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Intramolecular Interaction between Hydroxyl Group and Carbonyl Moiety in Keto-alcohols[1)]

Michinori Ōki, Hiizu Iwamura, Jun-ichi Aihara and Hiroshi Iida

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo

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The O–H stretching absorption (ν_{O-H}) spectra of some keto-alcohols have been examined. The ν_{O-H} shift to the lower frequency due to the intramolecular O–H···O bonding can roughly be correlated to the geometry of the hydroxyl group relative to the *n*-electrons on the carbonyl oxygen. When the bonding is forbidden because of the conformational restriction, a weaker interaction between the hydroxyl group and the π-electrons on the carbonyl group is observable as the lower shift of the ν_{O-H} by 10—30 cm^{-1} as far as the conformation is favorable for the interaction.

It has been well established by physico-chemical methods that the π-electrons on the olefinic and aromatic hydrocarbons function as a proton acceptor in the interaction with the hydroxyl group.[1,2)] As a nautral extension of the survey for a new type of the hydrogen bond acceptor, the π-electrons on the carbonyl double bond, a typical example of the multiple bonds carrying a hetero-atom, have now been taken into account. In addition to a pair of π-electrons, the carbonyl group has two lone-pairs of electrons, one of which can be regarded approximately of 2s character while the other of 2p character (n-electrons).[3)] The basicity or the donor ability of the carbonyl compounds in forming metallic and hydrogen bonded complexes has been ascribed entirely to the latter electrons, because these are more easily donated to an electron acceptor owing to the lower ionization potential (*ca.* 10 eV) and to the open nature to the attacking electrophile.[4)] The donor character of the carbonyl π-electrons which are assumed to have the ionization potential of *ca.* 12 eV, to the contrary, seems to have been less recognized.[5)] In order to observe the interaction of the carbonyl π-electrons with the hydroxyl group, some geometrical devices are necessary which exclude the preferential interaction involving the carbonyl n-electrons. In the present paper, the intramolecular interaction between the hydroxyl and the carbonyl groups in keto-alcohols has been investigated through the O–H stretching absorption (ν_{O-H}) spectra. In fulfilment of the above requirement, special emphasis has been laid on some conformationally-fixed keto-alcohols in which the hydroxyl group is so oriented as to approach the carbonyl group only from the upper side of the π-electrons clouds and perpendicularly to the n-electrons.

1) Part XXIII of "Intramolecular Interaction between Hydroxyl Group and π-Electrons." For part XXII see M. Ōki, H. Iwamura, T. Onoda and M. Iwamura, *Tetrahedron*, in press.

2) a) M. Tichý, "Advances in Organic Chemistry, Methods and Results," Vol. 5, ed, by R. A. Raphael, E. C. Taylor and H. Wynberg, Interscience Publishers, (1965) p. 115; b) Z. Yoshida and E. Osawa, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 509 (1966); c) M. Ōki, *Kagaku no Ryōiki*, **13**, 839 (1959); d) H. Iwamura, *Kagaku to Kōgyō*, **17**, 617 (1964).

3) G. Berthier and J. Serre, "The Chemistry of the Carbonyl Group," ed. by S. Patai, Interscience Publishers, London (1966), Chapter 1.

4) a) H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952); b) G. J. Brealey and M. Kasha, *J. Am. Chem. Soc.*, **77**, 4462 (1955); c) D. Cook, *ibid.*, **80**, 49 (1958); d) G. P. Rossetti and B. P. Susz, *Helv. Chim. Acta*, **47**, 289, 299 (1964).

Results and Discussion

Typical ν_{O-H} absorption curves are shown in Figs. 1 to 3. In Tables 1 and 2 are summarized the spectral parameters of all the keto-alcohols

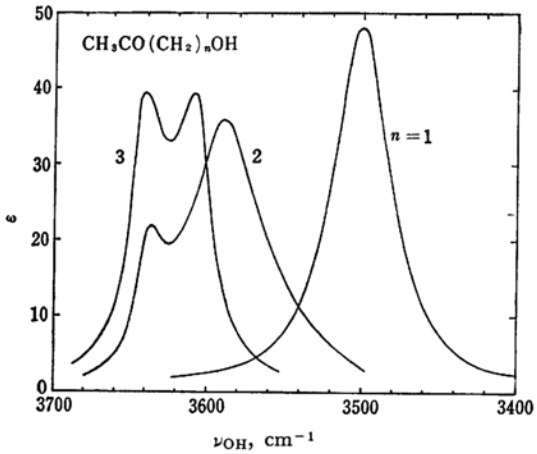


Fig. 1. ν_{O-H} absorptions of ω-hydroxy-2-alkanones.

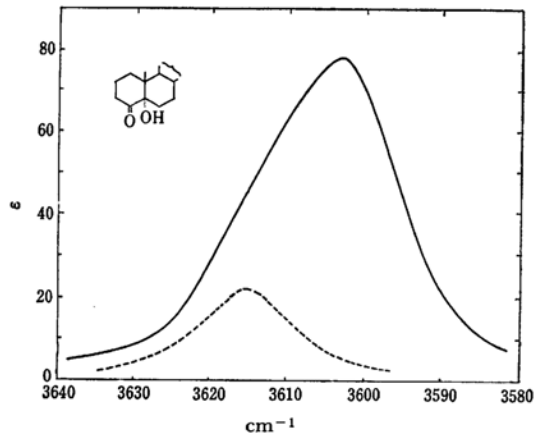


Fig. 2. ν_{O-H} absorption of 5α-cholestan-5α-ol-4-one (I).

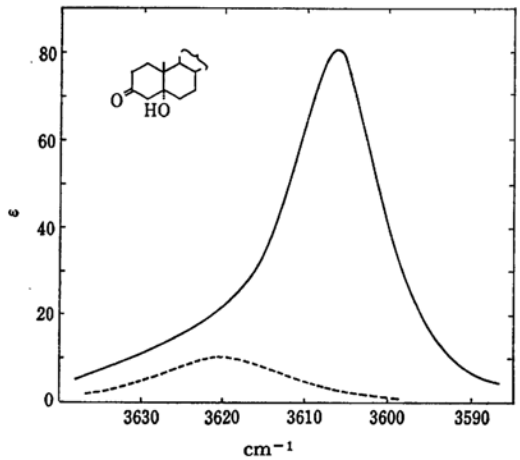
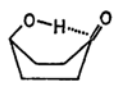


Fig. 3. ν_{O-H} absorption of 5α-cholestan-5α-ol-3-one (II).

5) In this connection the following papers deserve mention. It had once been considered that the band at 3427 cm^{-1} of 4-hydroxycyclohexanone might be due to the hydroxyl group intramolecularly bonded (i) (W. von E. Doering and A. A.-R. Sayigh, *J. Org. Chem.*, **26**, 1365 (1961)). The possibility was, however, eliminated by observing the survival of the band when the OH group was transformed into an OD group by deuterium exchange, and thus the 3427 cm^{-1} absorption was reassigned to the first overtone of the carbonyl stretching vibration at 1725.5 cm^{-1} (R. D. Stolow, *J. Am. Chem. Soc.*, **84**, 686 (1962)). Dalton and coworkers[6] have reported the anomalously low O-H stretching maxima in 5α-cholestan-5α-ol-3-one, 5β-cholestan-5β-3-one and the decalone analogs, but did



i

not notice the role of the π-electrons of the carbonyl group. The shape of the broad band due to the O-H stretching vibration of the hydrogen bond complexes of phenol with ketonic proton acceptors has been studied (H. Fritzsche, *Z. phys. Chem.*, **43**, 154 (1964); *Spectrochim. Acta*, **21**, 799 (1965)). It deviates from the normal symmetric type. The phenomenon was interpreted by assuming the superposition of two symmetrical bands and ascribed to the presence of two types of the hydrogen bond, the model for the second band requiring the participation of the π-electrons. Lately, the O-H stretching maximum at 3588 cm^{-1} of 2-hydroxy-4, 6-di-*t*-butylbenzophenone has been assigned to the hydroxyl group interacting with the π-electrons of the carbonyl group (A. T. Shulgin and H. O. Kerlinger, *Chem. Commun.*, **1966**, 249). However, the possibility of the interaction with the π-electrons of the phenyl group may not be ruled out, since the phenomenon is observed also in the structurally analogous 2-benzylphenol, the ν_{O-H} being at 3560 cm^{-1} (M. Ōki and H. Iwamura, This Bulletin, **33**, 681 (1960)).

6) F. Dalton, J. I. McDougall and G. D. Meakins, *J. Chem. Soc.*, **1963**, 4068.

examined together with some of those reported in the literature.

O–H···O Hydrogen Bond. As has been pointed out,[7,8] α-, β- and γ-keto-alcohols whose molecules are not fixed have ν_{O-H} maxima shifted to the lower frequency, and it is clear that the ordinary O–H···O hydrogen bond to form five, six and seven membered rings is taking place to a certain extent. The apparent ν_{O-H} shifts ($\Delta\nu_{O-H}$) are 135, 48 and 31 cm^{-1} for 1-hydroxy-2-propanone, 4-hydroxy-2-butanone and 5-hydroxy-2-pentanone, respectively. The trend is in sharp contrast with that of the inetrnal O–H···O bonding in α, ω-alkanediols and ω-methoxyalkanols, in which the value of $\Delta\nu_{O-H}$ increases on going from

7) V. S. Korobkov, *Doklady Mezhvuz. Nauch. Konf. po Spektroskopii i Spektr. Analizu, Tomsk. Univ.*, **1960**, 97; *Chem. Abstr.*, **56**, 115i (1962).

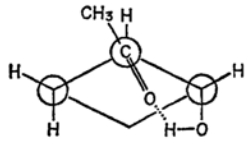
8) Tables on pp. 210—214 and papers cited therein, of Ref. 2.

Table 1. ν_{O-H} data for keto-alcohols
(O-H···O Hydrogen bond)

Compound	ν_{max} cm^{-1}	$\Delta\nu^{a}_{1/2}$ cm^{-1}	$A\times10^{-3}$ $mol^{-1}\,l\,cm^{-2}$	$\Delta\nu_{O-H}$[a] cm^{-1}
CH_3COCH_2OH	3501	44	9.8	135
2-Hydroxycyclohexanone	3500	46	—	127
5β-Cholestan-5β-ol-4-one	3480	42	11.7	138
5β-Cholestan-5β-ol-6-one	3481	45	13.3	137
2-Hydroxycyclododecanone	3497	45	9.0	130
$CH_3COCH_2CH_2OH$	3637	16	0.70	48
	3589	63	8.2	
$CH_3COCH_2CHMeOH$[9]	3600			
	3557	90	9.3	70
$CH_3COCH_2CMe_2OH$[9]	3612	25	0.68	
	3532	56	10.9	80
2-(Hydroxymethyl)cyclohexanone	3642	16	0.46	
	3584	40	8.0	58
(+)-10-Nor-8-oxoneomenthol (ii)[10]	3625	20	0.53	
	3537	87	14.4	88
(−)-10-Nor-8-oxomenthol[10]	3625	14	1.0	
	3598	60	7.7	27
Methyl icterogenin	3635[11]		(25)[b]	
	3518		(35)	117
$CH_3COCH_2CH_2CH_2OH$	3639	14	3.5	
	3608	14	3.5	31
11α-Hydroxy-25D-5β-spirostan-2-one	3534[12]			93
12β-Hydroxy-12α-methyl-5α-pregnane-3,20-dione	3463[13]			155
3β,14β-Dihydroxy-12β-benzoyloxypregn-5-en-20-one	3437[12]			181
3β-Acetoxy-14β,15α-dihydroxypregn-5-en-20-one	3434[12]			184
3β-Acetoxy-5α-hydroxy-9α-ergostan-11-one	3418[14]		(170)[b]	200

a) When the free ν_{O-H} is not observable, it is assumed to be 3636, 3627 and 3618 cm^{-1} for primary, secondary and tertiary alcohols, respectively.
b) ε

vicinal to 1, 4-difunctional derivatives, where it attains its maximum.[16] The difference between the two series may be due mainly to the different geometry around the proton accepting functions.



ii

Thus the carbonyl carbon atom is sp^2-hybridized and the α-carbon atom lies always on the same plane with the n-orbital of the oxygen atom. In 2-(hydroxymethyl)cyclohexanone and the derivatives, molecular models indicate even the hydroxylic oxygen atom is placed nearly on the very plane. The planar cyclic hydrogen bond is formed resulting in the ν_{O-H} shift of *ca.* 130 cm^{-1} which does not change materially over a whole range of examples.[8,9,11,17] Judging from the nearly equivalent $\Delta\nu_{O-H}$, the conformation of 1-hydroxy-2-propanone and other unfixed α-keto-alcohols may also be planar. Under the circumstances, the hydroxylic hydrogen atom participating in the hydrogen bond will be situated just on the extension line of the n-orbital of the carbonyl oxygen, as shown in

9) M. St. C. Flett, *Spectrochim. Acta*, **10**, 21 (1957).
10) Samples were provided through the courtesy of Dr. T. Suga by whom the conformation of the acetyl group is assigned as ii (T. Suga, Y. Shishibori and T. Matsuura, 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967. Abstract 3Y-020).
11) A. R. H. Cole and G. T. A. Müller, *J. Chem. Soc.*, **1959**, 1224.
12) T. Kubota, M. Takasuka and Y. Matsui, *Ann. Rep. Shionogi Research Lab.*, No. 16, 63 (1966).
13) Y. Matsui, M. Takasuka and T. Kubota, *ibid.*, No. 15, 125 (1965).
14) C. J. W. Brooks, G. Eglinton and L. Hanaineh, *Spectrochim. Acta*, **22**, 131 (1966).
15) J. Rigaudy and P. Courtot, *Compt. rend.*, **248**, 3016 (1959).
16) $\Delta\nu_{O-H}$'s of butane-1, 4-diol and 4-methoxybutan-1-ol are 156 and 184 cm^{-1}, respectively.
17) A number of examples are available for α-keto-alcohols in the following literatures and their ν_{O-H}'s fall always in the region of 3480—3500 cm^{-1}; R. N. Jones, P. Humphries, R. F. Herling and K. Dobriner, *J. Am. Chem. Soc.*, **74**, 2820 (1952); C. Duculot, *Compt. rend.*, **241**, 1738, 1925 (1955); J. Elks, G. H. Phillips, T. Walker and L. J. Wyman, *J. Chem. Soc.*, **1956**, 4330; G. DeStevens, *J. Org. Chem.*, **23**, 1752 (1958).

TABLE 2. ν_{O-H} DATA FOR KETO-ALCOHOLS
(O-H···π Hydrogen bond)

Compound	ν_{max} cm^{-1}	$\Delta\nu^{a}_{1/2}$ cm^{-1}	$A\times10^{-3}$ mol^{-1} l cm^{-2}	$\Delta\nu_{O-H}$[a] cm^{-1}
5α-Cholestan-5α-ol-4-one	3614	15	1.2	
	3603	17	4.4	11
5α-Cholestan-5α-ol-6-one	3614	13	1.1	
	3602	16	4.4	12
(−)-2-Hydroxyisopinocamphone	3586	18	5.4	32
α-Digiprogenin 3β-acetate	—[12]			
	3603			15
5α-Cholestan-5α-ol-3-one	3620	20	0.63	
	3606	12	3.5	14
5β-Cholestan-5β-ol-3-one	3620	18	0.40	
	3609	13	3.8	11
10β-Hydroxy-9β-methyl-3-decalone	3610[6]	19	(60)[b]	8
5α-Hydroxyergosta-7,22-dien-3-one	3608[6]	21	(55)[b]	10
	3594	25	(50)	24
Methyl hederagonate	3630[11]		very weak	
	3602		(40)	34
	3540		(20)	96
4-Hydroxycycloheptanone[15]	3624	10	3.3	
	3601	10	3.3	23

a), b) See footnotes of Table 1.

Fig. 4, effecting strong hydrogen bond formation.[18] In contrast with the α-keto-alcohols, the conformation about the ethylene glycol and 2-methoxyethanol has been shown not to be eclipsed but staggered and not only the distance between the bonding groups but also the angle are not most favorable for the intramolecular hydrogen bond.[19]

In β-keto-alcohols, the values of $\Delta\nu_{O-H}$ range from 30 to 120 cm^{-1}. The variety may be due to the difference in the conformation of the bonding species which has been considered to be unaltered in α-keto-alcohols. It may be argued that the bonding form of 4-hydroxy-2-butanone is planar because stabilization by hydrogen bond formation overwhelms the conformational energy. If it were the case, however, the distance between the hydroxylic hydrogen and the carbonyl oxygen would amount to 1.2 Å, and the stronger interaction which is reflected by greater shift to the lower frequency than those of α-keto-alcohols would have been observed. Therefore, in the bonding form of 2-(hydroxymethyl)cyclohexanone, the hydroxymethyl group is assumed to be equatorial with the hydroxyl group staggered between the axial hydrogen and the carbonyl carbon atoms. If the hydroxyl hydrogen is staggered between a methylene hydrogen and the ring carbon to which the hydroxymethyl group is attached, the distance between the hydroxyl hydrogen and the carbonyl oxygen atoms in this model becomes

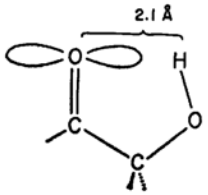


Fig. 4. Geometry of intramolecular hydrogen bond in α-keto-alcohols.

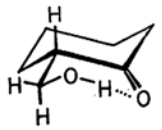


Fig. 5. Bonding conformation of 2-(hydroxymethyl)cyclohexanone.

18) When methanol and acetone are mixed in carbon tetrachloride to make a solution of 0.012 and 0.45 mol/l with respect to each component, a broad band due to the intermolecular hydrogen bond formation appears at 3534 cm^{-1}. Since there seems to be no geometrical restriction in the intermolecular association, the interacting groups are mutually so disposed that the greatest enthalpy of the interaction is attained. The fact that $\Delta\nu_{O-H}$ as a measure of the enthalpy of the interaction in α-keto-alcohols is greater even than those intermolecular bonding may suggest a factor which is advantageous to the intramolecular bonding. A possible electronic interaction through hyperconjugation of the intervening methylene group is excluded because α, α-disubstituted derivatives have similarly intensified hydrogen bond. It may be an explanation that the electrostatic field effect on the hydrogen bond is playing a great role, since the dipolar O–H and C=O groups are, as shown in Fig. 4, placed nearly anti-parallel with the result of some additional stabilization.

19) P. J. Krueger and H. D. Mettee, *J. Mol. Spectrys.*, **18**, 131 (1965); H. Matsuura and T. Miyazawa, This Bulletin, **40**, 85 (1967); P. Buckley and P. A. Giguere, *Can. J. Chem.*, **45**, 397 (1967).

nearly 2.1 Å coincident with those of α-keto-alcohols, but the angle made by the direction of the carbonyl n-orbital and the line connecting the hydroxyl hydrogen with the carbonyl oxygen atoms amounts to as high as 40° (see Fig. 5). It follows, therefore, that $\Delta\nu_{O-H}$ is reduced nearly to half of that in α-keto-alcohols.[20]

In an attempt to find correlation between the conformation and $\Delta\nu_{O-H}$ due to hydrogen bonding,

Table 3. The geometrical relation between hydroxyl and carbonyl groups in keto-alcohols as defined by Fig. 6

Compound	R, Å	θ
α-Keto-alcohols (1—3)	2.1	8
4-Hydroxy-2-butanones (4—6)	2.1	40
2-(Hydroxymethyl)cyclohexanone (7)	2.3	35
(+)-10-Nor-8-oxoneomenthol (8)	2.0	30[10]
(−)-10-Nor-8-oxomenthol (9)	2.3	55[10]
Methyl icterogenin (10)	1.9	25[21]
11α-Hydroxy-25D-5β-spirostan-2-one (11)	1.9	40
12β-Hydroxy-12α-methyl-5α-pregnane-3,20-dione (12)	1.8	20
3β,14β-Dihydroxy-12β-benzoyloxy-pregn-5-en-20-one (13)	1.6	20
3β-Acetoxy-14β,15α-dihydroxypregn-5-en-20-one (14)	1.6	20
3β-Acetoxy-5α-hydroxy-9α-ergostan-11-one (15)	1.4	35

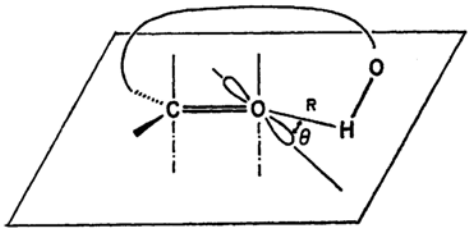


Fig. 6. Parameters representing the geometrical relation between hydroxyl and carbonyl groups.

the latter values have been plotted against $\cos\theta/R$, in which R and θ are defined as shown in Fig. 6, and estimated by examination of a Dreiding model (Table 3). The parameters were tentatively employed because it is easily expected that the enthalpy of the hydrogen bond increases as the distance between the interacting groups is shortened and the overlap between them becomes heavilier.

It is rather surprising that a smooth relationship has been obtained as shown in Fig. 7, when one considers that, to the hydrogen bond, several mechanisms such as electrostatic interaction, delocalization energy, repulsive force and dispersion force[22] are contributing which should be expressed in terms of a complex function of R and θ. It is beyond the purpose of the present authors to discuss the relative contribution of the above mechanisms from the relationship now obtained, but the atuhors would like to point out that $\Delta\nu_{O-H}$ due to the intramolecular hydrogen bond in keto-alcohols is dependent on the distance between the two groups and the direction of approach of the hydroxyl group to the head of the n-orbital on the carbonyl oxygen.[23] A few examples of γ-keto-alcohols and the higher homologs also conform to the same relationship and are included in Fig. 7.

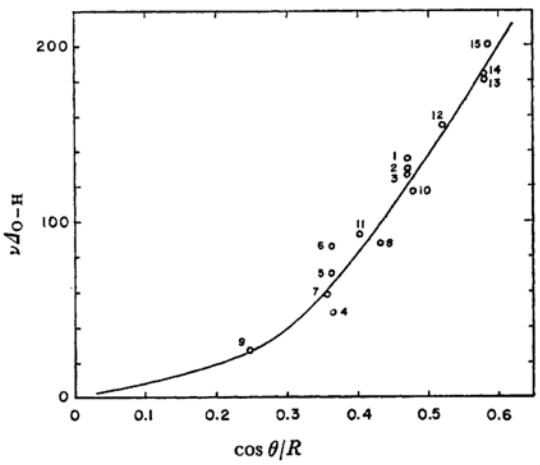


Fig. 7. Relation between the conformation and $\Delta\nu_{O-H}$ due to hydrogen bonding in keto-alcohols (numbers in Table 3).

O–H···π Interaction. In Table 2 are collected ν_{O-H} data of keto-alcohols in which R is not shorter than 3 Å, $\cos\theta/R$ parameter smaller than 0.9, and consequently the contribution to the hydrogen bond by n-electrons can be regarded geometrically

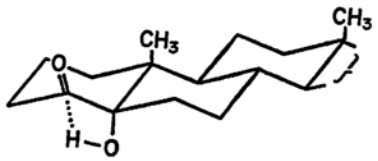
20) There seems to be a controversy as to the hybridization of the proton accepting n-orbital of the carbonyl group. W. G. Schneider (*J. Chem. Phys.*, **23**, 27 (1955)) regarded the hybridization of the carbonyl oxygen to be sp^2 in his electrostatic interpretation of the hydrogen bond, while a self-consistent field calculation of formaldehyde (P. L. Goodfriend, F. W. Birss and A. B. F. Duncan, *Rev. Mod. Phys.*, **32**, 307 (1960)) shows a clearly defined 2p-lone pair on the oxygen atom. Since trigonal sp^2 lone pair would have been more favorable geometrically for the hydrogen bond formation in β-keto-alcohols than for α-homologs, the above observations may provide another support for the 2p-character of the oxygen lone pair.

21) Contrary to the original authors,[11] the ring A of methyl icterogenin and methyl hederagonate was assumed to be a boat which has frequently been encountered in the lanostan-3-one derivatives (E. L. Eliel, N. L. Allinger, S. J. Angyal and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York (1965), p. 469).

22) C. A. Coulson, "Hydrogen Bonding," ed. by D. Hadzi and W. H. Thompson, Pergamon Press, London (1959), p. 339.

23) Kubota and co-workers[12] found an empirical relation, $\Delta\nu_{O-H}=-143R+412$ (cm^{-1}).

forbidden. According to the relationship found in Fig. 7, any low-frequency band may not be expected ($\Delta\nu_{O-H}<10\ cm^{-1}$). In these examples, however, the apparent ν_{O-H} maxima are always shifted to the lower frequency and a shoulder band is usually observed at the higher frequency side which is located at the normal position of the free ν_{O-H} (Figs. 2 and 3). Instead of the *n*-electrons, π-electrons on the carbonyl group are now situated favorably for accepting the hydroxyl hydrogen as depicted in Fig. 8, and it is postulated that the lower frequency bands are assigned to the ν_{O-H} due to the O–H···π interaction. The ν_{O-H} shifts range from 8 to 34 cm^{-1} and are roughly in accord with the degree of overlap between the orbitals of the hydroxyl group and π-electrons as estimated by the Dreiding model.[21,24] $\Delta\nu_{O-H}$ of 11, 14 and 34cm^{-1} in 5α-cholestan-5α-ol-4-one (I), 5α-cholestan-5α-ol-3-one (II) and methyl hederagonate (III), respectively, may be compared with those of structurally analogous 5-*trans*-*t*-butyl-2-methylenecyclohexanol ($\Delta\nu_{O-H}=9\ cm^{-1}$), epicholesterol (34 cm^{-1}) and 3β-acetoxychlolest-5-en-19-ol (52 cm^{-1}).[1] In these latter examples, the ethylenic π-electrons are playing the role of the proton acceptor. Near parallelism in the order of $\Delta\nu_{O-H}$'s between the keto-alcohols and the olefinic alcohols can be noted and, when structurally related alcohols in which only the C=O group is replaced by C=C are compared, $\Delta\nu_{O-H}$ in the former series is about half of the latter series. The trend is interpretable in terms of the reduced basicity of the carbonyl π-electrons compared to that of the ethylenic π-electrons as indicated by the higher ionization potential of the former.[3,4,25] Best illustration of the competition between the basicity of the carbonyl group and the ethylenic linkage is afforded by 5α-hydroxyergosta-7, 22-dien-3-one (V),[6] in which, under the nearly equivalent geometrical environment, $\Delta\nu_{O-H}$ is 10 and 24cm^{-1}, respectively. α-Axial keto-alcohols,[26] 5α-cholestan-5α-ol-4-one, -6-one and α-digiprogenin 3β-acetate, are rather exceptional in that $\Delta\nu_{O-H}$'s are even larger than those of the corresponding α-axial olefinic alcohols. This may be due to the strengthened interaction as a result of the enhanced acidity of the hydroxyl group which is located α



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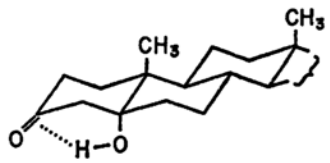

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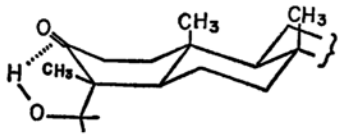
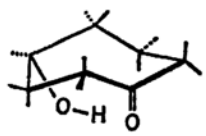
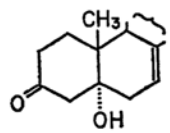


III



IV



V

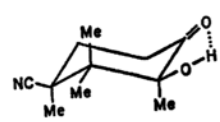
Table 4. $\nu_{C=O}$ data for keto-alcohols

Compound	ν_{max}	ε
CH_3COCH_2OH	1727	(406)
2-Hydroxycyclohexanone	1718	(—)
5β-Cholestan-5β-ol-4-one	1703	(650)
5β-Cholestan-5β-ol-6-one	1704	(598)
$CH_3COCH_2CH_2OH$	1716	(303)
$CH_3COCH_2CMe_2OH$	1712[30]	
2-(Hydroxymethyl)cyclohexanone	1705	(442)
$CH_3COCH_2CH_2CH_2OH$	1720	(293)
5α-Cholestan-5α-ol-4-one	1718	(597)
5α-Cholestan-5α-ol-6-one	1718	(528)
(−)-2-Hydroxyisopinocamphone	1721	(505)
5α-Cholestan-5α-ol-3-one	1721	(448)
5β-Cholestan-5β-ol-3-one	1720	(430)
5α-Hydroxyergosta-7,22-dien-3-one	1722	(430)[6]

24) The similarity of the ν_{O-H} absorption spectra between 5α-cholestan-5α-ol-4-one (I) and 5α-cholestan-5α-ol-6-one, and 5α-cholestan-5α-ol-3-one and 5β-cholestan-5β-ol-3-one provides a support for the normal chair conformation of the ring-A cyclohexanone in I and 5β-3-keto-steroid (N. L. Allinger and C. L. Neumann, *Tetrahedron*, **23**, 1279 (1967)). The 3540 cm^{-1} absorption of methyl hederagonate (III) may be due to the O–H···O bonding in a ring-A chair conformation which is in equilibrium with the boat form.[21] The conformation of 4-hydroxycycloheptanone was regarded to be chair (IV) (N. L. Allinger, *J. Am. Chem. Soc.*, **81**, 5727 (1959)). For 2-hydroxyisopinocamphone see, R. L. Erskine and S. A. Knight, *Chem. & Ind.*, **1960**, 1160.

25) Polarization of the carbonyl π-electrons in the sense $C\overset{\delta+}{=}O\overset{\delta-}{}$ will also be contributing, because in the pertinent examples the hydroxyl group is interacting with the π-electrons on the carbon atom rather than that on the oxygen atom geometrically.

26) Recently an intramolecular O–H···O bonding has been reported for iii, but no interaction is noticed in the OH-epimer (A. G. Yurchenko, *Zh. Organokhim.*, **2**, 1604 (1966); *Chem. Abstr.*, **66**, 64933b (1967)).



iii

to the electron-attracting carbonyl function. A support for this inductive effect may be obtained by the relatively low free ν_{O-H}'s at 3614 cm^{-1} of these α-keto-alcohols which should otherwise be expected to occur at 3618—3620 cm^{-1}.

Experimental

All the samples were of analytical purity and the physical constants agreed well with those in the literature.[27]

Spectral measurement was carried out as described in the previous papers.[1,28] Special care was taken to employ a little more dilute solution ($c \leq 10^{-3}$ mol/l) in carbon tetrachloride than usual, because it has often been mentioned[6,29] that in keto-alcohols the association through intermolecular hydrogen bond survives rather tenaciously even in *ca.* 5×10^{-3} mol/l solution.

The C=O stretching bands were measured in a sodium chloride cell of 0.55 cm optical length, and the data are summarized in Table 4. As has been pointed out,[30] the effect of the hydroxyl group in shifting the $\nu_{C=O}$ is not clear especially in the O–H$\cdots\pi$ interaction.

27) 2-Hydroxycyclohexanone is notorious for its spontaneous formation of a dimer with the hemiacetal structure (J. C. Sheehan, R. C. O'Neill and M. A. White, *J. Am. Chem. Soc.*, **72**, 3376 (1950)), and so the freshly distilled (bp, 87°C/18 mmHg) sample was used within five minutes after distillation.

28) M. Ōki and H. Iwamura, This Bulletin, **32**, 567 (1959).

29) H. M. Fales and W. C. Wildman, *J. Am. Chem. Soc.*, **85**, 784 (1963).

30) H. Minato, This Bulletin, **36**, 1020 (1963).