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IN DYNAMIC NMR SPECTROSCOPY

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## Topological and group theoretical analysis in dynamic NMR spectroscopy

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Abstract

A method is developed for constructing NMR reaction graphs which give the NMR signal and intensity ratio patterns. This is done by generating the irreducible representations spanned by nuclei (whose NMR are of interest) with generating functions obtained from group cycle indices (GCCIs). The method generates the symmetry species spanned by the nuclei both in the rigid and non-rigid groups without having to know the Character of the representation spanned by nuclei. For non-rigid molecules which exhibit internal rotations the GCCIs can be obtained without having to know their character tables. We outline a double coset technique to obtain the equivalence classes of nuclei and thus to construct NMR reaction graphs. Using this technique one can obtain the NMR signal and intensity ratio patterns. We introduce the concept of restricted character cycle indices (RCCIs) which generate the irreducible representations spanned by a given equivalence class of nuclei. This in turn enables the prediction of coalescence, splitting patterns and intensity ratios of NMR signals in dynamic processes. Applications to spontaneous generation of chiral signals are outlined, where a non-rigid molecule which possesses no chiral signals suddenly possess chiral signals (which can be resolved with chiral shift reagents) at lower temperatures.

## 1. Introduction

Topological and group theoretical analysis of dynamical systems such as molecules exhibiting large amplitude non-rigid motions is of considerable interest in recent years.<sup>1-13</sup> Several of these topological schemes describe essentially interrelationship among a set of isomers which get interconverted in to one another by non-rigid motions. They provide insight not only into pathways and mechanisms which interconvert such isomers but also several important experimental applications such as spontaneous generation of optical activity. Even though the area of isomerization reactions and reaction graphs obtained thus seem to be quite well studied this is not the case in the area of dynamic NMR spectroscopy. Dynamic NMR is potentially useful in understanding large amplitude non-rigid motions and interconversions that take place in molecules as a function of temperature at experimentally feasible conditions.

Experimentally one observes coalescence and splitting of certain signals which is a consequence of some dynamic exchanges that are so rapid that at high temperatures one sees only an average effect. (Coalescence of signals). The recent advent of dynamic NMR spectrometers, however, has enabled resolution of these coalesced signals at experimentally feasible conditions by appropriately adjusting the shutter speeds. While rapid experimental progress has been accomplished in this field, theoretical understanding and representations of these dynamic phenomena seems to be in progress. We undertake the present investigation with the intent of understanding dynamic NMR coalescence and intensity patterns with/<sup>a</sup>topological scheme. We develop generating function techniques which provide for not only the number of NMR signals (by way of generating the number of totally symmetric representations spanned by nuclei) but also all irreducible representations spanned by the nuclei present in the molecule whose NMR is of interest. Using the method of subdued repre-

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sentations one can correlate the symmetry species spanned by the nuclei from a larger group to its subgroup which enables the prediction of the splitting patterns of NMR signals. We also develop double coset methods which provide the intensity patterns of both coalesced and split signals in dynamic NMR spectroscopy. The methods developed here should be applicable to not only dynamic systems but also systems which exhibit distortions such as Jahn-Teller distortions. We also apply the techniques developed here to an interesting problem namely spontaneous generation of chiral NMR signals in dynamic processes. In section 2 we outline theoretical methods, Section 3 discusses double coset methods for intensity patterns, in Section 4 we obtain generators for symmetry species in the equivalence classes of nuclei using the concept of RCCI's, Section 5 outlines an application of the techniques developed here to the phenomenon of spontaneous generation of chiral signals and in the last section we give an example.

## 2. Theoretical Methods

### A. Preliminaries and Definitions

Let  $G$  be the rotational subgroup or the full point group of the molecule. Note that we will let  $G$  be the rotational subgroup if NMR can differentiate chiral nuclei by appropriate chiral shift reagents. Otherwise  $G$  is the point group. Let  $D$  be the set of nuclei whose magnetic resonance is under consideration. Let  $|D|$  denote the number of elements in  $D$ . Let  $R$  be a set containing just 2 labels which we denote by  $\alpha_1$  and  $\alpha_2$ . Consider a map  $f_1$  from  $D$  to  $R$  defined as follows.

$$f_i(d_j) = \begin{cases} \alpha_1 & \text{if } i \neq j, \\ \alpha_2 & \text{if } i = j. \end{cases} \quad (2.1)$$

$d_j \in D, j = 1, 2, \dots, |D|.$

To illustrate we could consider the five  $^{19}\text{F}$  nuclei as the D set. Then, for example the map  $f_1$  is shown below where we represent  $d_j$  by  $j$ .

$$\begin{aligned} f_1(1) &= \alpha_2 \\ f_1(2) &= \alpha_1 \\ f_1(3) &= \alpha_1 \\ f_1(4) &= \alpha_1 \\ f_1(5) &= \alpha_1 \end{aligned} \quad (2.2)$$

Two maps  $f_i$  and  $f_j$  are said to be equivalent if there exists a  $g$  in  $G$  such that

$$f_i(d) = f_j(gd) \text{ for every } d \in D. \quad (2.3)$$

For example, if one considers the rotational group  $D_3$  of the rigid  $\text{PF}_5$  molecule and if 1, 2 and 3 are equatorial and 4 and 5 are axial nuclei then the maps  $f_1$  and  $f_2$  are equivalent since they are transformable into one another by 3-fold rotation. It can be seen that if two maps  $f_i$  and  $f_j$  are equivalent then the nuclei  $i$  and  $j$  are also magnetically equivalent. Thus the group  $G$  divides  $D$  into equivalence classes, the number of equivalence classes gives the number of NMR signals and the ratio of the number of elements in various classes give the intensity ratios of these signals.

## B. Generating function techniques

The problem is to develop a general method which will give the number of equivalence classes and the ratios of the number of elements in various equivalence classes. The present author developed a method for the former problem using cycle indices and Pólya's theorem.<sup>1,14</sup> In this paper we consider more general techniques for studying coalescence and intensity patterns in dynamic NMR. With each element  $r \in R$  let us associate a weight  $w(r)$  which is just a formal symbol used to book keep the number of  $\alpha_1$ 's and  $\alpha_2$ 's in any function  $f_1$ . For example, we may associate a weight  $\alpha_1$  with  $\alpha_1$  and a weight  $\alpha_2$  with  $\alpha_2$ . Define the weight of any map  $f_1$  to be

$$W(f_1) = \prod_{d_j \in D} w(f_1(d_j)) \quad (2.4)$$

It can be easily seen that

$$W(f_1) = \alpha_1^{n-1} \alpha_2 \quad (2.5)$$

where  $n$  is the number of nuclei. Define the generalized character cycle index (GCCCI) of a group  $G$  corresponding to the irreducible representation  $\Gamma$  whose character is  $\chi$  as

$$P_G^\chi = \frac{1}{|G|} \sum_{g \in G} \chi(g) x_1^{b_1} x_2^{b_2} \dots \quad (2.6)$$

where a  $g \in G$  has  $b_1$  cycles of length 1,  $b_2$  cycles of length 2 etc. Equivalently the cycle type of  $g$  is  $(b_1, b_2, \dots)$ .

Then using the projection operator methods,<sup>15</sup> Williamson/and more recently Merris<sup>16</sup> (for higher dimensional representations) proved that the generating



function for the number of irreducible representation in  $F$ , the set of maps from  $D$  or  $R$  is given by

$$G \cdot f^X = P_G^X [x_k + \sum_{r \in R} (w(r))^k]. \quad (2.7)$$

The coefficient of a term  $\alpha_1^{n_1} \alpha_2^{n_2}$  in  $G \cdot f^X$  gives number of times  $\chi$  occurs in the set of maps from  $D$  to  $R$  with the weight  $\alpha_1^{n_1} \alpha_2^{n_2}$ . In particular, the coefficient of  $\alpha_1^{n-1} \alpha_2$  in  $G \cdot f^X$  gives the number of times  $\chi$  occurs in the representation spanned by the set of nuclei. This is indeed quite elegant and advantageous over conventional techniques in that it does not require the character of the representation spanned by the nuclei. Further GCCI's for the symmetry groups of non-rigid molecules can be obtained from GCCI's of much smaller groups.<sup>17,18</sup>

We will now illustrate (2.7) with the non-rigid  $PF_5$  molecule which exhibits Berry pseudo rotation. The rotational subgroup of the non-rigid  $PF_5$  is  $S_5$ . If one considers  $^{19}F$  NMR of  $PF_5$  then the set  $D$  consists of 5  $^{19}F$  nuclei. Consider for example, the  $G_1$  representation of this molecule. The corresponding GCCI and  $G \cdot f^X$  are shown below.

$$GCCI^{G_1} = \frac{1}{120} [4x_1^5 + 20x_1^3x_2 + 20x_1^2x_3 - 20x_2x_3 - 24x_5] \quad (2.8)$$

$$\begin{aligned} G \cdot f^{G_1} &= \frac{1}{120} [4(\alpha_1 + \alpha_2)^5 + 20(\alpha_1 + \alpha_2)^3(\alpha_1^2 + \alpha_2^2) + 20(\alpha_1 + \alpha_2)^2(\alpha_1^3 + \alpha_2^3) - \\ &20(\alpha_1^2 + \alpha_2^2)(\alpha_1^3 + \alpha_2^3) - 24(\alpha_1^5 + \alpha_2^5)] \\ &= \alpha_1^4 \alpha_2 + \alpha_1^3 \alpha_2^2 + \alpha_1^2 \alpha_2^3 + \alpha_1 \alpha_2^4 \end{aligned} \quad (2.9)$$

The coefficient of  $\alpha_1^4 \alpha_2$  in (2.9) is 1 implying there is one  $G_1$  representation spanned by the 5  $^{19}\text{F}$  nuclei. Table 1 shows the total generating function for the non-rigid  $\text{PF}_5$  molecule. In this table we follow the notation for the irreducible representations of an earlier paper of the author. By collecting all the coefficients of  $\alpha_1^4 \alpha_2$  one can immediately conclude that the representation spanned by the  $^{19}\text{F}$  nuclei is given by 2.10.

$$\Gamma_{^{19}\text{F}} = A_1 + G_1 \quad (2.10)$$

This is, of course, a trivial example but we used this for the sake of illustration. The number of  $A_1$  (totally symmetric representations) representations in the representation spanned by nuclei gives the number of NMR Signals by Pólya's theorem. This is because the number of  $A_1$  representations is obtained from GCCI which is also just the ordinary cycle index defined by Pólya<sup>19</sup> for the enumeration of equivalence classes. Thus number of  $A_1$  representations gives the number of equivalence classes and thus the number of NMR Signals. The present author introduced a topological description for the interconversion of nuclei in dynamic processes.<sup>2</sup> In that scheme nuclei are represented by vertices and the possible interconversions among them by edges. A NMR reaction graph is a graph in which two nuclei are connected if they are transformable in to one another by an operation in the rotational subgroup. Such a diagram for the  $^{19}\text{F}$  nuclei of the non-rigid  $\text{PF}_5$  molecule is shown in fig. 1. In the next section we will consider the splitting patterns of NMR graphs by way of correlation of the symmetry species spanned by these diagrams.

### C. Correlation of symmetry species and NMR reaction graphs

The symmetry group of the rigid  $\text{PF}_5$  molecule is  $D_{3h}$  and its rotational

subgroup is  $D_3$ . In this example there are no enantiotopic protons in both the rigid and non-rigid molecular groups so that one can treat both the cases by rotational subgroup. The set of irreducible representations spanned by the nuclei in the rotational group of the rigid molecule can be found by two methods. One method is to obtain the generating functions in the group  $D_3$ . Such a generating function is shown in Table 2. Note that by collecting the coefficients of  $\alpha_1^4 \alpha_2$  in various irreducible representations we find  $\Gamma_F$  in  $D_3$  to be

$$\Gamma_F = 2A_1 + A_2 + E \quad (2.11)$$

The same expression can also be obtained by correlating the symmetry species of  $S_5$  to  $D_3$  by way of subduced representation. The  $A_1$  representation of  $S_5$  correlates to  $A_1$  of  $D_3$  and  $G_1$  splits in to  $A_1 + A_2 + E$  so that expression (2.10) correlates to 2.11. Note that there are two  $A_1$  representations in  $\Gamma_F$  in the group  $D_3$  indicating there are 2 equivalence classes for the rigid molecule. This establishes the fact that a single NMR signal of the non-rigid molecule splits into 2 signals in dynamic NMR at lower temperatures. The NMR reaction graph of the rigid molecule is shown in figure 2 which contains 2 components. Number of components in the NMR reaction graph corresponds to the number of NMR signals and the ratio of the number of vertices in various components gives the intensity ratios of the corresponding NMR signals. Thus we can infer that the single NMR peak of the non-rigid molecule splits into two signals with the intensity ratio 3:2. The method outlined here eventhough enables the prediction of the splitting and coalescence patterns of the NMR signals it does not quite enable construction of the NMR reaction graph (since it gives only the number of components and not the number of vertices in each

component) and thus cannot predict the intensity patterns in dynamic processes. For this purpose we outline a double coset method in the next section.

### 3. Double Coset Method for Constructing The NMR Reaction graph and prediction of Coalescence and intensity patterns.

Let  $S_n$  denote the complete permutation group containing  $n!$  Permutations of nuclei. Since we are choosing  $n-1$   $\alpha_1$  labels and 1  $\alpha_2$  label to label the nuclei the group  $S_{n-1}XS_1$  ( $S_1$  is the group containing just the identity element) is known as the label subgroup  $L$  which is isomorphic to  $S_{n-1}$ .  $L$  is in general a subgroup of  $S_n$ . Recall that  $G$  is the rotational subgroup or the point group of the molecule. For an element  $s \in S_n$  the set  $LsG$  is known as the double coset of  $L$  and  $G$ . Any map  $f_1$  defined in Section 2.4 can be considered as an element in  $S_n$ . This is because we can consider the identity element of  $S_n$  as the map  $f_n$  which maps first  $n-1$  nuclei to  $\alpha_1$  and the  $n$ th nucleus to  $\alpha_2$  by definition. Then any other map can be obtained by applying  $s \in S_n$  on  $f_n$ . To illustrate consider  $PF_5$ . The map  $f_5$  labels the nuclei  $\alpha_1 \alpha_1 \alpha_1 \alpha_1 \alpha_2$ . Then for example, the permutation (12345) generates the following labeling of nuclei:  $\alpha_2 \alpha_1 \alpha_1 \alpha_1 \alpha_1$ . Thus the map  $f_1$  can be considered as an element in  $S_5$ .

Two elements  $s_1$  and  $s_2$  are said to be in the same double coset if

$$s_1 = Ls_2G. \quad (3.1)$$

Then it can be seen that the maps corresponding to  $s_1$  and  $s_2$  are equivalent and consequently, the corresponding nuclei are also equivalent. It can be

proved that (3.1) is an equivalence relation and thus the double cosets generate equivalence classes of nuclei. The elements of a set  $S = \{s_1, s_2, \dots, s_n\}$  are said to be distinct representatives of the double cosets or the equivalence classes of nuclei if the group  $S_n$  can be obtained as a disjoint decomposition of the double cosets formed by the elements of  $S$ . In symbols, the elements of  $S$  are distinct representatives if

$$S_n = \bigcup_{i=1}^M Ls_i G \quad (3.2)$$

and

$$(Ls_i G) \cap (Ls_j G) = \emptyset \text{ if } i \neq j$$

Where  $\emptyset$  is the null set. The number of elements in  $S$ ,  $M$ , can be found using the generating function techniques outlined in Section 2B. by way of generating number of  $A_1$  representations in the set of nuclei.

The number of elements in any double coset  $LsG$  is given by (3.3)

$$|LsG| = |L||G|/|s^{-1}Ls \cap G| = |L||G|/|L \cap sGs^{-1}| \quad (3.3)$$

Thus using (3.3) one can obtain the number of elements in the double coset without having to construct the coset. This is indeed quite advantageous because for our present purpose we only need to know the number of nuclei in each equivalence class (in fact ratio of nuclei in various classes) for the prediction of intensity ratio patterns. The number of elements in a double coset in general, is not equal to the number of elements in the corresponding equivalence class of nuclei. This is because two elements in a double coset

can generate the same map. To illustrate for the  $PF_5$  molecule the identity in  $S_5$  and the permutation (1234) generates the same map  $f_5$ . Nevertheless, in general the ratio of the number of elements in various double cosets is exactly the ratio of the number of elements in the corresponding equivalence classes. This is indeed very useful since we are interested in the intensity ratios of various peaks which corresponds to the ratio of the number of elements in the corresponding equivalence class. Thus we arrive at the following important relation. For a set of distinct representatives  $S = \{s_1, s_2, \dots, s_m\}$ , which generate the double coset decomposition of  $S_n$  we have

$$\begin{aligned}
 & |Ls_1G| : |Ls_2G| : \dots : |Ls_mG| \\
 & = |L||G|/|L \cap s_1Gs_1^{-1}| : |L||G|/|L \cap s_2Gs_2^{-1}| : |L||G|/|L \cap s_mGs_m^{-1}|. \quad (3.4)
 \end{aligned}$$

Thus the intensity ratios of various signals is given by (3.5)

$$\frac{1}{|L \cap s_1Gs_1^{-1}|} : \frac{1}{|L \cap s_2Gs_2^{-1}|} : \dots : \frac{1}{|L \cap s_mGs_m^{-1}|}$$

Also the number of elements in an equivalence class of nuclei corresponding to the double coset  $Ls_1G$  is given by (3.6).

$$\left. \begin{array}{l} \text{Number of elements in an} \\ \text{equivalence class of nuclei} \end{array} \right\} = \frac{|Ls_1G| \cdot n}{|s_n|}. \quad (3.6)$$

The double cosets of nuclei also facilitate elegant correlation of equivalence classes of nuclei in dynamic processes such as large amplitude motions. Each double coset generates an equivalence class of nuclei. The

number of totally symmetric representations in any double coset is unity. The splitting patterns of equivalence classes of nuclei in dynamic processes can be found by correlating the symmetry species in the equivalence classes of nuclei.

We will now illustrate the above method of double cosets with the example of  $\text{PF}_5$ . For the non-rigid molecule the rotational group is  $S_5$ . Thus  $G = S_5$  and  $L = S_4$ . This is a trivial case where  $G$  is isomorphic to  $S_n$ . Thus any  $s \in S_n$  is a distinct representative and there is only one such double coset since for any  $s \in S_n$ ,  $LsG = S_5$ . Thus all the five nuclei are equivalent and they span a single equivalence class  $C = \{1, 2, 3, 4, 5\}$ . The irreducible representations contained in  $C$  are  $A_1$  and  $G$ , (cf. 2.10). Thus when one considers rigid molecule whose rotational group  $G = D_3$  the class  $C$  splits into 2 classes  $C_1$  and  $C_2$ . In terms of the double cosets the single double coset splits into 2 double cosets. We will now look at this in detail as an illustration. The group  $G$  is

$$G = D_3 = \{e, (123), (132), (12)(45), (13)(45), (23)(45)\}$$

$$L = S_4 = \{e, (12), (13), (14), (23), (24), (34), (123), (132), (124), (142), (234), (134), (143), (1234), (1243), (1324), (1342), (1423), (1432), (12)(34), (14)(23), (13)(24)\}$$

We have to look for  $S = \{s_1, s_2\}$  such that

$$Ls_1G \cup Ls_2G = S_5 \text{ and}$$

$$Ls_1G \cap Ls_2G = \emptyset.$$

One obvious choice is  $s_1 = e \in S_5$  where  $e$  is the identity. The number of elements in this double coset is

$$|LeG| = |L||G|/|L \cap e^{-1}Ge| = \frac{|L||G|}{|L \cap G|} = \frac{24 \cdot 6}{3} = 48$$

Thus the number of elements in the corresponding equivalence class of nuclei is given by

$$n \frac{|LeG|}{|S_5|} = \frac{5 \cdot 48}{5!} = 2.$$

The elements of the equivalence class  $C_1$  can be generated by first operating  $e$  on  $f_5$  which is  $f_5$  and any other element in  $G$  or the double coset  $LeG$ . Thus it can be seen that  $C_1 = \{f_5, f_4\}$ . By choosing  $s_2$  to be (12345) we obtain the second double coset. We choose  $s_2 = (12345)$  since this is not present in the product  $LG$ . The number of elements in this double coset is

$$|Ls_2G| = \frac{|L||G|}{|L \cap s_2^{-1}Gs_2|} = \frac{24 \cdot 6}{2} = 72.$$

consequently the number of element in the second equivalence class is given by

$$n \frac{|Ls_2G|}{|S_5|} = \frac{5 \cdot 72}{5!} = 3.$$

The second class is easily constructed by operating (12345) on  $f_5$  and generating the other elements by either operating the resulting map by elements of  $G$ . It can be seen that  $C_2 = \{f_1, f_2, f_3\}$ . One can immediately obtain NMR reaction graph by connecting all elements in any  $C_i$ . The graph thus obtained



is shown in fig. 2. Of course, to predict the nature of intensity and splitting patterns of NMR Signals it is not necessary to explicitly construct all the double cosets. We need to know only the number of double cosets and the ratio of the number of elements in all double cosets which in turn give the number and intensity ratios of NMR Signals, respectively. The number of double cosets can be found by generating number of  $A_1$  representations as shown in Sec. 2c. The ratio of the number of elements in all the double cosets is obtained with the formula (3.5). Thus one immediately infers using these techniques that the single  $^{19}\text{F}$  NMR peak splits into 2 peaks in dynamic NMR with the intensity ratio  $1/2 : 1/3$  or  $3:2$  at lower temperatures. Conversely, the peaks with this intensity ratio will coalesce into a single peak at higher temperatures. For several applications one needs to know the irreducible representations contained in each equivalence class of nuclei. A technique for this is in the next section.

#### 4. Generation of Symmetry Species in Each Class of Nuclei and The Assignment of Splitting and Coalescence Patterns.

In order to completely assign the splitting and coalescence pattern of each signal it is necessary to know the symmetry species contained in each equivalence class of nuclei generated by the double cosets. In earlier sections we had a method to generate only the symmetry species spanned by all nuclei rather than equivalence classes of nuclei. However, in order to know whether a given signal will split or not (or conversely coalesce) it is necessary to know the irreducible representations spanned by the equivalence class of nuclei which gives rise to that NMR Signal. For this purpose we define

and use a new restricted character cycle index (RCCI) which generates symmetry species in each equivalence class. We define a RCCI as a character cycle index restricted to an equivalence class of nuclei. For an equivalence class C of nuclei we know that any  $g$  in the symmetry group  $G$  permutes nuclei only within the class  $C$ . Thus the cycle product of any  $g \in G$  over all nuclei can be separated and restricted only to the class  $C$ . Define a RCCI corresponding to a class  $C$  and an irreducible representation  $\Gamma$  with character  $\chi$  as

$$\text{RCCI}^{\chi}(C) = \frac{1}{|G|} \sum_{g \in G} \chi(g) x_1^{C(b_1)} x_2^{C(b_2)} \dots \quad (4.1)$$

Where  $C(b_1)$ ,  $C(b_2)$ , ... are the number of 1, 2 cycles generated in the equivalence class  $C$  when  $g$  is applied on  $C$ . To illustrate, the two equivalence classes of nuclei for  $\text{PF}_5$  in  $D_3$  are  $C_1 = \{1,2,3\}$  and  $C_2 = \{4,5\}$ . The RCCI's for the various representations of  $D_3$  restricted to  $C_1$  and  $C_2$  are shown below.

$$\text{RCCI}^{A_1}(C_1) = \frac{1}{6} (x_1^3 + 3x_1x_2 + 2x_3)$$

$$\text{RCCI}^{A_2}(C_1) = \frac{1}{6} (x_1^3 - 3x_1x_2 + 2x_3)$$

$$\text{RCCI}^E(C_1) = \frac{1}{6} (2x_1^3 - 2x_3)$$

$$\text{RCCI}^{A_1}(C_2) = \frac{1}{6} (3x_1^2 + 3x_2) = \frac{1}{2} (x_1^2 + x_2)$$

$$\text{RCCI}^{A_2}(C_2) = \frac{1}{6} (3x_1^2 - 3x_2) = \frac{1}{2} (x_1^2 - x_2)$$

$$\text{RCCI}^E(C_2) = \frac{1}{6} (2x_1^2 - 2x_2) = 0$$

The restricted generating function  $\text{RGF}^{\chi}(C)$  restricted to a class  $C$  generates the number of irreducible representations whose character is  $\chi$  restricted to  $C$ . It is obtained as follows:

$$\text{RGF}^{\chi}(C) = \text{RCCI}(\chi_k \rightarrow \sum_{r \in R} (w(r))^k).$$

To illustrate let us obtain the generating functions corresponding to RCCI's of  $\text{PF}_5$  in  $D_{3h}$  representations.

$$\begin{aligned} \text{RGF}^{A_1}(C_1) &= \frac{1}{6} [(\alpha_1 + \alpha_2)^3 + 3(\alpha_1 + \alpha_2)(\alpha_1^2 + \alpha_2^2) + 2(\alpha_1^3 + \alpha_2^3)] \\ &= \alpha_1^3 + \alpha_1^2 \alpha_2 + \alpha_1 \alpha_2^2 + \alpha_2^3 \end{aligned}$$

$$\text{RGF}^{A_2}(C_1) = 0$$

$$\text{RGF}^E(C_1) = \alpha_1^2 \alpha_2 + \alpha_1 \alpha_2^2$$

$$\text{RGF}^{A_1}(C_2) = \frac{1}{2} [(\alpha_1 + \alpha_2)^2 + (\alpha_1^2 + \alpha_2^2)] = \alpha_1^2 + \alpha_1 \alpha_2 + \alpha_2^2$$

$$\text{RGF}^{A_2}(C_2) = \alpha_1 \alpha_2$$

The coefficient of  $\alpha_1^{|C_1| - 1} \alpha_2$  in  $\text{RGF}^{\chi}$  generates the number of times  $\Gamma$  occurs (whose character is  $\chi$ ) in the equivalence class  $C_1$  where  $|C_1|$  is the number of elements in the class  $C_1$ . Thus by collecting the coefficient of  $\alpha_1^2 \alpha_2$  in RCIC's one can immediately infer that the nuclei in  $C_1$  span  $A_1 + E$  representation and similarly nuclei in  $C_2$  span  $A_1 + A_2$  representation. The technique

outlined above thus generates symmetry species in each class without having to know the character of the representation spanned by the nuclei present in that class. This is indeed very advantageous for large molecules which have several equivalence classes containing varied number of nuclei.

In order to theoretically predict if a given signal will split in dynamic NMR at lower temperatures all that we need to do is to correlate the symmetry species spanned by the nuclei which give rise to that signal to rigid molecular group.

#### 5. Spontaneous Generation of Chiral Signals.

In this section we consider an important application of the techniques outlined in the earlier sections to spontaneous generation of chiral signals. A molecule which does not have any chiral nuclei at higher temperatures when it exhibits very large amplitude motions may have chiral (enantiotopic) nuclei at lower temperatures. The chiral nuclei can be resolved with the use of chiral shift reagents. This phenomenon can be called spontaneous generation of chiral NMR signals. Let us consider the proton NMR of propane which exhibits this phenomenon. The rotational group of the non-rigid molecule can be represented by the generalized wreath product group  $C_2[C_3, E]$ , where  $E$  corresponds to the identity group acting on the methylene protons. The rotational group of the rigid molecule, however, contains only the identity and a 2-fold rotation. Under the group  $C_2[C_3, E]$  there are 2 double cosets and 2 equivalence classes of nuclei denoted by  $C_1 = \{1, 2, 3, 6, 7, 8, \}$ ,  $C_2 = \{4, 5, \}$  where 1, 2, 3, 6, 7, 8, are methyl protons and 4 and 5 are methylene protons. Chiral nuclei can be differentiated in the rotational group. However, they become equivalent in the point group. It can be easily seen that the class

structure remains unaltered if inversion operations are included in the rotational subgroup of the non-rigid molecule. Thus there are no chiral nuclei for the non-rigid molecule. The corresponding NMR graph is shown in fig. 3. The irreducible representations spanned by  $C_1$  and  $C_2$  are  $A_1 + A_2 + G$  and  $A_1 + A_2$  where  $A_1$  and  $A_2$  are totally symmetric and antisymmetric representations,  $G$  actually has 2 degenerate two dimensional representations. The representation  $A_1$  and  $A_2$ , and  $G$  correlate to  $A_1$ ,  $A_2$  and  $2(A_1 + A_2)$  in the rotational group  $C_2$  of the rigid molecule so that the class  $C_1$  of the non-rigid molecule contains 3  $A_1$  representations in the rigid molecular group. Consequently, the class  $C_1$  of the non-rigid molecule splits into 3 classes. The double cosets analysis shows that these are  $C_{11} = \{1,6\}$ ,  $C_{12} = \{2,8\}$  and  $C_{13} = \{3,7\}$ . The class  $C_2$  of the non-rigid molecule remains unaltered. The corresponding reaction graph is shown in Fig. 4. If we, however, introduce the inversion operation in the rigid group then the group becomes  $C_{2h}$  for the equilibrium conformation. The species  $A_1$ ,  $A_2$  and  $G$  correlate to  $A_1$ ,  $A_2$  and  $A_1 + A_2 + A_3 + A_4$ , representation in  $C_{2h}$ . Thus the class  $C_1$  contains only  $2A_1$  representation in  $C_{2h}$ . The double coset analysis with  $G = C_{2h}$  gives  $C_{11} = \{1,6\}$ ,  $C_{12} = \{2,8,3,7\}$ .

Thus the two classes  $C_{12}$  and  $C_{13}$  in the group  $C_2$  coalesce into a single class in  $C_{2h}$  indicating the presence of chiral protons. The proton pairs (2,3) and (7,8) are equivalent chiral pairs. We can thus indicate 3 as  $\bar{2}$  (mirror image of 2) and 8 as 7. (See Fig. 4 and 5.) The corresponding NMR graph is in Fig. 5. The analysis outlined here thus shows that there are 2 NMR signals for the non-rigid molecule at high temperature with the intensity ratio 3:1. The higher intensity peak generates chiral signals at lower temperature 2 of which are chiral (and therefore can be differentiated only with chiral reagents) and the other is achiral. The over all spectrum has 4

signals with equal intensity. In the absence of chiral shift reagents the intensity pattern is 2:1:1. There are several such systems which exhibit this phenomenon of spontaneous generation of chiral NMR signals.

## 6. An Example

In this section we consider the molecule  $B(CH_3)_3$  as an example to illustrate all the concepts outlined in earlier sections. This molecule was considered by Longuet-Higgins<sup>20</sup> as an illustration of a non-rigid molecule. The symmetry group of the non-rigid  $B(CH_3)_3$  is  $D_{3h}[C_3]$ . For the non-rigid molecule which has 3 methyl rotors exhibiting internal rotation it can be easily seen that there is only one class of protons. Generating function for all the irreducible representation are shown in Table 3. Collecting the coefficients of  $\alpha_1^8 \alpha_2$  under various irreducible representations we immediately infer that the protons of this non-rigid molecule span the representation  $A_1 + E_1 + I_3$ . The molecule in its equilibrium configuration (shown in Fig. 6) belongs to the point group  $C_{3h}$ . The rotational subgroup is  $C_3$ . Generating functions for all irreducible representation of  $C_{3h}$  are shown in Table 4. From this table we infer that the protons now span a representation shown below:

$$C_{3h}: 2A^+ + A^- + 2E_x^+ + 2E_y^+ + E_x^- + E_y^-$$

Equivalently, we could have obtained the above result by subducing the representations  $A_1$ ,  $E_1$  and  $I_1$  from  $D_{3h}[C_3]$  to  $C_{3h}$  which correlate to  $A^+$ ,  $E_x^+ + E_y^+$  and  $A^+ + A^- + E_x^+ + E_y^+ + E_x^- + E_y^-$ , respectively. However, the latter method needs the character table of the non-rigid molecule, while the former method does not need the character tables / the generating functions can be obtained without knowing the character tables.<sup>17,21</sup> In this sense generating function

techniques are more elegant than the method of subducing representations. Note that protons  $B(CH_3)_3$  span 2 totally symmetric representations in the group  $C_{3h}$ . Consequently, there are two equivalence classes of nuclei. The double coset analysis in  $C_{3h}$  shows they are  $C_{11} = \{1,4,7\}$  and  $C_{12} = \{2,3,8,9,5,6\}$  (see Fig. 6). If one considers the rotational group of the molecule in its equilibrium configuration, the generating functions are shown in Table 5. Thus the nuclei span the following representations in the  $C_3$  group:

$$C_3: 3A_1 + 3E_x + 3E_y.$$

There are 3 totally symmetric representations for the molecule in  $C_3$  group. The three equivalence classes are  $C_{11} = \{1,4,7\}$ ,  $C_{12} = \{2,5,9\}$  and  $C_{13} = \{3,5,8\}$ . Since the number of equivalence classes in  $C_3$  and  $C_{3h}$  differ one immediately infers the existence of chiral nuclei for non-rigid molecule. The nuclei pairs (2,3), (5,6), and (8,9) are chiral pairs. The non-rigid molecule, however, did not have any chiral centers. Thus this molecule is an example of a molecule which exhibits spontaneous generation of chiral signal. The NMR reaction graph of this non-rigid molecule is shown in Fig. 7. The corresponding reaction graphs of the rigid molecule in  $C_{3h}$ ,  $C_3$  groups are in Figures 8 and 9, respectively. A single NMR signal of the non-rigid molecule splits into 3 signals with equal intensity, 2 of which are chiral. The chiral signals coalesce in the absence of chiral shift reagents resulting in 2 signals with the intensity ration 2:1.

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Table 1. Total Generating Function for the Non-rigid  $\text{PF}_5$ . The Coefficient of  $\alpha_1^4 \alpha_2$  Under each Irreducible Representation Generates the Number of that Irreducible Representation in the Equivalence Classes of Nuclei. The Coefficient of  $\alpha_1^4 \alpha_2$  in the  $A_1$  Representation Generates the Number of NMR Signals

$\Gamma$	$\alpha_1^5$	$\alpha_1^4 \alpha_2$	$\alpha_1^3 \alpha_2^2$	$\alpha_1^2 \alpha_2^3$	$\alpha_1 \alpha_2^4$	$\alpha_2^5$
$A_1$	1	1	1	1	1	1
$A_2$	0	0	0	0	0	0
$G_1$	0	1	1	1	1	0
$G_2$	0	0	0	0	0	0
$H_1$	0	0	1	1	0	0
$H_2$	0	0	0	0	0	0
$I$	0	0	0	0	0	0

Table 2. Total Generating Function for the Rigid  $\text{PF}_5$  Molecule. Note that the Coefficient of  $\alpha_1^4 \alpha_2$  of  $A_1$  in Table 2 is 2 while it was 1 in Table 1 Indicating the Splitting of NMR Signals

$\Gamma$	$\alpha_1^5$	$\alpha_1^4 \alpha_2$	$\alpha_1^3 \alpha_2^2$	$\alpha_1^2 \alpha_2^2$	$\alpha_1 \alpha_2^4$	$\alpha_2^5$
$A_1$	1	2	3	3	2	1
$A_2$	0	1	1	1	1	0
E	0	1	3	3	1	0

Table 3. Generating Functions for the Irreducible Representations  
Spanned by the Protons of the Non-rigid  $B(CH_3)_3$  Molecule

$\Gamma$	$\alpha_1^9$	$\alpha_1^8 \alpha_2$	$\alpha_1^7 \alpha_2^2$	$\alpha_1^6 \alpha_2^3$	$\alpha_1^5 \alpha_2^4$	$\alpha_1^4 \alpha_2^5$	$\alpha_1^3 \alpha_2^6$	$\alpha_1^2 \alpha_2^7$	$\alpha_1 \alpha_2^8$	$\alpha_2^9$
$A_1$	1	1	2	3	3	3	3	2	1	1
$A_2$	0	0	0	0	0	0	0	0	0	0
$A_3$	0	0	0	0	0	0	0	0	0	0
$A_4$	0	0	0	1	1	1	1	0	0	0
$E_1$	0	1	2	3	4	4	3	2	1	0
$E_2$	0	0	0	0	0	0	0	0	0	0
$E_3$	0	0	0	1	1	1	1	0	0	0
$E_4$	0	0	0	0	0	0	0	0	0	0
$G$	0	0	0	0	1	1	0	0	0	0
$I_1$	0	0	1	2	3	3	2	1	0	0
$I_2$	0	0	0	1	1	1	1	0	0	0
$I_3$	0	1	2	3	4	4	3	2	1	0
$I_4$	0	0	1	2	3	3	2	1	0	0
$I_5$	0	0	0	1	2	2	1	0	0	0
$I_6$	0	0	0	0	1	1	0	0	0	0
$I_7$	0	0	1	2	3	3	2	1	0	0
$I_8$	0	0	0	1	1	1	1	0	0	0

Table 4. Generating Function for the Protons of  $B(CH_3)_3$  in its Equilibrium Conformation. From the Coefficient of  $\alpha_1^7 \alpha_2$  One can Immediately Infer that the Nuclei Span the Representation  $2A^+ + A^- + 2E_x^+ + 2E_y^+ + E_x^- + E_y^-$

$\Gamma$	$\alpha_1^9$	$\alpha_1^8 \alpha_2$	$\alpha_1^7 \alpha_2^2$	$\alpha_1^6 \alpha_2^3$	$\alpha_1^5 \alpha_2^4$	$\alpha_1^4 \alpha_2^5$	$\alpha_1^3 \alpha_2^6$	$\alpha_1^2 \alpha_2^7$	$\alpha_1 \alpha_2^8$	$\alpha_2^9$
$A^+$	1	2	7	17	23	23	17	7	2	1
$A^-$	0	1	5	13	19	19	13	5	1	0
$E_x^+$	0	2	7	15	23	23	15	7	2	0
$E_y^+$	0	2	7	15	23	23	15	7	2	0
$E_x^-$	0	1	5	12	19	19	12	5	1	0
$E_y^-$	0	1	5	12	19	19	12	5	1	0

Table 5. Generating Function for the Irreducible Representations of  $B(CH_3)_3$  in the Group  $C_3$

$\Gamma$	$\alpha_1^9$	$\alpha_1^8\alpha_2$	$\alpha_1^7\alpha_2^2$	$\alpha_1^6\alpha_2^3$	$\alpha_1^5\alpha_2^4$	$\alpha_1^4\alpha_2^5$	$\alpha_1^3\alpha_2^6$	$\alpha_1^2\alpha_2^7$	$\alpha_1\alpha_2^8$	$\alpha_2^9$
$A_1$	1	3	12	30	42	42	30	12	3	1
$E_x$	0	3	12	27	42	42	27	12	3	0
$E_y$	0	3	12	27	42	42	27	12	3	0

## Figure Captions

Figure 1. NMR reaction graph of non-rigid  $\text{PF}_5$ .

Figure 2. NMR reaction graph of rigid  $\text{PF}_5$  in  $D_{3h}$  symmetry. Number of components in the graph gives number of  $^{19}\text{F}$  signals and the ratio of the number of vertices corresponds to the intensity ratio.

Figure 3. NMR reaction graph of non-rigid propane.

Figure 4. NMR reaction graph of rigid propane in  $C_2$  symmetry. The proton pairs (2,3) and (7,8) are chiral pairs. Enantiotopic protons will be denoted by bars.

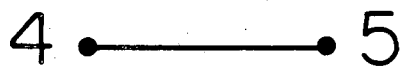
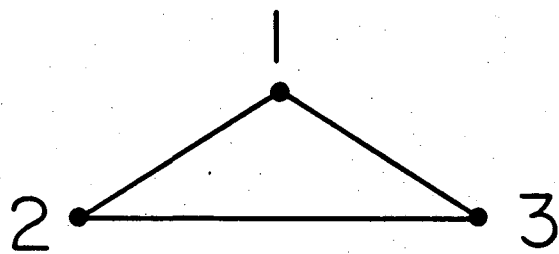
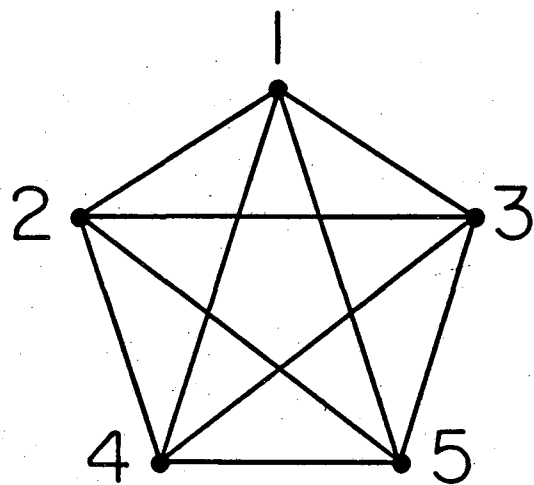
Figure 5. NMR reaction graph of rigid propane in  $C_{2h}$  or  $C_{2u}$  symmetry.

Figure 6. Equilibrium geometry of  $\text{B}(\text{CH}_3)_3$ .

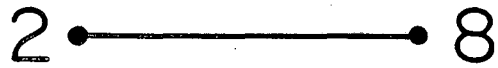
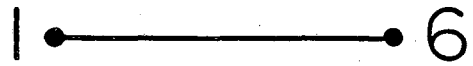
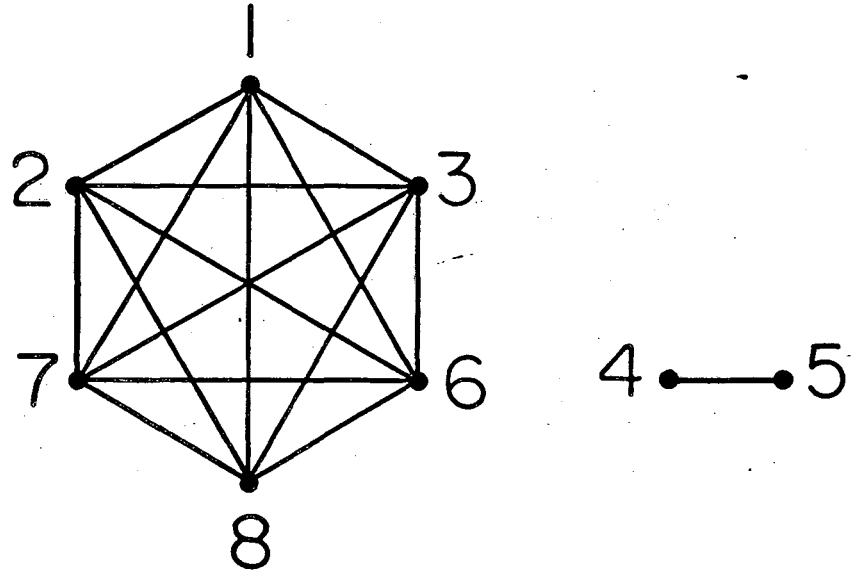
Figure 7. NMR reaction graph of non-rigid  $\text{B}(\text{CH}_3)_3$ .

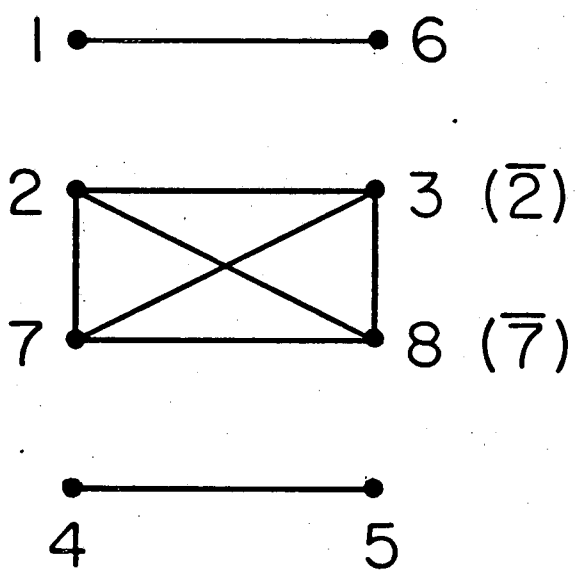
Figure 8. NMR reaction graph of rigid  $\text{B}(\text{CH}_3)_3$  in  $C_3$  group.

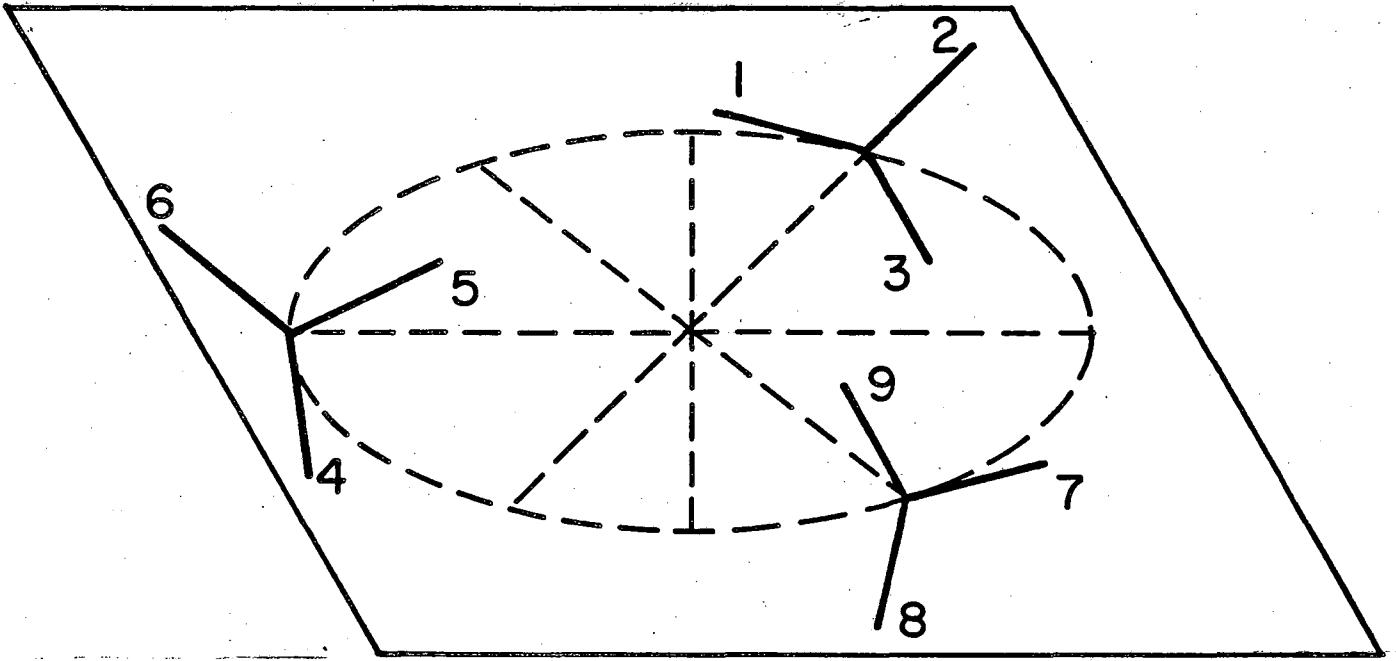
Figure 9. NMR reaction graph of rigid  $\text{B}(\text{CH}_3)_3$  in  $C_{3h}$  group.

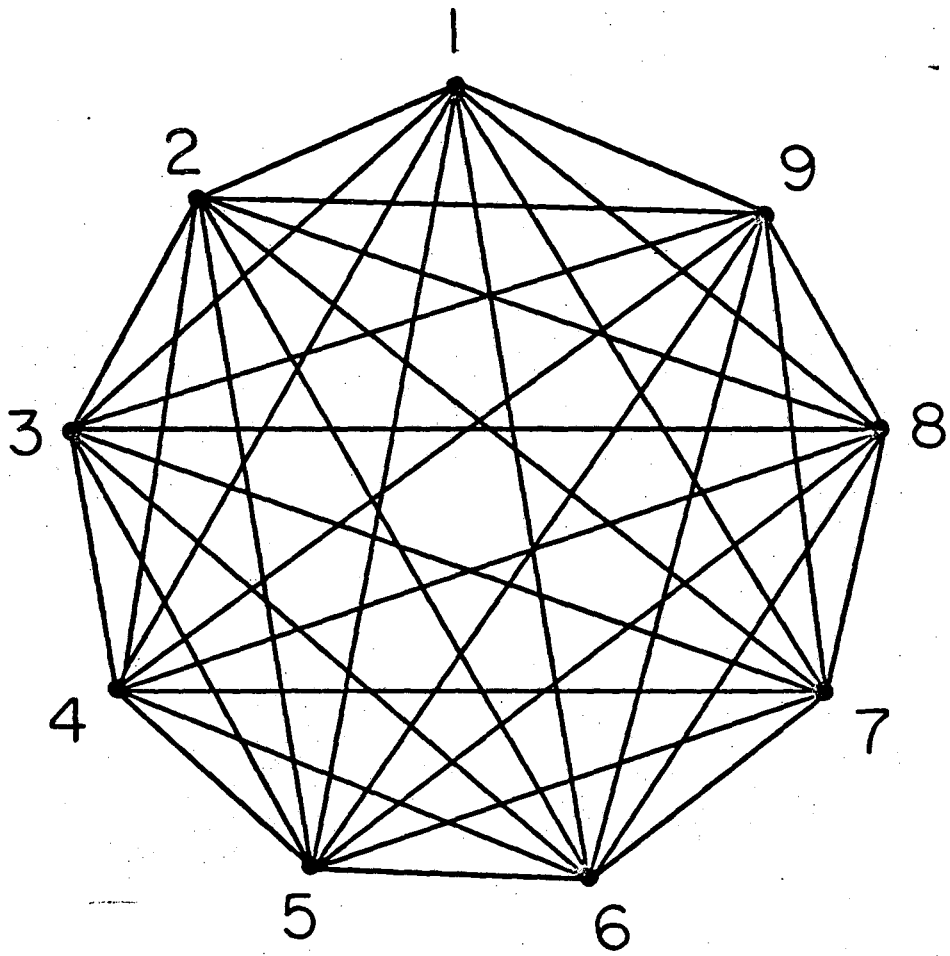


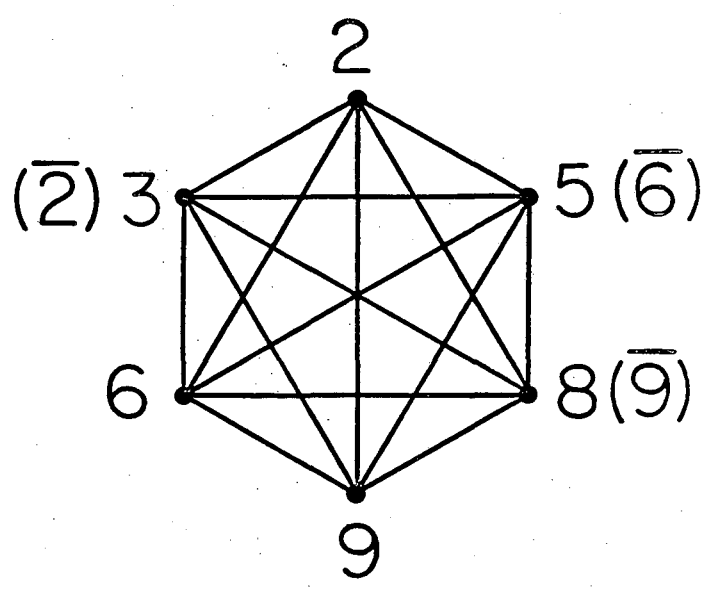
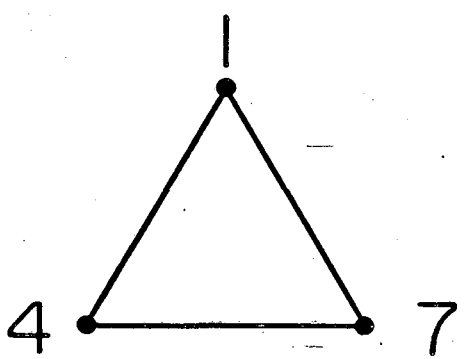
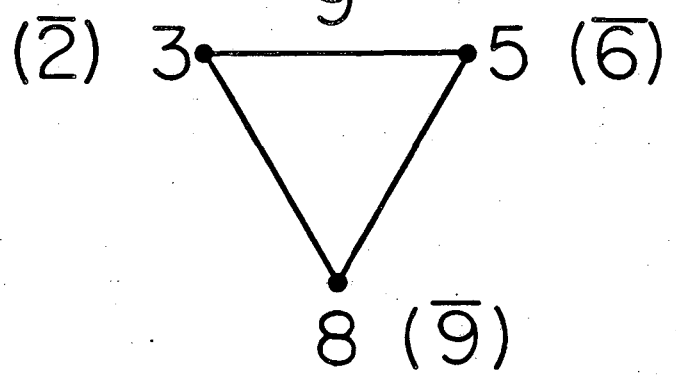
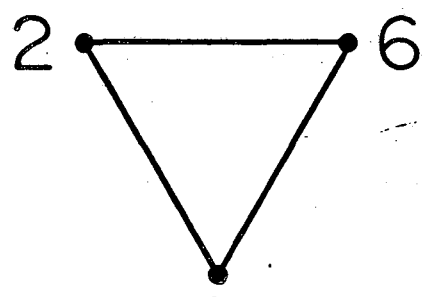
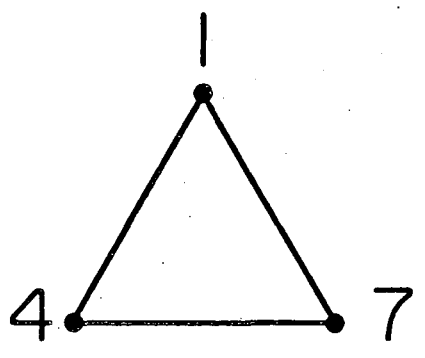












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