68. *The Infra-red Spectra of Cresols and Xylenols and the Analysis of Cresylic Acid.*

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The infra-red spectra of cresols and xylenols have been measured over a wide spectral range. Details have been given of a method for the rapid analysis of cresylic acid, and the basis for similar work on mixtures of xylenols has been explained. Some correlations of the spectra with molecular structure have been outlined, and the effect of the substituent groups on a vibration frequency of benzenoid substances has been considered. The possibility of formulating general rules by which *o*-, *m*-, and *p*-derivatives may be distinguished regardless of the particular substituents has been considered, and similar considerations have been applied to trisubstituted benzenes. A peculiarity in the spectra of some of the phenolic compounds has been discussed in relation to molecular association.

THE quantitative analysis of mixtures of *o*-, *m*-, and *p*-cresol by chemical methods is difficult, not very accurate, and unreliable if certain other related substances are also present. A more satisfactory method than those in

FIG. 1.
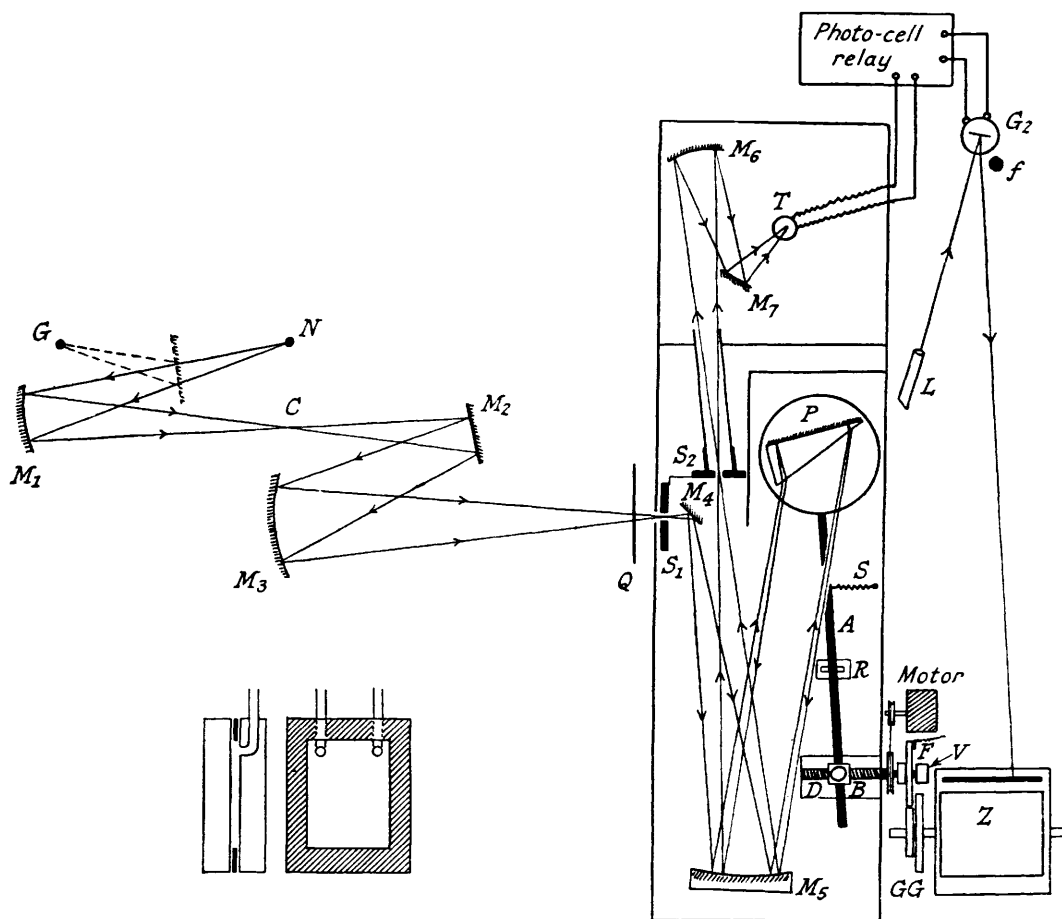
current use is therefore desirable. We have recently measured the infra-red absorption spectrum of each of these substances over the range of wave-lengths 7—14 μ as part of a general programme on the correlation of vibrational spectra with molecular structure, and also in connexion with similar work on the structure of resins and condensates between phenol or cresol and formaldehyde. It became clear that the infra-red absorption spectrum would provide a quick and simple method for the analysis of cresylic acid. Similar measurements have also been made with xylenols, which form a basis for the analysis of these isomers.

EXPERIMENTAL.

The infra-red spectrometer was an automatically recording instrument built in this laboratory and shown diagrammatically in Fig. 1. Although the main optical arrangement is fairly well known, it will be useful for purpose of future reference to describe its main features and dimensions, since it was designed to have high resolving power without being unnecessarily elaborate.

Radiation from a Nernst glower N (or heated Globar rod G) is focused by aluminised mirrors M_1, M_2, M_3 on to the entrance slit of the spectrometer S_1. M_1 and M_3 are concave mirrors of about 60 cm. radius of curvature and about 8 cm. in diameter. M_2 is a plane mirror and the source N (or G) is placed at the centre of curvature of M_1 so as to form a primary image at C, where the absorption cell is usually placed. Mirrors M_2 and M_3 form a second image on S_1. The absorption cell can also be placed just in front of the slit S_1, but with a cell made of a pair of polished rock-salt plates each about 5 mm. thick, a better focus on the slit is obtained with the cell at C, and this is essential if thin solid films of plastics, rubber or other materials with an irregular surface are being studied.

Behind S_1 a small plane mirror M_4 diverts the entrant beam on to the off-axis paraboloid mirror M_5, of focal length 60 cm. A parallel beam of radiation is then directed at the 30° prism P (rock-salt, quartz or potassium bromide) which has a reflecting back face of gold or aluminium. The prism has a reflecting face 10 cm. in length and 60 mm. in height, and is set up in Littrow mounting. After two refractions the beam returns to the mirror M_5 and is thereby focused on the second slit S_2, through which it passes on to M_6 and M_7, and is collected by the Schwarz compensated thermocouple T. The E.M.F. obtained is amplified by a twin photocell relay using a divided Eel selenium cell, a Cambridge d'Arsonval galvanometer of 10 ohms resistance as primary, and a similar galvanometer of higher resistance as secondary. A spot lamp L with line aperture is directed at the secondary galvanometer G_2 and the beam is returned to the camera Z, a cylindrical drum around which the photographic paper is fixed, moving behind a cylindrical lens. With the prism set at a given angle to the beam of radiation from M_5, a definite wave-length returns to the slit S_2 and the energy at this wave-length is recorded by the throw of the galvanometer G_2 from its zero position. As the prism rotates, the galvanometer throw is recorded on the camera, which is geared to the rotatory motion of the prism, both being driven by a D.C. motor. Smooth, slow rotation is obtained by allowing a machined aluminium rod A, supported at R on a ball race and restrained by a light spring S, to be propelled by another circular ball race B fixed to a nut through which the fine screw D is driven. By this mechanism the camera records a curve showing how the energy falls off as a function of increasing wave-length, and simulating the fall-off curve of a black-body radiator. Absorption bands appear as troughs in the background curve and percentage absorption can be calculated by measurement of this photographic trace at desired points. By means of suitable gears GG, the curve may be compressed or spread out along the camera paper.

As the main driving screw rotates, a contact F is made at five equal intervals during each complete revolution of the screw, causing a small filament bulb f near G_2 to flash and produce a line across the camera paper. These lines are calibrated in wave-lengths by reference to the well-established absorption bands of water, ammonia, and other substances. The main drive can be de-clutched and the prism table rapidly brought back to any desired setting, a revolution counter V enabling measurements to be started at the wave-length required.

The main parts of the spectrometer are mounted on steel plates fixed along a length of H girder, and the whole enclosed in a wooden box with loose panels in the top above the slit S_2 and prism P. The thermocouple T is sealed off from the remainder of the instrument in a separate compartment, into which the radiation is led from the slit S_2 through a narrow cylindrical tube fixed around the circumference of the slit mount. It is very desirable to isolate the thermocouple in this way if proper thermal stability is to be obtained.

For the shutter Q, metal, glass, quartz or other materials are used according to the particular spectral range under investigation. For the region 7—14 μ, a quartz shutter being used, the scattered radiation of false wave-length was very small.

The absorption cell was usually made by separating a pair of polished rock-salt plates by a metal washer of the desired thickness and cementing the whole together with a thin film of seccotine. Such cells had a pair of small gaps in the upper edge of the washer for filling and emptying. Since, in the present work, solutions in carbon disulphide had to be used, some form of sealed cell had to be employed. This was achieved by drilling holes about 2 mm. in diameter into one of the rock-salt plates as shown in the diagram. Into these holes were cemented short lengths of copper tubing, and after being filled with the solution the copper tubes were fitted with rubber caps. Such a cell was usually painted around the edges with porcenam cement.

We are particularly indebted for purified samples of the cresols to Bakelite Ltd., for the xylenols to Monsanto Ltd., and to Courtaulds Ltd. Other laboratory specimens were also used. In cases where more than one sample of a given compound was available, the identity of the spectra was a valuable check on purity. The detection of a small amount (1—2%) of m-cresol in one sample of 2 : 6-dimethylphenol, and of a trace of unidentified impurity in a sample of 3 : 4-dimethylphenol also served to illustrate the value and power of this analytical method.

The samples of phenol, carbon disulphide, and *cyclo*hexane used were purified commercial products.

Results.—Fig. 2 shows the absorption spectra of the three cresols, obtained from measurements on solutions in carbon disulphide over the range 700—1300 cm.$^{-1}$ (14—7·5 μ). Correlation of all the absorption bands with particular normal vibrational modes must be deferred, but for the present purpose it can be seen that each isomer has an intense absorption band in the region 750—800 cm.$^{-1}$ (12—13 μ), and another region of intense absorption between 1200 and 1300 cm.$^{-1}$. The band in the region 12—13 μ is characteristic of benzenoid substances with substituents attached to the nucleus, and it is almost certainly related to the intense absorption band of benzene at 671 cm.$^{-1}$. The latter has been assigned by Ingold and others (J., 1936, 971) to a motion involving the deformation of C–H bonds out of the plane of the nucleus. There is a shift of this " aromatic " band towards higher frequencies in passing along the series o-, m-, p-, and this seems to occur with most disubstituted benzenes regardless of the particular substituent groups. With o-cresol it is found at 750 cm.$^{-1}$, with m- at 776 cm.$^{-1}$, and with p- at 815 cm.$^{-1}$. The band is so intense with each isomer that it still gives a conveniently large optical density when most of the other bands in the spectrum are feeble, and these are ideal circumstances for infra-red analysis.

For qualitative analysis, inspection of the spectrum of a mixture at once reveals whether peaks are present at the wave-lengths characteristic for each component. If the usual absorption laws hold, the amount of a component present can then be correlated with the percentage absorption at its key wave-length in the usual way. Thus, for a pure component the extinction coefficient ε_i will be given by $\varepsilon_i = [\log(I_0/I)]/c_iL = d_i/c_iL$, where c_i is the concentration, L_1 the path length of solution, I_0 and I the intensities of radiation before and after absorption, and d_i the optical density. Strictly, this relationship applies to monochromatic radiation, but experience shows that in many cases it is satisfactory with the high resolving power such as has been used here, and when the intensities are related to the percentage absorption A at the peaks of a band by the relation $I_0/I = 100/(100 - A)$. Even if this relationship embodying Beer's law is not strictly valid. as discussed below, empirical calibration can be set up to give the required result (see Wright, *Ind. Eng. Chem. Anal.*, 1941, **13**, 1; Barnes, Liddel, and Williams, *ibid.*, 1943, **15**, 659). If we can assume, however, that the optical densities are additive in a mixture, we have, for a given wave-length, $d = \Sigma d_i = (c_1\varepsilon_1L + c_2\varepsilon_2L_2 + \ldots)$. For a given absorption cell, L being constant, we require to know the value of εL for each pure component at a series of key wave-lengths at each of which $d = \log 100/(100 - A)$ is measured. Equations are thus obtained from which the concentrations $c_1, c_2, \ldots$ are obtained.

In the present case of o-, m-, and p-cresol, at the key wave-length for any particular component, the optical densities

due to the other components can be ignored in almost all cases if suitably dilute solutions are used (Fig. 3), so that no equations have to be solved and the results can be read directly from a single graph. There is one small complication with cresols which requires consideration before the detailed analytical results are given. With *o*-cresol the band at 752 cm.$^{-1}$ remains as a single peak as the dilution is increased, but with both the *m*- and the *p*-isomer the corresponding peaks at 776 and 815 cm.$^{-1}$ split at lower concentrations into a double band with components whose relative intensity alters with changing dilution. The limiting spacing of the doublet with *p*-cresol is about 11 cm.$^{-1}$, and with *m*-cresol about 6 cm.$^{-1}$. For calibration, the stronger of the pair of peaks in each doublet has been used, since its wave-length remains almost constant. Until the exact reason for this doubling of the band with *m*- and *p*-cresol is understood, the theoretical basis for the analytical procedure is uncertain, and it is therefore to be regarded as semi-empirical. This does not, however, affect its serviceability for analysis. The doubling phenomenon is discussed below.

Figs. 3 and 4 incorporate the calibration data. It was decided to use *cyclo*hexane as solvent, since it is less offensive for general use than carbon disulphide, and is completely transparent between 12 and 14 μ. The wave-lengths of some of the absorption bands are slightly affected, not only by changes from the liquid to the solid state, but also in some cases by the particular solvent used. There is no difference between carbon disulphide and *cyclo*hexane in this respect. The absorption cell was about 0·1 mm. thick; since the same cell was used throughout, its exact thickness was not required. The absorption of solutions of *o*-cresol containing 0·5—3% by weight was measured between 700 and 850 cm.$^{-1}$ (Fig. 3). In Fig. 4 the optical density, log I_0/I, is plotted as a function of concentration. With this range of dilute solutions the plot is nearly linear, suggesting that Beer's law is roughly satisfied, though this may be accidental. Similar data were

FIG. 2.

Cresols in carbon disulphide : (1) 1%; (2) 5%; (3) 20%.
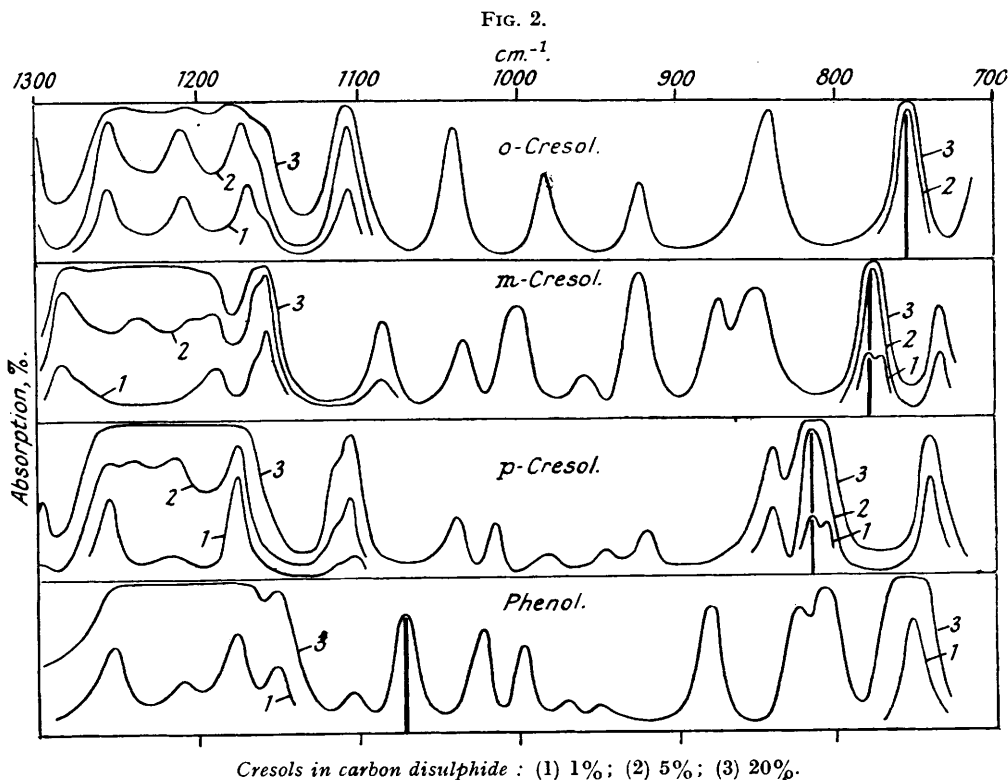
obtained for *m*- and *p*-cresol. Here again, the plots are almost linear over this range of concentration. In measuring the percentage absorption, readings were taken from the smooth background of the photographic trace as base line, so that the absorption or reflection losses from the absorption cell itself are eliminated. If necessary these can be allowed for (see Nielsen and Smith, *Ind. Eng. Chem. Anal.*, 1943, **15**, 609). If the plots of Fig. 4 were strictly linear, passing through the origin, the slope $d/c = \varepsilon L$ would be a measure of the extinction coefficients. It is noteworthy that, whereas the extinction coefficients for *m*- and *p*-cresol appear to be roughly equal, that of *o*-cresol is noticeably greater, although it must again be emphasised that this difference may be in part connected with the singlet nature of the *o*-cresol band, and the exact equality of the *m*- and the *p*-derivative may be accidental.

In analysing a mixture, the spectrum of a solution in *cyclo*hexane was measured over the range 700—850 cm.$^{-1}$, and the percentage absorption at 752, 776, and 815 cm.$^{-1}$ determined. The concentration was chosen so as to give the optimum conditions for accurate measurement at the three peaks; usually, about 3 g. of sample per 100 c.c. (0·3 g. per 10 c.c.) was suitable; *e.g.*, sample *B* (Fig. 3) contained 2·93 g. per 100 c.c. The absorption percentages at the *o*-, *m*-, and *p*-peaks were 14·5, 50, and 41, which gives :

|				
o-Cresol	....	0·15 g. per 100 c.c.		5% ± 0·5%
m- ,,	....	1·55 ,, ,,		53% ± 1%
p- ,,	....	1·20 ,, ,,		42% ± 1%
Total	....	2·90 (2·93 g. per 100 c.c. taken).		

The estimated errors are based on possible errors in measuring the optical densities, and are rather greater when the optical density is very low or if it is very high. A chemical determination on this sample carried out independently in

another laboratory gave : *m*- 52·6, *o*- 5·3%. The method was tested on synthetic mixtures, and typical results are as follows :

|			G. per 100 c.c.				Percentage.		
		o-.	*m*-.	*p*-.	Total.	*o*-.	*m*-.	*p*-.
M_1.	Taken	0·31	1·61	1·41	3·33	9·3	48·4	42·3
	Found	0·30	1·60	1·45	3·35	8·9	47·8	43·3
M_2.	Taken	0·60	1·61	1·27	3·48	17·2	46·2	36·6
	Found	0·60	1·65	1·30	3·55	16·9	46·4	36·7

Another test sample was examined and found to contain 12, 39, and 34% respectively of *o*-, *m*-, and *p*-cresol, with 15% unaccounted for. The residue was subsequently found to consist of other components such as xylenols and phenol. The

Fig. 3.

cm.$^{-1}$
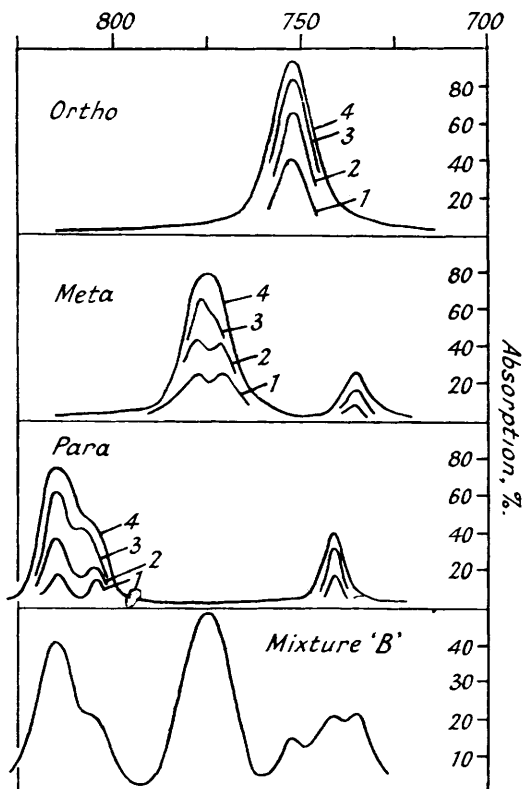
Cresols in cyclohexane : (1) 0·5%; (2) 1·0%; (3) 2·0%; (4) 3·0%.

Fig. 4.

$d = \log I_0/I$.

Concentration, G./100 c.c.
Cresols in cyclohexane.

○ Ortho
● Meta
◐ Para
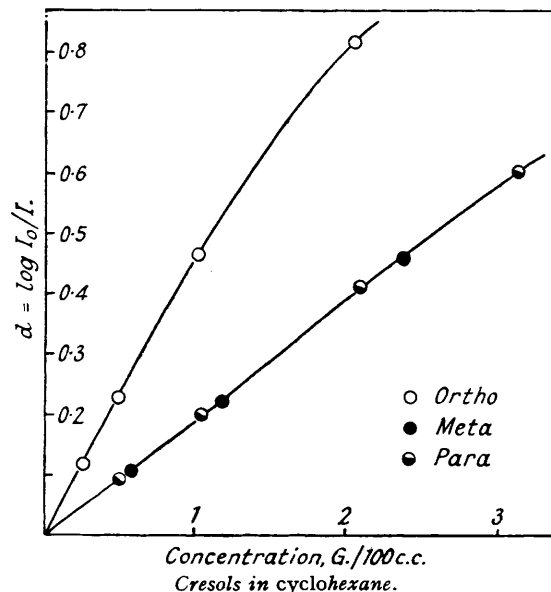
amount of material required for an analysis is very small, and the spectroscopic determination can be carried out in about ten minutes.

In Fig. 2, the spectrum of phenol is shown over the same spectral range. It is seen that small amounts of phenol in cresylic acid could be detected by means of its band at 1070 cm.$^{-1}$.

Fig. 5 shows the corresponding spectra of the six isomeric xylenols, as determined with solutions in carbon disulphide. These spectra are rather more complex than those of the cresols, but there are characteristic features, and an analysis of mixtures can be carried out in similar fashion, the accuracy obtainable being determined by the complexity of the mixture and the care taken in setting up reference calibrations. If mixtures of xylenols are first fractionated, the analysis is much simplified. For instance, 2 : 6-dimethylphenol distils off first, and if it enters a cresylic acid fraction, it can be detected by means of its bands at 1090 and 904 cm.$^{-1}$; 2 : 4- and 2 : 5-dimethylphenol next distil off together within a few degrees. Key bands for the former might be 770, 804, 873 cm.$^{-1}$, and for the latter 800, 850, and 993 cm.$^{-1}$. If 2 : 3-dimethylphenol entered this fraction, it could well be determined from the band at 1066 cm.$^{-1}$. In the top fraction 3 : 4- and 3 : 5-dimethylphenol can be measured, the former from bands at 730, 807, 855, 1116, and 1295 cm.$^{-1}$, and the latter from the band at 830 cm.$^{-1}$. Although preliminary fractionation is obviously to be avoided if possible, yet it is desirable for an initial examination, since the infra-red spectra provide indisputable evidence of the identity of the particular components present, and once this has been established an analysis may be possible without exhaustive fractionation.

It is also clear that with some suitable preliminary fractionation ethylphenols, if present, may also be identified in crude xylenol samples. In all analyses it is advantageous to use dilute solutions, unless small amounts of some particular component are being sought.

As regards the correlation of structure with vibrational spectrum, several points emerge. The most important concerns the " aromatic " band, used in particular in the analysis of cresols. As already explained, in the case of benzene

this frequency (671) has been assigned to a motion involving the oscillation of the six-carbon ring as a rigid structure through the plane of the six hydrogen atoms. With monosubstituted benzenes, regardless of the particular substituent, the frequency shifts to a value 740—760 cm.$^{-1}$, as shown in Table I. The data for the alkylbenzenes given in this and subsequent tables have been taken from a joint programme of work carried out by Dr. G. B. B. M. Sutherland and others with ourselves, and to be published shortly elsewhere.
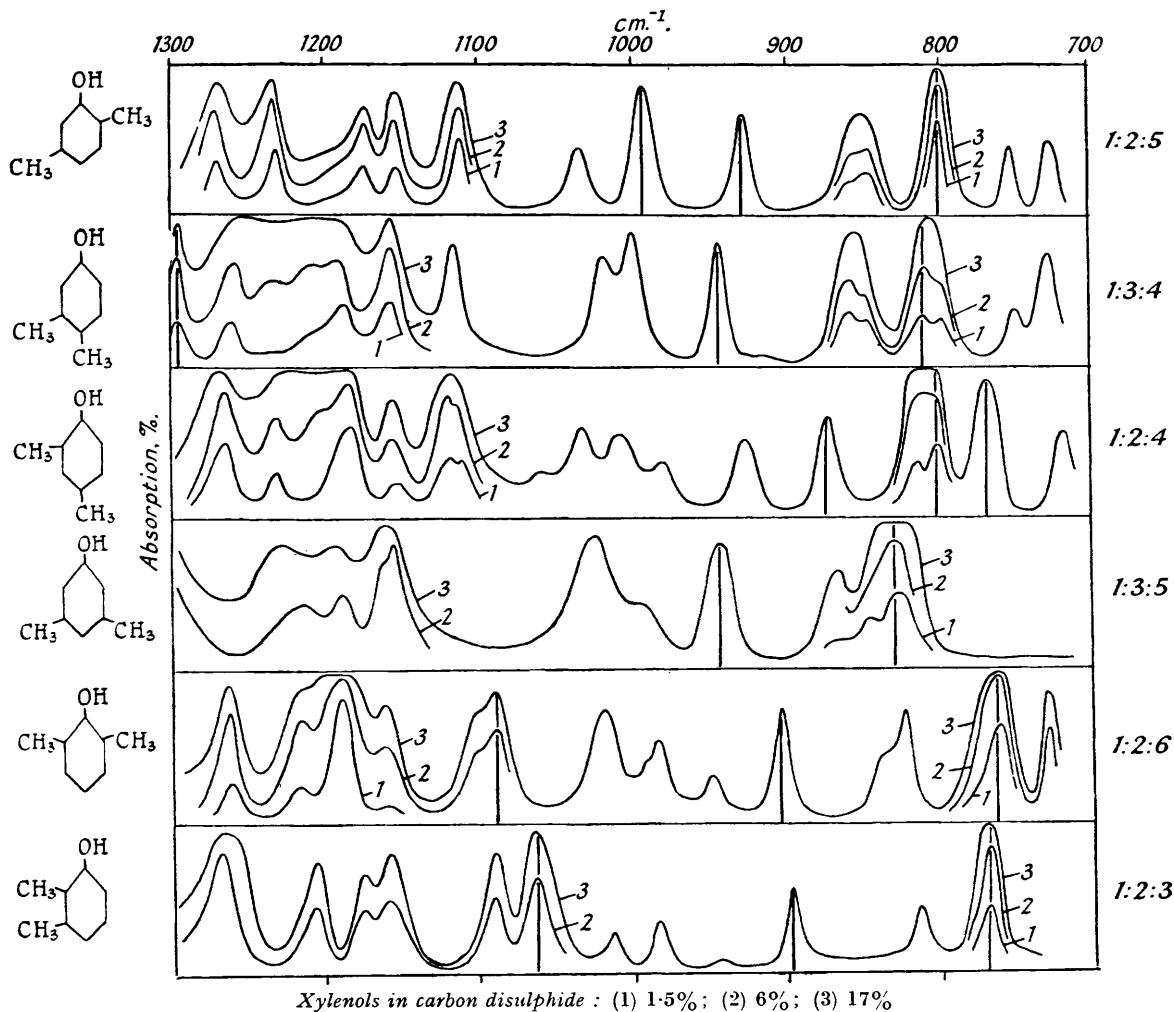
FIG. 5.

Xylenols in carbon disulphide : (1) 1·5%; (2) 6%; (3) 17%

TABLE I.

Phenol	751	Toluene	730	Diphenyl	752
Anisole	754	Ethylbenzene	745	Diphenylmethane	735
Aniline	753	*n*-Propylbenzene	740	*tert.*-Butylbenzene	762
N-Methylaniline	750	*iso*Propylbenzene	761	Chlorobenzene	742
NN-Dimethylaniline	749	Diphenylamine	747	Bromobenzene	740
NN-Diethylaniline	748				

With disubstituted benzenes (Table II) the corresponding vibration frequency moves steadily towards higher frequencies in passing along the series *o*-, *m*-, *p*, independently of the nature of the substituent groups. With each class of isomer, the frequency remains within fairly close limits, but measurements are needed with other compounds before rules can be set up to express how the small variations are connected with the particular nature of the substituent groups, or with steric effects.

TABLE II.

	o-.	*m*-.	*p*-.		*o*-.	*m*-.	*p*-.
Xylenes	743	765	790	*NN*-Dimethyltoluidines	—	—	806
Ethyltoluene	752	782	826	*NN*-Diethyltoluidines	—	—	813
Diethylbenzenes	—	792	828	*N*-Methyltoluidines	—	—	810
Toluidines	753	774	810	Di*iso*propylbenzenes	—	793	827
Cresols	752	775	827	Di-*tert.*-butylbenzenes	—	—	829
Dichlorobenzenes	750	—	818				

The corresponding intense absorption band appears with the xylenols, and the exact value of the frequency depends on the arrangement of the substituent groups; *e.g.*, all those having a 1 : 2 : 4-grouping, *viz.*, 1 : 2 : 5-, 1 : 3 : 4-, and 1 : 2 : 4-xylenol, have the band at 800—810 cm.⁻¹; those with the 1 : 2 : 3-grouping, *viz.*, 1 : 2 : 3- and 1 : 2 : 6-xylenol, have the band at 760—770 cm.⁻¹, and that with a 1 : 3 : 5-grouping at 833 cm.⁻¹. As with the disubstituted benzenes, it seems that the frequency rises in value as the substituent groups are spread around the aromatic nucleus, and is smallest when these groups are in closest proximity. Moreover, the value of this particular vibration frequency of trisubstituted benzenes seems to be to a large extent independent of the nature of the substituent groups. Table III gives results for xylenols, xylidines, and trimethylbenzenes.

TABLE III.

Type 1 : 2 : 3.				Type 1 : 2 : 4.				Type 1 : 3 : 5.			
(1).	(2).	(3).	cm.⁻¹.	(1).	(2).	(4).	cm.⁻¹.	(1).	(3).	(5).	cm.⁻¹.
CH_3	CH_3	CH_3	766	OH	CH_3	CH_3	804	CH_3	CH_3	CH_3	834
CH_3	CH_3	OH	770	CH_3	CH_3	CH_3	806	CH_3	CH_3	OH	830
CH_3	OH	CH_3	761	CH_3	OH	CH_3	800	CH_3	CH_3	NH_2	828
CH_3	NH_4	CH_3	761	CH_3	CH_3	OH	807				
				CH_3	NH_2	CH_3	797				
				CH_3	CH_3	NH_2	810				
				NH_2	CH_3	CH_3	813				

Apart from these structural correlations, the other interesting feature of the " aromatic " band is the doubling shown with some compounds at lower concentrations. As stated already, *o*-cresol shows no splitting, but *m*- and *p*-cresol do. In order to find possible causes for this effect, we have measured the spectra of a large number of mono- and di-substituted benzenes in dilute solution over the relevant range of wave-lengths. None of the monosubstituted derivatives listed in Table I shows a double band, nor any of the disubstituted derivatives of Table II, with the possible exception of *o*-dichlorobenzene. In the latter case, however, the spectrum suggests that there are two bands which accidentally fall close together, and it seems improbable that the effect is due to the same cause as with *m*- and *p*-cresol. As regards the xylenols, there is no splitting of the bands of the 1 : 2 : 6- or the 1 : 2 : 5-isomer at 761 and 800 cm.⁻¹, respectively, but doubling occurs with each of the other isomers.

The most natural hypothesis is to assume that the doubling phenomenon results from association through hydroxyl groups, although the exact mechanism is not clear. It might be possible to explain the absence of doubling in some cases by diminished association due to steric hindrance caused by methyl groups protecting the hydroxyl group. Further, there are peculiar variations of the absorption bands with concentration in the region 1100—1300 cm.⁻¹ with many of the hydroxylic compounds, particularly those showing a doubling of the " aromatic " band. This effect can well be seen by comparing the spectra of a solution of phenol in carbon disulphide with that of liquid phenol (Barnes, Liddel, and Williams, *loc. cit.*), and the variations are not merely due to slight displacement of bands by change of solvent or state of aggregation. These variations are almost certainly connected with the effect of varying association on the deformational frequency of the O–H bond. On the other hand, these explanations are not very satisfactory, for the phenol band at 751 cm.⁻¹ is single, and until further data on this phenomenon are available, further discussion must be postponed.