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

Structures and π-Electron Spectra. III. Triphenylmethane Dyes[1,2,3]

BY CATHERINE WORSFOLD LOONEY AND WILLIAM T. SIMPSON

RECEIVED JUNE 18, 1954

The results of a spectroscopic investigation of crystal violet, *p*-methoxy malachite green, malachite green, *p*-nitro malachite green, and Michler's hydrol blue are presented. The positions, intensities and symmetry classifications of the visible and near ultraviolet bands are given. The observed transition energies and polarizations for crystal violet and methoxy malachite green were used in paper II as input data for a theoretical treatment using the methods of the structure representation. The observed intensities for crystal violet are here used similarly. Using only these input data the transition energies for malachite green, and the intensities for methoxy malachite green and malachite green are here calculated theoretically and compared with experiment. Electric moments of the structures are obtained. The transition energies and intensities of *p*-nitro malachite green and Michler's hydrol blue are also treated theoretically. Finally a set of relative basicities is deduced from the spectral data, spectroscopic resonance energies are obtained, and heats of carbinol formation predicted.

Introduction

In "Structures and Electron Spectra II. The Transition Matrix" (hereafter called paper II) a theoretical scheme was developed using the observed transition energies and polarizations of the first three bands in the visible and near ultraviolet of crystal violet (CV) and *p*-methoxy malachite green (mMG). A matrix $\mathbf{S}^{-1}$ was found for CV giving[4]

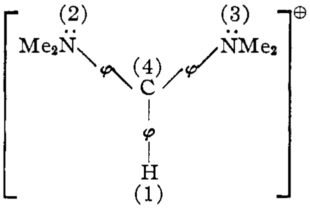
$$\mathbf{E}'(\mathrm{CV}) = \mathbf{S}^{-1}\mathbf{E}(\mathrm{CV})\mathbf{S}$$

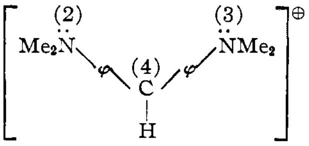
with the property that a very simple relation holds

$$\mathbf{E}'(\mathrm{mMG}) = \mathbf{E}'(\mathrm{CV}) + \begin{pmatrix} \delta E'_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

The equation for $\mathbf{E}'$ (mMG) is exact in the sense that on diagonalization, $\mathbf{E}'$ (mMG) gives the observed transition energies correctly.

In the present paper we obtain the transition energies and polarizations for CV and mMG, which in a sense are the experimental basis for the last part of paper II. We then go on to apply the method of the structure representation in making predictions. The main quantities predicted are the transition energies of malachite green (MG) and the intensities of mMG and MG. We also treat *p*-nitro malachite green (nMG) and Michler's hydrol blue (MHB) (which has no structure (1)) though these latter two dyes are relatively less similar to CV and mMG. The intensity predictions require some further development of the theory, so a separate section is employed having to do exclusively with the calculation of intensities and comparison with experiment.





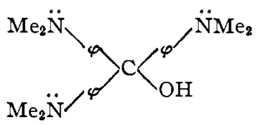
In the final section we deal with the possibility of correlating thermodynamic and spectroscopic quantities. In particular we obtain spectroscopic resonance energies and the related quantities, heats of carbinol formation; and we build up a basicity scale describing the substituents which distinguish the various dyes.

All of the experimental material is presented together, even though some of it is to be used as input data, enabling predictions to be made about the remainder of the data.

Experimental

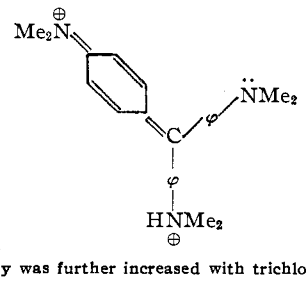
This section is divided into three parts, dealing with Purity, Absorptions and Polarizations.

1. **Purity.**—The dyes were obtained as the color bases, or carbinols, *e.g.*, for CV



and purified by recrystallization of the carbinols from solvents of the type of benzene and ligroin. The recrystallizations were repeated until spectroscopic behavior, including intensity, was constant. (MHB is an exception. Although chromatography on alumina was employed to some advantage, constant spectroscopic behavior was not ever strictly obtained, but this is reflected in the larger limits of error listed for the compound.) The dyes were weighed as the carbinols.

The spectra were run in glacial acetic acid, a solvent chosen to ensure that the carbinols would be instantaneously and completely converted to the dyes. The acidity is high



---

[1] Presented in part at the Spectroscopy Symposium, The Ohio State University, Columbus, Ohio, June, 1954.

[2] Supported under Contract R-351-20-2 Air Research and Development Command.

[3] Taken from the Ph.D. thesis of C. W. Looney.

[4] The notation is that of paper II; hence $\mathbf{E}'$ is the electronic energy in the structure representation, $\mathbf{E}$ in the Heisenberg representation. Structures$_1$ are classical, structures$_2$ are quantum mechanical. ψ_i's are state ψ's and ψ^i's are structure ψ's. The location of the plus charge gives the serial number of a structure (i) and the corresponding ψ^i.

[5] The acidity was further increased with trichloroacetic acid but no accompanying increase in the intensity of the main bands was found.

[6] R. J. Goldacre and J. N. Phillips, *J. Chem. Soc.*, 1724 (1949).

[7] N. F. Hall, THIS JOURNAL, **52**, 5115 (1930).

enough so that the carbinols of nMG and MHB were all converted to the dye, and these dyes are derived from the most stable carbinols.[5-7] The acidity is low enough so that none of the green second ion of CV was present, and CV most readily forms the second ion (as shown).

In the case of CV and MHB there was considerable contamination from Michler ketone making it hard to be sure at first whether the dyes themselves absorbed light in the region around 370 mμ, where Michler ketone absorbs strongly. By careful examination of the shapes of the curves, and by other experiments, it was concluded that surely for CV and almost surely for MHB there is absorption in the 370 mμ region.

2. **Absorptions.**—The absorptions were measured on a Beckman DU spectrophotometer, in a concentration region for which Beer's law is obeyed (optical densities of 0.4–0.5 for 1-cm. path length). The standard practice in low resolution absorption spectrophotometry of using the wave length of $\epsilon_{max.}$ as indicating the transition energy was followed. For the long wave length band of CV, which consists of two overlapping regions belonging to separate electronic transitions, some difficulty in determining the wave lengths was encountered. The procedure used was to plot the spectrum on a scale linear in energy, then by various means to estimate the shape of the low energy component, and finally to subtract giving the high energy component. It might be thought that the most reliable procedure for separating the components would be to use the polarizations and this was tried, but in practice it was considered better to estimate the shape of a single component intuitively.[8] What is needed for CV for comparison with theory is a single value of the transition energy corresponding to a virtual molecule for which the upper state is exactly twofold degenerate. The value assumed was the mean of the separate transition energies obtained by the decomposition procedure just described.

An interesting point is the nature of the splitting of the main band of CV.[9] We have attempted to consider the question carefully using the theory developed by Sponer and Teller, and taking note of the possibility of a Jahn–Teller effect.[10] Briefly, our conclusion is that the interpretation in reference 9 is not necessary. The splitting is the result of a large number of different effects. The contributions of these effects and their variation with experimental conditions would be difficult to predict so that use of a simple mean to characterize the first two transition energies is indicated.[11]

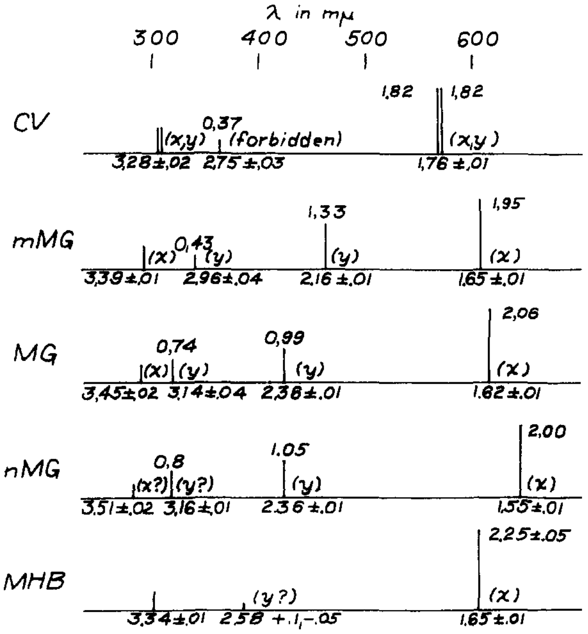


Fig. 1.—Summary of spectra of triphenylmethane dyes. Transition energies are listed on the base lines in cm.$^{-1}$ × 10^{-4}. Transition moments are on top of the schematic absorptions, in Å. Polarizations are in parentheses. Lengths of the lines are proportional to the transition moments.

The use of the wave length of $\epsilon_{max.}$ to give transition energies is equivocal, because as the upper state nuclear displacements increase, the difference between the vertical transition energies and zero–zero energies increases. The theory of the structure representation could conceivably be better suited for calculating zero–zero energies, as can be inferred intuitively: Considering the ground state of an amide as

$$R_2\ddot{N}{-}CH{=}O$$

and the first excited state as

$$R_2\overset{\oplus}{N}{=}CH{-}\overset{\cdot\cdot\ominus}{O}$$

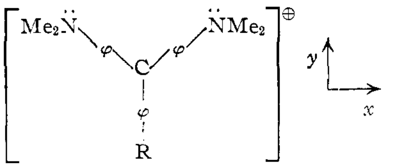
one finds that the representation of the upper state may be interpreted as embodying a modification in nuclear configuration. Still there does not at present seem to be a better plan than the adoption of the reciprocal of the wave length of maximum absorption for the transition energies. The values obtained are in Fig. 1. The energy units are such that one unit is 10^4 cm.$^{-1}$. The limits of error refer only to difficulties in estimating λ of $\epsilon_{max.}$ and are largest for some of the ultraviolet bands where there is strong overlapping.

The intensities were obtained from the areas of the absorption curves, and using

$$\left| \int \epsilon d \log_{10} \lambda \right| = 1.090 \times 10^{19} q^2$$

the transition moments q in cm. were calculated. They are listed in Fig. 1. The error from weighing, dilution, purity and spectrophotometry is believed no greater than 1% for the visible bands, except for MHB where there were particular difficulties in purifying the carbinol. The ultraviolet band moments may be in error by as much as ten per cent.

3. **Polarizations.**—The direction of the electric vector for excitation in the various bands was determined, wherever possible, using the method of polarized fluorescence. This method gives only the polarization relative to the emitting band, but it is assumed that the emitting band, which is the mirror image of the long wave length absorption band, is x, referring to the following general formula and coördinate system.



(and except where R is Me_2N- (CV)).

The group to which CV belongs is assumed to be C_{3v} with species and polarizations[12]

$$A_1, A_2, E(xy)$$

The group to which the perturbed molecule belongs is assumed to consist of the identity and reflection in the yz-plane. It has the species and polarizations

$$A(y), B(x)$$

The correlation between the groups is that A_1 goes into A, A_2 into B, and E into A and B. Some of the polarization determinations were a repetition of other work. The long wave length band of CV had already been analyzed by Feofilov[13] and some of the polarizations for MG had been obtained previously.[14]

The polarizations are listed in Fig. 1. In the case of the absorption in the region 370 mμ for CV it is assumed from the low intensity that the band is probably forbidden, and it seems clear from an examination of the spectra of the series CV, mMG, MG that the band becomes allowed y

---

(8) The shapes of the components as determined from polarizations were deemed implausible.

(9) G. N. Lewis, T. T. Magel and D. Lipkin, THIS JOURNAL, **64**, 1774 (1942), asserted that the splitting reflects the existence of isomers.

(10) H. Sponer and E. Teller, *Rev. Mod. Phys.*, **13**, 75 (1941).

(11) For a detailed discussion of the main band of CV see Appendix II, Ph.D. thesis, Catharine E. Looney, University of Washington.

(12) Totally symmetric ground states are assumed.

(13) P. P. Feofilov, *Doklady Akad. Nauk*, *S.S.S.R.*, **57**, 447 (1947).

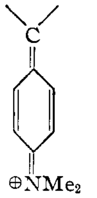
(14) G. N. Lewis and J. Bigeleisen, THIS JOURNAL, **65**, 2102 (1943).

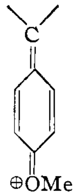
(and moves to the blue). Assignment of the upper state to A_1 follows. The second band for MHB is assigned as A → A mainly on theoretical grounds, because emission from Michler ketone jammed the polarization experiments. The experiments gave only the result that there was appreciable y absorption in the 360 mμ region. The technique of examining the fluorescence visually did not make it possible to determine any but the first two polarizations for nMG; however, the next band, may, perhaps, be assigned by correlation.

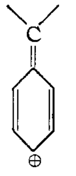
The transition moments are not given for the bands in the region 290–300 mμ, but it was found that the intensity for CV in this region is greater than for the other dyes by a factor of 1.8 to 3. It is assumed that this intensity change can be correlated with the polarization change. Thus for CV there is assumed to be a degenerate upper state for the 3.28 transition, but for the other dyes the y polarized component has apparently moved farther out into the ultraviolet, leaving only the x component.

The data in Fig. 1 for CV and mMG, except for the absorptions in the 290–300 mμ region, were incorporated into a structure representation formalism in paper II. Although the treatment in paper II may have value from the standpoint of classification, the predictive value is limited to the conclusion that the four most obvious classical structures_1 fit the observed polarizations. The work in paper II should therefore be considered to be mainly the solution of a preliminary problem which paves the way for predictions.

Transition Energies.—We wish now to use the structures_1 for MG and the formalism of paper II to predict the transition energies for MG. Structure_1 (1) for CV, mMG and MG is, respectively







This suggests, in view of the fact that $\delta\mathbf{E}'$ for mMG is

$$\begin{pmatrix} 0.940 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

that the matrix in the structure representation giving the change away from $\mathbf{E}'$ (CV) for MG be taken with the same simple form. That is, in

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

all the matrix elements of $\delta\mathbf{E}'$ should be taken as zero except $\delta E'_{11}$.

This is a particular assumption and in this case is the core of the application of the structure representation method.[15] Now we should be able to find the value of $\delta E'_{11}$ from the spectrum of MG, using trace invariance just as in paper II. (We are using a datum for MG, so the number of predicted transition energies is perhaps best considered as reduced by one.)

The observed trace of CV is $0 + 1.760 + 1.760 + 2.750 = 6.270$. Using $E_{11} = 0$ for CV we have for MG a trace of

$$x + (x + 1.62) + (x + 2.36) + (x + 3.14)$$

(see Fig. 1) and must find x. The energy difference between the first transition energy for CV (1.760) and for MG (1.620) is 0.140. This difference is x, the ground state energy of MG, (that is, E_{11} (MG)) because the upper level has the wave function

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

for both CV and MG and $\delta E'_2 = \delta E'_{33} = \delta E'_{23} = 0$, so that the upper levels have the same energy. The trace for MG is therefore 7.680, which is greater than the CV trace by 1.410. This difference in the traces is invariant on transformation into the structure representation and hence is the trace of $\delta\text{E}'$ or simply $\delta E'_{11} = 1.410$.

The energy matrix for MG in the structure representation is obtained directly from the matrix for CV in paper II. Differing only in the E'_{11} value, it is

$$\mathbf{E}'(\text{MG}) = \begin{pmatrix} 3.042 & -0.128 & -0.128 & -0.794 \\ -0.128 & 1.632 & -0.128 & -0.794 \\ -0.128 & -0.128 & 1.632 & -0.794 \\ -0.794 & -0.794 & -0.794 & 1.375 \end{pmatrix}$$

The calculation of the transition energies for MG is now the mechanical problem of diagonalizing this matrix. The predicted energy matrix in the Heisenberg representation is

$$\mathbf{E}(\text{MG}) = \begin{pmatrix} 0.140 & 0 & 0 & 0 \\ 0 & 1.760 & 0 & 0 \\ 0 & 0 & 2.37 & 0 \\ 0 & 0 & 0 & 3.40 \end{pmatrix}$$

with transition energies 1.62, 2.23 and 3.26 (observed, 1.62, 2.36, and 3.14). The eigenvectors of $\mathbf{E}'$ form the columns of

$$\mathbf{S}^{-1}(\text{MG}) = \begin{pmatrix} 0.2405 & 0 & 0.4109 & 0.8794 \\ 0.4498 & 0.7071 & -0.5311 & 0.1252 \\ 0.4498 & -0.7071 & -0.5311 & 0.1252 \\ 0.7332 & 0 & 0.5168 & -0.4420 \end{pmatrix}$$

The contributions of the structures_2 may be obtained from the $\mathbf{S}^{-1}$ matrix. For example for the ground state the contribution of structure_2 (1) is $(0.2405)^2 = 0.06$.

Several questions now arise. How much better is this scheme than a simple extrapolation procedure in which the energy for, say, the MG 1-3 transition is predicted by projecting the data for CV and mMG a "distance" obtained by referring to the 1,2-transition energies? The advantage in the quantal calculation of transition energies shows up best for larger $\delta E'_{11}$ values, where the theory predicts that the 1-3 transition energy fails to increase without limit but actually turns back slightly for $\delta E'_{11} > 3$. This predicted behavior is realized for nMG in water where the absorption of the 1,3-transition is at slightly longer wave lengths than the corresponding band in MG, though in glacial acetic acid the two transition energies are the same. A further advantage in using the structure representation is that the parameter which expresses the change from CV may be found from the trace. Still another advantage is that there is more information obtained than just transition energies, *e.g.*, the $\mathbf{S}^{-1}$ matrix, which leads to intensity predictions; the relative ground

---

[15] For predictions the structure representation method does at bottom require particular assumptions to be made; mainly because, though quantum mechanical in pattern, it does not contain commutation rules for the operators. Frequently however the nature of a particular assumption follows from a consideration of structures_1 with a naturalness that amounts to inevitability.

state energies; and matrix elements in the structure representation, which may be considered as giving thermodynamic properties.

Another question arising is how much better is it to use the four-dimensional than the three-dimensional treatment (see paper II). The three-dimensional treatment can be used to furnish good predictions about the position and intensity of the first band, but gives a 1,3-transition energy which continues to increase as $\delta E'_{11}$ increases in disagreement with experiment, and an intensity for the 1,3-transition which is too high. This probably means that the actual presence of two y-bands, lying close together, requires that each be considered explicitly in the theory. We shall now consider nMG and MHB, though each represents a rather large structural extrapolation from CV.

A study of Fig. 1 will show that the second y-band (3.14 transition of MG) is moving into a region formerly occupied by another y-band.[16] The situation for nMG is believed to be approximately as follows. The second y-band involving structures (1), (2), (3) and (4) lies far in the ultraviolet, having crossed over the third y-band. Therefore the band at 3.16 for nMG is no longer to be described using the structures originally assumed. It will be seen from Fig. 1 that already for mMG and MG the y absorption in the region of 3.4 has been "driven away" by the approaching band (3.14 transition of MG). In consequence it is not entirely appropriate to consider even the 3.14 transition of MG as involving exclusively states derived from the structures (1) to (4).

We do not use the trace to make a structure representation calculation for nMG because of the considerations in the last paragraph. Instead we have found that, using

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

together with

$$\delta\mathbf{E}'_{11} = 2.800, \text{ all other } \delta\mathbf{E}'_{ij} = 0$$

we can match the 1,2-transition energy empirically.[17]

The transition energies, calculated after diagonalizing $\mathbf{E}'$(nMG) are (1.56), 2.29 and 4.43 compared with observed 1.55, 2.36, —. Note that the 1,3-transition energy, 2.29, is only very slightly different from the value calculated for MG(2.23) even though E'_{11} has gone from 1.410 to 2.800. Both theory and experiment show, for a small perturbation of CV, a large change in the 1,3-transition energy and a small change in the 1,2-transition energy; and for a large perturbation of CV, essentially the reverse.

The transformation matrix for nMG is

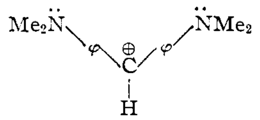
$$\mathbf{S}^{-1}(\text{nMG}) = \begin{pmatrix} 0.1662 & 0 & 0.4901 & 0.9683 \\ 0.4637 & 0.7071 & -0.5333 & 0.0230 \\ 0.4637 & -0.7071 & -0.5333 & 0.0230 \\ 0.7365 & 0 & 0.6296 & -0.2471 \end{pmatrix}$$

The contribution of structure$_2$ (1) with the plus charge on or adjacent to the nitro group is seen to be very small ($(0.1662)^2 = 0.03$).

Finally we consider MHB. One would hope to obtain the energy matrix in the structure representation by setting $\delta E'_{11} = \infty$, which is the same as taking the second, third and fourth rows and columns of the CV matrix, to give

$$\begin{pmatrix} 1.632 & -0.128 & -0.794 \\ -0.128 & 1.632 & -0.794 \\ -0.794 & -0.794 & 1.375 \end{pmatrix}$$

(compare the structures$_1$ of CV and MHB). However, the transition energies calculated from the $\mathbf{E}'$ (MHB) above are 1.46 and 2.25 compared with 1.65 and 2.58, observed. It is not unreasonable to suppose, however, that removing one phenyl alters structure$_2$ (4)



in the direction that more charge goes into the remaining two rings. In any event, if the 2,4- and 3,4-interaction is increased by 18% giving

$$\mathbf{E}'(\text{MHB}) = \begin{pmatrix} 1.632 & -0.128 & -0.940 \\ -0.128 & 1.632 & -0.940 \\ -0.940 & -0.940 & 1.375 \end{pmatrix}$$

diagonalization leads to transition energies of (1.65) and 2.66, to be compared again with the observed values, 1.65 and 2.58. The transition energy for the second band is a prediction. The transformation matrix is

$$\mathbf{S}^{-1}(\text{MHB}) = \begin{pmatrix} 0.4878 & 0.7071 & 0.5119 \\ 0.4878 & -0.7071 & 0.5119 \\ 0.7239 & 0 & -0.6899 \end{pmatrix}$$

Note that the ground state is composed of structures$_2$ (2), (3) and (4) with the contribution of (4) roughly equal to the combined contributions of the structures with the charge on the nitrogen, just as with CV for which (4) contributes 0.5.

Intensities.—The central idea for making predictions is to begin by putting some observed quantities into the structure representation, for a given molecule or molecules. After the change of representation, it is attempted to find these quantities for a related molecule. For the prediction of intensities we should start with the observed electric moment matrices for CV, $\mathbf{X}$(CV) and $\mathbf{Y}$(CV), transform so as to obtain $\mathbf{X}'$(CV) and $\mathbf{Y}'$(CV) and then from these, guided by the equivalence

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

attempt to obtain $\mathbf{X}'$(mMG) and $\mathbf{Y}'$(mMG). In the final step, which is mechanical, we must put $\mathbf{X}'$ and $\mathbf{Y}'$ for mMG back into the Heisenberg representation.

We already have obtained transformation matrices for all the dyes considered. Moreover the transformation matrix $\mathbf{S}^{-1}$(mMG) is, in a sense, exact. We are confronted with a difficulty, however, in that the matrices $\mathbf{X}$(CV) and $\mathbf{Y}$(CV) have matrix elements which have not, and perhaps cannot, in any

---

(16) This other y-band, and the companion x, (absorbing together at 3.28 for CV) probably should be assigned together as arising from excitation of the nature of $A_{1g} \rightarrow B_{2u}$ in the individual phenyls (local symmetry). See S. I. Weissman, *J. Chem. Phys.*, **18**, 1258 (1950); **22**, 21 (1954).

(17) We did not attempt to match the transition energy perfectly, but were content with a deviation of 0.01.

ordinary sense, be observed. The X moment connecting the excited states ψ_2 and ψ_3 is an example.

The plan for circumventing the difficulty is to attempt to construct matrices **x** and **y** which have matrix elements equal to the observed values where the observations have been made, and which are in other respects satisfactory. We call these matrices electric moment matrices, but the use of lower-case letters reminds us that they are not exact, even for CV. The scheme adopted for constructing **x** and **y** is to assume that electric moment is diagonal in the structure representation. It is possible to give some justification for this assumption on wave mechanical grounds (non-interaction of structure ψ's through the electric moment operator is related to the nature of their orthogonality) but it is reasonable anyway that as long as there is no very great change away from $\mathbf{S}^{-1}$(CV) the approximation should be good.

For CV, trigonometry gives the result that $x'_{22} = -x'_{33}$ and the other diagonal elements are zero (the center carbon is taken as origin). The y' elements differing from zero are $y'_{22} = y'_{33}$ and $y'_{11} = -2y'_{22}$. We also have the result that $x'_{33} = \sqrt{3}\, y'_{22}$. One number is required for the fixing of $\mathbf{x}'$ and $\mathbf{y}'$ and this is found from the observed[15] $x_{12} = y_{13} = 1.82$ Å., with the result

$$\mathbf{x}'(\mathrm{CV}) = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & -3.144 & 0 & 0 \\ 0 & 0 & 3.144 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

and

$$\mathbf{y}'(\mathrm{CV}) = \begin{pmatrix} -3.630 & 0 & 0 & 0 \\ 0 & 1.815 & 0 & 0 \\ 0 & 0 & 1.815 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

The matrices in the Heisenberg representation are

$$\mathbf{x}(\mathrm{CV}) = \begin{pmatrix} 0 & -1.815 & 0 & 0 \\ -1.815 & 0 & 1.815 & -1.815 \\ 0 & 1.815 & 0 & 0 \\ 0 & -1.815 & 0 & 0 \end{pmatrix}$$

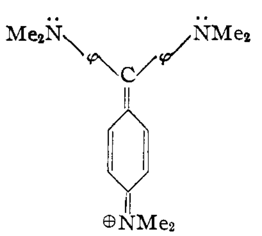
and

$$\mathbf{y}(\mathrm{CV}) = \begin{pmatrix} 0 & 0 & -1.815 & 0 \\ 0 & 1.815 & 0 & 0 \\ -1.815 & 0 & -1.815 & -1.815 \\ 0 & 0 & -1.815 & 0 \end{pmatrix}$$

The 1,2-transition is seen to be polarized x with a transition moment 1.82 while the 1,3-transition is y, also with a moment of 1.82, as is required.[18] The states ψ_2 and ψ_3 are seen to have y electric moments. This is the result of our choice of a particular phase for E of C_{3v} in paper II.

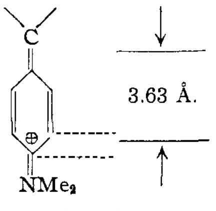
The value $y'_{11} = -3.63$ Å. gives the effective distance from the origin of the plus charge in structure$_2$ (1).

The classical structure$_1$ (1) is

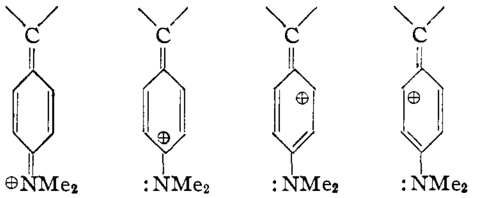


(1)

The charge is actually as indicated



This shows that the electric moments of the structures$_2$ are not very different from the literal values which would be assigned on the basis of structures$_1$. In fact, if one assumes equal contributions of the following



and a literal view about the location of the charge for each structure$_1$ he finds a predicted value for $|y'_{11}|$ of 3.5 Å. Now let us go on to consider predictions.

The particular assumption is made that for mMG the matrices $\mathbf{x}'$(mMG) and $\mathbf{y}'$(mMG) are the same as for CV.[15] This is suggested by the structures$_1$ for mMG. Thus all the burden for the calculation of differences in intensity from CV falls on the transformation matrices, or, in effect, on changes in the contributions of the structures. We have

$$\mathbf{x}(\mathrm{mMG}) = \mathbf{S}(\mathrm{mMG})\mathbf{x}'(\mathrm{CV})\mathbf{S}^{-1}(\mathrm{mMG})$$

and a similar equation for y giving

$$\mathbf{x}(\mathrm{mMG}) = \begin{pmatrix} 0 & -1.961 & 0 & 0 \\ -1.961 & 0 & 2.253 & -0.980 \\ 0 & 2.253 & 0 & 0 \\ 0 & -0.980 & 0 & 0 \end{pmatrix}$$

$$\mathbf{y}(\mathrm{mMG}) = \begin{pmatrix} 0.420 & 0 & -1.402 & -0.429 \\ 0 & 1.815 & 0 & 0 \\ -1.402 & 0 & -0.282 & -2.014 \\ -0.429 & 0 & -2.014 & -1.955 \end{pmatrix}$$

We have thus predicted the 1,2-, 1,3- and 1,4-intensities to be 1.96, 1.40 and 0.43 Å., respectively, (observed 1.95, 1.33 and 0.44 Å.). The agreement is noteworthy, particularly considering the simplicity of the underlying assumption.

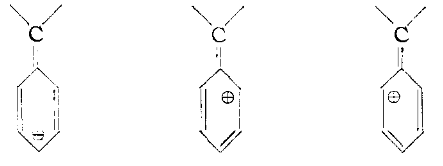
The increase in the x intensity from that for CV arises from the fact that the contributions of ψ^2 and ψ^3 to the ground state increase as the energy of ψ^1 is raised.

A similar procedure is followed for MG except that now it is not reasonable to assume that the

---

[18] Note that the moments in the structure representation are positive for a displacement of positive charge in the positive x and y directions. The signs of the transition moments are, however, not significant. The whole question of phases in the structure representation should perhaps be clarified.

charge for structure$_2$ (1) is located at $y = -3.63$ A. Instead we estimate the location using structures$_1$



and assume that each contributes equally.[15] The x′ matrix is as before, but the y′ matrix becomes

$$y'(\mathrm{MG}) = \begin{pmatrix} -2.780 & 0 & 0 & 0 \\ 0 & 1.815 & 0 & 0 \\ 0 & 0 & 1.815 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

The calculated transition moments turn out to be 2.00, 1.14 and 0.39 Å. for the 1,2-, 1,3- and 1,4-transitions, respectively (observed, 2.06, 0.99, and 0.74 Å.). The comparatively poor agreement for the 1,4-transition indicates that the accuracy of the prediction of the 1,4-transition moment for mMG may be somewhat fortuitous.

The intensities for nMG and MHB were also calculated. The assumption is made for nMG that the electric moment matrices are the same as for CV, and for MHB the equivalent assumption is made with allowance for the loss of one dimethylaminophenyl. For nMG we obtain, calculated, 2.06, 1.01 and 0.55 Å. (observed, 2.00, 1.05 and 0.8 Å.); for MHB, calculated, 2.17 and 0.91 Å. (observed 2.25 ± 0.05 and a very small value, probably less than 0.3 Å.). It is a little surprising that the observed intensity for the 1,2-transition in nMG is less than for MG. This may be caused by interaction with the nitro group. The axis of abnormally high polarizability for the nitro is parallel and alongside of the x oscillation for the 1,2-transition, which certainly could result in a diminution of intensity and a shift to shorter wave lengths for the band. The intensity calculated for the 1,2-transition for MHB is in good agreement with experiment, but the 1,3-intensity is not described well by the calculation. This means either that y'_{44} has an appreciable positive value, and/or that y'_{22} and y'_{33} are not as large as expected.

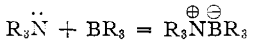
Generally speaking one ought not attempt to give detailed explanations of discrepancies when the expectation of unvarying success for the structure representation method has not been established. Nevertheless the agreement found for the intensities of mMG and MG indicates that the method has predictive value.

Thermodynamic Quantities.—The theory so far in this paper deals mainly with predictions. There is some value in the application of structure representation methods even when no new information is produced; but observed spectral quantities are merely combined through the transformations to give other quantities. These other quantities, which may be thermodynamic in nature, make possible a systemization of the spectral data along lines familiar to chemists. An example in paper II was the determination of a vertical spectroscopic resonance energy for benzene.

We shall first discuss the extent to which thermodynamic quantities may be satisfactorily determined from matrix elements in the structure representation. Next we shall consider as examples the base strengths of substituent groups in the dye series, and the dye resonance energies in relation to heats of carbinol formation.

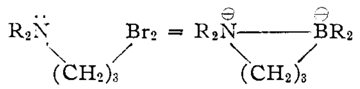
We shall be considering transitions among the structures as being like chemical reactions, and energy expectation values (diagonal matrix elements) in the structure representation as furnishing information about heats of reaction.

As a preliminary we examine briefly ordinary chemical reactions. When we write the equation for a reaction such as



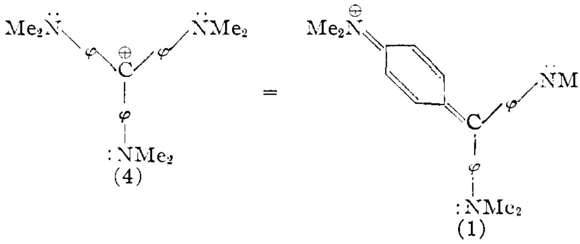
$$\mathrm{R_3\ddot{N}} + \mathrm{BR_3} = \mathrm{R_3\overset{\oplus}{N}\overset{\ominus}{B}R_3}$$

we realize firstly that the structures may be little more than formally correct in depicting the chemical species participating; nevertheless, there still are definite species involved, and experimentally as well as conceptually a ΔE/mole is unambiguously determined. Secondly, if the parts reacting are connected by chemical bonds as in the following reaction



still a value of ΔE is meaningful.

In the work with spectra and structures, reactions similar to the above make an appearance, but they are qualitatively different. To see this we consider these structures$_2$ of CV

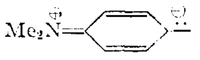


(4) (1)

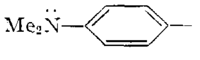
We may consider the transition from (4) to (1) to be analogous to an ordinary reaction in which a base neutralizes a Lewis acid, and for the heat of this reaction we have

$$\Delta E = E'_{11} - E'_{44}$$

We call the reaction a pseudo-reaction. Firstly we note that the representation of the base may be inaccurate. For example we may wonder if it would not be better to use



in place of



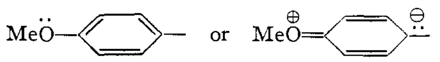
but this does not introduce anything to set the above apart from ordinary reactions. Secondly, we note also that the reacting parts are connected, so that they belong to the same molecule, but this again does not introduce anything new.

In the case of a *bona fide* chemical reaction the participating species are unambiguously defined by the experimental ΔE. In the CV case this determination cannot be made unambiguously, because ΔE depends on which structure representation is being employed. This is the qualitative difference from true reactions, the reason for the name pseudo-reaction. Nevertheless the wave functions corresponding to structures are conceptually well defined in that they are linear combinations of true wave functions for true electronic stationary states. The ambiguity, which we have described in detail in paper II, results from the existence of whole families of linear combinations which transform the same way (same general shape but different detailed shapes).

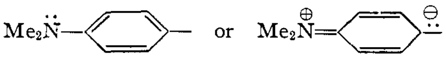
In paper II we treated CV in two different ways, obtaining $\mathbf{E}'$(CV) corresponding to the ψ^i's (4×4 case) and $\mathbf{E}''$(CV) corresponding to the φ^i's (3×3 case). The values of $E'_{11} - E'_{44}$ and $E''_{11} - E''_{44}$ (respectively, 0.257 and -1.577) are understandably quite different, but the quantities $\delta E'_{11}$ and $\delta E''_{11}$ representing the change to mMG are not as different

$$\delta E'_{11} = 0.94 \quad (26.9 \text{ kcal./mole})$$
$$\delta E''_{11} = 0.62 \quad (17.7 \text{ kcal./mole})$$

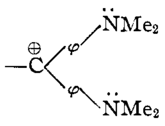
We may take either of the δE_{11} values as a measure of the basicity of



relative to



because formally the reference acid in the neutralization pseudo-reaction is the same for both bases, namely



Each value, $\delta E'_{11}$ or $\delta E''_{11}$ is determined from the spectra quite sharply by arguments based on trace invariance, and each seems plausible.

Estimates of the basicity of amines relative to ethers can be made from Gordy's work[19] and one finds superficially that $\delta E''_{11}$ is about right. It should be realized, however, that the change in structure is not simply from amine to ether. We may imagine that for the basic group to function at the carbonium ion position (center carbon) the strongly basic part has to "break through" the benzene resonance. It is possible that $Me_2\ddot{N}$– can break through effectively while $Me\ddot{O}$– cannot, so that the presence of the benzene ring could exaggerate the basicity difference between amines and ethers. In Table I we list the various $\delta E'_{11}$ values, based on the treatment using structures (1) to (4) for all the dyes in the series. This way the ambiguity is by-passed, by uniform adoption of what is considered to be in all likelihood the best convention. The δE values are converted to δpK values at 298° using $\delta \Delta F° = -2.302\, RT\delta pK$ (and as is customary, $\Delta S° = 0$).

TABLE I

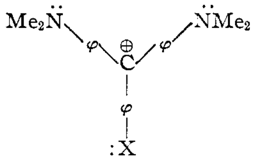
BASICITIES AT THE *para*-POSITION

Substituent	$\delta E'_{11}$	δpK
$Me_2\ddot{N}$–	0	+29.0
$Me\ddot{O}$–	0.940	+ 9.7
H–	1.410	0
O_2N–	2.800	−28.7

Note that through the use of spectra we have been able to construct a basicity scale which is well-defined and quantitative, and at the same time enormously expanded, covering here a range of 58 *pK* units.

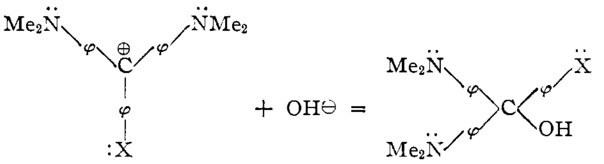
Let us next consider a different set of thermodynamic quantities for the triphenylmethane dyes, the ground state energies. These increase going along the series from CV because $\delta E'_{11}$ is increasing, but not as rapidly as one might think, because the contribution of ψ^1 to the ground state decreases. We measure the energies from E'_{44} which is the same over the series. This gives a set of spectroscopic resonance energies relative to the structure$_2$, having the lowest energy, (4). These resonance energies are ΔE for the pseudo-reaction

dye =



(4)

If we add to this pseudo-reaction another



(4)

the sum of the two is a true chemical reaction

$$\text{dye} + \text{OH}^{\ominus} = \text{dye carbinol}$$

In consequence we should have for the ΔE of carbinol formation the sum of the values for the pseudo-reactions. The changes in ΔE of carbinol formation along the series should follow the changes in resonance energies to the extent that ΔE for the second pseudo-reaction remains constant.

We are now able to make a set of predictions of a kind which is characteristic of work in the structure representation. On the basis of the equivalence: structures$_1$ ≈ structures$_2$ we make the particular assumptions that ΔE for carbinol formation from structure (4) is constant over the series.[15] This leads to the values in Table II for $\delta \Delta E$ of carbinol formation.

The entry in the experimental column was obtained from the determination by Goldacre and Phillips[6] of equilibrium constants for carbinol formation for crystal violet and malachite green. We have assumed entropy effects cancel and have converted to the units used mainly in this paper. The close agreement between calculated and observed values in the one case for which the comparison is possible should be noted.

---

(19) W. Gordy, *J. Chem. Phys.*, **9**, 215 (1941).

TABLE II

RESONANCE ENERGIES AND CHANGES IN HEAT OF CARBINOL FORMATION FOR COMPOUNDS RELATED TO CRYSTAL VIOLET

Compound	Resonance energies	Heats of carbinol formation referred to crystal violet[a] Theoretical	Heats of carbinol formation referred to crystal violet[a] Experimental
Crystal violet	1.38 (39 kcal./mole)	(0)	(0)
p-Methoxy malachite green	1.27	−0.11	....
Malachite green	1.24	− .14	−0.12
p-Nitro malachite green	1.17	− .21	....

[a] Note that by virtue of the nature of ψ_2 the values in the theoretical column may be quickly computed from the observed 1,2-transition energies. They are simply the negative of the ground state energy differences from CV.

Before concluding this section we need to call attention to a situation which is easy to interpret incorrectly. One might think that if the only difference between pseudo-reactions and bona-fide reactions is in the ambiguity associated with different structure representations, then in some cases there would be no difference at all. For example in paper II we treated benzene under the assumption $n = 2$ (two Kekulé structures) and found no formal ambiguity (no arbitrary constants in S^{-1}). However it must be kept in mind that in all the analysis with the structure representation we deal with an $n \times n$ upper block of an infinitely large matrix **E** in the Heisenberg representation. The freedom of choice of n, while necessary from the standpoint of fitting structures$_1$ (which may be few in number) to observed levels, gives always an ambiguity in a larger sense. Hence expectation values in the structure representation cannot strictly be interpreted as E values for working out heats of reaction.

This rule has one exception, the case in which the structure representation is the same as the Heisenberg representation (no interactions among the structures, or in structure$_1$ language, no mesomerism). This is the limiting case for which the equivalence relation

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

holds perfectly: the domain of applicability of classical valence theory.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM PHYSICAL CHEMISTRY LABORATORY, OXFORD]

An Experimental Study of the Transfer of Energy of Excitation between Unlike Molecules in Liquid Solutions[1]

BY EDMUND J. BOWEN AND ROBERT LIVINGSTON

RECEIVED JULY 6, 1954

In solutions containing two fluorescent solutes, where the emission spectrum of the first (A) overlaps the absorption spectrum of the second (B), the fluorescence of A is quenched, and the fluorescence of B is sensitized. The intensities of the fluorescence of each component were measured for the following pairs of aromatic hydrocarbons: chloroanthracene–perylene, chloroanthracene–rubrene and cyanoanthracene–rubrene. The transfer of energy of excitation between these compounds is much more efficient than can be accounted for by a process of emission and reabsorption. The data are consistent with the postulate that the non-radiative transfer of energy is a bimolecular interaction between an excited molecule of A and a normal molecule of B. The rate of this interaction is not determined by diffusion, being apparently independent of the viscosity of the solvent and (even in benzene) at least ten-fold faster than a diffusion-controlled process. Furthermore, it is not due to the formation of dimers, as is demonstrated both by the nature of the concentration dependence of the fluorescence and by the validity of Beer's law when applied to the mixed solutions.

The transfer of the energy of electronic excitation between like molecules in liquid solutions results in the depolarization and the self-quenching of the fluorescence of such solutions.[2a,b] Between unlike molecules, the corresponding transfer process results in the quenching of the fluorescence of one species and the sensitization of the fluorescence of the other.[3] Such an energy transfer can be due either to a radiative or to a non-radiative process. The former, commonly referred to as "absorption and remission" or as the "trivial process," is relatively unimportant for most solutions. The non-radiative process, which we shall designate as "classical resonance," has been analyzed theoretically[4,5] (especially by Professor Förster), and its existence has been demonstrated experimentally.[6–9] Of the systems investigated, the chloroanthracene–perylene[9] pair appears to be especially suitable for quantitative study. Measurements of the sensitized fluorescence and concurrent quenching are reported in the present paper for the following pairs of compounds: 1-chloroanthracene and perylene, 9-cyanoanthracene and rubrene, 1-chloroanthracene and rubrene and 9-aldehydoanthracene and rubrene.

Experimental Methods and Materials

The several hydrocarbons were purified chromatographically before use. All the solvents were of Analar grade and

---

(1) This work was performed while one of us (RL) was on Sabbatical Furlough from the University of Minnesota, Minneapolis, Minn. and was the recipient of a grant from the Guggenheim Memorial Foundation.

(2) (a) Th. Förster, "Fluoreszenz Organischer Verbindungen," Vandenhoeck and Ruprecht, Göttingen, 1951, pp. 172–180, 230–238; (b) P. Pringsheim, "Fluorescence and Phosphorescence," Interscience Publ. Inc., New York, N. Y., 1949, pp. 349–352, 378–379.

(3) Th. Förster, ref. 2a, p. 182.

(4) S. Vavilov, *J. Phys.* (*URRS*), **7**, 141 (1943).

(5) Th. Förster, *Ann. Physik*, **2**, 55 (1958).

(6) Th. Förster, *Z. Elektrochem.*, **53**, 93 (1949); *Z. Naturforsch.*, **4a**, 321 (1949).

(7) W. F. Watson and R. Livingston, *J. Chem. Phys.*, **18**, 802 (1950).

(8) L. N. M. Duysens, *Nature*, **168**, 548 (1951).

(9) E. J. Bowen and B. Brockelhurst, *Trans. Faraday Soc.*, **49**, 1131 (1953).