The reaction graph of the Cope rearrangement in bullvalene

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The concept of mode of rearrangement is used to analyse the connectedness of the reaction graph for the Cope rearrangement in bullvalene.

1. Introduction

In a recent paper [1], Klin, Tratch and Zefirov discussed a criterion for the connectedness of a reaction graph. Their demonstration was illustrated by several examples, including the reaction graph for the Cope rearrangement of bullvalene, for which they compared several models. According to these authors, the properties of the reaction graph depend on the "selection of an adequate model" which "requires two separate decisions: one about the subgroup H and one about the coset which is adjacent to H in the reaction graph".

In fact, the models discussed in ref. [1] differ from each other by the different treatment of improper symmetry operations. The main purpose of the present work is to show that the concept of mode of rearrangement provides an unambiguous way to construct reaction graphs, as far as one agrees about the mechanism (here the Cope rearrangement) and the skeleton symmetry (here C_{3v}). The models of ref. [1] are then analyzed in terms of the mode of rearrangements approach. Finally, the relation between ref. [1] and previous work on Longuet–Higgins groups [2] and on residual stereoisomerism [3] is pointed out.

2. Theoretical background

We recall some definitions which are useful for the subsequent discussion. Details may be found elsewhere [4]. Let G be the permutation group expressing the molecular symmetry and A the subgroup of G which contains only proper rotations:

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

where $\cup$ stands for "union" and σ is any improper operation. For chiral molecules

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

For a skeleton with n sites, the $n!$ permutations in the symmetric group S_n of degree n are to be considered. A general permutation $x \in S_n$ represents a given rearrangement. To such a permutation, one might associate a "A coset" Ax or a "G coset" Gx. Of course,

$$Gx = Ax \cup A\sigma x \tag{3}$$

is a union of two A cosets. The coset Ax represents a configuration, i.e. a potential minimum or a set of permutations which are rotationally equivalent to x (they differ from x by a proper rotation).

The number p of configurations is

$$p = \frac{|S_n|}{|A|} = \frac{n!}{|A|} , \tag{4}$$

where $|A|$ is the order of A.

As shown in eq. (3), Gx represents a pair of enantiomeric configurations Ax and $A\sigma x$, which correspond to completely different rearrangements when starting from the configuration represented by A. For instance, let us consider NF_3 and NH_3, of C_{3v} structure. In this case $S_n = S_3 = G$ and $p = 2$. The two configurations are represented by A and $A\sigma$. Applying A to a starting configuration means performing an always feasible rigid rotation whereas $A\sigma$ represents umbrella inversion which is feasible [2] at ordinary temperatures for NH_3 but not for NF_3.

We may also define A subclasses and G subclasses. The A subclass of elements $a^{-1}xa, a \in A$, contains all the permutations conjugate to x by a proper operation; $\{g^{-1}xg; g \in G\}$ is defined similarly by using proper and improper operations and is a G subclass.

We now recall a fundamental definition: a mode of rearrangements [4–7], is the set $M(x)$ of permutations which are indistinguishable from x because
(a) they generate the same final configuration as x, starting from a given one and/or
(b) they must occur with the same probability as x.

Clearly condition (a) leads to consider Ax whereas (b) leads to consider either $g^{-1}xg$ in achiral environment or $a^{-1}xa$ in chiral environment [4,7]. Hence, one obtains

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

in achiral situations and

$$M(x) = AxA \tag{6}$$

in chiral ones. In the case of degenerate rearrangements, i.e. when starting and

final configurations are isoenergetic, x and x^{-1} also occur with the same probability. Nourse [8] has introduced the important distinction between self-inverse (SI) and non self-inverse (NSI) rearrangements. It has been shown that $M(x)$ and $M(x^{-1})$ are identical or distinct according to whether the rearrangement is SI or NSI [9]. In the last case the extended mode

$$M_{\text{ext}}(x) = M(x) \cup M(x^{-1}) \tag{7}$$

has to be considered instead of $M(x)$ [10–12].

Since Ax and $A\sigma x$ represent enantiomeric configurations let us define [6]

$$M(\sigma x) = (A\sigma xA) \cup (Ax\sigma^{-1}A), \tag{8}$$

which generates the configurations enantiomeric to those generated by $M(x)$. Therefore $M(x)$ and $M(\sigma x)$ are called a pair of enantiomeric modes. The set

$$M(x) \cup M(\sigma x) = GxG \tag{9}$$

is called a racemic mode of rearrangements since it generates pairs of enantiomeric configurations.

It could happen that $M(x)$ itself generates pairs of enantiomeric configurations. Hence, $M(\sigma x)$ also does and in this case $M(x) = M(\sigma x)$ are both racemic modes and are equal to GxG.

Using the above definitions, one may unambiguously associate a reaction graph to any mode $M(x)$. The vertices of the graph represent the Ax cosets or configurations. A given initial configuration is transformed into δ_x final ones by $M(x)$. These transformations are represented by δ_x edges starting from the initial vertex. The connectivity [13] δ_x of the mode $M(x)$ is the degree of the (regular) reaction graph. It is easy to show that [14]

$$\delta_x = \frac{|R|}{|x^{-1}Rx \cap R|}, \tag{10}$$

where the Hougen group [15] is given by

$$R = A \cup a\sigma J$$

(J is inversion about the center of mass). The δ_x final vertices are in turn transformed by application of $M(x)$ and so on until no new configurations are generated, after, say f, such steps. Then the set

$$P(x) = \bigcup_{n=1}^{f} [M(x)]^n \tag{11}$$

is a group containing the permutations representing all the configurations reached during these successive steps [16–20]. The number of such configurations is

$$p' = \frac{|P(x)|}{|A|}, \tag{12}$$

where $p' \leqslant p$ since $P(x)$ is a subgroup of S_n (see. eq. (4)).

3. Discussion

In ref. [1], the groups $P(x)$ are defined by the set of permutations generating the group H which is either G or A and by a permutation characteristic of the rearrangement at hand. From the discussion of the preceding section (eqs. (5), (6), (9) and (11)), it is easy to find the generating set of $P(x)$ [21]:

in chiral environment : $P(x) = \langle \{a_i\}, x \rangle$,   (13a)

in achiral environment : $P(x) = \langle \{a_i\}, x, \sigma x \sigma^{-1} \rangle$,   (13b)

and when GxG is used instead of $M(x)$:

$$P(x) = \langle \{g_i\}, x \rangle,$$ (14)

where $\langle \, \rangle$ has the same meaning as in [1] (i.e., the group generated by the enclosed elements) and where $\{a_i\}$ and $\{g_i\}$ are the sets of generators for A and G, respectively.

We now discuss the case of bullvalene along the same lines as in ref. [1]. In fig. 1, the Cope rearrangement is represented. It is easy to see that $x = (1027548) (39)$ is one of the permutations representing the Cope process. The sets of permutations

$$Ax = (1027548) (39), (18) (25) (30) (49) (67), (1926438) (40),$$ (15)

$$A\sigma x = (1948) (267530), (18) (25) (39) (40), (1038) (276549)$$ (16)

are readily obtained by multiplication of the proper operations of the C_{3v} skeleton

$$A = I, (234) (567) (890), (243) (576) (809)$$

and of its improper operations

$$A\sigma = (34) (67) (90), (24) (57) (80), (23) (56) (89)$$

by x. It appears immediately that the permutation $g = (18) (25) (39) (40)$ of ref. [1] appears in $A\sigma x$ and not in Ax (see eqs. (15) and (16)).
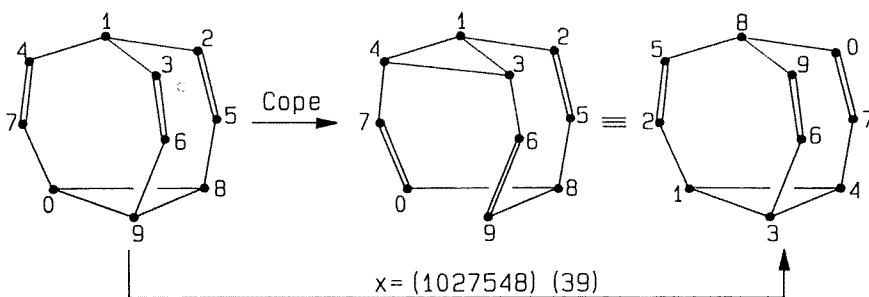

Fig. 1. The Cope rearrangement in bullvalene.

Hence the x obtained in fig. 1 and the g used in ref. [1] belong to enantiomeric configurations. Clearly x represents a Cope rearrangement. Does $g = \sigma x$ also do so? The answer is yes if and only if $M(x) = M(\sigma x)$, i.e. if the Cope mode is racemic (generates pairs of enantiomeric configurations). This is however *not* the case: $M(x)$ contains only odd permutations while $M(\sigma x)$ contains only even ones (see eqs. (5) or (6) and remember that A contains only even permutations). Therefore x and g belong to different modes: they are the representatives of a pair of distinct enantiomeric modes (see eq. (8)). *The permutation g does not represent the rearrangement known as a Cope rearrangement*: its relation with a Cope rearrangement is the same as the relation of umbrella inversion in NH_3 with molecular rotation.

We may now apply eqs. (13) and (14) to the case of bullvalene. We use successively

(a) the permutation x representing the Cope rearrangement (see fig. 1) or, equivalently, the permutation $\tilde{g}$ of ref. [1], which belongs to the same A coset (see eq. (15));

(b) the permutation $\sigma x = g$ of ref. [1] which represents the enantiomer of the Cope rearrangement. The groups $P(x)$ obtained in this way are given in table 1. The columns refer to the use of eqs. (13a), (13b) and (14), respectively. Note that eqs. (13a) and (13b) lead to identical results since $AxA = A\sigma x\sigma^{-1}A$ for both the Cope rearrangement and its enantiomer. Hence chiral situations and achiral ones need not to be treated separately (see eqs. (5) and (6)). The results of table 1 are readily obtained by using the arguments of ref. [1].

It appears that in both chiral and achiral situations, the chemical graph for the Cope rearrangement is connected ($p = p' = 10!/3$; see eqs. (4) and (12)) since the p configurations are reached by successive steps. For the enantiomer of this rearrangement however, half of the p possible configurations are reached ($p' = p/2$). The use of racemic mode GxG deserve special comments (last column in table 1). In this case, no distinction is made between a rearrangement and its enantiomer, i.e. a configuration Ax and its enantiomer $A\sigma x$ are considered as equivalent. The vertices of the chemical graph representing the GxG racemic mode represent no longer "A cosets" but "G cosets", i.e. Gx; its edges represent interconversions of pairs of enantiomeric configurations. In this case, eqs. (4) and (12) are to be replaced by $p = |S_n|/|G|$ and $p' = |P(x)|/|G|$, respectively. Such graphs have been studied in the literature. For instance, it has been shown that the Petersen graph represents the exchange of axial and equatorial ligands in trigonal bipyramids, disregarding differentiation between enantiomers [22–24].

Table 1
The groups $P(x)$.

	Chiral	Achiral	GxG
Cope rearrangement	S_{10} (IIb)	S_{10} (IIb)	S_{10} (I)
Enantiomer of Cope rearrangement	A_{10} (IIa)	A_{10} (IIa)	S_{10} (I)

The symbols I, IIa, IIb in table 1 refer to the models discussed in ref. [1]. From the above discussion, it appears that only model IIb (and not IIa) corresponds to the graph for Cope rearrangement. Model I has been defined with a generator g describing the enantiomer of this rearrangement. However, since $GxG = G\sigma xG$, the graphs generated by x (Cope) or $\sigma x = g$ (enantiomer of Cope) are identical when differentiation between enantiomers is disregarded, as in model I.

4. Conclusion

We conclude with some comments about the existence of two connected components, which is of course an interesting possibility. According to the arguments of the present work, it is ruled out for Cope rearrangement but is effective for its enantiomer. It is a direct consequence of the parity of the permutations. There exists numerous examples of stereochemical changes leading to multiple connected components [25]. For instance, in trigonal bipyramidal skeleta the so-called even modes with generators $x = (ae)\,(ae)$ or (aee) ($a = $ axial, $e = $ equatorial) give rise to two connected components. In this case also, enantiomeric configurations belong to different components [4]. Similar situations have been described for instance in the case of XeF_6 interconversions [26,27] and for interconversions of octacoordinate square antiprisms [21,28]. The existence of multiple connected components is related to

(a) the existence of sets of *residual stereoisomers* such that isomers within a given set are interconverted by the considered rearrangement mode while isomers belonging to different sets are not [3].

(b) the Longuet–Higgins groups i.e. the sets of permutations (and permutations-inversions) of identical nuclei which describe feasible transformations [2]. Examples may be found in refs. [16–21]. For a recent review see ref. [29].

We think that the concept of mode of rearrangements provides an unambiguous way to construct reaction graphs and to enumerate their connected components.

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