of toluene, cycloheptatriene, and norbornadiene cations in these matrix experiments suggests that the former may be an important intermediate in gaseous $C_7H_8^{+\cdot}$ cation rearrangements. The argon matrix is an effective medium for the investigation of photochemical rearrangement processes in molecular cations.

helpful discussions with D.S. Kelsall, and a copy of the unpublished spectrum of cycloheptatriene cation in a Freon matrix from T. Shida.

La Coupe du Roi and Its Relevance to Stereochemistry. Combination of Two Homochiral Molecules To Give an Achiral Product

Frank A. L. Anet,*[1a] Steve S. Miura,[1a] Jay Siegel,[1b] and Kurt Mislow*[1b]

Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024, and the Department of Chemistry, Princeton University, Princeton, New Jersey 08544. Received October 11, 1982

Abstract: The problem of dividing finite geometric objects into isometric segments is examined, including the special case in which an achiral object is bisected into isometric homochiral halves (la coupe du roi). Segmentations that are applicable to molecular systems are shown to be limited to four classes, depending on whether or not the object (molecular model) is achiral, whether or not the combination of the cut and the object (cut–object) is achiral, and whether or not there are mirror elements that pass through the segments. These segmentations have a bearing on previously developed relationships among atoms or groups of atoms in molecules and on chemical fragmentations and combinations of molecules. A chemical analogue for the assembly of two homochiral objects into one achiral object (the reverse of la coupe du roi) is provided by the self-coupling of (+)-4-(bromomethyl)-6-(mercaptomethyl)[2.2]metacyclophane ((+)-**15**) to give, in a stereospecific manner, the achiral cis dimer **11** (C_{2v} symmetry). In contradistinction, self-coupling of racemic **15** gives a 1:1 mixture of the above cis dimer and of the trans dimer **12** (C_{2h}): corresponding segments that are homochiral in **11** are heterochiral in **12**.

Consider an apple as an achiral object with the stem at the top (Figure 1). Two vertical half-cuts are made through the apple, one from the top to the equator and the other, perpendicular to the first, from the bottom to the equator. Two nonadjacent, horizontal quarter-cuts are then made along the equator to connect the vertical cuts, and the apple separates into two halves (Figure 1). This parlor trick, known among some families in France as la coupe du roi, is remarkable in that the two halves are homochiral.[2,3] At a first glance, the two halves, which are obviously

chiral, might be thought to be mirror images of one another, since together they constitute an achiral object. Not only is this not the case, but it is actually impossible to cut an apple in this way, i.e., into two heterochiral[3] parts. Of course, it is possible to cut an apple in a coupe-du-roi manner in two different but mirror-image related ways, depending on the direction of the quarter-cuts. Such mirror-image related halves, obtained from two different apples, do not however mesh properly to reconstitute an object that looks like a single complete apple (Figure 1). This property is obviously shared by geometric objects such as right circular cones ($C_{\infty v}$) in general, and by right circular cylinders ($D_{\infty h}$) and spheres (K_h) for bisections. However, a moment's reflection reveals that there exists another class of objects in which bisection cannot result in homochiral halves, as exemplified by a triangular pyramid with C_s symmetry or a distorted cube with C_i symmetry.

These considerations piqued our curiosity and provided the impetus for the present work. In this paper we examine the general problem of dissecting finite objects into isometric[3] segments, including the special case of la coupe du roi, and show that this and other segment compositions bear a significant relationship to chemical structures and processes. Finally, we provide a chemical example of such a process.

(1) (a) University of California, Los Angeles. (b) Princeton University.

(2) (a) Martin Gardner has given a description of this "curious way of dividing an apple into two identical parts" [Gardner, M. "Encyclopedia of Impromptu Magic"; Magic: Chicago, 1978; pp 7 and 8]. Gardner has also pointed out [Gardner, M. *Sci. Am.* **1978**, *239* (5), 22] that this division performed on a sphere has been set in stone by the Swiss artist Max Bill in his granite sculpture "Half Sphere around Two Axes". He additionally notes that this shape "suggests a three-dimensional version of the yin-yang bisection of a circle into asymmetric, congruent parts". (b) The homochiral relationship between the two halves was discovered in 1937 by Alain Horeau, then working in the laboratory of Marcel Delépine (Horeau, A., private communication).

(3) Because our exposition requires the use of stereochemical terminology that may be unfamiliar to the general reader, a brief glossary is provided. Two objects are *isometric*[4a] if they are properly (directly) or improperly (oppositely) congruent; otherwise they are *anisometric*. This definition is applicable to the model of a molecule.[4b] Alternativley phrased,[4c] nuclear configurations are isometric if their labeled graphs are the same, the labeling being by nuclear charge and mass for the vertices and by internuclear distances for the edges. The terms[4d] *homochiral* and *heterochiral* as used in this text refer to relations between isometric chiral objects or models of chiral molecules: homochiral objects are only properly congruent, whereas heterochiral (enantiomorphous) objects are only improperly congruent (isometric achiral objects are both). In the context of the present discussion, there is no need to place an additional restriction on the meaning of these terms.[4e] All of the above terminology may be extended to portions of objects or of models of molecules. If such portions are related by a symmetry operation of the ensemble, they are *homotopic* or *enantiotopic*, depending on whether the symmetry operation is of the first or only of the second kind, respectively.

(4) (a) For an excellent discussion of the concept of isometry, see: Coxeter, H. S. M. "Introduction to Geometry", 2nd ed.; Wiley: New York, 1969. (b) Mislow, K. *Bull. Soc. Chim. Belg.* **1977**, *86*, 595. (c) Bauder, A.; Meyer, R.; Günthard, Hs. *Mol. Phys.* **1974**, *28*, 1305. (d) Kelvin, Lord "Baltimore Lectures"; Clay: London, 1904; pp 618–619. The application of this terminology to geometric objects is sanctioned by Kelvin's statement: "For example, let the given bodies be halves (oblique or not oblique) of any parallelepiped on the two sides of a dividing plane through a pair of parallel edges. The two halves are homochirally similar." (e) Ruch, E. *Acc. Chem. Res.* **1972**, *5*, 49. Ruch, E. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 65.
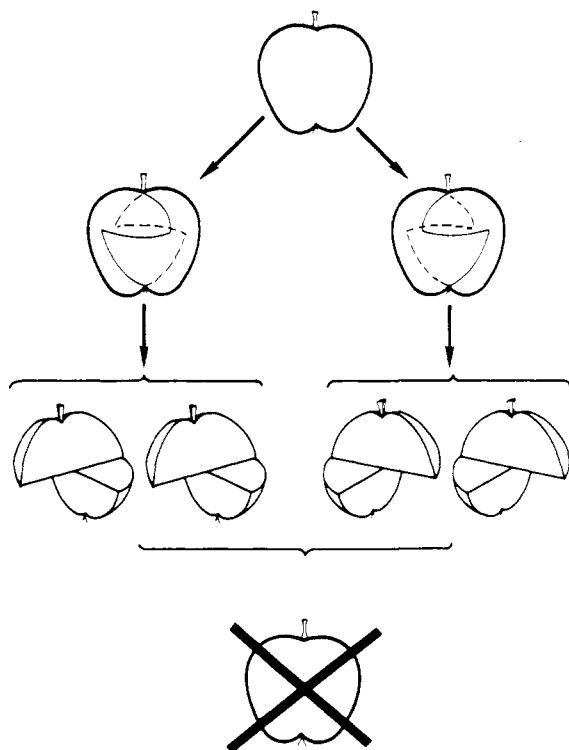
Figure 1. La coupe du roi. The sense of chirality depends on the direction of the cut. Each apple yields a pair of homochiral segments, but segments from the cut on the left are heterochiral (enantiomorphous) to those on the right. Two heterochiral segments, one from each apple, cannot be reassembled to form an apple.

Geometric Considerations

We begin by considering the general problem of dividing a finite geometric object into isometric segments and then go on to discuss those segmentations that are applicable to molecular systems.

In the general case, no limitations are placed on the shape or symmetry of finite objects and their isometric segments: the object may be chiral or achiral and the segments achiral, homochiral, or heterochiral.[5] Nor, in general, are limitations placed on the number of segments. Indeed, among the myriad combinations of objects and segments in two or three dimensions, only five types are disallowed, two in E^2 and three in E^3. Objects with $C_{\infty v}$ symmetry (i.e., the geometric counterparts of an apple) cannot be dissected into heterochiral segments; likewise, the planar D_∞ symmetry of circular objects precludes such segmentation. This attribute of objects with $C_{\infty v}$ and D_∞ symmetry is due to the presence of a C_∞ as its sole rotation axis (the center of the circle acts as such an axis in E^2): if heterochiral segments were to be formed from an object with this symmetry, they would have to be infinite in number and infinitesimal in size. In addition, special behavior is found in objects lacking rotational symmetry, i.e., in objects with C_s or C_i symmetry in E^3 or D_1 symmetry in E^2. Starting with these symmetries, one may construct objects, as in the examples given above, that cannot be divided into homochiral segments.

We next focus attention on objects that model molecular symmetry and point out some problems that are encountered in their segmentation. Consider bisection of a model of D_3-ethane by a plane containing the three C_2 axes: the segments (methyl groups) are necessarily homochiral (C_3).[6] As this example illustrates, *it is not possible to dissect chiral molecular models into achiral,*
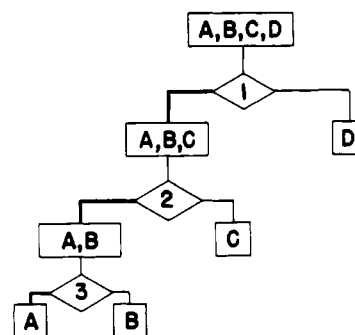

Figure 2. Flowchart for the classification of C/O's into four classes, indicated by capital letters. The decisions in response to questions are given by heavy (yes) and light (no) lines. The questions are as follows: (1) Is the object achiral? (2) Is the C/O achiral? (3) Are there mirror elements that pass through the segments?

isometric segments. A problem of a different sort is encountered in molecules exemplified by the meso compound $(1R,2S)$-1,2-dichloro-1,2-dibromoethane. In either of its achiral conformations (C_s or C_i), bisection of the model leads to heterochiral CHClBr moieties. In all of its other conformations, however, the molecule is asymmetric, and a model that appropriately represents this system in these conformations is therefore not segmentable into isometric moieties. A hypothetical meso conformation with isometric CHClBr groups such as might be obtained from one of the achiral conformations by *rigid* rotation ($0 < \phi < \pi$) about the central bond is therefore unrealistic; the proper representation is a model with anisometric moieties. As this example illustrates, *it is not possible to dissect chiral molecular models into heterochiral, isometric segments.*

Molecular Models and Their Segmentation

As the previous examples indicate, limitations are imposed on the ways in which objects can be segmented when such objects represent models of molecules. In the discussion to follow, our use of the term "object" refers to a rigid molecular model, i.e., to an abstract representation of the molecular system under observation,[7] and our use of "segmentation" to an operation on this geometric object. We do not mean chemical cleavage or fragmentation. The problem of fragmentation represents a separate issue that will be addressed below.

In order to elucidate the nature of these limitations, we introduce the following definitions and restrictions. (1) The point symmetry of the object must faithfully represent the symmetry of the molecular system. Except for its symmetry, the shape of the object is immaterial.[8] (2) We define a cut-object (C/O) as the ensemble of isometric segments in the shape of the object with the cut in place. Thus, if the object is an uncut apple, the two ensembles at the top of Figure 1 are examples of C/O's. (3) The segments must be related by a symmetry operation of the C/O. Accordingly, the segments may not contain any symmetry element that does not also belong to the object. It also follows that the number of segments is an integral factor of the order of the C/O symmetry group. (4) The segments may be disassembled so long as they maintain their relative positions in space. That is, the segments must not only be isometric but they must also be related by a symmetry operation of the ensemble of segments.[9]

---

(5) With respect to chirality, any set of isometric objects or segments of objects falls into one of four classes: achiral, homochiral, pairwise heterochiral, and nonpairwise heterochiral.

(6) To remain faithful to the molecular symmetry, the chirality of the segments must be expressed in the distribution of electrons, for it is easily seen that no representation of CH_3 in D_3-ethane as a set of four point-atoms is capable of assuming C_3 symmetry. Similarly, the chirality of the segments (C_1) in C_2-H_2O_2 can only be expressed in the distribution of electrons.

(7) Much in the same way, in speaking of la coupe du roi, we imply a model with the properties of a hypothetical, idealized object (e.g., a right circular cone) that is the geometric counterpart of the apple. On the subject of geometrizing physical objects, see: Mislow, K.; Bickart, P. *Isr. J. Chem.* **1976/77**, *15*, 1.

(8) Our treatment does not extend to systems whose symmetry can ony be represented by supergroups (such as the Longuet–Higgins molecular symmetry group) that are not isomorphic to point groups. See: Reisse, J.; Ottinger, R.; Bickart, P.; Mislow, K. *J. Am. Chem. Soc.* **1978**, *100*, 911, ref 5.

(9) This restriction does not apply to geometric figures or to objects that do not represent models of molecules. Segments of such objects may be isometric without being related by a symmetry operation of the ensemble of segments.
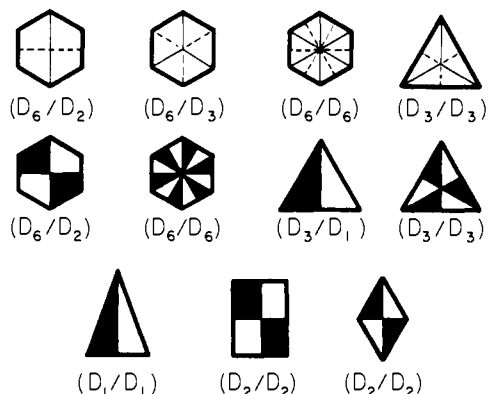
La Coupe du Roi and Its Relevance to Stereochemistry

J. Am. Chem. Soc., Vol. 105, No. 6, 1983 1421

Figure 3. Selected examples illustrating the dissection of planar, achiral objects into achiral (class A) and heterochiral (class B) segments. The symmetries of the object and the C/O are given in parentheses: (top row) class A, solid lines are cuts, dashed lines are mirror lines through the segments; (middle and bottom rows) class B, heterochiral segments are differentiated by shading.

Since the segments may not contain any symmetry element that does not also belong to the object, it follows that chiral objects cannot be dissected into achiral segments, as was shown above. Furthermore, since two heterochiral segments can only be related by a symmetry operation of the second kind, and since such an operation cannot belong to a group that describes the symmetry of a chiral molecule, it follows that chiral objects cannot be dissected into pairwise heterochiral segments, as was also shown above. Accordingly, chiral objects can only be dissected into homochiral segments. Similar limitations do not apply to achiral objects, which may (depending on the symmetry of the object and the nature of the cut) be dissected into achiral, heterochiral, or homochiral segments.

Classification of Cut–Objects. The preceding considerations provide the basis for classifying molecular C/O's. Our classification scheme is three-tiered (Figure 2). We wish to know, first, whether or not the object is achiral, second, whether or not the C/O is achiral, and, third, whether or not there are mirror elements that pass through the segments. According to this scheme, all C/O's belong to one of four classes, three (A–C) stemming from achiral objects and one (D) from chiral objects.

Class A: Object, cut, and C/O are all achiral, and there exists a mirror element that passes through the segments. The segments are achiral.

Class B: Object, cut, and C/O are all achiral, but, if mirror elements exist, none pass through the segments. The segments are pairwise heterochiral.

Class C: The object is achiral, and the cut and the C/O are chiral. The segments are homochiral.

Class D: The object and the C/O are both chiral. The segments are homochiral.

These somewhat abstract considerations can be easily illustrated by examples from E^2. In the Euclidean plane every achiral object has planar D_n symmetry. Cuts along mirror lines (achiral cuts) generate C/O's with achiral or pairwise heterochiral segments, depending on the type of cut. Figure 3 shows selected examples of C/O's in classes A and B that result from such cuts. Particularly instructive are the C/O's resulting from cuts along both mirror lines of the rectangle (D_2) and the rhombus (D_2); four rectangular segments are formed in the case of the former and four triangular segments in the case of the latter. By virtue of being scalene, the triangular segments are obviously chiral. However, the rectangular segments are also chiral because neither one of the two mirror lines in the original rectangular figure passes through the segments (see restrictions 3 and 4, above). That is, each rectangular segment resides in (and cannot be divorced from) the chiral environment provided by the three remaining segments.

Cuts that do not lie along mirror lines (chiral cuts) yield homochiral segments. The C/O's thus belong to class C or D (Figure 4); they are chiral and have planar C_n ($n > 1$) symmetry. Because such cuts lie in general positions, an infinite number exist for a
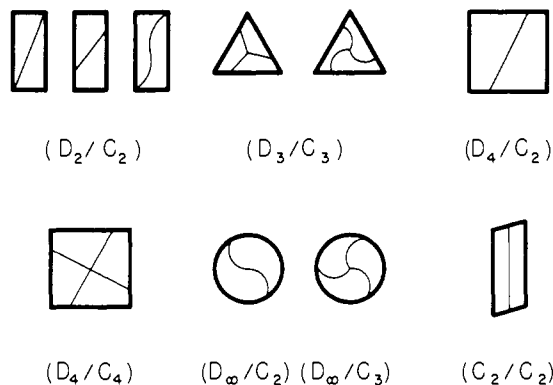

Figure 4. Selected examples illustrating the dissection of planar objects into homochiral segments (classes C and D). The symmetries of the object and the C/O are given in parentheses. The rhomboid (bottom row, right) is chiral (class D); all other objects are achiral (class C).

given object and a given number of segments. In addition, since the number of segments can be any divisor of n in D_n other than unity, a circular object (D_∞) may be divided into any number of homochiral (or achiral) segments.[10]

Much of the preceding analysis may be directly applied to objects in E^3. Thus, la coupe du roi is seen to be the analogue in E^3 of the chiral bisection of a circle in E^2 (Figure 4),[2a] and the C/O's in Figure 1 are seen to belong to class C. Because the cut lies in a general position, it is not constrained to any one particular shape such as that in Figure 1 but may, for example, take the form of a helical ribbon centered along the C_∞ axis. In further analogy with the desymmetrization of a circular object, any cut of C_n symmetry divides the apple into n homochiral segments. La coupe du roi is thus recognized to be just one of an infinite number in this class of segmentations.

Another point of general significance, again in analogy to segmentations in E^2, is that different cuts may lead to different classes of C/O's for the same object. We content ourselves with three examples. For an object with S_4 symmetry, any cut that contains the C_2 axis yields two homochiral moieties (class C), whereas a cut perpendicular to this axis yields two heterochiral moieties (class B). For the bisection of an object with C_{2h} symmetry, any planar or other achiral cut that contains the C_2 axis yields two achiral moieties (class A), whereas any other achiral cut through the center of symmetry yields two heterochiral moieties (class B). In addition, a cut along the C_2 axis in the manner of la coupe du roi yields a C/O with C_2 symmetry and two homochiral moieties (class C). Finally, for an object with C_{2v} symmetry, bisection leads to class C if the cut contains the C_2 axis but no σ plane and class A if it contains only one σ plane. Quadrisection leads to class B if the cut contains both σ planes.

The present classification scheme is a general one, and is easily applied to any molecular system.

Relationships among Groups in Molecules. We have shown that in the dissection of objects (molecular models) into isometric segments, the relationship among the segments is dictated by the symmetry of the C/O. This is not surprising since previously it had been shown that the relationship among atoms in a molecule is similarly dictated by the symmetry of the molecule.[12] Consider, for example, compound 1, in which G_R and G_S represent heterochiral groupings. In the S_4 conformation shown, a cut containing the C_2 axis leads to two homochiral arrays (class C) and to homotopic pairings H_1/H_3, H_2/H_4, etc., between these arrays. However, a planar cut through the center of the molecular model

(10) Shubnikov and Koptsik[11] have listed all the ways in which "parallelogons" (figures that fill a plane with no gaps or overlap when subjected to parallel translations) can be divided into equal parts ("planigons"). Planigons are isometric and are sometimes achiral, homochiral, or pairwise heterochiral. This treatment is restricted to parallelograms of any shape or hexagons in which opposite sides are equal and parallel.

(11) Shubnikov, A. V.; Koptsik, V. A. "Symmetry in Science and Art"; Plenum: New York, 1974; pp 171–174.

(12) Mislow, K.; Raban, M. *Top. Stereochem.* **1967**, *1*, 1.

1422 *J. Am. Chem. Soc., Vol. 105, No. 6, 1983*

Anet et al.
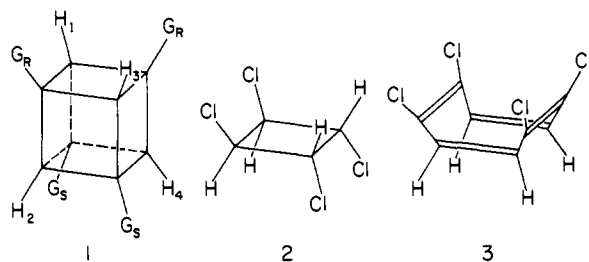
and at right angles to the C_2 axis leads to two heterochiral arrays and to enantiotopic pairings H_1/H_2, H_1/H_4, etc., corresponding to class B.

Similarly, in the C_{2h} isomer of 1,2,3,4-tetrachlorocyclobutane (2), the hydrogen and chlorine atoms that are related by a proper rotation (C_2) are homotopic (class A), whereas those that are related by an improper rotation (σ_h or i) are enantiotopic (class B). As a last example, in 1,2,5,6-tetrachlorocyclooctatetraene (C_{2v}, 3), bisection may lead to class A or C, depending on the nature of the cut, and quadrisection to class B, as discussed above. Here too, all chlorine or hydrogen atoms are pairwise either homo- or enantiotopic.

As an example of the dissection of a chiral molecular model, consider (1*R*,2*R*)- or (1*S*,2*S*)-1,2-dichloro-1,2-dibromoethane (C_2). A cut with C_2 symmetry through the central bond bisects this object into homochiral moieties. Bisection of a [n]helicene (C_2, n = odd) will similarly lead to homochiral segments whose constituent atoms are pairwise homotopic. All these molecular C/O's belong to class D.

Chemical Fragmentations and Combinations of Molecules

The separate particles that are produced in the chemical fragmentation of molecules have properties that differ to a greater or lesser extent from those of the same particles in their bonded state in the intact molecule.[13] A clear distinction must therefore be drawn between such chemical fragments and the C/O segments discussed above, and if we wish to consider the products of fragmentation we must treat them de novo as independent objects.[14]

If, in the general case of a chemical fragmentation (or its reverse, the combination of molecular fragments), any arbitrary change in nuclear position and electronic distribution were allowed, only trivial statements could be made concerning chirality.[15] We have therefore chosen to restrict the chemical relaxation involved in such reactions by requiring that the chirality class[5] of the fragment molecules be the same as that of the segments in the corresponding C/O of the whole molecule.[16,17] For example, the
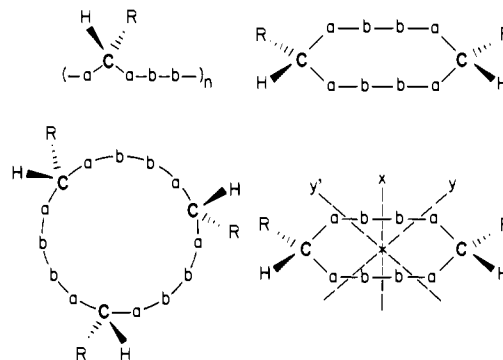

Figure 5. Cyclic oligomerization of the generalized fragment shown on the upper left ($n \geq 2$): (upper right) dimer; (lower left) trimer; (lower right) segmentation of the dimer by cut x (class A) and by cuts y and y' (class C).

Diels–Alder dimerization of 1,3-butadiene is excluded because the segments in the C/O of the dimer are not isometric. The cleavage of 4 to 5 is also excluded because the segments in the C/O of 4 are homochiral, whereas the molecular fragments (5) of 4 are achiral.
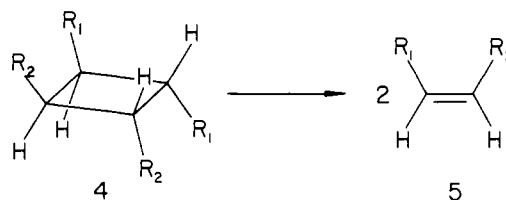
The cleavage of chiral molecules into homochiral fragment molecules (corresponding to segments in class D) and the reverse reaction are well-known. An unusual example[19] is the combination of four homochiral molecules of lactone 6 to give the chiral, cyclic tetramer 7, which has nearly C_4 symmetry in the crystalline state.[19]
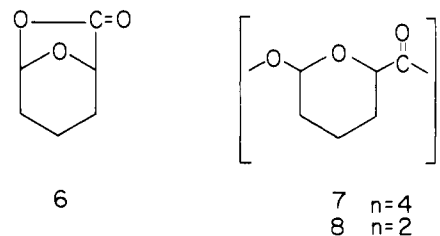
This reaction is a strict tetramerization and does not involve the gain or loss of small molecules such as H_2O or HBr. This distinction will be ignored in subsequent examples, since the main fragment molecules will always remain isometric.

The cleavage of achiral molecules into achiral, isometric fragments (class A segmentation) and the reverse reaction requires no documentation; cleavage to give heterochiral fragments (class B segmentation) is also well-known.[20] An interesting example in the reverse direction is the dimerization of racemic 6 to give an achiral product (8) with exact C_i symmetry in the crystalline state.[19]

A Chemical Analogy to la Coupe du Roi. We now address the problem of reactions in which the molecules are achiral and the fragments homochiral, since this feature is at the heart of la coupe du roi. The two essential features of this segmentation are, first, that certain achiral objects can be bisected into homochiral halves (and, conversely, that two homochiral objects can be combined

(13) The chemical fragmentation will always change the electron densities and internuclear distances within a fragment molecule from what these quantities were in the original molecule.

(14) This point is well illustrated by the examples discussed above.[6] The methyl radicals that result from cleavage of the central bond in D_3-ethane are expected to become achiral (C_{3v} or D_{3h}, depending on the time scale) upon relaxation, the hydroxyl radicals formed by homolysis of C_2-H_2O_2 are achiral ($C_{\infty v}$), and the CHClBr radicals resulting from cleavage of (1*R*,2*S*)-1,2-dichloro-1,2-dibromoethane become isometric (chiral or achiral) upon relaxation. In all these cases, the products in a homolysis—or, conversely, the educts in a dimerization—must be represented by objects that obviously differ in symmetry from the same fragments in the bonded state, i.e., from the segments in a molecular C/O that represent the intact educt or product molecule.

(15) All that could be said is that in the absence of a chiral influence (reagent, catalyst, etc.) achiral compounds are not expected to give rise to fragmentation products that exhibit chirality phenomena (e.g., optical activity).

(16) Corresponding segments and fragments (i.e., fragment molecules) contain the same sets of nuclei.

(17) According to terminology recommended by Hirschmann and Hanson,[18] isolated ligands, i.e., atoms or groups of atoms separated from the molecule of which they are part, are "homomorphic" if they are properly congruent and "enantiomorphic" if they are only improperly congruent. The usefulness of the "morphic" nomenclature lies in the distinction it affords between the "topic" relationship among ligands within the intact molecule[12] and the relationship among ligands in the absence of perturbations from the rest of the molecule.

(18) Hirschmann, H.; Hanson, K. R. *Tetrahedron* 1974, *30*, 3649. Hirschmann, H.; Hanson, K. R. *Top. Stereochem.*, in press.

(19) Tanaka, I.; Tajima, I.; Hayakawa, Y.; Okada, M.; Bitoh, M.; Ashida, T.; Sumitomo, H. *J. Am. Chem. Soc.* 1980, *102*, 7873.
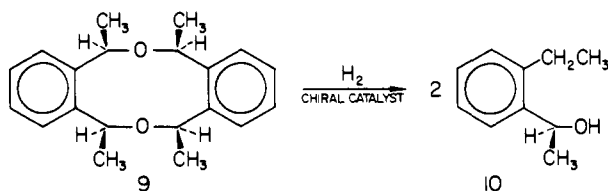
(20) For example, hydrolysis of the achiral macrotetrolide antibiotic nonactin to a single racemic hydroxyacid. See: Keller-Schierlein, W.; Gerlach, H. *Fortschr. Chem. Org. Naturs.* 1968, *26*, 161 and references therein.

La Coupe du Roi and Its Relevance to Stereochemistry

J. Am. Chem. Soc., Vol. 105, No. 6, 1983 1423

to give an achiral whole), and, second, that the same objects cannot be bisected into heterochiral halves. To the best of our knowledge, no examples are reported in the literature that demonstrate the first of these two features in a chemical reaction.[21]

What are the symmetry characteristics for such a molecule? To begin with, we must exclude molecules with C_∞ axes since they cannot be chemically cleaved along this axis. Thus, in contrast to an idealized apple,[7] which cannot be dissected into C/O's in class B *regardless* of the number of segments, any achiral molecule that can be cleaved into (or formed from) homochiral fragments can also be cleaved into (or formed from) an even number (not necessarily two) of heterochiral fragments, provided that the line of cleavage does not pass through a nucleus. Molecules with C_s and C_i symmetry are excluded since bisection can only be in class B. Of the remaining achiral symmetries, C_{2v} is the simplest in which bisection of a molecule can only lead to achiral or homochiral but not to heterochiral fragments. Conversely, it is also the simplest symmetry for a molecule that cannot be constructed from only two heterochiral fragments.

As a hypothetical example, consider the set of cyclic oligomers in Figure 5 that have C_{nv} symmetry ($n \geq 2$ and finite) on the appropriate time scale. In principle, these oligomers may be cleaved into n isometric molecular fragments. As illustrated for the dimer in Figure 5, these fragments may all be achiral (cleavage at x) or all chiral (cleavage at y and y'); in the latter case the enantiomeric excess depends on the extent to which unequal cleavage at y and y' is induced by a chiral reagent. In the limit, exclusive cleavage at, say, y would result in exclusively homochiral fragments. Conversely, these molecules may in principle be synthesized by oligomerization of achiral or homochiral fragments.

Along similar lines, Horeau has suggested the possibility that if hydrogenolysis of the meso compound **9** (which has C_{2v} sym-

metry on the appropriate time scale) leads to homochiral products, hydrogenolysis by a chiral reducing agent might lead to the predominance of one enantiomer, e.g., **10**.[22]

In all of the above reactions, a cyclic bonding array is made or broken, and the question naturally arises whether it is possible to obtain homochiral fragments by cleavage of an acyclic array in an achiral molecule; after all, it is easy to fragment an achiral molecule into two achiral radicals (R–R → 2R·, class A) or into two heterochiral radicals (R–R → $R_{R'}$ + $R_{S'}$, class B) by this type of cleavage. However, it turns out that under the constraints which we have imposed, a similar cleavage in class C (R–R → $R_{R'}$ + $R_{R'}$, R–R → $R_{S'}$ + $R_{S'}$) is not possible in practice, since the chirality of the cut cannot be maintained within the fragments after relaxation.[13] *In general, a central cyclic array is a necessary condition for the cleavage of an achiral molecule into homochiral fragments or for its formation from such fragments.*[23]

A reaction that fulfills all the requirements of symmetry and chemical feasibility in the context of the previous discussion is now reported. It is based on the work of Misumi and co-workers,[24–26] who synthesized the layered metacyclophanes **11** and **12**

Scheme I

Scheme II

13, X = Y = CH$_2$Br	**18**, X = CH$_2$OH; Y = CO$_2$H
14, X = Y = CH$_2$SH	**19**, X = CH$_2$Br; Y = CO$_2$CH$_3$
15, X = CH$_2$SH; Y = CH$_2$Br	**20**, X = CH$_2$SCN; Y = CO$_2$CH$_3$
16, X = Y = CH$_3$	**21**, X = CH$_2$SH; Y = CH$_2$OH
17, X = Y = CH$_2$OH	

(for convenience, these compounds will be referred to as the cis and trans "dimer", respectively) by the coupling of the dibromide **13** with the dithiol **14** or by the reaction of **13** with Na$_2$S. In both cases, approximately equimolar mixtures of the two dimers were obtained. Our plan was to synthesize the bromothiol **15** in an optically active form (**15a** or **15b**). The self-coupling of two homochiral molecules of **15** can only give the achiral cis dimer **11** (C_{2v} time-averaged symmetry), whereas the coupling of two heterochiral molecules of **15** can only give the achiral trans dimer **12** (C_{2h} time-averaged symmetry) as shown in Scheme I. In the cis dimer **11**, the fragments are joined together to form a new ring, as required.

The bromothiol precursor **15** should be obtainable in configurationally (and optically) stable form since the functionalities (CH$_2$SH and CH$_2$Br) have a meta relationship to one another on the benzene ring and are therefore unlikely to undergo in-

(21) It is obviously impossible to provide an experimental demonstration of the second feature.
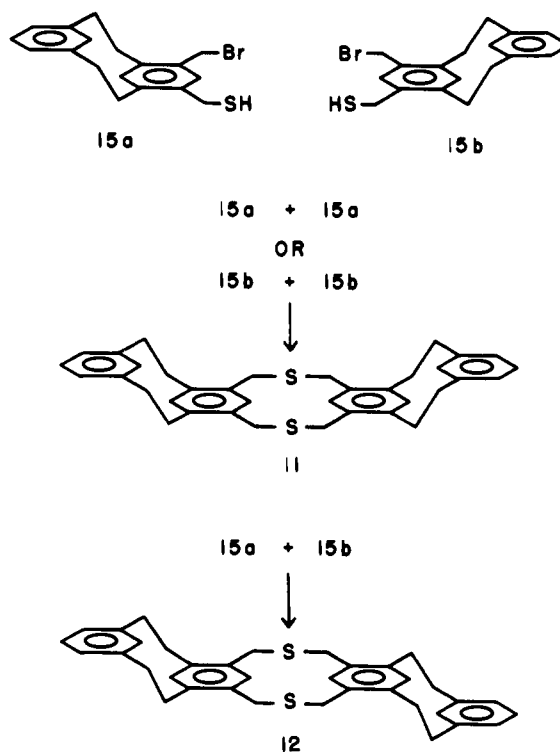
(22) Horeau, A., private communication. In the absence of a chiral reagent, the product will be racemic since each homochiral pair is statistically matched with the enantiomeric pair. In an extension of this idea, one might conceive of a hypothetical enzyme with C_2 symmetry that cleaves an achiral substrate into homochiral moieties.

(23) Note that by breaking a cyclic instead of an acyclic bonding array, heterolytic as well as homolytic cleavages can be performed.
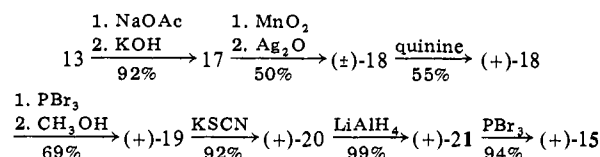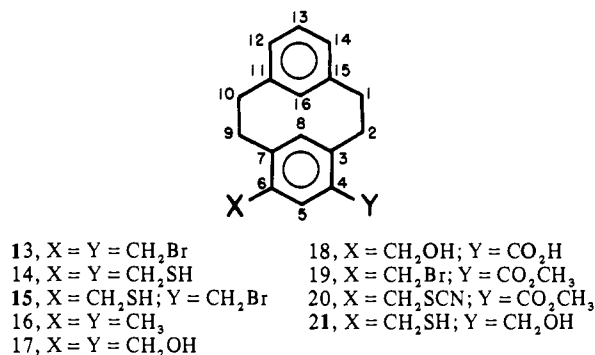
(24) Umemoto, T.; Otsubo, T.; Sakata, Y.; Misumi, S. *Tetrahedron Lett.* **1973**, 593.

(25) Umemoto, T.; Otsubo, T.; Misumi, S. *Tetrahedron Lett.* **1974**, 1573.

(26) Umemoto, T. Ph.D. Thesis, Osaka University, Osaka, Japan, 1976. We thank Professor Misumi for providing us with this data.

Table I. ^{1}H NMR Parameters of Compounds 11 through 21[a]

com-pound	^{1}H type[b]	δ	pat-tern[c]	$|J|$, Hz	com-pound	^{1}H type[b]	δ	pat-tern[c]	$|J|$, Hz
11	$H_{1a}, H_{2a}, H_{9a}, H_{10a}$	1.91, 2.41	td	12, 3	17	$H_{1a}, H_{2a}, H_{9a}, H_{10a}$	1.92, 2.15	td	12, 3
	$H_{1e}, H_{2e}, H_{9e}, H_{10e}$	3.13, 3.49	dt	12, 3		$H_{1e}, H_{2e}, H_{9e}, H_{10e}$	3.13, 3.47	dt	12, 3
	CH_2S	3.74, 3.96	q	14.5		H_8	4.25	s	
	H_8	4.07	s			H_{16}	4.35	br s	
	H_{16}	4.60	br s			CH_2O	4.76, 4.84	qd[d]	12, 4
	H_5	6.62	s			H_{12}, H_{14}	7.07	d	7
	H_{12}, H_{14}	7.09	d	7.5		H_{13}	7.30	t	7
	H_{13}	7.31	t	7.5		H_5	7.40	s	
12	$H_{1a}, H_{2a}, H_{9a}, H_{10a}$	1.67, 2.16	td	12, 3	18	$H_{1a}, H_{2a}, H_{9a}, H_{10a}$	1.85, 1.95, 2.20, 2.30	td	12, 3
	$H_{1e}, H_{2e}, H_{9e}, H_{10e}$	2.91, 3.24	dt	12, 3		$H_{1e}, H_{2e}, H_{9e}, H_{10e}$	3.19, 3.21, 3.55, 4.34	dt	12, 3
	H_8	3.67	s			OCH_3	3.90	s	
	CH_2S	3.99	s			H_8, H_{16}	4.37	s	
	H_{16}	4.03	br s			CH_2O	4.78, 4.86	q	12
	H_{12}, H_{14}	6.91	d	7.5		H_{12}, H_{14}	7.10, 7.12	d	7.5
	H_{13}	7.15	t	7.5		H_{13}	7.35	t	7.5
	H_5	7.17	s			H_5	8.15	s	
13	$H_{1a}, H_{2a}, H_{9a}, H_{10a}$	1.97, 2.36	td	12, 3	19	$H_{1a}, H_{2a}, H_{9a}, H_{10a}$	1.80, 2.00, 2.25, 2.40	td	12, 3
	$H_{1e}, H_{2e}, H_{9e}, H_{10e}$	3.16, 3.47	dt	12, 3		$H_{1e}, H_{2e}, H_{9e}, H_{10e}$	3.20, 3.20, 3.50, 4.20	dt	12, 3
	H_8	4.15	s			H_8	4.25	s	
	H_{16}	4.50	br s			H_{16}	4.42	br s	
	CH_2Br	4.58	s			CH_2Br	4.62	s	
	H_{12}, H_{14}	7.10	d	7.5		H_{12}, H_{14}	7.10	d	7
	H_{13}	7.35	t	7.5		H_{13}	7.30	t	7
	H_5	7.37	s			H_5	7.95	s	
14	SH	1.82	t	7	20	$H_{1a}, H_{2a}, H_{9a}, H_{10a}$	1.75, 1.90, 2.07, 2.23	td	12, 3
	$H_{1a}, H_{2a}, H_{9a}, H_{10a}$	1.92, 2.27	td	12, 3		$H_{1e}, H_{2e}, H_{9e}, H_{10e}$	3.08, 3.13, 3.25, 4.22	dt	12, 3
	$H_{1e}, H_{2e}, H_{9e}, H_{10e}$	3.11, 3.40	dt	13, 3		OCH_3	3.84	s	
	CH_2S	3.75, 3.85	qd	13, 7		CH_2S	4.01, 4.13	q	12
	H_8	4.17	s			H_8	4.25	s	
	H_{16}	4.42	br s			H_{16}	4.32	br s	
	H_{12}, H_{14}	7.10	d	7.5		H_{12}, H_{14}	7.02, 7.06	d	7
	H_5	7.23	s			H_{13}	7.29	t	7
	H_{13}	7.32	t	7.5		H_5	7.87	s	
15	$H_{1a}, H_{2a}, H_{9a}, H_{10a}$	1.92, 1.96, 2.27, 2.38	td	12, 3	21	$H_{1a}, H_{2a}, H_{9a}, H_{10a}$	1.88, 1.95, 2.13, 2.25	td	12, 3
	SH	1.82	t	7		SH	1.82	t	6
	$H_{1e}, H_{2e}, H_{9e}, H_{10e}$	3.13, 3.13, 3.43, 3.45	dt	12, 3		$H_{1e}, H_{2e}, H_{9e}, H_{10e}$	3.10, 3.12, 3.24, 3.26	dt	12, 3
	CH_2S	3.75, 3.85	qd	13, 7		CH_2S	3.78, 3.88	qd	13, 6
	H_8	4.15	s			H_8	4.20	s	
	H_{16}	4.45	br s			H_{16}	4.40	br s	
	CH_2Br	4.60	s			CH_2O	4.72, 4.82	q	12
	H_{12}, H_{14}	7.10	d	7		H_{12}, H_{14}	7.10	d	7
	H_5	7.30	s			H_5	7.30	s	
	H_{13}	7.32	t	7		H_{13}	7.32	t	7
16	$H_{1a}, H_{2a}, H_{9a}, H_{10a}$	1.82, 2.08	td	12, 3					
	CH_3	2.33	s						
	$H_{1e}, H_{2e}, H_{9e}, H_{10e}$	3.02, 3.30	dt	12, 3					
	H_8	4.20	s						
	H_{16}	4.29	br s						
	H_{12}, H_{14}	7.06	d	7.5, 1.5					
	H_5	6.98	s						
	H_{13}	7.28	t	7.5					

[a] All spectra were measured at 200 MHz in $CDCl_3$ except for compound 20, which was measured in 4:1 $CDCl_3-C_6D_6$ because this solvent gave a better spread of chemical shifts. $SiMe_4$ was used as an internal standard. [b] Subscripts a and e refer to axial and equatorial orientations of the protons in the 10-membered ring of the metacyclophane system. [c] s = singlet, d = doublet, t = triplet, q = AB-type quartet. In the case of dt, td, and qd, the first letter refers to the splitting with the larger coupling constant (i.e., in the order given in the J column). For the case of broad singlets (br s), the line widths at half peak height are about 2–2.5 Hz. [d] An ABX spectrum was only observed with $CDCl_3$ freshly treated with alumina.

tramolecular cyclization[27] or, by the same token, racemization through a reversibly formed achiral cyclic intermediate. Also, the benzene rings in simple metacyclophanes cannot pass one another under ordinary conditions,[24–26] so that 15 should not racemize by such a mechanism.

Scheme II shows the sequence of reactions for the synthesis of 15. The MnO_2 oxidation of the diol 17 gives predominantly the monoaldehyde, presumably because the latter is less strongly adsorbed on the reagent than is the diol. The hydroxyacid (±)-18 is easily resolved with quinine. Fortunately, the two diastereomeric

salts, which most likely exist as ion pairs in $CDCl_3$, have observably different ^{1}H chemical shifts, and this allowed an easy monitoring of the resolution and showed that the enantiomeric purity of 18 in the salt after three crystallizations was about 90%.

NMR of Metacyclophane Derivatives. All of the new compounds (15–21) have easily interpretable high-field (200 MHz) ^{1}H NMR spectra (Table I). The metacyclophane system provides sufficient chemical shift dispersion so that the spectra of the symmetrical compounds show virtually no multiplet overlap and are close to first order, except for the CH_2 protons at C-4 and C-6. These protons give rise to characteristic and strongly coupled AB quartets (or occasionally a single line) or to the AB part of ABX systems. The CH_2–CH_2 bridge protons give four well-

(27) Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978; p 160.
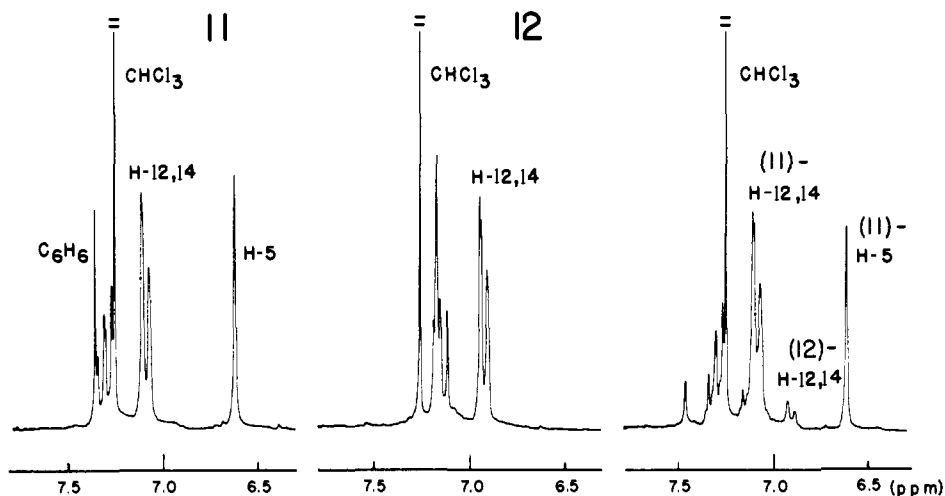
Figure 6. 200-MHz ^{1}H NMR spectra of the low-field aromatic region of dimers **11** (left) and **12** (center) and of the dimer mixture obtained from 90% enantiomerically pure (+)-**15** (right).

separated multiplets. Each bridge carbon has an axial (a) and an equatorial (e) proton. The multiplets of the axial protons are the result of large and nearly equal $^2J_{ae}$ and $^3J_{aa}$ and of a smaller $^3J_{ae}$. The equatorial protons have one large and two small coupling constants ($^2J_{ae}$, $^3J_{ae}$, and $^3J_{ee}$, respectively). In the unsymmetrical derivatives, the two bridges are different so that their multiplets, although still first order, show mutual overlaps for corresponding protons. The H-12, H-13, and H-14 protons have typical aromatic shifts and are AB$_2$ or ABC systems with an additional small meta coupling of H-12 and H-14 to H-16. In the unsymmetrical compounds, H-12 is slightly different from H-14. The internal protons (H-8 and H-16) have the very high field chemical shifts typical of the *anti*-metacyclophane ring system.[28] Whereas H-8 is relatively sharp, H-16 is distinctly broad because of unresolved couplings to H-12 and H-14.

The cis and trans dimers (**11** and **12**) have very different ^{1}H NMR spectra, and this allows an easy analysis to be made of the composition of a mixture of the two dimers. The ^{1}H NMR spectra reported by Misumi and co-workers[24-26] for these compounds agree precisely with our findings.

The central heterocyclic rings in the dimers probably exist very largely in the syn conformation, with the two metacyclophane moieties folded together, as has been found for the simpler 2,11-dithia[3.3]metacyclophane,[28] and this probably is the reason that the two dimers have very different ^{1}H NMR spectra. Inversion of the heterocyclic ring in all these compounds is very fast at room temperature, unlike that of the metacyclophane rings.[24-26] The latter do invert slowly above 200 °C, as shown by the interconversion of the two dimers **11** and **12** under these conditions.

Self-Coupling of the Bromothiols (+)-15 and (±)-15. The bromothiol (+)-**15** was self-coupled under basic conditions. The dimer fraction was optically inactive. NMR analysis of this fraction showed the presence of the dimers **11** and **12** in the ratio of about 10:1. Since the enantiomeric purity of the bromothiol used was ca 90%, some of the dimer **12** was expected. The self-coupling of (±)-**15**, by contrast, gave approximately equal amounts of the two dimers, as did the previously reported unsymmetrical coupling of achiral dibromide, **13**, with achiral dithiol, **14**. From these results it is clear that there is almost no selectivity in the initial S$_N$2 reaction; i.e., (+)-**15** reacts as fast with another (+)-**15** molecule as it does with a (−)-**15** molecule. The nature [cis (C_{2v}) or trans (C_{2h})] of the dimer is determined entirely by the initial carbon–sulfur bond formation; the subsequent ring closure by an internal S$_N$2 reaction follows a predetermined course. With the assumption of zero selectivity in the initial S$_N$2 reaction, the product from a precursor of 90% enantiomeric purity (i.e., 95% (+)-**15** and 5% (−)-**15**) is a ca. 9:1 ratio of the cis and trans

dimers (**11** and **12**), as found experimentally. With the same lack of selectivity, the products from (±)-**15** should consist of a 1:1 ratio of the cis and trans dimers, also as observed.

It is possible to correct for the lack of complete enantiomeric purity in (+)-**15** from the experimental data given above. The corrected result shows that enantiomerically pure (+)-**15** gives only the cis dimer **11** and none of the trans dimer **12**. This proves experimentally that (+)-**15** does not racemize during the coupling reaction. Thus, the self-coupling of the bromothiol (+)-**15** to give an achiral compound (cis dimer **11**) is a chemical analogue of the reassembly of a pair of homochiral coupe-du-roi apple halves to give back an achiral apple.

Experimental Section

Melting points were determined on a Mel-Temp apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker WP-200 Fourier transform spectrometer at 200 MHz. Mass spectra were obtained on an AEI MS-9 mass spectrometer. Optical rotations were obtained on a Perkin Elmer 241 MC polarimeter. The workup of reaction mixtures, unless otherwise stated, was carried out by extraction with CH$_2$Cl$_2$, washing of the extract with water, and drying of the organic phase with MgSO$_4$, followed by solvent removal under reduced pressure.

4,6-Bis(bromomethyl)[2.2]metacyclophane (13) was prepared by a sequence of reactions[24] starting from *m*-xylene and *m*-bis(bromomethyl)benzene (Aldrich).[29] The only modification made to the published procedure was that thiols were prepared from the corresponding halides via the thiocyanates followed by reduction with LiAlH$_4$[30] (as described below for **21**) rather than by the direct reaction of the halides with NaSH. In the preparation of **13** by bromination of the dimethyl compound **16** with *N*-bromosuccinimide, it was found necessary to use dilute solutions of **16** in CCl$_4$, as otherwise there was a vigorous evolution of HBr and Br$_2$ and little or no **13** was produced.

4,6-Bis(hydroxymethyl)[2.2]metacyclophane (17). A solution of 0.48 g (1.22 mmol) of **13** and 2.25 g (27 mmol) of sodium acetate in 50 mL of acetic acid was refluxed for 2.5 h. The solution was poured into water, and the product obtained after workup was refluxed with 70 mL of CH$_3$OH containing 0.65 g of KOH for 1.5 h. After workup (CHCl$_3$ extraction), the diol was purified by column chromatography over silica gel with 1:1 CHCl$_3$–ethyl acetate as the eluant to give 0.30 g (92%) of **17**: mp 177–180 °C after recrystallization from 1:1 CHCl$_3$–ethyl acetate. NMR in Table I.

Anal. Calcd for C$_{18}$H$_{20}$O$_2$, m/e (M$^+$) 268.1464. Found: m/e 268.1460.

4-Carboxy-6-(hydroxymethyl)[2.2]metacyclophane ((±)-18). The diol **17** (0.11 g, 0.41 mmol) was added to a suspension of 0.52 g of activated manganese dioxide[31] in 120 mL of CH$_2$Cl$_2$. The mixture was stirred, and the reaction was monitored by TLC on silica gel with 1:1 CHCl$_3$–ethyl acetate as the eluant. After 1 h, the monoaldehyde predominated. The

(28) Anker, W.; Bushnell, G. W.; Mitchell, R. H. *Can. J. Chem.* **1979**, *57*, 3080 and references therein.

(29) We thank Ed Hill for the preparation of some of the dimethyl compound **16** used in this investigation.
(30) Strating, J.; Backer, H. J. *Recl. Trav. Chim. Pays-Bas* **1950**, *69*, 638.
(31) Pratt, E. F.; Van de Castle, J. F. *J. Org. Chem.* **1961**, *26*, 2973.

product was purified by column chromatography over silica gel with 1:1 CHCl₃–ethyl acetate as the eluant. The resulting clear oil was further oxidized with 0.12 g (0.7 mmol) of AgNO₃ and 0.45 g (11 mmol) of NaOH in 20 mL of 9:1 CH₃OH–H₂O. After 2 h, the mixture was treated with dilute HCl. Workup gave a product that was dissolved in CH₂Cl₂ and extracted with dilute aqueous NaOH. Slow acidification of the aqueous layer gave (±)-**18**, which was collected by filtration to give 58 mg (50%) of a white solid: mp 194–197 °C. NMR in Table I.

Anal. Calcd for $C_{18}H_{18}O_3$, *m/e* (M⁺) 282.1256. Found: *m/e* 282.1254.

Optical Resolution of (±)-18 with Quinine. Dissolution of 0.305 g of (±)-**18** and 0.406 g of quinine in a minimum voume of warm CHCl₃ followed by slow cooling to room temperature gave a nicely crystalline salt. The ¹H spectrum of the crude salt in CDCl₃ showed two sets of AB quartets for the methylene protons of the CH₂OH group. The less soluble salt had δ_{AB} 4.526 and 4.602, and the more soluble salt had δ_{AB} 4.496 and 4.592, with J_{AB} = 12.5 Hz in both salts. Three recrystallizations of the crude salt gave 0.2 g of the quinine salt of (+)-**18**, which contained about 5% of the quinine salt of (−)-**18**. One half of this product was converted to the free acid by treatment with dilute HCl to give after workup (CHCl₃ extraction) 42 mg (55%) of (+)-**18** as a white solid: $[\alpha]^{20}{}_D$ +15.4° (*c* 1.68, CHCl₃).

(+)-4-(Carboxymethyl)-6-(bromomethyl)[2.2]metacyclophane ((+)-19). A solution of 42 mg (0.15 mmol) of (+)-**18** in 0.6 mL of PBr₃ was heated to 50–60 °C for 2 h. The solution was cooled in an ice bath and slowly added to 20 mL of cold CH₃OH. After the addition of 40 mL of ether, the solution was washed four times with water and dried over MgSO₄. Removal of the solvent left 37 mg (69%) of (+)-**19** as a light yellow oil: $[\alpha]^{20}{}_D$ +32.6° (*c* 0.43, CHCl₃). NMR in Table I.

Anal. Calcd for $C_{19}H_{19}O_2Br$, *m/e* (M⁺) 360.0549. Found: *m/e* 360.0533.

(+)-4-(Carboxymethyl)-6-(thiocyanatomethyl)[2.2]metacyclophane ((+)-20). A solution of 37 mg (0.10 mmol) of resolved **19** and 45 mg (0.46 mmol) of KSCN in 6 mL of acetone were refluxed for 1 h. After workup, the product was purified by column chromatography over silica gel with CHCl₃ as the eluant to give 32 mg (92%) of (+)-**20** as a white solid: $[\alpha]^{20}{}_D$ +31.7° (*c* 0.13, CHCl₃). NMR in Table I.

Anal. Calcd for $C_{20}H_{19}NO_2S$, *m/e* (M⁺) 337.1138. Found: *m/e* 337.1135.

(+)-4-(Hydroxymethyl)-6-(mercaptomethyl)[2.2]metacyclophane ((+)-21). To 10 mg of LiAlH₄ in 2 mL of ether was added a solution of 32 mg (0.095 mmol) of (+)-**20** in 6 mL of 3:1 ether–THF. The mixture was refluxed for 1 h and then quenched with water. A small amount of dilute HCl was added, and the solution was extracted with ether. After drying over MgSO₄, the solvent was removed from the ether extract, leaving 27 mg (99%) of (+)-**21** as a white solid: $[\alpha]^{20}{}_D$ +23.5° (*c* 0.27, CHCl₃). NMR in Table I.

Anal. Calcd for $C_{18}H_{20}OS$, *m/e* (M⁺) 284.1236. Found: *m/e* 284.1230.

(+)-4-(Bromomethyl)-6-(mercaptomethyl)[2.2]metacyclophane ((+)-15). A solution of 27 mg (0.095 mmol) of (+)-**21** in 0.65 mL of PBr₃ was heated to 50–60 °C for 2 h. The cooled solution was then slowly added to 10 mL of cooled CH₃OH. After the addition of 40 mL

of ether, the solution was washed four times with water. The ether extract was dried over MgSO₄ and the solvent evaporated to give 31 mg (94%) of (+)-**15** as a white solid: $[\alpha]^{20}{}_D$ +8.7° (*c* 0.31, CHCl₃). NMR in Table I.

Anal. Calcd for $C_{18}H_{19}BrS$, *m/e* (M⁺) 348.0372. Found: *m/e* 348.0366.

Self-Coupling of (+)-15. To a refluxing solution of 75 mg of KI in 325 mL of 95% EtOH was added 31 mg (0.089 mmol) of (+)-**15** (90% enantiomerically pure) in 10 mL of CHCl₃. After the addition of 4 mg (0.1 mmol) of NaOH in 2 mL of 95% EtOH, the solution was refluxed for 1.5 h and then another 4 mg of NaOH in EtOH was added. After a further 0.5 h of reflux, the solvent was evaporated. Chloroform and water were added to the residue, the chloroform layer was dried over MgSO₄, and the solvent was removed. The 200-MHz ¹H NMR spectrum of the crude reaction mixture showed the presence of a preponderance of the cis dimer **11** together with polymeric products and a small amount of the trans dimer (**12**). Chromatography over silica gel with 2:1 hexane–CHCl₃ as the eluant removed the polymeric products: $[\alpha]^{20}{}_D$ 0.0 ± 0.1° (*c* 1.11, *l* = 1, CDCl₃). The 200-MHz ¹H NMR spectrum then showed only the cis dimer **11** and the trans dimer **12** in a ratio of about 10:1. Figure 6 shows the low-field aromatic signals of this mixture.

Self-Coupling of (±)-15. The reaction was carried out as described for (+)-**15**. The sample of (±)-**15** was prepared in exactly the same way as that of (+)-**15**, except that the resolution step was omitted. The cis and trans dimers **11** and **12** were present in the crude product in approximately equal amounts, as shown by ¹H NMR.

Cis and Trans Dimers[32] 11 and 12.[24-26] The procedure described above for the self-coupling of (+)-**15** was used to couple **13** with **14**. The dimers, which are formed in about equal amounts, were separated by column chromatography over silica gel. The cis dimer **11** was eluted first. TLC showed that the two dimers interconvert at their melting points (>200 °C), which therefore tend to be broad and not useful for identification purposes. NMR in Table I.

Registry No. **11**, 54275-30-8; **12**, 54275-29-5; **13**, 51657-11-5; **14**, 62075-95-0; (+)-**15**, 84118-74-1; (±)-**15**, 84118-81-0; **16**, 40933-70-8; **17**, 84118-75-2; (±)-**18**, 84118-76-3; (+)-**18**, 84118-80-9; (+)-**19**, 84118-77-4; (+)-**20**, 84118-78-5; (+)-**21**, 84118-79-6.

(32) The *Chemical Abstracts* names of these compounds are (stereoisomers of) 3,19-dithiaheptacyclo[19.11.1.1⁵,¹⁷.1⁶,¹⁶.1⁹,¹³.1²²,³².1²⁵,²⁹]octatriaconta-1-(33),5,9,11,13(38),16(37),17(36),21,25,27,29(35),32(34)-dodecaene. A simpler name, which shows the chemical origin of these compounds is 4,4′,6,6′-bis(1,3-(2-thiapropanediyl))bis(metacyclophane). The cis and trans designations given to the two stereoisomers are self-evident.