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REPLACING TRADITIONAL (CHIRALITY-BASED) STEREOCHEMICAL NOMENCLATURE WITH A SYSTEM BASED SOLELY ON STEREOGENICITY

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ABSTRACT: In order to understand the underlying mathematical foundation of stereoisomers and to assign unique canonical names to each member of that class, an expansion beyond the limitations imposed by history and tradition is formulated. Not only must such a nomenclature be viable in all of the historical "fiefdoms" of 'organic', 'inorganic', 'polymer', 'organometallic', etc. chemistry, it must also lead to an understanding of the relationship between "stereogenecity" vs. "chirotopicity". The raison d'etre for creating such a new system of nomenclature was to promulgate a global, in contradistinction to the historically-evolved, mating of local nomenclature systems that were based on often inconsistent perspectives. This report, which is an extension of a previously developed proposed new nomenclature,[1] was created in order that there be a common nomenclature that is universally applicable to all of chemistry. In this report the precepts of that monograph are extended into that subset of chemistry commonly referred to as stereochemistry.

1. NOMENCLATING CIS-TRANS ISOMERS

A complication in assigning canonical names to chemical moieties arises whenever more than one geometrical arrangement of atoms and bonds can be described by a particular graph theoretical model. We begin by defining "stereoisomers"[2] as "Isomers that have equal graph theoretical distances (GTDs) between corresponding modules". Historically, the first two types of stereoisomers occurred in the "organic" domain wherein the focus was either on the bond joining a pair of carbon atoms (originally designated as “geometrical isomerism” but now preferentially referred to as “cis-trans isomers”) or on a single carbon atom having four different ligands (designated as “optical isomerism”). We further define the term “stereocenter” as a module for which different positioning of the ligands produces configurations that have different geometrical descriptors.

In the original concept referred to as “geometrical isomers”, one envisioned free rotation about single bonds, but hindered rotation about higher order bonds. This perception was incorporated into determining where to draw the line separating the ideas embodied in the terms “conformation” vs. “configuration”[1]. The result of such a perspective is that the same canonical name should be ascribed to all conformations of a configuration. Adopting this historical perspective, one encounters a major difference in the metric distances (MDs)[3] between selected corresponding atoms in the various stable configurations vs. their graph theoretical distance (GTDs)[4]. Additionally, the energy expended in rotation about a single bond between two carbon atoms is 3-6 kilocalories per mole vs. about 63 kcal/mol to break the pi bond component of a double bond, and thereby facilitate rotation between two doubly-bonded carbon atoms[5].

As part of the overall scheme to distinguish between isomers in the nomenclature, Cahn, Ingold and Prelog created what is now known as the CIP rules[6]. For cis-trans isomers, one augments as a prefix either the letter E (from the German word “entgegen” meaning apart) or the letter Z (German “zusammen” = together) to the isomer being named, depending on the inter-relation of the four ligands surrounding the two atoms connected by the double bond. This is illustrated in Figures 1 and 2 wherein the metric distance between ligands attached to the atoms adjacent to the stereocenter is the parameter determining E vs. Z. The priority used in the selection process is by atomic number, rather than like atoms. Meanwhile, noting the coordination of four about the double bond module and the fact that two of the four coordinators are part of the principal chain, the remaining two coordinators may be viewed as ligands to this chain.

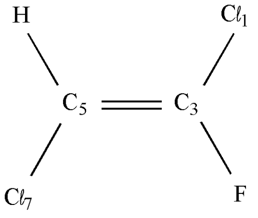

Figure 1: An E “geometrical” isomer

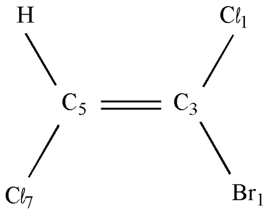

Figure 2: A Z “geometrical” isomer

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[1] This traditional perspective was predicated on all of chemistry being done at room temperature and pressure. The extension to a more modern approach, which also considers chemical moieties at very low temperatures or very high pressures, blurs the distinction between configuration and conformation given as definition (10) in Ref. 1.

In a slight modification to the IUPAC protocol, wherein the stereo designator precedes the rest of the name, this descriptor ***could*** be introduced into the systemic nomenclature as superscripts to the double bond; namely:

$C\ell 1C2^{E}C1C\ell$: $^{(3)}(1F);^{(5)}(1H)$ (Figure 1) (1)

and

$Br1C2^{Z}C1C\ell$: $^{(3)}(1C\ell);^{(5)}(1H)$ (Figure 2) (2)

Before progressing further, attention is directed to what are called “identity transformations”; namely, those operations on an object (in particular on the model of a chemical moiety) for which the resulting image following the transformation is congruent to the starting model. Three such congruence-preserving transformations, which impact all of physics (including chemistry), are grouped together by the term “metric motions”; namely, translation, rotation and reflection [7]. Of these three, both translation and rotation are differential operations, represented respectively using Cartesian and polar coordinate systems. These occur in the embedding space of the object being “transformed”. Reflection, on the other hand, is performed through an embedding space that is smaller than the object being reflected and is a discontinuous operation. This is notwithstanding that both the object and its image may both be continuous.

Note that reflection of a planar model through a point yields an image that may be translated so as to be congruent with the object **without leaving the plane** (Figure 3).

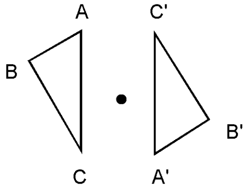

Figure 3: Reflection through a point

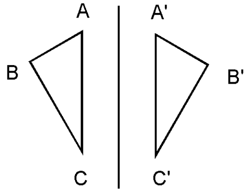

Figure 4: Reflection through a line

On the other hand, reflection of that same planar model through a line creates an image that is superimposable on the object **only** if one can rotate the object outside the embedding space (i.e., in the third dimension) This is illustrated in Figure 4. Such figures are designated as “symmetric”, rather than congruent. In a similar manner, in a three dimensional embedding space, reflection of a three dimensional object through a line will form a congruent image; however, through either a point or a plane, the image will be symmetric. This will play an important part in designing a nomenclature system for chemistry inasmuch as one can assume that the physical space of chemical moieties is three dimensional. In other words, any mathematical extension into a higher dimensional space, either Euclidean or relativistic, is NOT a consideration and we know of no use for imaginary dimensions in chemistry. This is in contradistinction to their usage in modern physics.

Returning to the two geometrical isomers depicted in Figures 1 and 2, we formulate an alternate standardized description that uses **ONLY** those two metric motions which are continuous (translation and rotation) — **NOT REFLECTION** Because of the above described fundamental difference in the geometry (and thus the physics) associated with translation and rotation vs. reflection, the nomenclature being promulgated in this report shall focus on the stereogenic, while downplaying the chirotopic, aspects that have been the cornerstone of traditional nomenclature practices for well over a century.

In this depiction, the principal chain of the model of the molecule is oriented as though it had been projected onto a straight line that runs from left to right. Conceptually, this corresponds to "squaring off" the approximately 120° trigonal angles so that each is either 90° or 180°. By this motion, the off-principal chain ligands are now either above or below this chain and the bonds connecting them to the principal chain are nomenclated with a superscripted **a** (for "above") or **b** (for "below"). Moreover, because all six atoms lie in a single plane, rotation of the model 180° in the plane of the model yields an image congruent to the original figure. Therefore, choose as the standardized orientation that one in which the first off-principal chain ligand is in the "above" orientation, The second off-principal chain ligand will now be either **a**bove the reference line, namely what traditionally has been called the cis configuration or **b**elow this line in the trans configuration. This same protocol shall be used when the restraining factor is a ring, rather than a double bond – which may be viewed as a degenerate ring. Figures 5 and 6 respectively illustrate the standardized orientations of the molecules represented as Figures 1 and 2. In other words, the IUPAC descriptor E or Z has been replaced by an **a** or **b** descriptor at the exiting ligand of the double bond. The entering ligand is, by this protocol, above the principal line and thus a descriptor locating this ligand need not be included in the canonical name. By this protocol the names (1) and (2) become:

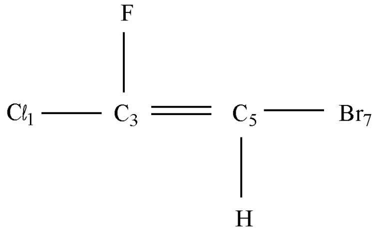

Figure 5: Standardized orientation of Figure 1

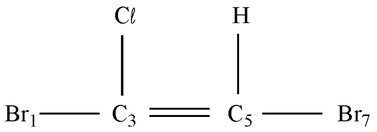

Figure 6. Standardized orientation of Figure 2

Cℓ1C2C1Cℓ: $^{(3)}$(1F);$^{(5b)}$(1H) (Figure 5) (3)

and

Br1C2C1Cℓ: $^{(3)}$(1Cℓ);$^{(5a)}$(1H) (Figure 6) (4)

This is now readily extended to theoretically possible compounds having even higher order (e.g., triple), as well as multiple double (or higher order) bonds. The molecule shown in Figure 7, if it were to be made, could follow the E and Z of IUPAC protocol and have the systemic name:

$$\mathrm{H_1 1\underline{\underline{\underline{C}}}_3 1P_5 3^{Z}P_7 1C_9 2^{E}\underline{C}_{11} 1\underline{\underline{\underline{C}}}_{13} 1H_{15}\!:\, {}^{(5)}(1O1H);\ {}^{(7)}(1\underline{N}1H);\ {}^{(9)}(1\underline{\underline{\underline{C}}}1H);\ {}^{(11)}(1H)} \tag{5}$$

or alternately, using the proposed standardized orientation of Reference #1 (Figure 8), have as the canonical name in that system:

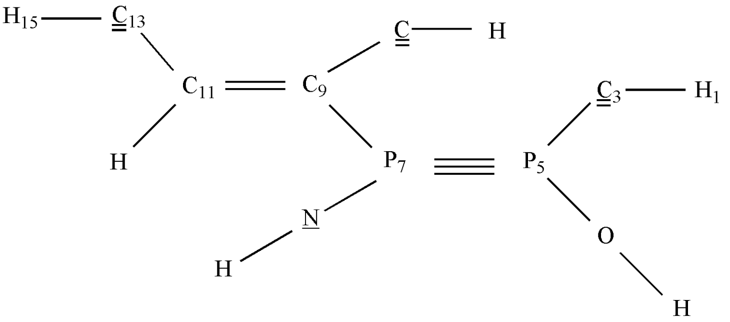

Figure 7: A theoretical compound containing a triple bond and a double bond

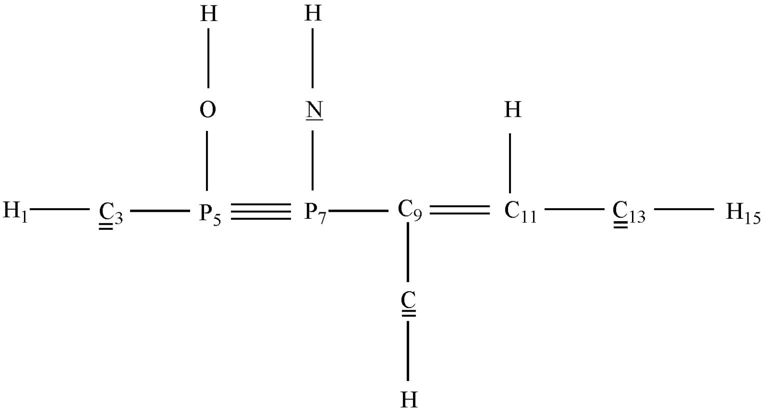

Figure 8: Standardized version of theoretical compound depicted in Figure 7

$$\mathrm{H_1 1\underline{\underline{\underline{C}}}_3 1P_5 3P_7 1C_9 2\underline{C}_{11} 1\underline{\underline{\underline{C}}}_{13} 1H_{15}\!:\, {}^{(5)}(1O1H);\ {}^{(7a)}(1\underline{N}1H);\ {}^{(9b)}(1\underline{\underline{\underline{C}}}1H);\ {}^{(11a)}(1H)} \tag{6}$$

Although every one of the ligands, **including hydrogen**, is spelled out in both sets of systemic canonical names, this second form is more readily extendable to other four coordinate stereocenters. In particular, attention is next directed to that second form of cis-trans isomerism wherein the restraint to motion is the presence of a ring. Observe that a cycloalkyl ring, although not strictly coplanar because of the Coulomb forces between ligands on adjacent carbon atoms, still has a marked difference between substituent ligands when they are on the same side of the projection of the cycloalkane onto a theoretical plane vs. when they are on opposite sides of that plane. This creates different metric distances between corresponding atoms attached to a cycloalkyl ring, in exactly the same manner as had been noted above for a double bond. At this point it is important to remember that by the nomenclature algorithm developed in Reference # 1, not only does the length of the longest chain take precedence over the higher atomic number of the ligand, also a small ring takes precedence over a large chain. For example, let the double bond in Figure 9 [which may be envisioned as a degenerate (two member) ring] be replaced by a three atom cycle (Figure 10). Observe that this third carbon atom, which

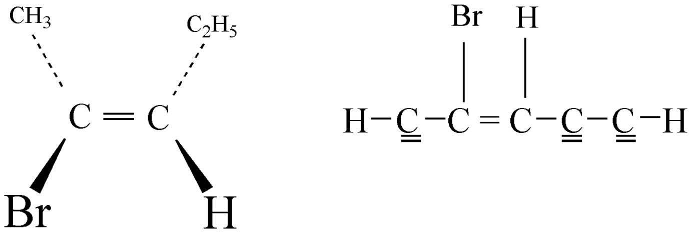

Figure 9: The different priorities used in nomenclating the molecule IUPAC names as 2-Bromo-2-pentene

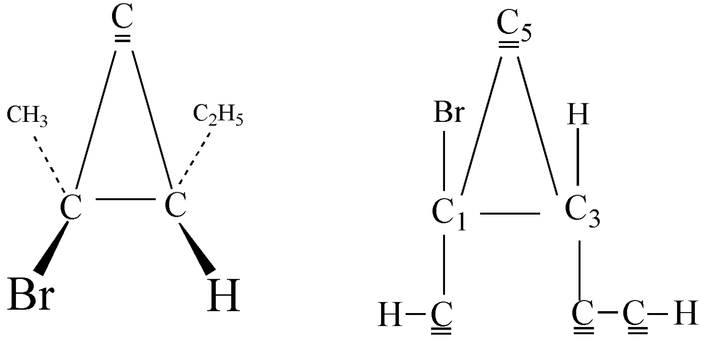

Figure 10: The different priorities used in nomenclating the molecule IUPAC names as (E)-1-Bromo-1-methyl-2-ethylcyclopropane

is being introduced between the two atoms previously double bonded together, thereby forming the (three member) ring, might be depicted as having been inserted **either** "above" the double bond, as indicated in Figure 10, **or** "below" it.

Consistency in the historical pictures of the stereocenter being either a line or a plane requires insertion of the methylene group so as to maintain the postulated counterclockwise arrangement of the ligands in decreasing priority. For this example this is above the double bond. In this way, the orientation about the reference line (of the double bond) is retained with the methyl and ethyl ligands remaining behind the newly formed reference (cyclopropyl) plane. On the other hand, had the inserted module been a difluoromethylene group (instead of the dihydromethylene group), counterclockwise orientation would have produced an inversion in the CIP system, but would be unambiguously represented in the proposed nomenclature.

As illustrated in Figure 9, the two above-described potential systemic names for the molecule which IUPAC names as (E)-2-Bromo-2-pentene:

$$\mathrm{H1\underline{\underline{C}}1C2^{E}C1(\underline{\underline{C}}1)_{2}H{:}^{(5)}(1Br);^{(7)}(1H)} \tag{7}$$

and

$$\mathrm{H1\underline{\underline{C}}1C2C1(\underline{\underline{C}}1)_{2}H{:}^{(5)}(1Br);^{(7a)}(1H)} \tag{8}$$

are based on different priorities; consequently, it is wrong to expect that Z will always be replaced by an **a** in the second superscript, while E would be represented by **b**.

Applying this procedure next to the molecule illustrated in Figure 10 that IUPAC names as: (E)-1-Bromo-1-methyl-2-ethylcyclopropane, the highest priority of the six ligands to the ring is the bromine atom. This atom, algorithmically, is oriented above the plane of the cyclopropane and is thus represented using a larger font than that used for the carbon atoms of the ring. Because priority among ligands in secondary and higher chains is determined starting from the principal chain (or ring), it is often the case that shorter chains with higher priority bonds or atoms are selected before longer chains. In this example the ligand containing the single Br atom has the highest priority, rather than either of the longer chain ligands of ethyl or methyl.

In the standardized drawing, the ring is now drawn in a counterclockwise orientation in the XY plane with all ligands that are on the same side of the ring as the bromine atom having their superscript locant number supplemented with an **a**, as well as their being pictured using larger font. Similarly those on the other side of the ring are in smaller font with their superscript supplemented by a **b**. Although it is redundant, the **a** descriptor is usually included with the superscript for the reference atom (Br) as well as the descriptors for the other ligands of the ring. This protocol assigns 3a as the locant number of the hydrogen atom on locant #3 carbon, and 3b as the locant number for the ethyl group. Consequently, the canonical systemic name is[2]:

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[2] An alternate name (Figure 11), (NOT the canonical name) akin to the linear names given respectively for cyclohexane and benzene as (23) and (24) in Chapter 6 of Reference #1 would be:

$$(C1)_3{:}^{(1a)}(1Br);^{(1b)}(1\underline{\underline{C}}1H);^{(3a)}(1H);^{(3b)}(1\underline{\underline{C}}1\underline{\underline{C}}1H);^{(5a,5b)}(1H) \qquad (9)$$

Moreover, if one or both of the hydrogen atoms at locant 5 had been replaced by a ligand of lower priority than the bromine. they would be unambiguously placed either on the same side as the Br (with a superscript 5a) or on the opposite side (with a superscript 5b). Similarly, if the replacing atom was iodine, this would now be the reference for a vs. b for all of the other ligands attached to this ring compound.

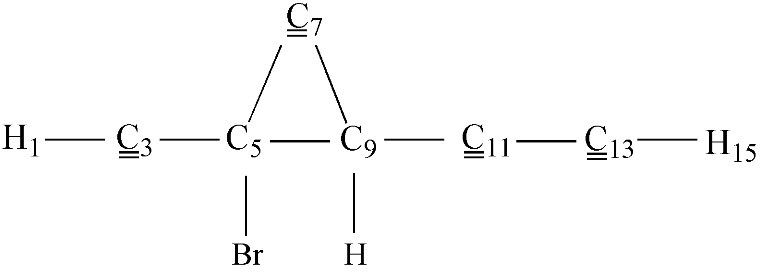

Figure 11: Locant numbering for the alternate depiction of the molecule in Figure 10

$$H1\underline{\underline{C}}1C1\underline{\underline{C}}1C1(\underline{\underline{C}}1)_2H{:}^{(5\text{-}9)}(1);^{(5b)}(1Br);^{(9b)}(1H) \qquad (10)$$

Note that for nomenclature purposes a cycle has priority over ligands and is thus above the principal chain (even though this makes the locant numbering of the cycle clockwise). On the other hand, had the Br ligand been a F ligand, there would be appreciable hydrogen bonding between the vicinal F and H atoms. This would result in the appropriate geometry being a five-membered bicyclic hydrogen-bonded ring compound. In this compound the stereogenicity has been suppressed by the formation of the bicyclic ring system; i.e., the locant numbering and canonical name are as shown in Fig. 12 and name (11):

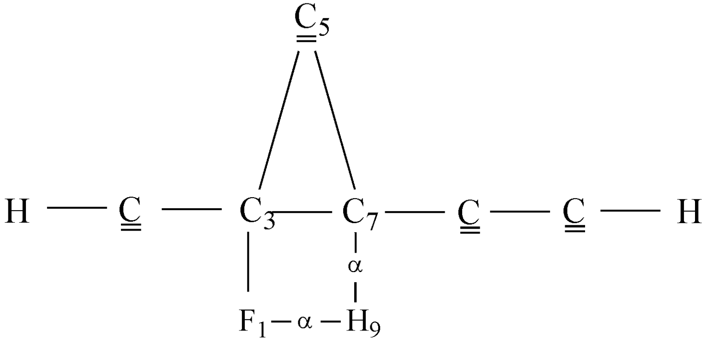

Figure 12: Locant numbering for the bicyclic molecule formed from Figure 11

$$F1C1\underline{\underline{C}}1C\alpha H\alpha{:}^{(3\text{-}7)}(1);^{(3)}(1\underline{\underline{C}}1H);^{(7)}(1\underline{\underline{C}}1\underline{\underline{C}}1H) \qquad (11)$$

2. NOMENCLATING MOLECULES WITH CHIRAL CENTERS

Continuing the development of the above idea, we next focus on the various sugars. For example, to assign the canonical systemic name to α-D-(+)-Glucopyranose, one notes that the Haworth formula[8] is most convenient from a nomenclature perspective in that it spells out precisely which hydroxyl groups are above the plane and which are below it (Figure 13).[3] The proposed canonical name for this molecule is thus:

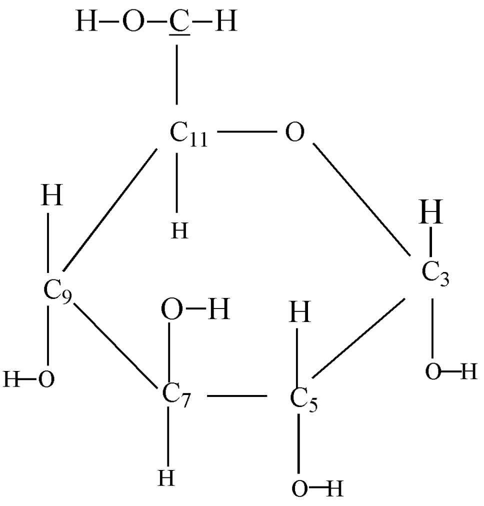

Figure 13: The Haworth formula for one of the hemiacetal forms of D-(+)-glucose

$$O1(C1)_5{:}^{(3a,5a,7b,9a,11b)}(1H);^{(3b,5b,7a,9b)}(1O1H);\,^{(11a)}(1\underline{\underline{C}}1O1H) \qquad (12)$$

Here one notes that just as each of the five carbon atoms of the glucose ring has four different ligands attached to it, every time such a local picture (of a single atom as a stereocenter with four or more ligands) is created, there is the opportunity for that second type of stereoisomerism traditionally referred to as "optical isomerism" The historical roots of the term "optical" isomerism, with its reliance on in which direction a beam of polarized light is rotated, like the subordination of the concept of "chirotopicity" to "stereogenicity", may be disregarded in the systemic nomenclature being developed here. Instead, the inherent geometry/topology is center stage.[4]. For example, consider the tri-

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[3] To many chemists, the Haworth formula is of academic interest ONLY. They view this representation as not as desirable as one that emphasizes the non-planarity of the hemiacetal ring. Meanwhile, one notes that the Haworth formula selects the terminal CH_2OH group as the reference ligand, which is positioned above the assumed planar hexagon. This is in contrast to our assigning the descriptor **a** to the first ligand of the stereocenter. It is this first ligand that is positioned above the presumed planar hexagon.

[4] The historical roots of the term "optical" isomerism, with its reliance on in which direction a beam of polarized light is rotated, like the subordination of the concept of "chirotopicity" to "stereogenicity", may be disregarded in the systemic nomenclature being developed here. Instead, the inherent geometry/topology is center stage.

substituted methane with IUPAC name Bromofluoroiodomethane. Because of inherent properties of three-dimensional Euclidean space, there are now two possible orientations which, more than coincidentally, are mirror images of each other. In other words, that topological relationship commonly described as "isomorphism with respect to reflection in a mirror" may also be characterized using only stereogenic properties. To do so, one selects an appropriate coordinate system in which the molecular model is described. In other words, the "chiral properties" [9], which had been the basis for traditional nomenclature, can be subordinated to, and thus be subsumed by, the stereogenic description.

Unlike the CIP system, for purposes of nomenclature, chirality may be viewed as a derived, rather than a fundamental, property. Chirality, which is a by-product of the third of the above described metric motions (reflection), occurs when the appropriate orientations of two isomers are in evidence. This is comparable to asserting that had one been able to give a pragmatic depiction in a four dimensional Euclidean space, your left hand would be superimposable on your right hand, which is the definition that one gives to the concept referred to as "congruent". Note that the very term "congruent" is a primitive concept (see the footnote following definition #6 in Chapter 1 of Reference #1) with the heuristic interpretation of superimposable in the given embedding space. Inasmuch as one does not have a heuristic interpretation of a four-dimensional Euclidean space, a different heuristic, called "symmetry" had to be formulated.

Returning focus to the CIP system, the orientation of a molecule "having a chiral center" is designated as either R or S by positioning the molecule with the smallest ligand (H in this case) behind the central (carbon) atom and the three larger ligands forming a plane in front of the central atom. These three front ligands may now be viewed as lying on a circle. If the ligands decrease in size in the clockwise direction, the molecule is denoted as R (from the Latin word "rectus" for right). Similarly, if the decrease is counterclockwise, this is denotes as S (from the Latin "sinister" for left). Figure 14 illustrates one of what is called "optical isomers" of Bromo-fluoro-iodomethane. By the CIP Rules, rotate this molecule around the line I-C-Br so that the smaller of the two remaining ligands (H) is directly behind the C and focus on the plane formed by the larger one (F) with I and Br. These three atoms (first I, then Br, then F) are in a

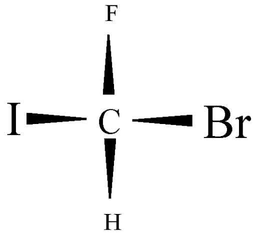

Figure 14: Example of a 4-coordinated atom

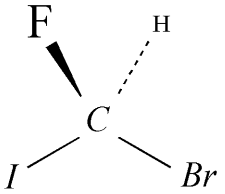

Figure 15: Rotation to place molecule in standard orientation

counterclockwise orientation. Consequently, the molecule is designated as (S)-Bromofluoro-iodomethane in the CIP system. Now even without a ring to determine "planar" sense with its specification of "above" vs. "below", one can envision such a "reference plane" for any tetrahedrally-oriented four-coordinated atom by selecting as the three points which determine that plane (indicated in Figure 15 in bold face italics) the four-coordinated atom along with its "entry" and "exit" ligands on the principal line. This produces as the canonical systemic name:

$$\mathrm{I1C1Br:}^{(3a)}\mathrm{(1F);}^{(3b)}\mathrm{(1H)} \qquad (13)$$

Although such an example seems to duplicate the CIP system, whenever the central atom is part of a longer chain, there is a different priority, exactly as above for "geometrical isomers". This is illustrated in Figure 16 for the molecule which IUPAC names as (2R,3S)-2,3-Dibromo-2-iodobutane. The systemic name for this compound is found by first noting that the longest chain has six atoms. The locant numbers on this principal line are next assigned and stereocenters at locant numbers 5 and 7 are recognized. The local geometry at locant #5 has the carbon atom at locant # 3 as the entry atom and the carbon at locant #7 as the exit. Since I has priority over Br, the molecule is oriented so that I is above the principal plane and is indicated in the name with superscript 5a. The bromine atom attached to C_5 is thus denoted with superscript 5b. Since there exists another stereocenter on this principal path, one views this path as though it had been part of a coplanar cycle and allocates all other a and b descriptors accordingly; i.e., at C_7 the Br ligand is above, while the H ligand is below this theoretical plane. Consequently, the canonical name for Figure 16 is[5]:

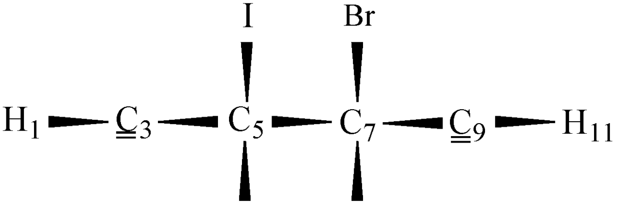

Figure 16: An optically active compound with 2 stereocenters

$$\mathrm{H1}\underline{\underline{\mathrm{C}}}\mathrm{1C1C1}\underline{\underline{\mathrm{C}}}\mathrm{1H:}^{(5a)}\mathrm{(1I);}^{(5b,7a)}\mathrm{(1Br);}^{(7b)}\mathrm{(1H)} \qquad (14)$$

Some advantages of this assignment scheme include:

(1) For each complete stereocenter (multiple bond, ring or "block"[6]), the focus is on the global, rather than on a local, orientation; however, for isolated stereocenters,

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[5] Note superscript designators for multiple occurrences of a common ligand can be grouped together. These will be listed with the first occurrence of that ligand. The order of these descriptors is lexicographic according to the first descriptor.

[6] A "block" is a "maximally non-separable subgraph of a given graph"

assignment of a vs. b is independent of the previous stereocenters. This is compatible with the assumption of free rotation about single bonds in a chain[10]. Such rotation is repressed in a ring.

(2) The orientation about each stereocenter is completely delineated in the successive individual bonds, rather than there being as a combined prefix to the whole name. This eliminates possible ambiguity as well as simplifying the nomenclature when there is no stereocenter. In that case, the bond connecting the ligand to the principal chain is designated by a single number (without an alphabetic descriptor).

(3) All of the ligands are located in the canonical name; i.e., the smallest ligand is spelled out, rather than just being implied.

(4) The logical basis for extension to other coordinations is laid. This will be illustrated below.

At this point, we focus on a "optical" isomer of tetrodotoxin (Figure 17).

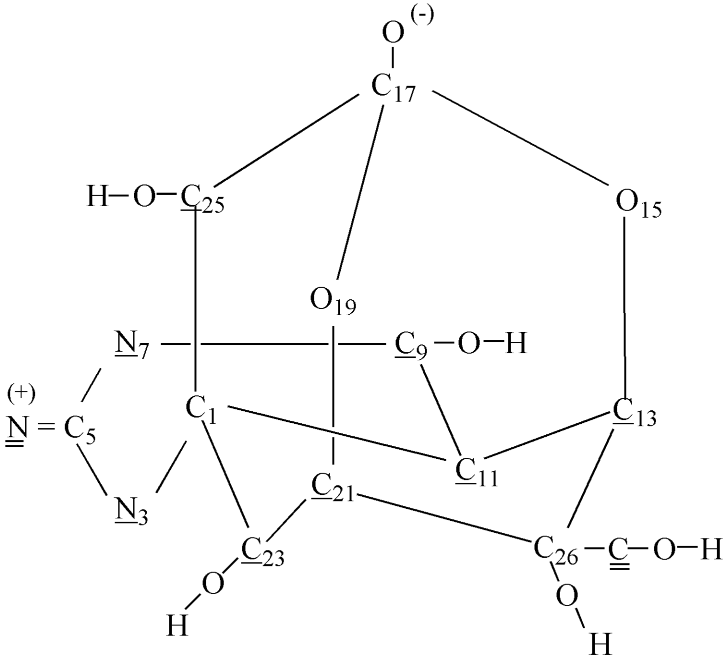

Figure 17: An optical isomer of tetrodotoxin

Observed that ten of the eleven carbon atoms have four ligands (only C_5 has only 3) and that one of these ten (the carbon atom attached to C_{26}) has a pair of like ligands (the two hydrogen atoms of the methoxy group); consequently, there are nine stereocenters that must be assigned either an R or S in IUPAC nomenclature or an a or b in the proposed nomenclature. This is done, in both instances, by narrowing the focus to the central atom and its neighbors extended to the first atom or bond of difference along each ligand. For IUPAC nomenclature one regards the smallest of the four ligands as lying behind the plane of the other three and assigns an R or S depending on whether these three are in a clockwise (R) or counterclockwise (S) orientation. This is done irrespective where in the molecule such a stereocenter is located. In the proposed system, on the other hand, the highest order (usually the principal) ring or chain determines the "entering" and "exiting" ligands to each stereocenter which are projected onto the x-axis of a three dimensional Cartesian coordinate system with the stereocenter located at the origin, the entering ligand on the negative x-axis and the exiting ligand on the positive x-axis. For example, with C_1 at the origin, the entering ligand is C_{23} and the exiting ligand is N_3. Now rotating the molecule to fit this orientation the bond connecting C_{25} to C_1 is above, while the bond connecting C_{11} is below.[7] Similarly, each of the other stereo-centers is designated by an **a** or a **b**. This creates as the full canonical name:

$$(\mathrm{C1\underline{N}1})_2(\mathrm{C1})_3(\mathrm{O1C1})_2\mathrm{C1}:^{(1\text{-}17)}(1^{a}\mathrm{C}^{(=25)}1);^{(13\text{-}21)}(1^{b}\mathrm{C}^{(=26)}1);^{(1\text{-}11)}(1^{b});\ ^{(3,7,9a,11b,13a,21b,\ 23b,2\overline{5a}}(1\mathrm{H});^{(5)}(2\underline{\underline{\mathrm{N}}}^{(+)});^{(9b,23a,25b,26b)}(1\mathrm{O1H});^{(17a)}(1\mathrm{O}^{(-)});^{(26a}(1\underline{\underline{\mathrm{C}}}1\mathrm{O1H}) \qquad (15)$$

Meanwhile observe that when the central atom is surrounded by less than four different ligands, every positioning that this molecule can assume by the metric motions of translation and/or rotation is superimposable on the original molecule. However, with the introduction of a fourth (or more) ligand(s) (in the assumed three dimensional space of molecules), a pair of molecules can be formed that are not superimposable in this (three dimensional) "embedding space". These are mirror image of each other; i.e., they are the result of the third of the metric motions, reflection. Because these two molecules have not only equal GTDs between corresponding atoms, but also equal MDs, graph theory alone is insufficient to distinguish between such isomers. Instead, with this picture of four ligands attached to a stereocenter, one may standardize the orientation by using the *a* vs. *b* descriptors developed above. Moreover in the systemic nomenclature being developed, standard positions for all of the other relevant static, stable geometric structures will be postulated, along with an examination of selected dynamic geometric orientations that are useful in describing molecular configurations when such a static geometrical environment is not viable.

3. OTHER COORDINATION = 4 STEREOISOMER SCENARIOS

Before formulating the nomenclature for higher coordination systems, an examination of other scenarios (in a three dimensional embedding space) in which a coordination of 4 is encountered is undertaken. In particular, one notes that, because three (non-co-linear) points uniquely determine a plane, when the molecule is positioned in standardized orientation, the focus of attention is that plane formed using the stereocenter and the two "entering" ligands of the leftmost double bond. By such a choice of reference plane, the set of cumulenes may be partitioned into "even" (2n) vs. "odd" (2n+1) subsets, where n is the number of double bonds in the cumulene.[8] Moreover, the

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[7] This corresponds to IUPAC's designation of R as the stereo descriptor at this location.

[8] An alternate perspective, rather than whether the cumulene has an odd or an even number of double bonds as its stereocenter, is the nature of the central "element" of the stereocenter ─ where here the term

smallest member of each subset, designated by n = 0, is respectively, a single coordination equal four atom in “optical isomerism” and a single double bond in “geometrical isomerism”.

Continuing to the larger cumulenes, as well as the associated multi-spiro combinations, one notes that, in this standardized orientation, even cumulenes (including n = 0) have the third and fourth ligands above and below the plane formed by the first two ligands and the stereocenter (be it a single point or a line coplanar with the two “initial” points), while odd cumulenes (including n = 1) are coplanar and have stereogenic properties associated with being either above or below a line through the defining atoms of the stereocenter. Using the symbolism of “polymers” (more accurately of oligomers), this is illustrated as Figures 18 and 19. Remember that α, β, γ and δ are standardized locations in space, that might be filled by any size ligand. This is true despite that when generalizing the assignment process, it is common to assign designators in order of decreasing priority, say, α = I, β= Br, γ = F and δ = H:

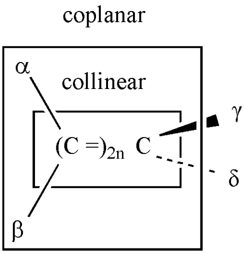

Figure 18: A general even cumulene

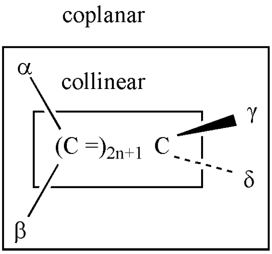

Figure 19: A general odd cumulene

I1C1Br: $^{(3a)}$(1F);$^{(3b)}$(1H) (n = 0) repeat of (13)

I1C2C1Br:$^{(3a)}$(1F);$^{(5a)}$(1H) (n = 0) (16)

I1(C2)$_2$C1F:$^{(3a)}$(1Br);$^{(7a)}$(1H) (n = 1) (17)

I1(C2)$_3$F:$^{(3a)}$(1Br);$^{(9a)}$(1H) (n = 1) (18)

I1(C2)$_4$C1F:$^{(3a)}$(1Br);$^{(11a)}$(1H) (n = 2) (19)

I1(C2)$_5$F:$^{(3a)}$(1Br);$^{(13a)}$(1H) (n = 2) (20)

etc.

“element” is from set theory in mathematics and denotes one of the constituent parts into which the object under consideration has been subdivided. Note that even cumulenes have an atom as the graph theoretical center, whereas odd cumulenes have a double bond as the center.

Note that mathematically, inasmuch as α refers to the entering ligand (which is in the upper left position in the standardized orientation), any of the three other ligands to this stereocenter may be located at position β. Now, whenever n > 0, one of the two remaining ligands may be designated as γ; i.e., in the three dimensional embedding space of this cumulene, one can form 6 different structural isomers, provided all of the ligands are different. Moreover, once β (which is exactly GTD =2 from α) has been chosen, the number of stereoisomers that must be distinguished in the nomenclature for each coordination = 4 atom in the principal chain has been reduced to two. Note that both α and β are at GTD greater than two from the other two ligands (γ and δ) for this longer stereocenter. This is in contrast to the scenario when n = 0 which is the traditional "optical" isomerism for the even cumulenes and "geometrical" isomerism for odd cumulenes, as was indicated in the nomenclature formulas (13) and (16) above.

An important extension of this type isomerism occurs when one of the double bonds of a cumulenic central atom is replaced by a ring. This ring is given priority over the cumulenic "chain" in formulating the canonical nomenclature. This is illustrated in Figure 20 as follows:

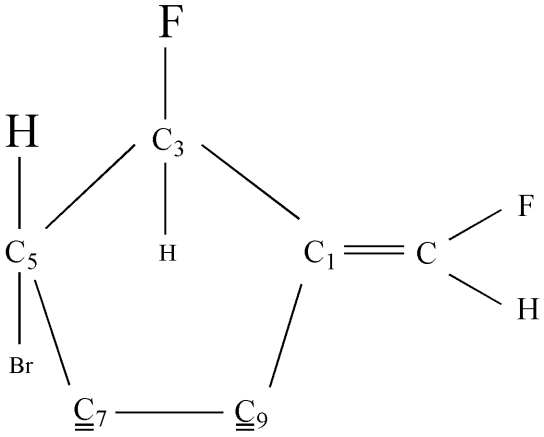

Figure 20: Example of a ring substituted even cumulene

(1) the carbon atom of the ring containing the double bond becomes locant #1;

(2) the direction of progression to locant #2 is the standard established in Reference 1; namely, since all the bonds of this ring are single bonds and all of the atoms are alike, the choice is made by focusing on the first atom to have different ligands (namely C_3) and then positioning the highest priority ligand in the ***a***bove orientation. The orientation for this particular example is counterclockwise;

(3) the orientation of each of the other ligands of this ring (a vs. b) is thus determined. HOWEVER, the orientation of ligands on the double bond or second ring needs further evaluation. In particular, since the given molecule is an even cumulene, above vs. below is NOT relevant and one has to resort to some other criterion,

such as the use of E vs. Z of traditional IUPAC nomenclature. Using that protocol the larger of the ligands on the double bond (F) has a smaller metric distance to the reference atom attached to locant #3 of the ring and thus is Z, while the smaller ligand (H) is E:

$$(C1)_5{:}^{(1)}[2C1^{Z}F{:}^{(3E)}(1H)];^{(3a)}(1F);^{(3b,5a,7a,7b,9a,9b)}(1H);^{(5b)}(1Br) \qquad (21)$$

Alternately, this name can be shortened to:

$$C1(\underline{C}1)_2(\underline{\underline{C}}1)_2{:}\ ^{(1)}(2\underline{C}1^{Z}F);^{(3a)}(1F);\ ^{(5b)}(1Br) \qquad (22)$$

where the underscore advises that a hydrogen atom is singly connected at all of the default positions. This problem does not arise for odd cumulenes inasmuch as there exists the same unequivocal above vs. below relationship for both the ring and the ligands (Figure 20).

$$C1(\underline{C}1)_2(\underline{\underline{C}}1)_2{:}\ ^{(1)}(2C2\underline{C}1^{b}F);^{(3a)}(1F);\ ^{(5b)}(1Br) \qquad (23)$$

Consequently, there is not the need to formulate a second, **unrelated**, set of descriptors such as the Z and E in (21) and (22).

Note that the fluorine atom attached to the ring at locant #3 determined the orientation for all of the other ligands of this molecule; consequently, had Figure 21 been

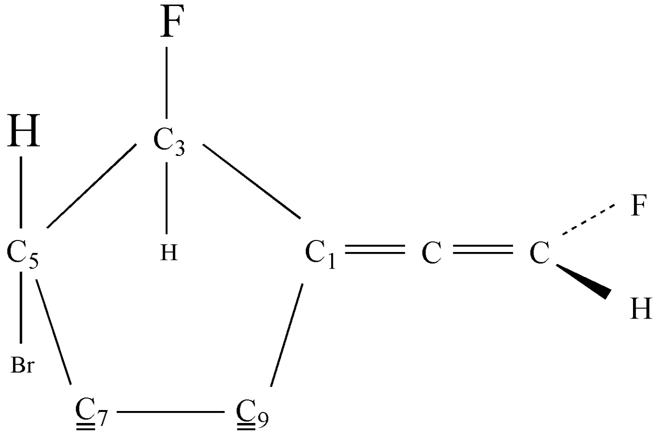

Figure 21: Example of a ring substituted odd cumulene

drawn with the cumulene in the left orientation and the ring on the right; i.e., a 180° rotation out of the plane, one initially would have created a alternate name that had all of the a vs. b descriptors interchanged while the rest of the name was unchanged; i.e.,

$$C1(\underline{C}1)_2(\underline{\underline{C}}1)_2\text{:}\ ^{(1)}(2C2\underline{C}1^{a}F);^{(3b)}(1F);\ ^{(5a)}(1Br) \qquad (24)$$

The decision as to which of these two names should be the canonical name was predicated on giving priority to ligands on the ring over ligands at the end of the cumulene. In other words the algorithm agreed upon made (23) the canonical name despite that formula (24) is lexicographically lower.

Before applying this protocol to molecules containing spiro rings, we note the existence of a special type of (quote) geometrical (unquote) isomerism that exists in "inorganic" chemistry, which is due to the co- planarity of the ligands with the central atom. In many respects, this category of isomerism, is closer to the diastereoisomerism associated with the "optical" isomerism of "organic" molecules in that single bonds, rather than multiple bonds, are prevalent. Nevertheless, this type of isomerism is categorized as "cis-trans" because there exist different metric distances between the corresponding atoms. Most of the molecules that exhibit this type of isomerism are ones that have been held in a static equilibrium by the presence of electron pairs, which function as phantom ligands; at least that is true in the classical domain of "organic" chemistry. Because of these phantom ligands, presentation of examples and a formal assignment of canonical names shall be deferred until later in the chapter, when hexa-coordinated atoms are described.

4. STEREOCHEMISTRY OF ORGANOLITHIUM COMPOUNDS

At this point, a major "wrinkle" in the development of cis-trans isomerism is noted in the classical domain of organolithium chemistry[11]. Namely, as well as the anticipated form of dilithiomethane (Figure 22), whose systemic canonical name is:

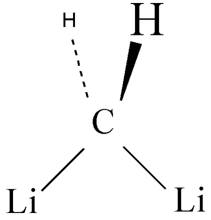

Figure 22: The anticipated isomer of dilithiomethane

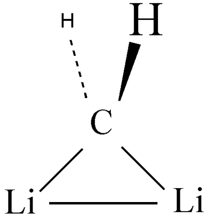

Figure 23: An isomer of dilithiomethane containing a lithium-lithium bond

$$Li1\underline{\underline{C}}1Li \qquad (22)$$

and which follows all of the familiar "rules" of valence and geometry (tetrahedral), one also encounters dilithiomethanes that violate each of these "presumptions"[12]. The first of these occurs when the two lithium atoms have a bond between them (Figure 23). Now, in order to accommodate the valence of -4 for carbon, which worked so well for Figure 22, one is hard pressed to justify how one characterizes the bond strength between the two lithium atoms. Should one assume that one of the two 1s electrons in each of the lithium atoms has been hybridized to parity with its 2s electron and represent this with a traditional single bond, or should one assume a lower bond order?[9] We have, in order to maintain simplicity, rather than for verifiable science that we are aware of, assumed the first choice and systemically nomenclate this molecule as:

$$\underline{\underline{\mathrm{C}}}1(\mathrm{Li}1)_2 \qquad (23)$$

Another variation that both Streitwieser's and Schleyer's [13] groups have investigated jettisons the traditional tetrahedral carbon atom and examines a coplanar molecule that both has and does not have a bond between the two lithium atoms. In order to produce canonical names for the molecules pictured in Figures 24 and 25, we have elected to supplement the bond descriptor with a letter superscript in a manner analogous to the **a** and **b** used above. For Figure 24 it is sufficient to use a superscripted letter, say **p**, to indicate planar; thereby producing as the canonical name:

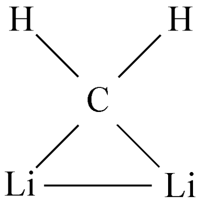

Figure 24: A planar isomer of dilithiomethane containing a lithium-lithium bond

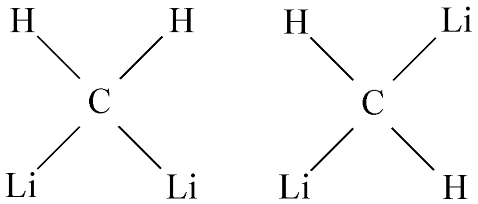

Figure 25: Two other planar isomers of dilithiomethane (orthogonal and straight)

$$\mathrm{C}1(\mathrm{Li}1)_2{:}^{(1\mathrm{p},1\mathrm{p})}(1\mathrm{H}) \qquad (24)$$

Note that, for this scenario, one can not use the underscore convention, as such a convention would default to the traditional tetrahedral geometry, rather than the desired planarity — ***which must be spelled out.***

Such a ploy, however, is not adequate for the two molecules illustrated in Figure 25, inasmuch as the name $\mathrm{Li}1\mathrm{C}1\mathrm{Li}{:}^{(3\mathrm{p},3\mathrm{p})}(1\mathrm{H})$ would apply to both of these different molecules. Instead, it is necessary to further spell out whether the principal chain is straight or orthogonal. This may be readily done by addending the letter superscipt (**s** or **o**) on the bond designator in the principal chain (without the need for the bond designators on the branches); namely for the two halves of Figure 25 the respective canonical names are:

$$\mathrm{Li}1\underline{\underline{\mathrm{C}}}1^{\mathrm{s}}\mathrm{Li} \qquad \text{and} \qquad \mathrm{Li}1\underline{\underline{\mathrm{C}}}1^{\mathrm{o}}\mathrm{Li} \qquad (25)$$

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[9] such as an α or a ζ bond (as developed in Reference #1).

5. NOMENCLATING SPIRANS

Returning the focus to the more familiar (usually organic) scenario in which the molecules being nomenclated contain spiro rings (such molecules are referred to as "spirans"). One notes that the nomenclature for a singly spiro compound as well as for both multiple and multiply-spiro combinations that have the appropriate symmetry were developed in Chapter 6 of Reference #1. When such symmetry is not evident one needs to addend orientation descriptors to the relevant bonds. Unfortunately, of the two previous options for nomenclature (bridged and redundant path) developed therein, there is a liability in each that is only partially corrected in the other. Consequently various hybrid systems of locant numbering could be postulated. One such system is to:

(1) Select as ring #1 the largest of the spiro connected end rings. The atoms of this "principal" ring are regarded as coplanar (in the XY-plane), irrespective how warped out of the plane they really are in 3-space. The spiro atom is designated as Locant #1.

(2) Following the protocol of Reference # 1 sequential locant numbers are assigned to the members (bonds and atoms) of the principal ring. In Figure 26 of Chapter 6 of that monograph, either neighbor of C_1 might have been chosen as C_3 (the chosen C_3 or C_{11}). So long as there are no multiple bonds or non-hydrogen atom ligands, it makes no difference. When there is either a bond or ligand difference, the selection has been determined. In Figure 26 (which has selected ligands

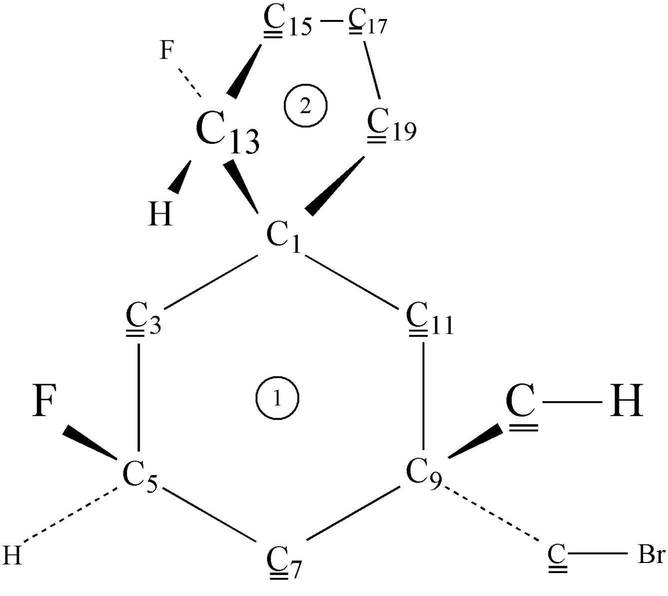

Figure 26. Nomenclating part of a multiple-spiran with stereocenters

attached to a part of Figure 26 of Chapter 6 of Reference #1) the first difference occurs two atoms removed from C_1. The F ligand has priority (over the methyl,

$$(C1\underline{\underline{C}}1)_3{:}^{(5a)}(1F);^{(5b)}(1H);^{(9a)}(1\underline{\underline{C}}1H);\ ^{(9b)}(1\underline{\underline{C}}1Br) \qquad (26)$$

(3) The ring spiro to the principal ring (designated as ring #2 and lying in the XZ-plane) may now be oriented in two possible ways (on the same side of the principal ring as **a**; hence the descriptor Z; or on the opposite side, denoted by E). Since the plane formed by C_{13}, C_1, C_{19} is perpendicular to the principal ring and C_{13} is nearer to the reference atom F (on C_5), the C_1 - C_{13} bond is Z, while the C_1 - C_{19} bond is E. The complete canonical name for the molecule represented by Figure 26 is thus:

$$(C1\underline{\underline{C}}1)_3{:}^{(1\text{-}1)}[1^{Z}C^{(=13)}(1\underline{\underline{C}})_2 1^{E}];^{(5a)}(1F);^{(5b)}(1H);^{(9a)}(1\underline{\underline{C}}1H);\ ^{(9b)}(1\underline{\underline{C}}1Br);\ ^{(13a)}(1H);^{(13b)}(1F) \qquad (27)$$

(4) Continuing to add a third spiro ring at locant #19, the local reference plane is determined by C_1, C_{17} and C_{19} and the reference ring will lie in the YZ-plane. Now because there is yet another spiro atom with its potential for multiple choices, there is no need to be concerned with locants on this spiro ring. Instead the focus is on which is the longer chain to this third spiro atom. Consequently, it is necessary to designate which of these chains is above this local plane and which one is below. By the protocol that the locant number sequencing continues along the longer chain; this chain is designated by descriptor b; also the next spiro atom is locant #27.

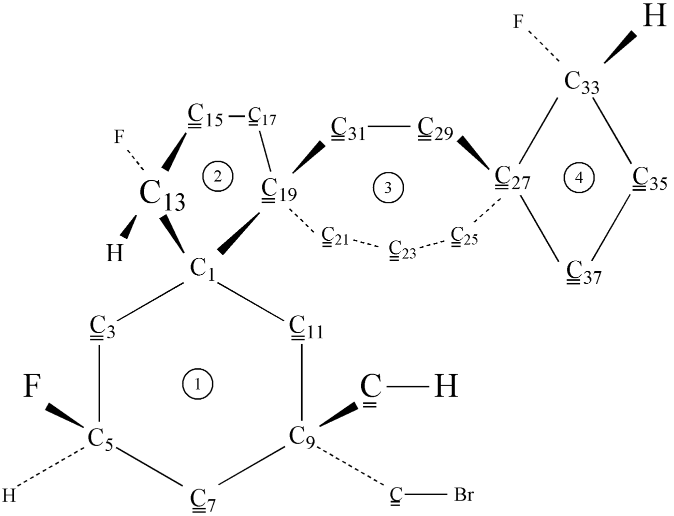

Figure 27: Completing the nomenclating of a multiple-spiran with stereocenters

(5) Because the final ring (#4) is perpendicular to ring #3, it is roughly coplanar with the principal ring (#1) and ligands attached to it will be denoted by a and b, as in ring #1. Consequently, the locant numbering is as shown in Figure 27 and the canonical name is:

$$(\mathrm{C}1\underline{\underline{\mathrm{C}}}1)_3\!:^{(1\text{-}1)}\{1^{Z}\mathrm{C}^{(=13)}(1\underline{\underline{\mathrm{C}}})_2 1^{E}\!:^{(19a\text{-}19b)}\{1(\underline{\underline{\mathrm{C}}}1)_3\mathrm{C}^{(=27)}1(\underline{\underline{\mathrm{C}}}1)_2\}\!: {}^{(27\text{-}27)}[1^{Z}\mathrm{C}^{(=33)}(1\underline{\underline{\mathrm{C}}})_2 1^{E})]\};{}^{(5a,13b,33b)}(1\mathrm{F});{}^{(5b,13a,33a)}(1\mathrm{H});{}^{(9a)}(1\underline{\underline{\mathrm{C}}}1\mathrm{H});{}^{(9b)}(1\underline{\underline{\mathrm{C}}}1\mathrm{Br}) \qquad (28)$$

6. STEREOISOMERISM INDUCED BY STERIC INTERFERENCE

Next, just as appropriate substitutions on a spiro assembly creates the opportunity for stereoisomerism, similarly, so might substitutions on a biaryl compound. For example, were there to be large bulky ligands replacing the hydrogen atoms at C_5 and C_{19} in the biphenyl illustrated in Figure 40 of Chapter 6 of Reference #1, there would be steric interference between these ligands[10] and the free rotation postulated about the bond connecting the two rings would be further restricted. This produces a pair of "conformational" isomers. This restriction would be even greater were there also bulky ligands on C_{13} and C_{27}. This is illustrated in Figure 28, in which a propyl and a methyl

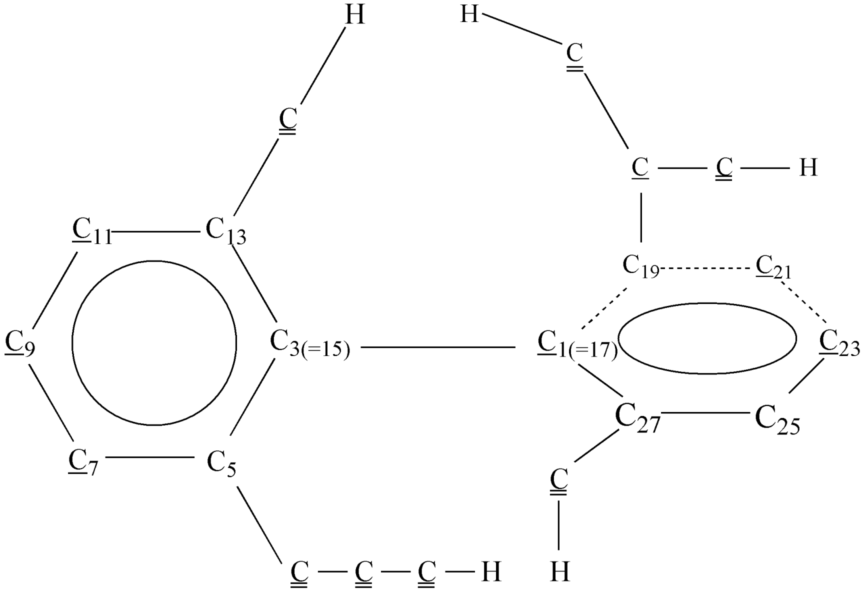

Figure 28: A sterically hindered biphenyl ring compound

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[10] Despite the representation, which was based on Patterson's drawing convention, the metric distance from C_5 to C_{19} is equal to that between C_{13} and C_{27}.

ligand are adjacent to the connecting bond of one benzene ring while an isopropyl and a methyl group are adjacent to the other benzene ring of a biaryl compound. Although neither the propyl nor the isopropyl ligands are on the principal part of the canonical name, the third carbon from the ring in the propyl ligand has precedence over the hydrogen atom at that position in the isopropyl ligand; consequently, for purposes of nomenclating, the propyl benzene ring is in the XY-plane and the isopropyl benzene is in the XZ- plane. Now, if one had allowed for rotation about the single bond between the two rings, there would be steric interference between the two three carbon substituents on the biphenyl rings. Instead, because the ring with the isopropyl substituent must be behind the XY-plane, this must be indicated in the nomenclature with a **b** superscript addended to the single bond connecting the two rings. For example, when the isopropyl ligand is behind the propylbenzene plane, the canonical name is:

$$\begin{array}{l}\mathrm{C1(C\beta)_2(\underline{C}\beta)_3C\beta C^{(15=3)}1^{(16=2)}C^{(17=1)}\beta^{b}C\beta(\underline{C}\beta)_3\underline{C}:^{(5)}[1(\underline{\underline{C}}1)_3H];} \\ \mathrm{{}^{(13,27)}(1\underline{\underline{C}}1H);^{(19)}[1\underline{C}1\underline{\underline{C}}1H:^{(5)}(1\underline{\underline{C}}1H)]}\end{array} \qquad (29)$$

This type of isomerism would be applicable to the compound depicted in Figure 25 of Chapter 3 of Reference #1 had the hydrogen atoms at C_9 and C_{63} been larger ligands. Consequently, one would need to specify as either **a** or **b** the orientation allocated to the bonds between C_{15} and C_{61} and between C_{45} and C_{73}. A similar scenario exists for steric interference between C_{21} and C_{71}, between C_{39} and C_{83}, and between C_{51} and C_{75}.

7. A MOLECULE WITH A TWO-DIMENSIONAL STEREOCENTER

The concept of "geometrical isomerism" is not limited to the historical domain of organic chemistry. An interesting inorganic compound[14] has as its stereocenter a two dimensional geometric figure (a rhombus). In this molecule two magnesium atoms form a hydrogen bonded ring with two hydrogen atoms. Now, instead of the familiar valence of 2 traditionally associated with magnesium, dative bonding by each of two molecules of tetrahydrofuran to the two magnesium atoms forms the molecule depicted in Figure 29. The simplest way to assign a canonical name to this molecule is to ignore a single edge from each of the two terminal tetrahydrofuran rings and to consider the selected edge as a bridge thereby forming a "linear" segment [in the manner of (24) in Chapter 6]. Similarly, one of the hydrogen atoms and its two hydrogen bridges is viewed as a third bridging segment. This geometrical isomer (Figure 29) has its canonical name:

$$\mathrm{(\underline{\underline{C}}1)_4O1Mg\alpha H\alpha Mg1O1(\underline{\underline{C}}1)_4:^{(1\text{-}9,17\text{-}25)}(1);^{(11\text{-}15)}(\alpha H\alpha);^{(11a,15b)}(1C\ell)} \qquad (30)$$

The "cis" isomer name differs only in the superscript (11a,15a) for the two chlorine atoms.

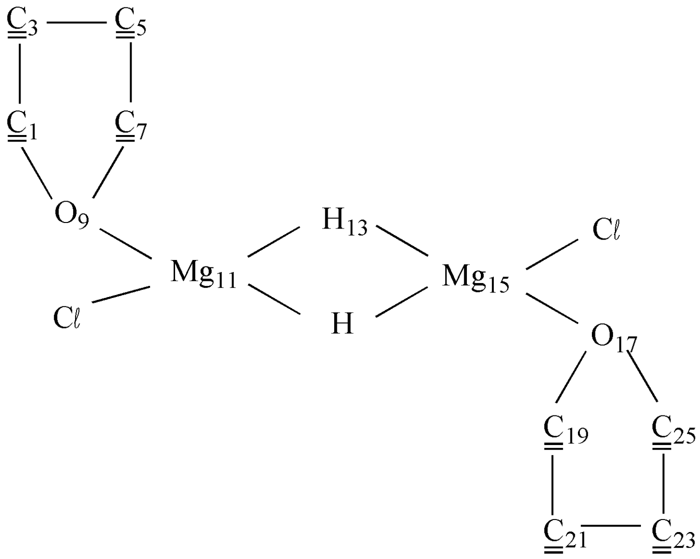

Figure 29: A molecule having a two dimensional stereocenter
– IUPAC name: trans-[HMgCℓ(thf)]$_2$

8. HELICENES

Returning focus to the more prevalent organic domain, one encounters a slightly different form of geometrical isomerism wherein the fusion of aromatic rings creates overlapping rings that aggregate into a helical pattern[15]. These were dubbed as "helicenes". Beginning from the tetrabenzene molecule illustrated as in Reference #1 as part 4 of Figure 10 in Chapter 2, one notes that the hydrogen atoms at C_9 and C_{17} are sufficiently far apart so that they do not appreciably affect one another. However, when one addends a fifth benzene module adjacent to the edge designated as locant number 18 this produces the pentabenzene shown as Figure 30, which has as its canonical name:

$$(C\beta)_{22}{:}^{(1\text{-}11,13\text{-}39,15\text{-}33,17\text{-}27)}\beta{:}^{(3,5,7,9,19,21,23,25,29,31,35,37,41,43)}(1H) \tag{31}$$

Here one observes a repulsion between the hydrogen atoms at C_9 and C_{19}, which serves to slightly warp the molecule out of the plane. Because this distortion is small, the ability to isolate distinct isomers at anywhere near STP (standard temperature and pressure) is unlikely. Instead, this is construed as a form of conformational isomers, and the nomenclature is unaffected. On the other hand, readily isolatable isomers may be created by:

(1) appreciable lowering of temperature;
(2) continuing the process of replacing a hydrogen atom with a larger substituent, such as a methyl group, at locant numbers 9 or 19;

(3) addending a sixth or more benzene ring in a continuing circular pattern, etc.

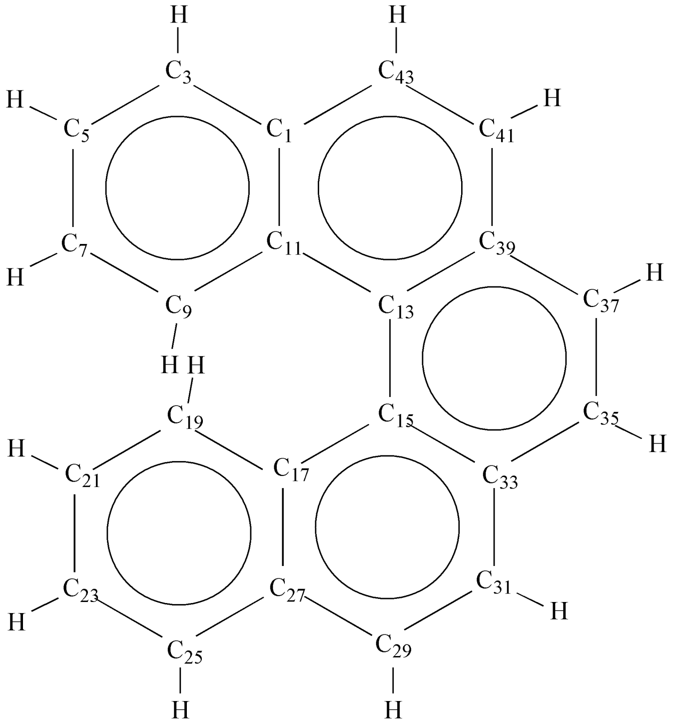

Figure 30: Distortion due to hydrogen atom interference in a helical pentabenzene

For nomenclature purposes, the first of the rings in such a circular pattern, is construed as the reference plane. Now, as more rings are addended beyond the first five, these are characterized as being either above or below this reference plane. For example, when a methyl group is attached at C_{19} and it lies below the reference plane, the canonical name for this molecule is:

$$(C\beta)_{22}:^{(1-11,13-39,15-33,17,27)}\beta:^{(9)}(1^{a}H);\ ^{(19)}(1^{b}\underline{\underline{C}}1H);\ ^{(3,5,7,21,23,25,29,31,35,37,41,43)}(1H) \tag{32}$$

Note that the hydrogen atom at C_9 was perfunctorily assigned as **a.** A more common, **but deliberately avoided so that the focus would stay on the stereogenicity, rather than the chirotopicity**, alternate way of describing this orientation is that when the methyl group is above the reference plane the direction of progression is counterclockwise vs. when it is below and the direction of progression is clockwise.

In a similar manner, by addending a sixth benzene ring in this continuing pattern three important forms can be created: two distinct three dimensional helicenes with molecular formula: $C_{26}H_{16}$ and one coplanar molecule containing two fewer carbon and four fewer hydrogen atoms (common name: coronene) which was nomenclated in Chapter 2 of Reference #1. The helicenes are differentiated from each other in the nomenclature by the superscript containing either an **a** or a **b**. For the sixth ring above the reference plane, the canonical name is:

$$(C\beta)_{26}:^{(1\text{-}11,17\text{-}51,23\text{-}49,29\text{-}47,35\text{-}45)}(\beta);^{(3b,5b,7,9,13,15,19,21,25,27,331,33,37,39,41a,43a)}(1H) \qquad (33)$$

while had the sixth ring been behind the reference (first) ring, the a and b superscripts on the hydrogen atoms would have been reversed:

$$(C\beta)_{26}:^{(1\text{-}11,17\text{-}51,23\text{-}49,29\text{-}47,35\text{-}45)}(\beta);^{(3a,5a,7,9,13,15,19,21,25,27,331,33,37,39,41b,43b)}(1H) \qquad (34)$$

9. MOLECULES MODELED AS A REGULAR TETRAHEDRAL CAGE

Before expanding our focus to molecules formed from atoms having a higher coordination than 4, the stereogenicity associated with regular polyhedron-shaped molecular cages wherein there are different ligands emanating from the respective vertices is probed.[11] Topologically, this may be represented by points on a sphere which circumscribe the polyhedron. Superficially it appears that such a geometry would be better served by a spherical, rather than a Euclidean, nomenclature; however, such is NOT the case.. Because there are different ligands on the otherwise equivalent vertex atoms, spherical symmetry does not extend to the entire molecule. To the contrary; the anticipated advantage that the spherical symmetry of the core introduces is negated and Cartesian nomenclature is of much greater pragmatic value.

In the formulation of canonical names for such a set of molecules, one selects as the reference plane that face of the polyhedron which contains the highest priority ligand along with as many as possible of the second largest, third largest, etc. of the remaining ligands. Note that the specification of regularity contains the provision of convexity, which, in turn, prevents this reference plane from containing the center of the circumscribing sphere. By default, this point must now be situated either above or below this reference plane. This circumcenter is the location of a phantom stereocenter, which is designated by the mathematical symbol for the empty set (Φ). The vertices in this planar face are next labeled in a counterclockwise orientation. Having developed such a geometrical model, one can now assign canonical names to the various stereoisomers, in exactly the same manner as though a single atom had been the stereocenter. This is illustrated for the regular tetrahedron. The nomenclature applicable to different ligands at the vertices of the four other Platonic solids will be developed in a later section following the nomenclating of molecules having higher coordinate atoms as the stereocenter.

At this point, our attention is directed to the two tetrahedral analogs of Bromofluoroiodomethane. Figure 31 illustrates the (S)-isomer. The above-described

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[11] For large enough polyhedra, some duplication of ligands may be encountered; however, no new principles would be involved, only that there will be a smaller number of possible isomers than is the case when all of the ligands are different.

reference plane is formed from the three vertices having the highest priority based on sequential atomic number; i.e., from the three carbon atoms having the halogen ligands in Figure 31. Additionally one takes note of the line passing perpendicular to the reference plane and continuing through the circumcenter and the lowest priority vertex (i.e., the fourth carbon atom (with its hydrogen atom ligand). Because of the requirement that the three highest priority ligands be in counterclockwise orientation, there are two possible locations for this reference plane: either above or below the stereocenter. These potential orientations are denoted by either an **a** or **b**. One thus incorporates stereochemistry into a canonical Cartesian name as:

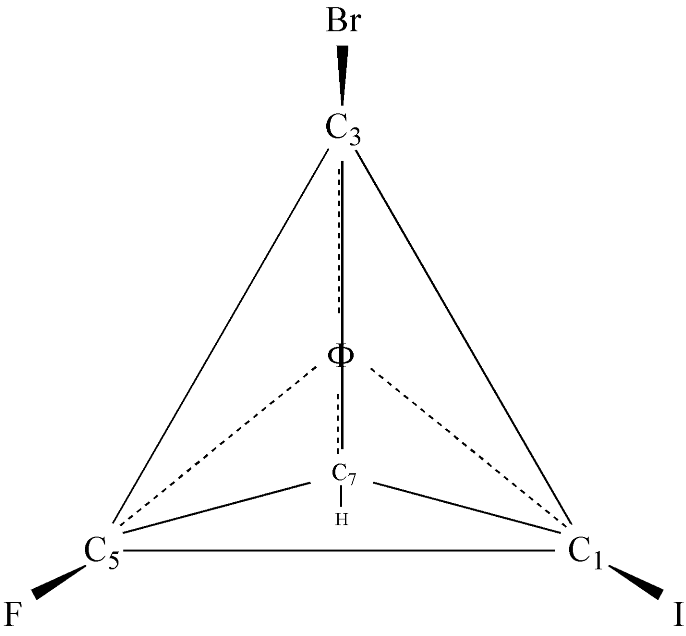

Figure 31: (S)-Bromofluoroiodomethane

$$(\mathrm{C1})_4{:}^{(1\text{-}5,3\text{-}7)}(1);^{(1)}(1^{a}\mathrm{I});^{(3)}(1^{a}\mathrm{Br});^{(5)}(1^{a}\mathrm{F});^{(7)}(1^{b}\mathrm{H}) \qquad (35)$$

for the S isomer and as:

$$(\mathrm{C1})_4{:}^{(1\text{-}5,3\text{-}7)}(1);^{(1)}(1^{b}\mathrm{I});^{(3)}(1^{b}\mathrm{Br});^{(5)}(1^{b}\mathrm{F});^{(7)}(1^{a}\mathrm{H}) \qquad (36)$$

for (R)-Bromofluoroiodomethane. Additionally, considering the stereocenter as a phantom atom with locant number 0 and the bond orders from this phantom stereocenter to any atom also 0, one assigns as the canonical spherical name for the S isomer:

$$\Phi\text{: }^{(0a)}(0C_1 1I);\ ^{(0a)}(0C_3 1Br);\ ^{(0a)}(0C_5 1F);\ ^{(0b)}(0C_7 1H)\text{: }(C_1)_4;^{(1\text{-}5,3\text{-}7)}(1) \qquad (37)$$

Similarly, the R isomer would have the superscripts a and b interchanged and its canonical spherical name:

$$\Phi\text{: }^{(0a)}(0C_7 1H);\ ^{(0b)}(0C_1 1I);\ ^{(0b)}(0C_3 1Br);\ ^{(0b)}(0C_5 1F)\text{: }(C_1)_4;^{(1\text{-}5,3\text{-}7)}(1) \qquad (38)$$

Now, because it is desirable to include all mathematically possible combinations, especially since some scenarios may arise unexpectedly, attention is next focused on the topology of a molecular “cage”; in particular, when a single atom (or combination of atoms) may be inside or penetrating, as well as outside such a cage. In this regard, in Chapter 7 of Reference #1, attention was directed to molecules containing one or more ligands interior to a cage. A theoretical extension ***could*** consider ligands interior to a tetrahedral cage; however, pragmatically, such a problem does NOT arise for small cages. On the other hand, it is important for large cages having coordination of 3 for all vertices, especially the fulleranes. Consequently, we adopt the simplification that *it will be indicated to the contrary when one should NOT assume that all of the ligands are exterior for any cage being nomenclated.* This exception will be indicated in the nomenclature by addending an **i** (for interior) to the bond descriptor. A more complex modification of this type stereogenicity, which is referred to as “adamantoid”, was described by the CIP team[16]. An example of such a molecule, which was created by Stetter and Bänder[17], is illustrated in Figure 32. Note that were it not for the hydroxyl groups on C_3 and C_{11}, there would be a plane of symmetry through $C_3 – C_7 – C_{13}$. In the standard orientation one may position the larger (hydroxyl) group on C_{11} to the left; thereby relegating the hydrogen atom to the right. There are now two possible locations for the hydroxyl ligand on C_3: above or below the reference ($C_3 – C_7 – C_{13}$) plane. The choice of which fits neatly into the proposed canonical name. The canonical name of the molecule illustrated in Figure 32 is thus:

$$\begin{array}{l}[(C1)_3\underline{\underline{C}}1]_2\text{:}^{(1\text{-}9)}[1\underline{\underline{C}}^{(=17)}1];^{(5\text{-}13)}[1\underline{\underline{C}}^{(=18)}1];^{(1,5,9,13)}[1C1O1H\text{:}^{(3)}2O];\\ ^{(3)}(1^aO1H;1^bH);^{(11)}(1^aH;\ 1^bO1H)\end{array} \qquad (39)$$

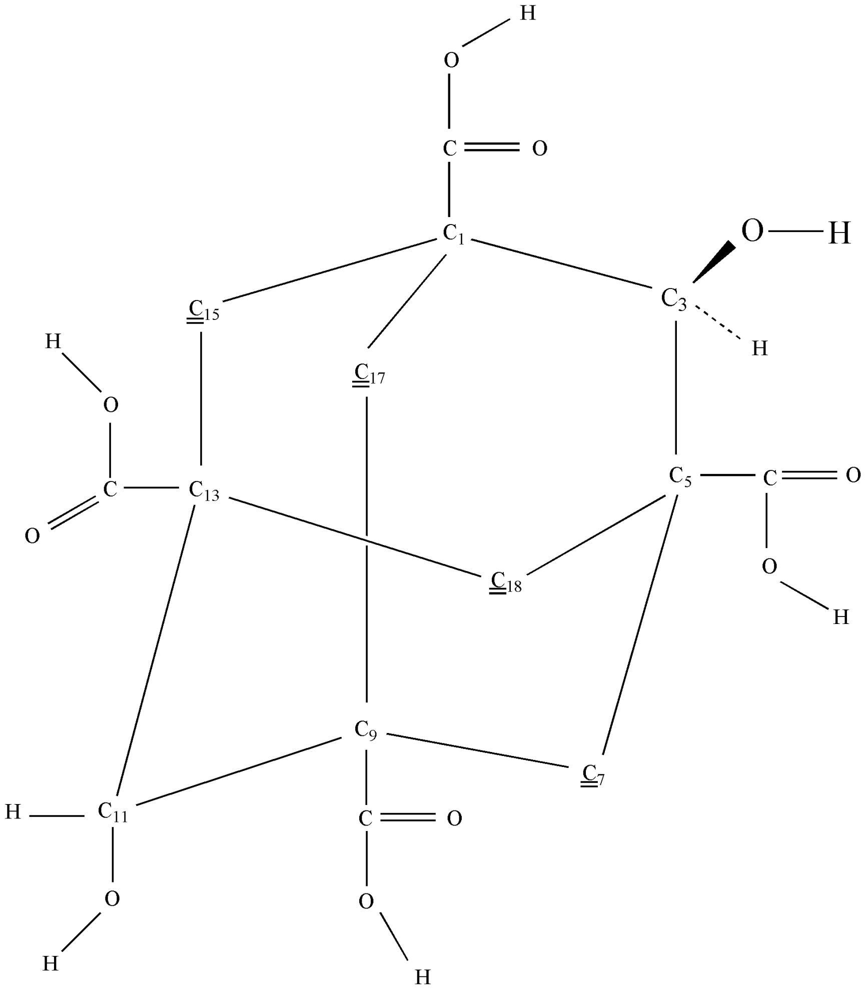

Figure 32: Nomenclating an adamantoid

10. DIASTEREOISOMERISM AT A SINGLE STEREOCENTER

A special type of geometrical isomerism, which may be viewed as a "diastereoisomerism at a single stereocenter" occurs in the traditional "inorganic" domain. One such example, which has four ligands (a ≥ b ≥ c ≥ d) attached to a central atom, differs from the tetrahedral orientation of the ligands in that here the ligands are coplanar with the central atom. Because of this coplanarity, the atom diametrically opposite to the largest ligand can be any one of the three remaining ligands. However, unlike when the embedding space is three-dimensional, there are, at most, only three (NOT six) viable isomers[12] (Figure 33) — rotation through 180° bring the larger of the two ligands not on the principal line to the standardized location above that line when forming the canonical name. Such a coplanarity is usually the result of there existing two pairs of unshared electrons on the central atom and thus a coordination of six — only four of which are atom ligands. This may be expressed in the canonical nomenclature by a special symbol for each set of unpaired electrons. In other words, the tetra-coordination of atom ligands about the stereocenter is only a part of chemical geometry. In addition, one views the paired electrons as phantom ligands, which need to be incorporated into the nomenclature; thereby producing, in effect, hexa-coordination. This will be described below.

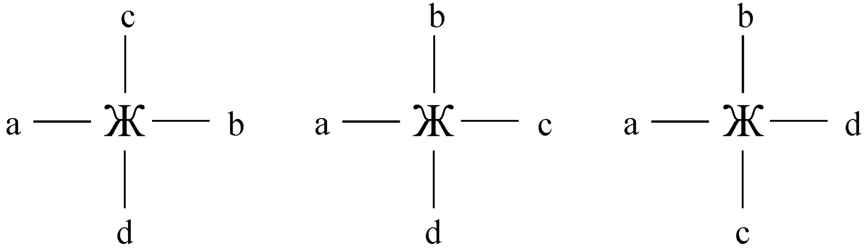

Figure 33: Theoretically possible orientations of ligands in a coplanar molecule

11. STEREOISOMERS HAVING HIGHER COORDINATION

In addition to the above described stereoisomers wherein the modules involved had a maximum coordination of 4, there exist additional classes of stereoisomers having higher coordination. In the process of nomenclating such molecules, one refocuses on the observation that, in contradistinction to the existence of a regular polygon of any number of sides (greater than 2) in a two dimensional space, there exists **only** five simple regular polyhedra in three dimensional Euclidean space. A consequence of this in chemistry is that, because of Coulomb attraction and repulsion, certain geometrical orientations are the preferred “islands of stability”. The first and most familiar of these is the association of the tetrahedron with the carbon atom; i.e., much of traditional organic chemistry may be directly inferred from this geometry. Furthermore, in a manner analogous to the chemistry associated with tetrahedral orientation, for each of the remaining four “Platonic solids”, attention is next directed to molecules likely to exist in a static stable equilibrium. In particular, we shall focus our attention on two important classes of molecules which often give rise to stereoisomerism — those having a star[13] and those with a cage[14] geometry.

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[12] The number of viable isomers will be less (two or one) when any of the ligands are alike.

[13] See page 17 in Reference #1.

[14] See page 150 in Reference #1.

In order to establish the canonical nomenclature for molecules having atoms with coordination higher than four, various standardized math models have been created. One major property of the larger Platonic solid models is their inherent three dimensionality. This is in contradistinction to the above tetrahedral system (number of vertices, V =4), which could be viewed as being mapped onto a two dimensional Cartesian coordinate system with the stereocenter at the origin and with one of the four ligands “entering” along the X-axis and a second ligand “exiting” that stereocenter at an angle other than 180^o. This determined the XY-plane. The nomenclature associated with this system focused on the remaining two ligands, which were viewed as being located above or below the reference line formed by the previous two ligands and the stereocenter. Mostly, this resulted in distorting the actual geometry from $109^o28.5'$ and 120^o angles so as to form 90^o and 180^o angles. Such a simplification is not amenable to the larger Platonic solids.

An octahedral[15] system (V=6), for example, directly uses the geometry associated with three dimensional Cartesian coordinates with the molecular model being mapped directly onto a set of Cartesian (orthogonal) axes. The stereocenter module, designated by Cyrillic letter Ж, is located at the origin of the Cartesian system and the six ligands are located at the positive and negative “unit” points along the three coordinate axes. Standardized names for the ligands located at each of these six positions are formulated as follows: select any one of the six ligands as the entry vector to the stereocenter and locate it along the negative X-axis (call it **a**). Having done this, there exists a unique representation for the ligand diametrically opposed (on the positive X-axis). Before assigning a standardized generic name to this ligand, one notes that when each of the ligands is a single atom, the GTD between any pair of ligands = 2; however, some of the MDs between ligands are different. We, therefore, elect to sequentially assign successive letters to the nearest set of ligands to a; namely, because there are four ligands an equal MD from a, these will be designated as **b**, **c**, **d** and **e**, with b being arbitrarily chosen. Next, in the plane containing b, c, d and e (which is the YZ-plane) assign **b** along the positive Y-axis, **c** along the positive Z-axis, **d** along the negative Y-axis and **e** along the negative Z-axis. These four locant descriptors are now in a clockwise orientation when that plane is approached from **a**. Moreover, the MD from each of these four locations (in a unit system) is $\sqrt{2}$. The final ligand from the stereocenter (which lies along the positive X-axis) has MD=2 from the starting ligand and is designated as **f**. In other words, once the arbitrary choice of **a** has been made, there are five different ligands that might be located at **f**. Similarly, once these two choice have been made, because the coordinate system may be freely rotated prior to assigning the location of the Y and Z axes, the choice of **b** from the remaining set of four ligands is completely arbitrarily. Likewise, because **d** is diametrically opposed to **b**, it may be any one of three remaining ligands. Finally, the choice of **c** is one of two remaining locations and **e** is detemined. In other words, the total number of different isomers that have to be assigned a canonical name = 5 * 3 * 2 = 30. Additionally, the choice made for **e** will determine which of two mirror images had been selected. The different canonical names for each of the 30 mathematically possible “star” orientations of generic ligands about a hexa-coordinated

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[15] Also referred to as a “square” or “tetragonal” bipyramid ─ especially when one wishes to partition the set of vertices into two “polar” and four “equatorial” vertices.

stereocenter[18] are tabulated in Table 1. Additionally, Figure 34 illustrates one of these theoretically possible molecules: (1) in Table 1.

Table 1:
Canonical names for various theoretical hexa-coordinated sulfur molecules

	Ligand located at position						Cartesian canonical name
	a	b	c	d	e	f	
(1)	I	Cℓ	F	D	H	Br	$\mathrm{I1S1^{f}Br{:}^{(3)}(1^{b}C\ell);^{(3)}(1^{c}F);^{(3)}(1^{d}D);^{(3)}(1^{e}H)}$
(2)	I	Cℓ	F	H	D	Br	$\mathrm{I1S1^{f}Br{:}^{(3)}(1^{b}C\ell);^{(3)}(1^{c}F);^{(3)}(1^{d}H);^{(3)}(1^{e}D)}$
(3)	I	Cℓ	D	F	H	Br	$\mathrm{I1S1^{f}Br{:}^{(3)}(1^{b}C\ell);^{(3)}(1^{c}D);^{(3)}(1^{d}F);^{(3)}(1^{e}H)}$
(4)	I	Cℓ	D	H	F	Br	$\mathrm{I1S1^{f}Br{:}^{(3)}(1^{b}C\ell);^{(3)}(1^{c}D);^{(3)}(1^{d}H);^{(3)}(1^{e}F)}$
(5)	I	F	Cℓ	D	H	Br	$\mathrm{I1S1^{f}Br{:}^{(3)}(1^{b}F);^{(3)}(1^{c}C\ell);^{(3)}(1^{d}D);^{(3)}(1^{e}H)}$
(6)	I	F	Cℓ	H	D	Br	$\mathrm{I1S1^{f}Br{:}^{(3)}(1^{b}F);^{(3)}(1^{c}C\ell);^{(3)}(1^{d}H);^{(3)}(1^{e}D)}$
(7)	I	Br	F	D	H	Cℓ	$\mathrm{I1S1^{f}C\ell{:}^{(3)}(1^{b}Br);^{(3)}(1^{c}F);^{(3)}(1^{d}D);^{(3)}(1^{e}H)}$
(8)	I	Br	F	H	D	Cℓ	$\mathrm{I1S1^{f}C\ell{:}^{(3)}(1^{b}Br);^{(3)}(1^{c}F);^{(3)}(1^{d}H);^{(3)}(1^{e}D)}$
(9)	I	Br	D	F	H	Cℓ	$\mathrm{I1S1^{f}C\ell{:}^{(3)}(1^{b}Br);^{(3)}(1^{c}D);^{(3)}(1^{d}F);^{(3)}(1^{e}H)}$
(10)	I	Br	D	H	F	Cℓ	$\mathrm{I1S1^{f}C\ell{:}^{(3)}(1^{b}Br);^{(3)}(1^{c}D);^{(3)}(1^{d}H);^{(3)}(1^{e}F)}$
(11)	I	Br	H	F	D	Cℓ	$\mathrm{I1S1^{f}C\ell{:}^{(3)}(1^{b}Br);^{(3)}(1^{c}F);^{(3)}(1^{d}D);^{(3)}(1^{e}H)}$
(12)	I	Br	H	D	F	Cℓ	$\mathrm{I1S1^{f}C\ell{:}^{(3)}(1^{b}Br);^{(3)}(1^{c}F);^{(3)}(1^{d}H);^{(3)}(1^{e}D)}$
(13)	I	Br	Cℓ	D	H	F	$\mathrm{I1S1^{f}F{:}^{(3)}(1^{b}Br);^{(3)}(1^{c}C\ell);^{(3)}(1^{d}D);^{(3)}(1^{e}H)}$
(14)	I	Br	Cℓ	H	D	F	$\mathrm{I1S1^{f}F{:}^{(3)}(1^{b}Br);^{(3)}(1^{c}C\ell);^{(3)}(1^{d}H);^{(3)}(1^{e}D)}$
(15)	I	Br	D	Cℓ	H	F	$\mathrm{I1S1^{f}F{:}^{(3)}(1^{b}Br);^{(3)}(1^{c}D);^{(3)}(1^{d}C\ell);^{(3)}(1^{e}H)}$
(16)	I	Br	D	H	Cℓ	F	$\mathrm{I1S1^{f}F{:}^{(3)}(1^{b}Br);^{(3)}(1^{c}D);^{(3)}(1^{d}H);^{(3)}(1^{e}C\ell)}$
(17)	I	Br	H	Cℓ	D	F	$\mathrm{I1S1^{f}F{:}^{(3)}(1^{b}Br);^{(3)}(1^{c}H);^{(3)}(1^{d}C\ell);^{(3)}(1^{e}D)}$
(18)	I	Br	H	D	Cℓ	F	$\mathrm{I1S1^{f}F{:}^{(3)}(1^{b}Br);^{(3)}(1^{c}H);^{(3)}(1^{d}D);^{(3)}(1^{e}C\ell)}$
(19)	I	Br	H	Cℓ	F	D	$\mathrm{I1S1^{f}D{:}^{(3)}(1^{b}Br);^{(3)}(1^{c}H);^{(3)}(1^{d}C\ell);^{(3)}(1^{e}F)}$
(20)	I	Br	H	F	Cℓ	D	$\mathrm{I1S1^{f}D{:}^{(3)}(1^{b}Br);^{(3)}(1^{c}H);^{(3)}(1^{d}F);^{(3)}(1^{e}C\ell)}$
(21)	I	Br	Cℓ	F	H	D	$\mathrm{I1S1^{f}D{:}^{(3)}(1^{b}Br);^{(3)}(1^{c}C\ell);^{(3)}(1^{d}F);^{(3)}(1^{e}H)}$
(22)	I	Br	Cℓ	H	F	D	$\mathrm{I1S1^{f}D{:}^{(3)}(1^{b}Br);^{(3)}(1^{c}C\ell);^{(3)}(1^{d}H);^{(3)}(1^{e}F)}$
(23)	I	Br	F	Cℓ	H	D	$\mathrm{I1S1^{f}D{:}^{(3)}(1^{b}Br);^{(3)}(1^{c}F);^{(3)}(1^{d}C\ell);^{(3)}(1^{e}H)}$
(24)	I	Br	F	H	Cℓ	D	$\mathrm{I1S1^{f}D{:}^{(3)}(1^{b}Br);^{(3)}(1^{c}F);^{(3)}(1^{d}H);^{(3)}(1^{e}C\ell)}$
(25)	I	Br	Cℓ	D	F	H	$\mathrm{I1S1^{f}H{:}^{(3)}(1^{b}Br);^{(3)}(1^{c}C\ell);^{(3)}(1^{d}D);^{(3)}(1^{e}F)}$
(26)	I	Br	Cℓ	F	D	H	$\mathrm{I1S1^{f}H{:}^{(3)}(1^{b}Br);^{(3)}(1^{c}C\ell);^{(3)}(1^{d}F);^{(3)}(1^{e}D)}$
(27)	I	Br	D	Cℓ	F	H	$\mathrm{I1S1^{f}H{:}^{(3)}(1^{b}Br);^{(3)}(1^{c}D);^{(3)}(1^{d}C\ell);^{(3)}(1^{e}F)}$
(28)	I	Br	D	F	Cℓ	H	$\mathrm{I1S1^{f}H{:}^{(3)}(1^{b}Br);^{(3)}(1^{c}D);^{(3)}(1^{d}F);^{(3)}(1^{e}C\ell)}$
(29)	I	Br	F	Cℓ	D	H	$\mathrm{I1S1^{f}H{:}^{(3)}(1^{b}Br);^{(3)}(1^{c}F);^{(3)}(1^{d}C\ell);^{(3)}(1^{e}D)}$
(30)	I	Br	F	D	Cℓ	H	$\mathrm{I1S1^{f}H{:}^{(3)}(1^{b}Br);^{(3)}(1^{c}F);^{(3)}(1^{d}D);^{(3)}(1^{e}C\ell)}$

An alternate "spherical" name, recommended primarily when all of the ligands are single atoms, as in Table 1, is created by listing the center first and then all of the ligands, rather than following the longest path. For molecule # (1) in Table 1 this would be:

$$\mathrm{S{:}^{(1a)}1I;^{(1b)}1C\ell;^{(1c)}1F;^{(1d)}1D;\ ^{(1e)}1H;\ ^{(1f)}1Br} \qquad (40)$$

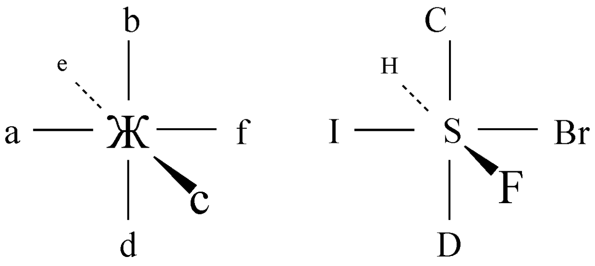

Figure 34: The generic locant positioning for hexa-coordination and that isomer for which the locants are in decreasing size; viz. (1) in Table 1

The first molecule created with a triply bonded lead atom[19] (Figure 35) is an example of a hexa-coordinated molecule recently in the news. The principal path includes the molybdenum atom at locant #7, which is approached along a single bond at locant #6 from a phosphorus atom and continues along the triple bond at locant #8 leading to the lead atom. This triple bond is situated in the standardized model at orientation d. Consequently, in the systemic name one affixes a superscript d to the bond descriptor at locant #8. Each of the other four ligands to the molybdenum are next identified: the largest (Br) has descriptor b, while the three additional phosphorus trimethyl groups are oriented at standardized positions c, e and f. Note that the descriptor a is implied and need not be included. On the other hand, it is recommended that even though one could always ascertain which ligand is descriptor f from the other descriptors given, it be included in the canonical name:

$$\begin{aligned}&\mathrm{H1\underline{\underline{C}}1P1Mo3^{(d)}Pb1(C\beta)_2(\underline{C}\beta)_3C1(C\beta)_2\underline{C}\beta C\beta\underline{C}\beta C1\underline{C}1\underline{\underline{C}}1H{:}^{(11\text{-}21,23\text{-}33,41\text{-}51)}(\beta);}\\&\mathrm{{}^{(5,5)}(1\underline{\underline{C}}1H);\ {}^{7b)}(1Br);^{(7c,7e,7f)}[1P1\underline{\underline{C}}1H{:}^{(3,3)}(1\underline{\underline{C}}1H)];^{(13)}[1C^{(=41)}\beta C^{(=43)}\beta\underline{C}^{(=45)}\beta\, C^{(=47)}\beta}\\&\mathrm{\underline{C}^{(=49)}\beta C^{(=51)}1\underline{C}^{(=53)}1\underline{\underline{C}}^{(=55)}1H^{(=57)}];\ {}^{25.29.43.47)}[1\underline{C}1\underline{\underline{C}}1H{:}^{(3)}1\underline{\underline{C}}1H];^{(35,53)}(1\underline{\underline{C}}1H)}\end{aligned}\tag{41}$$

Applying this perception of octahedral orientation to the earlier mentioned molecules that have a co-planar geometry, such as the "cis" and "trans" dichlorodiamino-platinum (II) molecules (Figure 36), this co-planarity is attributed to the presence of electron pairs acting as phantom ligands. Such an idea is readily incorporable into the nomenclature by designating the phantom locant (electron pair) by an artificial symbol such as a lower case *ep*, which replaces both the bond and it associated atom symbol; namely, one **might** select for the trans isomer:

$$\mathrm{H1\underline{N}1Pt1\underline{N}1H{:}^{(5b,5d)}(1C\ell);^{(5c,5e)}(ep)}\tag{42}$$

vs. for the cis isomer:

$$\mathrm{H1\underline{N}1Pt1\underline{N}1H{:}^{(5d,5f)}(1C\ell);^{(5c,5e)}(ep)}\tag{43}$$

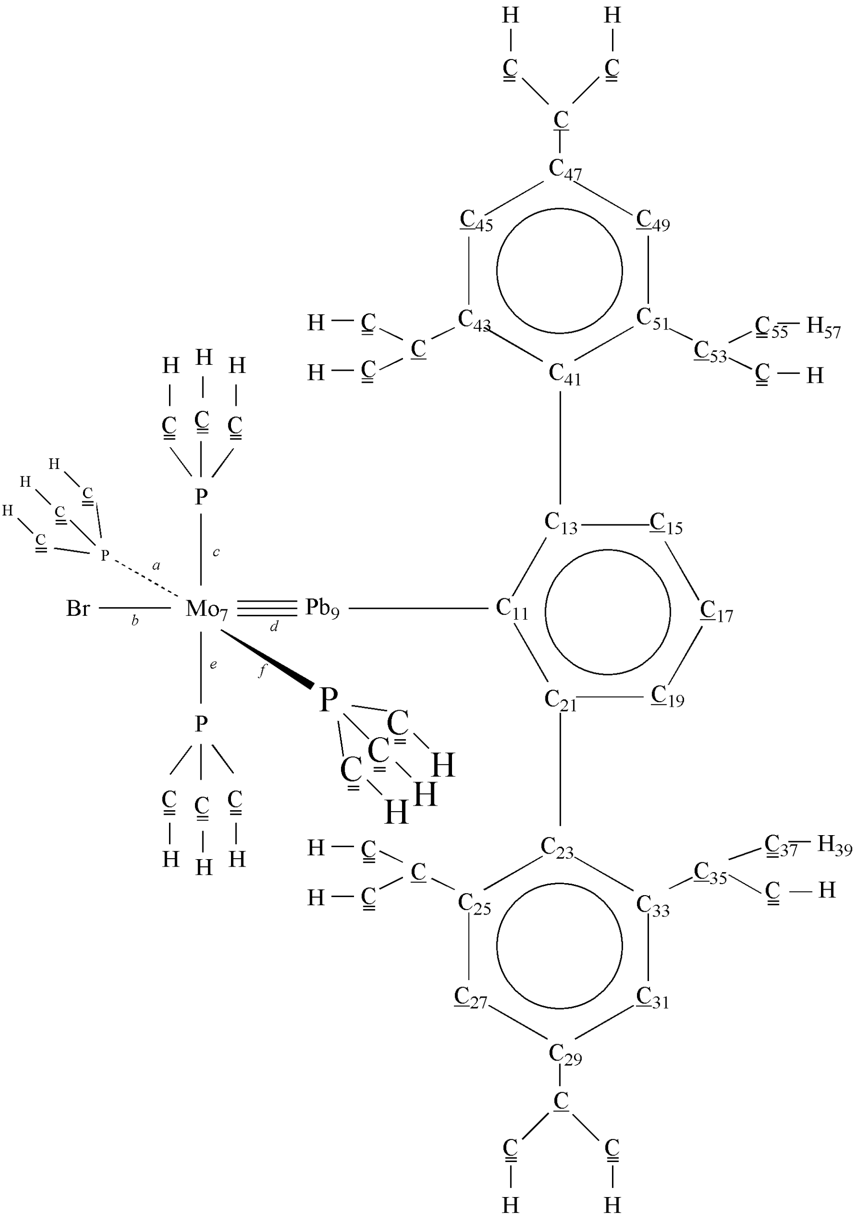

Figure 35: Hexa-coordination (including an atom with a valence of 8) in a recently created molecule containing a triply bonded lead atom

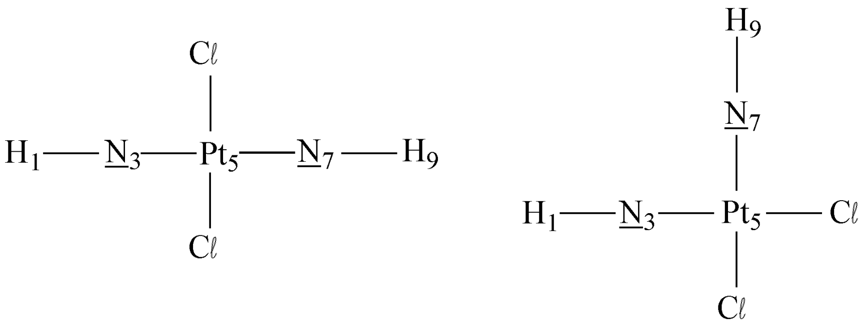

Figure 36: Trans vs. cis dichlorodiaminoplatinum (II)

However, in order to prevent ambiguity, inclusion of descriptors on the entering (a for both isomers) vs. leaving (f for the trans vs. b for the cis) bonds of the coordination six stereocenter is recommended; namely:

$$\mathrm{H1\underline{N}1^{(4a)}Pt1^{(6f)}\underline{N}1H{:}^{(5b,5d)}(1C\ell);^{(5c,5e)}(ep)} \tag{44}$$

and

$$\mathrm{H1\underline{N}1^{(4a)}Pt1^{(6b)}\underline{N}1H{:}^{(5d,5f)}(1C\ell);^{(5c,5e)}(ep)} \tag{45}$$

respectively.

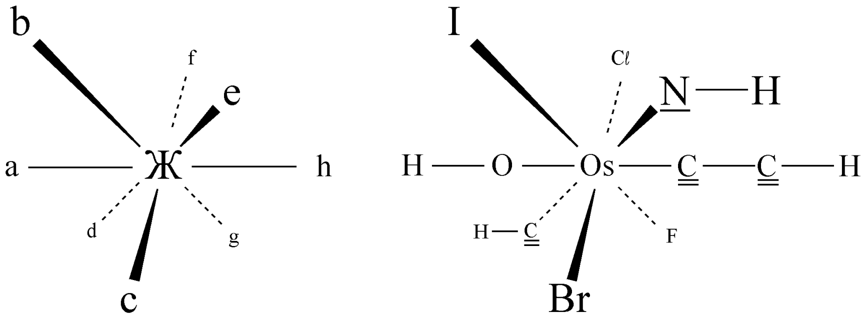

Figure 37: The generic Cartesian locant positioning for octo-coordination with a theoretical example

Returning our focus to the next largest regular polyhedron[16], the cube (V = 8), a standardized model analogous to Figure 34, namely Figure 37, may be created despite that steric considerations make the formation of an eight vertex star rare. This is true since the repulsive Coulomb force between like charged ligands more than counterbalances the attractive Coulomb force between the center atom and the individual ligands. Nevertheless, because such a scenario is not impossible, it is desirable that the applicable nomenclature be included at this point. To do this, one denotes the incoming" ligand (**a)** as lying on the negative X-axis with coordinate = -1, three ligands to the left of the YZ-plane with MD from a = 1 as **b**, **c** and **d**, three more to the right of the YZ-plane (**e**, **f**, and **g**) with MD from a = √2, and the eighth ligand (**h**) along the positive X-axis with coordinate +1 with MD from a = √3. The Cartesian name that would be assigned to such a potential molecule (assuming such an aggregation existed) would be formed from the longest possible chain with either the next to highest priority ligand first and the highest priority ligand last (when these ligands are longer than a single atom as in Figure 31) or vice versa (as would be the case if all of the ligands were only single atoms. For Figure 37, the canonical name is:

$$\mathrm{H1O1Os1(\underline{\underline{C}}1)_2H{:}^{(5b)}(1I);^{(5c)}(1Br);^{(5d)}(1\underline{\underline{C}}1H);^{(5e)}(1\underline{N}1H);^{(5f)}(1C\ell);^{(5g)}(1F)} \qquad (46)$$

The spherical counterpart of (46) lists the stereocenter first (Ж), followed by a colon and then the various ligands according to a different priority scheme. Figure 38 denotes the ligands using Greek, rather than Latin, letters in order to emphasize a different priority algorithm; namely, starting from the stereocenter and ordering by nearest bonds and atoms emanating from this stereocenter, rather than by the length of the chain of atoms comprising the ligand. In other words, α corresponds to the highest atomic number ligand (I) in the theoretical example of Figure 37; β, the largest of the three ligands nearest to α, etc. This produces as the spherical canonical name:

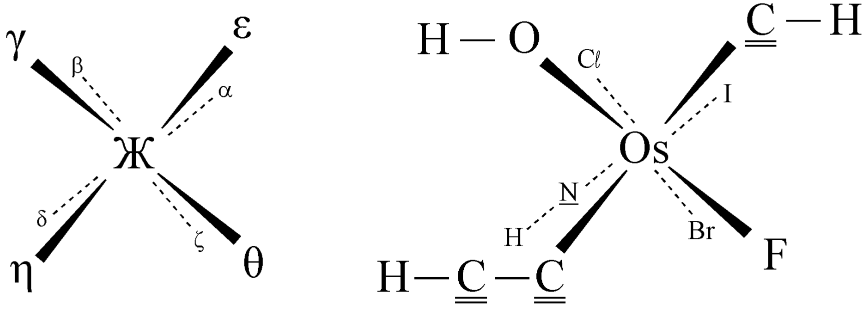

Figure 38: The generic spherical locant positioning for octa-coordination using the theoretical example of Figure 37

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[16] Note that the number of faces of this regular polyhedron is NOT a parameter of importance in this particular chemistry description, only the number of atoms (vertices) and edges (bonds).

$$\mathrm{Os}:^{(1\alpha)}(1\mathrm{I});^{(1\beta)}(1\mathrm{C}\ell);^{(1\gamma)}(1\mathrm{O}1\mathrm{H});^{(1\delta)}(1\underline{\mathrm{N}}1\mathrm{H});^{(1\varepsilon)}(1\underline{\underline{\mathrm{C}}}1\mathrm{H});^{(1\zeta)}(1\mathrm{Br});^{(1\eta)}[1(\underline{\underline{\mathrm{C}}}1)_2\mathrm{H}];\ ^{(1\theta)}(1\mathrm{F}) \tag{47}$$

Perhaps, a more viable octa-coordinated atom might be achievable by saturating the triple molybdenum-lead bond in Figure 35; however, even then the probability of encountering isomerism is minimal, inasmuch as one would also have to have not repeated ligands . Meanwhile one observes that, although there do exist some coordination = 5 and even some coordination = 6 carbon atoms[20], it is beyond the capacity of classical “organic” chemistry for an octahedral star to exhibit stereoisomerism. On the other hand, the possibility of producing some “inorganic” atom, such as osmium, with eight different ligands, although seemingly remote, can not be ignored. Consequently, ***AT PRESENT***, it would probably be viewed as pedantry to further develop this extension to the chemical nomenclature.

On the other hand, octa-coordination in a cage, rather than a star configuration is readily viable. For example, the vertex carbon atoms of cubane each have a valence = 4, but have used only three of these bonds to form the cage; consequently each of the fourth bonds is available for further bonding. In other words, it is desirable to nomenclate the various stereoisomers formed when seven or eight different ligands replace the hydrogen atoms on a molecule of cubane. The systematic development of a canonical name that differentiates each of the 1680 stereoisomers (840 pairs supplemented with an R or an S of conventional IUPAC nomenclature) was formulated earlier[21]. This name is predicated on the assumption that each of the ligands is external to the cage. Consequently, as above, the total number of stereoisomers for a hepta- or octa-substituted cubane (with all different ligands) is increased by a factor of $2^8 = 256$. In other words, 430,080 different stereoisomers are theoretically possible, even though, from a strictly steric consideration, at most one (or maybe two) ligands could be interior to the cage, rather than the mathematically possible scenario in which all eight ligands are interior. As above, each interior ligand will have its superscript addended with an *i*.

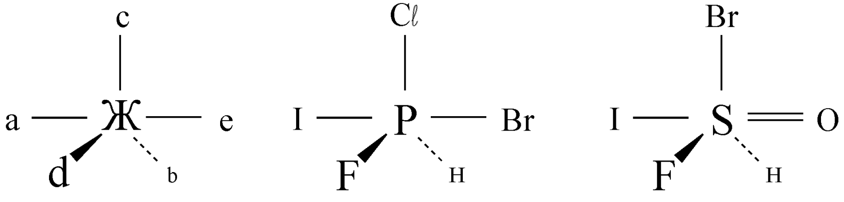
Continuing to the last two of the regular polyhedra, for reasons identical to the above for smaller Platonic solids, only icosa-coordination of the dodecahedral cage [22] is of current interest to chemistry. Moreover, upon considering the possibility of interior as well as exterior ligands in a cage compound, even the enormously large number ($>4 * 10^{16}$) of potential stereoisomers indicated in that report as being mathematically viable is too small by a factor of 2^{20}. Consequently, one could theoretically differentiate between each of the greater than $4 * 10^{22}$ such stereoisomers using the above described techniques.

12. NOMENCLATING MOLECULES MODELED BY NON-REGULAR POLYHEDRA

A logical, but highly impractical (even with the most modern, sophisticated computing facilities) extension of the previous paragraph would be to examine the various stereoisomers of the fulleranes, with its astronomically large number of potential isomers. Instead, our focus is returned to the more mundane nomenclature problem of assigning canonical names to selected molecules whose geometrical structure is described using a non-regular polyhedron: In particular, attention is focused on molecules containing coordinating atoms having five or seven different ligands (i.e., star) or a coordinating cage with this number of "leaves"[17]. For these, as well as for all other numbers of ligands besides the five associated with the vertices of a regular polyhedron, precisely because there does not exist a static, stable orientation of ligands about a central atom, other strategies need to be adopted. Two familiar ones are: polymerization and ionization[23]. Examples of these (which do not involve stereoisomerism) include polymerization to bypass the non-existence of a five vertex regular polyhedron in the oxides of phosphorus (see Chapter 3 of Reference #1) and ionization of iodine heptafluoride (see Chapter 7 of Reference #1). The need to include stereoisomer descriptors when nomenclating such molecules arises ***only if*** all, or all but one, of the oxygen or fluorine atoms were to be replaced by distinguishable isotopes or other atoms.

For a coordination of five, two important geometries are suggested with the assumption that they are in a state of constant pseudo-rotation[24,25]; namely, the instantaneous geometry is either a trigonal bipyramid or a square pyramid. Consequently. the best that one can do is to nomenclate one or more of the various conformers:

(1) The Cartesian model for the trigonal bipyramidal conformer (Figure 33) differs from Figure 28 only in that there are now three (not four) ligands in the YZ-plane. Moreover, there are ten ways in which the five ligands can occupy the axial positions and two ways that the three equatorial ligands can be oriented (clockwise and counterclockwise). In order to maintain consistency with the standardized model for hexa-coordination, the standardized model for penta-coordination positions the larger of the two axial ligands ahead of the equatorial YZ plane, designated with *a*, and the other axial ligand behind the equatorial plane and designated by *e*. Figure 39 illustrates the generic trigonal bipyramid and two theoretical examples. A tabulation of the twenty Cartesian canonical names of the example having a penta-coordinating central atom with



a. Generic

b. A theoretical pentavalent example

c. A theoretical hexavalent example

Figure 39: Penta-coordination in the form of a trigonal bipyramidal orientation

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[17] Although the word "leaf" (see chapter 1 of Reference #1) in graph theory is traditionally applied only to trees (non-cyclic graphs), the concept is readily extended to any vertex connected to a "block" such that deletion of the connecting edge partitions the graph into that single vertex and a smaller connected graph)

Table 2
Example of the canonical Cartesian names for a theoretically possible penta-coordinated bi-pyramidal (phosphorus) molecule having five different ligands

	Ligand located at position					Cartesian canonical name
	axial		equatorial			
	a	b	c	d	e	
(1)	I	Br	Cℓ	F	H	$\mathrm{I}^{(a)}1\mathrm{P}1\mathrm{Br}^{(b)}:{}^{(3c)}(1\mathrm{C}\ell);{}^{(3d)}(1\mathrm{F});{}^{(3e)}(1\mathrm{H})$
(2)	I	Br	Cℓ	H	F	$\mathrm{I}^{(a)}1\mathrm{P}1\mathrm{Br}^{(b)}:{}^{(3c)}(1\mathrm{C}\ell);{}^{(3e)}(1\mathrm{F});{}^{(3d)}(1\mathrm{H})$
(3)	I	Cℓ	Br	F	H	$\mathrm{I}^{(a)}1\mathrm{P}1\mathrm{Br}^{(c)}:{}^{(3b)}(1\mathrm{C}\ell);{}^{(3d)}(1\mathrm{F});{}^{(3e)}(1\mathrm{H})$
(4)	I	Cℓ	Br	H	F	$\mathrm{I}^{(a)}1\mathrm{P}1\mathrm{Br}^{(c)}:{}^{(3b)}(1\mathrm{C}\ell);{}^{(3e)}(1\mathrm{F});{}^{(3d)}(1\mathrm{H})$
(5)	I	F	Br	Cℓ	H	$\mathrm{I}^{(a)}1\mathrm{P}1\mathrm{Br}^{(c)}:{}^{(3d)}(1\mathrm{C}\ell);{}^{(3b)}(1\mathrm{F});{}^{(3e)}(1\mathrm{H})$
(6)	I	F	Br	H	Cℓ	$\mathrm{I}^{(a)}1\mathrm{P}1\mathrm{Br}^{(c)}:{}^{(3e)}(1\mathrm{C}\ell);{}^{(3b)}(1\mathrm{F});{}^{(3d)}(1\mathrm{H})$
(7)	I	H	Br	Cℓ	F	$\mathrm{I}^{(a)}1\mathrm{P}1\mathrm{Br}^{(c)}:{}^{(3d)}(1\mathrm{C}\ell);{}^{(3e)}(1\mathrm{F});{}^{(3b)}(1\mathrm{H})$
(8)	I	H	Br	F	Cℓ	$\mathrm{I}^{(a)}1\mathrm{P}1\mathrm{Br}^{(c)}:{}^{(3e)}(1\mathrm{C}\ell);{}^{(3d)}(1\mathrm{F});{}^{(3b)}(1\mathrm{H})$
(9)	Br	Cℓ	I	F	H	$\mathrm{I}^{(c)}1\mathrm{P}1\mathrm{Br}^{(a)}:{}^{(3b)}(1\mathrm{C}\ell);{}^{(3d)}(1\mathrm{F});{}^{(3e)}(1\mathrm{H})$
(10)	Br	Cℓ	I	H	F	$\mathrm{I}^{(c)}1\mathrm{P}1\mathrm{Br}^{(a)}:{}^{(3b)}(1\mathrm{C}\ell);{}^{(3e)}(1\mathrm{F});{}^{(3d)}(1\mathrm{H})$
(11)	Br	F	I	Cℓ	H	$\mathrm{I}^{(c)}1\mathrm{P}1\mathrm{Br}^{(a)}:{}^{(3d)}(1\mathrm{C}\ell);{}^{(3b)}(1\mathrm{F});{}^{(3e)}(1\mathrm{H})$
(12)	Br	F	I	H	Cℓ	$\mathrm{I}^{(c)}1\mathrm{P}1\mathrm{Br}^{(a)}:{}^{(3e)}(1\mathrm{C}\ell);{}^{(3b)}(1\mathrm{F});{}^{(3d)}(1\mathrm{H})$
(13)	Br	H	I	F	Cℓ	$\mathrm{I}^{(c)}1\mathrm{P}1\mathrm{Br}^{(a)}:{}^{(3d)}(1\mathrm{C}\ell);{}^{(3b)}(1\mathrm{F});{}^{(3e)}(1\mathrm{H})$
(14)	Br	H	I	Cℓ	F	$\mathrm{I}^{(c)}1\mathrm{P}1\mathrm{Br}^{(a)}:{}^{(3d)}(1\mathrm{C}\ell);{}^{(3e)}(1\mathrm{F});{}^{(3b)}(1\mathrm{H})$
(15)	Cℓ	F	I	Br	H	$\mathrm{I}^{(c)}1\mathrm{P}1\mathrm{Br}^{(d)}:{}^{(3a)}(1\mathrm{C}\ell);{}^{(3b)}(1\mathrm{F});{}^{(3e)}(1\mathrm{H})$
(16)	Cℓ	F	I	H	Br	$\mathrm{I}^{(c)}1\mathrm{P}1\mathrm{Br}^{(e)}:{}^{(3a)}(1\mathrm{C}\ell);{}^{(3b)}(1\mathrm{F});{}^{(3d)}(1\mathrm{H})$
(17)	Cℓ	H	I	F	Br	$\mathrm{I}^{(c)}1\mathrm{P}1\mathrm{Br}^{(e)}:{}^{(3a)}(1\mathrm{C}\ell);{}^{(3d)}(1\mathrm{F});{}^{(3b)}(1\mathrm{H})$
(18)	Cℓ	H	I	Br	F	$\mathrm{I}^{(c)}1\mathrm{P}1\mathrm{Br}^{(d)}:{}^{(3a)}(1\mathrm{C}\ell);{}^{(3e)}(1\mathrm{F});{}^{(3b)}(1\mathrm{H})$
(19)	F	H	I	Br	Cℓ	$\mathrm{I}^{(c)}1\mathrm{P}1\mathrm{Br}^{(d)}:{}^{(3e)}(1\mathrm{C}\ell);{}^{(3a)}(1\mathrm{F});{}^{(3b)}(1\mathrm{H})$
(20)	F	H	I	Cℓ	Br	$\mathrm{I}^{(c)}1\mathrm{P}1\mathrm{Br}^{(e)}:{}^{(3d)}(1\mathrm{C}\ell);{}^{(3a)}(1\mathrm{F});{}^{(3b)}(1\mathrm{H})$

the five ligands being the four halide atoms and hydrogen is given in Table 2. Because in each of these conformations the GTD between ligands is always 2, we tabulate the longest MD (between axial ligands) before the colon and the remaining ligands to the coordinating atom after the colon and separated by semicolons. Likewise, the punctuation chosen to differentiate the various square pyramidal conformations positions the colon separating the axial ligand from the remaining four equatorial ligands, with the same orientation as in Figure 38. The thirty canonical Cartesian names for these conformers is given in Table 3.

Although it might seem logical to continue in the systematic development of the canonical nomenclature by next examining molecules having one or more atoms with coordination = 7, neither the pentagonal bipyramid, nor even worse the hexagonal pyramid, are suitable models for minimizing Coulomb repulsions between seven like ligands about a central atom.

Table 3
Example of the canonical Cartesian names for a theoretically possible penta-coordinated square-pyramidal (phosphorus) molecule having five different ligands

	Ligand located at position					Cartesian canonical name
	apical	equatorial				
	a	b	c	d	e	
(21)	I	Br	F	Cℓ	H	$I^{(a)}P{:}^{(3b)}(1Br);^{(3d)}(1C\ell);^{(3c)}(1F);^{(3e)}(1H)$
(22)	I	Br	H	Cℓ	F	$I^{(a)}P{:}^{(3b)}(1Br);^{(3d)}(1C\ell);^{(3e)}(1F);^{(3c)}(1H)$
(23)	I	Br	Cℓ	F	H	$I^{(a)}P{:}^{(3b)}(1Br);^{(3c)}(1C\ell);^{(3d)}(1F);^{(3e)}(1H)$
(24)	I	Br	H	F	Cℓ	$I^{(a)}P{:}^{(3b)}(1Br);^{(3e)}(1C\ell);^{(3d)}(1F);^{(3c)}(1H)$
(25)	I	Br	Cℓ	H	F	$I^{(a)}P{:}^{(3b)}(1Br);^{(3c)}(1C\ell);^{(3e)}(1F);^{(3d)}(1H)$
(26)	I	Br	F	H	Cℓ	$I^{(a)}P{:}^{(3b)}(1Br);^{(3e)}(1C\ell);^{(3c)}(1F);^{(3d)}(1H)$
(27)	Br	I	F	Cℓ	H	$Br^{(a)}P{:}^{(3b)}(1I);^{(3d)}(1C\ell);^{(3c)}(1F);^{(3e)}(1H)$
(28)	Br	I	H	Cℓ	F	$Br^{(a)}P{:}^{(3b)}(1I);^{(3d)}(1C\ell);^{(3e)}(1F);^{(3c)}(1H)$
(29)	Br	I	Cℓ	F	H	$Br^{(a)}P{:}^{(3b)}(1I);^{(3c)}(1C\ell);^{(3d)}(1F);^{(3e)}(1H)$
(30)	Br	I	H	F	Cℓ	$Br^{(a)}P{:}^{(3b)}(1I);^{(3e)}(1C\ell);^{(3d)}(1F);^{(3c)}(1H)$
(31)	Br	I	Cℓ	H	F	$Br^{(a)}P{:}^{(3b)}(1I);^{(3c)}(1C\ell);^{(3e)}(1F);^{(3d)}(1H)$
(32)	Br	I	F	H	Cℓ	$Br^{(a)}P{:}^{(3b)}(1I);^{(3e)}(1C\ell);^{(3c)}(1F);^{(3d)}(1H)$
(33)	Cℓ	I	F	Br	H	$C\ell^{(a)}P{:}^{(3b)}(1I);^{(3d)}(1Br);^{(3c)}(1F);^{(3e)}(1H)$
(34)	Cℓ	I	H	Br	F	$C\ell^{(a)}P{:}^{(3b)}(1I);^{(3d)}(1Br);^{(3e)}(1F);^{(3c)}(1H)$
(35)	Cℓ	I	Br	F	H	$C\ell^{(a)}P{:}^{(3b)}(1I);^{(3c)}(1Br);^{(3d)}(1F);^{(3e)}(1H)$
(36)	Cℓ	I	H	F	Br	$C\ell^{(a)}P{:}^{(3b)}(1I);^{(3e)}(1Br);^{(3d)}(1F);^{(3c)}(1H)$
(37)	Cℓ	I	Br	H	F	$C\ell^{(a)}P{:}^{(3b)}(1I);^{(3c)}(1Br);^{(3e)}(1F);^{(3d)}(1H)$
(38)	Cℓ	I	F	H	Br	$C\ell^{(a)}P{:}^{(3b)}(1I);^{(3e)}(1Br);^{(3c)}(1F);^{(3d)}(1H)$
(39)	F	I	Cℓ	Br	H	$F^{(a)}P{:}^{(3b)}(1I);^{(3d)}(1Br);^{(3c)}(1C\ell);^{(3e)}(1H)$
(40)	F	I	H	Br	Cℓ	$F^{(a)}P{:}^{(3b)}(1I);^{(3d)}(1Br);^{(3e)}(1C\ell);^{(3c)}(1H)$
(41)	F	I	Br	Cℓ	H	$F^{(a)}P{:}^{(3b)}(1I);^{(3c)}(1Br);^{(3d)}(1C\ell);^{(3e)}(1H)$
(42)	F	I	H	Cℓ	Br	$F^{(a)}P{:}^{(3b)}(1I);^{(3e)}(1Br);^{(3d)}(1C\ell);^{(3c)}(1H)$
(43)	F	I	Br	H	Cℓ	$F^{(a)}P{:}^{(3b)}(1I);^{(3c)}(1Br);^{(3e)}(1C\ell);^{(3d)}(1H)$
(44)	F	I	Cℓ	H	Br	$F^{(a)}P{:}^{(3b)}(1I);^{(3e)}(1Br);^{(3c)}(1C\ell);^{(3d)}(1H)$
(45)	H	I	Cℓ	Br	F	$H^{(a)}P{:}^{(3b)}(1I);^{(3d)}(1Br);^{(3c)}(1C\ell);^{(3e)}(1F)$
(46)	H	I	F	Br	Cℓ	$H^{(a)}P{:}^{(3b)}(1I);^{(3d)}(1Br);^{(3e)}(1C\ell);^{(3c)}(1F)$
(47)	H	I	Br	Cℓ	F	$H^{(a)}P{:}^{(3b)}(1I);^{(3c)}(1Br);^{(3d)}(1C\ell);^{(3e)}(1F)$
(48)	H	I	F	Cℓ	Br	$H^{(a)}P{:}^{(3b)}(1I);^{(3e)}(1Br);^{(3d)}(1C\ell);^{(3c)}(1F)$
(49)	H	I	Br	F	Cℓ	$H^{(a)}P{:}^{(3b)}(1I);^{(3c)}(1Br);^{(3e)}(1C\ell);^{(3d)}(1F)$
(50)	H	I	Cℓ	F	Br	$H^{(a)}P{:}^{(3b)}(1I);^{(3e)}(1Br);^{(3c)}(1C\ell);^{(3d)}(1F$

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