CROATICA CHEMICA ACTA CCACAA **69** (1) 215–222 (1996)

ISSN 0011-1643
CCA–2298

Preliminary Communication

Bulvallene Reaction Graph

Tomislav P. Živković

The Rugjer Bošković Institute, 10000 Zagreb, Croatia

Received June 24, 1995; revised October 5, 1995; accepted October 9, 1995

The Monster Graph describing a rapidly reversible degenerate Cope rearrangement of bullvalene molecule is considered. Some global properties of this 1209600-vertex reaction graph, such as shell counts, properties of geodesics connection enantiomers *etc.*, are discussed.

INTRODUCTION

The Cope rearrangement of bullvalene $C_{10}H_{10}$ is the most famous example of a degenerate rearrangement. The existence of this highly unusual molecule was predicted by Doering and Roth[1] in 1963, and bullvalene was synthesized the very next year by Schroder.[2] The reaction graph of bullvalene describing a fast Cope rearrangement is extremely large. It contains as many as 1209600 vertices and, for this reason, it was named »Monster Graph«.[3–5]

The first reaction graphs treated in the literature were rather small, containing up to 20 or 30 vertices.[5,6] The largest reaction graph treated relatively completely in the literature is the reaction graph describing the intramolecular rearrangement of the P_7^{3-} ion.[3] This reaction graph has 1680 vertices. Though this graph is almost two orders of magnitude larger than reaction graphs previously considered in the literature, it is still three orders of magnitude smaller than the Monster Graph! Not surprisingly, very little is known about the Monster Graph. Oth, Muller, Gilles and Schroder[7] report the following properties of this graph:

- Each point of the graph is common to three minimal cycles.
- Each line is common to two minimal cycles.
- The graph is most likely nonplanar.
- The shortest cycle (graph girth) counts 14 points.
- The graph consists of 10!/3 = 1209600 points.

The only non-obvious statement, that about the dimension of the shortest cycle, is not correct! As shown by Randić, Oakland and Klein,[3] the Monster graph contains some cycles of size 12. Even the connectivity of the Monster Graph is not firmly established. Thus Klin, Tratch and Zefirov consider three different models for a Cope rearrangement of bullvalene.[4] One of these models (model IIA) implies that the Monster graph contains two connectivity components containing 10!/6 = 604800 vertices each.

Figure 1 shows the bullvalene skeleton and a Cope-type mechanism of breaking and forming bonds. This is a standard mechanism assumed by most authors, and it corresponds to model IIB of Klin *et al.*[4] Each structure ϕ is represented as an ordered string of ten labels that correspond to ten bullvalene carbon atoms. Thus, ϕ = *abc de fg hi j* represents the initial arrangement of Figure 1. Following Randić *et al.*,[3] we call such strings *codes*. Code labels are grouped in one triplet, three doublets and one singlet: the triplet (*abc*) describes three atoms of the bullvalene base ring, and by convention atoms *a*, *b* and *c* are listed clockwise, if one looks at a bullvalene molecule from the direction of the base ring; doublets (*de*), (*fg*) and (*hi*) describe the three bullvalene double bonds in such a way that atoms *d*, *f*, and *h* are adjacent to the base triangle atoms *a*, *b* and *c*, respectively; finally, the last label belongs to the carbon atom at the apex of the structure. Since the three atoms describing a base ring can be cyclically reordered, there is some ambiguity in the structure notation. In perticular, the three codes

$$\begin{aligned} &abc\ de\ fg\ hi\ j \\ &bca\ fg\ hi\ de\ j \\ &cab\ hi\ de\ fg\ j \end{aligned} \tag{1}$$

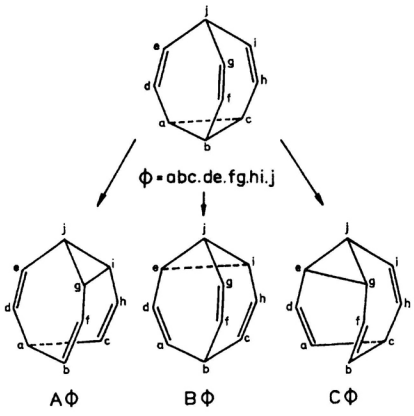

Figure 1.

represent the same structure. This ambiguity is fixed with the requirement that the first label of the triplet is alphabetically the first. With such a convention, there is a unique code for each bullvalene structure.

Granting the above convention, the three rearrangements shown in Figure 1 are:

$$\begin{aligned} \mathrm{A}(abc\ de\ fg\ hi\ j) &= gji\ fb\ ed\ hc\ a \\ \mathrm{B}(abc\ de\ fg\ hi\ j) &= eij\ da\ hc\ gf\ b \\ \mathrm{C}(abc\ de\ fg\ hi\ j) &= ejg\ da\ ih\ fb\ c\ . \end{aligned} \tag{2}$$

One easily finds that these rearrangements effect permutations (of carbon atoms) of odd parity. Further, the convention that the first lable of a triplet should be alphabetically the first does not cause any ambiguity concerning structure parity. This follows from the fact that the three codes Eq. (1) which differ only in a cyclic permutation of a base ring and which represent the same structure, are of the same parity. Hence, each structure has a well defined parity, and structures connected by Cope rearrangements are of the opposite parity. We also note that the code $\bar{\phi} = acb\ de\ hi\ fg\ j$ corresponds to the enantiomer of the structure $\phi = abc\ de\ fg\ hi\ j$, and that structures ϕ and $\bar{\phi}$ are of the opposite parity.

SOME PROPERTIES OF THE BULLVALENE MONSTER GRAPH

In a Monster graph G, each vertex represents one bulvalene structure, while each bond represents one Cope-type rearrangement. As shown above, each vertex has a well defined parity, and each bond connects vertices of the opposite parity. The bullvalene Monster Graph is so huge, that it is impossible to draw this graph, as this is the case with small reaction graphs containing a few tens of vertices.[5,6] Hence, one has to describe this graph in terms of some global properties, such as the graph diameter (largest distance between two graph vertices), graph connectivity (is a Monster Graph connected?), »radial« distribution of neighbours at different shells (distances) from the the initial vertex, distance between enantiomers, graph girth (dimension of the shortest cycle), cyclic and ring structure, *etc.* Here, we present some of these properties.

The most important global property of a Monster graph is probably its shell distribution. This is a radial distribution of neighbours, as seen from the initial »seed« vertex. A Monster Graph is regular of degree three, and all its vertices are equivalent. It is, hence, of no consequence which vertex is chosen as the initial seed vertex. Without loss of generality, one can choose the initial vertex to be $\phi = abc\ de\ fg\ hi\ j$. Starting from this initial vertex, we build various shells at continuously increasing distances. Thus,

TABLE I

Shell structure of a Monster graph. In the k-th shell there are P_{ki} vertices with i predecessors, and the total number of vertices is N_k.

Shell	P_{ki}	P_{k2}	P_{k3}	N_k
0	0	0	0	1
1	3	0	0	3
2	6	0	0	6
3	12	0	0	12
4	24	0	0	24
5	48	0	0	48
6	90	3	0	93
7	171	6	0	177
8	330	9	0	339
9	633	18	0	651
10	1200	42	0	1242
11	2214	111	2	2327
12	4143	198	0	4341
13	7599	438	3	8040
14	13737	936	9	14682
15	24315	1989	39	26343
16	42360	3999	87	46446
17	69627	9090	304	79021
18	105336	19239	1510	126085
19	141708	37617	4323	183648
20	153633	66792	11272	231697
21	116217	89796	26083	232096
22	47472	72945	42956	163373
23	8436	26931	35197	70564
24	624	3978	11741	16343
25	18	282	1548	1848
26	9	39	77	125
27	0	6	15	21
28	0	3	0	3
29	0	0	1	1

the 0-th shell contains only one vertex, the initial vertex ϕ. The first shell contains three vertices which are at distance one from the initial vertex, *etc.* In general, the k-th shell contains N_k vertices. These are all the vertices that are at distance k from the initial vertex. Since each bond connects vertices of the opposite parity, the Monster Graph is bipartite, all vertices in the k-th shell have the same parity, and no two vertices of the k-th shell are mutually connected. Out of N_k vertices contained in the k-th shell, P_{k1} vertices are connected to only one vertex of a previous shell, P_{k2} vertices are connected to two vertices of a previous shell, and P_{k3} vertices are connected to three

vertices of a previous shell. Since there is no connection between vertices of the same shell, and since each vertex is connected to exactly three other vertices, one has $P_{k1} + P_{k2} + P_{k3} = N_k$ ($k \neq 0$). The case $k = 0$ is excluded, since a single vertex ϕ contained in the initial shell is connected to no previous vertex.

The shell distribution of a Monster Graph is shown in Table I. This table contains a lot of information about the Monster Graph.

First, one easily finds that the sum of all counts N_k equals the total number of vertices in a Monster Graph. This graph is hence connected. Next, since according to Table I, the Monster Graph has 30 shells, the graph diameter is $D = 29$. Further, a single vertex in a shell 29 can be shown to correspond to the enantiomer $\bar{\phi} = acb\ de\ hi\ fg\ j$ of the structure representing the initial vertex $\phi = abc\ de\ fg\ hi\ j$. We call enantiomers at the maximal distance antipodal.[9] Vertices in shells 0 and 29 are thus antipodes, and the distance between each pair of enantiomers equals the graph diameter 29. One also observes in Table I that shell 6 contains (for the first time) vertices connected to two vertices of the previous shell. Since $P_{62} = 3$, there are three such vertices, and these three vertices must complete three cycles of size 12. This confirms the result obtained by Randić, Oakland and Klein that the girth of a graph is 12. In the next shell, there are six such vertices. Hence, at this level, one completes six cycles. Three out of these six cycles should

TABLE II

Shell counts of vertices incident to geodesic lines connecting antipodes ϕ and $\bar{\phi}$. The total number of such vertices is 12548.

k	M_k	k	M_k
0	1	15	1272
1	3	16	1188
2	6	17	1068
3	12	18	918
4	24	19	684
5	48	20	477
6	93	21	303
7	177	22	177
8	303	23	93
9	477	24	48
10	684	25	24
11	918	26	12
12	1068	27	6
13	1188	28	3
14	1272	29	1

TABLE III

An example of a geodesic connecting antipodes
ϕ = *abc de fg hi j* and $\bar{\phi}$ = *acb de hi fg j*

abc de fg hi j → gji fb ed hc a → acd bf hi ej g →
fjg ba ed ih c → chd ab ig ej f → bjf ac ed gi h →
dhi ej ca gf b → abf ch je gi d → die hc gf jb a →
acb fg hd je i → eig jb dh fa c → ahc fg di bj e →
egj id fa bc h → chd bj af ie g → efg id ah jb c →
bhc jg af di e → eif gj dc ah b → bjh cd ge af i →
die cb fa gj h → abh fi cd jg e → eig dc fa jh b →
bch af de jg i → fgi ab jh ed c → bdc af ei hj g →
gji fa hc ed b → adb fg ei ch j → hij cb ed gf a →
abf de ch gj i → eji da gf hc b → acb de hi fg j →

correspond to three 12-cycles initiated at shell 1, while the remaining three should complete a 14-cycle. There are, hence, three 14-cycles containing the initial vertex. In addition, since the Monster graph is bipartite, all cycles in the bullvalene reaction graph are even. A more detailed discussion of the cyclic and ring structure of the Monster Graph will be given elsewhere.[8]

Besides shell distribution, another important feature of a reaction graph is the structure of geodesics (the shortest path connecting two vertices) connecting antipodes ϕ and $\bar{\phi}$ in shells 0 and 29, respectively. Let G_g be a graph which is a subgraph of a reaction graph G, and which contains all the vertices contained in at least one geodesic connecting ϕ and $\bar{\phi}$. Graph G_g contains the initial vertex ϕ and its antipode $\bar{\phi}$, as well as all geodesics connecting these two vrtices. Out of N_k vertices contained in the k-th shell, only M_k are contained in a graph G_g. Quantities M_k are shown in Table II. Since all vertices are equivalent, the pattern of geodesic lines as seen from the initial vertex ϕ is identical to this pattern as seen from its antipode $\bar{\phi}$. Hence, $M_k = M_{29-k}$. One further finds that the sum of all M_k equals 12548, wich is the order of graph G_g. Graph G_g is almost a hundred times smaller than the reaction graph G. This shows that only about 1% of all bullvalene structures participated in the shortest conversion path of the initial structure ϕ to its enantiomer $\bar{\phi}$.

In Table III, an example is given of a geodesic π connecting the initial structure ϕ with its antipode $\bar{\phi}$. The first structure in this Table is the initial

structure ϕ, while the last structure is its antipode. Following the rearrangement rules shown in Figure 1, one can easily verify that 30 structures shown in this Table really form a path connecting the initial structure to its antipode. Since this path is geodesic, it represents the shortest conversion pathway between two enantiomes.

Replacing each structure in path π by its antipode, one forms an antipode path $\bar{\pi}$. This path is another geodesic connecting structures ϕ and $\bar{\phi}$. Following the reasoning similar to the one given in Ref. 3, one can show that paths π and $\bar{\pi}$ close a 58-ring.[8] This is the largest ring theoretically possible in the Monster Graph.

CONCLUSION

This is a preliminary report on a bullvalene rearrangement graph, known as Monster Graph. A more detailed account of this graph, as well as a description of the computer program that was used to derive various graph properties, will be given elsewhere.[8] Though the Monster Graph contains as many as 1209600 vertices, this program developed by the author, runs quite successfully on a 386-PC under DOS.

REFERENCES

1. W. von E. Doering and W. R. Roth, *Tetrahedron* **19** (1963) 715; W. von E. Doering and W. R. Roth, *Angew. Chem.* **75** (1963) 27.
2. G. Schroder, *Chem. Ber.* **97** (1964) 3140; R. Morenyi, J. F. M. Oth, and G. Schroder, *Chem. Ber.* **97** (1964) 3150.
3. M. Randić, D. O. Oakland, and D. J. Klein, *J. Comput. Chem.* **7** (1986) 35.
4. M. H. Klin, S. S. Tratch, and N. S. Zefirov, *J. Math. Chem.* **7** (1991) 135.
5. A. Balaban, in: *Graph Theoretical Approaches to Chemical Reactivity* D. Bonchev and O. Mekenyan) (Eds.), Kluwer Academic Publishers, 1994.
6. A. T. Balaban, D. Farcasiu, and R. Banica, *Rev. Roum. Chim.* **11** (1966) 1205.
7. J. F. M. Oth, K. Muller, J. M. Gilles, and G. Schroder, *Helv. Chim. Acta* **57** (1974) 1415.
8. T. P. Živković, in preparation.
9. In Ref. 3, there is a Conjecture stating that for an arbirary reaction graph (subject to some mild conditions) the distance between enantiomers equals diameter D of the isomerization graph. If true, this Conjecture would imply that each enantiomer pair is antipodal. As shown in the present paper, this is the case of the Monster Graph, and this is also the case of the reaction graph that was studied in Ref. 3 and which describes rearrangement of the P_7^{3-} ion. However, this conjecture is not generally true, and reaction graphs can be constructed where the distance between enantiomers is smaller than the graph diameter.[8] There are, hence, genuine enantiomer pairs that are not antipodal.

SAŽETAK

Reakcijski graf bulvalena

Tomislav P. Živković

Razmatran je tako zvani »graf monstrum« koji opisuje reverzibilnu Copeovu pregradnju molekule bulvalena. Diskutirana su neka globalna svojstva tog reakcijskog grafa koji sadrži 1209600 verteksa, kao na primjer statistika ljusaka koja opisuje radijalnu raspodjelu susjedstva, svojstva geodetskih linija koje povezuju enantiomere, itd.