

# The Apparent Symmetry of Cyclohexane

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**Abstract:** Although planar projection formulas have long been employed to represent ring compounds, the justification of their use has seldom been satisfactory. Pólya's method is employed to show that their use in counting isomers is allowed because the permutation symmetry of such formulas is equivalent to that of a nonplanar ring in which interconversion between conformers occurs. The general applicability of the method presented for the counting of isomers of nonrigid molecules is briefly discussed.

The use of planar projection formulas to count the isomers of cyclic compounds is both venerable<sup>2</sup> and often misunderstood, although the usefulness of this procedure is apparent. One is readily convinced by inspection of the formulas in Figure 1, for example, that there are only three stereoisomers of 1,2-dibromocyclohexane. This fact is not, however, immediately evident from examination of the more proper perspective formulas of chair form cyclohexane shown in Figure 2. Even after rejection of I and II on the grounds of conformational instability, four rather than three isomers are counted. The discrepancy is overcome, of course, by showing that III and IV can be interconverted by conformational change alone. The apparent rigidity of the perspective formulas is misleading. By experience it has been found that the planar projection formulas, which ignore conformation, give a more accurate count of isomers in such systems.

Such a useful procedure should have something more than an empirical justification. In the literature three different types of justification have been offered. (1) The oldest argument posits a planar transition state through which the molecule passes in conformational change. The argument continues with the reasonable statement that the molecule, therefore, exhibits the highest symmetry that it attains.<sup>3</sup> The difficulty with this justification is that the planar transition state is a convenient fiction; it is energetically prohibitive relative to the twist-boat forms. (2) A more sophisticated argument is that the time-averaged state of the system, which involves both enantiomorphs, has an apparent higher symmetry than either separate form.<sup>4</sup> This argument leaves unanswered, however, the question of why this apparent symmetry is that of a planar ring. (3) The usual approach to this question is silence. Even authors who emphasize the importance of conformational analysis will ignore the difficulty of using planar rings to count the isomers of nonplanar molecules.<sup>5</sup>

It is argued here that the application of simple combinatorial principles allows a rigorous justification for the use of planar projection formulas in isomer counting, and that the further application of these principles is a useful tool for counting the isomers of nonrigid molecules.

In 1936 Pólya showed that the number of distinguishable ways of labeling the vertices of an achiral skeleton of any type could be counted using group theory considerations alone.<sup>6</sup> Since adequate descriptions of Pólya's method are in the literature,<sup>7</sup> only the essential elements of it are given here. In the case of chemical structures, a symmetry group  $G$  can be assigned by considering the point group operations which relate the substituent positions on the molecular skeleton. This point group  $G$  can also be described in terms of the permutations of these positions which are produced by

the point group operations. Figure 3 shows a perspective formula of chair form cyclohexane with its numbered substituent positions. The permutation element  $\pi_E$  for the identity operation  $E$  can be represented in terms of 12 disjoint sets (cycles), each describing the permutation of only one position.

$$\pi_E = \begin{pmatrix} 1 \\ 1 \end{pmatrix} \begin{pmatrix} 2 \\ 2 \end{pmatrix} \begin{pmatrix} 3 \\ 3 \end{pmatrix} \begin{pmatrix} 4 \\ 4 \end{pmatrix} \begin{pmatrix} 5 \\ 5 \end{pmatrix} \begin{pmatrix} 6 \\ 6 \end{pmatrix} \begin{pmatrix} 7 \\ 7 \end{pmatrix} \begin{pmatrix} 8 \\ 8 \end{pmatrix} \begin{pmatrix} 9 \\ 9 \end{pmatrix} \times \begin{pmatrix} 10 \\ 10 \end{pmatrix} \begin{pmatrix} 11 \\ 11 \end{pmatrix} \begin{pmatrix} 12 \\ 12 \end{pmatrix}$$

In this form the permutation indicates that the identity operation takes position 1 into position 1, position 2 into position 2, etc. This is an operation of 12 cycles of length one. Using the same numbering and notation system, the  $C_3$  operation (which contains four cycles of length three) is written as

$$\pi_{C_3} = \begin{pmatrix} 159 \\ 591 \end{pmatrix} \begin{pmatrix} 2 & 6 & 10 \\ 6 & 10 & 2 \end{pmatrix} \begin{pmatrix} 3 & 7 & 11 \\ 7 & 11 & 3 \end{pmatrix} \begin{pmatrix} 4 & 8 & 12 \\ 8 & 12 & 4 \end{pmatrix}$$

In general, a permutation  $\pi$  of a set  $S$  containing  $|S|$  elements can be described by  $c_1$  cycles of length 1,  $c_2$  cycles of length 2, . . . ,  $c_k$  cycles of length  $k$ , etc. Such a cycle structure representation of  $\pi$  can be written as a monomial

$$f_1^{c_1} f_2^{c_2} \dots f_k^{c_k} \dots$$

where the  $f_k$  are formal variables. For example,  $\pi_E$  and  $\pi_{C_3}$  are represented by  $f_1^{12}$  and  $f_3^4$ , respectively. (Note that the algebraic sum of the exponents is equal to 12, the degree of the group; the permutation of each of the 12 positions is accounted for.) In this manner each operation of the group can be represented in terms of its cycles, and the entire group  $G$  can be represented by the sum of these cycles, normalized by dividing by  $|G|$ , the order of the group. The general form of such a cycle index is then given by

$$Z(G; |S|) = (1/|G|) \sum_{\pi \in G} f_1^{c_1} f_2^{c_2} \dots f_k^{c_k} \dots$$

where the terms are defined as described above, and the sum is over all permutations in  $G$ . The cycle indices for the rotation group  $D_3$  and the rotation-reflection group  $D_{3d}$  are given in Table I, where the set  $S$  describes the substituent positions of chair form cyclohexane. The name of the index,  $Z(D_3; 12)$ , for example, indicates that a figure of 12 points is permuted by the symmetry group  $D_3$ . Table I also gives the cycle indices for the rotation group  $D_6$  and the rotation-reflection group  $D_{6h}$ , each applied to planar-projection cyclohexane.

Pólya showed various ways that the cycle index can be used to solve problems involving combinatorial enumera-

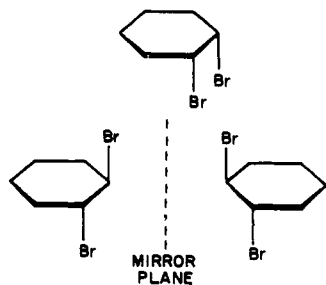


Figure 1. Planar projection formulas for 1,2-dibromocyclohexane.

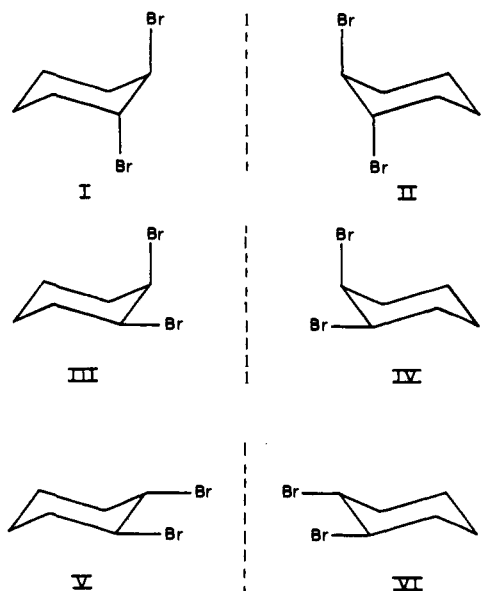


Figure 2. Perspective formulas for conformers of 1,2-dibromocyclohexane.

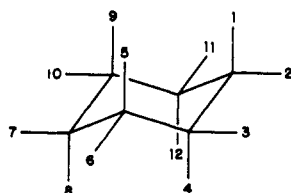


Figure 3. Numbering system for cyclohexane.

tion, but in the present paper we will confine our interest simply to its structure. Two observations on the isomer numbers can be made without further calculation. In both the threefold and sixfold groups the rotation group cycle index is not identical with the rotation-reflection cycle index, and hence both chair form and planar-projection cyclohexane can have enantiomeric isomers. Furthermore, there is no identity between the cycle indices for the rotation groups of the threefold and sixfold groups, nor for their rotation-reflection group cycle indices. Hence, there are different isomer numbers for the two skeletons whether one is counting all stereoisomers (rotation group) or only diastereomers (rotation-reflection group). Since the sixfold group has a higher order, it has fewer isomers of either type. The application of Pólya's method to rigid skeletons, then, has merely confirmed our empirical observation that there are fewer isomers for a planar-projection structure.

In attempting to represent the operations corresponding to nonrigid motions of molecular skeletons, it was found that the symmetry of cyclohexane can be adequately represented by introducing a new symmetry element  $R_6$  which combines a sixfold rotation with a flip motion of the ring in-

Table I. Cycle Indices for Calculating Cyclohexane Isomer Numbers

Chair Form Cyclohexane	
$Z(D_3;12)$	$= \frac{1}{6} [f_1^{12} + 3f_2^6 + 2f_3^4]$
$Z(D_{3d};12)$	$= \frac{1}{12} [f_1^{12} + 4f_2^6 + 2f_3^4 + 2f_6^2 + 3f_1^4 f_2^4]$
Planar-Projection Cyclohexane	
$Z(D_6;12)$	$= \frac{1}{12} [f_1^{12} + 7f_2^6 + 2f_3^4 + 2f_6^2]$
$Z(D_{6h};12)$	$= \frac{1}{24} [f_1^{12} + 12f_2^6 + 2f_3^4 + 6f_6^2 + 3f_1^4 f_2^4]$

Table II. Comparison of the Groups and Subgroups of  $D_{6h}$  and  $D_{3d}R_6$

Rotation Groups	
$D_3R_6$	$E, 2C_3, 3C_2, 2R_6, R_6^3, 3R_6 \cdot C_2$
$D_6$	$E, 2C_3, 3C_2, 2C_6, C_2, 3C_2'$
$Z(D_3R_6;12)$	$= Z(D_6;12) = \frac{1}{12} [f_1^{12} + 7f_2^6 + 2f_3^4 + 2f_6^2]$
Rotation-Reflection Groups	
$D_{3d}R_6$	$D_3R_6 + i, 2S_6, 3\sigma_v, 2R_6^5, R_6^3 \cdot i, 3\sigma_v \cdot R_6$
$D_{6h}$	$D_6 + i, 2S_6, 3\sigma_v, 2S_3, \sigma_h, 3\sigma_d$
$Z(D_{3d}R_6;12)$	$= Z(D_{6h};12) = \frac{1}{24} [f_1^{12} + 12f_2^6 + 2f_3^4 + 6f_6^2 + 3f_1^4 f_2^4]$

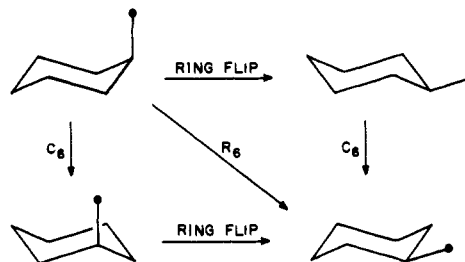


Figure 4. The ring flip-rotation operator  $R_6$ .

terconverting one chair form to another (Figure 4). The effect of this sixfold ring flip-rotation operator is to permute all the positions on the same side of the ring. The double application of this operator ( $R_6^2$ ) is identical with the simple rotation operation  $C_3$ . By combining this element with the groups  $D_3$  and  $D_{3d}$  two new groups can be generated which are designated  $D_3R_6$  and  $D_{3d}R_6$ . Table II summarizes the operations and cycle indices of these two groups and gives a comparison of their structures with  $D_6$  and  $D_{6h}$ . It is immediately obvious that the cycle indices of the two rotation groups are identical, and similarly for the two rotation-reflection groups. It is known from Pólya's work that, though two isomorphic groups operating on sets of the same degree must have the same cycle index, the converse is not always true. Hence, it is not immediately obvious that the two groups are isomorphic. However, a detailed comparison shows that they are in fact isomorphic permutation groups.

The permutation symmetry of the cyclohexane ring can be represented by a planar ring because the conversion of one chair form ring into the other leads to a permutation group whose combinatorial properties are identical with  $D_{6h}$ . This method of justifying the use of planar projection formulas emphasizes the necessity of conformational change in making planar representation allowable. Consequently, where such interconversion is impossible, as in bicyclo[2.2.0]hexane, the correct isomer number cannot be obtained from a planar representation.

If this method of analysis were limited to the algebraic solution of a problem (the isomer numbers of cyclohexane) which has previously been fully worked out from models, it

would be of little use indeed. However, it is a more powerful tool than is indicated by this example alone. Traditionally, Pólya's method has been applied primarily to molecules such as benzene,<sup>6</sup> octahedral and tetrahedral coordination complexes,<sup>7</sup> and polynuclear coordination complexes<sup>7,8</sup> which are characterized by rigid skeletons. The element  $R_6$  is only a single example of internal symmetry operations which occur in nonrigid molecules. In addition to the ring flip-rotation operation, internal symmetry elements which have been investigated include internal rotation (in ethane and metallocene compounds) and inversion (in amines).<sup>9</sup>

Furthermore, the investigation of isomerism in nonrigid molecules has become an important field of chemical investigation. Permutation group properties have been applied to the analysis of these systems, both theoretically<sup>10</sup> and applied.<sup>11,12</sup> In work carried out by Gillespie and his colleagues, the power of the permutation group method has been illustrated for a number of nonrigid systems.<sup>11</sup> They note that monocyclic ring systems, in particular the cyclohexane system, exhibit a dynamic skeletal symmetry which is equivalent to the symmetry of a hypothetical planar ring. They obtain the dynamic skeletal symmetry, group  $D$ , by obtaining the product of the permutation group  $G$  representing the rigid skeletal system of the ring and the permutation group  $F$  representing the flexions:  $D = G \times F$ .

The advantages of the point group method proposed herein over the permutation group method are similar to those leading to the adoption of point groups for most chemical applications: (a) the symmetry elements bear logical and easily visualized relations to chemical/physical notions of the molecule's properties; (b) the group of symmetry operation can be obtained from the product  $G \times F$  in a manner which allows for visualization and description; and (c) the description of the dynamic skeletal symmetry group is independent of the numbering of the skeleton.

It is our hope that the present method of describing the dynamic skeletal symmetries of molecules will serve as a fruitful tool for making the chemist's intuition of internal molecular motions into a theoretically precise notion.

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## Excited States and Photochemistry of Saturated Molecules. I. General Approach and Application to Propane

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**Abstract:** Following Ruedenberg, we suggest that a useful measure of chemical binding is the two-center, one-electron interference contribution to the energy in the electronic state of interest. Using this conceptual framework, the vertical valence excited states of propane in the optimal ground state geometry are examined using INDO in its original parametrization. The results are compared with available experimental information. The calculations yield bond energies which are consistent with observed decomposition modes for ground states of small alkanes and excited states of propane. Configuration interaction calculations are discussed in the case of propane. Inclusion of all single excitations from the ground state results in considerable rearrangement of the order of excited states; however, the relative bond energies within each state are unaffected.

With the exception of ethane, absorption or electron impact spectra of small ( $n \leq 6$ ) acyclic alkanes contain little discernible information. The broad, essentially featureless spectra<sup>1,2</sup> give little in the way of structural information about the excited state. Recently Lipsky<sup>3</sup> observed that the separation between absorption onset and fluorescence maxi-

mum of linear alkanes decreases with increasing chain-length and increases with branching. Based on these results and energy transfer studies, he concluded that these frequencies are related to the extent of nuclear distortion in the excited states. Numerous photochemical studies of small acyclic alkanes have established the striking predomi-