

From Chemical Topology to 3D Geometry[†]

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The first part presents a survey of how ideas originating in chemical topology can be applied for stereochemistry; diastereoisomerism can be more easily encoded in matrix form than enantiomerism. Chirality in two or three dimensions is examined, and the simplest elements of chirality ("protochirons") are described. Their assembly into chiral or achiral geometries with chemical relevance, including regular and semiregular polyhedra, is described. Examples of topological stereoisomerism are discussed. The second part is a bibliography including a particularization of Euler's famous formula for three-dimensional polyhedra, including cage compounds, which takes into account the possible presence of vertices of degrees two and/or four; chemical applications of this special formula are various cage hydrocarbons, fullerenes, fullerocoronands with oxygen heteroatoms, and nanotubes with oxygen or nitrogen heteroatoms which may form complexes with metallic cations; the heteroatoms serve to remedy dangling bonds at the ends of nanotubes.

1. INTRODUCTION

Organic chemistry really became a science in the third quarter of the last century, when isomerism was clearly understood. Organic compounds consist of only a few elements: carbon (and hydrogen in most cases) is the essential element; in addition, the most important organic compounds occurring in living organisms or synthesized for their various applications also contain oxygen, nitrogen, sulfur, and/or phosphorus. Isomerism is therefore so utterly characteristic of organic compounds that it puzzled chemists (Liebig, Wöhler, and Berzelius) from the beginning. In the last 50 years, synthetic chemistry used also several other elements (halogens, silicon, arsenic, boron, and a few metals) for developing medicinal drugs, fertilizers, pesticides, detergents, plastics, fibers, etc., contributing thus to present day civilization.

Thanks to several chemists (Kekulé, Couper, Crum Brown, and Butlerov), the simplest form of isomerism, namely chemical constitution, was firmly established as the way atoms are connected. For hydrocarbons, constitutional formulas are equivalent to unlabeled and nondirected multigraphs, and the corresponding enumeration problem can be solved by graph-theoretical approaches such as the applications of Polya's theorem.^{1–3}

However, chemical structure involves more than constitution or connectivity. Though Van't Hoff and Le Bel advocated in 1876 stereochemical models based on the tetrahedral geometry of saturated carbon or the trigonal geometry for double-bonded carbon, and though Werner in 1900, for metallic complexes, generalized these ideas to higher coordination numbers than 4, it was only at the beginning of this century that such stereochemical ideas became generally accepted. With the advent of quantum mechanics, of Pauling's concept of hybridization, and of Gillespie's concept of valence shell electron pair repulsion (VSEPR), one understands nowadays the reasons why the *geometry of molecules* must also be taken into account, in

addition to connectivity data. For the enumeration of stereoisomers, mathematical techniques involve, along with Polya's theorem, applications of Redfield's ideas⁴ and of double cosets.⁵

2. CHEMICAL TOPOLOGY AND ISOMERISM

2.1. Constitutional Isomerism. Apparently, enumerative problems involving simple unlabeled graphs (nondirected graphs without loops or multiple edges) can be always solved. As indicated above, Polya's theorem can solve any enumeration problem for such graphs. When multiple edges are present, restricted rotation for double bonds can give rise to geometrical (*cis-trans*) isomerism, and aromatic bond equalization can reduce the number of regioisomerism such as for *ortho*- or *meta*-disubstituted benzene derivatives; one should, however, mention the recently discovered cyclohexatrienic structures when special substitution patterns are present in some benzene derivatives;^{6,7} in such systems, as in antiaromatic annulenes,⁸ bond equalization does not occur.

Coding and nomenclature are essential for coping with the rapidly increasing flow of papers and of new compounds. Despite the computerized storage and retrieval of chemical information, the present IUPAC nomenclature is not the logically simplest one: when the name of an alkane is based on the longest linear chain, a complicated set of priority rules must be appended. Read's system based on the graph center⁹ is much simpler to apply for acyclic graphs. For cyclic graphs the situation is somewhat more complicated, but substantial progress has been made for defining generalized graph centers.^{10–12}

Polycyclic benzenoid hydrocarbons (PAHs) form an important class of compounds, deserving special attention. Their dualist graphs have been of considerable assistance,^{13–19} and many studies have been published on a systematic approach for PAHs by Randić,²⁰ Trinajstić,²¹ Gutman,²² Cyvin,^{22,23} Dias,²⁴ Herndon,²⁵ and others.

2.2. Stereoisomerism. For molecules with identical constitution, there are two types of stereoisomerism, namely diastereoisomerism and enantiomerism. The latter ("mirror-image" isomerism) manifests itself in differences of proper-

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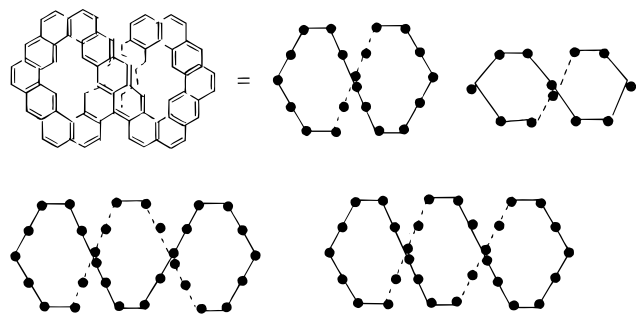


Figure 1. (A) Upper row: two chiral coronoid catafusenes and dualist graphs (with centers of hexagons as vertices). Lower row: two diastereomeric coronoid catafusenes (dualist graphs only); the left-hand one (B) is achiral, and the right-hand one (C) is chiral, therefore it will give rise to two enantiomers. Dotted lines of the dualist graph and of the coronoid are *behind* the full lines.

ties only when interactions with chiral forms of energy (e.g., polarized light) or matter (e.g., other chiral molecules) are involved; otherwise, enantiomers have identical properties—such as thermodynamic or thermochemical properties. Diastereoisomerism in turn may be classified as geometrical isomerism (when geometrical distances between non-bonded atoms differ, e.g., *cis/trans* diastereomerism) and “polychiral diastereomerism” (illustrated by aldoses with four or more asymmetric carbon atoms). The former type can be encoded easily in “topographic matrix” form, patterned after distance matrices in which topological matrices have been replaced by geometrical (Euclidean) distances.²⁶

Different classification schemes for constitutional isomers and stereoisomers have been reviewed.^{27,28}

Enumeration problems for stereoisomers can be solved by several mathematical techniques: Polya’s theorem (for instance, enumeration of chiral alkanes),²⁹ double cosets (e.g., for metallic complexes with coordination numbers 5 or 6),³⁰ or by special procedures (illustrated by Balasubramanian’s approaches to enumeration of NMR signal multiplicities).³¹

Restricted rotation around single bonds can also give rise to stereoisomerism. Atropisomerism in sterically congested polyaryls has been known for a long time. Dynamic NMR techniques have considerably increased the range of observable hindered rotation processes. Staggered rotamers of alkanes may be observed at low temperature, and the corresponding graph-theoretical enumeration problems have been examined³² but not yet fully solved. By dynamic NMR methods, diastereoisomeric configurations of annulenes and conformations of cycloalkanes have been experimentally observed, and the corresponding mathematical enumerations have been discussed.^{33–35}

2.3. Topological Stereoisomerism. In addition to the isomers discussed above, other types of isomerism are possible, depending on the molecular topology. Catenanes, rotaxanes, and other “molecules without chemical bonds” have been synthesized and reviewed.³⁶ Some of them have also been observed by electron microscopy in strands of nucleic acids.

Topological stereoisomers form a smaller subset of such systems. So far, the discussion has been mostly theoretical for normal *versus* Möbius-type ribbons of aromatic rings,³⁷ but Stoddart and co-workers have published interesting experimental approaches to this problem.³⁸ Figure 1 illustrates other possible topological stereoisomers, which so far are only theoretical predictions: each chiral system of

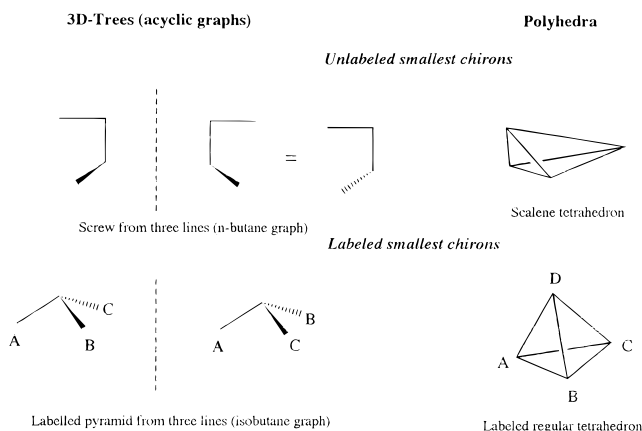


Figure 2. Three-dimensional unlabeled and labeled protochirons. The vertical dotted line is a mirror plane.

Figure 1 (parts A and C) should exist as a pair of enantiomers.³⁷

3. CHIRALITY IN TWO OR THREE DIMENSIONS

3.1. Definitions and Simplest Elements of Chirality (Protochirons). A chiral *n*-dimensional object is, by definition, nonsuperimposable on its mirror image by any rotation in the *n*-dimensional space.

Ever since the publication of the essay “Flatland”,³⁹ the general public has become aware of the interesting problems raised by fictional universes with any number of dimensions. In a 2D-universe, Flatlanders would see the letters F, G, J, L, N, P, Q, R, S, Z as chiral objects. For nondirected graphs, we can thus consider the letter L (with two unequal straight segments at any angle $\alpha < 180^\circ$) as the simplest unlabeled 2D-protachiron. When labeled nondirected graphs are considered, then the simplest protochiron would be a letter L with equal sides and different labels at the two ends. An equivalent statement on the simplest nondirected 2D-protachirons is in terms of polygons: for the unlabeled case, this is a scalene triangle; for the labeled case this is an equilateral triangle labeled with three different labels. Of course, by lifting these protochirons into the third dimension and returning them to Flatland, one may convert one 2D-enantiomer into its antipode.

If directed graphs (digraphs) are considered, then the directed letter L with equal sides, or a directed circular planar segment, would be the unlabeled protochiron. However, since for molecular graphs such digraphs are not relevant, we shall not pursue further the discussion on chiral digraphs.

The nondirected 3D-protachirons are considered to be for unlabeled graphs, the *gauche* rotamer of the *n*-butane hydrogen-depleted graph (or any equivalent path of length three with any angles different from 180°): this is the simplest proto-helix (3D-protachirons); and for labeled graphs, a pyramidal letter Y with three different labels at the three endpoints (Figure 2). In terms of polyhedra, the equivalent for the latter case is a regular tetrahedron whose vertices have four different labels (e.g., an asymmetric carbon atom); the equivalent of the former case is a scalene tetrahedron.

By analogy with the 2D-case, if one would take a 3D-chiral object in the fourth dimension, it would become superimposable on its mirror image after “rotating” it and returning it to the 3D-space. The same result would be



Figure 3. A regular tetrahedron formed from two protohelices of opposite chirality, denoted by open circles and black circles, respectively, as endpoints: perspective view (left-hand) and Schlegel diagram (right-hand).

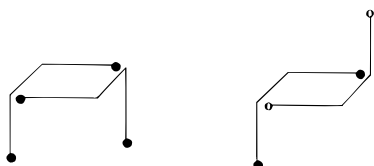


Figure 4. (A) Left-hand figure: a semicube formed by concatenation of two protohelices with the same chirality. (B) If the protohelices have opposite chirality, the right-hand figure results, which cannot give rise to a cube. Both figures have a plane of symmetry, hence they are achiral.

obtained in chemical practice by inverting an asymmetric tertiary amine or phosphine or an ammonia molecule labeled isotopically with one deuterium and one tritium atom (i.e., NHDT being inverted into NHTD).

3.2. Concatenation of 3D-Protohelices into Regular Polyhedra. By definition, *concatenation* will denote the association of two or more protohelices such that two vertices merge into one. One can consider several cases, e.g., an endpoint of a protohelix will become fused either with another endpoint (vertex of degree 1) or with a kink (vertex of degree 2) of another protohelix; alternatively, two vertices of degree two merge into one vertex of degree four.

One should note that the five regular (Platonic) polyhedra are achiral, yet they can be obtained by concatenation of protohelices. Among the 13 semiregular Archimedean polyhedra, two are chiral. Buckminsterfullerene is one of the achiral semiregular Archimedean polyhedra.

Two enantiomeric protohelices with angle of 60° may be concatenated yielding a tetrahedron (Figure 3). In this figure and subsequent ones, endpoints of protohelices with the same chirality will be represented by similar types of circles (black or white).

Two protohelices of the same chirality with right angles can be assembled into a semicube (half-cube) which is no longer chiral (Figure 4A). One should note that an antipodal pair of such protohelices does not form by concatenation a half-cube but forms instead a different aggregate (Figure 4B).

Since a cube may be formed from two half-cubes, the constituent four protohelices may either all have the same chirality, or they may be two pairs of antipodes (Figure 5A). It should also be noted that, as shown in Figure 5B, the turn of such a protohelix spans two cubes. Figure 5C indicates how a "boat-cyclohexane" (as a part of a cube) results by concatenation of two identical protohelices, and Figure 5D shows a "chair-cyclohexane" formed by concatenation of two antipodal protohelices.

A different kind of semicube, this time a chiral one, may be formed from a pair of antipodal helices, as shown in Figure 6A. Two such identical semicubes may be assembled into a cube which will therefore consist of two pairs of antipodal helices (Figure 6B). If we denote the two protohelix antipodes by H and H', then antipodal semicubes will be obtained when concatenations differ: either concat-

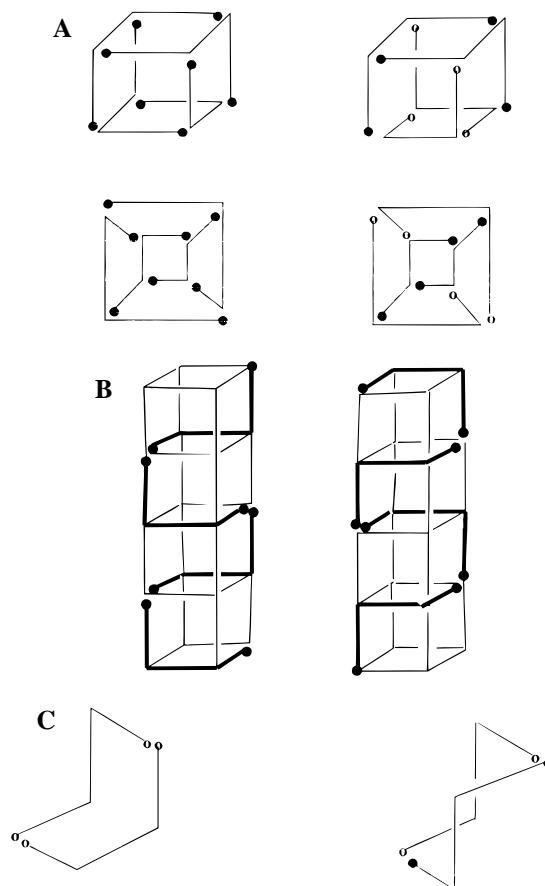


Figure 5. (A) Two cubes made of achiral semicubes: left-hand side with all protohelices with the same chirality (upper row with perspective view, lower row with Schlegel diagram); right-hand side with the semicubes from protohelices of opposite chirality. (B) Left-hand side: the pitch of the helix formed from two protohelices spans two cubes. Right-hand side: if each protochiron is inverted, the helix is also inverted. The two cyclohexane conformers: the boat conformer (C) consists of two homochiral protochirons on the left, whereas the chair conformer (D) consists of two enantiomeric protochirons.

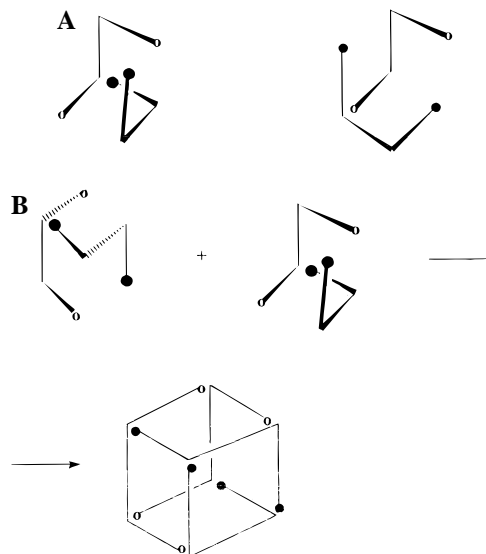


Figure 6. (A) Two enantiomeric chiral semicubes consisting each of two enantiomeric protohelices. (B) Two identical (homochiral) chiral semicubes, each formed from two enantiomeric protohelices, yield an achiral cube.

enation of an endpoint of H with a vertex of degree 2 of H', or vice-versa.

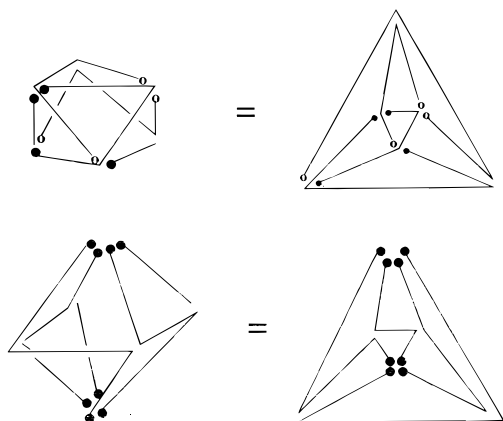


Figure 7. (A) Concatenation of regular octahedra from two pairs of enantiomeric protoheli-ces (upper row) or (B) from four homo-chiral protoheli-ces (lower row). Left-hand figures are perspective views, and right-hand figures are corresponding Schlegel diagrams.

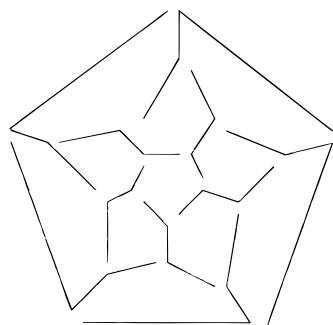


Figure 8. Concatenation leading to the regular pentagonal dodecahedron (Schlegel diagram) from ten homochiral protochirons.

For obtaining a regular octahedron by concatenation of protoheli-ces, one may start either from protoheli-ces with two angles of 60° (in which case four protoheli-ces with the same chirality will concatenate all their endpoints together, and separately endpoints of degree 2 together, Figure 7A) or from a protoheli-ces with 60° and 90° angles (in which case two pairs of antipodal heli-ces will concatenate as shown in Figure 7B, namely two endpoints with a vertex of degree 2).

A regular dodecahedron may be formed from ten protoheli-ces, all with the same chirality (Figure 8).

A different type of aggregating protoheli-ces is the *assembly*, which consists in merging two edges from two different protoheli-ces into one. This process is exemplified by Figure 9, in which one may see how the assembly of two homochiral unlabeled protochirons yields a chiral 3D-path of length five. The labeled counterpart (assembly of two labeled protochirons by merging of the edges whose endpoint has label C) is presented in Figure 10.

An interesting case of chiral polyhedra is represented by some fullerene isomers. Among the constitutional isomers of proper fullerenes, formed by 12 pentagons and any number (different from 1) of hexagons, many of them are chiral. Balasubramanian has enumerated such isomers.⁴⁰ Of considerable interest are fullerene isomers with isolated (non-abutting) pentagons; only one of the 1812 constitutional isomers of C_{60} , namely buckminsterfullerene, fulfills this condition. Also, only one isolated-pentagon isomer exists for C_{70} . However, for larger fullerenes than C_{74} , several isolated-pentagon isomers exist. In the case of C_{76} and C_{78} such isomers include chiral ones,⁴¹ and the chiral C_{76} was

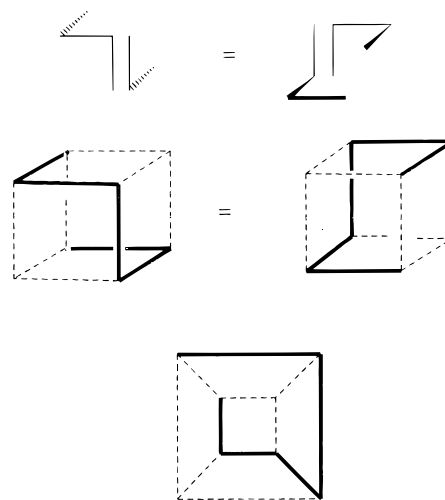


Figure 9. Assembly of two simplest homochiral unlabeled protochirons by merging two edges into one. The result is a chiral path of length five. The first two rows indicate how the assembly proceeds, and the last row is a Schlegel diagram of the cube underlying the chiral path.

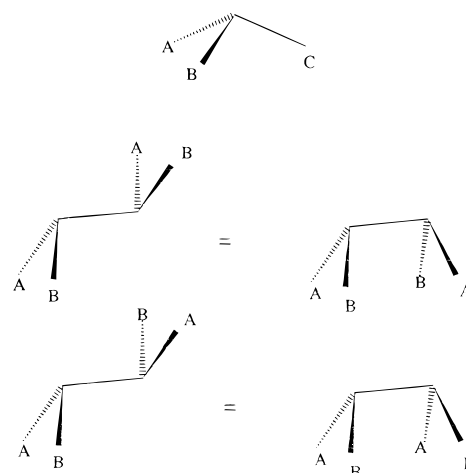


Figure 10. Assembly of two labeled protochirons (upper row) by merging one edge (with label C). Middle row: formation of a chiral labeled composite from two homochiral labeled protochirons. Lower row: formation of an achiral labeled composite from two enantiomeric labeled protochirons. Free rotation is assumed.

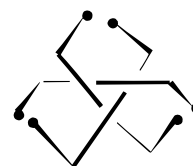


Figure 11. A trefoil knot formed from three protoheli-ces.

isolated in 1991 and resolved kinetically into an optically active form by asymmetric osmylation.⁴²

3.3. Knots. Far from being topological curiosities, knots⁴³ have been experimentally proved to exist both in natural (DNA) and in synthetic polymers. Mislow and co-workers⁴⁴ argued convincingly that a precise definition of knots must lead to some restrictions against the indiscriminate use of the word knot; "open knots" are tolerated, but the literature contains mistaken use of the term knots for structures which actually are "unknots".

The simplest knot ("trefoil knot") may be formed from the concatenation of three protoheli-ces (Figure 11); it is chiral.

4. BIBLIOGRAPHIC SURVEY OF THEORETICAL CONTRIBUTIONS TO HETEROATOM-DECORATED CARBON CAGES

4.1. A Special Case of Euler's Formula for Cage Compounds. Euler's relationship for polyhedra containing V vertices, F faces, and E edges is

$$V + F = E + 2 \quad (1)$$

When m_f faces are f -membered polygons, and when n_v vertices have degree v (the degree of a vertex is the number of vertices to which it is directly connected), the following relationships hold:

$$\sum_f m_f = F \quad (2)$$

$$\sum_v n_v = V \quad (3)$$

$$2E = \sum_v v n_v = \sum_f f m_f \quad (4)$$

$$2 \sum_v n_v (3 - v) + \sum_f m_f (6 - f) = 12 \quad (5)$$

In a polyhedron formed only from m_5 five-membered rings, m_i large i -membered rings ($i > 6$), and m_6 six-membered rings, and having only n_2 vertices of degree two and n_3 vertices of degree three, the above equation indicates that m_6 and n_3 (the numbers of hexagons and of vertices with degree 3, respectively, as in graphite sheets, whose coefficients are zero) can have any arbitrary values, and the equation reduces to⁴⁵

$$m_5 - \sum_i (i - 6) m_i + 2n_2 = 12 \quad (6)$$

If one applies eq 6 to buckytubes having their ends or end-caps decorated with divalent heteroatoms such as oxygen atoms, then one can devise various possibilities for buckytubes capped with coronand cavities.

4.2. Buckytubes Capped with Coronand Cavities. In a previous paper,⁴⁶ fullerocoronands were described. These were fullerenes that had "holes" bordered by oxygen heteroatoms so as to offer the possibility for coordinating alkali metal cations. The fate of the anions in such cases was not considered in detail.

Scuseria and co-workers⁴⁷ presented theoretical evidence for a "window" mechanism in excited fullerenes which could allow various kinds of atoms to be trapped endohedrally. Oxygen-bordered "windows" in ground-state systems such as the fullero-coronands would be attractive for a variety of reasons.

The above ideas may be extended to graphitic nanotubes (buckytubes, nanowires) paying specific attention to the anions in order to obtain electrically charged systems that may be oriented or bent when applying an external electric field.⁴⁵

4.3. Corona-Tubulenes with Hemispherical Caps and/or Coronand Cavities at Each End. The simplest case is that of buckytubes with two open ends bordered by oxygen heteroatoms.⁴⁵ Extreme cases are with C—C bonds parallel to the axis of the cylinder or orthogonal to the axis of the cylinder. The length and the diameter of the cylinder can

be varied, but eq 6 puts some restrictions on these two variable parameters.

We can apply eq 6 for the former type of "corona-tubulene" with $m_5 = 0$, $m_i = 2$ and $i = n_2$; for the latter type of "corona-tubulene" we must have $m_5 = n_2$, $i = 3n_2/2$, $m_i = 2$.

The size of the coronand cavity (and implicitly the diameter of the tubulene) influences the steric strain. For eq 6 to be satisfied we must have $m_5 = 6 + n_2$, $i = 3n_2$, $m_i = 1$.

4.4. Aza-Buckytubes. When at the ends of an open buckytube a carbon atom is connected only to two other carbon atoms, its replacement by a nitrogen heteroatom "cures" the dangling bond by replacing the singly occupied σ -orbital by an electron lone pair. Thus the nitrogen-bordered open ends of a buckytube may coordinate metal atoms or ions, similarly to what is assumed to happen in fulleropolycoronands or in corona-tubulenes. Again there are two extreme ways with some C—C bonds oriented either in parallel or orthogonal fashion to the cylinder axis. In the former case, after aza-substitution, the benzenoid rings at the ends of the buckytube are replaced by pyridinic rings, and the electronic structure leads to quinonoid formulas which are energetically unfavorable. In the latter case, many rings have three double bonds inside each ring as in Clar-structures, but the end-rings are pyridazinic, with two adjacent nitrogen heteroatoms. Such rings with *cis*-azo structures have higher energy than isomeric diazinic (pyrimidinic or pyrazinic) rings, but for aza-buckytubes which are long enough this effect will be counterbalanced by the aromatic stabilization of the whole structure.⁴⁸ The possibility of avoiding dangling bonds by having aza-heterocyclic rings at the ends of buckytubes is an interesting alternative to capping these buckytubes.

5. CONCLUSIONS

The application of topological methods can inspire approaches for dealing with the more complicated problems of including information on three-dimensional molecular structure. The most difficult problem is that of enantiomerism. So far, few authors have attacked this problem: Schultz et al.⁴⁹ proposed an interesting idea. It is hoped that prochirons (labeled or unlabeled) may help in devising new ways of dealing with chirality; the fact that homochiral objects may be assembled into either a chiral or an achiral object, as shown here and as mentioned earlier by Mislow,⁵⁰ indicates that the dissection of chiral molecules into 3D-subgraphs must be made with considerable discrimination.

Other ideas on the title theme can be found in the first chapter of a book edited recently by the present author.⁵¹

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