255. *Absorption Spectra of Hydroxy-aldehydes, Hydroxy-ketones, and their Methyl Ethers.*

By R. A. Morton and A. L. Stubbs.

The ultra-violet absorption spectra of *o*-, *m*-, and *p*-hydroxy-aldehydes, hydroxy-ketones, and their methyl ethers are described and discussed. The spectra are dominated by absorption maxima which are benzenoid in origin but show considerable displacements. Selective absorption undergoes second-order modifications when hydrogen-bond formation and interaction between hydroxylic solutes and polar solvents occur.

The interpretation of ultra-violet absorption spectra for the larger polyatomic molecules in solution or in the state of vapour is not easy. This applies not only to such vibrational and rotational fine structure as is ascertainable within a broad electronic band, but also to unresolved selective absorption, the problem being to determine the site of the main electronic process concerned in the act of absorption. Perhaps the safest approach is still the study of groups of structurally related compounds, with a view to achieve a more convincing correlation between broad absorption bands and chromophoric groups. The most significant result is the recognition that quite large displacements of selective absorption may occur without affecting the basic electronic process. Such displacements imply that the "environment" of simple chromophores ($C{=}O$, $C{=}C$, or $-N{=}N-$) polarises valency electrons in such a way that electronic processes, which in the simpler molecules (*e.g.*, in $CH_3{\cdot}CO{\cdot}CH_3$) require large quanta, may come to require smaller quanta (*e.g.*, in $CH_3{\cdot}CO{\cdot}CH{:}CMe_2$). The term "environment" must include (*a*) intramolecular factors such as those arising from conjugation of double bonds, substitution in the benzene ring, and hydrogen-bond formation, (*b*) intermolecular forces such as association in all its aspects and solvent–solute interactions, including those involving changes in p_H value.

One of the major difficulties in dealing with solution spectra has been the doubt whether the wave-length of maximum absorption in broad electronic bands possesses any fundamental significance. In the absence of a more precise datum, however, it is best to assume provisionally that $\lambda_{max.}$ is an indication of the size of the quantum concerned in the electronic process *and* of the most probable vibrational change.

We now submit data for simple hydroxy-aldehydes and hydroxy-ketones and consider them from the point of view that widely different absorption spectra can be assembled in an orderly way if it be accepted (i) that a very limited number of essentially similar electronic processes occur, (ii) that changes in the "environment" of the simple chromophores result in discontinuous displacements of $\lambda_{max.}$ (and therefore discontinuous changes in the energy requirement for a given electronic process), and (iii) that these discontinuous displacements correspond in the main with simple "vibrational" quanta.

A convenient notation for specifying the presumed site of the electronic process corresponding with a given absorption band is as follows. If it is argued that an absorption band in benzaldehyde is characteristic of the benzoyl group, but the electron affected appears to be located in the carbonyl group, the chromophore may be written as $C_6H_5{-}\overset{*}{C}{=}O$, whereas, if it appears to be located in the benzene ring, the notation is $\overset{*}{C}_6H_5{-}C{=}O$. The asterisk indicates the site of the act of absorption and at the same time implies that the characteristic absorption of the simple chromophore has been influenced by the conjugation existing in the complex chromophore.

The Phenyl Chromophore.—Benzene itself, in hexane solution, shows a group of eight narrow bands between 2300 and 2700 A., the value of $\varepsilon_{max.}$ varying from about 60 to 300. The subdivision into narrow bands being neglected, the value of $\lambda_{max.}$ for the envelope may be taken as about 2550 A., with log $\varepsilon_{max.}$ 2·48. There is also a region of more intense selective absorption near 1900 A., with log $\varepsilon_{max.}$ about 4·0. The whole spectrum characteristic of benzene, free from the influence of substituents, differs from that exhibited by molecules containing three conjugated double bonds in a straight chain, in that the cyclic structure brings about a great diminution in $\varepsilon_{max.}$:

	$\lambda_{max.}$, A.	$\varepsilon_{max.}$		$\lambda_{max.}$, A.	$\varepsilon_{max.}$
$CH_3\cdot[CH{:}CH]_3\cdot CH_3$ ……	2600	*ca.* 8000	*cyclo*Hexadiene …………	2600	*ca.* 4550
Benzene …………………	2550	*ca.* 230			

This makes it clear that the act of absorption in benzene is associated with $(\cdot C{:}C\cdot)_{ar.}$, but it is convenient to consider the phenyl group as a distinct chromophore.

Substitution in the benzene ring tends, in all cases, to displace the position of $\lambda_{max.}$ towards longer wave-lengths, at the same time bringing about an increase in $\varepsilon_{max.}$, and in a large number of cases there is also diminished resolution of the band into subsidiary maxima.

Introduction of transparent groups by substitution. (i) *Monosubstitution.* (1) Alkyl groups and halogens have little effect on the position and intensity of the benzenoid absorption, as shown by the data for the following compounds in alcoholic solution:

	$\lambda_{max.}$, A.	log $\varepsilon_{max.}$		$\lambda_{max.}$, A.	log $\varepsilon_{max.}$
Benzene …………………	2543	2·48	Chlorobenzene …………	2640	2·51
Toluene …………………	2620	2·48			

The general effect is a slight displacement of $\lambda_{max.}$ towards longer wave-lengths and a small increase in intensity of absorption. (2) Certain other substituents which are, in themselves, transparent in this region exert a more marked effect:

	$\lambda_{max.}$, A.	log $\varepsilon_{max.}$		$\lambda_{max.}$, A.	log $\varepsilon_{max.}$
$C_6H_5\cdot CN$	2700	2·90	$C_6H_5\cdot OH$	2730	3·25
	2250	4·10		2150	4·00
$C_6H_5\cdot CO_2H$	2670	3·25	$C_6H_5\cdot OCH_3$	2720	3·35
	2270	4·15	$C_6H_5\cdot NH_2$	2845	3·24
				2340	4·06

The most noteworthy point is the displacement of the long-wave benzenoid band, with a 3- to 10-fold increase in the intensity of absorption. In addition, the short-wave benzenoid band has been displaced towards longer wave-lengths with apparently little change in intensity. There seems little doubt that both these bands must be considered as benzenoid in origin, *i.e.*, the chromophore is written as $\overset{*}{C}_6H_5$—X. This leads to the conclusion that certain substituents, not in themselves sites of selective absorption in this region of the spectrum, can appreciably modify absorptive processes located in the benzene ring.

(ii) *Disubstitution.* (1) Methyl groups and halogens.

	o-Compounds.		*m*-Compounds.		*p*-Compounds.	
	$\lambda_{max.}$, A.	log $\varepsilon_{max.}$	$\lambda_{max.}$, A.	log $\varepsilon_{max.}$	$\lambda_{max.}$, A.	log $\varepsilon_{max.}$
$C_6H_4Me_2$	2633	2·52	2652	2·49	2680	2·68
$C_6H_4Cl_2$	2696	2·56	2707	2·62	2720	2·59
$CH_3\cdot C_6H_4Cl$	2650	2·52	2670	2·52	2770	2·71

The effects of substitution are again small although wave-length displacements increase in the order *o*-, *m*-, *p*-.

(2) Substituents which produce considerable effects in mono-derivatives:

	o-Compounds.		*m*-Compounds.		*p*-Compounds.	
	$\lambda_{max.}$, A.	log $\varepsilon_{max.}$	$\lambda_{max.}$, A.	log $\varepsilon_{max.}$	$\lambda_{max.}$, A.	log $\varepsilon_{max.}$
$C_6H_4(OH)_2$	2780	3·42	2760	3·30	2940	3·49
$C_6H_4(CO_2H)_2$	2810	3·09	2880	3·05	2950	3·18
	2740	3·01	2800	3·11	2840	3·24
			2270	4·16	2380	4·15
$C_6H_4(NH_2)_2$	2927	3·58	2928	3·43	2905	3·51
	2366	3·88			2440	4·12

The second group has thus less effect than the first. In all cases the wave-length displacement is comparatively small, and is again greatest for the *p*-isomerides.

(3) Substituents different, and when taken separately exerting considerable effects.

	o-Compounds.		*m*-Compounds.		*p*-Compounds.	
	$\lambda_{max.}$, A.	log $\varepsilon_{max.}$.	$\lambda_{max.}$, A.	log $\varepsilon_{max.}$.	$\lambda_{max.}$, A.	log $\varepsilon_{max.}$.
$C_6H_4(OH)\cdot CO_2H$	3055	3·68	2990	3·48	2547	4·20
	2360	3·95	2330	3·96		
$C_6H_4(NH_2)\cdot CO_2H$	3375	3·67	3205	3·63	2890	4·30
	2470	3·83	~2450	3·80	2180	3·90
	2180	4·40	2200	4·30		
$C_6H_4(NH_2)\cdot OH$	2860	3·60	2860	3·52	3015	3·43
	2330	3·86			2340	3·90

~ denotes an inflexion in the absorption curve.

The spectra of the hydroxyanilines are very similar to those of the corresponding phenylenediamines. For the hydroxy- and amino-benzoic acids, the absorption curves are in sharp contrast to those already discussed. In the first place, the displacement of the long-wave band is greatest for the *o*-compounds, and the increase in intensity of absorption is considerable. The *p*-derivatives show only one band and that is of very high intensity. The explanation of this " para-effect " appears to be a large displacement of the short-wave benzenoid band associated with a comparatively small displacement of the long-wave band. This brings about superposition of the two bands, so that an apparently single band of high intensity is recorded. This means that in contrast with (1) and (2), the displacement of the long-wave benzenoid band increases in the order *p*-, *m*-, *o*-, and that of the short-wave band in the reverse order. This tendency has already been noted with regard to the phenylenediamines. *p*-Hydroxybenzoic acid behaves similarly, and its spectrum in hexane + 10% ether shows the displacement of the short-wave band, without complete masking of the long-wave band (Castille and Klingstedt, *Compt. rend.*, 1923, **176**, 749).

$\lambda_{max.}$, A.	log $\varepsilon_{max.}$.	$\lambda_{max.}$, A.	log $\varepsilon_{max.}$.	$\lambda_{max.}$, A.	log $\varepsilon_{max.}$.	$\lambda_{max.}$, A.	log $\varepsilon_{max.}$.
2840	3·18	2780	3·40	2750	3·54	2525	4·18

This " para-effect " is referred to later, in connection with *p*-hydroxy- and -methoxy-aldehydes.

All three hydroxybenzoic acids also show, in hexane + 10% ether (*loc. cit.*), a band in the far ultra-violet :

	o-Compound.		*m*-Compound.		*p*-Compound.	
	$\lambda_{max.}$, A.	log $\varepsilon_{max.}$.	$\lambda_{max.}$, A.	log $\varepsilon_{max.}$.	$\lambda_{max.}$, A.	log $\varepsilon_{max.}$.
$C_6H_4(OH)\cdot CO_2H$	2060	4·32	2070	4·33	~2100	4·06

These bands appear to correspond to those observed in the far ultra-violet for the three aminobenzoic acids, and it may be suggested that they represent the selective absorption of the carboxyl group. Simple fatty acids show strong absorption in this region, and it seems possible that, although the carboxyl group has no selective absorption near 2700 A., it does possess the very short-wave band characteristic of the carbonyl group.

Phenyl and Carbonyl Chromophores combined.—When the phenyl and the carbonyl chromophore occur in the same molecule, as in benzaldehyde or acetophenone, the effects of the two groups are superimposed, but each absorption is modified by the proximity of the other group. The spectra of acetophenone and benzaldehyde are almost identical, and for the purpose of correlating absorption spectra and chromophoric groups may be taken as :

$\lambda_{max.}$, A.	3200	2780	2400	1990
log $\varepsilon_{max.}$	1·7	3·02	4·12	4·3

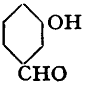
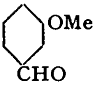
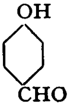
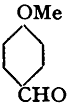
It seems evident from its intensity that the 3200 A. band is due to the carbonyl chromophore, influenced by the phenyl group (compare the conjugation of the carbonyl group with the ethylenic double bond in mesityl oxide, where the carbonyl band appears at 3270 A. with log $\varepsilon = 1\cdot 6$). By means of comparisons with phenol, benzoic acid, aniline, etc., it also appears highly probable that the 2780 A. band is benzenoid in origin, *i.e.*, the chromophore is $\overset{*}{C}_6H_5\text{—}C{<}^{O}_{R}$, and from similar comparisons it is suggested that the

2400 A. band is the short-wave benzenoid band, observed at 2150 A. with log ε 4·0 in phenol, 2270 A., log ε 4·15 in benzoic acid, and 2340 A., log ε 4·06 in aniline, whilst the 1990 A. band corresponds to the short-wave carbonyl absorption, observed near 1900 A., log ε 4·0 in acetone, near 2100 A., log ε 4·3 in the hydroxybenzoic acids, and near 2200 A., log ε 4·3 in the aminobenzoic acids. The carbonyl group, therefore, is similar in its effect on the benzenoid chromophore to $-OH$, $-CO_2H$, $-NH_2$, etc., and in addition the characteristic selective absorption of the carbonyl chromophore itself is superimposed.

Hydroxy- and Methoxy-aldehydes and -ketones (Table I and Figs. 1—11).—These results are discussed in the following steps: (1) The identification of the sites of processes giving rise to the various absorption bands, using only the data obtained from the study of alcoholic solutions. (2) A discussion of the effects of possible hydrogen-bond formation on the ultra-violet absorption spectra, together with effects brought about by changing the type of solvent used.

TABLE I.

Maximum Values of λ (*in* A.) *and* log ε.

Substance.	Fig.	Hexane.		Alcohol.		Water.		1 Equiv. NaOH.		Excess NaOH.		Vapour.
		λ.	log ε.	λ.	log ε.	λ.	log ε.	λ.	log ε.	λ.	log ε.	λ.
	1, 2	~3430	3·28	—	—	—	—	3790	3·70	3780	3·74	3200
		3285	3·51	3250	3·48	3250	3·43	~3270	3·10	—	—	—
		2550	4·00	2550	4·00	2550	4·00	2610	3·85	2650	3·81	2515
	3	3100	3·75	3195	3·63	—	—	—	—	—	—	2990
		2465	4·08	2530	4·07	—	—	—	—	—	—	2385
	4, 5	3290	3·63	3270	3·50	3245	3·52	3410	3·50	3590	3·71	3210
		2555	4·02	2515	3·97	2525	4·01	2540	3·88	2565	3·755	2500
		2495	4·025	—	—	—	—	—	—	—	—	2430
	6	~3300	2·00	—	—	—	—	—	—	—	—	—
		3000	3·58	3050	3·58	—	—	—	—	—	—	2885
		2425	3·90	2460	4·06	—	—	—	—	—	—	—
	7, 8	~3330	2·78	—	—	—	—	~3520	3·15	3590	3·47	2320
		3080	3·69	3160	3·46	3150	3·42	3210	3·27	~3120	2·78	2960
		~2820	3·17	~2930	3·04	—	—	~2570	3·90	~2640	3·81	—
		2470	4·20	2540	3·93	2530	4·00	2390	4·13	2370	4·37	2390
	9	3090	3·46	3145	3·45	—	—	—	—	—	—	2965
		2490	3·93	2525	3·92	—	—	—	—	—	—	2400
	10	—	—	~3320	2·25	~3330	2·78	3290	4·36	3300	4·42	—
		—	—	2840	4·24	2840	4·24	~2880	3·75	~2750	3·35	~2980
		—	—	2210	4·14	2200	4·06	2400	3·81	2390	3·93	—
		—	—	—	—	—	—	—	—	—	—	2520
	11	2655 (f.s.)	4·29	2770	4·17	—	—	—	—	—	—	—
		3000—3500 (f.s.)	2·0—1·6	2190	4·07	—	—	—	—	—	—	—
	—	—	—	2760	4·13	—	—	3250	4·18	3250	4·39	—
		—	—	2205	4·03	—	—	~2780	3·79	—	—	—
		—	—	—	—	—	—	2360	3·70	2350	3·81	—
		—	—	—	—	—	—	2250	3·71	—	—	—

~ Denotes an inflection. f.s. Denotes fine structure.

(1) By the comparison

	$\lambda_{max.}$, A.	log $\varepsilon_{max.}$.	$\lambda_{max.}$, A.	log $\varepsilon_{max.}$.	$\lambda_{max.}$, A.	log $\varepsilon_{max.}$.
Benzaldehyde	3250	1·25	2790	3·25	2430	4·2
Salicylaldehyde	3250	3·48	2550	4·0	—	—

it would seem at first sight that the 3250 A. band of salicylaldehyde is due to a transition localised in the carbonyl group, since it agrees in position with the low-intensity carbonyl band of benzaldehyde. This view is, however, untenable in the light of the following data :

FIG. 1.

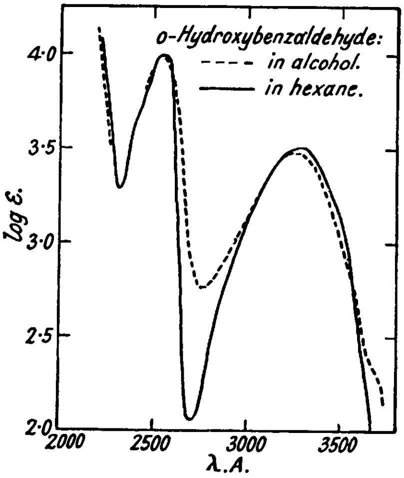


FIG. 2.

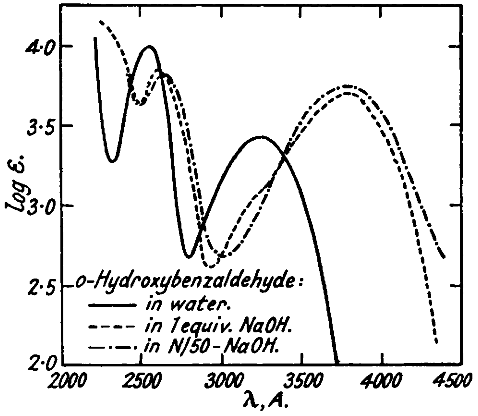


FIG. 3.

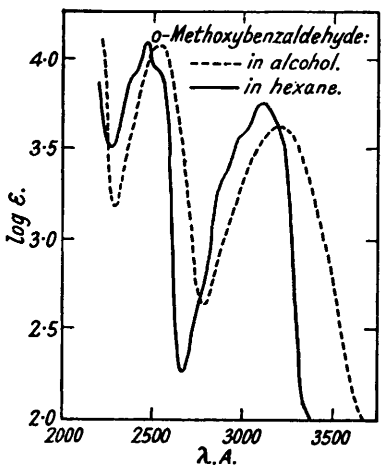
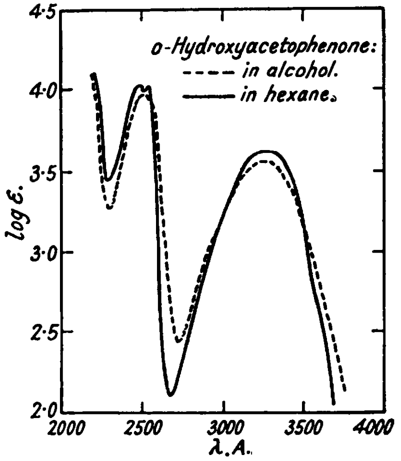


FIG. 4.



C_6H_4 a	OMe	OH	OMe	OH	NH_2
	(*o*-)	(*m*-)	(*m*-)	(*o*-)	(*o*-)
b	CHO	CHO	CHO	CO_2H	CO_2H
$\lambda_{max.}$, A.	3195	3160	3145	3055	3375
log $\varepsilon_{max.}$	3·63	3·46	3·45	3·68	3·67

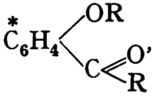
All these compounds show a band similar as regards both intensity and location to the 3250 A. band of salicylaldehyde. The first three compounds, *i.e.*, *o*-methoxybenzaldehyde, *m*-hydroxybenzaldehyde, and *m*-methoxybenzaldehyde, cannot undergo chelation, whereas *o*-hydroxybenzoic acid and *o*-aminobenzoic acid have no true carbonyl band in this region. It must therefore be concluded that the benzene ring is the site of this absorption band and that it corresponds in fact to the 2790 A. band of benzaldehyde displaced towards longer wave-lengths by the introduction of the hydroxyl group, the intensity being only slightly increased. This displacement is analogous to that produced by the introduction of a hydroxyl group into benzene itself, a process which results in a displacement of $\lambda_{max.}$ from 2600 to 2730 A., although in this case there is a big increase in intensity. It is similarly to be concluded that all the maxima observed in the region from 3050 to 3270 A. for *o*- and *m*-hydroxybenzaldehyde and *o*-hydroxyacetophenone and their methyl ethers are due primarily to the phenyl chromophore and may be represented as  $\overset{*}{C_6H_4}\langle^{OR}_{C\langle^{O}_{R}}$, any absorption due to the carbonyl group being completely masked. The second maximum near 2550 A. is strikingly constant in position, and only slightly less so in respect of intensity, for all the *o*- and *m*-derivatives. From its position and intensity, it is almost certainly the 2400 A. band of benzaldehyde moved towards longer wave-lengths by the introduction of the hydroxyl or methoxyl group. As has been suggested in discussing the spectrum of benzaldehyde, this band is also due to the benzene nucleus. The maximum recorded at 1990 A. for benzaldehyde, and here ascribed to the carbonyl group, has not been observed

Fig. 5.

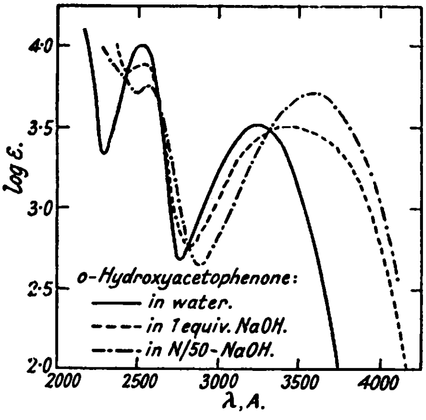


Fig. 6.

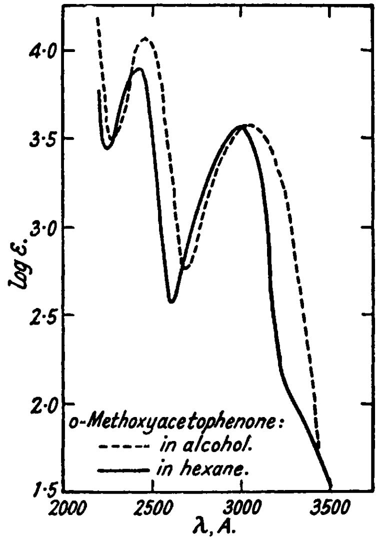


Fig. 7.

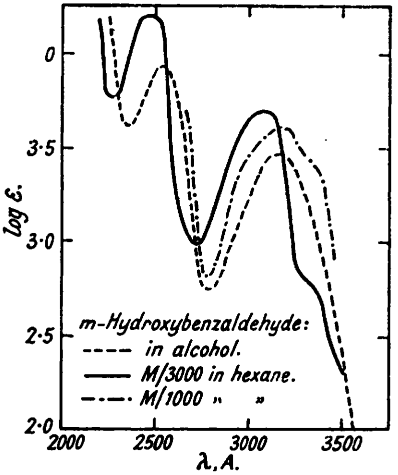
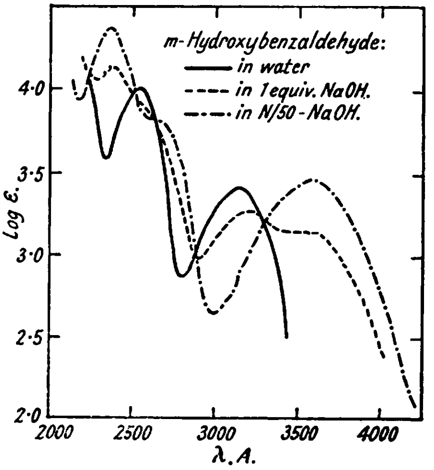


Fig. 8.



for these *o*- and *m*-derivatives, although the curves show a steeply rising intensity near this region.

It is obvious that the spectra of all the *o*- and *m*-compounds studied can be interpreted in general terms on the same basis, without reference to any possible hydrogen-bond formation, and furthermore, these spectra reflect, in the main, the influence of substituents on the benzenoid absorption. The *p*-derivatives all show the band of high intensity which has already been discussed for *p*-amino- and *p*-hydroxy-benzoic acids. As before, this single band is probably analogous to the 2790 A. band of benzaldehyde which is little affected by the introduction of *p*-hydroxyl, whilst the short-wave benzenoid band undergoes a large displacement towards longer waves, the result being a single summation band of high intensity. The band of high intensity observed near 2200 A. for the *p*-derivatives

FIG. 9.

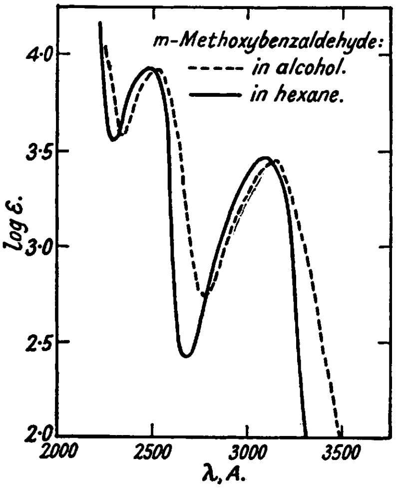


FIG. 10.

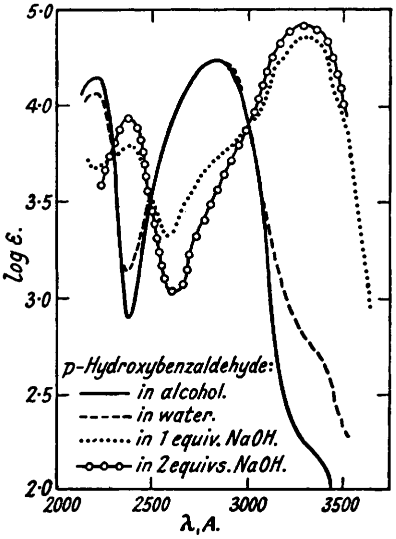
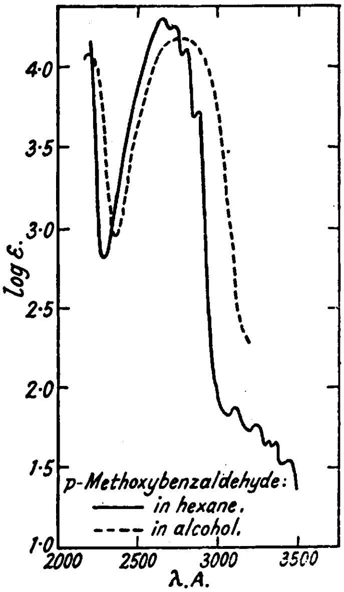
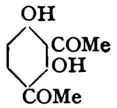


FIG. 11.

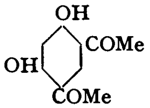


apparently corresponds to the 1990 A. band of benzaldehyde and acetophenone, and is ascribed to the carbonyl chromophore. The low-intensity carbonyl band is observed near 3300 A. for *p*-hydroxybenzaldehyde, and also for *p*-methoxybenzaldehyde in hexane, in which case the band is split into sub-maxima. Thus, as for the *o*- and *m*-derivatives, the *p*-derivatives reflect, in the main, the influence of substituents on the benzenoid absorption, but in contrast with the former, the principal effect is on the short-wave benzenoid band. Also, the carbonyl absorption is no longer masked, and both the long- and the short-wave carbonyl bands are observed.

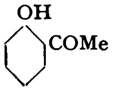
The spectra of the diacetylresorcinols,† (I) and (II), are of interest in this connection :



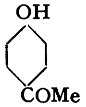
(I.)



(II.)



(III.)



(IV.)

	$\lambda_{max.}$, A.	log $\varepsilon_{max.}$	$\lambda_{max.}$, A.	log $\varepsilon_{max.}$	$\lambda_{max.}$, A.	log $\varepsilon_{max.}$	$\lambda_{max.}$, A.	log $\varepsilon_{max.}$
(*a*)	3375	3·81	3230	3·79	3270	3·55	—	—
(*b*) Persistence poor	2665	4·21	2800	4·07	—	—	2760	4·13
(*c*)	2465	4·35	2530	4·66	2515	3·97	2205	4·03
		Dimethyl ethers.				Methyl ethers.		
	2900	3·66	3100	3·78	3050	3·58	—	—
	2660	4·09 *	2750	4·21 *	—	—	2770	4·17
	2280	4·08	2460	4·48	2460	4·06	2190	4·07

* Definition improved as compared with (I) and (II).

(I) and (II) may both be considered as *o*-hydroxy- and *p*-hydroxy-acetophenone derivatives, and it is apparent in (II) and its dimethyl ether that the spectrum corresponds qualitatively to a summation of the curves of the *o*- and the *p*-compound (III) and (IV). The wave-lengths of the maxima are apparently little disturbed, but the ε values suggest that the additivity is not simple, for the maxima near 3250, 3070, and 2500 A. are considerably more intense. From the improvement in definition which occurs in the band showing a maximum at 2750 A. following methylation, the *p*-orientation becomes more significant as the possibility of chelation disappears. It is not easy to interpret the data for (I) in a completely convincing way, but the following approach is not unreasonable. Simple additivity for the *o*-hydroxyacetyl arrangement involves :

$\lambda_{max.}$, A.	log $\varepsilon_{max.}$	$\lambda_{max.}$, A.	log $\varepsilon_{max.}$
3270	$3·55 + 0·301 = 3·85$	2515	$3·97 + 0·301 = 4·27$

so that the intensities of the (*a*) and the (*c*) bands are more or less as might be expected. The displacements to 3375 and 2465 A. are both of the order of a vibrational quantum and do not weaken the ascription of (*a*) and (*c*) to the *o*-orientation. The maximum at 2665 A. is not very persistent and is probably due to a partly suppressed effect due to *p*-orientation. The striking difference between (I) and its dimethyl ether shows how methylation has enhanced the importance of *p*-orientation and diminished the part played by *o*-orientation. It is noteworthy that the (*b*) band is less affected by methylation than the (*a*) and (*c*) bands.

Solvent Effects, and the Consequences of Hydrogen-bond Formation on Ultra-violet Absorption Spectra.—It has been noted for aliphatic compounds (Morton and Rosney, J., 1926, 706) that chelation through hydrogen coincides with an approximately 100-fold increase in the intensity of the carbonyl absorption band without change in $\lambda_{max.}$. This cannot be extended to the *o*-hydroxy-aldehydes and -ketones, but the systems are different in the sense that enolisation involves the introduction of a new double bond. In determining the consequences of chelation on ultra-violet absorption spectra, comparisons should

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† These absorption spectra were determined by Dr. W. T. Earlam, on specimens kindly supplied by Dr. Wilson Baker.

be made in hexane solution, where there is a minimum possibility of solvent–solute interaction :

Solvent : hexane.	$\lambda_{\text{max.}}$, A.	log $\varepsilon_{\text{max.}}$.	$\lambda_{\text{max.}}$, A.	log $\varepsilon_{\text{max.}}$.
o-Hydroxybenzaldehyde	3285	3·51	2550	4·0
o-Methoxy ,,	3100	3·75	2465	4·08
o-Hydroxyacetophenone	3290	3·63	2555	4·02
			2495	4·025
o-Methoxy ,,	3000	3·58	2425	3·9
m-Hydroxybenzaldehyde (M/3000)	3080	3·69	2490	3·93
,, ,, (M/1000)	3180	3·62	—	—
m-Methoxy ,,	3090	3·46	2490	3·93

The spectrum of *m*-hydroxybenzaldehyde (M/3000) in hexane is almost identical with that of its methyl ether : this is in agreement with the normal effect of methylation. On the other hand, salicylaldehyde and *o*-hydroxyacetophenone differ appreciably from their methyl ethers. For both bands (long- and short-wave), the hydroxy-compounds show $\lambda_{\text{max.}}$ appreciably nearer the long-wave end of the spectrum. *m*-Hydroxybenzaldehyde does not obey Beer's law. Unfortunately its solubility in hexane is not much more than M/1000; nevertheless, on passing from a concentration of M/3000 to one of M/1000, $\lambda_{\text{max.}}$ is displaced towards longer waves. The only explanation of this departure from Beer's law seems to be increased association of this compound in the more concentrated solution. This is considered to take place by a process analogous to chelation through hydrogen (Fox and Martin, *Proc. Roy. Soc.*, 1937, *A*, **162**, 419), and it is therefore suggested that both processes give rise to a displacement of the benzenoid absorption towards longer waves. Since methylation in itself is known to have little effect on the spectra, the effect of chelation may be taken as a displacement from $\lambda_{\text{max.}}$ 3100 A. for *o*-methoxybenzaldehyde in hexane to $\lambda_{\text{max.}}$ 3285 A. for *o*-hydroxybenzaldehyde in hexane. This corresponds with $\Delta(1/\lambda)$ 1820 cm.$^{-1}$, whilst the displacement due to association, *viz.*, 3080 to 3180 A., is only 1020 cm.$^{-1}$. It must be emphasised that these displacements are not (as is the case with displacements due to hydroxyl in the infra-red region) measures of the energies of the bonds, but rather they represent a variation in the induction effects of the groups concerned upon the intrinsic benzenoid absorption.

One of the primary differences between chelated and unchelated compounds is that the latter contain a free hydroxyl group. On the basis of the foregoing discussion, therefore, unchelated compounds should show larger variations of $\lambda_{\text{max.}}$ on passing from a non-polar to a polar solvent (hexane to alcohol) whenever the possibility exists of intermolecular hydrogen-bond formation :

Data for the long-wave band.

Chelated compounds.	$\Delta(1/\lambda)$, cm.$^{-1}$.	Chelated compounds.	$\Delta(1/\lambda)$, cm.$^{-1}$.
o-Hydroxybenzaldehyde	−330	*o*-Hydroxyacetophenone	−180
Unchelated compounds.		Unchelated compounds.	
o-Methoxybenzaldehyde	960	*m*-Hydroxybenzaldehyde	820
o-Methoxyacetophenone	543	*m*-Methoxybenzaldehyde	460

It will be seen that the displacements for unchelated compounds are appreciably greater and in the direction of *longer* wave-lengths. It must therefore be presumed that all three possibilities, *viz.*, (1) chelation through hydrogen, (2) association, and (3) intermolecular hydrogen-bond formation, result in displacements of the benzenoid absorption towards longer waves, the value of $\Delta(1/\lambda)$ varying for different compounds, apparently in accordance with the strength of the bond.

Vapour Spectra.—The only compound in this series to show highly resolved vapour absorption is salicylaldehyde. At room temperature the vapour pressure is sufficiently high for a 5-cm. layer to show the characteristic absorption. Two spectrographs have been used in this work : a Littrow model (Hilger E1) in conjunction with a cadmium spark, which possesses a good continuous background, and a medium instrument (Hilger E3) in conjunction with a high-tension (Tesla) spark running under water between tungsten electrodes; 27 bands, each about 3 A. wide without rotational fine structure, were measured

TABLE II.

Vapour Absorption : Salicylaldehyde.

λ, A.	ν, obs., cm.$^{-1}$.	ν, calc., cm.$^{-1}$.	Series.	p.	q.
2548·21	39243·2	—	—	—	—
2544·95	39293·5	—	—	—	—
2541·34	39349·3	—	—	—	—
2534·96	39448·4	39442·1	I	0	−3
2531·67	39499·6	39499·7	I	0	−2
2527·98	39557·3	39557·3	I	0	−1
2524·30	39614·9	39614·9	I	0	0
2516·05	39744·8	39742·3	I	+1	−2
2512·41	39802·4	39799·9	I	+1	−1
2508·94	39857·5	39857·3	I	+1	0
2502·29	39963·4	—	—	—	—
2500·36	39994·2	39984·9	I	+2	−2
2493·81	40099·3	40100·1	I	+2	0
2482·23	40286·4	40285·1	I	+3	−1
2480·73	40310·7	40312·5	II	0	−1
2479·17	40336·1	40342·7	I	+3	0
2477·08	40370·1	40370·1	II	0	0
2466·29	40546·7	40555·1	II	+1	−1
2463·84	40587·0	40585·3	I	+4	0
2454·18	40746·8	40740·1	II	+2	−2
2452·79	40769·9	40770·3	I	+5	−1
2450·80	40803·3	40797·7	II	+2	−1
2438·06	41016·2	41012·9	I	+6	−1
2432·81	41104·7	41097·9	II	+3	0
2414·39	41418·3	—	—	—	—
2412·71	41447·2	41440·5	I	+8	−2
2410·03	41493·3	41498·1	I	+8	−1

in the region 2400—2550 A. (see Table II). The bands are well accounted for by the expressions :

$$1/\lambda,\ \text{cm.}^{-1} = 39614{\cdot}9 + 242{\cdot}6p + 57{\cdot}6q \text{ (Series I) ; } p \text{ 0 to 8; } q \text{ 0 to } -5.$$
$$1/\lambda,\ \text{cm.}^{-1} = 40370{\cdot}1 + 242{\cdot}6p + 57{\cdot}6q \text{ (Series II) ; } p \text{ 0 to 3; } q \text{ 0 to } -2.$$

The frequency difference between the two series is 40370·1 − 39614·9 = 755·2 cm.$^{-1}$.

With the smaller spectrograph the following additional bands were detected, but were not quite so accurately measurable :

λ, A.	1/λ, cm.$^{-1}$ (obs.).	1/λ, cm.$^{-1}$ (calc.).	Series.	p.	q.
2497·09	40046·6	40042·5	I	2	−1
2463·15	40598·4	40612·7	II	1	0
2441·22	40963·1	40955·3	I	6	−2
2434·75	41072·0	41070·5	I	6	0
2428·21	41199·6	41197·9	I	7	−2
2423·41	41264·2	41255·5	I	7	−1

The constant frequency differences cannot be accounted for with certainty, but the following points are suggestive. The commonest Δ(1/λ) value in benzene and its derivatives is about 900—950 cm.$^{-1}$, those for, *e.g.*, benzene, phenol, and benzaldehyde being 922, 938, and 953 cm.$^{-1}$, respectively. There is no evidence of such a constant frequency difference in salicylaldehyde vapour absorption, and the principal Raman frequencies are 768 and 1029 cm.$^{-1}$. The vapour spectrum of *o*-cresol (Savard, *Ann. Chim.*, 1929, **11**, 287) exhibits vibrational fine structure associated with the long-wave ultra-violet benzenoid absorption :

$$1/\lambda,\ \text{cm.}^{-1} = \begin{matrix}(a)\ 36248\\ (b)\ 36412\end{matrix} + 704(p' - p_0) - 69p_0 + 245(q' - q_0) - 48q_0.$$

	(*a*).	(*b*).
$p' - p_0$	0 to 2	0 to 2
p_0	−1 to 3	−1 to 5
$q' - q_0$	−2 to 4	−2 to 2
q_0	−1 to 1	0 and 1

The wave-number differences 704, 245, and 69 cm.$^{-1}$ are fairly close to the 755, 242·6, and 57·6 cm.$^{-1}$ differences of salicylaldehyde, but there is not sufficient evidence to indicate how the energy absorbed by the (benzenoid) electronic transition sets up these vibrational frequencies. The only other compound in this series which exhibits fine structure within the absorption band near 2500 A. is *o*-hydroxyacetophenone, but the narrow bands are ill-developed and only four were capable of reasonably accurate measurement :

λ, A.	1/λ, cm.$^{-1}$.	Δ(1/λ), cm.$^{-1}$.
2503	39,950	
2495	40,070	120
2459	40,670	600
2452	40,790	120

o-Methoxyacetophenone shows only continuous absorption in the vapour state. On the other hand, *o*-methoxybenzaldehyde shows five fairly wide (10 A.) continuous bands near 3000 A.:

λ, A.	$1/\lambda$, cm.$^{-1}$.	$\Delta(1/\lambda)$, cm.$^{-1}$.
3117	32,080	
		470
3072	32,550	
		330
3041	32,880	
		460
2999	33,340	
		420
2962	33,760	

The vapour absorption of *m*-compounds is characterised by a number of moderately well-defined bands between 2430 and 2520 A.

m-Hydroxybenzaldehyde.

λ, A.	$1/\lambda$, cm.$^{-1}$.	$\Delta(1/\lambda)$, cm.$^{-1}$.
2495	40,080	
		80
2490	40,160	
		140
2481	40,300	
		110
2475	40,410	
		90
2469	40,500	
		130
2461	40,630	
		170
2451	40,800	
		180
2440	40,980	
		190
2429	41,170	

m-Methoxybenzaldehyde.

λ, A.	$1/\lambda$, cm.$^{-1}$.	$\Delta(1/\lambda)$, cm.$^{-1}$.
2530	39,530	
		100
2523	39,630	
		160
2513	39,790	
		150
2504	39,940	
		140
2495	40,080	
		110
2487	40,190	
		170
2478	40,360	
		160
2468	40,520	
		150
2459	40,670	

The *p*-derivatives show narrow bands on the long-wave side of the main absorption:

p-Hydroxybenzaldehyde.

λ, A.	$1/\lambda$, cm.$^{-1}$.	$\Delta(1/\lambda)$, cm.$^{-1}$.
2852	35,070	
		40
2848	35,110	
		90
2841	35,200	
		30
2839	35,230	
		570
2793	35,800	
		90
2786	35,890	
		140
2775	36,030	
		210
2759	36,240	
		220
2743	36,460	
		110
2735	36,570	
		80
2728	36,650	

p-Methoxybenzaldehyde.

λ, A.	$1/\lambda$, cm.$^{-1}$.	$\Delta(1/\lambda)$, cm.$^{-1}$.
2858	34,990	
		220
2840	35,210	
		60
2836	35,270	
		700
2780	35,970	
		80
2774	36,050	
		110
2765	36,160	
		360
2738	36,520	
		160
2726	36,680	
		100
2719	36,789	

The degree of resolution yet effected is inadequate for any attempt at analysis, but the use of lower temperatures and longer absorption cells may provide the necessary data.

Absorption Spectra in Alkaline Solution.—All the hydroxy-compounds, when studied in alkaline solution, show displacements of the long-wave band in the direction of longer wave-lengths. This is qualitatively in agreement with the effect of alkali on the spectrum of phenol. However, the magnitudes of the various displacements show little agreement:

Substituent.	Change of medium.	$\Delta(1/\lambda)$, cm.$^{-1}$.
OH	H_2O to NaOH	2000
OH,CHO (*o*-)	H_2O to 1 equiv. NaOH	4380
	H_2O to excess NaOH	4310
OH,CO·CH$_3$ (*o*-)	H_2O to 1 equiv. NaOH	1480
	H_2O to excess NaOH	2950
OH,CHO (*m*-)	H_2O to 1 equiv. NaOH	600
	or	3340 (see Fig. 8)
	H_2O to excess NaOH	3890
OH,CHO (*p*-)	H_2O to 1 equiv. NaOH	4710
	H_2O to excess NaOH	4810

It has already been pointed out that the spectra of salicylaldehyde and *o*-hydroxyacetophenone are remarkably similar in hexane, alcohol, and water, as well as in the vapour state. On passing to alkaline solution, however, there are very noticeable differences, shown most obviously in the case of the long-wave band. In the presence of 1 equiv. of sodium hydroxide, salicylaldehyde shows the full displacement which is observed in the presence of excess alkali, but for *o*-hydroxyacetophenone, the displacement brought about by 1 equiv. is appreciably less than that effected by excess of alkali. Even in the presence of excess alkali, the displacement observed for the long-wave absorption band of *o*-hydroxyacetophenone is much less than the corresponding displacement for salicylaldehyde.

In the case of *m*-hydroxybenzaldehyde, the differences between the spectra shown by solutions containing 1 equiv. and excess of sodium hydroxide respectively are distinct from those cited above. The long-wave band appears to be displaced by approximately the same amount in both alkaline solutions, but from the intensities of absorption in the solution containing 1 equiv. of alkali only about half the molecules seem to be absorbing at the new wave-length of 3590 A., whilst the remainder are absorbing at the original wave-length. With regard to the short-wave absorption, it is difficult to say whether in excess of alkali a new band has appeared at 2370 A., or the original maximum near 2550 A. has been moved towards shorter wave-lengths. Since there is an inflexion near 2640 A. in excess alkali (cf. $\lambda_{max.}$ 2650 A. for salicylaldehyde), the former alternative seems the more probable. For *p*-hydroxybenzaldehyde, the absorption curves for the two alkaline solutions are almost identical, except that, as in the case of the meta-compound, the change is not quite complete in the presence of 1 equiv.

Three points worth further enquiry are: (*a*) the difference between salicylaldehyde and *o*-hydroxyacetophenone in alkaline solution; (*b*) the change in $\lambda_{max.}$ shown by *o*-hydroxyacetophenone in passing from 1 equiv. to excess of alkali; (*c*) the very close agreement between $\lambda_{max.}$ for *o*-hydroxyacetophenone and *m*-hydroxybenzaldehyde in the presence of excess alkali.

The observed difference between the positions of maximum absorption for salicylaldehyde and *o*-hydroxyacetophenone in 1 equiv. and in excess of alkali is 1470 cm.$^{-1}$, whereas the difference between the maxima of *p*- and *o*-hydroxyacetophenone (both in excess alkali) is 2910 cm.$^{-1}$, *i.e.*, 2×1455 cm.$^{-1}$. It would appear, therefore, that the values of $\lambda_{max.}$ observed for these compounds in alkaline solution are related by a constant frequency difference of approximately 1450 cm.$^{-1}$.

Benzene derivative.	Medium.	$\lambda_{max.}$, A.	$1/\lambda$, cm.$^{-1}$.
OH,CO·CH$_3$ (*p*-)	Excess alkali	3250	
OH,CO·CH$_3$ (*o*-)	1 Equiv. alkali	3410	1440
OH,CHO (*m*-) and	Excess alkali	3590	1470
OH,CO·CH$_3$ (*o*-)			1400
OH,CHO (*o*-)	Excess alkali	3780	

A further point is that for the short-wave band, the difference between the maxima of salicylaldehyde (2650 A.) and *o*-hydroxyacetophenone in excess of sodium hydroxide (2565 A.) is 1360 cm.$^{-1}$, which is within the experimental error of the constant differences already recorded.

Unless these constant frequency differences are fortuitous, they supply a partial answer to the questions raised earlier and suggest a discrete series of values of $\lambda_{max.}$ for the benzenoid chromophore under the influence of substituents. A significant frequency difference of about 1450 cm.$^{-1}$ should not be restricted to alkaline solutions, and the suggestions may be tested by extending it to the data for other media:

Derivative.	Medium.	$\lambda_{max.}$, A. (obs.).	$1/\lambda_{max.}$, cm.$^{-1}$ (calc.).		$\lambda_{max.}$, A. (calc.).
OH,CHO (*o*-)	Excess alkali	3785	26,420		3785
			add 1,450		
OH,CO·CH$_3$ (*o*-)	,, ,,	3590	27,870	=	3588
OH,CHO (*m*-)	,, ,,		add 1,450		
OH,CO·CH$_3$ (*o*-)	1 Equiv. alkali	3410	29,320	=	3411
OH,CHO (*o*-)	Hexane	3430			
OH,CHO (*o*-)	EtOH or H$_2$O	3250	add 1,450		
OH,CO·CH$_3$ (*p*-)	Excess alkali	3250	30,770	=	3250
OH,CO·CH$_3$ (*o*-)	Alcohol	3270			
OH,CO·CH$_3$ (*o*-)	Water	3245	add 1,450		
OMe,CHO (*o*-)	Hexane	3100	32,220	=	3104
OH,CHO (*m*-)	,,	3080			
OMe,CHO (*m*-)	,,	3090			

Consecutive additions of 1450 cm.$^{-1}$ give values of $\lambda_{max.}$ including 2847 A. (cf. benzaldehyde in hexane, 2830 A.), 2735 A. (cf. phenol in alcohol 2728 A.) and 2534 A. (cf. most intense narrow band of benzene itself in alcohol, 2543 A.). The following main values of $\lambda_{max.}$ (in A.) could therefore be predicted for the long-wave benzenoid band by using $\Delta(1/\lambda) = 1450$ cm.$^{-1}$: 3785, 3588, 3411, 3250, 3104, 2970, 2847, 2735, 2631, 2534.

Further (calculated) values of $\lambda_{max.}$ can be obtained, agreeing well with practically all the remaining observed values, by adding or subtracting 910 cm.$^{-1}$. This quantity is the mean value of the frequency differences between the narrow bands of benzene itself in alcoholic solution, and is therefore apparently connected with a vibrational frequency within the benzene nucleus.

Such a method of predicting values of $\lambda_{max.}$ can obviously be carried to a point where it becomes too flexible to be serviceable. For this reason it is undesirable to push the argument too far, but it is impossible to evade the fact that very nearly the same values of $\lambda_{max.}$ recur again and again for a variety of substituted benzene derivatives. The possibility that such values form a discrete series must therefore be studied, but cannot be easily settled. The data submitted show regularities which are scarcely fortuitous.

The existence of such a discrete series of values for $\lambda_{max.}$ would raise many points of theoretical interest and the implications of the hypothesis may be pointed out: (1) The actual position of maximum absorption (within the envelope of vibrational and rotational sub-maxima) is given significance. (2) The effect of substituents on the benzenoid absorption is, in general, to displace the spectrum as a whole in the direction of longer wavelengths. If this is taken to imply a changed initial energy state, *in the sense that a smaller quantum of energy can now effect essentially the same electronic transition*, the induction effect of substituents must be such as to bring this about. (3) The existence of a discrete series of $\lambda_{max.}$ values corresponding with a common electronic transition would seem to imply that the induction effect consists in the stabilisation of valency electrons, at energy levels differing by integral steps fixed by natural vibrational frequencies.

EXPERIMENTAL.

Preparation of Compounds.—Salicylaldehyde was purified through the bisulphite compound and redistilled in an atmosphere of nitrogen (b. p. 196°). Methylation of salicylaldehyde (methyl sulphate) afforded a product (b. p. 245°) which did not solidify readily and showed in the vapour state a large number of narrow bands, the most intense of which (2748·3, 2691·8, 2678·2, 2637·9, 2625·3, 2612·9, 2574·5 A.) are known to be characteristic of anisole (Horio, *Mem. Coll. Eng. Kyoto*, 1933, **7**, No. 4). After seeding with authentic *o*-methoxybenzaldehyde, the liquid solidified and could be recrystallised from alcohol, m. p. 35° (Perkin, J., 1889, **55**, 550, records a modification, m. p. 2·7—3°, which on addition of a crystal of the form melting at 35° changes completely into the latter). The recrystallised material no longer showed the vapour absorption due to anisole. *m*-Hydroxybenzaldehyde (Eastman Kodak) was twice recrystallised from hot water, m. p. 102—103°. The methoxy-derivative, b. p. 228°, was obtained by treatment with methyl iodide and potassium hydroxide. *p*-Hydroxybenzaldehyde (Eastman Kodak), recrystallised from hot water, m. p. 117°, was methylated (methyl iodide and potassium hydroxide), and the methoxy-compound, b. p. 250°, was obtained as an oil and further purified through the bisulphite compound.

o-Hydroxyacetophenone, prepared from phenol, glacial acetic acid, and zinc chloride and purified (b. p. 213°) through the copper derivative, contained phenol, as shown by the spectra of the vapour and of hexane solutions. Purification through the semicarbazone gave in poor yield a phenol-free product. Interaction of phenyl acetate and aluminium chloride (Fries and Pfaffendorf, *Ber.*, 1910, **43**, 215) proved satisfactory and yielded *o*-hydroxyacetophenone as an oil which was readily purified (b. p. 216—217°) through the semicarbazone. The product was methylated (methyl sulphate) without difficulty, and the ether (b. p. 241°) purified through the semicarbazone.

We are indebted to Dr. Wilson Baker for specimens of *p*-hydroxyacetophenone and the diacetylresorcinols and their ethers (cf. J., 1934, 1684).

UNIVERSITY OF LIVERPOOL. [*Received, July* 19*th*, 1940.]