘min’ is the minimum Clar number over all isomers of fullerene graph. Similarly, column ‘max’ represents the maximum Clar number over all isomers of fullerene graph. Column ‘average time’ is average CPU time for computing the Clar number over all isomers of fullerene graph.

Fullerene	Number of isomers	Max	Min	average time (sec.)
C24	1	2	2	0.001
C26	1	1	1	0.015
C28	2	2	1	0.015
C30	3	2	1	0.016
C32	6	2	2	0.023
C34	6	3	2	0.029
C36	15	4	2	0.028
C38	17	3	2	0.030
C40	40	4	2	0.032
C42	45	5	3	0.039
C44	89	4	3	0.038
C46	116	5	3	0.043
C48	199	6	3	0.047
C50	271	5	3	0.048
C52	437	6	4	0.048
C54	580	7	4	0.055
C56	924	6	4	0.055
C58	1205	7	5	0.070
C60	1812	8	4	0.072
C62	2385	7	5	0.078
C64	3465	8	5	0.077
C66	4478	9	5	0.085
C68	6332	8	4	0.089
C70	8149	9	6	0.151

Table 1. The Clar number for fullerenes isomers C24-C70

Since there are too many isomers for each fullerene F_n , $n \geq 72$, we obtained the Clar numbers for 3500 isomers of each fullerenes C72-C300. The results are reported in Table 2.

Fullerene	max	min	average time	Fullerene	max	min	average time	Fullerene	max	min	average time
C72	10	6	0.162	C150	23	18	0.787	C226	35	29	2.421
C74	9	6	0.157	C152	22	18	0.827	C228	36	29	2.495
C76	10	6	0.146	C154	23	19	0.859	C230	35	29	2.930
C78	11	6	0.165	C156	24	19	0.855	C232	36	30	3.096
C80	10	6	0.190	C158	23	19	0.953	C234	37	30	2.677
C82	11	7	0.197	C160	24	19	0.961	C236	36	30	3.113
C84	12	7	0.222	C162	25	20	0.909	C238	37	31	2.691
C86	11	7	0.245	C164	24	20	0.997	C240	38	31	2.938
C88	12	8	0.244	C166	25	20	0.972	C242	37	31	3.302
C90	13	8	0.245	C168	26	21	1.003	C244	38	31	3.871
C92	12	8	0.281	C170	25	21	1.047	C246	38	32	3.191
C94	13	9	0.286	C172	26	21	1.174	C248	38	32	3.829
C96	14	9	0.297	C174	26	21	1.081	C250	39	32	3.799

C98	13	9	0.330
C100	14	10	0.342
C102	14	10	0.353
C104	14	10	0.414
C106	15	11	0.420
C108	16	11	0.395
C110	15	11	0.422
C112	16	12	0.432
C114	17	12	0.453
C116	16	12	0.485
C118	17	13	0.520
C120	18	13	0.507
C122	17	13	0.560
C124	18	14	0.576
C126	19	14	0.532
C128	18	14	0.603
C130	19	15	0.590
C132	20	15	0.590
C134	19	15	0.623
C136	20	16	0.678
C138	20	16	0.673
C140	20	16	0.749
C142	21	17	0.745
C144	22	17	0.718
C146	21	17	0.735
C148	22	18	0.778
C176	26	22	1.290
C178	27	22	1.250
C180	28	22	1.265
C182	27	23	1.242
C184	28	23	1.364
C186	29	23	1.234
C188	28	23	1.412
C190	29	24	1.514
C192	30	24	1.539
C194	29	24	1.553
C196	30	25	1.638
C198	31	25	1.555
C200	30	25	1.661
C202	31	25	1.662
C204	32	26	1.797
C206	31	26	1.681
C208	32	26	1.930
C210	32	27	1.936
C212	32	27	2.212
C214	33	27	1.953
C216	34	27	2.192
C218	33	28	2.217
C220	34	28	2.143
C222	35	28	2.153
C224	34	29	2.454
C252	40	33	3.446
C254	39	33	3.620
C256	40	33	4.163
C258	41	33	4.625
C260	40	34	4.238
C262	41	34	4.393
C264	42	34	4.473
C266	41	35	4.523
C268	42	35	5.267
C270	42	35	187.127
C272	42	36	14.319
C274	42	36	45.758
C276	44	36	26.893
C278	42	36	102.866
C280	44	37	29.189
C282	44	37	195.805
C284	44	37	86.838
C286	44	37	389.084
C288	46	38	51.083
C290	44	38	23.667
C292	46	38	99.778
C294	46	39	95.154
C296	46	39	141.220
C298	46	39	237.279
C300	48	40	41.816

Table 2. The Clar number for fullerenes isomers C72-C300

4 Conclusion

The Clar number of a fullerene is a parameter that is related to the stability of fullerene. It was claimed that there is a direct relationship between the Clar number of a fullerene and its stability, i.e., fullerene with larger Clar number is more stable. In this paper, a binary integer linear programming model was proposed for determining the Clar number of a fullerene. The model was implemented on many fullerene graphs with sufficiently large number of vertices using CPLEX 12.6. The results and computation time show that our proposed model is trustworthy in determining the Clar number of fullerenes.

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