Intramolecular Interaction between Hydroxyl Group and π-Electrons. IV[1]. *Rotational Isomers of Alcohols and Shift of ν_{O-H} Absorptions in Phenyl Substituted Alcohols*

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The authors have found[2] an unsymmetric ν_{O-H} absorption band for 10-undecen-1-ol in the course of the investigation of the intramolecular interaction between the hydroxyl group and π-electrons of an isolated double bond. But the origin of the second minor band, obtained by dividing the band on the assumption that the unsymmetric band is an overlap of two symmetric bands which can be expressed by the Lorentz function, has been unknown. The present author expected that saturated aliphatic alcohols, such as ethanol, may also possess two ν_{O-H} absorptions as 10-undecen-1-ol does in spite of the improbable internal interaction. This has been found to be true.

Experimental

Measurement and Calculation.—They were carried out similarly as described previously[2].

Materials. — The materials, all being known compounds, were purified as stated in the literature. Their physical constants agreed with those reported.

Results and Discussion

The apparent curves for methanol, ethanol, isopropyl alcohol and *tert*-butyl alcohol are given in Fig. 1. The ν_{O-H} absorption is one of the best explored and

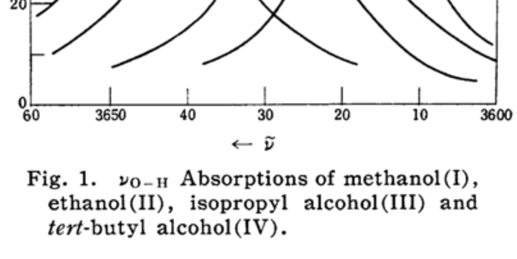

Fig. 1. ν_{O-H} Absorptions of methanol(I), ethanol(II), isopropyl alcohol(III) and *tert*-butyl alcohol(IV).

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[1] Part III of this series: M. Ōki and H. Iwamura, This Bulletin, 32, 306 (1959).

[2] M. Ōki and H. Iwamura, ibid., 32, 567 (1959).

it is accepted that the wave number where the absorption maximum appears shifts to the lower side as the alcohol varies from primary to secondary and then to tertiary. The results obtained agree with the above rule, except that ethanol and isopropyl alcohol possess unsymmetric bands which were found with high resolvability of the grating spectrophotometer. The unsymmetric band is divided into two symmetric bands, on the assumption that the unsymmetric curve is an overlap of the two symmetric ones which obey the Lorentz function. The results are given in Table I with those of other aliphatic alcohols.

TABLE I. ν_{O-H} ABSORPTION OF ALIPHATIC ALCOHOLS

R	Band	ν_{max} (cm^{-1})	$\Delta\nu^a_{1/2}$ (cm^{-1})	$A\times10^{-3}$ (mol^{-1}·l.·cm^{-1})	A_I/A_{II}
Primary alcohols (RCH_2OH)					
H		3643.8	22.2	3.99	—
CH_3	I	3637.3	18.2	2.80	1.8
	II	3627	19	1.6	
C_2H_5	I	3639.7	19.5	3.36	2.6
	II	3626	18	1.3	
$C_2H_5CH_2$	I	3639.3	17.6	2.81	2.2
	II	3627	20	1.3	
$(CH_3)_2CH$	I	3641.5	17.9	3.61	2.0
	II	3628	22	1.8	
$(CH_3)_3C$	I	3642.0	20.7	4.83	6.0
	II	3632	18	0.8	
Secondary alcohols (RCH_3CHOH)					
CH_3	I	3627.1	13.8	2.42	1.7
	II	3617	26	1.4	
C_2H_5	I	3628.8	20.0	3.35	3.3
	II	3615	27	1.0	
$(CH_3)_2CH$	I	3631.6	21.0	3.55	2.2
	II	3618	33	1.6	
$(CH_3)_3C$	I	3635.6	17.4	3.42	2.5
	II	3621	23	1.4	
Tertiary alcohols [$R(CH_3)_2COH$]					
CH_3		3616.9	15.2	3.46	—
C_2H_5		3617.3	20.0	3.46	—

The origin of the second minor peak can not be the formation of the dimer, because Liddel and Becker[3] reported that they observed no dimer band at the concentration of 0.001~0.003 mol./l. at which the present measurement was carried out. Neither can be the origin the hydrogen bonding between the solute and the chlorine atom of carbon tetrachloride, since methanol, tertiary alcohols and phenols always show symmetric bands. Therefore it should be sought elsewhere.

Richards[4], Barrow[5] and Flett[6] tried to explain the shift of the ν_{O-H} absorption maxima, as the alcohol varies from primary to secondary and then to tertiary, on the basis of the mesomeric or inductive effect of the substituent. That is to say, the contribution of the resonance structure $H^-CH_2=O^+-H$ or $H^+CH_2=O^--H$ will increase as the result of stabilization due to the presence of the alkyl groups on the carbon atom to which the hydroxyl group is attached, and the resulting weaker force constants cause the ν_{O-H} absorption to appear at a lower wave number. However, this explanation is not convincing, since it does not explain the presence of the two bands for O–H stretching.

Badger and Bauer[7] found two ν_{O-H} absorptions for the primary alcohols and tried without success to assign them to the rotational isomers, because they failed to observe a doublet for the secondary alcohols. However, the idea of the rotational isomerism is attractive to the present authors, since this is a promising explanation for the existence of the two ν_{O-H} absorptions. Though the energy barrier for the rotational isomers around the O–C axis of the alcohols is estimated to be even lower than that of the rotation around the C–C axis of ethane derivatives, a 0.8 or 0.9 kcal./mol. energy barrier would suffice for the presence of the isomers at room temperature. Barrow[8] estimated the energy barrier 0.8 kcal./mol. for ethanol and Weltner and Pitzer[9] estimated 0.9 kcal./mol. for methanol around the O–C axis by comparison of the values obtained by computation and by observation of heat capacities and entropies. The energy barrier is also estimated by the microwave method as 1 kcal./mol.[10]

Now, let us consider the rotational isomers of aliphatic alcohols in respect of the O–C axis. In Fig. 2, the isomers are projected through the O–C axis and the oxygen atom is on the upper side. The circle indicates a carbon atom to which the hydroxyl group is attached.

In type I, the hydrogen atom of the hydroxyl group is situated between the two hydrogen atoms which are attached

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[3] U. Liddel and E. D. Becker, *Spectrochim. Acta*, **10**, 70 (1957).

[4] R. E. Richards, *Trans. Faraday Soc.*, **44**, 40 (1948).

[5] G. M. Barrow, *J. Phys. Chem.*, **59**, 1129 (1955).

[6] M. St. C. Flett, *Spectrochim. Acta*, **10**, 21 (1957).

[7] R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **4**, 711 (1936).

[8] G. N. Barrow, ibid., **20**, 1739 (1952).

[9] W. Weltner and K. S. Pitzer, *J. Am. Chem. Soc.*, **73**, 2606 (1951).

[10] E. V. Ivash and D. M. Dennison, *J. Chem. Phys.*, **21**, 1804 (1953).

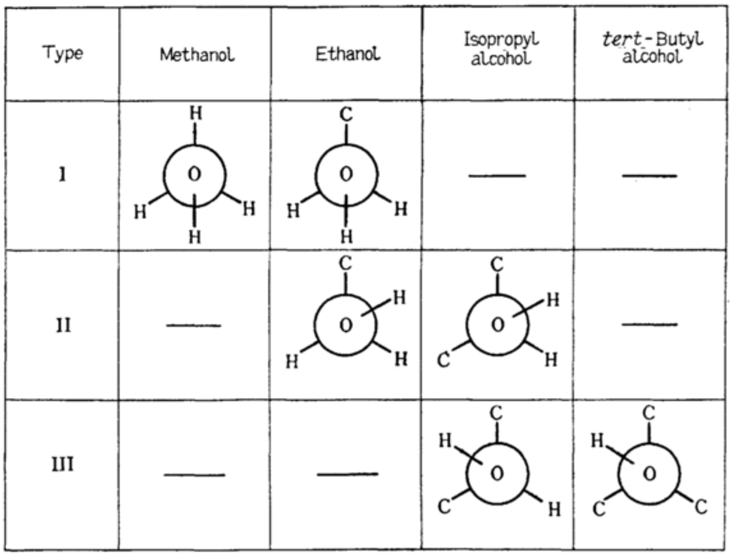

Fig. 2.

to the next carbon atom; in type II, between carbon and hydrogen atoms; and in type III, between two carbon atoms. Then, it is quite understandable that methanol and *tert*-butyl alcohol have single symmetric bands because they have only one rotational isomer and that also ethanol, higher primary alcohols and secondary alcohols have two bands which form an apparently unsymmetric band because they have two rotational isomers.

It is also expected from the above models that the force field will be almost the same in type I, irrespective of the other part of the molecules, and the same situation is also expected for type II or III. Therefore, the type of the rotational isomers of the alcohols determines the wave number where the ν_{O-H} band appears. This turned out to be really the case. The ν_{O-H} absorption of type I appears at about 3640 cm^{-1}, that of type II at about 3626 cm^{-1} and that of type III at about 3617 cm^{-1} irrespective of the nature of the alcohols. The main peak for the primary alcohols comes from type I and that for the secondary alcohols comes from type II.

The reason for such assignment is as follows. When Table I is examined, it is obvious that primary alcohols possess the property of methanol to some extent, because they show one of the ν_{O-H} bands at about 3640 cm^{-1}. Thus the absorption at ca. 3640 cm^{-1} is assigned to type I. Comparison of the absorptions of secondary alcohols with those of tertiary alcohols in a similar way indicates that the band at about 3617 cm^{-1} must be assigned to type III. The remaining band at about 3626 cm^{-1} is assigned to type II.

The probability of type I for primary alcohols is considered one third and that of type II two thirds. Although such expectation does not agree with the results obtained with the primary alcohols, it does agree with those for the secondary alcohols. One of the possibilities which may explain this phenomenon is repulsion between the hydrogen atom of the hydroxyl group and the alkyl group attached to the alpha carbon. In order to clarify this point, a bulky substituent, such as isopropyl or *tert*-butyl group, is introduced to the primary or secondary alcohols. As to the integrated intensities, the steric effect of the substituent is clearly observed in the primary alcohols but not in the secondary alcohols; since the integrated intensity the ν_{O-H} band, affected by the steric environment, is the minor one in the former, while, in the latter both types are affected as far as the present compounds are concerned. The error included in dividing the unsymmetric band may not allow the drawing of a clear-cut conclusion, but it is still clear that the most stable point for the hydrogen atom of the hydroxyl group is pushed toward the hydrogen rather than the bulky group because of the steric effect and consequently the wave number at which ν_{O-H} absorption appears is heightened. Thus the main peak for *tert*-butylmethylcarbinol appears very close to the main peak of the primary alcohols (type I). The same phenomenon is also observed in the primary alcohols, but in this case the more outstanding feature is the increase of the ratio of the integrated intensity of type I to that of type II. In other words, in neopentyl alcohol, A_I/A_{II} increased to 6.0 from about 2.0 for the other primary alcohols and the increase in the integrated intensity of type I must be attributed to the greater number of the molecules due to the steric requirement.

Thus, it is now evident that the second minor peaks of ν_{O-H} absorption found in 4-penten-1-ol, 5-hexen-1-ol and 10-undecen-1-ol[2] do not represent the intramolecular interaction between the hydroxyl group and the π-electrons of the double bond, but are attributable to the existence of the two rotational isomers which can be represented by types I and II.

It is expected from the above results that the idea of rotational isomerism will be applicable to the phenyl substituted alcohols and therefore the authors have extended their work to benzyl alcohol and its derivatives. The results are shown in Table II.

TABLE II. ν_{O-H} ABSORPTION OF PHENYLCARBINOLS

Compounds	Band	ν_{max} (cm^{-1})	$\Delta\nu^a_{1/2}$ (cm^{-1})	$A\times10^{-3}$ (mol^{-1}·l.·cm^{-2})
$C_6H_5CH_2OH$	I	3636.3	24.0	2.52
	II	3617.1	17.0	4.26
$C_6H_5CH(CH_3)OH$	I	3627.0	21.0	1.15
	II	3616.0	16.3	4.32
$C_6H_5C(CH_3)_2OH$	I	3620.6	15.4	1.61
	II	3607.1	15.0	3.43
$C_6H_5C(C_2H_5)_2OH$	I	3618.2	17.8	3.49
	II	3608.2	19.0	1.38
$(C_6H_5)_2CHOH$	I	3619.0	15.6	4.92
	II	3609.8	21.4	2.40
$(C_6H_5)_2C(CH_3)OH$	I	3613.0	14.8	4.26
	II	3608.0	20.0	1.85
$(C_6H_5)_2C[CH(CH_3)_2]OH$	I	3617.3	13.2	4.39
	II	3609.7	13.0	0.89
$(C_6H_5)_3COH$		3610.7	15.6	5.95

Ethylmethylphenylcarbinol and ethyldiphenylcarbinol are not included in Table II, because they show a nearly symmetric band which may be an overlap of two similar symmetric bands and can not be divided by the present technique.

It has long been in question why benzyl alcohol and allyl alcohol show an absorption band at about 3620 cm^{-1} in spite of the fact that they are primary alcohols, the only observation of the two bands for benzyl alcohol having been made by Fox and Martin[11]. Quite recently Schleyer, Trifan and Bacskai[12] also reported the existence of the two bands for the O–H stretching absorption of allyl and benzyl alcohols, their results being in good agreement with the present ones. Although the present authors as well as Schleyer et al. attributed the band at 3619 cm^{-1} to the intramolecular interaction between the hydroxyl group and π-electrons, it now seems probably correct to introduce the concept of rotational isomers involving the interaction mentioned above for the explanation of the phenomenon, because type IV shows the absorption band at 3636 cm^{-1} where the normal primary alcohols do, type V at 3618 cm^{-1} and type VI at 3610 cm^{-1}.

The fairly large shifts (7∼8 cm^{-1}) between types II and V and between types III and IV are most conveniently explained by introducing the concept of neutralization or the intramolecular interaction between the hydroxyl group and the π-electrons. That is, when a π-electron exists at the β-carbon atom of the alcohol, the interaction takes place and the extension of the O–H bond length occures. Thus the force constant is weakened and the weaker force constant gives rise to the shift of the absorption maximum toward the lower wave number.

Then the rotational isomers represented in Fig. 3 must be somewhat different from those in Fig. 2. In benzyl alcohol it is understood that the hydrogen atom of the hydroxyl group is not in the midst of the two atoms attached to the α-carbon, different from the cases of aliphatic alcohols, but is located closely to the carbon atom which possesses a π-electron. But the O–H bond can not be *cis* in respect of the C_{Ph}–C_α bond; since, if it were, there should not be any difference between types V and VI or between benzhydrol and triphenylcarbinol. The intramolecular interaction in allyl alcohol may be of this type, because its interacted form shows an absorption band at 3619.4 cm^{-1}.

It is also noticed that the band intensity of type V is greater than that of type IV in benzyl alcohol in contrast with the reverse in the primary aliphatic alcohols. This fact can be attributed to greater stabilization of type V in benzyl alcohol

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[11] J. J. Fox and A. E. Martin, *Trans. Faraday Soc.*, 36, 897 (1940).

[12] P. von R. Schleyer, D. S. Trifan and R. Bacskai, *J. Am. Chem. Soc.*, 80, 6691 (1958).

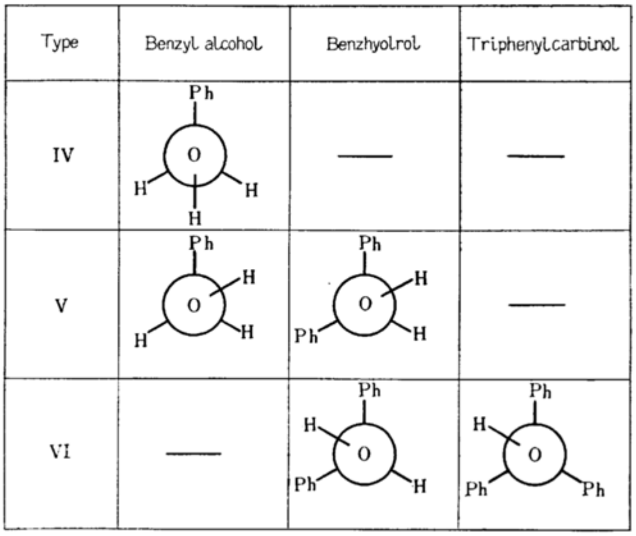

Fig. 3.

than of type IV in aliphatic alcohols because of the intermolecular interaction.

The only unknown ν_{O-H} absorption for the rotational isomers in the alcohols now is the one which should be assigned to the type in which the hydrogen atom of the hydroxyl group is situated between the aromatic carbon and the aliphatic carbon (type VII). The example is provided by alkyldiphenylcarbinols. The absorption at 3617 cm^{-1} is assigned to this, since the other absorption at 3609 cm^{-1} has been assigned to type VI.

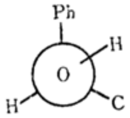

Fig. 4.

Theoretically, it is expected that alkylphenylcarbinols exhibit three ν_{O-H} absorptions, because they have the possibility of taking three types represented by II, V and VII. However, the ν_{O-H} absorptions of the types V and VII are so closely located that it is impossible to resolve them and consequently only two bands are observed for type II and for a mixture of types V and VII with methylphenylcarbinol.

There are some exceptions which are represented by dialkylphenylcarbinols. In these cases, the absorptions occur at 3620 cm^{-1} and at 3607 cm^{-1}, the latter being in the same position as type VI. However, the steric interference between the two alkyl groups and the ortho hydrogen atoms of the benzene nucleus causes the different situation from the others and the case is more complicated. The authors tentatively attribute this abnormality to the internal rotation around the C_{Ph}-C_α axis which is forced by the environment. Although the shift in wave number may be too great to assign the bands in an analogous way, it may still be valid that type VII of dialkylphenylcarbinol shows an absorption band at a lower wave number than type III because of the lowered force constant. Thus, the band at 3608 cm^{-1} is tentatively assigned to type VII and that at 3620 cm^{-1} to type III.

Summary

The authors observed symmetric ν_{O-H} absorptions for methanol and tertiary alcohols and unsymmetric bands for primary and secondary alcohols. The unsymmetric band was divided into two bands, assuming that the band is an overlap of the two symmetric bands. The idea of the rotational isomerism was successfully introduced for assigning the band and the following points were concluded.

1) Types I and IV show absorption bands at 3644~3636 cm^{-1}, type II at 3626~3629 cm^{-1}, type III at 3615~3618 cm^{-1}, type V at 3616~3619 cm^{-1}, type VI at 3608~3611 cm^{-1}, and type VII at 3613~3617 cm^{-1}.

2) The exception is dialkylphenylcarbinols which show the ν_{O-H} absorptions at about 3620 cm^{-1} and 3608 cm^{-1}, the former being assigned to type III and the latter to type VII. This ruling-out may be

attributed to the steric effect and the rotation around the C_{Ph}-C_{α} axis.

The steric effect on the integrated intensities and on the wave number where ν_{O-H} absorption falls is also discussed. The differences between types II and IV and between types III and VI were attributed to the existence of the intramolecular interaction between the hydroxyl group and π-electrons of the benzene nucleus. The same reason may cause allyl alcohol to show its main ν_{O-H} absorption at about 3620 cm^{-1}.

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