TABLE II

PRINCIPAL ABSORPTION BANDS OF PROMETHIUM

| Wave length, mμ | Molar extinction coefficient, ε × 10³ |
|---|---|
| 459.5 ± 0.5 | 0.7 |
| 493 ± 0.5 | 1.2 |
| 548 ± 0.5 | 2.3 |
| 629.0 ± 1.0 | 0.5 |
| 568 ± 0.2 | 2.3 |
| 685 ± 0.2 | 1.3 |
| 702.7 ± 0.2 | 1.6 |
| 737.2 ± 0.2 | 1.9 |
| 785.0 ± 0.2 | 1.1 |
| 810.0 ± 0.1 | 0.6 |

remaining spectral bands of samarium, however, do not appear in concentrations of promethium which are three to four times as high as is illustrated in Fig. 2. Due to the fact that measurement of absorption in solution does not distinguish between two adjacent absorption bands separated by only a few ångströms, comparisons with the absorption by the crystals will be undertaken soon. It is hoped that this would also establish whether this weak band at 402.5 ± 0.5 mμ belongs to samarium or to promethium.

It was observed that the crystalline salts, chloride and nitrate, of promethium displayed different colorings. This introduced the question of whether if in solution these salts would have the same optical absorption characteristics; however, when this test was made, it was noted that the coloring of the solutions were visibly the same, *i. e.*, pink or rose. This fact was later indicated by the failure to find any apparent difference in the two spectra.

Other chemical forms of promethium, such as the hydroxide, oxalate and oxide all appear pink or rose.

It was of interest to compare the results of this study of the synthetic element with those reported in 1926 on natural material by B. S. Hopkins, *et al.*[10] Harris and Hopkins concluded that the most probable bands were in the positions 581.6 mμ and 512.3 mμ. A description of the methods used by Hopkins, *et al.*, in studying absorption is not given in the papers cited. The absorption data presented here were obtained with the element in solution and in that form the presence of these lines is not indicated.

## Summary

1. The absorption bands of promethium in the visible spectrum are observed to resemble those of neodymium, both in number and in intensity but are distinctly separable from the neodymium bands by at least 8 mμ.

2. The absorption bands of promethium are in the same position and of the same magnitude for both the chloride and nitrate solutions.

3. The most prominent absorption bands for a solution of promethium are to be found in positions 493.5 ± 0.5 mμ, 548.5 ± 0.5 mμ, 568.0 ± 0.2 mμ, 685.0 ± 0.1 mμ, 702.7 ± 0.3 mμ, 737.2 ± 0.2 mμ, and 785.0 ± 0.1 mμ.

OAK RIDGE, TENN. RECEIVED AUGUST 29, 1949

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[CONTRIBUTION FROM THE GULF RESEARCH & DEVELOPMENT COMPANY]

# Absorption Spectroscopic Studies of Hydrogen Bonding and Isomeric Forms in Bis-phenol Alkanes

BY NORMAN D. COGGESHALL

The present report is of infrared and ultraviolet absorption spectroscopic investigations made on a series of bis-phenol alkanes. These compounds are formed by the bridging of two phenolic nuclei through an aliphatic group which may be of various forms. Such materials have been referred to elsewhere as dihydroxyphenols or in some cases as diphenylolmethanes.[1] During some molecular structure determination work it was discovered that the bis-phenol alkanes had unusual hydrogen bonding characteristics. It was found that some members of the species may exist in three states, with regard to the hydrogen bonding. Some molecules may be intermolecularly bonded, some may be in a *cis*-isomeric form and some may be in a *trans*-isomeric form. The *cis*- and *trans*-isomeric forms, as used here, are not true isomeric forms but refer to orientation configurations. The *cis* form is that orientation wherein the two hydroxyl groups on the two phenolic nuclei are close together and hydrogen bonded to each other. The *cis* form hence exhibits intramolecular hydrogen bonding. The *trans* form is that orientation wherein the two hydroxyl groups are sufficiently removed from each other that no hydrogen bond exists and yet the hydroxyls are not members of intermolecular bonds. The fact that a *trans* form can exist in concentrated solutions of some of the phenols is due to the steric hindrance offered by ortho substituted *t*-butyl groups. The steric hindrance to intermolecular bonding offered by large ortho substituted alkyl groups in the mono-nuclear phenols has been previously discussed[2,3] and some of the results are applied here.

## Experimental Details

**Infrared Absorption.**—The infrared absorption data were obtained with an automatic recording Perkin–Elmer Model 12B infrared spectrometer. A LiF prism which gives excellent dispersion in the 2.6–3.0 μ region was used. The quantitative data were obtained with a cell-in-cell-out arrangement previously described.[4]

Each compound was examined under four different conditions. As received, the materials were generally a powder of small crystals which had not at any time been exposed to melting temperatures. Since melting sometimes changes the distribution among the various states the materials

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(1) H. L. Bender and A. G. Farnham, U. S. Patent 2,464,207.

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

(3) N. D. Coggeshall and E. M. Lang, *ibid.*, **70**, 3283 (1948).

(4) E. L. Saier and N. D. Coggeshall, *Anal. Chem.*, **20**, 812 (1948).

were examined as mineral oil smears. In addition each material was examined in low and high concentration solutions and in recrystallized form. The latter was prepared by melting the material between two salt plates with subsequent cooling. The solvent used was C.P. carbon tetrachloride.

**Ultraviolet Absorption.**—The ultraviolet absorption data were obtained with a standard Beckman quartz spectrophotometer. Absolute ethanol was used as the primary solvent. Any effects due to residual traces of benzene were eliminated by the use of the same solvent in both the sample and comparison cells. The most significant data in the ultraviolet absorption were those in which sodium hydroxide in an aqueous solution was added to the ethanol. The same concentration of sodium hydroxide was always used in both the sample and comparison cells.

The bis-phenol alkanes used were kindly supplied by Dr. Donald R. Stevens and Mr. A. C. Dubbs of this Laboratory. They were prepared by condensing various substituted phenols with different aldehydes and ketones in glacial acetic acid. The materials were believed to be better than 99% pure in each case.

## Infrared Absorption Results

**Bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-methane.**—The infrared absorption data for this compound may be seen in Fig. 1. Here may be seen the molecular structure diagram as well as the absorption bands for the material under three different condition. These curves, and later ones, are vertically displaced from one another for clarity. They were obtained by automatic scanning and give the amount of transmitting energy as a function of wave length. Curve A is for a solution of $1.0 \times 10^{-2}$ mole/liter. At this strength it is known from previous work[2] that negligible intermolecular hydrogen bonding can occur due to the large average separation between molecules. In this spectrum a sharp absorption band at 2.76 μ is the characteristic "free" hydroxyl absorption band, *i. e.*, absorption due to hydroxyl groups which are not members of hydrogen bonded complexes. In addition may be seen a strong, broad band centering at 2.85 μ. Since the concentration is too low to permit intermolecular bonding this latter band must be ascribed to intramolecular bonding. We hence have the surprising result that this material may exist in two forms in dilute solutions. The 2.76 μ band is ascribed to molecular configurations wherein the phenolic groups are so oriented relative to the bridging group that the two hydroxyl groups are widely separated and hence are free of hydrogen bonding effects. This we call the *trans*-isomeric form. The 2.85 μ band is ascribed to molecular configurations wherein the phenolic nuclei are so oriented that there is intramolecular bonding between the hydroxyls. This we call the *cis*-isomeric form.

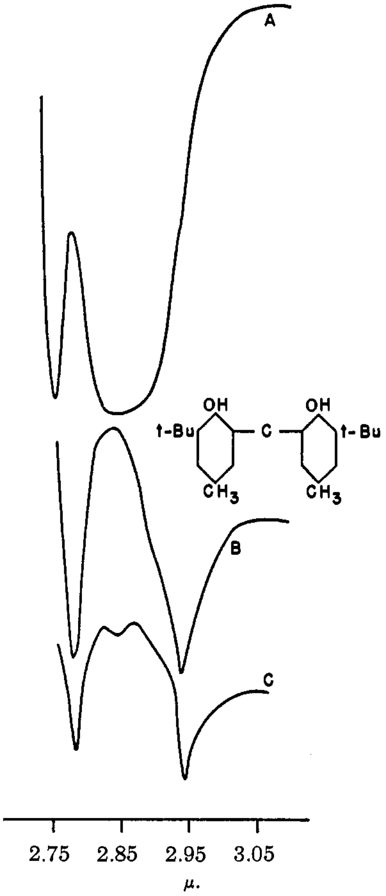

Fig. 1.—Infrared absorption spectra in the hydroxyl region of various forms of bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-methane.

In Curve B may be seen the spectrum for the recrystallized melt. Note that the free hydroxyl band remains strong but that the intramolecular bonding at 2.85 μ has disappeared and there is a new band occurring at 2.94 μ. The latter is known to be characteristic of hydroxyl groups which are members of strong intermolecular hydrogen bonds. Curve C is the spectrum for the material as a smear. There is, in addition to the free hydroxyl band and the intermolecular bonding band, a faint band characteristic of the *cis*-isomeric form. The wave lengths of the bands and the assignment to the different types for these data may be seen in Table I.

TABLE I

WAVE LENGTHS AT WHICH HYDROXYL ABSORPTION OCCURS IN BIS-(2-HYDROXY-3-*t*-BUTYL-5-METHYLPHENYL)-METHANE

| Sample | Wave length, μ | State of existence |
|---|---|---|
| Powder (smear) | 2.94 | Intermolecular bonding |
| | 2.78 | *trans*-Isomer |
| Recrystallized melt | 2.94 | Intermolecular bonding |
| | 2.78 | *trans*-Isomer |
| 0.5 m./l. solution | 2.85 | *cis*-Isomer |
| | 2.76 | *trans*-Isomer |
| 0.01 m./l. solution | 2.85 | *cis*-Isomer |
| | 2.76 | *trans*-Isomer |

These data show that this material may exist in three different states. It is to be noted that at a concentration of 0.5 m./l. no intermolecular bonding occurs. This concentration is sufficient to produce strong intermolecular bonding unless the material is sterically hindered. The ortho substituted *t*-butyl groups provide this hindrance in solution. As the material goes into the crystalline phase there is apparently a re-orientation which allows the *cis*-isomeric material to become intermolecularly bonded.

**1,1-Bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-ethane.**—The data for this material are given in Fig. 2. Curves A and B give the spectra of solutions of strength $1.0 \times 10^{-2}$ and 0.5 m./l., respectively. In each appears the free hydroxyl absorption band representing the *trans*-isomer form. In addition, in each there is the 2.86 μ band due to intramolecular bonding and which represents the *cis*-isomeric form. No intermolecular bonding is evident for the stronger solution indicating the effectiveness of the steric hindrance due to the *t*-butyl groups. Curve C gives the spectrum for the material after melting and cooling. Here we observe the presence of the *cis*- and *trans*-isomeric forms and no intermolecular bonding.

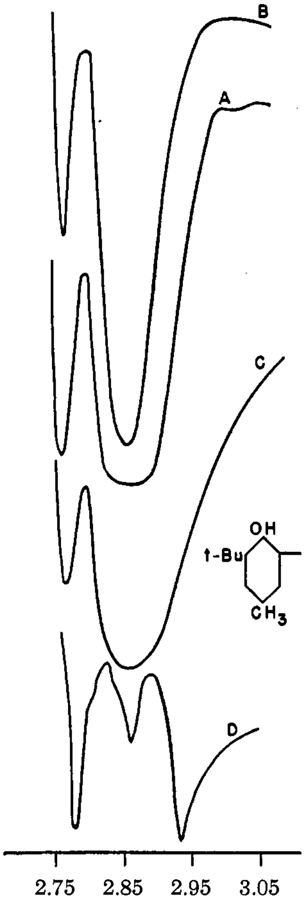

Fig. 2.—Infrared absorption spectra in the hydroxyl region of various forms of 1,1-bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-ethane.

The spectrum of the material as a smear is given in Curve D. Note that there is a strong *trans*-isomeric band at 2.78 μ, a weaker *cis*-isomeric form band at 2.86 μ and a strong, sharp intermolecular bonding band at 2.93 μ. Thus, the material exists in substantial proportions in all forms in the original powder state. After the material is melted it does not recrystallize but forms a glass. This is significant in view of the differences between Curves C and D. After melting and cooling there is no intermolecularly bonded form. The conclusion from these differences is that for the original material to crystallize there must be a definite distribution between the three states. When the material is melted this distribution is altered and the material cannot recrystallize. Table II gives the wave lengths at which this compound evidences hydroxyl absorption.

TABLE II

WAVE LENGTHS AT WHICH HYDROXYL ABSORPTION OCCURS IN 1,1-BIS-(2-HYDROXY-3-*t*-BUTYL-5-METHYLPHENYL)-ETHANE

| Sample | Wave length, μ | State of existence |
|---|---|---|
| Powder (smear) | 2.93 | Intermolecular bonding |
| | 2.86 | *cis*-Isomer |
| | 2.78 | *trans*-Isomer |
| Glass | 2.86 | *cis*-Isomer |
| | 2.76 | *trans*-Isomer |
| 0.5 m./l. solution | 2.86 | *cis*-Isomer |
| | 2.76 | *trans*-Isomer |
| 0.01 m./l. solution | 2.86 | *cis*-Isomer |
| | 2.76 | *trans*-Isomer |

**1,1-Bis-(2-hydroxy)-3-*t*-butyl-5-methylphenyl)-isobutane.**—The spectra for this compound will not be shown. It also showed the existence of the *cis*- and *trans*-isomeric forms in a solution of $1.0 \times 10^{-2}$ m./l. concentration. A spectrum for a solution strength of 0.5 m./l. was not possible due to the low solubility in carbon tetrachloride. In both the recrystallized melt and the smear only one band appeared. This was centered at about 3.12 μ and is ascribed to a very strong type of intermolecular bonding. This is a surprising result as strong bonding would not be expected in view of the *t*-butyl groups substituted ortho to the hydroxyls. This compound is also anomalous in comparison to the above two in that neither *cis*

TABLE III

WAVE LENGTHS AT WHICH HYDROXYL ABSORPTION OCCURS IN 1,1-BIS-(2-HYDROXY-3-*t*-BUTYL-5-METHYLPHENYL)-ISOBUTANE

| Sample | Wave length, μ | State of existence |
|---|---|---|
| Powder (smear) | 3.12 | Intermolecular bonding |
| Recrystallized melt | 3.12 | Intermolecular bonding |
| $1.0 \times 10^{-2}$ m./l. solution | 2.75 | *trans*-Isomer |
| | 2.86 | *cis*-Isomer |

nor *trans* forms are observed for the solid state. The wave lengths observed are given in Table III.

**Bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-phenylmethane.**—The data for this compound may be seen in Fig. 3. Here Curve C is for the smear. It exhibits the absorption of the *cis*-isomeric form as a doublet but shows no evidence for either the *trans* isomer or the intermolecularly bonded form. When the material is examined as a recrystallized melt it again shows no evidence for the latter two forms but shows only the *cis*-isomeric form, although the doublet structure is destroyed. When the material is in solution it is interesting that a weak but definite *trans* absorption band appears.

The fact that the spectrum of the smear shows only the *cis* form implies that either the material was synthesized entirely in the *cis* form or that there is a conversion of the existing *trans* form to the *cis* form at the time of the initial crystallization. The low intensity of the *trans* band for the solutions infers that conversion, through rotation about the saturated valence bonds of the bridging group, of the *cis* isomer to *trans* isomer is possible but not probable. From the size of the phenyl ring group attached to the bridging carbon it would be expected that such rotation might be completely blocked. An investigation with Fisher–Hirschfelder molecular models[5] shows that this rotation is possible although sterically hindered. The absorption wave lengths for this material are given in Table IV. It is interesting as a type of bis-phenol intermediate between those of above in which the *cis* and *trans* isomers are represented in roughly equal proportions and those to be described immediately below which exist only in the *cis* form.

TABLE IV

WAVE LENGTHS AT WHICH HYDROXYL ABSORPTION OCCURS IN BIS-(2-HYDROXY-3-*t*-BUTYL-5-METHYLPHENYL)-PHENYLMETHANE

| Sample | Wave length, μ | State of existence |
|---|---|---|
| Powder (smear) | 2.83 | *cis*-Isomer |
| | 2.82 | *cis*-Isomer |
| Recrystallized melt | 2.85 | *cis*-Isomer |
| 0.5 m./l. solution | 2.85 | *cis*-Isomer |
| | 2.75 (weak) | *trans*-Isomer |
| 0.01 m./l. solution | 2.85 | *cis*-Isomer |
| | 2.75 (weak) | *trans*-Isomer |

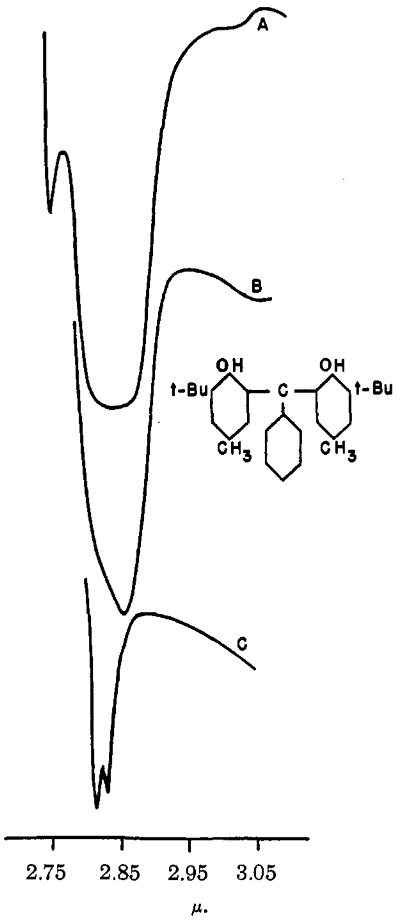

Fig. 3.—Infrared absorption spectra in the hydroxyl region of various forms of bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-phenylmethane.

**2,2-Bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-butane, 2,2-Bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-propane, and 1,1-Bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-cyclohexane.**—These three bis-phenols are grouped because they possess the common characteristic of existing only in the *cis* form. The data for one, the 2,2-butane type, may be seen in Fig. 4. Here Curves A and B are solutions of $1.0 \times 10^{-2}$ m./l. and 0.5 m./l., respectively, Curve C is for the recrystallized melt and Curve D is for a smear. For Curves A, B and C the maximum of absorption occurs at 2.87 μ and for Curve D it appears at 2.88 μ. It is clear that this band must in every case represent only the *cis*-isomeric form. No *trans* form nor intermolecularly bonded form appears in any state in which the material was examined. This is significant as it implies that the material was originally synthesized in the *cis* form completely.

The behavior of the 2,2-bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-propane, for which the data are not shown was very similar to the material above. It was examined as a smear, as the recrystallized melt, in a solution at 0.5 m./l., and in a solution at $1.0 \times 10^{-2}$ m./l. In each case only one band appeared. This was at 2.87 μ in each case and is ascribed to the *cis*-isomeric form.

The data for the third of these compounds, *i. e.*, 1,1-bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-cyclohexane are given in Fig. 5. Here Curves A and B are for solutions of $1.0 \times 10^{-2}$ and 0.5 m./l., respectively, and Curve C is for the original material which in this case was a liquid. Again we observe only the characteristic *cis*-isomeric band. The common center of the band in this case was at 2.85 μ.

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(5) Available from Fisher Scientific Co., Pittsburgh, Pennsylvania.

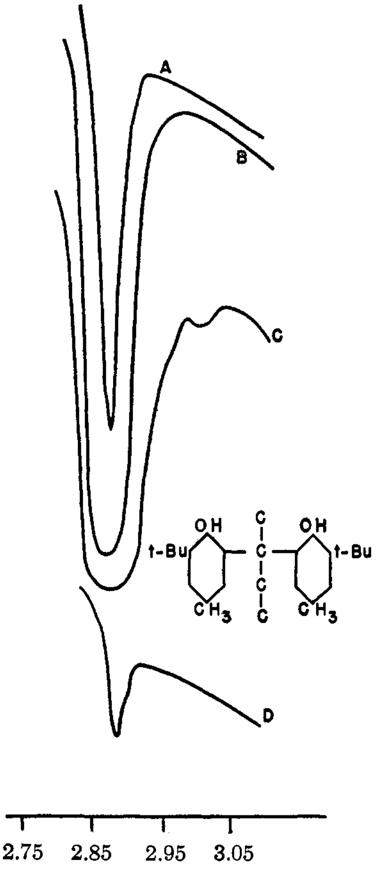

Fig. 4.—Infrared absorption spectra in the hydroxyl region of 2,2-bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-butane under various conditions.

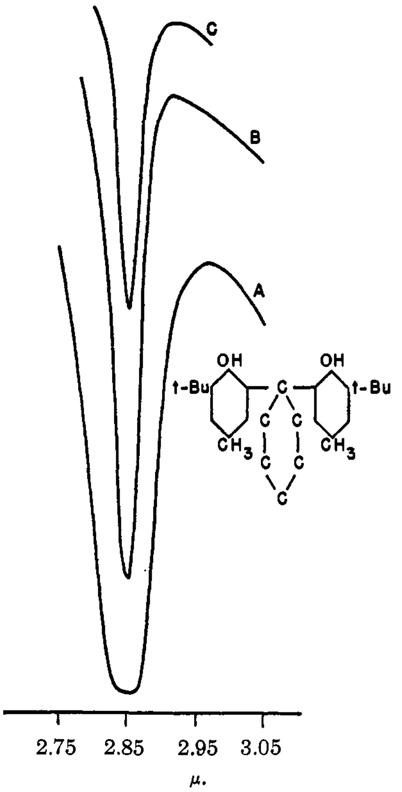

Fig. 5.—Infrared absorption spectra in the hydroxyl region of 1,1-bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-cyclohexane under various conditions.

The compounds just discussed are remarkable in that they exist in only the *cis*-isomeric form. As was remarked this indicates that in the synthesis only the *cis* form was created. Each of these materials is characterized by the size of the bridging group or the manner of substitution on it. For two of them the bridging is across the number 2 carbon atom in the chain. In the other the effective appendage (the remainder of the cyclohexyl group) on the bridging carbon atom is large due to the unsaturation. These are important items since the materials are found only in the *cis* form. With these types of bridging groups there is so much hindrance to rotation that a *cis* isomer cannot pass to the *trans* form. This may be verified by examination of the corresponding molecular models. These compounds are different in another respect from the earlier ones. There is no tertiary hydrogen atom on the bridging carbon atoms. What effect this has on the molecular properties cannot be conclusively stated. The fact that the materials are synthesized in the *cis* form indicates that the *trans* form is either forbidden because of large steric hindrance effects or that the *cis* form exists in a lower energy state and hence is preponderantly much more probable.

**Bis-(2-hydroxy-3-methyl-5-isoöctylphenyl)-methane.**—This material is of interest because of the smaller substituents ortho to the hydroxyl groups. As previously remarked[2,3] large ortho groups are very effective in hindering the formation of intermolecular bonds. We should expect this compound to exhibit very strong intermolecular bonding in the solid state and in the 0.5 m./l. solution. The data are given in Fig. 6. Curve A is for a $1.0 \times 10^{-2}$ m./l. solution, Curve B is for a 0.5 m./l. solution and Curve C is for the material recrystallized after melting. Note that in the latter case only absorption ascribable to intermolecular bonding is observed. This is also

TABLE V

WAVE LENGTHS AT WHICH HYDROXYL ABSORPTION OCCURS IN BIS-(2-HYDROXY-3-METHYL-5-ISOÖCTYLPHENYL)-METHANE

| Sample | Wave length, μ | State of existence |
|---|---|---|
| Powder (smear) | 2.95 | Intermolecular bonding |
| Recrystallized melt | 2.95 | Intermolecular bonding |
| 0.5 m./l. solution | 2.95 | Intermolecular bonding |
| | 2.77 | *trans*-Isomer |
| $1.0 \times 10^{-2}$ m./l. solution | 2.88 | *cis*-Isomer |
| | 2.77 | *trans*-Isomer |

true of the spectrum (not shown) of the material when examined as a smear. In a medium strength solution such as 0.5 m./l. there is still very strong intermolecular bonding although a fairly strong *trans* absorption band also appears. This is seen in Curve B. In the weaker solution of $1.0 \times 10^{-2}$ m./l. (Curve A) such that intermolecular effects are removed the spectrum shows both the *cis* and *trans* form. In Table V are given the wave lengths at which hydroxyl absorption maxima are observed.

**Discussion.**—From the above data it may be seen that the bis-phenol alkanes wherein the bridging group is ortho to the hydroxyls may be divided into two classes: those that admit of both *cis*- and *trans*-isomeric forms and those that are found only in the *cis* form. It may be further seen that the latter class are those such that the bridging groups offer very large steric hindrance to passage from a *cis* to a *trans* form. Either the bridging is through 2,2-substitution on a chain or the bridging group is very large. As remarked earlier these materials are apparently synthesized directly into the *cis* form as no evidence for the *trans* is found under any of the conditions used.

Among those bis-phenols which exist in both the *cis*- and *trans*-isomeric forms there are large variations in individual behavior. This was exhibited primarily in their hydrogen bonding behavior in the solid state or in concentrated solution as compared to that in dilute solution. For the latter case they all exhibited the *cis* and *trans* forms. However, several variations with respect to the distribution among the *cis* and *trans* forms and intermolecular bonding are observable. From this we may then conclude that the detailed distribution among these forms in the solid state is a specific function of particular bridging group.

The percentages of each compound present in the *cis* and *trans* forms when in dilute solution have been calculated. We may express Beer's law of absorption as

$$D = \log (I_0/I) = ACl$$

where $D$ is the optical density, $I_0$ and $I$ are the incident and transmitted energies, respectively, $A$ is the extinction coefficient, $C$ is the concentration of absorbing material, and $l$ is the cell thickness. In a previous study of a large number of substituted phenols it has been found that $A$ for the free hydroxyl absorption at about 2.76 μ is essentially constant for all. For the present case we therefore assume that the absorption per free hydroxyl group in a *trans* isomer is the same as the absorption per free hydroxyl group in a hindered phenol. For the latter 2,6-di-*t*-butyl-4-methylphenol was used. With the concentration expressed in m./l. it yielded an $A$ with a numerical value of 136.

The optical density for the free hydroxyl band was then determined for each bis-phenol alkane and divided by twice the $A$ obtained for the hindered phenol of above to yield the concentration of *trans*-isomer present. This was then combined with the known concentration of the bis-phenol to yield the per cent. of *cis*-isomer present. The results are given in Table VI. The difference per

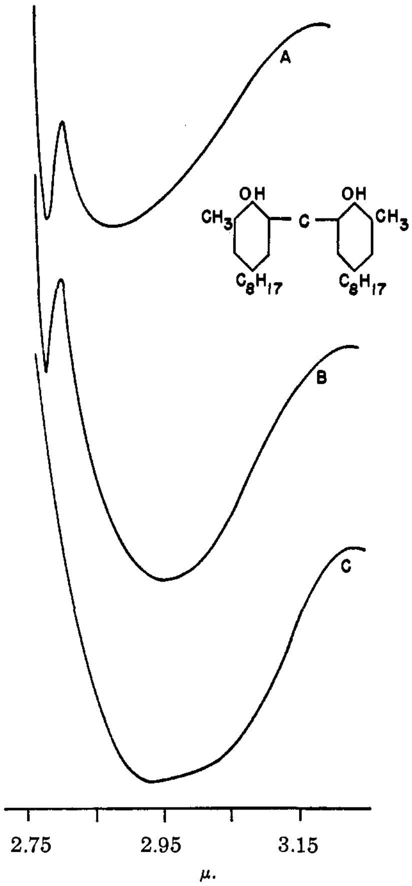

Fig. 6.—Infrared absorption spectra in the hydroxyl region of bis-(2-hydroxy-3-methyl-5-isoöctylphenyl)-methane under various conditions.

TABLE VI

DISTRIBUTION BETWEEN *cis*- AND *trans*-ISOMERIC FORMS AND VALUES OF *A* FOR THE INTRAMOLECULARLY BOUND HYDROXYL GROUP

| Compound | % *trans* | % *cis* | *A* |
|---|---|---|---|
| Bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-methane | 30.3 | 69.7 | 202 |
| 1,1-Bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-ethane | 18.3 | 81.7 | 229 |
| 1,1-Bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-isobutane | 45.3 | 54.7 | 181 |
| Bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-phenylmethane | 7.7 | 92.3 | 102 |
| Bis-(2-hydroxy-3-methyl-5-isoöctylphenyl)-methane | 55.8 | 44.2 | 196 |
| Bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-cyclohexane | .. | 100 | 82 |
| 2,2-Bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-propane | .. | 100 | 442 |
| 2,2-Bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-butane | .. | 100 | 552 |

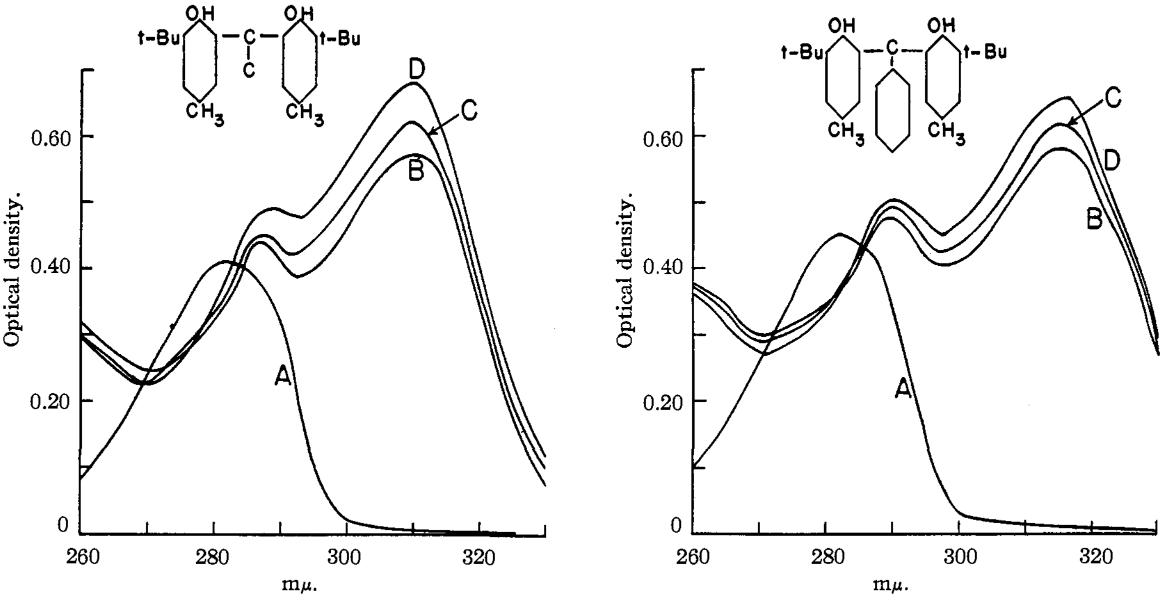

Fig. 7.—Ultraviolet absorption spectra of (a) 1,1-bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-ethane and (b) bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-phenylmethane in: A, ethanol; B, ethanol plus 1.0 × $10^{-1}$ m./l. of sodium hydroxide; C, ethanol plus 5 × $10^{-1}$ m./l. of sodium hydroxide; D, ethanol plus 5.0 m./l. of sodium hydroxide.

cent. of *cis*-isomer present is then used with the optical density for the bound hydroxyl band to yield a value of $A$ for the latter in each case. These are also given in Table VI.

The validity of the data in Table VI rests upon the assumption that the absorption per free hydroxyl group in a bis-phenol alkane is the same as for the hindered phenol. This assumption was used in the calculation of the per cent. distribution between the two isomeric forms. Those data were in turn used in the determination of the $A$ values. With the data obtained there was no way to make an independent check on the above assumption. Since group absorption coefficients are ordinarily reasonably constant in progressing through a series of compounds it is surprising that that $A$ values, *i. e.*, the absorption coefficients for the intramolecularly bound hydroxyls, varied as much as they did. They are constant only to within an order of magnitude. The variations exhibited are presumably due to differences in types of bridging groups and the manner of bridging.

The observations above permitted an interesting prediction of the ionization behavior of the two classes of bis-phenols. In the *cis*-isomeric form the two hydroxyl groups are hydrogen bonded to each other. Since material existing totally in the *cis* form exhibits no free hydroxyl absorption it is known that both hydroxyl protons are involved. The assumed model of the bonding is one of dipole–dipole attraction wherein the proton of each hydroxyl group is attracted to the oxygen atom of the other. Such a configuration allows the electrostatic field due to the dipole moment of one hydroxyl group to essentially cancel out the field due to the other. The electrostatic field about the molecule is at best then a weak quadrupole field. This is in contrast to the two dipole fields attendant to each *trans* isomer. We may therefore expect the *cis*-isomeric form to be less acidic than the *trans* form. We may also expect them to be less acidic for another reason. This is due to the negative potential energy associated with the formation of the intramolecular bond in the *cis* isomer. This results in a higher ionization potential for the *cis* isomers. This expected decrease of acidity is found to be true by ultraviolet absorption measurements which will be discussed below.

The above observations now make available a tool for the determination of substitution in bis-phenols of uncertain structure since their distribution between *cis* and *trans* forms in dilute solution is known to depend on the type and size of the bridging group.

## Ultraviolet Absorption Results

When a phenol molecule becomes ionized the ultraviolet absorption due to the phenyl ring chromophore shifts to the red by about 20 mμ. Thus, ultraviolet absorption spectroscopy provides a useful tool for the study of ionization in phenols. In a recent study[6] of the ionization in a series of substituted phenols it was shown that large alkyl groups ortho to the hydroxyl group are very effective in reducing acidity. Thus the partially hindered phenols are much weaker acids than the unhindered phenols and the hindered phenols are much weaker acids than the partially hindered phenols. This is a result of the smaller differences between energies of solvation of

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[6] N. D. Coggeshall and A. S. Glessner, Jr., THIS JOURNAL, **71**, 3150 (1949).

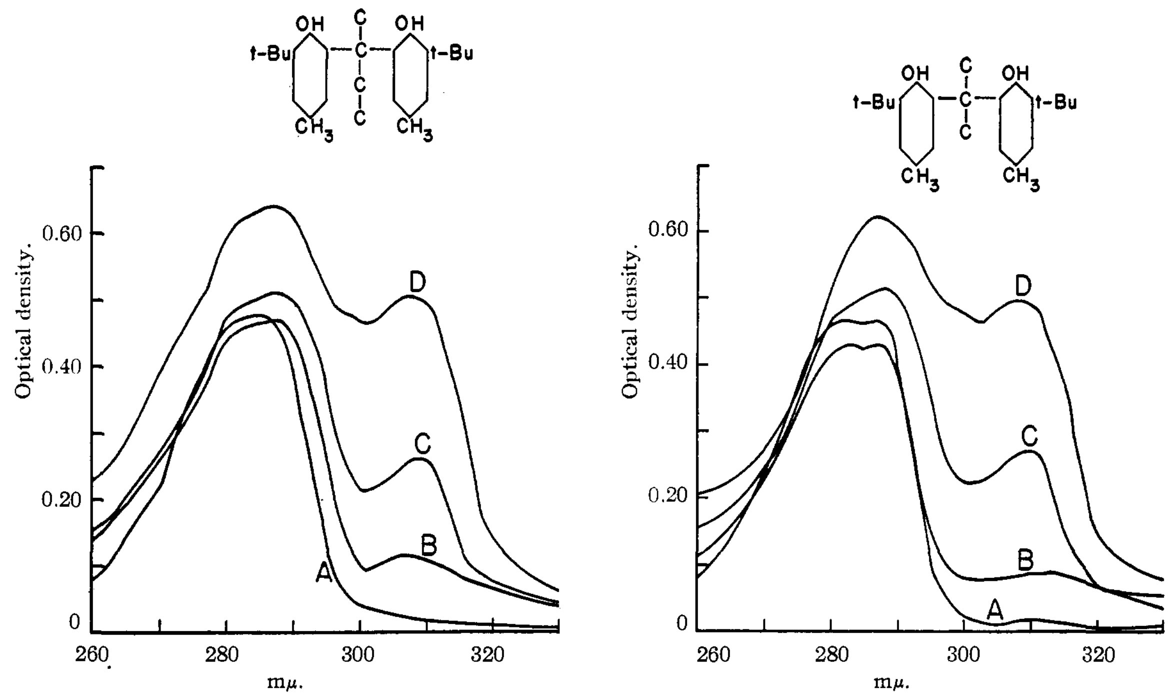

Fig. 8.—Ultraviolet absorption spectra of (a) 2,2-bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-butane and (b) 2,2-bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-propane in: A, ethanol; B, ethanol plus $1.0 \times 10^{-1}$ m./l. of sodium hydroxide; C, ethanol plus $5.0 \times 10^{-1}$ m./l. of sodium hydroxide; D, ethanol plus 5.0 m./l. of sodium hydroxide.

the ions and un-ionized molecules for the hindered materials. In view of the above results we would expect a material existing totally in the *cis* form due to the bridging to remain in the *cis* form after ionization. Thus it would be expected that bis-phenols in the *cis*-isomeric form would be less acidic than those in the *trans*-isomeric form as there would be a large steric hindrance to interaction between the ions and the solvent and hence less increase of energy of solvation upon ionization. The steric hindrance here is due to the *t*-butyl groups ortho to the hydroxyls.

**Bis-phenol Alkanes Existing in *cis*- and *trans*-Isomeric Forms.**—Typical data for two of these materials, the 1,1-bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-ethane and the bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-phenylmethane may be seen in Fig. 7(a) and (b). Curve A refers to the material in ethanol solution and Curves B, C and D to ethanol plus $1.0 \times 10^{-1}$, $5.0 \times 10^{-1}$ and 5.0 m./l. of sodium hydroxide, respectively. For each compound characteristic phenol absorption, centering near 280 mμ, is obtained when examined in ethanol. When sodium hydroxide is added a new and very intense band appears at a longer wave length which is due to the phenolate ion. In the present case the presence of the sodium hydroxide is responsible for an apparent shift of the absorption of the un-ionized material about 5 mμ to the red. This is due to two effects: a virtual shift due to the superposition of absorption due to ionized and un-ionized material and the usual shift to the red due to a change of solvent properties.

Although the addition of $1.0 \times 10^{-1}$ m./l. of sodium hydroxide produces a large change of spectra, further increase of sodium hydroxide concentration by factors of 5 and 50 produce little further change. This is interpreted as follows: the addition of $1.0 \times 10^{-1}$ m./l. of base ionizes most of the *trans*-isomeric material present with little effect on the *cis*-isomeric material; further additions of base have little effect since most of the readily ionizable material is already ionized and the remainder is of the *cis* form which is highly resistant to ionization. This interpretation is consistent with and confirms the predictions of above regarding ionization.

Bis-(2-hydroxy-3-methyl-5-isoöctyl-phenyl)-methane behaves in a class by itself with respect to ionization. Almost complete ionization is achieved with the addition of only 1.0 × $10^{-1}$ m./l. of sodium hydroxide. This is ascribed to the unhindered nature of this phenol, *i.e.*, the lack of large alkyl groups, which allows the close approach between the hydroxyl groups and other molecules or ions with subsequent ionization.

**Bis-phenol Alkanes Existing in the *cis* Form Only.**—Data for two of thes materials, the 2,2-bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-butane and the 2,2-bis-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-propane, are given in Fig. 8(a) and (b). Curve A refers to the material in pure ethanol and Curves B, C and D to the material in ethanol plus $1.0 \times 10^{-1}$, $5.0 \times 10^{-1}$ and 5.0 m./l. of sodium hydroxide, respectively. In contrast to the bis-phenols existing in *cis* and *trans* forms the addition of $1.0 \times 10^{-1}$ m./l. of base produces very little ionization. Also the effects of increasing the base from $1.0 \times 10^{-1}$ to 5.0 m./l. are relatively much larger. However, even the heaviest concentration of base does not produce strong ionization. These observations confirm the predictions of above that such materials would be highly resistant to ionization. Since in the *cis* form the hydroxyls are bonded together and produce a cross cancellation of dipole fields the molecule as a whole possesses at most only small electric fields. It thus has the property of an essentially non-polar material.

As the hydrogen bonding behavior, as observed by infrared absorption, may be used for structure determination so also may the ionization behavior, as observed by ultraviolet absorption. The above data, for example, demonstrate how differentiation may be made between a bis phenol allowing *cis* and *trans* forms and one allowing the *cis* form only.

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## Summary

A series of bis-phenol alkanes have been examined by infrared and ultraviolet absorption spectroscopy. These materials were found to exist in three distinct states, with regard to their hydrogen bonding characteristics. They exist in *cis*- and *trans*-isomeric forms and with intermolecular hydrogen bonding. This *cis*-isomeric form is one wherein the phenolic nuclei are so oriented relative to each other that there is intramolecular hydrogen bonding between the hydroxyl groups. The *trans* form is one wherein the orientation is such that the hydroxyl groups do not influence each other.

Bis-phenol alkanes with a 2,2-substitution on the bridging group or with a bridging group having a very large appendage are restricted to existence in the *cis* form only. They are shown to have been originally synthesized completely in that form.

The distribution between *cis* and *trans* forms is given for those compounds that exist in both states. The distribution in each case appears to be unique to the compound. On the basis of intramolecular hydrogen bonding whereby the two hydroxyl groups effect a cross cancellation of dipole fields it was predicted that those materials existing in the *cis* form only would be less acidic than those existing in *cis* and *trans* forms. This prediction was confirmed by ultraviolet absorption measurements on the materials in alkaline solutions.

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# The Dielectric Constant of Water at High Temperatures and in Equilibrium with its Vapor

By G. C. Akerlof and H. I. Oshry[1]

The dielectric constant of water is one of the most important parameters in all modern theories of aqueous solutions. It is known with considerable accuracy between 0° and 100°.[2,3] Data for temperatures above the boiling point are not to be found in the literature. Thus it was felt to be of considerable value to fill this gap in our knowledge of the properties of one of our most common substances.

**Experimental Theory.**—Ordinary methods for measuring the dielectric constant of a liquid fail when it has a conductivity as high as that of water above its normal boiling temperature. Methods involving standing waves are difficult to handle at high temperatures and pressures as in the present case. Conventional resonance methods are unsatisfactory due to variable stray capacitance errors at the high frequencies required.

Wyman[3] has described a modified resonance method utilizing a rigid reactor immersed in the liquid and where the frequency of the oscillator is matched with that of the resonant frequency of the reactor. For our purposes we adopted a variation of this method. Let us assume that we have a resonant circuit with the capacitance $C$, resistance $R$ and inductance $L$. Its impedance $z$ at the frequency $\omega$ is given by the expression

$$z = \left[R^2 + \left(\omega L - \frac{1}{\omega C}\right)^2\right]^{1/2}$$

The impedance will pass through a minimum when the frequency has the value

$$\omega = 1/\sqrt{LC}$$

If $C_0$ is the capacitance of the circuit in air and

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[1] From the thesis of H. I. Oshry presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Pittsburgh, Pa.

[2] Akerlof, This Journal, **54**, 4125 (1932).

[3] Wyman, *Phys. Rev.*, **35**, 623 (1930); *cf.* Drake, Pierce and Dow, *ibid.*, **35**, 613 (1930).