176. *The Ultra-violet Absorption Spectra of Some Benzoic Acids With Electron-repelling Substituents.*

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The ultra-violet absorption spectra of benzoic acids, mono- and 2 : 6-di-substituted with the following substituents, methyl, chloro, bromo, methoxyl, and hydroxyl, have been measured from 2000 A. towards the visible region. The three bands that are generally observed have been designated as the A, B, and C bands. It is found that the frequency of the absorption of A is largely independent of, .B is very dependent upon, and C is somewhat dependent upon the nature and position of the substituent group. The spectra are discussed in the light of currently accepted hypotheses concerning absorption in the near ultra-violet region.

ALTHOUGH the ultra-violet absorption spectra of a number of classes of organic molecules have been measured, those of aromatic acids have been measured only in a random fashion. In view of the importance of such acids, it seemed desirable to measure the spectra of a number of substituted benzoic acids in a systematic manner in order to provide a further basis for the elucidation of the relationship of ultra-violet spectra to molecular structure. We therefore report the ultra-violet absorption spectra of numerous benzoic acids, *o*-, *m*-, and *p*-monosubstituted and 2 : 6-di-substituted with the following substituent groups—methyl, chloro, bromo, methoxyl, and hydroxyl. The spectra of some of these acids have been previously determined in a number of solvents, but there are only a few measurements recorded of the spectra of organic molecules in the region near 2000 A.

TABLE I.

Ultra-violet absorption characteristics of substituted benzoic acids.

Acid.	A Band.		B Band.		C Band.		Method of prepn.
	$\lambda_{max.}$.	log ε.	$\lambda_{max.}$.	log ε.	$\lambda_{max.}$.	log ε.	
Benzoic	2020	3·90	2280	4·00	2710	2·88	1
					2790	2·74	—
o-Toluic	2050	4·09	2280	3·71	2790	2·86	1
m-Toluic	2050	4·12	2320	3·95	2790	3·01	1
p-Toluic	2040	4·12	2360	4·14	—	—	1
2 : 6-Dimethylbenzoic	2020	4·24	—	—	2700	2·86	2
o-Chlorobenzoic	2020	4·27	~2290 [a]	3·71	2780	2·88	1
m-Chlorobenzoic	2040	4·31	2300	3·92	2840	2·98	1
p-Chlorobenzoic	2020	4·17	2340	4·18	—	—	1
2 : 6-Dichlorobenzoic	2040	4·43	—	—	2640	2·64	3
	~2160	4·01	—	—	2740	2·70	—
o-Bromobenzoic	2050	4·17	~2240	3·80	2620	2·75	1
					2820	2·88	—
m-Bromobenzoic	2060	4·41	~2250	3·92	2800	2·92	1
p-Bromobenzoic	2050	4·17	2400	4·10	—	—	1
2 : 6-Dibromobenzoic	2050	4·48	—	—	2620	2·97	4
	~2260	4·00	—	—	2720	2·94	—
o-Anisic	2060	4·22	2300	3·79	2910	3·43	1
m-Anisic	2060	4·42	2300	3·83	2930	3·39	1
p-Anisic	2050	4·15	2490	4·14	—	—	1
2 : 6-Dimethoxybenzoic	2050	4·43	—	—	2820	3·27	5
Salicylic	2040	4·36	2360	3·86	3070	3·57	1
m-Hydroxybenzoic	2030	4·36	2360	3·78	3010	3·39	1
p-Hydroxybenzoic	2010	4·18	2510	4·09	—	—	1
γ-Resorcylic	2080	4·21	2500	3·80	2770	3·29	6
	~2180	4·15	—	—	3110	3·54	—

[a] ~ indicates approximate point of inflection.

(1) Purchased from Eastman Kodak Company, Rochester, New York. (2) Berger and Olivier, *Rec. Trav. chim.*, 1927, **46**, 600. (3) Reich *et al.*, *Bull. Soc. chim.*, 1917, **21**, 222. (4) Olivier, *Rec. Trav. chim.*, 1924, **43**, 872. (5) Mauthner, *J. pr. Chem.*, 1929, **121**, 259. (6) Limaye and Kelkar, *J. Indian Chem. Soc.*, 1935, **12**, 788.

The experimental data are recorded in Figs. 1—5 and Table I. The source of the compounds is indicated in Table I. All samples, either commercially obtained or synthesized, were recrystallized from suitable solvents until a constant melting point was obtained that was in agreement with values in the literature.

FIG. 1.

Ultra-violet absorption spectra of : (1) *benzoic acid ;* (2) o-*chlorobenzoic acid ;* (3) m-*chlorobenzoic acid ;* (4) p-*chlorobenzoic acid ;* (5) 2 : 6-*dichlorobenzoic acid.*

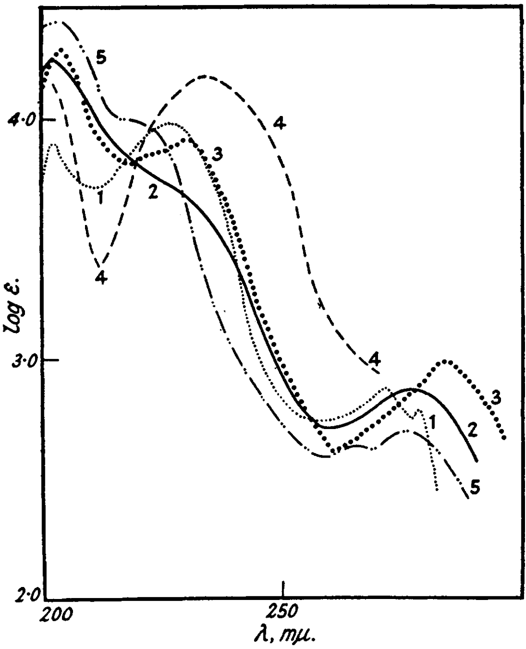


FIG. 2.

Ultra-violet absorption spectra of : (1) *benzoic acid ;* (2) o-*anisic acid ;* (3) m-*anisic acid ;* (4) p-*anisic acid ;* (5) 2 : 6-*dimethoxybenzoic acid.*

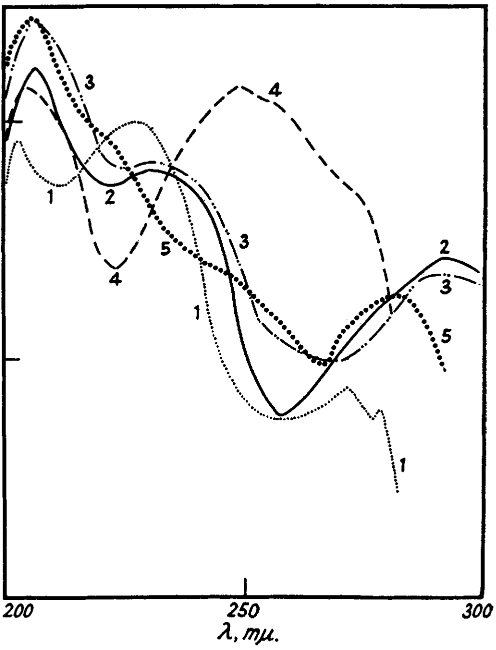


FIG. 3.

Ultra-violet absorption spectra of : (1) *benzoic acid ;* (2) o-*toluic acid ;* (3) m-*toluic acid ;* (4) p-*toluic acid ;* (5) 2 : 6-*dimethylbenzoic acid.*

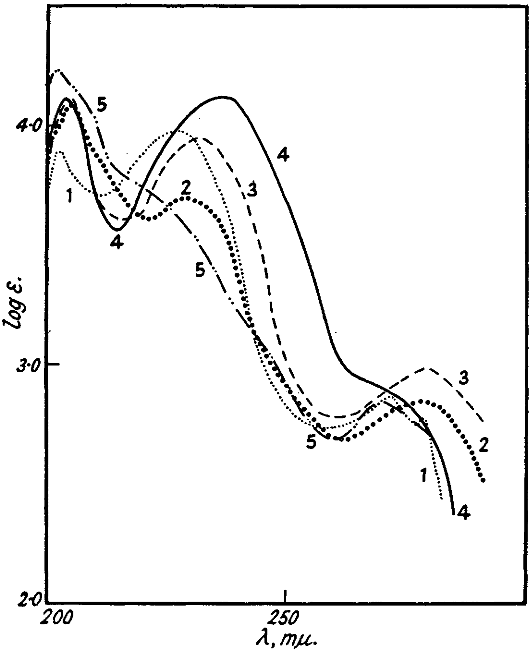
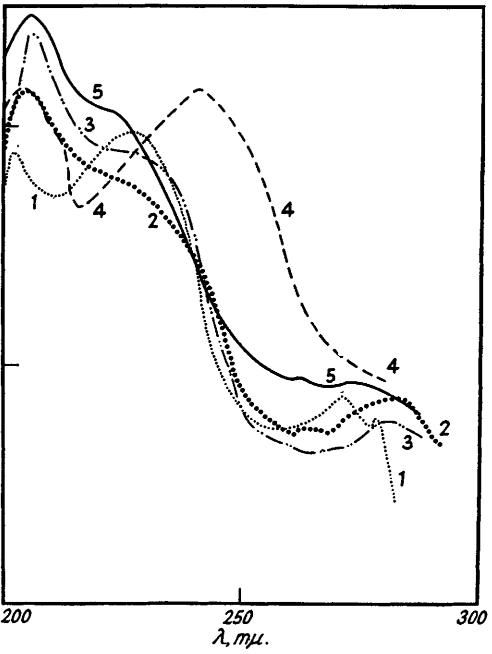


FIG. 4.

Ultra-violet absorption spectra of : (1) *benzoic acid ;* (2) o-*bromobenzoic acid ;* (3) m-*bromobenzoic acid ;* (4) p-*bromobenzoic acid ;* (5) 2 : 6-*dibromobenzoic acid.*

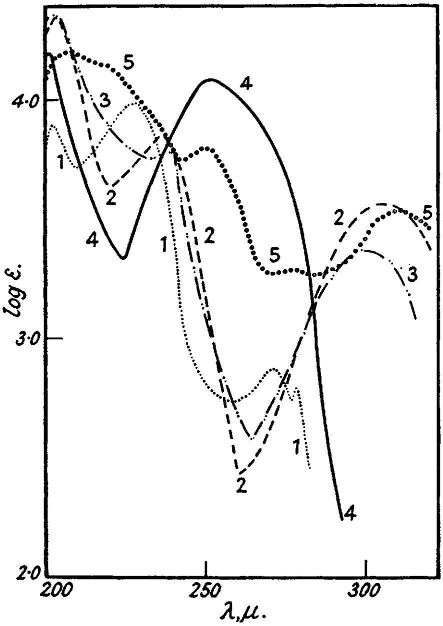


The spectrum of benzoic acid exhibits maxima at the following wave-lengths : 2020, 2280, 2710, and 2790 A. (log ε 3·90, 4·00, 2·88, and 2·74, respectively). The last two maxima in all probability represent vibrational fine structure of one electronic transition. For convenience, the band at 2020 A. will be labelled the A band, that at 2280 A. the B band, and the other two peaks the C band. We now consider the displacements brought about in these bands by further substitution of the benzene ring.

With substitution in the *para*-position to the carboxyl group by electron-repelling substituents, the A band remains essentially constant in frequency, although somewhat more intense than the corresponding band in benzoic acid. The B band undergoes a considerable bathochromic shift from the position of this band in benzoic acid, the amounts of shift with various substituent groups being in the order OH > OMe > Br > Me > Cl. The C band is not evident in these *para*-substituted acids, but it is probably hidden by the very broad B band rather than having disappeared from the spectra. In a mixture of hexane and ether the spectrum of *p*-hydroxybenzoic acid shows the C band clearly (Castille and Klingstedt, *Compt. rend.*, 1923, **176**, 749). The maxima are as follows : ~2100, 2525, 2750, 2780, 2840 A. (log ε 4·06, 4·18, 3·54, 3·40, 3·18, respectively). It would be of interest to determine the spectra of the other *para*-substituted acids in a hydrocarbon solvent; it seems likely that the C band would be visible in those compounds also.

FIG. 5.

Ultra-violet absorption spectra of : (1) benzoic acid ; (2) salicylic acid ; (3) m-*hydroxybenzoic acid; (4)* p-*hydroxybenzoic acid ; (5) γ-resorcylic acid.*



In the *ortho*-substituted compounds it is seen that the A band of benzoic acid again is essentially unchanged in the frequency of absorption. The position and intensity of the B band, however, are considerably dependent upon the nature of the substituent group. The displacement toward longer wave-lengths of the B band of the *ortho*-substituted acids (when compared with the B band of benzoic acid) is in the following order : OH > OMe > Me ≃ Cl > Br. It is to be particularly noted that the B band of *o*-bromobenzoic acid appears only as a weak inflection and is hypsochromically displaced by about 40 A. from its position in benzoic acid. All B bands of the *ortho*-substituted acids are displaced to shorter wave-lengths when compared with the B bands of the corresponding *para*-substituted acids.

The C bands of the *ortho*-substituted acids are well defined. They are all displaced towards the visible when compared with the C band of benzoic acid, and the displacement is in the following order : OH > OMe > Br > Cl > Me. The C bands of *o*-anisic and salicylic acid are considerably more intense than those of the other *ortho*-substituted acids and of benzoic acid.

The spectra of the *meta*-substituted acids in general show considerable similarity to the spectra of the corresponding *ortho*-substituted acids. The frequency of the A bands remains very close to that of benzoic acid and of the acids substituted in the other positions, but their intensity is greater than that of the latter acids. The B and C bands also occur at nearly the same frequency as in the corresponding *ortho*-acids, although the intensity is usually greater.

In the 2 : 6-disubstituted acids the A band again maintains nearly constant frequency of absorption. In three acids (*viz.*, chloro-, bromo-, and hydroxy-) the band appears to be split so that a reasonably well-defined inflection also occurs to the long wave-length side of the usual position of the A band. In only one acid (γ-resorcylic acid) does the B band appear; the position is shifted to longer wave-lengths when compared with the B band of salicylic acid and is almost equal in frequency to that of *p*-hydroxybenzoic acid. The C bands of three disubstituted acids (methyl-, chloro-, and bromo-) are similar in intensity and frequency of absorption to the C band of benzoic acid. The C band of 2 : 6-dimethoxybenzoic acid is slightly shifted toward longer wave-lengths from its position in benzoic acid and is more intense; the C band of γ-resorcylic acid is considerably shifted to longer wave-lengths than that of benzoic acid (from 2720 to 3110 A.) and is even more intense than the C band of 2 : 6-dimethoxybenzoic acid. In addition, there appears to be a weakly-defined peak near 2770 A. (log ε 3·29) in γ-resorcylic acid.

DISCUSSION.

One of the more generally used hypotheses for a qualitative understanding of ultra-violet spectra might be called the " resonance " theory. Braude *et al.* (*J.*, 1949, 1890) have recently restated the general principles that underlie this approach and have particularly emphasized the relationship between steric inhibition of resonance and electronic spectra. On the basis of these principles the behaviour of the B bands of the *ortho*- and *para*-substituted acids can be rationalized at least with partial success. The structural change that results in going from benzoic acid to the *para*-substituted acids increases the conjugation, and, as elaborated by Braude *et al.* (*loc. cit.*), decreases the energy of excitation, thus resulting in a bathochromic shift of this band. On the basis of resonance considerations alone, the position of the B band in the corresponding *ortho*- and *para*-acids should be nearly the same. The observed hypsochromic shift that has taken place in the spectra of the *ortho*-acids when compared with the B band of the corresponding *para*-acids would be explained on the basis of steric interference to co-planarity between the *ortho*-substituent and the carboxyl group.

Whether the increase of energy of excitation of the *ortho*-acids is primarily due to steric interference can probably be deduced from the following considerations. If the increase in energy of excitation is proportional to the size of the *ortho*-substituent, then the hypothesis of the steric interference to spectra would be at least partially substantiated. This has been done in Table II, with the energy differences translated into cm.$^{-1}$ units.

TABLE II.

Group.	Increase in energy of excitation (cm.$^{-1}$) of B band in going from *para*- to *ortho*-substituted acid.	Van der Waals radius (A.).[a, b]
Methyl	1487	2·0
Chloro	1125	1·8
Bromo	2193	1·95
Methoxyl	3155	*c*
Hydroxyl	2532	*c*

[a] Values obtained from Pauling, " The Nature of the Chemical Bond," p. 188, Cornell Univ. Press (1940). [b] Braude *et al.* (*loc. cit.*) have suggested that the van der Waals radii are probably too large a measure of the intramolecular interference properties of atoms. Even if this is true, a corrected measure of interference should be proportional to the van der Waals radii. [c] The van der Waals radii for the hydroxyl and the methoxyl group are not given by Pauling. The value given for oxygen is 1·40 A. An inspection of molecular models of salicylic acid and *o*-anisic acid indicates that there is very little interference in the former compound, but that it is considerable in the latter.

It will be observed that there appears to be little direct relationship between the increase in energy and the size of the substituent group. Particularly interesting is the low value for the increase in the energy of excitation observed for the methyl group, even though the size of this group would indicate that the energy of excitation should be very considerable, and the high value for the small hydroxyl group. It may be that the shifts in frequency of the B band should not be assigned alone to steric interference with coplanarity. Klevens and Platt (*J. Amer. Chem. Soc.*, 1949, **71**, 1014) have stated that changes in *location* of bands that are observed in other derivatives may be partly due to inductive and similar effects of the substituent on the ring, but changes of *intensity* observed in the bands are to be accounted for almost entirely by steric interference to resonance. Although it is generally assumed that the resonance effects of any substituent group in the *ortho*- and *para*-positions are the same, the inductive effects would not be, and they no doubt play a part in the energy of excitation, though the exact amount cannot yet be determined. In such a geometrically small group as the hydroxyl group the difference in inductive effect appears to be rather considerable.

In the 2 : 6-disubstituted acids the steric interference to coplanarity would be expected to be very considerable, and the absence of a B band in all these compounds except γ-resorcylic acid is not surprising. An examination of a molecular model of γ-resorcylic acid indicates that there is only a small amount of steric interference between the carboxyl group and the two *ortho*-hydroxyl groups.

The interpretation of the B bands of the *meta*-substituted acids on this basis is rather more complex. Since there is no resonance interaction between the substituent and the carboxyl group, it might be assumed, as a first approximation, that the effect of the substituents on the displacement of the corresponding band in benzene that occurs near 2035 A. would be nearly additive after allowance for a small hypsochromic shift due to cross-conjugation effects (Branch and Calvin, " The Theory of Organic Chemistry," p. 172, Prentice-Hall, New York, 1940). This assumption was tested upon Doub and Vandenbelt's data (*J. Amer. Chem. Soc.*, 1947, **69**, 2714; 1949, **71**, 2414) for the frequency of the B band in the monosubstituted benzene compounds. The agreement between the calculated and measured values for the frequency of the B bands of the *meta*-substituted acids varied from rather good in the case of *m*-hydroxybenzoic acid to rather poor in that of *m*-anisic acid. It would seem that the simple assumptions made for the calculation are not sufficient accurately to account for the B bands of the *meta*-substituted acids.

It is of interest to observe the close similarity in the frequency of absorption of the B bands of the corresponding *meta*- and *ortho*-substituted acids. This similarity has been observed in the spectra of a large number of *ortho*- and *meta*-disubstituted benzenoid compounds by Doub and Vandenbelt (*loc. cit.*). Their suggestion that stabilization of the photo-excited state might be able to take place across *meta*-positions, even though this is not possible in the ground state, would not appear to account for the position of the B band of *m*-bromobenzoic acid, which is shifted to shorter wave-lengths than that of benzoic acid. It is noteworthy in connection with the B band of *m*-bromobenzoic acid that, although an inspection of the molecular model of this acid indicates that there is no steric interference to coplanarity between the bromine atom and the carboxyl group, nevertheless the band appears only as a reasonably well-defined inflection. It would appear that other factors than steric interference to coplanarity are able to bring about shifts of bands to shorter wave-lengths and to diminish the intensity of absorption. An explanation offered (see below) to account for the similarity of the position of the C bands of corresponding *ortho*- and *meta*-substituted acids may also hold for the similarity of the position of the B bands.

Inspection of the data reveals that the C bands also are very similar in both the corresponding *ortho*- and *meta*-substituted acids. However, it will be seen that steric interference between the carboxyl group and another atom or group apparently has no effect upon this band. For example, the B band is barely visible in the spectrum of *o*-bromobenzoic acid while the C band is as intense as the C band of benzoic acid and has undergone a bathochromic shift of approximately 110 A. from the position of this band in benzoic acid. In 2 : 6-dibromobenzoic acid, where there is considerable steric interference between the bromine atoms and the carboxyl group, the C band is similar in position and intensity to that of benzoic acid.

The similarity in frequency of absorption of the C bands of the corresponding *ortho*- and *meta*-substituted acids has received a quantum-mechanical explanation by Förster (*Z. Naturforsch.*, 1947, **2a**, 149) based on geometrical symmetry considerations. It is possible that a similar explanation would hold for the similarity of the B bands.

Both the bands that have been labelled B and C in this paper have usually been associated with benzenoid absorption. They have been assumed to arise by the displacement of the bands of benzene occurring near 2035 and 2540 A. that has been brought about by substitution of the benzene ring. Qualitatively, these bands have been accounted for on the assumption that light is absorbed along non-identical optical axes, perpendicular to each other (Lewis and Calvin, *Chem. Reviews*, 1939, **25**, 273; Jones, *ibid.*, 1948, **43**, 429; Cram and Cranz, *J. Amer. Chem. Soc.*, 1950, **72**, 595). This conception has received support from Coulson's LCAO calculations (*Proc. Physical Soc.*, 1948, **60**, 257). If this should be a satisfactory explanation for these bands, it is of considerable interest to ascertain why steric interference to resonance has a marked effect upon the B band but apparently none on the C band.

The A bands in these acids remain, through numerous changes of position and substituent group, reasonably constant in frequency of the maxima although varying rather considerably in intensity. Morton and Stubbs (*J.*, 1940, 1347) suggested that the bands observed by Castille and Klingstedt (*loc. cit.*) near 2060 A. in the monohydroxybenzoic acids are due to the selective absorption of the carboxyl group. It might appear that, since all the acids reported in this paper also show bands in this region, the suggestion has been strengthened. However, the intensity of the band that appears in the region in the spectra of numerous aliphatic acids is of the order of log ε 1·7—2·0 (Ley and Arends, *Z. physikal. Chem.*, 1932, **17**, *B*, 177), while the bands reported in this paper are of the order of log ε 4·0. The intensity of the A band is thus probably too high to be ascribed to the carboxyl group and should probably be ascribed to benzenoid absorption also. In this case the band would be the displacement of the band in benzene that occurs near 1870 A. The splitting of this band that is visible in the spectra of 2 : 6-dichlorobenzoic, 2 : 6-dibromobenzoic, and γ-resorcylic acid is to be ascribed to the absorption of light along perpendicular axes (Platt, *J. Chem. Physics*, 1949, **17**, 484).

In all probability the most consistent explanation of the observed spectra that can now be offered is that the bands are due to the displacement of those of benzene. No simple explanation can yet be advanced as to why the perturbations of the individual bands are so different. Only a quantum-mechanical theory going in detail into the effect of substituent groups on the general potential field of the molecule and electron interactions is likely to provide an analysis of the ultra-violet spectra which will hold for more than a few special cases. Such a study is now in progress.

Experimental.—The spectra were measured with the aid of a Beckman quartz spectrophotometer, Model DU, equipped with a hydrogen lamp obtained from Mr. A. G. Nestor, Lansdowne, Pennsylvania. The spectra were determined in 95% ethanol from 2200 A. towards the visible region. Although it has been reported by Harrison, Lord, and Loofbourow ("Practical Spectroscopy," New York, 1948, p. 418), that carefully purified 95% ethanol (Leighton, Cary, and Schipp, *J. Amer. Chem. Soc.*, 1931, **53**, 3017) yields a solvent sufficiently good for work to 2000 A., we were not able to purify 95% ethanol so that it was sufficiently transparent at shorter wave-lengths than 2150 A. to be suitable as a solvent (a complete description of the attempted purification will be published elsewhere). Therefore, a mixture of 99·5% of distilled water +0·5% of 95% ethanol (carefully purified) was used as the solvent in the region from 2000 A. to 2200 A. A comparison of our data in alcohol with those for the same compounds in water (Doub and Vandenbelt, *loc. cit.*) indicates that the spectra are essentially the same. In alcohol the peaks are usually shifted by 10—20 A. towards shorter wave-lengths and are slightly less intense.

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