

Enumeration of Internal Rotation Reactions and Their Reaction Graphs

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Threefold and twofold internal rotation reactions and their reaction graphs are enumerated using the generalized wreath product method developed by the author in an earlier paper. The correspondence between reaction directed graphs (digraphs) and finite topologies on isomers is established. It is shown that the reaction digraphs can be represented by Borel fields. Atropisomerism in polyphenyl compounds is discussed. Applications to spontaneous generation of optical activity and NMR spectroscopy are considered. Borel fields are enumerated by bumping squares of the upper rows of Young diagrams starting from the Young diagram containing just one row.

Key words: Rotation reactions – Borel fields – Atropisomerism – Optical activity, spontaneous generation of \sim – NMR spectra

1. Introduction

While the topological representation and the enumeration of permutation isomerization reactions of inorganic complexes has been well studied [1–4], the isomerization reactions and the reaction graphs due to internal rotations in organic compounds have not been enumerated. One of the problems was to construct a group that includes the point group operations and the permutations induced by internal rotations. Davidson [5] and Balasubramanian [6] observed that internal rotations in ethane can be described by wreath product groups. Balasubramanian [7] (hereafter referred to as paper I) further extended this to a generalized wreath product group for characterizing internal permutations and for enumerating the stereo and position isomers of polysubstituted organic compounds. Leonard [8, 9] enumerated the isomers of non-rigid cyclohexane molecules. Balaban [10] enumerated the reaction graphs of degenerate rearrangements via 1–2 shifts of carbenium ions derived from

homovalenes. Balaban [11] recently enumerated the graphs of intramolecular rearrangements of tetragonal-pyramidal complexes. Klein and Cowley [12] enumerated the permutational isomers with bidentate ligands and other constraints using the double coset method of Ruch *et al.* [13]. Extensive expositions of the chemical applications of graph theory are available in the review papers of Rouvray [14, 15] and the book of Balaban [16]. We use the combinatorial theorem of Pólya [17] and the readers can find the preliminary concepts related to this theorem elsewhere [18]. The present paper of the author uses the results and the theorems developed in I. Discussions on the cycle index of generalized wreath product groups that appear in I will not be repeated here.

The object of the investigation is to obtain the graphs describing the interrelationship of isomers induced by internal rotations and to develop an efficient abstract representation of internal rotation reactions which is achieved through finite topologies. Further, we outline the theoretical basis of spontaneous generation of optical activity. The methods expounded are used for representing the interconversions of magnetically equivalent protons (or any nuclei) and, therefore, the effect of internal rotation on the NMR spectrum is discussed. The unlabelled Borel fields which correspond to internal rotation reactions are enumerated by generating Young diagrams through a "bump algorithm".

2. Theory of the Enumeration of Isomerization Reactions

The enumeration of configurations under a group action reduces first to obtaining the cycle index of a permutation group and then generating a configuration counting series using the theorem of Pólya. The cycle index of a permutation group is defined as

$$P_G(s_1, s_2, \dots) = \frac{1}{|G|} \sum_{g \in G} s_1^{a_1} s_2^{a_2} \dots$$

where $s_1^{a_1} s_2^{a_2} \dots$ is a representation of a typical permutation g in G having a_1 cycles of length 1, a_2 cycles of length 2 and so on. The number of isomers of a molecule containing b_1 substituents of the type F_1 , b_2 substituents of the type F_2 etc., is given by the coefficient of $\alpha_1^{b_1} \alpha_2^{b_2} \dots$ in the configuration counting series,

$$C = P_G \left(s_k \rightarrow \sum_i \alpha_i^k \right)$$

where α_i is the weight assigned to the substituent F_i ; the symbol $s_k \rightarrow \sum_i \alpha_i^k$ stands for the operation of replacing every cycle of length k with $\sum_i \alpha_i^k$ in P_G .

To enumerate the internal rotation reactions, the configuration counting series for both the rigid and non-rigid molecules are generated. If two isomers of a rigid molecule are transformed into each other by a mechanism which introduces non-rigidity, then they are said to belong to the same class. Thus, isomers of different classes cannot be transformed into each other. The coefficients of $\alpha_1^{b_1} \alpha_2^{b_2} \dots$ in the configuration counting series of rigid and non-rigid molecules give the number of isomers and the number of classes of isomers respectively. We indicate the possible interconversions among isomers by suitable arrows.

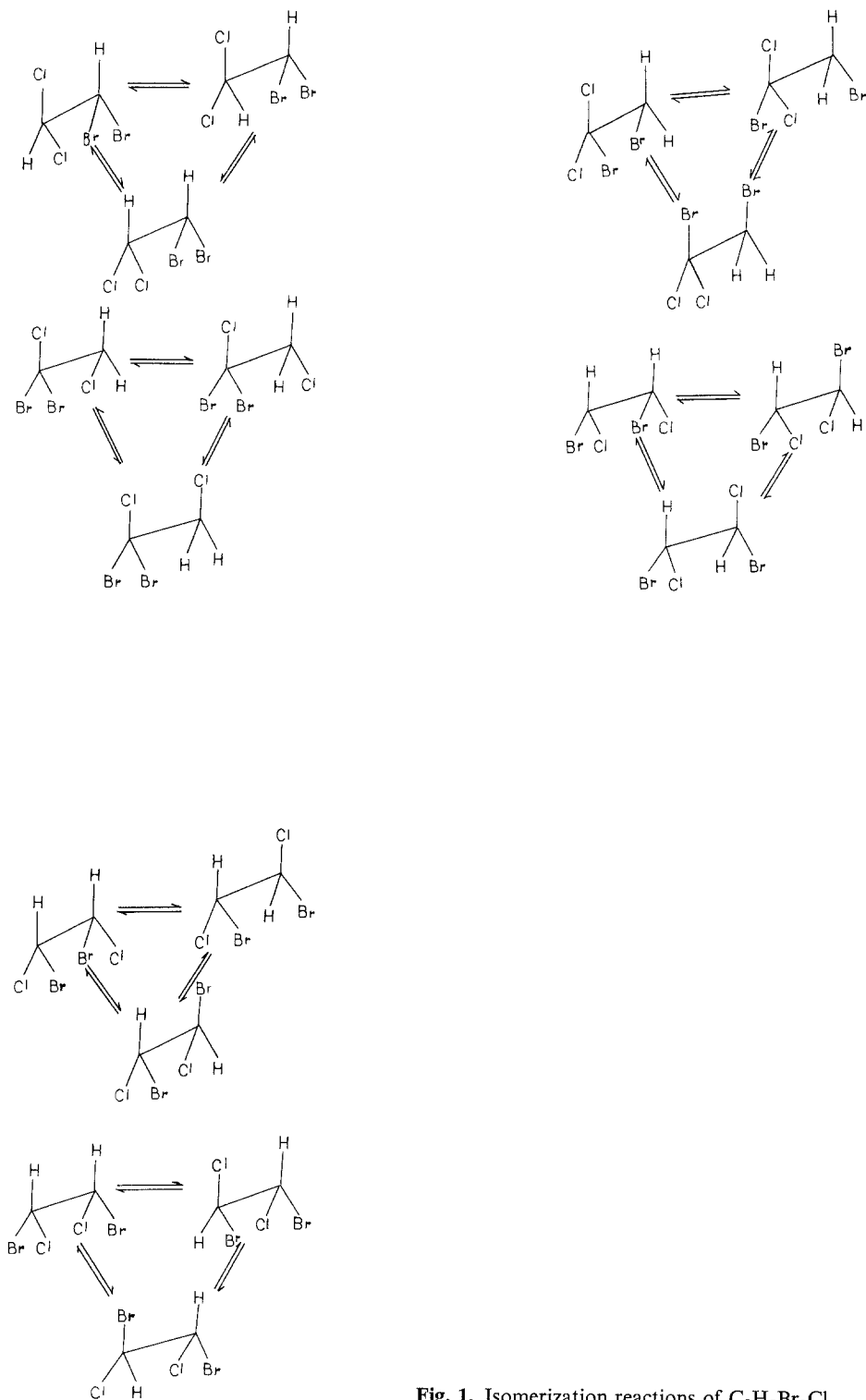


Fig. 1. Isomerization reactions of $C_2H_2Br_2Cl_2$

Example: Substituted ethanes

Consider the non-rigid ethane molecule in the eclipsed conformation. (The staggered conformation, however, does not drastically alter the treatment.) The rotational subgroup of the point group can be seen to be D_3 . The cycle index of D_3 acting on the six unspecified vertices is given by (1).

$$P_G = \frac{1}{6}(s_1^6 + 2s_3^2 + 3s_2^3). \quad (1)$$

If one maps the six vertices into substituents of the type, F_1, F_2, \dots , the following configuration counting series is generated by Pólya's theorem.

$$C = \frac{1}{6}\{(\alpha_1 + \alpha_2 + \dots + \alpha_6)^6 + 2(\alpha_1^3 + \alpha_2^3 + \dots + \alpha_6^3)^2 + 3(\alpha_1^2 + \alpha_2^2 + \dots + \alpha_6^2)^3\} \quad (2)$$

where α_i is the weight assigned to F_i . For example, the number of isomers of the rigid molecule $C_2H_2Br_2Cl_2$ is the coefficient of $\alpha_1^2\alpha_2^2\alpha_3^2$ in (2), which is

$$\frac{1}{6}\left\{\binom{6}{2 \ 2 \ 2} + 3\binom{3}{1 \ 1 \ 1}\right\} = 18.$$

The rotational subgroup of the non-rigid ethane molecule is $C_2[C_3]$ which stands for the wreath product of C_2 with C_3 . The cycle index is obtained by letting $n = 2$

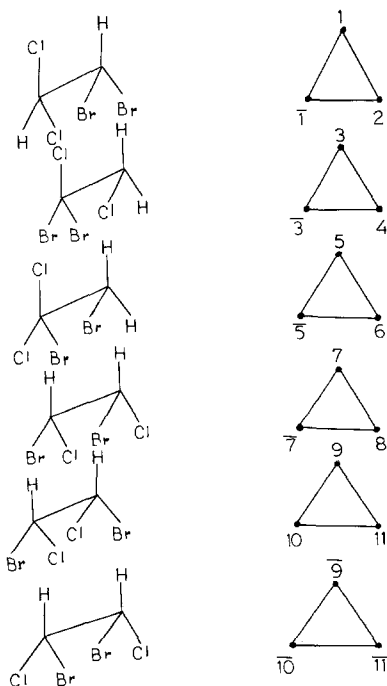


Fig. 2. The components of the reaction graph of $C_2H_2Br_2Cl_2$ and the isomers of the non-rigid molecule $C_2H_2Br_2Cl_2$. The vertices with and without the bar are mirror images of each other

in the general expression already derived in Ref. [7] for linear substituted alkanes. The configuration counting series is given by Eq. (3).

$$C = \frac{1}{18}[(\alpha_1 + \alpha_2 + \cdots + \alpha_6)^6 + 4(\alpha_1 + \alpha_2 + \cdots + \alpha_6)^3 \\ \times (\alpha_1^3 + \alpha_2^3 + \cdots + \alpha_6^3) + 4(\alpha_1^3 + \alpha_2^3 + \cdots + \alpha_6^3)^2 \\ + 3(\alpha_1^2 + \alpha_2^2 + \cdots + \alpha_6^2)^3 + 6(\alpha_1^6 + \alpha_2^6 + \cdots + \alpha_6^6)]. \quad (3)$$

For example, the number of non-rigid isomers of $C_2H_2Br_2Cl_2$ is given by the coefficient of $\alpha_1^2\alpha_2^2\alpha_3^2$ in (3), which is

$$\frac{1}{18}[90 + 18] = 6.$$

The isomers and the isomerization reactions are shown in Fig. 1.

A graph is constructed with the vertices as isomers of the rigid molecule. Two vertices i and j will be connected if there exists an operation in the rotational subgroup of the non-rigid molecule that transforms the isomer i into j . Such a reaction graph for $C_2H_2Br_2Cl_2$ is shown in Fig. 2.

3. Properties of Reaction Graph

We start with certain terminologies. A path in the reaction graph that connects enantiomers is called a *dl*-path. If a non-rigid molecule is optically active, then there is no operation in the rotational sub-group of the non-rigid molecule that can convert it into its enantiomer. Hence, all the rigid isomers of this pair of non-rigid enantiomers will belong to different classes. Consequently, the rigid isomers of a non-rigid *dl*-pair are the vertices of different components of the reaction graph and there will be no *dl*-path in each component. If a non-rigid molecule is optically inactive, and if any of its rigid isomers are optically active, then there will necessarily be a *dl*-path in the component formed by these rigid isomers. The reaction graph will be connected only if the isomer count of the corresponding non-rigid molecule is one. The number of components of the reaction graph is the isomer count of the non-rigid molecule. All the non-trivial components of the reaction graph containing three or more vertices are Hamiltonian. We represented the isomerization reactions by undirected graphs. Actually, since the reactions are directed, their graphs can be undirected only if there is a back reaction for every reaction. If one envisages a directed reaction graph, then the following theorems immediately follow. Theorem 1 justifies the undirected representation. The following theorems are true for all the reaction graphs arising from internal rotations.

Theorem 1. If there is an edge from the vertex i to the vertex j in the graph, then there is also an edge from j to i .

Proof. There is an edge from i to j if there exists a permutation g in the rotational subgroup of the non-rigid molecule that can convert i to j . Since the inverse of every element exists in a group, and since g^{-1} converts j to i , the result follows.

Theorem 2. If there are edges from i to j and j to k in the reaction graph, then there is also an edge from i to k .

Proof. Let g_1 and g_2 be the permutations in the rotational subgroup of the non-rigid molecule that converts i to j and j to k respectively. g_1g_2 is also in the group and it converts i to k . Consequently, the result follows.

A directed graph is said to be transitive if the existence of the edges ij and jk implies the existence of the edge ik . Let S be a set of n elements. Then a finite collection of subsets of S (includes the null set \emptyset and the whole set S) that is closed under union and intersection is called a finite labelled topology on n points. Alternatively, a finite topology contains the union and intersection of any two sets in the collection. Evans *et al.* [19] established the correspondence between a transitive directed graph on n points (hereafter called *trans* digraph) and a finite labelled topology on n points. Thus, in fact, internal rotation reactions can be represented in an abstract form by the finite topology on isomers. Given a *trans* digraph, a finite topology (all topologies under discussion are labelled) is constructed stipulating that i will be in every neighborhood of j (i.e., i will be in every subset of S containing j) if and only if there is an edge from i to j in the *trans* digraph (reaction digraph). Let us illustrate this construction using $C_2H_2Br_2Cl_2$ as an example. (See Fig. 2.) The finite topology that characterizes the internal rotation reactions of $C_2H_2Br_2Cl_2$ is

$$[\emptyset, \{1, \bar{1}, 2\}, \{3, \bar{3}, 4\}, \{5, \bar{5}, 6\}, \{7, \bar{7}, 8\}, \{9, 10, 11\}, \{\bar{9}, \bar{10}, \bar{11}\}]$$

where the square bracket stands for the union-span of the elements inside the square bracket. A union-span of a set is a collection of all possible unions of the elements in the set. There will be 2^6 objects in the union-span of the set shown above for $C_2H_2Br_2Cl_2$, which is a finite topology on the isomers of $C_2H_2Br_2Cl_2$.

A labelled Borel field on n points is a labelled topology such that if i is in the neighborhood of j then j is also in the neighborhood of i . As a consequence of Theorem 1, the finite topologies representing internal rotation reactions are Borel fields. The fact that the topologies on isomers are Borel fields leads to the following theorem.

Theorem 3. The components of the reaction digraph are either trivial or they are complete.

Proof. We shall prove the theorem by induction. If a component is non-trivial and contains two vertices, then by Theorem 1 it is complete. If the component contains three vertices then the existence of any arbitrary edges ij and jk implies the existence of the edge ik , by Theorem 2. Now, by Theorem 1, there are edges ji , kj , and ki in the reaction graph. Hence the component is complete. Let us therefore assume that all components containing m or less vertices are complete. Let C_m be a component containing m vertices. Let us add the vertex $(m + 1)$ to C_m and show that the resulting component C_{m+1} is complete. Since, by definition, a component is connected, there exists at least one edge, $i, m + 1$ connecting a vertex i in C_m and the vertex $(m + 1)$. By induction hypothesis, C_m is complete and, hence, the existence of the edges $1i, 2i, \dots, ji, \dots, mi$ is assured in both C_m and C_{m+1} . ($j \neq i$). As a consequence of Theorem 2, the existence of these edges and the edge $i, m + 1$ will imply the existence of the edges $(1, m + 1), (2, m + 1), \dots, (m, m + 1)$. Thus by Theorem 1, there exist edges $(m + 1, 1) \cdots (m + 1, m)$ in the reaction graph. Hence C_{m+1} is complete.

This property of the completeness of the components of a reaction digraph, enables simplification of the representation of the reaction digraph in terms of topologies.

Introduce a binary operation \oplus on the elements of the Borel field. For any two sets S_1 and S_2 in the Borel field, define

$$S_1 \oplus S_2 = S_1 \cup S_2 - S_1 \cap S_2.$$

where \cup and \cap stand for the union and intersection of two sets. It can be verified that the Borel field is closed under \oplus . Moreover, it forms a group under the operation \oplus . \emptyset , the null set is the identity. Every element is its inverse. It also forms a vector space over the field \mathcal{F} of scalars containing two elements, namely, 0 and 1 with the definition that for any S in the Borel field

$$1 \cdot S = S, \quad 0 \cdot S = \emptyset.$$

Now, one can introduce the concept of linear independence and basis. A set of elements in the Borel field is said to be linearly independent, if and only if

$$\sum_{\oplus} \lambda_i S_i = \emptyset$$

implies all $\lambda_i = 0$; where $\lambda_i \in \mathcal{F}$, S_i 's are the elements of the set whose linear independence is under consideration; \oplus sign below \sum indicates that it is a linear combination with respect to \oplus . The span of a set A , $[A]$, is the set of all linear combinations of the elements of A . A linearly independent set that can span the Borel field is called a basis of the Borel field. The number of elements in the basis is the dimension of the Borel field. To illustrate, consider the molecule $C_2H_2Br_2Cl_2$. The following set forms a basis for the Borel field of $C_2H_2Br_2Cl_2$ (see Fig. 2).

$$B = \{\{1, \bar{1}, 2\}, \{3, \bar{3}, 4\}, \{5, \bar{5}, 6\}, \{7, \bar{7}, 8\}, \{9, 10, 11\}, \{\bar{9}, \bar{10}, \bar{11}\}\}.$$

It is interesting to note that the elements of B are the non-rigid group-equivalence classes of $C_2H_2Br_2Cl_2$, wherein two isomers are equivalent if one is transformable into another by an element of the rotational subgroup of the non-rigid molecule. Thus a basis of the Borel field can be generated by the non-rigid group-equivalence classes. However, note that the non-rigid group-equivalence classes need *not* be the only basis. For example, the set B' shown below is also a basis for the reaction graph of $C_2H_2Br_2Cl_2$.

$$B' = \{\{1, \bar{1}, 2\}, \{1, \bar{1}, 2, 3, \bar{3}, 4\}, \{\bar{5}, 5, 6, 7, \bar{7}, 8\}, \{7, \bar{7}, 8\}, \{9, 10, 11, \bar{9}, \bar{10}, \bar{11}\}, \{\bar{9}, \bar{10}, \bar{11}\}\}.$$

Nevertheless, one can always construct B from B' or vice versa using the binary operation \oplus . For any given basis B , there will be an edge from i to j in the reaction graph if i is in every set containing j in the basis.

4. General Cases

Consider, now, in general a molecule containing any number of carbon atoms. The permutation group of such a non-rigid molecule is the generalized wreath product.

Expressions for isomers have already been derived in Ref. [7]. In this paper we shall only state the results that we need. The number of isomers of linear $C_nH_{2n+2-k}X_k$ is given by (4) if k is odd and by (5) if k is even. We indicate them by I_{k^-} and I_{k^+} respectively.

$$I_{k^-} = \frac{1}{18} \left\{ \binom{2n+2}{k} + 4 \binom{2n-1}{k} + 4 \binom{2n-1}{k-3} + 4 \binom{2n-4}{k} + 8 \binom{2n-4}{k-3} + 4 \binom{2n-4}{k-6} \right\} \quad (4)$$

$$I_{k^+} = \frac{1}{18} \left\{ 18I_{k^-} + 3 \binom{n+1}{k/2} + 6 \binom{n-2}{k/2} + 6 \binom{n-2}{(k-6)/2} \right\} \quad (5)$$

where I_{k^-} in (5) is given by (4). The rotational subgroup of the corresponding rigid molecule is C_2 . The cycle index is given by (6) for both the parities of n .

$$P_G = \frac{1}{2}(x_1^{2n+2} + x_2^{n+1}) \quad (6)$$

It can be seen from the counting series generated from (6) that the number of isomers of rigid linear $C_nH_{2n+2-k}X_k$ is given by (7) if k is odd and by (8) if k is even.

$$I'_{k^-} = \frac{1}{2} \binom{2n+2}{k} \quad (7)$$

$$I'_{k^+} = \frac{1}{2} \left\{ \binom{2n+2}{k} + \binom{n+1}{k/2} \right\} \quad (8)$$

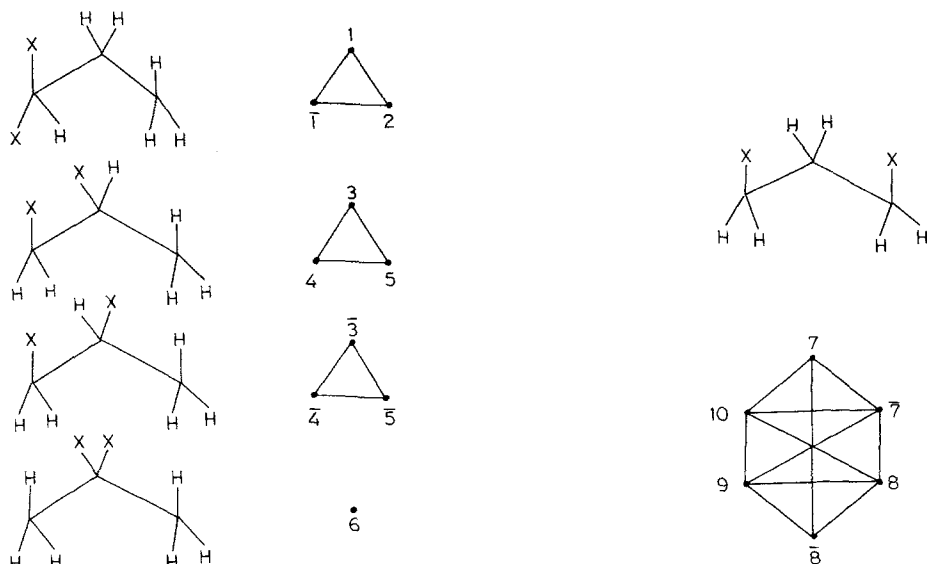


Fig. 3. The components of the reaction graph and the isomers of the non-rigid molecule $C_3H_6X_2$

The isomers obtained from (7) or (8) are partitioned into equivalence classes, applying the criterion of (non-rigid) group-equivalence introduced before. The number of classes or the dimension of the Borel field is given by (4) or (5). Internal rotation reactions can be enumerated using the elements of the Borel field. For example, for $C_3H_6X_2$, the isomer counts of rigid and non-rigid structures are 16 and 5 respectively. A basis of the Borel field can be easily constructed by generating the (non-rigid) group-equivalence classes. Suppose the rigid isomers are numbered such that the enantiomer pairs bear the numbers i and \bar{i} , then the following set is a basis of the Borel field of $C_3H_6X_2$.

$$B = \{\{1, \bar{1}, 2\}, \{3, 4, 5\}, \{\bar{3}, \bar{4}, \bar{5}\}, \{6\}, \{7, \bar{7}, 8, \bar{8}, 9, 10\}\}.$$

The reaction graph for $C_3H_6X_2$, which can be easily constructed using the one-to-one correspondence, between a finite topology and a transitive digraph, is shown in Fig. 3.

5. Atropisomerism in Polyphenyl Compounds

In this section we use the Sheehan's [20] generalization of Pólya's theorem. First, the Sheehan's procedure is briefly outlined.

Let Y_1, Y_2, \dots, Y_l be a partition of a set D into l subsets. Let R_1, R_2, \dots, R_l be a partition of the set R . Consider the set \mathcal{F} of all functions from D to R with the restriction

$$\mathcal{F}(Y_i) \subseteq R_i, \quad i = 1, 2, \dots, l.$$

Let G be a permutation group acting on D such that all its orbits are contained in the same Y -set. Two functions f_1 and f_2 from D to R are G -equivalent if there exists a $g \in G$ such that

$$f_1(y_{ij}) = f_2(gy_{ij})$$

where $y_{ij} \in Y_i, j = 1, 2, \dots, |D_i|, i = 1, 2, \dots, l$.

Since all the orbits of $g \in G$ are contained in the same Y -set, the cycle index of G is of the form

$$P_G = \frac{1}{|G|} \sum_{g \in G} \prod_i \prod_j S_{ij}^{C_{ij}(g)}$$

where $C_{ij}(g)$ denotes the number of j -cycles of g contained in the set Y_i ; S_{ij} is a representation of a j -cycle in the set Y_i . Let α_{ji} be the weight assigned to an element $y_{ji} \in R_i$. In this set-up we have the Theorem 4.

Theorem 4 (Sheehan). The generalized configuration counting series is obtained with the following substitution in P_G .

$$P_G(S_{ij} \rightarrow \sum_k \alpha_{kit}^k)$$

where $k = 1, 2, \dots, |R_i|$.

Now consider a string of n phenyl rings in one plane. Insert $(n - 1)$ phenyl rings in the "gaps" in between two successive rings, in a plane perpendicular to both of them. Thus, in the resulting polyphenyl of $2n - 1$ rings, the rings are alternately in planes perpendicular to each other. We map *only the vertices of a phenyl ring that face the adjacent rings into substituents*. It can be seen that the number of such vertices is $4(n - 1) + 4(n - 2) + 4$. The rigid arrangement of such rings has D_2 rotational symmetry. The rings 1 and $2n - 1$, 2 and $2n - 2$ etc. transform into each other under certain operations of D_2 . Hence, it is appropriate to partition the set of rings into sets Y_1, Y_2, \dots , each consisting of two rings except when n is odd. If n is odd, the central ring is itself a set. Let S_{ij} denote a j cycle generated in the set Y_i by an element in the group. Then it can be seen that the cycle index of such a rigid linear polyphenyl system is given by (9).

$$P_G = \frac{1}{4} \left\{ S_{11}^4 \left(\prod_{i=2}^{n-1} S_{i1}^8 \right) S_{n1}^4 + 3 S_{12}^2 \left(\prod_{i=2}^{n-1} S_{i2}^4 \right) S_{n2}^2 \right\}. \quad (9)$$

The configuration counting series is obtained using Theorem 4 and it is given by (10). In (10), α_{ij} denotes the weight assigned to a functional group F_i , attached to an element in the set Y_j .

$$C = \frac{1}{4} \left[\left(\sum_{j=1}^4 \alpha_{j1} \right)^4 \left\{ \prod_{i=2}^{n-1} \left(\sum_{j=1}^8 \alpha_{ji} \right)^8 \right\} \left(\sum_{j=1}^4 \alpha_{jn} \right)^4 + 3 \left(\sum_{j=1}^4 \alpha_{j1}^2 \right)^2 \left\{ \prod_{i=2}^{n-1} \left(\sum_{j=1}^8 \alpha_{ji}^2 \right)^4 \right\} \left(\sum_{j=1}^4 \alpha_{jn}^2 \right)^2 \right]. \quad (10)$$

For example, the number of atropisomers of the triphenyl $C_6H_4X \cdot C_6a_2b_2 \cdot C_6H_4X$, is the coefficient of $\alpha_{11}^2 \alpha_{12}^2 \alpha_{21}^2 \alpha_{22}^2$ in (10), with $n = 2$, which is

$$\frac{1}{4} \left\{ \binom{4}{2 \ 2} \binom{4}{2 \ 2} + 3 \binom{2}{1 \ 1} \binom{2}{1 \ 1} \right\} = 12.$$

The cycle index of non-rigid polyphenyls can be obtained using Theorem 1 of I. Davidson [5] also derived the cycle index of the corresponding non-rigid polyphenyls using the wreath product groups. For the triphenyl under consideration, the cycle index can be seen to be (11).

$$P_G = \frac{1}{16} [(S_{11}^4 + 2S_{11}^2 S_{12} + S_{12}^2)(S_{21}^4 + S_{22}^2) + 4S_{22}^2(S_{12}^2 + S_{14})]. \quad (11)$$

The corresponding counting series is given by (12)

$$C = \frac{1}{16} \left\{ \left[\left(\sum_{j=1}^4 \alpha_{j1} \right)^4 + 2 \left(\sum_{j=1}^4 \alpha_{j1} \right)^2 \left(\sum_{j=1}^4 \alpha_{j1}^2 \right) + \left(\sum_{j=1}^4 \alpha_{j1}^2 \right)^2 \right] \times \left[\left(\sum_{j=1}^4 \alpha_{j2} \right)^4 + \left(\sum_{j=1}^4 \alpha_{j2}^2 \right)^2 \right] + 4 \left(\sum_{j=1}^4 \alpha_{j2}^2 \right)^2 \left[\left(\sum_{j=1}^4 \alpha_{j1}^2 \right)^2 + \left(\sum_{j=1}^4 \alpha_{j1}^4 \right) \right] \right\}. \quad (12)$$

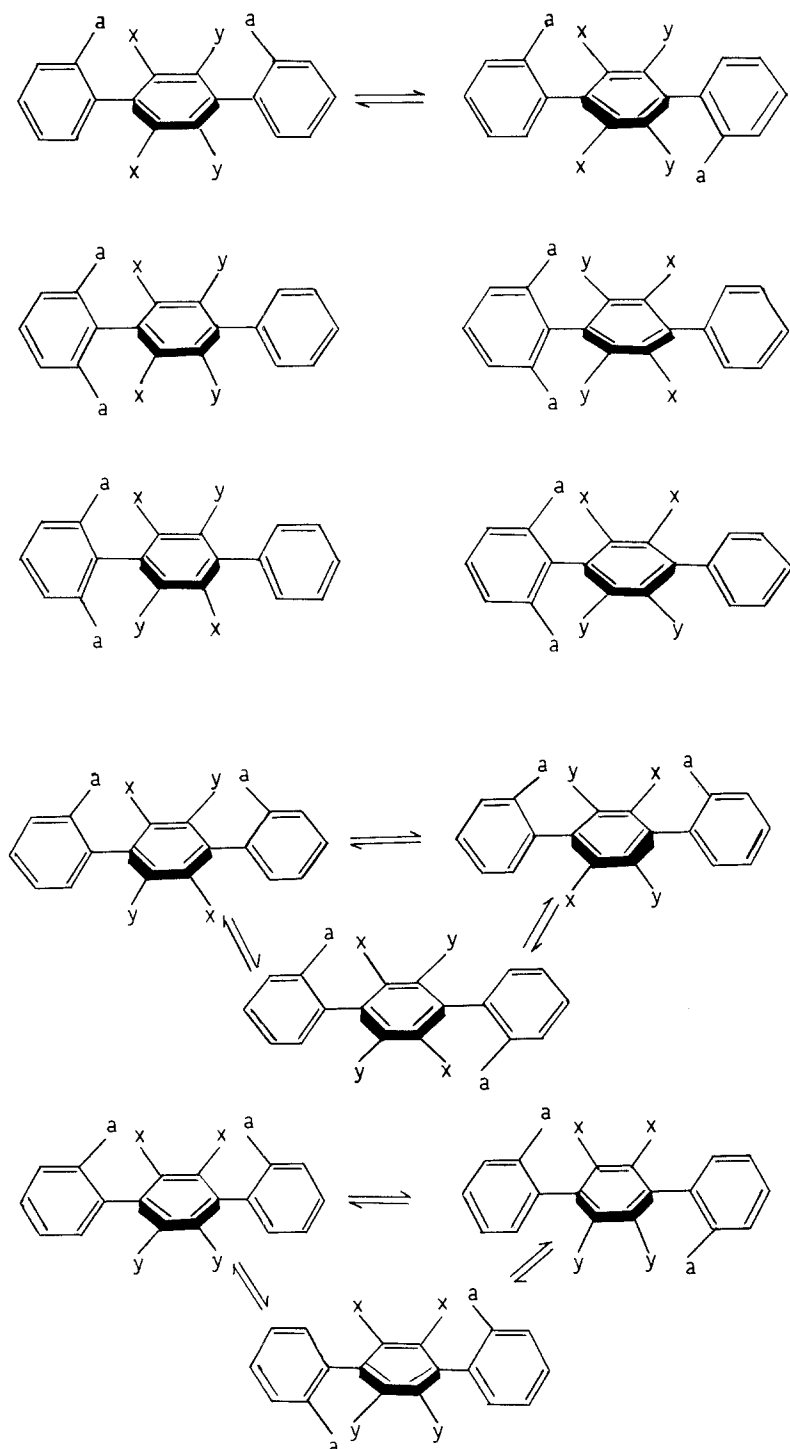


Fig. 4. Isomerization reactions due to twofold rotations in a triphenyl

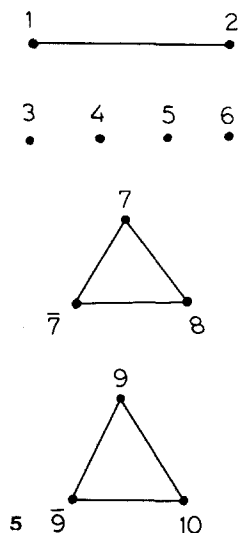


Fig. 5. The reaction graph of the isomerization reaction shown in Fig. 4

The coefficient of $\alpha_{11}^2 \alpha_{12}^2 \alpha_{21}^2 \alpha_{22}^2$ in (12), which gives the number of isomers of non-rigid $C_6H_5X \cdot C_6a_2b_2 \cdot C_6H_5X$, is

$$\frac{1}{16} \left[\left\{ \binom{4}{2 \ 2} + 2 + 2 + \binom{2}{1 \ 1} \right\} \left\{ \binom{4}{2 \ 2} + \binom{2}{1 \ 1} \right\} + 4 \binom{2}{1 \ 1} \binom{2}{1 \ 1} \right] = 7.$$

The rotation reactions are shown in Fig. 4 and the reaction graph is shown in Fig. 5.

6. Spontaneous Generation of Optical Activity

Spontaneous generation of optical activity is a topic of current interest [21]. In this section we present a graph theoretical method of identifying the number of phases into which a compound solidifies, and the number of phases that will be optically active. Since enantiomers have identical thermodynamic potentials, the equality of potentials of two chiral phases is always satisfied. This introduces an additional degree of freedom, and thus the thermodynamic stability of two enantiomorphic phases is explained. Consequently, an achiral molecule may solidify into distinct chiral (enantiomorphic) yet stable phases. The phenomenon is referred to as the spontaneous generation of optical activity, [21]. If there is a *dl*-path in the reaction digraph, then, when the corresponding molecule solidifies it will resolve into enantiomorphic phases and thus lead to spontaneous optical resolution. One can predict from the reaction graph whether an achiral molecule, when it solidifies, will lead to spontaneous optical resolution or not. The number of optically active phases in the solid state can be obtained from the reaction graph. In the Borel field representation the necessary and sufficient condition for spontaneous optical resolution of a *dl*-pair is the presence of both the enantiomers in any set of a basis that contains one of them. For example, the achiral molecule $CH_2X \cdot CH_2 \cdot CH_2X$

(see Fig. 3) will solidify into six phases four of them optically active, wherein there are two classes of chiral phases.

7. Application to NMR Spectroscopy

Balasubramanian [7] has already shown that the coefficient of $\alpha_1^M - 1\alpha_2$ in the configuration counting series gives the number of NMR signals of a compound containing M protons. Here we compare the results of both the rigid and non-rigid molecules and represent the possible interconversions among the protons by a basis of the Borel field. Consider the molecule $\text{CH}_3\text{CHClCH}_2\text{Cl}$. Starting from the methyl protons, number the protons. The NMR inventory [7] of the non-rigid molecule $\text{CH}_3\text{CHClCH}_2\text{Cl}$ is given by (13).

$$C = \frac{1}{3}[(\alpha_1 + \alpha_2)^6 + 2(\alpha_1^3 + \alpha_2^3)(\alpha_1 + \alpha_2)^3]. \quad (13)$$

Consequently, the number of NMR signals is given by the coefficient of $\alpha_1^5\alpha_2$ in (13), which is

$$\frac{1}{3} \left[\binom{6}{5 \ 1} + 2 \binom{3}{2 \ 1} \right] = 4.$$

The six protons are partitioned into the classes $\{1, 2, 3\}$, $\{4\}$, $\{5\}$, $\{6\}$.

When the molecule is rigid, the point group of the root-to-root product [7] is the group containing only the identity. The configuration counting series is given by (14).

$$C = (\alpha_1 + \alpha_2)^6. \quad (14)$$

As a result, the number of NMR signals at low temperature, when the molecule is essentially rigid, is

$$\binom{6}{5 \ 1} = 6.$$

Now, every proton is itself a class. The possible interconversions among the protons are indicated by their reaction graph in Fig. 6. A basis of the Borel field of the reaction graph is

$$B = \{\{1, 2, 3\}, \{4\}, \{5\}, \{6\}\}.$$

Note that the set $B' = \{\{1, 2, 3, 4\}, \{1, 2, 3\}, \{5, 6\}, \{6\}\}$ is also a basis, for the same reaction graph. This clearly shows that the methylene protons 5 and 6 can never be interconverted by internal rotation, since in any basis 6(5) occurs in a set where 5(6)

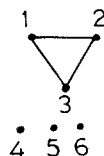


Fig. 6. The NMR reaction graph of the molecule $\text{CH}_3\cdot\text{CHCl}\cdot\text{CH}_2\text{Cl}$. The vertices are the protons. The labels 1, 2, 3 correspond to the methyl protons; number 4 corresponds to the proton in CHCl group and 5 and 6 are the methylene protons

is not present. Although this is a well-known result, we have here a general approach for any molecule. Thus, the effect of non-rigidity is to coalesce the three NMR signals due to methyl protons into a single signal. This will explain the classical and well-known result that the NMR spectrum of the molecule PCl_5 contains only one signal. Even though, the point group of the rigid PCl_5 molecule is D_{3h} , the group of the non-rigid molecule, the non-rigidity introduced through the Berry mechanism, is S_5 . (S_5 stands for the symmetric group, containing 5! elements.) The coefficients of $\alpha_1^4\alpha_2$ in the NMR inventories [15] and [16] of rigid and non-rigid molecules can be seen to be 2 and 1 respectively, explaining one NMR signal contrary to two signals.

$$\frac{1}{12}[(\alpha_1 + \alpha_2)^5 + 2(\alpha_1 + \alpha_2)^2(\alpha_1^3 + \alpha_2^3) + 3(\alpha_1 + \alpha_2)(\alpha_1^2 + \alpha_2^2)^2 + (\alpha_1 + \alpha_2)^3(\alpha_1^2 + \alpha_2^2) + 2(\alpha_1^2 + \alpha_2^2)(\alpha_1^3 + \alpha_2^3) + 3(\alpha_1 + \alpha_2)^3(\alpha_1^2 + \alpha_2^2)], \quad (15)$$

$$\frac{1}{120}[(\alpha_1 + \alpha_2)^5 + 10(\alpha_1 + \alpha_2)^3(\alpha_1^2 + \alpha_2^2) + 20(\alpha_1 + \alpha_2)^2(\alpha_1^3 + \alpha_2^3) + 30(\alpha_1 + \alpha_2)(\alpha_1^4 + \alpha_2^4) + 15(\alpha_1 + \alpha_2)(\alpha_1^2 + \alpha_2^2)^2 + 20(\alpha_1^2 + \alpha_2^2)(\alpha_1^3 + \alpha_2^3) + 24(\alpha_1^5 + \alpha_2^5)]. \quad (16)$$

A non-trivial example exemplifying the effect of internal rotation on the NMR spectrum is propane. The symmetry groups of rigid and non-rigid molecules are C_{2v} and $C_{2v}[C_3, E]$ respectively. The NMR inventories of the rigid and non-rigid propane are given by (17) and (18) respectively.

$$\frac{1}{4}[(\alpha_1 + \alpha_2)^8 + 2(\alpha_1 + \alpha_2)^2(\alpha_1^2 + \alpha_2^2)^3 + (\alpha_1^2 + \alpha_2^2)^4], \quad (17)$$

$$\frac{1}{36}[(\alpha_1 + \alpha_2)^8 + 4(\alpha_1 + \alpha_2)^5(\alpha_1^3 + \alpha_2^3) + 4(\alpha_1 + \alpha_2)^2(\alpha_1^3 + \alpha_2^3)^2 + 3(\alpha_1^2 + \alpha_2^2)^4 + 6(\alpha_1^2 + \alpha_2^2)(\alpha_1^6 + \alpha_2^6) + 12(\alpha_1 + \alpha_2)^2(\alpha_1^2 + \alpha_2^2)^3 + 6(\alpha_1 + \alpha_2)^2(\alpha_1^6 + \alpha_2^6)]. \quad (18)$$

The coefficients of $\alpha_1^7\alpha_2$ in (17) and (18) are (19) and (20) respectively.

$$\frac{1}{4}\left[\binom{8}{7 \ 1} + 2\binom{2}{1 \ 1}\right] = 3 \quad (19)$$

$$\frac{1}{36}\left[\binom{8}{7 \ 1} + 4\binom{5}{4 \ 1} + 4\binom{2}{1 \ 1} + 12\binom{2}{1 \ 1} + 6\binom{2}{1 \ 1}\right] = 2. \quad (20)$$

If one labels the two sets of methyl protons {1, 2, 3} and {6, 7, 8} and if the methylene protons are labelled 4 and 5 the eight protons are partitioned into the following 3 classes at very low temperatures with the convention that a σ_v plane of the C_{2v} group passes through the protons 1 and 6.

$$\{1, 6\}, \{4, 5\}, \{2, 3, 7, 8\}.$$

Thus, at low temperature this method predicts 3 NMR signals, 2 due to 2 classes of methyl protons and one attributed to methylene proton with the intensity ratio 1:2:1. However, at high temperature the eight protons are partitioned into just 2 classes shown below.

$$\{1, 2, 3, 6, 7, 8\}, \{4, 5\}.$$

Consequently, at high temperature one observes only 2 signals with the intensity ratio 3:1 and the effect of internal rotation is to coalesce the 2 NMR signals (1:2) due to methyl protons into 1 signal.

8. Enumeration of Unlabelled Borel Fields and a Dissection of the Numbers P_n^m

The one-to-one correspondence established between Borel fields and reaction digraphs yields a concrete procedure for enumerating the possible types of internal rotation reactions, since unlabelled Borel fields on n points can be enumerated. Krishnamurthy [22] showed that the labelled Borel fields on n points can be enumerated by a dissection of the Stirling numbers of the second kind. He introduced the combinatorial numbers $\lambda(n:r:p)$, the number of labelled Borel fields on n points containing p components and r 2-cycles. The enumeration of unlabelled Borel fields which is of interest to us can be done in an analogous manner. Since each component of a Borel field is trivial or complete, the number of unlabelled Borel fields on n points containing p components corresponds to the number of ways of distributing n indistinguishable objects into p indistinguishable cells. This can be done in P_n^p ways, where P_n^p denotes the number of unordered partitions of the integer n into p parts. A generating function for P_n^p can be readily obtained [23]. It is

$$F(x) = x^p(1 - x)^{-1}(1 - x^2)^{-1} \dots (1 - x^p)^{-1}. \tag{21}$$

The coefficient of x^n in (21) gives P_n^p .

With every unordered partition of an integer n we can associate a Ferrer's diagram also known as Young's diagram in the literature of physics and chemistry. The number of squares in each row decreases as we descend from top to bottom. The number of squares in any column decreases as we move from left to right. For example, the Ferrer's diagram which corresponds to the partition $4 + 3 + 1$ is shown in Fig. 7. To a partition of an integer n into m parts we can assign a Ferrer's diagram containing m rows. Given a Ferrer's diagram corresponding to a partition of n into m parts, an unlabelled Borel field is determined as follows. Let the number of squares in the i th row of Ferrer's diagram be n_i . Then a Borel field is constructed on n vertices containing m components. The i th component contains n_i vertices and the number of edges in this component is $2\binom{n_i}{2}$. Thus the Borel field (unlabelled) is uniquely determined. To illustrate, the Borel field which corresponds to Ferrer's diagram in Fig. 7 is shown in Fig. 8. Hence unlabelled Borel fields can be enumerated if we can enumerate all Ferrer's diagrams corresponding to the partition of a given integer n . The number of partitions can be found easily using generating functions. We formulate here an algorithm which we shall call the "bump algorithm" for generating the unlabelled Borel fields on n points. The motivation for

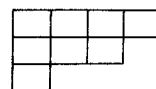


Fig. 7. The Ferrer's diagram which corresponds to the partition $4 + 3 + 1$

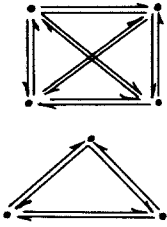


Fig. 8. The Borel field which corresponds to the Ferrer's diagram shown in Fig. 7

this algorithm takes its origin from the algorithm "Insert" used by Krishnamurthy [24], wherein certain entries of the Young Tableau are "bumped" to enumerate finite topologies.

Start with the partition of the integer n into one part whose Ferrer's diagram contains just one row with n squares. Then a square at the extreme right in an upper row containing more than one square is pushed down (bumped) and either a new row is created or the length of a lower row is increased. The bumping process should be executed in such a way that the properties of the Ferrer's diagram (outlined above) are preserved. This process is continued until one reaches Ferrer's diagram which corresponds to the partition of the integer n into n parts. The

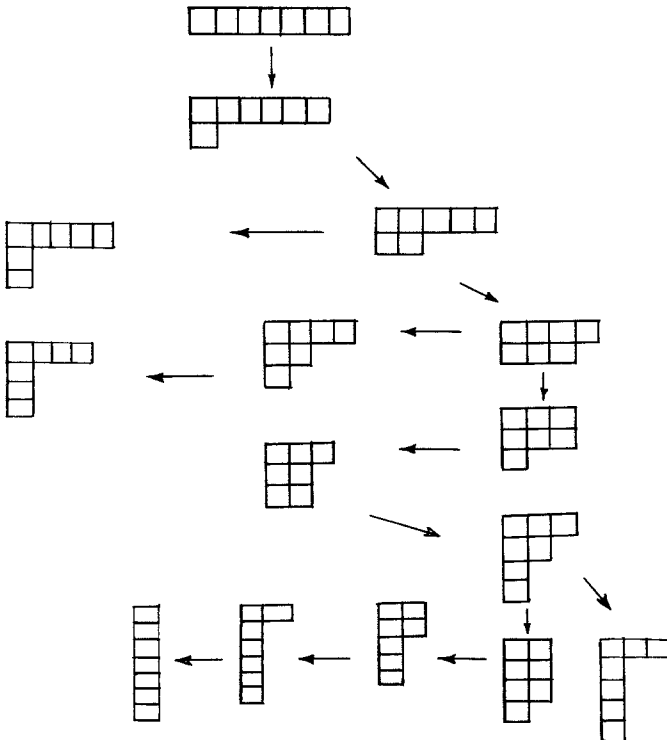


Fig. 9. The spanning tree of Young diagrams containing 7 squares generated by bump algorithm

algorithm can be most efficiently executed by growing a spanning tree. This can be effected stipulating that

- 1) a square is always bumped from an upper to a lower row and never in the reverse direction;
- 2) a square is bumped from an upper row to the first lower row that can accommodate the square;
- 3) the tree will not be grown from a diagram which has more than two squares in the first row and a square in all lower rows; such vertices can be called leaves;
- 4) bumping from lower rows are continued, keeping the length of the first row constant until one reaches a leaf.

The algorithm is illustrated by finding all the Ferrer's diagrams which correspond to the partitions of the integer 7 in Fig. 9.

This enumeration of unlabelled Borel fields provides the possible types of isomerization reactions arising from internal rotations. Alternatively, any inter-relationship among isomers can be described by one of the Borel fields. Further, this enumeration gives insight into the possible NMR spectra of non-rigid molecules containing a set of n nuclei possessing magnetic moment. For example, Table 1 shows non-rigid molecules containing four protons and their NMR spectra as obtained from their Borel fields.

Table 1. Non-rigid molecules containing four protons, their Borel fields and NMR spectra

S-No.	Non-rigid molecule	Ferrer's diagram	Borel field	NMR Spectrum	
				Number of peaks	Intensity ratio
1.	Hydrazine $\text{CH}_2\text{Cl} \cdot \text{CH}_2\text{Cl}$			1	—
2.	$\text{CH}_3 \cdot \text{CHCl}_2$			2	3:1
3.	$\text{CHCl}_2\text{CH}_2\text{CHCl}_2$			2	2:2
4.	$\text{CHCl}_2 \cdot \text{CH}_2 \cdot \text{CHBr}_2$			3	2:1:1
5.	$\text{CH}_2\text{Cl} \cdot \text{CHCl} \cdot \text{CHCl}_2$			4	1:1:1:1

9. Conclusion

In this paper we enumerated the reaction graphs of non-rigid molecules. There are interesting cases where the problem is not straightforward. For example, the enumeration of stable stereo and position isomers of polysubstituted alcohols involves the principle of inclusion and exclusion under a group action on the set of properties [25]. Thus, the corresponding reaction digraphs and the Borel fields should be enumerated by incorporating the principle of inclusion and exclusion.

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