[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 516]

Note on the Interpretation of the Infra-red Absorption of Organic Compounds Containing Hydroxyl and Imino Groups

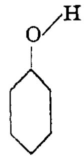
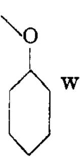
BY LINUS PAULING

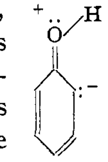
The extremely interesting and important quantitative studies of the infra-red absorption spectra of organic compounds in carbon tetrachloride solution being carried on by Wulf and his co-workers[1] promise to provide much information regarding the structure of molecules after the theory of the phenomenon has been formulated. In this note I suggest a simple interpretation of the observed spectra of compounds containing hydroxyl and imino groups.

Let us assume that the absorption observed in the neighborhood of 7000 cm.$^{-1}$ is due to the first overtone of the OH or NH oscillation, as stated by Wulf and Liddel, and that the large electric moment associated with the OH or NH oscillation is available for only one normal mode of vibration of the molecule, this being essentially the vibration of the hydrogen atom relative to the rest of the molecule. The explanation offered for the complexity of the observed spectra of some molecules is that the absorption is caused by two or more types of hydroxyl or imino groups, with different characteristic frequencies—the different groups being in different molecular species (*o*-chlorophenol) or in the same molecule (catechol).

Of the 32 compounds containing hydroxyl and imino groups studied by Wulf and Liddel, 21 show a single sharp absorption peak in the region between 6200 and 7200 cm.$^{-1}$. This indicates that for each of these latter substances (methanol, ethanol, isopropanol, methylisopropylcarbinol, methylphenylcarbinol, triphenylcarbinol, phenol, 2,4,6-trichlorophenol, *m*-nitrophenol, resorcinol, hydroquinone, *p*-hydroxybenzaldehyde, *p*-hydroxyacetophenone, carbazole, acetonylpyrrole, tetraphenylpyrrole, fluorenonimine, phenanthraquinonimine, diphenylamine, di-*n*-butylamine, and *o*-methoxybenzyl alcohol[2]) the OH or NH groups in all the dissolved molecules have nearly the same characteristic frequencies, and, moreover, that in the molecules containing two or more OH or NH groups (resorcinol, hydroquinone, acetonylpyrrole) there is very little interaction between these groups.

Phenol, 2,4,6-Trichlorophenol, and *o*-Chlorophenol

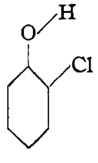
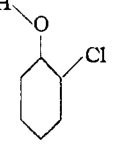
In phenol (and substituted phenols) the C–O bond has some double-bond character, resulting from resonance with structures such as I (in addition to the more important Kekulé-type structures). This double-bond character tends to cause the hydrogen atom to lie in the plane of the rest of the molecule. The phenol molecule can thus assume either of the two configurations  and  which, however, are equivalent, so that we expect for phenol only one molecular species and a sharp OH absorption peak, as observed at 7050 cm.$^{-1}$.



I

Similarly the two configurations for 2,4,6-trichlorophenol are equivalent, and we expect a single sharp absorption peak for this substance also. However, we can predict that it will occur at a lower frequency. Both the carbon–chlorine and the oxygen–hydrogen bonds have considerable ionic character, giving the chlorine atom a resultant negative charge and the hydrogen atom a resultant positive charge. These charges will cause the hydrogen atom to be attracted by the chlorine atom[3] and pulled away from the oxygen atom; by Badger's rule[4] we predict that this will lead to a decrease in the OH frequency. The decrease is observed, the peak for this substance occurring at 6890 cm.$^{-1}$.

For *o*-chlorophenol the two configurations

 (*cis*) and  (*trans*)

are not equivalent. We expect these two molecu-

---

[1] O. R. Wulf and U. Liddel, THIS JOURNAL, **57**, 1464 (1935); see also U. Liddel and O. R. Wulf, *ibid.*, **55**, 3574 (1933); and G. E. Hilbert, O. R. Wulf, S. B. Hendricks and U. Liddel, *Nature*, **135**, 147 (1935).

[2] The peaks for the last three are not so sharp as for the others.

[3] The effect may be intensified by interaction of the hydrogen atom and an adjacent unshared electron pair of the chlorine atom.

[4] R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934).

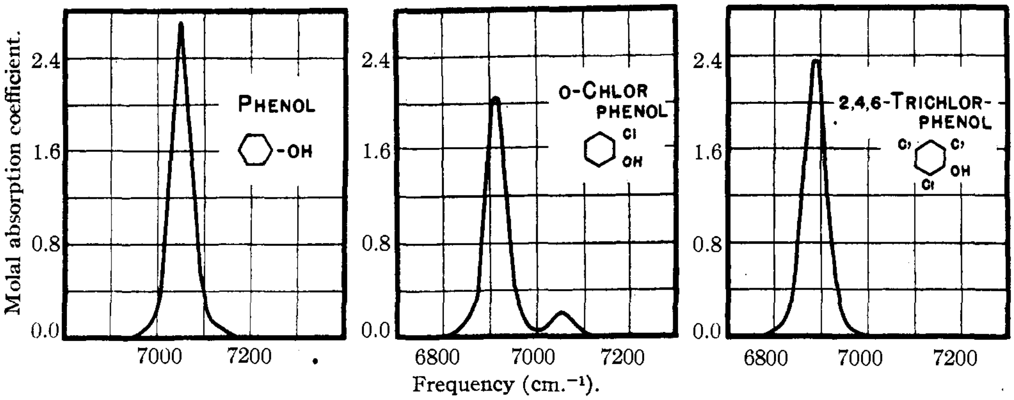


Fig. 1.—Absorption curves for phenol, *o*-chlorophenol and 2,4,6-trichlorophenol (from Wulf and Liddel).

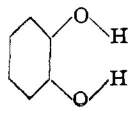
lar species to be present in solution, with the *cis* form outnumbering the *trans* because of the stabilizing effect of the H–Cl interaction. Hence we can predict that the spectrum of this substance should show two peaks, one at 7050 cm.$^{-1}$ (*trans* form, frequency as in phenol, the H–Cl interaction being negligible) and one at 6890 cm.$^{-1}$ (*cis* form, frequency as in 2,4,6-trichlorophenol), the peak at 6890 cm.$^{-1}$ being the larger. This is in complete agreement with experiment; two peaks are observed, at 7050 cm.$^{-1}$ and 6910 cm.$^{-1}$, the area of the latter being about ten times that of the former.

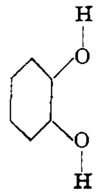
Thus from the infra-red absorption we learn that in solution in carbon tetrachloride *o*-chlorophenol consists of about 91% *cis* and 9% *trans* molecules, the free energy difference of the two forms being about 1400 cal./mole. It is interesting that the peaks are well resolved, showing that molecules with intermediate configurations are not present in appreciable amounts.

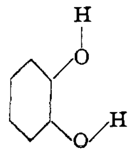
A straightforward test of this interpretation of the spectrum of *o*-chlorophenol can be made by determining the effect of change of temperature on the relative areas of the two peaks. This investigation has been begun by Wulf and Liddel.

The Structure of Catechol

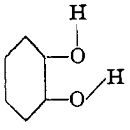
Catechol shows two nearly equal peaks, with wave numbers 6970 cm.$^{-1}$ and 7060 cm.$^{-1}$. For this substance we predict the three configurations







We expect, however, that the third of these is more stable than the other two, inasmuch as it is stabilized relative to the second by an O–H interaction, while the first is made unstable by repulsion of the similarly charged hydrogen atoms. If only the third configuration is represented by the solute molecules, we expect two absorption peaks of the same size, one at about 7050 cm.$^{-1}$, as in phenol, due to the *trans* OH, and one at a lower frequency, due to the *cis* OH, the hydrogen atom of which is attracted by the *trans* oxygen atom.[5] The agreement with experiment (especially the equal areas of the two peaks) supports the prediction that the *cis-cis* and *trans-trans* molecular species are not represented to an appreciable extent, the *cis-trans* form being the stable form in solution.



The wave number change in catechol, 90 cm.$^{-1}$, is less than that in *o*-chlorophenol, 140 cm.$^{-1}$, showing the attraction of the hydrogen atom by the negative atom to be less in catechol than in *o*-chlorophenol.

Proton Attraction in Other Molecules

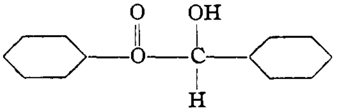
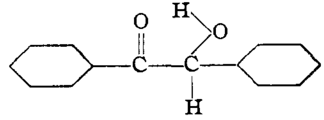
In catechol and *o*-chlorophenol the attraction of the partially shielded proton (hydrogen atom with some positive charge) by a negative atom is large enough to stabilize the configuration in which the O–H axis is directed toward the attracting atom. We might describe such a configuration as involving a weak hydrogen bond. (The energy of this bond we have evaluated as 1400 cal./mole in *o*-chlorophenol, as compared with 5000–8000 cal./mole for a strong hydrogen bond.)

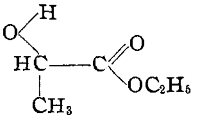
---

(5) We have assumed that the interaction of the two OH's is small compared with the interaction of the *cis* H and the *trans* O, the two normal modes of vibration then being essentially located in the two OH groups.

It has been shown by Hilbert, Wulf, Hendricks, and Liddel[6] that the formation of a strong hydrogen bond leads to extinction of the absorption in the 7000 cm.$^{-1}$ region, this extinction thus providing a very important means for testing for the presence of strong hydrogen bonds. The mechanism of extinction of the absorption band in this region through hydrogen-bond formation is not understood. It may be related to the broadening and decrease in area of the peaks for some substances, such as *o*-methoxybenzyl alcohol, as discussed by Wulf and Liddel.

The absorption curves given by Wulf and Liddel can be interpreted as showing proton attraction and weak hydrogen-bond formation in several molecules other than those already mentioned.

Benzoin.—The absorption curve for benzoin  consists of a large broad peak at about 6740 cm.$^{-1}$ and a small broad peak at about 7080 cm.$^{-1}$. The first we interpret as showing the presence of a large number of molecules with the configuration  and the second as due to other configurations. The proton attraction in this molecule is large, causing a wave number change of 340 cm.$^{-1}$, which indicates that the hydrogen bond is over twice as strong as in *o*-chlorophenol. This is no doubt the result of the large negative charge on the ketonic oxygen atom, the dipole moment of ketones being very large (about 2.8×10^{-18} e. s. u.).

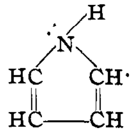
Ethyl Lactate and Ethyl Tartrate.—Each of the substances ethyl lactate and ethyl tartrate[7] shows a large broad peak at about 6900 cm.$^{-1}$ and a small peak at 7050 cm.$^{-1}$. (In addition some absorption is observed out to 7400 cm.$^{-1}$.) The peaks at 6900 cm.$^{-1}$ we attribute to the configuration  for the lactate and a similar one for the tartrate, and the small peaks at 7050 cm.$^{-1}$ to other configurations. The magnitude of the proton attraction indicated by the observed wave number change is about the same as in *o*-chlorophenol.

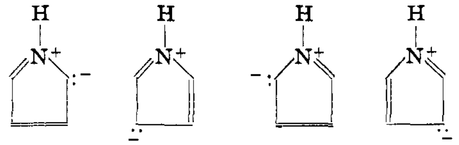
Other Substances.—We would interpret the large broad peak at 6600 cm.$^{-1}$ and the small broad peak at 6830 cm.$^{-1}$ shown by 8-hydroxyquinoline as due to *cis* and *trans* configurations (relative to the nitrogen atom), respectively, except for the fact that we expect for the latter[8] the wave number 7050 cm.$^{-1}$. The discrepancy makes this interpretation doubtful.

o-Methoxybenzyl alcohol and ethylene glycol monoacetate show broad peaks at 7050–7100 cm.$^{-1}$, the latter with indication of a doublet. There is accordingly only very little proton attraction in molecules of these substances.

The Structure of Pyrrole and Related Substances

The absorption curve for pyrrole consists of a large sharp peak with a small (not completely resolved) satellite on the low frequency side, the separation of the two being about 50 cm.$^{-1}$. Wulf and Liddel have suggested that this splitting is the result of interaction of the NH group with adjacent CH groups, whereby the effective electric moment of the NH group is divided between two normal modes of vibration involving both NH and CH. In the following paragraphs an alternative interpretation is offered.[9]

The valence bond structure usually written for pyrrole is  For this structure the hydrogen atom attached to nitrogen would not lie in the plane of the ring, but to one side, so as to give the angles of the nitrogen bonds approximately the tetrahedral value. However, the normal pyrrole molecule resonates between this structure and the four structures



these four tending to keep the hydrogen atom in the plane of the ring. We do not have enough knowledge of resonance to predict confidently the configuration of the resonating pyrrole molecule. It is possible that the potential function for the

---

(6) Ref. 1; see also J. Errera and P. Mollet [*J. phys. radium*, **6**, 281 (1935)] who have made similar studies on pure liquids.

(7) No. 32, Fig. 3, Wulf and Liddel, ref. 1.

(8) Dr. Wulf has informed me that there is some evidence for a very small peak at 7050 cm.$^{-1}$.

(9) A decision between the two suggestions could be made by studying the effect of change of temperature of the solution on the absorption curve, the first interpretation requiring that there be no effect, and the second that the satellite become larger with increasing temperature.

hydrogen atom has three minima, one in the plane of the ring (resulting from the contribution of the four ionic structures) and one on each side of this plane[10] (resulting from the contribution of the usual valence bond structure). There would then be two molecular species in a solution of pyrrole, consisting of the coplanar and the non-coplanar molecules, respectively, and a splitting of the N–H absorption would be observed. We attribute the observed large peak to the coplanar molecules and the small peak (at smaller wave number) to the non-coplanar molecules.

A more detailed description of the pyrrole molecule in its normal electronic state according to this conception may be given. For each configuration of the nuclei the molecule has a definite electronic structure and corresponding electronic energy, the energy function having its minimum value when all the nuclei are coplanar, and in addition having minima also for two configurations in which the imino hydrogen is displaced to one side of the plane of the ring. For each configuration the actual electronic structure can be approximated closely as a combination of the valence bond structures represented above. The contribution of these structures is dependent to some extent on the configuration, that of the usual valence bond structure being somewhat greater for the non-coplanar configuration than for the coplanar configuration; for each configuration, however, all five structures contribute appreciably.

Some support for this interpretation is provided by the absorption curves for other substances. Many more ionic structures can be written for carbazole and tetraphenylpyrrole than for pyrrole, so that the coplanar configuration should be further stabilized for these molecules. This is supported by the observation of a single sharp peak for these molecules. (We would also expect the satellite for indole to be smaller than for pyrrole, for the same reason; the observed absorption curves for the two compounds are, however, actually closely similar.) Moreover, the bond angles in acetonylpyrrole require that the four pyrrole rings be nearly coplanar. This would bring the hydrogen atoms within about 1.5 Å. of one another for the configuration in which each is coplanar with its pyrrole ring. The usual minimum distance of approach of non-bonded hydrogen atoms is about 2 Å. Hence we expect each pyrrole group to assume a non-coplanar configuration, two hydrogen atoms lying on one side and two on the other side of the plane of the entire molecule. This is in agreement with the observation of a single sharp absorption peak at lower frequency than for other pyrrole derivatives.

Phenanthraquinonimine shows a single absorption peak at about the same wave number as for fluorenonimine. This indicates that the attraction of carbonyl oxygen for imino hydrogen is much less than for hydroxyl hydrogen, the *cis* and *trans* forms not giving resolvable peaks. The two peaks of acetanilide we consequently interpret as due not to proton attraction (which would indeed be expected to make the low-frequency *cis* peak larger than the other, contrary to observation) but rather to the presence of coplanar and non-coplanar forms, as for pyrrole. The same effect may be operative to a small extent in diphenylamine and dinaphthylamine, the peaks being not resolved, however.

Several explanations of the observed doubling of the absorption curve for hydrazobenzene can be offered, a decision among them being difficult at present.

It should be pointed out that the interpretation of the observed structure of infra-red absorption spectra given here as arising in part from more than one molecular species may be extended into other fields of spectroscopy, such as the Raman effect, to account for the observation of a larger number of lines than anticipated for a single molecular configuration.

I am indebted to Dr. Oliver Wulf for calling my attention to this field by discussing with me his observations and various interpretations of them, and for giving much advice in regard to the interpretation suggested in this note.

Summary

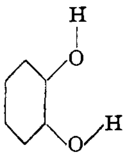
The infra-red absorption spectra of substances in carbon tetrachloride solution obtained by Wulf and Liddel are interpreted to lead to the following conclusions.

1. *o*-Chlorophenol exists in a *cis* form (91%) and a *trans* form (9%), the *cis* form being more stable than the *trans* by 1400 cal./mole, as a result of attraction of the partially shielded proton by the chlorine atom (weak hydrogen bond formation).

2. The catechol molecule has the *cis-trans* configuration

---

[10] These minima would be displaced somewhat toward the plane from the tetrahedral positions as a result of incomplete resolution from the more pronounced minimum in the plane.



3. Proton attraction by oxygen atoms also occurs in benzoin, ethyl lactate and other molecules.

4. It is suggested that pyrrole molecules exist in solution in a coplanar form, the NH hydrogen being in the plane of the ring, and also (to a smaller extent) in a non-coplanar form. Only the coplanar molecules of carbazole and tetraphenylpyrrole and the non-coplanar molecules of acetonylpyrrole occur in appreciable quantities.

PASADENA, CALIFORNIA RECEIVED NOVEMBER 25, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Induced Substitution of Pentene by Chlorine

BY T. D. STEWART AND BERNHARDT WEIDENBAUM

We have previously[1,2] reported the reactions of chlorine with benzene and *n*-pentane, as induced by ethylene. The present work is a study of the coupled reactions

$$C_2H_5CH{=}CH{-}CH_3 + Cl_2 \longrightarrow C_2H_5{-}CHCl{-}CHCl{-}CH_3 \quad (1)$$

$$C_2H_5CH{=}CH{-}CH_3 + Cl_2 \longrightarrow C_2H_5{-}CH{=}CH{-}CH_2Cl + HCl \quad (2)$$

2-Pentene and chlorine were dissolved separately in carbon tetrachloride, in known concentrations, and measured volumes of the two solutions mixed rapidly.

Preparation of Materials

Purification of most of the reagents has been described.[2] 2-Pentene (E. K. Co.) was fractionated, and the portion of b. p. 36.2–36.4° was used. 2-Chloropropene was prepared from acetone and phosphorus pentachloride,[3] and distilled at 23.0°. Kahlbaum allyl chloride was used without further purification. 1-Phenyl-2-propene was prepared from phenylmagnesium bromide and allyl bromide.[4] The fraction distilling from 155–157° was used. All reagents were carefully dried.

Experimental Results

In Table I the concentrations of reagents given refer to the calculated initial concentrations after mixing of the stock solutions. By induction factor is meant the ratio of the moles of chlorine producing hydrogen chloride to the moles of chlorine reacting by addition. Fifteen seconds were allowed for completion of the reaction. From two to four experiments were made at each dilution, varying the order of addition of the reactants.

TABLE I

THE RELATIVE AMOUNTS OF SUBSTITUTION AND ADDITION BY CHLORINE REACTING WITH 2-PENTENE IN PURE CARBON TETRACHLORIDE, IN THE ABSENCE OF OXYGEN

Concentration in moles/liter Chlorine	2-Pentene	Induction factor
0.101	0.097	1.23
.0464	.097	1.60–1.64
.101	.051	0.57
.0464	.051	0.88–0.93
.00954	.051	3.04–3.24
.0464	.0097	0.72–0.78

The substitution reaction was favored by a relative increase in the 2-pentene concentration, or by a relative decrease in the chlorine concentration.

Similar results were obtained in the presence of oxygen, *p*-thiocresol and when commercial carbon tetrachloride was used as solvent.

TABLE II

EXPERIMENTS IN THE PRESENCE OF OXYGEN (A), *p*-THIOCRESOL, 0.018 *M* (B) AND COMMERCIAL CCl_4 (C)

	Concentration in moles/liter Chlorine	2-Pentene	Induction factor
A	0.0104	0.0122	1.11–1.20
	.0064	.0122	2.03
	.0021	.0122	3.22
B	.0104	.0122	1.28–1.31
C	.00954	.0097	1.17–1.32

In Table III are given the results of a series of experiments performed at −10° and at 25.1°. Change of temperature produces little change in the induction factor.

Other attempts to cause a significant change in the induction factor under constant initial concentration of reagents failed; the presence of water, hydrogen chloride and powdered glass, respectively, had no effect.

When 1-phenyl-2-propene was used instead of 2-pentene, the reaction was found to be rapid, but

---

[1] Stewart and Hanson, THIS JOURNAL, **53**, 1121 (1931).

[2] Stewart and Hanson, *ibid.*, **57**, 2036 (1935).

[3] Friedel, *Ann.*, **112**, 236 (1859).

[4] Tiffeneau, *Compt. rend.*, **139**, 482 (1904).