

238. Vibrational Spectra of Phenolic Derivatives and Phenolic Resins.

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The vibrational spectra of some substituted phenols and related compounds, and of some resins formed from phenols and aldehydes, have been examined. The possibility of formulating correlation rules for use in determining structural features of the resins has been explored. From the bands observed in the region 700—900 cm^{-1} it may be possible to infer the type of substitution around the aromatic nuclei in these complex molecules. The absorption of hydroxyl groups in the region 3200—3650 cm^{-1} reveals differences in the types of hydrogen bonds in the different compounds and suggests that differences between resins made from the same materials may be related to this particular structural feature. Some of the compounds have been measured both as solids and as liquids and spectral differences in the two states of aggregation have been found.

INFRA-RED spectroscopy has recently been used in examining compounds of high molecular weight, and some results have emerged which might not have been derivable by other methods (Thompson and Torkington, *Trans. Faraday Soc.*, 1945, **41**, 246; *Proc. Roy. Soc.*, 1945, **184**, A, 3, 21). Among other classes of compound we have studied the resins formed by condensation of phenols with aldehydes, the aim being to discover more about the mechanism of condensation and the nature of cross linkage in these structures. Whilst some empirical spectral differences between different resins were of immediate practical interest, it became clear that the only satisfactory way of understanding the spectra would be to collect results for a large number of structurally related simpler molecules from which closer correlations with molecular structure could be made. In the course of this investigation some interesting facts have emerged about the association which occurs with these hydroxylic compounds, and the nature of the hydrogen bridges which arise. Some of the results are given in the present paper.

EXPERIMENTAL.

The spectra between 6 and 15 μ were measured on a single-beam recording spectrometer with rock-salt prism (Whiffen and Thompson, *J.*, 1945, 268). The measured frequencies were accurate to $\pm 5 \text{ cm}^{-1}$ at 7 μ , and to $\pm 2 \text{ cm}^{-1}$ at 15 μ . Between 2.5 and 6 μ a double-beam recording spectrometer was used (see preceding paper). With this spectrometer, the frequencies of bands near 7 μ could be determined to $\pm 3 \text{ cm}^{-1}$, and at 3 μ to $\pm 8 \text{ cm}^{-1}$ depending upon their breadth. At 3 μ it was possible to resolve bands 20 cm^{-1} apart, although when the instrument was used as a single-beam spectrometer rather better resolution was possible.

Solutions in carbon disulphide were measured in rock-salt cells about 0.1 mm. thick. Solutions in carbon tetrachloride were studied at 3 μ in rock-salt cells of thickness 2 mm., 3.5 cm., and 7.8 cm., according to the dilution being used. Solids were examined either by melting them and allowing them to crystallise between a pair of rock-salt plates, or by the method of a paste in paraffin used in the preceding paper. Measurements at higher temperatures were made with an electrically heated cell (Richards and Thompson, *Trans. Faraday Soc.*, 1945, **41**, 183).

Many of the phenolic derivatives were kindly supplied by Messrs. Bakelite Ltd. or by the Chemical Laboratory, Teddington. Others were commercial samples purified in this laboratory in the appropriate manner. The resins were supplied by Messrs. Bakelite Ltd. and by other firms.

RESULTS AND DISCUSSION.

Figs. 1 and 2 show the spectra between 700 and 1500 cm^{-1} (14—6.5 μ) of some phenols, aromatic alcohols, and other compounds likely to have a bearing on the structure of the resins themselves. Each of the spectra is complex, and few correlations are immediately obvious. All the compounds show one or more intense bands in the region 700—870 cm^{-1} , and these are of particular interest since it has previously been found that substituted benzenes have more or less characteristic frequencies in this range, according to the number and position of the substituents and in great measure independent of their exact nature (Thompson and Torkington, *loc. cit.*; Whiffen and Thompson, *loc. cit.*). The normal vibration of benzene in which the group of six carbon atoms moves in a rigid plane perpendicularly to the plane containing the six

hydrogen atoms has a frequency of 671 cm^{-1} . Previous results have shown that when the substituent is attached to the ring, this type of vibration, which is essentially a deformation of the remaining C-H bonds, is displaced to 740—760 cm^{-1} . With disubstituted benzenes, the corresponding vibration has a frequency which depends on the relative position of the substituents; with *o*-derivatives it usually lies at 740—760 cm^{-1} , with *m*-compounds at 770—790 cm^{-1} , and with *p*-compounds at 810—830 cm^{-1} . With tri- and tetra-substituted benzenes the corresponding deformations of the residual C-H bonds also appear to have fairly definite frequencies. The earlier work suggested for the 1 : 2 : 3-derivatives a band at 760—770 cm^{-1} , for 1 : 2 : 4-compounds a band at 800—820 cm^{-1} , and for 1 : 3 : 5-compounds at 825—860 cm^{-1} . With the 1 : 2 : 3 : 5- or 1 : 2 : 4 : 5-compounds the band lies in the region 850—880 cm^{-1} .

The present results appear in most cases to conform with these correlations. Thus, mono-substituted benzenes include :

Benzyl alcohol	745 cm^{-1}	Diphenyl ether	752 cm^{-1}
β -Phenylethyl alcohol	748 ,,	Diphenylmethane	735 ,,
Dibenzyl ether	746 ,,		

Typical disubstituted benzenes include the following :

<i>ortho</i> -		<i>para</i> -	
Fluorene	741 cm^{-1}	4 : 4'-Dihydroxydiphenylmethane ...	816 cm^{-1}
Diphenylene oxide	750 ,,	2 : 4'-Dihydroxydiphenylmethane ...	810 ,,
2 : 4'-Dihydroxydiphenylmethane.....	752 ,,	4 : 4'-Dihydroxydiphenylmethane ...	827 ,,
2 : 2'-Dihydroxydiphenylmethane.....	754 ,,		

Some compounds show simultaneously the mono- and di-substituted type, such as

	Mono.	<i>o</i> -Di.	<i>p</i> -Di.
<i>p</i> -Hydroxydiphenyl	755	—	830
<i>o</i> - ,, ,,	730	754	—

Polysubstituted benzenes include the following :

3-Hydroxymethyl- <i>p</i> -cresol (1 : 2 : 4)	815 cm^{-1}
3 : 5-Bishydroxymethyl- <i>p</i> -cresol (1 : 2 : 3 : 5) ..	864 ,,
5-Hydroxymethyl- <i>o</i> -4-xyleneol (1 : 2 : 4 : 5)...	856 ,,

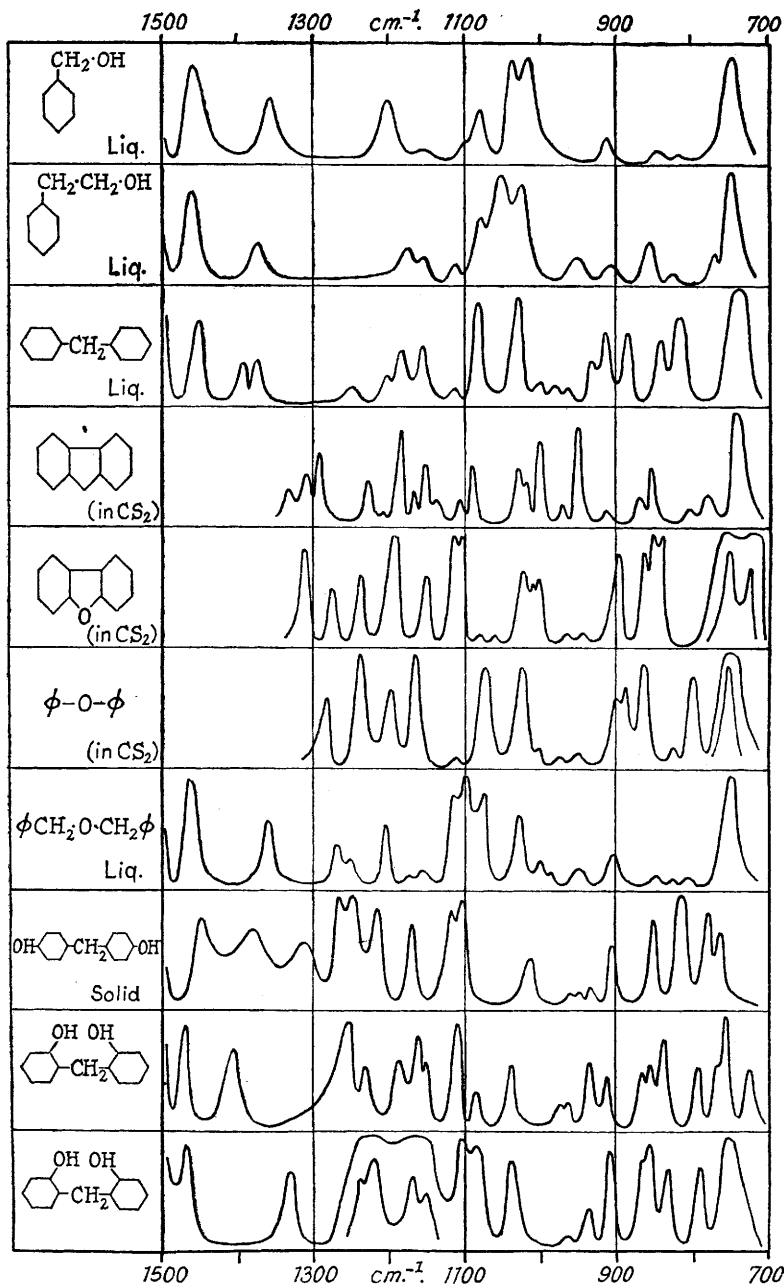
It is clear, therefore, that these correlation rules are fairly widely applicable, although it is obvious that since there are small variations within a given class there may in some cases be ambiguity and the rules must be used with caution. Also, whilst the correlations do not seem to be seriously affected by a change of state of the substance being measured, this possibility must not be excluded.

It is impossible to assign the bands between 1000 and 1500 cm^{-1} to particular normal modes, although this region will include vibrations of the groups C—O—C, C—O—H, CH_2 , and CH_3 , as well as of the skeleton of the aromatic rings. It is, however, apparent that in these cases the exact position of a particular band depends upon the environment of the group within the molecule. It is hoped shortly to explore this region in greater detail under higher resolving power.

Some of the substances given in Figs. 1 and 2 were measured in the solid and in the liquid state, or in solution. In some cases there are striking changes of spectrum with change of state, which have been noted already in other connexions (Thompson and Torkington, *Trans. Faraday Soc.*, 1945, **41**, 260; Thompson, *Nature*, 1946, **158**, 234). In order to eliminate the possibility of decomposition on melting, the procedure was to measure the spectrum of the liquid first, then to allow it to crystallise between the rock-salt plates, and then to measure the solid film again. The spectrum of this solid film was also compared with that obtained by measuring the paste formed by grinding with paraffin. The spectrum of the monoalcohol of *m*-4-xyleneol was measured at 100° and 250°, but showed no appreciable change, and other liquids showed no change of spectrum with temperature. It seems certain, therefore, that the marked changes of spectrum at the melting point must be connected with fresh influences which come into play in the arrangement of the molecules in the solid. The spectra of the solids usually show sharper bands than those of the liquids, and new bands appear which are absent with the latter. This whole problem is being examined more systematically, and a detailed consideration of the physical principles involved will therefore be deferred.

In Fig. 3 (Nos. 1, 2, 3, 4, 5) the spectra around 3 μ are shown of some simple *p*-substituted phenols in the solid state, and of dilute solutions in carbon tetrachloride. In the dilute solutions the normal sharp band of the hydroxyl group occurs at 3615 cm^{-1} . With the solids, this band

FIG. 1.

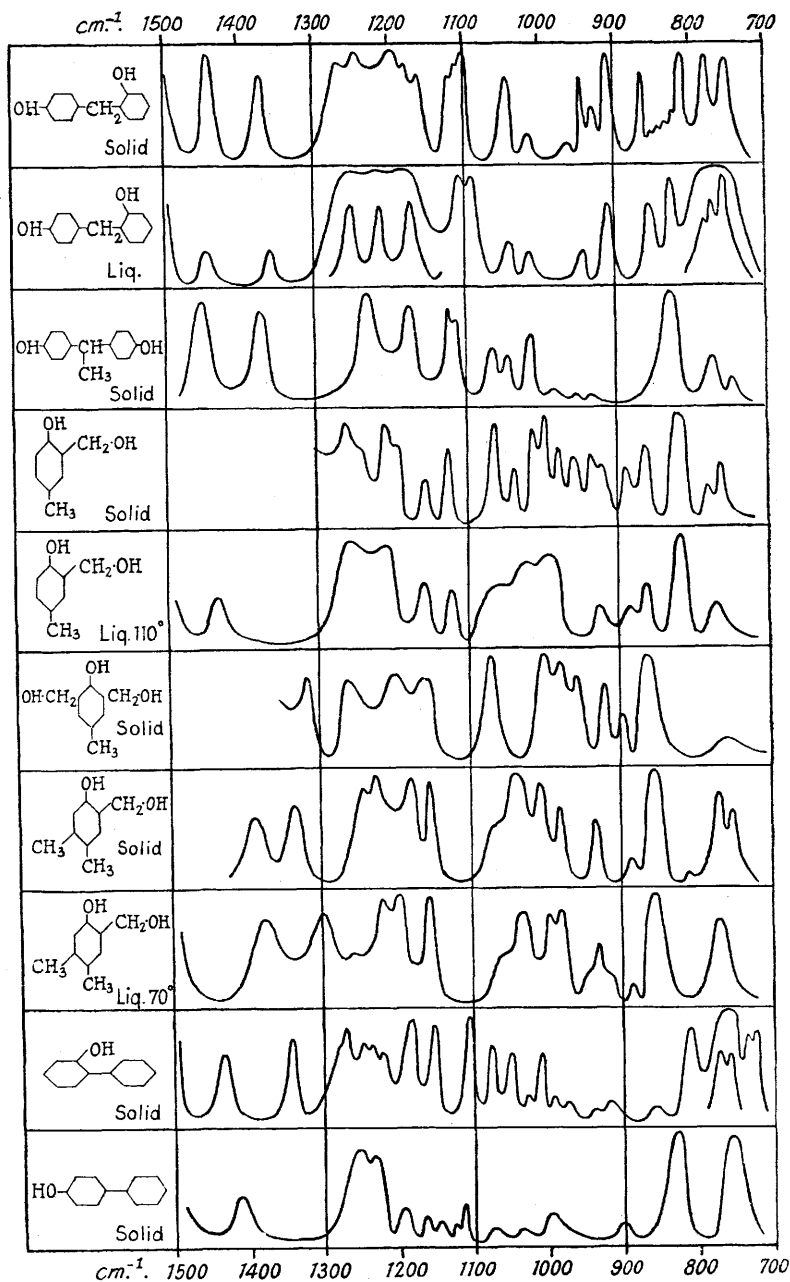


1. Benzyl alcohol (liquid).
2. β -Phenylethyl alcohol (liquid).
3. Diphenylmethane (liquid).
4. Fluorene (in carbon disulphide).
5. Diphenylene oxide (in carbon disulphide).
6. Diphenyl ether (in carbon disulphide).
7. Dibenzyl ether (liquid).
8. 4:4'-Dihydroxydiphenylmethane (solid).
9. 2:2'-Dihydroxydiphenylmethane (solid).
10. 2:2'-Dihydroxydiphenylmethane (liquid).

is replaced by a broader band with centre at 3200—3250 cm^{-1} , corresponding to the “bonded” hydroxyl group. With concentrated solutions, both the normal and the “association” band may appear simultaneously. These relationships correspond to those already examined by Fox and Martin, and others.

When there is a substituent in the *o*-position to the hydroxyl group (Fig. 4, Nos. 1, 2, 3, 4) the position of the "normal" hydroxyl group band in dilute solution is again at about 3615 cm^{-1} , but the association band with the solids lies at rather higher frequencies than in the above cases of the simple *p*-substituted phenols. This implies that the screening of the hydroxyl

FIG. 2.

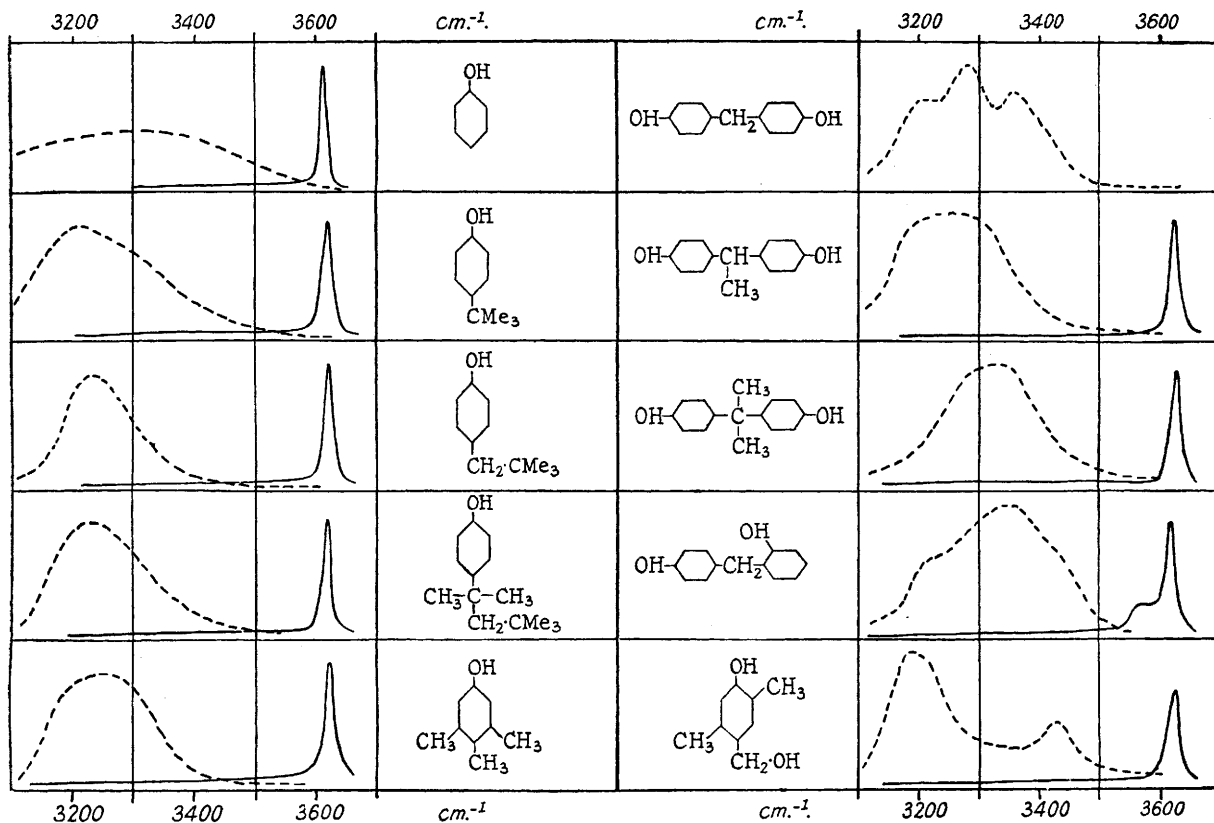


1. 2 : 4'-Dihydroxydiphenylmethane (solid).
2. 2 : 4'-Dihydroxydiphenylmethane (liquid).
3. 4 : 4'-Dihydroxy-*aa*-diphenylethane (solid).
4. 3-Hydroxymethyl-*p*-cresol (solid).
5. 3-Hydroxymethyl-*p*-cresol (liquid).
6. 3 : 5-Bishydroxymethyl-*p*-cresol (solid).
7. 5-Hydroxymethyl-*o*-4-xyleneol (solid).
8. 5-Hydroxymethyl-*o*-4-xyleneol (liquid).
9. 2-Hydroxydiphenyl (solid).
10. 4-Hydroxydiphenyl (solid).

group by the neighbouring groups decreases the strength of the hydrogen bridges which may be formed. With diphenylcarbinol and triphenylcarbinol (Fig. 4, Nos. 7, 8) this steric influence is well marked. In these connexions *o*-hydroxydiphenyl appears to be an exception, and will be discussed below.

When there are two hydroxyl groups in the molecule (Fig. 3, Nos. 6—10; Fig. 4, Nos. 6, 9—16) the dilute solutions again show the "normal" hydroxyl band at about 3615 cm^{-1} , but in the solid state a given compound may simultaneously show several "association" bands. When there are two neighbouring hydroxyl groups (Fig. 4, Nos. 9—16) the dilute solutions

FIG. 3.



1. Phenol.
2. p-tert.-Butylphenol.
3. p-tert.-Amylphenol.
4. p-tert.-Octylphenol.
5. s.-Hemimelliténol.

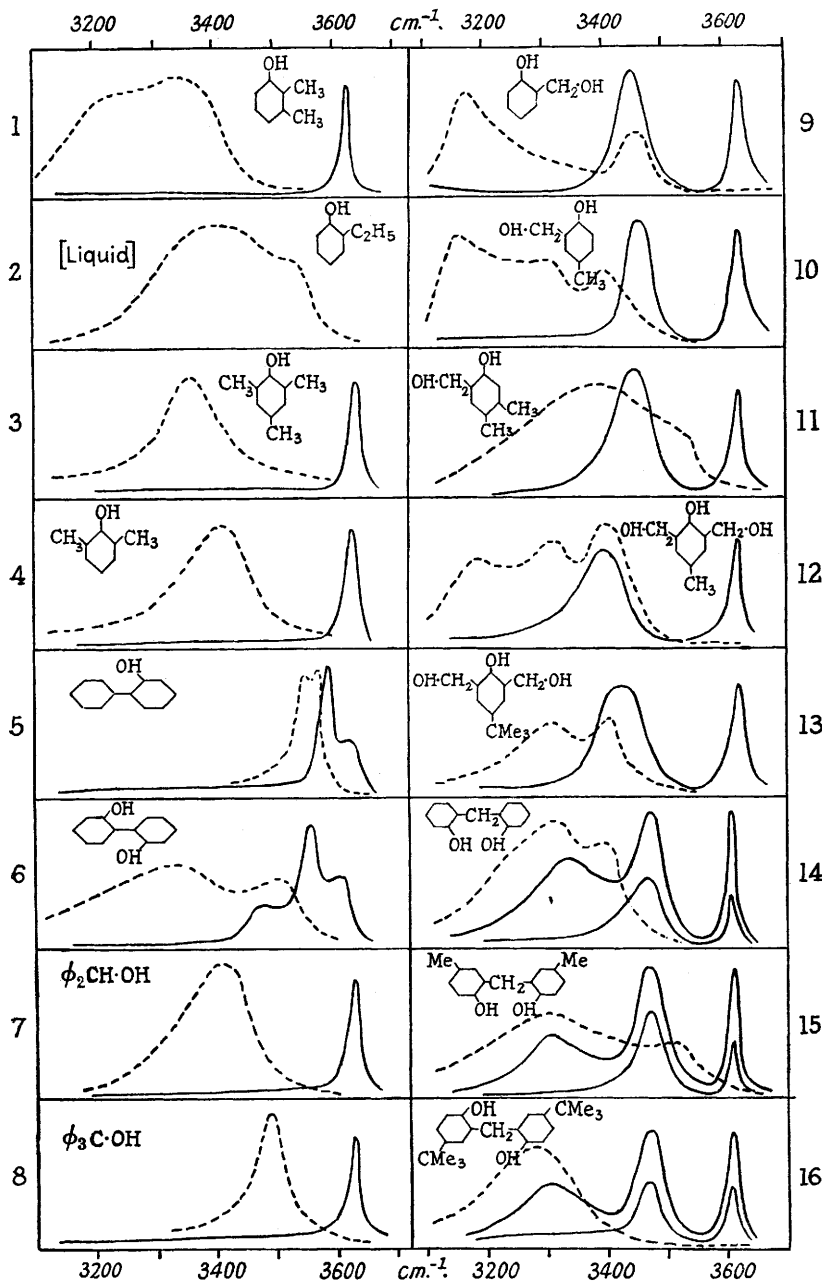
6. 4,4'-Dihydroxydiphenylmethane.
7. 4,4'-Dihydroxy- $\alpha\alpha$ -diphenylethane.
8. 4,4'-Dihydroxy- $\beta\beta$ -diphenylpropane.
9. 2,2'-Dihydroxydiphenylmethane.
10. 5-Hydroxymethyl-p-3-xylénol.

----- solid.
 ----- solution in CCl_4 .

show, in addition to the normal hydroxyl band, another fairly sharp band at about 3450 cm^{-1} , which generally persists in the solid state. This band is sharper than the customary "association" bands, but behaves as if it were due to internal hydrogen bonding not markedly affected by dilution. Just as with *o*-hydroxydiphenyl already mentioned, so, too, 2,2'-dihydroxydiphenyl appears to be anomalous.

In the case of *o*-hydroxydiphenyl, a dilute solution shows the main hydroxyl band at 3590 cm^{-1} , although there is a weak shoulder in the usual position at about 3610 cm^{-1} . In the solid a close doublet appears at 3560 cm^{-1} . Reference to a scale model of the molecule suggests that the size of the OH group is such that the planes of the two aromatic rings may be slightly oblique to each other. In any case, however, the distance between the oxygen atom and the 2'-carbon atom is within the value which would allow of a hydrogen bond being formed of the

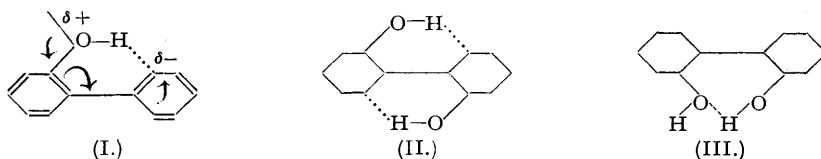
FIG. 4.



- | | |
|------------------------------|--|
| 1. <i>o</i> -3-Xylenol. | 9. <i>o</i> -Hydroxybenzyl alcohol. |
| 2. <i>o</i> -Ethylphenol. | 10. 3-Hydroxymethyl- <i>p</i> -cresol. |
| 3. <i>Mesitol</i> . | 11. 5-Hydroxymethyl- <i>o</i> -4-xenol. |
| 4. <i>m</i> -2-Xylenol. | 12. 3 : 5-Bishydroxymethyl- <i>p</i> -cresol. |
| 5. 2-Hydroxydiphenyl. | 13. 2 : 6-Bishydroxymethyl- <i>p</i> -tert.-butylphenol. |
| 6. 2 : 2'-Dihydroxydiphenyl. | 14. 2 : 2'-Dihydroxydiphenylmethane. |
| 7. Benzhydrol. | 15. 2 : 2'-Dihydroxy-5 : 5'-dimethyldiphenylmethane. |
| 8. Triphenylcarbinol. | 16. 2 : 2'-Dihydroxy-5 : 5'-di-tert.-butylphenylmethane. |

----- solid.
 ——— solution in CCl_4 .

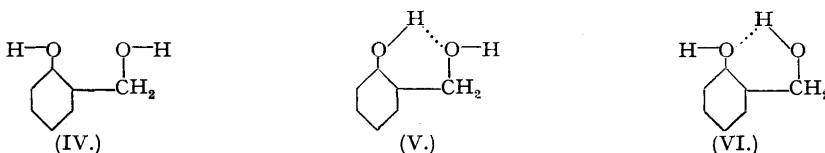
type $\text{-O-H}\cdots\text{C-}$. In this particular case the formation of such a bond might be assisted by the fractional charge which the 2'-carbon atoms may acquire owing to electronic displacements depicted in (I). The formation of $\text{-C-H}\cdots\text{O-}$ bridges has been established by infra-red and



other methods (*e.g.*, Gordy, *J. Chem. Physics*, 1940, **8**, 170; 1941, **9**, 204, 215; *J. Amer. Chem. Soc.*, 1938, **60**, 605; 1941, **63**, 1094; Buswell, Rodebush and Roy, *ibid.*, 1938, **60**, 252), and it is not unreasonable to expect $\text{-O-H}\cdots\text{C-}$ bonds in favourable circumstances. If there is internal bonding of this kind, it is not surprising to find only a small shift of the absorption band on passing from the solution to the solid. In this connexion, too, it is worth noting that *o*-hydroxydiphenyl melts at a much lower temperature than its *p*-isomer.

2 : 2'-Dihydroxydiphenyl in dilute solutions shows some similarities to *o*-hydroxydiphenyl. It may be noted that the strong band at 3560 cm.^{-1} is due to internal bonding of the type $\text{-O-H}\cdots\text{C-}$, as in (II), the broad band at 3610 cm.^{-1} to some unassociated hydroxyl groups, and the weak band at 3470 cm.^{-1} to bonded hydroxyl group of the type shown in (III).

With dilute solutions of compounds containing two close hydroxyl groups, two sharp bands were found at about 3610 and 3450 cm.^{-1} . The former must be due to free hydroxyl groups as in (IV). Internal bonding as in (V) or (VI) may give rise to the sharp band at 3450 cm.^{-1} which is sometimes hardly affected, or only slightly displaced, on passing to the solid. In the solid state there is indication of intermolecular bonding giving broader bands at lower frequencies ($3200\text{--}3350\text{ cm.}^{-1}$), as well as the intra-molecular bonding.



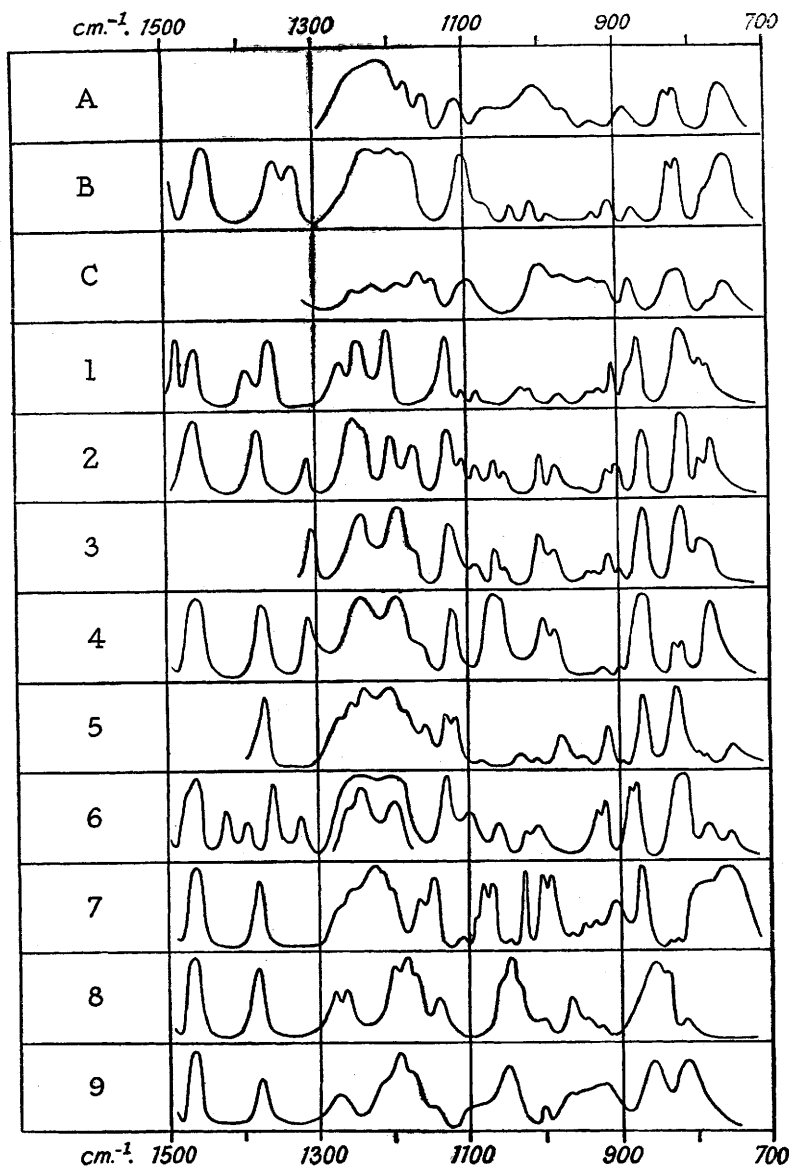
Some exploratory attempts have been made to measure the relative intensities of the bands due to the free and the bonded hydroxyl groups at different temperatures, since this should lead to a quantitative estimate of the strengths of the hydrogen bonds. The low boiling point of carbon tetrachloride makes it an unsuitable solvent, but carbon tetrabromide has been used in thickness up to 5 cm. at $3\ \mu$. The spectra of *o*-hydroxybenzyl alcohol in carbon tetrachloride at 20° , and in carbon tetrabromide at 100° , show a profound change in the relative intensities of the free and the bonded hydroxyl group bands. It is hoped shortly to extend these measurements by an improved method.

Fig. 5 shows the spectra between 700 and 1500 cm.^{-1} of some resins formed by the condensation of phenols with formaldehyde or acetaldehyde at various stages of the condensation, and there are examples of pairs of resins made from the same starting materials but having different physical properties, *e.g.* (2) and (3) from *p-tert.*-amylphenol and formaldehyde. The samples were measured either as solid films made by melting and allowing to solidify between rock salt plates, or by grinding to a paste with "Nujol." Undoubtedly a little free phenol must have been present in some of the starting materials, and there are signs that small amounts were present in the final resins. This must be taken into account in drawing conclusions from the measurements.

Clear differences exist between the spectra of the phenol-formaldehyde resins at different stages of condensation. In particular, the two-stage fusible resin differs from the one-stage resin in having a stronger band at about 1105 cm.^{-1} , and weaker absorption between 950 and 1050 cm.^{-1} . The two-stage infusible resin shows the band at 880 cm.^{-1} relatively more strongly, and has intense absorption between 900 and 1000 cm.^{-1} . All the other resins show significant differences in the region $900\text{--}1500\text{ cm.}^{-1}$. For example, (2) and (3), novolacs of different melting point made from *p-tert.*-amylphenol and formaldehyde, differ in the region $1100\text{--}1300\text{ cm.}^{-1}$, and the resol (4) has a strong band near 1070 cm.^{-1} which is probably connected with the $\text{-CH}_2\cdot\text{OH}$ group. The differences between the spectra of (8) and (9) reflect the different nature of the xylenols used in their preparation.

The spectral differences in the range 700—900 cm^{-1} are especially important, since as already explained the intense bands in this region may be associated with C-H deformations of different kinds of substituted benzene nucleus. In the one-stage phenol-formaldehyde resin the band

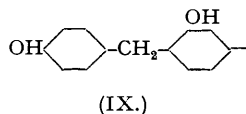
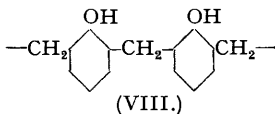
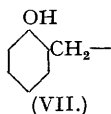
FIG. 5.



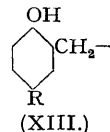
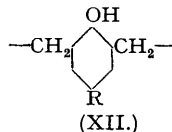
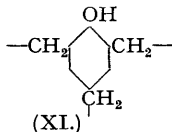
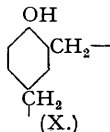
- | | |
|--|--|
| <p>A. Phenol-formaldehyde resin, one-stage.
 B. Phenol-formaldehyde resin, two-stage, fusible.
 C. Phenol-formaldehyde resin, two-stage, infusible.
 1. p-tert.-Butylphenol-formaldehyde, novolac.
 2. p-tert.-Amylphenol-formaldehyde, novolac.
 3. p-tert.-Amylphenol-formaldehyde, high m.p. novolac.</p> | <p>4. p-tert.-Amylphenol-formaldehyde, resol.
 5. p-tert.-Octylphenol-formaldehyde, novolac.
 6. p-tert.-Butylphenol-acetaldehyde, novolac.
 7. p-a-Phenylethylphenol-formaldehyde, novolac.
 8. Xylenol-formaldehyde, high m.p. novolac.
 9. Xylenol-formaldehyde, novolac.</p> |
|--|--|

at 750—760 cm^{-1} will be due to *o*-substituted nuclei, and to any residual free phenol. Such *o*-substituted groups will presumably be as in (VII), the end groups of a chain, and the intensity of the band suggests that such groups are relatively so numerous that the chain length must be

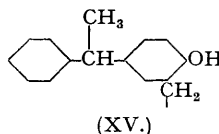
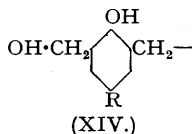
fairly short, say 4—8 aromatic nuclei. The weaker band at about 780 cm.^{-1} in the two-stage resins is probably due to 1 : 2 : 3-substituted rings of the type (VIII). The bands at 815 —



830 cm.^{-1} probably arise from *p*-substituted rings such as (IX), or 1 : 2 : 4-substituted rings such as (X). The band at about 880 cm.^{-1} may be due to tetra-substituted rings such as (XI), and it may be noted that in the two-stage infusible resin this band is strengthened, as would arise from further cross linking.



Resins (1), (2), (3), (5), and (6) all show strong bands at about 820 and 870 cm.^{-1} . The latter can be correlated with tetra-substituted nuclei as in (XII), and the former with 1 : 2 : 4-substituted nuclei such as (XIII). With the resol from *p-tert.*-amyphenol (4), the weak band at 820 cm.^{-1} may arise because the end groups are of the type (XIV), rather than (XIII). The



resol from *p-α*-phenylethylphenol is peculiar in having no appreciable band near 820 cm.^{-1} , and has intense absorption near 750 cm.^{-1} and 790 cm.^{-1} . The latter can be interpreted as arising from the monosubstituted phenyl group in (XV), and the strong shoulder at about 790 cm.^{-1} from the 1 : 2 : 4-substituted rings. The xylenol resins also differ from the others in this region, as might be expected since the nuclei must in this case be either tetra- or penta-substituted.

These examples serve to illustrate how useful structural correlations can be made, but it would be premature to discuss them in greater detail until resins can be examined which have been made from purer starting materials and by controlled methods of condensation.

The resins differ, however, in one other important feature, namely, the position of the band near 3μ due to the stretching vibration of the hydroxyl group. All the solid resins show a more or less broad band due to the hydrogen-bonded hydroxyl group, but its exact position varies in the different resins between 3200 and 3550 cm.^{-1} . Dilute solutions in carbon tetrachloride show a weak sharp band at about 3615 cm.^{-1} due to unassociated hydroxyl groups, together with the association band found with the solids and lying in about the same position as in the latter case. The results are shown in Fig. 6. It is noteworthy that (10) and (11), both novolac resins made from *p-tert.*-octylphenol and formaldehyde, have their bonded hydroxyl group bands at noticeably different frequencies.

The results show that in the resins there are hydrogen bridges of varying strengths. In some cases, more than one association band appears [*e.g.*, Fig. 6, Nos. (7), (1), and (2)]. This might arise from impurities in the starting materials, but is more probably due to different types of hydrogen bond within the same resin. With the exception of the weak band at 3615 cm.^{-1} in dilute solutions there is a close similarity between the spectra of a solid resin and of its solution. This suggests that the majority of the hydrogen bonds may be intramolecular, which would agree with the comparatively low melting points of these particular resins, and also with the inactivity of their hydroxyl groups towards diazomethane. If this is so, one factor in the "curing" of the resins might be a change from intra- to inter-molecular association. In the final heating intramolecular bonds may be opened, and larger complexes formed by inter-molecular association. Whilst such changes may only be one factor in the "curing" process, it might cause a considerable rise of melting point and hardness quite apart from that caused by further chemical condensations. The differences in the strengths of the hydrogen bonds in the solid novolacs are to some extent paralleled by differences in their physical properties.

This was well marked in the resins (10) and (11) shown in Fig. 6. A more exhaustive and controlled survey of this question is desirable.

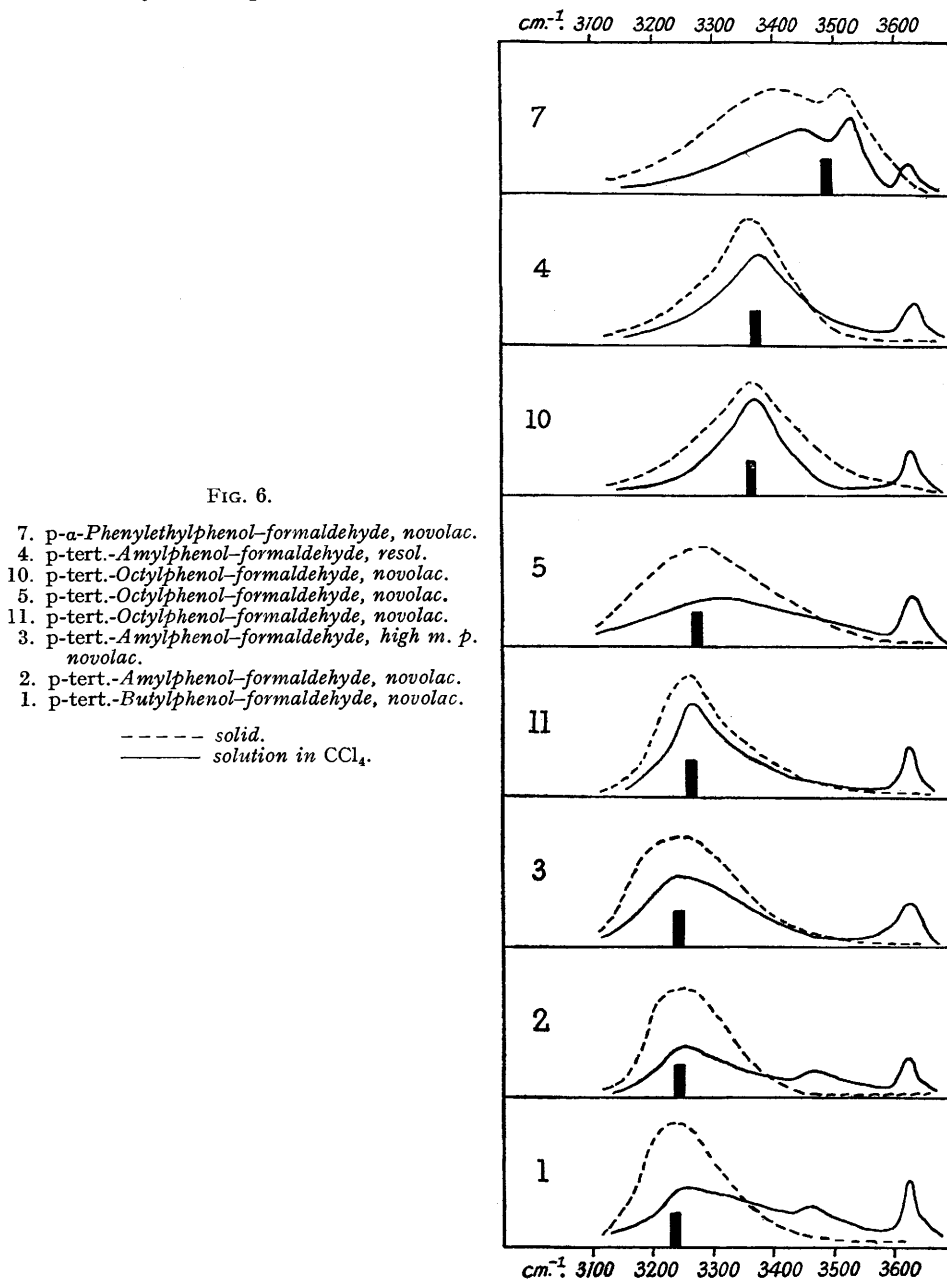


FIG. 6.

7. *p*-*a*-Phenylethylphenol-formaldehyde, novolac.
4. *p*-*tert*-Amylphenol-formaldehyde, resol.
10. *p*-*tert*-Octylphenol-formaldehyde, novolac.
5. *p*-*tert*-Octylphenol-formaldehyde, novolac.
11. *p*-*tert*-Octylphenol-formaldehyde, novolac.
3. *p*-*tert*-Amylphenol-formaldehyde, high m. *p*. novolac.
2. *p*-*tert*-Amylphenol-formaldehyde, novolac.
1. *p*-*tert*-Butylphenol-formaldehyde, novolac.

----- solid.
 ----- solution in CCl₄.

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