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## Absorption of Polysubstituted Benzene Derivatives\*

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The intensification, by nonchromophoric substitutions, of the forbidden,  ${}^1A_{1g} \rightarrow {}^1B_{2u}$ , transition in benzene is due, on the one hand, to the unsymmetrical distortion of the ring by the normal vibrations and, on the other hand, to the transition moment produced at the equilibrium position by the migration of charge from the substitution into the ring or vice versa. The latter effect is treated by the method of antisymmetrical molecular orbitals, all calculations being limited to the first order. The rules for combining transition moments due to the various groups in a polysubstituted benzene are calculated. It is shown that,

for weak nonchromophoric substitutions, the intensity ratios (except for the less important variation in the normal vibrations) are for  $C_6H_5X$ :  $oC_6H_4X_2$ :  $mC_6H_4X_2$ :  $pC_6H_4X_2$ : 1,3,5  $C_6H_3X_3$ : 1,2,3  $C_6H_3X_3$ : 1,2,4  $C_6H_3X_3$  = 1 : 1 : 1 : 4 : 0 : 0 : 3. It is further shown that if one substitutes benzene by a meta-directing group,  $M$ , and by an ortho-para-directing group,  $P$ , of the same intensifying power, the ratios for the mono : ortho : meta : para-derivatives should be 1 : 3 : 3 : 0. These ratios are shown to be in good qualitative agreement with experimental data.

### INTRODUCTION

THE effect of substitutions upon the intensity of the characteristic absorption bands of a chromophoric nucleus depends both upon the nature of the substituting group and upon the nature of the electronic transition associated with the absorption. The various substituting radicals may be first subdivided into chromophoric and non-chromophoric classes. The former (e.g.,  $-NO_2$ ) possesses a resonating system independent of the chromophore to which they are attached and cause new long wave-length electronic bands in the derivative. The effect of such radicals will be considered in a later paper. Here we will be concerned with those groups which in themselves do not have a resonating system either because the group is saturated or because one of the structures has a considerably lower energy than all others. Each class of radicals may now be further broken up into weak and strong types, depending upon the magnitude of the interaction between the radical and the nucleus on which it is substituted. There is, of course, no sharp dividing line between these classes. We shall consider only those radicals whose effect on the electronic states is sufficiently small to be handled as a first-order correction only.

The nature of the electronic transition in the chromophore nucleus also plays an essential role

in determining the effect of the substitution. The intensity of a strong band associated with an allowed transition will not be much affected percentually by a weak substitution which does not form an enlarged chromophore. However, the intensity of a weak band whose weakness is due to the geometrical symmetry of the molecular nucleus will in general be greatly enhanced percentually by substitutions which destroy symmetry.

The long wave-length electronic band of benzene at 2600A has been shown to be due to a transition of the latter type,<sup>1</sup> appearing weakly in benzene itself only through the distortion of the ring by unsymmetrical vibrations. The intensification of this band by a monosubstitution has been attributed<sup>2</sup> to the migration of unsaturation electrons<sup>3</sup> into or out from the aromatic nucleus. It was shown that such a migration produces a transition moment in the plane of the ring at right angles to the ring-substituent axis.<sup>2</sup>

This transition moment alone determines the entire intensity of the band only if the nuclei are held fast in their equilibrium position. The interaction of unsymmetrical vibrations, just as in the case of unsubstituted benzene, will cause

<sup>1</sup> A. L. Sklar, J. Chem. Phys. **5**, 669 (1937); M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys. **6**, 645 (1938); H. Sponer, G. Nordheim, A. L. Sklar, and E. Teller, J. Chem. Phys. **7**, 207 (1939).

<sup>2</sup> A. L. Sklar, J. Chem. Phys. **7**, 984 (1939).

<sup>3</sup> R. S. Mulliken, J. Chem. Phys. **7**, 123 (1939); **7**, 353 (1939).

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additional bands.<sup>4</sup> The occurrence of two such superimposed spectra, one having the appearance of an allowed transition (migration moment) and one that of a forbidden transition (vibration moment) has recently been discussed for the case of monochlorobenzene.<sup>5</sup>

From a chemical point of view one can separate the various substitutions into two classes,<sup>6</sup> meta-directing (e.g., NO<sub>2</sub>, COOH) and ortho-para-directing (e.g., CH<sub>3</sub>, Cl, OH, NH<sub>2</sub>). It has been shown<sup>7</sup> that (except for a few unimportant cases) the ortho-para-directing groups send charge into the benzene ring whereas the meta-directing groups attract charge from the ring. One must accordingly consider separately the transition moment caused by ortho-para-(*P*) and meta-(*M*) directing groups.

In the following we will consider the combined effects of several groups in various positions upon the intensity of the 2600Å band of benzene.

#### INTENSITIES IN C<sub>6</sub>H<sub>6-n</sub>P<sub>n</sub>

##### Group Theoretical Discussion

The combined effect of a number of identical weak non-chromophoric substitutions (*P* or *M*) can be most quickly seen from a group theoretical point of view. The 2600Å band of benzene (*D*<sub>6h</sub> group) has been shown<sup>1</sup> to be a  ${}^1A_{1g} \rightarrow {}^1B_{2u}$  transition. The coordinate perpendicular to the plane of the ring<sup>2</sup> transforms like  $A_{2u}$  while the two coordinates in the plane (*x*, *y*) transform like the degenerate representation  $E^-_{2u}$ . Since neither  $A_{1g}A_{2u}B_{2u}(=B_{1g})$  nor  $A_{1g}E^-_{2u}B_{2u}(=E^+_{2g})$  contain  $A_{1g}$  the transition in benzene is forbidden. Now it is clear that a perturbation symmetrical to a reflection in the plane of the ring cannot give a transition moment in the *Z* direction since both the ground and excited state contain the same number of  $P_z$  electrons and no others. Since the induction effect,<sup>8</sup> which is the only perturbation in the plane molecule in its equilibrium position not necessarily symmetrical to a reflection in the plane, has only a negligible

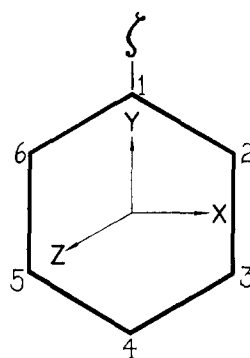


FIG. 1. Orientation of coordinate system in a monosubstituted benzene and notation for positions of substitution.

effect<sup>2</sup> on the intensity we need consider only the transition moment in the plane of the ring. Now in order to have a first order transition moment in the plane of the ring it is both necessary and sufficient that the perturbation either mix an  $E^+_{2g}$  component into the ground ( $A_{1g}$ ) state or an  $E^-_{2u}$  component into the excited ( $B_{2u}$ ) state. Now both of these admixtures can be brought about only by a perturbation which transforms like  $E^+_{2g}$ . If we now consider any perturbation, say that of a single substitution which has only axial symmetry, as expanded into a series in the normal coordinates of *D*<sub>6h</sub> symmetry, it is clear that only the  $E^+_{2g}$  term can affect the transition moment. Now a perturbation of symmetry  $E^+_{2g}$  transforms under rotations in the plane like  $e^{2i\varphi}$ . Since the transition moment is proportional, in the first order, to the perturbation, the relative intensity of

$$C_6H_5P_2 : o-C_6H_4P_2 : m-C_6H_4P_2 : p-C_6H_4P_2$$

will be

$$1 : \left| 1 + \exp\left(2i\frac{\pi}{3}\right) \right|^2 : \left| 1 + \exp\left(4i\frac{\pi}{3}\right) \right|^2 \\ : \left| 1 + \exp\left(6i\frac{\pi}{3}\right) \right|^2 \quad \text{or} \quad 1 : 1 : 1 : 4.$$

That is, one can find the combined action of two or more identical weak non-chromophoric substituents by adding the perturbations as vectors whose angular displacement is twice as great as that of the substitutions.

##### Non-Group Theoretical

The above results may also be obtained by a less general argument which, however has the compensating merit of being able to yield more

<sup>4</sup> G. Herzberg and E. Teller, *Zeits. f. physik. Chemie* **B21**, 410 (1933).

<sup>5</sup> H. Sponer and S. A. Wollman, *Phys. Rev.* **57**, 1078 (1941).

<sup>6</sup> E. Emmet Reid, *College Organic Chemistry* (D. Van Nostrand), p. 498.

<sup>7</sup> G. W. Wheland and L. Pauling, *J. Am. Chem. Soc.*, **57**, 2086 (1935).

<sup>8</sup> E. Hückel, *Zeits. f. Physik* **72**, 310 (1931).

detailed information such as the difference between the effect of an ortho-para-directing group and that of a meta-directing group. Group theory can only tell us that the transition moments for both types of substitutions will be collinear,\* but not whether they will reinforce or interfere.

We will first treat the case of two identical ortho-para-directing (*P*) substitutions whose relative orientation is either ortho, meta, or para. It is known<sup>7</sup> that such substituents send charge into the ring. The effect of a single *P* group on the intensity of absorption has been treated in a previous paper<sup>2</sup> in the following manner. One writes a molecular orbital including not only the six  $P_z$  (unsaturation) electrons in the ring but also a pair of  $P_z$  electrons on the substitution. The atomic orbitals for the six  $P_z$  ring electrons are the same as in unsubstituted

benzene while the atomic orbitals for the pair of electrons on the radical are linear combinations of radical functions and benzene orbitals.

If one writes  $K(\nu)$  for the  $P_z$  atomic function of the  $k$ th carbon atom in the ring, the benzene orbitals may be written in the following real form:

$$\left. \begin{aligned} \varphi_0(\nu) &= \frac{1}{\sqrt{6}} \sum_k K(\nu), \\ \varphi_l(\nu) &= \frac{1}{\sqrt{3}} \sum_k \cos\left(\frac{2\pi}{6}lk\right) \cdot K(\nu) \\ \varphi_{-l}(\nu) &= \frac{1}{\sqrt{3}} \sum_k \sin\left(\frac{2\pi}{6}lk\right) \cdot K(\nu) \\ \varphi_3(\nu) &= \frac{1}{\sqrt{6}} \sum_k (-1)^k K(\nu), \end{aligned} \right\} l=1, 2, \quad (1)$$

where  $k=0, 1, 2, \dots, 5$ .

The orbitals for the pair of radical electrons on a substituent attached to carbon atom zero is then:

$$\psi(\nu) = \sum_{j=1}^3 a_j \varphi_j(\nu) + b \zeta(\nu) \quad (2)$$

where  $\zeta$  is the atomic orbital of the radical and  $\lambda_j = a_j/b$  is determined by minimizing the energy.<sup>2</sup> In Eq. (2) the summation runs over the positive values of  $j$  only since  $\zeta$  and  $\varphi_{-j}$  are, respectively, even and odd with respect to a rotation by  $\pi$  about the ring-radical axes and hence do not interact.

The antisymmetrized molecular orbitals for the ground,  $\Psi_0$  and excited state,  $\Psi'$ , corresponding to the 2600Å band<sup>1</sup> become,<sup>9</sup> after neglecting terms containing squares of  $\lambda_j$ :

$$\begin{aligned} \Psi_0 &= (8! \mu_0)^{-\frac{1}{2}} \sum_P (-1)^P P \varphi_0(1) \varphi_0(2) \varphi_1(3) \varphi_1(4) \varphi_{-1}(5) \varphi_{-1}(6) \\ &\quad \times \{ \zeta(7) \zeta(8) + \sum_j \lambda_j [ \varphi_j(7) \zeta(8) + \zeta(7) \varphi_j(8) ] \} \chi_0, \\ \Psi' &= (8! 2\mu')^{-\frac{1}{2}} \sum_P (-1)^P P \varphi_0(1) \varphi_0(2) [ \varphi_1(3) \varphi_1(4) \varphi_{-1}(5) \varphi_2(6) + \varphi_{-1}(3) \varphi_{-1}(4) \varphi_1(5) \varphi_{-2}(6) ] \\ &\quad \times \{ \zeta(7) \zeta(8) + \sum_j \lambda_j [ \varphi_j(7) \zeta(8) + \zeta(7) \varphi_j(8) ] \} \chi', \end{aligned} \quad (3)$$

where  $\mu$  is the normalization factor and the spin functions  $\chi$  are:

$$\begin{aligned} \chi_0 &= \alpha_1 \beta_2 \alpha_3 \beta_4 \alpha_5 \beta_6 \alpha_7 \beta_8, \\ \chi' &= \alpha_1 \beta_2 \alpha_3 \beta_4 \frac{1}{\sqrt{2}} (\alpha_5 \beta_6 - \beta_5 \alpha_6) \alpha_7 \beta_8. \end{aligned}$$

The transition moment,  $e \int \Psi_0 \mathbf{x} \Psi' d\tau$ , may then be evaluated directly, yielding the oscillator strength,  $f$ .<sup>2,10</sup>

\* It is easily seen that the transition moment induced in the  $A_{1g} \rightarrow B_{2u}$  transition by a monosubstitution, whether ortho-para- or meta-directing, is along the  $X$  axis (cf. Fig. 1). This follows from the fact that both the reflection in the plane ( $\sigma_h$ ) and the rotation by  $\pi$  about the  $Y$  axis ( $C'_2$ ) are symmetry operations of the substituted molecule. The former operation shows that there is no component of the transition moment along the  $Z$  axis since

$$\sigma_h \times [A_{1g} Z B_{2u}] = -[A_{1g} Z B_{2u}].$$

The  $Y$  component is likewise zero since  $C'_2 \times (A_{1g} Y B_{2u}) = -(A_{1g} Y B_{2u})$ . One can accordingly say that the transition moment is along the  $X$  axis for any type of group  $S$ ; one cannot, however, say in this manner whether both types of group will give a moment in the positive direction.

<sup>9</sup> In the previous paper (reference 2) the minus sign in Eq. (9) should be a plus sign.

<sup>10</sup> R. S. Mulliken, J. Chem. Phys. 7, 14 (1939).

If  $\zeta$  is the atomic orbital of a radical attached to carbon atom  $k=0$  and  $\xi$  that of a second radical oriented either ortho, meta, or para with respect to the first, one can write one-electron functions for the  $P_z$  electrons of the two substituents.

$$\begin{aligned}\psi(\nu) &= \sum_j a_j \varphi_j(\nu) + b \xi(\nu), \quad j=1, 2, 3, \\ \bar{\psi}(\nu) &= \sum_j \bar{a}_j \varphi_j(\nu) + \bar{b} \xi(\nu), \quad j=\pm 1, \pm 2, 3.\end{aligned}\quad (2')$$

If one writes the variation function for  $\bar{\psi}(\nu)$  as a linear combination of  $\varphi_j$ , the summation runs over negative as well as positive values of  $j$ , since the ring-radical axis to  $\xi$  is not a symmetry axis for the degenerate  $\varphi_j$ 's. It is, however, no loss of generality to write the function  $\bar{\psi}(\nu)$  in terms of the rotated orbitals,  $\bar{\varphi}_j$ , which do have the ring- $\xi$  radical axis as a symmetry axis, since the  $\varphi_{\pm j}$  are linear combinations of the  $\bar{\varphi}_{\pm j}$ . In this case the summation runs only over positive values of  $j$ , as in the case of  $\psi(\nu)$ , and the coefficients  $a_j$  are exactly the same in  $\bar{\psi}$  as in  $\psi$  if the substitutions are identical. Hence:

$$\bar{\psi}(\nu) = \sum_j a_j \bar{\varphi}_j(\nu) + b \xi(\nu), \quad j=1, 2, 3. \quad (2'')$$

One can now form the molecular orbitals  $[3']$  for the six ring and two pairs of radical electrons, again neglecting higher powers of  $\lambda$ .

$$\begin{aligned}\Psi_0 &= [10! \mu_0]^{-\frac{1}{2}} \sum_P (-1)^P P \varphi_0(1) \varphi_0(2) \varphi_1(3) \varphi_1(4) \varphi_{-1}(5) \varphi_{-1}(6) \{ \zeta(7) \zeta(8) \xi(9) \xi(10) \\ &\quad + \sum_j \lambda_j [\zeta(7) \varphi_j(8) + \varphi_j(7) \zeta(8)] \xi(9) \xi(10) + \zeta(7) \zeta(8) \sum_j \lambda_j [\xi(9) \bar{\varphi}_j(10) + \bar{\varphi}_j(9) \xi(10)] \} \chi_0, \\ \Psi' &= [10! 2\mu']^{-\frac{1}{2}} \sum_P (-1)^P P \varphi_0(1) \varphi_0(2) \{ \varphi_1(3) \varphi_1(4) \varphi_{-1}(5) \varphi_2(6) + \varphi_{-1}(3) \varphi_{-1}(4) \varphi_1(5) \varphi_{-2}(6) \} \\ &\quad \times \{ \zeta(7) \zeta(8) \xi(9) \xi(10) + \sum_j \lambda_j [\zeta(7) \varphi_j(8) + \varphi_j(7) \zeta(8)] \xi(9) \xi(10) \\ &\quad + \zeta(7) \zeta(8) \sum_j \bar{\lambda}_j [\xi(9) \bar{\varphi}_j(10) + \bar{\varphi}_j(9) \xi(10)] \} \chi',\end{aligned}\quad (3')$$

where  $\varphi_{\pm j}$  and  $\bar{\varphi}_{\pm j}$  are the benzene orbitals, and the spin functions  $\chi_0, \chi'$  are the product of  $\alpha\beta\beta_{10}$  and the corresponding  $\chi_0, \chi'$  of Eq. (3).

One can now proceed to form the transition moment

$$\mathbf{M} = e \int \Psi_0^* \mathbf{r} \Psi' d\tau,$$

which may be done in two parts. Let us first form the moment  $\mathbf{M}_\tau$  which is obtained by deleting from Eqs. (3') the summation over  $j$  which has  $\zeta(j)\zeta(j+1)$  as a factor;<sup>11</sup> and separately form  $\mathbf{M}_\xi$  which is similarly obtained by deleting the summation over  $j$  having  $\xi(j)\xi(j+1)$  as a factor. Since the overlap function  $\int \zeta(\nu) \xi(\nu) d\tau$  is completely negligible and since the unperturbed transition is forbidden we may write  $\mathbf{M} = \mathbf{M}_\tau + \mathbf{M}_\xi$ .

Before considering separately the vectors  $\mathbf{M}_\tau$  and  $\mathbf{M}_\xi$  it is first necessary to notice the behavior of  $\Psi_0$  and  $\Psi'$ , Eqs. (3'), under symmetry operations. Each of the functions  $\varphi_{\pm j}(\nu)$ ,  $\xi(\nu)$ ,

and  $\xi(\nu)$  are  $P_z$  orbitals and hence change sign under a reflection in the plane of the ring ( $\sigma_h$ ).  $\Psi_0$  and  $\Psi'$ , being homogeneous functions of an even degree in  $\varphi_{\pm j}(\nu)$ ,  $\xi(\nu)$ , and  $\xi(\nu)$ , are both symmetrical to  $\sigma_h$ . It is accordingly clear that both  $\mathbf{M}_\tau$  and  $\mathbf{M}_\xi$  contain no component along the  $Z$  axis.

Let us consider, for the moment, only  $\mathbf{M}_\tau$  which is formed by deleting from Eqs. (3') those terms containing  $\zeta(j)\zeta(j+1)$  as factor of a sum. Both  $\Psi_0$  and  $\Psi'$  then contain as a factor  $\xi(l)\xi(l+1)$  which does not affect the transition moment  $\mathbf{M}_\tau$ . Now the  $\varphi_{+j}(\nu)$  and  $\xi(\nu)$  are even with respect to a rotation by  $\pi$  about the  $Y$  axis ( $C'_2$ ), whereas the  $\varphi_{-j}(\nu)$  are odd with respect to  $C'_2$ , which is a symmetry operation of the deleted  $\Psi$ 's without the inactive factor  $[\xi(j)\xi(j+1)]$ .  $\Psi_0$ , being homogeneous of the second degree in  $\varphi_{-j}$ , is symmetrical with respect to  $C'_2$ .  $\Psi'$ , however, contains the  $\varphi_{-j}$  only singly or as triple products and is accordingly antisymmetrical with respect to  $C'_2$ . It follows, then, that  $\mathbf{M}_\tau$  contains no component along the  $Y$  axis. Accordingly,  $\mathbf{M}_\tau$  is parallel to the  $X$  axis. Whether it is directed along the positive or

<sup>11</sup> The wave function so obtained is one in which the substituent  $\zeta$  sends an electron into the ring while the substituent  $\xi$  keeps its  $P_z$  electrons to itself. The latter, therefore, do not influence the moment  $\mathbf{M}_\tau$ , which comes out the same as if  $\zeta$  had been the only substituent.

negative  $X$  axis depends<sup>12</sup> on the arbitrary choice of the sign of the  $\varphi_{\pm j}(\nu)$  in Eq. (1).

Let us now consider  $\mathbf{M}_\xi$  which is obtained by deleting in Eq. (3') the terms containing the factor  $\xi(j)\xi(j+1)$  in front of a summation over  $j$ . The moment  $\mathbf{M}_\xi$  is complicated only by the occurrence of both  $\varphi_j(\nu)$  and  $\bar{\varphi}_j(\nu)$  functions; the  $\varphi_j$  and  $\bar{\varphi}_j$  differing in that  $k$  is counted from the carbon atom joined to  $\zeta$  and  $\xi$ , respectively. The moment  $\mathbf{M}_\xi$  is, however, easily obtained if one expresses the  $\varphi_{\pm j}(\nu)$  in terms of the  $\bar{\varphi}_{\pm j}(\nu)$ . If one introduces the complex  $\phi_{\pm j}$

$$\phi_j = \frac{1}{\sqrt{2}}(\phi_j + \phi_{-j}), \quad \phi_{-j} = \frac{-i}{\sqrt{2}}(\phi_j - \phi_{-j}), \quad (4)$$

the transformation is easily made since

$$\bar{\phi}_{\pm j}(\nu) = \exp[i(\pm j)(\zeta, \xi)] \cdot \phi_{\pm j}, \quad (5)$$

where  $(\zeta, \xi)$  is the angle between the radius vectors from the center of the benzene ring to  $\zeta$  and  $\xi$ . It is thus easily checked that<sup>13</sup>

$$\Psi_0 = \bar{\Psi}_0 \quad \text{and} \quad \Psi' = \bar{\Psi}' \exp[3i(\zeta, \xi)], \quad (6)$$

where the  $\Psi$ 's are the  $\Psi$ 's without the terms in  $\lambda$ ; that is, without migration. The moment  $\mathbf{M}_\xi$ , then, differs from  $\mathbf{M}_\zeta$  in only two respects. First it has a factor  $\exp[3i(\zeta, \xi)]$  and second  $\bar{\varphi}_{\pm j}$  functions appear uniformly instead of  $\varphi_{\pm j}$ . The latter causes the vector moment  $\mathbf{M}_\xi$  to be turned through an angle  $(\zeta, \xi)$  with respect to  $\mathbf{M}_\zeta$  and the former causes it to be reversed every sixty degrees, that is, to be reversed in sign for ortho- and para- but not for meta-orientated groups. Since the intensity depends on the square of the vector sum of the moments the intensity ratios for  $\text{C}_6\text{H}_5\text{P} : \text{C}_6\text{H}_4\text{P}_2 : m\text{-C}_6\text{H}_4\text{P}_2 : p\text{-C}_6\text{H}_4\text{P}_2$  is 1 : 1 : 1 : 4, in agreement with the result obtained group theoretically. One can in this way also form intensity ratios for polysubstituted products,  $\text{C}_6\text{H}_{6-n}\text{P}_n$ . If the substituted radicals are not all the same, that is in  $\text{C}_6\text{H}_{6-m-n}\text{P}_n\text{P}_m'$ , the ratios will differ from the above but are easily obtained by adding unequal vectors whose lengths may be estimated from  $\text{C}_6\text{H}_5\text{P}$  and  $\text{C}_6\text{H}_5\text{P}'$ , as will be discussed later. These ratios will be discussed and compared with experimental data in a later section.

#### INTENSITIES IN $\text{C}_6\text{H}_{6-n}\text{M}_n$

It is immediately clear from a group theoretical point of view that the relative intensity ratios for  $\text{C}_6\text{H}_{6-n}\text{M}_n$  are the same as for  $\text{C}_6\text{H}_{6-n}\text{P}_n$  since the arguments depended only on the symmetry and not upon the nature of the interaction. The general theory, however, does not tell us how to combine moments due to ortho-para-directing groups with those due to meta-directing ones. In order to find the effect of a meta-directing group ( $M$ ) let us consider an  $M$ -monosubstituted benzene. We cannot use the orbitals of Eq. (3) since they consider only migration into the benzene ring and we are now concerned with migration of charge out from the ring into the radical.<sup>7</sup> One can form an appropriate variation function which permits migration out from the ring by replacing the benzene orbitals in the function for unsubstituted benzene by linear combinations<sup>14</sup> of benzene functions and radical function, that is,

$$\phi_j = \varphi_j + \lambda_j \zeta. \quad (7)$$

The variation function for the ground and excited state after neglecting higher powers of  $\lambda$  becomes

$$\begin{aligned} \Xi_0 &= [6! \mu_0]^{-\frac{1}{2}} \sum_P (-1)^P P \{ \varphi_0(1) \varphi_0(2) \varphi_1(3) \varphi_1(4) \varphi_{-1}(5) \varphi_{-1}(6) + \lambda_0 (\varphi_0(1) \zeta(2) + \zeta(1) \varphi_0(2)) \\ &\quad \times \varphi_1(3) \varphi_1(4) \varphi_{-1}(5) \varphi_{-1}(6) + \lambda_1 \varphi_0(1) \varphi_0(2) (\varphi_1(3) \zeta(4) + \zeta(3) \varphi_1(4)) \varphi_{-1}(5) \varphi_{-1}(6) \} \chi_0, \\ \Xi' &= [6! 2\mu']^{-\frac{1}{2}} \sum_P (-1)^P P \{ (\varphi_0(1) \varphi_0(2) + \lambda_0 [\varphi_0(1) \zeta(2) + \zeta(1) \varphi_0(2)]) (\varphi_1(3) \varphi_1(4) \varphi_{-1}(5) \varphi_2(6) \\ &\quad + \varphi_{-1}(3) \varphi_{-1}(4) \varphi_1(5) \varphi_2(6)) + \lambda_1 \varphi_0(1) \varphi_0(2) ([\varphi_1(3) \zeta(4) + \zeta(3) \varphi_1(4)] \varphi_{-1}(5) \varphi_2(6) \\ &\quad + \varphi_{-1}(3) \varphi_{-1}(4) \zeta(5) \varphi_2(6)) + \lambda_2 \varphi_0(1) \varphi_0(2) \varphi_1(3) \varphi_1(4) \varphi_{-1}(5) \zeta(6) \} \chi', \end{aligned} \quad (8)$$

<sup>12</sup> The choice made in Eq. (1) leads, as can be shown, to an  $\mathbf{M}_\zeta$  along the positive  $X$  axis, but that is not essential to the argument. Only the relative orientations of the transition moments are important.

<sup>13</sup>  $\Psi_0$  and  $\Psi'$  contain products of  $\phi_j$ 's in which the sum of the  $j$  values over all factors in the product is zero for  $\Psi_0$  and three for  $\Psi'$ .

<sup>14</sup>  $\psi$  is used for a one-electron function;  $\Psi$  is a molecular orbital without migration;  $\Psi'$  is a molecular orbital with migration into the ring; and  $\Xi$  is used to represent migration out from the ring.

where

$$\begin{aligned}\chi_0 &= \alpha_1\beta_2\alpha_3\beta_4\alpha_5\beta_6, \\ \chi' &= \alpha_1\beta_2\alpha_3\beta_4 \frac{1}{\sqrt{2}}(\alpha_5\beta_6 - \beta_5\alpha_6).\end{aligned}$$

One can now calculate the transition moment for the meta-directing substitution

$$\mathbf{M}_m = \int \Xi_0 \mathbf{r} \Xi' d\tau.$$

The result easily follows that the transition moment is in the  $X$  direction (Fig. 1) and its magnitude is:

$$\mathbf{M}_m = (2\lambda_1 T_1 + \lambda_1^2) \int \varphi_{-1} \chi \varphi_2 d\tau, \quad (9)$$

where

$$T_j = \int \varphi_j(\nu) \xi(\nu) d\tau.$$

The transition moment for an ortho-para-directing group has been discussed earlier.<sup>2</sup> Using the orbitals of Eq. (3) one finds that the transition moment  $M_{op}$  for an ortho-para-directing group is:<sup>15</sup>

$$\mathbf{M}_{op} = (\lambda_1 T_1 + \lambda_2 T_2 + \lambda_2^2) \int \varphi_{-1} \chi \varphi_2 d\tau - \lambda_3 T_1 \int \varphi_3 \chi \varphi_{-2} d\tau. \quad (10)$$

Now it is easily checked that:

$$\int \varphi_1 \chi \varphi_{-2} d\tau = - \int \varphi_{-1} \chi \varphi_2 d\tau,$$

and further that  $\int \varphi_3 \chi \varphi_{-2} d\tau$  has the same sign as  $\int \varphi_{-1} \chi \varphi_2 d\tau$ . It is accordingly clear that  $\mathbf{M}_m$  is exactly antiparallel to  $\mathbf{M}_{op}$ .

Although this result is important in discussing  $C_6H_{6-n-m}P_nM_m$  compounds, it does not in itself imply that  $C_6H_{6-n}M_n$  obey the same combination rule as the  $C_6H_{6-n}P_n$  compounds. This, however, is clear from the group theoretical discussion and should follow from extending Eqs. (8) to polysubstitutions in the same way that Eqs. (3) were extended.

#### INTENSITIES IN $C_6H_{6-n-m}P_nM_m$

As previously discussed the transition moment due to an ortho-para-directing radical  $\xi$  attached to the carbon atom on the positive  $Y$  axis is directed along the  $X$  axis. We may summarize the rules for combining transition moments as follows:

I. The transition moment of a second ortho-para-directing radical in the position  $\xi$  is rotated from the  $X$  axis by an angle  $\tau = (\xi_0\xi)$  and multiplied by  $(-1)^{3\tau/\pi}$ .

II. The transition moment of a meta-directing radical is  $180^\circ$  out of phase from the moment of a para-group located at the same place in the ring.

<sup>15</sup> Formula (10) is an intermediate formula used in obtaining formula (13) of reference 2.

If the monosubstituted benzenes  $C_6H_5P$  and  $C_6H_5M$  have nearly the same intensity of absorption, then the ratio of intensity of the monosubstituted : ortho- $C_6H_4PM$  : meta- $C_6H_4PM$  : para- $C_6H_4PM$  is, accordingly, 1 : 3 : 3 : 0. The previously discussed ratio of  $C_6H_5P$  :  $o$ - $C_6H_4P_2$  :  $m$ - $C_6H_4P_2$  :  $p$ - $C_6H_4P_2$  was 1 : 1 : 1 : 4 as is also the ratio of  $C_6H_5M$  :  $o$ - $C_6H_4M_2$  :  $m$ - $C_6H_4M_2$  :  $p$ - $C_6H_4M_2$ . The transition in the symmetrical trisubstituted benzene  $C_6H_3P_3$ , as might be expected, is still forbidden by symmetry and the increase in intensity should be zero. The 1 : 2 : 4  $C_6H_3P_3$  should have three times the intensity of the monosubstituted derivatives. In 1 : 2 : 3  $C_6H_3P_3$ , although the transition is

no longer forbidden by symmetry, the intensification should still be zero since the contributions annul one another in the first order. Before one can compare these statements with empirical data the effect of the normal vibrations, which also contribute to the intensity, must be discussed.

#### EFFECT OF NORMAL VIBRATIONS

Until now we have, in effect, been considering the transition moments of substituted benzenes which are constrained to their equilibrium position in both the ground and excited electronic states. In addition to the previously discussed transition moment, there is also the moment which arises from the distortion of the molecule by certain unsymmetrical vibrations. In order to decide how to combine the effect of a migration of charge and that of a vibrational distortion we may proceed as follows.

During a vibration the electronic wave functions will be functions of the normal coordinates. Neglecting, for the moment, the migration of charge, one may expand the  $\Psi(q)$  into a series in terms of the  $\Psi(q_0)$ ,  $q_0$  being the equilibrium position:

$$\Psi^k(q) = a_0^k \Psi^k(q_0) + \sum_i a_i^k(q) \Psi^i(q_0). \quad (11)$$

If one now makes a first-order perturbation calculation for  $a_j^k$  the perturbing potential (4) is clearly a periodic function of the time whose frequency is the same as that of the vibration. We may accordingly write:

$$a_j^k(q) = \sum_l a_{jl}^{0k} \exp(2\pi i \nu_l t), \quad (12)$$

where  $a_{jl}^{0k}$  is independent of  $q$ , the summation over  $l$  meaning a possible summation over different normal vibrations.

We can include the effect of the migration of charge into Eq. (11) by replacing the  $\Psi(q_0)$  by the  $\Psi^0(q_0)$  given in Eqs. (3'). Equation (11), after neglecting higher powers in  $\lambda_s$  and  $a_{jl}^{0k}$ , becomes:

$$\Psi^k(q) = a_0^k [\Psi^k(q_0) + \sum_s \lambda_s \Phi(q_0)] + \sum_i \sum_l a_{il}^{0k} \exp(2\pi i \nu_l t) \Psi^i(q_0). \quad (13)$$

in which the boldface functions are those which express, as before, a migration of charge, and  $\lambda_s$  is independent of  $t$ .

We can now form the transition moments

$$\int \Psi_0(q) \{ \mathbf{x}, \mathbf{y}, \mathbf{z} \} \Psi'(q) d\tau.$$

$$M_{\{x, y, z\}} = \sum_s \lambda_s M_{\{x, y, z\}}^s + \sum_l M_{\{x, y, z\}}^l \exp(2\pi i \nu_l t), \quad (14)$$

in which the quadratic terms in the  $\lambda_s$  and  $a_{jl}^{0k}$  have been neglected. The first sum is the moment due to migration of charge and the second sum is that due to vibrational distortion.

Since the intensity of absorption is proportional to the time average of  $MM^*$  we may write:

$$I \sim \overline{MM^*} = [\sum_s \lambda_s M_{\{x, y, z\}}^s]^2 + \sum_l [M_{\{x, y, z\}}^l]^2, \quad (15)$$

the cross products vanish on averaging over time.

It is accordingly clear that, at least to a first order, the intensity of absorption produced by the migration of charge and that caused by vibrations are additive.<sup>16</sup>

The vibrational intensity is not small enough to be neglected in comparison with the intensity produced by weak non-chromophoric substitutions. This can be seen from the comparison of the intensities of benzene and  $C_6X_6$ , which have no migrational intensity. In order to obtain quantitative data on the migration intensity it would be necessary to investigate theoretically the effect of substitution on the vibrational intensity, both as regards the mass and the orientation of the substituents. In the absence of a theoretical analysis of the effect of substitution on the vibrational intensity, one might anticipate that the relative orientation of the substitutions does not sensitively affect the vibrational intensity. Which particular vibrations appear in the spectrum should depend on the orientation but the total effect might be expected to depend predominantly on the kind and number of substituents, since the latter determine the amplitudes of vibration. This is,

<sup>16</sup> In expressing the dependence of the electronic wave function on the normal coordinates (Eq. (13)) it was assumed that one could write the total wave function as a product of an electronic and of a vibrational function. It is, however, clear that the inclusion of terms into Eq. (13) which represent the deviation from the product representation will not affect the argument for Eq. (15) in the first order, since the coefficients of these new terms will be periodic functions with vibrational frequencies.



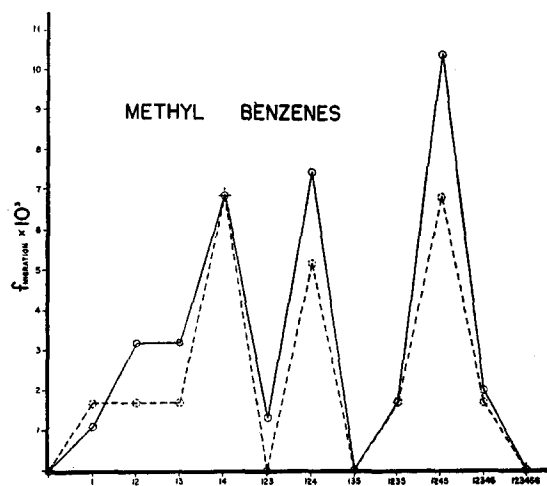


FIG. 2. Migrational oscillator strengths of the methyl benzenes. The experimental  $f$  values (reference 17) are plotted against the various positions (cf. Fig. 1) of substitution as a solid line; the theoretical values by a dashed line.

indeed, borne out by the fact that, in both the halogen and methyl benzene series, the 1, 3, 5 trisubstituted benzene is intermediate in intensity to benzene and the hexa-substituted product. In all these cases the symmetry is such that electron migration will not affect the intensity, so that the whole effect is due to vibration. But the symmetry of the vibrations in the 135 trisubstituted compound is lowered, so that more vibrations make the transition allowed than in benzene or the hexa-derivatives. Nonetheless, the intensity of the trisubstituted compounds lies between those of benzene and the hexa-derivatives.

That the vibrational intensity is not the sensitive factor in determining the relative intensities in isomeric substituted benzenes can furthermore be seen by comparing the effects of inserting a methyl group into the para positions in toluene and benzo-nitrile. The total absorption intensity of para-xylene is double that of toluene whereas the total intensity of para-tolu-nitrile is less than that of benzo-nitrile. That  $P$ - $P$  derivatives are consistently found to follow different intensity rules than  $M$ - $P$  derivatives, as is shown below, indicates clearly that the qualitative features, at least, are to be sought in the migrational effect on the intensity.

One can either apply the intensity rules for migrational intensity in a qualitative way or one can make a semi-quantitative comparison

by estimating the vibrational intensity from symmetrical molecules, where the vibrations alone are responsible for the intensity. The zero-zero transition is forbidden by symmetry for benzene, 1, 3, 5  $C_6H_3X_3$ , and for  $C_6X_6$ . One can make a crude estimate of the vibrational intensity by plotting the oscillator strengths of these three compounds against molecular weight and interpolating for the other members of the same series. For each substituent  $X$ , a separate curve is drawn, one for the chlorobenzenes and one for the methylbenzenes. The  $f$  values found by this interpolation are given in the tables as "vibrational  $f_v$ "; subtracting these  $f_v$ 's from the total  $f$  values gives the "migrational  $f_m$ " in the table.

#### COMPARISON WITH EXPERIMENT

We can first test the intensity rules in a qualitative manner by the total oscillator strength. We must limit our qualitative comparisons to isomeric molecules, that is molecules which differ only in that the substitutions are shuffled.

For the  $P$ - $P$  disubstituted benzenes, we should expect from the foregoing that the ortho- and meta-derivatives be equally intense and that the para-derivative be considerably more intense than both. That this is indeed so for the dichlorobenzenes and for the xylenes may be seen from Table I and also from Figs. 2 and 3. In  $M$ - $P$  disubstituted derivatives, on the other hand,

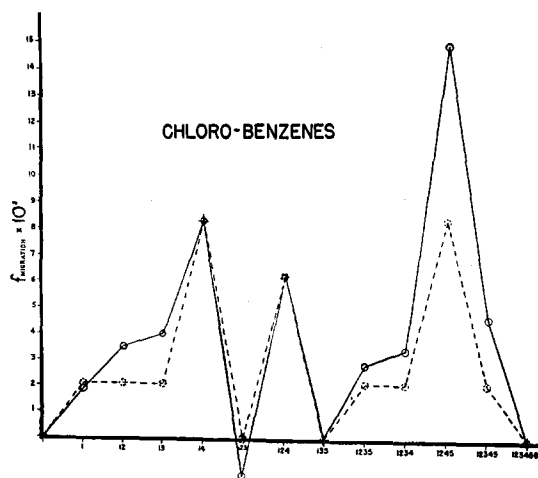


FIG. 3. Migrational oscillator strengths of the chlorobenzenes. The experimental  $f$  values (reference 17) are plotted against the various positions (cf. Fig. 1) of substitution as a solid line; the theoretical values by a dashed line.

the para-compound should be very much weaker than the ortho- or meta-isomers; the latter should again be equally intense. This is indeed the case, as is borne out by the chloronitriles, toluonitriles, chloroisonitriles and toluoisonitriles (cf Figs. 4 and 5).

Striking confirmation of the rules is also afforded by the three trisubstituted derivatives. That 1, 3, 5,  $C_6H_3X_3$  has a very weak absorption is clear independently of these rules since the electronic transition is forbidden by symmetry. However, the transition in 1, 2, 3,  $C_6H_3X_3$  is not forbidden by symmetry but is forbidden, in the first order, by these rules and is indeed found to be of the same order of intensity as the 1, 3, 5

TABLE I.\*

	$f \times 10^3$	Experimental $f_e \times 10^3$	$f_m \times 10^3$	Theoretical estimate $f_m \times 10^3$
Benzene	2.7	2.7	(0)	0
Toluene	5.3	4.2	1.1	1.7
O-xylene	8.8	5.6	3.2	1.7
M-xylene	8.8	5.6	3.2	1.7
P-xylene	12.5	5.6	6.9	(6.9)
123 trimethylbenzene	8.4	7.1	1.3	0
124 trimethylbenzene	14.6	7.1	7.5	5.2
135 trimethylbenzene	7.1	7.1	(0)	0
1235 tetramethylbenzene	8.8	7.1	1.7	1.7
1245 tetramethylbenzene	17.6	7.1	10.5	6.9
penta methylbenzene	9.2	7.2	2.0	1.7
hexa methylbenzene	7.3	7.3	(0)	0
chlorobenzene	4.9	3.0	1.9	2.1
O-dichlorobenzene	6.8	3.2	3.5	2.1
M-dichlorobenzene	7.2	3.2	4.0	2.1
P-dichlorobenzene	11.5	3.2	8.3	(8.3)
123 trichlorobenzene	2.1	3.5	-1.4	0
124 trichlorobenzene	9.7	3.5	6.2	6.2
135 trichlorobenzene	3.5	3.5	(0)	0
1235 tetrachlorobenzene	6.3	3.5	2.8	2.1
1234 tetrachlorobenzene	6.9	3.5	3.4	2.1
1245 tetrachlorobenzene	18.3	3.5	14.8	8.3
pentachlorobenzene	8.2	3.6	4.6	2.1
hexachlorobenzene	3.7	3.7	(0)	0

\* The experimental data for this table were taken from reference 17.

TABLE II.\*

	$f \times 10^3$	Experimental $f_e \times 10^3$	$f_m \times 10^3$	Theoretical estimate $f_m \times 10^3$
Benzene	2.4	2.4	(0)	0
Toluene	4.7	3.1	1.6	1.2
O-xylene	5.7	3.9	1.8	1.2
M-xylene	6.0	3.9	2.1	1.2
P-xylene	8.6	3.9	4.7	(4.7)
Chlorobenzene	4.3	2.7	1.6	1.3
O-dichlorobenzene	5.5	2.8	2.6	1.3
M-dichlorobenzene	5.4	2.8	2.6	1.3
P-dichlorobenzene	8.0	2.8	5.2	(5.2)
Benzonitrile	10.4	2.9	7.5	(7.5)
O methyl benzonitrile	21.7	3.7	18.0	11.6
M methyl benzonitrile	18.7	3.7	15.0	11.6
P methyl benzonitrile	9.7	3.7	6.0	2.8
O chloro benzonitrile	20.7	3.0	17.7	11.9
M chloro benzonitrile	15.9	3.0	12.9	11.9
P chloro benzonitrile	8.0	3.0	5.0	2.6
Benzoisotrile	6.5	2.9	3.6	(3.6)
O methyl benzoisotrile	20.7	3.7	17.0	6.8
M methyl benzoisotrile	7.2	3.7	3.5	7
O chloro benzoisotrile	10.7	3.0	7.7	7.1
M chloro benzoisotrile	10.3	3.0	7.3	7.1
P chloro benzoisotrile	6.4	3.0	3.4	1.2

\* The experimental data for this table was taken from reference 18.

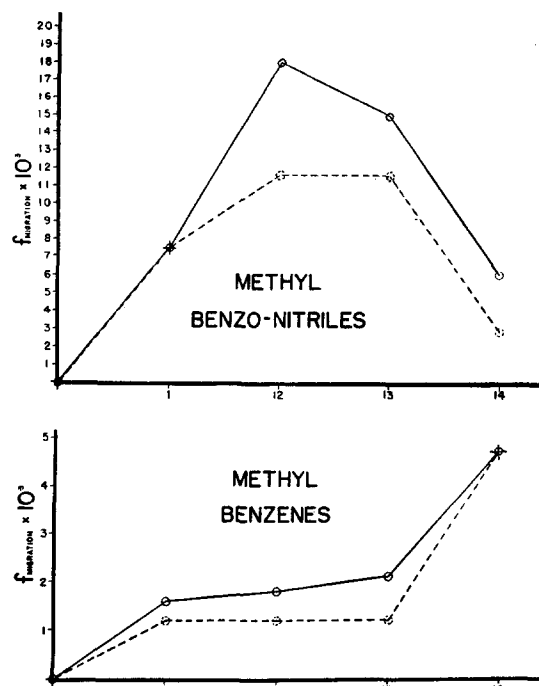


FIG. 4. The migrational oscillator strengths of the methyl benzenes ( $C_6H_4P_2$ ) are contrasted with those of the methyl benzo-nitriles ( $C_6H_4MP$ ). The experimental values (reference 18) are plotted against the various positions of substitution as a solid line; the theoretical values by a dashed line.

isomer, slightly less in the trichloro series and slightly more in its trimethyl series. This is perhaps the most striking evidence for these rules. The 1, 2, 4 derivative is, of course, quite strong and of the expected intensity.

The tetra- and penta-substitution products are also in agreement with the rules but, of course, add nothing new qualitatively.

Table I contains the oscillator strengths of a number of substituted benzene derivatives with weak auxochromes of the type  $C_6H_{6-m}P_m$ . The most complete series of this type are the methylbenzenes and chlorobenzenes investigated by Conrad-Billroth;<sup>17</sup> the  $f$  values calculated from his measurements are given in the first column of Table I. Some scattered measurements on the compounds of this series were also made by Wolf and co-workers<sup>18</sup> and are given in Table II for comparison. The vibrational  $f_e$  in the second

<sup>17</sup> H. Conrad-Billroth, Zeits f. physik. Chemie **B19**, 76 (1932); **B29**, 170 (1935).

<sup>18</sup> K. L. Wolf and W. Herold, Zeits f. physik. Chemie **B13**, 201 (1931); K. L. Wolf and O. Strasser, *ibid.* **B21**, 389 (1933).

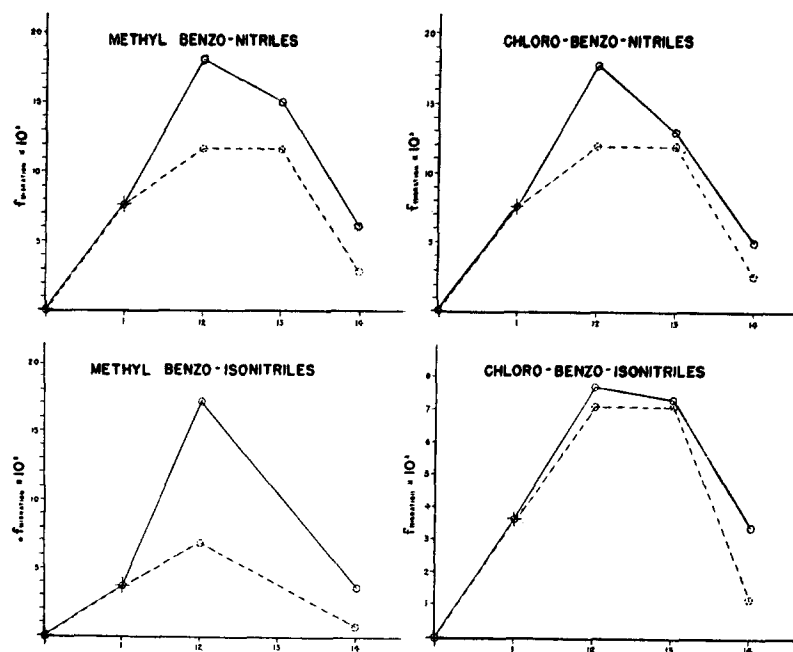


FIG. 5. Oscillator strengths of  $C_6H_4MP$ . The experimental values (reference 18) are plotted against the various positions of substitution as a solid line; the theoretical values by a dashed line.

column is obtained, as discussed before, by interpolating between the  $f_v$ 's (in column 1) of those compounds which owe their entire intensity to vibration. The experimentally estimated migration effects  $f_m$  are the differences between the first and second column, and are plotted as solid lines in Fig. 2 for the various methyl benzenes and in Fig. 3 for the chlorobenzenes. Those points which have been used to calculate the vibrational  $f_v$  are marked with a cross. To calculate the theoretical curves in Figs. 2 to 5 one needs the value of the migrational effects for  $CH_3$  and for  $Cl$ . This is obtained from the  $f_m$  of the para-disubstituted derivative. This compound is selected since it should have the largest  $f_m$  and a smaller  $f_v$  than the 1245 substituted derivative which is the only other compound having as large a predicted  $f_m$ . Half the square root of the  $f_m$  of para  $C_6H_4P_2$  is taken as a measure of the magnitude of the transition moment induced by the migration of charge from group  $P$ .

The experimental oscillator strengths for compounds of the type  $C_6H_{6-2}MP$  are given in Table II. Since a complete series of this type is not available, the vibrational  $f$  had to be estimated from other series. The mean of the interpolated  $f_v$  value for the monomethyl and

monochloro derivatives was taken as the  $f_v$  for benzonitrile and isonitrile, since the mass of the nitrile group is the mean of the masses of the methyl and chloro groups. The  $f_v$  for the di-substitutions was obtained by adding to the  $f_v$  of the nitrile the difference between the interpolated  $f_v$  of  $C_6H_4P_2$  and that of  $C_6H_5P$ . The  $f_m$ 's so obtained are plotted in Fig. 5 as a solid line. The square root of the  $f_m$  for  $C_6H_5M$  is taken as the transition moment due to  $M$ . This moment and the one of the para-directing group obtained previously are combined according to the rules developed and the intensities plotted in Fig. 5 as dashed lines.

The large difference between the effect of an ortho-para-directing group, ( $P$ ), on the absorption intensity of  $C_6H_5P$  as compared with its effect on the intensity of  $C_6H_5M$  is brought out in Fig. 4, in which the oscillator strengths of the xylenes,  $[C_6H_4 \cdot CH_3 \cdot CH_3]$  are contrasted with those of the methyl benzonitriles,  $[C_6H_4 \cdot CH_3 \cdot CN]$ .

In conclusion the author would like to express his indebtedness to Professor K. F. Herzfeld for continued inspiration and discussion and also to Sister M. Ann Elizabeth Waters C.S.C. for assistance in computing the experimental oscillator strengths.