

Symmetry Guidelines for the Design of Convergent Syntheses. On Narcissistic Coupling and La Coupe du Roi

Santiago Alvarez* and Félix Serratosa*

Contribution from the Departament de Química Inorgànica and Departament de Química Orgànica, Universitat de Barcelona, 08028 Barcelona, Spain. Received February 21, 1991

Abstract: A symmetry point group study of different segmentation patterns for molecules is presented as an aid for their retrosynthetic analysis. Symmetry properties of the target molecule allow the design of synthetic routes using either achiral, homochiral, or heterochiral isometric segments. It is found that chiral molecules can only be dissected into homochiral segments, whereas achiral molecules can only be fragmented into achiral or heterochiral segments in most cases. The only achiral molecules which can be dissected into homochiral segments (la coupe du roi) are those belonging to the C_{nv} or D_{nd} point groups, in two particular dissection modes.

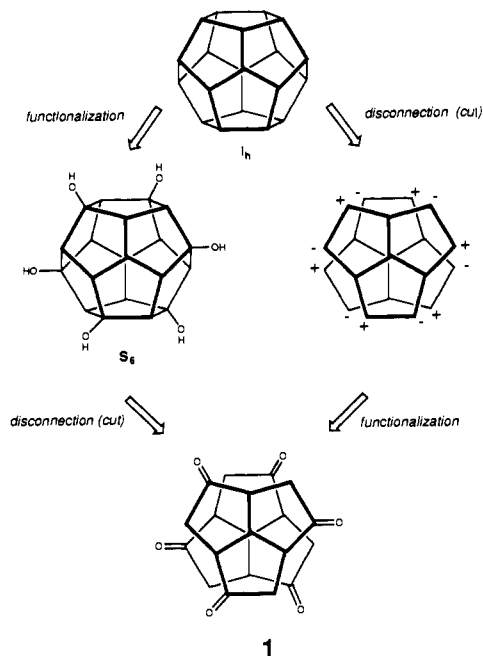
Introduction

The design of a chemical synthesis is based on a retrosynthetic analysis¹ in which the target molecule is conceptually dissected into smaller fragments or *synthons* through the disconnection of bonds. High-symmetry molecules can sometimes be conveniently synthesized by joining together isometric segments^{1,2} through a convergent synthesis.⁴ In this case, the segments may be identical (achiral or *homochiral* segments) or enantiomeric pairs (*heterochiral* segments).

The convergent synthesis from homochiral segments and its reciprocal process, the bisection of an achiral molecule into homochiral fragments, are usually referred to as *la coupe du roi*.³ A recent example of the bisection of a molecule in a *la coupe du roi* mode has been reported by Cinquini et al. for *cis*-3,7-dimethyl-1,5-cyclooctanedione.⁵ On the other hand, the coupling of heterochiral segments to produce an achiral molecule has been named *narcissistic coupling*.⁶ This strategy has two major advantages: it is convergent and reflexive,⁷ and it does not require the resolution of the starting materials into optically pure enantiomers. Such a strategy has been proposed by Serratosa and co-workers⁸ for the synthesis of dodecahedrane.

Once the target molecule has been submitted to retrosynthetic analysis, the different ways in which some of the bonds may be disconnected must be evaluated. A symmetry point group⁹ study should allow us to establish some rules to determine which bond disconnections might lead to achiral, homochiral, or heterochiral segments. The aim of this study is to analyze the different possible disconnections of a molecule into isometric segments according to its symmetry and the relationship between the resulting segments for each case. In what follows, we will consider bond disconnections (or bond *cutting*) as if they were always homolytic. Therefore, a heterolytic bond disconnection between two symmetry-related atoms may be conceptually considered in two

successive steps: some asymmetry ("functionalization") is first introduced into the bond, which is then cut ("disconnection"). Alternatively, the bond is first cut ("disconnection"), and alternate positive and negative charges (indicating the electrophilic and nucleophilic character of the atoms) are assigned to the "disconnected" atoms (in the resulting fragments), which are then properly "functionalized" in order to attain the formal charges assigned. Both approaches are summarized in 1.



Although the methodologies and strategies discussed here have been developed mainly in the area of organic chemistry, the formation of transition metal coordination compounds can be also considered in a similar way. Multinuclear transition metal compounds with either metal-metal bonded skeletons or bridging ligands can also be imagined to be formed by isometric fragments which could eventually undergo self-assembly reactions.

In a slightly different approach, coordination compounds can be considered as *supermolecules* in which the metal ion(s) hold the ligands together. Ligand dissociation can then be considered, within the framework of this paper, as the fragmentation of the complex into isometric segments (the ligands), disregarding the presence of the metal ion(s). An example of such an approach is given by the case of the double helicates synthesized by Lehn and co-workers.¹⁰ Moreover, the bond connection-disconnection terminology and the analysis of the relationships between segments

(1) Corey, E. J. *Q. Rev. Chem. Soc.* **1971**, *25*, 455; *Chem. Soc. Rev.* **1988**, *17*, 111.

(2) Two molecules are isometric if their labeled graphs are the same, i.e., if the atoms and their connectivity (bonds) are the same. See ref 3 and references therein.

(3) Anet, F. A. L.; Miura, S. S.; Siegel, J.; Mislow, K. *J. Am. Chem. Soc.* **1983**, *105*, 1419.

(4) Velluz, L.; Valls, J.; Mathieu, J. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 778. Bertz, S. H. *J. Chem. Soc., Chem. Commun.* **1984**, 218.

(5) Cinquini, M.; Cozzi, F.; Sannicolò, F.; Sironi, A. *J. Am. Chem. Soc.* **1988**, *110*, 4363.

(6) "Narcissistic, from *Narkissos*, youth who fell in love with his reflection in water", *The Oxford English Dictionary* [cf. L. A. Salem, J. Durup, G. Bergeron, D. Cazes, X. Chapuisat, H. Kagan (*J. Am. Chem. Soc.* **1970**, *92*, 4472), "a reaction is defined as narcissistic if reactant(s) and product(s) are mirror images with respect to a fixed plane and if the image of the reactant(s) undergoes the reverse 'reaction' to the image of the product(s)"].

(7) Bertz, S. H. *J. Am. Chem. Soc.* **1982**, *104*, 5801.

(8) Carceller, E.; Garcia, M. L.; Moyano, A.; Pericàs, M. A.; Serratosa, F. *Tetrahedron* **1986**, *42*, 1831.

(9) Cotton, F. A. *Chemical Applications of Group Theory*, 3rd ed.; J. Wiley: New York, 1990.

(10) Lehn, J. M.; Rigault, A.; Siegel, J.; Harrowfield, J.; Chevrier, B.; Moras, D. *Proc. Natl. Acad. Sci. USA* **1987**, *84*, 2565.

could also be applied in template syntheses,¹¹ since the presence of a transition metal ion at the center of symmetry of the molecule does not affect the symmetry of the ligand array (typically a macrocyclic system).

Mislow and co-workers³ have recently examined the problem of dividing finite geometric objects into isometric segments, including the special case of la coupe du roi. Our systematic analysis based on symmetry point groups corroborates some of the statements made by these authors and establishes more general rules and some new conclusions.

Symmetry Relationships between a Molecule and Its Segments

In order to study how the symmetry of a molecule dictates the ways in which it can be isometrically segmented and to define the relative chirality of the resulting segments, the following premises must be first stated.

(1) The molecule belongs to a symmetry point group *G*. When several conformers are possible around the bond to be cut, the highest symmetry conformer will be considered.

(2) If the molecule can be fragmented into isometric segments, these are necessarily related by a symmetry operation *R*, *R* being an element of *G*.

(3) In the general case, the molecule can be fragmented in several different ways, depending on the symmetry operation chosen to define the isometric segments. For each fragmentation pattern, the number of segments produced is thus determined by symmetry.

(4) In order to generate isometric segments, a complete set of bonds related through one of the symmetry operations of *G* must be cut. Notice that in polycyclic molecules it may be necessary to cut more than one set of bonds in order to obtain independent segments. Notice also that a complete set of bonds is not necessarily formed by the *n* bonds related through *C_n*, for example, since there are only *n/m* bonds related through *C_{n/m}*.

(5) The symmetry operation which relates the isometric segments of a molecule is not a symmetry operation of the segments. As a result, the point group of a segment, *S*, is a subgroup of *G*. All of the symmetry operations in *G* can be obtained by successive application of the powers of *R* and the symmetry operations in *S*, i.e., *G* = *S* × *R*.¹² It is obvious that all of the isometric segments belong to the same symmetry group *S*. The special case of molecules of low symmetry with fragments of higher local symmetry, in which *S* might not be a subgroup of *G*, will not be considered in this paper.

(6) If the isometric segments are related by a proper rotation, *C_n*, they are superimposable (i.e., they may be either achiral or homochiral, but never heterochiral).

(7) Chiral segments related in the molecule through an *S_n* operation (including reflections, *S₁*, and inversion, *S₂*) are enantiomers (heterochiral segments).

(8) When a molecule has at least one atom sitting on a symmetry element, nonisometric segments are also necessarily obtained. This is the case of mononuclear coordination compounds, in which dissociation reactions would produce several isometric segments (ligands) plus the central atom.

Dissection Patterns and Molecular Symmetry

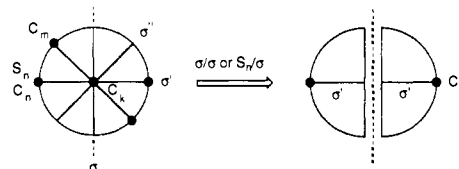
When a molecule is fragmented into isometric segments, the symmetry operation which converts the segments into each other is lost. For the subsequent discussion it is important to know the relationships between the particular dissection pattern applied to

Table I. Effect of Different Dissection Patterns on the Existing Symmetry Operations

| dissection pattern | operations preserved | operations destroyed | operation relating segments |
|--------------------|--|--|-----------------------------|
| σ/σ | σ^\perp, C_n^\perp | $\sigma^\parallel, C_n^\parallel, S_n^\perp, S_n^\parallel, i$ | σ |
| S_n/σ | $C_{n/2}$ (<i>n</i> even), σ^\perp | $C_n^\parallel, S_n^\parallel, S_n^\perp, \sigma^\perp$ | σ |
| C_n/σ_v | σ_v (<i>n</i> odd), σ_h, C_2^\perp | C_n, S_n^\perp | C_n |
| | σ_d (<i>n</i> even), σ_h, C_2^\perp | C_n, σ_v, S_n^\perp | C_n |
| C_2/C_n | C_n^\perp | | C_2 |
| C_n/g | σ_h | C_n, σ_v, σ_d | C_n |
| S_n/gc | $C_{n/2}$ (<i>n</i> even) | S_n, σ_h | σ |
| S_n/g | none | | σ |
| i/i | | <i>i</i> | σ |
| i/g | | <i>i</i> | σ |

the molecule, the symmetry elements that are lost or retained by the segments, and those which remain in each segment. Let us identify each dissection pattern by a symbol of the type *R/p*, where *R* is the symmetry operation which relates the resulting segments and *p* refers to the position of the disconnected bonds relative to the symmetry elements of the molecule. The parameter *p* can be either σ for a bond passing across a symmetry plane (or a pseudosymmetry plane; see below), *C_n* for a bond across a proper rotation axis but not across a symmetry plane, or *g* for a bond in a general position and not passing through a symmetry plane or a proper rotation axis. Other types of positions *p* will be introduced later.

We start by looking at those bond disconnections which split the molecule into two halves. In other words, we cut all of the bonds that go across a reference plane. Any molecule can be idealized as a sphere with some symmetry elements, and its stereographic projection may be represented as in 2. Even if the



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cutting plane is a symmetry plane of the molecule, it is not a symmetry plane of each fragment, i.e., that plane is lost upon cutting. All symmetry elements not perpendicular to the cutting plane (*C_m*, *C_k*, and σ'' in 2) exchange pieces of both fragments, i.e., the associated symmetry operations are lost upon fragmentation. What symmetry elements are retained by the fragments? Only the mirror planes and proper rotation axes perpendicular to the cutting plane are retained (*C_n*, σ' , and the plane of the paper). If a perpendicular improper rotation axis is present (e.g., *S_n* in 2), it is also lost upon cutting since its reflection component converts pieces of both fragments into each other.

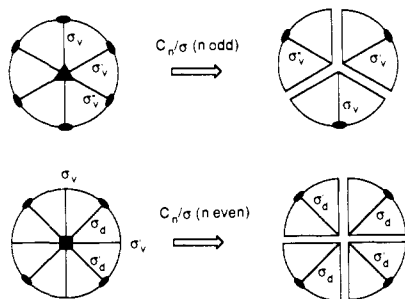
Now, not every plane can be used as a cutting plane. The two fragments are required to be isometric, so they must be related by a symmetry operation. We consider two possible cases: in one, the cutting plane is a symmetry plane, the resulting segments are mirror images of each other, and the dissection pattern will be abbreviated σ/σ in the following. In the second case, the cutting plane is the reflection component of an improper rotation (not necessarily a symmetry plane, but we can consider it as a pseudosymmetry plane), and the dissection strategy should be abbreviated S_n/σ , indicating that the resulting fragments are related in the molecule by the improper rotation *S_n* and that the disconnected bonds cross a pseudosymmetry plane. It is enough to rotate one of the disconnected segments by an angle of $2\pi/n$ to find that it is the mirror image of the other one (i.e., if the segments are disymmetric, they must be heterochiral). The only difference between the σ/σ and S_n/σ cases is that the existence of a pseudosymmetry plane implies a perpendicular improper axis *S_n*. We have already stated that improper rotations are lost when cutting through a plane; a proper rotation *C_{n/2}* colinear with *S_n* must exist

(11) For accounts on template syntheses, see: (a) Melson, G. A., Ed. *Coordination Chemistry of Macrocyclic Compounds*; Plenum: New York, 1979. (b) Black, D. St. C. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Vol. 6, p 155. (c) Healy, M. de S.; Rest, A. J. *Adv. Inorg. Chem. Radiochem.* 1978, 21, 1. (d) Gerbeleu, N. V.; Zhovmir, F. K. *Russ. J. Inorg. Chem.* 1982, 27, 309. (e) Mertes, K. B.; Lehn, J.-M. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Vol. 2, p 915. (f) Vogel, E.; et al. *Angew. Chem., Int. Ed. Engl.* 1988, 27, 406, 409, 411.

(12) For an account of the relationships between symmetry operations in a symmetry point group, see: Hall, L. H. *Group Theory and Symmetry in Chemistry*; McGraw-Hill: New York, 1969.

for even n and a colinear C_n for odd n . Since these proper rotation axes are perpendicular to the cutting plane, they are retained by the fragments. All of this is summarized in Table I.

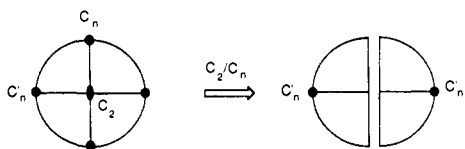
A different strategy consists of splitting the molecules into two or more fragments related by a proper rotation C_n . Let us first study those cases in which there are n symmetry planes containing the rotation axis ($\sigma_v, \sigma_v', \sigma_v'',$ and σ_d in 3). Bonds can then be disconnected across equivalent symmetry planes, i.e., separated by angles of $2\pi/n$, as shown in 3. This strategy is therefore called



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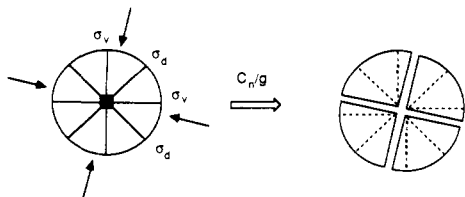
C_n/σ . For odd n , each segment retains one of the σ_v planes. For even n , the σ_v planes are lost, but there are always σ_d planes which are retained by the segments. The proper rotation C_n interconverts the segments, but it is not a symmetry operation of each segment. If there are binary rotation axes at the intersection of the remaining planes and the plane of the paper, they continue to be symmetry operations of the segments. All other rotations are lost upon segmentation. If a σ_h symmetry plane exists in the molecule, each segment will keep such a symmetry plane. Notice that the existence of σ_h together with σ_v implies the existence of C_2 and, conversely, the existence of σ_v and C_2 implies the existence of σ_h . A brief summary of the results for the C_n/σ strategy is presented in Table I.

If the bonds to be cut are not across a symmetry plane but across a C_2 axis, as represented by the stereographic projection 4, a perpendicular axis C_n (if present) is retained in each fragment, but other symmetry elements disappear. In the absence of a symmetry plane, the two isometric segments are related through a C_2 rotation. Hence, these are C_2/C_n dissection patterns.



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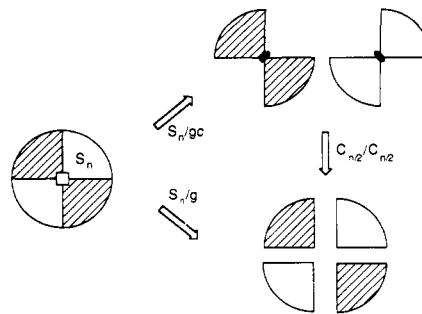
One can also choose to disconnect bonds that are related by a proper rotation C_n but do not cross symmetry planes or axes, which may not even be present in a particular molecule. This is a C_n/g dissection pattern. We can now use the stereographic projection 5 and cut the bonds at the positions indicated by the arrows. It is clear that C_n and the symmetry planes σ_v and σ_d are lost. Other rotation axes are also lost. Only a σ_h plane, if present, remains as a symmetry element of each segment.



5

If we disconnect bonds related by an improper rotation S_n , but not by a perpendicular symmetry plane nor by the coaxial proper

rotation of the same order, the improper rotation and any perpendicular symmetry planes are lost. A $C_{n/2}$ rotation can be preserved, depending on the connectivity of the molecule. In 6, the two shaded pieces (above the plane of the paper) remain connected after dissection, retaining a $C_{n/2}$ rotation, and the same applies for the two white pieces (below the plane of the paper).



6

This will be referred to as an S_n/gc dissection, the *c* referring to the fact that some connectivity between the smallest possible isometric segments remains after dissection. This is what happens if there are two atoms or two bonds sitting on the improper rotation axis. If there are no additional bonds connecting such pieces (the S_n/g pattern), isometric segments result with no symmetry element. Notice that S_n/g is equivalent to the successive application of S_n/gc and $C_{n/2}/C_{n/2}$. Other types of S_n/p dissection patterns will be discussed later during the analysis of the D_{nd} point groups.

When a bond located at a center of inversion is cut and the molecule is split into two segments related *only* through the inversion, this symmetry operation is lost and the resulting segments are mirror images of each other. This dissection pattern is naturally called *i/i*. Similarly, if two bonds related *only* through inversion are cut, in an *i/g* dissection pattern, two mirror-related segments result with no inversion center.

Finally, two geometric restrictions apply to bond cutting: If one or more atoms are sitting on a symmetry element *Q*, neither the *Q/p* nor the *R/Q* dissection is allowed (i.e., they would not produce isometric segments). The above analysis of the relationships between bond disconnections and symmetry operations retained by the segments provides us with most of the information needed to decide which cutting strategy can split a molecule of known symmetry into either achiral, homochiral, or heterochiral segments. In general, for each possible dissection pattern in a particular point group *G*, we can easily identify, from Table I, which symmetry operations are lost and find the point group of the segments, *S*. Also, the dissection pattern chosen determines whether the segments generated are related through a rotation (i.e., superimposable) or mirror images (see Table I). In the following, a systematic study of the results of the above dissection patterns for each family of point groups is presented, together with some examples of applications to real molecules.

Segmentation of Chiral Molecules: C_n and D_n Groups

The only symmetry operations available in a chiral molecule are the proper rotations C_n and consequently they can only belong to point groups D_n or C_n (disymmetric molecules) or to C_1 (asymmetric molecules). Since no isometric segments can be generated from an asymmetric molecule, we do not consider the C_1 point group here (see below). All of the subgroups of the C_n and D_n point groups are also of the C_n or D_n types; hence all isometric segments of C_n or D_n molecules are necessarily chiral (premise 5). Furthermore, all isometric segments of C_n or D_n molecules *must* be related by a proper rotation and are therefore homochiral, according to premise 6. A detailed summary of the results for C_n molecules is presented in Table II.

Molecules belonging to a D_n group can be fragmented in different ways: either into n segments related by the C_n rotation (C_n/p dissections) or into two segments related by C_2 (C_2/p dissections). In the first case, depending on the position of the

Table II. Summary of the Different Patterns for Dissection of a Molecule into Isometric Segments^a

| G | dissection pattern | number of segments | chirality of segments | S | examples ^b |
|----------|---------------------------------|--------------------|-----------------------|---|-----------------------|
| C_1 | no | 1 | | | |
| C_1 | i/g | 2 | C_1 hetero | | |
| C_n | C_n/g | n | C_1 homo | | s |
| D_n | C_n/C_2 | n | C_2 homo | | s |
| | C_n/g | n | C_1 homo | | s |
| | C_2/g | 2 | C_1 homo | | |
| | C_2/C_n (n even) | 2 | C_2 homo | | |
| | C_2/C_n (n odd) | 2 | C_1 homo | | |
| C_s | σ/σ | 2 | C_1 hetero | | |
| C_{nv} | σ_v/σ_v (n even) | 2 | C_s achiral | | s |
| | σ_v/σ_v (n odd) | 2 | C_1 hetero | | s |
| | C_n/g | n | C_1 homo | | s |
| | C_n/σ_v | n | C_s achiral | | s |
| | $2C_n/\sigma_v$ | $2n$ | C_1 pairwise hetero | | s |
| C_{nh} | σ_h/σ_h | 2 | C_n hetero | | Figure 3 |
| | C_n/g | n | C_s achiral | | s |
| | C_2/C_2 | 2 | C_s achiral | | Figure 3 and s |
| | S_n/gc | 2 | $C_{n/2}$ hetero | | |
| | S_n/g | n | C_1 pairwise hetero | | |
| S_n | S_n/gc | 2 | $C_{n/2}$ hetero | | Figure 4 and s |
| | S_n/g | n | C_1 pairwise hetero | | Figure 4 and s |
| D_{nd} | σ_d/σ_d (n even) | 2 | C_s achiral | | |
| | σ_d/σ_d (n odd) | 2 | C_2 hetero | | |
| | C_n/C_2 | n | C_2 homo | | s |
| | C_n/g | n | C_1 homo | | s |
| | $S_{2n}/\sigma_d c$ | 2 | D_n hetero | | |
| | S_{2n}/σ_d | $2n$ | C_2 pairwise hetero | | |
| | $S_{2n}/C_2 c$ | 2 | C_{nv} achiral | | s |
| | S_{2n}/C_2 | $2n$ | C_s achiral | | s |
| | S_{2n}/gc | 2 | C_n hetero | | 10 |
| | S_{2n}/g | $2n$ | C_1 pairwise hetero | | 10 and s |
| | C_2/C_2 | 2 | C_s achiral | | s |
| D_{nh} | σ_v/σ_v (n even) | 2 | C_{2v} achiral | | s |
| | σ_v/σ_v (n odd) | 2 | C_s achiral | | s |
| | σ_h/σ_h | 2 | C_{nv} achiral | | s |
| | C_n/σ_v | n | C_{2v} achiral | | s |
| | C_n/g | n | C_s achiral | | s |
| | S_n/gc | n | C_s achiral | | |

^aG and S are the symmetry point groups of the molecule and the segments, respectively. ^bAn s in this column indicates that an example is provided as supplementary material.

disconnected bonds relative to the C_2 axis, the segments will be either asymmetric (C_1 point group) or disymmetric (C_2 point group). Similar results are found for the C_2/p dissection patterns (Table II).

A good example of fragmentation of disymmetric molecules is provided by the double-stranded helicates reported by Lehn et al.¹⁰ (Figure 1). These compounds belong to the D_2 point group for any length of the double helix. Consequently, the only conceivable fragmentation mode for the double-stranded helicates yields only two homochiral segments (ligands).

According to statement 2 above, asymmetric molecules cannot be fragmented into isometric segments. However, molecules such as (1*R*,2*R*)-1,2-dichloro-1,2-dibromoethane or (1*R*,2*S*)-1,2-dichloro-1,2-dibromoethane, which are asymmetric in the general conformation, must be analyzed in their most symmetric conformation according to statement 1. Thus, these molecules should not be considered as asymmetric but rather as belonging to the C_2 and C_s point groups, respectively, and both can be split into two isometric segments.

Segmentation of Achiral Molecules

Achiral molecules possess at least one improper rotation S_n , considering reflections and inversion as S_1 and S_2 , respectively. They belong to any symmetry group other than C_1 , D_n , or C_n . Fragmentation of such molecules can yield either chiral or achiral segments, depending on the fragmentation pattern chosen. We will focus mainly on the generation of chiral segments in the following section.

When the fragmentation pattern is such that isometric chiral segments are related through a C_n rotation, these are homochiral. Notice the fragmentation of an achiral molecule into segments

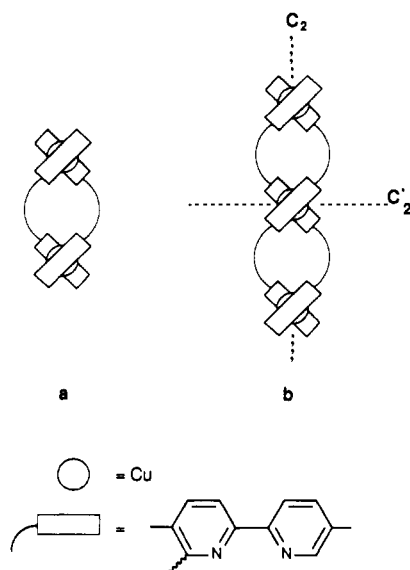


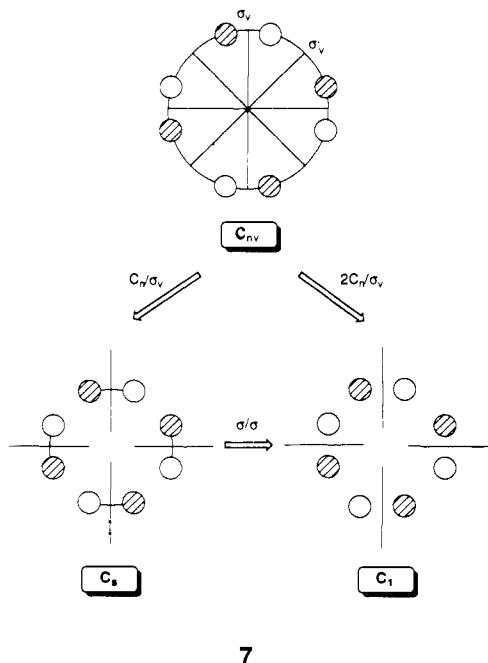
Figure 1. Schematic representation of di- (a) and trinuclear (b) helicates belonging to the D_2 point group. The two sets of ligands are related through C_2 , and each retains C_2' as a symmetry operation.

related by a proper rotation is not a sufficient condition for the segments to be chiral, since for many symmetry groups other symmetry operations must be simultaneously destroyed. If the segments are related through a reflection, an inversion, or an improper rotation, they will be heterochiral, according to premise 7. These segments can be further fragmented into smaller homochiral segments according to what is described in the preceding section, resulting in n segments of each chirality. It is clear that the appropriate choice of the fragmentation pattern would allow the dissection an achiral molecule into either homo- or heterochiral segments. Whether both kinds of fragmentation or only one of them is possible depends on the symmetry group of the molecule and will be analyzed below.

A molecule belonging to the point group C_s can only be cut into isometric segments along its symmetry plane (σ/σ pattern). Obviously, the two segments are mirror images of each other, i.e., they are heterochiral.

C_{nv} Groups. Generalization of La Coupe du Roi. Taking into account the symmetry relationships shown in Table I, it is easy to deduce the results of the different dissection patterns on a general molecule of symmetry C_{nv} (Table II). It is noteworthy that only molecules with an odd symmetry axis can be decomposed into heterochiral halves. Notice, however, that the fragments produced through σ_v/σ_v and C_n/σ_v strategies belong to the C_s point group and can be further fragmented into heterochiral segments. In the last case, one could refer to the whole process as a $2C_n/\sigma_v$ dissection pattern (7, segments represented by white and shaded circles are mirror images of each other), since two sets of C_n -related bonds are disconnected. This strategy produces $2n$ segments which are pairwise heterochiral.

It is interesting to apply our analysis to the particular case of the linear point groups, using as an example an idealized apple ($C_{\infty v}$ point group). La coupe du roi (Figure 2a) is just a fragmentation pattern that produces two homochiral apple pieces. In order to achieve this, we need to separate two fragments related by a rotation C_2 , while simultaneously destroying the symmetry planes (achieved through the horizontal cut) in what could be formally described as a C_2/g dissection. With this in mind, we can generalize la coupe du roi by replacing the C_2/g by a C_n/g strategy: Any number of homochiral fragments of an apple can be generated by means of two sets of vertical C_n cuts performed on the upper and lower part of the apple, respectively. The cuts on the same half of the apple must be separated by an angle of $2\pi/n$ (where n is the number of fragments to be generated), and the upper and lower cuts must be displaced by an angle β in the range $0 < \beta < 2\pi/n$ (Figure 2b). Perhaps this technique should be called *la coupe du parlement*.¹³



Unfortunately, there are no molecular apples. Any molecule belonging to the C_{nv} or D_{nh} point groups must have all of its atoms on the symmetry axis and cannot be split into isometric segments related by one of the C_n or σ_v operations unless we trade chemistry for nuclear physics. Isometric fragmentation of a linear molecule through σ_h (or C_2) would result in achiral C_{nv} segments. We can therefore conclude that linear molecules cannot produce chiral isometric segments.

Conversely, one can ask whether an apple could be cut into heterochiral parts. The C_{nv} point group is just a particular case of C_n with $n = \infty$. There are two ways in which a C_n object can produce heterochiral segments (Table II). In one case, a σ/σ cut (n odd) can yield heterochiral halves because of the absence of a perpendicular symmetry plane. This route is not operative since in C_{nv} every symmetry plane is perpendicular to another one. On the other hand, to obtain heterochiral pairs through a C_{2n}/σ_v strategy, an infinite number of cuts must be applied. Hence an apple cannot be dissected into heterochiral segments, as previously found by Anet et al.³ Other fruits belonging to C_n point groups with odd n can be split in two heterochiral halves through a σ/σ cut (an example might be an orange with an odd number of segments).

C_{nh} Groups. These point groups can be obtained as a product of the corresponding C_n group and a perpendicular symmetry plane σ_h . In contrast with the C_n groups, the proper rotations and a perpendicular symmetry plane are independent, as discussed above. As a consequence, the main results which arise for different fragmentation patterns are as follows (Table II): (i) σ/σ cuts produce two heterochiral segments, each having C_n as a symmetry operation (C_n point group); (ii) C_n/g dissections yield n achiral segments which retain the symmetry plane (C_s point group); and (iii) a C_n/C_n dissection is only possible for C_2 rotations. For any other C_n , there are no bonds across the symmetry axis.

Thus, it is clear that molecules belonging to C_{nh} point groups cannot be fragmented into homochiral segments only. All of this can be illustrated through the example of tetrachlorocyclobutane proposed by Anet et al.³ (Figure 3a). This molecule belongs to the point group C_{2h} . A C_2/C_2 cut (Figure 3b) results in achiral segments according to the above rules (point group C_1). On the other hand, if the molecule is cut through the symmetry plane σ_h (σ_h/σ_h cut, Figure 3c), heterochiral segments (point group C_2) are obtained.

(13) As the general way to cut an apple into any number of homochiral slices describes a more advanced technique than the partition into two pieces known as la coupe du roi, we propose a name which assumes parliamentary democracy as a higher degree of social organization than monarchy.

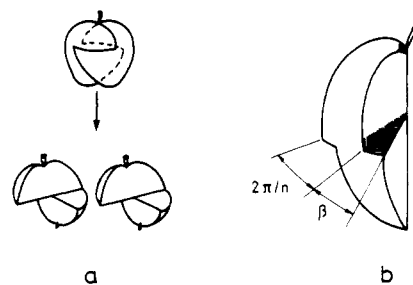


Figure 2. Technique for the dissection of a C_{nv} object into two homochiral halves (la coupe du roi, a) and for its dissection into n homochiral pieces (la coupe du parlement¹³, b).

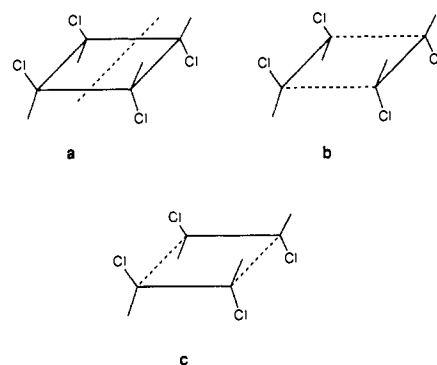


Figure 3. Two dissection patterns for tetrachlorocyclobutane (a), a molecule of C_{2h} symmetry: C_2/C_2 (b) and σ/σ (c).

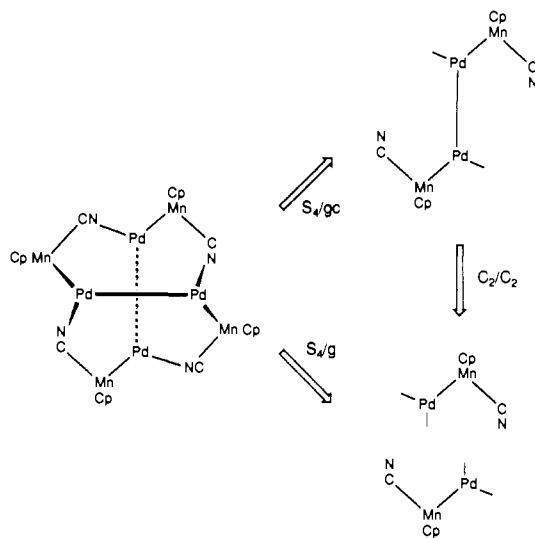


Figure 4. Schematic representation and dissection patterns for $[(OC)-Pd(\mu-NC)Mn(\eta-Cp')(CO)_2]$.

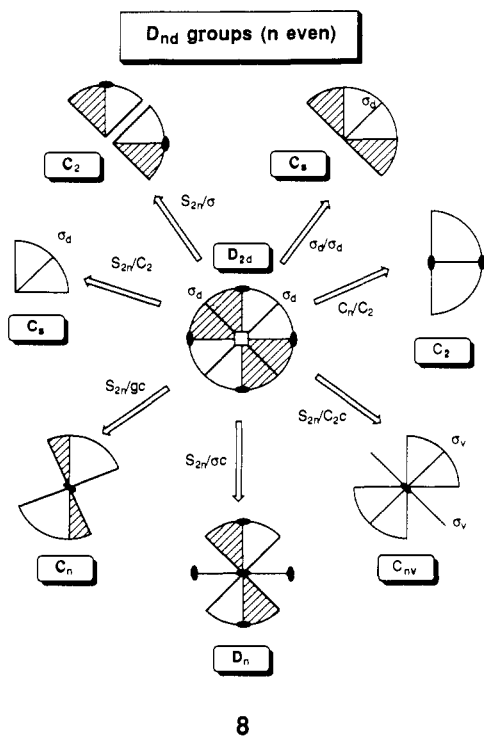
S_n Point Groups. These are cyclic groups generated by the powers of improper rotations S_n , where n is even, and they possess no symmetry planes. Several segmentation choices exist for such point groups according to the above analysis of the symmetry of cuts when an improper rotation is present (see Table I): (i) When an S_n/c cut is applied, two reflection-related segments result. They still possess a proper rotation $C_{n/2}$ and are consequently heterochiral. (ii) A $C_{n/m}/g$ cut yields n/m segments related through $C_{n/m}$, while simultaneously destroying the S_n operations. The segments belong to point group C_1 and are homochiral. (iii) The combined action of the two strategies is equivalent to an S_n/g cut (Table II).

Even if there is no clear-cut definition of which bonds are in a g position and which are in a c position, the S_n/g and S_n/gc dissection patterns can be clearly differentiated because the first one results in n segments and the latter always produces two.

An illustrative case of an S_n molecule is provided by $[(OC)-Pd(\mu-NC)Mn(\eta-Cp')(CO)_2]$, a tetranuclear cluster recently re-

ported by Braunstein et al.,¹⁴ which belongs to the S_4 point group. This compound, schematically represented in Figure 4, can be dissected through an S_4/gc cut, producing two heterochiral segments (point group C_2). Further disconnection via a C_2/C_2 cut splits each fragment into two homochiral halves. The net result, a set of n pairwise heterochiral segments, could be obtained directly through an S_n/g dissection of the starting molecule.

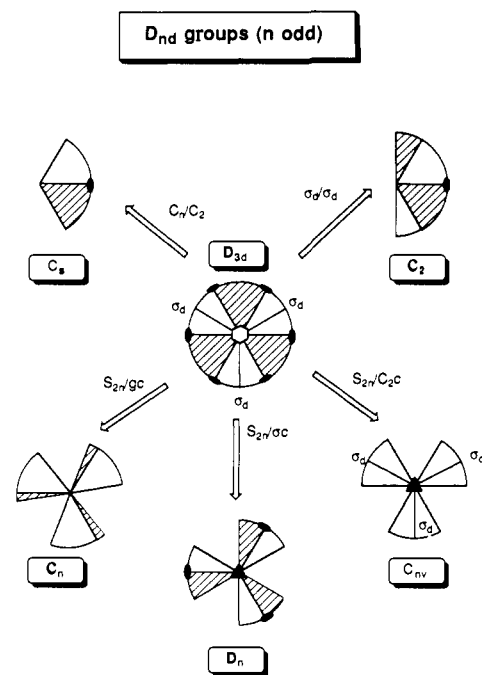
D_{nd} Point Groups. These groups can be generated by adding a σ_v reflection to a D_n group. As a σ/σ cut destroys all rotations around coplanar axes, the resulting segments retain only the perpendicular symmetry plane (which exists only for n even), they belong to the C_s point group, and they are therefore achiral. For n odd, on the other hand, there are no perpendicular symmetry planes, but there is a perpendicular C_2 axis; the σ/σ pattern produces heterochiral segments of C_2 symmetry. Stereographic views of such dissection patterns are presented in 8 (for n even) and 9 (n odd), where the white and shaded regions represent the parts of the molecule lying above and below the plane of the paper, respectively. Of course, this strategy can only be applied when there are no atoms sitting on the σ_d symmetry plane.



C_n/C_2 cuts always preserve a perpendicular C_2 axis (see 8 and 9), but all of the symmetry planes are destroyed since they are not coplanar with the binary axes. Thus, n homochiral segments of C_2 symmetry are produced. If bonds at general positions are disconnected (C_n/g cut), all symmetry elements are destroyed and n asymmetric homochiral segments result.

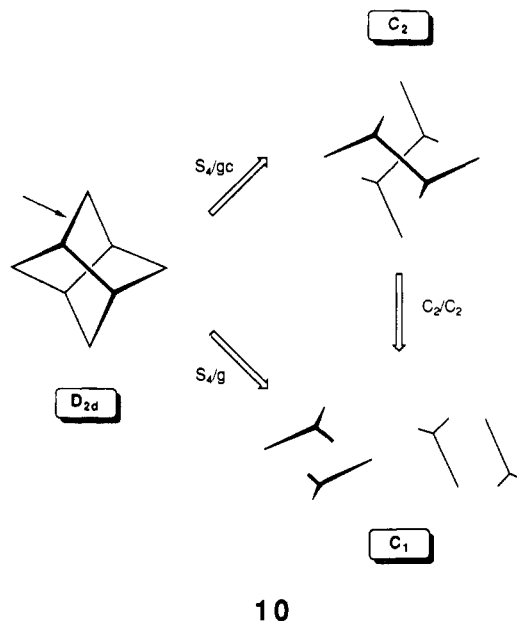
The D_{nd} point groups can also be generated by S_{2n} and perpendicular C_2 rotations. Since we have seen that S_{2n}/pc cuts can be imagined which preserve the proper rotation C_n it is clear that segments with D_n , C_n , or C_2 symmetries can, in principle, be generated. S_{2n}/σ_c dissection yields two heterochiral segments of D_n symmetry, as shown in 7 and 8, and further disconnection (S_{2n}/σ pattern) yields $2n$ segments of C_2 symmetry which are pairwise heterochiral. Other choices can be seen in 7 and 8 and are summarized in Table II.

Finally, one could choose to cut the molecule into two pieces related by the C_2 rotations, dissecting bonds perpendicular to either the C_n or another C_2 axis. In the former case, the result is different for the odd and even groups: a C_2/C_n dissection yields two homochiral segments of C_2 symmetry when n is even, but two



achiral C_s segments when n is odd. The result of a C_2/C_2 dissection is presented in Table II.

An example of a D_{2d} molecule is provided by bisnoradamantane¹⁵ (10). Despite the large number of dissection



patterns available for D_{nd} molecules, most of them cannot be applied to this molecule: σ_d/σ_d , C_n/C_2 , S_{2n}/σ_c , S_{2n}/σ , S_{2n}/C_2 , and σ_d patterns are forbidden because there are atoms sitting on the corresponding symmetry elements. C_n/g and C_2/C_n patterns do not disconnect this molecule. Thus, we are left with only S_{2n}/gc and S_{2n}/g strategies to cut this molecule in isometric segments. In the S_{2n}/gc pathway, we cut a bond in a general position (indicated by an arrow in 10) and all of the equivalent bonds related through S_4 rotations. The result is two heterochiral segments of C_2 symmetry (Table II), which could be further disconnected to yield four pairwise heterochiral asymmetric fragments.

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only cases in which homochiral segments can be assembled into achiral molecules and constitute a generalization of la coupe du roi, generally used for C_{nv} molecules only.

The first conclusion may have some relevance to the fact that living beings prefer homochirality, i.e., they use only the L series of amino acids in proteins and only the D family of nucleotides in nucleic acids, a fact closely related to the origin of life.^{22,23} Since chain compounds can be regarded as cyclic systems with an infinite number of members,²⁴ our symmetry analysis above indicates that,

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in proteins or nucleic acids, an enantiomeric chain compound can only be obtained from homochiral building blocks.

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Supplementary Material Available: Drawings of 35 fragmentation patterns for 23 molecules (9 pages). Ordering information is given on any current masthead page.

(24) See: Gerstein, B. C. *J. Chem. Educ.* 1973, 50, 316.

On the Photodecomposition Mechanism of *o*-Diazonaphthoquinones

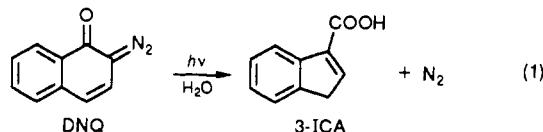
Mónica Barra,¹ T. A. Fisher,² G. J. Cernigliaro,² R. Sinta,^{*2} and J. C. Scaiano^{*1,3}

Contribution from the Department of Chemistry, University of Ottawa, Ottawa, Canada K1N 6N5, Shipley Company, Inc., 455 Forest Street, Marlboro, Massachusetts 01752, and Steacie Institute for Molecular Sciences, National Research Council, Ottawa, Canada K1A 0R6. Received July 2, 1991

Abstract: The mechanism for the photodecomposition of several *o*-diazonaphthoquinones has been examined in acetonitrile solution using time-resolved laser flash photolysis techniques. It is concluded that the Wolff rearrangement, which involves the formation of a ketene intermediate, can be regarded as a concerted process in the nanosecond time scale. It is suggested that the reaction of the ketene with water, which is well known to yield 3-indenecarboxylic acids, involves the intermediacy of a ketene hydrate. Pyridine, a molecule frequently employed as a carbene trap/probe, efficiently traps the ketene in these systems; this scavenging reaction can be employed as a probe for the study of the dynamics of ketene reactions, but in some systems it may represent a problem in carbene studies if the possibility of ketene reactions is not considered.

Introduction

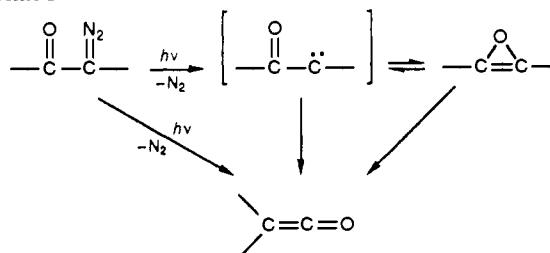
The phototransformation of 2-diazo-1,2-naphthoquinones (DNQs) into the corresponding 3-indenecarboxylic acids (3-ICAs) (eq 1) via the Wolff rearrangement has been widely studied and has numerous applications in photoresist technology.⁴



It is well known that the photodecomposition of DNQs produces an intermediate ketene, which upon reaction with water yields the corresponding 3-ICA. It has been suggested that in some cases a long-lived intermediate ketene (the transient decay time is of the order of seconds) can absorb another photon, leading to unwanted photochemistry, which in the photoresist field is usually referred to as a reciprocity failure.⁵

The conversion of *o*-diazo ketones into ketenes involves a 1,2 migration of a carbon atom, which is known as the Wolff rearrangement. Despite many investigations, the mechanism involved in this process is still being debated. The focus of the discussion is whether the loss of nitrogen and the 1,2 migration of the carbon

Scheme I



atom occur in a concerted manner or the Wolff rearrangement is a two-step reaction which involves an α -keto carbene and/or an oxirene-like intermediate, as represented in Scheme I. On the basis of the studies already reported, one must point out that the mechanism will depend on the specific type of *o*-diazo ketone being studied.⁶

The mechanism for the photoconversion of DNQs into 3-ICAs in solution is a matter of some discussion and controversy. There have been different results on the number, sequence, and spectroscopic properties of the intermediates formed, such as the ketene.⁷⁻¹²

(1) University of Ottawa.

(2) Shipley Co., Inc.

(3) National Research Council.

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