

INTRAMOLECULAR INTERACTION BETWEEN A HYDROXYL GROUP AND π -ELECTRONS—XXII¹

RELATIONSHIP BETWEEN CONFORMATION AND FREQUENCY SHIFT BY INTRAMOLECULAR O—H $\cdots\pi$ INTERACTION IN OLEFINIC ALCOHOLS

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Abstract—In olefinic alcohols the intramolecular interaction between the OH group and the π -electrons is observed as a shift to the lower frequency of the O—H stretching band ($\nu_{\text{O—H}}$), when the molecule is fixed in a conformation in which both groups are mutually in proximity or when it can adopt such a conformation. The closer the interacting groups, the greater the value of the $\nu_{\text{O—H}}$ shift, and $\Delta\nu_{\text{O—H}}$ can be correlated to the degree of the overlap between the orbitals of the OH group and the π -electrons.

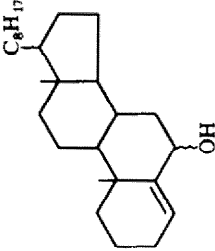
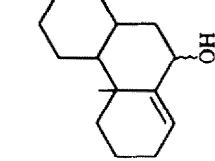
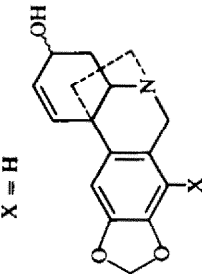
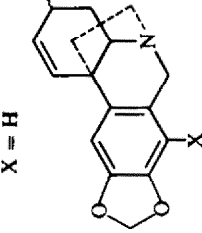
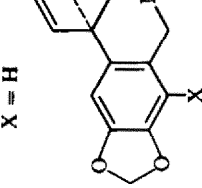
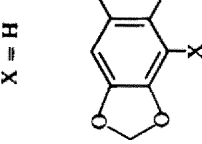
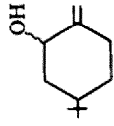
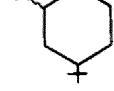
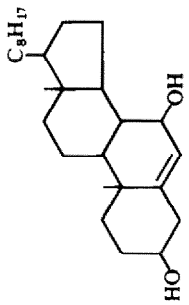
INFRARED data of unsaturated alcohols in which there is intramolecular interaction between the OH group and the π -electrons have been accumulated in the 3μ region of the O—H stretching absorption ($\nu_{\text{O—H}}$). It has also been shown that the presence of an interacting $\nu_{\text{O—H}}$ band may be used to assign the configuration and/or conformation of the molecule.² The configuration of the OH group has successfully been deduced in haemanthamine-epihaemanthamine,³ isomeric decahydroanthracene-9,10-diol,⁴ epimeric bicyclo[2.2.2]oct-2-en-5-ols,⁵ 5(10)-estren-3-ol derivatives,⁶ bicyclo[3.3.1]non-2-en-9-ol derivatives,⁷ synthetic octalols⁸ etc. There are, however, some compounds which appear to favor the internal interaction, but lack this $\nu_{\text{O—H}}$ band. Schleyer *et al.*^{1,9} failed to observe the O—H $\cdots\pi$ bonding in cholest-4-en-6 β -ol, 5-*endo*-hydroxymethylbicyclo[2.2.1]hept-2-ene and 4-hydroxymethylcyclohexene. 4-Hydroxycyclohexene¹⁰ and 7-*syn*-hydroxymethylbicyclo[2.2.1]hept-2-ene^{9,11} have also been shown to lack this O—H $\cdots\pi$ interacting band, although the tertiary analog of the latter exhibits strong O—H $\cdots\pi$ interaction.

It is the purpose of the present paper to determine the factors governing the internal O—H $\cdots\pi$ interaction in olefinic alcohols and to account for exceptions cited above. Since both the interacting groups are highly directional, it may be possible to correlate the spectral parameters with those of the molecular geometry as is the case in the O—H \cdots O type hydrogen bonding of diols.¹²

RESULTS AND DISCUSSION

Allylic alcohols. In connection with the intramolecular O—H $\cdots\pi$ interaction in olefinic alcohols, Schleyer *et al.*^{2a} observed doublet and singlet $\nu_{\text{O—H}}$'s for cholest-4-en-6 α - and -6 β -ols, respectively, and assigned the singlet at 3614 cm^{-1} of the latter to the free OH group. The assignment is, however, unattractive, since the 6 β -hydroxyl group is situated axially and is more favorably disposed to interact with the π -electrons on the C₄-C₅ double bond than the 6 α -epimer. A similar IR characteristic

TABLE I. ν_{O-H} DATA FOR ALLYLIC ALCOHOLS

No.	Compound	$\nu_{max} (\Delta\nu^a)$ cm ⁻¹	$A \times 10^{-3}$ mole ⁻¹ l. cm ⁻²	$\Delta\nu_{O-H}^b$ cm ⁻¹	Ref	$R_1(A)^c$ (θ)	$R_2(A)$ (θ)
1	$CH_2=CHCH_2OH$	3635 (23) 3619 (16)	23 29	8	15	—	—
2		α 3619 3605	sh.	13	2a	2.65 (63)	2.74 (64)
3		β — 3614	13	13	2a	2.61 (42)	3.19 (53)
4	X = H 	β 3626 3611	sh.	7	13	2.65 (47)	3.63 (60)
5		α 3620 (30)	7	7	13	2.58 (51)	3.67 (64)
6		β 3626 3611	sh.	7	13	2.65 (47)	3.63 (60)
7	X = OMe 	α 3619 (21)	8	8	13	2.58 (51)	3.67 (64)
8		cis 3622 (21) 3605 (18)	40 0.9	13	present work	2.65 (63)	2.74 (64)
9		trans — 3618 (15)	5.9	9	present work	2.61 (42)	3.19 (53)
10		3623 (24) 3608 (15)	109 81 ^d	10	present work	2.65 (47)	3.63 (60)

^a Position of the interacting bands referred to the standard free ν_{O-H} which is taken to be 3636, 3627 and 3618 cm⁻¹ according to the isomerism brought about by rotation around the C—O bond (type I, II and III in text).

^b Defined as shown in Fig. 1.

^c Overlapped with 3 β -OH.

has been reported by Fales and Wildman¹³ in the epimeric pairs of crinine and powelline, as shown in Table 1. It has now been established that a model pair (8 and 9) of these fixed allylic alcohols behave similarly (8 with the equatorial OH group shows doublet $\nu_{\text{O-H}}$ while 9 with the axial OH singlet), and that the apparent reversal of the band feature is a general phenomenon.*

In order to account for the contradiction, either the overlap between the OH group and π -electrons in the axial allylic alcohols is too small to bring about any observable $\nu_{\text{O-H}}$ shift, or the singlet bands at $3614 \sim 3620 \text{ cm}^{-1}$ should be assigned to the interacting OH group. As a measure of overlap of the orbitals belonging to the OH group and π -electrons, it is adequate to employ the overlap integral, $S(R, \theta)$,¹⁶ as a function of the distance and the angle defined as shown in Fig. 1 between the ethylenic

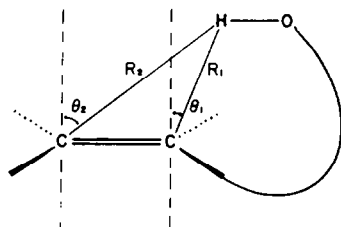
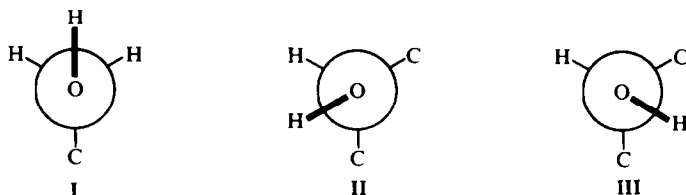


FIG. 1. Parameters expressing the overlap.

carbons and the OH hydrogen.¹ Dreiding models indicate that the most favorable overlap in the 2-methylenecyclohexanols is realized by an OH axial epimer with a conformation in which the O—H group eclipses the C_{α} — C_{β} bond. According to this model, S is as high as 0.14, and it is very improbable that olefinic alcohols 3, 5, 7 and 9 have a free or only weakly interacting OH group. The eclipsed conformation is also disregarded for the following reasons. In previous papers,¹⁷ it was established that the free $\nu_{\text{O-H}}$ maxima of alcohols are determined primarily by the conformational isomerism with respect to the C—O bond. Thus different $\nu_{\text{O-H}}$ frequencies appear corresponding to the three potential energy minima represented by Newman projections of types I, II and III. The potential barrier around this three-fold axis has been shown to be about one kcal/mole.¹⁸ Judging from the minor $\nu_{\text{O-H}}$ shift under

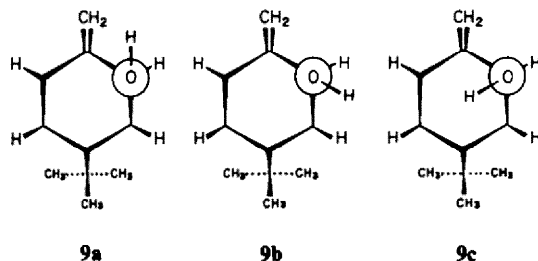


discussion, the energy gained by the $\text{O-H} \cdots \pi$ interaction¹⁹ may be only a fraction of one kcal/mole. The shape of the potential curve, therefore, can be assumed to be only slightly changed by the interaction with the π -electrons. As far as the O—H staggered conformations are concerned, three conformations exist, of which the contribution of the OH inside conformation 9c may be neglected due to 1,3-diaxial

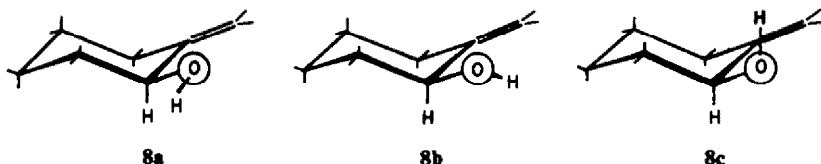
* It is also the case in the epimeric 1-tetralols which are conformationally fixed by the bulkier 3-substituents; *cis*-3-phenyl-1-tetralol (OH, pseudo-equatorial) at 3622 and 3600 cm^{-1} , *trans*-epimer (OH, pseudo-axial) at 3617 cm^{-1} .¹⁴

steric interference.* It then follows that the $\nu_{\text{O-H}}$ of **9** should appear at ca. 3627 cm^{-1} corresponding to the type II environment of the OH group in **9a** and **9b**. It is, therefore, concluded that alcohols **3**, **5**, **7** and **9** prefer conformation **9a** and that the observed singlet bands at $3614 \sim 3620\text{ cm}^{-1}$ are $\nu_{\text{O-H}}$'s shifted from ca. 3627 cm^{-1} as a result of the internal interaction with the π -electrons. $\Delta\nu_{\text{O-H}}$ as a potential measure of strength of the $\text{O-H}\cdots\pi$ interaction should be $7 \sim 13\text{ cm}^{-1}$, and the overlap integral S now ca. 0.09 which is, as shown later, not in conflict with rather weak interaction.†

As shown in Table 1, O—H equatorial alcohols always exhibit a doublet $\nu_{\text{O-H}}$, the lower frequency band of which can be assigned to the interacting ones, although



apparently this geometry precludes any such interaction. The equatorial OH groups on a cyclohexane ring have been shown²⁰ to absorb at a slightly lower frequency than the axial epimer due to the contribution of type III conformation which was excluded from the latter. Considering **8a**, **8b** and **8c**, $\nu_{\text{O-H}}$ should appear at 3627 cm^{-1} in **8a** and **8b** and around 3618 cm^{-1} in **8c** when no interaction with π -electrons is taking place. The overlap integrals amount to nearly zero, 0.019 and 0.072, respectively. The last value is almost equivalent to that of **9a** and, therefore, the corresponding shift to the lower frequency of about 10 cm^{-1} is expected. Thus the lower frequency bands at $3603 \sim 3611\text{ cm}^{-1}$ in compounds **2**, **4**, **6**, **8** and **10** are assigned to the interacting OH group in the conformation **8c**. The higher frequency bands are of course "free" $\nu_{\text{O-H}}$ in **8a** and **8b**. A minor shift to the lower frequency of these bands in **2**, **8** and **10** may be attributed to the preference of **8b** conformation which is slightly affected by the π -electrons.



* Aaron *et al.*²⁰ have attributed $\nu_{\text{O-H}}$ of a little higher frequency of the axial OH group of the cyclohexanols to contribution of the steric interference, in the case of O—H stretching, from OH inside conformation (such as **9c**).

† $3\beta,6\beta$ -Diacetoxy-5-methyl-19-nor-5 β -cholest-9-11 β -ol shows sharp singlet $\nu_{\text{O-H}}$ at 3590 cm^{-1} , with $\Delta\nu_{\frac{1}{2}} = 26\text{ cm}^{-1}$ and $A = 1.13 \times 10^4\text{ mole}^{-1}\text{ cm}^{-2}$. It was once considered that this band is shifted due to the strong $\text{O-H}\cdots\pi$ interaction, but since the 11 β -hydroxyl group is situated axially the frequency is too low to be assigned in this way. Together with the information of the enhanced band intensity A , it seems to be more natural to ascribe the band to the $\text{O-H}\cdots\text{O}=\text{C}$ type hydrogen bonding with the 6 β -acetoxy group. The occurrence of such intramolecular hydrogen bonding is compatible only with the model of Jones and Summers (6 β -axial) for 5 β -methyl-19-nor-5 β -cholest-9-ene skeleton.²¹

Homoallylic alcohols. Table 2 tabulates homoallylic alcohols in which the intramolecular O—H $\cdots\pi$ interaction can be observed in the $\nu_{\text{O-H}}$ absorptions, some of which are reproduced in Fig. 2. They cover primary (compounds Nos 11, 12), secondary (Nos 13 ~ 29) and tertiary alcohols (Nos 30 ~ 42), with a variety of

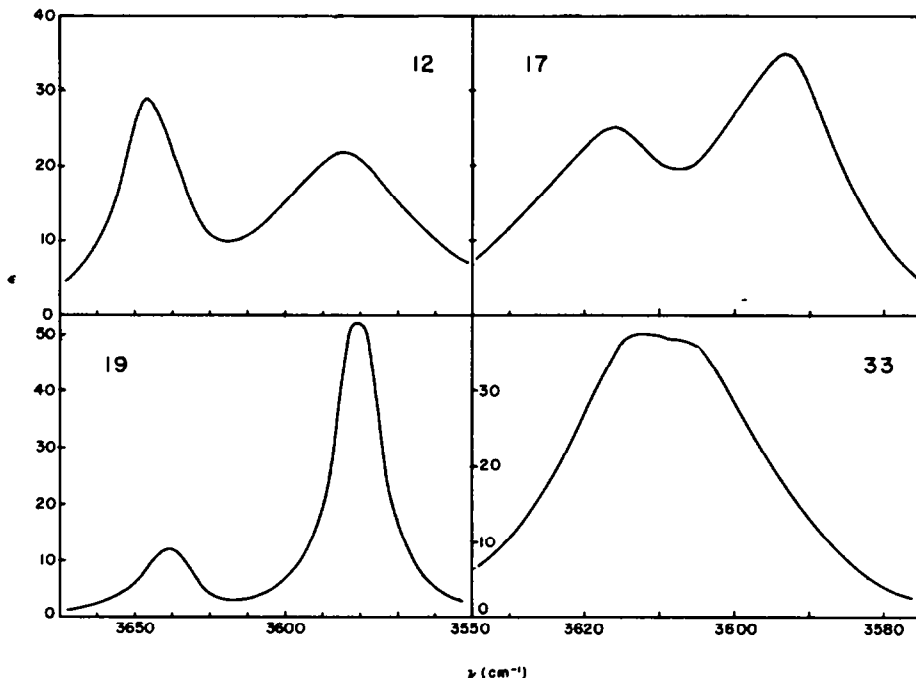


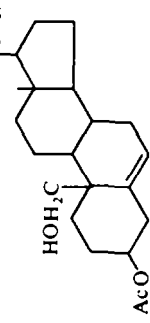
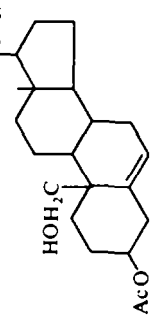
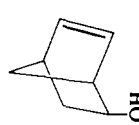
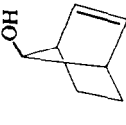
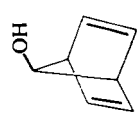
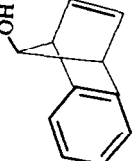
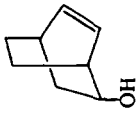
FIG. 2. $\nu_{\text{O-H}}$ Absorptions of homoallylic alcohols 12, 17, 19 and 33.

spectral parameters. The apparent frequency shifts vary from 14 cm^{-1} (No 33) to 67 cm^{-1} (No 15) as a result of the interaction. As to the intensity, the interacting bands are revealed only as a shoulder against the strong free $\nu_{\text{O-H}}$ band in compound 27, while they are the single absorption band in many other compounds.

Since the proposal of Badger and Bauer,²² there has been a general acceptance of the empirical rule that the $\nu_{\text{O-H}}$ shift ($\Delta\nu_{\text{O-H}}$) provides a good measure of the enthalpy of the hydrogen bonding.³⁴ It has also been shown by Kuhn^{12, 35} that $\Delta\nu_{\text{O-H}}$ provides a measure of both the strength and the distance (OH \cdots O) of the hydrogen bond in diols, although recently Singh *et al.*³⁶ indicated that a linear $\Delta\nu_{\text{O-H}}$ vs $-\Delta H^\circ$ relation does not hold when one considers hydrogen bonding of a variety of OH compounds with a series of electron donors. The examples presently under consideration have the alcoholic OH group as a proton donor and the ethylenic double bond as a proton acceptor in common, and therefore seem to fit the linear $\Delta\nu_{\text{O-H}}$ vs $-\Delta H^\circ$ relation fairly well.

It is not correct to regard the free $\nu_{\text{O-H}}$ of each sample as a standard for expressing $\Delta\nu_{\text{O-H}}$ as the location of the free $\nu_{\text{O-H}}$ has been shown to depend primarily on the conformational isomerism around the C—O bond and in this respect the environment

TABLE 2. ν_{O-H} DATA FOR HOMALLYLIC ALCOHOLS

No.	Compound	$\nu_{max} (\Delta\nu_{OH}^a)$ cm^{-1}	$A \times 10^{-3}$ $mole^{-1} l. cm^{-2}$	$\Delta\nu_{O-H}^b$ cm^{-1}	Ref.	$R_1(A)^c$ (6)	$A_2(A)$ (6)
11	$CH_2=CHCH_2CH_2OH$ 	3635 (24) 3596 (32)	3.3 1.9	31	present work	—	—
12		3637 (18) 3585 (45)	1.8 3.7	42	present work	2.54 (23)	2.77 (32)
13		3624 (21) 3592 (15)	2.6 1.7	26	present work	2.44 (12)	2.91 (35)
14		— 3572	—	46	11a	2.41 (22)	2.41 (22)
15		— 3551	—	67	11a	2.41 (22)	2.41 (22)
16		— 3559	—	59	23	2.41 (22)	2.41 (22)
17		3617 (20) 3593 (18)	1.5 2.1	25	present work	2.50 (14)	2.93 (34)

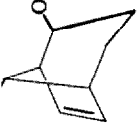
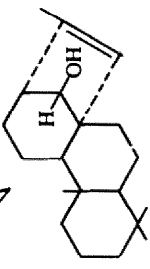
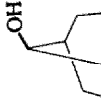
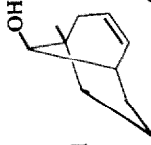
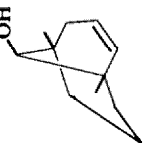
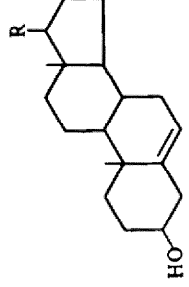
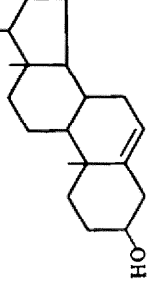
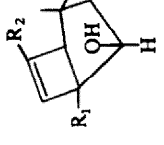
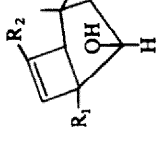
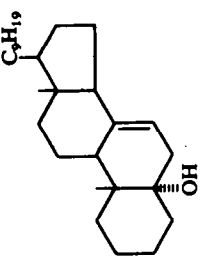
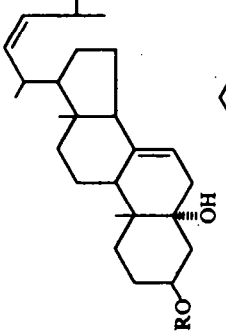
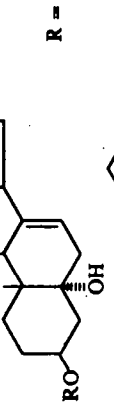
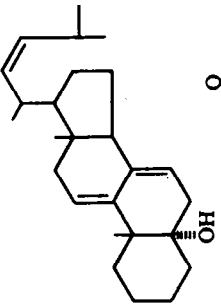
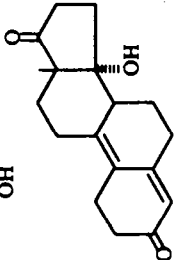
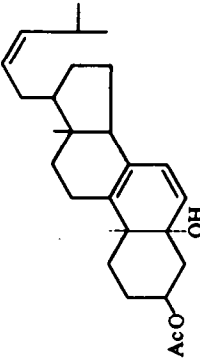
18		3628 ^c 3596	22	24	2.64 (27)	2.64 (27)
19		3631 (16) 3581 (14)	37	present work	2.50 (27)	2.50 (27)
20		3617 3578	40	25	2.16 (26)	2.32 (34)
21		3632 (18) 3587 (19)	31	present work	2.54 (35)	2.50 (33)
22		3640 (25) 3584 (18)	34	26	2.54 (35)	2.50 (33)
23		3624 (17) 3590 (32)	28	2b	2.50 (16)	3.12 (40)
24		3620 (20) ^f 3588 (31)	30	present work	2.50 (16)	3.12 (40)
25		R ₁ = Me R ₂ = H	12	27	2.66 (15)	2.92 (28)
26		R ₁ = H R ₂ = Me	13	27	2.66 (15)	2.92 (28)

TABLE 2—continued

No.	Compound	ν_{\max} ($\Delta\nu_1^a$) cm^{-1}	$A \times 10^{-3}$ $\text{mole}^{-1} \text{l. cm}^{-2}$	$\Delta\nu_0 - \nu^a$ cm^{-1}	Ref.	$R_1(A)^b$ (θ)	$R(A)^b$ (θ)
27 ¹⁸		3628 3605	sh.	13	6	2.76 (43)	2.68 (42)
28		— β 3598		29	3	2.40 (10)	2.88 (36)
29		— α 3591		36	3	2.40 (10)	2.88 (36)
30	$\text{CH}_2=\text{CHCH}_2\text{CMe}_2\text{OH}$	3616 (26) 3583 (21)	2.5 1.5	35	10		
31	$(\text{CH}_2=\text{CHCH}_2)_2\text{CMeOH}$	3615 (20) 3581 (25)	1.9 2.6	37	10		
32	$(\text{CH}_2=\text{CHCH}_2)_3\text{COH}$	3612 (20) 3578 (25)	1.2 3.9	40	10		
33		3616 (20) 3602 (21)	2.0 1.7	16	present work	2.57 (42)	2.49 (40)
34		— 3575		43	29	2.41 (22)	2.41 (22)
35		3613 (21) 3596 (18)	25 ^d 45 ^d	22	26	2.57 (42)	2.49 (40)
36		3623 3597		21	30	2.57 (42)	2.49 (40)

37		3614 (25) 3593 (29)	10 ^a 40 ^a	25	26	2.57 (42)	2.49 (40)
38		R = H 3627 ^b (17) 3591 (52)	70 ^a 40 ^a	27	31	2.57 (42)	2.49 (40)
39		R = Ac 3592 (40)	42 ^a	26	31	2.57 (42)	2.49 (40)
40		— 3583	—	35	26	—	—
41		— 3578	—	40	32	—	—
42		3619 3604	55 ^a 20 ^a	14	33	—	—

^a Not necessarily an apparent ν_{O-H} shift, but the shift of the interacting bands referred to the standard free ν_{O-H} which has been assumed to be 3636, 3627 and 3618 cm^{-1} according to the type I, II and III isomerism with respect to the rotation around the C—O bond, respectively, of the interacting species.

^b Defined as shown in Fig. 1.

^c Overlapped with another free ν_{O-H} .

of the OH hydrogen giving free $\nu_{\text{O-H}}$ is not equivalent to that of the interacting OH group. The free OH hydrogen of compounds **13**, **14**, **28** and **29**, for example, is staggered between a carbon and a hydrogen atom in the Newman projection (type II), while the interacting OH hydrogen is placed between two adjacent carbon atoms (type III) in **13** and **14**, and remains unaltered from the environment of the free OH group in **28** and **29**. Nor is it proper to employ, as a reference compound for the free $\nu_{\text{O-H}}$, the corresponding saturated alcohols or epimers whose OH group is pointing in the opposite direction to the π -electrons, because it has been noticed that the crowded environment of the OH group due to the branching on the adjacent carbon atoms or the presence of the *syn*-axial hydrogen atoms may shift the free $\nu_{\text{O-H}}$ to the higher frequency presumably owing to the van der Waals repulsion which effects shortening of the O—H bond.^{17, 20, 37, *}

With the above in mind, it is tentatively proposed to equate the free $\nu_{\text{O-H}}$ to 3636, 3627 and 3618 cm^{-1} according to the type I, II and III environment, respectively, of the interacting OH group with respect to the rotational isomerism around the C—O bond. $\Delta\nu_{\text{O-H}}$'s in Tables 1 to 3 are the shift of $\nu_{\text{O-H}}$ thus defined. The procedure is partly equivalent to comparing the position of the interacting $\nu_{\text{O-H}}$ without reference to the free $\nu_{\text{O-H}}$.^{9, 38}

As another index to test the linearity with $\Delta\nu_{\text{O-H}}$ thus far discussed, an overlap between the OH group and π -electrons is considered to be of prime importance in determining the enthalpy of the O—H $\cdots\pi$ interaction, because the strength of the proton donor and the acceptor under consideration is nearly equivalent throughout. Difference in π -basicity of the ethylenic double bonds due to substitution and variation in the sp^2 bond angle should contribute to a change in the enthalpy of the interaction, but the effect will be of secondary importance when considering a wide variety of olefinic alcohols of different geometry.† In order to express the degree of overlap between the orbitals of the OH group and the ethylenic π -electrons, it may be sufficient either to employ the distance between them as treated by Kuhn,³⁵ or the angle made by them as suggested in the preceding paper,¹ or a combination of the two. It seems, however, more appropriate to adopt the overlap integral tabulated by Mulliken *et al.*¹⁶ as a function of the combination of the two parameters, because the square of this integral has been shown to be proportional to the enthalpy of the charge-transfer force which is probably operating in the O—H $\cdots\pi$ interaction.¹ The parameters R and θ were determined with respect to the geometry defined as shown in Fig. 1 according to the known structural dimensions of the analogous skeletons.⁴⁰ The conformation determined by the rotation around the C—O bond was assumed to be one of the staggered which is more favorable for the internal O—H $\cdots\pi$ interaction of the three staggered forms. The calculated $S^2(R, \theta)$ vs $\Delta\nu_{\text{O-H}}$ plots give a correlation as shown in Fig. 3, in which the data of the allylic and bishomoallylic alcohols are included. There are some examples in which the staggered conformation apparently does not represent the interacting form correctly, and the eclipsed conformation of the OH group with the $\text{C}_\alpha\text{—C}_\beta$ bond may be preferred to the staggered because of the

* Rather high free $\nu_{\text{O-H}}$ of **22** may be this example. If the apparent free $\nu_{\text{O-H}}$ is employed for expressing the $\nu_{\text{O-H}}$ shift, $\Delta\nu_{\text{O-H}}$ comes up to 56 cm^{-1} which will be shown later to be an overestimation.

† When a series of geometrically equivalent samples are compared, the electronic effect will be of major importance.³⁹

more favorable overlap between the orbitals of the interacting groups. The overlap integrals of the eclipsed form in 12, 28, 29 as well as 3, 5, 7 and 9 are, however, too high to be placed on the smooth line in Fig. 3 with which the rest of the examples conform. This in turn may support the staggered conformation of the interacting OH group. In addition consideration of repulsive forces between the eclipsing groups

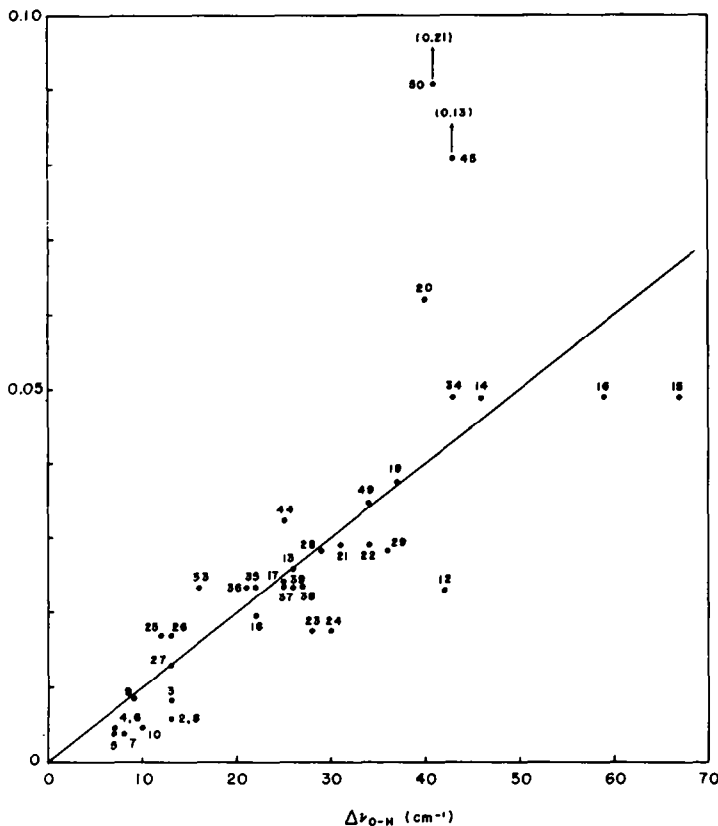
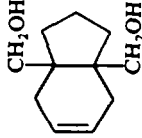
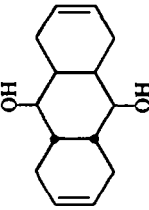
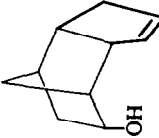


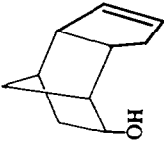
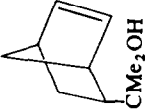

FIG. 3. Correlation between the overlap integral $S'(R, \theta)$ and the ν_{O-H} shift.

does not support the eclipsed conformation as stated before.* It has thus been demonstrated that the enthalpy of the intramolecular $O-H \cdots \pi$ interaction is dominated mainly by the degree of the overlap between the pertaining orbitals, and that a linear $-\Delta H^\circ$ vs $\Delta \nu_{O-H}$ relation holds, in which the slope amounts to $10^{-3}/\text{cm}^{-1}$ which is about three times as large as the gradient of the same relationship in

* In 12, $S^2(R, \theta)$ calculated on a fully staggered conformation in which the dihedral angle made by $C_{(10)}-C_{(19)}-O-H$ is just 60° gives a point far below the linear plot in Fig. 3. Judging from the relatively large $\Delta \nu_{O-H}$, the energy of the $O-H \cdots \pi$ interaction is no longer negligible compared to that of the conformational energy with respect to the rotation of the OH group. Location of the hydroxyl hydrogen must be determined by a compromise between the two factors, and it is probably the case that a slight deviation of the dihedral angle from 60° is happening in favor of the better overlap between the orbitals of the OH group and π -electrons.

TABLE 3. ν_{O-H} DATA FOR BISHOMOALLYLIC ALCOHOLS

No.	Compound	$\nu_{max} (\Delta \nu_{OH}^2)$ cm^{-1}	$A \times 10^{-3}$ $mole^{-1} l. cm^{-2}$	$\Delta \nu_{O-H}$ cm^{-1}	Ref.	$R_1(A)$ (θ)	$R_2(A)$ (θ)
43	$CH_2=CH(CH_2)_2OH$	3638 (21) 3625 (24)	40 1.8	—	15		
44		3635 3602 3480 (O—H...O)		25	9	2.28 (16)	2.90 (43)
45		— 3584		43	4	1.97 (20)	2.07 (27)
46		3624 3575		43	2a	1.36 (15)	1.68 (36)

47		3622 3591	27	2a	
48	$\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CMe}_2\text{OH}$	3617 (21)	42	present work	
49		3617 (17) 3584 (29)	1:2 4:8	present work	2:62 (19)
50		3617 3577	weak strong	11a	2:10 (45)

2-hydroxybiphenyls.¹ The difference may be rationalized by taking into account the increased proportionality constant as the result of enhanced acidity of the phenolic OH group compared with that of the alcoholic OH group. Deviation from linearity is marked when $S^2(R, \theta)$ is greater than 0.05. In these circumstances, the distance between the ethylenic carbon and the OH hydrogen atoms of the interacting form is shorter than 2A, and some repulsive forces may be operating resulting either in a reduced enthalpy of the interaction or a decreased $\Delta\nu_{\text{O-H}}$ due to the shortening of the O—H bond.^{20, 37} In short, the overlap integral does not represent the true enthalpy in these cases. In norbornadiene it is well known that transannular interaction between the two double bonds does exist as indicated by a series of absorptions centering at 205 $\text{m}\mu$ ($\epsilon = 2100$), and that the energy level of the highest occupied orbital is raised relative to the isolated double bond.⁴¹ In other words the basicity is apparently increased in this case. Thus the enthalpy of the internal O—H $\cdots\pi$ interaction should be greater than that estimated only by the orbital overlap, and the corresponding plot in Fig. 3 is placed well below the line. The enhanced shift to the lower frequency by 10 cm^{-1} from No 37 to 40 is not in line with the basicity order, because the latter is expected to have less basicity due to π -electron delocalization. Although the original authors²⁶ considered the change of the molecule into more flat geometry favourable for intimate interaction, an additional contribution from the overlap between the OH hydrogen and the π -orbital on $\text{C}_{(9)}$ -atom may also be an explanation.

Since the overlap integral S is approximately proportional to the inverse cube of the distance R when R is no shorter than ca. 1.5 A, the empirical formula (1), relating the distance R and the angle θ defined as shown in Fig. 1 to the $\nu_{\text{O-H}}$ shift, may be proposed for the internal O—H $\cdots\pi$ interaction of moderate strength (for the linear part in Fig. 3).*

$$\Delta\nu_{\text{O-H}} (\text{cm}^{-1}) = 2.3 \times 10^3 \left(\frac{\cos \theta_1}{R_1^3} + \frac{\cos \theta_2}{R_2^3} \right)^2 \quad (1)$$

Now that the frequency shift ($\Delta\nu_{\text{O-H}}$) upon internal interaction has been shown to be proportional to the enthalpy of the interaction, it is to be emphasized here that the relative intensity of the interacting band and/or the apparent presence or absence of the O—H $\cdots\pi$ interaction as observed in the 3μ region of the O—H stretching bands are governed by the free energy $-\Delta F^\circ$ of the interacting species, and not by its enthalpy.† This is clearly illustrated in Fig. 4 by a series of tertiary allyl carbinols, 30, 31 and 32. In these examples, the number of the proton accepting groups is changed so as to vary the statistical factor for the internal O—H $\cdots\pi$ interaction. As the number of allyl groups is increased, the intensity of the interacting bands is increased while $\Delta\nu_{\text{O-H}}$ is kept constant. Since the "distance" between the interacting groups is held constant by a two carbon chain, the $\nu_{\text{O-H}}$ shift and consequently the enthalpy of the

* The limitation is close to that in the empirical formula proposed by Kuhn¹² relating the OH \cdots O distance with $\Delta\nu_{\text{O-H}}$ for intramolecular hydrogen bonds.

† Even this enthalpy does not necessarily coincide with that of the O—H $\cdots\pi$ interaction which has been related with $\Delta\nu_{\text{O-H}}$ because the former includes in addition to the latter the conformational energy necessary for adopting the interacting form. 4-Hydroxycyclohexene, for example, may be endowed with $-\Delta H^\circ$ of the O—H $\cdots\pi$ interaction corresponding to that in 27, 33, 35, 36 and 37. But the conformational enthalpy of the axial hydroxyl group over the otherwise preferred OH equatorial epimer may exceed the gain of the O—H $\cdots\pi$ interaction with the actual result of the non-observance of the interaction in this example.⁴²

interaction are common for the three, and the changes in the relative intensity can be interpreted in terms of the entropy $-\Delta S^\circ$ of the interaction.^{10,*}

Bishomoallylic alcohols. In Table 3 the $\nu_{\text{O-H}}$ data of some bishomoallylic alcohols are given. Since $\text{O-H}\cdots\pi$ interaction depends on $-\Delta F^\circ$ as shown in the previous section, the examples of the bishomoallylic alcohols are reported less frequently

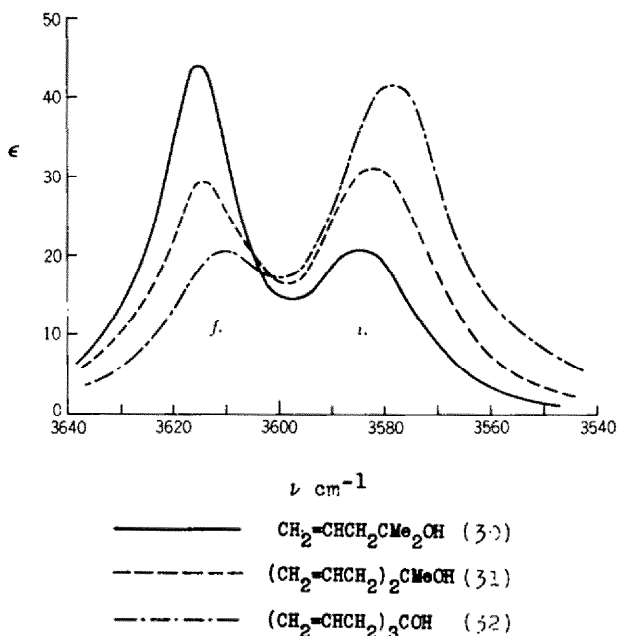


FIG. 4. $\nu_{\text{O-H}}$ Absorptions of the allylcarbinols, 30, 31 and 32.

than the lower homologs owing to the disadvantageous entropy factor introduced by one more $-\text{CH}_2-$ (see Nos 43 and 48). This is also the case in the partly fixed examples of 7-*syn*-hydroxymethylbicyclo[2.2.1]hept-2-ene^{9,11} and 5-*endo*-hydroxymethylbicyclo[2.2.1]hept-2-ene.^{9†} Only after the population of the rotational isomers around the $\text{C}_\alpha-\text{C}_\beta$ bond in the above examples is changed by substituting the methylenic hydrogens by two Me groups, is the $\text{O-H}\cdots\pi$ interaction detectable by the $\nu_{\text{O-H}}$ absorption (Nos 49 and 50).¹¹

In 45, 46, 47 and 50, even the staggered models with respect to the conformation of the OH group give the $S^2(\text{R}, \theta)$ vs $\Delta\nu_{\text{O-H}}$ plots far above the line in Fig. 3. It now must be decided whether the relatively short distance between the interacting two groups is incorrect and the overlap integral is overestimated, or whether this is the real case and the $\nu_{\text{O-H}}$ shift is apparently minimized by an overcrowding effect.³⁷

* Although Kuhn *et al.*⁹ are warning that the non-observance of the hydrogen bonding cannot be used with certainty to support an assignment of the configuration with the interacting two groups in non-proximity, it is now found that a careful conformational analysis can provide informative conclusion.

† $\nu_{\text{O-H}}$ max at 3637 cm^{-1} ($A = 3.2 \times 10^3 \text{ mole}^{-1}, 1 \text{ cm}^{-2}$) with a shoulder at 3625 cm^{-1} ($A = 1.2 \times 10^3$) characteristic of primary alcohols.

EXPERIMENTAL

Spectral measurements were carried out as described.^{1,15} As to the literature values, care was taken to pick up the reliable data measured in dil CCl₄ solution on the IR spectrometer equipped with a grating or a fluoride prism.

Sources of compounds. Compounds **8** and **12** were provided through the courtesy of Professor G. H. Whitham and Professor M. Shiota, respectively. Samples of **19** and **21** were kindly donated by Dr. T. Uda. 3 β ,6 β -Diacetoxy-5-methyl-19-nor-5 β -cholest-9-en-11 β -ol, **10** and **24** were supplied by Dr. K. Mori. Compounds **9**, **13**, **17**, **33**, **48** and **49** were prepared as described in the literature. All the above samples were of analytical purity, and the physical constants agreed well with those in the literature.*

* 5-*trans*-1-Butyl-2-methylenecyclohexanol (**9**) prepared according to B. Cross and G. H. Whitham, *J. Chem. Soc.* 1650 (1961) had m.p. of 49° which differed from m.p. 25° in the literature. (Found: C, 78.51; H, 12.09. Calc. for C₁₁H₂₀O: C, 78.51; H, 11.98 %).

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