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Numbering of Fullerenes

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ABSTRACT

Rules for numbering ($C_{60}-I_h$)[5,6]fullerene and ($C_{70}-D_{5h(6)}$)[5,6]fullerene were codified in a publication “Nomenclature for the ($C_{60}-I_h$)[5,6] and ($C_{70}-D_{5h(6)}$)[5,6]fullerenes” published in *Pure Appl. Chem.* **74**(4), 629-695, 2002. The current publication contains recommendations for numbering a wide variety of fullerenes of different sizes, and of various point group symmetries, including low symmetries such as C_s , C_i , and C_1 , as well as many fullerenes that have been isolated and structurally well characterized. These recommendations are based on the principles established in the earlier publication, and aim to identify well-defined, and preferably contiguous helical pathway for numbering. Rules for systematically completing the numbering of fullerene structures the numbering of which becomes discontinuous are presented.

Numbering of Fullerenes

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1. Introduction

In 1995 a preliminary survey on numbering and nomenclature for fullerenes was published [1]. It described two types of names for fullerenes, one proposed by some workers in the field and the one used by the Chemical Abstracts Service (CAS); and two systems for numbering fullerene skeletons, one proposed in a publication by R. Taylor [2], and one published by CAS [3]. In addition, alternative methods for naming derivatives of fullerenes were discussed. More recently, a document appeared reporting IUPAC recommendations for the nomenclature for the $C_{60}-I_h$ and $C_{70}-D_{5h(6)}$ -fullerenes and their derivatives [4]. This report was limited to these fullerenes because there are only a small number of known derivatives of only a few other fullerenes.

The present document contains recommendations for the numbering of fullerenes other than $(C_{60}-I_h)[5,6]$ fullerene and $(C_{70}-D_{5h(6)})[5,6]$ fullerene. The parenthetical prefix gives the carbon content and the point group symbol; the bracketed numbers indicate the ring sizes in the fullerene. The latter is important in fullerenes with rings other than five- and six-membered. The subscript parenthetical (6) following the point group symbol D_{5h} in the latter name indicates that the five-membered ring on the five-fold symmetry axis is surrounded by six-membered rings. This distinguished this fullerene from an isomeric $(C_{70}-D_{5h(6)})[5,6]$ fullerene having five-membered rings surrounding the five-membered ring on the five-fold symmetry axis designated by the name $(C_{70}-D_{5h(5)})[5,6]$ fullerene. In the present document, fullerene structures are unambiguously identified by CAS registry number and the reference numbers of *An Atlas of Fullerene*, if available [5]. The recommendations are largely based on those reported in ref. 4, and can be used for numbering all fullerenes. One of the aims for the development of these recommendations was to devise a numbering method simpler for the chemical public to use than the existing CAS procedures [3].

2. General Considerations on Fullerene Numbering

The identification of a well-defined and preferably contiguous helical numbering pathway is the cornerstone of fullerene numbering. Such a pathway represents a double-conical helix in the sense that, starting from a given atom (a "pole" of the spheroid), reaches all the other atoms of the fullerene moving in a clockwise or anticlockwise direction through the two "hemispheres" to reach the opposite "pole". (In a Schlegel diagram with the starting point of the numbering located at the center of the representation, the pathway corresponds to an expanding spiral.) The construction of

the pathway starts with the numbering of a whole simple ring of the fullerene. Then, the numbering proceeds to cover all of the other atoms keeping the pitch of the helix as small as possible (*i.e.* keeping the movement “as tight as possible”) and maintaining its clockwise or anticlockwise directionality.

2.1. Numbering for $(C_{60}-I_h)[5,6]$ fullerene and $(C_{70}-D_{5h(6)})[5,6]$ fullerene

The following rules were adopted for numbering $(C_{60}-I_h)[5,6]$ fullerene and $(C_{70}-D_{5h(6)})[5,6]$ fullerene [4]

Rule Fu-3.1.1: Proper rotation axes (C_n) are examined in sequence from the highest-order to the lowest-order axis, until at least one contiguous helical pathway is found that begins in a ring through which a proper rotation axis passes, or at the end of a bond bisected by a proper rotation axis, or at an atom through which a proper rotation axis passes. Numbering begins at the end of such a contiguous helical pathway, and the corresponding axis is called the “reference axis”.

Rule Fu-3.1.2: If there is a choice for the selection of a reference axis or for the end of the reference axis to begin the numbering, a ring is preferred to a bond which, in turn, is preferred to an atom.

Rule Fu-3.1.3: When there is a choice among helical numbering pathways, the preferred pathway terminates as close as possible, in terms of the number of bonds, to the reference axis.

The numberings of $(C_{60}-I_h)[5,6]$ fullerene and $(C_{70}-D_{5h(6)})[5,6]$ fullerene [4] illustrate the application of these rules.

2.1.1. Systematic numbering for $(C_{60}-I_h)[5,6]$ fullerene (Fig. 1) (Atlas [5] Ref. No. 60:1; CAS Reg. No. 99685-96-8).

This fullerene has six equivalent C_5 axes passing through opposite pentagons, each of which gives identical contiguous helical pathways in either direction from any atom of any pentagon (all atoms are equal in $(C_{60}-I_h)[5,6]$ fullerene). Any of these C_5 axes can be the reference axis. According to **Rule Fu-3.1.1**, it is not necessary to consider any of the lower-order C_3 and C_2 axes. The systematic numbering is given in Fig. 1.

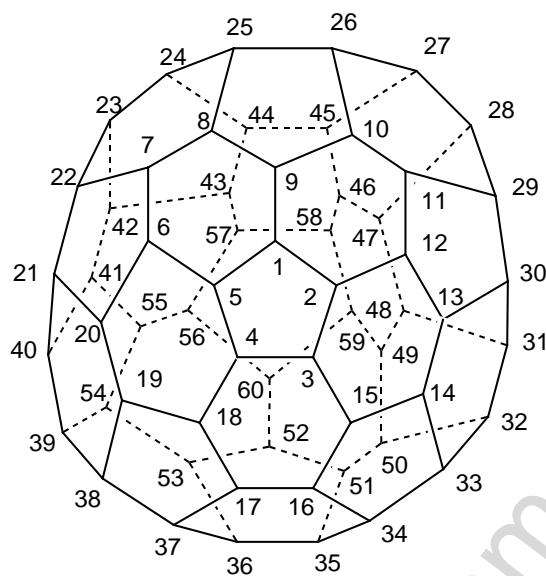


Fig. 1. Systematic numbering of $(C_{60}-I_h)[5,6]$ fullerene

2.1.2. Systematic numbering for $(C_{70}-D_{5h(6)})[5,6]$ fullerene (Fig. 2) (Atlas Ref. No. 70:1; CAS Reg. No. 115383-22-7).

The principal axis for this fullerene is the C_5 axis passing through opposite pentagons. There are no contiguous helical pathways from any atom in either pentagon (all equivalent) and therefore the C_5 axis cannot be the reference axis. Following **Rule Fu-3.1.1**, one of the five equivalent C_2 axes that pass through the center of a six-membered ring at one end and bisect the bond between two six-membered rings at the other end (see Fig. 2a) must be evaluated. Since, according to **Rule Fu-3.1.2**, a ring is preferred to a bond for the beginning of numbering, the search for a helical pathway must start in the six-membered ring. *A priori* there are twelve pathways, one in each direction, clockwise and anticlockwise, from each atom of the six-membered ring to be examined. However, because of symmetry, atoms **a** and **a'** in Fig. 2a are equivalent, as are atoms **b**, **b'**, **b''**, and **b'''** (throughout this document symmetry-related atoms are indicated by unprimed and primed identical letters). Therefore, there are only three different pathways to explore: clockwise **b'** to **a'** to **b''**, clockwise **a** to **b** to **b'**, and clockwise **b** to **b'** to **a'**. The pathway **b'** to **a'** to **b''** terminates at the atom marked **c** at the end of the bond bisected by the reference axis. The pathway **a** to **b** to **b'** terminates at the atom marked **d**, one bond removed from the bond at the end of the reference axis. The pathway **b** to **b'** to **a'** terminates at the atom marked **e**, two bonds removed from the bond bisected by the reference axis. According to **Rule Fu-3.1.3**, the preferred contiguous pathway for numbering is **b'** to **a'** to **b''**; the resulting systematic numbering is shown in Fig. 2b.

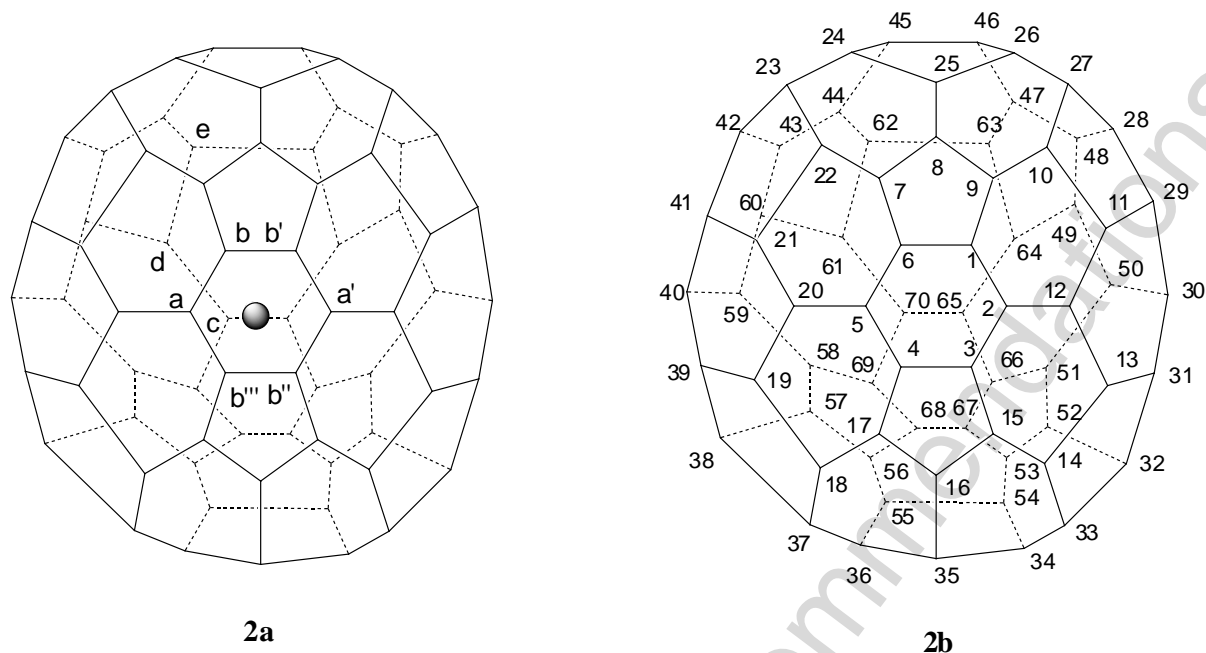


Fig. 2. Systematic numbering of $(C_{70}-D_{5h(6)})[5,6]$ fullerene

3. Numbering of fullerenes other than $(C_{60}-I_h)[5,6]$ - and $(C_{70}-D_{5h(6)})[5,6]$ -fullerene.

While **Rules Fu-3.1.1, Fu-3.1.2, and Fu-3.1.3** are sufficient to systematically number $(C_{60}-I_h)[5,6]$ fullerene and $(C_{70}-D_{5h(6)})[5,6]$ fullerene, the numbering of other fullerenes may require additional rules. Some of these rules have already been proposed [4].

Rule Fu-3.1.2.1: When there is a choice between rings for the beginning of numbering, a larger ring is preferred to a smaller one. When there is still a choice, the preferred ring contains the highest ranking atom at the first point of difference. The highest-ranking atom is defined as the common atom of the set of three largest rings. For example, in a [5,6]fullerene, an atom at the intersection of three six-membered rings (in short, a 6,6,6 atom) ranks higher than an atom at the intersection of two six-membered rings and a five-membered ring (a 6,6,5 atom).

Rule Fu-3.1.2.2: When there is a choice between bonds bisected by an axis for the beginning of numbering, the preferred bond contains the higher number of higher-ranking atoms.

Rule Fu-3.1.2.3: When there is a choice between atoms lying on an axis for the beginning of numbering, the numbering must start at the higher-ranking atom.

In addition to the recommendations of ref. 4 one new rule was adopted:

Rule Fu-3.1.4: When there is still a choice among helical pathways for numbering, they are evaluated by sequential comparison of the ranking of their atoms. The preferred pathway contains the highest-ranking atom at the first point of difference.

Based on the rules required for the numbering of their atoms, fullerenes considered in this document are divided into the following classes:

3.1 Fullerenes having at least one symmetry axis (C_n , $n > 1$) and a contiguous helical numbering pathway determined on the basis of rules **Fu-3.1.1** to **Fu-3.1.4**.

3.2 Fullerenes having at least one symmetry axis (C_n , $n > 1$) but no contiguous helical numbering pathway determined on the basis of rules **Fu-3.1.1** to **Fu-3.1.4**.

3.3 Fullerenes having a symmetry plane (σ) as sole symmetry element (point group C_s) and a contiguous helical numbering pathway determined unambiguously as described under 3.3 below.

3.4 Fullerenes having a center of inversion (i) or a C_1 axis as sole symmetry elements (point group C_i and C_1) and a contiguous helical numbering pathway determined unambiguously as described under 3.4 below.

~~**3.1.** Fullerenes having at least one symmetry axis (C_n , $n > 1$) and a contiguous helical numbering pathway determined on the basis of rules **Fu-3.1.1** to **Fu-3.1.4**.~~

There are fullerenes belonging to this class whose numbering can be devised solely on the basis of **Rules Fu-3.1.1** to **Fu-3.1.3**. Examples are given below.

3.1.1. Systematic numbering for (C_{20} - I_h)[5]fullerene (Fig. 3) (Atlas Ref. No. 20:1; CAS Reg. No. 104375-45-3).

For this fullerene any of the equivalent C_5 axes (the highest-order axis for this molecule), that pass through the centers of opposite faces, provides equivalent contiguous helical pathways in either direction from any atom of any pentagon (all atoms are symmetry equivalent). Because this fullerene is achiral, the clockwise or anticlockwise direction of the helical numbering pattern is not important (caution: the direction of numbering may become important for chiral derivatives, see ref. 4). Therefore, each of the C_5 axes can be the reference axis, and it is not necessary to examine the equivalent C_3 or equivalent C_2 axes which are of lower order. The numbering for this fullerene is given in Fig. 3.

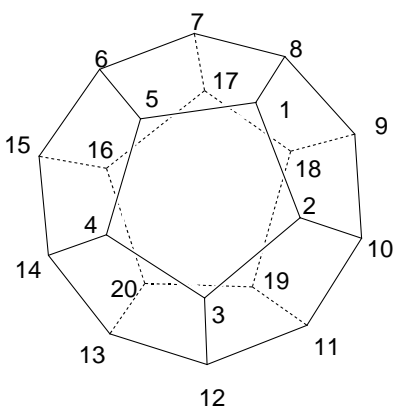


Fig. 3. Systematic numbering for $(C_{20}-I_h)[5]$ fullerene

3.1.2. Systematic numbering for $(C_{24}-O_h)[4,6]$ fullerene (Fig. 4) (CAS Reg. No.114153-97-8).

This fullerene contains only 6,6,4 atoms. A contiguous helical pathway cannot be obtained using the three equivalent C_4 axes passing through opposite tetragonal faces (Fig. 4a). Therefore, following **Fu-3.1.1**, the four equivalent C_3 axes passing through opposite symmetry-equivalent hexagons are examined (Fig. 4b). Only the clockwise or anticlockwise pathways (both are equivalent for this achiral fullerene) starting along one of the three symmetry-equivalent bonds connecting symmetry-equivalent atoms (**a** and **a'**) lead to contiguous numberings. The clockwise numbering is shown in Fig. 4c. Pathways around the lower-order C_2 axes do not need to be considered.

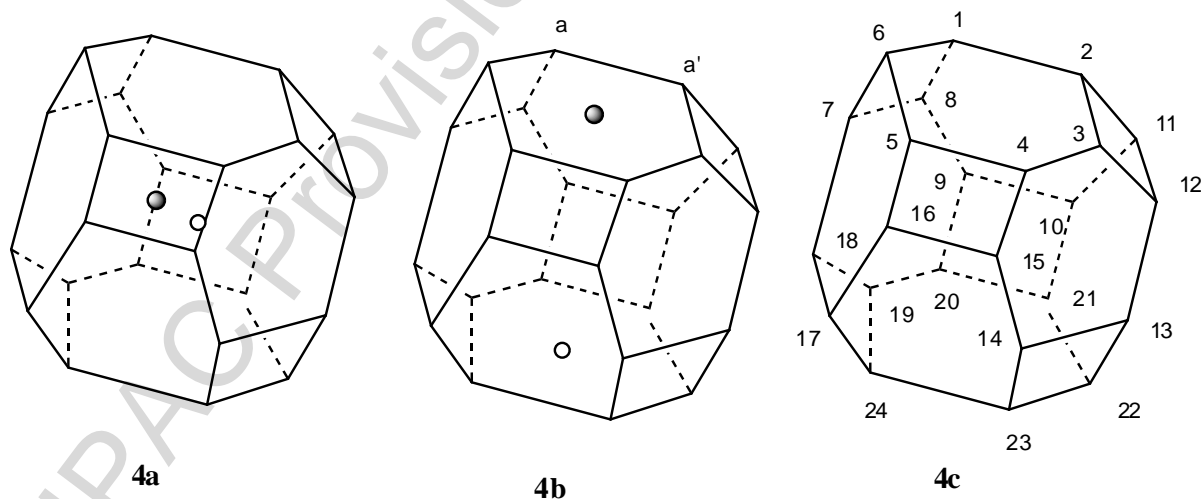


Fig. 4. Systematic numbering for $(C_{24}-O_h)[4,6]$ fullerene

3.1.3. Systematic numbering for $(C_{78}-C_{2v})[5,6]$ fullerene (Fig. 5) (Atlas Ref. No. 78:2; CAS Reg. No. 139707-96-3).

This fullerene contains a single C_2 axis which passes through the center of a six-membered ring on one side and the midpoint of a bond on the other side. According to **Fu-3.1.2** the ring is preferred for beginning the numbering. Because of symmetry there are only three pathways to be considered, namely clockwise **a** to **b** to **a'**, **b** to **a'** to **a''**, and **a'** to **a''** to **b'** (Fig. 5a). These lead to the contiguous helical numberings shown in Fig. 5b, 5c, and 5d, respectively. By application of **Rule Fu-3.1.3** the numbering of Fig. 5c is preferred because it terminates at an atom belonging to the bond bisected by the C_2 axis, whereas the other numberings terminate at an atom one (Fig. 5d) and two (Fig. 5b) bonds removed from the C_2 axis, respectively.

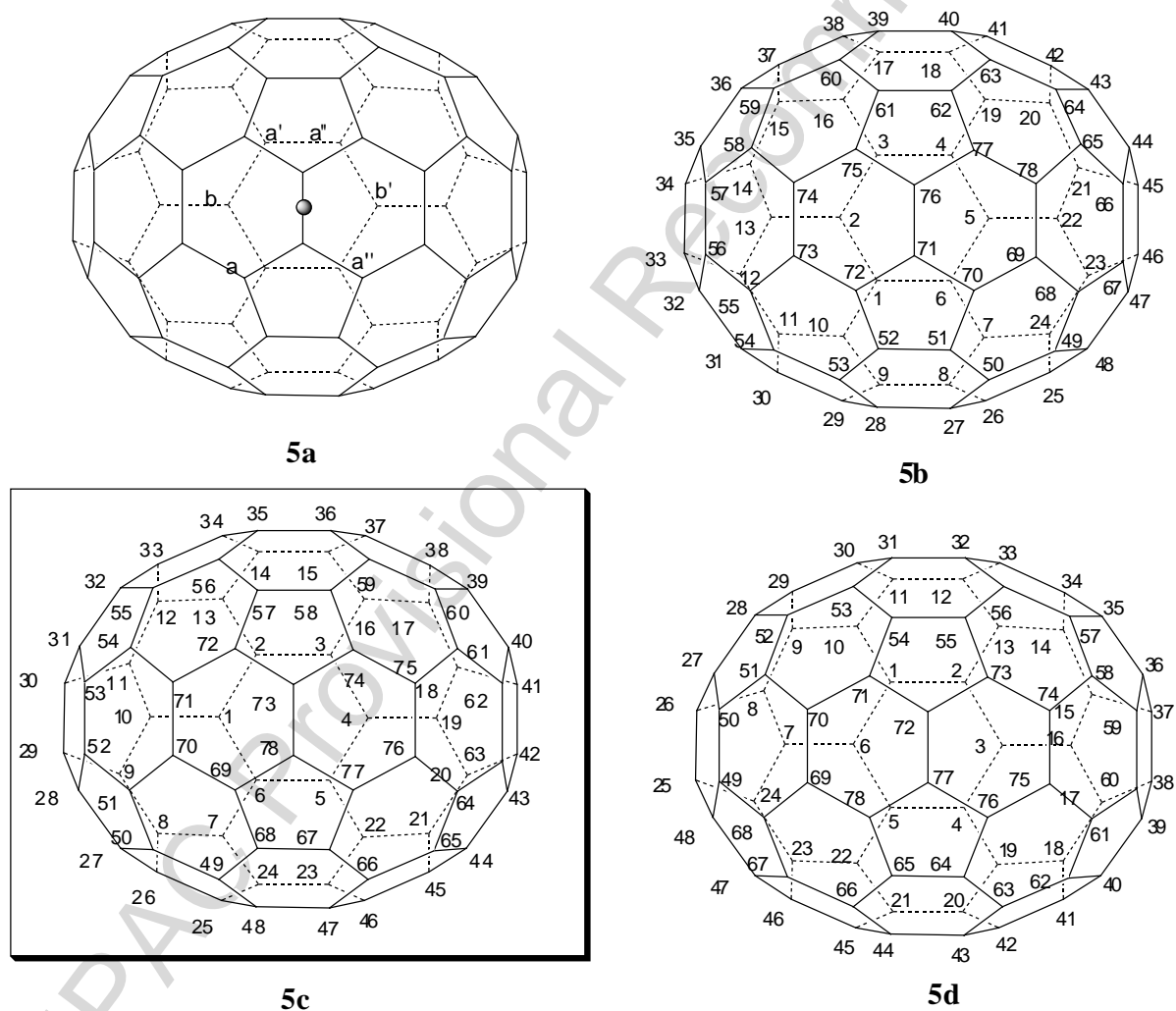


Fig. 5. Systematic numbering for $(C_{78}-C_{2v})[5,6]$ fullerene

3.1.4. Systematic numbering for (C₄₈-C₂)[5,6]fullerene (Fig. 6) (Atlas Ref. No. 48:163; CAS Reg. No. 150398-36-0; this fullerene is listed as C₁-symmetric CAS).

This is a chiral fullerene. The discussion will consider the enantiomer shown in Fig. 6a. The only symmetry element in this fullerene is a C₂ axis which bisects midpoints of opposite bonds (Fig. 6a). Both bonds connect 6,6,5 atoms (**a** and **a'** at the near end of the axis; **b** and **b'** at the far end). Based on **Fu-3.1.2.2** no selection between these bonds for beginning the numbering can be made. In Fig. 6a, the atoms indicated with the same letter (unprimed and primed) are identical for symmetry reasons. Also because of symmetry, only four pathways must be considered: **a** to **a'** to **c**; **a** to **a'** to **d**; **b** to **b'** to **e**; and **b** to **b'** to **f**. Of these, only the anticlockwise **b** to **b'** to **e** pathway results in a contiguous helical numbering that is shown in Fig. 6b. Because the pathway is clockwise for a viewer looking directly at the polygon where the numbering begins from the outside of the fullerene cage, the stereodescriptor for this inherently chiral fullerene is (^{f,s}C) (“f” = fullerene; “s” = systematic numbering; “C” = clockwise) [4]. The numbering of the (^{f,s}A), enantiomer, shown in Fig. 6c, is the mirror-image of that shown in Fig. 6b.

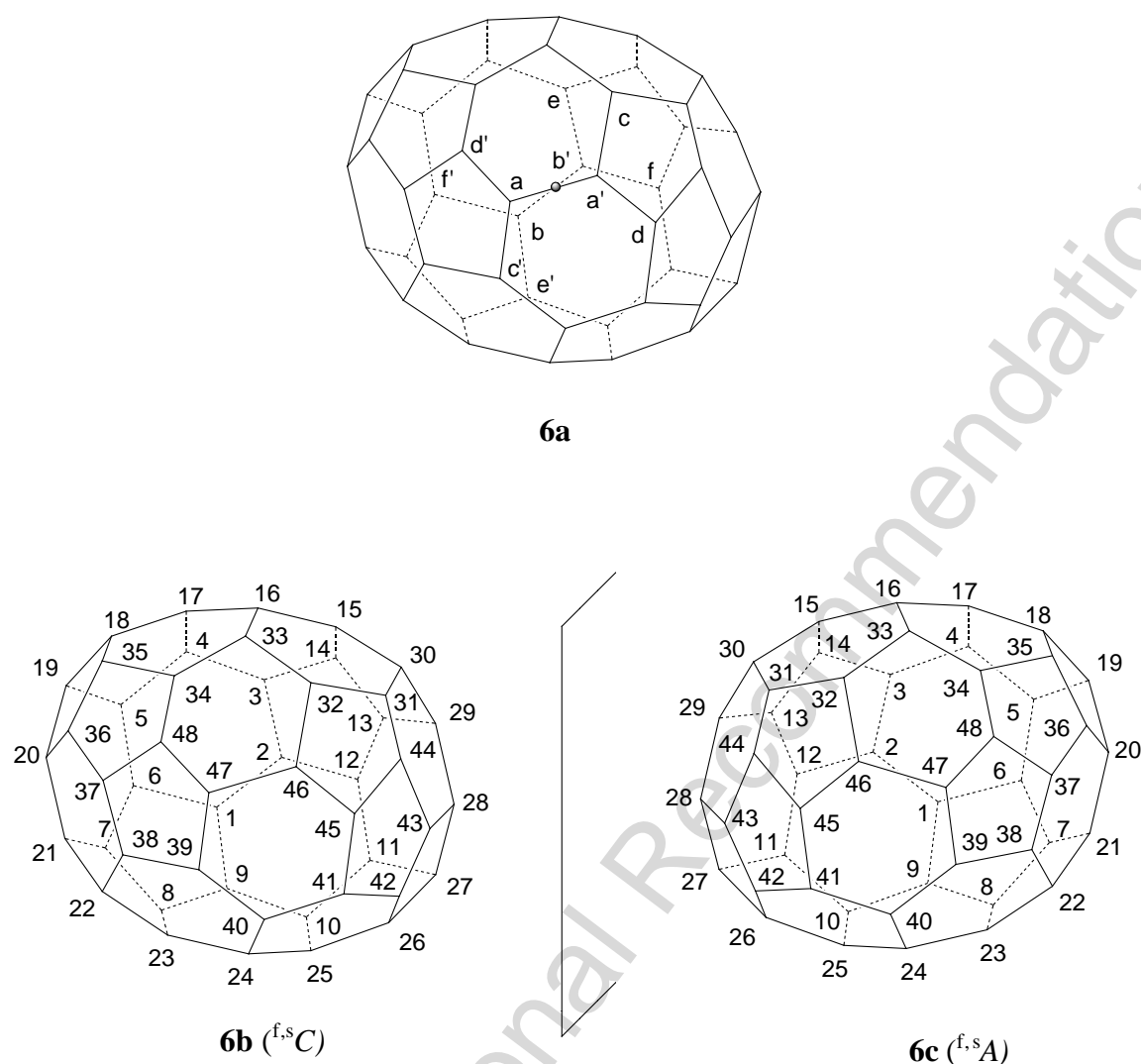


Fig. 6. Systematic numbering for the enantiomers of $(C_{48}-C_2)[5,6]$ fullerene

3.1.5. Systematic numbering for other fullerenes having at least one symmetry axis (C_n , $n > 1$) and a contiguous helical numbering pathway determined on the basis of rules **Fu-3.1.1** to **Fu-3.1.4**.

Rules Fu-3.1.1 to **Fu-3.1.3** were used to number the fullerenes reported in Appendix 1. However, fullerenes of this class do exist for which the application of **Rules Fu-3.1.1** through **Fu-3.1.3** does not allow to distinguish among several contiguous helical numberings. To solve this problem the additional **Rule Fu-3.1.4** has been adopted. The use of this new rule leads to numberings that in some cases are different from those obtained by CAS [3]. Examples of fullerenes whose numbering *requires* application of **Rule Fu-3.1.4** are described below.

3.1.6 Systematic numbering for $(C_{40}-D_2)[5,6]$ fullerene (Fig. 7) (Atlas Ref. No. 40:38; Cas Reg. No. 145646-78-2).

This structure is characterized by three different C_2 axes. One C_2 axis passes through opposite six-membered rings; the other C_2 axes pass through midpoints of opposite bonds. By application of **Fu-3.1.2** the axis passing through the ring has highest priority for selection as the reference axis. This axis is shown in Fig. 7a. The numbering should begin from one of the atoms belonging to either one of the two rings that are symmetry-equivalent. Because of symmetry, the six atoms of the ring form three pairs of equivalent atoms: **a/a'**, **b/b'**, and **c/c'**. Thus, there are only six pathways to be evaluated, clockwise and anticlockwise from **a**, from **b**, and from **c**. The pathway **c** to **b** to **a** does not result in a contiguous helical numbering. All the other five pathways [**a** to **c'** to **b'** (Fig. 7b); **a'** to **b'** to **c'** (Fig. 7c); **b'** to **a'** to **c** (Fig. 7d); **b'** to **c'** to **a** (Fig. 7e); **c'** to **a** to **b** (Fig. 7f)] do result in contiguous numberings and a choice must be made.

Application of **Rules Fu-3.1.1** through **Fu-3.1.3** is not sufficient to select the preferred numbering, since all numberings terminate at an atom belonging to the ring intersected by the axis. Inspection of the atom ranking using the new **Rule Fu-3.1.4** leads to selection of the pathway in Fig. 7e as the correct numbering since it contains the higher-ranking atom at the first point of difference (see Table 1). Indeed, the pathway in Fig. 7e begins at a 6,6,5 atom (and thus is preferred over the pathways in Figs. 7b and 7c), and contains a 6,6,5 atom at position 2, whereas both pathways in Figs. 7d and 7f contain a 6,5,5 atom at the same position. The stereodescriptor for the shown enantiomer of this inherently chiral fullerene is (^{f,s}A) [4]. Note that, once a numbering is discarded, further inspection of atom ranking is not required. Based on different rules [3], CAS selects the pathway in Fig. 7c as the preferred numbering.

Table 1. Rankings of atoms 1 and 2 for pathways in Figs. 7b-7f.

Atom	7b	7c	7d	7e	7f
1	6,5,5	6,5,5	6,6,5	6,6,5	6,6,5
2	-	-	6,5,5	6,6,5	6,5,5

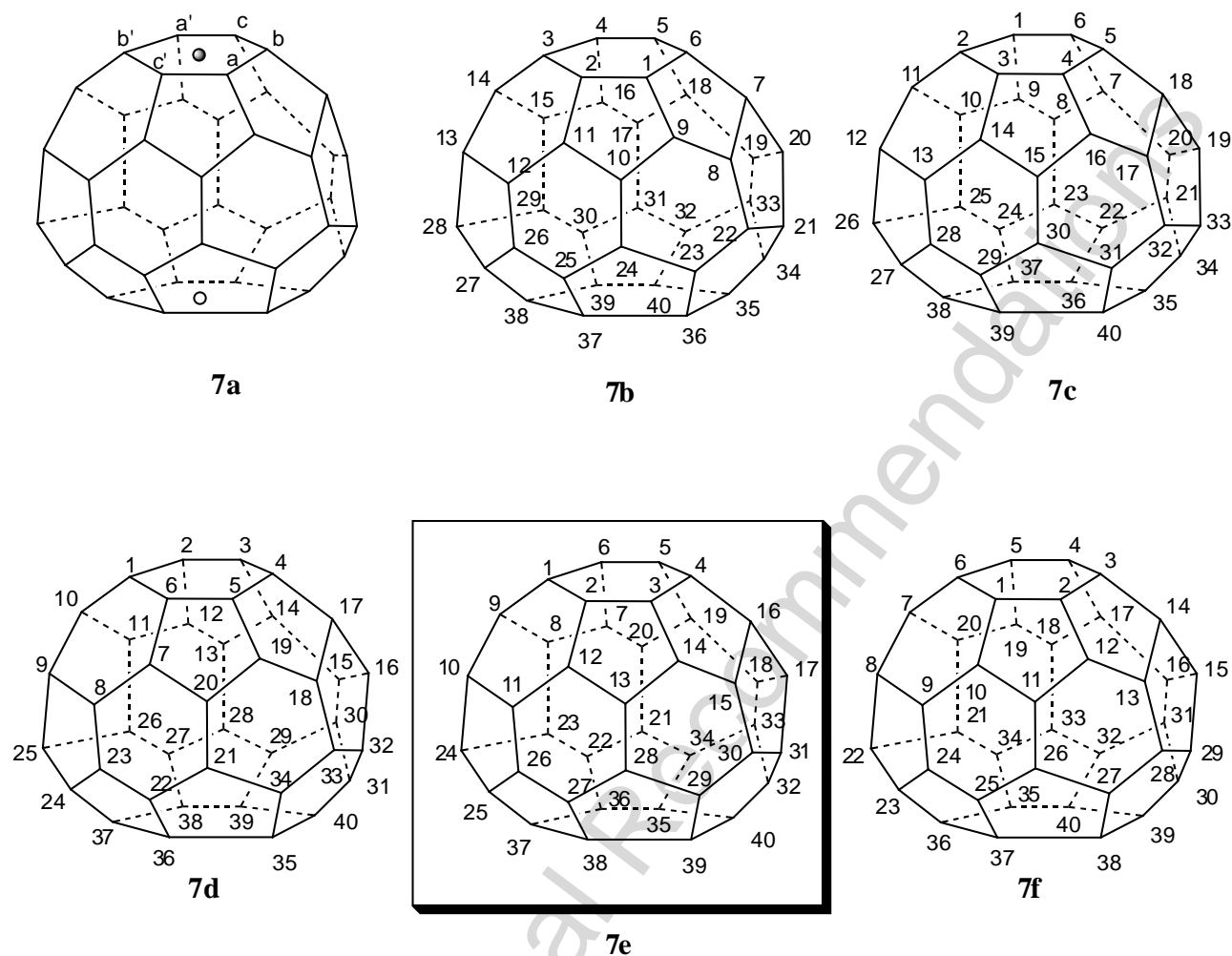


Fig. 7. Systematic numbering for $(f,sA)-(C_{40}-D_2)[5,6]$ fullerene

3.1.7 Systematic numbering for $(C_{76}-D_2)[5,6]$ fullerene (Fig. 8) (Atlas Ref. No. 76:1; CAS Reg. No. 142136-39-8).

This chiral fullerene has three C_2 axes, each intersecting the midpoint of a bond. These axes are indicated in Figs. 8a, 8b, and 8c. Application of **Fu-3.1.2.2** allows to discard the axis in Fig. 8b because it bisects bonds connecting only 6,6,5 atoms, whereas in the other cases the corresponding bonds connect 6,6,6 atoms. The two bonds at the end of each reference axis in Figs. 8a and 8c are symmetry-equivalent, and only the inspection of the pathways originating from the atoms of one of these bonds is necessary. For symmetry reasons, there are two possible beginnings for the numbering in each Fig. 8a and Fig. 8c. These have been indicated as **a** to **a'** to **b**, and **a** to **a'** to **c** in each of these figures. Thus, there are four pathways to be considered. All of them are contiguous. The **a** to **a'** to **b** numbering in Fig. 8c terminates at an atom one bond

removed from the bond bisected by the reference axis; the **a** to **a'** to **c** numbering in Fig. 8c terminates at an atom two bonds removed from the bond bisected by the axis; the two numberings in Fig. 8a terminate at atoms belonging to the bond bisected by the axis. According to **Rule Fu-3.1.3**, the latter two numberings, shown in Figs. 8d and 8e, are preferred pathways, but a selection must still be made between them. Inspection of the ranking of the atoms according to **Rule Fu-3.1.4** (Table 2) shows that the atom at position 3 of Fig. 8d is a 6,6,5 atom whereas the atom at the same position in Fig. 8e is a 6,6,6 atom. Therefore the numbering of Fig. 8e is preferred for the shown structure. In this case the numbering is the same as that selected by CAS [3]. The stereodescriptor for the shown enantiomer of this inherently chiral fullerene is (^f,^sC) [4].

Table 2. Rankings of atoms 1 to 3 for pathways in Figs. 8d and 8e.

Atom	8d	8e
1	6,6,6	6,6,6
2	6,6,6	6,6,6
3	6,6,5	6,6,6

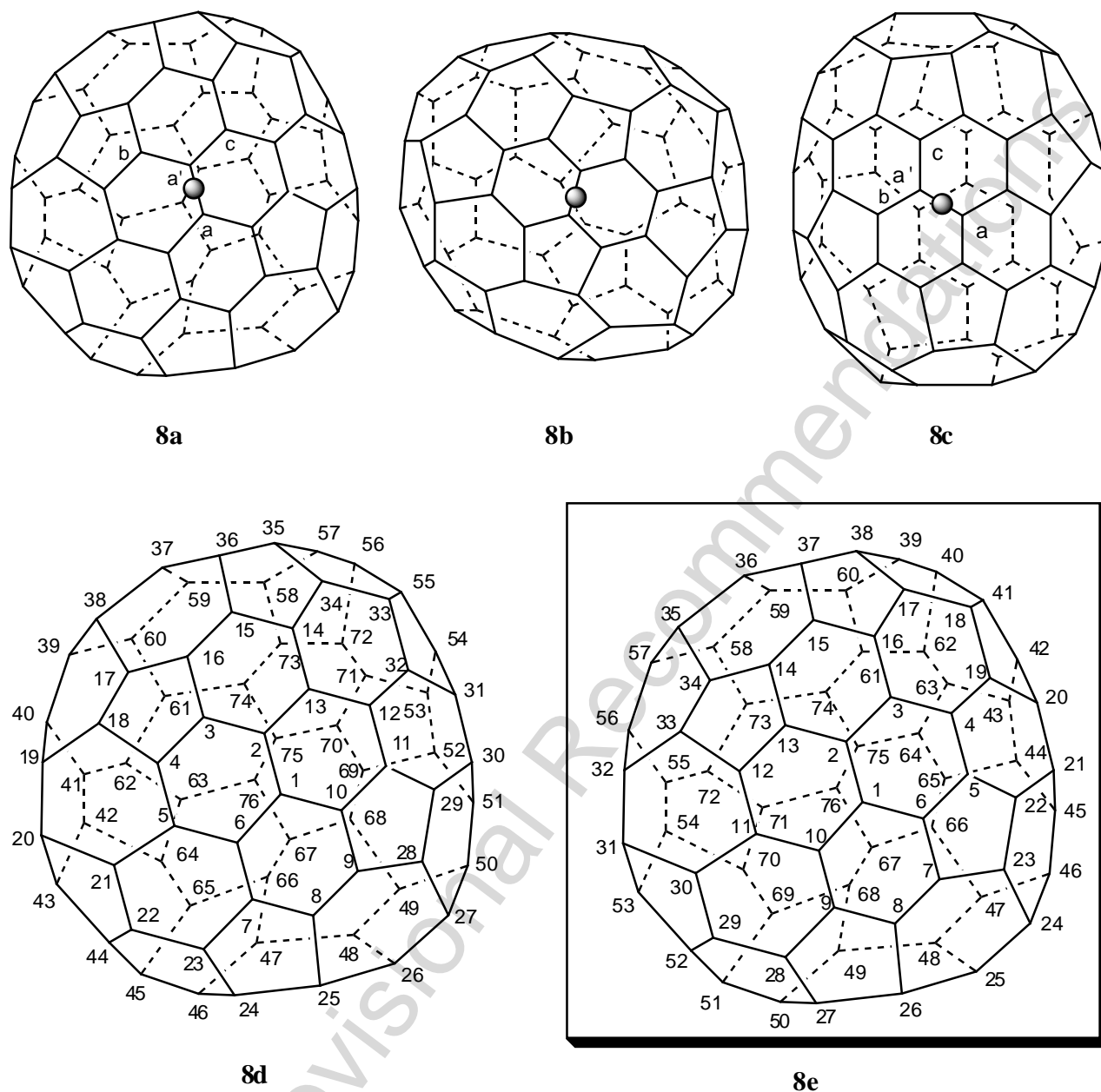


Fig. 8. Systematic numbering for $(f,sC)(C_{76}-D_2)[5,6]$ fullerene

3.1.8 Systematic numbering for $(C_{28}-D_2)[5,6]$ fullerene (Fig. 9) (Atlas Ref. No. 28:1; CAS Reg. No. 145393-14-2).

This chiral fullerene has three C_2 axes, shown in Figs. 9a, 9b, and 9c, respectively. The axis of Fig. 9a is preferred because it passes through the midpoint of two bonds connecting 6,6,5 atoms, whereas both the others axes pass through the midpoints of two bonds connecting lower-ranking atoms (**Fu-3.1.2.2**). Because of symmetry, only two possible pathways must be

considered, namely **a** to **a'** to **b** and **a** to **a'** to **c** (Fig. 9a) The resulting helical numberings are shown in Figs. 9d and 9e, respectively. Both numberings terminate at the same atom and application of **Fu-3.1.3** is inconclusive. Application of **Fu-3.1.4** (Table 3) shows that the two numberings differ at position 15, where there is a 6,5,5 atom in the numbering of Fig. 9d, but a 5,5,5 atom in the numbering of Fig. 9e. Therefore, the numbering of Fig. 9d is preferred. CAS selects the numbering of Fig. 9e [3]. The stereodescriptor for the shown enantiomer of this inherently chiral fullerene is (^{f,s}C) [4].

Table 3. Rankings of atoms 1 to 15 for pathways in Figs. 9d and 9e.

Atom	9d	9e
1	6,6,5	6,6,5
2	6,6,5	6,6,5
3	6,5,5	6,5,5
4	6,5,5	6,5,5
5	6,5,5	6,5,5
6	6,5,5	6,5,5
7	5,5,5	5,5,5
8	5,5,5	5,5,5
9	6,5,5	6,5,5
10	6,5,5	6,5,5
11	6,5,5	6,5,5
12	6,5,5	6,5,5
13	5,5,5	5,5,5
14	5,5,5	5,5,5
15	6,5,5	5,5,5

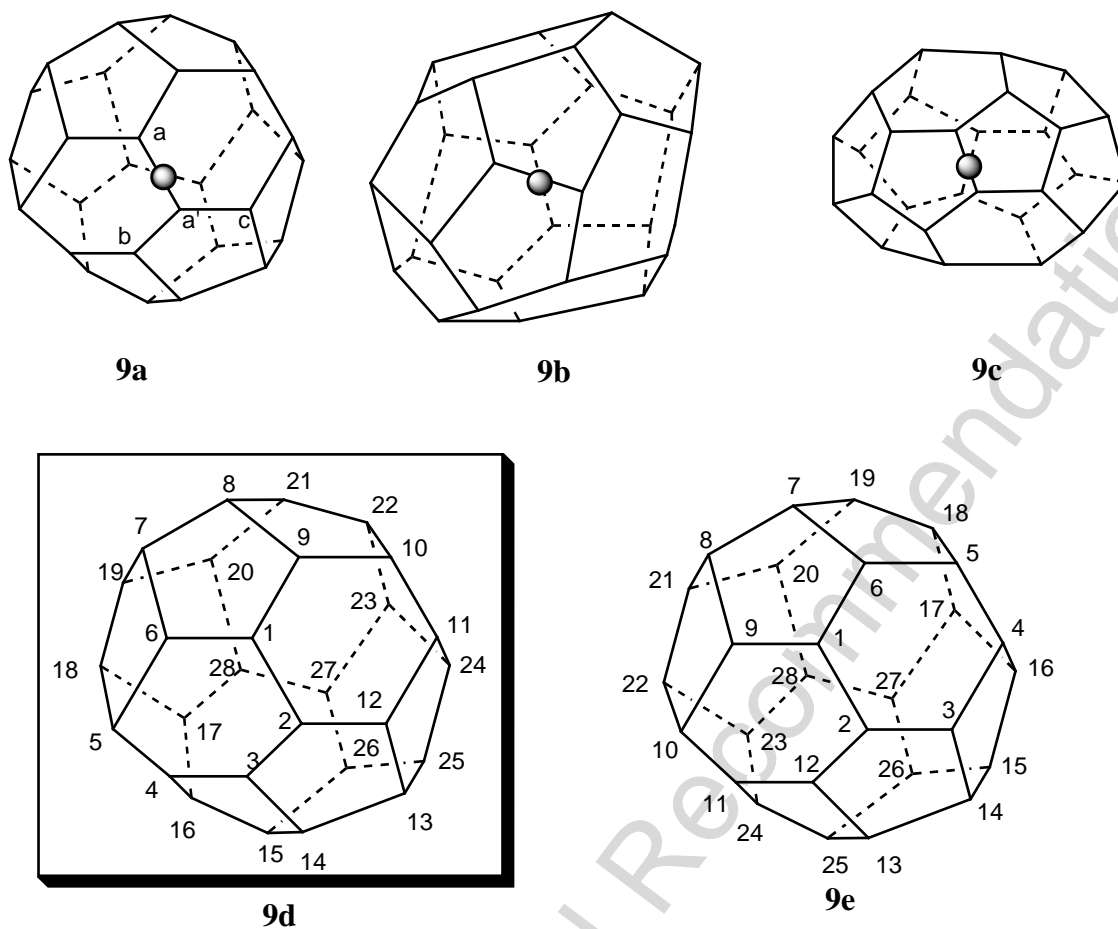


Fig. 9. Systematic numbering for $(f,sC)(C_{28}-D_2)[5,6]$ fullerene

3.1.9 Systematic numbering for $(C_{42}-D_3)[5,6]$ fullerene (Fig.10) (Atlas Ref. No. 42:45; CAS Reg. No. 145646-79-3).

The reference axis of this chiral fullerene is the C_3 axis passing through opposite and symmetry-equivalent six-membered rings (Fig. 10a). Numbering can begin in either one of these rings, the six atoms of which are symmetry-equivalent in two sets of three: **a** is equivalent to **a'** and **a''**, and **b** is equivalent to **b'** and **b''**. As a consequence there are four possible pathways to be considered: **a** to **b** to **a'**; **a** to **b''** to **a''**; **b** to **a'** to **b'**; **b** to **a** to **b''**. The pathway **b** to **a'** to **b'** does not lead to a contiguous numbering, whereas the other three pathways do. These are reported in Figs. 10b (**a** to **b** to **a'**), 10c (**a** to **b''** to **a''**), and 10d (**b** to **a** to **b''**). Since all three pathways terminate at an atom belonging to the six-membered ring bisected by the reference axis, application of **Rule Fu-3.1.3** is inconclusive. Inspection of the atom sequences of Figs. 10b, 10c, and 10d according to **Rule Fu-3.1.4** (Table 4) shows that the sequence in Fig. 10d has a 6,6,5 atom at position 7, whereas those in Figs. 10b and 10c both have a 6,5,5 atom at the same position. The numbering

of Fig. 10d is therefore preferred. CAS selects the same numbering [3]. The stereodescriptor for the shown enantiomer of this inherently chiral fullerene is (^{f,s}C) [4].

Table 4. Rankings of atoms 1 to 7 for the pathways in Figs. 10b, 10c, and 10d

Atom	10b	10c	10d
1	6,6,5	6,6,5	6,6,5
2	6,6,5	6,6,5	6,6,5
3	6,6,5	6,6,5	6,6,5
4	6,6,5	6,6,5	6,6,5
5	6,6,5	6,6,5	6,6,5
6	6,6,5	6,6,5	6,6,5
7	6,5,5	6,5,5	6,6,5

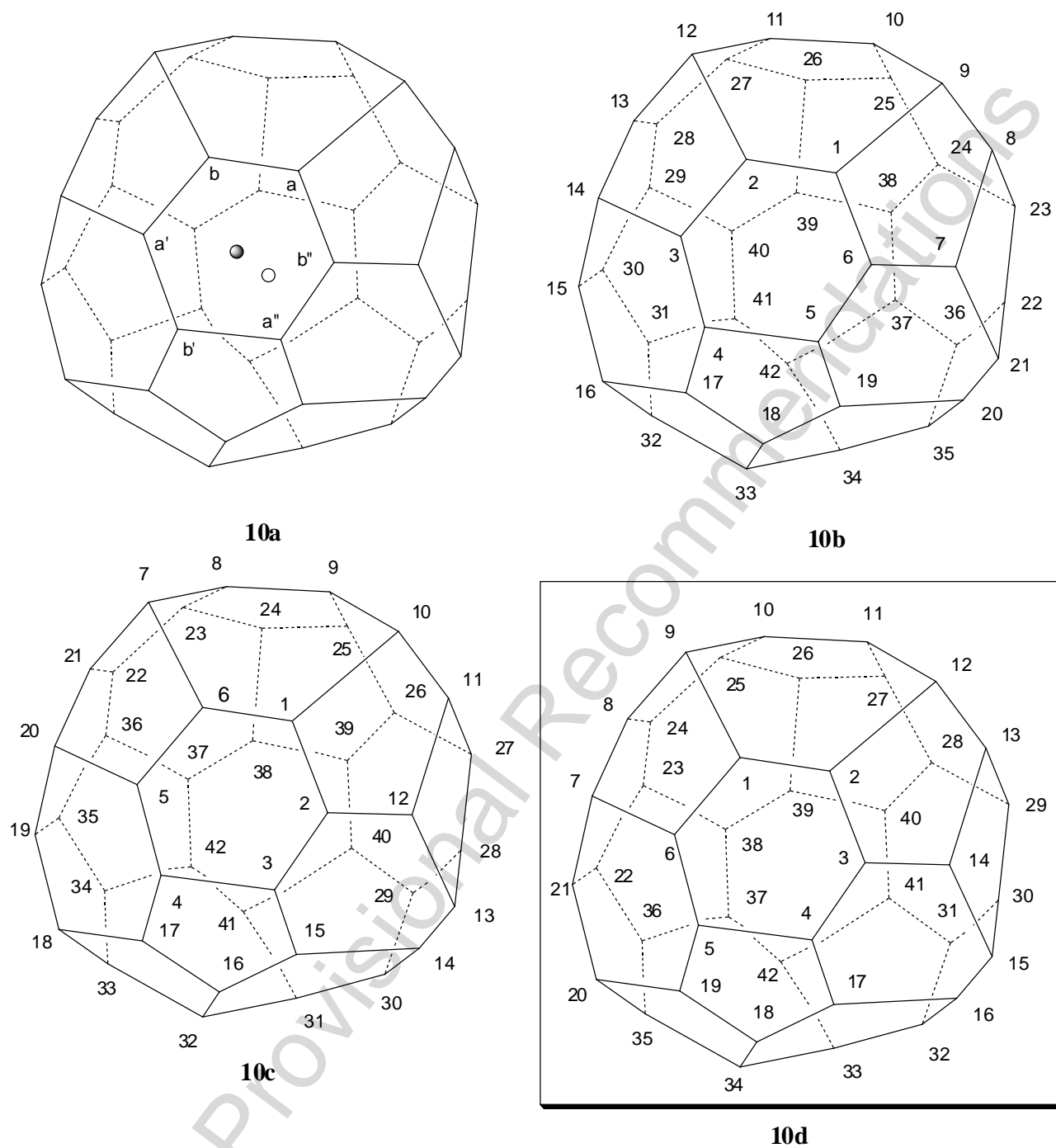


Fig. 10. Systematic numbering for $(I,SC)-(C_{42}-D_3)[5,6]$ fullerene

3.1.10 Systematic numbering for $(C_{34}-C_2)[5,6]$ fullerene (Fig.11) (Atlas Ref. No. 34:5; CAS Reg. No. 145646-75-9; this fullerene is listed as C_1 -symmetric by CAS).

The only C_2 axis in this fullerene is the reference axis. It passes through the center of the six-membered ring at the far end and bisects a bond at the near end of the structure in Fig. 11a. According to **Rule Fu-3.1.2** the numbering should begin in the ring which contains three pairs of symmetry-equivalent atoms indicated as **a/a'**, **b/b'**, and **c/c'**. There are six possible pathways to be evaluated: **a to b to c**; **a to c' to b'**; **b to c to a'**; **b to a to c'**; **c to a' to b'**; and **c to b to a**. Of these, **a to b to c** and **b to a to c'** do not yield a contiguous helical numbering, whereas the other four pathways do. Since they terminate at an atom belonging to the bond bisected by the C_2 axis, a selection among them cannot be made using **Rule Fu-3.1.3**. However, application of **Rule Fu-3.1.4** solves the problem. First, pathways **b to c to a'** (Fig. 11b) and **a to c' to b'** (Fig. 11c), that begin with 6,6,5 atoms, are preferred over the other two pathways that begin with 6,5,5 atoms. Then, inspection of the atom ranking shows that the numbering in Fig. 11b is preferred to that in Fig. 11c since it contains a 6,6,5 rather than a 6,5,5 atom at position 21. The stereodescriptor for the shown enantiomer of this inherently chiral fullerene is (f,sA) [4].

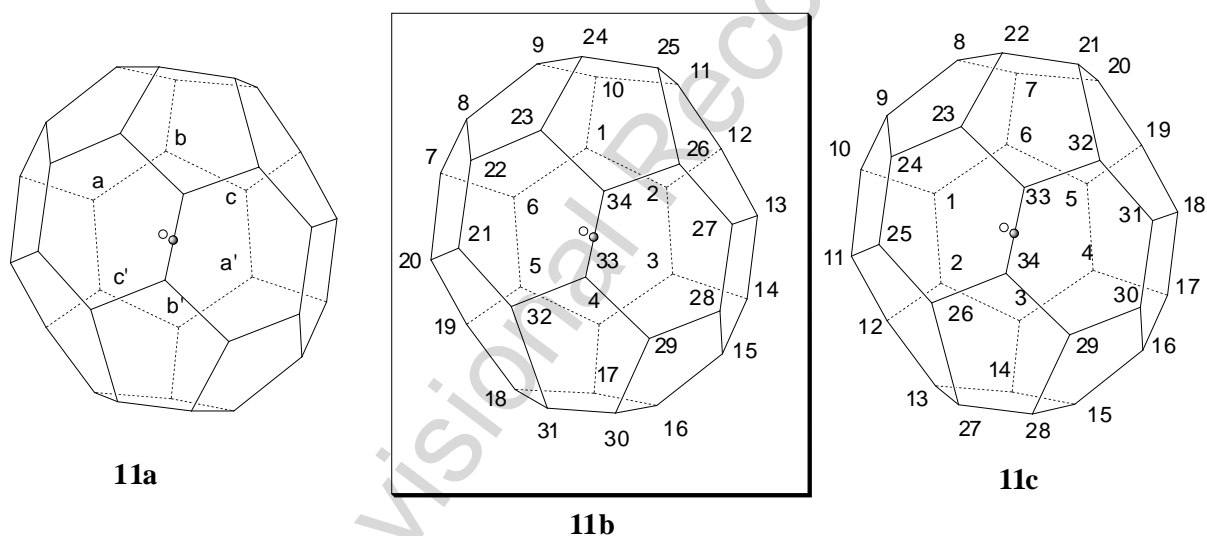


Fig. 11. Systematic numbering for (f,sA)($C_{34}-C_2$)[5,6]fullerene

3.1.11 Systematic numbering for ($C_{78}-D_3$)[5,6]fullerene (Fig. 12) (Atlas Ref. No. 78:1; CAS Reg. No. 139707-95-2).

This fullerene contains one C_3 axis, passing through the center of opposite and symmetry-equivalent six-membered rings (Fig. 12a), and three C_2 axes, perpendicular to the C_3 axis. According to **Fu-3.1.1** the highest order axis (C_3) must be examined first for contiguous helical pathways. The atoms of the six-membered ring are equivalent in sets of three (**a/a'/a''** and

b/b'/b''). There are four possible pathways to be considered: **b** to **a** to **b''**; **a** to **b** to **a'**; **b''** to **a** to **b**; and **a** to **b''** to **a''**. Only the first three (shown in Figs. 12b, 12c, and 12d) lead to contiguous helical numberings terminating at an atom belonging to the six-membered ring intersected by the C_3 axis. Rule **Fu-3.1.3** does not select among these numberings. Application of **Fu-3.1.4** first eliminates the numbering of Fig. 12d, in which there is a 6,6,5 atom at position 22 rather than a 6,6,6 atom as in the numberings of Figs. 12b and 12c. By continuing the atom ranking exploration for 12b and 12c, the numbering in Fig. 12b is preferred over that in Fig. 12c because it features a 6,6,6 rather than a 6,6,5 atom at position 40. The stereodescriptor for the shown enantiomer of this inherently chiral fullerene is (^{f,s}A) [4].

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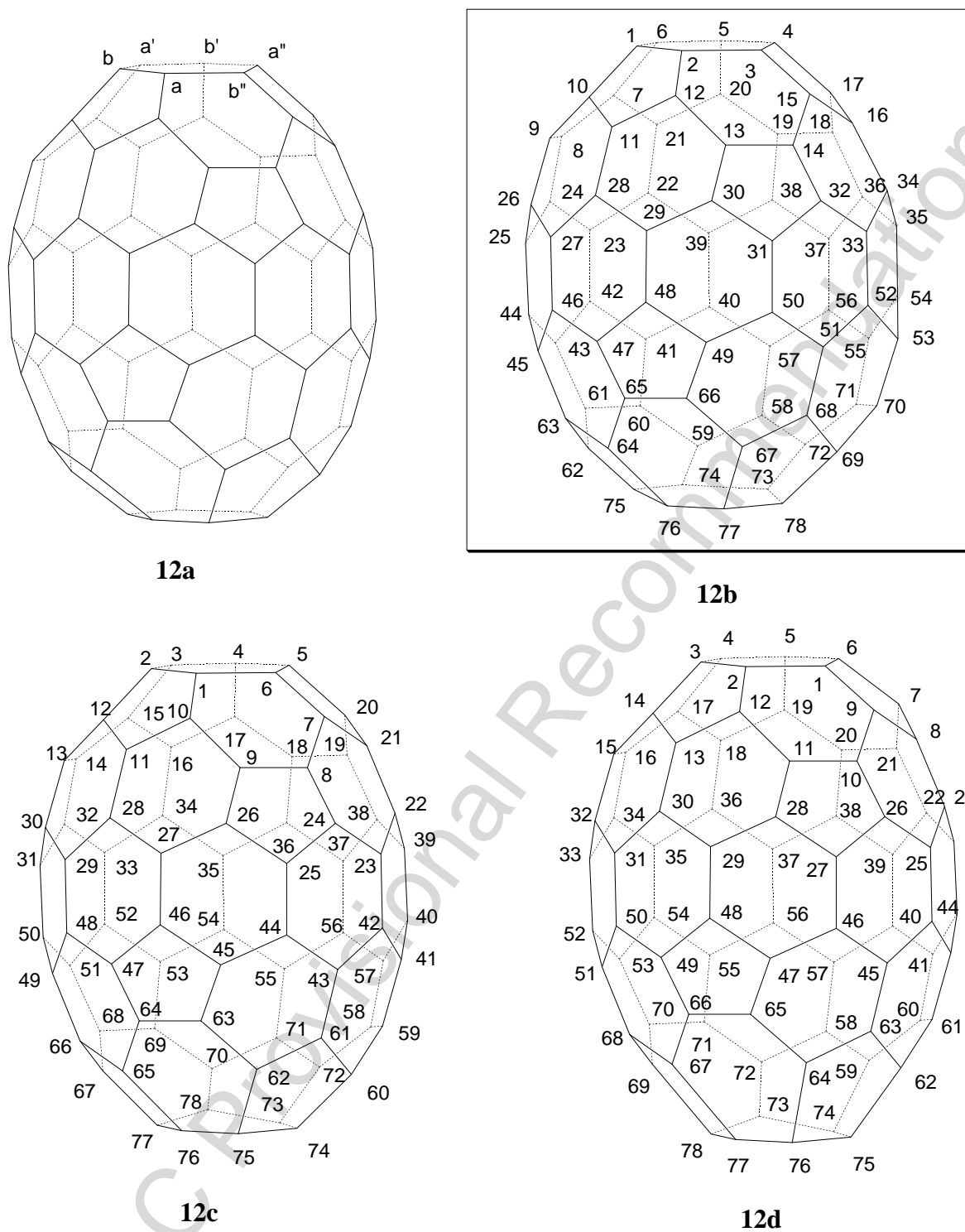


Fig. 12. Systematic numbering for $(f,sA)(C_{78}-D_3)[5,6]$ fullerene

3.1.12 Systematic numbering for $(C_{78}-C_{2v})[5,6]$ fullerene (Fig. 13) (Atlas Ref. No. 78:3; CAS Reg. No. 143974-29-2).

This fullerene contains a single C_2 axis at the intersection of two mirror planes; the axis passes through the center of a six-membered ring on one side and the midpoint of a bond on the other side. According to **Rule Fu-3.1.2** the ring is preferred for beginning the numbering. Because of symmetry there are only three pathways to be considered, namely **a to b to c**, **b to c to a'**, and **c to a' to b'** (Fig. 13a). The first pathway does not lead to a contiguous helical numbering. The other two (Figs. 13b and 13c) do. Both terminate at an atom belonging to the bond bisected by the reference axis, and application of **Rule Fu-3.1.3** is inconclusive. By inspection of the atom ranking according to **Rule Fu-3.1.4** the numbering of Fig. 13b is preferred because it begins with a 6,6,6 rather than with a 6,6,5 atom (Fig. 13c).

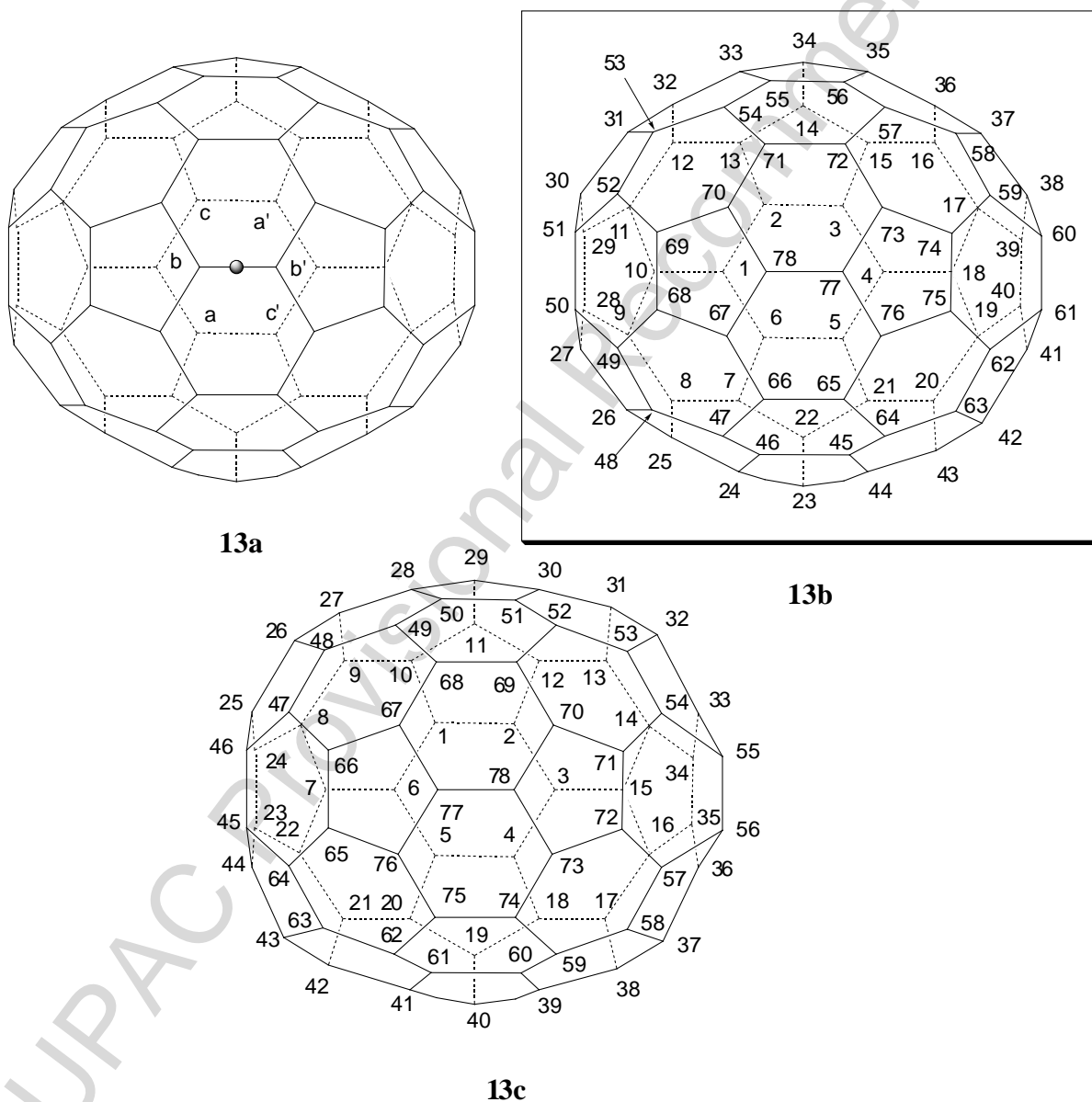
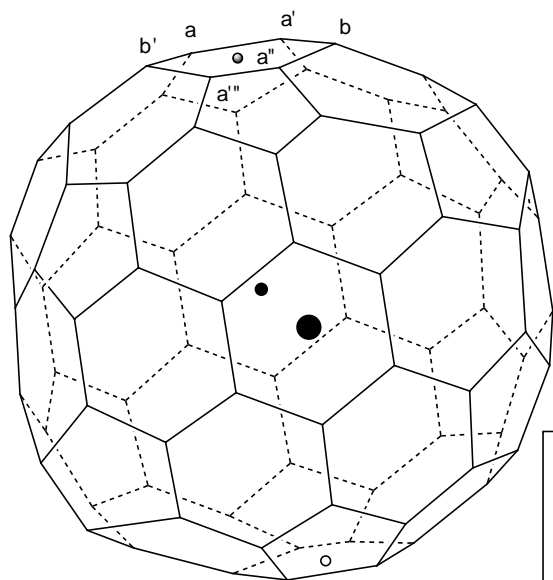


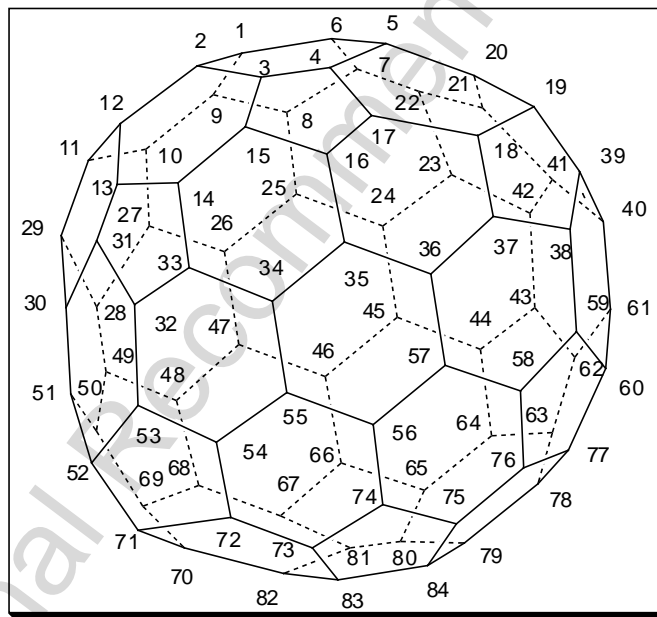
Fig. 13. Systematic numbering for $(C_{78}-C_{2v})[5,6]$ fullerene

3.1.13 Systematic numbering for $(C_{84}-D_{6h})[5,6]$ fullerene (Fig. 14) (Atlas Ref. No. 84:24; CAS Reg. No. 134847-09-9).

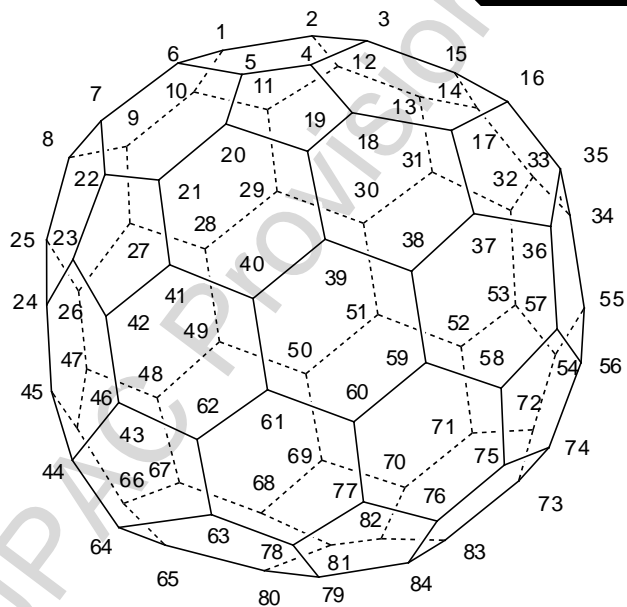
In this fullerene the principal axis is the C_6 axis passing through the midpoint of opposite and symmetry-equivalent hexagons (shown by black dots in Fig. 14a). However, no contiguous helical numbering can be found starting from the six symmetry-equivalent atoms of the two equivalent rings. Therefore, the six C_2 axes must be considered. Three of these are symmetry-equivalent axes passing through the midpoint of opposite hexagons (one is shown by grey and white dots in Fig. 14a); the remaining three symmetry-equivalent C_2 axes pass through the midpoints of opposite bonds, and are therefore less preferred according to **Fu-3.1.2**. Either one of the former C_2 axes can be used as the reference axis. Numbering can start in either one of the symmetry-equivalent hexagons. Because of symmetry, the atoms of this ring form two sets of atoms, indicated as **a/a'/a''/a'''**, and **b/b'**. There are three pathways to be evaluated: **a** to **b'** to **a'''**; **a** to **a'** to **b**; and **b'** to **a'''** to **a''**. Of these, the **b'** to **a'''** to **a''** pathway does not lead to a contiguous numbering, whereas the other two do. The numberings are shown in Fig. 14b (**a** to **b'** to **a'''**) and in Fig. 14c (**a** to **a'** to **b**). Since both terminate at an atom belonging to the ring intersected by the axis, a selection cannot be made on the basis of **Fu-3.1.3**. However, inspection of the atom ranking according to **Fu-3.1.4** shows that the numbering shown in Fig. 14b is preferred because it features a 6,6,6 rather than a 6,6,5 atom at position 2.



14a



14b



14c

Fig. 14. Systematic numbering for $(C_{84}-D_{6h})[5,6]$ fullerene

3.2. Fullerenes having at least one symmetry axis (C_n , $n > 1$) but having no contiguous helical pathway determined on the basis of rules **Rule Fu-3.1.1 through **Rule Fu-3.1.4****

Fullerenes with at least one symmetry axis C_n , $n > 1$ exist for which a contiguous helical pathway for numbering cannot be found using **Rules Fu-3.1.1** through **Fu-3.1.4**. The problem of numbering discountiguity in these fullerenes has already been tackled by previous publications [1,3], and solved using different and sometimes non-clearly established procedures. To devise unique numbering for these fullerenes in a clear and relatively straightforward way, it was decided to establish a modified set of rules adopting an approach similar to that used in the case of fullerenes with contiguous numbering.

If no contiguous helical numbering can be found in a fullerene with at least one rotational axis of symmetry C_n , $n > 1$ by application of **Rules Fu-3.1.1** to **Fu-3.1.4**, discontinuous numberings made up of two or more contiguous segments are examined, with the first of their segments being built around a proper rotation axis in complete analogy to the procedure employed in **Fu-3.1** to determine a contiguous pathway. If a preferred first segment is obtained based on **Rules Fu-3.2.1** through **Fu-3.2.3** (see below), its follow-up segment(s) is (are) constructed based on **Fu-3.2.4** (see below) to complete the preferred numbering. If there is still a choice after comparison of different first segments, subsequent segments are constructed (**Rule Fu-3.2.4**) and compared (**Rules Fu-3.2.1** through **Fu-3.2.3**) at each level n until a preference becomes apparent.

Rule Fu-3.2.1 (cf. **Rule Fu-3.1.1**):

- a. The n^{th} discountiguity must occur as late as possible in the numbering.
- b. Among different pathways having the n^{th} discountiguity at the same highest locant, the preferred numbering pathway is built around the proper rotation axis of higher order.

Rule Fu-3.2.2 (cf. **Fu-3.1.2**): If there is a choice among reference axes of the same order or between the end of a reference axis to begin the numbering, **Rule Fu-3.1.2** is applied.

Rule Fu-3.2.3 (cf. **Fu-3.1.4**; for practical reasons, no rules analogous to **Fu-3.1.3** is applied to segments of discontinuous numberings): When there is still a choice, the n^{th} segments are compared according to **Rule Fu-3.1.4**.

Once a preferred segment is identified based on **Fu-3.2.1** through **Fu-3.2.3** the numbering of the fullerene is completed by construction of the subsequent segment(s). The starting point of a new segment is defined according to **Rule Fu-3.2.4a** (see below), and numbering within a segment is continued according to **Rule Fu-3.2.4b**.

Rule Fu-3.2.4: After each discontinuity,

- a). the next atom to be numbered must be directly connected to one of the previously numbered atoms; among the latter, the atom with the highest locant is preferred.
- b). numbering continues by the shortest path, in terms of number of bonds, to reach an unnumbered atom that is directly connected to a numbered atom with the lowest locant already assigned. (In this way the sense of the numbering helix should be maintained and its pitch kept as small as possible.)

Some examples describing the discontinuous numbering of axial fullerenes assigned on the basis of these rules are reported below.

3.2.1. Systematic numbering for $(C_{24}-O_h)[3,8]$ fullerene (Fig. 15) (CAS Reg. No. 121498-50-8).

This fullerene, made up only of 8,8,3 atoms, possesses three equivalent C_4 axes (Fig. 15a), four equivalent C_3 axes (Fig. 15c), and six equivalent C_2 axes (not shown: these axes join midpoints of opposite 8,8 bonds). When one of the C_4 axes is used as the reference axis, a contiguous pathway cannot be found starting along the bond shared by two eight-membered rings. In this case (Fig. 15a) the numbering becomes discontinuous at position 14. The numbering in Fig. 15b, obtained again using one of the C_4 axes but starting along the bond shared by an eight- and a three-membered ring also becomes discontinuous at position 14. In Fig. 15c the numbering obtained using one of the C_3 axes as the reference axis is shown. In this case, numbering becomes discontinuous at position 18. The numbering obtained using a C_2 axis as the reference axis becomes discontinuous at a position with a lower locant. According to **Fu-3.2.1a** the numbering in Fig. 15c is preferred because the discontinuity occurs at a higher locant. According to **Rule Fu-3.2.4a**, the numbering proceeds to position 19, which is connected to the numbered atom with the highest locant within reach (17). Within the second segment, numbering proceeds by the shortest path to position 22 which is connected to the the numbered atom with the lowest locant within reach (6) (**Fu-3.2.4b**). After another discontinuity, a third segment starts at position 23 (connected to atom number 21 according to **Fu-3.2.4a**) and ends with the last unnumbered, neighboring atom (24).

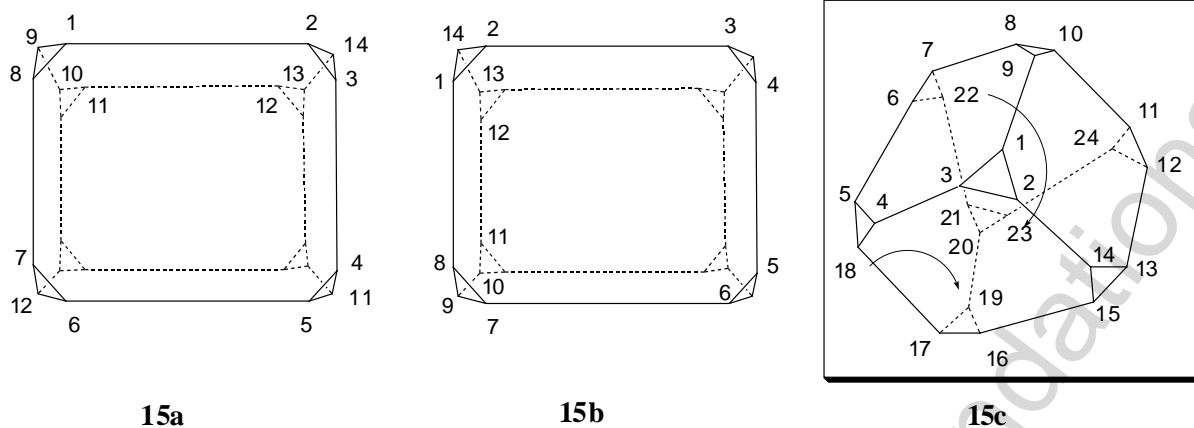


Fig. 15. Systematic numbering for $(C_{24}-O_h)[3,8]$ fullerene

3.2.2. Systematic numbering for $(C_{48}-O_h)[4,6,8]$ fullerene (Fig. 16) [(CAS Reg. No. 145985-79-1, as fulleride(2-)].

This fullerene, made up only of 8,6,4 atoms, possesses three equivalent C_4 axes (Fig. 16a), four equivalent C_3 axes (Fig. 16b), and six equivalent C_2 axes (not shown: the axes pass through the midpoints of opposite four-membered rings). When one of the C_4 axes is used as the reference axis (Fig. 16a) and the pathway begins along a bond shared by an eight- and a six-membered ring, the numbering becomes discontinuous at position 40. When, using the same axis, a bond shared by an eight- and a four-membered ring is selected to begin the numbering (namely, C-2 to C-3 in Fig. 16a), the discontinuity occurs at position 24. The numbering obtained using one of the C_3 axes as the reference axis and starting along a bond shared by an eight- and a six-membered ring is shown in Fig. 16b. In this case the discontinuity occurs at position 42. Using the same axis and starting along a bond shared by a six- and a four-membered ring (namely, C-2 to C-3 in Fig. 16b), the numbering becomes discontinuous at position 24. The use of a C_2 axis leads to numberings discontinuous at positions with lower locants. Therefore, on the basis of **Fu-3.2.1a** the numbering shown in Fig. 16b is preferred. According to **Fu-3.2.4a**, the numbering resumes at position 43 which is connected to 41, and then continues contiguously to position 48 according to **Rule Fu-3.2.4b**.

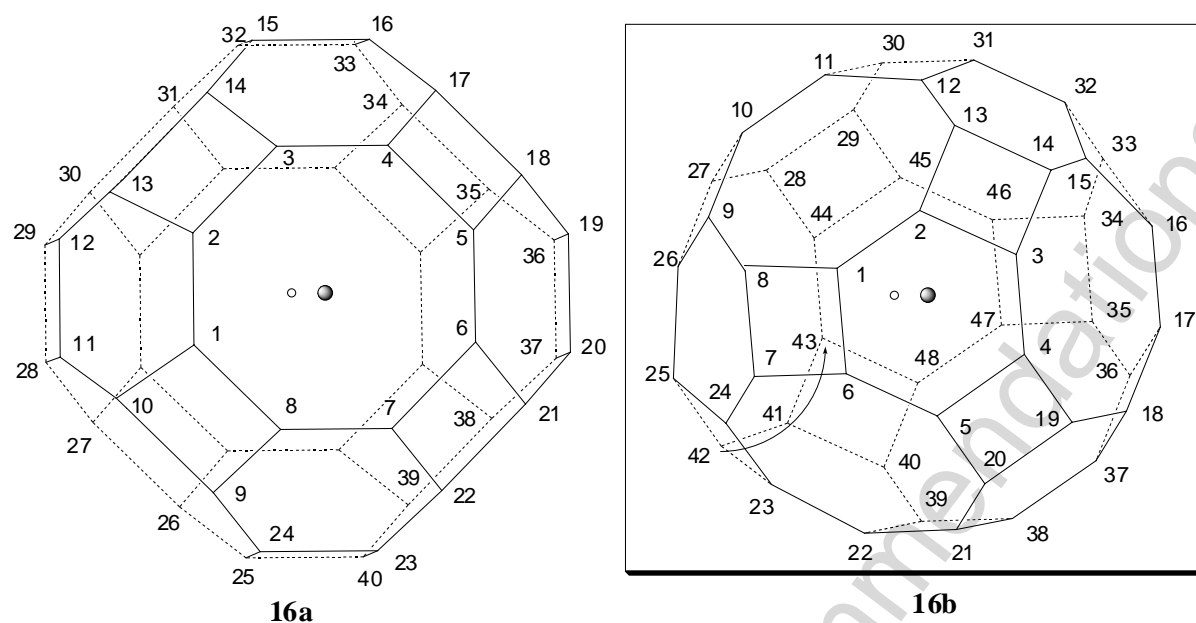


Fig. 16. Systematic numbering for $(C_{48}-O_h)[4,6,8]$ fullerene

3.2.3. Systematic numbering for $(C_{32}-O_h)[4,6]$ fullerene (Fig. 17) (CAS Reg. No. 146066-57-1).

This fullerene features three equivalent C_4 axes (Fig. 17a), four equivalent C_3 axes (not shown: they pass through opposite atoms at the intersection of three six-membered rings), and six equivalent C_2 axes (Fig. 17b). When one of the C_4 axes is used as the reference axis (Fig. 17a) there is only one possible pathway, and the numbering becomes discontinuous at position 28. Using one of the C_3 axes, the only possible pathway leads to a numbering discontinuous at position 25. Using one of the C_2 axes as the reference axis, there are three possible pathways that leads to numberings discontinuous at positions 25, 26, and 28, respectively. The latter is shown in Fig. 17b. Thus, two discontinuous numberings with a first segment of equal length are found. However, according to **Fu-3.2.1(b)**, the numbering reported in Fig. 17a is preferred, because its pathway uses the highest-order axis as the reference axis. From position 28, the numbering resumes as shown in Fig. 17a [**Rule Fu-3.2.4(a)**] to reach position 32 [**Rule Fu-3.2.4(b)**] without further discontinuity.

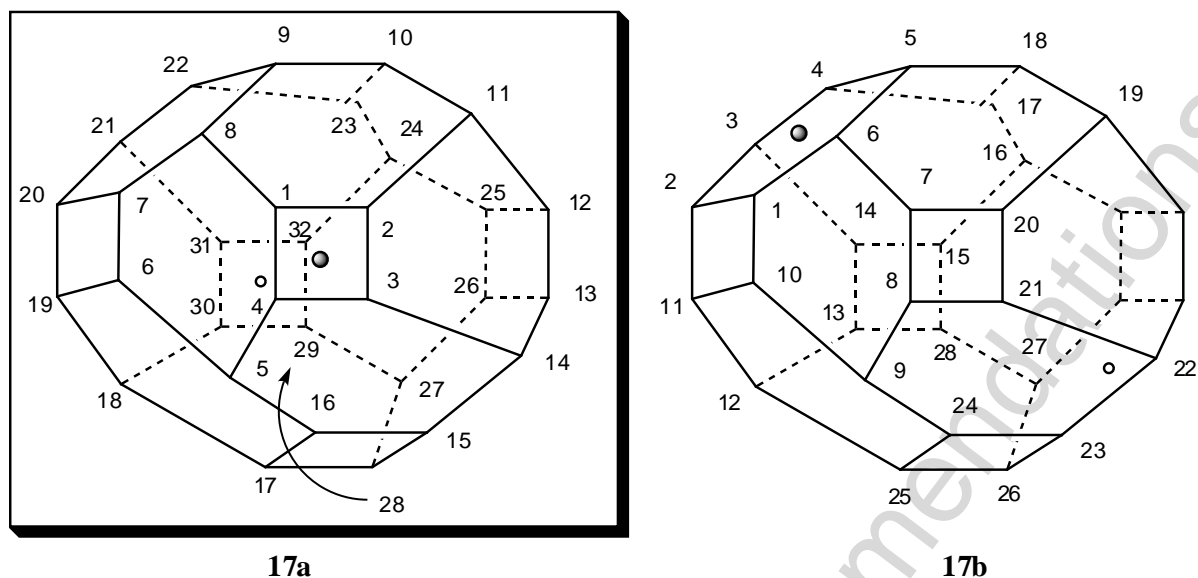


Fig. 17. Systematic numbering for $(C_{32}-O_h)[4,6]$ fullerene

3.2.4 Systematic numbering for $(C_{34}-C_{2v})[4,6]$ fullerene (Fig. 18) (CAS Reg. No. 181425-29-6 as $B_{17}N_{17}$).

This fullerene contains one C_2 axis intersecting the midpoint of a six-membered ring at the near end and of a 6,6 bond at the far end (Fig. 18a). The six atoms of the ring form two sets of symmetry equivalent atoms: $\mathbf{a/a'}$ and $\mathbf{b/b'/b''/b'''}$. Three pathways must be considered: \mathbf{a} to \mathbf{b} to $\mathbf{b'}$; \mathbf{b} to $\mathbf{b'}$ to $\mathbf{a'}$; and \mathbf{b} to \mathbf{a} to $\mathbf{b''}$. These lead to discontinuous numberings terminating at positions 20, 28 (Fig. 18b), and 25, respectively. The two atoms \mathbf{x} and $\mathbf{x'}$ (Fig. 18a) connected by the bond at the far end of the axis are symmetry-equivalent. The anticlockwise pathway from \mathbf{x} becomes discontinuous at position 32 (Fig 18c), and is therefore preferred on the basis of **Fu-3.2.1a**. The completion of this numbering according to **Fu-3.2.4** is shown in Fig. 18c.

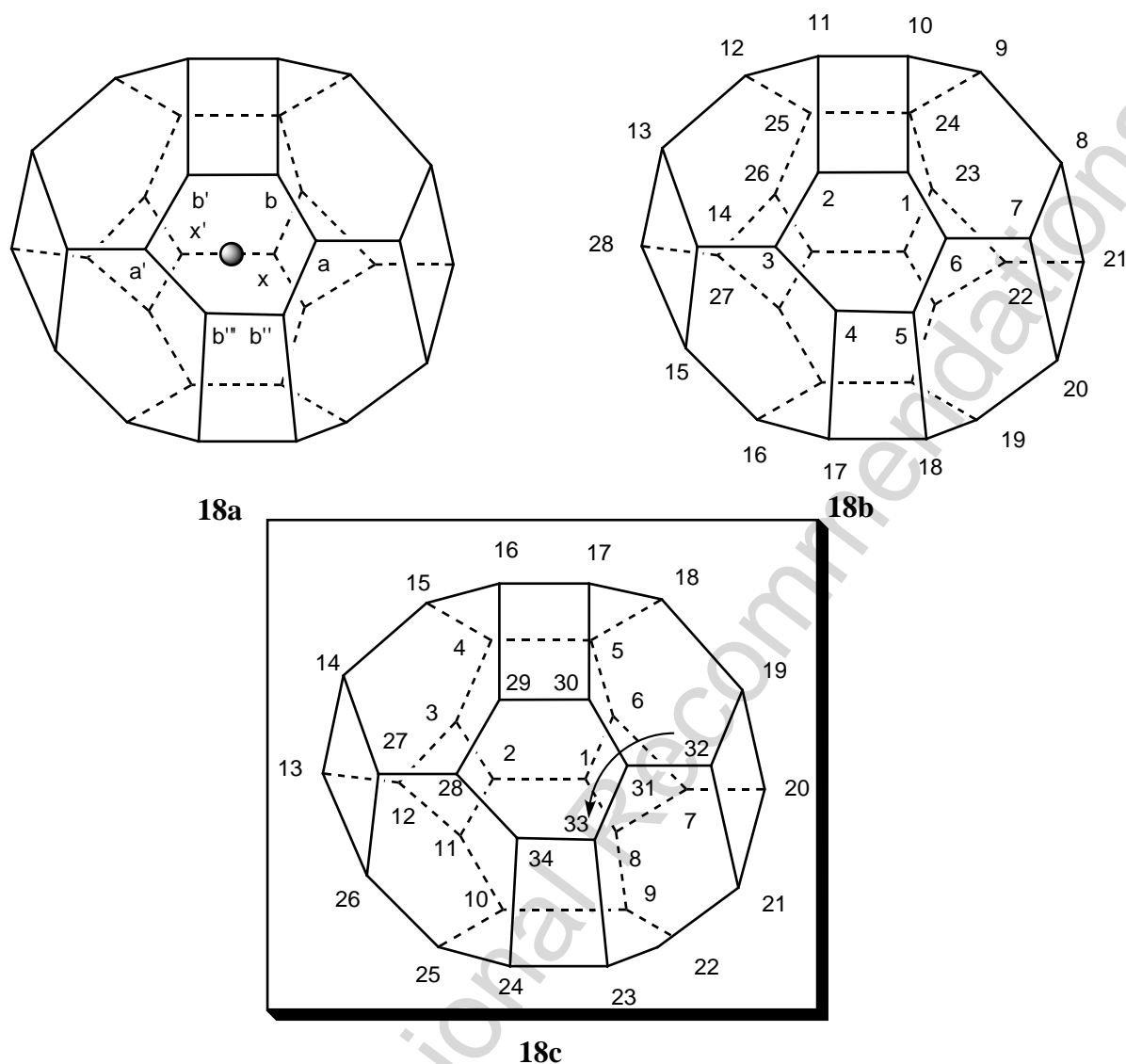
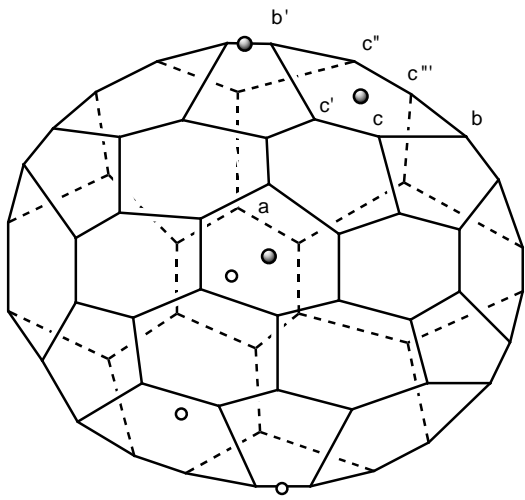


Fig. 18. Systematic numbering for $(C_{34}-C_{2v})[4,6]$ fullerene

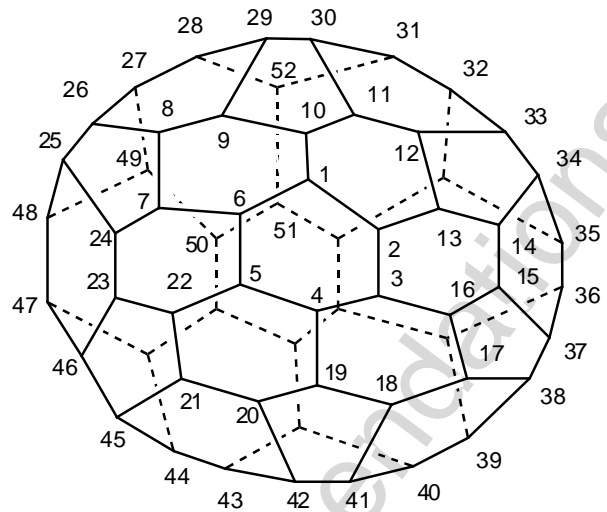
3.2.5 Systematic numbering for $(C_{60}-D_{6h})[5,6]$ fullerene (Fig. 19) CAS Reg. No. 112303-18-1)

This fullerene features one C_6 axis, passing through the midpoints of opposite hexagons (centers of coronene substructures), three equivalent C_2 axes, also passing through the midpoints of opposite hexagons, and three equivalent C_2 axes, passing through the midpoint of opposite bonds (Fig. 19a). Starting from any of the six equivalent atoms **a** of the six-membered ring intersected by the C_6 axis does not lead to a contiguous helical pathway. The relative numbering (Fig. 19b) becomes discontinuous at position 52. Three pathways must be considered for beginning the numbering based on one of the C_2 axes passing through opposite hexagons: **c** to **c'** to **b'**; **c** to **b'** to **c''**; and **b'** to **c''** to **c'''**. These pathways lead to numberings discontinuous at

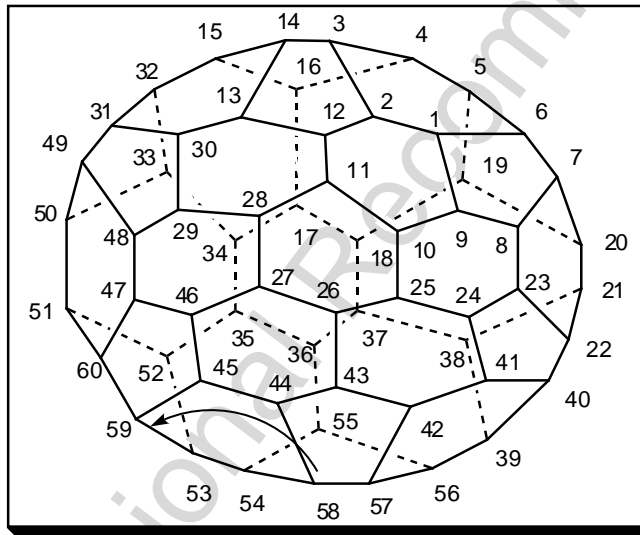
position 58 (Fig. 19c), 56 (not shown), and 58 (Fig. 19d), respectively. Finally, one pathway can also be constructed around one of the remaining C_2 axes passing through the midpoints of opposite bonds. This pathway results in the numbering shown in Fig. 19e that is discontinuous at position 58. To select among the three numberings having the discontinuity at the same position and built around axes of the same order (Figs. 19c, 19d, and 19e), **Fu-3.2.2** is first applied. The two numberings beginning in a ring (Figs. 19c and 19d) are preferred over the one beginning at a bond bisected by a C_2 axis (Fig. 19e). Furthermore, according to **Fu-3.2.3**, the numbering beginning with a 6,6,5 atom (Fig. 19c) is preferred over the one beginning with a 6,5,5 atom (Fig. 19d). The completion of the numbering of Fig. 19c is straightforward on the basis of **Rule Fu-3.2.4**.



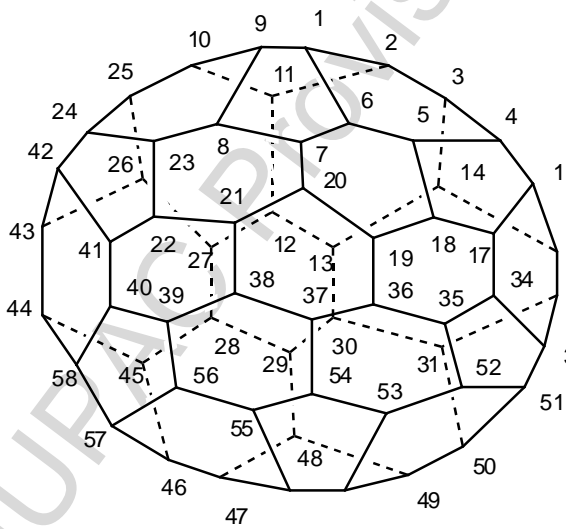
19a



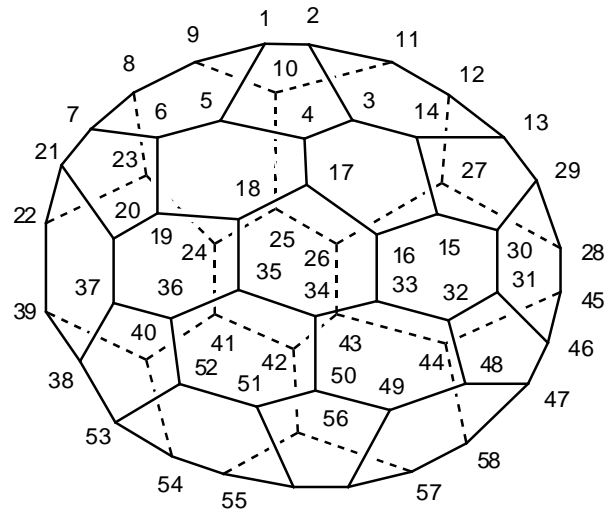
19b



19c



19d



19e

Fig. 19. Systematic numbering for $(C_{60}-D_{6h})[5,6]$ fullerene

3.2.6 Systematic numbering for $(C_{70}-C_{2v})[5,6]$ fullerene (Fig. 20) (CAS Reg. No. 163479-23-0).

This fullerene contains a single C_2 axis connecting the center of a six-membered ring at the near end and the midpoint of a bond at the far end, as shown in Fig. 20a. For symmetry reasons, three pathways must be considered in the ring: **a** to **b** to **a''**; **a** to **a'** to **b'**; and **b** to **a** to **a'**. They lead to numberings that become discontinuous at positions 54, 55, and 59, respectively (not shown). The only pathway that starts from the bond [(**x** to **x'**) is equivalent to (**x'** to **x**), Fig. 20a] leads to the numbering shown in Fig. 20b; since this becomes discontinuous only at position 63 it is preferred on the basis of **Rule Fu-3.2.1(a)**. The completion of the numbering represents an interesting example of the application of **Rule Fu-3.2.4** (see arrows in Fig. 20b). From position 63 a discontinuous step leads to atom 64 which is bound to atom 62 [**Rule Fu-3.2.4(a)**]. Moving on from atom 64 there are two possibilities, but the one going to the atom connected to atom 44 is preferred by **Rule Fu-3.2.4(b)**. Atom 66 is selected again on the basis of **Rule Fu-3.2.4(a)**, and **Rule Fu-3.2.4(b)** allows the numbering to reach atoms 67 and 68. A final application of **Rule Fu-3.2.4** allows the last segment of the numbering for this fullerene to be completed.

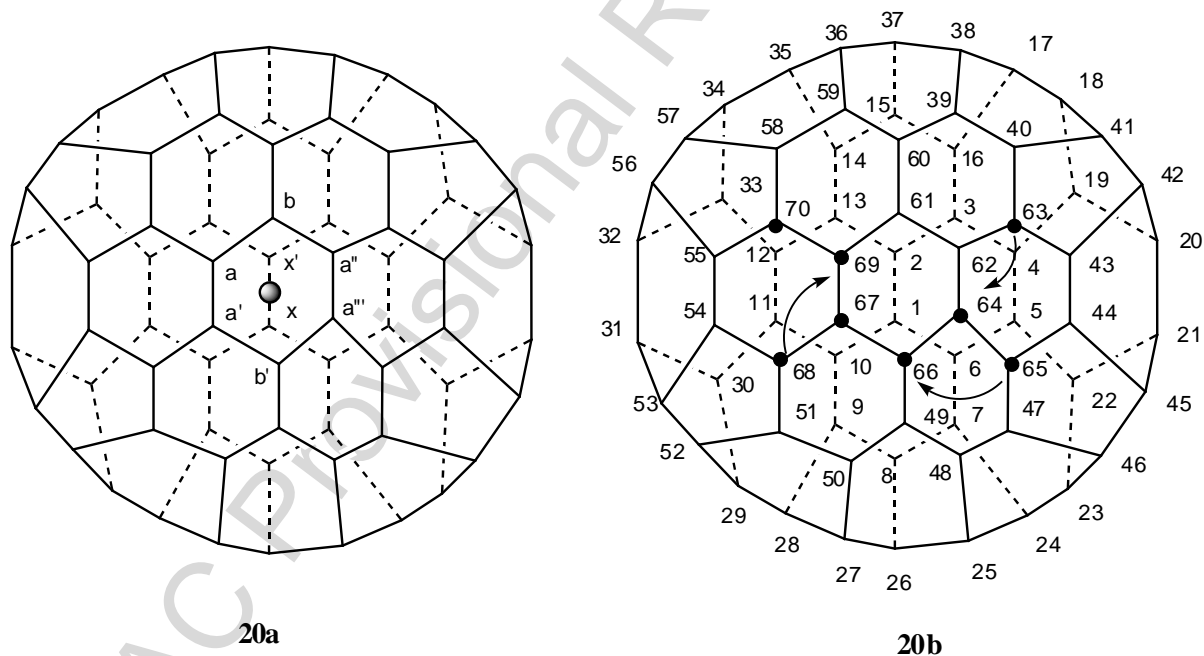


Fig. 20. Systematic numbering for $(C_{70}-C_{2v})[5,6]$ fullerene

3.2.7. Systematic numbering for $(C_{80}-I_h)[5,6]$ fullerene (Fig. 21) (Atlas Ref. No. 80:7; CAS Reg. No. 133947-14-5).

This fullerene features six equivalent C_5 axes (connecting midpoints of opposite five-membered rings), ten equivalent C_3 axes (connecting atoms at the intersection of three six-membered rings), and fifteen equivalent C_2 axes (passing through the midpoints of opposite hexagons). These axes are shown in Fig. 21a. When one of the C_5 axes is used as the reference axis, the pathway can begin at any one of the five symmetry-equivalent atoms of the pentagon (indicated as **a** in Fig. 21a); the numbering (shown in Fig. 21b) becomes discontinuous at position 75. When one of the C_3 axes is used as the reference axis only one pathway from atom **m** must be considered; this pathway becomes discontinuous at position 66, and is therefore discarded (**Fu-3.2.3**). When one of the C_2 axes is used as the reference axis there are three pathways to be considered: **x** to **y** to **z**; **y** to **z** to **x'**; **z** to **x'** to **y'**. One of these leads to the numbering becoming discontinuous at position 75 (not shown); the others lead to numberings in which the discontinuities occur at positions 72 and 66. According to **Fu-3.2.1** the two numberings built around the C_2 axis are discarded. The correct numbering is therefore that shown in Fig. 21b. The completion of the numbering by application of **Fu-3.2.4** is straightforward.

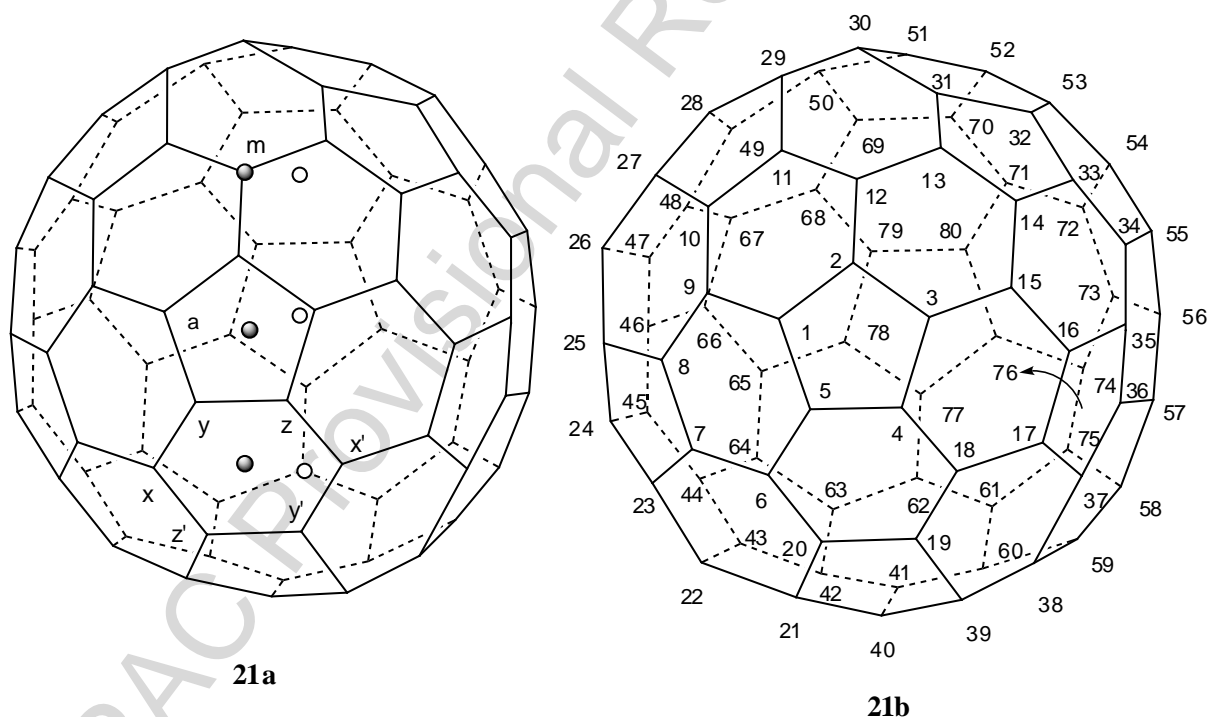
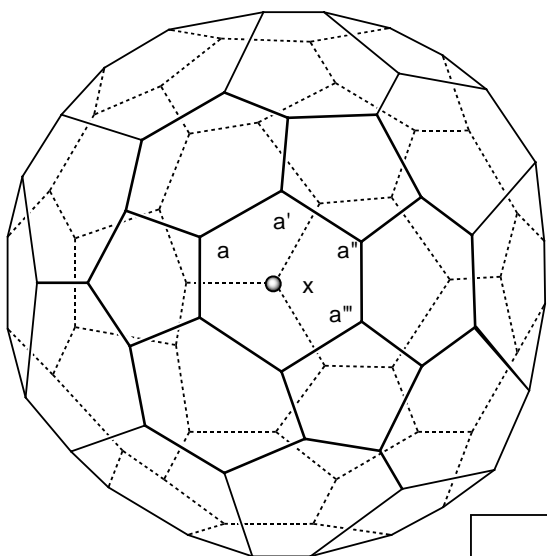


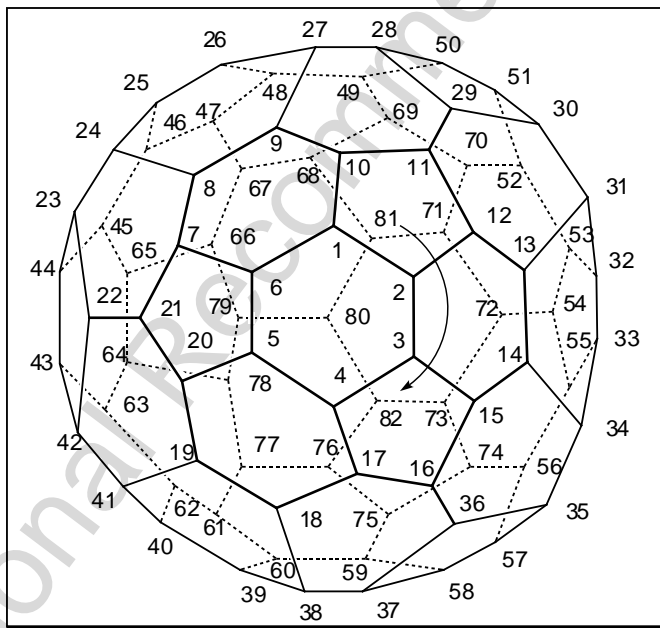
Fig. 21. Systematic numbering for $(C_{80}-I_h)[5,6]$ fullerene

3.2.8. Systematic numbering for $(C_{82}-C_{3v})[5,6]$ fullerene (Fig. 22) (Atlas Ref. No. 82:8; CAS Reg. No. 147230-79-3).

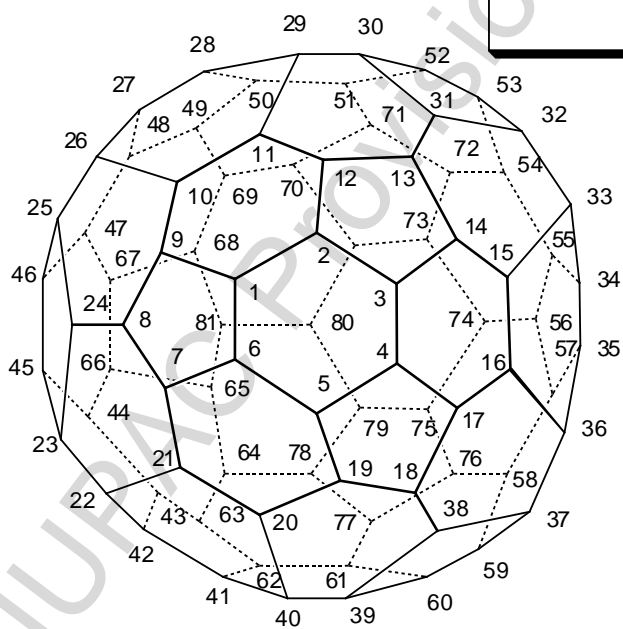
This fullerene features one C_3 axis connecting the center of a six-membered ring at the near end and an atom at the intersection of three six-membered rings at the far end (Fig. 22a). For symmetry reasons two pathways starting in the ring must be considered: **a** to **a'** to **a''** and **a'** to **a''** to **a'''**. They both lead to numberings that become discontinuous at position 81, as shown in Figs. 22b and 22c, respectively. The pathway starting from the atom at the far end of the axis leads to a numbering discontinuous at position 66 (not shown), that is discarded on the basis of **Fu-3.2.1**. Selection between the remaining two numberings is made on the basis of **Fu-3.2.3**. By comparing the ranking of the atoms of the two sequences (cf. **Fu-3.1.4**), it is found that the atom at position 8 of the numbering in Fig. 22b is a 6,6,6 atom whereas the numbering shown in Fig. 22c features a 6,6,5 atom at the same position. The former is therefore preferred. The completion of the numbering is obvious, because the unassigned site is reduced to a final isolated unnumbered atom which receives the last number in the sequence.



22a



22b



22c