16. Configurational Description of Chiral Fullerenes and Fullerene Derivatives with a Chiral Functionalization Pattern

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Dedicated to Prof. *Vladimir Prelog* on the occasion of his 90th birthday

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Simple recommendations for the configurational description of chiral fullerenes and fullerene derivatives with a chiral functionalization pattern are presented in detail and illustrated with examples for different types of compounds. The descriptor system is based on the fact that the numbering schemes proposed for fullerenes are chiral (helical) and, thus, constitute an ideal reference for differentiating between enantiomers of chiral carbon cages and of fullerene derivatives with a chiral functionalization pattern. A single descriptor is sufficient to specify the configuration of the chiral spheroids, regardless of their functionalization degree. According to the helicity of the numbering scheme to be used, the descriptors are $^f C$ (clockwise) or $^f A$ (anticlockwise). The proposed configurational description can also be extended to related classes of compounds such as chiral bowl-shaped condensed ring systems and their derivatives with a chiral functionalization pattern.

1. Introduction. – After the discovery of the structural principles of fullerenes had led to the occurrence of chiral fullerenes and nanotubes being envisioned [1], these carbon spheroids became of practical interest for the first time with the isolation and characterization of D_2-symmetric C_{76} [2] and D_3-symmetric C_{78} [3]. Shortly afterwards, another chiral carbon molecule, a D_2-symmetric isomer of C_{84}, was characterized spectroscopically in a mixture together with an achiral isomer, D_{2d}-C_{84} [3c] [4] and, very recently, the isolation of a D_2-symmetric isomer of C_{80} was reported [5] (*Fig. 1*). These inherently chiral higher fullerenes were obtained as racemic mixtures in 1–100 mg quantities by HPLC (high performance liquid chromatography) purification of fullerene soot extract [6] which had been previously depleted from the far more abundant C_{60} and C_{70} [3c] [4] [5] [7] [8]. By asymmetric *Sharpless* osmylation, *Hawkins et al.* [9] accomplished the kinetic resolution of very small amounts of the allotropes D_2-C_{76}, D_3-C_{78}, and D_2-C_{84}, and characterized them by their circular dichroism spectra.

In 1992, the first enantiomerically pure covalent fullerene adducts, fullerene sugar conjugates, were prepared [10]. With the explosive development of covalent fullerene chemistry during the past years [11], an increasing number of chiral C_{60} and C_{70} derivatives have been published, sometimes without their stereochemical properties even being addressed. In many of these cases, the chirality is neither inherent to the core of the unfunctionalized carbon cage, nor is it due to stereogenic units in the addends, but it can be attributed to an addition pattern characterized by the absence of an S_n axis [12].

As the number of chiral fullerene derivatives is increasing, the need for their configurational description is becoming more and more apparent besides the problem of fullerene nomenclature [13]. In a recent paper describing synthesis and characterization
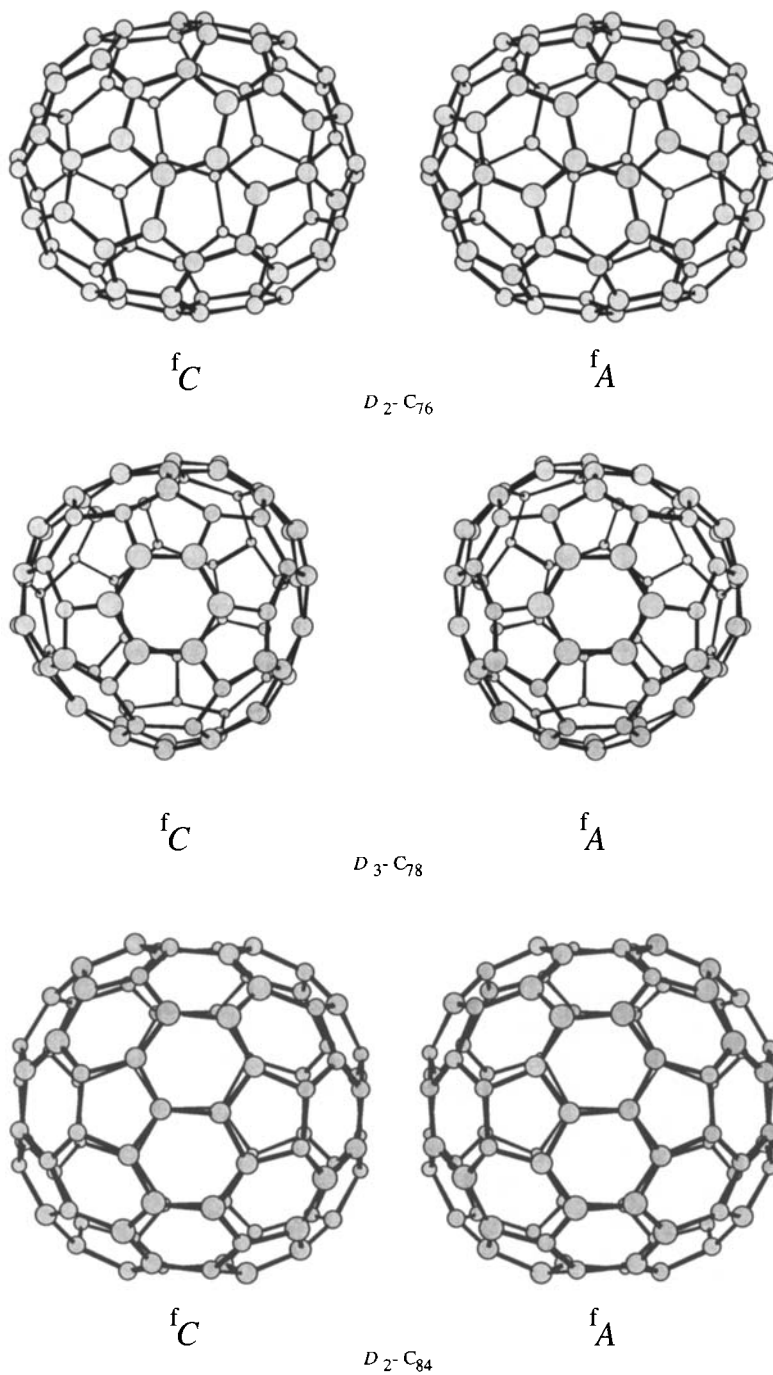
^fC ^fA

D_2-C_{76}

^fC ^fA

D_3-C_{78}

^fC ^fA

D_2-C_{84}

Fig. 1. *Enantiomeric pairs of* D_2-C_{76}, D_3-C_{78}, *and* D_2-C_{84}, *the inherently chiral fullerenes which have been character-ized and resolved so far*

of bis-, tris-, and tetrakis-adducts of C_{70} with chiral addition patterns [14], we outlined recommendations for the assignment of a single configurational descriptor to a carbon spheroid with a chiral addition pattern. Here, these recommendations are presented in a more detailed and clearly structured way, extended to other kinds of chiral fullerene derivatives, and illustrated with examples mostly taken from literature.

2. Scope and Limitations. – The main motivation for proposing a new configurational descriptor system for fullerene derivatives with a chiral addition pattern was the degree of complexity encountered, when using the *CIP* (*Cahn, Ingold, Prelog*) system [15], with this class of compounds. In fact, the simple and powerful set of rules, while perfectly appropriate to unambiguously describe the configuration of the stereogenic centers involved, generally implies a lengthy and unintuitive procedure for determining all necessary descriptors. When starting from a given configurational description on the other hand, it may require a similar effort to deduce the corresponding molecular structure. Furthermore, inherently chiral fullerenes do not have any stereogenic centers to be configurationally specified by the *CIP* system. A new convention recently proposed for C_{60} derivatives, which is based on edge labelling of the icosahedron and also allows configurational specification of chiral molecules, does not seem to be much easier to handle [16].

Even though the complexity of the molecules discussed here will always be reflected somehow in a structural description, an alternative to the *CIP* system should be relatively easy to apply and rely on concepts that are familiar to fullerene chemists and easy to understand for other scientists. Furthermore, computers playing an important role in structural studies of fullerenes [17] as well as in naming compounds, easy machine handling of a newly developed configurational descriptor system would be of great advantage.

We tried to make use of existing definitions and rules wherever this was possible and useful. Among the most important such definitions are the numbering schemes which have been developed from geometrical considerations on the carbon spheroids and proposed to the *IUPAC* for the nomenclature of fullerenes and their derivatives [13]. It has to be stressed, however, that the configurational description, while making use of these numbering schemes, is independent from the names of the compounds. In fact, the basic concept proposed here is fully applicable to any helical (chiral) fullerene numbering system, *e.g.*, the one developed at the *Chemical Abstracts Service*[1]) [18].

Besides these practical guiding principles, two crucial points to be considered are the unambiguity of the configurational specification system and the complementarity of the descriptors. This means that only a single descriptor can be associated with the configuration of each chiral molecule, and the opposite descriptor has to be used for its mirror image. Even though the validity of these requirements is difficult to establish rigorously, we have, by testing our system on many existing and a number of conceivable compounds, not found a counter-example.

In this context, another question has to be addressed: to which compounds exactly can the new descriptor system be applied? If an unambiguous definition can be given for fullerenes themselves [17] [19], this is not applicable as such to their derivatives, the core of

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[1]) All the examples given in this paper refer to the numbering schemes defined in [13].

which may include saturated C-atoms, heteroatoms, broken bonds, missing atoms *etc.* In a stricter sense, the system should be valid for all fullerenes and their derivatives having a core framework that is unaltered with respect to the number of atoms and to the connections between them, if no distinction is made between formal single and double bonds. In practice, however, it may appear convenient to use the proposed configurational description for all compounds that are relatively closely related to the carbon spheres, and to which fullerene nomenclature can be easily applied, *e.g.*, partially and fully saturated fullerenes (adducted fullerenes), heterofullerenes, isotopically labelled fullerenes and other fullerene-like structures (fulleroids), as well as the endohedral inclusion complexes of all these species.

The system should also allow the configurational specification of endohedrally adducted fullerenes, where addends are located inside the cage. Such cases may occur with small addends like H, and the prefix *in* is proposed for designating endohedral addends, independently of the actual configuration, or even the compound being chiral or not. Accordingly, the prefix *out* can be used for emphasizing the fact that an addend is located on the outer side of the spheroid. These additional stereodescriptors do not affect the configurational description of the addition pattern as it is proposed below.

As far as fullerene derivatives are concerned, it should finally be noted that the present recommendations deal with the configurational description of molecules with a chiral addition pattern only. Stereogenic units in the addends are described in the usual way by the *CIP* system [15] and are considered only in cases where the interplay between different such addends leads to a chiral addition pattern (*cf. Fig. 10*).

3. Discussion. – 3.1. *Basis of the Configuration Specification System for Fullerene Compounds.* In principle, the configuration of fullerene derivatives with a chiral addition pattern could be described by indicating the configuration of each stereogenic sp^3-hybridized center of the cage. This procedure, however, seems of little practical use, because the multiple branching of the fullerene framework may require the development of very complex hierarchic digraphs (showing nature and connectivity of the atoms in the molecule) [15b] with a difference in *CIP* priority becoming apparent only for high generations of connected atoms, if the distance between addends is large on the surface of the spheroid. This is illustrated by *Fig. 2, b*, showing the hierarchic digraph for the stereogenic center C(1) of a recently synthesized chiral bis-adduct of C$_{60}$ (*Fig. 2, a*) [20]. For multiply functionalized fullerenes, this procedure would have to be repeated for all stereogenic centers that are not related by symmetry, and result in a multitude of configurational descriptors.

A different, maybe more reasonable way of looking at fullerene derivatives with a chiral addition pattern is considering them as examples for planar chirality, the 'plane' in this case being the curved fullerene surface. It can be easily seen that inverting both the addends with respect to the surface and turning the fullerene shell inside out (the latter operation leaves the configuration of stereogenic centers unchanged) leads to the enantiomeric addition pattern. However, the way to apply the existing rules for planar chiral molecules to fullerene compounds does not seem to be obvious [15].

These considerations illustrate the convenience of having a simple convention for describing the absolute configuration of fullerene adducts with a chiral addition pattern by a single descriptor. Appropriate rules could even be extended to unfunctionalized
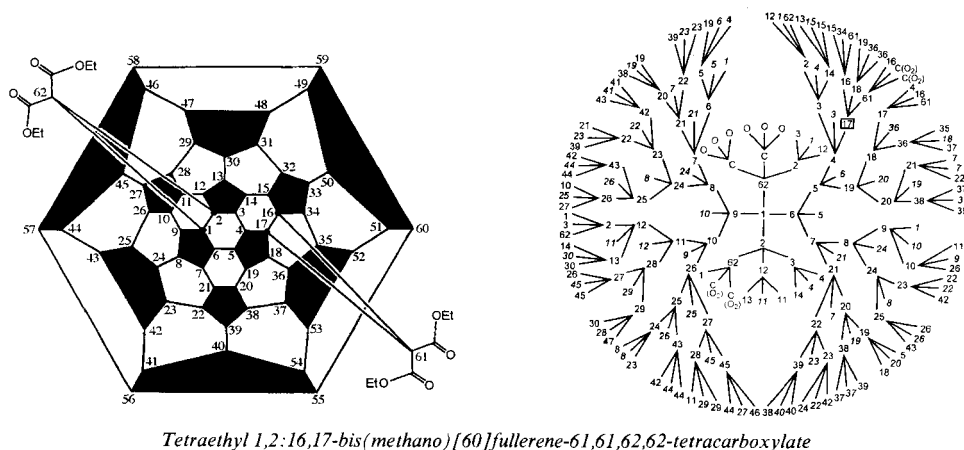
Tetraethyl 1,2:16,17-bis(methano)[60]fullerene-61,61,62,62-tetracarboxylate

Fig. 2. a) Schlegel *diagram of one enantiomer of tetraethyl 1,2:16,17-bis(methano)[60]fullerene-61,61,62,62-tetra-carboxylate and* b) *the corresponding hierarchic digraph for the stereogenic center* $C(1)$; *the development of each branch is stopped after its priority over others has become apparent.* Whereas the *CIP* priorities of the ligand branches C(62) (O-atoms (higher atomic number) *vs.* C-atoms) and C(2) (higher number (nine) *vs.* lower number (six) of C-atoms) can already be assigned as first and second, respectively, in the third generation; the overall priority order can be established only in generation 6 with 48 C-atoms in the C(6) *vs.* 45 C-atoms in the C(9) ligand branch. The priority of the C(6) over the C(9) branch appears plausible by the fact that the shortest path from C(1) to the quaternary C(17) (framed) leads *via* C(6) rather than C(9). Application of the sequence rules thus leads to the assignment of the (*R*)-configuration to C(1) in the shown enantiomer. The configurational description of the whole molecule requires repetition of this procedure for the remaining stereogenic centers. In case of more distant addends, development into even higher ligand generations is necessary to determine *CIP* priority orders.

chiral fullerenes which do not contain any stereogenic centers, or to chiral heterofullerenes and isotopically labelled fullerenes, in which one or several C-atoms of the spheroid have been replaced by other elements or isotopes. At a stereogenic center, the four tetrahedrally arranged substituent positions are equivalent due to symmetry, and chirality can only result from a different nature of the substituents. For the description of a given fullerene C_n or its derivative, however, we have to consider an arrangement of up to n different points at the surface of a spheroid. A simple distinction between enantiomeric patterns in such a complex arrangement is possible by taking as a reference the numbering schemes which have been developed for the nomenclature of fullerenes and their derivatives, and which can be developed with a number of rules from their structure [13] [18].

In a three-dimensional model, the pathway following the sequence of numbered C-atoms is made up of a helix (in case of a contiguous numbering) or of helical segments (if contiguous numbering is not possible), and, therefore, it is chiral. As a consequence, two geometrically equivalent, mirror-symmetric numbering schemes can be applied to an achiral parent fullerene, as shown in *Fig. 3* for *Schlegel* diagrams of C_{60}. For a specific enantiomer of an inherently chiral carbon spheroid, on the other hand, the numbering scheme is unique, and its mirror image has to be applied to the other optical antipode (*cf. Fig. 4*).

For a chiral derivative resulting from a specific addition pattern of an achiral parent fullerene, there is a unique numbering scheme leading to the lowest set of locants for the
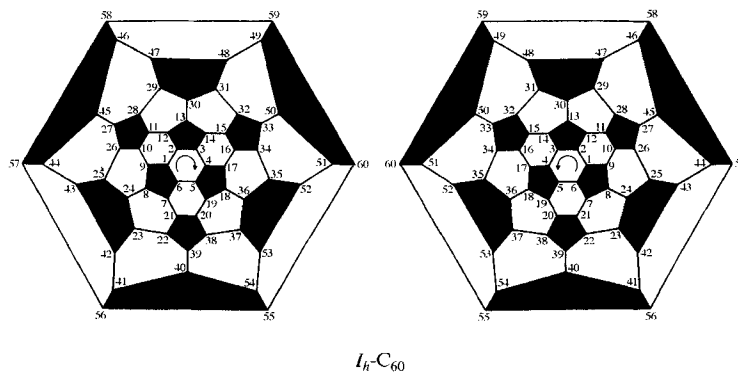
$I_h\text{-}C_{60}$

Fig. 3. Schlegel *diagrams of C_{60} with enantiomeric numbering schemes according to* [13c]. As the parent buckminster-fullerene is achiral, both numbering schemes are equivalent in this case. The arrow in the central hexagon, which is the one closest to the viewer, indicates the path of the numbering commencement (clockwise on the left, anticlockwise on the right side).

addends[2]). A description of the handedness of the numbering scheme leading to the lowest set of locants is sufficient to unambiguously characterize the absolute configuration of the adduct. Again, it should be kept in mind that, despite the concept of the 'lowest set of locants' being taken from the nomenclature rules of organic compounds for practical reasons, the resulting descriptor is independent of the name of the compound.

The configurational descriptor of the adduct is defined identical to that of the numbering scheme affording the lowest set of locants and determined in the following way by using a three-dimensional representation, or more easily, a *Schlegel* diagram[3]) of the derivative. After determining the appropriate numbering scheme, the viewer, looking at the polygon of the numbering commencement from the outside of the fullerene cage, traces a path from C(1) to C(2) to C(3) which are never aligned in a fullerene structure. If the path describes a *c*lockwise motion, the configuration of the adduct is termed ^{f}C, if it describes a counter- or *a*nti-clockwise motion, the descriptor is ^{f}A (the superscript 'f' refers to 'fullerene').

In practice, configurations should be most easily determinable with an appropriate computer program. In many cases, the following procedure also appears to be quite convenient: mirror images of the numbering scheme [13] [18] fitting a *Schlegel* diagram of the achiral parent fullerene in question are copied on a transparency and, according to the recommendations given above, assigned the descriptors ^{f}C and ^{f}A. *Fig. 13* (appendix) provides appropriate patterns to do this for C_{60} and C_{70}. The obtained templates can be easily rotated in any required orientation and used to determine which one allows for the lowest set of locants in a *Schlegel*-type representation of the chiral fullerene derivative. The absolute configuration of the adduct is assigned the descriptor of the numbering scheme fulfilling this criterion. To realize a maximum of useful orientations with the templates, the *Schlegel* diagram should reflect the highest possible number of symmetry

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[2])   For the definition of the lowest set of locants, see *Sect. R-0.2.4.2* in [21].
[3])   The convention that the central polygon of the *Schlegel* diagram is facing the viewer [13c] is used here.

elements of the compound. Finally, it has to be kept in mind that *Schlegel* diagrams obtained by facing different sides of the three-dimensional model of a fullerene derivative are not superimposable in general, and finding the actual lowest set of locants may require testing several of them.

According to structural criteria of chiral fullerene compounds, a distinction is made between three different types of core functionalization patterns: They can be *1*) inherently chiral, *2*) non-inherently chiral, and *3*) achiral (chirality resides in addend(s)), and are discussed in detail as well as illustrated with examples below. The actual type of functionalization pattern can be easily recognized with the help of a simple substitution test (*Scheme*) consisting in *a*) replacing *all* addends or substituents[4]) with the *same achiral* test-addend, *b*) replacing *(non)identical* addends or substituents with *(non)identical achiral* test-addends, and *c*) considering the original molecule. After each step, the resulting structure of increasing degree of complexity is checked for chirality; as soon as it is found, the type of functionalization pattern can be identified.

Scheme. *Scheme for Classifying Different Types of Fullerene Spheroid Chirality by Applying a Simple Substitution Test*
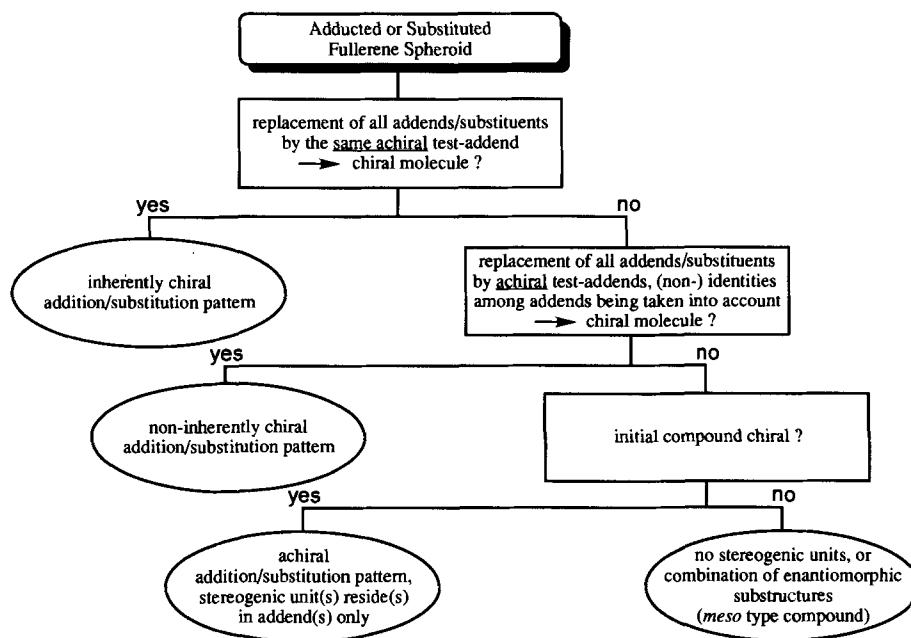
3.2. *Inherently Chiral Fullerenes and Their Derivatives*. This class of compounds includes inherently chiral fullerenes, heterofullerenes, and isotopically labelled fullerenes and heterofullerenes, as well as their adducts [2–5] [7] [9] [22]. For these compounds, each one of the two mirror-symmetric, geometrically equivalent numbering schemes fits only

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[4])   In this context, the term 'substituent' refers to the substitution of C-atoms of the fullerene core by heteroatoms or specific isotopes, 'substitution' being used in a purely structural, not a mechanistic sense.

one of the two parent fullerene enantiomers. Hence, it is the chirality of the parent
fullerene that determines the numbering scheme to be used, and, therefore, the descriptor
^fC or ^fA for the specification of the absolute configuration of these carbon spheroids and
their derivatives, regardless of the addition or substitution pattern (*Fig. 4*). It should be
noted that, contrarily to the case of achiral parent fullerenes, a given enantiomer of an
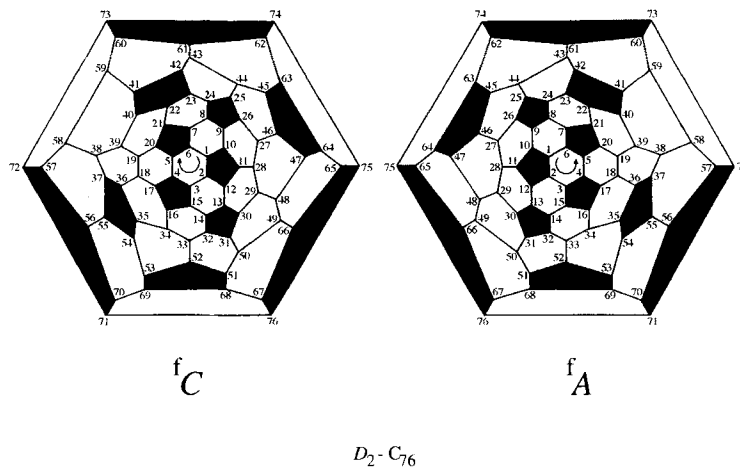inherently chiral fullerene cannot be combined with functionalization patterns that are
enantiomeric.

$$^fC \qquad\qquad ^fA$$

$$D_2 \text{-} C_{76}$$

Fig. 4. Schlegel *diagrams of the enantiomers of the inherently chiral fullerene* D_2-C_{76}. Because of the lack of mirror
symmetry, each numbering scheme fits only a single optical antipode. For the left-side structure, the numbering
commences in a clockwise direction (C(1) → C(2) → C(3)) and accordingly, the structure is assigned the configura-
tional descriptor ^fC. Analogously, the anticlockwise numbering commencement for the enantiomer on the right
side leads to the descriptor ^fA.

An alternative way of specifying the configuration of inherently chiral parent fuller-
enes, which is independent of the numbering scheme, has been suggested [13c]. However,
its application depends on the drawing of a geometrically appropriate *Schlegel* diagram
which may require knowledge of actual bond lengths and angles. On the other hand, the
descriptor system proposed here is simple and unambiguous, once the numbering scheme
has been established. A further advantage is its general applicability ranging from
inherently chiral fullerenes themselves over their derivatives to cage compounds that are
chiral due to the functionalization pattern only.

3.3. *Derivatives of Achiral Parent Fullerenes with an Inherently Chiral Addition or
Substitution Pattern.* We define a fullerene functionalization pattern as inherently chiral if
the possibility for the existence of enantiomeric species is inherent to the geometric
arrangement of the actual addition (substitution) sites within the fullerene core, regard-
less of the addends (substituents) being identical or different (*Scheme*). Compounds
derived from inherently chiral fullerenes have inherently chiral functionalization pat-
terns[5]); they are the object of the preceding section. The molecules considered here are all

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[5])   Besides the actual functionalization positions of the fullerene core resulting from addition or substitution, the
        unaltered part of the carbon shell also has to be considered as a part of the functionalization pattern.

derived from achiral parent cores and include fullerene adducts, heterofullerenes, isotopically labelled fullerenes or heterofullerenes, as well as their adducts [7] [14] [20] [23]. The C-atom numbering of the achiral parent fullerene can be achieved with either one of the two mirror-symmetric numbering schemes. For a particular enantiomer of its derivatives with an inherently chiral functionalization pattern, however, a single numbering scheme only leads to the lowest set of locants. This is shown in *Fig. 5* for the enantiomers of a tris-adduct of C$_{60}$ obtained as a racemate by *Hirsch et al.* [23a]. The configuration is determined as indicated above, and the according descriptor is assigned to the enantiomer in question.
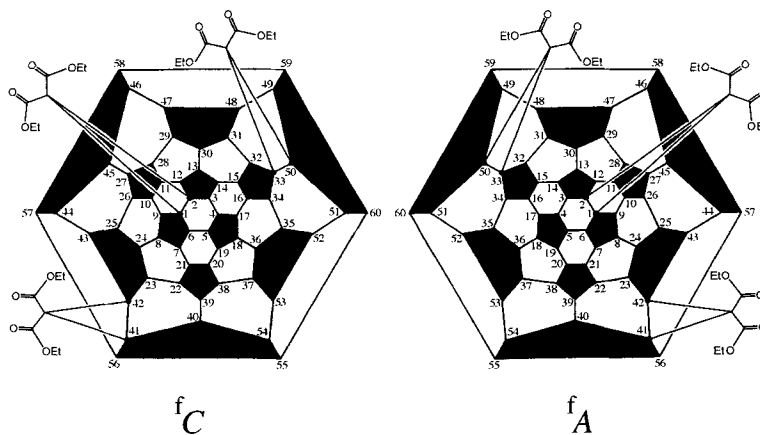
Hexaethyl 1,2:33,50:41,42-tris(methano)[60]fullerene-61,61,62,62,63,63-hexacarboxylate

Fig. 5. Schlegel *diagrams of the enantiomers of hexaethyl 1,2:33,50:41,42-tris(methano)[60]fullerene-61,61,62,62, 63,63-hexacarboxylate* (*trans*-3,*trans*-3,*trans*-3 isomer), *a C$_{60}$ adduct with an inherently chiral addition pattern.* Interchange of the numbering schemes, and, therefore, of the descriptors, would afford the locant set 1,2:39,40:48,49 for the addends which is higher than 1,2:33,50:41,42 and, therefore, unacceptable.

3.4. Derivatives with a Functionalization Pattern That Is Chiral Due to the Nonidentity of Addends or Substituents (Non-inherently Chiral Functionalization Patterns).

The enantiomers of all fullerene adducts with a chiral addition pattern discussed so far can be unambiguously described with the simple set of rules given above. However, other derivatives can be conceived of, where the chirality is neither inherent to the parent fullerene nor to an inherently chiral pattern of addition or substitution, but is due to the geometric arrangement of addends or substituents, all of which must not be identical (non-inherently chiral functionalization patterns, *Scheme*) [12] [24]. This category is closely related to the stereogenic center with a tetrahedral arrangement of ligands, where chirality occurs only if – in this case all four – substituents are different[6]). Similarly to other types of stereogenic elements, the connection of enantiomorphic fullerene units may result in an achiral *meso*-type compound (*Fig. 6*; *cf.* also *Fig. 10*) [12] [24d].

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[6])   For the general problem of 'pseudoasymmetry', which can occur with enantiomorphic ligands in the case of stereogenic centers as well as of non-inherently chiral fullerene addition patterns, see [15b].
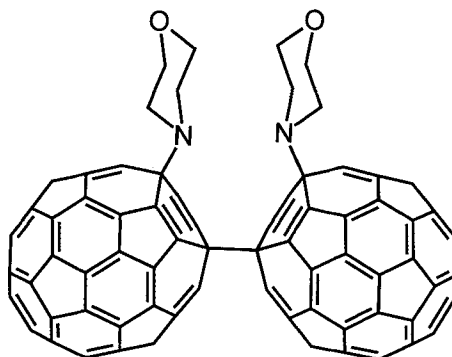
Fig. 6. meso-*Compound resulting from the direct connection of two fullerene units, each representing a 1,4-adduct of* C_{60} *with a non-inherently chiral addition pattern.* Due to opposite configurations, the units are enantiomorphic and the molecule as a whole is achiral.

In all cases of non-inherently chiral addition or substitution patterns associated with an achiral parent fullerene, no distinction between enantiomers is possible on the base of the criteria enunciated above: the same lowest set of locants is obtained with both mirror-symmetric numbering schemes. For a discrimination, a classification of addends or substituting atoms is necessary. It can be achieved in a most convenient way by use of the *CIP* system, a simple hierarchic ordering scheme for residues differing in constitution or configuration, which has proven very efficient in the configurational description of stereogenic centers [15]. For the fullerene derivatives considered in this section, substituting heteroatoms and addends are treated in a similar way by starting the comparison of the substructures according to the *CIP* rules at the atom located within the fullerene core and then progressively moving outwards until a priority difference emerges. In case two enantiomorphic fullerene structures have to be compared according to *CIP*, we suggest that, in addition to *Sequence Rule 5* (priority of *R* over *S* and of *M* over *P*) [15b], ^fC is given priority over ^fA. Of the two mirror-symmetric numbering schemes leading to the lowest set of locants, that one assigning the lower locant to an addend of higher *CIP* priority at the first point of difference is preferred and confers its descriptor to the enantiomer in question. Typical representatives of this category are 1,4-adducts of C_{60} with two different addends [24] (*Fig. 7*).

It should be noted that this is not necessarily the same numbering scheme used to compose the name of the compound. Nomenclature, in such a case, assigns lowest locant priority according to different criteria, *e.g.*, alphabetical order of prefixes (*cf.* [21], *Rules R-0.1.8* and *R-4*) (*Fig. 8*). The possible need for having to use mirror-symmetric numbering schemes for the configurational description and the nomenclature may seem inconvenient at first view, but it illustrates well the independence of the two systems. Whereas the numbering schemes and the simple rule of the lowest set of locants – combined with *CIP* priorities of addends or substituents if necessary – are sufficient to describe the configuration of all examples known so far and were chosen identical to those used in nomenclature for reasons of convenience, nomenclature rules alone do not allow a distinction between enantiomers.
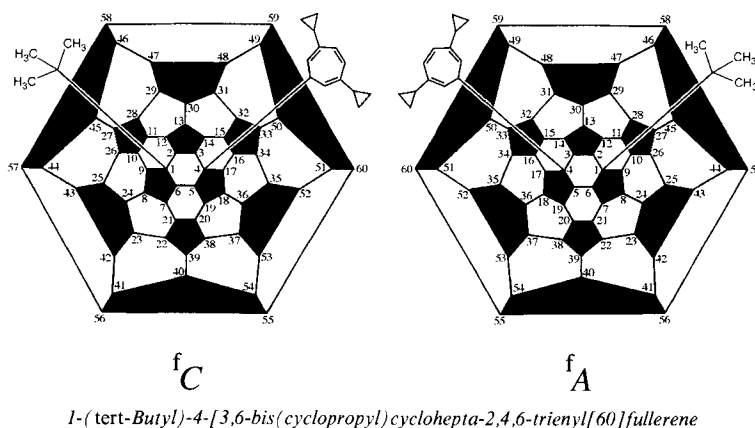
1-(tert-Butyl)-4-[3,6-bis(cyclopropyl)cyclohepta-2,4,6-trienyl[60]fullerene

Fig. 7. Schlegel *diagrams of the enantiomers of 1-(tert-butyl)-4-[3,6-bis(cyclopropyl)cyclohepta-2,4,6-trienyl]-[60]fullerene, having an addition pattern which is chiral only because both addends are (constitutionally) different (non-inherently chiral addition pattern)* [24c]. The *t*-Bu residue has to be assigned the lower locant 1, because its *CIP* priority is higher than that of the 3,6-bis(cyclopropyl)cyclohepta-2,4,6-trienyl group.
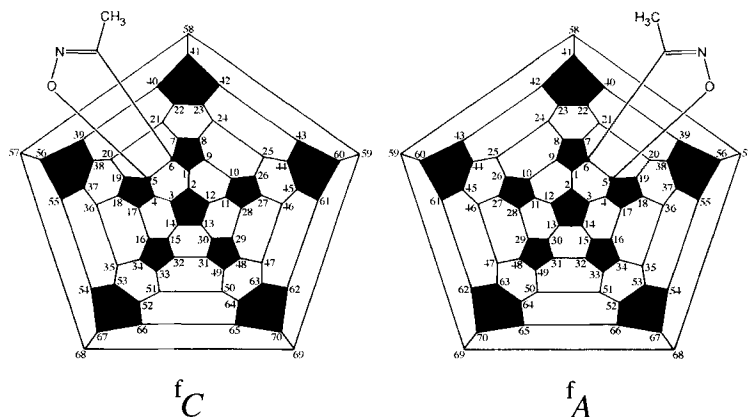

73-Methyl-6,5-epoxynitrilometheno[70]fullerene or 3'-Methyloxazolo[4',5':5,6][70]fullerene

Fig. 8. Schlegel *diagrams of the enantiomers of 73-methyl-6,5-epoxynitrilometheno[70]fullerene* [24b]. In this case of a non-inherently chiral addition pattern, different numbering schemes have to be used for the configurational description (lowest locant (5) for the addend of highest *CIP* priority (O); as shown in the diagram) and for nomenclature (nomenclature rules for bridged condensed ring systems containing heteroatoms in the bridge: the lowest bridge locant (71) has to be connected to the bridgehead with the highest locant (6) and to be assigned to the bridge atom of highest heteroatom priority (O); this numbering is not shown). According to the fusion nomenclature adapted to fullerenes [13c], this compound can be alternatively named *3'-methyloxazolo[4',5':5,6][70]-fullerene.*

Finally, it must be mentioned that addition of residues comprising stereogenic units does not necessarily lead to chiral addition patterns (Scheme and Fig. 10, a–d) [10] [12] [14] [25]. In such cases, the configuration of the chiral addends only has to be specified in the usual way by using the CIP system [15]. If a chiral addition pattern is superimposed to chiral addends, the configuration of both types of stereogenic elements has to be indicated. Fig. 9 shows such a superimposition of stereogenic centers in the ester residues to an inherently chiral C_{70} addition pattern of methano addends [14]. Similarly to other molecules with chiral isoconstitutional substructures, the combination of distinct fullerene addition patterns with isomorphic or enantiomorphic chiral addends can lead to steric arrangements with a certain complexity. However, these can be easily analyzed with the substitution test outlined in the Scheme, and a selection of such C_{60} and C_{70} derivatives with chiral side chains – still awaiting their syntheses – is shown in Fig. 10.

3.5. Related Chiral Bowl-Shaped Molecules. It has been mentioned earlier in this paper that the proposed configuration specification, even though rigorously applicable only to fullerenes in a stricter sense, as defined in Sect. 2, may be extended to other molecules that can be considered as derived from them. An interesting class of such derivatives is obtained upon progressive removal of atoms or interatomic connections from the spheroid leading to holes in the fullerene shell [26], and – depending on the hole size – to bowl-shaped molecules ('buckybowls' [27]). Two prominent examples of this category are 1(6)a-homofullerene ('6,5-open' $C_{61}H_2$ structure) [28] and corannulene [29], one of the basic subunits of fullerenes. As opposed to the closed carbon cages, these molecules additionally have a rim that can be functionalized, and, in combination with the bowl
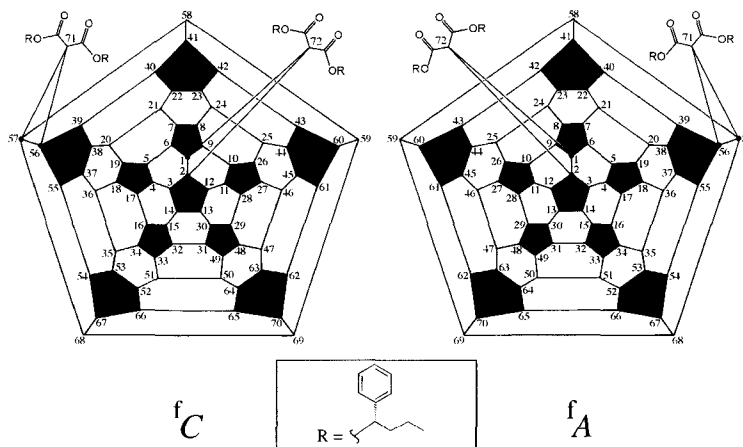
Tetrakis[(S)-1-phenylbutyl] 1,2:56,57-bis(methano) [70]fullerene-71,71,72,72-tetracarboxylate

Fig. 9. Schlegel diagrams of tetrakis[(S)-1-phenylbutyl] (^{f}C)- and (^{f}A)-1,2:56,57-bis(methano)[70]fullerene-71,71,72,72-tetracarboxylate, a compound in which the chirality of the addends ((S)-configured stereogenic center in the alcohol component of the ester groups) is superimposed to an inherently chiral addition pattern of the fullerene core. The two types of stereogenic units are independent from each other, and the configuration of both has to be specified for a full structural description of the molecules. As can be seen from the combinations (S)-(^{f}C) and (S)-(^{f}A), the depicted molecules are diastereoisomers.
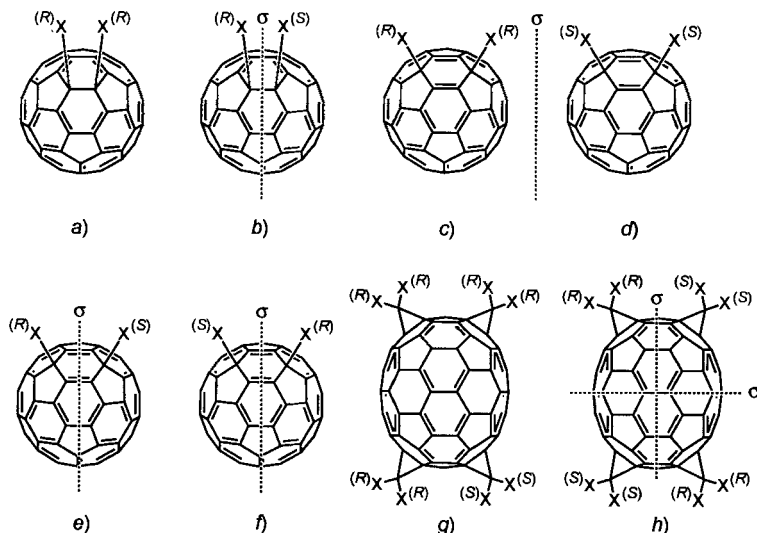
Fig. 10. *Some combinations of two well known C_{60} addition patterns and a potential C_{70} addition pattern with chiral addends $X^{(R)}$ or $X^{(S)}$* (the superscript indicates the configurational descriptor of the addends; $X^{(R)}$ and $X^{(S)}$ are enantiomorphic). *a*) Chiral 1,2-adduct of C_{60}: the addition pattern is achiral and the chirality resides in the addends only; *b*) achiral 1,2-adduct of C_{60}: an achiral addition pattern is combined with enantiomorphic addends (*meso*-form); *c*) chiral 1,4-adduct of C_{60}: the addition pattern is achiral and the chirality resides in the addends only; *d*) enantiomer of *c*); *e*) achiral 1,4-adduct of C_{60}: a non-inherently chiral addition pattern is combined with enantiomorphic addends ('pseudoasymmetric' addition pattern, *meso*-form); *f*) achiral 1,4-adduct of C_{60}: diastereoisomer of *e*) (same combination of stereogenic units) obtained from the latter by addend interchange; *e*) and *f*) are also diastereoisomeric to *c*) and *d*); *g*) chiral 1,2:13,30:41,58:69,70-adduct of C_{70}: chirality resides in a combination of a non-inherently chiral addition pattern and chiral addends; *h*) achiral 1,2:13,30:41,58:69,70-adduct of C_{70}: a non-inherently chiral addition pattern is combined with enantiomorphic addends ('pseudoasymmetric' addition pattern, *meso*-form); interchange of the enantiomorphic methano addends again leads to a diastereoisomer; *h*) is also diastereoisomeric to *g*).

shape of the core, an appropriate functionalization pattern gives rise to enantiomerism [30]. The configurational description of 'opened cage' molecules that are relatively closely related to fullerenes, *e.g.*, the first C_{60} derivative containing an 11-membered ring as a hole in the core [31], can be based on the C-atom numbering of the parent fullerene (*Fig. 11*). Provided a numbering scheme similar to that of fullerenes is defined for bowl-shaped molecules, a configuration specification can be done according to the principles enunciated above by a viewer facing the positive curvature side of the core, as shown in *Fig. 12* for a rim-substituted corannulene [30a].

4. Conclusion. – The proposed system allows specification of the configuration of chiral fullerenes and fullerene derivatives with a chiral functionalization pattern by using a single descriptor, ^fC (clockwise) or ^fA (anticlockwise), regardless of the number of addends or stereogenic centers present on the core. On the other hand, it should be kept in mind that however simple a descriptor system may be, it has to include the structural information in its total complexity. In the present case, most of the latter is contained in the fullerene numbering schemes, and, therefore, a convenient graphical representation of

R = CH₂OCH₂CH₂OCH₃

^{f}C ^{f}A
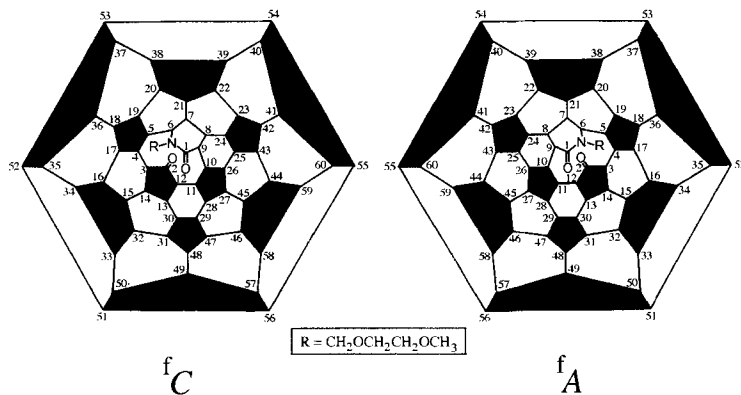
1(6)a-[(2-Methoxyethoxy)methyl]-1(6)a-aza-1(6)a-homo-1,2-seco[60]fullerene-1,2-dione

Fig. 11. Schlegel *diagrams of the enantiomers of 1(6)a-[(2-methoxyethoxy)methyl]-1(6)a-aza-1(6)a-homo-1,2-seco[60]fullerene-1,2-dione, an 'opened cage' molecule containing an eleven-membered ring, which can be considered as a C₆₀ derivative with an inherently chiral functionalization pattern.* It becomes clear that the more the molecular framework differs from the parent fullerene, the more difficult it is to apply the numbering scheme of the latter, and rules may have to be developed for systematically numbering bowl-shaped molecules.
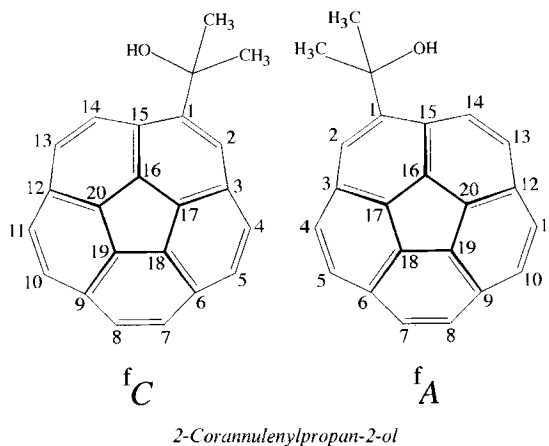

^{f}C ^{f}A

2-Corannulenylpropan-2-ol

Fig. 12. *Enantiomers of 2-corannulenylpropan-2-ol, a bowl-shaped condensed ring system substituted at the rim.* It represents another molecule with an inherently chiral functionalization pattern and has been tentatively assigned a contiguous numbering scheme starting at the rim (largest ring) which allows a configurational description according to the principles enunciated above.

the molecular structures is indispensable. The patterns provided in the *Appendix* should facilitate the application of the proposed system to chiral derivatives of the most common fullerenes C_{60} and C_{70}.
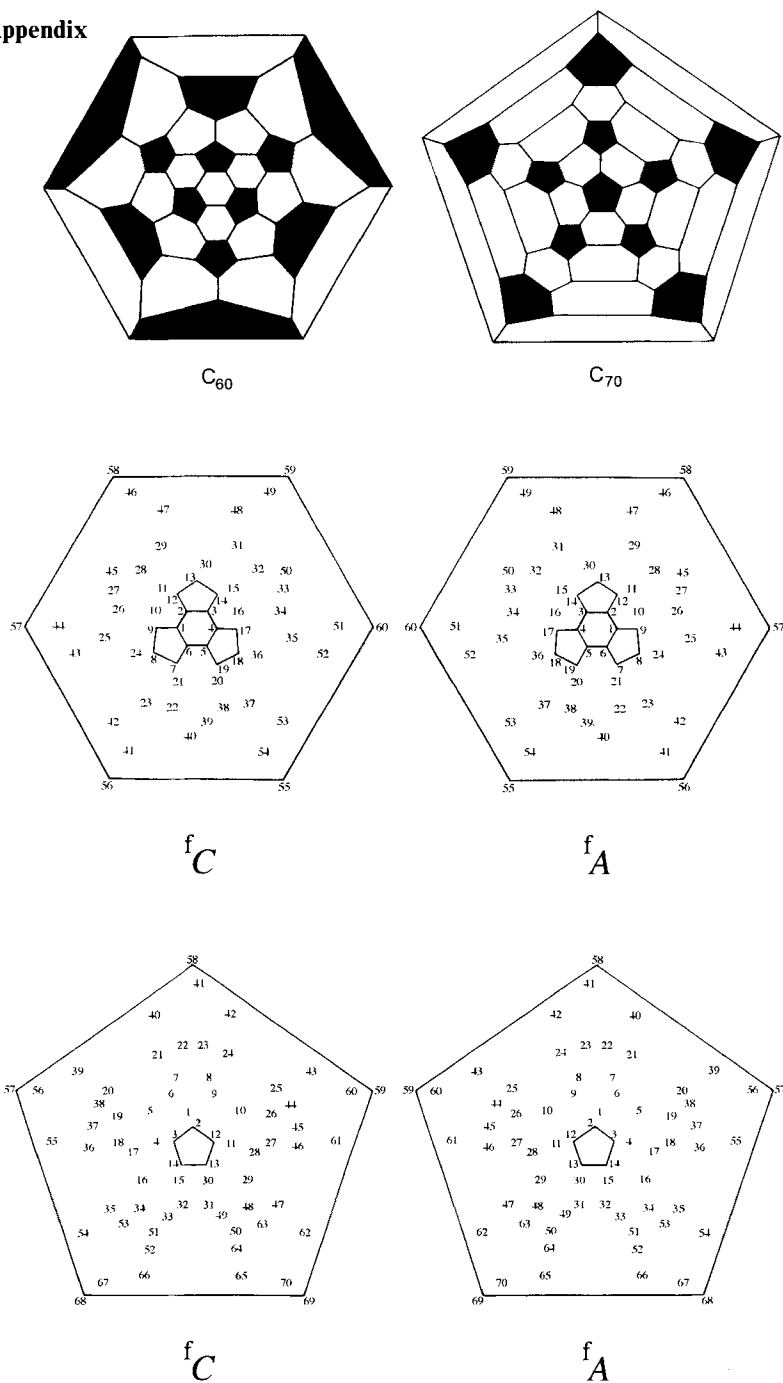
5. Appendix

Fig. 13. Schlegel *diagrams of* C_{60} *and* C_{70} *with the respective* ^fC *and* ^fA *numbering schemes having the appropriate size for being used as templates with the* Schlegel *representations after being copied on a transparency*

REFERENCES

[1] a) D. E. Manolopoulos, *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2861; b) P. W. Fowler, R. C. Batten, D. E. Manolopoulos, *ibid.* **1991**, *87*, 3103; c) D. E. Manolopoulos, *Scientist* **1993**, *7*, 16.

[2] a) F. Diederich, R. Ettl, Y. Rubin, R. L. Whetten, R. Beck, M. Alvarez, S. Anz, D. Sensharma, F. Wudl, K. C. Khemani, A. Koch, *Science (Washington D. C.)* **1991**, *252*, 548; b) R. Ettl, I. Chao, F. Diederich, R. L. Whetten, *Nature (London)* **1991**, *353*, 149; c) R. H. Michel, M. M. Kappes, P. Adelmann, G. Roth, *Angew. Chem.* **1994**, *106*, 1742; *ibid. Int. Ed.* **1994**, *33*, 1651.

[3] a) F. Diederich, R. L. Whetten, C. Thilgen, R. Ettl, I. Chao, M. M. Alvarez, *Science (Washington D. C.)* **1991**, *254*, 1768; b) R. Taylor, G. J. Langley, J. S. Dennis, H. W. Kroto, D. R. M. Walton, *J. Chem. Soc., Chem. Commun.* **1992**, 1043; c) K. Kikuchi, N. Nakara, T. Wakabayashi, S. Suzuki, H. Shiromaru, Y. Miyake, K. Saito, I. Ikemoto, M. Kainosho, Y. Achiba, *Nature (London)* **1992**, *357*, 142.

[4] a) C. Thilgen, F. Diederich, R. L. Whetten, in 'Buckminsterfullerenes', Eds. W. E. Billups and M. A. Ciufolini, VCH Publishers Inc., New York, 1993, p. 59; b) F. Diederich, R. L. Whetten, *Acc. Chem. Res.* **1992**, *25*, 119.

[5] F. H. Hennrich, R. H. Michel, A. Fischer, S. Richard-Schneider, S. Gilb, M. M. Kappes, D. Fuchs, M. Bürk, K. Kobayashi, S. Nagase, *Angew. Chem.* **1996**, *108*, 1839; *ibid. Int. Ed.* **1996**, *35*, 1732.

[6] W. Krätschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman, *Nature (London)* **1990**, *347*, 354.

[7] A. Herrmann, F. Diederich, C. Thilgen, H.-U. ter Meer, W. H. Müller, *Helv. Chim. Acta* **1994**, *77*, 1689.

[8] a) K. Kikuchi, N. Nakahara, T. Wakabayashi, S. Suzuki, K. Saito, I. Ikemoto, Y. Achiba, *Synth. Met.* **1993**, *55–57*, 3208; b) R. H. Michel, H. Schreiber, R. Gierden, F. Hennrich, J. Rockenberger, R. D. Beck, M. M. Kappes, C. Lehner, P. Adelmann, J. F. Armbruster, *Ber. Bunsenges. Phys. Chem.* **1994**, *98*, 975; c) K. Jinno, H. Ohta, Y. Saito, T. Uemura, H. Nagashima, K. Itoh, Y.-L. Chen, G. Luehr, J. Archer, J. C. Fetzer, W. R. Biggs, *J. Chromatogr.* **1993**, *648*, 71; d) M. R. Banks, I. Gosney, A. C. Jones, D. S. Jones, P. R. R. Langridge-Smith, R. J. McQuillan, P. Thorburn, *Chromatographia* **1993**, *35*, 631; e) J. C. Fetzer, E. J. Gallegos, *Polycycl. Arom. Comp.* **1992**, *2*, 245; f) C. J. Welch, W. H. Pirkle, *J. Chromatogr.* **1992**, *609*, 89; g) D. Herren, C. Thilgen, G. Calzaferri, F. Diederich, *ibid.* **1993**, *644*, 188.

[9] a) J. M. Hawkins, A. Meyer, *Science (Washington D. C.)* **1993**, *260*, 1918; b) J. M. Hawkins, M. Nambu, A. Meyer, *J. Am. Chem. Soc.* **1994**, *116*, 7642.

[10] a) A. Vasella, P. Uhlmann, C. A. A. Waldraff, F. Diederich, C. Thilgen, *Angew. Chem.* **1992**, *104*, 1383 *ibid. Int. Ed.* **1992**, *31*, 1388; b) P. Uhlmann, E. Harth, A. B. Naughton, A. Vasella, *Helv. Chim. Acta* **1994**, *77*, 2335.

[11] a) F. Diederich, C. Thilgen, *Science (Washington D. C.)* **1996**, *271*, 317; b) Tetrahedron Symposia-In-Print Number 60, Fullerene Chemistry, Ed. Amos B. Smith III, *Tetrahedron* **1996**, *52*, issue 14 (April 1).

[12] For review see: F. Diederich, C. Thilgen, A. Herrmann, *Nachr. Chem. Tech. Lab.* **1996**, *44*, 9, and ref. cit. therein.

[13] a) R. Taylor, *J. Chem. Soc., Perkin Trans. 2* **1993**, 813; b) P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor, D. R. M. Walton, *J. Chem. Soc., Chem. Commun.* **1995**, 683; c) E. W. Godly, R. Taylor, 'IUPAC Report of the Working Party on Fullerene Nomenclature and Terminology', 1993; we thank Dr. R. Taylor for sending us a copy of the manuscript.

[14] A. Herrmann, M. Rüttimann, C. Thilgen, F. Diederich, *Helv. Chim. Acta* **1995**, *78*, 1673.

[15] a) R. S. Cahn, S. C. Ingold, V. Prelog, *Angew. Chem.* **1966**, *78*, 413; *ibid. Int. Ed.* **1966**, *5*, 385; *errata ibid.* p. 511; b) V. Prelog, G. Helmchen, *Angew. Chem.* **1982**, *94*, 614; *ibid. Int. Ed.* **1982**, *21*, 567.

[16] Y. Nakamura, M. Taki, J. Nishimura, *Chem. Lett.* **1995**, 703.

[17] P. W. Fowler, D. E. Manolopoulos, 'An Atlas of Fullerenes', Clarendon Press, Oxford, 1995.

[18] A. L. Goodson, C. L. Gladys, D. E. Worst, *J. Chem. Inform. Comput. Sci.* **1995**, *35*, 969.

[19] a) H. W. Kroto, *Nature (London)* **1987**, *329*, 529; b) T. G. Schmalz, W. A. Seitz, D. J. Klein, G. E. Hite, *J. Am. Chem. Soc.* **1988**, *110*, 1113.

[20] J.-F. Nierengarten, V. Gramlich, F. Cardullo, F. Diederich, *Angew. Chem.* **1966**, *108*, 2242; *ibid. Int. Ed.* **1996**, *35*, 2101.

[21] R. Panico, W. H. Powell in 'A Guide to IUPAC Nomenclature of Organic Compounds', Ed. J.-C. Richter, Blackwell Scientific Publications, Oxford, 1993.

[22] A. Herrmann, F. Diederich, *Helv. Chim. Acta* **1996**, *79*, 1741.

[23] a) A. Hirsch, I. Lamparth, H. R. Karfunkel, *Angew. Chem.* **1994**, *106*, 453; *ibid. Int. Ed.* **1994**, *33*, 437; b) J. M. Hawkins, A. Meyer, M. Nambu, *J. Am. Chem. Soc.* **1993**, *115*, 9844; c) Q. Lu, D. I. Schuster, S. R. Wilson, *J. Org. Chem.* **1996**, *61*, 4764.

[24] a) A. Hirsch, A. Soi, H. R. Karfunkel, *Angew. Chem.* **1992**, *104*, 808; *ibid. Int. Ed.* **1992**, *31*, 766; b) M. S. Meier, M. Poplawska, A. L. Compton, J. P. Shaw, J. P. Selegue, T. F. Guarr, *J. Am. Chem. Soc.* **1994**,

116, 7044; c) T. Kitagawa, T. Tanaka, Y. Takata, K. Takeuchi, K. Komatsu, *J. Org. Chem.* **1995**, *60*, 1490; d) G. Schick, K.-D. Kampe, A. Hirsch, *J. Chem. Soc., Chem. Commun.* **1995**, 2023.

[25] a) S. R. Wilson, Y. H. Wu, N. A. Kaprinidis, D. I. Schuster, C. J. Welch, *J. Org. Chem.* **1993**, *58*, 6548; b) L. Isaacs, F. Diederich, *Helv. Chim. Acta* **1993**, *76*, 2454; c) C. Toniolo, A. Bianco, M. Maggini, G. Scorrano, M. Prato, M. Marastoni, R. Tomatis, S. Spisani, G. Palú, E. D. Blair, *J. Med. Chem.* **1994**, *37*, 4558; d) F. Novello, M. Prato, T. Da Ros, M. De Amici, A. Bianco, C. Toniolo, M. Maggini, *J. Chem. Soc., Chem. Commun.* **1996**, 903; e) S. R. Wilson, Q. Lu, J. Cao, Y. Wu, C. J. Welch, D. I. Schuster, *Tetrahedron* **1996**, *52*, 5131; f) A. Bianco, M. Maggini, G. Scorrano, C. Toniolo, G. Marconi, C. Villani, M. Prato, *J. Am. Chem. Soc.* **1996**, *118*, 4072.

[26] a) P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor, D. R. M. Walton, *J. Chem. Soc., Chem. Commun.* **1995**, 1869; b) M.-J. Arce, A. L. Viado, Y.-Z. An, S. I. Khan, Y. Rubin, *J. Am. Chem. Soc.* **1996**, *118*, 3775.

[27] a) P. W. Rabideau, A. H. Abdourazak, H. E. Folsom, Z. Marcinow, A. Sygula, R. Sygula, *J. Am. Chem. Soc.* **1994**, *116*, 7891; b) A. H. Abdourazak, Z. Marcinov, A. Sygula, R. Sygula, P. W. Rabideau, *ibid.* **1995**, *117*, 6410; c) Z. Marcinow, F. R. Fronczek, Y.-H. Liu, P. W. Rabideau, *J. Org. Chem.* **1995**, *60*, 7015; d) P. W. Rabideau, A. Sygula, in 'Advances in Theoretically Interesting Molecules', Ed. R. P. Thummel, Jai Press Inc., Greenwich, Connecticut, 1995, Vol. 3, p. 1.

[28] a) T. Suzuki, Q. Li, K. C. Khemani, F. Wudl, *J. Am. Chem. Soc.* **1992**, *114*, 7301; b) L. Isaacs, A. Wehrsig, F. Diederich, *Helv. Chim. Acta* **1993**, *76*, 1231; c) M. Prato, V. Lucchini, M. Maggini, E. Stimpfl, G. Scorrano, M. Eiermann, T. Suzuki, F. Wudl, *J. Am. Chem. Soc.* **1993**, *115*, 8479; d) A. B. Smith III, R. M. Strongin, L. Brard, G. T. Furst, W. J. Romanow, K. G. Owens, R. J. Goldschmidt, R. C. King, *ibid.* **1995**, *117*, 5492.

[29] a) W. E. Barth, R. G. Lawton, *J. Am. Chem. Soc.* **1971**, *93*, 1730; b) L. T. Scott, M. M. Hashemi, D. T. Meyer, H. B. Warren, *ibid.* **1991**, *113*, 7082.

[30] a) L. T. Scott, M. M. Hashemi, M. S. Bratcher, *J. Am. Chem. Soc.* **1992**, *114*, 1920; b) A. Sygula, P. W. Rabideau, *J. Chem. Soc., Chem. Commun.* **1994**, 1497.

[31] J. C. Hummelen, M. Prato, F. Wudl, *J. Am. Chem. Soc.* **1995**, *117*, 7003.