[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY, OXFORD UNIVERSITY]

# The Hydrogen Bond. I. Intra- and Intermolecular Hydrogen Bonds in Alcohols[1]

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The OH bands of a number of dihydroxy compounds have been measured in the 3 micron region. The presence of an intramolecular hydrogen bond was detected by the appearance of two OH bands. The separation of these bands, Δν, is a measure of the length of the hydrogen bond. The effects of substituents and structural changes upon Δν is explained on the basis of changes in the geometry of the molecule. The values of Δν for intra- and intermolecular hydrogen bonds are discussed.

The purpose of this work is to gain further information on the relationship between molecular structure and intramolecular hydrogen bond formation in diols and conversely, to learn something about molecular structure from measurements of the hydrogen bond. Some miscellaneous observations are also reported which shed additional light on the hydrogen bond in mono- and dihydric alcohols.

Previous workers have shown that when the OH groups of a dihydroxy compound are sufficiently close together they will form an internal hydrogen bond. Thus, catechol[3] and *o*-hydroxybenzyl alcohol[4] possess a hydrogen bond whereas resorcinol and hydroquinone do not.[3] Wall and Clausser[5] studied a series of glycols and their monomethyl ethers having the formula $HOCH_2(CH_2)_n$-OH where $n = 1$ to 7. Some of these compounds have now been re-examined because the spectrometer used by these authors was equipped with a rock salt prism instead of a LiF prism and did not give the necessary resolution either to enable them to recognize the hydrogen bond in ethylene glycol and its monomethyl ether or to give sufficiently precise values for the OH frequencies.

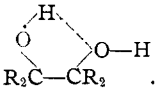
In the present work the OH bands in the 3 micron region have been measured for a number of cyclic and acyclic dihydroxy compounds in $CCl_4$ solution. The concentration, which did not exceed 0.005 molar, was such that intermolecular bonding would not be expected to take place. Certain of the compounds studied possess two OH bands while others have only one. Compounds having two OH bands exist in the form,[6]  $R_2C—CR_2$ (O and O—H, bridged by H). The high frequency band is due to the free OH and the low frequency band is due to the bonded OH. The reasons for believing that the duplicity of bands is due to intramolecular hydrogen bonding are as follows: (a) only those compounds in which the calculated length of the hydrogen bond is less than 3.3 Å. have two bands, (b) the ratio of intensities of the two bands is independent of concentration, (c) by working with more concentrated solutions the band due to intermolecular bonded OH appears and it is at considerably lower frequency than the intramolecular bonded OH. The length of the hydrogen bond is here defined as

TABLE I

FREQUENCY OF OH BANDS IN CM.$^{-1}$

| | | Intramol. | concentrated | |
|---|---|---|---|---|
| Compound | Free OH | Bonded OH | Solution | Crystal |
| *cis*-Cyclopentane-1,2-diol | 3633 | 3572 | | |
| *trans*-Cyclopentane-1,2-diol | 3620 | | | |
| *cis*-Cyclohexane-1,2-diol | 3626 | 3587 | 3405 | 3400, 3260 |
| *trans*-Cyclohexane-1,2-diol | 3634 | 3602 | | 3310 |
| *cis*-Cyclohexane-1,3-diol | 3619 | 3544 | | 3260 |
| *trans*-Cyclohexane-1,3-diol | 3620 | | | 3310, 3220 |
| *cis*-Cyclohexane-1,4-diol | 3629 | | | 3290 |
| *trans*-Cyclohexane-1,4-diol | 3630 | | | 3250 |
| *cis*-Tetrahydronaphthalene-1,2-diol | 3618 | 3575 | | |
| *trans*-Tetrahydronaphthalene-1,2-diol | 3615 | 3582 | | |
| *trans*-1,2-Dihydroxydihydronaphthalene | 3608 | | | |
| *trans*-1,2-Dihydroxydihydroanthracene | 3607 | | | |
| *cis*-9,10-Dihydroxydihydrophenanthrene | 3605 | 3567 | | |
| *trans*-9,10-Dihydroxydihydrophenanthrene | 3605 | | | |
| *cis*-1,2-Dimethylolcyclohexane | 3633 | 3496 | 3293 | |
| *trans*-1,2-Dimethylolcyclohexane | 3631 | 3479 | 3268 | |
| Catechol | 3616 | 3567 | | |
| Resorcinol | 3610 | | | |
| Ethylene glycol | 3644 | 3612 | | |
| Ethylene chlorohydrin | 3630 | 3600 (weak) | | |
| Ethyl cellosolve | | 3607 | | |
| Trimethylene glycol | 3636 | 3448 | | |
| Tetramethylene glycol | 3634 | 3478 | | |
| Hexamethylene glycol | 3639 | | | |
| *d*-Butane-2,3-diol | 3633 | 3588 | 3415 | |
| *meso*-Butane-2,3-diol | 3630 | 3591 | 3450 | |
| Tetramethylethylene glycol | 3626 | 3583 | 3477 | |
| Benzophenone pinacol | 3608 | 3567 | | 3609, 3568 |
| Fluorenone pinacol | 3600 | 3574 | 3462 | 3572, 3365 |
| Cyclohexanone pinacol | 3512 | 3567 | | 3485, 3375 |
| Cyclopentanone pinacol | 3618 | 3578 | 3490 | 3415 |

Monohydric Alcohols

| | Free OH | Dimer | Polymer | ROH---OEt$_2$ | φOH---ROH |
|---|---|---|---|---|---|
| Methanol | 3462 | 3525 | 3341 | 3491 | 3390 |
| *n*-Butyl alcohol | 3634 | 3506 | 3338 | 3484 | 3377 |
| 2-Butanol | 3627 | 3498 | 3384 | 3492 | 3366 |
| *t*-Butyl alcohol | 3614 | 3495 | 3344 | 3486 | 3344 |
| Phenol | 3608 | 3472 | 3338 | 3330 | |

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(1) Presented at the International Union of Chemistry Meeting, New York, N. Y., Sept., 1951.

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(3) M. Davies, *Trans. Faraday Soc.*, **34**, 1427 (1938).

(4) M. Davies, *ibid.*, **36**, 1114 (1940).

(5) F. T. Wall and W. F. Claussser, THIS JOURNAL, **61**, 2679 (1939).

(6) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p. 320.

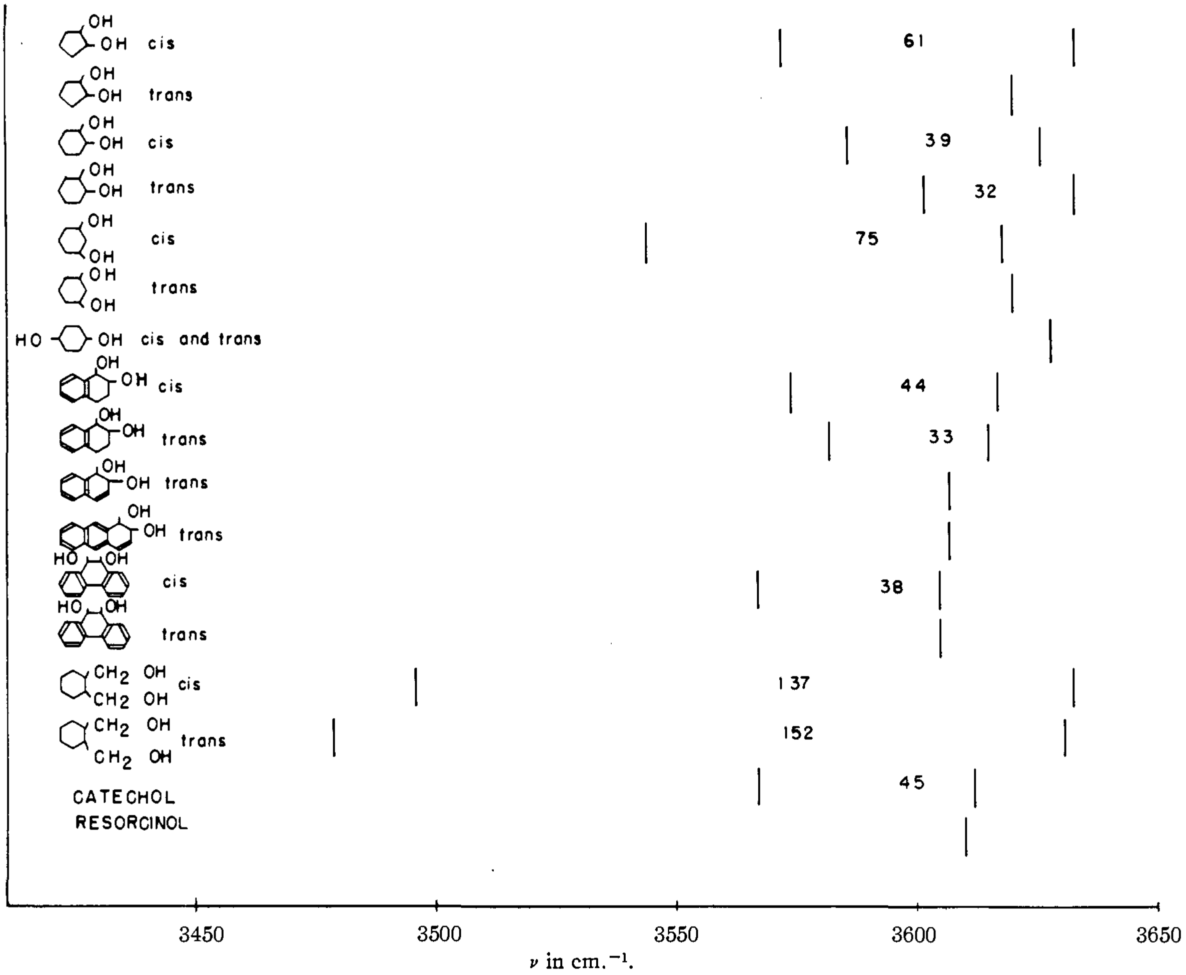

Fig. 1.—OH bands of cyclic diols.

the distance between the hydrogen atom of one OH and the oxygen atom of the other. The bond is designated by the symbol H---O.

## Experimental

The compounds used were purified by distillation or recrystallization and their boiling or freezing points checked with those in the literature. The $CCl_4$ used as solvent was distilled over $P_2O_5$ and stored over $P_2O_5$ until used. The measurements were taken with a Perkin-Elmer model 12B spectrometer equipped with a LiF prism. For the bands due to unassociated molecules, solutions were made up to be 0.005 molar; however in many cases the compound was not soluble to this extent and a saturated solution was used which was less than 0.005 molar. A cell of 20-mm. thickness was used. The frequencies could be measured to an accuracy of ± 1 $cm.^{-1}$ although the absolute values of the frequencies may be off by slightly more than 1 $cm.^{-1}$. The lower frequency bands were usually broad and for this reason could not be measured as accurately as the sharper, higher frequency bands.

To prove that the bond is intra- rather than intermolecular the intensities of the two bands were measured at two concentrations which differed by a factor of approximately two. If the bonding were intermolecular the low frequency band would decrease and the other would increase with dilution, hence the ratio of intensities, low frequency/high frequency, should be less at the lower concentration. The following data give the name of the compound, the ratio at low concentration and ratio at higher concentration: *meso*-butane-2,3-diol, 98, 85; *trans*-cyclohexane-1,2-diol, 1.26, 1.31; catechol, 92, 93. There is no regular change in intensity ratio with concentration, hence the hydrogen bond must be intramolecular.

The frequencies of all the bands studied are given in Table I.

**Cyclic Compounds.**—Figure 1 contains the results obtained with cyclic diols. The vertical lines represent the OH bands and the numbers indicate the difference in wave numbers ($cm.^{-1}$) between the free and bonded OH bands. For convenience this difference will be designated by $\Delta\nu$, The observed differences in $\Delta\nu$ are attributed to differences in H---O distance. Badger[7] has shown that the stronger the hydrogen bond the greater is $\Delta\nu$. One would thus expect that the value of $\Delta\nu$ would vary inversely with the length of the hydrogen bond. Table I contains the calculated H---O distances and the values of $\Delta\nu$ for some of the compounds studied. The former were obtained using the

TABLE II

RELATIONSHIP BETWEEN H---O DISTANCES AND $\Delta\nu$

| Compound | $\Delta\nu$ | $\varphi$ | H---O dist., Å. |
|---|---|---|---|
| *cis*-Cyclopentane-1,2-diol | 61 | 0 | 1.84 |
| *trans*-Cyclopentane-1,2-diol | 0 | 120° | 3.3 |
| *cis*-Cyclohexane-1,2-diol | 39 | 60° | 2.34 |
| *trans*-Cyclohexane-1,2-diol | 32 | | |
| (equatorial) | | 60° | 2.34 |
| (polar) | | 180° | >3.3 |
| *cis*-Cyclohexane-1,3-diol | 75 | | |
| (polar) | | | 1.64 |
| (equatorial) | | | >3.3 |
| *trans*-Cyclohexane-1,3-diol | 0 | | >3.3 |
| *cis*- and *trans*-Cyclohexane-1,4-diol | 0 | | >3.3 |

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[7] R. F. Badger, *J. Chem. Phys.*, **8**, 288 (1940).

following values[6] for bond distances and bond angles: C–C 1.54, C–O 1.42, O–H 0.96 Å., C–C–O 109° 28′, C–O–H 108°. The assumption is made that the orientation around the C–O bond is such that the H—O distance is a minimum. In picturing the H—O distances in compounds containing OH groups on adjacent carbon atoms it is convenient to consider the angle, $\varphi$, which is defined as the angle that one observes bounded by the two C–O bonds when the eye of the observer and the two carbon atoms are on a straight line. These angles are also included in Table II.

Each carbon of cyclohexane has a polar and an equatorial bond.[8] The former are more or less perpendicular to the plane of the ring and the latter are in the plane of the ring. In *cis*-cyclohexane-1,2-diol one OH group occupies a polar position and the other an equatorial position. In the *trans*-compound there are two possibilities: each OH may be polar or each may be equatorial. In the *trans*-cyclohexane-1,3-diol one OH is polar and the other equatorial. In the *cis*-compound there are again two possibilities: each may be polar or each may be equatorial. The data in Table II show that in the *trans*-1,2-diol the OH groups are equatorial and in the *cis*-1,3-diol they are polar. If the OH groups were in the other positions they would be farther apart than in *trans*-cyclopentane-1,2-diol and hence would have no hydrogen bond. The molecules seem to assume the position which enables the OH groups to be as close together as possible. On the basis of thermodynamic data, previous workers[8] have shown that in dimethylcyclohexanes the more stable forms are those in which the methyl groups are in equatorial positions. These are the positions which allow a maximum distance between methyl groups and between methyl groups and hydrogen atoms.

As shown in Table II, both *cis*- and *trans*-cyclohexane-1,2-diols have the same calculated H---O distance and yet the *cis*-compound has the larger $\Delta\nu$. The attraction between the OH groups in forming a hydrogen bond will tend to produce a rotation around the C–C bond thus reducing the angle $\varphi$. As shown in Fig. 2 this will make the ring more planar in the *cis*-compound and more puckered in the *trans*. The potential energy curve for rotation around a C–C bond of cyclohexane has two minima and the ring goes through the planar form in going from one minimum to the other, hence the curve is not symmetrical around a minimum but has a steeper slope in going toward the more puckered shape as compared with going toward the more planar shape. For a given expenditure of energy the OH groups of the *cis*-compound can get closer together than those of the *trans*. This can be readily demonstrated with models and explains why $\Delta\nu$ is larger for the *cis* than for the *trans*-compound.

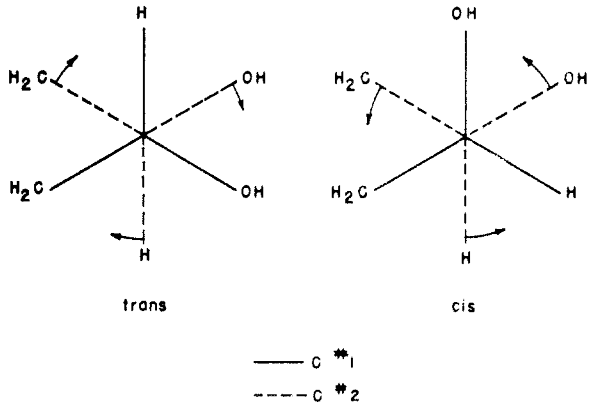

Fig. 2.—Cyclohexane-1,2-diol.

When a benzene ring is fused to a cyclohexane molecule as in tetrahydronaphthalene it is no longer possible to have a chair form because carbon atoms 1 and 4 of the hydrogenated ring must be in the plane of the benzene ring. Two strainless or almost strainless forms of this molecule can be made with models. As shown in Fig. 3 the hydrogenated ring may be in either a boat form or in what may be called a semi-puckered form. In the boat form, $\varphi = 60°$ for both *cis*- and *trans*-tetrahydronaphthalene-1,2-diol. In the semi-puckered form $\varphi = 60°$ for the *cis*- and *trans*-compounds when the OH groups are in positions 1 and 2 as shown in Fig. 3, but when the OH groups are in positions 3 and 4, $\varphi < 60°$ for the *cis*- and $\varphi > 60°$ for the *trans*-compound. The values of $\Delta\nu$ given in Fig. 1 indicate that the *cis*-compound is in the semi-puckered form with the OH groups in positions 3 and 4, and that the *trans*-compound is either in the boat form, or in the semi-puckered form with the OH groups in positions 1 and 2.

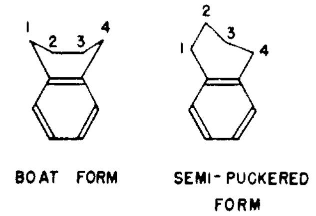

Fig. 3.—Tetrahydronaphthalene.

The hydrogenated rings of 1,2-dihydronaphthalene and 1,2-dihydroanthracene must be planar which means that in these *trans*-1,2-diols $\varphi = 120°$. As might be expected these compounds, like the planar cyclopentanediols, have no hydrogen bond. The *cis*-isomer was not available for study. The 9,10-dihydrophenanthrene-9,10-diols also appear to be almost, if not completely, planar for the *trans*-compound has no hydrogen bond. The *cis*-compound has a $\Delta\nu$ of 38 cm.$^{-1}$ which is smaller than one might expect since $\varphi$ should be about 0°. This ring however is strained and a calculation of the H—O distance is impossible. *cis* and *trans*-bishydroxymethylcyclohexane each possess two OH bands with the relatively large separation of 137 and 152 cm.$^{-1}$, respectively. The H---O distances in these compounds are less than that in any of the compounds previously discussed and were not possible to calculate because the closest approach of the two atoms is less than 0.96 Å., the length of a covalent bond.

The data relating H—O distance with $\Delta\nu$ which are given in Table II are shown graphically in Fig. 4. A curve of somewhat similar shape has been found for $\Delta\nu$ *versus* energy of the hydrogen bond.[7] In the range of values of H—O distance which was available, namely, 1.6 to 3.3 Å., a linear relationship was found between $\Delta\nu$ and the reciprocal of the H—O distance as shown in Fig. 4. This relationship can be expressed by the equation

$$\Delta\nu = \frac{250 \times 10^{-8}}{L} - 74$$

where $L$ is the H---O distance in cm. These relationships apply only to an intramolecular bond between two OH groups or to an intermolecular bond in a dimeric monohydric alcohol in $CCl_4$ solution. As will be shown shortly, when the OH group interacts with two neighboring groups as in polymeric associated alcohols or with more than two neighboring groups as in crystals, $\Delta\nu$ will be much larger for a given H—O distance than that given in Fig. 4. For associated poly-

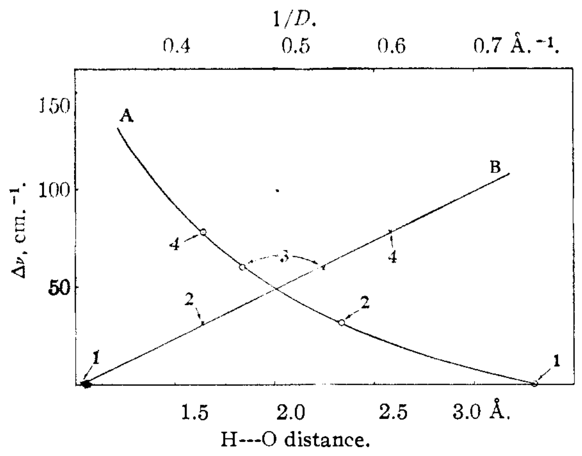

Fig. 4.—A, H---O distance *vs.* $\Delta\nu$; B, $1/D$ *vs.* $\Delta\nu$: 1, *trans*-cyclopentane-1,2-diol; 2, *trans*-cyclohexane-1,2-diol; 3, *cis*-cyclopentane-1,2-diol; 4, *cis*-cyclohexane-1,3-diol.

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[8] C. W. Beckett, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2488 (1948).

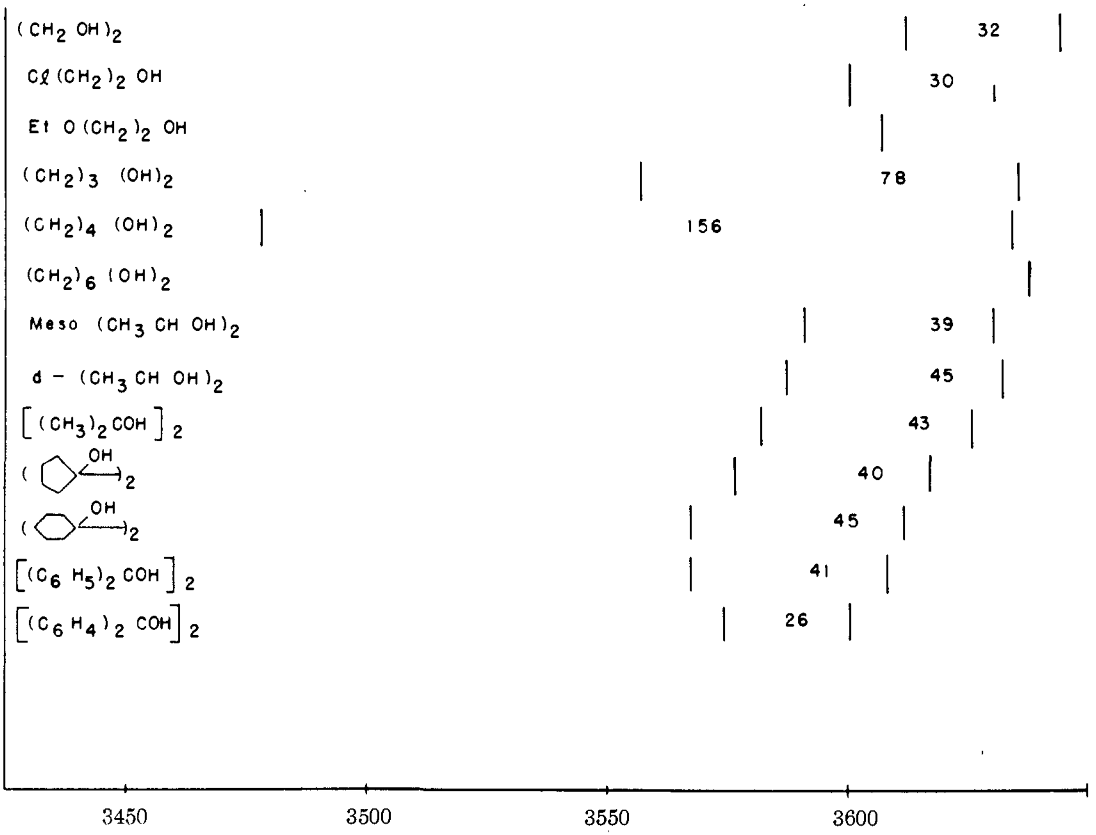
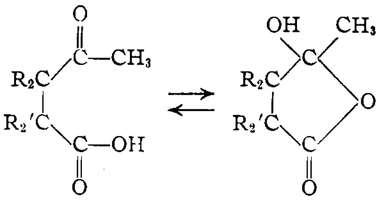


Fig. 5.—OH bands of glycols and related compounds.

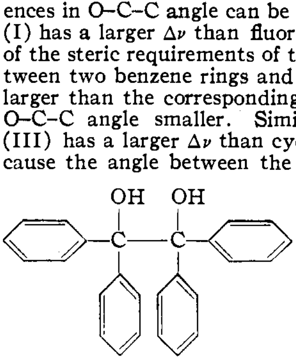
meric alcohols $\Delta\nu$ is approximately 300 cm.$^{-1}$ and for crystalline alcohols it can be greater than 400 cm.$^{-1}$. The largest value of $\Delta\nu$ that has been found in this work, 156 cm.$^{-1}$ for tetramethylene glycol, corresponds to an H---O distance of 1.1 Å. which is not much larger than the O–H distance of 0.96 Å. The H—O distance in dimeric monohydric alcohols, for which $\Delta\nu$ = 120–130 cm.$^{-1}$, is 1.2 to 1.3 Å, which corresponds to an O–H—O distance of 2.2–2.3 Å. The O–H---O distance in crystalline alcohols from X-ray data is about 2.7 Å. Because these distances are shorter than one would expect them to be and because they were obtained by a rather large extrapolation from a few points these values must be accepted with suspicion.

**Acyclic Compounds.**—In this group are included a number of substituted ethylene glycols and related compounds which are shown in Fig. 5. The differences in $\Delta\nu$ between closely related compounds are again believed to be due to differences in H---O distance. In substituted ethylene glycols this distance may be considered to be dependent upon $\varphi$ and upon the O–C–C angle. A weaker bond is found in *meso*- than in *d*-butane-2,3-diol which is believed due to a difference in $\varphi$. As $\varphi$ is decreased a methyl group becomes aligned with a methyl in the *meso*-compound whereas in the *d*-compound the methyl group becomes aligned with a hydrogen. Since the repulsion between a methyl and a hydrogen is less than the repulsion between two methyl groups $\varphi$ will be smaller in the *d*-compound.

In the series of compounds ethylene glycol, *meso*-butane-2,3-diol, and tetramethylethylene glycol the respective values of $\Delta\nu$ are 32, 39 and 43 cm.$^{-1}$. For reasons which will appear later, the increase in $\Delta\nu$ which results, upon the replacement of hydrogen by methyl, is believed to be due not to a change in polarity of the OH groups but to a decrease in the H---O distance. Since the angle, $\varphi$, would be expected to be larger in tetramethylethylene glycol than in ethylene glycol one must conclude that the replacement of hydrogen by methyl reduces the O–C–C angles. This alteration of bond angles is not without precedent. It is known as the Thorpe–Ingold deformation theory which says that when one of the angles at a carbon atom is increased the opposite angle is decreased. This theory was used to explain the fact that in certain types of ring chain tautomerism, the equilibrium



is displaced toward the cyclic form when R or R' is methyl instead of hydrogen.[9] Several other examples of differences in O–C–C angle can be found in Fig. 4. Benzpinacol (I) has a larger $\Delta\nu$ than fluorenone pinacol (II). Because of the steric requirements of the benzene rings the angle between two benzene rings and a central carbon atom in I is larger than the corresponding angle in II thus making the O–C–C angle smaller. Similarly, cyclohexanone pinacol (III) has a larger $\Delta\nu$ than cyclopentanone pinacol (IV) because the angle between the non-planar cyclohexane rings



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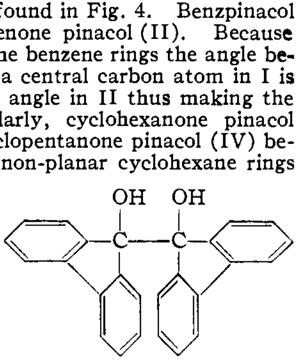
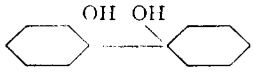
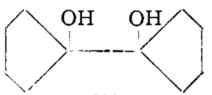


II



III



IV

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[9] J. W. Baker, "Tautomerism," G. Rutledge and Sons, Ltd., London, 1934, p. 179.

and a central carbon atom is larger than the angle between the planar cyclopentane rings and the central carbon atom thus making the O–C–C angles of III smaller than those of IV. These comparisons can easily be seen with the aid of molecular models.

The frequency of the OH band of cellosolve (ethylene glycol monoethyl ether) indicates that it has an intramolecular hydrogen bond. It has also been found to exist in the bonded form in the vapor phase.[10] Because it has two OH bands ethylene chlorohydrin probably exists in two forms which are rotational isomers. The isomer in which there is a hydrogen bond predominates for the low frequency band is much the stronger. Whether this isomerism is due to rotation around the C–C bond or around the C–O bond has not been ascertained. In the homologous series of polymethylene glycols, $\Delta\nu$ increases in going from ethylene glycol, 32 cm.$^{-1}$, to trimethylene glycol, 78 cm.$^{-1}$, to tetramethylene glycol, 156 cm.$^{-1}$, because of the decrease in H---O distance. The similarity between the values of $\Delta\nu$ for the members of this series and for the compounds *trans*-cyclohexane-1,2-diol, *cis*-cyclohexane-1,3-diol and *trans*-1,2-bis-hydroxymethylcyclohexane, is striking and indicates that the H---O distances are about the same for the corresponding members of the two series which is what one would expect. This strengthens the belief that $\Delta\nu$ is a sensitive measure of the H---O distance. There is no bond in hexamethylene glycol.

The bands of some of the substances studied are shown in Fig. 6 to illustrate some of the differences in band shapes.

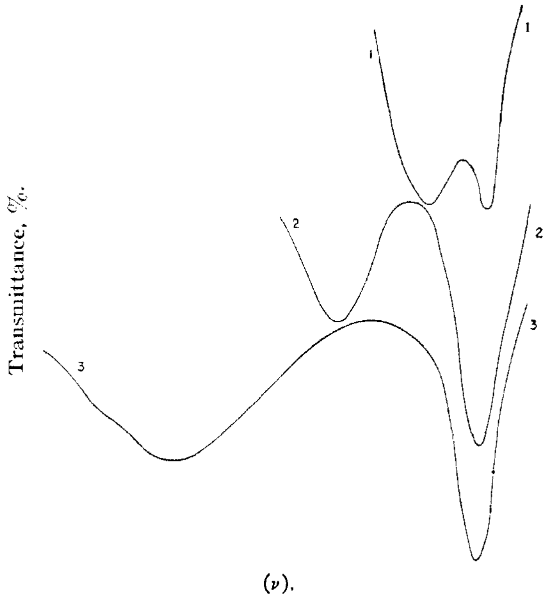

Fig. 6.—1, Ethylene glycol; 2, trimethylene glycol; 3, tetramethylene glycol.

The larger the value of $\Delta\nu$ the broader and less intense is the bonded OH band. The broadness of certain bonded OH bands has been frequently observed[11] and can be correlated to the strength of the bond or to $\Delta\nu$. If all of the hydrogen bonds present in a solution of a diol are not exactly the same length but have a range of lengths of, say, 0.1 Å., then from Fig. 4 the bonded OH band would be 3 cm.$^{-1}$ wide if the H---O distance were 2.5 Å., but would be about 15 cm.$^{-1}$ wide if the H-O distance were 1.5 Å. because of the change in slope of the curve. The relative intensities of free and bonded OH bands seem to vary in closely related compounds as shown in Fig. 7. In ethylene glycol and *d*-butane-2,3-diol the free and bonded OH bands are of about the same intensity, whereas in *meso*-butane-2,3-diol and in tetramethylethylene glycol the free OH band is considerably stronger than the bonded OH band. In the cyclohexane-1,2-diols the two bands of the *cis* are of the same intensity whereas in the *trans* the bonded band is much the stronger. In benzpinacol the bonded OH band is much stronger than the free OH while in fluorenone pinacol the reverse is true. The reason for these differences is not understood.

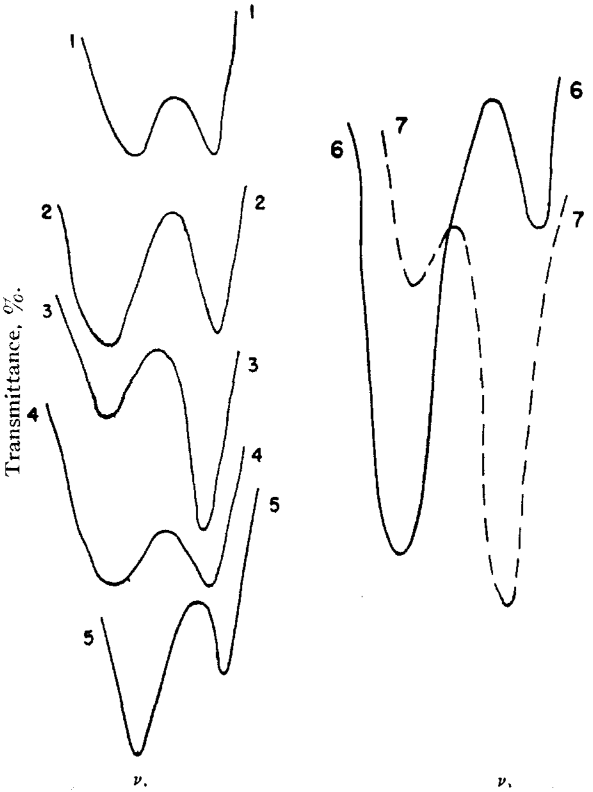

Fig. 7.—OH bands of some dihydroxy compounds: 1, ethylene glycol; 2, *d*-butane-2,3-diol; 3, *meso*-butane-2,3-diol; 4, *cis*-cyclohexane-1,2-diol; 5, *trans*-cyclohexane-1,2-diol; 6, benzpinacol; 7, fluorenone pinacol.

**Intermolecular Bonds.**—Those diols which are sufficiently soluble in $CCl_4$ were studied in solutions of such concentration that intermolecular bonding takes place. In addition to the bands due to free and intramolecular bonded OH, these solutions have a third band which is at lower frequency than the first two and which is due to intermolecular bonded OH, as shown in Fig. 8. The extinction coefficient of this band decreases with dilution and at concentrations less than 0.004 molar the band is imperceptible. For purposes of comparison the OH bands of some simple monohydric alcohols were also measured and are shown in Fig. 8. At suitable concentrations these also have three bands which, as previous workers have shown, are due to free OH, bonded OH in dimers and bonded OH in polymers.[12]

Those molecules, such as tetramethylene glycol and dimethylolcyclohexane, the geometry of which places no restriction upon the H---O distance, have values of $\Delta\nu$ which are slightly larger than the $\Delta\nu$ of dimeric monohydric alcohols. This may be due to the fact that the distance between non-bonded atoms in the same molecule can be considerably smaller than the distance between non-bonded atoms in different molecules.

The value of $\Delta\nu$ (polymer) is larger than that of $\Delta\nu$ (dimer) because the bonded OH in the dimer, $\overset{R}{\mathrm{O}}\text{–H---}\overset{R}{\mathrm{O}}\text{–H}$, like the intramolecular bonded OH, interacts only with a hydrogen acceptor, whereas in the polymer, $\overset{R}{\mathrm{O}}\text{–H---}\overset{R}{\mathrm{O}}\text{–H---}\overset{R}{\mathrm{O}}\text{–H}$, the bonded OH interacts on one side with a hydro-

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(10) L. R. Zumwalt and R. Badger, This Journal, **62**, 305 (1940).

(11) *Discussions of the Faraday Soc.*, **9**, 212 (1950).

(12) (a) J. J. Fox and A. S. Martin, *Proc. Royal Soc.* (*London*), **162**, 419 (1937); (b) J. Errera, R. Gaspart and H. Sack, *J. Chem. Phys.*, **8**, 63 (1940); (c) F. A. Smith and E. C. Creitz, *J. Research Natl. Bur. Standards*, **46**, 145 (1951).

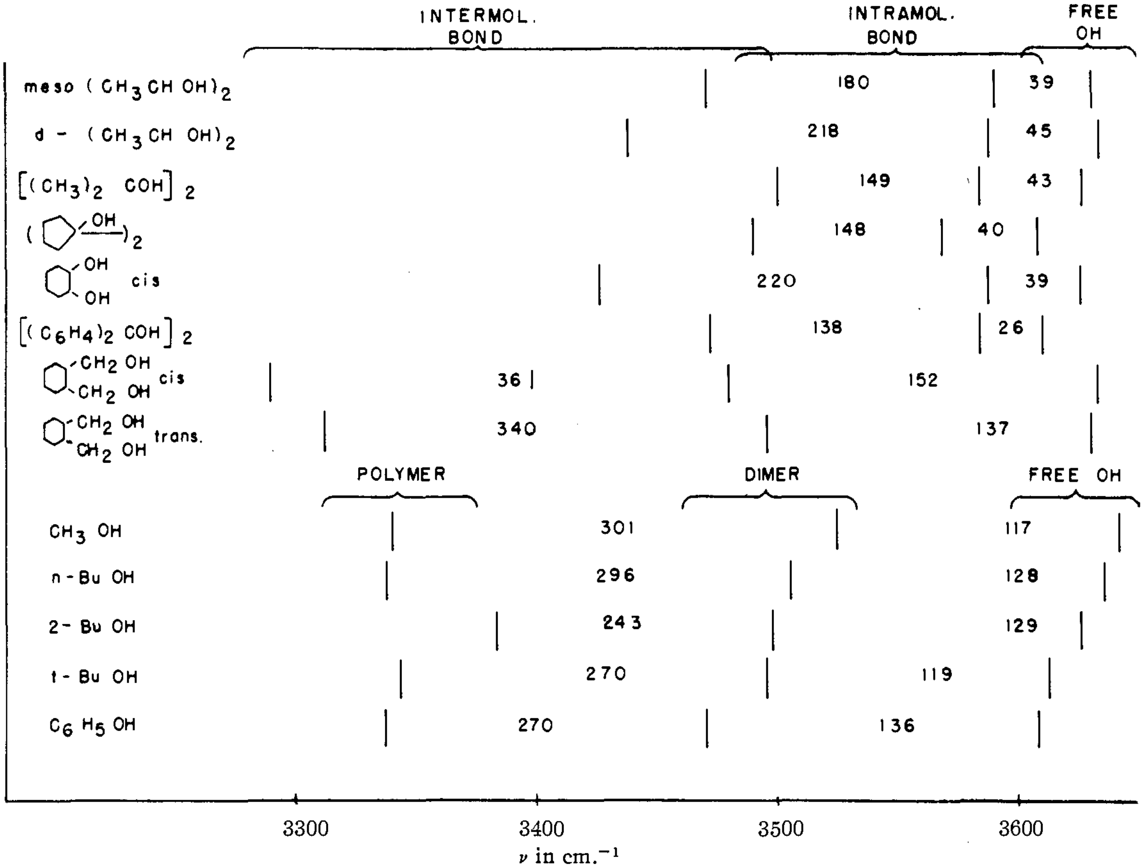


Fig. 8.—OH bands of some mono- and dihydric alcohols.

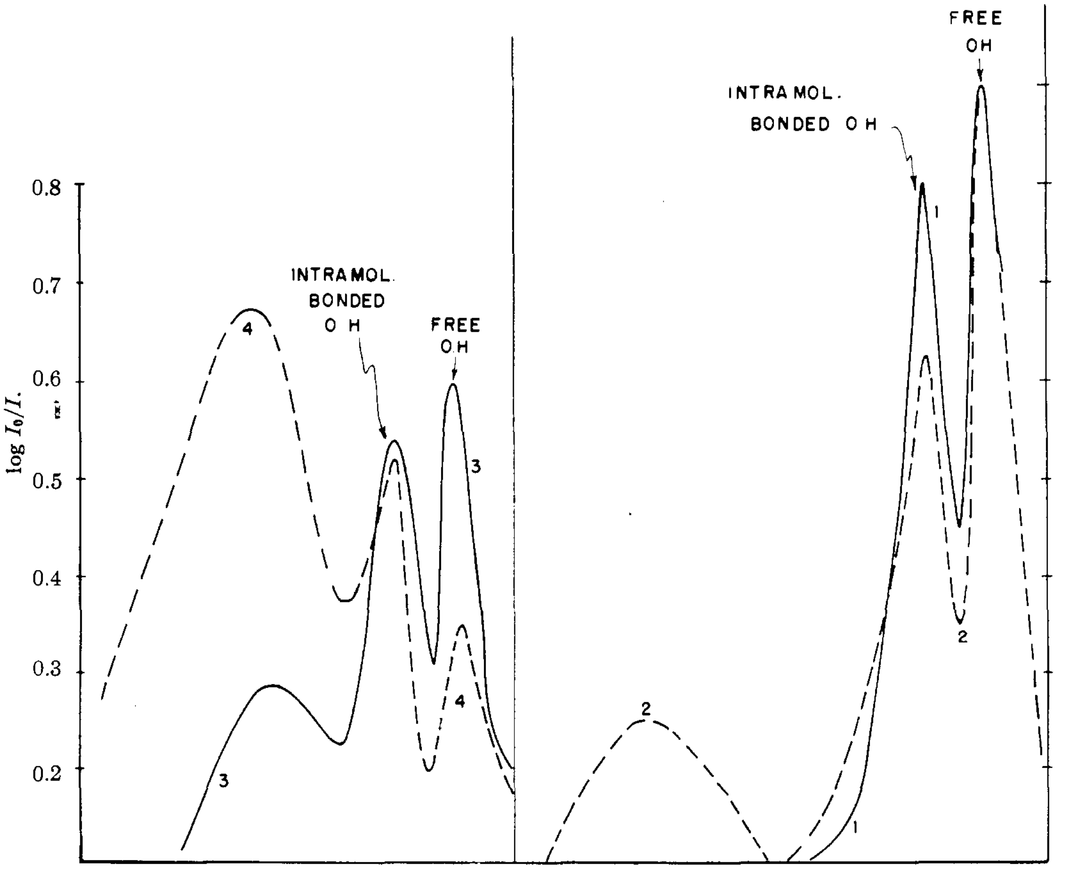
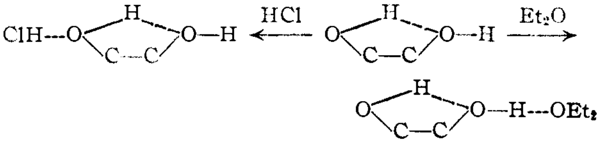


Fig. 9.—(1) 0.006 molar tetramethylethylene glycol (TEG); (2) 0.006 molar TEG plus dry HCl; (3) 0.05 molar TEG; (4) 0.05 molar TEG, 0.1 molar ethyl ether. Cell thickness: (1) and (2) 20 mm.; (3) and (4) 1.6 mm.

gen acceptor and on the other side with what we may call an electron acceptor. Evidence for the validity of this explanation is shown in Fig. 9. A 0.05 molar solution of tetramethylethylene glycol has three bands due to polymeric, internally bonded, and free OH, respectively, the first being very weak at this concentration. Upon the addition of ethyl ether, which acts as a hydrogen acceptor, the free OH band becomes weaker, the internally bonded OH is unchanged and the polymeric band becomes stronger. If, instead of ether, dry HCl which acts as an electron acceptor is added, the free OH band remains unchanged and the internally bonded band is weakened because some of it is converted to the polymeric OH. These reactions can be pictured as



The hydrogen acceptor may be considered to be a base and the electron acceptor an acid in the Lewis sense. Gordy[13] has in fact shown that the more basic is the hydrogen acceptor the stronger is the hydrogen bond as measured by $\Delta\nu$. One would expect, although it has never been demonstrated, that in the presence of a given hydrogen acceptor the hydrogen bond formed by various alcohols would be stronger the more acidic the alcohol. Figure 10 shows the associated OH band for 0.1 molar *t*-butyl alcohol and for 0.1 molar phenol. When equal parts of these solutions are

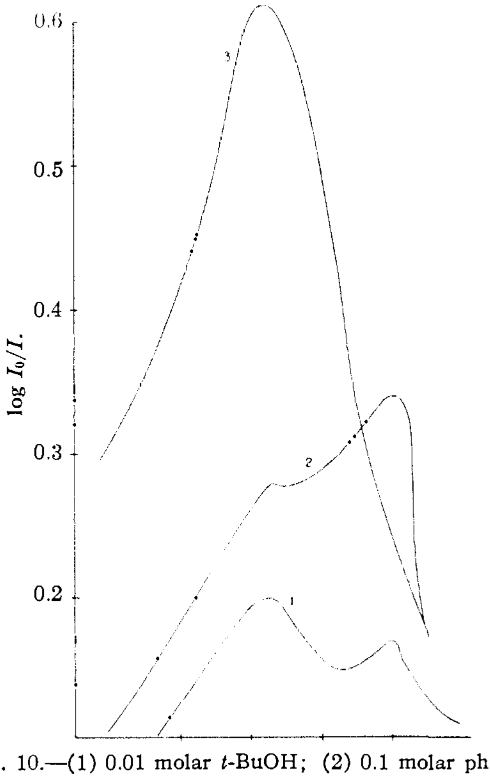
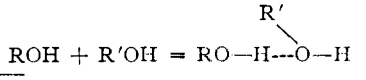


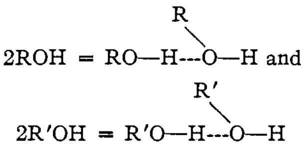
Fig. 10.—(1) 0.01 molar *t*-BuOH; (2) 0.1 molar phenol; (3) 0.05 molar *t*-BuOH, 0.05 molar phenol; cell thickness. 2 mm.

mixed, a solution 0.05 molar with respect to each solute is obtained which has a markedly different associated OH band than the original solutions. The large increase in band intensity shows that the equilibrium constant for the reaction



$$\mathrm{ROH + R'OH = RO{—}H{---}\overset{R'}{O}{—}H}$$

is much larger than the equilibrium constants for the reactions



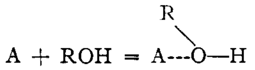
$$\mathrm{2ROH = RO{—}H{---}\overset{R}{O}{—}H} \text{ and}$$

$$\mathrm{2R'OH = R'O{—}H{---}\overset{R'}{O}{—}H}$$

where R is phenyl and R′ is *t*-butyl. The OH band of the mixture which is a dimer band, is at a much lower frequency than the dimer band of either phenol or *t*-butyl alcohol. In fact it is at about the same frequency and hence has the same $\Delta\nu$ as the polymeric OH band of phenol or *t*-butyl alcohol, which indicates that the hydrogen bond between phenol and *t*-butyl alcohol is much stronger than the bond between two molecules of phenol or two molecules of *t*-butyl alcohol. Phenol is the stronger acid and *t*-butyl alcohol is the stronger base. The dimerization reactions can be considered to be reactions between a strong acid and a weak base in the case of phenol and between a weak acid and a strong base in the case of *t*-butyl alcohol. The association of the two together involves a strong acid and a strong base. The values of $\Delta\nu$ have been determined for a series of alcohols, ROH, in the presence of ethyl ether and are shown in Fig. 11. The order of decreasing acidity is R = $C_6H_5 > CH_3 >$ *n*-Bu > 2-Bu > *t*-Bu, and this is the order of decreasing $\Delta\nu$. The values of $\Delta\nu$ for a series of alcohols in the presence of phenol were determined and are also shown in Fig. 11. Here $\Delta\nu$ is the difference in frequency between the free OH band of phenol and the bonded OH band of the compound, $\mathrm{C_6H_5O{-}H{---}\overset{R}{O}{-}H}$. Now the order of decreasing $\Delta\nu$ is reversed, for in the presence of ether the alcohols act as acids whereas in the presence of phenol they act as bases, and the order of decreasing basicity is R = *t*-BuOH > 2-BuOH > *n*-BuOH > MeOH.

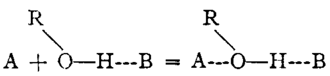
As shown in Fig. 8 there is no regular order of $\Delta\nu$ (dimer) for the various alcohols. This is so because the order of decreasing acidity is the reverse of decreasing basicity. It is for this reason that the increase in $\Delta\nu$ for the intramolecular bonded OH that is observed in going from ethylene glycol to tetramethylethylene glycol is believed to be due to a difference in H—O distance rather than to a change in polarity of the atoms involved.

There is no significant difference in frequency between the free OH bands of tetramethylene glycol and of hexamethylene glycol although the former has an internal hydrogen bond and the free OH may be considered to be interacting with an electron acceptor. The latter compound contains no intramolecular bond and hence the OH group is not influenced by an electron acceptor. In other words, the reaction



$$\mathrm{A + ROH = A{---}\overset{R}{O}{—}H}$$

where A is an electron acceptor results in no change in frequency of the OH band. On the other hand, as shown in an earlier paragraph, the reaction



$$\mathrm{A + \overset{R}{O}{—}H{---}B = A{---}\overset{R}{O}{—}H{---}B}$$

results in a large decrease in frequency of the OH band. The reason for this difference in behavior is obscure.

The OH bands of some crystalline diols were also examined. In some instances compounds which show two bands in dilute solution also show two bands in the solid, for example, *cis*-cyclohexane-1,2-diol. The *trans*-compound on the other hand shows only one very broad band which may be two closely spaced bands. *trans*-Cyclohexane-1,3-diol which has one band in dilute solution has two bands in the solid, while the *cis*-compound which has two bands in dilute solution has only one band in the solid. In each of these cases the bands of the solids are at much lower frequency than the bands of the dilute solutions. There seems to be no correlation between the number of OH bands in dilute solution and the number in the solid. The number of bands in dilute solution depends upon the geometry of the molecule whereas in the solid it probably depends upon the geometry of the crystal. Benzpinacol has two bands in

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[13] W. Gordy and E. C. Stanford, *J. Chem. Phys.*, **8**, 170 (1940); **9**, 204 (1941).

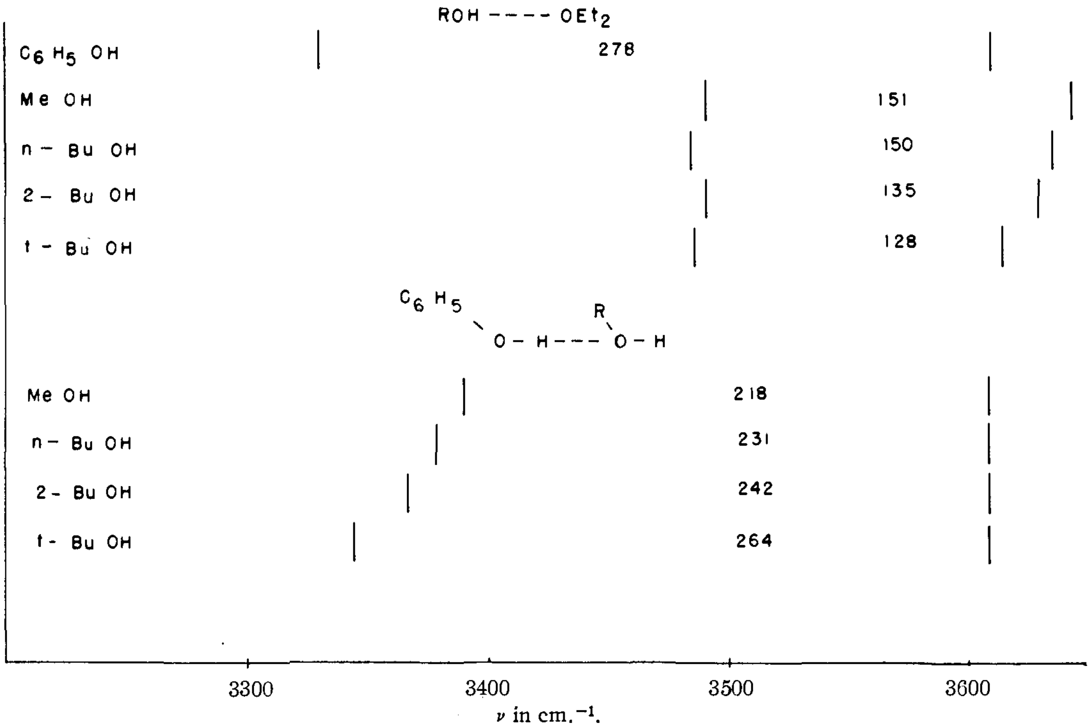

Fig. 11.—OH bands of alcohols in presence of (a) hydrogen acceptor, $OEt_2$ and (b) electron acceptor, $C_6H_5OH$.

both dilute solution and in the solid, the frequencies being the same in each state, 3567 and 3608 cm.$^{-1}$. Fluorenone pinacol has two bands in dilute solution at 3574 and 3600 cm.$^{-1}$. In the solid the 3600 cm.$^{-1}$ band is replaced by a band at 3365 but the 3570 band remains unchanged. These are the first recorded instances in which no frequency shift of an OH band is observed in going from a dilute solution to a solid. According to Davies,[14] the frequency of an OH band necessarily shifts toward lower frequency in going from a dilute solution to the solid. In view of the results obtained with benzpinacol and fluorenone pinacol this hypothesis is open to some question. In general, the value of $\Delta\nu$ for solids will be larger than that for concentrated solutions because in solution an OH group interacts with one hydrogen acceptor and one electron acceptor whereas in the solid it can interact with one hydrogen acceptor and two electron acceptors as has been shown to be the case in ice.[15]

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ABERDEEN PROVING GROUND, MD.

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(14) M. Davies, *J. Chem. Phys.*, **8**, 577 (1940).

(15) Reference 6, p. 301.