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# The Kekulé Covalent Bond Arrangements of $C_{60}$

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We present an algorithm that enumerates all 12,500 arrangements of double bonds on $C_{60}$ in which each carbon atom forms a single bond with two of its neighbors and a double bond with the third. We then present statistics concerning the symmetry groups of the arrangements and the number of double bonds along pentagonal faces. We exhibit a generating function for the allowed arrangements whose factorization suggests there should be a direct combinatorial solution to the enumeration. We conclude by exhibiting a complete list of double bond arrangements, up to symmetry.

## 1. Introduction

A *Buckyball* is a molecule comprised of 60 carbon atoms placed at the vertices of a truncated icosahedron, or soccer ball. There are 90 edges, forming 12 pentagons and 20 hexagons. There are 60 *pentagonal bonds* along the edges of the pentagons and 30 *hexagonal bonds* sandwiched between two hexagons. The *Kekulé* bond configurations are those in which each carbon atom forms a double bond with one neighboring carbon atom and a single bond with each of two other neighboring carbon atoms. The most symmetric configuration of double bonds is the one in which the hexagonal bonds are all double bonds and the pentagonal bonds are all single bonds; however, this is only one of the 12,500 distinguishable Kekulé bond arrangements which it is the purpose of this paper to enumerate and describe.

We begin in Section 2 by describing an algorithm to enumerate all the Kekulé bond arrangements. A numerical breakdown of the types of arrangements according to their symmetry group and number of pentagonal double bonds is presented in Section 3. In Section 4, we reformulate the problem mathematically as a weighted matching problem, exhibit an interesting generating function, and note that Kasteleyn's formula for weighted matchings in a graph agrees with the results of the enumeration. We conclude with a comprehensive pictorial list of the possible double bond arrangements, up to symmetry.

## 2. An algorithm for enumerating Kekulé bond arrangements

To enumerate the Kekulé bond arrangements, we first note that an arrangement of double bonds among the hexagonal bonds uniquely determines the arrangement of double bonds among the pentagonal bonds, if one is possible at all: a pentagon incident with one hexagonal double bond has two pentagonal double bonds formed on the remaining four carbons; a pentagon incident with three consecutive hexagonal double bonds has one pentagonal double bond formed on the remaining two carbons; and a pentagon whose carbons are all in hexagonal double bonds has no pentagonal double bonds. Hence, if we reduce each pentagon to a single vertex to obtain an icosahedron, we may formulate an equivalent problem: find all the ways to select edges on the icosahedron so that there are one, three consecutive, or five selected edges around each vertex.

Figure 1 is a planar representation of an icosahedron: the vertices are connected by non-crossing edges in a single plane, and the same vertex and edge adjacency relations hold as in the three-dimensional icosahedron, though the shape and size of the edges had to be altered to achieve this. We now break the 30 edges of the icosahedron into 8 groups, as shown in this figure. We will go

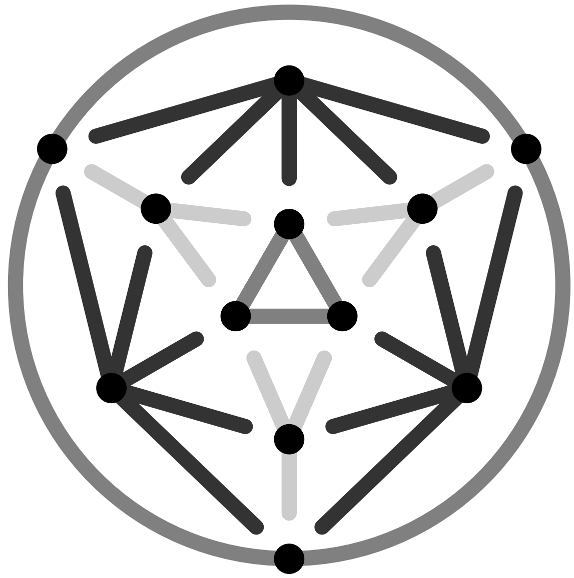


Fig. 1. A planar representation of the icosahedron, broken into eight groups of edges. The icosahedron's edges correspond to hexagonal bonds. We configure the double and single bonds on the five-edge groups, then the "Y"-shaped groups, and finally the triangle and circle.

through the groups in sequence, *configuring* the edges in each group by designating some edges as *selected* and the rest as *unselected*, in a manner that results in a permitted configuration of edges around each vertex.

The first three edge groups are shown as 5-pronged fans. Each of these groups may be independently configured in eleven ways, as there are five ways to have one edge selected, five ways to have three cyclically consecutive edges selected, and one way to have all five edges selected.

The next three groups are the three "Y"-shaped groups. At the center of each group is a vertex which now has two "old" edges already configured in the first three groups, and the "new" edges of the "Y." If both old edges are selected, we must either select all three new edges or only the base of the "Y." If one old edge is selected, we select none of the new edges, so that the vertex has only one selected edge, or in one of two ways select two edges of the "Y" so that the vertex has three consecutive selected edges. Finally, if neither old edge is selected, we select any one of the three new edges. Hence, depending on how the first three groups were configured, each of the second three groups may be configured in 2 or 3 ways.

The last two groups of edges are the triangle at the center and the "circle" on the outside; of course, on the three dimensional icosahedron, both of these are triangles. In both triangles, each vertex has two unconfigured edges and three edges already configured from the first six groups. The nine configured edges already touching a triangle may be in any of 512 configurations, and each one of these permits at most two configurations of the triangle's three unconfigured edges: configure one of the edges in either of the two possible ways, and then since each vertex must have an odd number of selected edges, there is at most one way to configure the remaining two edges.

An upper bound on the number of configurations is thus $11^3 \cdot 3^3 \cdot 2^2 = 143,748$. This number is sufficiently small that it is feasible for a computer program to quickly list all valid configurations of edges by configuring groups of edges in the manner prescribed above, and to analyze the list of configurations so obtained.

## 3. Analysis of the enumeration

A complete list of Kekulé configurations was generated via the algorithm in Section 2. There are 12,500 Kekulé configurations in all. Many of these configurations can be obtained from others by rotations and reflections. If we count configurations as the same when they may be obtained from each other via proper symmetries (rotations), there are 260 different classes of configurations, and if

TABLE I
Symmetry group vs. number of pentagonal double bonds

| p | $C_1{}^a$ | $C_s$ | $C_2{}^a$ | $C_3{}^a$ | $D_2{}^a$ | $C_{2h}$ | $C_{2v}$ | $D_3{}^a$ | $C_{3v}$ | $D_{3d}$ | other | total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 24 | | | 1/60 | | 1/30 | | | 1/20 | | 1/10 | 1/5 $T_d$ | 5/125 |
| 23 | 4/480 | 2/120 | | | | | | | | | | 6/600 |
| 22 | 4/480 | 1/60 | 7/420 | | | 1/30 | 1/30 | | | | | 14/1020 |
| 21 | 3/360 | 3/180 | | 3/120 | | | | | | | | 9/660 |
| 20 | 4/480 | 1/60 | 1/60 | | 1/30 | | | | | | 1/6 $D_{5d}$ | 8/636 |
| 19 | 14/1680 | 2/120 | | | | | | | | | | 16/1800 |
| 18 | 9/1080 | 4/240 | 2/120 | 1/40 | | | 1/30 | 1/20 | | 1/10 | 1/20 $S_6$ | 20/1560 |
| 17 | | 2/120 | | | | | | | | | | 2/120 |
| 16 | 6/720 | 4/240 | 4/240 | | 1/30 | 1/30 | | | | | | 16/1260 |
| 15 | 13/1560 | 6/360 | | 1/40 | | | | | | | 1/12 $C_{5v}$ | 21/1972 |
| 13 | 2/240 | 2/120 | | | | | | | | | | 4/360 |
| 12 | 8/960 | 4/240 | 3/180 | 1/40 | | 1/30 | 1/30 | | 1/20 | | 1/10 $T^a$ | 20/1510 |
| 10 | | | | | | | 1/30 | | | | 1/6 $D_{5d}$ | 2/36 |
| 9 | 3/360 | 4/240 | | 1/40 | | | | | 1/20 | | | 9/660 |
| 6 | | 1/60 | 1/60 | | | | 1/30 | | | 1/10 | | 4/160 |
| 3 | | | | | | | | | 1/20 | | | 1/20 |
| 0 | | | | | | | | | | | 1/1 $I_h$ | 1/1 |
| total | 70/8400 | 36/2160 | 19/1140 | 7/280 | 3/90 | 3/90 | 5/150 | 2/40 | 3/60 | 3/30 | 7/60 | 158/12500 |

Number of configuration classes modulo symmetry / total number of configurations.
[a] As this group contains only proper symmetries, each configuration class possessing this symmetry splits into two mirror-image components; accounting for this yields 260 classes of bond configurations up to proper motions.

we count configurations as being the same when they may be obtained from each other by improper symmetries (combinations of reflections and rotations) as well, these classes collapse into only 158 different classes.

In Table I, we tally the number of double bond configurations according to the number of pentagonal double bonds and the symmetry group of the bond arrangement, giving both the number of configurations up to symmetry and the number of configurations without reducing by symmetry. In Figure 2, we exhibit one representative of each of the 158 classes of bonds.

## 4. Weighted matchings

The problem of arranging double bonds on the Buckyball may be viewed mathematically as follows. Find a matching in the graph whose vertices are the Buckyball's carbons and whose edges are the bonds, where a matching is a set of edges in the graph such that each vertex of the graph is incident with exactly one edge in the set.

Assign each edge in this graph a *weight*, such as a numeric value or a symbolic value. The weight of a matching is the product of the weights of the edges in the matching, and the weight of a set of matchings is the sum of the weights of the matchings in the set. If we assign all edges on the Buckyball weight 1, then each matching has weight 1 and the total weight of all matchings is 12,500. If we assign all pentagonal edges weight $p$ and all hexagonal edges weight 1, the total weight of all matchings is the generating function

$$\begin{aligned} f(p) &= 125p^{24} + 600p^{23} + 1020p^{22} + 660p^{21} + 636p^{20} + 1800p^{19} + 1560p^{18} + 120p^{17} + 1260p^{16} + \\ &\quad 1972p^{15} + 360p^{13} + 1510p^{12} + 36p^{10} + 660p^{9} + 160p^{6} + 20p^{3} + 1 \\ &= (1 + p^2 + 2p^3 + p^4)^3(1 + 2p + 2p^3 + 5p^4)^2(1 - 4p + 9p^2 - 10p^3 + 5p^4). \end{aligned}$$

The coefficient of $p^i$ is the number of double bond arrangements with precisely $i$ pentagonal edges. This was computed by analyzing an enumeration of all Kekulé configurations. It is interesting that the polynomial has a nontrivial factorization, for this suggests there might be a direct combinatorial way of counting the number of matchings with different weights by decomposing the Buckyball into groups of edges corresponding to the factors of the polynomial, making independent choices as to what the weight contribution should be from each group of edges, and putting these choices together to produce the matchings. The author has not found such a decomposition.

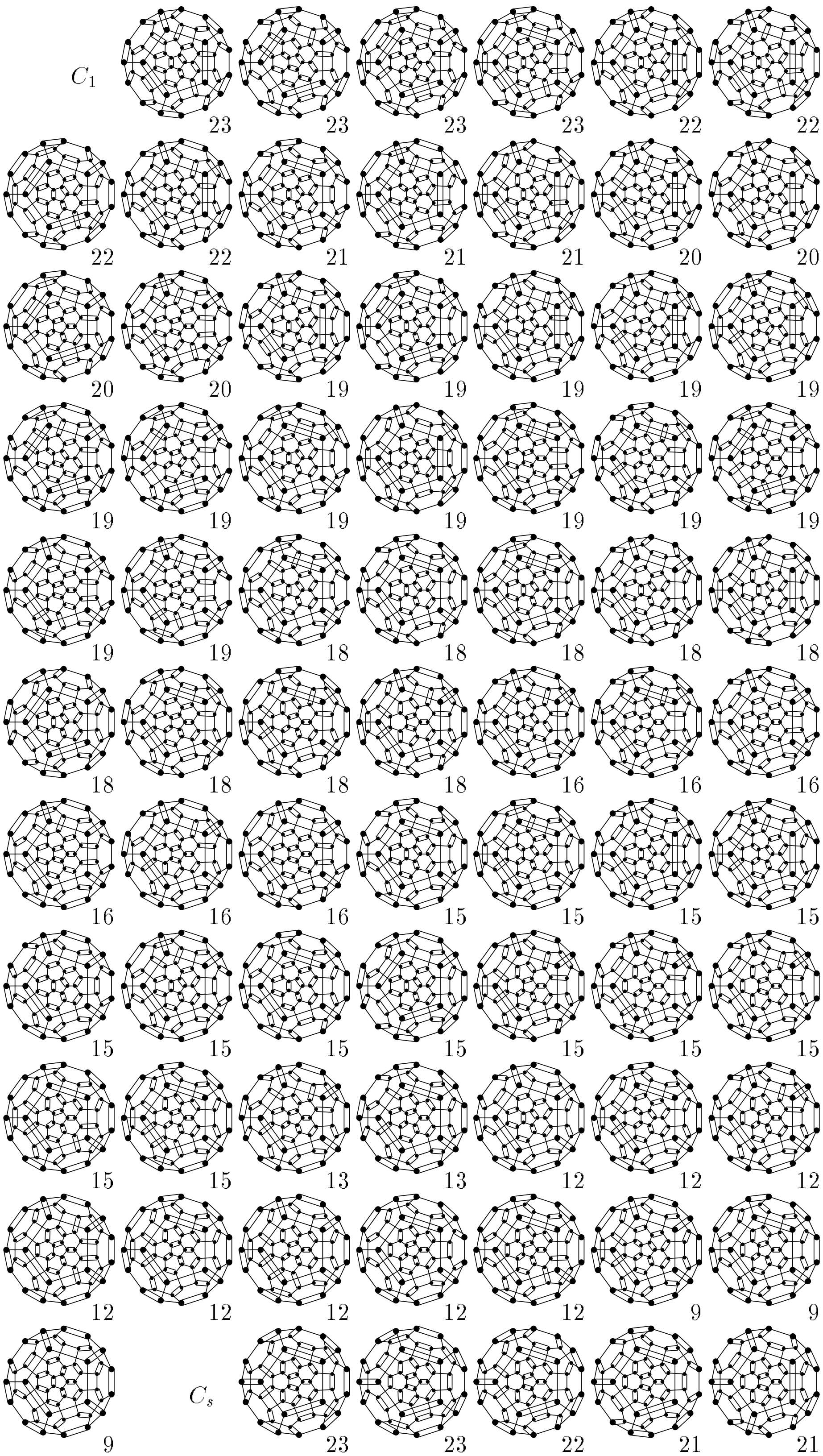
Kasteleyn [1] developed a method to count weighted matchings in a planar graph. The Buckyball is a planar graph with 60 vertices, as we may stereographically project it onto the plane without any edges crossing. Kasteleyn shows that in any planar graph it is possible to direct the edges (by putting arrows on them pointing to one end or the other) so that each finite face in the plane has an odd number of edges pointing clockwise. Form a matrix $A = (a_{ij})$ whose rows and columns are indexed by the vertices of the graph. If there is an edge $(i, j)$ directed from vertex $i$ to vertex $j$, set $a_{ij} = -a_{ji} =$ weight of edge $(i, j)$; if there is no edge between $i$ and $j$, set $a_{ij} = -a_{ji} = 0$. Kasteleyn shows that $\det A$ is the square of the weight of the set of all matchings in the graph!

If all weights are set to 1, it is straightforward to compute this determinant, to obtain 12,500 matchings. If hexagonal edges are given weight 1 and pentagonal edges are given weight $p$, the weight of all matchings obtained by Kasteleyn's method also agrees with $f(p)$. In theory, we could assign all edges distinct symbolic weights, and compute the square root of the determinant of the 60 by 60 matrix corresponding to these weights, to obtain a list of all the matchings, but such a computation is not currently feasible.

## 5. Acknowledgments

I would like to thank Robert Hellwarth, Professor of Physics at USC, for suggesting the problem addressed in this paper.

Fig. 2. A representative of each class of bond arrangements equivalent up to symmetry, drawn from the perspective of a close-up view of a soccer-ball through a front pentagonal face, and arranged by point symmetry group. The subscript is the total number of double bonds on pentagons. The arrangements are oriented so that the highest order rotational axis or symmetry plane is located in a standard position. A five-fold rotation, if present, is about the front-facing pentagon. A three-fold rotation, if present, is about the lower front left hexagon. If neither of these rotations are present but a two-fold rotational axis is present, one bisects the front left edge. If there are no rotational symmetries but there's a reflection, it is through the plane perpendicular to the page, bisecting the diagram from left to right. Beyond these characterizations of the highest order symmetry element, the orientation is arbitrary.


$C_1$
23 23 23 23 22 22
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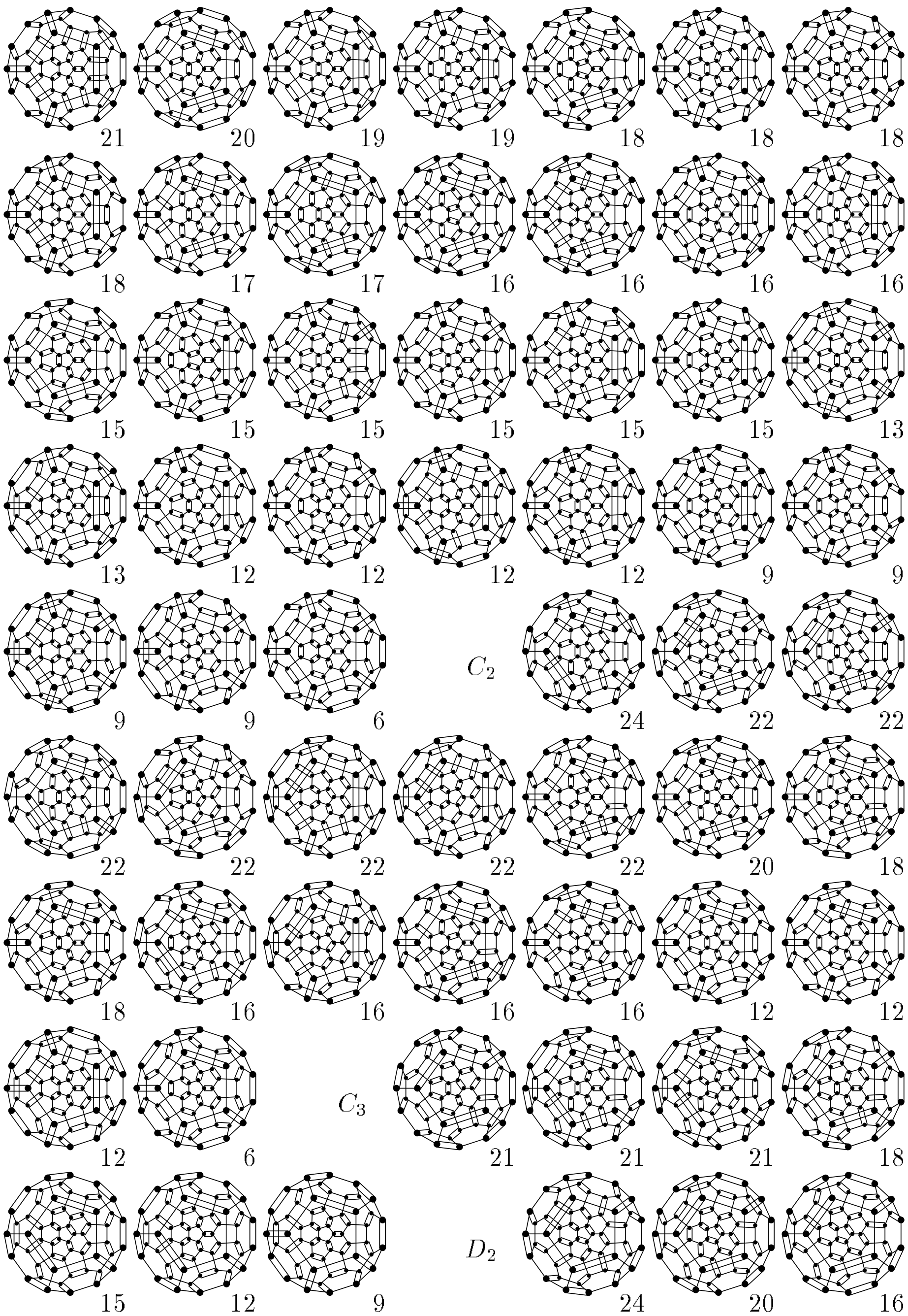
9
$C_s$
23 23 22 21 21


21 20 19 19 18 18 18
18 17 17 16 16 16 16
15 15 15 15 15 15 13
13 12 12 12 12 9 9
9 9 6
$C_2$
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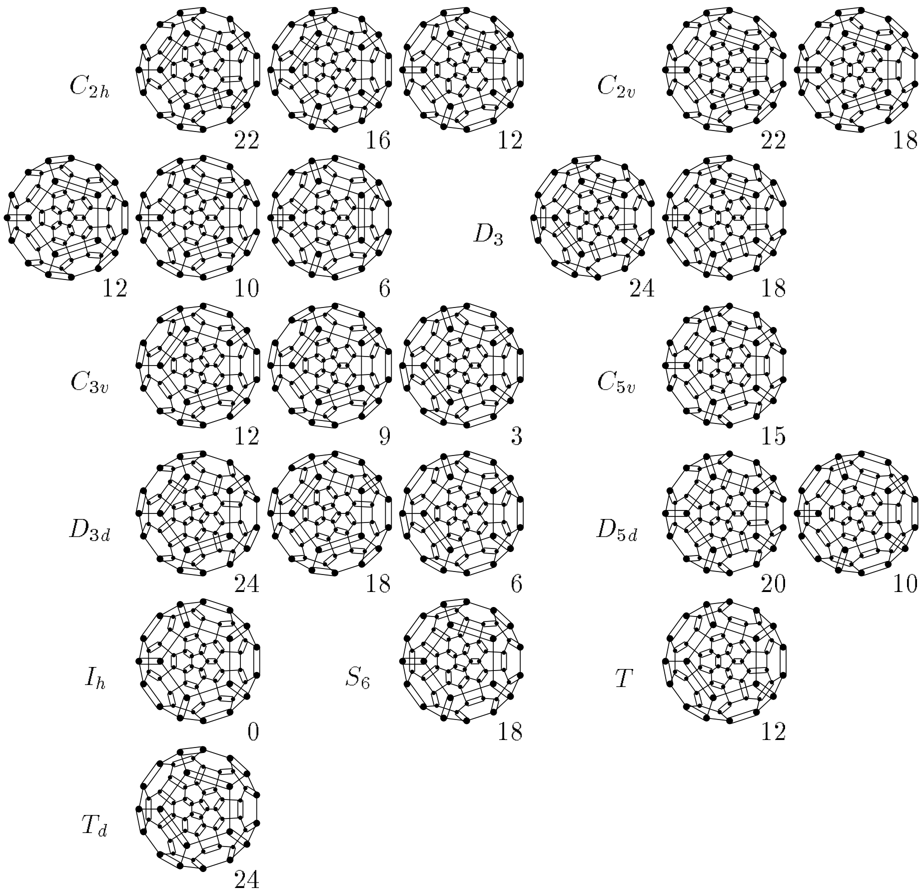
18 16 16 16 16 12 12
12 6
$C_3$
21 21 21 18
15 12 9
$D_2$
24 20 16



$C_{2h}$
22
16
12
$C_{2v}$
22
18
12
10
6
$D_3$
24
18
$C_{3v}$
12
9
3
$C_{5v}$
15
$D_{3d}$
24
18
6
$D_{5d}$
20
10
$I_h$
0
$S_6$
18
$T$
12
$T_d$
24

## References

[1] P. W. Kasteleyn, "Graph Theory and Crystal Physics, in *Graph Theory and Theoretical Physics*," ed. Harary, F. (Academic Press, New York, NY), 1967, pp. 43-110.