

sociation constants from the second, fourth, fifth, and sixth most dilute points are, respectively, 1.7, 2.9, 4.0 and 3.3, averaging 3.0.

Potassium Metaperiodate.^{4c}— Λ_0 obtained = 128.05 ± 0.02 , giving 54.53 ± 0.02 for the metaperiodate ion. This is somewhat higher than the value of 54.38 given by Jones. Dissociation constants from the third, fourth and fifth most dilute points are, respectively, 0.55, 0.56 and 0.59, averaging 0.57.

Potassium Perrhenate.—^{4c} Λ_0 obtained = 128.47 ± 0.02 , giving 54.95 ± 0.02 for the perrhenate ion, again somewhat higher than the quoted value of 54.68. Dissociation constants from the four most dilute points are 0.15, 0.17, 0.21 and 0.23, respectively, averaging 0.19.

Silver Chlorate.^{4d}— Λ_0 obtained = 126.50 ± 0.02 , giving 64.58 ± 0.02 for the chlorate ion (based on 61.92 for the silver ion,¹⁰ corrected to the standard of Jones and Bradshaw⁷); this is somewhat lower than the quoted value of 64.65. Dissociation constants calculated from the first,

second and fourth most dilute points are 0.54, 0.57 and 0.71, respectively, averaging 0.6.

Summary

The conductance of potassium iodate has been measured over the range 0.0002 to 0.004 molar at 25°. The Owen method² of extrapolation has been found to be satisfactory in this and some other cases where the Shedlovsky method³ fails. The dissociation constants of this and some other salts are reported. From the results the following anion conductances are evaluated: iodate = 40.75, bromate = 55.84, perchlorate = 67.31, metaperiodate = 54.53, perrhenate = 54.95 and chlorate = 64.58, all within 0.02 to 0.03 unit. The following dissociation constants were obtained using the method of Davies⁵: potassium iodate = 1.7, potassium bromate = 4.0, potassium perchlorate = 3.0, potassium metaperiodate = 0.57, potassium perrhenate = 0.19 and silver chlorate = 0.6.

ABERYSTWYTH, WALES

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Influence of Solvent, Hydrogen Bonding, Temperature and Conjugation on the Ultraviolet Spectra of Phenols and Aromatic Hydrocarbons¹

BY NORMAN D. COGGESHALL AND ELEANOR M. LANG^{1a}

It is well known that for some ultraviolet absorbing compounds the absorption spectra are dependent on the nature of the solvents used. For example, the spectrum obtained from a simple phenol in a paraffin solvent will be considerably different for that obtained with ethyl alcohol as the solvent. For the latter the spectrum is changed in shape from the former and shifted to the red. This phenomenon is quite general among the polar substituted aromatics.

It has been assumed that highly polar structures make a greater contribution to the excited than to the ground states of such compounds as polar substituted aromatics.² From this it follows that any factors which stabilize these structures will decrease the energy of transition and shift the absorption bands to longer wave lengths. The shifts to longer wave lengths that occur for such compounds when examined in a polar solvent as compared to similar data obtained for a neutral solvent may then be explained on this basis.

The present investigation was concerned with some of the factors expected to be effective in stabilizing the excited polar structures. Such stabilization would result from electrostatic or dipole

interaction of the hydrogen bonding type, between the ionic structure of the excited state of the solute molecule and the polar component of the solvent molecule. Recent studies, by infrared absorption, of steric hindrance to hydrogen bonding in substituted phenols³ furnish useful information for the correlation of these spectral shifts with the known hydrogen bonding characteristics of the phenols. It was shown from the infrared data that large alkyl groups such as *t*-butyl on one or both the ortho positions of a phenol are effective in hindering inter-molecular hydrogen bonding. These studies gave a classification of phenols into three classes: hindered, partially hindered, and unhindered. The same series of phenols were studied in this investigation.

Errera and Sack⁴ found that the population of intermolecular complexes between ethyl alcohol and dioxane in a carbon tetrachloride solution is very strongly reduced by a change in temperature from 20 to 55°. From the infrared spectral changes it is believed that the energy per complex for association between a phenol and an alcohol solvent will be of the same order of magnitude as for the type of complex studied by Errera and Sack. Consequently, the ultraviolet spectra of the phenols in alcohol solution as a function of temperature should clarify the role of stable com-

(1) Presented in part before the Division of Physical Chemistry at the 112th American Chemical Society meeting, New York, September, 1947.

(1a) Now at Camp Detrick, Frederick, Maryland.

(2) C. Curran, Paper P6, American Chemical Society meeting, Chicago, September, 1946.

(3) N. D. Coggeshall, *THIS JOURNAL*, **69**, 1620 (1947).

(4) J. Errera and H. Sack, *Trans. Faraday Soc.*, **34**, 728 (1938).

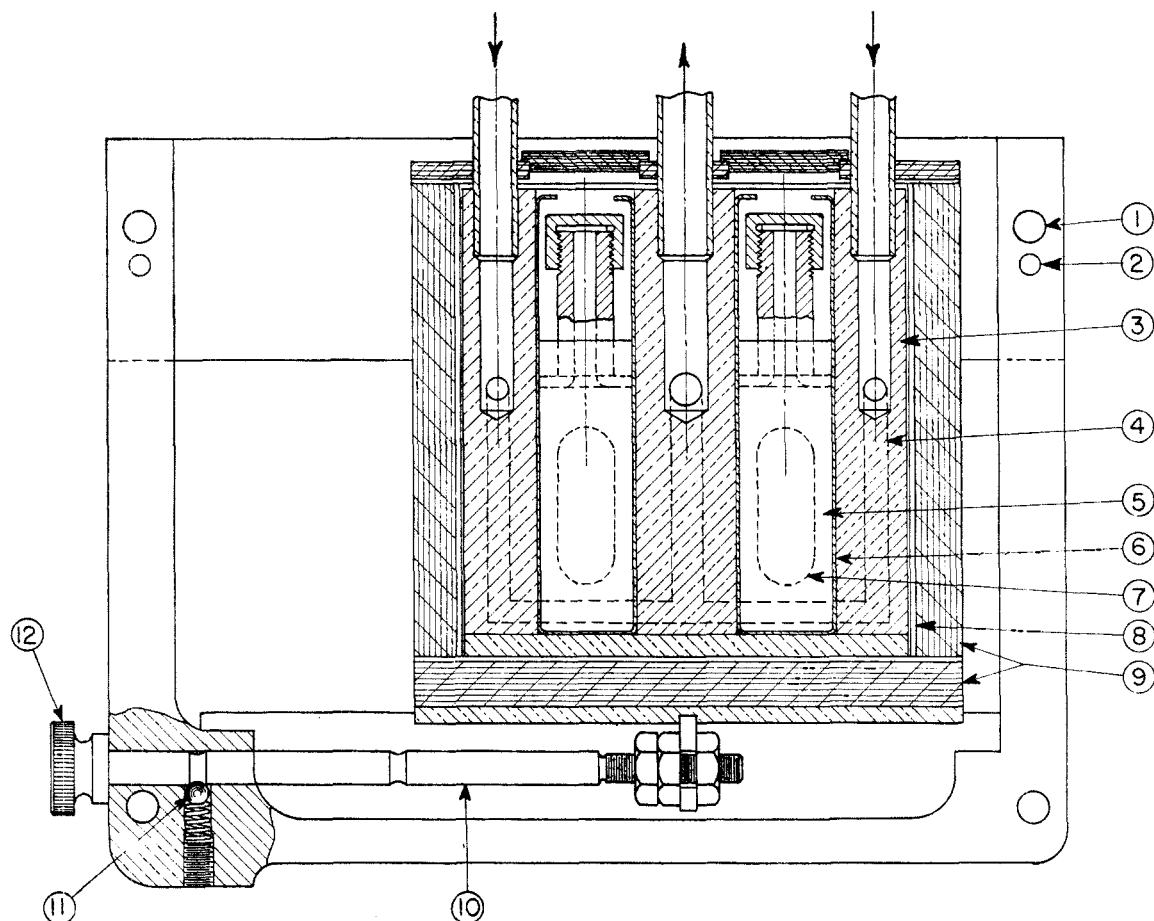


Fig. 1.—Schematic diagram of temperature controlled absorption cell compartment.

plexes in the processes responsible for the spectral changes. For this reason a temperature controlled cell compartment was constructed and utilized.

Since the instantaneous dipole moment of the polar form of an excited molecule will depend upon its geometrical extension, a number of aromatic compounds of varying degrees of conjugation and extension were studied. An effect was found for the diphenylbenzene isomers which confirms the above assumptions concerning the alteration of the spectra. Consideration has been given to the change of shape of the spectra as well as to the shifting of bands to the red. Tentative explanations, based on considerations of the intermolecular interactions, have been formulated for the observed results.

Experimental

All the absorption spectroscopic data were obtained with a standard Beckman Quartz Spectrophotometer. The substituted phenols were prepared in this Laboratory^{5,6} and each was believed to be at least 99% pure. The other compounds were the best obtainable commercially and, when necessary, were further purified by recrystallization.

(5) D. R. Stevens, *Ind. Eng. Chem.*, **35**, 655 (1943).

(6) G. H. Stillson, D. W. Sawyer and C. K. Hunt, *THIS JOURNAL*, **67**, 303 (1945).

The solvents used were isoöctane (2,2,4-trimethylpentane), absolute ethanol and distilled water. Effects due to benzene in the ethanol were eliminated by using the solvent for the sample and for the comparison cell from the same bottle.

In order to study the temperature dependence of the various spectra a constant temperature cell compartment suitable for use with the Beckman Spectrophotometer was designed. In the design of this, which is in some ways similar to the one recently described by Bell and Stryker,⁷ a number of specific objectives were kept in mind: the assembly would be kept at constant temperature by the circulation of water from a commercial constant temperature bath, all essential components would be integrated in a removable assembly, and this assembly would occupy the place of the regular cell compartment.

The essential elements of this assembly are seen in Fig. 1. Here 1 represents one of the four holes through which the retaining screws pass. The small hole 2 is one of two dowel holes which serve to position the unit relative to the body of the spectrometer. The heart of the device is represented by 3. It is a machined brass block through which the water circulates. There are two inlet and one outlet ports for the water, as indicated by the arrows. The channels for these are drilled about halfway through the block. Each then divides into two smaller channels, one of which is represented by 4. These smaller channels are located symmetrically relative to the center plane of the block which is represented by the figure. Also, in the block are milled two square holes which accommodate the cells, one of which is represented by 5. These cells are

(7) P. H. Bell and C. R. Stryker, *Science*, **105**, 414 (1947).

enclosed on three sides by metal strips 6, which are used for insertion and removal.

Two windows, indicated by 7, are cut through the brass block to communicate with each hole containing a cell. The light passes through these in a direction perpendicular to the plane of the figure.

The brass block is surrounded by a Bakelite housing 9. Between the Bakelite and the block are strips of felt 8. This combination has proven to be quite effective insulation. Openings are cut in front and back sides to match the windows in the block. Onto the Bakelite and over these openings are sealed thin quartz windows (about $\frac{3}{32}$ " thick). The assembly is moved back and forth by the rod 10, to which is attached the knurled knob 12. It is held in either one of two pre-determined positions by a ball-lock 11.

Since the samples under examination are varied in temperature, it is necessary that the cells be vapor tight. A cross section of such a cell is seen in Fig. 2. Here the cell body is represented by 17. The unit 16 is a filling port. Units 16 and 17 are sealed together by means of Sauer-eisen⁸ cement 13. Units 16 and 15 are of Invar metal. A solid lead washer 14 is used to make a seal when the cap is tightened on 16.

Fig. 2.—Schematic diagram of vapor-tight absorp-tion cell.

Data and Discussion

A. Behavior of the Substituted Phenols; Spectral Changes and Steric Hindrance to Hydrogen Bonding.—Since the phenols as a class exhibit strong dependence of spectra on the type of solvent used, and since definite information concerning their hydrogen bonding characteristics is now available,³ a large part of this investigation deals with them. In Fig. 3 may be seen the data for the unhindered phenol *p-t*-butylphenol. Two major differences between the spectra are observable. The spectrum for the ethanol solvent is shifted considerably to the longer wave lengths, or red portion of the spectrum. The other difference is in the shape and intensity of the bands. We note that the detailed structure of the band near 280 $m\mu$ as obtained in the isoöctane is almost completely blurred out when the alcohol is used. These two effects are characteristic, in varying degrees, of all the phenols. The results for another unhindered phenol may be seen in Fig. 4, which refers to *p*-cresol. The same two effects of wave length shift to the red and blurring of band structure are rather prominently displayed here.

An example of one of the partially hindered phenols may be seen in Fig. 5, for 2,4-di-*t*-butylphenol. Here again the same two effects may be seen. It is also to be noticed that the degree of detailed structure for the fundamental band centering near 275 $m\mu$ in iso-octane is less than observed for the simpler phenols. The behavior of this phenol is essentially representative of the other partially hindered phenols examined.

The results for one of the hindered phenols may

(8) Mfd. by Sauereisen Cements Co., Pittsburgh, Pa.

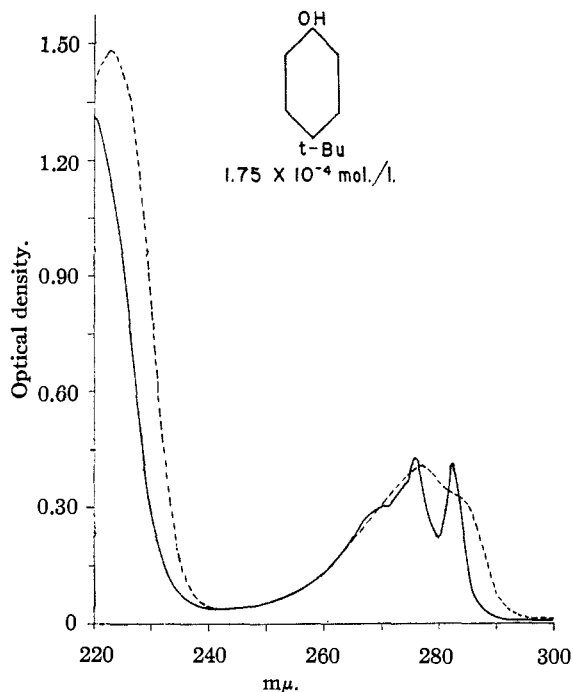


Fig. 3.—Ultraviolet absorption spectra of *p-t*-butylphenol, solid curve for isoöctane solution, dashed curve for alcohol solution.

be seen in Fig. 6, which is for 2,6-di-*t*-butyl-4-cyclohexylphenol. We note here that the shift to the red of the fundamental absorption band is greatly reduced, in comparison to the above com-

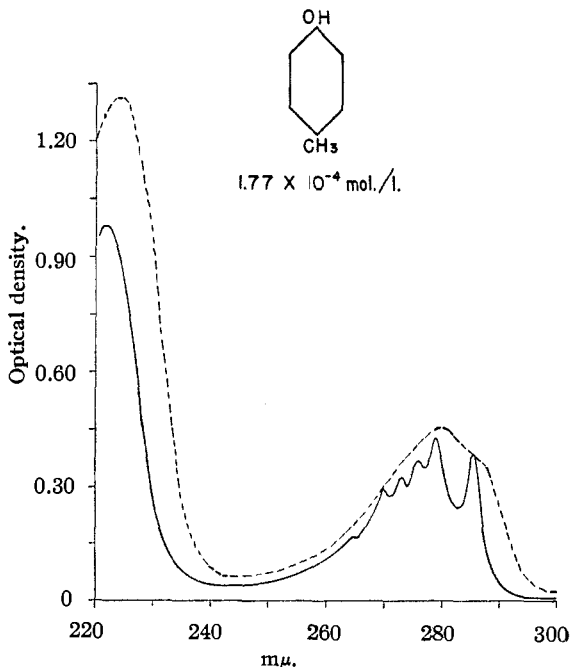


Fig. 4.—Ultraviolet absorption spectra of *p*-cresol, solid curve for isoöctane solution, dashed curve for alcohol solution.

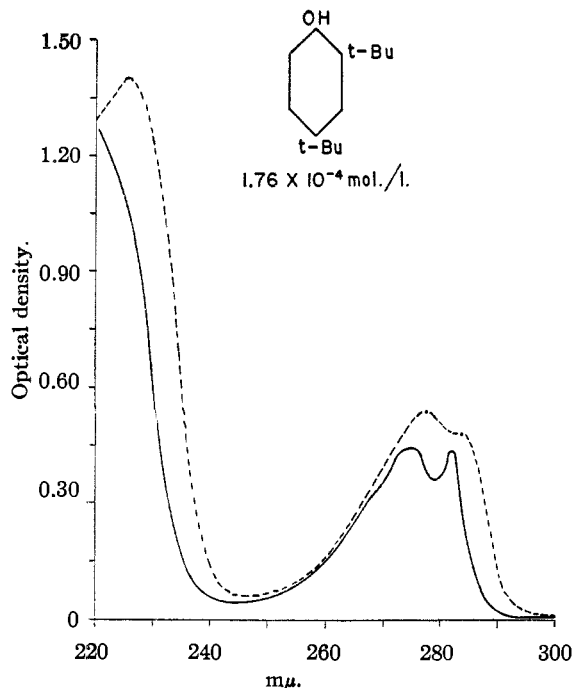


Fig. 5.—Ultraviolet absorption spectra of 2,4-di-*t*-butylphenol, solid curve for isoöctane solution, dashed curve for alcohol solution.

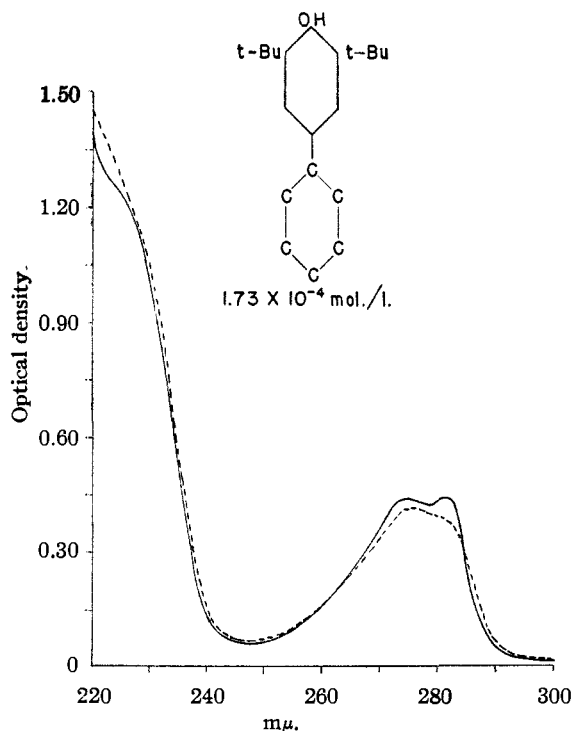


Fig. 6.—Ultraviolet absorption spectra of 2,6-di-*t*-butyl-4-cyclohexylphenol, solid curve for isoöctane solution, dashed curve for alcohol solution.

pounds. Another hindered phenol, exhibiting a very small shift to the red, is seen in Fig. 7 which

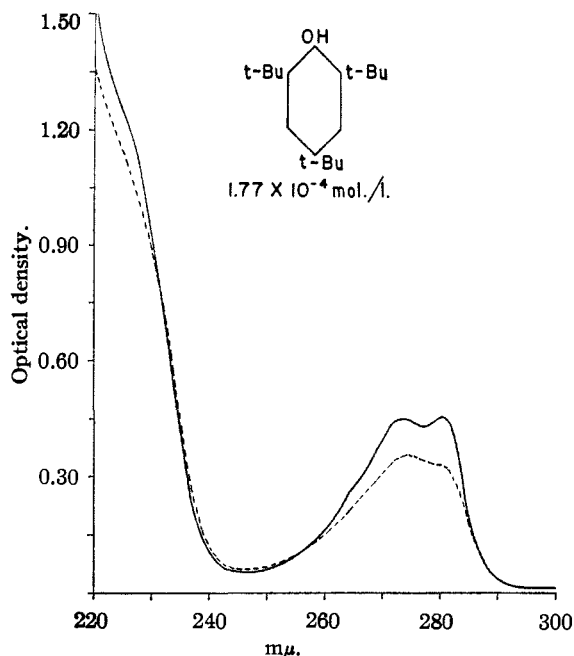


Fig. 7.—Ultraviolet absorption spectra of 2,4,6-tri-*t*-butylphenol, solid curve for isoöctane solution, dashed curve for alcohol solution.

represents 2,4,6-tri-*t*-butylphenol. Note that there is practically no detailed structure in the 280 $m\mu$ absorption for either solvent. This is to be expected from the more complex nature of the molecules, *i. e.*, more allowable vibrational states due to the larger substituent groups.

Although the data are shown for only a few of the phenols examined, further curves would be superfluous as the examples chosen are representative of their classes. An examination of the absorption spectra leads one to conclude that the unhindered and partially hindered phenols behave essentially as a single class with respect to the solvent dependence of their spectra. In contrast to this behavior the hindered phenols behave as a distinct class, since the red shift for them is so slight.

These results are based on visual observations of the spectra and it is desirable to verify them from quantitative data. For that reason a "center of gravity" of the spectral bands is defined and used. If we regard optical density as corresponding to mass and the wave length values as corresponding to distance then our spectral "center of gravity" is analogous to the mechanical concept. The spectral center of gravity will lie on a wave length $\bar{\lambda}$ determined by

$$\bar{\lambda} = \frac{\int_{\lambda_1}^{\lambda_2} \lambda D(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} D(\lambda) d\lambda} \quad (1)$$

where the effective wave length limits for the absorption band under consideration are λ_1 and λ_2 , and $D(\lambda)$ is the optical density for wave length λ .

It is clear from the figures that a change in

solvent from isoöctane to ethyl alcohol shifts the center of gravity of the fundamental band to the red for each of the above compounds. The use of the center of gravity concept allows a quantitative calculation of these shifts. For this Eq. 1 was evaluated for each compound by numerical integration by using the equation

$$\bar{\lambda} = \frac{\sum \lambda_i D(\lambda_i)}{\sum D(\lambda_i)} \quad (2)$$

where $\lambda_{i+1} - \lambda_i = 1 \text{ m}\mu$. The wave length shift $\Delta\bar{\lambda}$ occurring in going from one solvent to another was obtained for each phenol by determining the difference in $\bar{\lambda}$ calculated for the two solvents. In Table I may be seen these values for the unhindered phenols.

TABLE I

VALUES OF $\bar{\lambda}$ AND $\Delta\bar{\lambda}$ IN $\text{m}\mu$ FOR THE UNHINDERED PHENOLS FOR ISOÖCTANE AND ETHYL ALCOHOL SOLVENTS

Compound	$\bar{\lambda}$ (iso-octane)	$\bar{\lambda}$ (alcohol)	$\Delta\bar{\lambda}$
Phenol	268.3	270.5	2.2
<i>o</i> -Cresol	269.4	271.6	2.2
<i>m</i> -Cresol	270.6	275.7	5.1
<i>p</i> -Cresol	273.9	275.8	1.9
<i>p-t</i> -Amylphenol	271.6	273.5	1.9
<i>p-t</i> -Butylphenol	271.9	274.0	2.1
2,6-Dimethyl-4- <i>t</i> -butylphenol	272.5	273.3	0.8
Average $\Delta\bar{\lambda} = 2.3 \text{ m}\mu$.			

For each of the compounds in Table I and for the other substituted phenols examined the band over which the $\bar{\lambda}$'s and the $\Delta\bar{\lambda}$ were calculated was taken as extending from 245 $\text{m}\mu$ to 310 $\text{m}\mu$. Calculations were not made for the lower wave length band as complete data were not available for it. Results for the partially hindered phenols are given in Table II.

TABLE II

VALUES OF $\bar{\lambda}$ AND $\Delta\bar{\lambda}$ FOR THE PARTIALLY HINDERED PHENOLS

Compound	$\bar{\lambda}$ (iso-octane)	$\bar{\lambda}$ (alcohol)	$\Delta\bar{\lambda}$
2-Methyl-4,6-di- <i>t</i> -butylphenol	272.1	273.2	1.1
2,4-Di- <i>t</i> -butylphenol	272.3	274.4	2.1
2- <i>t</i> -Butyl-4-methylphenol	274.5	276.9	2.4
3-Methyl-6- <i>t</i> -butylphenol	270.7	272.7	2.0
2- <i>t</i> -Amyl-4-methylphenol	275.3	277.5	2.2
4-Ethyl-6- <i>t</i> -butylphenol	273.6	276.0	2.4
Average $\Delta\bar{\lambda} = 2.1 \text{ m}\mu$.			

The results for the hindered phenols are seen in Table III. Inspection of these shows that some of the $\Delta\bar{\lambda}$'s and the average $\Delta\bar{\lambda}$ for the hindered phenols are negative. It is not true, however, that the spectra for those cases have been shifted to the blue, *i. e.*, to shorter wave lengths. These negative values result from the change of shape of the spectral bands together with the manner of computing $\bar{\lambda}$. In Fig. 7 may be seen an example of this. Here the fundamental band, centering near 280 $\text{m}\mu$, has two poorly resolved branches for the

isoöctane solution. It is clear that the longer wave length one will contribute more to the calculated value of $\bar{\lambda}$. The same band for ethyl alcohol solution shows two even more poorly resolved branches, the one at shorter wave length now predominating. This weights the calculation in such a manner as to induce an "apparent" blue shift. From the shoulders and sides of the band it is apparent, however, that there is a slight red shift. The same type of band-shape change also occurs for the other compounds in the table exhibiting negative $\Delta\bar{\lambda}$'s. With this in mind we see from a comparison of the tables that the red shifts for the hindered phenols are much smaller than for the unhindered and partially hindered phenols. Also, we see that these latter two classes are essentially the same with regard to this shift.

TABLE III

VALUES OF $\bar{\lambda}$ AND $\Delta\bar{\lambda}$ IN $\text{m}\mu$ FOR THE HINDERED PHENOLS

Compound	$\bar{\lambda}$ (iso-octane)	$\bar{\lambda}$ (alcohol)	$\Delta\bar{\lambda}$
2,6-Di- <i>t</i> -butyl-4-cyclohexylphenol	273.0	273.1	0.1
2,4,6-Tri- <i>t</i> -butylphenol	273.0	272.0	-1.0
2,6-Di- <i>t</i> -butyl-4-methylphenol	274.8	274.2	-0.6
2,6-Di- <i>t</i> -butyl-4-ethylphenol	273.3	273.6	0.3
2,6-Di- <i>s</i> -butyl-4-methylphenol	275.0	274.1	-0.9
2- <i>t</i> -Butyl-6- <i>t</i> -amyl-4-methylphenol	273.8	273.8	0.0
2,6-Di- <i>t</i> -butyl-4-diisobutylphenol	271.6	272.0	0.4
Average $\Delta\bar{\lambda} = -0.2 \text{ m}\mu$.			

One hindered phenol, 2,6-di-*t*-butyl-4-phenylphenol, exhibited anomalous behavior in comparison to the others. This behavior, to be seen in Fig. 11, is believed to be due in part to the conjugation between the two phenyl rings. For that reason it is not included in the above tables nor considered in drawing conclusions from these tables.

On the assumption that hydrogen bonding between solute and solvent molecules is important to the processes responsible for the alteration of spectra, the fact that the unhindered and partially hindered phenols behave as a single class would seem in variance with the infrared results. It must be remembered, however, that the classification from infrared studies is based on the steric hindrance to hydrogen bonding between like molecules. Two unhindered phenol molecules may associate very strongly. Two partially hindered phenols will be partially hindered in their association by the large alkyl groups on the ortho positions. However, due to the relatively small dimensions of the ethanol molecule it may associate easily with either unhindered or partially hindered phenol molecules. This may be easily seen by the use of atom models. This equal ease of association explains the similar behavior of these two classes of phenols. The reduced alteration of spectra observed for the hindered phenols is ascribed to the hindrance the large alkyl groups on the ortho positions offer to the approach of the ethanol molecules to the phenol hydroxyl groups.

It would thus seem that a direct correlation

might be made between the observed degree of spectral change and the strength of intermolecular hydrogen bonding. However, we cannot conclude that it is hydrogen bonding itself which is to be correlated with the spectral changes but rather the distance of approach of the ethanol molecule to the hydroxyl group of the phenol.

B. Temperature Effects.—As was stated earlier, it was decided to study the spectra as a function of temperature to determine the importance of hydrogen bonded complexes. If it were true that such complexes were necessary to produce the spectral changes then a progressive rise in temperature should progressively modify the alcohol solution spectrum to resemble the iso-octane solution spectrum. This would be true as the population of complexes would be progressively reduced by the increase of temperature.

Phenol was chosen as the compound to examine and its spectra in iso-octane and alcohol solution at room temperature may be seen in Fig. 8.

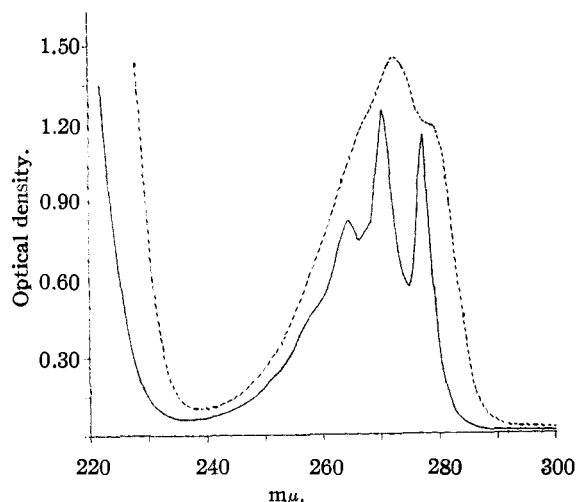


Fig. 8.—Ultraviolet absorption spectra of phenol, solid curve for iso-octane solution, dashed curve for alcohol solution.

In Fig. 9 may be seen a series of temperature runs made with the temperature-controlled cell compartment described above. Here the successive spectra are shifted vertically for clarity. There are no discernible changes in the spectra even though the temperature change is quite adequate to destroy the hydrogen bonded complexes. Similar tests were made with other compounds. Aniline shows large spectral changes between the spectra obtained in iso-octane and water solutions. However, when a water solution of aniline was examined through a series of increasing temperatures as for phenol no changes of spectra were found. Acetylacetone shows a large red shift between the spectra for iso-octane and ethyl alcohol solutions. No changes of spectra were found for it when an alcohol solution was examined through a similar series of temperature.

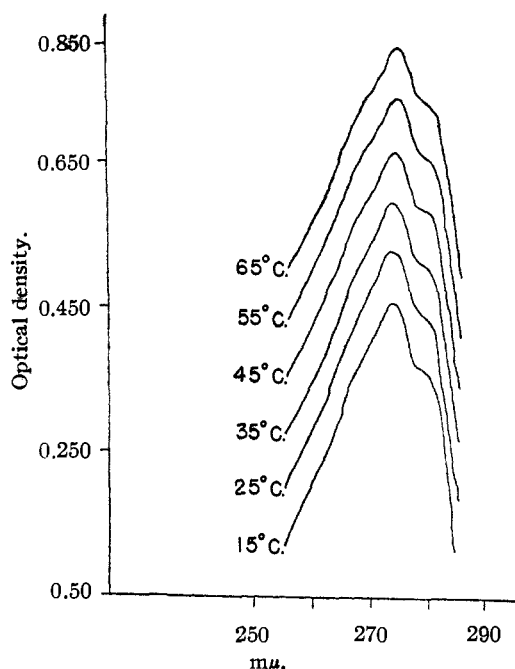


Fig. 9.—Spectra of phenol in ethanol solution at various temperatures.

Since these tests show no dependence of spectra on temperature, we may conclude that stable hydrogen bonded complexes are not necessary for the change of spectra observed for ethyl alcohol solutions. These observations together with those on the substituted phenols indicate that the spectral changes are due to the close proximity between the hydroxyl groups of the ethanol and phenol molecules. The stabilization of the polar excited states may be assumed to be due to electronic interaction between the dipole moment of the alcohol and the ionic form of the excited state. This interaction is evidently non-specific in the sense of not depending upon stable complexes.

As a further test of the temperature dependence of the spectra a series of runs was made of a solution of phenol in a solvent consisting of 0.2 mole per liter of ethanol in iso-octane. These results are seen in Fig. 10. Again the spectra are vertically displaced for clarity. At the end of the series the sample was returned to approximately room temperature to ascertain if any permanent changes had been produced in the solution. This spectrum is the top one in the figure. It shows no significant differences from the initial one. It is to be observed in this series of curves that the spectra at increasing temperatures approach nearer and nearer the spectrum for phenol in iso-octane. The trend of these spectra is the same as achieved when a series of similar solutions containing progressively smaller concentrations of alcohol are examined. In view of the results and the above temperature studies, it is believed that the phenomenon of spectral change with temperature seen in Fig. 10 is due to changes in the im-

mediate surroundings of the solute molecules. Due to dipole-dipole interactions between the phenol molecules and the alcohol molecules there will be a tendency for the former to be in close proximity with one or more of the latter. An increase in temperature, however, will tend to disperse such clusters due to thermal agitations. Thus an increase in temperature will create the observed effect which is the same as reducing the concentration of the alcohol in the solvent.

C. Smoothing and Asymmetrical Broadening of the Absorption Bands.—It is well known that the band structure observed in the ultraviolet is the result of transitions from the vibrational energy levels of one electronic configuration to the vibrational energy levels of another.⁹ With an increase of atomic groupings in the molecule there will be more allowable vibrational levels and the detailed band structure will be less distinct. This may be observed from Figs. 3, 4, 5, 6, 7 and 8. It is noted that the partially hindered phenols possessing more alkyl substitution than the unhindered phenols have less detailed band structure. In turn the hindered phenols have even less structure. These observations are true of all the phenols examined.

In examining the same set of figures as above, it may be observed that in each case the band structure is almost lost in the ethanol solutions. Before proposing an explanation for this, let us consider another effect. It is to be observed, particularly in Figs. 3, 4 and 5, that, in passing from isoöctane to ethanol solution, the fundamental band centering near 280 m μ is asymmetrically broadened. It is extended into the red with very little change in behavior on the short wave length side. This phenomenon is characteristic of all the phenols examined, especially the unhindered and partially hindered ones. This asymmetrical broadening is not observed for the aromatic hydrocarbons even though they may exhibit appreciable values of $\Delta\lambda$. This latter fact together with the effects of temperature variation lead us to explanations for the present phenomena based on the proximity of the hydroxyl groups of alcohol and phenol molecules.

Due to the dipole-dipole interaction between the hydroxyl groups there will be a tendency for the alcohol and phenol molecules to approach very closely to each other and at room temperature and somewhat above to form complexes. However, due to thermal agitations, all phenol molecules in the solution will not be members of complexes. Rather, at any instant, there will be a weighted statistical distribution over the dipole-(phenol)-dipole(alcohol) distance. It is known from the above data that this distance influences the degree of spectral shift. The spectra for an alcohol solution will be the superposition of the spectra for all values of the dipole-dipole distance. Those phenol molecules with their hy-

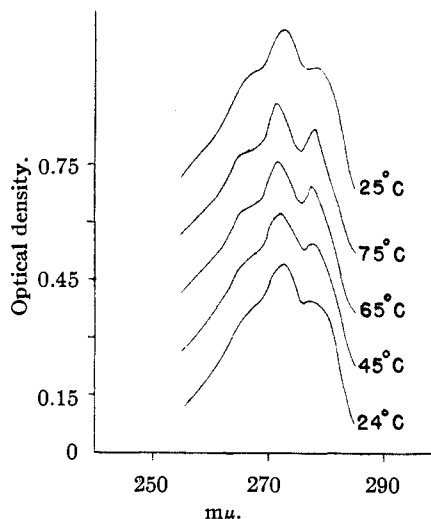


Fig. 10.—Spectra of phenol at various temperatures for a concentration of 2.88×10^{-4} mol./l. in a solvent comprising 0.2 mol./l. of ethanol in isoöctane.

droxyl groups in close proximity to the hydroxyl groups of alcohol molecules would be expected to contribute heavily to the red side of the band. Those with large or normal distances would be expected to absorb approximately as if they were in an isoöctane solution. This latter statement is based on results obtained for benzene and toluene, to be discussed later. It is clear then that such a superposition would lead to an asymmetrical broadening as observed. It would also lead to a blurring of the band structure.

In addition to the blurring due to a spread in dipole-dipole distances there are two other effects expected to contribute to it. One is the effect of the electric fields due to the dipoles of the hydroxyl groups in the alcohol molecules. At short distances the intensity of the electric fields of such a dipole is very large. Therefore, for the phenol molecules in close proximity to ethanol molecules we would expect a smoothing or displacement of band structure due to the perturbing effects of the large electric fields. The other effect expected to contribute to the smoothing of the band structure is inherent in the strong dipole-dipole attractions between the phenol and alcohol molecules. Because of these strong forces, a phenol molecule may be regarded as mechanically coupled in a non-rigid manner to one or more neighboring alcohol molecules. Since this is somewhat equivalent to adding further substituent groups we would expect a reduction of band structure for the same reasons that the addition of further groups on a simple phenol reduces the structure.

D. Effects Obtained with Conjugated Aromatics.—As was mentioned above, 2,6-di-*t*-butyl-4-phenylphenol behaves anomalously compared to the other phenols. Its spectra may be seen in Fig. 11. We note that it not only exhibits a quite large wave length shift, but it does not show

(9) See, for example, G. N. Lewis and M. Calvin, *Chem. Rev.*, **25**, 273 (1939).

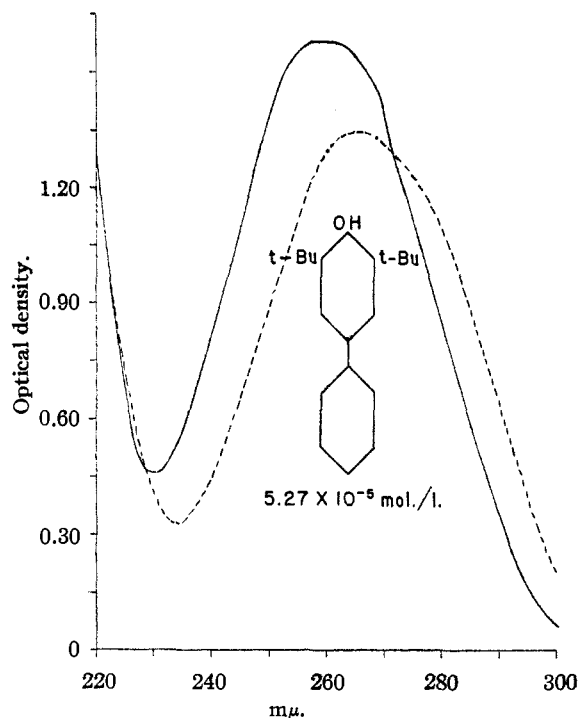


Fig. 11.—Ultraviolet absorption spectra of 2,6-di-*t*-butyl-4-phenylphenol, solid curve for isoöctane solution, dashed curve for alcohol solution.

the asymmetrical band broadening. The calculated values for this compound are: $\bar{\lambda}$ (isoöctane) = 265.1 m μ , $\bar{\lambda}$ (alcohol) = 269.8 m μ , and $\Delta\bar{\lambda}$ = 4.7 m μ . We have assumed that this anomalous behavior is due to the conjugation of the phenyl and phenol groups. Confirming evidence for this may be seen below wherein wave length shifts are observed for conjugated aromatic systems.

In order to appraise the degree of spectral shift

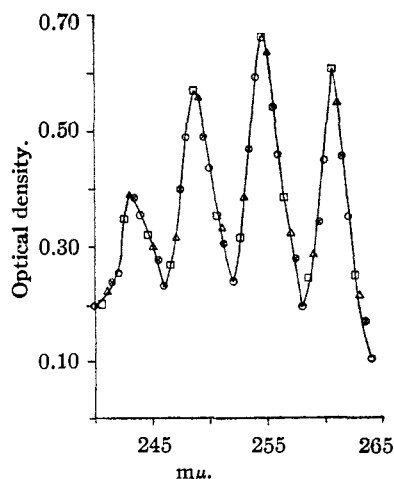


Fig. 12.—Absorption spectra of benzene under various solvent conditions: O, isoöctane; Δ, ethyl alcohol; □, ethyl alcohol + sodium chloride; ⊗, ethyl alcohol + water.

for conjugated hydrocarbon systems a number of aromatic hydrocarbons were examined. In Fig. 12 may be seen the results for benzene examined under four different conditions. The solvents for these were isoöctane, ethanol, ethanol containing water in equal concentrations to the solute an ethanol saturated with sodium chloride. No significant spectral changes nor wave length shifts are observable. Toluene was also examined in isoöctane and alcohol with no observable shift. In Fig. 13 may be seen the spectra in isoöctane and ethanol of naphthalene. Here a definite shift to

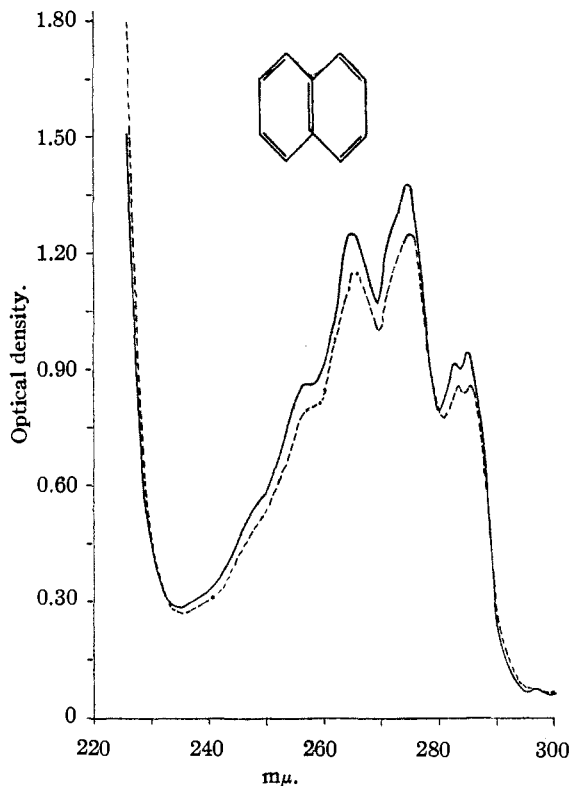


Fig. 13.—Ultraviolet absorption spectra of naphthalene, solid curve for isoöctane solution, dashed curve for alcohol solution.

the red is observable. It would be even more so were it not that two slightly different concentrations were used. A number of other hydrocarbons possessing a degree of conjugation greater than benzene were examined and the results for these are tabulated in Table IV. As the wave length regions considered are different for the various compounds they are also included.

In Fig. 14 may be seen the results for another of the aromatic hydrocarbons, *p*-diphenylbenzene. In this figure it may be seen that the complete fundamental band in the 280 m μ region is shifted to the red rather than asymmetrically broadened as for the phenols. This effect of complete band shift rather than asymmetrical broadening was observed for all the aromatic hydrocarbons examined. It suggests a definite difference, between

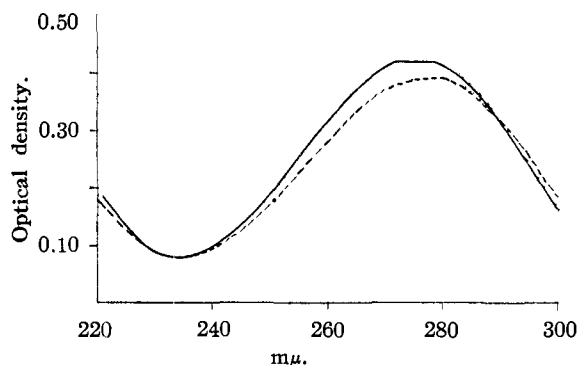


Fig. 14.—Ultraviolet absorption spectra of *p*-diphenylbenzene, solid curve for iso-octane solution, dashed curve for alcohol solution.

the phenols and aromatic hydrocarbons, in the processes responsible for the alteration of spectra.

TABLE IV
VALUES OF $\bar{\lambda}$ AND $\Delta\bar{\lambda}$ IN $m\mu$ FOR VARIOUS AROMATIC HYDROCARBONS

Compound	Wave length region, $m\mu$	μ (iso-octane)	$\bar{\lambda}$ (alcohol)	$\Delta\bar{\lambda}$
Styrene	220–265	242.9	243.3	0.4
Naphthalene	235–305	257.4	257.8	.4
Diphenyl	220–290	247.8	248.6	.8
<i>o</i> -Diphenylbenzene	224–255	237.4	237.5	.1
<i>m</i> -Diphenylbenzene	222–290	250.6	250.9	.3
<i>p</i> -Diphenylbenzene	239–320	272.9	273.7	.8

Since the aromatics of Table IV all have more conjugation than benzene and toluene we may assume that the dipole moments of their polar excited states will be correspondingly larger. We may further assume that it is the interaction of these larger dipole moments with the surrounding ethanol molecules that accounts for the red shift. Since these aromatic hydrocarbons in the ground state are not possessed of strong dipole moments there will not be the same tendency for preferential alignment and complex formation between them and the alcohol molecules as for the phenols. Therefore, when an aromatic hydrocarbon is raised to an excited state it should find an "average" state of affairs as regards the neighboring alcohol molecules. This would account for the complete shift of the band rather than an asymmetrical broadening.

When a dipole is imbedded in a dielectric the interaction energy will be a function of the dipole strength. We would, therefore, expect larger wave length shifts for molecules possessed of larger dipole moments of the excited states. It is interesting to observe the behavior of the diphenylbenzene isomers. Due to spatial extension it is to be expected that the dipole moment of the excited state of the para isomer will be larger than that of the meta isomer which in turn will be greater than that of the ortho isomer. The wave length shifts would then be expected to have the

same order. An examination of Table IV shows this to be true.

E. Behavior of the bis-Phenols.—Interesting results were obtained on several bis-phenols kindly supplied us by Dr. D. Stevens and Mr. A. C. Dubbs of this Laboratory. The data for one of these may be seen in Fig. 15. The dashed

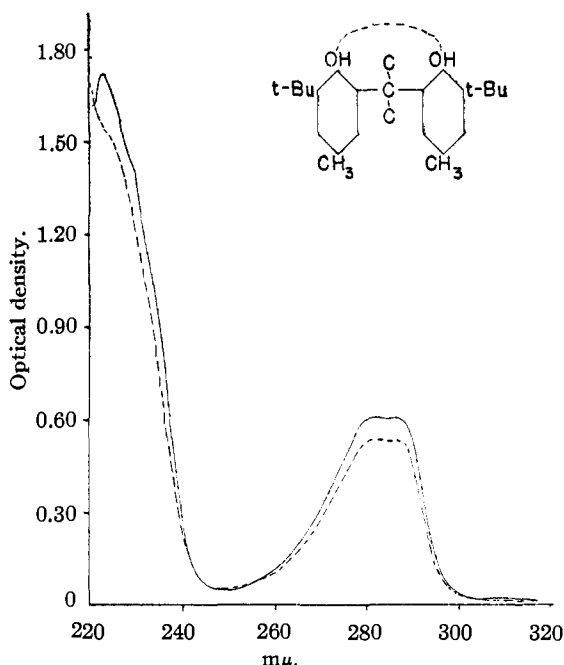


Fig. 15.—Ultraviolet absorption spectra of 2,2-bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)propane, solid curve for iso-octane solution, dashed curve for alcohol solution.

line joining the hydroxyl groups in the figure is meant to represent the existence of an intramolecular hydrogen bond. It was found by infrared absorption studies that in each of these compounds studied there was very good evidence of such internal hydrogen bonds.¹⁰ The manner of representing the structure used in Fig. 15 does not indicate that the hydroxyls can achieve enough proximity to hydrogen bond. However, an examination using atom models shows that such proximity is possible. The values of the $\bar{\lambda}$'s and $\Delta\bar{\lambda}$'s found for these compounds may be seen in Table V.

TABLE V
VALUES OF $\bar{\lambda}$ AND $\Delta\bar{\lambda}$ IN $m\mu$ FOR THE BIS-PHENOLS

Compound	$\bar{\lambda}$ (iso-octane)	$\bar{\lambda}$ (alcohol)	$\Delta\bar{\lambda}$
bis-(2-Hydroxy-3- <i>t</i> -butyl-5-methylphenyl)-methane	280.1	279.7	-0.4
2,2-bis-(2-Hydroxy-3- <i>t</i> -butyl-5-methylphenyl)propane	280.5	280.6	.1
2,2-bis-(2-Hydroxy-3- <i>t</i> -butyl-5-methylphenyl)butane	280.9	280.9	.0
1,1-bis-(2-Hydroxy-3- <i>t</i> -butyl-5-methylphenyl)isobutane	281.4	281.6	.2

(10) Unpublished results.

The values of $\Delta\bar{\lambda}$ are approximately the same as for the hindered phenols. This is to be expected in view of the steric hindrance the *t*-butyl groups on the ortho positions will offer to the approach of ethanol molecules and to the fact that in the intramolecular hydrogen bond the dipole moments of the hydroxyls will partially cancel each other, thus reducing the attraction of such a molecule for the alcohol molecules.

It is interesting to note that the center of the fundamental band for each of these compounds is about 280 μ . This is further to the red than the centers of the corresponding band for the simpler phenols. Part of this displacement may be thought to be due to the hydrogen bonding or close proximity effects of the two phenol rings on each other. The positioning of one phenol group in close proximity to another should be expected to produce a red shift just as ethyl alcohol solvent does for a simpler phenol. Therefore, the spectra of a bis-phenol in isoöctane solution would be expected to show the center of its fundamental band at longer wave lengths than a simple phenol.

Acknowledgment.—Acknowledgment is gratefully made to Dr. D. Stevens, Dr. G. Stillson and Mr. A. C. Dubbs for furnishing some of the compounds studied. We also wish to express acknowledgment to Brother C. Curran of Notre Dame University for discussions of the subject, to Mr. A. Glessner for aid in taking some of the data, and to Paul D. Foote, Executive Vice-President of Gulf Research & Development Company, for permission to publish this material.

Summary

A study has been made of the changes in ultra-violet absorption spectra for twenty-one phenols that occur when the solvent is changed from a paraffin to an alcohol. Three different effects are observed: a shift of the spectral center of gravity to longer wave lengths, a smoothing of the band structure, and an asymmetrical broadening of the fundamental absorption band. It is found that that the spectral change depends upon the degree of steric hindrance offered to the approach of the alcohol molecules to the hydroxyl group of the phenol. In alcohol solutions the spectra of the phenols and other compounds do not change with increasing temperature, indicating that the processes primary to the spectral changes do not depend on stable hydrogen bonded complexes. Data are given for the unhindered, partially hindered and hindered phenols.

Tentative explanations are provided for some of the temperature effects, the smoothing of the band structure, and the asymmetrical broadening of the bands. These are based on considerations of the intermolecular interactions. No significant spectral changes were observed for benzene or toluene whereas a shift to the red was observed for aromatic hydrocarbons of higher conjugation. This is discussed in terms of the stabilization of the excited polar states through interactions with the alcohol molecules. Data and discussion are provided for four bis-phenols.

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Correlated Molecular Orbitals¹

BY ARTHUR A. FROST, JERRY BRAUNSTEIN AND WARREN SCHWEMER

The molecular orbital method of Hund, Mulliken, Lennard-Jones and others for the approximate quantum mechanical treatment of the electronic structure of molecules has the advantage over the valence bond method of Heitler and London, Pauling, Slater and others^{1a-5} in being simpler in concept and simpler for the calculation of numerical results. The molecular orbital method has the disadvantage, however, in that it overemphasizes ionic structures, permitting electrons to pile up without restriction on any given atom of the molecule. This is due to the fact that the po-

tential energy of repulsion of the various electrons is brought in only indirectly through its average effect, the interelectronic distances not appearing in the wave function. That these interelectronic distances should appear explicitly is shown by their required presence for the accurate calculations of Hylleraas⁶ on the helium atom and of James and Coolidge⁷ on the hydrogen molecule. The "correlated" motions of electrons in solids has been considered by Wigner and Seitz,^{8,9} and it is this previous use of this word that gives the title to the method considered here.

When antisymmetrized molecular orbitals¹⁰ are used no more than two electrons are in the

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