

ionone under the same conditions employed for β -ionone.¹¹ After separating the insoluble β -*i*-methylionone, the *n*-methyl isomer was regenerated from the bisulfite solution. Final fractionation yielded 160.0 g. of β -*n*-methylionone, b. p. 86–88° at 1 mm., n_{20} 1.5155. The m. p. of the semicarbazone was 145° (reported m. p. 145°¹¹).

β -*i*-Methylionone (VI).—Starting with 90 g. of crude β -*i*-methylionone the semicarbazone was prepared and hydrolyzed according to Young's procedure⁷ for the purification of β -ionone. The yield of β -*i*-methylionone semicarbazone after two recrystallizations from 60% alcohol was 49 g. (42.5% yield) melting at 181° (cor.) (reported m. p. 183°¹¹). Hydrolysis of 40 g. of the semicarbazone gave 18.3 g. of distilled β -*i*-methylionone and 13.2 g. of unchanged semicarbazone (m. p. 179–181°). Based on the semicarbazone that reacted the yield was 87%. The hydrolyzed material was fractionated with a 12" column packed with glass helices and yielded 11.1 g., b. p. 78° at 0.5 mm., n_{20} 1.5051–1.5054.

α -*i*-Methylionone (V).—The semicarbazone of crude α -*i*-methylionone was prepared by the same procedure. Four recrystallizations from 70% alcohol gave a 46% yield of semicarbazone melting at 203.5° (cor.) (reported m. p. 203°¹¹). Thirty-eight grams of the semicarbazone, 80 cc. of benzene, and 165 g. of 30% phosphoric acid were refluxed for twelve hours. Seven and five-tenths grams of starting material (m. p. 202.5°) was collected by filtration. The benzene layer was separated, washed with sodium carbonate solution, and the solvent removed by dis-

tillation at 40 mm. Distillation of the residue gave 13.2 g. of α -*i*-methylionone (55% yield based on the semicarbazone that reacted) which was fractionated with a 10" column packed with glass helices. Eight and two-tenths grams was obtained, b. p. 83° at 1 mm., n_{20} 1.5008.

Pseudoionone (b. p. 107° at 1 mm., n_{20} 1.5339), ***n*-methylpseudoionone (I)** (b. p. 115–116° at 1 mm., n_{20} 1.5281) and ***i*-methylpseudoionone (II)** (b. p. 118 at 1 mm., n_{20} 1.5265) were purified through the bisulfite compound using the same procedure as given for α -*n*-methylionone.

The pseudomethylionones and the methylionones are commercially available compounds. Absorption spectra were determined in 95% ethanol by means of a Beckman spectrophotometer.

Summary

The ultraviolet absorption spectra have been determined for *i*-methylpseudoionone, *n*-methylpseudoionone and the four methylionones derived from them.

The position of the band maxima has been correlated with the structure of the chromophore.

Spectrophotographic evidence suggests that the structure previously assigned to "beta-*i*-methylionone" is incorrect.

EAST RUTHERFORD, N. J. RECEIVED DECEMBER 20, 1948

(11) Royals, *Ind. Eng. Chem.*, **38**, 546 (1946).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, PARKE, DAVIS & Co.]

The Ultraviolet Absorption Spectra of Simple Unsaturated Compounds. II. *m*- and *o*-Disubstituted Benzene Derivatives

BY LEONARD DOUB AND J. M. VANDENBELT

In the previous paper of this series¹ on simple benzene compounds it was shown that the longer wave length maxima of the mono- and *p*-disubstituted derivatives could be related to the parent bands of benzene near 200 $m\mu$ and at 254 $m\mu$, called the first primary and the secondary bands, respectively. In addition, with derivatives showing considerably displaced absorption, a third band appeared at short wave length which was termed the second primary band. The present study indicates that the concepts developed there can be applied to an analysis of the spectra of *m*- and *o*-disubstituted benzene derivatives.

Methods and Materials.—A Model DU Beckman quartz spectrophotometer with hydrogen discharge tube source was used for all measurements. Extinction coefficients were calculated by dividing the density observed in matched cells by the molar cell concentration. Band peaks were read in the density range 0.4–0.8 at a spectral band width of approximately 1 $m\mu$. Readings at extremely low wave lengths were obtained by balancing the instrument for 100% transmission through the solvent cell at the 0.1 switch position. To indicate a decreased accuracy at the end of the accessible region, principally

as a result of the increase in scattered radiation, some values in Table I are given in italics.

Melting points of solids after recrystallization and the boiling points of liquids upon distillation were accepted as confirmation of identity and purity. Water was used as the solvent throughout. With substances relatively insoluble in water, methanol was used first for solution, followed by a larger dilution in water. A blank containing an equal amount of methanol was prepared for instrument reading. The methanol concentration was restricted to 1 or 2% in these cases.²

Presentation of Data.—Figure 1 gives curves of *m*- and *o*-hydroxyacetophenone which serve to illustrate the absorption characteristics of this general class of compounds. It can be seen that there is considerable similarity in the spectra of these derivatives. The pattern exhibited is that of three bands decreasing in intensity with displacement in an almost stepwise fashion from a rather intense short wave length band. The displacement of the bands upon ionization is similar to that observed in mono- and *p*-disubstituted

(2) The spectra of many of the compounds given here have been reported previously in the literature. However, the diversity of solvents and uncertainty below 220 $m\mu$ justify repetition for this study.

(1) Doub and Vandenbelt, *THIS JOURNAL*, **69**, 2714 (1947).

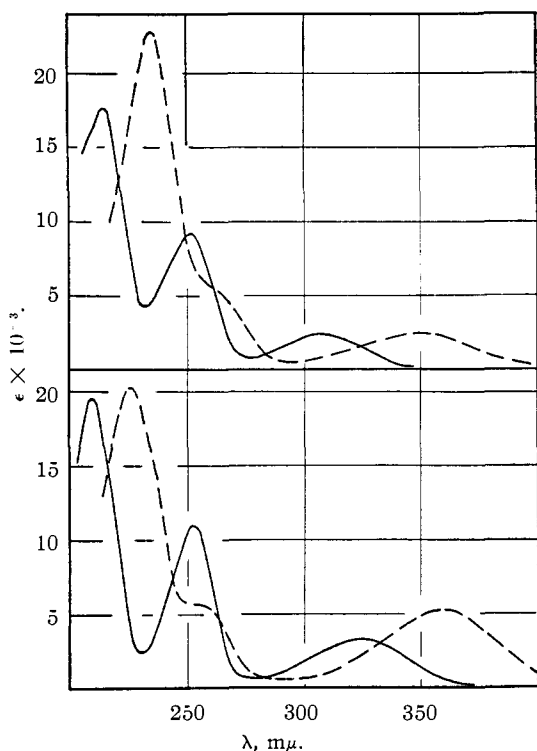


Fig. 1.—Ultraviolet absorption of (top) *m*- and (bottom) *o*-hydroxyacetophenone: solid lines, in 0.1 *N* HCl; broken lines, in 0.1 *N* NaOH.

derivatives.¹ With some variation this is typical of most of the *o*- and *m*-disubstituted compounds studied. The only major exception to this pattern so far found is that of the nitro derivatives, a typical example being that of *m*-nitrophenol shown in Fig. 2. The spectra of these compounds exhibit an additional shorter wave length band but otherwise conform to the general picture.

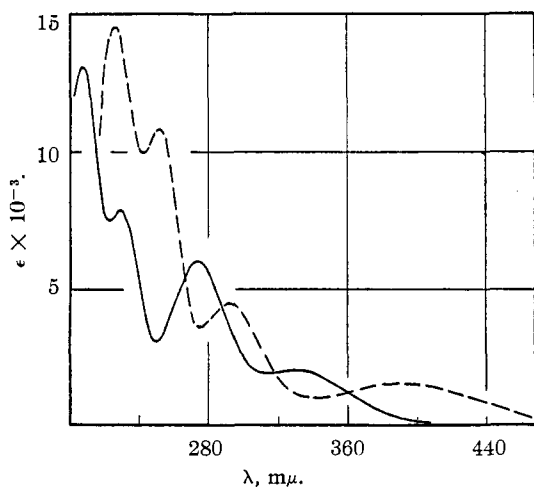


Fig. 2.—Ultraviolet absorption of *m*-nitrophenol: solid line, in pH 3; broken line, in 0.1 *N* NaOH.

Table I gives the absorption characteristics of the compounds included in this study. Following roughly the criteria laid down in the previous paper the maxima have been listed as the secondary band, and the first, second, etc., primary bands proceeding from long to short wave length. Since this assignment is arbitrary, being based largely on similarity of position and intensity, it is of interest to investigate whether these do, in fact, correspond to the similarly named bands of mono- and *p*-disubstituted compounds.³

Band Relationships: the Effects of Disubstitution with Groups of Complementary Electronic Character (*i. e.*, Containing an *o-p* and a *m* Directing Group).—Since the nitro compounds appear exceptional by virtue of their additional short wave length band and were

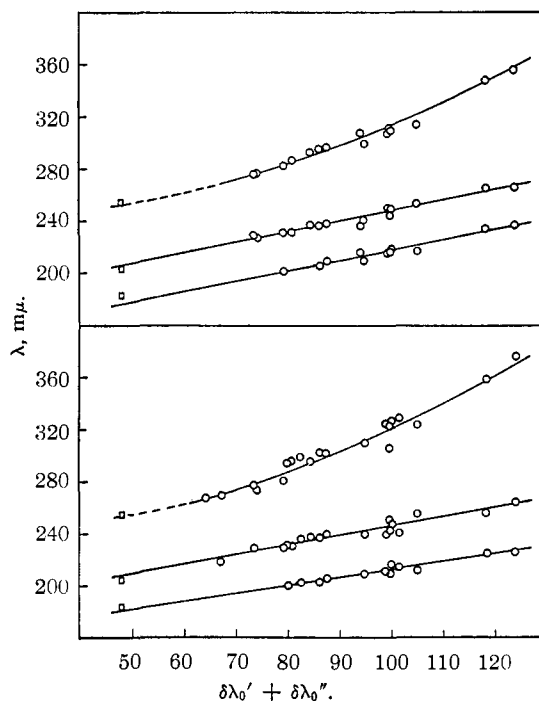


Fig. 3.—Plot of the various bands of (top) *m*- and (bottom) *o*-derivatives (except nitro compounds) in Table I, containing *o-p* vs. *m* directing groups, against the sum of the $\delta\lambda_0$ values of the groups. The upper, middle and lower curves represent the secondary, first primary and second primary bands, respectively, in each set.

(3) These bands have received other designations in the literature. Particular attention should be directed on the one hand to their interpretation in quantum mechanical terms [*e. g.*, cf. Mulliken, *J. Chem. Phys.*, **7**, 353 (1939), and Sklar, *Rev. Mod. Phys.*, **14**, 232 (1942)], and on the other to the concept of x and x' bands [Kumler, *This Journal*, **68**, 1184 (1946)]. The extension of these concepts to encompass the bands of a large number of diverse simple benzene derivatives involves many considerations beyond the scope of this immediate study. The designation of secondary, first primary, etc., bands was set up deliberately to avoid these implications and to arrive at a simple, convenient naming system for these bands in benzene derivatives. These terms were originally defined¹ both by wave length position and intensity. It should be noted that the intensity criteria do not always strictly apply in the compounds studied here, especially in the case of the secondary bands.

interaction of some of the groups should alter their relation to the benzene ring.

The development in paper I ascribed a $\delta\lambda_0$ effect to hydrogen as a substituent. If the various bands of benzene⁶ are plotted using as abscissa twice this value, the points represented as squares in Fig. 3 are obtained. The near coincidence of these points representing the parent benzene bands with the trends established by the various families of bands in *m*- and *o*-disubstituted compounds is strong evidence for their fundamental relationship.

In the previous paper the secondary and first primary bands were associated with the corresponding benzene maxima. It is particularly interesting that the second primary band whose origin was previously uncertain can now be identified with the benzene maximum at 183.5 $m\mu$.⁶ Thus the total evidence would seem to picture the ultraviolet absorption spectra of the majority of simple mono-, and *p*-, *m*- and *o*-disubstituted benzene derivatives as arising by displacement of the bands of benzene by substitution.

With this thesis in mind it is of interest to compare the effect of position of substitution on the rate of displacement of the benzene bands with increasing displacement power of the substituent groups. This is shown in the composite plot of Fig. 4, where representative datum points for mono- and *p*-disubstituted derivatives from Paper I (except nitro compounds),⁷ are compared with the curves of the *m*- and *o*-disubstituted compounds which are reproduced from Fig. 3. Limiting immediate attention only to the curves, it is apparent that, within the degree of approximation involved here, they are identical. This leads to the important observation that *m* or *o* disubstitution with pairs of groups of complementary type has approximately the same displacing effect on all of the bands of benzene.⁸

In Fig. 4, the large circles represent a plot of *p*-disubstituted compounds (containing *o*-*p* vs. *m* orienting groups); the small circles represent monosubstituted compounds plotted following the convention of assigning hydrogen a $\delta\lambda^0$ value¹; the squares representing the parent bands of benzene are presented on the same basis; the arrows indicate that for the more displaced *p*-disubstituted compounds a secondary band,

(6) The wave length positions of the secondary and first primary bands of benzene are taken from Paper I; the second primary band is identified with a band at 183.5 $m\mu$; Platt and Kleven, *Chem. Rev.*, **41**, 301 (1947).

(7) In Paper I the plot of the position of the first primary bands of mono- and *p*-disubstituted derivatives vs. the product of the $\delta\lambda_0$ values of the two groups approximated a straight line. In the present case, the band position was graphed vs. the sum of the $\delta\lambda_0$ values of the two groups. The product plot gives a smoother curve for the first primary band of *p*-disubstituted compounds, and this series of data can also be represented as a product plot which satisfactorily describes the relationships between the bands. However, the sum plot is possibly superior in the present instance in that the convergence at shorter wave length is better represented.

(8) This has been pointed out previously for what is referred to here as the secondary bands: see reference 14.

if present and of the usual order of magnitude, does not occur at longer wave length than designated.

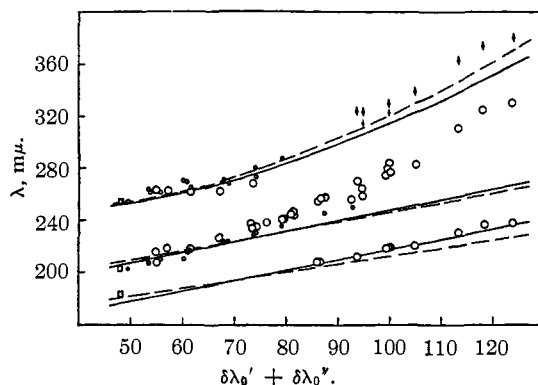


Fig. 4.—Composite plot of mono- and disubstituted derivatives (except nitro compounds) based on the $\delta\lambda_0$ values of the groups. The curves from Fig. 3 are reproduced: solid lines, *m*-derivatives; broken lines, *o*-derivatives. The large circles represent *p*-disubstituted compounds containing *o*-*p* vs. *m* orienting groups; the small circles represent monosubstituted compounds considering hydrogen as a substituent. The arrows indicate that, for the more displaced *p*-disubstituted derivatives, a secondary band, if present and of the usual order of magnitude, does not occur at longer wave length than that indicated at the point of the arrow.

While the dispersion of data comprising Fig. 4 emphasizes the approximate nature of the trends shown, the over-all correlation is sufficient to warrant some limited conclusions being drawn.

The most clearly defined trend is shown by the second primary bands of *p*-disubstituted compounds (lower curves of Fig. 4). These points coincide distinctly well with the curves representing the second primary bands of *m*- and *o*-disubstituted compounds. This would seem to justify the conclusion that the position of the second primary band is determined (with *o*-*p* vs. *m* orienting groups) principally by the nature of the substituent pair and is roughly independent of the position of substitution.

It is tentatively proposed that the same interpretation may apply in the case of the secondary bands (top curve of Fig. 4). Within the dispersion of the data this is clearly indicated with not only the monosubstituted compounds (small circles) but also those *p*-disubstituted compounds with moderate displacement having a defined secondary band (large circles). With those *p*-disubstituted compounds containing more effective groups the first primary band has been displaced into the region of the secondary and with its broadening tends to obliterate this band. Although no definite wave length can be assigned for the position of the secondary band in these cases, asymmetry of the first primary band in this

region frequently indicates that it may still be present. With the very considerably displaced *p*-disubstituted compounds, a careful examination of the absorption curves at the immediately longer wave lengths (points of the arrows in Fig. 4) confirms that the secondary band cannot have been displaced appreciably beyond the positions occupied in *m*- and *o*-disubstituted derivatives, unless its intensity simultaneously has been reduced greatly beyond that usually occurring in benzenoid compounds.

The trends of the points in Fig. 4 representing the first primary bands of mono- and *p*-disubstituted compounds presents a more complex pattern than that of the other bands. They merge at short wave length with the curves (center lines, Fig. 4) of *m*- and *o*-disubstituted compounds as is required if they all may be represented as arising from the first primary band of benzene (the square in this plot). The monosubstituted compounds throughout appear to follow fairly well the same trend as the *o*- and *m*-disubstituted compounds. In the case of the *p*-disubstituted compounds, with increasing displacement of the spectrum, the position of the first primary band diverges increasingly toward longer wave length, compared to the position of this band in *m*- and *o*-disubstituted compounds.

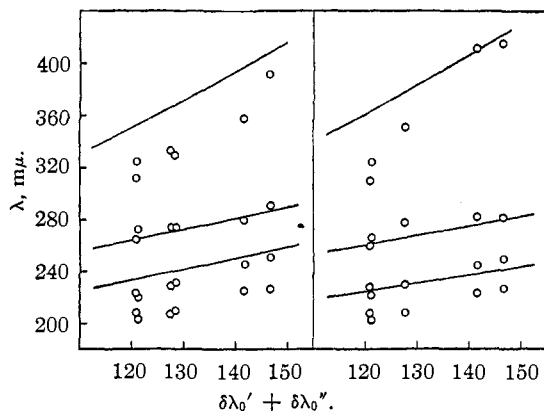


Fig. 5.—Wave length maxima of (left) *m*- and (right) *o*-derivatives containing a nitro group vs. an *o-p* orienting group plotted against the sum of the $\delta\lambda_0$ values of the two groups. The solid lines representative of the non-nitro compounds are reproduced from Fig. 3.

It would appear from the above that the first primary is unique among the bands of benzene in that its wave length position is particularly sensitive to *para* disubstitution with opposite types of groups. It is extremely interesting that, with this single exception (and some uncertainty regarding the secondary band of *p*-disubstituted compounds), the effect of complementary disubstitution (*i. e.*, *o-p* vs. *m* orienting groups) is broadly the same regardless of the position of substitution. This is in sharp contrast to the distinct difference to be expected between the *meta*,

ortho, and *para* positions from a knowledge of chemical reactivity.

Interaction of Groups of Like Electronic Character.—As indicated in the previous paper of this series, the displacing power of a group in *p*-disubstituted compounds may be markedly altered when incorporated in the benzene ring with another group of the same kind. A similar phenomenon is exhibited in *m*- and *o*-disubstituted compounds. With *m*-aminobenzoic acid, for instance, the three bands are at 218.5, 250 and 310 $m\mu$. *m*-Phenylenediamine and isophthalic acid contain groups the sum of whose $\delta\lambda_0$ values would be identical with those of *m*-aminobenzoic acid and by Fig. 3 might be expected to give bands in the same positions. Yet the bands of these latter compounds are at 10–30 $m\mu$ shorter wave length than would be predicted (Table I).

It is thus apparent that the band displacing effects are altered quantitatively when both groups are of the same electronic type.

Nitro Compounds.—As pointed out earlier in this paper the *m*- and *o*-disubstituted compounds containing the nitro group occupy an exceptional position among the simple benzene derivatives described thus far. Figure 5 gives a plot of the various bands of these derivatives containing an *o-p* orienting group vs. the sum of the values of the groups. The curves describing the non-nitro compounds are reproduced from Fig. 3. The small number of compounds presented for these plots seriously restricts the scope of generalization allowable. Although the coherence of the data leaves much to be desired it would appear that again the bands of the various derivatives form a series of continuities which justify regarding them as related within each trend. The curves representing the first and second primary bands of the non-nitro compounds seem to represent fairly well the two intermediate bands of these *m*- and *o*-substituted nitro compounds. This probably justifies considering them all produced by the same kind of electronic transition responsible for these bands in benzene itself. The same conclusion would seem to hold for the secondary bands of these derivatives, but the spread of the points representing these compounds from the curve of the non-nitro compounds emphasizes its approximate nature.

The unique feature of the plot of these nitro compounds is the appearance of an additional family of bands at short wave length. These bands are given in Table I in parentheses, and represent a third primary band. The significance of this set of bands is uncertain. It may, of course, arise from the nitro group itself, which is known to absorb strongly in this region, or it may represent the displacement of a band of benzene occurring in the spectrum of that compound at shorter wave length than the 183.5 $m\mu$ band. However, studies in the vacuum ultra-

violet region would be needed to evaluate these points.⁹

Discussion

The most important single fact which emerges from the study of simple mono- and disubstituted benzene derivatives is that their absorption spectra usually can be accounted for by a regular displacement of similar bands in benzene itself. This relation has been established on an empirical semiquantitative basis. The quantitative concepts involved, while clearly needing improvement as judged by a lack of the smooth correlation usually met in physical data,¹⁰ nevertheless seem adequate for the broad integration in which they have been employed. Except for the nitro compounds, whose position in the correlation framework is less certain, the usual deviation of the 91 points representing the bands of the *m*- and *o*-disubstituted compounds in Fig. 3 is less than $\pm 5 m\mu$ (76 points). Only 15 points deviate more than $5 m\mu$ and 1 point more than $10 m\mu$ ($13 m\mu$) from the apparent trends.¹¹

Recent developments in the concepts of light absorption have emphasized that the wave length of light absorbed corresponds to the energy difference between the normal or ground state and an excited state. On this basis changes in the position of absorption with substitution reflect changes in the relative stability of the excited and normal forms of the absorbing sub-

(9) If this band occurs in the non-nitro derivatives and follows the trend shown in the nitro compounds themselves it would fall at wave lengths too short to be accessible to the instrument in the case of the great majority of compounds in this study. The spectra of two non-nitro compounds, *m*-hydroxyacetophenone anion and *m*-hydroxybenzaldehyde anion, representing the longest wave lengths obtained, were examined for the presence of this band as far as the transmission of the solvent would permit. In 0.1 *N* sodium hydroxide this limit was *ca.* $216 m\mu$, somewhat higher than would be expected for the band in these two derivatives. While this paper was in press, Klevens and Platt, *THIS JOURNAL*, **71**, 1714 (1949), reported measurements below $200 m\mu$ with dimethylaniline and derivatives. They observed bands in these compounds which would seem to correspond to this third primary band. If these are plotted in an extension of Fig. 5, the trend identifies the origin of this band at *ca.* $150 m\mu$, approximately corresponding to the first member of a Rydberg series of benzene discovered by Price and Wood, *J. Chem. Phys.*, **3**, 439 (1935).

(10) Attempts have been made by the authors to improve the quantitative concepts by measuring the displacement effects of the substituent groups in frequency and in cm.^{-1} . These units have the advantage that their magnitude is proportional to energy throughout the entire spectrum whereas displacements measured in millimicrons cover greatly differing energy ranges depending upon the spectral region under consideration. While translation to frequency units does improve the correlations obtained in Papers I and II to some extent, the gain is probably not sufficient to justify a change at this time from the $m\mu$ basis so well established in the spectroscopy of organic compounds.

(11) As pointed out in Paper I, groups themselves absorbing strongly in this region might be expected to give anomalous results. Iodine as a substituent group may be an example of this type. Unreported measurements show that iodobenzene possesses a strong band at $227 m\mu$, which is in the region of a band present in aliphatic iodo compounds and probably reflects the absorption of iodine *per se* in this type of substitution. This position of absorption corresponds to a $\Delta\lambda$ value of 23.5, whereas the $\delta\lambda_0$ values derived from selected *p*-disubstituted compounds is of the order of that of the other halogens.

stance. Price¹² has pointed out that, with ionization potentials where ionic forms play an important role in the resonance of the excited state, changes in the stability of the ground state can probably be neglected so that gross changes in absorption position with substitution primarily reflect changed resonance stabilization of the excited form. This possibly applies also to light absorption in polar substituted benzene derivatives (*e. g.*, aniline, benzonitrile, benzaldehyde, etc.). Here the ground state is stabilized by 4–7 kcal. per mole relative to that of benzene, which can be taken for this comparison as the reference zero.¹³ The excitation energy for these compounds in the light absorption process runs from 10–30 kcal. per mole less than that of benzene. Since these quantities are additive, the photoexcited state of these derivatives has been stabilized relative to the excited state of benzene by *ca.* 15–40 kcal. per mole. Thus the stabilization of the excited state is generally more important quantitatively than that of the ground state. However, where small differences are under consideration or where ionic forms may be less important in the excited state, consideration of the ground state would be imperative.

Almost invariably monosubstitution moves all of the benzene bands toward the visible to some degree. With disubstitution the displacement is considerable if the groups are of opposite type (*o-p vs. m* directing); if the substituents are of the same type (*o-p vs. o-p; m vs. m*), the displacement is usually much less. This points to the importance of ionic forms in the excited state of benzene derivatives since opposite types of groups are uniquely capable of accommodating both species of charge resulting from charge separation. The rule for predicting ionization shifts developed in Paper I also illustrates the importance of charge separation in the photoexcited state. Where ionization polarizes the group favorably with respect to the charge separation occurring on that group in the excited state of the un-ionized molecule, displacement toward longer wave length results coincident with considerable stabilization of the excited state; where the charge resulting from ionization opposes that present on the group in the excited state of the parent molecule, the excited state loses stability leading to a hypsochromic effect. In Paper I this rule was restricted to the first primary band of mono- and *p*-disubstituted compounds. It is noteworthy that the present study indicates that the same general effect is shown in *m*- and *o*-disubstituted compounds and apparently applies to all of the bands, *i. e.*, secondary and second primary as well as first primary.

It has been noted that *o-p vs. m* disubstitution whether in the *m*, *o* or *p* positions has qualitatively

(12) Price, *Chem. Rev.*, **41**, 257 (1947).

(13) Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1945, p. 139.

the same displacing effect on all the benzene bands; and, except for the first primary and possibly the secondary band of *p*-disubstituted compounds, these effects are semiquantitatively comparable. The equivalency of *m*- and *o*-disubstitution is especially surprising in view of the decided difference associated with the *ortho* and *meta* positions in chemical substitution.¹⁴ Possibly this allows some insight into the nature of the photoexcited state in these compounds.

It seems logical that if considerable stabilization is conferred on the photoexcited state by charge separation resonance across *meta* positions there should be some direct interaction in this state between carbon atoms in the *meta* positions. Such bonds are probably negligible in the ground state,¹⁵ but appear to be important in the photoexcited state of benzene derivatives.

Complementary substitution (*i. e.*, with opposite types of groups) in the *para* position causes displacement of the first primary band considerably more than the same *meta* or *ortho* substitution (Fig. 4). This associates the excited state corresponding to this band with an electronic vibration whose symmetry is determined in some manner by the *para* positions of the benzene ring. It would be of considerable interest to assign symmetry characteristics to the secondary and second primary band but the present data do not allow a clear decision in this respect.

In both this paper and in Paper I the relative intensities of the various bands have been given only cursory attention. To date no decisive overall correlations have been obtained in this respect but certain patterns are evident. The parent bands of benzene increase in intensity stepwise on proceeding from the secondary ($\epsilon = 204$) to the first primary ($\epsilon = 7400$) and the second primary band ($\epsilon = 46,000$).⁶ For comparison, where the second primary band has been displaced sufficiently to be measured in these studies,

(14) This feature of benzenoid absorption (or what has been referred to in this paper as secondary absorption) has been given a quantum mechanical explanation by Förster. *Z. Naturforschung*, **2a**, 149 (1947). It is not immediately apparent from this development that this equivalency should apply to the other major bands of benzene and also to some of the bands of *p*-disubstituted compounds.

(15) Pauling, *ibid.*, p. 146.

the band intensity relationships obtaining in benzene itself are roughly preserved in *m*- and *o*-disubstituted derivatives. Substitution causing displacement toward the visible usually leads to some increase in intensity of the secondary band. This holds true for the mono-, *m*- and *o*-derivatives and those *p*-disubstituted compounds where it can be distinguished. In the *p*-disubstituted derivatives, coincident with its progressive marked displacement, the intensity of the first primary band becomes much greater.¹ This is accompanied by a loss of intensity of the second primary band if it is compared with the intensity of the 183.5 $m\mu$ band of benzene.

Acknowledgment.—We are pleased to thank Miss Denise Lundquest and Miss Jere Saladonis for their enthusiastic assistance.

Summary

The empirical semiquantitative concepts developed previously have been extended to demonstrate that the absorption bands of benzene are displaced in a regular manner with *m*- and *o*-disubstitution. The position of these bands in derivatives containing *o-p* vs. *m* directing groups can be predicted approximately.

The nitro compounds fit less exactly into the correlation and have an additional band at shorter wave length, the significance of which is uncertain.

As in the case of the *p*-disubstituted compounds, substitution with like electronic groups has quantitatively less displacing effect on the spectrum than with groups of complementary character (*i. e.*, with *o-p* vs. *m* directing groups).

Complementary disubstitution in any position with the same pairs of groups has an approximately equal displacing effect on each of the major bands in the spectrum of benzene except in the case of the first primary band, which is particularly sensitive to *p* substitution. Possibly this gives some indication of the symmetry of the electronic vibration involved in the photoexcited state corresponding to this band.

The importance of ionic forms in the resonance of the photoexcited state is inferred.

DETROIT, MICHIGAN

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