Properties of Reaction Graphs for XeF_6

J. Brocas

Chimie Organique, Faculté des Sciences, Université Libre de Bruxelles, 50, av. F.D. Roosevelt, 1050 Bruxelles, Belgium

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In this study of the automorphism group of some reaction graphs for XeF_6 interconversions, there exists a close relation between these groups and the algebraic structure of the modes of rearrangements of this molecule. Two of these groups are of big order (10^6 and 10^8). The relation between the present reaction graphs and those for trigonal bipyramids is discussed. In one case, the distance between enantiomers appears to be smaller than the diameter of the graph.

INTRODUCTION

Reaction graphs are an efficient tool to represent degenerate rearrangements. Their use has been developed extensively since Balaban's work, more than 25 years ago.[1] They provide a compact and aesthetically appealing representation of complex interconversions between molecular configurations, at least when the number of configurations (vertices) does not exceed say 50. When this number increases, the graphs are no longer explicitly available, but, even in the case of P_7^{3-} (1680 vertices) or, hopefully, bullvalene (1.209.600 vertices), interesting graph properties can be deduced such as cycle length, maximal distance between vertices, number of vertices at a given distance from a given vertex, automorphism group, and so on.[2]

For medium size graphs, pictorial representations are available or can be constructed. For a given number of vertices (order of the graph) and a given number of edges meeting at each vertex (degree of the vertices), the legibility of these regular graphs depends strongly on the way they are represented, and, generally speaking, the more symmetrical drawings provide a better insight into the graph properties. Of course, a two-dimensional picture is unable to account for the very big number of symmetry operations of some graphs, e.g., 10^8 (vide infra) or 10^9 [3] in the case of some square antiprism interconversions.

The knowledge of the symmetry operations, i.e., of the graph automorphism group is per se an important step on the way to characterize the graph. It also provides a possibility to draw symmetrical pictures of the graph. For instance, if one knows that an n-fold "axis" is present in the graph automorphism group and if one knows its permutational expression, it is an easy matter to obtain a representation of the graph where this n-fold "axis" appears clearly.

The automorphism groups of reaction graphs have been studied by Randić and co-workers in a series of papers starting 15 years ago. For details about the methods used and the results obtained, the reader should consult recent papers by this author and work cited there.[2,4,5]

In the present paper, we derive and study the automorphism groups of some graphs for XeF_6 interconversions. A complete permutational analysis of the dynamics of this molecule has been given and has been compared to previous theoretical and experimental work (see ref 6 and 7 and work cited there). Graphical representations have been obtained[8] for the modes of rearrangements[9−12] where at most 40 configurations can be reached starting from a given one. It seems useful to recall some concepts and notations related to the forthcoming discussion. Details may be found in ref 6−12.

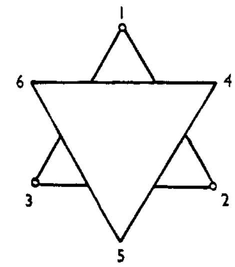

Figure 1. The XeF_6 framework.

We assume that the XeF_6 molecule has C_{3v} symmetry. It is represented in Figure 1 where the open circles denote the skeletal sites on the triangular face with the free electron pair. The ligand labels (1, 2, ..., 6) represent the six fluorine atoms. The permutational expression of the molecular C_{3v} symmetry group is given by

$$G = A \bigcup A\sigma$$

$$A = I, (123)(456), (132)(465)$$

$$A\sigma = (12)(56), (13)(45), (23)(46)$$

where $\cup$ means union, A and $A\sigma$ denote, respectively, proper and improper symmetry operations, I stands for identity operation, and σ is any improper operation.

The ligands may be permuted by the operations of S_6, the symmetric group of permutations of degree 6. The number of configurations reached in this way is

$$t = \frac{|S_6|}{|A|} = 240$$

where $|A|$ means order of A.

Six digits symbols may be used to label the configurations: the triangular face (big) with the electron pair is below, as in Figure 1; the first digit of the symbol is the lowest among the labels of the ligands on the big face, the second and third digits are the labels appearing clockwise on the

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Table 1. Correspondence between Letters and Configuration Symbols

o	123.456	f	145.236	l	465.231
a	264.531	g	253.641	m	465.123
b	345.612	h	163.542	n	123.564
c	156.423	i	156.423	p	356.241
d	364.125	j	465.312	q	164.352
e	256.314	k	123.645	r	245.163

big face. One then inserts a dot followed by the labels of the ligands on the small face in clockwise order and starting from the ligand of the small face which is between the two first ligands on the big face. For instance, the symbol of the configuration of Figure 1 is 123.456. In the present paper, the vertices of the graphs will be labeled with letters. The correspondence between configuration symbols and letters is given in Table 1.

The internal dynamics of nonrigid molecules may be analyzed in terms of modes of rearrangements:[9−12] a mode $M(x_i)$ is the set of permutations describing rearrangements pathways which are indistinguishable from the permutation x_i for symmetry reasons. In the present case, the group S_6 may be partitioned into 52 such modes. To each mode $M(x_i)$ it is possible to associate an enantiomeric mode $M(\sigma x_i)$. Starting from a given configuration, $M(\sigma x_i)$ generates the mirror images of the configurations generated by $M(x_i)$. In the present case, the 52 modes may be grouped into 26 pairs of enantiomeric modes.

Among these modes, we consider the opposite jump, i.e., a movement where the free electron pair jumps from the triangular face 123 to the opposite face 456. It leads from configuration 123.456 to 456.123; the permutation describing this jump will be noted u_o whereas ν_o is the product of u_o and the enantiomerization σ (noted σ_o from now on). Using the four permutations $I = x_o$, σ_o, u_o, and ν_o it is easy to show that

(a) the 240 configurations may be grouped into 60 quartets of the type $\{o, \bar{o}, \underline{o}, \bar{\underline{o}}\}$ where $\bar{o}$, $\underline{o}$, and $\bar{\underline{o}}$ are obtained by applying σ_o, ν_o, and u_o, respectively, to configuration o and

(b) the 52 modes may be grouped into 13 quartets of modes $\{x_i, \sigma_i, u_i, \nu_i\}$ $(i = 0, 1, 2, ... 12)$.

Starting from a given configuration, say o, repeated application of a given mode $M(x_i)$ generates a set of configurations. The number p_i of configurations reached in this way is equal to or smaller than the number t of possible configurations (here $t = 240$).

Hence, to each mode $M(x_i)$, it is possible to associate a graph having p_i vertices (of order p_i) and whose edges represent the interconversions of the p_i configurations (vertices) when applying mode $M(x_i)$.

The automorphism groups of these graphs are obtained below by using a computer program[13] which also permits to investigate some structural properties of these groups such as classes, character tables, or invariant subgroups. It will appear

(a) that the relation between the modes which has been analyzed in terms of the operators σ_o (enantiomerization), u_o (opposite jump), and their product ν_o[6] is reflected in some symmetry properties of the graphs and

(b) that some of these properties are identical to those of the apparently unrelated graphs for trigonal bipyramids interconversions.

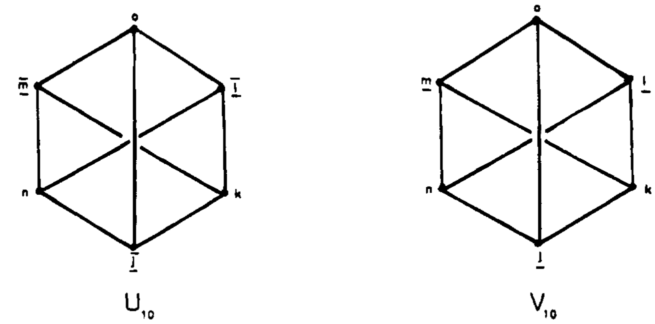

Figure 2. The graphs for modes u_{10} and ν_{10}.

AUTOMORPHISM GROUPS

In previous work,[8] the reaction graphs of the rearrangements of XeF_6 have been obtained, as far as their order does not exceed 40. The automorphism groups of these graphs are now discussed.

The groups of the graphs for (a) x_o, σ_o, u_o, ν_o; (b) x_1, σ_1, u_1, ν_1; (c) x_5, σ_5, u_5, ν_5; and (d) x_{12}, σ_{12} do not deserve further comments since these graphs are either trivial (cases (a) and (c)) or isomorphic to well-known polyhedra (cases (b) and (d)). This appears clearly in Figures 2−4, 12, and 13 of ref 8. The groups of the other graphs are discussed below.

Graphs for u_{10} and ν_{10}. They are represented in Figure 2. These four-cage graphs of order six and degree three are the well-known complete bipartite graph $K_{3,3}$. In the graph for ν_{10}, each vertex of the set {o, k, n} is adjacent to all the vertices of the set $\{\underline{l}, \underline{m}, \underline{j}\}$. Hence, the group $G(\nu_{10})$ of this graph contains all the permutations within each of these sets and the permutation α of the sets among each other:

$$G(\nu_{10}) = \{S_3(o, k, n) \otimes S_3(\underline{l}, \underline{m}, \underline{j})\} \wedge \{I, \alpha\}$$

where

$$\alpha = (o, \underline{l})\,(k, \underline{m})\,(n, \underline{j})$$

where ⊗ and ∧ mean direct and semidirect product,[14] respectively, and where S_n denotes the symmetric group of degree n. Of course the order $|G(\nu_{10})|$ of this group is 72.

Graphs for x_{10} and σ_{10}. The graph for x_{10} is represented in Figure 5 of ref 8. It is a directed graph since it corresponds to a non self-inverse mode.[15] The graph for σ_{10} is obtained by inverting the arrows. We discuss the group $G(x_{10}, \sigma_{10})$ corresponding to the graph where the arrows are omitted, i.e., the graph for the union of the two mutually inverse[12] modes x_{10} and σ_{10} (see Figure 3).

In this complete bipartite graph $K_{6,6}$ of order 12 and degree 6 each vertex of the set $\{\underline{o}, \bar{o}, k, \bar{k}, \underline{n}, \bar{n}\}$ is adjacent to all the vertices of the set $\{l, \bar{l}, m, \bar{m}, j, \bar{j}\}$. Hence

$$G(x_{10}, \sigma_{10}) = \{S_6(o, \bar{o}, k, \bar{k}, n, \bar{n}) \otimes S_6(l, \bar{l}, m, \bar{m}, j, \bar{j})\} \wedge \{I, \beta\}$$

where

$$\beta = (o, l)\,(\bar{o}, \bar{l})\,(k, m)\,(\bar{k}, \bar{m})\,(n, j)\,(\bar{n}, \bar{j})$$

permutes the two sets.

The order of this group is

$$|G(x_{10}, \sigma_{10})| = 6! \times 6! \times 2 = 1.036.800$$

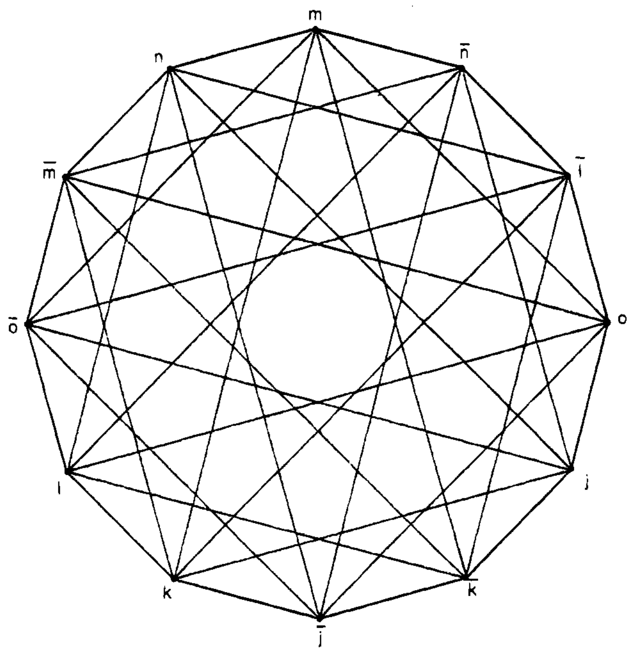

Figure 3. The graph for the union of the two mutually inverse modes x_{10} and σ_{10}.

Table 2. Labels of the Vertices

	o	a	b	c	d	e	f	g	h	i
o, etc. ...	1	10	9	3	7	8	4	6	2	5
ō, etc. ...	11	20	19	13	17	18	14	16	12	15
$\underline{o}$, etc. ...	21	30	29	23	27	28	24	26	22	25
$\underline{\bar{o}}$, etc. ...	31	40	39	33	37	38	34	36	32	35

Graphs for x_4 and σ_4. The vertices of these graphs are o, a, b, c, d, e, f, g, h, and i and their enantiomers. The vertices of the graphs ν_4 and u_4, discussed further, also contain the vertices obtained from those of x_4 and σ_4 by the action of the operators u_o or ν_o defined elsewhere.[6,7] The symbols used to designate these vertices are o, ō, $\underline{o}$, $\underline{\bar{o}}$, etc.[8] In order to avoid the use of upper and lower bars in lengthy permutational expressions, we label the vertices by the numerals 1, 2, ... 40. The correspondence between the two notations is given in Table 2. It is seen that the action of the operators σ_o, ν_o, u_o on the vertices 1, 2, ..., 10 is merely obtained by adding 10, 20, and 30 to the label of these vertices.

The graphs for x_4 and σ_4 are not isomorphic.[8] In spite of this, their automorphism groups $G(x_4)$ and $G(\sigma_4)$ are identical and spanned by the three following generators:

$$a = (2,12)\,(4,8)\,(5,6)\,(9,10)\,(14,18)\,(15,16)\,(19,20)$$

$$b = (2,5)\,(3,4)\,(7,10)\,(8,9)\,(12,15)\,(13,14)\,(17,20)\,(18,19) \quad (1)$$

$$c = (1,2)\,(3,6)\,(4,19)\,(5,17)\,(7,15)\,(9,14)\,(11,12)\,(13,16)$$

Moreover

$$|G(x_4)| = |G(\sigma_4)| = 240$$

The fact that $G(x_4)$ and $G(\sigma_4)$ are identical implies that it is possible to find for the graph σ_4 a representation displaying the same D_{10h} symmetry as for the graph for x_4.[8] Similar representations of both graphs are indeed shown in Figure 4. From Table 3 in Appendix 1, it is seen that $G(x_4)$ and $G(\sigma_4)$ do not have higher than tenfold symmetry.

Table 3: Class Structure of (a) $G(x_4)$, (b) $G(P_3)$, and (c) L

cycle structure				
(a)	(b)	(c)	order	length
1^{20}	1^{20}	1^{40}	1	1
2^{10}	2^{10}	2^{20}	2	1
$1^2\,2^9$	$1^8\,2^6$	$1^{16}\,2^{12}$	2	10
$1^6\,2^7$	2^{10}	2^{20}	2	10
$1^4\,2^8$	$1^4\,2^8$	$1^8\,2^{16}$	2	15
2^{10}	2^{10}	2^{20}	2	15
$1^2\,3^6$	$1^2\,3^6$	$1^4\,3^{12}$	3	20
4^5	$2^2\,4^4$	$2^4\,4^8$	4	30
4^5	$2^2\,4^4$	$2^4\,4^8$	4	30
5^4	5^4	5^8	5	24
$1^2\,6^3$	$2^1\,6^3$	$2^2\,6^6$	6	20
$2^1\,3^2\,6^2$	$1^2\,3^2\,6^2$	$1^4\,3^4\,6^4$	6	20
$2^1\,6^3$	$2^1\,6^3$	$2^2\,6^6$	6	20
10^2	10^2	10^4	10	24

We now use the well-known fact that all the mode operators commute with σ_o (see [6 and 10] and refs cited there). As a consequence, the operation p simultaneously exchanging the members of each pair of enantiomeric configurations is one of the automorphisms of any reaction graph for degenerate rearrangements (note that this operation could exchange vertices belonging to different components of a disconnected graph when the rearrangement at hand does not lead to enantiomerization). In the present case, this operation is written

$$p = (1, 11)\,(2, 12)\,...\,(10, 20) \quad (2)$$

and $G(x_4)$ and $G(\sigma_4)$ may be expressed as a product of two of their invariant subgroups

$$G(x_4) = G(\sigma_4) = G \otimes \{I, p\} \quad (3)$$

The group G itself may be factorized as follows

$$G = H \wedge \{I, g\} \quad (4)$$

where g is any permutation of order 2 belonging to G but not to H, e.g.,

$$g = (1,11)\,(3,13)\,(4,18)\,(5,16)\,(6,15)\,(7,17)\,(8,14)\,(9,20)\,(10,19) \quad (5)$$

and where H, another invariant subgroup of $G(x_4)$, is isomorphic to A_5, the alternating group of degree 5. Details about the permutational expressions of $G(x_4)$, G, and H are given in Appendixes 1−3, respectively.

The factorization of $G(x_4)$ shown in eq (3) corresponds to an homomorphic mapping[16] of the graphs of Figure 4, i.e., the pairs of vertices {1, 11}, {2, 12}, ... corresponding to enantiomers are replaced by the single vertices 1, 2, ..., respectively. More precisely, the internal vertices of these graphs are suppressed; the external ones are the vertices of a decagon and labeled from 1 to 10, as shown on Figure 5A. An edge connects a pair i, j of these 10 vertices if and only if there was an edge connecting i or $\bar{i}$ to j or $\bar{j}$ in the graphs of Figure 4. The resulting graph is the same whether starting from the graph for x_4 or σ_4, and it is shown in Figure 5A. Surprisingly, it is isomorphic to the Desargues graph for mode P_2 represented by (aee) of the trigonal bipyramid (a means axial and e equatorial). A graphical representation of P_2 showing fivefold symmetry is shown in Figure 5B. The vertices labels refer to configuration symbols of the trigonal bipyramid (see ref 12 and work cited there). It is

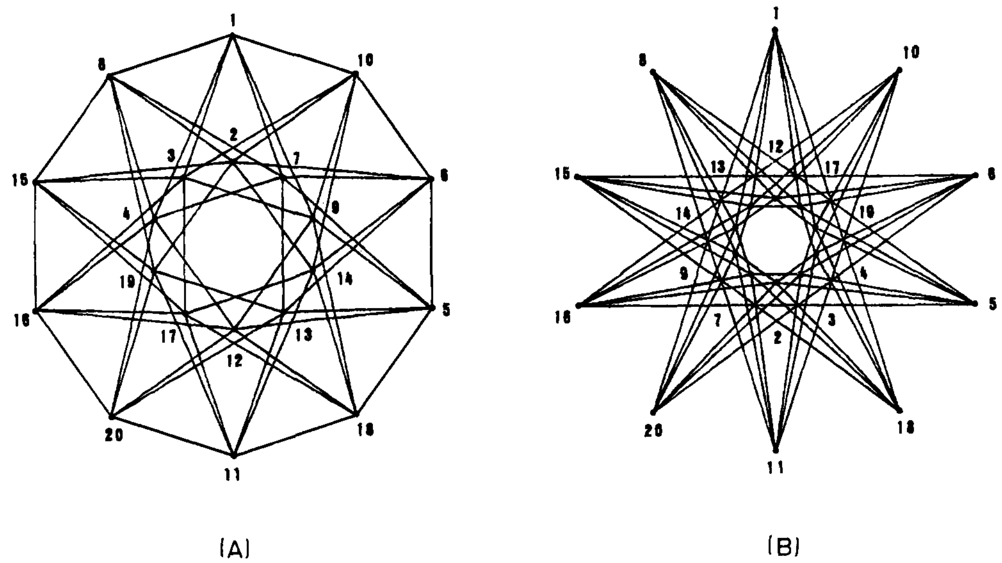

Figure 4. The D_{10h} symmetry in the graphs for x_4 (A) and σ_4 (B).

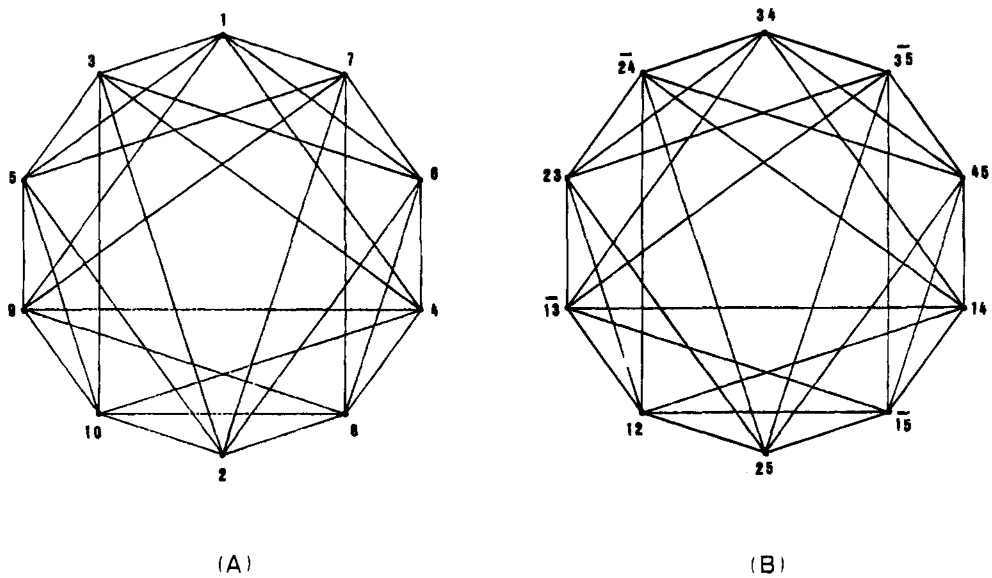

Figure 5. (A) Homomorphic reduction of the graphs of Figure 4 and (B) the graph for mode P_2 (trigonal bipyramid).

well-known that the Petersen graph for P_4 (represented by $(ae)^2$) and the Desargues graph for P_2 are complementary[4,17], i.e., their union is the complete graph of order 10. Hence, they have the same automorphism group, namely a group isomorphic to S_5, the symmetric group of degree 5.[17,18] Indeed, the group G, given in eq 4 and displayed in Appendix 2, is effectively isomorphic to S_5.

Incidentally, it should be noted that the graph for mode P_3[12] of the trigonal bipyramid represented by (ae) is also of order 20 and degree 6. It is drawn in Figure 6 and shows a striking similarity with the graph for x_4 in Figure 4A. It is labeled in the same way as Figure 4A. By homomorphic reduction it yields the graph of Figure 5B where an edge ij plays the role of the pair of edges ij and $\bar{i}\bar{j}$ in Figure 6. The graph for P_3 is bipartite since edges only connect even configurations to odd ones.[12] Hence P_3 has only cycles of even length. Its girth—the length of its shortest cycle—is four, as is obvious from Figure 6. It is not isomorphic neither to the graph for x_4 nor to the graph for σ_4 which have both cycles of length 3, i.e., $1 \to 3 \to 9 \to 1$ (Figure 4A) and $1 \to 13 \to 17 \to 1$ (Figure 4B).

The automorphism group $G(P_3)$ of this graph is closely related to $G(x_4)$ (see eq 3 and 4). It is also of order 240 and may be written

$$G(P_3) = J \otimes \{I,p\} \tag{6a}$$

$$J = \{K \wedge \{I,j\}\} \tag{6b}$$

and where p is given in eq 2 and

$$j = (4,18)\,(5,16)\,(6,15)\,(8,14)\,(9,20)\,(10,19) \tag{7}$$

The relation between the cycle structure of $G(P_3)$ and that of $G(x_4)$ is shown in Table 3 of the Appendix 1. The group K in eq 6b is isomorphic to A_5, and its generators are given in the Appendix 3 as well as its class structure. Details about the group J are discussed in Appendix 2.

Graphs for v_4. This graph is isomorphic to the graph for u_4 and has 40 vertices instead of 20 for the graphs corresponding to x_4 and σ_4 (see Figure 10 of ref 8). This graph is also represented in Figure 7 where the omitted vertex labels are easy to retrieve. Indeed, the labels i, $i + 10$, $i + 20$, and $i + 30$ are on the same diameter, and $i + 20$ is close

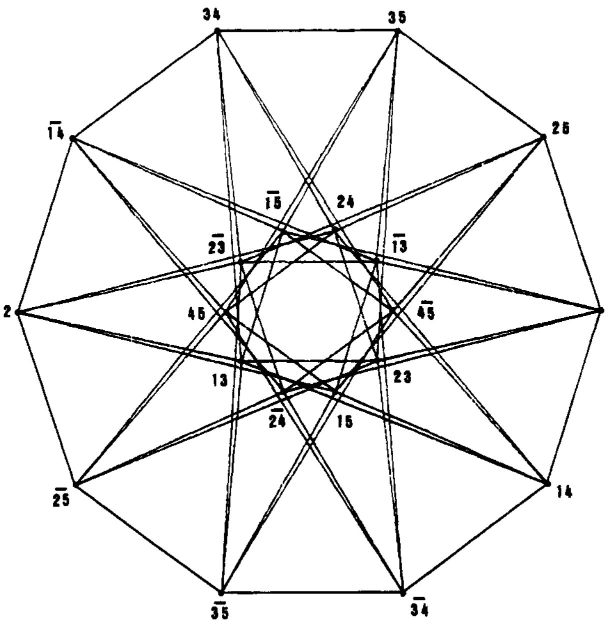

Figure 6. The graph for mode P_3 (trigonal bipyramid).

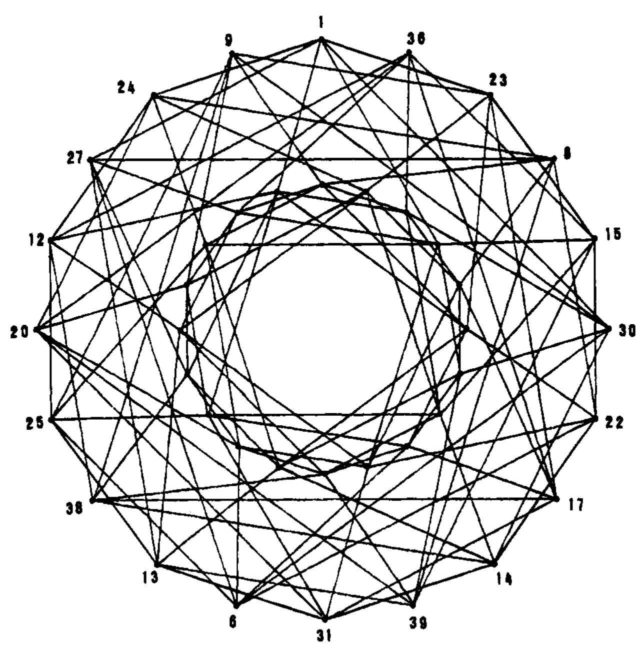

Figure 7. The graph for mode ν_4.

to i. Its automorphism group is of order 480. It has four generators: a', b', c', and q'. The generator q' exchanges simultaneously the members of each pair of vertices related to each other by the operation ν_o and is written

$$q' = (1{,}21)\,(2{,}22)\,...\,(19{,}39)\,(20{,}40) \tag{8}$$

whereas a', b', and c' may be obtained by replacing any transposition (i, j) in a, b, and c (see eq 1) by the product of transpositions (i, j) $(i + 20, j + 20)$.

For this reason, the group $G(\nu_4)$ may be factorized similarly to $G(x_4)$ and $G(\sigma_4)$ (see eq 3 and 4):

$$G(\nu_4) = G' \otimes \{I, p'\} \otimes \{I, q'\} \tag{9}$$

where p' plays the same role as p (see eq 2) and is written

$$p' = (1{,}11)\,(2{,}12)\,...\,(10{,}20)\,(21{,}31)\,...\,(30{,}40) \tag{10}$$

The group G' is given by (see eq 4)

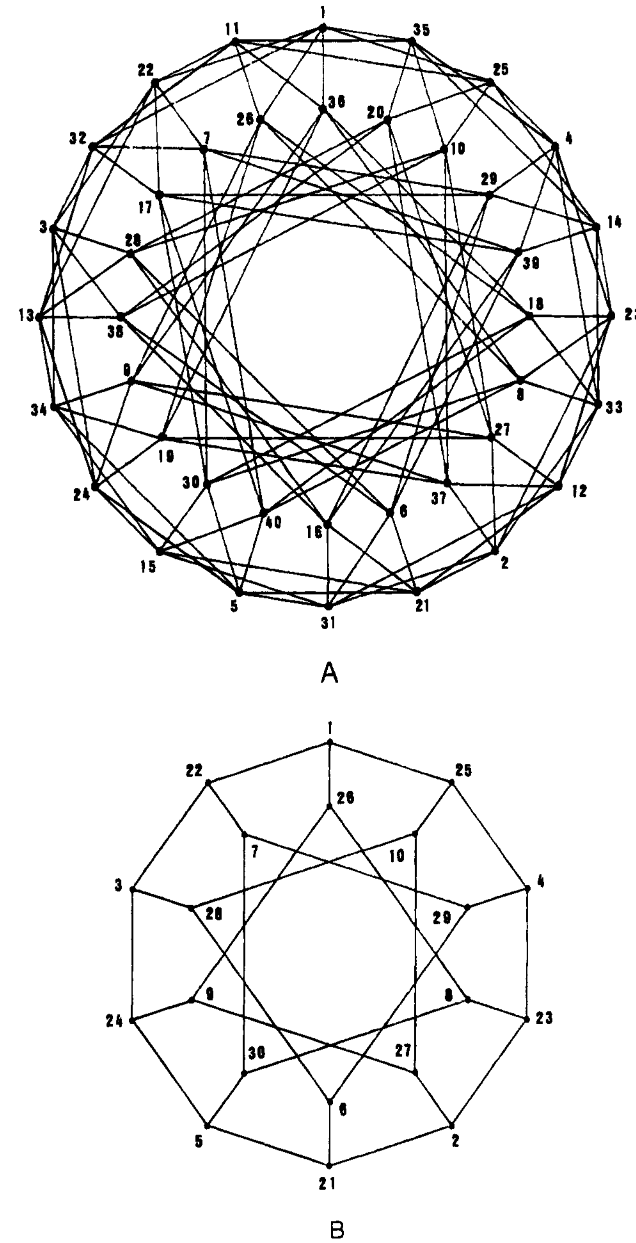

Figure 8. (A) The graph for mode u_{12} and (B) its homomorphic reduction.

$$G' = H' \wedge \{I, g'\} \tag{11}$$

where the relation between g and g' is the same as that between p and p'. The properties of G' and H' are obtained, mutatis mutandis, from those of G and H found in Appendixes 2 and 3. The homomorphic reduction from $G(\nu_4)$ to G' (eq 9) gives also rise to the graph in Figure 5B.

Graphs for u_{12}. Since u_{12} and ν_{12} are mutually inverse we discuss the graph for their union (see Figure 8A).

In spite of the fact that it has the same number of vertices and edges as the graph for ν_4, the order of the automorphism group this graph is much bigger:

$$|G(u_{12})| = 2^{24} \times 3 \times 5 = 251.658.240$$

This is due to the fact that it has a special property: any vertex is the neighbor of both vertices of an enantiomeric pair (see Figures 14 and 15 of ref 8 and Figure 8A of the present work). As a consequence, this graph is invariant for the individual exchange of the two vertices corresponding to any pair of enantiomers.

Hence

$$G(u_{12}) = L \otimes E \tag{12}$$

$$E = \{I, (1,11)\} \otimes \{I, (2,12)\} \ldots \otimes \{I, (30,40)\} \tag{13}$$

is a group of order 2^{20} and L is merely of order 240.

The factorization of eq 12 corresponds to a homomorphic reduction where each pair of enantiomeric vertices $\{i, \bar{i}\}$ in Figure 8A is represented by a single vertex i in Figure 8B and where the quadruple of edges $\{(ij), (i\bar{j}), (\bar{i}j), (\overline{ij})\}$ in Figure 8A is represented by a single edge (ij) in Figure 8B. The graph resulting from this reduction is the famous Desargues–Levi graph for mode P_1 (Berry mechanism) of the trigonal bipyramid,[12] a quite unexpected result. This graph has been discussed extensively since Balaban's proposal[1] and its automorphism group has been obtained by Randić.[18] The group L is eq 12 is, of course, closely related to the Randić group, in spite of the fact that its degree is 40 instead of 20 for the group of the Desargues–Levi graph. Its generators are

$$1_1 = [4,8]\ [5,6]\ [9,10]$$

$$1_2 = [2,5]\ [3,4]\ [7,10]\ [8,9]$$

$$1_3 = [1,2,3,4,5] \tag{14}$$

and the permutation q' exchanging simultaneously the members of each pair of configurations related to each other by the operation $\nu_o{}^6$ (see eq 8). In eq 14,

$$[4,8] = (4,8)\ (14,18)\ (24,28)\ (34,38) \tag{15}$$

and similar meaning for the other square bracketed expressions.

The group L may be factorized along the same lines as $G(x_4)$, $G(P_3)$, and G' (eqs 3, 4, 5, and 11):

$$L = M \otimes \{I, q'\} \tag{16a}$$

$$M = \{N \wedge \{I, 1_4\}\} \tag{16b}$$

where, for instance

$$1_4 = [3,7]\ [4,10]\ [8,9] \tag{17}$$

and where N is isomorphic to A_5. Details about the groups L, M, and N are collected in Appendixes 1–3, respectively.

CONCLUSION

The graph $G(\nu_{10})$ for ν_{10} and u_{10} and the graph $G(x_{10}, \sigma_{10})$ for the union of x_{10} and σ_{10} are of related structure. They are both complete bipartite graphs of order p and degree $p/2$ ($p = 6$ or 12, respectively). Their automorphism group is of the form $\{S_{p/2} \otimes S_{p/2}\} \wedge C_2$ where C_2 exchanges the components of the bipartite set. Note that the graph for mode $\theta_{10}{}^3$ is another example of this type ($p = 8$), whereas the square illustrates the trivial case where $p = 4$.

Let us consider a homomorphic mapping of the graph $G(x_{10}, \sigma_{10})$ where each pair of enantiomeric configurations (e.g., $\{o,\bar{o}\}$) is replaced by a single configuration o and where each quartet of edges (e.g. $\{om, \bar{o}m, o\bar{m}, \overline{om}\}$ is replaced by a single edge om. Such a mapping gives rise to a graph isomorphic to $G(\nu_{10})$ (see Figure 2). This shows the relation between graphs generated by a given quartet of modes, here $\{x_{10}, \sigma_{10}, u_{10}, \nu_{10}\}$.

The graphs for the modes x_4, σ_4, and ν_4 (isomorphic to the graph for u_4) are very closely related to the reaction graph for P_2 (e.g., cyclic exchange of one axial and two equatorial ligands) of the trigonal bipyramid (the Desargues graph), which is obtained by homomorphic mapping of the graphs for x_4, σ_4, and ν_4. The homomorphic mapping to be applied replaces a pair of enantiomeric vertices by a single vertex in the case of x_4 and σ_4 and replaces a quartet (of the type $o, \bar{o}, \underline{o}, \underline{\bar{o}}$) by a single vertex in the case of ν_4. The reaction graph of P_3 (e.g., exchange of one axial and one equatorial ligand) of the trigonal bipyramid also yields the graph of P_2 by the same homomorphic mapping as the one applied for the graphs for x_4 and σ_4. However the graphs for x_4, σ_4, and P_3 are not isomorphic.

The graph for the mode u_{12} bears also a surprising relation with the reaction graph for the Berry mechanism P_1 of the trigonal bipyramid (the Desargues–Levi graph) since a homomorphic mapping of the former gives rise to the latter when a pair of enantiomeric vertices is mapped onto a single vertex.

The common and remarkable feature of the automorphism groups of the reaction graphs for P_2 and P_3 (trigonal bipyramid), on the one hand, and the automorphism groups $G(x_4) = G(\sigma_4)$, $G(\nu_4) = G(u_4)$ and $G(u_{12})$, on the other hand, is that they all have a subgroup isomorphic to A_5.

We also want to comment about a conjecture by Randić, Oakland, and Klein.[2] According to these authors, "for isomerization graphs of achiral molecules with distinct enantiomeric configurations connected via a sequence of isomerization steps, the distance between enantiomers is the diameter D of the isomerization graph". Let us consider the case of a reaction graph for a racemic mode of rearrangement.[10,12] In this particular case, the set of configurations reached from a starting configuration s in one step of that mode consists only of pairs of enantiomeric configurations. This means that there exist an edge from s to f and one from s to $\bar{f}$ (f and $\bar{f}$f are enantiomeric configurations). Hence, when the mode is racemic, the distance d between enantiomers is equal to two. It is then tempting to look for "big" graphs where the diameter D is likely to be bigger than 2. This is indeed the case for the graph of u_{12} where $d = 2$ and $D = 5$, a graph for a racemic mode where the above conjecture fails. It seems, however, not easy to find other examples of this type: in the case of XeF_6 discussed in the present work, the other nontrivial graphs leading to interconversion of enantiomers are those from x_{10}, x_4, and ν_4 (x_{10} is the only racemic one). They all verify the conjecture ($d = D = 2$, 3, and 4, respectively). Other geometries have been investigated: square antiprism,[3] octahedra,[12] tetragonal pyramids,[12] and trigonal bipyramids.[12] In these four cases, the conjecture is verified even when the mode happens to be racemic, such as the diagonal twist of octahedral molecules.

To conclude, it appears that modes of rearrangements play an important role in the properties of the corresponding reaction graphs. Repeated application of a given mode $M(x_i)$ to a starting configuration gives rise to a set of p_i configurations. The corresponding graph has p_i vertices (its order is p_i) and its edges represent the interconversions of the p_i configurations when mode $M(x_i)$ is operative. The Longuet-Higgins[19] group (which is the symmetry group of a nonrigid molecule) is the set of feasible permutations (and permutations-inversion) of identical nuclei. The permutations of this group may be obtained from $M(x_i)$, if this mode is considered as feasible. Hence, the mode $M(x_i)$ determines unambiguously, on the one hand, the reaction graph and, as a result, its automorphism group and, on the other hand, the Longuet-Higgins group. These two groups are, however, distinct. The Longuet-Higgins group permutes identical nuclei, while the graph automorphism group permutes the vertices of the graph, i.e., the configurations. The order of the Longuet-Higgins group is $p_i|G|$. Such a simple relation does, of course, not hold for the order of the graph automorphism group.

APPENDIX 1: GROUPS OF ORDER 240

The classes of the groups $G(x_4)$ (see eqs 1–5), $G(P_3)$ (eqs 6 and 7); and L (eqs 14–17) are given in Table 3. These three groups of order 240 have identical order and length of their classes. The groups $G(x_4)$ and $G(P_3)$ shown in columns (a) and (b) of Table 3 differ by their cycle structure. The groups $G(P_3)$ and L (columns (b) and (c)) have similar cycle structure since, for each class, the number of cycles of given length in L is twice the number of cycles of the same length in $G(P_3)$.

The similarity between the columns (b) and (c) of Table 3 suggests that the groups $G(P_3)$ and L could be isomorphic if there were a one-to-one correspondence between a cycle (a, b, c, ...) in a permutation belonging to $G(P_3)$ and a product of two cycles (a, b, c, ...) (a + 20, b + 20, and c + 20) in a permutation belonging to L. This is, however, not the case. The eventual isomorphism between $G(x_4)$, $G(P_3)$, and L could be related to the fact that they all have a subgroup isomorphic to A_5.

APPENDIX 2: GROUPS OF ORDER 120

The group G of eq 3 is spanned by the following generators:

$$g_1 = (1,8)\,(2,3)\,(4,7)\,(5,20)\,(6,16)\,(9,19)\,(10,15)\,(11,18)\,(12,13)\,(14,17)$$

$$g_2 = (1,4)\,(2,13)\,(3,12)\,(5,15)\,(6,19)\,(7,8)\,(9,16)\,(10,20)\,(11,14)\,(17,18)$$

$$g_3 = (1,9)\,(2,17)\,(3,10)\,(4,5)\,(6,16)\,(7,12)\,(8,18)\,(11,19)\,(13,20)\,(14,15)$$

and the generator given by eq 5. Its class structure is given in Table 4 (column labeled (a)).

One should, however, keep in mind that the factorization of $G(x_4)$ of the form of eq 3 is not unique: $G(x_4)$ has two invariant subgroups whose direct product with $\{I, p\}$ gives $G(x_4)$. The first one is G itself (used in eq 3), and the second one is another group having generators and cycle structure different from those of G, but the same order and length of the classes than G. Similar comments apply to the factorization of $G(P_3)$ (eq 6a) and L (eq 16a) and to the nonunicity of J and M in Table 4.

Table 4. Class Structure of (a) G, (b) J, and (c) M

cycle structure				
(a)	(b)	(c)	order	length
1^{20}	1^{20}	1^{40}	1	1
$1^2\,2^9$	$1^8\,2^6$	$1^{16}\,2^{12}$	2	10
2^{10}	$1^4\,2^8$	$1^8\,2^{16}$	2	15
$1^2\,3^6$	$1^2\,3^6$	$1^4\,3^{12}$	3	20
4^5	$2^2\,4^4$	$2^4\,4^8$	4	30
5^4	5^4	5^8	5	24
$1^2\,6^3$	$1^2\,3^2\,6^2$	$3^4\,6^4$	6	20

Table 5. Class Structure of (a) H, (b) K, and (c) N

cycle structure				
(a)	(b)	(c)	order	length
1^{20}	1^{20}	1^{40}	1	1
2^{10}	$1^4\,2^8$	$1^8\,2^{16}$	2	15
$1^2\,3^6$	$1^2\,3^6$	$1^4\,3^{12}$	3	20
5^4	5^4	5^8	5	12
5^4	5^4	5^8	5	12

APPENDIX 3: GROUPS OF ORDER 60

The classes of the groups H (see eq 4), K (see eq 6b), and N (see eq 16b) are given in Table 5. It is seen that the order and length of the classes are those of A_5, the alternating group of degree 5. Since A_5 is the only group of order 60 displaying these order and length of classes,[13] it is clear that H, K, and N are all isomorphic to A_5.

The groups K and N have similar cycle structure. The cycle structure of H, K, and N is unique, in contradistinction to the cycle structure of G, J, and M (see Appendix 2): indeed the groups $G(x_4)$, $G(P_3)$, and L have only one invariant subgroup of order 60.

The generators of H are g_1, g_2, and g_3 given in Appendix 2. The group K is spanned by the generators:

$$k_1 = (1,2)\,(3,5)\,(6,17)\,(7,16)\,(8,10)\,(11,12)\,(13,14)\,(18,20)$$

$$k_2 = (1,2)\,(3,16)\,(4,9)\,(5,7)\,(6,13)\,(11,12)\,(14,19)\,(15,17)$$

$$k_3 = (1,6)\,(2,9)\,(3,14)\,(4,13)\,(5,8)\,(11,16)\,(12,19)\,(15,18)$$

The group N is spanned by the generators l_2, l_5, and l_6 where l_2 is given in eq 14 whereas

$$l_5 = [3,7]\,[4,9]\,[5,6]\,[8,10]$$

and

$$l_6 = [1,3]\,[4,5]\,[6,8]\,[9,10]$$

The square brackets are defined in eq 15.

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