

## Topological Considerations Subtly Inherent in the Formation and Subdivision of Fused vs. Bridged Ring Compounds

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Exploration of what common elements should be used for taxonomy purposes is undertaken by employing the standard IUPAC system in conjunction with the geometrical descriptive properties of paddlanes and propellanes. Such an exploration leads to a reexamination of the concepts, both stated and implied, in the dichotomy between compounds that are classified as "fused" vs. "bridged" and also between compounds classified as "ortho-fused" vs. "ortho- and peri-fused". In this process the foundations of undefined words in a language are probed, with emphasis on the difference between words that may be designated as "primitive" vs. "ill-defined". Also, the difference between geometrical models and the actual physics being modeled becomes pronounced, with the geometrical model inevitably resulting in an oversimplified picture, which, in turn, forms the foundation for distorted descriptions of these compounds.

Exactly one topological model—which was apropos for most of the earlier (simpler) compounds that had been discovered—underlies nearly all of the traditional taxonomy processes for subdividing ring systems. This topological model is a plane or, more precisely, a projection onto a planar surface. The manifestation of this model was formalized in the postulation of SSSR (smallest set of smallest rings)—where smallest ring takes precedence over smallest set.<sup>1,2</sup> However, because of the formulation, during the past few decades, of many compounds that were once considered unimaginable and the ability to create compounds of theoretically inspired geometry, this perspective is seen to be grossly inadequate. Furthermore, fundamental problems have been shown to be associated with the use of SSSR.<sup>3</sup> Consequently, a reexamination of the problem is required.

In order to better manage information about compounds containing ring systems (description, taxonomy, nomenclature, etc.), one important question arises, How many different basic models need to be considered? Because of the vast number of presently known, different types of compounds, the specification of a different model for each type of compound becomes unwieldy. Therefore, it is desirable to be able to group compounds according to some set of what may be called "essential common properties". However, the selection of what common properties are essential in order to define such unifying classes involves, as it must, a great degree of heuristic reasoning—where to draw the dividing lines between classes.

This article focuses on the standard system used by IUPAC<sup>4</sup> for purposes of ring taxonomy and two particular classes of compounds that are, at best, ill-defined by such a system.<sup>5</sup> However, before an examination of this system can be made, it is necessary to clarify and subdivide the class of undefined words.

Undefined words are a necessary part of any system. This is true since words can only be defined in terms of other words. Thus some starting, or "primitive", words must be accepted as understood; otherwise, there is no way of defining anything. Note that a primitive word in one system may be a word that has a precise definition in another system. Which words you choose as primitive depends on your individual bias. For example, a "line" might be undefined (as was assumed by Euclid) or else may be defined as a "one-dimensional homoloidal manifold", where the terms "dimension", "homoloidal", and "manifold" are considered more primitive than "line". In other words, it is a heuristic decision what is the base of knowledge, and thus reference.

A word is considered "well-defined" in mathematical logic if it divides the set in question into exactly two disjoint subsets—one having the property and the other not having that

property. Every "knowledgeable"<sup>6</sup> person confronted by this word should have an identical understanding of it; i.e., there are NO excluded cases and also NO cases both having and not having this property simultaneously. Any word allowing ambiguity is "ill-defined". The demarcation line as to what words are well-defined vs. ill-defined is based on a set of heuristic assumptions that hopefully will be the same set for both the speaker and the listener; however, such an intersection cannot be guaranteed. For example, assuming that the word figure is well-defined in geometry, all attempts to delineate what is a simple figure are doomed to failure. Many properties that you would expect in a simple figure are, in fact, well-defined, such as simply closed, simply connected, orientable, etc.; however, the overall picture is far from clear. Before we are ready to apply the above discussion of the different connotations of undefined words to "ortho-fused", "ortho- and peri-fused" and "bridged" ring systems, let us first consider what meaning is to be connoted by the words "fused" and "bridged".

(a) Fused: An undefined (primitive) word based on the assumption that rings are joined by sharing a common edge, i.e., bond (and consequently sharing the two adjacent vertices, i.e., atoms).

(b) Bridged: An undefined (ill-defined) word describing compounds having a "valence bond or an atom or an unbranched chain of atoms connecting two different parts of a molecule".<sup>7</sup>

Observe the fuzzy line of demarcation between these two words. For example, a collection of atoms joined in a single ring and also having one valence bond between two nonadjacent atoms (Figure 1) or else having a connected chain of atoms between two nonadjacent atoms (Figure 2) may be viewed as either (1) a set of two rings fused together or (2) a single ring that has been bridged.

Also note that, irrespective of how this fused or bridged common pathway in a compound was formed, the taxonomy classification of this compound was supposed to be based solely on the final configuration; namely, the dividing line between fused vs. bridged should be the presence of two vs. more than two atoms along the common path. By this perspective Figure 1 would be relegated to the category of fused and Figure 2 to bridged. In practice, however, because (among other things) of the lack of a precise line segregating tautomer, conformer, resonance structure, and transition state, the taxonomy scheme that evolved was wed to previous biases. For example, the resonance form of benzene having a central bond (Figure 3) was, for a long time, not recognized as being a fused bicyclic compound with chemical properties far remote from those of benzene. Instead, it was regarded as a bridged compound with

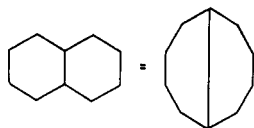


Figure 1.

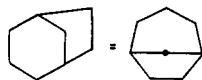


Figure 2.

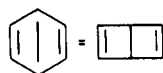


Figure 3.



Figure 4.

the common name of Dewar benzene. In this way it maintained its supposed relation to the more familiar compound (benzene) while simultaneously not negating its similarity to cross-bonded structures (Figure 4). This is equivalent to stating that a trivial name profoundly influenced the thinking of chemists with regard to chemical taxonomy.

Furthermore, it should be noted that this type of fiction is perpetuated even to this date in IUPAC nomenclature. For example, the smallest fused compound described anywhere in IUPAC's rules (A-21.2 and A-21.3)<sup>8</sup> is pentalene—a compound containing two more carbon atoms in the skeleton than does Dewar benzene and four more than the theoretical minimum: bicyclo[1.1.0]butane.

The rationale for such a choice lay not only in the historical bias to five- and six-membered rings but also in the fact that the word "fused" was never clarified—instead, it kept its primitive (undefined and thus intuitive) connotation. This had the concomitant advantage that for any number of successively fused rings and also for exactly two bridged rings such a compound can be represented by a purely coplanar picture, even though a realistic geometrical picture of such a compound is one in which these rings are highly puckered, i.e., noncoplanar. Nevertheless, IUPAC Rules A-21-A-31<sup>9</sup> view all compounds described therein as though they were, in fact, planar in the physical world. For bridged hydrocarbons containing three or more rings, on the other hand (from Rule A-32 on),<sup>10</sup> the perspective abruptly shifts to a three-dimensional one.

With the above set of biases in mind, and with the desire to be more precise in subdividing and naming compounds, let us focus attention on the two classes of compounds referred to as paddlanes<sup>11</sup> and propellanes<sup>12</sup> (Figures 5 and 6). Examining Figure 5, one may view the "global model" of a paddlane as two intersecting rings with the common set being two nonadjacent atoms. If one wanted to maintain the SSSR description, this can be done by giving precedence to SS (the smallest set of covering rings in this case is two) over SR, instead of the usual order; however, little is gained by such an ad hoc solution.

Next notice that, using such an inversion of perspective with respect to SSSR, it would be possible to envision propellanes as being formed by two intersecting rings with the common set being two adjacent atoms (and consequently their common bond); however, such an interpretation is almost as distorted as the planar picture using the usual SSSR. Instead, a global picture of three semicircles in a three-dimensional embedding space sharing a common diameter is more appropriate, as may

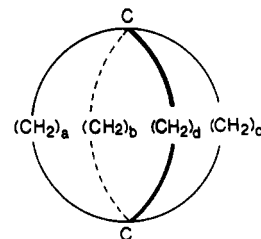


Figure 5.

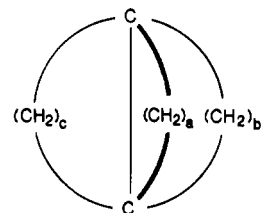


Figure 6.

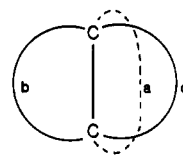


Figure 7.

be seen by examining Figure 6.

In the physical world, however, even the above global model descriptions are oversimplifications. In a large enough (unstrained) propellane, the three chains emanating from the tetravalent carbon atoms are, more realistically, geometrically located above the plane perpendicular to the axis formed by the two tetravalent carbon atoms and containing one of these tetravalent carbon atoms (Figure 7). When these chains are long enough to avoid strain (geometrical distortion), the assumption of tetrahedral orientation (i.e.,  $109^\circ 28'$ ) at the tetravalent carbon atoms is a good one. Therefore, instead of the rigidity and ordering of the chains, as implied in Figure 6, a dynamic equilibrium exists in which the relative positioning of the individual methylene chains is frequently interchanged—much as in the case of two jump ropes of different lengths held together pairwise at the ends and being twirled (in either the same or opposite direction). Similarly, even for a paddlane, the presence of all four bonds on the same side of any plane through one of the tetravalent carbon atoms—with its intuitive mating of semicircles to form a complete circle (as implied by Figure 5)—is unlikely. This, however, does not negate the interpretation of intersecting rings. Rather, because each path between the tetravalent carbon atoms is noncoplanar, all three permutations of pairing "half-circles" must be examined. This is in contradistinction to the oversimplified picture, which allows for the intuitive pairing that occurs with a set of two simple convex planar polygons. Note that the presence of tetrahedral ( $109^\circ 28'$ ) angles for the unstrained saturated carbon atoms would tend to form nearly coplanar pentagons (actually coplanar were it not for the presence of the hydrogen atoms of the methylene groups eclipsing one another).<sup>13</sup> Thus if two chains were a single carbon and two carbon atoms, respectively, this would be one of the more desirable pairs of half-rings to consider as a full-ring. The other two pairs, by default, become the "other" intersecting ring. In a similar manner, the association of paths forming a six-membered ring is the next most desirable combination, etc. In other words, the intuition that five- or six-membered rings form a natural affinity is a first choice for selecting which pairs of half-rings should be grouped together

in designating the intersecting rings.

In contrast to both the actual physical picture just described and the intuitive model description given immediately prior, tradition and consistency with other (unrelated) compounds have resulted in the formulation of an interpretation in terms of the union of planar segments that is counterproductive. Because a synthesis of some type of module to form the desired end product is required, in the case of fundamentally three-dimensional compounds such as a paddlane or propellane, let the module chosen be a lune of a sphere, with the vertices of the lune being the tetravalent carbon atoms.

Three different modular pictures now have been alluded to: (1) coplanarity, as modeled by SSSR; (2) purely spherical,<sup>14</sup> such as the intuitive picture of a paddlane; and (3) a hybrid planar-spherical picture, such as the intuitive picture of a propellane.

Before we progress further, it is desirable to determine in what sense these modular pictures are truly different and also whether two, or maybe even all three, of these modular pictures have some essential common properties that should be exploited. Toward this end let us use the term "topological transformation" to denote the mapping of one point set (figure) onto another, with the property that the mapping is (1) biunique (each point on the object corresponds to exactly one point on the image) and (2) continuous in both directions (if the distance between two points on the object approaches zero, then the corresponding distance in the image also approaches zero).<sup>16</sup> Physically, this is equivalent to saying that the object can be stretched or twisted, but not torn or overlapped and rejoined.

At this point it should be noted that, by means of a topological transformation, pictures 2 and 3 are equivalent, but differ from picture 1. An entire sphere is transformable into a 2-sided circle, but NOT into an ordinary circle of only one side. A coplanar model, on the other hand, is topologically transformable into a (1-sided) circle.

With these clarifications in mind, an examination of the definitions of the two disjoint types of fused compounds employed by IUPAC<sup>17</sup> is in order.

(c) Ortho-fused: "Polycyclic compounds in which two rings have two, and only two, atoms in common". This definition is followed by the sentence: "such compounds have  $n$  common faces and  $2n$  common atoms".

(d) Ortho- and peri-fused: "Polycyclic compounds in which one ring contains two, and only two, atoms in common with each of two or more rings of a continuous series of rings". It, too, is followed by a statement: "Such compounds have  $n$  common faces and less than  $2n$  common atoms".

Whether these follow-on sentences are to be considered as a part of the definition or a statement of clarification in the general case is of more than trivial interest inasmuch as they contain a built-in bias toward one particular topological system (the projection onto a plane)<sup>18</sup>—in preference to any essentially three-dimensional one, which would be more relevant.

This built-in bias resides first in the word "face" with its implication of planarity.<sup>19</sup> Notice that the graph-theoretical concept being described is one of an edge of a, usually skew, polygon. Second, the word "common" refers to atoms in pairs, irrespective of any commonality in triplets, etc. A third problem area also exists in the intended interpretation of the word "continuous".

Although, from a formal logic perspective, one might take exception to applying the terms "ortho-fused" and "ortho- and peri-fused" to compounds that have not been unambiguously accepted as being fused, the definitions given by IUPAC do not make such a limitation. Instead, because there is no clear delineation as to whether a given compound is fused, there are two logical alternatives:

(1) Reserve these two terms for only the traditionally accepted "fused compounds" (which, according to IUPAC's Rules A-21–A-28 appear to be either conjugated systems or else hydrogenated systems whose parents<sup>20</sup> are conjugated).

(2) Accept the formal definitions given above—without regard to whether the definitions of these terms are internally consistent with the heuristics of fused.

Using the first alternative, consistency dictates that we evade the issue by not considering compounds such as paddlanes and propellanes—a scientifically nonviable course of action. Therefore, let us look to the second alternative.

This second alternative is probed by answering the set of four questions posed by the two definitions (c and d) and the two classes of figures (paddlanes and propellanes):

QUESTION 1: Are the rings in a propellane ortho-fused?

ANSWER: It is true that each pair of two rings has only one common face and two common atoms. This, however, is not equivalent to saying that the totality of rings in the compound has  $n = 1$  common faces and  $2n = 2$  common atoms. While it is true that each pair of rings has these properties, no technique was anticipated for counting a vertex or edge common to three rings in the broad category of fused. All such compounds were relegated to the category of bridged rings. In other words, if we are willing to overlook this difficulty, there are at least two valid interpretations: (1) There are exactly one edge and two atoms in common. (2) There are exactly three edges (all overlapping) and six vertices (overlapping in triplets). Note that both with and without the qualifying sentence, propellanes are strictly ortho-fused.

QUESTION 2: Are the rings in a propellane ortho- and peri-fused?

ANSWER: Select any one ring as "primary". This ring does contain two, and only two, atoms in common with each of the other rings; also, the rings are, in fact, a continuous series of rings—despite the fact that the continuity is about a common line, rather than lying in a common plane. This is equivalent to saying that the first requirement is fulfilled BUT in a way that is different from what had been anticipated. The follow-on statement, on the other hand, is NOT fulfilled inasmuch as there are exactly  $2n$  common atoms, rather than less than  $2n$ . In other words, the answer to the stated question is predicated upon the inclusion or omission of the qualifying sentence.

QUESTION 3: Are the rings in a paddlane ortho-fused?

ANSWER: Taking the above-described global picture without the follow-on sentence, these intersecting rings have only the tetravalent carbon atoms in common. Consequently, the answer is positive. HOWEVER, with the follow-on sentence, there are zero common faces, i.e.,  $n = 0$ , and there are two common atoms, i.e.,  $n = 1$ . Since there does not exist a consistent value for  $n$ , the answer to this question must be negative.

QUESTION 4: Are the rings in a paddlane ortho- and peri-fused?

ANSWER: By the perspective of exactly two rings, the basic requirement of three rings is NOT met, thus the answer is unequivocally negative!

Note that despite the strained description of a propellane, in order to make it into a paddlane having one chain of zero additional methylene groups, the answers to questions 1 and 3 and to questions 2 and 4 are not identical. In fact, if one is to use IUPAC terminology, an important consideration is that the concept of peri-fused was intended to include a group of compounds that are fused, not bridged, but are, in some way, different from ortho-fused; i.e., the two definitions (ortho-fused vs. ortho- and peri-fused) were intended to be disjoint. Because of the above, a far more salient question than ANY of the four questions that were asked is "Using these

two selected classes of compounds, have any of the above-described lines of demarcation fulfilled the intent of their definition?", and the unambiguous answer is NO.

An important advance in taxonomy occurred with Balaban and Harary's<sup>22</sup> division of fused compounds into cata- vs. peri-condensed for the limited class of polycyclic aromatic hydrocarbons of ring size six. Note that by this deliberate limitation of focus the problems of consistency are not encountered. A far more profound subtlety, however, is the substitution of the neutral word "condensed" in place of the related, but somehow different, word "fused" and the dropping of "ortho" from both terms. (Notice that bridged compounds could be condensed just as well as could fused compounds.)

In a similar manner, there have been many other techniques, such as Taylor's<sup>23</sup> attempt to create a new understanding of fused by subdividing the class into unifilar, polyfilar, and reticular and Goodson's extension of Taylor's classification by further breaking off another class from the reticular category,<sup>24</sup> which he called fisular.

Although this creation of the fisular category is of significance in that it recognizes the importance of dimension in the general scheme of taxonomy, none of the systems produced to date have recognized and successfully attacked the central topological problem—weaning away from the use of projection onto a plane (with its inherent limitations, as well as its admittedly desirable property of allowing simple representation in the printed media) when a three-dimensional module is required. This is equivalent to asserting that the present system with its good points, as well as its inadequacies, might well become a proper subset<sup>25</sup> of a new expanded system, yet to be formulated, that recognizes the importance of dimension; i.e., the new system will default to approximately the present system when the requisite approximation to coplanarity is fulfilled and will be shunted for compounds such as adamantane and the higher polymantanes<sup>26</sup> in which their chemical properties are formed, in large measure, by their intrinsic geometry.

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- (4) International Union of Pure and Applied Chemistry *Nomenclature of Organic Chemistry*; Pergamon: Oxford, England, 1979; Section A.
- (5) Although this is merely one particular standard and two particular classes of compounds that have been selected for examination, this examination leaves no doubt as to the inadequacy of the presently used system.
- (6) Note that the word "knowledgeable" implies a meta system. In other words, absolute consistency (the desired goal) is an impossibility.
- (7) International Union of Pure and Applied Chemistry *Nomenclature of Organic Chemistry*; Pergamon: Oxford, England, 1979; Section A, p 32 footnote.
- (8) Reference 7, pp 22-25.
- (9) Reference 7, pp 22-33.
- (10) Reference 7, pp 33-38.
- (11) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic: New York, 1978; pp 366-369.
- (12) Reference 11, pp 343-362.
- (13) Reference 11, pp 65.
- (14) Note that the implication of the word "spherical" is that of a two-dimensional surface, in contradistinction to the three-dimensional volume that is enclosed by this surface. The segment enclosed by this boundary<sup>15</sup> is referred to as a ball.
- (15) Elk, S. B. "Topologically Different Models To Be Used as the Basis for Ring Compound Taxonomy". *J. Chem. Inf. Comput. Sci.* **1985**, *25*, 17-22.
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- (17) See ref 4, p 25 footnote.
- (18) See ref 15.
- (19) See ref 1.
- (20) "CAS defines the term Parent Compound as a member of the general class of substances which comprise the fundamental building blocks of CA index nomenclature. Parent Compounds are specific molecules upon which derivation of CA index substances names is based".<sup>21</sup>
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