

is in preparation,<sup>31</sup> including theoretical plots of  $k_2$  vs.  $A$ . These preliminary results suggest the statistical theory approach may well be appropriate for these systems, but the more complete analysis, in progress, is necessary to confirm this suggestion.

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# Generalized Selection Rules: Symmetry Rules for Molecules or Chromophores in Perturbing Fields

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**Abstract:** Generalized selection rules are developed for any interaction process involving a species of given symmetry in the presence of perturbing fields (such as static electric and magnetic or radiation fields, or that due to the presence of another species). It is suggested that the selection rules be defined in two stages: those giving the combinations of operators allowed under the symmetry of the species (operator selection rules) and those giving the allowed intermediate states (state selection rules). The former are shown to reduce to the symmetry rules of the classical tensor describing the molecular response, and lead to the concept of an invariant operator characteristic of the point group of the molecule corresponding to the classical tensorial observable. The method is illustrated by application to some simple interaction processes.

## Introduction

Selection rules are of such fundamental importance and widespread use in chemistry that it is easy to overlook that they are basically of two quite distinct types: classical selection rules (which are essentially the symmetry rules describing the conditions under which the classical observable must vanish under the molecular symmetry) and quantum mechanical selection rules (which are the corresponding symmetry rules for the matrix elements in the quantum mechanical expressions describing the same process). We can illustrate this with recourse to the familiar concept of polarizability.

The interaction of a molecule  $A$  with an electrostatic field

$E$  leads to the following classical expression for the resultant induced dipole moment of  $A$ :

$$\delta\mu = \hat{\alpha}^c E \quad (1)$$

$\hat{\alpha}^c$  is the classical polarizability tensor with elements  $\alpha_{ij}^c$ , where  $i, j$  are Cartesian indexes. If the molecule has a symmetry higher than  $C_1$  (containing only the identity), certain elements of the polarizability tensor will be related by symmetry, or vanish. Definition of these conditions lead to the classical tensor selection rules, which have been discussed in some detail by Birss<sup>1</sup> in a monograph directed at solid state problems. The quantum equivalent of the above expression has the form

$$\delta\mu = \hat{\alpha}^q \mathbf{E} \quad (2)$$

where

$$\alpha_{ij}^q = 2 \sum_{s \neq 0} \frac{\langle 0 | \mu_i | s \rangle \langle s | \mu_j | 0 \rangle}{\epsilon_s} \quad (3)$$

and 0,  $s$  specify the ground and an excited state of A, respectively, with  $\mu_i$  the  $i$ th Cartesian component of the electric dipole operator centered at the origin of A.  $\epsilon_s$  is the transition energy of state  $s$  relative to the ground state. The quantum selection rules must summarize the conditions under which the matrix elements in the numerator must vanish, or are related by symmetry. As the symmetry conditions now involve the symmetry properties of the states 0,  $s$  and the operators  $\mu_i$ ,  $\mu_j$ , it is not immediately obvious how the classical selection rules and the quantum selection rules are related.

In this paper, this relationship is examined in detail. The quantum selection rules of the general matrix element products that arise from perturbation expansions of the interaction of a molecule or chromophore A (with point symmetry  $G_A$ ) with perturbing fields is developed in two stages. Using the above as an example, these are (1) the *operator selection rules*, which define the combinations of operators ( $\mu_i, \mu_j$ ) that are allowed under  $G_A$  (i.e., which polarization combinations are allowed); (2) the *state selection rules*, which define those states  $s$  that lead to finite matrix elements for a given ground state symmetry.

In this way, it is shown that the operator selection rules reduce to the classical selection rules of the corresponding tensor if the symmetry of the molecule is not appreciably reduced by the perturbation, and that the state selection rules are then additional quantum mechanical restraints on the possible intermediate states leading to finite contributions in the sum over states. In the procedure, any operator product is expressed in terms of a set of *invariant operators*, characteristics of  $G_A$ . These invariant operators may be interpreted as the quantum mechanical operators corresponding directly to finite classical observables.

The application of the procedure to polarizabilities is relatively trivial; the utility of the method is manifest, however, in applications to more complex perturbation expansions where the matrix element products may be larger or involve higher multipole operators. For example, in theories of induced circular dichroism,<sup>2</sup> the products

$$\langle 0 | Q_{ij} | s \rangle \langle s | m_k | 0 \rangle \quad (4)$$

and

$$\langle 0 | \mu_i | t \rangle \langle t | \mu_j | s \rangle \langle s | m_k | 0 \rangle \quad (5)$$

where  $Q_{ij}$  is a quadrupole operator and  $m_k$  the  $k$ th component of the magnetic dipole operator on A, describe quite different mechanisms for inducing circular dichroism in A (which is achiral in this case). As will be discussed later, application of the operator selection rules to elicit the nonvanishing terms leads to important physical consequences, and is capable of predicting purely on symmetry grounds which mechanism should predominate. As the operator selection rules reduce to the classical selection rules of the corresponding tensor, the results of the procedure described in the first section of this paper may also be derived using other tensorial techniques such as the use of vector coupling coefficients and the irreducible tensor method. The state selection rules, however, are also of vital importance in such problems, especially if the energy denominators in the perturbation expansion are fairly rapidly convergent as the summation over intermediate states is taken to states of increasingly higher energy; this highlights the limitations of classical tensorial approaches to molecule-field interaction problems.

The aim of this paper is therefore to provide the general

chemist with a simple, unified procedure for determining the generalized selection rules for direct application to perturbation expansions of interaction processes, without the restriction of using purely classical procedures. For the operator selection rules, character tables and the concept of irreducible representations are completely avoided, and the ambiguities for degeneracies that are a well-known limitation of conventional character tables are resolved. As the operator selection rules are generally significantly more restrictive than the state selection rules, such a procedure has distinct advantages over the usual procedure of using character tables for each separate matrix element.

### Observables and the Totally Symmetric Projection Operator

The definition of the operator selection rules necessitates some familiarity with the effects of symmetry operations on operators and observables, which may be developed in the following way. Consider the molecule or chromophore A to be of point symmetry  $G_A$ , with the symmetry operations of  $G_A$  denoted as  $R_\xi$ . The index  $\xi$  runs over the various operations; i.e., from 1 to  $h$ , where  $h$  is the order of the group. The operations  $R_\xi$  leave the molecule unchanged, so that symbolically

$$R_\xi A = A \text{ for all } \xi \quad (6)$$

This simply means that if any sequence or combinations of the symmetry operations  $R_\xi$  are performed on the molecule between the times  $t, t'$ , we will not be able to perceive any *measurable* difference in that molecule observed at time  $t$  and  $t'$ . It follows that any measurements made at time  $t$  must have the same value at time  $t'$ , be it energy, polarizability, permanent moments, shape, orientation, and so on. Thus any *observable* (i.e., any finite measurable quantity)  $O_b$  must also be invariant to all operations  $R_\xi$ ; i.e.,

$$R_\xi O_b = O_b \text{ for all } \xi \quad (7)$$

In group theory terms, we say that any observable must be totally symmetric to all operations of  $G_A$ , and must therefore be a basis for the totally symmetric representation of  $G_A$ .

The importance of this quantum mechanically is that the operators corresponding to such observables must also be totally symmetric for all the symmetry operations. For example, the Hamiltonian (the operator corresponding to the observable energy) also satisfies eq 7. For observables such as polarizability and circular dichroism, the definition of the corresponding operator is not as obvious because of the intermediate states; it is, in fact, the problem of defining such operators leading to a finite classical observable that forms the basis of the development of the operator selection rules. It follows from the above that a molecular observable can only be finite or measurable if the corresponding operator is totally symmetric. (This will be proved later.) This may be generalized in the following way.

Consider an operator  $f$  which correspond to an observable such that

$$R_\xi f = f \text{ for all } \xi \quad (8)$$

A more useful formulation of this criterion involves the projection operator  $\mathbf{P}^0$  of the totally symmetric representation of  $G_A$  which is simply defined as

$$\mathbf{P}^0 = \frac{1}{h} \sum_{\xi=1}^h R_\xi \quad (9)$$

For the operator  $f$  above, it follows directly from eq 8 that

$$\mathbf{P}^0 f = f \quad (10)$$

In the more general case where an operator  $f'$  does not satisfy eq 10, then  $\mathbf{P}^0$  will *project out* any totally symmetric component that  $f'$  may contain; i.e. either

$$P^0 f' = f^0 \quad (11)$$

where  $f^0$  corresponds directly to an observable (nonzero) as it satisfies eq 10, or

$$P^0 f' = 0 \quad (12)$$

if there is no observable corresponding to the operator  $f'$ . The conditions 11 and 12 form the basis of the operator selection rules.

### The Operator Selection Rules

**Matrix Element Products.** A proper understanding of the application of the generalized selection rules is facilitated by some knowledge of how the matrix element products arise in physical problems. The states of A are solutions of the free molecule Hamiltonian  $H_A$  of A such that

$$H_A |s\rangle = E_s |s\rangle \quad (13)$$

The effects of radiation or static fields lead to a perturbation  $V$  which is generally small with respect to  $H_A$ , so that the states of the perturbed Hamiltonian  $H_A + V$  may be determined as a perturbation expansion in the free molecule states  $s$ . Consider, for example, a simple perturbation by static fields, for which the perturbed state  $S$  is given by

$$|S\rangle = |s\rangle - \sum_{t \neq s} \frac{\langle t|V|s\rangle}{\Delta\epsilon_{ts}} |t\rangle + \dots \quad (14)$$

where  $V = -\boldsymbol{\mu} \cdot \mathbf{E}$  (for a static electric field) and  $V = -\mathbf{m} \cdot \mathbf{B}$  (for a static magnetic field), in the dipole approximation.  $\boldsymbol{\mu}$  and  $\mathbf{m}$  are the electric and magnetic dipole operators centered on A, and  $\Delta\epsilon_{ts} = \epsilon_t - \epsilon_s$ . Any observable will now involve matrix elements of states  $S$ , which in turn are expanded in terms of the free molecule states according to eq 14 above; i.e., any observable reduces to matrix element products involving only the free molecule states of a connected by operators centered only on A, plus other quantities such as field strengths and energy denominators which are completely independent of A coordinates. Equation 14 applies strictly to nondegenerate states. Degeneracies are readily incorporated by firstly determining the states  $s_j$  of a degenerate set by degenerate perturbation theory, and then applying eq 14 to each member of the set with the constraint that the sum over  $t$  omits all states  $s_j$ . As  $\Delta\epsilon_{ts_j}$  is approximately constant for all  $s_j$  for most perturbations of interest, it follows that any matrix element product on A may be simply summed over the relevant degeneracy and the energy denominator extracted outside such a summation.

For radiation fields, the A response may again be separated explicitly. The perturbation has the form<sup>3</sup>

$$H_{int} = -\boldsymbol{\mu} \cdot \mathbf{e}^\perp - \mathbf{m} \cdot \mathbf{b} \quad (15)$$

where  $\mathbf{e}^\perp$ ,  $\mathbf{b}$  are the radiative electric and magnetic fields, whose exact form need not concern us here as they factor outside of the molecular matrix elements. Higher multipole terms are readily incorporated into the above Hamiltonian. The radiative perturbation is time dependent, but the results are similar: the matrix element product on A may be factorized out, and any remaining factors will be independent of A coordinates. For molecule-molecule (or chromophore-chromophore) interactions, it is necessary to make a separable chromophore assumption (in which it is assumed that there is negligible electron overlap between the different chromophores) in order to get the matrix element products on A to factorize completely. The perturbation has the symbolic form

$$V = V_{AB}(dd) + V_{AB}(dQ) + V_{AB}(Qd) + V_{AB}(QQ) + \dots \quad (16)$$

where  $V_{AB}(Qd)$  is the operator representing the interaction of the quadrupole on A with a dipole on B, and so on. Each multipole operator acts only on the coordinates on the appropriate chromophore. Again, use of perturbation theory leads to an A-matrix element product, a B-matrix element product, and a term containing quantities independent of the coordinates of A and B.

It follows then that the observables from such perturbations will always reduce to terms of the general form

$$F = CF_A F_B \dots F_f \quad (17)$$

where  $F_A$  contains all matrix elements centered on A,  $F_B$  all those on B, and so on,  $F_f$  the factors pertaining directly to the perturbing fields, and  $C$  all other quantities such as energy or radial denominators. If A has point group symmetry  $G_A$ , it then follows that group theory will restrict the possible combinations of operator and state symmetries that give finite values of the matrix element product  $F_A$ .

The derivation of the operator selection rules proceeds through an important theorem which appears complex, but is actually conceptually simple and equally simple to apply. It may be stated in its most general form as follows.

*The operator selection rule theorem.*

If

$$F_A = \sum_a \sum_{\gamma, \lambda, \dots} \langle o_\gamma^i | P_\alpha^a | r_\lambda^j \rangle \langle r_\lambda^j | P_\alpha^a | \dots | P_\alpha^a | o_\gamma^i \rangle$$

and

$$P^0 \sum_a \prod_\alpha P_\alpha^a = \sum_b \prod_\alpha P_\alpha^b$$

then

$$F_A = \sum_b \sum_{\gamma, \lambda, \dots} \langle o_\gamma^i | P_\alpha^b | r_\lambda^j \rangle \langle r_\lambda^j | P_\alpha^b | \dots | P_\alpha^b | o_\gamma^i \rangle \quad (18)$$

$P^0$  is the projection operator of the totally symmetric representation defined in eq 9. The basis functions for A are assumed bases for the irreducible representations of  $G_A$  such that  $r_\lambda^j$  transforms as the  $\lambda$ th row of the  $j$ th irreducible representation  $\Gamma^j$ . The meaning of the summation over  $a$  will become clearer later, but allows for flexibility when linear combinations of matrix element products differing only in the nature of the operators appear in a certain physical problem. The summation over  $\gamma, \lambda, \dots$  is over all degeneracies. The product of the operators is defined in such a way that

$$R_\xi \left( \prod_\alpha P_\alpha^a \right) = \prod_\alpha (R_\xi P_\alpha^a) \quad (19)$$

It is important to note that as the operators generally connect different states, the above products are not necessarily commutative so that the order should be carefully retained.

To understand the meaning of this theorem, we can first ignore the sum over  $a$ , and treat each matrix element product separately. The theorem then states that we can replace the corresponding operator product (derived from simply ignoring all the wave functions) by its totally symmetric projection. If this projection vanishes, we have the situation of eq 12 where the matrix element product does not correspond to an observable, and vanishes. If the projection is finite, then the projected operator product satisfies eq 10 and corresponds to a finite observable. In particular, if

$$P^0 \prod_\alpha P_\alpha = \sum_b \prod_\alpha P_\alpha^b \quad (20)$$

then the initial matrix element product may be replaced by the sum of matrix element products formed by substituting the ordered wave functions back into each term of the projected operator product sum. This will then lead directly to an observable. Noting that the projected operator product sum

satisfies eq 11, it follows that it is totally symmetric, and we shall therefore refer to it as an *invariant operator*. Such an invariant operator corresponds directly to an observable, and any operator product will project under  $\mathbf{P}^0$  (and thus may be replaced by) one of the invariant operators characteristic of the point group, or zero.

In this way, we have generalized the simple procedure described earlier (eq 10-12) so that each invariant operator has a direct one-to-one correspondence to a classical observable. Furthermore, the invariant operators constitute the simplest set of operator product sums that are linearly independent and cannot be further reduced by symmetry. Any of the original matrix element products that are related by symmetry will manifest this interdependence in leading to projections in terms of the same invariant operators. The isomorphism of the classical observable and the invariant operator implies that they will be tensors of the same rank and type, and thus they must have analogous symmetry properties. It follows that the operator selection rules are, in effect, the exact quantum analogue of the classical selection rules for the macroscopic tensorial observable.

We return now to the sum over  $a$ . This may be used in certain physical problems (for example, when the molecule is averaged over all orientations with respect to the perturbing field) where the observable of interest is a simple sum of matrix element products which differ only in the nature of the operators, and have the same coefficients. This will be clarified in a later section, but suffice it to say at this stage that the projection of such a sum will generally be a *sum* of invariant operators.

**Proof of the Theorem.** An understanding of the theorem does not require a detailed understanding of the proof. We shall, however, include the proof here for completeness, and it may be developed from the following lemmatae.

*Lemma 1.*  $\sum_{\lambda} |r_{\lambda}^j\rangle \langle r_{\lambda}^j|$  is a basis for the totally symmetric representation of  $G_A$ .

Each operator  $R_{\xi}$  of  $G_A$  is unitary, so that if the set of degenerate functions  $\{r_{\lambda}^j\}$  span the space of  $\Gamma^j$ , then the set  $\{r_{\lambda\xi}^j\}$  span the same space, where

$$|r_{\lambda\xi}^j\rangle = R_{\xi}|r_{\lambda}^j\rangle$$

Then

$$\begin{aligned} \mathbf{P}^0 \sum_{\lambda} |r_{\lambda}^j\rangle \langle r_{\lambda}^j| &= \frac{1}{h} \sum_{\xi} \sum_{\lambda\xi} |r_{\lambda\xi}^j\rangle \langle r_{\lambda\xi}^j| \\ &= \sum_{\lambda\xi} |r_{\lambda\xi}^j\rangle \langle r_{\lambda\xi}^j| \\ &= \sum_{\lambda} |r_{\lambda}^j\rangle \langle r_{\lambda}^j| \end{aligned}$$

*Lemma 2.*  $\sum_{\lambda} \langle r_{\lambda}^j | Op | r_{\lambda}^j \rangle = \sum_{\lambda} \langle r_{\lambda}^j | \mathbf{P}^0 Op | r_{\lambda}^j \rangle$ .

The proof in this case follows the same lines:

$$\begin{aligned} \mathbf{P}^0 \sum_{\lambda} \langle r_{\lambda}^j | Op | r_{\lambda}^j \rangle &= \frac{1}{h} \sum_{\xi} \sum_{\lambda\xi} \langle r_{\lambda\xi}^j | R_{\xi} Op | r_{\lambda\xi}^j \rangle \\ &= \sum_{\lambda\xi} \langle r_{\lambda\xi}^j | \frac{1}{h} \sum_{\xi} R_{\xi} Op | r_{\lambda\xi}^j \rangle \\ &= \sum_{\lambda} \langle r_{\lambda}^j | \mathbf{P}^0 Op | r_{\lambda}^j \rangle \end{aligned}$$

The proof of the final theorem in the text now follows from noting that

$$\begin{aligned} F_A &= \sum_a \sum_{\gamma, \lambda, \dots} \langle o_{\gamma}^i | P_a^q | r_{\lambda}^j \rangle \langle r_{\lambda}^j | P_a^q | \dots | P_a^q | o_{\gamma}^i \rangle \\ &= \sum_{\gamma} \langle o_{\gamma}^i | Op | o_{\gamma}^i \rangle \end{aligned}$$

where

$$Op = \sum_a \left\{ P_a^q \left( \sum_{\lambda} |r_{\lambda}^j\rangle \langle r_{\lambda}^j| \right) P_a^q (\dots) P_a^q \right\}$$

Using lemma 2 for the operator defined above, and noting from lemma 1 that each projection operator sum in round brackets must transform as the totally symmetric representation of  $G_A$ , it follows that if

$$\mathbf{P}^0 \sum_a \prod_{\alpha=1}^N P_{\alpha}^a = \sum_b \prod_{\alpha=1}^N P_{\alpha}^{b'}$$

then

$$\mathbf{P}^0 Op = \sum_b \left\{ P_b^{b'} \left( \sum_{\lambda} |r_{\lambda}^j\rangle \langle r_{\lambda}^j| \right) P_b^{b'} (\dots) P_b^{b'} \right\}$$

This is the required result.

**Generalizations.** The application of the operator selection rules is not merely restricted to  $A$ .  $F_B$  must satisfy similar conditions under the symmetry of  $B$ , and  $F_f$  must satisfy the selection rules under the symmetry of the charge system leading to the field quantities about the chosen origin. In the latter case, the origin at which the field quantities are evaluated must also be used as the origin of the point group of the charge distribution. An example of this is the case where the ligand field about a central metal ion is represented by its electric field and the derivatives thereof at the central ion; the field products arising from such perturbations must be totally symmetric under the operations of the symmetry group of the ligand field.

Another generalization that is important in processes such as Raman scattering or vibronic coupling relates to the appearance of vibrational matrix elements in the product for  $A$ . If simple perturbation theory is used, the matrix element products may be written in the form

$$F_A = F_A^e F_A^v$$

where  $F_A^e$  is the matrix element product depending only on the electronic coordinates of  $A$  (for a fixed nuclear configuration), and  $F_A^v$  that product depending solely on nuclear coordinates. The operator selection rules may then be applied to  $F_A^e$  and  $F_A^v$  separately, as the symmetry operations of  $G_A$  may be applied either to all the electronic coordinates or all the nuclear coordinates.

### Transformations of Operator Products

The beauty of expressing perturbation expansions in terms of tensorial operators such as multipole moment operators lies not only in their generality, but also in their simple transformation properties under point symmetry operations. This may be illustrated with reference to the quadrupole moment operator, which may be defined for our purposes as

$$Q_{\alpha\beta} = e\alpha\beta \tag{21}$$

where  $\alpha, \beta$  run over the Cartesian operators  $x, y$  and  $z$ , and  $e$  is the electronic charge. (The general definition may be taken to be  $\hat{Q} = e\mathbf{r}\mathbf{r}$ , where  $\mathbf{r}$  is the Cartesian vector  $\mathbf{r} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k}$  and  $\mathbf{i}, \mathbf{j}, \mathbf{k}$  are unit vectors along the respective Cartesian axes.) The application of  $R_{\xi}$  to this particular quadrupole operator may be written

$$R_{\xi} Q_{\alpha\beta} = e(R_{\xi}\alpha)(R_{\xi}\beta) \tag{22}$$

The transformation properties of the electric multipole operators may thus be found directly from a knowledge of the transformation properties of the Cartesian operators  $x, y, z$ . These may be determined in the following way. Letting  $\mathbf{i}, \mathbf{j}, \mathbf{k}$  be the unit vectors in the  $x, y, z$  directions as above, the operation of  $R_{\xi}$  to these unit vectors may be written as

$$R_{\xi}\mathbf{i} = a_{xx}^{\xi}\mathbf{i} + a_{xy}^{\xi}\mathbf{j} + a_{xz}^{\xi}\mathbf{k} \tag{23}$$

$$R_{\xi} \mathbf{j} = a_{jx}^{\xi} \mathbf{i} + a_{jy}^{\xi} \mathbf{j} + a_{jz}^{\xi} \mathbf{k} \quad (24)$$

$$R_{\xi} \mathbf{k} = a_{kx}^{\xi} \mathbf{i} + a_{ky}^{\xi} \mathbf{j} + a_{kz}^{\xi} \mathbf{k} \quad (25)$$

The  $a_{\alpha\beta}^{\xi}$  are simply the direction cosines of the transformed basis vectors relative to the original set. Returning to the quadrupole operator, we have

$$\begin{aligned} R_{\xi} Q_{\alpha\beta} &= e \left( \sum_{\delta} a_{\alpha\delta}^{\xi} \delta \right) \left( \sum_{\delta'} a_{\beta\delta'}^{\xi} \delta' \right) \\ &= \sum_{\delta, \delta'} a_{\alpha\delta}^{\xi} a_{\beta\delta'}^{\xi} Q_{\delta\delta'} \end{aligned} \quad (26)$$

$\delta, \delta',$  etc., also run over the Cartesians  $x, y, z$ . This is readily generalized to any electric multipole product. For example, if  $\boldsymbol{\mu} = e\mathbf{r}$  is the electric dipole operator,

$$\begin{aligned} R_{\delta} \mu_{\alpha} Q_{\beta\gamma} &= (R_{\xi} \mu_{\alpha})(R_{\xi} Q_{\beta\gamma}) \\ &= \sum_{\delta, \delta', \delta''} a_{\alpha\delta}^{\xi} a_{\beta\delta'}^{\xi} a_{\gamma\delta''}^{\xi} \mu_{\delta} Q_{\delta'\delta''} \end{aligned} \quad (27)$$

Electric multipole moment operators are basically defined in terms of  $\mathbf{r}$ , which is a *polar vector*. The transformation properties of such a vector are essentially those of a directed arrow (e.g., antisymmetric to inversion). The magnetic dipole operator  $\mathbf{m}$ , however, is proportional to a vector product of two polar vectors; viz.  $\mathbf{r} \times \mathbf{p}$ , where  $\mathbf{r}$  is the Cartesian vector from the moment origin to the linear momentum vector  $\mathbf{p}$ . As each of these polars separately changes sign under inversion, the magnetic dipole moment operator is symmetric, and is referred to as an *axial vector*. The cross product has the properties of a current loop, so that the transformation properties of the magnetic moment are not those of the directed arrow, but rather those of the current loop from which it derives. The direction of the vector  $\mathbf{m}$  is determined from that of the transformed current loop using the usual right-hand rule. These transformation properties are, however, simply related to those of a polar vector in that

$$R_{\xi} m_{\alpha} = (-1)^I \sum_{\delta} a_{\alpha\delta}^{\xi} m_{\delta} \quad (28)$$

where  $I = 0$  if  $R_{\xi}$  is a proper rotation, and  $I = 1$  if  $R_{\xi}$  is an improper rotation. Polar and axial vectors transform in the same way for proper rotations, but in an opposite sense for improper rotations.

Any operator comprising tensorial operators (axial or polar) may thus be determined directly if the set of direction cosines  $a_{\alpha\beta}^{\xi}$  is known for the basis vectors for each symmetry operation of the relevant group. These quantities are not generally available, and have therefore been conveniently tabulated in the Appendix for the finite point groups. For the operator selection rules, we will see that these tables are more useful and complete than the conventional character tables.

### Applications of the Operator Selection Rules

One of the areas where these rules have proved extremely useful to this author is the field of circular dichroism, which is essentially the interaction of a molecule or chromophore with circularly polarized radiation fields (or, alternatively, with chiral photons). The examples to be discussed in this section are therefore drawn from this general area. It is stressed, however, that the methods are of widespread application, and it is hoped that they will prove as useful in other areas as they have been to this author in theories of circular dichroism.

**Natural Circular Dichroism.** The operator selection rules may be used to determine which of the point groups can lead to natural circular dichroism (CD). The expression for the CD of the 0 to  $s$  transition of a molecule  $A$  (averaged over all orientations of the molecule relative to the radiation field) has the form

$$R_{0s} = \sum_{\alpha} \text{Im} \langle 0 | \mu_{\alpha} | s \rangle \langle s | m_{\alpha} | 0 \rangle \quad (29)$$

We shall in particular consider the groups  $C_4$  and  $S_4$ . It is worth discussing briefly how the selection rules could be determined for these cases using conventional character tables.<sup>4</sup> Applying the usual rules for each matrix element (i.e., that the integrand of each matrix element must be totally symmetric) and assuming for simplicity that the ground state is totally symmetric, then the molecule will be CD active if there exists a state  $s$  such that

$$\Gamma^s \otimes \Gamma(\mu_{\alpha}) \subset \Gamma^0$$

and

$$\Gamma^s \otimes \Gamma(m_{\alpha}) \subset \Gamma^0$$

where  $\Gamma(\mu_{\alpha})$  is the irreducible representation generated by  $\mu_{\alpha}$ ,  $\Gamma^0$  is the totally symmetric representation, and so on. For  $\alpha = z$  (the symmetry axis), the  $A$  to  $A$  transition will be CD active for  $C_4$ , but not for  $S_4$ . For the  $A$  to  $E$  transition, however, the character tables *suggest* that this transition is *potentially* active for both point groups. This is simply the result of the character tables containing incomplete information for degenerate representations.

We now apply the operator selection rules directly, and thus illustrate how the tables in the Appendix contain *all* the information we require. The second condition of eq 18 is applied directly, so that for  $C_4$ ,

$$\begin{aligned} \mathbf{P}^0 \sum_a \prod_{\alpha} P_{\alpha}^a &= \mathbf{P}^0 (\mu_x m_x + \mu_y m_y + \mu_z m_z) \\ &= (\mu_x m_x + \mu_y m_y + \mu_z m_z) \end{aligned}$$

The operator product corresponds directly to an observable. This should clarify why the sum over  $a$  was incorporated into the general theorem. Note, however, that  $\mathbf{P}^0$  acting on the operator product *sum* will not necessarily give a single invariant operator, but must give a sum of invariant operators (or zero) as we shall presently. For  $S_4$ , it follows immediately that

$$\mathbf{P}^0 \sum_{\alpha} \mu_{\alpha} m_{\alpha} = 0$$

so that  $S_4$  is unambiguously an achiral point group. There can be no CD activity for any state.

To find the invariant operators, the projections of the separate matrix element products must be determined. For  $C_4$ ,

$$\begin{aligned} \mathbf{P}^0(\mu_{\alpha} m_{\beta}) &= 0 \quad \alpha \neq \beta \\ \mathbf{P}^0(\mu_x m_x) &= \mathbf{P}^0(\mu_y m_y) = 1/2(\mu_x m_x + \mu_y m_y) \\ \mathbf{P}^0(\mu_z m_z) &= \mu_z m_z \end{aligned}$$

so that the invariant operators are  $1/2(\mu_x m_x + \mu_y m_y)$  and  $\mu_z m_z$ . For  $S_4$ ,

$$\begin{aligned} \mathbf{P}^0(\mu_{\alpha} m_{\beta}) &= 0 \quad \alpha \neq \beta \text{ or } \alpha = \beta = z \\ \mathbf{P}^0(\mu_x m_x) &= -\mathbf{P}^0(\mu_y m_y) = 1/2(\mu_x m_x - \mu_y m_y) \end{aligned}$$

The only invariant operator is  $1/2(\mu_x m_x - \mu_y m_y)$ . Although this corresponds potentially to an observable, it does not correspond to the observable for CD, which requires an operator product of the form  $1/2(\mu_x m_x + \mu_y m_y)$ .

The above is a simple example, but it highlights some significant features: (1) Conventional character tables are inadequate in dealing with operator or state degeneracies. (2) Irreducible representations do not enter the selection rules. (3) The operator selection rules are generally extremely restrictive; for the above groups, the general tensor  $\boldsymbol{\mu}\mathbf{m}$  has no finite off-diagonal elements. (4) The number of invariant operators is generally significantly smaller than the possible number of

operator products. (5) The projection of a single operator product will always be zero or generate an invariant operator (multiplied by at most a numerical constant), but the projection of an operator product sum may be zero or generate a linear combination of the invariant operators. (6) The invariant operators are explicitly determined through a purely algebraic procedure. The manipulative algebra increases with the order of the operator products from which the invariant operators are generated, but the method remains conceptually simple, and general.

**Induced Circular Dichroism.** We conclude this section with an example from the recent literature comparing two possible dynamic coupling mechanisms for the induction of CD in an achiral chromophore. No attempt will be made here to detail the mechanisms, as this is fully discussed elsewhere.<sup>5,6</sup> Suffice it to say that the CD appearing at the magnetic dipole allowed 0 to *s* transition of the achiral chromophore A for the two mechanisms give rise to eq 4 and 5 as the relevant matrix element products on A. The product of eq 4 arises from first-order perturbation theory, but involves a higher multipole transition moment. The product of eq 5 is purely dipolar, but comes from second-order perturbation theory. The two mechanisms may therefore be competitive.

It is possible, however, to differentiate between them purely on symmetry grounds. Consider the following possible symmetries for the achiral chromophore. (These symmetries arise commonly for the metal ion chromophore in metal complexes).

$$O_h D_{4h} D_{2d} C_{4v} C_{2v}$$

Each group is a subgroup of  $O_h$  with decreasing symmetry toward  $C_{2v}$ . Both of the above products have the transformation properties of the product  $(\alpha\beta m_\gamma)$ , which may be summarized as follows:

$$\text{All groups: } \mathbf{P}^0(\alpha\beta m_\gamma) = 0 \quad \text{if any of } \alpha, \beta, \gamma \text{ are the same} \quad (30)$$

$$\begin{aligned} O_h: \mathbf{P}^0(xym_z) &= \mathbf{P}^0(yzm_x) = \mathbf{P}^0(zxm_y) \\ &= -\mathbf{P}^0(yxm_z) = -\mathbf{P}^0(zym_x) \\ &= -\mathbf{P}^0(xzm_y) = 1/6[(xy - yx)m_z \\ &\quad + (yz - zy)m_x + (zx - xz)m_y] \end{aligned} \quad (31)$$

$$\begin{aligned} D_{4h}, D_{2d}, C_{4v}: \mathbf{P}^0(xym_z) &= -\mathbf{P}^0(yxm_z) \\ &= 1/2[(xy - yx)m_z] \end{aligned}$$

$$\begin{aligned} \mathbf{P}^0(yzm_x) &= -\mathbf{P}^0(xzm_y) = 1/2[yzm_x - xzm_y] \\ \mathbf{P}^0(zxm_y) &= -\mathbf{P}^0(zym_x) = 1/2[zxm_y - zym_x] \end{aligned} \quad (32)$$

$$C_{2v}: \quad \mathbf{P}^0(\alpha\beta m_\gamma) = [\alpha\beta m_\gamma] \quad (33)$$

Thus there is only one invariant operator for  $O_h$ , three for  $D_{4h}$ ,  $D_{2d}$ , and  $C_{4v}$ , and six for  $C_{2v}$ . The products are not necessarily commutative as they may refer to transition moments between different states.

Consider first the mechanism described by eq 4. The quadrupole tensor element  $Q_{\alpha\beta}$  transforms as  $\alpha\beta$  so that the overall operator product transforms as  $\alpha\beta m_\gamma$  as above. However, as  $Q_{\alpha\beta}$  is an operator within a single transition moment, it follows from the symmetric nature of the quadrupole tensor that  $Q_{\alpha\beta} = Q_{\beta\alpha}$  so that  $Q_{\alpha\beta} - Q_{\beta\alpha} = 0$ . The above eq 30–33 then simplify to the following:

$$O_h: \quad \mathbf{P}^0(Q_{\alpha\beta} m_\gamma) = 0 \text{ for all } \alpha, \beta, \gamma \quad (34)$$

$$\begin{aligned} D_{4h}, D_{2d}, C_{4v}: \mathbf{P}^0(Q_{xy} m_z) &= 0 \\ \mathbf{P}^0(Q_{yz} m_x) &= \mathbf{P}^0(Q_{zy} m_x) = -\mathbf{P}^0(Q_{xz} m_y) \\ &= -\mathbf{P}^0(Q_{zx} m_y) = 1/2(Q_{yz} m_x - Q_{xz} m_y) \end{aligned} \quad (35)$$

$$C_{2v}: \quad \mathbf{P}^0(Q_{\alpha\beta} m_\gamma) = \mathbf{P}^0(Q_{\beta\alpha} m_\gamma) = Q_{\alpha\beta} m_\gamma \quad (36)$$

The important feature of the above is that all terms are zero for  $O_h$ , so that this mechanism cannot contribute to the CD induced in A for any magnetic dipole allowed transition. For  $D_{4h}$ ,  $D_{2d}$ , and  $C_{4v}$ , only transitions for which the magnetic dipole transition moment is *x* or *y* polarized may become CD active through this mechanism. We return to this anon.

For the purely dipolar mechanism of eq 5, there is no commutativity for the  $\alpha\beta$  products, as the individual operators  $\alpha, \beta$  appear in different matrix elements. The transformation properties are therefore precisely those of eq 30–33. It follows that the magnetic transition moment of the CD-active transition may have any polarization.

These deductions may be directly compared with experimental results. It is found that qualitatively comparable CD bands appear for all polarizations of the magnetic transition moment irrespective of the symmetry of the achiral chromophore.<sup>7</sup> This strongly supports the dipolar mechanism, and illustrates the potency of the procedure for somewhat more complex problems.

### State Selection Rules

The main thrust of this work has been directed at the operator selection rules for the simple reason that they are usually the most restrictive. The state selection rules, however, have important additional consequences.

The difficulty of defining the state selection rules as precisely as those for the operators stems from the simple fact that the wave functions for a molecule have no direct correspondence with classical observables in the way that an invariant operator has. The only restrictions arise from their being eigenfunctions of an invariant operator (the Hamiltonian), so that they must transform as one of the irreducible representations of the point group of the molecule. The wave function may thus be specified by the irreducible representation for which it forms a basis, but any further specification requires expansion in terms of some chosen basis set in such a way as to minimize the energy.

The state selection rules are therefore defined as the usual conditions for nonvanishing matrix elements—with the important simplification that only the components of the invariant operators need be tested; i.e., for the matrix element

$$\langle a | P | b \rangle$$

the state selection rule is simply

$$\Gamma^a \otimes \Gamma^P \otimes \Gamma^b \subset \Gamma^0 \quad (37)$$

where  $\Gamma^a$  is the irreducible representation generated by *a*,  $\Gamma^0$  is the totally symmetric representation, and so on. These conditions may be readily determined using conventional character tables; it is, in fact, for such problems involving quantities of unspecified functional form that conventional character tables are most studied. If the functional forms of the wave functions (written  $\psi_a, \psi_b$ ) are known, then we could generalize the state selection rules to

$$\langle a | P | b \rangle = \int [\mathbf{P}^0(\psi_a^* P \psi_b)] d\tau \quad (38)$$

i.e., only the totally symmetric projection of the integrand can contribute to the final matrix element.

The importance of the state selection rules is best illustrated with a particular example. Consider the matrix element







Table I (Continued)

Operation	Transformation of (x,y,z)		C <sub>1</sub>	C <sub>5</sub>	C <sub>i</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	D <sub>2</sub>	D <sub>3</sub>	D <sub>4</sub>	D <sub>5</sub>	D <sub>6</sub>	C <sub>2v</sub>	C <sub>3v</sub>	C <sub>4v</sub>
*S <sub>8</sub> <sup>7</sup> (001)	(x - y)/√2	(x + y)/√2	-z															
*S <sub>10</sub> (001)	c $\frac{\pi}{5}$ x + s $\frac{\pi}{5}$ y	-s $\frac{\pi}{5}$ x + c $\frac{\pi}{5}$ y	-z															
*S <sub>10</sub> <sup>3</sup> (001)	-s $\frac{\pi}{10}$ x + c $\frac{\pi}{10}$ y	-c $\frac{\pi}{10}$ x - s $\frac{\pi}{10}$ y	-z															
*S <sub>10</sub> <sup>7</sup> (001)	-s $\frac{\pi}{10}$ x - c $\frac{\pi}{10}$ y	c $\frac{\pi}{10}$ x - s $\frac{\pi}{10}$ y	-z															
*S <sub>10</sub> <sup>9</sup> (001)	c $\frac{\pi}{5}$ x - s $\frac{\pi}{5}$ y	s $\frac{\pi}{5}$ x + c $\frac{\pi}{5}$ y	-z															
*S <sub>12</sub> (001)	(√3x + y)/2	(-x + √3y)/2	-z															
*S <sub>12</sub> <sup>5</sup> (001)	(-√3x + y)/2	(-x - √3y)/2	-z															
*S <sub>12</sub> <sup>7</sup> (001)	(-√3x - y)/2	(x - √3y)/2	-z															
*S <sub>12</sub> <sup>11</sup> (001)	(√3x - y)/2	(x + √3y)/2	-z															
*σ (100)	-x	y	z													0	0	
*σ (010)	x	-y	z													0	0	
*σ (001)	x	y	-z	0														
*σ (110)	-y	-x	z															0
*σ (1̄10)	y	x	z															0
*σ (101)	-z	y	-x															
*σ (1̄01)	z	y	x															
*σ (011)	x	-z	-y															
*σ (01̄1)	x	z	y															
*σ (√310)	(-x - √3y)/2	(-√3x + y)/2	z															0
*σ (√3̄10)	(-x + √3y)/2	(√3x + y)/2	z															0
*σ (1√30)	(x - √3y)/2	(-√3x - y)/2	z															
*σ (1̄√30)	(x + √3y)/2	(√3x - y)/2	z															
*σ (c $\frac{\pi}{12}$ s $\frac{\pi}{12}$ 0)	(-√3x - y)/2	(-x + √3y)/2	z															
*σ (c̄ $\frac{\pi}{12}$ s $\frac{\pi}{12}$ 0)	(-√3x + y)/2	(x + √3y)/2	z															
*σ (s $\frac{\pi}{12}$ c $\frac{\pi}{12}$ 0)	(√3x - y)/2	(-x - √3y)/2	z															
*σ (s̄ $\frac{\pi}{12}$ c $\frac{\pi}{12}$ 0)	(√3x + y)/2	(x - √3y)/2	z															
*σ (c $\frac{\pi}{8}$ s $\frac{\pi}{8}$ 0)	(-x - y)/√2	(-x + y)/√2	z															
*σ (c̄ $\frac{\pi}{8}$ s $\frac{\pi}{8}$ 0)	(-x + y)/√2	(x + y)/√2	z															
*σ (s $\frac{\pi}{8}$ c $\frac{\pi}{8}$ 0)	(x - y)/√2	(-x - y)/√2	z															
*σ (s̄ $\frac{\pi}{8}$ c $\frac{\pi}{8}$ 0)	(x + y)/√2	(x - y)/√2	z															
*σ (c $\frac{\pi}{10}$ s $\frac{\pi}{10}$ 0)	-c $\frac{\pi}{5}$ x - s $\frac{\pi}{5}$ y	-s $\frac{\pi}{5}$ x + c $\frac{\pi}{5}$ y	z															
*σ (c̄ $\frac{\pi}{10}$ s $\frac{\pi}{10}$ 0)	-c $\frac{\pi}{5}$ x + s $\frac{\pi}{5}$ y	s $\frac{\pi}{5}$ x + c $\frac{\pi}{5}$ y	z															
*σ (s $\frac{\pi}{5}$ c $\frac{\pi}{5}$ 0)	s $\frac{\pi}{10}$ x - c $\frac{\pi}{10}$ y	-c $\frac{\pi}{10}$ x - s $\frac{\pi}{10}$ y	z															
*σ (s̄ $\frac{\pi}{5}$ c $\frac{\pi}{5}$ 0)	s $\frac{\pi}{10}$ x + c $\frac{\pi}{10}$ y	c $\frac{\pi}{10}$ x - s $\frac{\pi}{10}$ y	z															

product of eq 5. There are two important features arising from the explicit perturbation expansion which have been omitted:<sup>2</sup> (1) the sum over the intermediate states  $t$  (the observable being measured at the transition energy of a specified state  $s$ ); (2) an energy denominator containing the factor  $\Delta\epsilon_{ts} = \epsilon_t - \epsilon_s$  where  $\epsilon_t$ ,  $\epsilon_s$  are the transition energies of states  $t$  and  $s$ , respectively. For the matrix element product

$$\langle 0 | \mu_\alpha | t \rangle \langle t | \mu_\beta | s \rangle \langle s | m_\gamma | 0 \rangle$$

the state selection rules summarize the restrictions on the intermediate state  $t$  for given symmetries of the ground 0 and excited  $s$  states. These are

- (i)  $\Gamma^0 \otimes \Gamma^t \otimes \Gamma^{s'} \subset \Gamma^0$
- (ii)  $\Gamma^s \otimes \Gamma^t \otimes \Gamma^\beta \subset \Gamma^0$
- (iii)  $\Gamma^s \otimes \Gamma^0 \otimes \Gamma^{m_\gamma} \subset \Gamma^0$  (39)

Note that the operator selection rules have already restricted the  $\alpha\beta\gamma$  to certain combinations ( $xyz$  and permutations thereof for the groups discussed earlier) so that the symmetry of  $t$  will be severely restricted. The sum over states is then confined to

those satisfying the state selection rules (eq 39) for the invariant operators determined from the operator selection rules. If this were the only benefit of the generalized selection rules, we would still have quite a problem in summing over the limited set of states of the appropriate symmetry. However, the hitherto neglected energy denominators in many perturbation expansions may force a convergence in the overall contributions as we go to higher energy intermediate states. For example, if the energy denominator contains factors of the form  $\Delta\epsilon_{ts} = \epsilon_t - \epsilon_s$ , then the major contributions will come from states  $t$  for which  $\Delta\epsilon_{ts} \ll \epsilon_s \approx \epsilon_t$  (the close levels approximation). For some problems, only one intermediate state need be considered.<sup>2</sup>

In fact, use of the combination of the operator and state selection rules, coupled with a close examination of energy denominators and the nature of the particular problem, frequently simplifies a seemingly complex perturbation expansion to a few terms connecting only a small number of states. This can give much more insight into a molecular response property than an approach based purely on classical tensorial observables, and may in turn be utilized for assigning molecular states



group in whose vertical column it lies has the operation given horizontally at the left-hand side of the table, with the relevant transformation properties. The totality of entries in a vertical column thus corresponds to the total set of symmetry operations of that particular point group.

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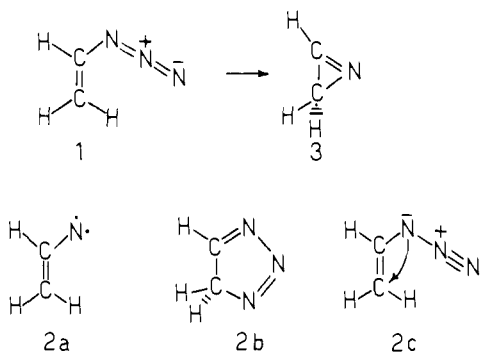
## Theoretical Study of the Vinyl Azide-*v*-Triazole Isomerization

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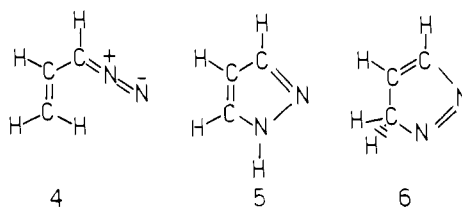
**Abstract:** The properties of the cyclization of vinyl azide to *v*-triazole are studied using the STO-3G minimal basis set to construct an energy hypersurface. Then, a split valence 4-31G basis set is used for the geometries found for the transition state, vinyl azide, and *v*-triazole. The activation energy,  $E_a$ , is 32.9 kcal/mol in STO-3G and 41.4 kcal/mol in 4-31G; the heat of reaction is  $-10.8$  kcal/mol in 4-31G. Various limited configuration interactions (CI) were employed for points around the SCF transition state but the new transition state differed only slightly. The various properties calculated, along with localized molecular orbitals, permit the reaction to be classed as a 1,5-dipolar electrocyclic reaction. In addition, using the geometry of the vinyl azide transition state as a start, a similar transition state was found for the isoelectronic species, protonated azidoazomethine. The activation energy in STO-3G is 42.9 kcal/mol, and is to be compared with 12.3 kcal/mol previously found for the cyclization of neutral azidoazomethine.

The thermolysis or photolysis of vinyl azides **1** give azirines **3** as products or as intermediates for final products.<sup>1</sup> Three mechanisms for the formation of azirines have been proposed,<sup>2</sup> the first of which, formation of a vinyl nitrene **2a**, has been



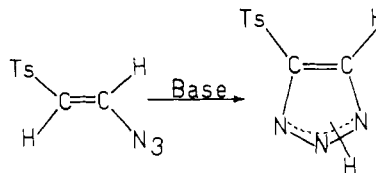
excluded on the basis of kinetic results which show that vinyl azides give moderate activation energies (26–30 kcal/mol) and low entropies of activation ( $-3$  to  $+5$  eu).<sup>3</sup> This is in contrast with the decomposition of aryl azides to nitrenes ( $\Delta E_a = 39$  kcal/mol,  $\Delta S^\ddagger = 19$  eu for phenyl azide).<sup>4</sup> Kinetic evidence has not been conclusive, however, in choosing between the two remaining proposed mechanisms. One would have the formation of *v*-triazole **2b** which would further lose  $\text{N}_2$  to give azirine **3**. The other one would have a concerted process **2c** wherein the loss of  $\text{N}_2$  is simultaneous with ring closure.

The present work is an ab initio theoretical study of the first part of the second proposed mechanism, closure of vinyl azide to *v*-triazole. Evidence for the involvement of this intermediate comes from the cyclization of diazopropene **4**, which is isoelectronic with vinyl azide **1**. An intermediate has been detected<sup>4</sup> in the formation of product 1*H*-pyrazole **5** and has been attributed<sup>4</sup> to 3*H*-pyrazole **6**. The kinetics of this reaction have

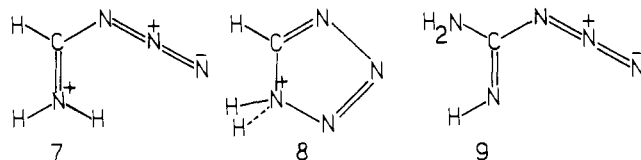


been studied<sup>3</sup> and found to be similar to those for vinyl azides ( $E_a = 32.0$  kcal/mol,  $\Delta S^\ddagger = -3.6$  eu).

Additional interest as to the involvement of *v*-triazole comes from the findings that vinyl azides possessing an acidic terminal H atom undergo a facile base-promoted cyclization to triazoles.<sup>5</sup>



In addition to the vinyl azide cyclization of this study, the geometries found for vinyl azide and the transition state are then used as starting points to study the closing of protonated azidoazomethine **7** to protonated tetrazole **8**. This expectation



of similar transition states has been used to explain the stability of the azide form of substituted azidoazomethines in acid solution. Neutral guanyl azide **9** cyclizes spontaneously to 5-aminotetrazole<sup>6</sup> but the salts  $[(\text{NH}_2)_2\text{CN}_3]^+\text{X}^-$  have the open azide structure.