Enantiomeric Labeling of Reaction Graphs

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We examine systematically the possibility that a given reaction graph connects enantiomers. We define an enantiomeric labeling as a way to dispose enantiomers on the graph according to specified conditions. Since reaction graphs have to be symmetric, we have derived the set of enantiomeric labelings for every symmetric graph having less than 20 vertices. For some of these graphs, this set is empty; for others it contains only one labeling. Unexpectedly, it appears that some graphs have many such labelings which may even have different distances between enantiomers. As a result, the distance between enantiomers is not always the diameter of the graph.

1. INTRODUCTION

A striking feature of the literature on reaction graphs is that dynamic processes of a quite different nature may give rise to isomorphic reaction graphs. This appeared already at the very beginning of the development of this area because the first reaction graph, namely the Desargues−Levy graph discussed by Balaban, Fărcaşiu and Bănică,[1] can describe as well interconversions of carbonium ions via 1,2-shifts as Berry[2] pseudorotations in phosphorus pentafluoride. Quite recently, it has been shown that the reaction graph of XeF_6 (mode u_{12})[3] is also related to the Desargues−Levy graph: the graph for u_{12} where a pair of enantiomeric vertices is mapped onto a single vertex gives rise to the Desargues−Levy graph. Hence, 1,2-shifts in carbonium ions, Berry pseudorotations in phosphorus pentafluoride, and interconversions of pairs of enantiomeric configurations via mode u_{12} in XeF_6 are stereochemically correspondent systems,[4,5] i.e., their static stereochemistry and conformational dynamics may be represented by the same abstract model namely the Desargues−Levy reaction graph. Loosely speaking, the rather frequent occurrence of such stereochemical correspondences suggests that the number of reaction graphs is small compared to the number of fluxional systems, at least when the number of vertices of the graph is not too big. This is one of the reasons why reaction graphs are an efficient tool to study such reaction systems. In the present paper, we focus our attention on a particular aspect of the behavior of fluxional systems, namely the transformation of a given configuration into its mirror image. Such a transformation may occur in one step (as, for instance, umbrella inversion of ammonia) or may need more than one step (at least five consecutive Berry pseudorotations are needed in order to transform an initial trigonal bipyramid configuration into its mirror image). It would however also happen that a given stereochemical interconversion does not transform a configuration into its mirror image (such as ethane internal rotation). We want to discuss the underlying problem without any reference to the static and dynamic stereochemical problem at hand. In other words, we address the following question: given an abstract connected reaction graph, is it possible to find an **enantiomeric labeling** of its vertices, i.e., a correspondence between the set of configurations $a, \bar{a}, b, \bar{b}, ...$ and the vertices of the graph (a and $\bar{a}$ are mirror image configurations), as will be seen in section 4.

2. PERMUTATIONAL DESCRIPTION

The permutational description of fluxional molecules is based on the concepts of configuration and of mode of rearrangements.[6−8] A detailed discussion[9] of these concepts and of their connection with reaction graphs[3,10,11] may be found in previous work. We briefly recall some definitions.

2.1. Configurations. We consider a molecule with n skeletal sites (n a positive integer) and reaction objects (ligands) of the same nature placed at those sites. Mathematically speaking this provides a skeleton consisting of a set of n points not all in one plane, called sites, in the three-dimensional euclidean space. We often need to label those sites from 1 to n. The groups A (respectively G) associated with the molecule are the permutational expressions (namely restrictions to the skeleton) of the groups of proper (respectively proper and improper) symmetries of three-space acting on the sites. Thus A (respectively G) consists of space rotations (respectively rotations and antirotations) fixing the center of mass and it is a subgroup of $SO(3)$ (*respectively* O(3)). The order of A is denoted by $|A|$. Both A and G obey the relation

$$G = A \cup A\sigma \tag{1}$$

where ∪ means union and σ is any improper symmetry

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operation. For chiral molecules

$$G = A \tag{2}$$

but this case will not be discussed here, hence we always assume that A is a subgroup of index *2* of G which means that σ exists. There are physical reasons to consider interconversions from an initial reference configuration to some final configuration of the molecule as any permutation x of the n sites up to the members of A and to express this on the basis of the labels from 1 to n put on the sites. Therefore we introduce the symmetric group S_n of degree n acting on the set of n sites. As a matter of fact A and G are subgroups of S_n We define a *configuration* of the molecule as a coset Ah of A in S_n consisting of all |A| permutations of the n sites differing from each other by a proper rotation leaving the skeleton invariant. The *n!* permutations in S_n give rise to

$$t = |S_n|/|A| = n!/|A| \tag{3}$$

configurations.

A key concept here is that the coset

$$A\sigma h = \sigma A h \tag{4}$$

represents the configuration which is **enantiomeric** (mirror image) to the configuration Ah, and these enantiomeric configurations are distinct because σ is not in A.

2.2. Modes of Rearrangement. Let x be any permutation belonging to S_n, describing a reaction interconversion of one configuration to another. A **mode of rearrangement** $M(x)$ *is* the set of permutations which are chemically indistinguishable from x either because they generate the same configuration as x from the initial one or because they occur with the same probability as x. It has been shown that[7,8]

$$M(x) = (AxA) \cup (A\sigma x\sigma^{-1}A) \tag{5}$$

provided $M(x)$ *is* self-inverse namely

$$M(x) = M(x^{-1})$$

When the mode is not self-inverse, i.e., when $M(x)$ and $M(x^{-1})$ are distinct, one has to consider

$$M_{\mathrm{ext}}(x) = M(x) \cup M(x^{-1}) \tag{6}$$

instead of $M(x)$, since x and x^{-1} are chemically equiprobable.[12−16] Here we will only consider self-inverse modes in order to simplify the arguments.

Mathematically speaking, we may consider (5) and (6) as the definition of a mode of rearrangement: it provides a partition of S_n or better, of the set of configurations. In terms of permutation groups, in the action of S_n on the cosets of A, the set $M(x)$ can be seen as the union of the orbits of the cosets Ax and $A\sigma x\sigma^{-1}$ under the configuration stabilizer A. More precisely, we define the graph Δ whose vertices are the right cosets of A in S_n and whose edges are the pairs $\{Ah, Ak\}$ such that $kh^{-1} \in M(x)$. If $\sim$ denotes the adjacency in Δ we have thus $Ah \sim Ak$ if and only if $A \sim Akh^{-1}$ which means that each edge of Δ is the image of an edge containing the vertex A by the permutation $\alpha(s)$ induced by some fixed element s $\in S_n$ on the vertices of Δ and such that for every $r \in S_n$ we get $\alpha(s)(Ar) = Ars$. We have

$$(M(x))^{-1} = (AxA)^{-1} \cup (A\sigma x\sigma^{-1}A)^{-1}$$
$$= (Ax^{-1}A) \cup (A\sigma x^{-1}\sigma^{-1}A) = M(x^{-1})$$

Since we suppose $M(x^{-1}) = M(x)$, this implies that, for every $h, k \in S_n$, $kh^{-1} \in M(x)$ if and only if $hk^{-1} = (kh^{-1})^{-1} \in M(x)$ and the graph Δ is well defined as an undirected graph.

For every $a \in A$, the permutation $\alpha(a)$ defined by

$$\alpha(a)(Ah) = Aha \text{ for every } h \in S_n$$

is an automorphism of Δ fixing the vertex A and the group of these automorphisms is acting transitively on each of the two subsets

$$A_1 = \{Ah | h \in xA\}$$

$$A_2 = \{Ah | h \in \sigma x\sigma^{-1}A\}$$

which form a partition of the vertices adjacent to A in Δ. Moreover the conjugation by σ also provides an automorphism σ^* of Δ fixing A defined by $\sigma^*(Ah) = A\sigma h\sigma^{-1} = \sigma Ah\sigma^{-1}$. For every $h, k \in S_n$, we have

$$(\sigma Ah\sigma^{-1}) \sim (\sigma Ak\sigma^{-1}) \text{ iff}$$

$$(A\sigma h\sigma^{-1}) \sim (A\sigma k\sigma^{-1}) \text{ iff}$$

$$\sigma kh^{-1}\sigma^{-1} \in M(x) \text{ iff}$$

$$kh^{-1} \in \sigma^{-1}M(x)\sigma = M(x) \text{ iff}$$

$$Ah \sim Ak$$

Since this automorphism exchanges A_1 and A_2, we see that A (acting by right multiplication) and σ (acting by conjugation) generate an automorphism group of Δ which fixes A and acts transitively on the neighbors of A. So S_n and σ generate an automorphism group of Δ acting transitively on the ordered pairs (Ah, Ak) of adjacent vertices. A graph having this property is called **flag-transitive or symmetric**. Now we restrict ourselves to the connected component of Δ containing A. Let Γ be the graph induced by Δ on this component. Then Γ is also a symmetric graph. The connectivity δ[17,18] of the mode $M(x)$ *is* the number of configurations reached in one step of this mode, starting from a given configuration. It is clear that

$$\delta = |M(x)|/|A| \tag{7}$$

is the degree of Γ.

The order of Γ, which is the maximum number of configurations reached in an arbitrary number of steps of $M(x)$ starting from a given configuration is denoted by m.

Coming back to the chemical point of view, if we start from a given configuration, the mode $M(\sigma x)$ generates in one step the configurations which are enantiomeric to those generated by $M(x)$. If $M(x)$ and $M(\sigma x)$ are disjoint, they are called enantiomeric modes. If they are not disjoint, it is easy to prove that $\sigma x \in M(x)$ and we have thus

$$M(\sigma x) = M(x) \tag{8}$$

Table 1. The Number of Connected VT-Graphs

m^{δ}	0	1	2	3	4	5	6	7	8	9	10	11	12	total
1	1													1
2	1													1
3			1											1
4			1	1										2
5			1		1									2
6			1	2	1	1								5
7			1		1		1							3
8			1	2	3	2	1	1						10
9			1		3		2		1					7
10			1	3	3	4	3	2	1	1				18
11			1		2		2		1		1			7
12			1	4	10	12	13	11	7	4	1	1		64
13			1		3		4		3		1		1	13
14			1	3	5	6	8	9	6	6	3	2	1	51
15			1		7		12		12		8		3	44
16			1	4	13	25	39	47	48	40	27	16	7	272
17			1		4		7		10		7		4	35
18			1	5	12	23	36	45	53	54	45	38	24	365
19			1		4		10		14		14		10	59
20			1	7	24	43	80	113	148	167	168	149	115	1190
21			1		10		28		48		56		48	235
22			1	3	9	18	36	52	78	94	108	109	94	807
23			1		5		15		30		42		42	187
24			1	11	60	152	359	640	1057	1469	1857	2063	2064	15422
25			1		8		25		57		86		104	461
26			1	5	13	29	67	117	201	286	396	466	522	4221

In this case the mode $M(x)$ *is* called racemic[7] since it generates pairs of enantiomeric configurations in one step from a given configuration.

3. SYMMETRIC CONNECTED GRAPHS

From now on we use the word graph always to mean a connected graph. Since reaction graphs are symmetric graphs, we now recall some results about these. We make use of existing tables of VT-graphs (vertex transitive graphs) where symmetric graphs[19−21] are listed as well.

In Table 1, the number of connected VT-graphs of m vertices and of degree δ up to $m = 26$ is listed.[19] Many interesting properties of VT-graphs with fewer than 20 vertices may be found in the paper by McKay.[20] For instance, this catalog provides the list of symmetric graphs for $m < 20$, i.e., those VT-graphs with $m < 20$ whose arc-transitivity is at least one. The number of such graphs is shown in Table 2. For $m = 24$, the list of symmetric graphs has been obtained by Royle−Praeger.[21]

Table 2. The Number of Connected Symmetric Graphs

$m\delta$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1																		
2		1																	
3			1																
4			1	1															
5			1		1														
6			1	1	1	1													
7			1				1												
8			1	1	1		1	1											
9			1		1		1		1										
10			1	1	2	1	1		1	1									
11			1								1								
12			1		2	2	2		1	1	1	1							
13			1		1		1						1						
14			1	1	2		1	1					1	1					
15			1		2		2		2		1		1		1				
16			1	1	2	1	3	1	1	1	1		1		1	1			
17			1		1				1								1		
18			1	1	2		2		2	1	1		1			1	1	1	
19			1				1												1

By comparing Tables 1 and 2 it appears that only a small number of VT-graphs are also symmetric. For instance among the 365 VT-graphs having 18 vertices, only 14 are symmetric graphs. It is also interesting to notice that, for $m \leq 19$ there exist very few symmetric graphs of given order and degree.

As pointed out in refs 20 and 21 many connected symmetric graphs can be some how expressed as kinds of products in terms of smaller graphs. To do this, we recall some standard graph theoretical constructions and notation. Assume that Γ is a connected symmetric graph. Then $q\Gamma$ denotes the graph having q connected components isomorphic to Γ. We use $\bar{\Gamma}$ for the complementary graph of Γ. We use C_m and K_m respectively, for the cyclic graph and the complete graph of m vertices. Let $m = qr$ where q, r are integers. Then $(\overline{qK_r})$ denotes the complete q-partite graph of m vertices which is of degree $m - r$. A particularly interesting situation occurs when a graph may be expressed as a product of two or more other graphs. We use the terminology and notation of ref 20 to describe three kinds of products of the graphs X and Y having each the vertex set $V(X) \times V(Y)$ where $V(X)$ and $V(Y)$ are the vertex sets of X and Y.

3.1. The Cartesian Product. $Z = X \times Y$ has the set of edges $E(Z) = \{(x_1,y_1), (x_2,y_2)|$ either $x_1 = x_2$ and $\{y_1,y_2\} \in E(Y)$ or $y_1 = y_2$ and $\{x_1, x_2\} \in E(X)\}$. Here, $\delta_z = \delta_x + \delta_y$.

3.2. The Tensor Product. $Z = X*Y$ has the set of edges $E(Z) = \{(x_1, y_1), (x_2, y_2)|\{x_1, x_2\} \in E(x)$ and $\{y_1, y_2\} \in E(y)\}$. Here, $\delta_z = \delta_x\delta_y$.

3.3. The Lexicographic Product $Z = X\,[Y]$. Here, $E(Z) = \{(x_1, y_1), (x_2, y_2)|$ either $\{x_1, x_2\} \in E(X)$ or $x_1 = x_2$ and $\{x_1, y_2\} \in E(Y)\}$. Now $\delta_z = \delta_x m_y + \delta_y$ where m_y is the order of Y.

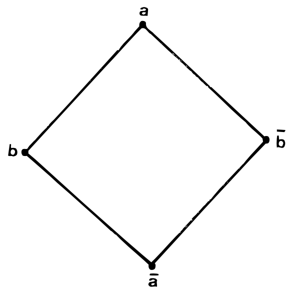

Figure 1. Cycle in a graph for an enantiomeric mode.

4. GRAPHS CONNECTING ENANTIOMERIC CONFIGURATIONS

4.1. The Role of σ. We now discuss the possibility that reaction graphs connect enantiomeric configurations. We suppose that the configuration a and its enantiomer $\bar{a}$ are vertices of a given connected symmetric graph. From eq 5 in section 2 it is easy to verify that in the graph derived from $M(x)$, if $b, c, d, ...$ are the neighbors of a, then $\bar{b}$, $\bar{c}$-, $\bar{d}$, ... are the neighbors of $\bar{a}$. Therefore, the graph automorphism group contains the permutation α interchanging simultaneously the members of each pair of enantiomeric vertices[3]

$$\alpha = (a, \bar{a})(b, \bar{b})(c, \bar{c})(d, \bar{d}) ... \qquad (9)$$

and the number of edges has to be even.

We now describe three mutually exclusive situations.

(a) The permutation x in eq 5 describing an interconversion is an improper symmetry operation, say σ defined in eq 1. In this case the interconversion is an enantiomerization, i.e., it transforms in one step any configuration a into the enantiomeric configuration $\bar{a}$. In this case $\delta = 1$ and the corresponding reaction graph is K_2. Ammonia inversion is of this type.

(b) $M(x)$ and $M(\sigma x)$ are disjoint, and x is not an improper symmetry operation of the molecule. Suppose that the graph for $M(x)$ has an edge $\{a,b\}$. Then the graph for $M(\sigma x)$ has an edge $\{a,\bar{b}\}$. The graph for $M(x)$ cannot have an edge $\{a,\bar{b}\}$ since this would imply $M(x) = M(\sigma x)$. Hence, when $M(x)$ and $M(\sigma x)$ are disjoint, no vertex can have a pair of enantiomers as neighbors.

(c) $M(x) = M(\sigma x)$ and the neighbors of any vertex consist exclusively of pairs of enantiomers. The degree of the graph is even. Since the graph is VT, this implies the existence of a cycle of length four shown in Figure 1. The distance between enantiomers is equal to two.

The existence of an edge $\{a,b\}$ implies the existence of edges $\{a,\bar{b}\}$, $\{\bar{a},b\}$, and $\{\bar{a},\bar{b}\}$. The number of edges is thus a multiple of four. The graph automorphism group contains any permutation[3] of the form

$$\beta = (a,\bar{a}) \qquad (10)$$

which expresses individual exchange of the vertices representing enantiomeric configurations.

4.2. Enantiomeric Labeling. We have seen in section 2.2 that the group S_n (acting by right multiplication) and σ (acting by conjugation) generate a flag-transitive automorphism group X of the graph Γ. This group leaves enantiomerization invariant since for every vertex Ah of Γ we have

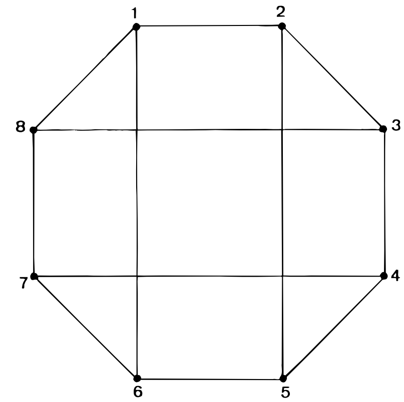

Figure 2. The graph of the cube.

•for every g in S_n, the pair of enantiomers $(Ah, A\sigma h)$ is mapped on $(Ahg, A\sigma hg)$ and the latter consists of enantiomers;

•similarly, σ maps the pair $(Ah, A\sigma h)$ on $(A\sigma h\sigma^{-1}, Ah\sigma^{-1})$ which are also enantiomers.

Moreover, X acts transitively on the vertices of Γ; this implies that X is also a flag-transitive automorphism group of the graph of connectivity one whose edges are the pairs $\{Ah, A\sigma h\}$ of enantiomeric vertices of Γ. If $p = Ah$ *is* any vertex of Γ, if x is an element of X and if we denote by $x(p)$ the image of p by x, we have $x(\bar{p}) = \overline{(x(p))}$ and thus

$$x(\sigma Ah) = \sigma x(Ah)$$

This shows that every element x of X has to commute with σ and so X is contained in the centralizer of σ in Aut(G). Therefore, an enantiomeric labeling EL of a symmetric graph Γ, mapping the vertex y on $\bar{y}$, has the following properties:

1. it belongs to the graph automorphism group Aut(G);
2. it is of order 2 and fixes no vertex;
3. the centralizer of σ in the full automorphism group is flag-transitive on the graph and on the enantiomerization;
4. a pair $\{y,\bar{y}\}$ is never an edge of Γ unless $\Gamma = K_2$.

Taking these four properties as axioms we have classified the enantiomeric labelings of each of the symmetric graphs having less than 20 vertices listed in the catalog of McKay.[20] The description of the computer program written in the CAYLEY[22] language and generating the set of enantiomeric labelings (SEL) is given in the Appendix. For instance, if Γ is the graph of the cube labeled as in Figure 2, the SEL is given by

$$\text{SEL} = \{(1,4)(2,7)(3,6)(5,8)\}$$

and it contains only one permutation. In this case, the pairs of mirror images are {1,4}, {2,7}, {3,6}, and {5,8}. Note however that a given graph may represent various stereoreaction processes. Among these processes, some may interconvert enantiomers, others may not. Hence, the fact that the SEL of a graph is nonempty *does not mean* that this graph can only represent a process interconverting enantiomers but *does mean* that if the process interconverts enantiomers, enantiomers have to be disposed on the graph in the way prescribed by the permutation(s) of the SEL.

The results are summarized in Table 3. In this table, we only list symmetric graphs whose number of vertices m and of edges are even, except K_2. The symbol $\Sigma\Gamma(m)_i$ in the first column stands for the ith symmetric graph having m

vertices and will be used in this paper to denote that graph. The second column characterizes the graph in terms of K_m, C_m, or as a complement of a graph having less edges, when possible. When available, familiar names such as cube or complement of Petersen are added. In the next columns the symbols δ, g and D refer respectively, to the degree, the girth, and the diameter of the graph. The notation $d(z)$ gives the number z of EL in which enantiomers are at distance d. The value $z = 1$ is omitted. In the last two columns, the symbol denoting the graph in McKay[20] is given, and, when possible, the graph is expressed as a lexicographic or a tensor product related to enantiomeric labeling (see sections 4.3 and 4.4). We now comment on the results displayed in Table 3.

4.3. Enantiomeric Configurations and the Tensor Product. We consider the tensor product $\Gamma = \gamma * K_2$ where K_2 is represented in Figure 3; one of its vertices is unlabeled, the other one has an upper bar meaning "mirror image of" or "enantiomer to".

Let γ be a connected symmetric bipartite graph with vertices 1, 1′, 2, 2′, ... and edges only connecting unprimed to primed vertices. Therefore, using the definition of the tensor product, Γ is a disconnected graph having two components γ_1 (with vertices $1, \bar{1}', 2, \bar{2}'$, ...) and γ_2 (with vertices $\bar{1}, 1', \bar{2}, 2'$, ...). Both components have edges only connecting unprimed to primed vertices and are isomorphic to γ. If γ is a connected symmetric but nonbipartite graph, with vertices 1, 2, 3, ... it has cycles of odd length, for instance $1 - 2 - 3 \ldots 1$ which gives rise to $1 - \bar{2} - 3 - \ldots - \bar{1}$ in Γ. Hence, Γ contains at least one pair of enantiomers 1, $\bar{1}$. Consider a path from 1 to any vertex k in γ. This leads to a path from 1 to k or $\bar{k}$ in Γ. We conclude that the set of vertices of Γ contains 1, $\bar{1}$ and k or $\bar{k}$. Since all the pairs play the same role, Γ is connected and bipartite (only edges between vertices with and without a bar). As an example we show in Figure 4 the tensor product of a nonbipartite graph (A) and of a bipartite graph (B) with K_2.

As a consequence of the above discussion, the graphs C_{2k} with even k cannot be expressed as $C_k * K_2$ (see graphs $\Sigma\Gamma(8)_1 = H4$, $\Sigma\Gamma(12)_1 = L6$, and $\Sigma\Gamma(16)_1 = P5$ in Table 3). These graphs possess however an EL where enantiomers are at distance k on the $2k$-gon. The graphs $\Sigma\Gamma(6)_1 = F4$, $\Sigma\Gamma(10)_1 = J4$, $\Sigma\Gamma(14)_1 = N4$, and $\Sigma\Gamma(18)_1 = R6$ are of the type $C_k * K_2$ (k odd). They also have an EL where enantiomers are at distance k on the $2k$-gon. The graphs $\Sigma\Gamma(8)_2 = H7$, $\Sigma\Gamma(10)_3 = J10$, $\Sigma\Gamma(12)_4 = L34$, $\Sigma\Gamma(14)_4 = N24$, $\Sigma\Gamma(16)_9 = P130$, $\Sigma\Gamma(18)_3 = R29$, $\Sigma\Gamma(18)_5 = R90$, and $\Sigma\Gamma(18)_7 = R173$ are of the type $\Gamma = \gamma * K_2$, where γ is a symmetric nonbipartite graph other than C_k (k odd). For all these graphs, the distance between enantiomers is the girth of γ, and for all of them, except $\Sigma\Gamma(18)_5 = R90$, $|SEL| = 1$. The graphs $\Sigma\Gamma(8)_2 = H7$, $\Sigma\Gamma(10)_3 = J10$, $\Sigma\Gamma(12)_4 = L34$, $\Sigma\Gamma(14)_4 = N24$, $\Sigma\Gamma(16)_9 = P130$, and $\Sigma\Gamma(18)_7 = R173$ are of the form $K_m * K_2$ (m = 4, 5, ..., 9). If we label the vertices K_m from 1 to m, then in $K_m * K_2$, vertex 1 is adjacent to $\bar{2}, \bar{3}, \ldots, \bar{m}$. In Figure 5, we show a convenient way to represent $K_m * K_2$ and to visualize its EL for even and odd m, respectively.

For even m (Figure 5A) the labels 1, 2, ..., m are disposed clockwise on an outer circle and $\bar{1}, \bar{2}, \ldots, \bar{m}$ on an inner one, in such a way that $\bar{1}$ is opposite to 1. Edges are drawn as shown, leading for $m = 4$ to the graph of the cube, where the only EL imposes that enantiomers are at opposite vertices.

Table 3. The Connected Symmetric Graphs Having an Even Number of Vertices and an Even Number of Edges

graph	description	δ	g	D	$d(z)$	ref 20	product
$\Sigma\Gamma(2)_1$	K_2	1		1	1	B_2	
$\Sigma\Gamma(4)_1$	$\overline{2K_2}$, C_4	2	4	2	2	$D3$	$K_2[2K_1]$
$\Sigma\Gamma(4)_2$	K_4, tetrahedron	3	3	1		$D4$	
$\Sigma\Gamma(6)_1$	C_6	2	6	3	3	$F4$	$K_3 * K_2$
$\Sigma\Gamma(6)_2$	$\overline{3K_2}$, octahedron	4	3	2	2	$F7$	$K_3[2K_1]$
$\Sigma\Gamma(8)_1$	C_8	2	8	4	4	$H4$	
$\Sigma\Gamma(8)_2$	cube	3	4	3	3	$H7$	$K_4 * K_2$
$\Sigma\Gamma(8)_3$	$\overline{2K_4}$	4	4	2	2(9)	$H8$	$\overline{2K_2}\,[2K_1]$
$\Sigma\Gamma(8)_4$	$\overline{4K_2}$	6	3	2	2	$H13$	$K_4\,[2K_1]$
$\Sigma\Gamma(8)_5$	K_8	7	3	1		$H14$	
$\Sigma\Gamma(10)_1$	C_{10}	2	10	5	5	$J4$	$C_5 * K_2$
$\Sigma\Gamma(10)_2$		4	4	2	2	$J9$	$C_5\,[2K_1]$
$\Sigma\Gamma(10)_3$		4	4	3	3	$J10$	$K_5 * K_2$
$\Sigma\Gamma(10)_4$	complement of Petersen	6	3	2			
$\Sigma\Gamma(10)_5$	$\overline{5K_2}$	8	3	2	2		$K_5[2K_1]$
$\Sigma\Gamma(12)_1$	C_{12}	2	12	6	6	$L6$	
$\Sigma\Gamma(12)_2$	$L(H7)$, cuboctahedron	4	3	3	3	$L20$	
$\Sigma\Gamma(12)_3$		4	4	3	2,3(8)	$L23$	$C_6[2K_1]$
$\Sigma\Gamma(12)_4$		5	4	3	3	$L34$	$K_6 * K_2$
$\Sigma\Gamma(12)_5$	icosahedron	5	3	3	3	$L37$	
$\Sigma\Gamma(12)_6$	$\overline{L30}$	6	3	2			
$\Sigma\Gamma(12)_7$	$\overline{2K_6}$	6	4	2	2(225)		$\overline{2K_3}[2K_1]$
$\Sigma\Gamma(12)_8$	$\overline{3K_4}$	8	3	2	2(27)		$\overline{3K_2}\,[2K_1]$
$\Sigma\Gamma(12)_9$	$\overline{4K_3}$	9	3	2			
$\Sigma\Gamma(12)_{10}$	$\overline{6K_2}$	10	3	2	2		$K_6[2K_1]$
$\Sigma\Gamma(12)_{11}$	K_{12}	11	3	1			
$\Sigma\Gamma(14)_1$	C_{14}	2	14	7	7	$N4$	$C_7 * K_2$
$\Sigma\Gamma(14)_2$		4	4	3	2	$N12$	$C_7[2K_1]$
$\Sigma\Gamma(14)_3$	dual of Heawood	4	4	3		$N13$	
$\Sigma\Gamma(14)_4$		6	4	3	3	$N24$	$K_7 * K_2$
$\Sigma\Gamma(14)_5$	$\overline{7K_2}$	12	3	2	2		$K_7[2K_1]$
$\Sigma\Gamma(16)_1$	C_{16}	2	16	8	8	$P5$	
$\Sigma\Gamma(16)_2$		3	6	4	4	$P12$	
$\Sigma\Gamma(16)_3$		4	4	4	2,4(16)	$P23$	$C_8[2K_1]$
$\Sigma\Gamma(16)_4$	*4* - cube	4	4	4	4	P27	$\overline{\mathrm{H7}} * K_2$
$\Sigma\Gamma(16)_5$	complement of Clebsch	5	4	2		$P55$	
$\Sigma\Gamma(16)_6$		6	3	2		$P81$	
$\Sigma\Gamma(16)_7$		6	4	3	2,3(16)	$P82$	$H7[2K_1]$
$\Sigma\Gamma(16)_8$	Shrikhande	6	3	2		$P84$	
$\Sigma\Gamma(16)_9$		7	4	3	3	$P130$	$K_8 * K_2$
$\Sigma\Gamma(16)_{10}$	$\overline{2K_8}$	8	4	2	2(225)		$\overline{2K_4}[2K_1]$
$\Sigma\Gamma(16)_{11}$	$\overline{P81}$	9	3	2			
$\Sigma\Gamma(16)_{12}$	$\overline{P55}$	10	3	2			
$\Sigma\Gamma(16)_{13}$	$\overline{4K_4}$	12	3	2	2(81)		$\overline{4K_2}[2K_1]$
$\Sigma\Gamma(16)_{14}$	$\overline{8K_2}$	14	3	2	2		$K_8[2K_1]$
$\Sigma\Gamma(16)_{15}$	K_{16}	15	3	1			
$\Sigma\Gamma(18)_1$	C_{18}	2	18	9	9	$R6$	$C_9 * K_2$
$\Sigma\Gamma(18)_2$		4	4	4	2	$R28$	$C_9\,[2K_1]$
$\Sigma\Gamma(18)_3$		4	4	3	3	$R29$	$(K_3 * K_3) * K_2$
$\Sigma\Gamma(18)_4$	dual of Pappus	6	4	3		$R88$	
$\Sigma\Gamma(18)_5$		6	4	3	3(216)	$R90$	$(K_3[3K_1]) * K_2$
$\Sigma\Gamma(18)_6$		8	3	2	2	$R171$	$(K_3 * K_3)[2K_1]$
$\Sigma\Gamma(18)_7$		8	4	3	3	$R173$	$K_9 * K_2$
$\Sigma\Gamma(18)_8$	$\overline{R126}$	10	3	2			
$\Sigma\Gamma(18)_9$	$\overline{3K_6}$	12	3	2	2(3375)		$\overline{3K_3}[2K_1]$
$\Sigma\Gamma(18)_{10}$	$\overline{9K_2}$	16	3	2	2		$K_9[2K_1]$

Figure 3. The graph K_2.

With this way of representing $K_m * K_2$ (even m), the enantiomers have to be disposed in opposite positions, one on each circle. For odd m (Figure 5B), the $2m$ vertices are disposed clockwise on a single circle and labeled 1, 2, ...,

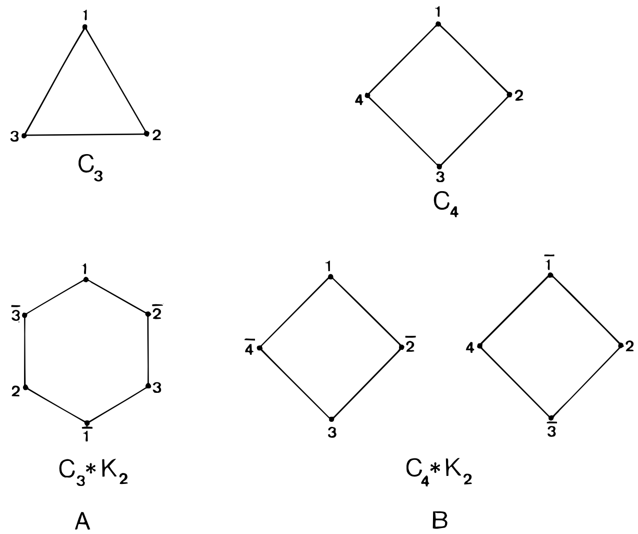

Figure 4. Tensor product of a nonbipartite graph (A) and a bipartite graph (B) with K_2.

m, $\bar{1}$, ..., $\bar{m}$. Labels with and without a bar appear at alternate positions. Edges are drawn as shown. With this way of drawing, the enantiomers have to be disposed in opposite positions. The graph $\Sigma\Gamma(18)_3 = R29 = (K_3^* K_3)^* K_2$ may be shown in a way similar to $K_m^*\ K_2$ (odd m). The result is shown in Figure 6.

The only EL of $\Sigma\Gamma(18)_3 = R29$ imposes that, in this drawing, enantiomers are at opposite vertices. The SEL of $\Sigma\Gamma(18)_5 = R90 = (K_3[3K_1])^*K_2$ deserves special comments. The graph $K_3[3K_1] = \overline{3K_3}$ is a symmetric nonbipartite graph of degree 6. The structure of $\Sigma\Gamma(18)_5 = R90$ is shown in Figure 7 where the vertices of the graph are represented by open circles and dots.

In $\Sigma\Gamma(18)_5 = R90$ each dot (circle) is adjacent to the circles (dots) which are not on the same line as it on the grid of Figure 7. The graph is bipartite. The three dots on a given line of the grid are at distance *3* from the three open circles on the same line. For instance, 1, 2, and 3 are each at distance 3 from 4, 5, and 6. In this graph, the enantiomer of a given vertex can be any vertex at distance 3 of it. Hence the enantiomer of 1 can be either 4, 5, or 6. Let it be 4; then the enantiomer of 2 is 5 or 6. One possibility remains for the enantiomer of 3. The SEL is given by SEL = {(1,4)(2,5)(3,6), (1,4)(2,6)(3,5), (1,5)(2,6)(3,4), (1,5)(2,4)(3,6), (1,6)(2,4)(3,5), (1,6) (2,5)(3,4)} × {(7,10)(8,11)(9,12), (7,10)(8,12)(9,11), (7,11)(8,10)(9,12), (7,11)(8,12) (9,10), (7,12)(8,10)(9,11), (7,12)(8,11)(9,10)} × {(13,16)(14, 17)(15, 18), (13,16) (14,18)(15,17), (13,17)(14,16)(15,18), (13,17)(14,18)(15,16), (13,18)(14,16)(15,17), (13,18)(14,17)(15,16)} and $|\mathrm{SEL}| = 6^3 = 216$. The last example of a graph of the form γ^*K_2 is $\Sigma\Gamma(16)_4 = P27$, the 4-cube (hypercube). Here γ is $\overline{H_7}$, the complement of the cube, a graph which is neither bipartite nor edge transitive. The graph $\Sigma\Gamma(16)_4 = P27$ may also be expressed as a Cartesian product $\gamma \times K_2$, where γ is the cube. However, using K_2 as shown in Figure 3, in this Cartesian product should produce a graph in which a cube with vertex labels $\bar{1}$, $\bar{2}$, ..., $\bar{8}$ and another cube labeled similarly $\bar{1}$, $\bar{2}$, ..., $\bar{8}$ are connected by edges $1\bar{1}$, $2\bar{2}$, ..., $8\bar{8}$. Such a representation leads to a contradiction since enantiomers may only be adjacent in the graph K_2.

The graph $\Sigma\Gamma(16)_4 = P27$ is shown in Figure 8 and its SEL is given by SEL = (1,6)(2,13)(3,12)(4,11)(5,10)(7,16)(8,15)(9,14). Since each vertex of $\Sigma\Gamma(16)_4 = P27$ has only one vertex at distance 4 from it, the permutation of SEL tells us that enantiomers may be disposed at distance 4 from each other. Arrows in Figure 8 show a Hamiltonian circuit.

4.4. Enantiomeric Labeling and the Lexicographic Product. Consider a graph Γ which may be expressed as a lexicographic product

$$\Gamma = \gamma[2K_1]$$

where $2K_1$ is shown in Figure 9.

One of its two vertices is unlabeled, and the other one has an upper bar meaning "mirror image of". Hence the set of vertices of Γ is {1, $\bar{1}$, 2, $\bar{2}$, 3, $\bar{3}$, ...} if {1, 2, 3, ...} is the set of vertices of the connected graph γ. From the above definition of the lexicographic product, any edge $\{a,b\}$ of γ, will give rise to the four edges $\{a,b\}$, $\{a,\bar{b}\}$, $\{\bar{a},b\}$, and $\{\bar{a},\bar{b}\}$. Hence any vertex a of Γ is adjacent to the pair of edges b and $\bar{b}$. Such a labeling of the graph Γ is called a *racemic labeling.* Conversely, any graph Γ showing a racemic labeling may be expressed as $\gamma[2K_1]$, where γ is the homomorphic reduction of Γ such that the pair of vertices a, $\bar{a}$ and the quartet of edges $\{a,b\}$, $\{a,\bar{b}\}$, $\{\bar{a},b\}$, and $\{\bar{a},\bar{b}\}$ of Γ are mapped, respectively, onto the vertex a and the edge $\{a,b\}$ of γ. As an example of graphs having a racemic labeling (in short racemic graphs), consider $\Gamma = \overline{qK_r}$, a connected graph of order $m = qr$. The vertex a belonging to one of the q subsets, say A, of r vertices is adjacent to the $(q - 1)r$ vertices of the $(q - 1)$ other subsets. If any of these $(q - 1)r$ vertices were to be a, the graph Γ would be of degree $\delta = 1$ (see case a) in section 4.1). The other possibility is that $\bar{a}$ belongs to A, which implies that A consists of pairs of enantiomeric vertices: a, $\bar{a}$, b, $\bar{b}$, ... Therefore $r = 2s$ ($s = 1, 2, ...$) is even. Hence the graphs $\Gamma = \overline{qK_{2s}}$ are racemic. It is easy to verify that

$$\overline{qK_{2s}} = \overline{qK_s}[2K_1]$$

and, when $s = 1$

$$\overline{qK_2} = K_q[2K_1]$$

For instance, for $q = 3$, $\overline{3K_2} = K_3[2K_1]$ *is* the octahedron, a racemic graph.

In Table 3, $\overline{4K_3}$ *is* the only graph of the types $\overline{qKr}$ (odd r). It has no EL. The graphs $\Sigma\Gamma(4)_1 = D_3$, $\Sigma\Gamma(6)_2 = F7$, $\Sigma\Gamma(8)_3 = H8$, $\Sigma\Gamma(8)_4 = H13$, $\overline{5K_2}$, $\overline{2K_6}$, $\overline{3K_4}$, $\overline{6K_2}$, $\overline{7K_2}$, $\overline{2K_8}$, $\overline{4K_4}$, $\overline{8K_2}$, $\overline{3K_6}$ and $\overline{9K_2}$ are all of the type $\overline{qK_{2s}}$($s = 1, 2, ...$) and may be expressed as $\overline{qK_s}[2K_1]$. For a graph $\Gamma = \overline{qK_{2s}}$, the number SEL of permutations of the SEL is easy to calculate. Indeed, for one of the q subsets the number of enantiomeric labelings is given by the Cauchy formula, i.e., $(2s)!/2^s s!$. Hence

$$|\mathrm{SEL}| = ((2s)!/2^s s!)^q \tag{11}$$

For instance, if $\Gamma = \overline{2K_4}$, $|\mathrm{SEL}| = 9$.

With the labelings of the vertices shown in Figure 10, the SEL of $\overline{2K_4}$ is SEL = {(1,3)(5,7),(1,5)(3,7),(1,7)(3,5)} × {(2,4)(6,8),(2,6)(4,8),(2,8)(4,6)}. Other examples of racemic graphs are provided by the family $C_n[2K_1]$ ($n = 5$, *6*, ...).

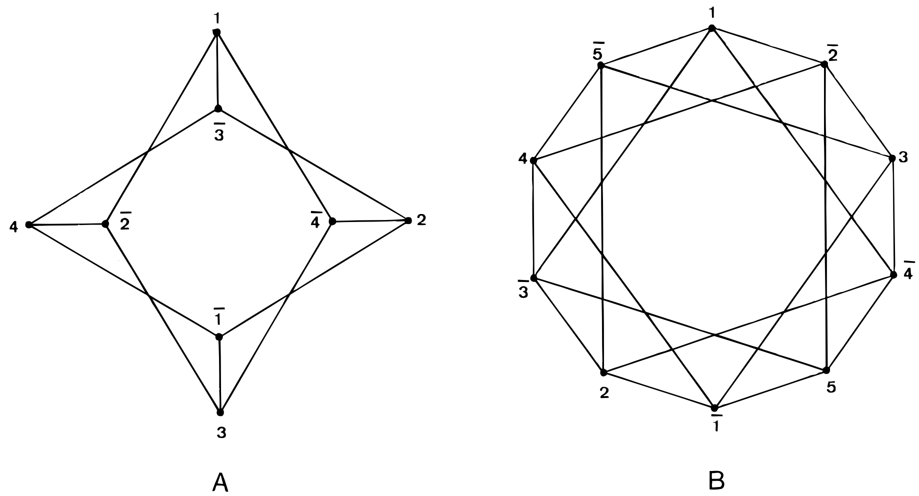

Figure 5. The EL structure of $K_m^* K_2$ for $m = 4$ (A) and $m = 5$ (B).

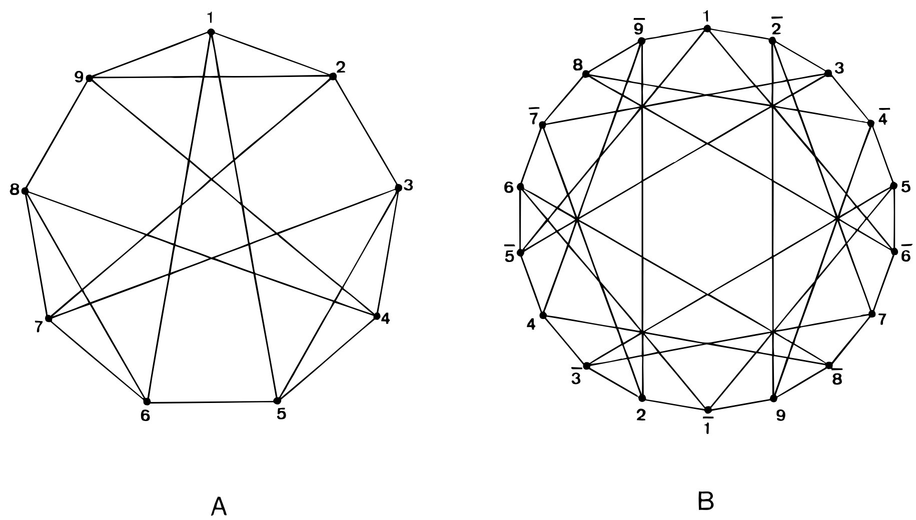

Figure 6. The graphs $K_3^* K_3$ (A) and $\Sigma\Gamma(18)_3 = R29 = (K_3^* K_3)^* K_2$ (B).

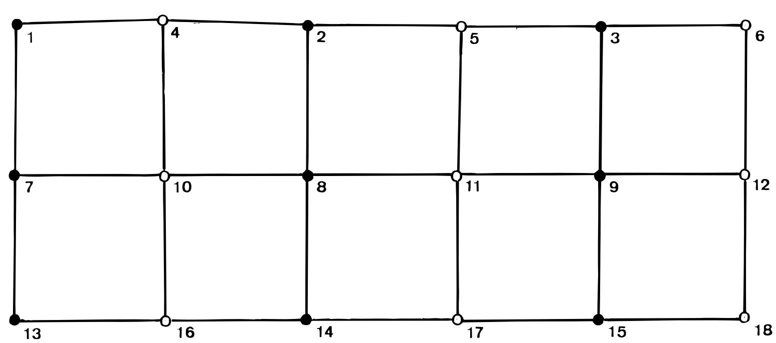

Figure 7. The structure of $\Sigma\Gamma(18)_5 = R90$.

The cases $n = 2$, 3, and 4 need no further discussion since they are respectively equal to $\overline{2K_2}$, $\overline{3K_2}$, and $\overline{2K_4}$.

The graphs $C_n[2K_1]$ are conveniently represented by a cycle of length $2n$ to which inner edges are added: they connect each vertex to the neighbors on the cycle of the vertex opposite to it. The case $n = 5$ is shown in Figure 11. Such graphs were first employed[23] for enumerating constitutional isomers of n-membered cycloalkanes and are called Balaban's B_{2n} graphs of degree 4.

The SEL for the graph of Figure 11 is

$$\mathrm{SEL} = \{(1,6)(2,7)(3,8)(4,9)(5,10)\}$$

When n is odd

$$|\mathrm{SEL}| = 1$$

for $C_n[2K_1]$. This is no longer true for even n.

Consider for instance $\Sigma\Gamma(12)_3 = C_6[2K_1]$ in Figure 12 for which the SEL is given by

$$\mathrm{SEL} = \mathrm{SEL}(2) \cup \mathrm{SEL}(3) \qquad (12)$$

where

$$\mathrm{SEL}(2) = \{(1,7)(2,8)(3,9)(4,10)(5,11)(6,12)\}$$

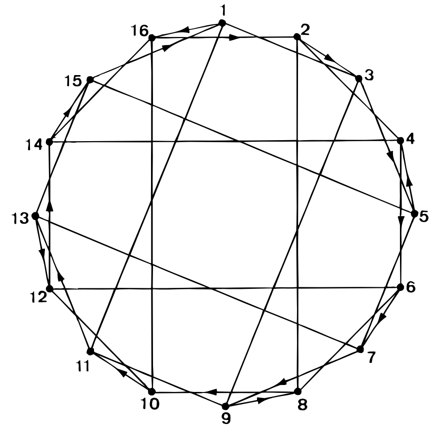

Figure 8. The graph $\Sigma\Gamma(16)_4 = P27$.

Figure 9. The graph $2K_1$.

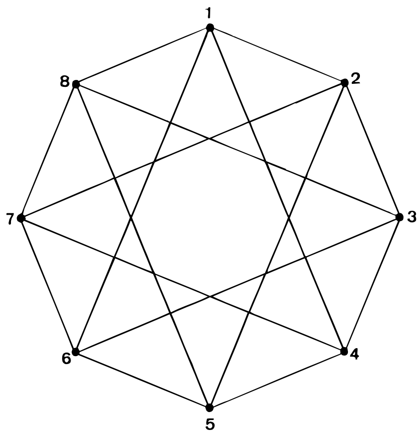

Figure 10. Labeling of $\overline{2K_4}$.

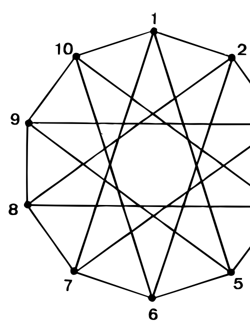

Figure 11. The graph $C_5[2K_1]$.

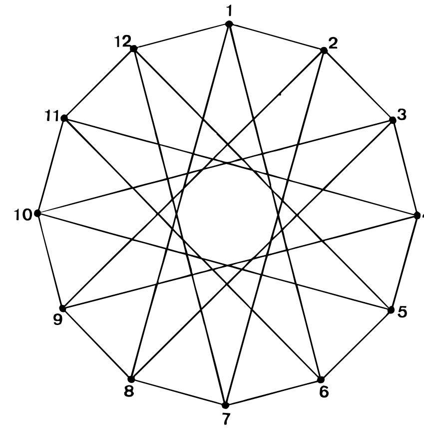

Figure 12. The graph $\Sigma\Gamma(12)_3 = C_6[2K_1]$.

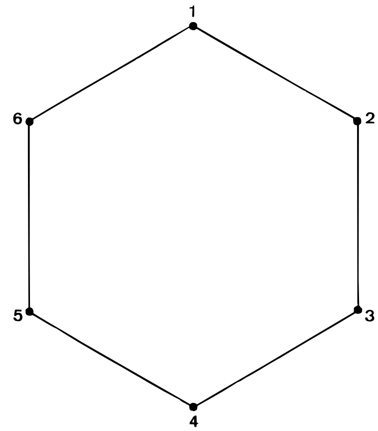

Figure 13. The graph $\Sigma\Gamma(6)_1 = C6$ (first labeling).

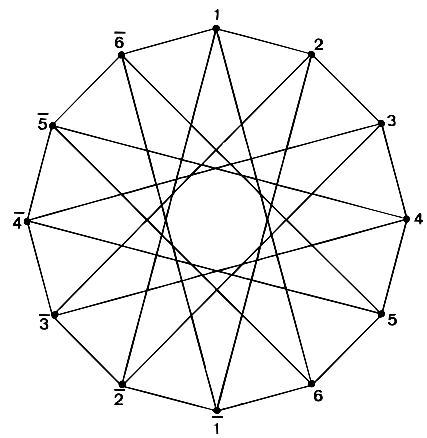

Figure 14. The graph $C_6[2K_1]$ (see Figure 13).

is a racemic labeling since it imposes that enantiomers are at distance 2, as in any racemic graph (see Figure 1) and

$$\mathrm{SEL}(3) = \{(1,4)(7,10),(1,10)(4,7)\} \times \{(2,5)(8,11),(2,11)(5,8)\} \times \{(3,6)(9,12),(3,12)(9,6)\} \quad (13)$$

does not contain racemic labelings since it imposes that enantiomers are at distance 3. To understand the above result, let us construct $\Sigma\Gamma(12)_3 = L23 = C_6[2K_1]$ in two different ways. First, we label C_6 as in Figure 13, and we perform the product of this labeled graph with $2K_1$ shown in Figure 9. The result is shown in Figure 14. By comparing this figure with Figure 12, it appears that the resulting racemic labeling is the permutation given in SEL(2) (see eq 12). Second, we label C_6 as in Figure 15A, and we perform the product of this labeled graph with the graph $2K_1$ shown in Figure 15B. The result is shown in Figure 16. It now appears that, in this figure, the enantiomers are at distance 3 from each other (as in Figure 15A). By comparing Figure 16 to Figure 12, the EL is shown to be (1,4)(2,5)(3,6)(7,-10)(8,11)(9,12), i.e., one of the elements of SEL(3) (see eq 13). Equation 13 shows that the labels of $C_6[2K_1]$ (see Figure 12) may be partitioned into three quartets, i.e., {1,4,7,10}, {2,5,8,11}, and {3,6,9,12}. Within each quartet enantiomers have to be at distance 3. Therefore the enantiomer of 1 is 4 (or 10) which imposes that the enantiomer of 7 is 10 (or 4), respectively. There are two partial ELs for each of the three quartets. Hence, for $C_6[2K_1]$

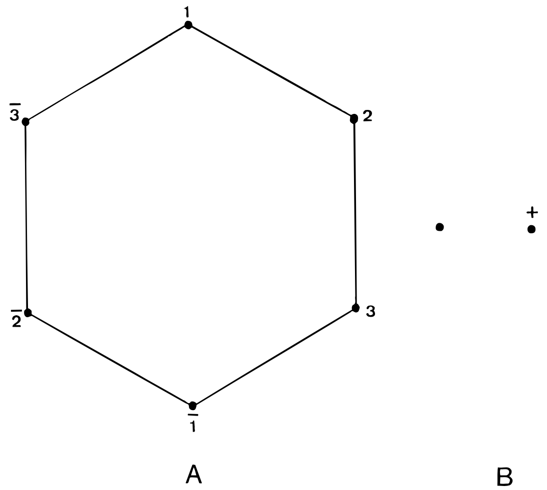

Figure 15. The graph $\Sigma\Gamma(6)_1 = C_6$ (second labeling) (A) and $2K_1$ (B).

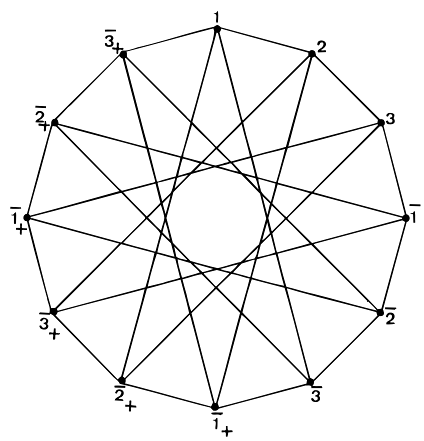

Figure 16. The graph $C_6[2K_1]$ (see Figure 15).

$$|\mathrm{SEL}(3)| = 2^3$$

These arguments suggest that for $C_{2k}[2K_1](k = 3, 4, ...)$

$$|\mathrm{SEL}(k)| = 2^k$$

as can be verified in Table 3, where it is seen that $\Sigma\Gamma(10)_2 = J9$, $\Sigma\Gamma(12)_3 = L23$, $\Sigma\Gamma(14)_2 = N12$, $\Sigma\Gamma(16)_3 = P23$, and $\Sigma\Gamma(18)_2 = R28$ are of the type $C_n[2K_1]$ ($n = 5, ..., 9$). Finally, notice that $\Sigma\Gamma(16)_7 = P82$ and $\Sigma\Gamma(18)_6 = R171$ are also graphs of the form $\gamma[2K_1]$. For $\Sigma\Gamma(16)_7 = P82$, γ is the graph of the cube. The graph $\Sigma\Gamma(16)_7 = P82$ has a SEL where enantiomers are either at distance 2, as in any racemic graph or at distance 3 as in the cube (see the discussion of eqs 12 and 13 above), i.e.,

$$\mathrm{SEL} = \mathrm{SEL}(2) \cup \mathrm{SEL}(3)$$

where

$$\mathrm{SEL}(2) = (1,9)(2,10)(3,11)(4,12)(5,13)(6,14)(7,15)(8,16)$$

and

$$\mathrm{SEL}(3) = \{(1,4)(9,12),(1,12)(4,9)\} \times \{(2,7)(10,15),(2,15)(7,10)\} \times \{(3,6)(11,14),(3,14)(6,11)\} \times \{(5,8)(13,16),(5,16)(8,13)\}$$

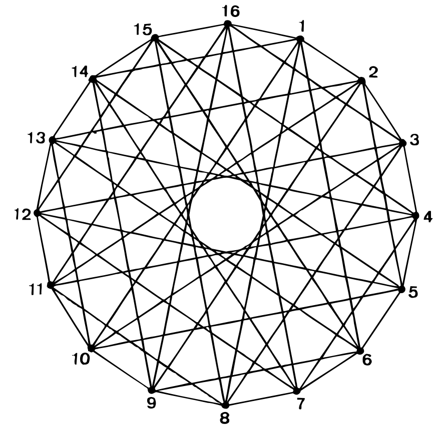

Figure 17. The graph $\Sigma\Gamma(16)_7 = P82$.

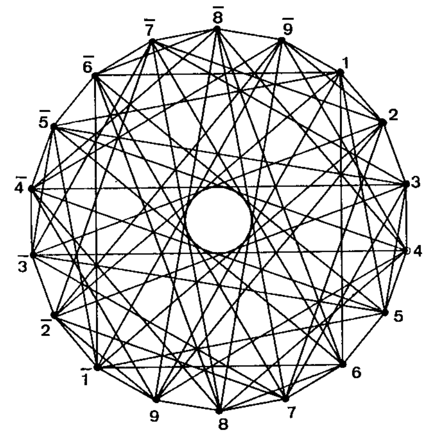

Figure 18. The graph $\Sigma\Gamma(18)_6 = R171$.

The labeling of $\Sigma\Gamma(16)_7 = P82$ and its relation to the cube of Figure 2 are shown in Figure 17. The structure of SEL-(3) given above may be understood as follows.

In $\Sigma\Gamma(16)_7 = P82$, each vertex has two vertices at distance 3 of it, e.g., vertices 4 and 12 are at distance 3 of vertex 1. They are also at distance 3 of vertex 9. Hence, in SEL(3), if 4 (or 12) is the enantiomer of 1, then 12 (or 4) is the enantiomer of 9. A similar argument holds for the three other quartets of vertices. As a result

$$|\mathrm{SEL}(3)| = 16$$

The graph $\Sigma\Gamma(18)_6 = R171 = (K_3 * K_3)[2K_1]$ is drawn in Figure 18 where its only EL is shown, whereas $(K_3 * K_3)$ may be found in Figure 6A.

4.5. Other Examples of Enantiomeric Labeling. In Table 3, it appears that three graphs, i.e., $\Sigma\Gamma(12)_2 = L20$ (cuboctahedron), $\Sigma\Gamma(12)_5 = L37$ (icosahedron) and $\Sigma\Gamma(16)_2 = P12$ all possess one EL but that they are not expressible as a product involving K_2 or $2K_1$. In the cuboctahedron (respectively icosahedron) enantiomeric pairs are located on the same 2-fold axis (respectively 5-fold axis). In the graph $P12$, related to the so-called 8_3 configuration of Coxeter-Möbius-Kantor, the unique EL is shown in Figure 19.

5. GRAPHS WITHOUT ENANTIOMERIC LABELINGS

The remaining graphs in Table 3 have no enantiomeric labelings. Among them, one finds the complete graphs K_m ($m = 4,8,12,16$) i.e., $\Sigma\Gamma(4)_2 = D4$, $\Sigma\Gamma(8)_5 = H14$, K_{12}, and K_{16}. If a complete graph were to have an EL, this should

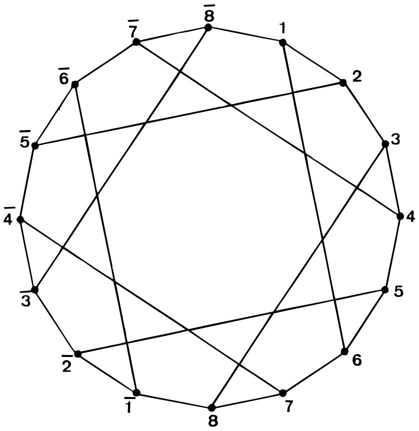

Figure 19. The EL of $\Sigma\Gamma(16)_2 = P12$.

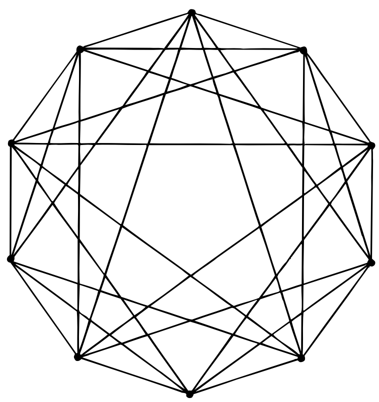

Figure 20. The graph $\Sigma\Gamma(10)_4$, the complement of the Petersen graph (Desargues graph).

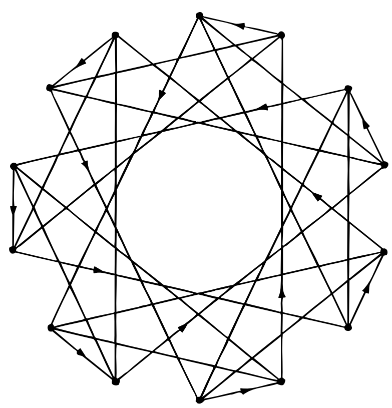

Figure 21. The graph $\Sigma\Gamma(14)_3 = N13$, the dual of the Heawood graph.

imply that there exists an edge between enantiomers. This is only possible for K_2. The fact that $\overline{4K_3}$ has no EL has been discussed previously: graphs of the type $\overline{qK_r}$ have ELs if and only if r is even.

Finally $\Sigma\Gamma(10)_4 = \overline{J7}$, $\Sigma\Gamma(12)_6 = \overline{L30}$, $\Sigma\Gamma(14)_3 = \overline{N13}$, $\Sigma\Gamma(16)_5 = \overline{P55}$, $\Sigma\Gamma(16)_6 = P81$, $\Sigma\Gamma(16)_8 = P84$, $\overline{\Sigma\Gamma(16)_6} = \overline{P81}$, $\overline{\Sigma\Gamma(16)_5} = \overline{P55}$, $\Sigma\Gamma(18)_4 = R88$, and $\Sigma\Gamma(18)_8 = \overline{R126}$ are also graphs for which no ELs exist. They are drawn in Figures 20−24 except the following graphs which are expressible as products of smaller graphs:

$$\Sigma\Gamma(12)_6 = \overline{L30} = K_3 * K_4$$

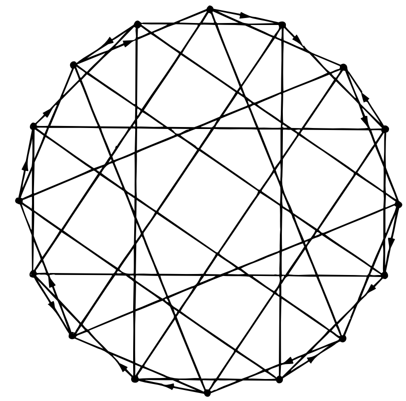

Figure 22. The graph $\Sigma\Gamma(16)_5 = P55$, the complement of the Clebsch graph.

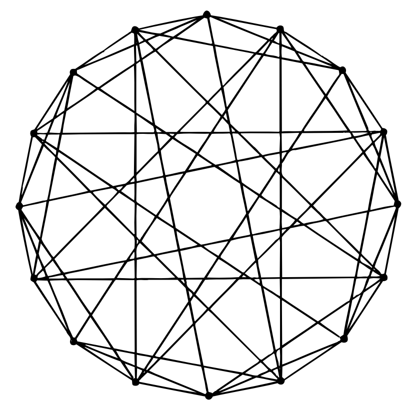

Figure 23. The graph $\Sigma\Gamma(16)_8 = P84$, the Shrikhande graph.

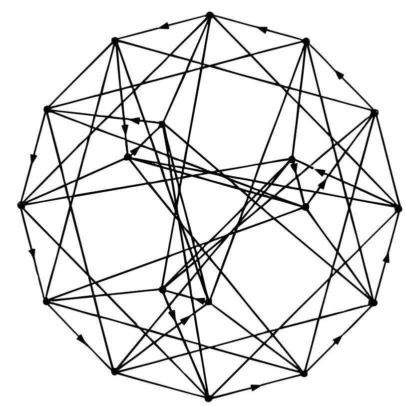

Figure 24. The graph $\Sigma\Gamma(18)_4 = R88$, the dual of the Pappus graph.

$$\Sigma\Gamma(16)_6 = P81 = K_4 \times K_4$$

$$\Sigma\Gamma(18)_8 = \overline{R126} = K_3 * K_6$$

Note that in Figures 21, 22, and 24, the arrows indicate Hamiltonian circuits.

6. CONCLUSIONS

In this work, we examined the possibility that reaction graphs allow enantiomeric interconversions. For some of them that possibility does not exist. We have tested the relation between possible enantiomeric labeling of a graph and its factorization into a product of the type $\gamma[2K_1]$ or $\gamma * K_2$.

We have shown that surprisingly some graphs possess many enantiomeric labelings. For instance $\Sigma\Gamma(8)_3 = H8 =$

Chart 1

```
" this CAYLEY library uses the following variables which have to be
  initialized before its execution :

   v  is the set containing the numbers 1, 2, ... n corresponding to the
      n vertices of the graph,
   ad is a sequence defining the graph : for each i in v, ad[i] is the
      set of vertices which are adjacent to i,
   e  is a sequence containing the edges of the graph, each element of e
      is a set of 2 elements of v,
   g  is the automorphism group of the graph presented as a permutation
      group on the set v.                                                  "

c = empty;
for each x in g do
  if order(x) eq 2 then
    if length(orbits(<x>)) eq (length(ad) / 2) then
      ok = true;
      for i = 1 to length(c) do
         if conjugate(g, x, c[i]) then ok = false; break;
         end;
      end;
      if ok then
         for i = 1 to length(e) do if e[i]^x eq e[i] then ok = false; break;
                                   end;
         end;
      end;
      if ok then c = append(c,x); end;
    end;
  end;
end;

" c is a sequence containing all the automorphisms of the graph which are
  involutions having no fixed vertex and no fixed edge.
  The elements of c are the candidates to induce enantiomeric labellings :
  the enantiomeric image of a vertex p by an element x of c is x(p).      "

s = empty;
for each x in c do
  ok = true;


  if (ad[1]^x eq ad[1]) then
    for i = 2 to length(ad) do
      if not(ad[i]^x eq ad[i])  then
         ok = false; break;
      end;
    end;

  " the boolean variable ok is true if the labelling induced by x is such
    that for every vertex p of the graph, the set of vertices adjacent to
    p is equal to the set of vertices adjacent to x(p). This corresponds
    to labellings in which the distance between enantiomers is equal to 2. "

  else if (ad[1]^x meet ad[1]) eq null then
          for i = 2 to length(ad) do
             if not ((ad[i]^x meet ad[i]) eq null) then
                ok = false; break;
             end;
          end;
       else ok = false;
       end;

  " here the variable ok is true if for any vertex p, the distance between
    p and x(p) is at least 3 ; this corresponds to the other class of
    enantiomeric labellings.                                               "

  end;
  if ok then s = append(s,x); end;
end;

" the sequence s contains the remaining candidates for enantiomeric
  labellings.                                                              "

r = empty;
```

Chart 1 (continued)

```
for i = 1 to length(s) do
  dd = empty;
  x = s[i];
  v1 = v;
  while v1 ne null do
    u = setrep(v1); u1 = u^x; dd = append(dd, [u,u1]); v1 = v1 - [u, u1];
  end;

  " dd is a sequence containing the pairs of enantiomeric vertices in the
    enantiomeric labelling induced by the element x of s                   "

  k = dd[1]^g;
  ok = true;
  for j = 2 to length(dd) do if position(k, dd[j]) eq 0 then ok = false;
                                                               break;
                             end;
  end;

  " ok is true if all the pairs of enantiomeric vertices are equivalent
    under the action of g.                                                 "

  if ok then r = append(r, x); end;
end;
print ad;
print g;
print '____________________________________________________________________';
for i = 1 to length(r) do
        x = r[i];
        cg = centralizer(g, x);
        ok = transitive(cg);
        if ok then cg1 = stabilizer(cg,1);
                   ok = card(setrep(ad[1])^cg1) eq  card(ad[1]);
                   if ok then
print '____________________________________________________________________';
print '____________________________________________________________________';
                              print x;
                              print card(class(g,x));
print '____________________________________________________________________';
                              print ' centralisateur : ';
                              print '------------------';
                              print cg;
                              if order(cg) le 1000 then
                                print subgroup lattice(cg);
                              end;
                   end;
        end;
end;
finish;
```

$\overline{2K_4}$, $\Sigma\Gamma(12)_3 = L23 = C_6[2K_1]$, $\overline{2K_6}$, $\overline{3K_4}$, $\Sigma\Gamma(16)_3 = P23 = C_8[2K_1]$, $\Sigma\Gamma(16)_7 = P82 = H_7[2K_1]$, $\overline{2K_8}$, $\overline{4K_4}$, $\Sigma\Gamma(18)_5 = R90 = (K_3[3K_1]) * K_2$ and $\overline{3K_6}$. Among these graphs, some display a quite unexpected property: there exist enantiomeric labelings that possess **different distances** between enantiomers. This is the case for $\Sigma\Gamma(12)_3 = L23$, $\Sigma\Gamma(16)_3 = P23$, and $\Sigma\Gamma(16)_7 = P82$. This property results from the fact that these graphs are of the type $\gamma[2K_1]$. Some of their ELs are due to the EL of γ itself; other ELs result from their factorization. We did also find examples of graphs where the diameter D and the distance d between enantiomers are different.[3,24] This is the case for $\Sigma\Gamma(12)_3 = L23$, $\Sigma\Gamma(14)_2 = N12$, $\Sigma\Gamma(16)_3 = P23$, $\Sigma\Gamma(16)_7 = P82$, and $\Sigma\Gamma(18)_2 = R28$. All of these graphs are of the type $\gamma[2K_1]$.[3]

Various graphs discussed in the present work have been used previously in connection to chemical applications. For instance, $\Sigma\Gamma(6)_2$, the octahedron, describes a possible interconversion of tetragonal pyramidal complexes.[25] The complement of Petersen graph,[26] i.e., $\Sigma\Gamma(10)_4$, represents a rearrangement of trigonal bipyramidal skeleta. The graphs $\Sigma\Gamma(6)_1$ (hexagon), $\Sigma\Gamma(8)_2$ (cube), and $\Sigma\Gamma(12)_7(\overline{2K_6})$ are related to XeF_6 interconversions,[3,10] while $\Sigma\Gamma(4)_1$ (square), $\Sigma\Gamma(8)_3(\overline{2K_4})$, and $\Sigma\Gamma(12)_8(\overline{3K_4})$ have been used as reaction graphs for square antiprism rearrangements.[11] Finding the reaction graph for a given interconversion is a difficult task when the number of configurations is big. However, knowing the group G of proper and improper symmetries of the molecular skeleton and the permutation x representing the interconversion (see sections 2.1 and 2.2), it is possible to obtain the degree and order of the reaction graph (see, for instance ref 27). The list of graphs of this given order and degree might perhaps be obtained from an atlas of graphs.[28] From this list and using the program given in the Appendix of the present work, it is then possible to select the graphs having enantiomeric labeling(s), and for such graphs to dispose enantiomers on the graph.

It may be worthwhile to relate the present interaction of chemistry, permutation groups, and graphs to ref 29.

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We want to thank Professor Balaban for having pointed out ref 23 and the Hamiltonian circuits in some of the graphs.

APPENDIX

We describe the program set up to list the ELs of a given graph ENANT4-mac.tex shown in Chart 1.

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