

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

The Near Ultraviolet Absorption Spectra of Monosubstituted Benzenes: the Effect of Certain Meta Directing Groups¹

BY W. F. HAMNER AND F. A. MATSEN

The effect of electron donating (*i.e.*, ortho-para directing) groups on the near ultraviolet absorption spectra of monosubstituted benzenes has been extensively investigated^{2,3} and the following trends established: the greater the extent of migration into the ring the longer the wave length of the O-O band, the higher the intensity of the spectrum as a whole and of the substitution sub-

spectrum (A, A + C, etc.)^{4b} relative to the benzene subspectrum (A + B, A + B + C, etc.).^{4a}

It was of interest therefore to investigate the spectra of electron attracting (*i.e.*, meta-directing) groups. According to the data of Flurschein and Holmes⁵ the per cent. meta compound formed upon nitration is as follows: toluene, 4.4; benzyl chloride, 11.6; benzal chloride, 32.8–33.3; benzotrichloride, 48.3–48.6. This is attributed to the increasing migration of electrons out of the ring due to the progressive replacement of the hydrogen atoms by strongly electronegative chlorine atoms. This series presents a gradual transition from ortho-para toward meta direction.

Experimental

The benzyl chloride, benzal chloride and benzotrichloride were donated by the Hooker Electrochemical Company, the β -phenylethyl chloride and γ -phenylpropyl chloride were Eastman Kodak Co. white label grade; the compounds were subjected to vacuum distillation or recrystallization to insure purity. The refractive indices of the fractions used are:

Compound	Temp., °C.	n_D
$C_6H_5CH_2Cl$	17.4	1.5391
$C_6H_5CHCl_2$	19.4, 20.0	1.55155, 1.55121
$C_6H_5-CCl_3$	19.2, 20.0	1.55841, 1.55806
$C_6H_5-CH_2CH_2Cl$	20.0	1.52760
$C_6H_5-CH_2CH_2CH_2Cl$	20.0	1.52237

The spectra of the vapor were photographed in the first order of a three-meter 15,000 line per inch, Eagle mounted grating spectrograph using a 2.5 kva hydrogen discharge tube. The cells were all-quartz connected by a side-arm to a reservoir which contained the sample, the temperature of which controlled the vapor pressure in the cell. The plates were scanned on a Leeds and Northrup microphotometer and the wave lengths determined by comparison with standard iron lines.

The solution spectra were obtained in cyclohexane solution with a Beckman quartz spectrophotometer.

Results

Microphotometer tracings of the vapor spectra are given in Fig. 1 along with that for toluene. The intensities of the spectra are not comparable since conditions were chosen to give maximum contrast. The chloroalkylbenzene spectra are more diffuse than that of toluene which appears to be due to the broadening of the rotational structure and to the interaction of a dissociative electronic level.

From Fig. 1 it will be seen that the substituent subspectrum becomes relatively more important as the number of chlorine atoms on the α atom of

(4) (a) The benzene subspectrum consists of bands containing the 500 cm^{-1} (B) the mode which makes the benzene spectrum allowed. (b) The substitution subspectrum consists of the additional bands which appear in substituted benzenes: 0 – 0(A), 0 + 900 (A + B) etc.

(5) Flurschein and Holmes, *J. Chem. Soc.*, 1607 (1928).

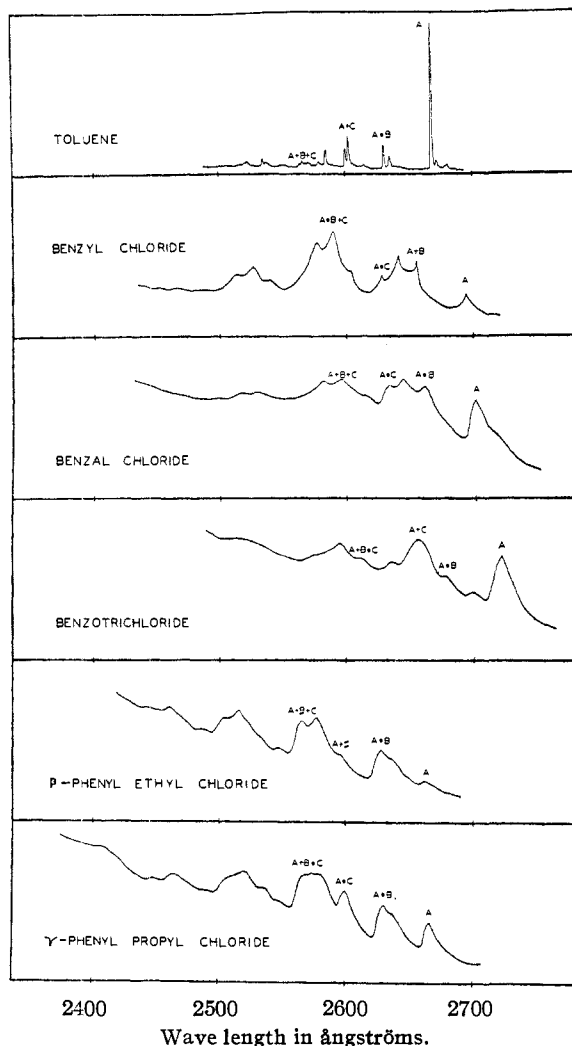


Fig. 1.—Microphotometer tracings of the vapor spectra of chloroalkyl substituted benzenes; intensity scale varies from compound to compound.

(1) Presented at the 112th meeting of the American Chemical Society New York, N. Y., September 15–19, 1947.

(2) A. L. Sklar, *Rev. Modern Phys.*, **14**, 232 (1942).

(3) F. A. Matsen, W. W. Robertson and R. L. Chouke, *Chem. Rev.*, **41**, 273 (1947).

the substituent is increased and as the chlorine atom is substituted successively β , γ and α .

The wave lengths, the relative intensities and assignments in terms of excited state fundamentals for the band maxima are given in Table I. These

TABLE I
WAVE LENGTHS, RELATIVE INTENSITIES, AND PROBABLE ASSIGNMENTS OF MAXIMA

\AA .	Cm.^{-1}	Relative intensity	Probable assignment
Benzyl chloride			
2694	37,110	MS	0 - 0
2655	37,650	S	0 + 540
2641	37,860	S	0 + 750
2628	38,040	M	0 + 930
2604	38,390	W	0 + 540 + 750
2589	38,620	VS	0 + 2 \times 750; 0 + 540 + 930
2577	38,790	S	0 + 750 + 930
2540	39,360	W	
2526	39,570	W	
2515	39,760	W	
Benzal chloride			
2701	37,020	VS	0 - 0
2661	37,570	MS	0 + 550
2644	37,810	MS	0 + 790
2634	37,950	S	0 + 930
2617	38,200	VW	
2596	38,510	M	0 + 550 + 930
2582	38,720	M	0 + 790 + 930
2522	39,640	M	
Benzotrichloride			
2721	36,740	VS	0 - 0
2629	37,040	W	0 + 300
2678	37,340	VW	0 + 600
2656	37,640	S	0 + 900
2635	37,940	W	0 + 300 + 900
2613	38,250	W	0 + 600 + 900
2595	38,520	W	0 + 2 \times 900
Phenylethyl chloride			
2662	37,560	W	0 - 0
2628	38,040	S	0 + 480
2595	38,520	W	0 + 960
2576	38,810	VS	0 + (730) + 480
2564	38,980	VS	0 + 480 + 960
2547	39,250	W	0 + (730) + 960
2514	39,760	MS	
2487	40,190	W	
2461	40,630	W	
Phenylpropyl chloride			
2664	37,530	MS	0 - 0
2638	38,040	S	0 + 510
2598	38,480	MS	0 + 950
2578	38,780	VS	0 + (740) + 510
2564	38,980	VS	0 + 510 + 950
2535	39,440	W	0 + 2 \times 950
2516	39,730	M	
2416	40,600	M	
2405	41,560	W	

spectra, due to their diffuseness, exhibit only a few of the fundamentals and combination bands exhibited by more discrete spectra.⁶ For β -phenylethyl chloride and γ -phenylpropyl chloride the 700 cm.^{-1} fundamental is lost on the shoulder of the stronger 900 cm.^{-1} fundamental but does appear in combinations. The wave numbers of the zero-zero bands lie in the following order: β -phenylethyl chloride > γ -phenylpropyl chloride > toluene > benzyl chloride > benzal chloride > benzotrichloride.

The solution data⁷ are given in Fig. 2. The spectra of β -phenylethyl and γ -phenylpropyl chloride lie so close to toluene that they were not included on the graph. The order of the intensities of absorptions are in the order benzotrichloride > benzal chloride > benzyl chloride \cong toluene > γ -phenylpropyl chloride > β -phenylethyl chloride.

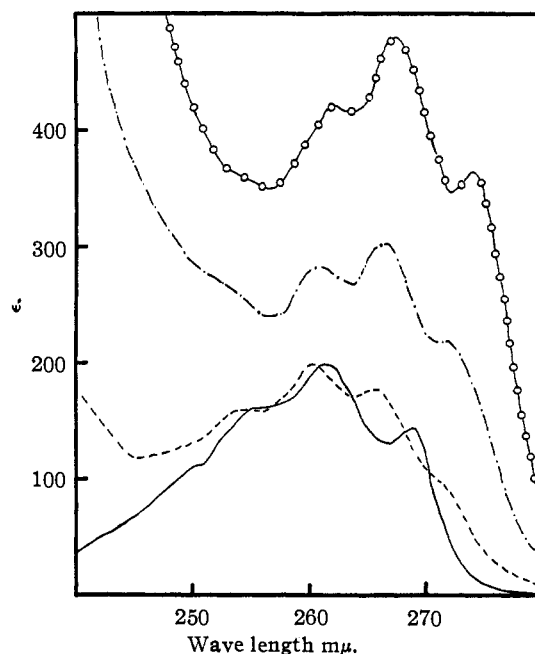


Fig. 2.—Ultraviolet absorption spectra in solutions of cyclohexane: —, toluene; ---, benzyl chloride; -·-·-, benzal chloride; ····, benzotrichloride; -o-o-o, benzotrichloride.

Conclusions

The migration of electrons out of the ring has qualitatively the same effect on the spectra as the migration into the ring.

The intensities of absorption and the importance of the substitution subspectrum are functions of the transition probability which is very low for benzene due to the hexagonal symmetry of the electron distribution. It has been proposed by Sklar² that the hexagonal symmetry is distorted by migration of electrons into the ring due to the substitution of ortho-para directing groups. This research shows that the distortion is also accom-

(6) See footnote 3 for particular references.

(7) See also L. J. Anderson and S. L. Linden, *THIS JOURNAL*, **69**, 2091 (1947).

plished by the migration of electrons out of the ring. Very qualitatively it appears that the migration in for toluene is of the same order as the migration out for benzyl chloride.

The position of the zero-zero bands is a function of the difference of zero point energies in the ground and excited state and the height of the excited state above the ground state. The former is influenced by the mass of the substituent and appears to become smaller as the mass of the substituent increases.³

The height of the excited above the ground state may be discussed from the point of view of resonance between valence structures or of molecular orbitals. From the former, there is resonance involving structures like the following



which will lower the excited state relative to the ground state. The substitution of more chlorine atoms produces more ionic structures with a resultant increased lowering of the excited state. From the molecular orbital point of view the withdrawal of electrons by the electronegative chlorine atoms tends to leave vacant a *p* orbital on the carbon atom. The molecule then possesses seven

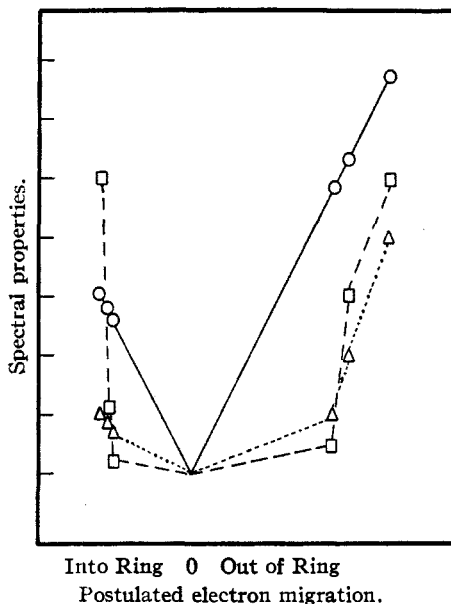
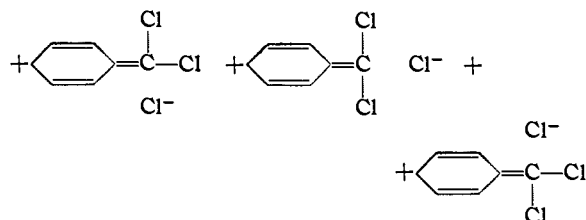


Fig. 3.—Spectral properties and postulated electron migration: The position of the zero-zero bands (O), the estimated intensity of the spectrum compared to that of benzene (Δ), and the estimated ratio of intensity of the substitution subspectrum to intensity of the benzene subspectrum (\square) are plotted as ordinates. From left to right the points correspond to compounds toluene, γ -phenylpropyl chloride, β -phenylethyl chloride, benzyl chloride, benzal chloride and benzotrichloride. The abscissa is a scale of electron migration so chosen as to make the points (O) fall on straight lines.



interacting *p* orbitals in which six π electrons move. This system may be compared to aniline and phenol which also possess seven interacting orbitals; however, eight electrons move in these orbitals. The seven orbital-six electron system may be shown to be more stable and to possess a relatively lower-lying excited state than a six-orbital-six electron system accounting for the observed spectral shifts.

The substitution of chlorine for hydrogen atoms reduces hyperconjugation, the principal mechanism by which the methyl group sends electrons into the ring. The direction of migration is reversed on the replacement of one hydrogen atom by a chlorine atom as may be seen by Fig. 3.

From left to right along the abscissa of Fig. 3 there is progression from migration into the ring to migration out of the ring. At some point there must be zero migration. Since the right side goes up continuously it seems necessary to locate the zero migration point between toluene and benzyl chloride; that is the direction of migration is reversed by the replacement of one hydrogen atom by a chlorine atom. This is substantiated by the spectrum of β -phenylethyl chloride which has a weaker substitution spectrum, a lower intensity and a zero-zero band which lies farther from the visible than either toluene or benzyl chloride. Thus the shift of the chlorine atom from an α - to a β -carbon atom reduces its effect enough to place β -phenylethyl chloride near the minimum of the curve in Fig. 3. In γ -phenylpropyl chloride the effect of the chloride is so reduced that the hyperconjugation with the ring becomes predominating which places the compound up on the left branch of the curve.

Assuming that in benzyl chloride the migration is out of the ring, the problem is raised as to why the per cent. meta formed is not higher than the 11.6% reported. If the substituent had no effect, 40 per cent. meta should be formed; if the substituent withdrew electrons a still higher per cent. meta should be formed. Several suggestions present themselves: (1) there is a permanent positive inductive (non-resonance) effect associated with carbon which will always be ortho-para directing, (2) there are polarizing effects in the substitution reaction of the kind discussed by Pauling and Wheland⁸ which are not detected spectroscopically.

Summary

1. The spectra of benzyl, benzal, benzotri-

(8) Wheland, *THIS JOURNAL*, **64**, 900 (1942); Pauling and Wheland, *ibid.*, **57**, 2086 (1935).

β -phenylethyl and γ -phenylpropyl chloride have been obtained in the vapor phase and in cyclohexane solution.

2. A theoretical discussion of the results is given.

AUSTIN, TEXAS

RECEIVED JANUARY 14, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

The Relation between the Absorption Spectra and the Chemical Constitution of Dyes. XX. Induced Non-Coplanarity in Symmetrical Benzidine Dyes¹

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In an earlier paper in this series³ an investigation was made on the separation of chromophores in disazo dyes by the introduction of insulating methylene, ethenylene and ethylene groups. This study was made on both symmetrical and unsymmetrical disazo dyes and from the data obtained it was shown that when two chromophores were separated by one or two methylene groups, the chromophores function almost as though they were in separate molecules. However, the frequency of each chromophore was slightly diminished by the presence of the other. This was considered due either to the mutual influence of the two chromophores or to added molecular weight. The closer the separated chromophores approached each other when directly connected, the greater their mutual effect. When the azo chromophores were connected by a well-defined conjugate system, each chromophore strongly influenced the electronic excitation of the other.

The observed shift of the principal absorption band to lower frequency caused by an increase in molecular weight of the compound was, however, of a low order of magnitude compared with the shift caused by the conjugation of chromophoric systems.

In azo dye structures, the conditions effecting the coplanarity of the dye molecule would also be expected to have considerable effect on their absorption spectra. As early as 1923, Ley and Rincke⁴ made comparisons of the absorption spectra of planar *trans*-stilbene with *trans*- α -methylstilbene. Interpretation of their results indicated that the methyl group in the latter crowds an ortho hydrogen of the more remote benzene ring. Planarity was therefore inhibited, as was, in consequence, the resonance interaction between the two benzene rings. The unsubstituted benzidine nucleus has been shown to exhibit some steric inhibition to complete coplanarity because of the bond angles and distances involved in

its structure.⁵ Moyer and Adams⁶ have shown that the compound 3,3'-diaminodimesityl, because of the steric effects of the methyl groups in the 2,2',6,6'-positions, was definitely non-coplanar. It was further predicted that the characteristic effect of the conjugation of the biphenyl molecule on the absorption spectra would vanish for compounds possessing this inhibited structure. This hypothesis was supported by observations conducted by Pickett.⁷ In this investigation it was shown that the absorption spectra of bimesityl was almost identical with that of mesitylene but differed significantly from biphenyl. Other examples of the effect of 2,2'-substitution on the absorption spectra of the biphenyl molecule have been recorded by Rodebush.⁸ Jones⁹ has also presented data and a general review on steric hindrance of resonance.

Experimental

The dyes prepared for this study were synthesized from intermediates of known purity by standard procedures for diazotization and coupling. The cresols used were available in grades of acceptable purity. Benzidine, 3,3'-dimethylbenzidine and 3,3'-dimethoxybenzidine obtained from Eastman Kodak Company were analyzed and shown to be of acceptable purity. The 2,2'-dimethyl¹⁰ and 2,2',6,6'¹¹-tetramethyl benzidine derivatives were synthesized and purified before use.

All the dyes prepared were purified by repeated recrystallization from dilute acetic acid until a constant purity resulted. The analysis for the purity of all dye samples was accomplished by the use of a standardized titanium trichloride solution.

Absorption measurements were made by the use of a Beckman quartz spectrophotometer. The properly diluted samples were introduced into 1.00-cm. fused silica cells and their absorption spectra determined using the corresponding solvent as a reference solution. Readings were generally taken at 10 m μ intervals, although in some places determinations were made at closer intervals to increase the accuracy of the measurements. A dilution to 0.000015 *M* served for obtaining the complete absorption spectra of all the dyes measured. In neutral solu-

(1) Presented before the Organic Chemistry Division at the New York meeting of the American Chemical Society, September 17, 1947.

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(3) W. R. Brode and J. D. Piper, *THIS JOURNAL*, **57**, 135 (1935); **63**, 1502 (1941).

(4) H. Ley and F. Rincke, *Ber.*, **56**, 771 (1923).

(5) J. M. Robertson and I. Woodward, *Proc. Roy. Soc. (London)*, **A142**, 333 (1933).

(6) W. W. Moyer and R. Adams, *THIS JOURNAL*, **51**, 630 (1929).

(7) L. W. Pickett, G. F. Walter and H. France, *ibid.*, **58**, 2296 (1936).

(8) B. Williamson and W. H. Rodebush, *ibid.*, **63**, 3018 (1941).

(9) L. A. Jones, *Chem. Reviews*, **32**, 1 (1943); *ibid.*, **63**, 1658 (1941); **67**, 2127 (1945).

(10) P. Jacobsen, *Ber.*, **28**, 2541 (1895).

(11) R. B. Carlin, *THIS JOURNAL*, **67**, 928 (1945).