spacings were, however, not reproducible and did not show any ordered pattern.

Orientation of the crystallites was not accomplished by stretching the melted polymers. It is obvious that additional study is necessary in order to understand more completely the structure and arangement of the crystallites.

Melting Points as a Function of the Length of the Straight Side Chains.[13-17]—The melting points of the even-numbered *n*-alkyl chain (12 to 18 carbon atoms) alcohols,[18] acids,[18,19] paraffins,[14] polymethacrylates and polyacrylates are plotted in Fig. 4 as a function of the number of carbon atoms in the chain. It may be noted in Fig. 4 that the curves (except for the polymethacrylates) are essentially similar in shape.

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(17) W. E. Garner, F. C. Madden and J. E. Rushbrooke, *ibid.*, 2491 (1926).

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BROOKLYN, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Structures and π-Electron Spectra. II. The Transformation Matrix[1,2]

BY WILLIAM T. SIMPSON AND CATHERINE WORSFOLD LOONEY

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A definite procedure is presented for the construction of a transformation matrix which relates π-electron spectra to structures. Arbitrariness in the transformation matrix which may exist even after the incorporation of symmetry is discussed. A method of removing the arbitrariness is shown, as applied to crystal violet and *p*-methoxy malachite green.

Introduction

In a previous paper,[3] hereafter called paper I, a scheme for using structures as an aid in understanding π-electron spectra was presented. The scheme usually requires the solution of a preliminary problem, preliminary in the sense that its solution does not lead directly to theoretical predictions but only "paves the way." The preliminary problem is to transform suitably to non-diagonal form a given observed set of term values arranged along the diagonal of a square matrix. The matrix before transformation is considered to be the dynamic variable electronic energy in the Heisenberg representation.

The actual method of computing the transformation matrix for forming a new non-diagonal matrix of the energy was not given in paper I (though an example of the procedure to be followed was given in Appendix I). In the present paper the object is to define a particular representation in which the energy is non-diagonal, and which is called the structure representation; and to show how to construct the transformation matrix. The transformation matrix is not always unambiguously determined, and the ambiguity is given detailed treatment. A particular method of removing the ambiguity is described, using as examples a given molecule (crystal violet) and another (*p*-methoxy malachite green) which is considered as a perturbation. This choice of examples is also a preparation for paper III of this series, which deals at length with triphenylmethane dyes, and which will illustrate the making of predictions using the scheme in paper I. We now give a formal statement of the object of this paper.

Given a diagonal energy matrix **E** the problem is to find the transformation matrix **S** such that

$$\mathbf{E}' = \mathbf{S}^{-1}\mathbf{E}\mathbf{S}$$

where **E′** is in the structure representation, a representation defined by the requirement that the matrix elements be labeled with indices which correspond to structures. Unit vectors in this representation refer to the same quantum states (not stationary states) as described by wave functions which correspond to structures, in that the squares of the wave functions transform like the corresponding structures.

Applying the methods of part I of paper I we consider as given (i) *n* structures and their behavior under the operations of the group of the molecule; (ii) *n* energy levels (the observed spectroscopic term values which are the elements of the diagonal matrix **E**) and their species. In addition we know that (iii) the transformation properties of the structures are consistent with the species of the states of the molecule.

Preliminary Discussion.—In this section we shall discuss qualitatively how the transformation matrix is to be calculated, but first shall present the notation that is to be used subsequently. The species of the levels are arranged serially in the order of the diagonal elements of **E**. There are *n* elements

$$E_{11}, E_{22}, E_{33}, \ldots, E_{nn}$$

with species[4]

$$\Gamma_\alpha, \Gamma_\beta, \Gamma_\gamma, \ldots, \Gamma_\nu$$

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(1) Presented in part at the Spectroscopy Symposium, Ohio State University, Columbus, Ohio, June 1953.

(2) Supported under Contract R-351-20-2 Air Research and Development Command.

(3) W. T. Simpson, THIS JOURNAL, **75**, 597 (1953).

(4) This notation is used in preference to $\Gamma_1, \Gamma_2, \Gamma_3, \ldots, \Gamma_n$ because conventionally Γ with a numerical subscript stands for a particular species, instead of one of serially numbered species for a particular dynamical system.

some of which may be the same. To these elements correspond n stationary state wave functions

$$\psi_1, \psi_2, \psi_3, \ldots, \psi_n$$

The wave functions are unknown, except in principle. The structures are also arranged serially.

$$(1), (2), (3), \ldots, (n)$$

(parentheses are used to denote structures) and the assumption is made that to each structure there corresponds a wave function (not an energy eigenstate except in unusual circumstances)

$$\psi^1, \psi^2, \psi^3, \ldots, \psi^n$$

and that the n wave functions are mutually orthogonal. Note that stationary state ψ's are labeled with subscripts and structure ψ's with superscripts.

The most common change of representation in matrix mechanics occurs with the diagonalization of a matrix. A matrix $\mathbf{E}'$ is made diagonal by the transformation

$$\mathrm{E} = \mathrm{SE'S^{-1}}$$

S and S^{-1} are obtained using a theorem in matrix algebra which states that the columns of S^{-1} are the normalized orthogonal eigenvectors of $\mathbf{E}'$.

In this paper the fundamental task is to perform the reverse transformation

$$\mathrm{E'} = \mathrm{S^{-1}ES}$$

that is, to find $\mathbf{S}$ (or S^{-1}). The idea for the solution of the problem is to use the fact that S is the same as in the companion diagonalization problem. Turning to the diagonalization problem, we find that we are already familiar with the process of finding an S which provides a transformation at least partially into the Heisenberg representation. This operation is usually referred to by another name, "factoring the secular equation." Since the transformation properties of the structures are known, we are able, as it were, to factor the secular equation for the problem of a linear variation method type calculation involving interactions among wave functions corresponding to structures. If the secular equation can be factored unambiguously (complete determination of ψ_i's as linear combinations of ψ^i's) S can be constructed unambiguously.

We have now to translate into the vectorial language of matrix mechanics the familiar secular equation factorization process.

Incorporation of Symmetry.—The usual method of factoring the secular equation is to set it up using linear combinations which belong to various species of the group. Those combinations which belong to different species do not interact, and if there is only one combination for each species, the secular equation is completely factored. We considered this case first, and for the present exclude degeneracy.

The linear combination (not normalized)

$$\psi_j = \sum_{i=1}^{n} t_{ij}\psi^i$$

where ψ_j belongs to a particular species, Γ_γ, is constructed by forming a fragment; that is, by operating on one member of a set of equivalent ψ^i's, say, ψ^k, as[5]

$$<\psi^k> = \sum_R \chi^{\Gamma_\gamma}(\mathrm{R})\mathrm{R}\psi^k$$

Here χ^{Γ_γ} (R) is the character for the operation R and the species Γ_γ, and $R\psi^k$ is the ψ_i obtained by operating on ψ^k with the operation R. The coefficients in this expression, when suitably grouped together, are the same as the t's. This results from

$$\int \psi^{l*}<\psi^k>\mathrm{d}\tau = \sum_{\mathrm{R(kl)}} \chi^{\Gamma_\gamma}(\mathrm{R(kl)})$$

where the sum is over all operations R(kl) that send ψ^k into ψ^l; and

$$\int \psi^{l*}\psi_j \, \mathrm{d}\tau = t_{lj}$$

so that with $\psi_j = <\psi^k>$ we have[6]

$$t_{lj} = \sum_{\mathrm{R(kl)}} \chi^{\Gamma_\gamma}(\mathrm{R(kl)})$$

Quantum mechanical transformation theory gives, if the t's are normalized

$$t_{lj} = S^{-1}{}_{lj}$$

or equivalently

$$t_{lj} = S_{jl}$$

so that the first problem is solved.

It should be noted that the character table for the group is required, and also a knowledge of which operations send ψ^k into ψ^l, that is, the transformation properties of the ψ^i's. We now consider the connection with structures: the ψ^i's are known only to the extent that the transformation properties of the $(\psi^i)^2$'s are the same as the transformation properties of the (i)'s (structures). As shown in paper I (Part I and Appendix I) for practical purposes this correspondence may often be simplified so that the transformation properties of the ψ^i's themselves are inferred from the (i)'s. Alternatively the fragments may be made-up directly from structures so that the quantity essential to the definition of the t's, R(kl), may be taken as one of the operations which sends structure k into structure l ((k) into (l)). We consider next the case in which a given species is represented more than once, but still assume no degeneracy.

Incomplete Determination by Symmetry.—If the full reduction of the secular equation cannot be accomplished on the basis of symmetry, or, equivalently, the transformation in the reverse direction is not completely determined, there will be more than one fragment belonging to at least one of the species. Extra fragments are always generated from non-equivalent[5] ψ^i's. (It follows that if all ψ^i's are equivalent the transformation is completely determined.)

The usual device in setting up the secular equation in the case where it cannot be completely factored is to use as a basis combinations of equivalent ψ^i's (fragments). In matrix notation this is the same as setting equal to zero the mixing coefficient between parts of an eigenvector of $\mathbf{E}'$, or column of S^{-1}. To illustrate, if ψ^1 and ψ^q are not equivalent, but ψ^1 up to ψ^q and ψ^q to ψ^r are equivalent, we would have, at least for the identity species Γ_0, two

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[5] If some R of the group can be found which sends ψ^r into ψ^s ψ^r and ψ^s are equivalent.

[6] Since Γ_γ is the species of the jth energy eigenstate, the formula could have been written with χ^j instead of χ^{Γ_γ}. The index k does not appear on the left because k only determines the phases of the t's (any ψ^i used to generate the fragment gives the same fragment). Therefore the indices match in the final equation for the t's.

fragments, $<\psi^1>$ and $<\psi^q>$ belonging, say, to Γ_α and Γ_δ. Two columns of $\mathbf{S}^{-1}$ would have the following appearance

$$\mathbf{S}^{-1} = \begin{array}{c} \\ \\ \psi^1 \\ \psi^2 \\ \vdots \\ \psi^{q-1} \\ \psi^q \\ \psi^{q+1} \\ \vdots \\ \psi^n \end{array} \begin{array}{c} \bar{\psi}_1\ \psi_2 \ldots \bar{\psi}_j \ldots \psi_n \\ \Gamma_\alpha\ \Gamma_\beta \ldots \Gamma_\delta \ldots \Gamma_\nu \\ \left(\begin{array}{cccc} t_{11} & & 0 & \\ t_{21} & & 0 & \\ \vdots & & \vdots & \\ t_{q-1,1} & & 0 & \\ 0 & & t_{qj} & \\ 0 & & t_{q+1,j} & \\ \vdots & & \vdots & \\ 0 & & t_{nj} & \end{array}\right) \end{array}$$

The first $q - 1$ t_{i1}'s are coefficients in $<\psi^1>$ and the remaining elements in the column are zero, while the non-zero t_{ij}'s come from $<\psi^q>$. The matrix above cannot, through a similarity transformation, be used to completely diagonalize $\mathbf{E}'$, but will factor it as much as symmetry allows. Concomitantly it would seem that the above matrix could not be used to change $\mathbf{E}$ to $\mathbf{E}'$. To understand this situation is the next aim.

Imagine that we have set up the secular equation

$$|\mathbf{E}' - \lambda\mathbf{I}| = 0$$

using a set of ψ^i's considered as known, that is with

$$E'_{ij} = \int \psi^{i*} H \psi^j d\tau$$

(H is the energy in the Schrödinger representation.) The eigenvectors of $\mathbf{E}'$ will be the columns of the matrix $\mathbf{S}^{-1}$ above, except that the mixing between fragments of ψ^i's of the same species is actually determined. More specifically, there is determined a matrix like the one above except that $\bar{\psi}_1$ is replaced by

$$\psi_1 = (1 - c^2)^{1/2}\bar{\psi}_1 + r\bar{\psi}_i$$

and also $\bar{\psi}_j$ by

$$\psi_i = c\bar{\psi}_j\ (1 - c^2)^{1/2}\bar{\psi}_i$$

(Note that orthogonality and normalization are preserved—also $0 \leqslant c \leqslant 1$.) The role of c in this instance is to mix fragments of non-equivalent ψ^i's so as to get the best approximation to the true energies. If the ψ^i's are perfect, the roots of the secular equation will be the true energies. For a given set of perfect ψ^i's a c is determined, say c_1.

Now imagine that we have linear combinations of perfect ψ^i's which transform the same way, called φ^i's.[7] From these we could again construct fragments, which could then be automatically mixed by the secular equation technique, leading to roots of the secular equation equal to the observed energies. The φ^i's are also perfect. However for the φ^i's a different c is determined, say c_2.

When we consider perfect ψ^i's or φ^i's we are in effect dealing with the structure representation, but now we must realize that the form of the functions is not known, only the transformation properties. That is, we do not know if we are dealing with the ψ^i's or the φ^i's and so we do not know what to take for c. This illustrates a fundamental ambiguity. In matrix notation the ambiguity arises from the fact that if $\mathbf{S}^{-1}$ and $\mathbf{S}$ are constructed with c incorporated as any number $0 \leqslant c \leqslant 1$, still

$$\mathbf{E}' = \mathbf{S}^{-1}\mathbf{E}\mathbf{S}$$

has the property that its eigenvalues are the diagonal elements of $\mathbf{E}$.

The generalization to cases with more constants or greater ambiguity is obvious.

Without knowing the shapes of the ψ^i's and the φ^i's we can say that for a particular structure (k), say, ψ^k and φ^k have the same general shape but different detailed shapes. The detailed shapes are related in some fashion to the values of c, and this relationship is discussed further in the last section of the paper.

Next, however, we consider the question of the actual number of arbitrary constants, which number was one in the example above. The most general transformation matrix has the fragments mixed, with coefficients incorporated as "unknowns." The number of mixing coefficients, or constants needed, and hence the number of constants in $\mathbf{E}'$ can be calculated by considering the individual normalized fragments as single matrix elements. For example the matrix above may be written as

$$\mathbf{S}^{-1} = \begin{array}{c} \begin{array}{cccc} \bar{\psi}_1 & & \bar{\psi}_j & \end{array} \\ \left(\begin{array}{cccc} <\psi^1> & \ldots & 0 & \ldots \\ 0 & \ldots & <\psi^q> & \ldots \end{array}\right) \end{array}$$

If for the particular species Γ_k, say, there are m fragments then there will be before normalization and orthogonalization m^2 constants. Normalization reduces this by m and orthogonalization by the number of pairs, $(m^2 - m)/2$, so the number remaining is

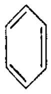
$$m^2 - m - (m^2 - m)/2 = (m^2 - m)/2$$

To find the total number of arbitrary constants we must sum over all species.

Incidentally, when $m = n$ (which would make $\Gamma_k = \Gamma_0$, the identity species) the number of arbitrary constants is $(n^2 - n)/2$ and there is no utilization of symmetry at all.

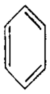
Next we take up a particularly straightforward example in which there is no ambiguity.

Benzene as an Example.—Consider benzene (see also paper I) with only the two equivalent structures



(1)

and



(2)

The symmetry group of the molecule is taken to be D_{6h} with the character table shown below.

The object is now to obtain the transformation matrix, $\mathbf{S}^{-1}$. The t's, which on normalization are the matrix elements of $\mathbf{S}^{-1}$, are obtained from the expression

$$t_{1i} = \sum_{R(kl)} \chi^{\Gamma\gamma}(R(kl))$$

However, in practice, instead of making explicit use of this formula we proceed in a manner analogous to the procedure for factoring the secular equation in a linear variation calculation and form fragments. Moreover, as explained in Paper I, we shall use structures, not ψ^i's. The t's are simply the coefficients of the structures in these fragments.

Using structure (1) we perform on it the operations of the group, writing down the serial numbers of the structures obtained, multiplied by the appro-

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(7) For example, consider the first and third energy eigen-ψ's for a harmonic oscillator, ψ_1 and ψ_3. $\varphi_1 = \psi_1 + \alpha\psi_3$ and $\varphi_3 = \psi_3 - \alpha\psi_1$ transform like ψ_1 and ψ_3 (even functions). Moreover one could, using the linear variaton method, obtain the true energies $E_1 = h\nu/2$ and $E_3 = 5h\nu/2$ using the φ's as "trial" fnuctions.

	E	C_2	$2C_3$	$2C_6$	$3C_2'$	$3C_2''$	iE	iC_2	$2iC_3$	$2iC_6$	$3iC_2'$	$3iC_2''$
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1
A_{1u}	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1
A_{2g}	1	1	1	1	−1	−1	1	1	1	1	−1	−1
A_{2u}	1	1	1	1	−1	−1	−1	−1	−1	−1	1	1
B_{1g}	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1
B_{1u}	1	−1	1	−1	1	−1	−1	1	−1	1	−1	1
B_{2g}	1	−1	1	−1	−1	1	1	−1	1	−1	−1	1
B_{2u}	1	−1	1	−1	−1	1	−1	1	−1	1	1	−1
E_{1g}	2	−2	−1	1	0	0	2	−2	−1	1	0	0
E_{1u}	2	−2	−1	1	0	0	−2	2	1	−1	0	0
E_{2g}	2	2	−1	−1	0	0	2	2	−1	−1	0	0
E_{2u}	2	2	−1	−1	0	0	−2	−2	1	1	0	0

priate characters for the particular species, and summing. There are twelve operations of the group which leave (1) unchanged and twelve operations which convert structure (1) into structure (2). Thus, using the characters for the species A_{1g} we obtain the fragment

$$12\,(1) + 12\,(2)$$

The process is repeated for all other species of the group and it is found that the only other fragment different from zero is

$$12\,(1) - 12\,(2)$$

belonging to the species B_{2u}. From the coefficients of the structures in the fragments, the vectors (before normalization) in the structure representation are found by inspection to be

$$\begin{pmatrix}12\\12\end{pmatrix}_{A_{1g}} \text{ and } \begin{pmatrix}12\\-12\end{pmatrix}_{B_{2u}}$$

On normalization these vectors form the columns of S^{-1} and therefore

$$S^{-1} = \begin{pmatrix}2^{-1/2} & 2^{-1/2}\\ 2^{-1/2} & -2^{-1/2}\end{pmatrix}$$

Thus S^{-1} is completely defined by the symmetry of the molecule and we can now make the transformation from the observed energy matrix to the structure representation. The observed energy of the $A_{1g} \rightarrow B_{2u}$[8] transition is 3.81 (energies in this paper are in units such that one unit is 10^4 cm.$^{-1}$). This gives

$$E = \begin{pmatrix}0 & 0\\ 0 & 3.81\end{pmatrix}$$

and

$$E' = S^{-1}ES = \begin{pmatrix}1.91 & -1.91\\ -1.91 & 1.91\end{pmatrix}$$

The difference in energy between a single Kekulé structure and the ground state of the molecule is 1.91 (55 kcal./mole). This quantity is the observed or experimental vertical resonance energy referred to the Kekulé structures as defined by the above transformation. As is well known there is no reason to suppose that this quantity should agree very well with thermochemical (non-vertical) resonance energy measurements (36 kcal./mole).[9]

Before proceeding to the examples of the triphenylmethane dyes we consider a new notation to distinguish structures as used in organic chemistry from structures in the more technical sense.

Semantic Considerations.—As in the concluding section of paper I two types of structures are to be distinguished. The structures which are "given," the transformation properties of which we use in defining the structure representation, are not considered to be quantum mechanical entities. They are considered to be defined instead by the classical phenomenological theory of valence in organic chemistry. They have been called by various names, including mesomers, electromers, resonance forms, and paper structures. We shall refer to these structures as structures$_1$.

On the other hand, matrix elements in the structure representation are, when derived from observed energies, exact quantum mechanical quantities. They may then certainly be considered to be derived from interactions among wave functions (structure functions) which, in suitable combinations, exactly represent the various energy eigenstates. The squares of these component wave functions are called structures$_2$. Less precisely the wave functions themselves, or unit vectors in the structure representation, are sometimes called structures$_2$. These unit vectors represent the same states, in the abstract sense, as are represented by the wave functions.

With the new notation it is possible compactly to characterize the theory of paper I. It is a suggestion to use structures$_1$ and hence the resources of classical organic chemistry, together with a quantum mechanical formalism, to make predictions. The postulate is to be tried that an equivalence with respect to transformation properties, energies and other properties holds

$$\text{structures}_1 \approx \text{structures}_2$$

The degree of success of the theory on many applications may afford an objective estimate of the degree of truth in the equivalence. This equivalence must be understood to be a relation which is not quantum-mechanical. It relates theory of a fundamental nature (quantum mechanics) to theory of a lower level (classical valence theory). Any such scheme would be unnecessary if it were not for the virtual impossibility of solving the equations of the fundamental theory.[10] The testing of the equivalence postulate is not itself a low level theory, but conceivably quite the reverse, in that use of modern inductive logic may be indicated.

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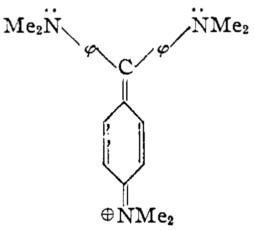
[8] A. S. Davydov, *Zhur. Ekspti. Teoret. Fiz.*, **21**, 673 (1951); A. C. Albrecht and W. T. Simpson, *J. Chem. Phys.*, **21**, 940 (1953).

[9] However, it agrees better with Hornig's value (~65 kcal./mole), D. F. Hornig, THIS JOURNAL, **72**, 5772 (1950).

[10] The equivalence is a limiting law in that it may be considered to hold exactly for molecules for which there is no interaction among the structures (domain of unquestioned applicability of classical valence theory).

Linus Pauling's name is strongly associated with this equivalence. In fact, in 1939 Pauling outlined a treatment of the color of dyes which in effect makes use of the equivalence and which in many ways anticipates the work in the present series of papers.[11]

Triphenylmethane Dyes with Three Structures.—In the remaining sections the material above is further illustrated, but with cases which introduce the problem of ambiguity and require the consideration of degeneracy. First we treat crystal violet using three structures. Following the procedure outlined in the Introduction we consider as given: (i) the three structures,[12]



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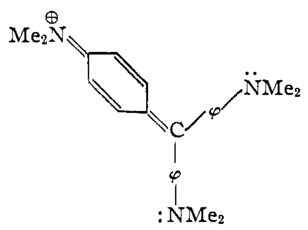

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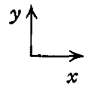

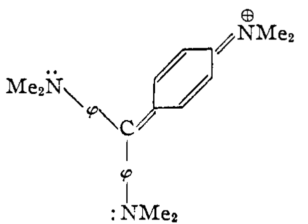

(3)

(ii) the first three energy levels $E_{11} = 0$, $E_{22} = 1.760$, $E_{33} = 1.760$ with species A_1, E, E, respectively,[13] and (iii) the fact that the species of the energy levels are consistent with the species of the fragments, as will be seen.

Crystal violet is considered to have at least C_{3v} symmetry, with the following character table

	E	σ_v^1	σ_v^2	σ_v^3	C_3^1	C_3^2
A_1	1	1	1	1	1	1
A_2	1	−1	−1	−1	1	1
E (x,y)	2	0	0	0	−1	−1

The fragment for the species A_1 is generated using structure (1), yielding

$$2\,(1) + 2\,(2) + 2\,(3)$$

Recalling that the coefficients of the structures in the fragments are the t's we have the normalized vector in the structure representation

$$\psi_1 = \begin{pmatrix} 3^{-1/2} \\ 3^{-1/2} \\ 3^{-1/2} \end{pmatrix}$$

The method outlined in paper I for generating fragments for the degenerate species E[14] made use of the matrix elements of the irreducible representations. In this paper the usual method of computing fragments, which requires only the characters of the E species, is used. Forming fragments with each structure in turn and using the characters of E we get

$$\begin{aligned} (a) &= 2(1) - (2) - (3) \\ (b) &= 2(2) - (3) - (1) \\ (c) &= 2(3) - (1) - (2) \end{aligned}$$

only two of which are linearly independent. The problem is now to pick suitable linearly independent and orthogonal fragments, chosen so that they also form bases for irreducible representations of the symmetry group of molecules which are to be considered as perturbed crystal violet. The direction of the perturbation will be taken along the y-axis (referring to the coördinate system for the structures) and it is sufficient to take as the character table for the group of the perturbed molecules

	E	σ_v
A(y)	1	1
B(x)	1	−1

where σ_v is the operation of reflection in the yz-plane. In order to find the new fragments which form bases for the irreducible representations of the new group we form fragments from the fragments (a), (b) and (c) using the character table for the group of the perturbed molecule. (a) already belongs to A of the new group. From (b) we find

$$\sum_R \chi(R)^{\Gamma_A} R(b) = [2(2) - (3) - (1)] + [2(3) - (2) - (1)] = -[2(1) + (2) + (3)] = -(a)$$

and

$$\sum_R \chi(R)^{\Gamma_B} R(b) = [2(2) - (3)\,(1)] - [2(3) - (2) - (1)] = 3(2) - 3(3)$$

The fragments obtained from (c) are the same as those from (b) (except for the sign, which is trivial) and thus the desired fragments are $2(1) - (2) - (3)$ belonging to the species A and $3(2) - 3(3)$ belonging to the species B. Thus the orthogonal vectors in the structure representation belonging to the species E are

$$\begin{pmatrix} 2 \\ -1 \\ -1 \end{pmatrix} \text{and} \begin{pmatrix} 0 \\ 3 \\ -3 \end{pmatrix}$$

which on normalization become

$$\begin{pmatrix} 2(6)^{-1/2} \\ -6^{-1/2} \\ -6^{-1/2} \end{pmatrix} \quad \begin{pmatrix} 0 \\ 2^{-1/2} \\ -2^{-1/2} \end{pmatrix}$$

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[11] L. Pauling, *Proc. Nat. Acad. Sci.*, **25**, 577 (1939).

[12] Each structure may be considered to contain all of the additional structures which arise from benzene type resonance in the phenyl groups.

[13] The experimental assignment of the levels and factors affecting numerical precision will be fully discussed in paper III. The transition energies are all based on measurements in glacial acetic acid.

[14] In paper I it was wrongly stated that only Γ_2^{11} and Γ_2^{21} appear. In fact, Γ_2^{12} and Γ_2^{22} also give non-vanishing fragments which are identical with those given. (Hence only two linearly independent fragments were generated.) This difficulty arose because of the "directional" properties of the matrices of E. If structure (3) (in the notation of paper I) had been used to generate the fragments, only two non-vanishing fragments would have been obtained. In addition, there is a typographical error in the character table for C_3v and $\sqrt{3/2}$ should read $\sqrt{3}/2$.

These vectors, together with the A_1 vector, give

$$\mathbf{S}^{-1}(\mathrm{CV}) = \begin{array}{c} \\ \psi^1 \\ \psi^2 \\ \psi^3 \end{array} \begin{array}{c} \begin{array}{ccc} \psi_1 & \psi_2 & \psi_3 \end{array} \\ \begin{pmatrix} 3^{-1/2} & 2(6)^{-1/2} & 0 \\ 3^{-1/2} & -6^{-1/2} & 2^{-1/2} \\ 3^{-1/2} & -6^{-1/2} & -2^{-1/2} \end{pmatrix} \end{array}$$

Note that except for the phase of the degenerate representation there is no ambiguity. We also find this result from the formula for the arbitrary constants in $\mathbf{S}^{-1}$

$$\sum_{A,E} (m^2 - m)/2$$

because

$$m = 1 \text{ for A and E}^{15}$$

When we adopt

$$\mathbf{E}(\mathrm{CV}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1.760 & 0 \\ 0 & 0 & 1.760 \end{pmatrix}$$

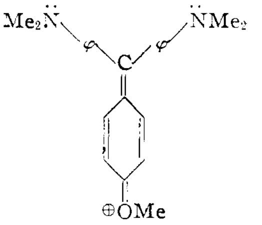
for the energy in the Heisenberg representation[13] we have, using

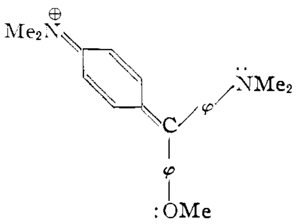
$$\mathbf{E}' = \mathbf{S}^{-1}\mathbf{E}\mathbf{S}$$

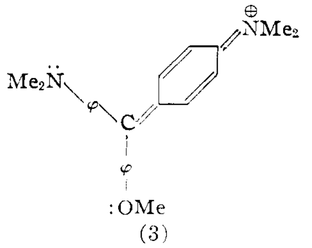
$$\mathbf{E}'(\mathrm{CV}) = \begin{pmatrix} 1.173 & -0.587 & -0.587 \\ -0.587 & 1.173 & -0.587 \\ -0.587 & -0.587 & 1.173 \end{pmatrix}$$

in the structure representation.

We turn now to methoxy malachite green. The observed energies from the spectrum referred to $E_{11} = 0$ for crystal violet are x, $x + 1.650$ and $x + 2.160$, where x is to be determined.[13] The species are A, B and A, respectively.[13] Using the character table of the perturbed molecule and the three structures


(1)


(2)


(3)

we obtain the fragments

(1) and (2) + (3)

belonging to A, and

(2) − (3)

belonging to B. Hence for A, $m = 2$, and there will be $(2^2 - 2)/2$ constants in $\mathbf{S}^{-1}$.

We saw in the section "Incomplete Determination by Symmetry" that with

$$\bar{\psi}_1 = \psi^1$$
$$\bar{\psi}_3 = 2^{-1/2}(\psi^2 + \psi^3)$$

to be completely general we must use

$$c\bar{\psi}_1 + (1 - c^2)^{1/2}\bar{\psi}_3$$

and

$$(1 - c^2)^{1/2}\bar{\psi}_1 - c\bar{\psi}_3$$

in constructing $\mathbf{S}^{-1}$. This gives for methoxy malachite green

$$\mathbf{S}^{-1}(\mathrm{mMG}) = \begin{array}{c} \\ \psi^1 \\ \psi^2 \\ \psi^3 \end{array} \begin{array}{c} \begin{array}{ccc} \psi_1 & \psi_2 & \psi_3 \end{array} \\ \begin{pmatrix} c & 0 & (1 - c^2)^{1/2} \\ 2^{-1/2}(1 - c^2)^{1/2} & 2^{-1/2} & -2^{-1/2}c \\ 2^{-1/2}(1 - c^2)^{1/2} & -2^{-1/2} & -2^{-1/2}c \end{pmatrix} \end{array}$$

The problem of selecting (not determining) the constant must be solved before we can find $\mathbf{E}'$ for the dye.

We now make an assumption characteristic of work with the structure representation, and based on the equivalence, structures$_1$ ≈ structures$_2$. The assumption, linking the two substances crystal violet and methoxy malachite green, is that

$$\mathbf{E}'(\mathrm{mMG}) = \mathbf{E}'(\mathrm{CV}) + \delta\mathbf{E}'$$

with

$$\delta\mathbf{E}' = \begin{pmatrix} \delta E'_{11} & \delta E'_{12} & \delta E'_{13} \\ \delta E'_{21} & 0 & 0 \\ \delta E'_{31} & 0 & 0 \end{pmatrix}$$

($\delta E'_{12} = \delta E'_{13} = \delta E'_{21} = \delta E'_{31}$, because of the symmetry of the matrix and of the molecule). The physical meaning of the assumption is that the detailed shapes (see the section "Incomplete Determination by Symmetry") of the ψ^i's for the perturbed molecule are picked in such a way that the energies and interaction energies not involving structure$_2$ (1) are unchanged. This is suggested, of course by the structures$_1$.

We now compute c in $\mathbf{S}^{-1}$ (mMG). First we perform the transformation $\mathbf{E}' = \mathbf{S}^{-1}\mathbf{E}\mathbf{S}$ using $\mathbf{S}^{-1}$ with its dependence on c. This gives E_{23} (mMG) as a function of c. The relation $\delta E_{23} = 0$, or

$$E'_{23}(\mathrm{CV}) = E'_{23}(\mathrm{mMG})$$

is then used to determine c. (The value is found to be 0.469). The zero of energy is determined similarly and it is found that $x = 0.110$. This gives

$$\mathbf{E}(\mathrm{mMG}) = \begin{pmatrix} 0.110 & 0 & 0 \\ 0 & 1.760 & 0 \\ 0 & 0 & 2.270 \end{pmatrix}$$

which after transformation into the structure representation is

$$\mathbf{E}'(\mathrm{mMG}) = \begin{pmatrix} 1.794 & -0.632 & -0.632 \\ -0.632 & 1.173 & -0.587 \\ 0.632 & -0.587 & 1.173 \end{pmatrix}$$

The E_{22} matrix element is understandably the same as for crystal violet because in each case

$$\psi_2 = 2^{-1/2}(\psi^2 - \psi^3)$$

and the E'_{ij} values not involving (1) are unchanged.

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(15) The correctness of the formula for the number of arbitrary constants in the case where there is degeneracy has not actually been proved. However if the phases of the degenerate representations are considered determined it is believed that the formula is correct with each degenerate set of fragments counted as one. If, for example, E of C_{3v} occurred twice there would result, after selection of the phase, one arbitrary constant in $\mathbf{S}^{-1}$. Consider each degenerate pair to consist of an A and a B part (group of lower symmetry). Then $\mathbf{S}^{-1}$ is restricted so that the mixing coefficient between the A parts is the same as the mixing coefficient between the B parts.

The transformation matrix is

$$S^{-1}(\text{mMG}) = \begin{array}{c} \\ \psi^1 \\ \psi^2 \\ \psi^3 \end{array} \begin{array}{ccc} \psi_1 & \psi_2 & \psi_3 \\ \end{array}$$

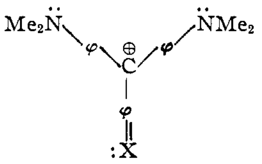
$$S^{-1}(\text{mMG}) = \begin{array}{cc} & \begin{array}{ccc} \psi_1 & \psi_2 & \psi_3 \end{array} \\ \begin{array}{c} \psi^1 \\ \psi^2 \\ \psi^3 \end{array} & \begin{pmatrix} 0.4694 & 0 & 0.8830 \\ 0.6244 & 0.7071 & -0.3319 \\ 0.6244 & -0.7071 & -0.3319 \end{pmatrix} \end{array}$$

and the matrix of the perturbation

$$\delta\mathbf{E}' = \begin{pmatrix} 0.621 & -0.045 & -0.045 \\ -0.045 & 0 & 0 \\ -0.045 & 0 & 0 \end{pmatrix}$$

It is encouraging to note that $\delta E_{11} > 0$ which is in accord with chemical intuition based on structures$_1$. It means simply that ethers are less basic than amines. The low value $\delta E'_{12}$ is also encouraging but no simple interpretation of the negative sign can be made (the 1–2 interaction is increased in magnitude by the perturbation). After we have discussed the dyes on the basis of four structures given we shall relate the 3 × 3 case to the 4 × 4 case, which will make it possible to understand $\delta E'_{12}$ for the 3 × 3 case.

Triphenylmethane Dyes with Four Structures.— Next we try to fit observed levels and structures together into a consistent scheme using (1), (2) and (3) as above and also


(4)

where X is $-\ddot{N}Me_2$ for crystal violet and $-\ddot{O}Me$ for methoxy malachite green. The observed energies for crystal violet are now 0, 1.760, 1.760 and 2.750; and the species are, respectively, A_1, E, E and A_1 of C_{3v}.[13] For methoxy malachite green the energies are x, $x + 1.650$, $x + 2.160$ and $x + 2.960$ with species, respectively, A, B, A and A.[13]

In incorporating four structures we cannot remove the ambiguity as neatly as in the last section. We begin by noting that for crystal violet itself, for the A_1 species $m = 2$, from the existence of the two fragments

$$(1) + (2) + (3) \text{ and } (4)$$

This means that $S^{-1}(\text{CV})$ is a function of c.[16] The main assumption we make is that

$$\mathbf{E}'(\text{mMG}) = \mathbf{E}'(\text{CV}) + \begin{pmatrix} \delta E_{11} & \delta E_{12} & \delta E_{13} & \delta E_{14} \\ \delta E_{21} & 0 & 0 & 0 \\ \delta E_{31} & 0 & 0 & 0 \\ \delta E_{41} & 0 & 0 & 0 \end{pmatrix}$$

just as for the 3 × 3 case. However in spite of $\delta E'_{12} = \delta E'_{13} = \delta E'_{21} = \delta E'_{31}$ we cannot determine all the arbitrary constants. We have to find c in $\mathbf{E}'$ (CV) and $\delta E'_{11}$, $\delta E'_{12}$ and $\delta E'_{14}$, all from the three observed colors of methoxy malachite green.

The difficulty can be overcome only if another condition is added. The condition chosen (after considerable exploration) was

$$\delta E'_{14} = 0$$

which resulted in the following values

$$c = 0.707$$
$$\delta E'_{11} = 0.940$$
$$\delta E'_{12} = \delta E'_{13} = 0$$

The value for $\delta E'_{11}$ is actually independent of c, as will be shown below. We note first that the value of $\delta E'_{11}$ is in accord with expectations based on structures$_1$ just as in the 3 × 3 case.[17] In addition $\delta E'_{12} = \delta E'_{13}$ has happily turned out to be zero. That is, when the detailed shape of the ψ^i's for methoxy malachite green is refined so that E'_{14} is not affected by the perturbation, then neither is E'_{12}. The result is that the perturbation is isolated to the diagonal.

To obtain $\delta E'_{11}$ we work with the observed traces

$$\text{trace } \mathbf{E}(\text{CV}) = 6.270$$
$$\text{trace } \mathbf{E}(\text{mMG}) = 4x + 6.770$$

For each molecule the second state is

$$\psi_2 = 2^{-1/2}(\psi^2 - \psi^3)$$

so that $E_{22}(\text{CV}) = E_{22}(\text{mMG})$. In consequence the 1–2 transition energy difference

$$[E_{22}(\text{CV}) - E_{11}(\text{CV})] - [E_{22}(\text{mMG}) - E_{11}(\text{mMG})]$$

gives x directly ($x = 1.760 - 1.650 = 0.110$). Now we find the difference

$$\text{trace } \mathbf{E}(\text{mMG}) - \text{trace } \mathbf{E}(\text{CV}) = 0.940$$

The difference of traces in the structure representation is also 0.940 by the trace invariance property. Moreover in the structure representation only E'_{11} changes, going from crystal violet to methoxy malachite green, so $\delta E'_{11} = 0.940$.

To find c and $\delta E'_{12}$ we use various c values to get various $\mathbf{E}'$ (CV). For each value and using $\delta E'_{11} = 0.940$ and $\delta E'_{14} = 0$ we obtain a trial matrix

$$\mathbf{E}'(\text{mMG}) = \mathbf{E}'(\text{CV}) + \delta\mathbf{E}'$$

This matrix is now dependent directly on $\delta E'_{12}$. When this matrix on diagonalization exactly reproduces the observed energy matrix, then c and $\delta E'_{12}$ are determined. As noted above this procedure was carried out numerically, with the result $\delta E'_{12} = 0 \pm 0.05$ and $c = 0.707 \pm 0.1$.[18]

To summarize, the 4 × 4 transformation matrix for Crystal Violet is

$$S^{-1}(\text{CV}) = \begin{array}{cc} & \begin{array}{cccc} \psi_1 & \psi_2 & \psi_3 & \psi_4 \end{array} \\ \begin{array}{c} \psi^1 \\ \psi^2 \\ \psi^3 \\ \psi^4 \end{array} & \begin{pmatrix} 0.4083 & 0 & 0.8165 & 0.4083 \\ 0.4083 & 0.7071 & -0.4083 & 0.4083 \\ 0.4083 & -0.7071 & -0.4083 & 0.4083 \\ 0.7071 & 0 & 0 & -0.7071 \end{pmatrix} \end{array}$$

Note that (4) contributes $(S^{-1}_{41})^2 = 0.5$ to the

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[16] In a manner analogous to that used to find S^{-1} (mMG) in the 3 × 3 case we find at this stage

$$S^{-1} = \begin{pmatrix} 3^{-1/2}(1 - c^2)^{1/2} & 0 & 2(6)^{-1/2} & 3^{-1/2}c \\ 3^{-1/2}(1 - c^2)^{1/2} & 2^{-1/2} & -6^{-1/2} & 3^{-1/2}c \\ 3^{-1/2}(1 - c^2)^{1/2} & -2^{-1/2} & -6^{-1/2} & 3^{-1/2}c \\ c & 0 & 0 & -1(1 - c^2)^{1/2} \end{pmatrix}$$

[17] The meaning to be attached to the fact that $\delta E'_{11}$ is somewhat different in the 3 × 3 and 4 × 4 cases will be clarified by the treatment in the next section.

[18] It was found, moreover, that c and $\delta E'_{12}$ cannot be varied in tandem so as to give an $\mathbf{E}'$ (mMG) which on diagonalization still gives the observed energies.

ground state. The energy in the structure representation is

$$\mathbf{E}'(\mathrm{CV}) = \begin{pmatrix} 1.632 & -0.128 & -0.128 & -0.794 \\ -0.128 & 1.632 & -0.128 & -0.794 \\ -0.128 & -0.128 & 1.632 & -0.794 \\ -0.794 & -0.794 & -0.794 & 1.375 \end{pmatrix}$$

For methoxy malachite green

$$\mathbf{S}^{-1}(\mathrm{mMG}) = \begin{pmatrix} 0.2811 & 0 & 0.5784 & 0.7663 \\ 0.4411 & 0.7071 & -0.5067 & 0.2204 \\ 0.4411 & -0.7071 & -0.5067 & 0.2204 \\ 0.7293 & 0 & 0.3902 & -0.5618 \end{pmatrix}$$

Note that the contribution to ψ_1 by structure$_2$ (1) (in which according to structure$_1$ (1) the oxygen acquires a positive charge) is only 0.08; while each nitrogen has the charge with a weight of 0.19. The E′ for methoxy malachite green is easily obtained from E′ (CV) because only $\delta E'_{11} \neq 0$.

It should be specially emphasized that in the Heisenberg representation all four diagonal elements must be changed to represent methoxy malachite green as related to crystal violet. In the structure representation, now for the 4 × 4 case, the perturbation is represented through the variation of only one matrix element. The reduction in the number of changing matrix elements is promising not only from the standpoint of classification of spectra, but also from the standpoint of making predictions.

Relation between the Two Treatments.—The question arises as to whether or not the 4 × 4 treatment is better than the 3 × 3. While there is more information involved in the 4 × 4 case, there is also an extra assumption needed. The ultimate decision about the most suitable number of structures to be incorporated must be made with reference to predictions. Since predictions for the triphenylmethane dye case are not made in this paper, but in paper III, we cannot say here which treatment is better. In this section we shall, however, compare the 3 × 3 and 4 × 4 cases from the standpoint of transformation theory.

A new matrix

$$\mathbf{R}^{-1}(\mathrm{CV}) = \begin{pmatrix} 3^{-1/2} & 0 & 2(6)^{-1/2} & 0 \\ 3^{-1/2} & 2^{-1/2} & -6^{-1/2} & 0 \\ 3^{-1/2} & -2^{-1/2} & -6^{-1/2} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

is first defined. It is the same as S^{-1} for the 3 × 3 case except that an extra dimension is appended trivially. (All structure representation matrices are really only upper corners of infinitely large matrices.) The fourth state can have any symmetry. Now let us consider $\mathbf{R}^{-1}$ as a modification of the 4 × 4 $\mathbf{S}^{-1}$(CV) given in the last section. This shifted point of view is to be understood as follows.

The $\mathbf{E}'$ in the 4 × 4 case considered in the last section can be conceived as being set up using particular ψ^{i}'s and

$$E'_{ij} = \int \psi^{i*} H \, \psi^{j} \mathrm{d}\tau$$

The S^{-1} matrix in the 4 × 4 case in the last section then shows how the ψ^{i}'s are combined to give the stationary state ψ's(ψ_j's). The $\mathbf{R}^{-1}$ matrix above tells how the same state ψ's are to be constituted. However since $\mathbf{R}^{-1} \neq \mathbf{S}^{-1}$ the description must necessarily be in terms of *different* structure ψ's which we may denote as φ's, as was done earlier in this paper. The φ^{i}'s have the same general shape as the ψ^{i}'s but a different detailed shape.

We next look for an expression for the φ^{i}'s in terms of the ψ^{i}'s. We had

$$\mathbf{E}(\mathrm{CV}) = \mathbf{SE}'(\mathrm{CV})\mathbf{S}^{-1}$$

Now denoting the particular structure representation obtained using **R** in place of **S** with a double prime, we have $\mathbf{E}'' = \mathrm{R}^{-1}\mathbf{ER}$ so that

$$\mathbf{E}''(\mathrm{CV}) = \mathrm{R}^{-1}\mathbf{SE}'(\mathrm{CV})\mathbf{S}^{-1}\mathrm{R}$$

Here R^{-1} **S** plays the role of a single transformation matrix from one structure representation to another. The rules of transformation theory give

$$\varphi^{i} = \sum_{i} (\mathrm{S}^{-1}\mathrm{R})_{ij}\psi^{i}$$

The matrix of the coefficients in this equation is

$$\mathbf{S}^{-1}\mathbf{R} = \begin{array}{c} \\ \psi^1 \\ \psi^2 \\ \psi^3 \\ \psi^4 \end{array} \begin{array}{cccc} \varphi^1 & \varphi^2 & \varphi^3 & \varphi^4 \\ \left(\begin{array}{rrrr} 0.9024 & -0.0976 & -0.0976 & -0.4083 \\ -0.0976 & 0.9024 & -0.0976 & -0.4083 \\ -0.0976 & -0.0976 & 0.9024 & -0.4083 \\ 0.4083 & 0.4083 & 0.4083 & 0.7071 \end{array}\right) \end{array}$$

The last column is $\varphi^4 = \psi_4$ which follows from the nature of the *R* representation. The first three columns show that φ^1 to φ^3 have a considerable amount of ψ^4 in them.

It is interesting to analyze matrix elements in the 3 × 3 case from the viewpoint of the transformation above. The rather large interaction, say

$$E''_{13} = \int \varphi^{1*} H \varphi^{3} \mathrm{d}\tau = -0.587$$

may be understood as compounded mainly from the small interaction

$$E'_{13} = \int \psi^{1*} H \psi^{3} \mathrm{d}\tau = -0.128$$

and the larger value for

$$E'_{14} = \int \psi^{1*} H \psi^{4} \mathrm{d}\tau = -0.794$$

It is possible, similarly, to understand the anomalous increase in $|E''_{12}| = |E''_{13}|$ going from crystal violet to methoxy malachite green which was observed in the 3 × 3 case; and the difference between $\delta E''_{11}$ and $\delta E'_{11}$.

It will be appreciated that absolute detailed shape of $\psi^{i}(c)$'s cannot strictly be obtained in the work with the structure representation; but that relative detailed shape can be found, as in the illuminating interpretation of the φ^{i}'s as related to the ψ^{i}'s above. In paper III, when we consider intensities, we shall see that some progress can be made toward estimating absolute detailed shapes of structures. However, there will not be a proliferation of information, as there seems to be in the case of fundamental theories like quantum mechanics. The structure representation method is a method of observable quantities; and the quantities observed in molecular spectroscopy, and related fields, are few.

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