ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, PARKE, DAVIS & COMPANY]

The Continuity of the Ultraviolet Bands of Benzene with Those of its Derivatives. Application to Certain Trisubstituted Derivatives[1]

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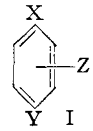
The principal bands of benzene are located in the spectra of its trisubstituted derivatives containing one *meta*- and two *ortho,para*-directing substituents in the arrangement of formula I. The bands of these compounds taken one at a time usually compare well both in form and wave length position with the most displaced corresponding band in the spectra of those disubstituted compounds containing the same groups.

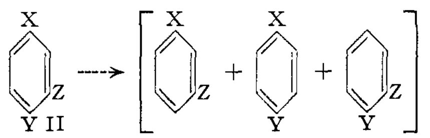
Previous papers of this series have supported the thesis that all of the accessible bands of benzene are displaced and can be identified in the spectra of its simple mono- and disubstituted derivatives.[2] Further, the wave length position of these bands was found to be roughly predictable. With this background it was of interest to inquire whether the introduction of yet another substituent group into disubstituted derivatives would lead to further large displacements of the benzene bands. A preliminary survey of the spectra of numerous trisubstituted compounds showed that further changes resulting from this additional substitution, besides being a function of the nature of the groups, are heavily dependent upon their relative position in the benzene ring.

For this study a number of derivatives of type I were selected



I

where X,Y and Z are substituent groups, only one of which is electron attracting (*i.e.*, *m*-directing) in nature. These are listed in Tables I and II. It was found that, within this class, there was frequently a remarkable resemblance of the spectra of these compounds, taken one absorption band at a time, to those of one of the three disubstituted compounds representing all possible permutations of groups. These permutations are shown in the accompanying formula II based on the preceding type formula I.



II

Trisubstituted compound

Constituent disubstituted compounds

The term "constituent compound" is defined in accord with the scheme of formula II and has been introduced to facilitate the presentation of these correlations.

Experimental.—Absorption spectra of the compounds studied were determined with a Beckman model DU spectrophotometer. Molar absorptivities were calculated by dividing the absorbance values in matched quartz cells by the molar concentrations of the solute. The solute concentrations were chosen to give peak absorbance values for each band in the range 0.4 to 0.8.

In the region below 220 mμ, 0.020-cm. cells were used; the reduced solvent absorption with these cells extends the range and promotes instrument accuracy. The slit opening at these wave lengths was held constant at 1.0 mm., and solute dilutions were prepared giving peak absorbances near 0.5. In view of the decreased accuracy which may be expected at low wave lengths, ϵ values in this region are reported in whole units.

Most of the compounds used in this study were obtained from commercial suppliers, principally Eastman Kodak Co. Some were graciously furnished by members of the Parke Davis research staff. Each sample was checked by standard physical methods with its literature value, and recrystallized to suitable constants when necessary.

Comparison of Representative Trisubstituted Compounds and their Constituent Disubstituted Compounds.—Figure 1 gives the spectrum of β-resorcylic acid and that of each of its constituent disubstituted compounds, salicylic acid, resorcinol and *p*-hydroxybenzoic acid. Since this case is representative, it will be examined at some length. In terms of our original correlations the bands of the disubstituted compounds have the following relations. The combination of hydroxyl and carboxyl groups in salicylic acid results in a displacement of the longer wave length band of benzene (secondary band) from 254 to 303 mμ, while the *ca.* 200 mμ band of benzene (first primary band) is displaced to 237 mμ. If these same groups are combined in *para* positions, the resulting *p*-hydroxybenzoic acid shows very different band displacement effects. Now the secondary band is apparent only as an inflection at *ca.* 273 mμ, less displacement than in the case of salicylic acid. On the

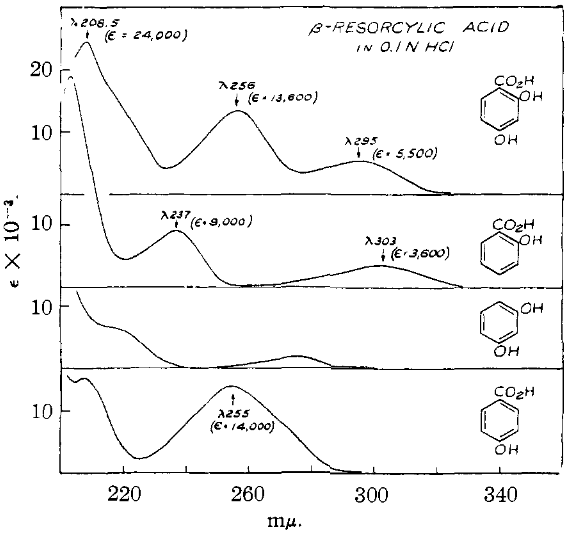


Fig. 1.—Ultraviolet absorption spectra of β-resorcylic acid and its constituent disubstituted compounds.

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(1) Presented in part at the Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, 1952.

(2) L. Doub and J. M. Vandenbelt, THIS JOURNAL, **69**, 2714 (1947); **71**, 2414 (1949).

other hand, the first primary band has undergone greater displacement to 255 mμ. Simultaneously, this band is considerably increased in intensity and has broadened. This pattern of band displacement and shape was found to be generally characteristic of disubstituted compounds containing one electron-attracting and one electron-repelling substituent.

Although the combination of one hydroxyl group with the carboxyl group in either salicylic acid or *p*-hydroxybenzoic acid caused striking wave length displacement of both the secondary and first primary bands of benzene, the addition of another hydroxyl group to form *β*-resorcylic acid causes only slight displacements of these bands. Further, the spectrum appearance now partakes of the features of both disubstituted compounds. The spectrum of the trisubstituted compound contains a first primary band at 256 mμ coinciding nicely with that of *p*-hydroxybenzoic acid at 255 mμ and closely resembling this band both in shape and intensity. Whereas *p*-hydroxybenzoic acid shows only an inflection in its spectrum corresponding to the secondary band, *β*-resorcylic acid exhibits a well-defined secondary band. This band is only a few mμ short of the wave length of the secondary band of salicylic acid, and is similar to it in intensity and form. It should be noted further that the first primary band of salicylic acid (λ_{max} 237 mμ) appears to have no analog in the spectrum of *β*-resorcylic acid; likewise, the inflection (secondary band) of *p*-hydroxybenzoic acid disappears in the spectrum of the trisubstituted compound.

The situation with respect to resorcinol, the third constituent disubstituted compound of Fig. 1, is less clear. Both the secondary band and first primary band are relatively weak and might be obscured if present in the spectrum of *β*-resorcylic acid. There is an inflection in the latter spectrum at 220–225 mμ which might correspond to the first primary band of resorcinol at *ca.* 220 mμ.

The band at 208.5 mμ in the spectrum of *β*-resorcylic acid is probably a second primary band. It corresponds well in wave length position to the second primary bands of both salicylic acid and *p*-hydroxybenzoic acid. It is most similar in intensity to the second primary band of salicylic acid.

In the examples to follow, the pattern of band displacement shown in *β*-resorcylic acid often will be representative and the following rules are suggested. The secondary or first primary bands of these trisubstituted derivatives each can be related to that band which is the most displaced among the corresponding bands of the constituent compounds. These bands not only correspond usefully close in wave length position but also often are similar in intensity and form. Frequently the remaining secondary and first primary bands of constituent compounds do not appear at all in the spectrum of the trisubstituted compound.[3]

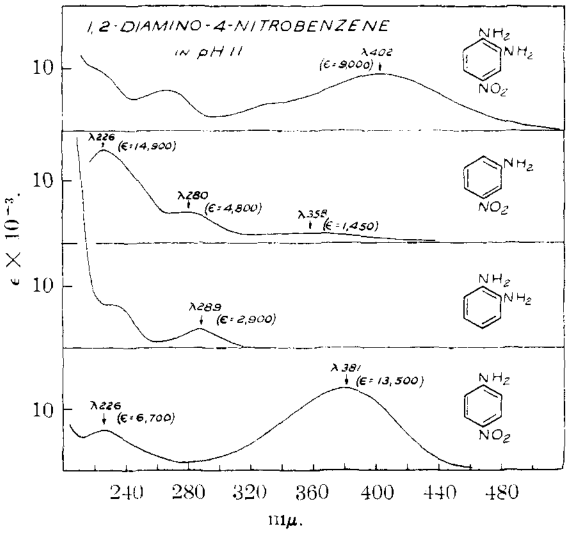

Fig. 2.—Ultraviolet absorption spectra of 1,2-diamino-4-nitrobenzene and its constituent compounds.

In succeeding discussion little attention will be paid to the second primary bands. While it is not unlikely that these bands in trisubstituted benzenes also correspond to the most displaced second primary band of constituent compounds, there is frequently a first primary band of a constituent compound to which it could also correspond.

In Fig. 2 is presented the spectrum of 1,2-diamino-4-nitrobenzene in comparison with the spectra of *m*-nitroaniline, *o*-phenylenediamine and *p*-nitroaniline. This example does not lend itself to quite the convincing visual argument the previous compound allowed. It was included, in spite of this, because of the very great displacement shown relative to benzene. The first primary band of *p*-nitroaniline at 381 mμ represents a nearly 180 mμ shift of the original first primary band of benzene. The introduction of an additional amino group to form the trisubstituted compound results in a further displacement of the first primary band of only 21 mμ. This example is unique, too, in respect to the fate of the secondary bands. Whereas in most other examples the introduction of an electron-contributing group into the *para* disubstituted constituent compound leads to clear definition of the secondary band from the broad first primary band of the original, in this instance no such separation of the secondary band occurs on the longer wave length side. No decision can be reached in terms of the above promulgated rules, because it is uncertain which constituent disubstituted compound has the more displaced secondary band. This arises because of the uncertainty regarding the fate of the secondary band in highly displaced *para* disubstituted compounds such as *p*-nitroaniline. If, as is possible on one interpretation, the secondary band is present in *p*-nitroaniline, possibly at longer wave length than the first primary band, it is of such low intensity as to be completely masked by the intense first primary band. On this basis the postulated rules hold and the spectrum of *p*-nitroaniline governs the position of both the secondary and first primary band in the trisubstituted compound. On the other hand, if it were assumed that the secondary band of *m*-nitroaniline was most displaced of those of the constituent compounds, then the plateau area at 328 mμ in the spectrum of 1,2-diamino-4-nitrobenzene might correspond to this band.

However these last points are resolved, it remains that the 402 mμ band of this trisubstituted compound corresponds well with the first primary band of *p*-nitroaniline, especially in view of the great displacement which might be expected because of the additional amino group.

Thus far the class of trisubstituted compounds has been considered in which the electron-attracting group is either X or Y of formula II; in the spectra of these, the broad intense first primary band of the *para* constituent compound has been preserved and contributes characteristically to the spectrum of the trisubstituted derivative (Table I). Now

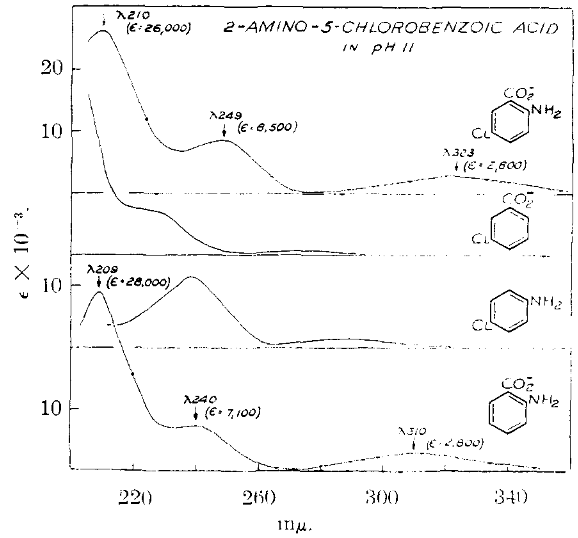

Fig. 3.—Ultraviolet absorption spectra of 2-amino-5-chlorobenzoic acid anion and its constituent compounds.

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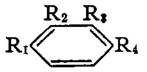
[3] Of course if these bands were reduced sufficiently in intensity they would be overlooked.

TABLE I

ULTRAVIOLET ABSORPTION CHARACTERISTICS OF TRISUBSTITUTED BENZENE DERIVATIVES (R_1 AND R_4 COMPLEMENTARY, R_2 OR R_3 *ortho,para* DIRECTING)



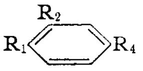
					Second primary band[g]		First primary band[g]			Secondary band[g]		
R_1	R_2	R_3	R_4	Solvent	λ	$\epsilon \times 10^{-3}$	λ[a]		$\epsilon \times 10^{-3}$	λ[a]		$\epsilon \times 10^{-3}$
Cl	...	Cl	CO_2H	*p*H 3	202	35	232	*p*	7.4	282	*o*	0.5
Cl	...	Cl	CO_2^-	*p*H 11	[b]	..	229	*p*	7.4	281	*o*	.4
Cl	Cl	...	CO_2H	*p*H 3	206	34	242	*p*	13.5	281	*m*	.8
Cl	Cl	...	CO_2^-	*p*H 11	203	41	237	*p*	11.3	279	*m*	.7
Cl	...	NH_2	CO_2H	*p*H 4	221	30	249	*o*	8.9	327	*o*	3.8
Cl	...	NH_2	CO_2^-	*p*H 7	216.5	32	247	*o*	8.5	314	*o*	3.5
CH_3	...	OH	CO_2H	*p*H 3	206.5	37	242	*p*	9.6	301	*o*	3.5
CH_3	...	OH	CO_2^-	*p*H 7	206	36	238	*p*	8.5	297	*o*	3.8
OH	...	OH	CO_2H	0.1 *N* HCl	208.5	24	256	*p*	13.6	295	*o*[c]	5.5
OH	...	OH	CO_2^-	*p*H 7	207.5	31	248	*p*	10.8	292	*o*[c]	4.9
O^-	...	OH	CO_2^-	*p*H 11	231 (209)	11.2 (21)	248	*p*	15.4	298	*o*[c]	13.0
OH	OH	...	CO_2H	*p*H 3	217	16	260	*p*	9.3	294	*m*[c]	4.8
OH	OH	...	CO_2^-	*p*H 7	[b]	..	251	*p*	7.8	288	*m*[c]	3.7
O^-	OH	...	CO_2^-	*p*H 11	230[d]	11	276	*p*	8.0	303	*m*[c]	9.5
OH	OCH_3	...	CO_2H	*p*H 3	217.5	20	260	*p*	11.1	291	*m*[c]	5.8
OH	OCH_3	...	CO_2^-	*p*H 7	204.5	28	251	*p*	9.9	286	*m*[c]	4.4
O^-	OCH_3	...	CO_2^-	0.1 *N* NaOH	225	12.1	280[d]	*p*	13	298	*m*[c]	14.9
OCH_3	...	OH	CO_2H	*p*H 3	206	33	254	*p*	12.4	294	*o*[c]	5.5
OCH_3	...	OH	CO_2^-	*p*H 7	[b]	..	250	*p*	12.0	291	*o*[c]	5.3
OCH_3	...	OCH_3	CO_2H	*p*H 3	207.5	23	257	*p*	13.1	291	*o*[c]	5.9
OCH_3	...	OCH_3	CO_2^-	*p*H 11	[b]	..	246	*p*	8.5	283	*o*[c]	3.6
OH	NH_2	...	CO_2H	*p*H 4.2	229	10.9	250[d]	*p*	8.4	302	*m*[c]	1.5
OH	NH_2	...	CO_2^-	*p*H 7	215	24	253	*p*	6.9	297	*m*[c]	3.5
O^-	NH_2	...	CO_2^-	*p*H 11	235[d] (214)	13 (18)	280	*p*	9.2	308	*m*[c]	9.1
NH_2	...	OH	CO_2H	*p*H 3.1	231 (204)	8.3 (26)	275	*p*	9.2	301	*o*[c]	9.9
NH_2	...	OH	CO_2^-	*p*H 7	228[d] (209)	11.3 (23)	265	*p*	13.2	299	*o*[c]	8.7
NH_2	...	CH_3	CO_2H	*p*H 3.6	223	9.6	288	*p*	12.1	[e]		..
NH_2	...	CH_3	CO_2^-	*p*H 11	[e]	..	266	*p*	12.2	293[d]	*o*[c]	6
NH_2	...	NH_2	CO_2H	*p*H 4.4	228	16.4	277	*p*	11.1	317[d]	*o*[c]	4.3
NH_2	...	NH_2	CO_2^-	*p*H 11	216	25	266	*p*	10.0	307	*o*[c]	4.2
NH_2	...	Cl	CO_2H	*p*H 3	225[d]	9.5	282	*p*	9.8	[e]		..
NH_2	...	Cl	CO_2^-	*p*H 7	[b]	..	256	*p*	9.0	294[d]	*o*[c]	2.3
$NHCH_3$	...	Cl	CO_2H	*p*H 3	230	8.3	302	*p*	13.2	[e]		..
$NHCH_3$	...	Cl	CO_2^-	*p*H 7	209	24	268	*p*	10.2	[e]		..
$N(CH_3)_2$	...	Cl	CO_2H	*p*H 3	233	6.5	313	*p*	13.9	[e]		..
$N(CH_3)_2$	...	Cl	CO_2^-	*p*H 7	211	22	275	*p*	11.4	[e]		..
Cl	...	Cl	$COCH_3$	H_2O[f]	212	21	252	*p*	8.9	290[d]	*p*	1.1
Cl	Cl	...	$COCH_3$	H_2O[f]	212	23	254	*p*	14.6	290[d]	*m*	1.5
OH	...	OH	$COCH_3$	*p*H 3	228 (211)	9.4 (17)	275	*p*	13.9	312	*o*[c]	6.8
O^-	...	OH	$COCH_3$	*p*H 11	248 (211)	6.5 (13)	328 (290[d])	*p*	25.6 (6)	[e]		..
OH	OH	...	$COCH_3$	0.1 *N* HCl	228 (205)	13.0 (15)	274	*p*	9.9	305	*m*[c]	7.4
O^-	OH	...	$COCH_3$	*p*H 11	248 (206)	10.2 (14)	342 (290[d])	*p*	16.3 (4.5)	[e]		..
NH_2	...	OH	$COCH_3$	*p*H 6	245 (210)	5.7 (16)	325 (290[d])	*p*	21.2 (10)	[e]		..
NH_2	...	O^-	$COCH_3$	0.1 *N* NaOH	250[d] (232)	10 (17)	298	*p*	9.8	348	*o*[c]	10.4
Cl	...	Cl	CHO	H_2O[f]	218	17	263	*p*	13.7	300[d]	*p*	2.0
OH	...	OH	CHO	*p*H 3	229 (211)	10.7 (15)	278	*p*	15.7	320[d]	*o*[c]	6.3
O^-	...	OH	CHO	*p*H 11	250[d] (230[d])	8 (12)	331	*p*	20.3	[e]		..
Cl	Cl	...	NO_2	H_2O[f]	225[d] (211)	9 (14)	276	*p*	9.2	320[d]	*m*[c]	2
OH	Cl	...	NO_2	0.1 *N* HCl	231 (210)	7.6 (13)	317	*p*	8.5	[e]		..
O^-	Cl	...	NO_2	0.1 *N* NaOH	265 (235[d])	4.0 (5)	400 (301)	*p*	17.4 (1.4)	[e]		..
CH_3	NH_2	...	NO_2	*p*H 11	245 (223)	10.4 (12)	293	*p*	5.8	358	*m*[c]	2.1
OH	NH_2	...	NO_2	*p*H 5	256 (221)	9.8 (11)	315	*p*	5.1	370	*m*[c]	4.7
O^-	NH_2	...	NO_2	*p*H 11	275 (226[d])	6.9 (9)	446 (345[d])	*p*	13.4 (3)	[e]		..
NH_2	OCH_3	...	NO_2	*p*H 7	257 (219)	6.0 (8)	400 (310[d])	*p*	12.3 (2.4)	[e]		..
OCH_3	NH_2	...	NO_2	*p*H 11	254 (221)	11.4 (12)	311	*p*	5.6	367	*m*[c]	4.6
NH_2	NH_2	...	NO_2	*p*H 11	266 (224[d])	6.6 (10)	402 (328[d])	*p*	9.0 (4)	[e]		..

[a] The *m*, *o* or *p* entry following each band in these columns designates that constituent compound whose corresponding band is used as abscissa in Fig. 4. [b] Below accessible wave length region. [c] In Fig. 4, this band is arbitrarily plotted *vs.* the

secondary bands of the designated *m*- or *o*-disubstituted constituent compounds. This was necessary because the position and even existence of the secondary bands of these particular *p*-disubstituted constituent compounds is uncertain. In view of the doubtful status of these points, they are separately identified in Fig. 4. [d] Band inflection. [e] Band fused with neighboring absorption. [f] Diluted from methanol solution. [g] Figures in parentheses are for unidentified bands in the spectrum.

TABLE II

ULTRAVIOLET ABSORPTION CHARACTERISTICS OF TRISUBSTITUTED BENZENE DERIVATIVES (R_1 AND R_4 *ortho,para* DIRECTING; R_2 *meta* DIRECTING)



R_1	R_2	R_4	Solvent	Second primary band		First primary band			Secondary band		
				λ	$\epsilon \times 10^{-3}$	λ^a		$\epsilon \times 10^{-3}$	λ^a		$\epsilon \times 10^{-3}$
OH	CO_2H	Cl	0.1 *N* HCl	208	34	233	*o*	7.7	314	*o*	3.5
OH	CO_2^-	Cl	*p*H 7	204.5	35	230	*o*	7.9	308	*o*	3.4
OH	CO_2H	Br	0.1 *N* HCl	210.5	36	233	*o*	8.4	314	*o*	3.3
OH	CO_2^-	Br	*p*H 7	206.5	37	232^d	*o*	8.4	308	*o*	3.3
OH	CO_2H	OH	0.1 *N* HCl	211	31	238	*m*	9.3	329	*o*	5.3
OH	CO_2^-	OH	*p*H 7	206	35	235^d	*m*	8.3	320	*o*	5.3
OCH_3	CO_2H	Br	*p*H 3	208	29	234^d	*o*	9.0	305	*o*	2.4
OCH_3	CO_2^-	Br	*p*H 11	201	30	230^d	*o*	9.4	289	*o*	2.1
NH_2	CO_2H	Cl	*p*H 3	218	22	250	*o*	5.2	340	*o*	2.3
NH_2	CO_2^-	Cl	*p*H 11	210	26	249	*o*	8.5	323	*o*	2.8
Cl	$COCH_3$	Cl	H_2O^b	215.5	25	240	*m*	6.2	296	*m*	1.1
OH	$COCH_3$	OH	0.1 *N* HCl	224	18.4	256	*o*	9.4	355	*o*	4.5
OH	CHO	Cl	*p*H 3	221.5	23.6	255	*o*	8.9	338	*o*	3.1
O^-	CHO	Cl	0.1 *N* NaOH	233.5	18.9	260^d	*o*	7.6	390	*o*	6.0
Cl	NO_2	Cl	H_2O^b	220	19	258	*m*	3.3	314	*m*	1.5
CH_3	NO_2	Cl	H_2O^b	213	18	262	*o*	4.8	315	*o*	1.7
OCH_3	NO_2	Cl	H_2O^b	220.5	19	265	*o*	3.9	349	*o*	2.7
OCH_3	NO_2	OCH_3	H_2O^b	218	16	273 (245^d)	*m*	3.3 (5.7)	372	*o*	2.6
NH_2	NO_2	Cl	H_2O^b	233	21.6	279	*o*	4.6	425	*o*	4.6
NH_2	NO_2	CH_3	H_2O^b	227.5	18.4	287	*o*	5.6	428	*o*	4.3
NH_2	NO_2	OCH_3	*p*H 11	230.5	19.9	285 (259^d)	*o*	5.2 $(5.7)^c$	448	*o*	4.7

[a] The *m* or *o* entry after each band in these cols. designates that constituent compound whose corresponding band is used as abscissa in Fig. 5. [b] Dild. from MeOH soln. [c] Figures in parentheses for unidentified bands in spectrum. [d] Band infl.

attention will be turned to those derivatives in which the electron-attracting group is Z of formula II (Table II).

An example of this type is shown in Fig. 3. Here are given the spectra of 2-amino-5-chlorobenzoic acid anion, *m*-chlorobenzoic acid anion, *p*-chloroaniline and *o*-aminobenzoic acid anion. It can be seen by inspection that greatest similarity exists between the trisubstituted derivative and *o*-aminobenzoic acid anion, a small shift to longer wave length for each band having resulted from the substitution. It is a moot point whether the first primary band of this last compound or that of *p*-chloroaniline should be related to the first primary band of the trisubstituted compound.

Some Quantitative Aspects of Band Comparison.—In Figs. 4 and 5 are shown the quantitative comparisons of the bands of these trisubstituted derivatives with those of the constituent compounds. At the top of these figures the secondary bands of the trisubstituted compounds are plotted as λ_{max} from the tables each *vs.* the *most displaced* secondary band of its set of three constituent compounds. The primary bands are similarly plotted below the figures.[4]

Figure 4 presents those trisubstituted compounds containing one constituent compound which is *para* disubstituted with electronically complementary groups. In terms of formula II, either X or Y is the electron-attracting group. The spectra of these compounds are illustrated by Figs. 1 and 2 and are characterized usually by a broad intense first primary band.

In Fig. 5 are presented those trisubstituted compounds in which Z of formula II is electron-attracting. Their spectra are of the type illustrated by Fig. 3.

In both Figs. 4 and 5 the solid lines represent a one-to-one correspondence and have no necessary relation to the straight line which, statistically, would best represent the data. This device has been used to emphasize the usually slight effect of adding the third substituent group to the selected disubstituted compounds (abscissas of the plots). The secondary bands at the top of Fig. 5 show some displacement to longer wave length resulting from this added substitution. However, to a useful approximation, all others of these band plots give a direct numerical correspondence.

The deviations from direct correspondence in these latter plots can be either to shorter or to longer wave length as compared with the appropriate constituent compound. This is in sharp contrast to the situation obtaining in simpler benzene derivatives, where the addition of a substituent group almost invariably shifts the absorption toward the visible to some extent. Whether the hypsochromic effects observed in the present study represent a real shift of the total band or whether they are due to changes in symmetry of the curves has not been determined.

Discussion.—Before proceeding it should be made very clear that the correlations discussed in this paper are meaningful only if viewed within their framework of limitations. Firstly, they apply to a particular class of trisubstituted compounds; secondly, it occasionally may happen that derivative spectra contain bands of constituent compounds other than those most displaced. Finally, in some instances the identification of bands is arbitrary. In order to achieve objectivity, in Figs. 4 and 5 only the most displaced appropriate band of the constituent compounds was used for each trisubstituted compound. Where the constituent compounds present an additional band only slightly less displaced there can be no pretense that the present correlations are adequate to discriminate which band is, in fact, represented in the spectrum of the trisubstituted compound.

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(4) Absorption data for most of the disubstituted constituent compounds containing *o,p*- *vs.* *m*-directing groups are given in previous papers of this series. Additional derivatives not in these papers, but necessary to the present correlations, are given in Table III.

TABLE III

ULTRAVIOLET ABSORPTION CHARACTERISTICS OF DISUBSTITUTED BENZENE DERIVATIVES USED IN FIGURES 4 AND 5 (*R*$_1$ *ortho,para* DIRECTING; R$_2$ *meta* DIRECTING)

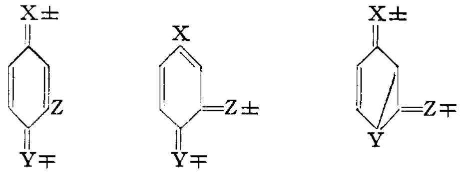
			Second primary band		First primary band		Secondary band	
R$_1$	R$_2$	Solvent	λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$	λ	$\epsilon \times 10^{-3}$
para								
Cl	$COCH_3$	H_2O	210^d	13	254.5	16.3	290^d	1.2
Cl	CHO	H_2O	210	14	259.5	17.4	292^d	1.9
$NHCH_3$	CO_2H	*p*H 3.3	224	7.6	303	13.6	[a]	..
$NHCH_3$	CO_2^-	*p*H 11	219^d	7	280	14.1	[a]	..
$N(CH_3)_2$	CO_2H	*p*H 3.5	226	7.9	315	16.4	[a]	..
$N(CH_3)_2$	CO_2^-	0.1 *N* NaOH	223^d	6.5	289	16.3	[a]	..
OCH_3	NO_2	H_2O	227	7.0	317	11.0	[a]	..
meta								
Br	CO_2H	*p*H 3	204	37	232^d	8.2	285	1.0
Br	CO_2^-	*p*H 11	202	41	226^d	8.4	278	0.6
OCH_3	CO_2H	*p*H 3	208	28	236.5	7.1	296	2.5
OCH_3	CO_2^-	*p*H 11	201.5	37	232^d	6.2	287	2.1
Cl	$COCH_3$	H_2O	208.5	26	245	10.6	293	1.2
Cl	CHO	H_2O	210	27	248.5	10.8	295	1.4
ortho								
CH_3	CO_2H	*p*H 3	[b]	..	231	7.1	279	1.4
CH_3	CO_2^-	*p*H 11	[b]	..	230^d	3.3	270	0.5
OCH_3	CO_2H	*p*H 3	203	31	236.5	7.5	296	3.3
OCH_3	CO_2^-	*p*H 11	...	..	232^d	4.7	279	2.2
Cl	$COCH_3$	H_2O	208.5	20	243	6.2	286	1.1
Cl	CHO	H_2O	210	21	253	10.0	301	1.7
OCH_3	NO_2	H_2O	232^d (211)	5.3 $(15)^c$	267	4.0	338	2.8

[a] Band fused with neighboring absorption. [b] Below accessible wave length region. [c] Identified in earlier studies as a third primary band. [d] Band inflection.

Rather, what is proposed is a point of view which seems to integrate a large mass of data. Whatever is the fate of the other bands in any given case, the most displaced bands of the constituent compounds do seem to appear in the spectra of these trisubstituted benzenes and frequently are either only slightly displaced or not displaced at all. This rests on the quantitative comparison of band position in Figs. 4 and 5 and is supported in band identification by the more subtle correspondences of form and intensity. Although it is not unlikely that this generalization also applies to the second primary bands, it is clearly apparent only for the secondary and first primary bands.

If this be valid, it should be possible to predict the main features of the spectra of these trisubstituted compounds. This may prove useful since proof of structure of such compounds often is laborious. The prediction can be achieved preferably by determining directly the spectra of appropriate disubstituted constituent compounds. If these compounds are unavailable, it will happen frequently that the positions of their bands can in turn be predicted with some confidence from previous correlations of this series.

The absorption of light can be associated with charge separation resonance in the excited state. The relationships here outlined suggest that for these trisubstituted benzenes this resonance has the important forms outlined in the accompanying formulas, in which only charge separation on the substituent atoms is considered.



III

It should be noticed that in each form one substituent group does not participate in the resonance. The effects of the third group would, on this basis, be limited largely to electrostatic and steric contributions. Since these last effects are usually small in absorption spectra, the formulas as written should not be far removed in energy from those of the disubstituted compounds which would result by removal of the non-participating atom. This comparison is congruent with that used in the present paper and gives identical constituent compounds. This qualitative reasoning, however, does not lead directly to one apparent result of this investigation, that often *only* the form of highest resonance energy is represented for each band in the spectrum of the trisubstituted derivatives. It seems likely that this result, insofar as it obtains, arises because the counterpart of this form in the ground state is also the most stable and contains electronic

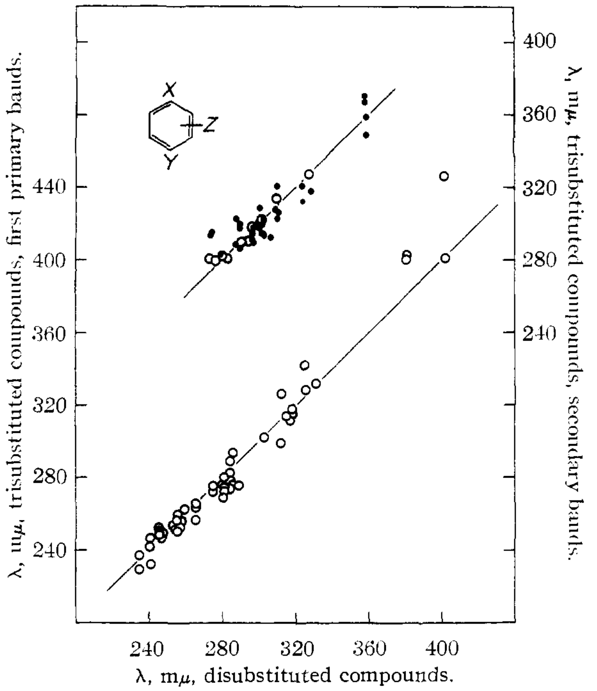


Fig. 4.—Wave lengths of trisubstituted compounds of Table I (only X or Y is *meta* directing) plotted *vs.* the most displaced bands of corresponding constituent disubstituted compounds: bottom, first primary bands; top, secondary bands. The ordinate axis for the secondary bands is at the right of the figure. In the upper group, solid points represent data identified by footnote *c* in Table I.

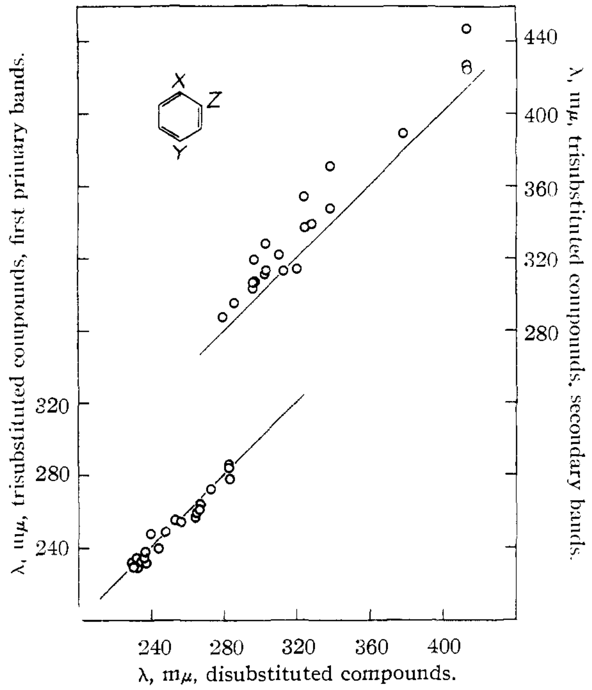


Fig. 5.—Wave lengths of trisubstituted compounds of Table II (only Z is *meta* directing) plotted *vs.* the most displaced bands of corresponding constituent disubstituted compounds: bottom, first primary bands; top, secondary bands. The ordinate axis for the secondary bands is at the right of the figure.

and vibrational symmetries which are exclusive of those required for the other resonance forms.

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[Contribution No. 1977 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology]

Exchange Reactions of Deuterated Benzene Derivatives with Potassium Amide in Liquid Ammonia[1a]

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The rates of deuterium-protium exchange have been determined for *o*-, *m*- and *p*-deuterated fluorobenzene, benzotrifluoride and anisole in liquid ammonia solution in the presence of potassium amide. The exchange rates were found to be greatest for the *ortho* compounds and smallest for the *para* compounds. Deuterobenzene and *o*-deuterotoluene reacted too slowly for convenient measurement. The results are interpreted on the basis of the operation of combined inductive and field effects of the substituents, mesomeric effects appearing to be of minor importance.

An understanding of the effect of substituents on the acidity of hydrogens located on benzene rings is important to the interpretation of the unusual rearrangements encountered in amination of aromatic halides.[2-4] For this reason, we have determined the rates of replacement of deuterium by protium for appropriate deuterated benzene derivatives in the presence of a strong base (NH_2^-) and a proton-donating solvent (NH_3).[5] Although, in principle, the rate constants k for removal of particular hydrogens need not necessarily be related to the equilibrium ionization constants K_A of the same hydrogens, in practice, the relation $\log k = x \log K_A + C$ (Brönsted catalysis law)[6] is generally observed for acids of similar structures. We will assume that this sort of parallelism between k and K_A holds for the compounds under discussion and,

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[1a] Supported in part by The Upjohn Company.

[1b] Faculty Fellow of The Fund for the Advancement of Education, 1953–1954.

[2] *Cf.* J. D. Roberts, H. E. Simmons, Jr., L. A. Carlsmith and C. W. Vaughan, This Journal, **75**, 3290 (1953).

[3] J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, *ibid.*, papers submitted for publication.

[4] J. D. Roberts, C. W. Vaughan, L. A. Carlsmith, H. E. Simmons, Jr., and D. A. Semenow, *ibid.*, papers submitted for publication.

[5] The feasibility of these experiments was first demonstrated qualitatively by H. E. Simmons, Jr., Ph.D. Thesis, Massachusetts Institute of Technology, 1954.

[6] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, pp. 222–227.