

[CONTRIBUTION FROM THE BALLISTIC RESEARCH LABORATORIES, ABERDEEN PROVING GROUND, MD.]

The Hydrogen Bond. VI. Equilibrium between Hydrogen Bonded and Nonbonded Conformation of α,ω -Diol Monomethyl Ethers

BY LESTER P. KUHN AND ROBERT A. WIRES

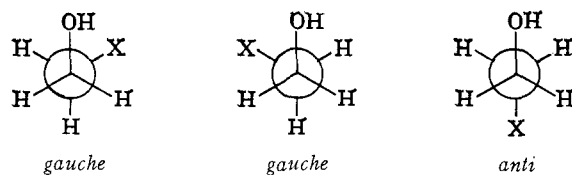
RECEIVED DECEMBER 27, 1963

From measurements of the intensities of the free and bonded OH bands, the equilibrium constant for the equilibrium, nonbonded conformations \rightleftharpoons hydrogen bonded conformations, was determined for 2-methoxyethanol (I), 3-methoxypropanol-1 (II), and 4-methoxybutanol-1 (III) in CCl_4 solution over the temperature range of 0 to 60°, and values of ΔF , ΔH , and ΔS were obtained. Similar data were also obtained for the association between 1-butanol and butyl ether. The half band width, $\nu_{1/2}$, and the change in intensity with temperature, dB/dT , are much larger for the intermolecularly bonded OH band than for the intramolecularly bonded OH band. Although $\Delta\nu$ increases by a factor of 6, there is little change in ΔH , indicating that the Badger-Bauer rule does not hold for intramolecular bonds. Hydrogen bond formation in I is more exothermic than expected because it is accompanied by loss in repulsive nonbonded interactions. Hydrogen bond formation in III is less exothermic than expected because it is accompanied by an increase in repulsive interactions. The Badger-Bauer rule is obeyed by II because in this instance the hydrogen bond interaction is the major contributor to ΔH . The equilibrium constant becomes smaller in going from I to III because $-\Delta S$ becomes larger. The change in entropy is related to the ratio, number of hydrogen bonded conformations/number of nonbonded conformations.

Introduction

Substituted alcohols in which the substituent can act as a hydrogen acceptor may exist in an intramolecularly bonded conformation and there is considerable literature containing data on the frequency shift of the OH band, $\Delta\nu$, due to hydrogen bonding in diols,¹ diol monoethers,² amino alcohols,³ etc. Even more work has been done on intermolecular hydrogen bonds between unsubstituted alcohols, especially phenol, and various hydrogen acceptors. In this work⁴ not only has $\Delta\nu$ been measured, but the equilibrium constant for the formation of the hydrogen bonded complex has been determined at various temperatures and the thermodynamic functions ΔH , ΔF , and ΔS have been evaluated and compared with $\Delta\nu$. In only one instance have such data been obtained for an intramolecularly bonded system and this was for a series of 1,3-diols.⁵

In the present work we have measured the equilibrium constant for the equilibrium between intramolecularly hydrogen bonded conformations and nonbonded conformations in the monomethyl ethers of ethylene glycol propane-1,3-diol and butane-1,4-diol. Measurements were made over the temperature range of 0 to 60°, and from these measurements, values of ΔH , ΔF , and ΔS were calculated. A dilute solution of a diol monomethyl ether in carbon tetrachloride has two OH bands, the high frequency band being due to a free OH group and the lower frequency band being due to the intramolecularly bonded OH group. 2-Methoxyethanol can exist in three conformations having a dihedral angle of 60° as shown in Fig. 1. Molecules having the two *gauche* conformations give rise to the



bonded OH band and molecules having the *anti* conformation give rise to the free OH band. The equilibrium that is measured in this case, then, is the equilibrium between *gauche* and *anti* conformations. 3-Methoxypropanol can have nine conformations having dihedral angles of 60°; two of these would have an intramolecular hydrogen bond and seven would not. 4-Methoxybutanol can have twenty-seven conformations, four with hydrogen bonds and twenty-three without.

The concentration of molecules having no hydrogen bond is determined from the intensity of the free OH band, using the extinction coefficient obtained from measurements with 1-butanol. It is assumed that the extinction coefficient of the free OH band of the compounds studied in this work is the same as the free OH band of 1-butanol. This appears to be a reasonable assumption since the extinction coefficient of a number of primary unbranched alcohols is constant.⁶ The concentration of molecules having a bonded OH group is the difference between the total concentration and the concentration of molecules having the free OH group. The measurements were made at a sufficiently high dilution that no intermolecular hydrogen bonds were present.

Results and Discussion

Having obtained the bonded OH bands, knowing the concentration of molecules having the bonded OH group, it is possible to calculate the intensity of the bonded OH band for each of the compounds studied. In order to compare the intramolecular hydrogen bond with the intermolecular hydrogen bond, a study was also made of the intermolecular hydrogen bond formed between 1-butanol and dibutyl ether. The spectroscopic properties of all of the bands are given in Table I and the dependence of the band intensities upon temperature is given in Fig. 1. The frequencies of the free and bonded OH of the glycol ethers bands are in good agreement with those in the literature² and the value for the intensity of the free OH of 1-butanol is in reasonable agreement with the value of Buc and Neel⁵ (5.4 vs. 4.5).

The increase in $\Delta\nu$ that accompanies the increase in the carbon chain from 2 to 4 has been attributed to the decrease in the length of the hydrogen bond.¹ The data show that there is also an increase in the half band

- (1) L. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952).
- (2) A. Poster, A. Haines, and M. Stacey, *Tetrahedron*, **16**, 177 (1961).
- (3) G. Drefahl and G. Haublein, *Chem. Ber.*, **94**, 915 (1961).
- (4) (a) M. D. Joesten and R. S. Drago, *J. Am. Chem. Soc.*, **84**, 3817 (1962); (b) T. Gramstad, *Spectrochim. Acta*, **19**, 497 (1963).
- (5) H. Buc and J. Neel, *Compt. rend.*, **255**, 2947 (1962).

- (6) M. Flett, *Spectrochim. Acta*, **10**, 21 (1957).

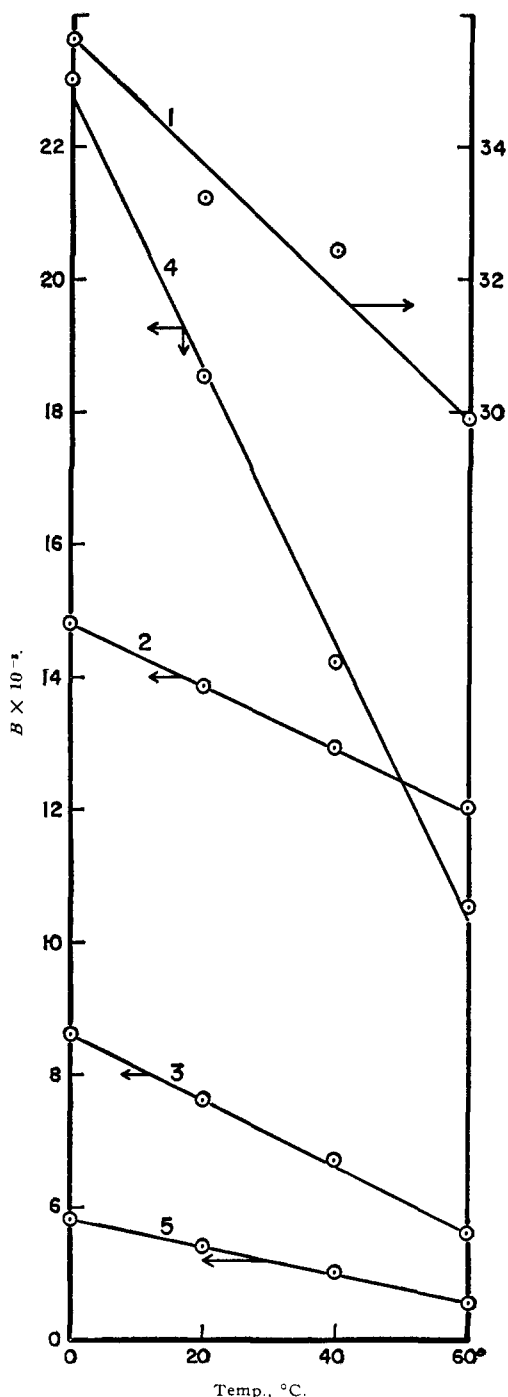


Fig. 1.—Intensity, B , of OH bands as a function of temperature: 1, $\text{CH}_3\text{O}(\text{CH}_2)_4\text{OH}$; 2, $\text{CH}_3\text{O}(\text{CH}_2)_3\text{OH}$; 3, $\text{CH}_3\text{O}(\text{CH}_2)_2\text{OH}$; 4, BuOH-OBu_2 ; 5, BuOH (free).

width, $\nu_{1/2}$, and the integrated intensity, B . A similar parallelism in the values of $\Delta\epsilon$, $\nu_{1/2}$, and B has been observed in intermolecular hydrogen bonds.⁷ If, instead of considering the absolute changes in the three band parameters, ν , $\nu_{1/2}$, and B , we consider the fractional changes in these parameters due to hydrogen bonding, we find that for the 1,4-diol $\Delta\nu/\nu$ is 0.05, $\Delta\nu_{1/2}/\nu_{1/2}$ is 3.2, and $\Delta B/B$ is 5.6; similarly, for the intermolecular hydrogen bond these values are 0.04, 3.5, and 2.6. Thus the half band width and the intensity undergo a greater fractional change due to H-bonding than does the frequency. There is no simple quantitative relationship between $\Delta\nu$ and $\nu_{1/2}$ or between $\Delta\nu$ and

(7) C. M. Huggins and G. C. Pimentel, *J. Phys. Chem.*, **60**, 1615 (1956).

B given in Table I. The half band width of the free OH of butanol is not meaningful because this unsymmetrical band has been shown to consist of two bands which are due to the presence of rotational isomers having different orientations around the C-O bond.⁸ The main band of primary straight chain alcohols has a $\nu_{1/2}$ of $22 \pm 2 \text{ cm.}^{-1}$. If we use this figure as the value of $\nu_{1/2}$ for the free OH group, then we find that the change in frequency due to hydrogen bonding, $\Delta\nu$, is proportional to the change in half band width due to hydrogen bonding, $\Delta\nu_{1/2}$

$$\Delta\nu = 2.5(\Delta\nu_{1/2})$$

where $\Delta\nu_{1/2}$ is $\nu_{1/2}(\text{bonded}) - 22$. This relationship does not hold for the intermolecularly bonded OH band which has a much larger half band width than the intramolecularly bonded OH of comparable $\Delta\nu$.

The frequency of the free OH band does not change with temperature over the temperature range 0 to 60° which we have used. The bonded OH band moves slightly to higher frequency as the temperature rises, producing a slight decrease in $\Delta\nu$ with increase in temperature. The effect which is never large is more pronounced for large than for small $\Delta\nu$ and is about the same in intermolecular bonds as in intramolecular bonds. The change in intensity with temperature, dB/dT , is quite significant, as shown in Fig. 1. Our value of -20 for the temperature coefficient of the free OH in butanol is in agreement with the value of -20 reported for ethanol.⁹ The value of dB/dT for the intermolecularly bonded OH band is larger than for the intramolecularly bonded OH band.

There is no detectable change in half band width over the 60° temperature range for the intramolecularly bonded OH bands which means that $-d\nu_{1/2}/dT < 0.1$. The intermolecularly bonded OH band, on the other hand, shows a significant change in half band width, $d\nu_{1/2}/dT = -0.4 \text{ cm.}^{-1}/\text{deg}$. This corresponds to a fractional change of -0.4×10^{-3} .

The thermodynamic data for the equilibrium between bonded and nonbonded conformations for the three glycol ethers and for the intermolecular hydrogen bonded system butyl alcohol-butyl ether are given in Table II. Our value for $-\Delta H$ of methoxypropanol, 2100 ± 500 , is in good agreement with the value of $-\Delta H$ found for propane-1,3-diol, 2000 ± 300 , by Buc and Neel.⁵ Previous workers have shown that in intermolecularly hydrogen bonded systems containing phenol and a variety of, but not all, acceptors, there is a linear relationship between ΔH and $\Delta\nu$, a rule first promulgated by Badger and Bauer.¹⁰ Joesten and Drago^{4a} showed that their and others' data for phenol with various acceptors fitted the equation

$$-\Delta H \pm 0.5 \text{ (kcal./mole)} = 0.016\Delta\nu + 0.63$$

Our data for butanol-butyl ether fit this equation. The Badger-Bauer rule has been found not to apply to equilibria in which alkyl halides are the hydrogen acceptor.¹¹ A striking feature of our data is that in going

(8) (a) M. Oki and H. Iwamura, *Bull. Chem. Soc. Japan*, **32**, 567 (1959); (b) F. Dalton, G. Meakins, J. Robinson, and W. Zaharia, *J. Chem. Soc.*, 1566 (1962).

(9) U. Liddel and E. Becker, *Spectrochim. Acta*, **10**, 70 (1957).

(10) R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 839 (1937).

(11) R. West, D. Powell, L. Whatley, M. Lee, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **84**, 3221 (1962).

TABLE I
 SPECTROSCOPIC PROPERTIES OF OH BANDS

| Compound | $\nu(\text{OH}),^a \text{ cm.}^{-1}$ | | $\Delta\nu^a$ | $\nu_{1/2}^{a,b}$ | $B^{a,c} \times 10^{-4}$ | Bonded OH | | |
|--|--------------------------------------|--------|---------------|-------------------|--------------------------|-------------------|---------|-----------------|
| | Free | Bonded | | | | $d(\Delta\nu)/dT$ | dB/dT | $d\nu_{1/2}/dT$ |
| $\text{HO}(\text{CH}_2)_4\text{OCH}_3$ | 3645 | 3465 | 180 | 92 | 33.6 | -0.3 | -95 | 0 |
| $\text{HO}(\text{CH}_2)_3\text{OCH}_3$ | 3644 | 3558 | 86 | 60 | 13.8 | -0.16 | -50 | 0 |
| $\text{HO}(\text{CH}_2)_2\text{OCH}_3$ | 3645 | 3615 | 30 | 32 | 7.6 | 0 | -50 | 0 |
| $\text{BuOH}-\text{OBu}_2$ | 3641 | 3505 | 136 | 98 | 18.8 | -0.25 | -210 | -0.4 |
| BuOH (free OH) | 3641 | ... | ... | 29 | 5.4 | 0 | -20 | 0 |

^a These measurements made at 20°. ^b Half band width in cm.^{-1} . ^c Integrated intensity, $B = 2.3\pi \log(I_0/I_{\text{max}})\nu_{1/2}/2cl$ in l. moles⁻¹ cm.^{-2} .

 TABLE II
 THERMODYNAMIC DATA AND FREQUENCY SHIFTS

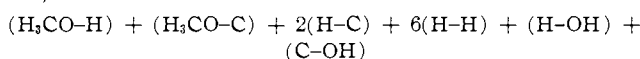
| Compound | Concn. $\times 10^4$, mole/l. | k_0 | $-\Delta H$, cal./mole | $-\Delta F$ | $-\Delta S$ | $\Delta\nu$ |
|--|--------------------------------|-------|-------------------------|-------------|-------------|-------------|
| $\text{HO}(\text{CH}_2)_4\text{OCH}_3$ (III) | 5.8 | 0.65 | 2700 ± 300 | -235 | 10.8 | 180 |
| | 7.7 | 0.68 | 2750 ± 300 | -210 | 10.8 | |
| $\text{HO}(\text{CH}_2)_3\text{OCH}_3$ (II) | 6.8 | 1.5 | 2100 ± 300 | 220 | 6.9 | 86 |
| | 9.2 | 1.5 | 2010 ± 300 | 220 | 6.5 | |
| $\text{HO}(\text{CH}_2)_2\text{OCH}_3$ (I) | 9.7 | 12.3 | 2200 ± 500 | 1360 | 3.0 | 30 |
| ROH-OR ₂ | 14.0 (ROH) | 2.4 | 2300 ± 300 | 470 | 6.7 | 136 |
| | 446 (R ₂ O) | | | | | |
| | 7.4 (ROH) | 1.9 | 2300 ± 300 | 350 | 7.1 | |
| | 480 (R ₂ O) | | | | | |

from 2-methoxyethanol to 4-methoxybutanol $\Delta\nu$ increases by a factor of 6 but ΔH hardly changes at all. In other words, the Badger-Bauer rule does not hold for these intramolecular hydrogen bonds. The reason for the failure of the Badger-Bauer rule in intramolecular hydrogen bonds is that $\Delta\nu$ is a measure of the strength of the interaction between the hydrogen donor (the OH group in this case) and the acceptor, whereas ΔH is a measure of the sum of all the interactions associated with the formation of the hydrogen bond. If the interaction between donor and acceptor is very large compared to all the other interactions, then the Badger-Bauer rule is obeyed. This is usually the case for intermolecular hydrogen bonds which do not involve a change in conformation but is not the case for intramolecular hydrogen bonds which, as stated earlier, do involve a change in conformation. Let us consider the interactions between nonbonded atoms on adjacent carbon atoms in the *gauche* (hydrogen bonded) and *anti* (nonhydrogen bonded) conformations of 2-methoxyethanol, shown in Fig. 1. In each conformation there are six interactions: *gauche*: hydroxy interacting with methoxy designated by (OH-OCH₃), methoxy interacting with hydrogen designated by (H₃CO-H), three hydrogen-hydrogen interactions 3(H-H) and one hydrogen-hydroxyl interactions (H-OH); *anti*: 2(H₃CO-H), 2(H-H), and 2(H-OH). To determine the interactions accompanying the formation of the hydrogen bond we subtract the interactions of the *anti* conformation from those of the *gauche* and we get (OH-OCH₃) - (H₃CO-H) + (H-H) - (H-OH). Now (OH-OCH₃) is an attractive force and is therefore exothermic; the other interactions are repulsive and therefore endothermic. In forming the hydrogen bond, two relatively strong repulsive interactions, (H-OH) and (H₃CO-H), are lost and one weak repulsive interaction, (H-H), is gained, thus making the process more exothermic than would be expected on the basis of the hydrogen bond alone. The difference between the observed $-\Delta H$, 2200 ± 500 cal./mole, and the $-\Delta H$ calculated from the Joesten-Drago equation, 1100 ± 500 cal./mole, is attributed to these lost interactions.

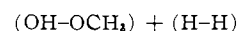
Each conformation of the 3-methoxypropanol has twelve 1,2-interactions and two 1,3-interactions

Bonded conformation

1,2-interactions

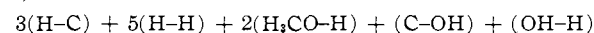


1,3-interactions



Nonbonded conformations

1,2-interactions



1,3-interactions



Subtracting the interactions of the nonbonded conformations from the interactions of the bonded conformation gives



Here, except for the hydrogen bond interaction, the interactions which are lost in going from nonbonded to bonded conformations are approximately equal to the interactions that are gained and so the ΔH is determined largely by (OH-OCH₃), the hydrogen bond interaction, and the Badger-Bauer rule is obeyed. ΔH calculated with the Joesten-Drago equation is -2100 cal./mole which is in excellent agreement with the experimentally determined value.

The 4-methoxybutanol has so many interactions and so many conformations that it is not worthwhile to treat them in the manner used above. The most stable nonbonded conformations, shown below, have their carbon atoms in the same arrangement as in the *anti* conformation of butane. The bonded conformations, on the other hand, have the carbon atoms arranged as in the *gauche* conformation of butane. Now the *gauche* conformation of butane is less stable than the *anti*; therefore the conversion nonbonded conformation \rightarrow bonded conformations will be less exothermic than would be expected on the basis of hydrogen bond interaction alone. The enthalpy difference between *anti*

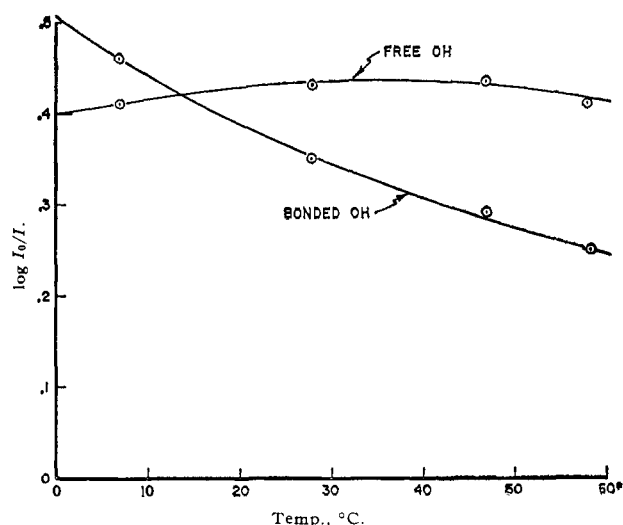
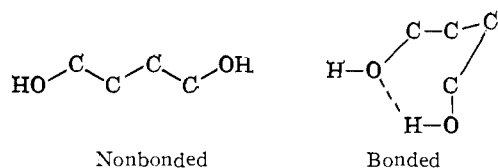


Fig. 2.—Peak height of OH bands of $\text{CH}_3\text{O}(\text{CH}_2)_4\text{OH}$ at various temperatures.

and *gauche* conformations of *n*-butane, 800 cal./mole,¹² is, in fact, the difference between our measured value of ΔH , -2700, and the calculated value, -3500 cal./mole.



The change in entropy, ΔS , that accompanies the formation of the intramolecular hydrogen bond is also of interest and can be explained in terms of conformational analysis. As shown in Table II, in contrast to ΔH , which hardly changes at all in going from 2-methoxyethanol to 4-methoxybutanol, ΔS changes by a factor of about 4. The formation of an intermolecular hydrogen bond is accompanied by a loss in entropy since the system experiences a loss in translational degrees of freedom. Although ΔS for the intramolecular hydrogen bond is comparable to the ΔS of the intermolecular bond, there is no loss of translational degrees of freedom associated with the former. The loss of entropy associated with the intramolecular hydrogen bond is due to the decrease in rotational degrees of freedom, which is related to the number of possible conformations of the bonded as compared with the nonbonded molecules. This ratio bonded/nonbonded conformations, considering only rotation around C-C bonds, is 2 for the methoxyethanol, $2/7$ for the methoxypropanol, and $4/21$ for the 4-methoxybutanol.¹³ Therefore the loss in entropy, $-\Delta S$, increases in going from the methoxyethanol to the methoxybutanol. Since the ratio for the methoxyethanol, given above, is greater than 1, the change in entropy should be positive. The fact that ΔS is negative indicates that there are other restrictions associated with the hydrogen bond formations. These restrictions involve rotation around the C-O bonds. In the molecules containing the free OH group we can picture three possible stag-

(12) N. Sheppard and G. Szasz, *J. Chem. Phys.*, **17**, 86 (1949).

(13) There are 23 possible nonhydrogen bonded conformations of the 4-methoxybutanol, but in two of them the distance between nonbonded atoms is very small, being about equal to the covalent bond distance, so only 21 need be considered.

gered conformations around each C-O bond. In hydrogen bonded molecules, on the other hand, the hydrogen of the OH group must be directed toward the ether oxygen and the methyl group of the ether must be directed away from the hydrogen thus reducing the number of possible conformations around the C-O bonds.

Finally, it is noteworthy that the equilibrium constant, K , and hence, the change in free energy, ΔF , vary in a manner opposite to that of $\Delta\nu$. The compound with the strongest hydrogen bond as measured by $\Delta\nu$ has the smallest equilibrium constant. The thermodynamic functions are related by the well known equations

$$\Delta F = -RT \ln K$$

$$\Delta F = \Delta H - T\Delta S$$

Since ΔH is about the same for all the compounds studied and ΔS varies considerably, it is the latter which has the greater influence on the equilibrium constant.

Experimental

Preparation of Materials.—2-Methoxyethanol was reagent grade which was further purified by v.p.c. using an F & M chromatograph equipped with a 0.5-in. diameter preparative column of DC-500 silicone oil on Chromosorb W. The 3-methoxypropanol and 4-methoxybutanol were prepared by methylation of the diols.¹⁴ The 3-methoxypropanol-1, b.p. 148–153°, was purified by v.p.c. Fractionation of 4-methoxybutan-1-ol gave a pure product, b.p. 76° (14 mm.). The purity of each compound as determined by v.p.c. was above 99%. Reagent grade carbon tetrachloride was distilled and stored over P_2O_5 before use.

Spectroscopic Measurements.—The OH bands were obtained with a Beckman DK-2 spectrophotometer, purged with dry argon while the measurements were taken, and which was set as follows: time constant, 0.2; gain, 1.11; expansion, 2X; speed, 50; 2-cm. quartz cells were used for the intramolecular bonds and 1-cm. cells were used for the intermolecular bonds. The cells were placed in a thermostated holder which fitted snugly in the cell compartment of the instrument and through which water was circulated from a constant temperature bath. The temperature of the solution in the sample cell was measured with an iron-constantan thermocouple which was immersed in the solution.

Butanol in CCl_4 was found to obey Beer's law over the concentration range of 0.002 to 0.008 *M*. The free OH band was then measured at two different concentrations of butanol (approximately 0.003 and 0.006 *M*) at various temperatures from 5 to 55° at approximately 10° intervals and a plot was made of $\log I_0/I$ at ν_{max} vs. temperature for each solution, which gave a straight line. Values of absorbance at 0, 20, 40, and 60° were obtained from these curves and these values were used to make a Beer's plot of the free OH band of 1-butanol at these four temperatures. These four straight lines were our calibration curves.

To determine the equilibrium constant for intramolecular hydrogen bonding, a CCl_4 solution of the hydroxy ether of known concentration, such that the absorbance of the free OH band was 0.2 to 0.7, was put in the sample cell and pure CCl_4 in the reference cell. The free and bonded OH bands were obtained at various temperatures as with the butanol. From these spectra a plot of absorbance vs. temperature was made for the free and bonded OH bands. A typical curve is shown in Fig. 2. The absorbance at 0, 20, 40, and 60° for the free OH band was taken from this curve and this was converted to concentration of free OH groups from the calibration curve for each of the four temperatures. Subtraction of this concentration from the total concentration gives the concentration of bonded OH groups. The equilibrium constant is the ratio (bonded OH/free OH); ΔH was obtained from a plot of $\log K$ vs. $1/T$. The intensity, B , of the bonded OH band was calculated with the formula, $B =$

(14) L. Smith and J. Sprung, *J. Am. Chem. Soc.*, **65**, 1378 (1943).

$2.3\pi A\nu_{1/2}/cl$, where A is the absorbance at ν_{\max} , $\nu_{1/2}$ is the half band width, c is concentration of bonded OH in moles per liter, and l is the cell length in centimeters. Correction was made for the thermal expansion of CCl_4 .

For the determination of the equilibrium constant of the intermolecular hydrogen bond between butanol and butyl ether, the alcohol and ether in CCl_4 were put in the sample cell and ether in CCl_4 at the same concentration were put in the reference cell.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TUFTS UNIVERSITY, MEDFORD 55, MASS.]

Conformational Studies. VI.¹ Intramolecular Hydrogen Bonding in Nonchair Conformations of *cis,cis,cis*-2,5-Dialkyl-1,4-cyclohexanediols²

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RECEIVED DECEMBER 2, 1963

cis,cis,cis-2,5-Dialkyl-1,4-cyclohexanediols, in dilute solution in carbon tetrachloride at 25°, give infrared spectra which show absorption at $3490 \pm 10 \text{ cm}^{-1}$ attributable to transannular intramolecular hydrogen bonding in nonchair conformations. For each diol, the relative absorbance near 3490 cm^{-1} is interpreted in terms of its nonchair population. The nonchair population increases with the sizes of the alkyl groups from about 5% for *cis,cis,cis*-2,5-dimethyl-1,4-cyclohexanediol (**6**) to >98% for *cis,cis,cis*-2,5-di-*t*-alkyl-1,4-cyclohexanediols (**2** and **3**). Intermediate nonchair populations are reported for *cis,cis,cis*-*p*-menthane-2,5-diol (**7**), *cis,cis,cis*-2-*t*-butyl-5-methyl-1,4-cyclohexanediol (**8**), both ca. 14%, and for *cis,cis,cis*-2,5-di-*sec*-alkyl-1,4-cyclohexanediols (**4** and **5**), ca. 80%. Preparations and configurations of the diols are discussed in addition to their conformational equilibria.

Examination of models of 1,4-cyclohexanediols suggests that intramolecular hydrogen bonding can occur only when the hydroxyl groups have the *cis* configuration, and then only in certain *nonchair* conformations.³ Infrared spectroscopic studies have shown that the population of intramolecularly hydrogen bonded nonchair conformations, while negligible for *cis*-1,4-cyclohexanediol (**1**) itself,⁴ is very large (probably >98%) for *cis,cis,cis*-2,5-di-*t*-alkyl-1,4-cyclohexanediols (**2** and **3**).^{1,3} Between these extremes, intermediate nonchair populations would be expected for diols like **2** and **3** in which one or both of the *t*-alkyl groups is replaced by a primary or secondary alkyl group. That is, a relationship would be expected between the nonchair population and the relative "sizes" of the alkyl substituents in *cis,cis,cis*-2,5-dialkyl-1,4-cyclohexanediols. We wish to report results of a study of such diols of intermediate nonchair population (**4**–**8**).

The frequencies and intensities of all resolved infrared absorption bands in the region 3100 – 3900 cm^{-1} are reported in Table I for 0.0040 M solutions of *cis,cis,cis*-2,5-dialkyl-1,4-cyclohexanediols (**2**–**8**) in carbon tetrachloride at ca. 25°. Each of the diols **2**–**8** exhibits a single, broad absorption band at $3490 \pm 10 \text{ cm}^{-1}$, plus absorption in the region 3618 – 3640 cm^{-1} , the latter ranging from a resolved doublet for **2** and **3**,

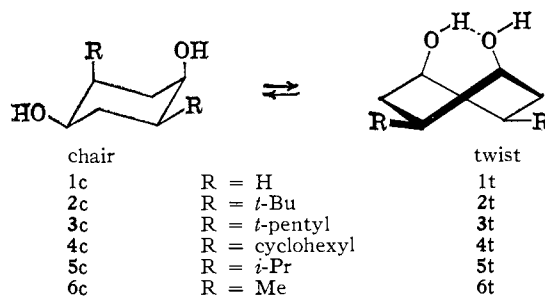


TABLE I

O–H BANDS OF THE 2,5-DIALKYL-1,4-CYCLOHEXANEDIOLS^a

| Diol | Free O–H ν , cm^{-1} (absorbance) | Bonded O–H ν , cm^{-1} (absorbance) | Bonded/ bonded- 2 absorbance ratio |
|-----------------------|--|--|---|
| 1 ^b | 3626 | ... | <0.01 |
| 2 ^c | 3640 (0.26) | 3480 (0.48) | 1.00 |
| | 3619 (.23) | | |
| 3 ^c | 3640 (.26) | 3480 (.47) | 1.0 |
| | 3618 (.23) | | |
| | | | |
| 4 | 3621 (.32) | 3491 (.36) | 0.8 |
| 5 | 3622 (.34) | 3492 (.40) | .8 |
| 6 | 3628 (.38) | 3497 (.026) | .05 |
| 7 | 3626 (.41) | 3492 (.062) | .13 |
| 8 | 3625 (.43) | 3490 (.067) | .14 |
| 9 ^d | 3623 (.48) | 3500 (<0.01) | <.02 |

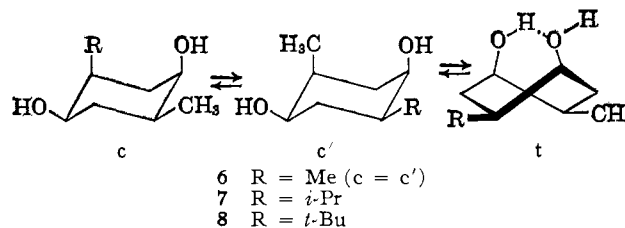
^a In 0.0040 M carbon tetrachloride solutions at 25°. ^b See ref. 4. ^c See ref. 1. ^d See ref. 8.

(1) Paper V: R. D. Stolow and M. M. Bonaventura, *J. Am. Chem. Soc.*, **85**, 3636 (1963).

(2) This work was presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 13, 1963, and was supported in part by National Science Foundation Grants NSF G12310 and GP-435 and in part by Public Health Service Research Grant GM-08813 from the National Institutes of Health. The authors gratefully acknowledge this assistance.

(3) R. D. Stolow, *J. Am. Chem. Soc.*, **83**, 2592 (1961).

(4) L. P. Kuhn, *ibid.*, **74**, 2492 (1952).



to a fairly symmetrical singlet for **6**. The absorbance of these bands varies linearly with the concentration at concentrations below 0.0040 M . Upon replacement of the hydroxyl hydrogens by deuterium, these absorption bands are replaced by new bands having similar relative intensities and appearing near 2580 and 2680 cm^{-1} . Therefore the results are consistent with interpretation of the absorption bands in the region 3100 – 3900 cm^{-1} in terms of O–H stretching vibrations of hydroxyl groups of the monomeric diol.⁵

The band near 3490 cm^{-1} may be assigned to hydroxyl groups, the hydrogen atoms of which form a transannular intramolecular hydrogen bond to oxygen

(5) See R. N. Jones and C. Sandorfy in "Chemical Applications of Spectroscopy," Vol. IX of A. Weissberger, "Technique of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, pp. 417–424.