

121. *The Infra-red Spectra of Solid and Liquid Alkylphenols.*

By T. A. KLETZ and W. C. PRICE.

The infra-red spectra of twelve phenols have been obtained in the liquid and in the solid state in the range 5—15 μ . One of the most striking features of the spectra is the formation of doublets on crystallisation. This is interpreted as being due to association involving hydrogen bonds. Another noteworthy feature is a tendency for the bands to move towards shorter wave-lengths. Considerable changes of intensity occur in some of the bands, particularly those associated with the C—O valency vibration. This is attributed to specific types of hydrogen bonding occurring in the crystal. Crystallisation is also accompanied by a decrease in band width which is apparently due to the greater order prevailing in the crystal and the consequent reduction in collision broadening.

RELATIVELY little work has been done on the comparison of the infra-red spectra of organic substances in the crystalline and the liquid state. This field of investigation appears to be a promising one and must be regarded as an important part of a more general spectroscopic attack upon the solid state which is now engaging the attention of many spectroscopists from both the theoretical and the experimental point of view. It is to be expected that from the changes in the spectrum accompanying the change of state, some information might be found concerning (a) the nature of the intermolecular forces which hold the individual molecules together in the crystal lattice, (b) the particular isomeric configurations which are likely to be associated with different crystalline modifications, (c) the extent to which inter- and intra-molecular hydrogen bonding when present are involved in the formation of the lattice, (d) the influence of the crystal symmetry on the molecular motions, (e) the possibility of elucidating the types of environment occurring in the unit cell, etc. Some work has already been done on the Raman spectra of crystals by the Indian school of physicists, and some general theoretical treatment of selection rules, relative intensities, etc., in crystals is available (Bhagavantam and Venkatarayudu, *Proc. Indian Acad. Sci.*, 1939, 9 A, 224; 1941, 13 A, 543; Halford, *J. Chem. Physics*, 1946, 14, 8). It would be desirable to record the spectra of the gas, the liquid, and the solid, but in the present work this was not possible. The object here has been to attempt to classify empirically the effects which occur in a set of related molecules.

The general conclusions which have been derived from X-ray work on organic crystals are that they are predominantly molecular structures (in contrast to most inorganic crystals which are largely macromolecules) and that the molecules remain as discrete units in the lattice. The arrangement in the crystal depends upon the stoichiometric relations and relative sizes of the atoms rather than abrupt changes of chemical bond type. The present work is concerned with alkylphenols which have melting points in the range 25—80°. The examination in the solid and the liquid condition of the spectra of substances melting in this range does not require very elaborate apparatus, and it appeared possible that any results obtained might be correlated in some degree with the structure of the different alkylphenols and might yield some information concerning the factors mentioned in the previous paragraph.

Experimental.—The spectrometer used was a Hilger D. 209. It was fitted with a rock-salt prism and operated on single beam. On account of the extremely strong absorption of the materials being investigated, it was necessary to use cells of only 0.01 mm. thickness. The cell was placed on an electrically heated stage of special construction situated in front of the slit of the spectrometer. It was then filled with the molten phenol and its temperature was kept just above the m. p. of the substance for the recording of the liquid spectrum which was taken over the range 5—15 μ . After the record had been obtained the heating current was switched off and the substance allowed to crystallise. The scatter of the resulting thin crystalline layer was found to be much less than when a solid film was deposited on a rock-salt plate. In order to correct for scatter by the solid film, the amplification was adjusted so that the recorder deflection at a wave-length where no bands are present was the same for the solid and the

liquid. Schematic diagrams of the spectra obtained for a number of different phenols are shown in the figures. The thick vertical lines correspond to the centre of the band, and the oblique lines give some indication of its width. The ordinates are in percentage absorption.

Discussion.—The results obtained for 12 phenols are summarised in the table. One of the most striking features of the spectra of the solids is the band splitting which occurs for 9 out of the 12 substances investigated. Certain bands which appear single in the spectrum of the liquid are split into two or even three components in that of the solid. These components can appear as sharply resolved doublets or as pronounced shoulders when the resolution is inadequate for complete separation. The cases in which this occurs are set out in cols. 1, 2, and 3 of the table. A few instances are found in which the reverse phenomenon occurs. For these exceptions, which are indicated by a negative sign in the table, well-marked doublets are not formed in going from solid to liquid, but a single band in the solid appears as a band plus a shoulder in the liquid. Col. 4 gives the cases in which a band plus a shoulder in the liquid appears as a doublet in the solid.

Summary of changes occurring in the infra-red spectra of alkylphenols in passing from the liquid to the solid state.

Substance.	1.	2.	3.	4.	5.	6.	7.	8.
Phenol	+1	+1 -1	+2 -1		+3	+5 -1	Several minor decreases	+1 -3
<i>o</i> -Cresol	+3		+3	+1	+1	+4	Several minor changes	+7 -3
<i>p</i> -Cresol	+1*	+2	+4			+4	Little change	+6 -2
<i>p</i> -Ethylphenol					+1	+1	1 Large decrease	+3 -5
<i>o</i> -3-Xylenol	+1		+1			+1	9 Large decreases	+11 -2
<i>m</i> -4-Xylenol	+1	+1	+2	+1		+2	Little change	+14 -0
<i>p</i> -Xylenol		-1	-1		+4	+4 -1	Several minor changes; 1 big decrease	+10 -2
<i>m</i> -2-Xylenol	+2		+2	+2		+2	Several minor decreases	+8 -3
<i>o</i> -4-Xylenol	+2	+2	+4	+1		+4	Little change	+4 -1
<i>m</i> -5-Xylenol	+3*	+3	+7			+7	3 Large decreases	+5 -3
4-Ethyl- <i>m</i> -cresol	+1		+1		+1	+1	Several minor increases	+7 -3
5-Ethyl- <i>m</i> -cresol		-1	-1		+1 -1	+1 -2	Several minor increases	+6 -2

Col. 1. Number of bands which form doublets (or triplets) on crystallisation; * indicates that one band is split into a triplet.

„ 2. Number of bands which acquire shoulders on crystallisation.

„ 3. Total number of new frequencies formed by processes (1) and (2).

„ 4. Number of bands with shoulders which form doublets on crystallisation.

„ 5. Number of entirely new bands formed on crystallisation.

„ 6. Total number of new frequencies formed on crystallisation, *i.e.*, (3) and (5).

„ 7. Intensity changes on crystallisation.

„ 8. Number of bands for which the solid has higher (plus) or lower (minus) frequencies than the liquid.

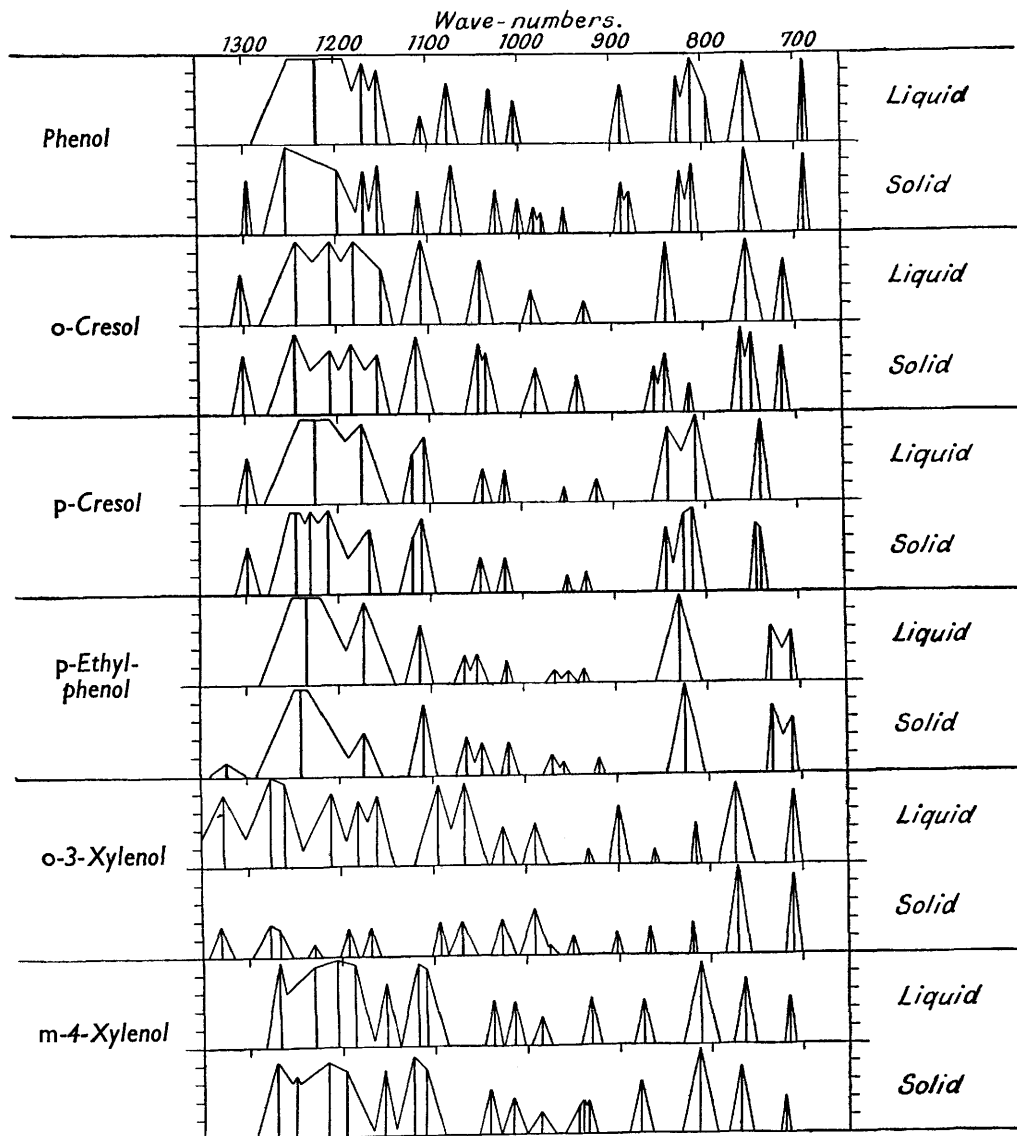
Throughout the table the negative sign refers to the reverse process.

The formation of new bands can arise from several causes. First, a decrease in band width may result in effectively higher resolution in the solid state. This is probably the explanation of the cases in which a band with a shoulder in the liquid appears as a doublet in the solid (col. 4), and possibly in some other cases as well. A similar effect can arise from a reduction in band intensity accompanying the change of state which might result in values of the per cent. absorption more favourable for resolution. The latter effect is almost certainly operative in the region of strong absorption around 1200 wave-numbers and accounts for some of the cases listed in cols. 1 and 2—*cf.* *p*-cresol. Other possible explanations of the formation of new bands are that a splitting of the energy levels may occur or that a transition forbidden in one state may become allowed in another as a result of the influence of the crystal symmetry and give rise to a new band in the immediate vicinity of a band common to both states. Such new bands would not, however, be expected to be strong in molecular crystals.

The explanations we favour for the appearance of such well-defined doublets as are present

e.g., in crystalline *o*-cresol at *ca.* 750, 850, and 1040 wave-numbers, are different from any of those cited above. The first is that two isomers are possible for many xylenols arising out of the two possible positions of the OH bond directed towards or away from an *o*-methyl group (resonance confines the OH bond to the plane of the ring but does not specify its direction). Although these two isomeric forms are possible in the liquid one may predominate on grounds of stability. On the other hand, the nature of the packing in the crystal may require the formation

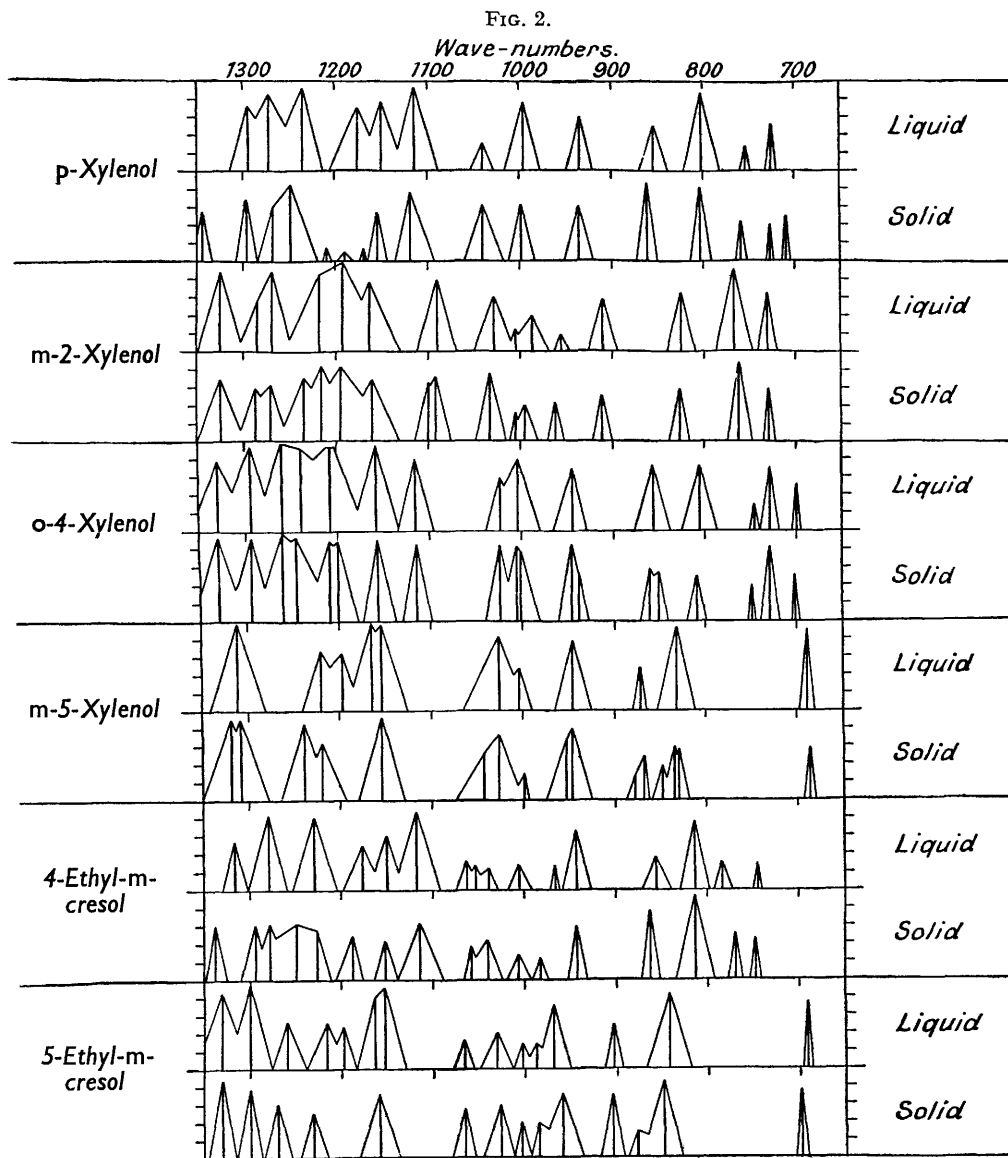
FIG. 1.



of a considerable proportion of the other. The second factor considered to be important is the occurrence in the unit cell of the crystal of two types of molecules differing in the nature of their environment. Even if all the molecules in the unit cell had the same isomeric form, it is highly probable that they could be classified according to their environment and these environmental effects are accentuated by the possibility of intermolecular hydrogen bonding. For example, some molecules in the unit cell may be packed in such a way that intermolecular hydrogen bonding may occur, while others may occupy positions in which such bonding is not possible.

It is noteworthy that the band in the region 730—840 wave-numbers, which has been interpreted as a deformation vibration involving the motion of the plane of the hydrogen atoms through the plane of the carbon atoms (Whiffen and Thompson, *J.*, 1945, 268), is sometimes split by the change from liquid to solid.

The absorption frequencies of corresponding bands in the solid and the liquid state usually differ by several wave-numbers, as can be seen from col. 8. In the great majority of cases the



frequency of the band in the solid is greater than that in the liquid. In previous work (Herzberg, "Infra-red and Raman Spectra of Polyatomic Molecules", Van Nostrand, N.Y., 1945, p. 532) it has been found that when the position of a band is altered in going from liquid to solid, the shift is generally to longer wave-lengths. This is in direct contradiction to what has been found here. The explanation appears to be that previous work has been concerned with substances like hydrogen chloride and hydrogen sulphide which probably form associative bonds in the solid which tend to weaken the original valency bond and thus to decrease the frequency of

vibrations in which it is involved. In the present case two possible causes are suggested to account for the increase in frequencies observed. In the long-wave-length region in which we have worked many of the bands arise from deformation vibrations. Although hydrogen bonding decreases the frequency of the valency vibrations, it should have the reverse effect upon deformation vibrations. The other possible cause of frequency increase is the repulsive forces between the peripheral atoms of molecules which come into operation whenever the latter approach closer than their van der Waals radii. The magnitudes of the observed shifts are usually of the order of 5 wave-numbers, which is small in comparison with shifts arising from associative effects in valency frequencies.

Col. 5 contains the number of bands appearing in the spectrum of the solid which do not occur in that of the liquid. Only in one case is a band present in the liquid spectrum but not in that of the solid.

Intensity changes in passing from solid to the liquid are summarised in col. 7. They are most marked in the region of strong absorption around 1200 wave-numbers, which is the region where modes involving the valency vibration of the strongly polar C-O bond are expected to occur. Of particular note are the large changes of intensity occurring in *o*-3-, *p*-, and *m*-5-xylenols. They probably arise from the partial annulment of the dipole-moment changes concerned in the absorption by the specific association present in the crystal. An increase of dipole moment occurring in the C-O bond is always accompanied by a decrease of dipole moment of the *associated* OH bond. This would have the effect of reducing the intensities of the bands involving vibrations in these bonds.

A phenomenon of very general occurrence is the decrease in band width which accompanies the passage from solid to liquid. This often results in the resolution in the spectrum of the solid of bands which only appear as shoulders in the spectrum of the liquid, as has been mentioned earlier in the discussion. Presumably this is to be related to the greater order prevailing in the crystal. In the liquid, intermolecular collisions result in a broadening of the energy levels, an effect which is not present in the case of the solid.

The hope that some of the liquid-solid changes might be correlated with the known structure of the different phenols has not yet been fulfilled to any extent. For instance, it was thought at first that doubling occurring in *o*-cresol might arise from the presence in the liquid of only one isomer in which the OH bond was directed towards the methyl group, and that in the crystal the isomer in which this bond was oppositely directed might also be present. However, doubling also occurs, though to a lesser extent, in *p*-cresol and *m*-5-xyleneol where only one isomer is possible. It thus appears that some other cause must be operative such as, for example, the presence in the unit cell of some molecules where the CO group is affected by hydrogen bonding and others where it is not. As more becomes known of the detailed structure of the xylenol spectra, further interpretation may become possible, and conversely, the study of the solid spectra may help in assigning the various bands. Although the present work has been confined to the long-wave region, it is intended also to investigate the shorter wave-length range, using a lithium fluoride prism. The simple valency vibrations involving hydrogen atoms occur in this range, and important changes in the spectrum may be expected to accompany crystallisation.

Our thanks are due to Dr. A. E. J. Vickers for his continued encouragement in the pursuit of problems of academic interest, and to Mr. A. Sumner for invaluable assistance with the experimental work.

RESEARCH DEPARTMENT, IMPERIAL CHEMICAL INDUSTRIES LIMITED,
BILLINGHAM DIVISION.

[Received, August 21st, 1946.]
