Fullerenes $C_{20}$–$C_{60}$: Combinatorial Types and Symmetry Point Groups

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Abstract—A series of fullerenes from $C_{20}$ to $C_{60}$ (a total of 5770) is obtained and their characterization in terms of symmetry point groups is performed for the first time. The most symmetric forms with the sixth and higher orders of automorphism groups (a total of 80) are represented in the Schlegel projection onto one of the faces. It is noted that, among the 5770 fullerenes obtained, only 12 fullerenes exhibit noncrystallographic symmetry. © 2002 MAIK “Nauka/Interperiodica”.

Considerable advances made in the crystallography and mineralogy of carbon over the last fifteen years are associated with the laboratory synthesis [1, 2] and the subsequent discovery [3–5] of $C_{60}$ stable clusters in nature. Fullerenes containing less than 60 atoms are unstable; furthermore, carbon clusters involving from 20 to 36 atoms fall within the so-called “forbidden gap” [6, 7]. However, it is this type of crystallization cavities that has been revealed in different clathrate compounds over the last fifty years [8]. In the present work, we derived all combinatorial types of fullerenes containing from 20 to 60 atoms and proposed their classification in terms of symmetry point groups. It should be noted that the problem of enumeration of fullerenes is dual of the problem of triangulation of a spherical surface. The latter problem has been intensively studied in the context of the problem concerning the closest packing of identical particles on the spherical surface.

Let us now consider a fullerene in the form of a simple polyhedron (each vertex is shared by three faces) in which only pentagonal and hexagonal faces are allowed. It is assumed that $f_5$ and $f_6$ are the numbers of pentagonal and hexagonal faces, respectively, and $f, e,$ and $v$ are the numbers of all faces, edges, and vertices in the polyhedron, respectively. Hence, from the relationships

$$f_5 + f_6 = f, \quad 5f_5 + 6f_6 = 2e$$

we obtain

$$f_5 = 6f - 2e.$$  

Next, from the relationships

$$f - e + v = 2, \quad 2e = 3v$$

we have

$$6f - 2e = 12.$$  

As a result, we obtain

$$f_5 = 12, \quad f = 12 + f_6$$

at any $f_6 \geq 0$.

Similarly,

$$v = 2f - 4 \geq 20, \quad f_6 = f - 12 = v/2 - 10.$$  

Thus, any fullerene can be characterized by the vertex ($C_{v}$-r) and face ($5_{12}^6$, $v_{12}^6$) formulas.

The general idea of representing a fullerene in the form of a Schlegel projection according to the face formula is as follows. Face $f$ is surrounded by other faces that are numbered clockwise. The same operation is repeated with faces 2, 3, etc. In the favorable case, the basal face of the Schlegel projection will be generated at the penultimate step. In particular, for the simplest formula $5_{12}$, the operation begins with the pentagonal face and leads to a dodecahedron (see figure, no. 1).

For fullerenes described by the formula $5_{12}6_m$, the above operation can begin with the hexagonal face. In order to exhaust all the possible variants, it is necessary to preliminarily enumerate the sequences (6, ... with all kinds of arrangement of $(n - 1)$ sextuples in $(n + 11)$ unoccupied positions. Then, pentagonal and hexagonal faces are generated in accordance with these sequences. For example, the sequence (6, 5, 5, ..., 5) with twelve quintuples does not lead to a polyhedron, because the $5_{12}6_1$ fullerene is nonexistent in nature. However, the $5_{12}6_2$ fullerene (figure, no. 2) exists and can be specified by the sequence (6, 5, ..., 5, 6).

The aforementioned operation is terminated in the following cases: (i) the fullerene is constructed according to the face formula; (ii) the fullerene is constructed prior to exhaustion of the formula; (iii) the fullerene is not constructed, but the formula is exhausted; and
(iv) at a certain step, the required face becomes neither pentagonal nor hexagonal. All the fullerenes constructed with the use of the given formula are sorted according to combinatorial type, and repetitions are rejected.

The forms thus obtained are characterized by symmetry point groups. The algorithm of their determination is reduced to the enumeration of all kinds of redesignation of vertices retaining contiguity. By certain criteria, each redesignation is identified as a fullerene symmetry element.

After executing this algorithm, we obtained 5770 combinatorially different fullerenes in which the number of vertices ranges from 20 to 60. The distribution of the fullerenes over automorphism group orders and symmetry point groups is given in the table. The vast majority of the forms involved have the symmetry 1, 2, or 3. For a fixed $v$, the diversity of forms drastically decreases with an increase in the order of the automorphism group. This is accompanied by an increase in the physical stability of the fullerene $[1, 2, 6, 7, 9]$. The most symmetric forms with the sixth and higher orders of automorphism groups are depicted in the figure. The symmetry point groups of these forms are as follows:

- $C_{20}$: 1 ($53m$); $C_{24}$: 2 ($122m$); $C_{26}$: 3 ($6m2$); $C_{28}$: 4 ($43m$); $C_{30}$: 5 ($10m2$); $C_{32}$: 6 (32); 7 ($3m$); 8 ($6m2$); $C_{34}$: 9 ($3m$); $C_{36}$: 10, 11 ($42m$); 12 ($6m2$); 13 ($6/mmm$); $C_{38}$: 14 (32); 15 ($3m$); 16 ($6m2$); $C_{40}$: 17 ($3m$); 18 ($mmm$); 19, 20 ($5m$); 21 ($43m$); $C_{42}$: 22 (32); $C_{44}$: 23, 24 (32); 25 (23); 26–28 ($3m$); 29, 30 ($6m2$); $C_{46}$: 31 (32); 32, 33 ($mmm$); 34, 35 ($12m2$); $C_{50}$: 36, 37 (32); 38 ($3m$); 39 ($6m2$); 40, 41 ($10m2$); $C_{52}$: 42, 43 ($3m$); 44, 45 ($mmm$); 46–50 ($42m$); 51 (23); $C_{54}$: 52 (32); 53 ($6m2$); $C_{56}$: 54–59 (32); 60 ($mmm$); 61 ($42m$); 62, 63 ($3m$); 64 ($43m$); $C_{58}$: 65, 66 ($3m$); $C_{60}$: 67–69 (32); 70 ($3m$); 71 ($mmm$); 72–75 ($42m$); 76 (52); 77 ($5m$); 78, 79 ($6/mmm$); 80 ($53m$).

Apart from the well-known form $C_{60}$ (80), the most probable fullerenes in the physical experiments are 34, 35, 40, 41, 64, and 77–79. Judging from the number of atoms, these fullerenes fall far beyond the forbidden gap and possess high symmetry. Except for forms 1, 2, 5, 19, 20, 34, 35, 40, 41, 76, 77, and 80, the fullerenes $C_{20}–C_{60}$ exhibit crystal symmetry and, without symmetry violation, can be considered as possible structural units of the crystalline compounds. The listed 12 forms are also encountered in crystalline compounds (for...