lected, ignited eventually to 800°, and weighed. Weights are corrected to vacuum.

The Atomic Weight of Protactinium

K₂PaF₇, g.	Pa₂O₃, g.	Ratio 2K₂PaF₇ : Pa₂O₃	At. wt. Pa
0.091907	0.056274	1.6332	230.4
.070047	.042913	1.6323	230.8
	Average	1.6328	230.6

The result seems to be in accord with the expectation that protactinium has the atomic weight 231.

Aston[14] by determination of packing fractions and abundance ratios with the mass spectrograph has obtained the following atomic weights.

Carbon	12.0080	Gallium	69.71
Calcium	40.076	Zirconium	91.24
Titanium	47.91	Silver	107.87
Iron	55.84	Cadmium	112.2
Nickel	58.68	Indium	114.80
		Hafnium	178.4

(14) Aston, Proc. Roy. Soc. (London) A149, 396 (1935).

The only serious discrepancy between these values and the International values is with cadmium.

Thorium and rhodium were found to be probably simple.

By comparison of doublets Aston[15] has obtained new values for several light atoms, although these are still regarded as provisional.

O¹⁶ = 16.0000	O = 16.0000
H = 1.0081	1.0079
D = 2.0148	2.0143
He = 4.0041	4.0031
C¹² = 12.0048	12.0018

If the abundance ratio of D is 1/5000 and that of C^{13} is 1/100, the atomic weights of hydrogen and carbon become 1.0081 and 12.012.

(15) Aston, Nature, 135, 541 (1935).

The Hydrogen Bond between Oxygen Atoms in Some Organic Compounds

By G. E. Hilbert, O. R. Wulf, S. B. Hendricks and U. Liddel

Bonding of hydrogen to two atoms has been recognized and described under such various terms as partial valence, secondary forces, hydrogen bond, chelate ring, coördination, Dimroth ring, association, intramolecular association and the "ortho effect." This very multiplicity of naming reflects the amorphous character of the concept and its partially uncorrelated appearance in the literature during the last twenty-five years.

Such a role of hydrogen in molecule formation seems to have been first postulated by Moore and Winmill[1] (secondary forces) to account for the differences in the basicity of the tertiary and quaternary ammonium bases. The concept was developed (hydrogen bond) within the scope of the Lewis valence theory by Huggins[2] and by Latimer and Rodebush[3] to account for the association of water and for the formation of such ions as HF₂⁻.[4]

It was extended to organic compounds (chelation) by Sidgwick[5] as a particular case of Werner's coördination theory for the formation of closed rings containing metal atoms.[6] This possibility was mentioned earlier by Pfeiffer and co-workers[7] but was not developed.

Various explanations for the formation of this type of atomic linkage have been advanced in terms of coeval theories. Thus partial valence was used by Winmill and others. Lewis wrote the following formula for the acid fluoride ion

$$: \ddot{F} : H : \ddot{F} :$$

whereas Pauling[8] pointed out that the binding must be electrostatic, F⁻H⁺F⁻, since the Pauli exclusion principle, namely, that two electrons cannot have the same quantum numbers, did not
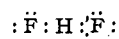
(1) Moore and Winmill, J. Chem. Soc., 101, 1635 (1912).

(2) Huggins, Undergraduate Thesis, University of California, 1919.

(3) Latimer and Rodebush, This Journal, 42, 1419 (1920).

(4) See G. N. Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York, 1923, p. 110.
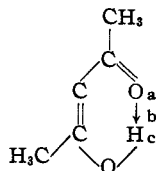
(5) Sidgwick, J. Chem. Soc., 127, 907 (1925).

(6) Werner, Ber., 34, 2586 (1901); 41, 1062 (1908); Morgan, J. Chem. Soc., 117, 1457 (1920).

(7) Pfeiffer, Fischer, Kuntner, Monti and Pros, Ann., 398, 137 (1913).

(8) (a) Pauling, Proc. Nat. Acad. Sci., 14, 359 (1928); (b) This Journal, 53, 1365 (1931).

permit the covalent linkages of Lewis' formula. Sidgwick wrote the enol form of acetylacetone as

in which the arrow indicates a "coördinate co-valence," *i. e.*, one in which the binding electrons are derived from atom a. Finally, Bernal and Megaw[9] suggest that the binding energy partially results from "exchange forces" due to interchange of hydrogen between two such positions as (b) and (c).

While the physical properties of some molecules are sufficiently striking in comparison with normal substances to have led to the concept of the hydrogen bond, absence of definite criteria has hindered general acceptance of the concept. In studying the phenomenon recourse has usually been had to comparison of such properties as association in non-polar solvents, solubility, melting point and volatility of analogous compounds.[10]

In the course of a general quantitative study of the absorption coefficients in the region of the first overtone of the OH absorption in the infrared[11] it was observed that some molecules supposedly containing hydrogen bonds did not give measurable characteristic OH absorption.[12] Similar results were found independently at approximately the same time by Errera and Mollet for liquid salicylaldehyde and o-nitrophenol.[13] Bawn[14] earlier had found that benzoylacetone and acetylacetone[15] (this also was examined by Ellis) when examined as liquids did not give the characteristic OH absorptions at 0.923, 1.55 and 3.00 μ.

We have continued our study of this phenomenon by measuring the absorptions in the region 6000 to 7500 cm.$^{-1}$ of various alcoholic and phenolic compounds. In this region[11] absorption characteristic of OH groupings is to be found as

had been established by empiric analysis. Compounds that according to current concepts and their logical extension might be expected to have hydrogen bonds between oxygen atoms were in general selected for study.

Preparation of Compounds

Such compounds as were available were purchased from the Eastman Kodak Company. In almost all cases these were recrystallized or redistilled and in every case certain of their properties checked with those recorded in the literature. In a number of cases special purification was necessary. For example, Eastman Kodak salicylaldehyde (from bisulfite compound) b. p. 73–74° (10 mm.) contained a small quantity of hydroxy compound and this was removed by converting the aldehyde first to the copper acetate complex and then to the bisulfite compound. Professor Taylor and Dr. Baker of Oxford University, England, supplied generous specimens of 1-benzoylnaphthol-2,3-nitrocatechol, 2-nitroresorcinol, 2,4- and 4,6-diacetylresorcinol, and 2,4- and 4,6-dinitroresorcinol. The hydroxyanthraquinone derivatives were gifts of Director Walter M. Ralph, Research and Development, National Aniline and Chemical Company. Derritol and dihydrorotenol were supplied by Dr. H. Haller, of the U. S. Department of Agriculture. The remainder of the compounds were synthesized by methods already outlined in the literature.

The experimental procedure was the same as in previous work from this Laboratory.[11] It is perhaps best to point out that compounds were studied in carbon tetrachloride solutions at concentrations that did not exceed 0.100 molal, and usually were below 0.03 molal: this since (1) the solvent should be one that does not have absorption in the region investigated, (2) the maximum absorption of the compound should best be suited for accurate measurement, and (3) the various compounds should be studied in equivalent environments. This choice of solvent naturally restricted somewhat the selection of compounds for study due to solubility requirements; thus sulfonic acids in general were excluded. In order to obtain requisite concentrations it was necessary in some instances to heat the solutions, usually to *ca.* 60°, and this is indicated by a parenthetical (h). Absence of such a distinguishing mark indicates that the compound was studied at room temperature.

Since many of the compounds examined did not give characteristic OH absorption in the region mentioned above, data from them are restricted to a statement of this fact. Data for compounds showing measurable absorption in the characteristic OH and NH region are shown in Fig. 2.

Geometrical Requirements

In order that selection of compounds for study might appear intelligible, it is first necessary to discuss some factors that have been suggested as influencing formation of the hydrogen bond. Among these are geometrical configuration, particularly the number of atoms in the ring through

(9) Bernal and Megaw, *Proc. Roy. Soc.* (London), **A151**, 384 (1935).

(10) See N. V. Sidgwick, "The Electronic Theory of Valency," Oxford University Press, Oxford, 1929, p. 147–151.

(11) Wulf and Liddel, THIS JOURNAL, **55**, 3574 (1933); **57**, 1464 (1935).

(12) Hilbert, Wulf, Hendricks and Liddel, *Nature*, **135**, 147 (1935).

(13) Errera and Mollet, *Compt. rend.*, **200**, 814 (1935); *J. phys. radium*, **6**, 281–288 (1935).

(14) Bawn, *J. Chem. Soc.*, 1189 (1932).

(15) Ellis, THIS JOURNAL, **51**, 1384 (1929).

the hydrogen bond[10] (pp. 236–255), electron affinity of atoms sharing the hydrogen bond[4,8a] and "resonance" in a conjugate system of double bonds.[16] We are to be concerned chiefly with the first of these factors.

Fig. 1.—Structural formulas showing probable interatomic distances. A converging line indicates that the line departs from the plane of the figure.

Although the data collected are for compounds in which the hydrogen bond if present is formed intramolecularly, information of value in discussing their geometrical aspects is to be derived from intermolecular compounds. Perhaps the most cogent example is formic acid, the structure of which has been determined by electron diffraction from the vapor.[17] In this compound, which can be represented by a planar formula

$$H{-}C\diagup_{OH\leftarrow\!\!-\!\!-O}^{O\rightarrow H{-}O}\diagdown C{-}H$$

the O-H←O distance is 2.67 Å. This also is approximately the distance found by crystal structure analysis in a number of inorganic salts and oxalic acid, specifically KH_2PO_4, 2.54 Å;[18] $NaHCO_3$, 2.55 Å.;[19] α-$(COOH)_2$, 2.55 $\pm$ 0.15 Å., β-$(COOH)_2$, 2.71 $\pm$ 0.15 Å.[20] The only compound in which the hydrogen bond is formed intramolecularly for which such geometrical information is available is 1,4-dihydroxy-5,8-naphthoquinone, naphthazarine.[21] The crystal structure analysis was not complete but it was found that the molecule has a center of symmetry which indicates average equivalence of the quinone and the hydroxyl oxygen and moreover from the probable separation of the 1,8-positons leads to approximately 2.50 Å. as the O-H←O distance. It thus would appear that 2.60 Å. is a reasonable value for the separation of the oxygen atoms in the hydrogen bond and this will be used throughout the remainder of the work.

The application of structural information derived from diffraction data obtained for a few simple compounds further makes it possible to find the probable separations of atoms in some of the compounds studied. Information for this purpose is perhaps best summarized by Robertson.[22] A possible model for a phenol with an ortho R=O substituent, for example o-hydroxyacetophenone which contains a hydrogen bond, is shown in Fig. 1.

The minimum distance of approach of the two oxygen atoms, a and b, is 2.60 Å. corresponding to the indicated plane configuration and in agreement with the expected O-H-O distance for the formation of a hydrogen bond. This model also holds for the six-membered ring of the enolic form of the β-diketones, for the o-nitrophenols and for the peri substituted aromatic compounds that are among the principal types of compounds in which hydrogen bonds are present.

Results and Discussion

The basis of our work, as stated earlier, is the observation that many hydroxylic compounds in which there are supposed to be hydrogen bonds fail to give detectable OH absorption in a region where such absorption has been found in other

(16) Sidgwick, Annual Reports of the Chemical Society, 1934.

(17) Pauling and Brockway, Proc. Nat. Acad. Sci., 20, 336 (1934).

(18) West, Z. Krist., 74, 330 (1930).

(19) Zachariasen, J. Chem. Phys., 1, 634 (1933).

(20) Hendricks, Z. Krist., 91, 48 (1935).

(21) Palacios and Salvia, Añales soc. españ. fis. quím., 32, 49 (1934).

(22) Robertson, Chem. Rev., 16, 417 (1935).

hydroxylic compounds for which the possibility of formation of a hydrogen bond is absent. This correlation was substantiated as far as ancillary information on hydrogen bond formation permitted and then was extended to cases in which other methods either had not been applied or gave indefinite results.

Characteristic OH absorption in the region studied was absent for acetylacetone, benzoylacetone and dibenzoylmethane. These compounds are typical β-diketones existing predominantly (ca. 85–99%) at equilibrium in their enolic forms and are considered as containing hydrogen bonds[10] (pp. 120, 240). They fulfil the geometrical conditions mentioned above for the formation of six-membered rings through hydrogen. That these geometrical conditions alone are not sufficient for the hydrogen bond formation is shown by the fact that β-hydroxybutyraldehyde (aldol) and α- and β-benzilmonoxime gave typical OH absorptions as shown in Fig. 2. Aldol is representative of substances having an OH group in the β-position of an aliphatic carbonyl compound that are generally considered as normal hydroxy compounds.

Measurements have also been made on a number of aliphatic compounds in which a hydrogen bond if formed would be in a five or seven membered ring. All of these absorb in the region of characteristic OH absorption, but the absorption is often different from that of simple alcohols. Benzoin, α- and β-benzoin oxime acetates, d-diethyl tartrate, d-n-dibutyl tartrate and meso-diethyl tartrate are compounds of this type (see Fig. 2). The hydroxyl groups of the tartaric esters are in both α- and β-positions relative to the carbonyl group, thus being similar both to the α-hydroxy ketone, benzoin, and the β-hydroxy ketone, aldol. In ethyleneglycolmonoacetate, the absorption curve of which has previously been published, the hydroxyl group is separated by two atoms from the one oxygen atom and by four atoms from the other. These observations are in agreement with the fact that none of these compounds has previously been considered as containing a hydrogen bond.

Availability of ortho substituted phenols permitted a rather extensive study of this type of compound. Molecules with a $\overset{\text{O}}{\underset{}{\underset{\text{—C—R}}{\parallel}}}$ group present in the (2) position and with the (3) position occupied by hydrogen did not give OH absorption. The geometrical conditions mentioned above are

satisfied by these substances and previous work on a number of them has shown that they probably contain hydrogen bonds. Compounds studied included the following, where x represents an o-hydroxy aromatic radical:

(A) x—$\overset{\text{H}}{\underset{}{\text{C}}}$=O   Salicylaldehyde, p-Homosalicylaldehyde

(B) x—$\overset{\text{OR}}{\underset{}{\text{C}}}$=O   Methyl salicylate, Phenyl salicylate, 3,5-Dibromomethylsalicylate

(C) x—$\overset{\text{O}}{\underset{}{\text{C}}}$—R   o-Hydroxyacetophenone, 2-Acetonaphthol-1, 1-Benzoylnaphthol-2, 2-Hydroxy-5-methyldiphenylketone, Dihydrorotenol, 1-Hydroxyanthraquinone

Presence of substituents in the (4), (5) or (6) positions of the o-carboxylphenols apparently does not prevent hydrogen bond formation. The naphthol derivatives are of interest in that they show that the bond is formed in at least two of the three possible types of ortho isomers. In dihydrorotenol neither the molecular complexity nor the presence of a heterocyclic ring in the (2) and (3) positions with respect to the OH group prevents formation of the hydrogen bond.

Salicyl amide (h), a compound of type C above, gave the absorption shown in Fig. 2. This absorption is to be compared with that of benzamide which is also shown in the figure. The close similarity of the two absorptions, which are probably due to the NH₂ group, indicates absence of OH absorption and therefore the presence of a hydrogen bond. Characteristic OH absorption was also absent for o-nitrophenol, 2,6-dinitrophenol, and 1-nitronaphthol-2, which are regarded as typical nitro compounds containing rings formed through hydrogen bonds. The only aliphatic nitro compound examined was 9-keto-10-nitro-methyl-9,10-dihydrophenanthrol-10, which gave the absorption shown in Fig. 2 and is considered not to contain a hydrogen bond.

The β-diketones, o-carbonylphenols, and o-nitrophenols tested above are representative of some of the principal types of compounds to which methods of studying the hydrogen bond have been applied successfully. We now shall consider some compounds of a more doubtful nature. Among these are catechol, o-chlorophenol, and 3-nitrocatechol that have been considered[23] as containing hydrogen bonds formed between hydroxyl

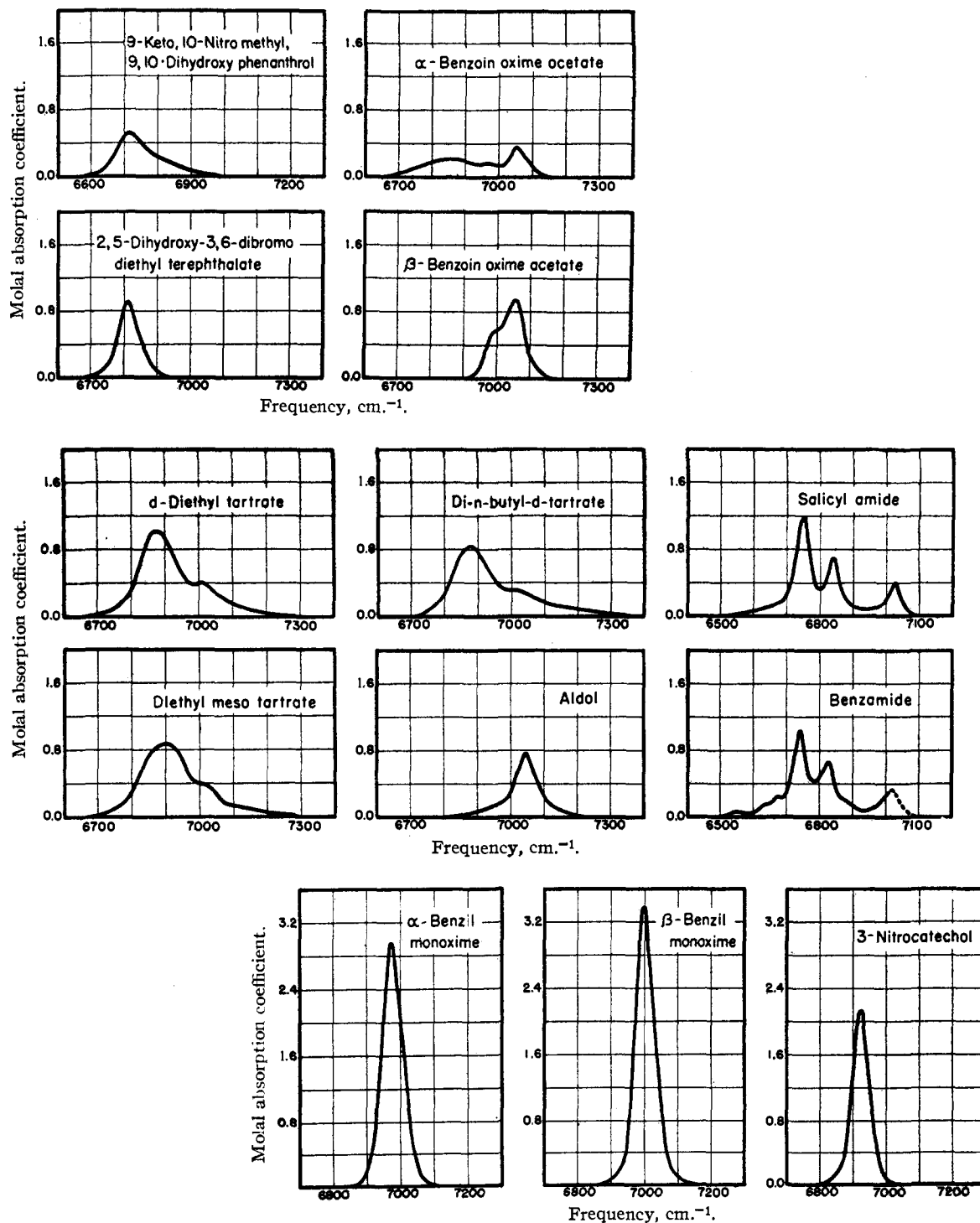(23) (a) Sidgwick, ref. 10, p. 245; (b) Baker, J. Chem. Soc. 1684 (1934).

Fig. 2.—Molal absorption coefficients for some compounds of interest in the question of hydrogen-bond formation. (In top left diagram for 9,10-dihydroxy phenanthrol read 9,10-dihydrophenanthrol-10.)

groups. Absorption curves for the first two of these compounds have been published previously and that for 3-nitrocatechol is shown in Fig. 2. Each shows characteristic OH absorption and

the absorption for 3-nitrocatechol is approximately equal in area to that of m-nitrophenol which has been measured previously. This indicates that a single hydrogen bond is present in 3-

nitrocatechol and that the other two compounds are normal phenols.

It is thought that the above results support the correlation between absence of characteristic OH absorption and hydrogen bond formation and further permits the use of the absorption method as a positive analytical device. The presence of more than one hydrogen bond within a molecule is shown by the absence of OH absorption for 1,4- and 1,5-dihydroxyanthraquinone (h), and 1,4-dihydroxy-5,8-naphthoquinone, naphthazarine. Each of these compounds contains two hydroxyl groups with carbonyl groups in neighboring *peri*-positions and their geometrical requirements can be illustrated by 1,5-dihydroxyanthraquinone.

2.6 Å.
O→H-O

O-H←O
2.6 Å.
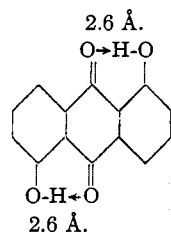
Two hydrogen bonds are also present in 2,4- and 4,6-diacetylresorcinol, and 2,4- and 4,6-dinitroresorcinol, each of which contains two hydroxyl groups with carbonyl or nitro groups *ortho* to them and none of which give OH absorption.

2,4-Dinitroresorcinol, moreover, presents the possibility of formation of two hydrogen bonds to a single group. Absence of OH absorption for 2-nitroresorcinol, which Baker[23b] has considered as containing two hydrogen bonds, indicates that such a structure is possible. Although the configuration of a nitro group has not yet been determined the following structure for 2-nitroresorcinol is reasonable, the entire molecule being in one plane (Fig. 1).

Another interesting example of formation of two hydrogen bonds to a single group is 2-naphthol-1-sulfone which has no hydroxyl absorption. This, moreover, affords an example of a compound in which one of the oxygen atoms is linked to an atom other than carbon or nitrogen. In this case, however, the geometrical arrangement of the atoms cannot reasonably be predicted and the possibility of formation of two hydrogen bonds to a single atom is not excluded. Such a possibility is clearly borne out by 2,2'-dihydroxybenzophenone and 1,8 - dihydroxyanthraquinone, both of which fail to give characteristic OH absorption. These observations indicate that the former compound has the configuration A, in a plane rather than B of Fig. 1, with free rotation around the link ab. A further example of this behavior is afforded by the compound derritol, which is considered to have the structure shown in Fig. 1, and which has no OH absorption. The compound is of particular interest in that the carbonyl group is separated from one of the benzene rings by a carbon atom and thus the ring containing the hydrogen bond is formed from seven atoms. Since this condition cannot obtain in a plane the two hydrogen bonds are not in coplanar rings.

That the steric effect of appropriately placed large atoms or groups can be sufficient to prevent hydrogen bond formation is shown by results obtained from 3,6-dibromo-2,5-dihydroxydiethyl-terephthalate (Fig. 2).[24] The OH absorption, which is appreciable, cannot be safely reduced to a molal value since the compound apparently exists in more than one form,[25,26] but it does indicate that at least part of the molecules do not have hydrogen bonds. This is probably brought about by the displacement of the carbethoxy group resulting from the proximity of the bromine atom. A suggested structure is shown in Fig. 1, in which the groups are rotated about the lines a, b so as not to be in the plane of the figure thus increasing the oxygen separations considerably beyond 2.60 Å., the value required for formation of a hydrogen bond. For purposes of comparison the OH absorption of the unsubstituted 2,5-dihydroxydiethylterephthalate where the steric factor is negligible was determined and found to be absent, thus indicating the presence of two rings formed through hydrogen bonds. The rotation out of the plane of the benzene ring of the carbethoxyl group in 3,6-dibromo-2,5-dihydroxydiethyltere-phthalate indicates the possibility of its existence in both *cis* and *trans* forms. Moreover, it suggests that a similar but asymmetric model, as for example 3-bromo-4- or 5-aminoalkylsalicylate, should be capable of resolution into enantio-morphs.

Discussion

The choice of compounds was sufficiently wide to test the factors, geometrical configuration, electron affinity of the hydroxyl group and resonance,

(24) The results given above for 2,4-diacetylresorcinol indicate that the steric influence of the hydroxyl group in the 3-position is not sufficient to produce such an effect.

(25) Boniger, *Ber.*, **21**, 1758 (1888).

(26) Hermann, *ibid.*, **19**, 2234 (1886).

previously suggested as influencing hydrogen bond formation. The formation of the hydrogen bond seems to be facilitated when the three following geometrical conditions are satisfied: (1) an O-H←O distance of 2.60 Å., and (2) a ring relatively free from strain with (3) a limited number of bonds in the ring about which there can be freedom of rotation. Five-membered hydrogen bonded rings were not encountered and it is to be noted that this type of cycle could only be formed by distortion of the normal valence angles when the O-H←O distance is 2.60 Å. Another contributing factor, perhaps the major one, is the repulsive force on the hydrogen produced by neighboring atoms which are closer in a five than in a six-membered ring. In every case but one the hydrogen bond was present only in six-membered rings. The lone exception is that of derritol (Fig. 1) and if the generally accepted structure is correct, the hydrogen bond forms a seven-membered ring which can be strainless. Freedom of rotation about the single bonds which would have a tendency to break the ring seems to be restricted by the nature of the adjacent large group. Since this condition would not be operative in most cases, seven and eight-membered rings containing hydrogen bonds would be expected to be rare.

Failure of formation of geometrically permissible six-membered rings can be accounted for by low electron affinity of at least one of the oxygen atoms. This is particularly well shown by α- and β-benzilmonoxime that not only have the requisite geometry and constrained rotation but also might contain a resonating system of conjugate double bonds. Low electron affinity is probably responsible in part at least for the absence of hydrogen bonds in alcoholic compounds such as aldol, the tartaric esters and 9-keto-10-nitromethyl-9,10-dihydrophenanthrol-10 that are weak acids compared to most phenolic compounds. The suggestion has been made that the formation of rings containing hydrogen bonds will be favored when the ring would contain either two conjugate double bonds or a double bond conjugate to an aromatic link since the resulting system could be a "resonating" one. That the criterion of high electron affinity is a necessary one and that "resonance" as expressed above or an alternate explanation of restricted rotation are not essential is shown by such molecules as (HF)₆ and γ-diethylaminopropanol, where double bonds are absent and where the hydrogen bonds formed probably result from the high electron affinities of the fluorine and nitrogen atoms.

Although many compounds containing intramolecular hydrogen bonds were studied, no example was encountered in which the hydrogen bonded species is in equilibrium with a detectable amount of a possible OH tautomer. In general absence of OH absorption would, therefore, seem to be a safe criterion for the presence of a hydrogen bond in an alcoholic or phenolic compound. This bears particularly on the results obtained from 4,6-diacetylresorcinol and 4,6-dinitroresorcinol, neither of which show OH absorption. Baker[23b] from his examination of their properties concluded that only a single hydrogen bond is present in each, which he interpreted as supporting Mills and Nixon's theory for fixation of double bonds in a benzene ring.[27] Since our results indicate the presence of two hydrogen bonds in each substance the information is probably not useful in testing the theory.

The most striking chemical property of intramolecular hydrogen bonded molecules is the ability to form coördinated metallic compounds, where the metal takes the place of the hydrogen in the ring. Thus characteristic for molecules containing hydrogen bonds are reactions with stannic chloride[7] to form (I) and with boron acetic acid anhydride[28] to form (II).
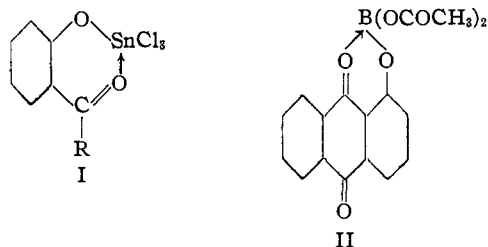
Formation of coördination compounds between 1-hydroxyanthraquinones and boric acid has been used to much advantage as a means for protecting the hydroxyl groups in certain oxidations and condensations. In 1,8-dihydroxyanthraquinone which contains two hydrogen bonds only one of the hydrogen atoms is replaced in the formation of the coördination compound and as far as we know the only exceptions to the replacement of hydrogen in the ring by another element occur when two hydrogen bonds are attached to a single

(27) Mills and Nixon, J. Chem. Soc., 2510 (1930).
(28) Dimroth and Faust, Ber., 54, 3020 (1921).

keto group. Another instance of this was encountered by Pfeiffer and co-workers,[29] who made particular use of the absence of double compound formation between sarcosine anhydride and molecules containing hydrogen bonds. Since one hydroxyl group in 2,2'-dihydroxybenzophenone was involved in forming a double compound with sarcosine anhydride the other was considered to be present in a hydrogen bond. Attention should also be called to the failure of many phenolic compounds containing hydrogen bonds to form brown colored addition compounds with triphenylmethyl chloride. Comparison of other type reactions indicates differences in degree rather than in kind. Although rates of reactions of the potential hydroxyl or keto groups in the simpler hydrogen bonded molecules, as salicyl aldehyde or methyl salicylate, are not greatly different than those in normal aromatic keto hydroxyl compounds, there is a marked depression in the rate of reaction when the freedom of rotation of

the keto group has been restricted. Well-known examples in which the hydroxyl group is difficult to methylate and also usually difficult to esterify are the 1-hydroxyanthraquinones, 1-hydroxyflavones and compounds in the rotenone series, where the OH is ortho to the carbonyl group.[30]

Summary

Infra-red absorption characteristic of hydroxyl groups has been measured quantitatively for a number of selected alcohols and phenols. Since the absence of characteristic OH absorption is found to be closely correlated with the presence of the hydrogen bond as indicated by evidence from other sources, it has been inductively concluded that the absence of such OH absorption constitutes a good criterion for the presence of a hydrogen bond. In the present work this method is used for testing various factors believed to influence the formation of a hydrogen bond between oxygen atoms.

(29) Pfeiffer, Angein, Wang, Seydel and Quehl, J. prakt. Chem., 126, 97 (1930).

(30) This has usually been attributed to "steric hindrance."

The Chemistry of the Citric Acid Fermentation. I. The Carbon Balance

BY P. A. WELLS, A. J. MOYER AND O. E. MAY

Various theories have been proposed to explain the formation of citric acid from sugars by fungi. Challenger[1] has reviewed the mechanisms suggested up to 1929. An appreciable portion of the more recent work recorded in the literature dealing with the citric acid fermentation has been concerned with mechanisms involving acetic acid as one of the important intermediate substances. Naturally the acceptance of such a role for acetic acid has led to the assumption that the appearance of this acid is preceded by a breakdown of glucose similar to that encountered in the alcoholic fermentation of yeast. However, there has been a growing tendency in the past few years to assume that the initial phases of the citric acid fermentation follow the general chemi-

cal equation which represents the alcoholic fermentation without any direct experimental evidence upon which to base such an assumption. The purpose of this communication is to indicate that there is no direct evidence for this assumption and that experimental data show that the usual alcoholic breakdown of glucose plays no part in the formation of citric acid by molds.

Chrzaszcz and Tiukow[2] first reported the biochemical transformation of acetic acid to citric acid by mycelia of *Aspergillus niger* and on the basis of this evidence proposed the theory that the first stage in the formation of citric acid proceeded in a manner similar to that of the alcoholic fermentation.

There is considerable evidence which apparently

(1) F. Challenger, Ind. Chem., 5, 181 (1929).

(2) T. Chrzaszcz and D. Tiukow, Biochem. Z., 229, 343 (1930).