Integrated Intensities of Hydroxy Stretching Vibration Bands in Some Bicyclic Systems containing a Hydroxy Group β to *o*-Benzeno, Etheno, Epoxy, or Epithio Functions

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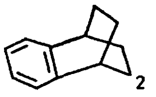
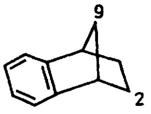
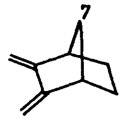
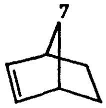
For the title class of compounds, OH stretching vibration bands, ν_{OH}, and integrated intensities, A_{OH}, were measured for dilute carbon tetrachloride solutions. When A_{OH} values were compared for f-structures which are incapable of intramolecular hydrogen bonding and b-structures in which intramolecular bonding takes place, the result was remarkable in that the A_{OH} values of free ν_{OH} bands in f-structures were greater than those for the hydrogen-bonded ν_{OH} bands in the b-structures. The C=O and C–O stretching vibration bands, $\nu_{C=O}$ and ν_{C-O}, for the corresponding acetates were also measured. The $\nu_{C=O}$ bands for the f-structures shifted to higher wavenumbers than those for b-structures, but the ν_{C-O} bands are shifted to lower wavenumbers. These results were ascribed to the through-space interaction between π- or n-electrons and the sp^3-hybridized carbon atom bearing hydroxy and acetoxy groups which affects on polarization of these groups.

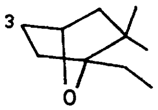
THE formation of a hydrogen bond by a hydroxy group causes a shift of the stretching vibration band, ν_{OH}, to lower wavenumber and increases the integrated intensity, A, providing much information on the bond character and electronic structure.[1-3] For intramolecular hydrogen bonds (OH · · · X system where X represents n-,[4-8] π-,[5,9,10] or σ-electrons[11]), the shift value, $\Delta\nu_{OH}$, varies with the spatial requirement of the hydroxy group and the proton acceptor, X. An increase in $\Delta\nu_{OH}$ generally enhances A_{OH} for intra-[6,12] and inter-molecular hydrogen bonds[13-16] in the OH · · · n system. This trend was also found for intermolecular hydrogen bonds in the OH · · · π-electron system,[17,18] though no information is available on intramolecular hydrogen bonds in this system. We studied hydroxy stretching bands in a given class of bicyclic compounds, as shown below, which contain a hydroxy group β to the *o*-benzeno, etheno, epoxy, or epithio function. These compounds have two epimers, one of which has a conformation incapable of forming an intramolecular hydrogen bond (f-structure) and the other which can (b-structure). We found that the integrated intensities, A_{OH}, of free ν_{OH} bands in f-structures are greater than those of the hydrogen-bonded ν_{OH} bands in b-structures. This observation is obviously at variance with the general situation mentioned above. In the acetates of the present compounds, while the stretching vibration bands, $\nu_{C=O}$, of the carbonyl groups in the f-structures are shifted to higher wavenumbers than those in the b-structures, the stretching vibration bands of the C–O groups, ν_{C-O}, are shifted to lower wavenumbers.

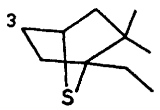












The mechanism of solvolysis of compounds (4)—(8) has attracted our interest for some years.[19,20] The great difference in solvolysis rates between the *anti*- and *syn*-epimers (or the *exo*- and *endo*-epimers) has been reasonably attributed to stabilization of the cationic transition state due to the participation of neighbouring π- or n-electrons. A recent view of Hoffmann[21] on through-space and through-bond interactions based on molecular orbital theory was applied to explain u.v.,[22] n.m.r.,[23-26] and photoelectron spectral results[27,28,†] obtained for related compounds. As an important factor in the i.r. observations, we suggest that through-space interaction between the π- or n-electrons and the sp^3-hybridized carbon atom bearing the hydroxy and acetoxy groups takes place.

EXPERIMENTAL

I.r. spectra were recorded on a JASCO DS-402G grating spectrometer calibrated in the usual manner. Compounds (4)—(9) and (14) were prepared as reported.[20] Compounds (10) and (11) were supplied by Sawa *et al.*[32] and (12), (13), (15), and (16) by Komeno *et al.*[33] Compounds(1)—(3) are known substances.[34,35] The solvent carbon tetrachloride was purified by distillation and stored over P_2O_5. Alcohols (1)—(13) were dissolved in carbon tetrachloride at a concentration (c) below 0.006M (cell length l = 2 or 5 cm) to exclude self-association of the hydroxy groups. The integrated intensity (A) was calculated by Ramsay's method,[36] defined as $A = (\pi/2)\cdot[\ln (I_0/I)/c\cdot l]\cdot\Delta\nu_{1/2}$ (mol^{-1} dm^3 cm^{-2}), where $\ln (I_0/I)/c\cdot l$ is the absorption coefficient (mol^{-1} dm^3 cm^{-1}) at the band maximum and $\Delta\nu_{1/2}$ is the band width (cm^{-1}) at half intensity. The accuracy of ν_{OH} and A_{OH} in the alcohols was within ±2 cm^{-1} and ±3%,[‡] respectively. The acetates (14)—(16) were also dissolved

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[†] From the photoelectron spectra,[28-31] it has been suggested that the vertical ionization energy of the π-system in norbornene and benzonorbornene is stabilized when a hydroxy or methoxy group is introduced into the *anti*-position.

[‡] Since the value of the integrated intensity is slightly dependent on the i.r. spectrometer used, the comparison of data from different sources is less reliable. However, the difference in magnitude between the integrated intensities observed with an identical spectrometer can be determined accurately.

at a concentration below 0.01M (l = 0.1 cm). The accuracy of $\nu_{C=O}$ and ν_{C-O} in the acetates was within ± 1 cm^{-1}. All measurements were carried out at room temperature (27 °C).

RESULTS AND DISCUSSION

(a) *Integrated Intensity*, A_{OH}, *of the* OH *Stretching Band*, ν_{OH}.

—The values of ν_{OH} and A_{OH} observed for alcohols (1)—(13) are shown in Table 1 and Figures 1—3. These alcohols, except (1)—(3) and (11), are bicyclic compounds containing a hydroxy group β to a functional group such as *o*-benzeno, etheno, epoxy, or epithio. Compounds (1)—(3) do not have any functional groups and compound (11) has a hydroxy group γ to the methoxyphenyl function. Normal A_{OH} values ($\times 10^{-4}$ mol^{-1} dm^3 cm^{-2}) of free ν_{OH} for saturated alcohols, R-OH, have been reported by us and others to be in the range 0.32—0.54 (average value 0.45).[6,15,37] In the present case, the A_{OH} values of (1)—(3) and (11f) [equatorial epimer of (11)] are in the same range. However, for alcohols (4)—(8) involving a π-electron function such as *o*-benzeno or etheno, the A_{OH} values for the free ν_{OH} in the f-structures (*exo*- and *anti*-epimers) are in the range 0.55—0.66; they are greater than A_{OH} for free ν_{OH} for the above described saturated alcohols and compounds (1)—(3) and (11f) and also greater than A_{OH} for hydrogen-bonded ν_{OH} for the corresponding b-structures (*endo*- and *syn*-epimers), though the hydrogen-bonded ν_{OH} as usual shifts to lower wavenumbers (Figure 1 and Table 1). Since A_{OH} generally increases with hydrogen bond formation as a result of increasing frequency shifts ($\Delta\nu_{OH}$),[6,12—16] the last finding seems unusual. However, no literature is available for the relation between A_{OH} and $\Delta\nu_{OH}$ for intramolecular hydrogen bonds in OH • • • π-electron systems. This lack of information is probably due to the fact that accurate estimation of A_{OH} is difficult, particularly for the case of weak intramolecular hydrogen bonds which are ordinarily observed in the majority of OH • • • π-electron systems. In these systems, the presence of both free and hydrogen-bonded ν_{OH} allows estimation of A_{OH} only by extrapolation to 100% formation of the hydrogen bond. However, an example of the A_{OH} increase with formation of an intramolecular hydrogen bond in a OH • • • π-electron system was obtained here with compound (11) which has a hydroxy group γ to the methoxyphenyl π system. The A_{OH} value, 1.01, for the hydrogen-bonded ν_{OH} of the axial epimer (11b) is *ca.* 2.5 times greater than that, 0.44, of free ν_{OH} for the

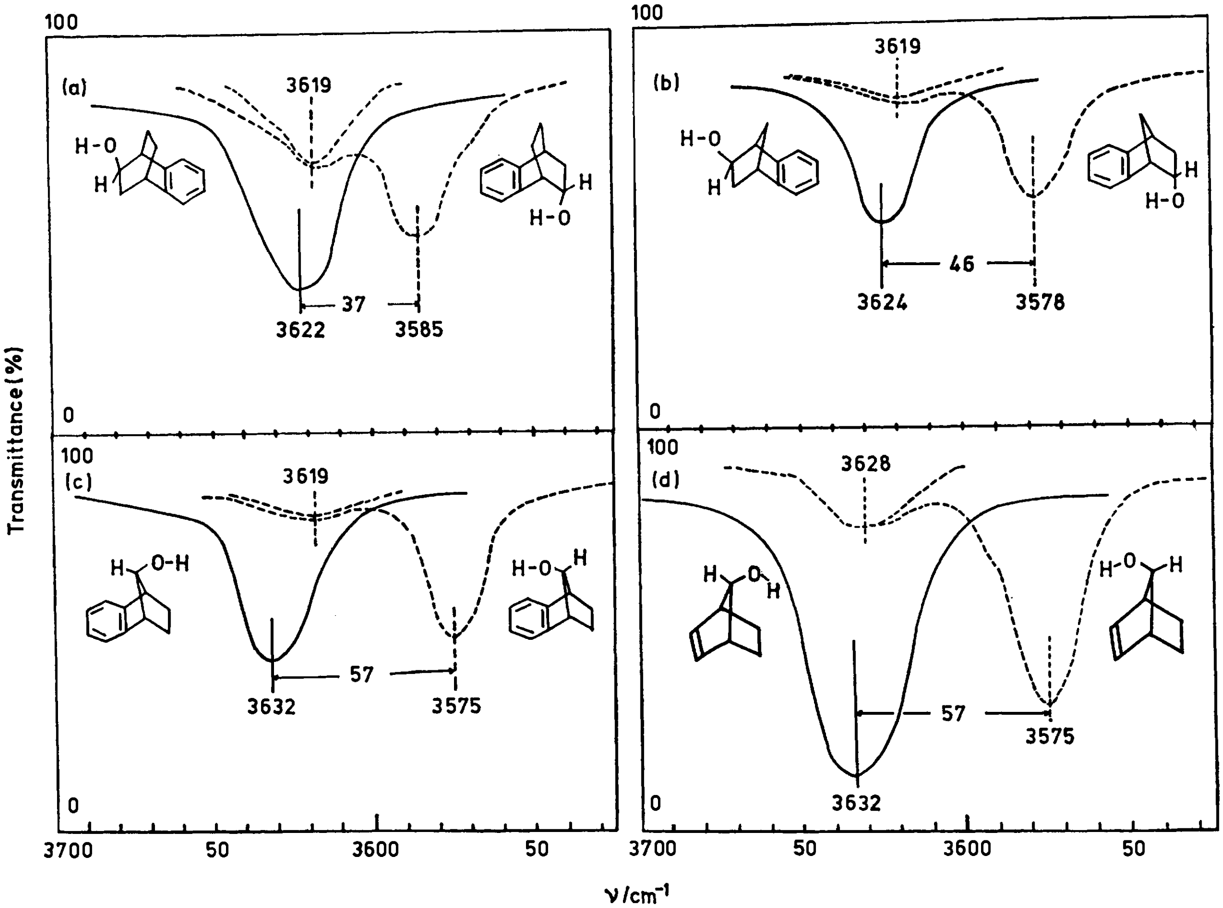


FIGURE 1 I.r. spectra of (a) *exo*- and *endo*-benzobicyclo[2.2.2]octen-2-ol (4f) (3.181 × 10^{-3}M) and (4b) (3.157 × 10^{-3}M); (b) *exo*- and *endo*-benzonorbornen-2-ol (5f) (1.446 × 10^{-3}M) and (5b) (1.454 × 10^{-3}M); (c) *anti*- and *syn*-benzonorbornen-9-ol (7f) (2.033 × 10^{-3}M) and (7b) (2.042 × 10^{-3}M); and (d) *anti*- and *syn*-norbornen-7-ol (8f) (5.711 × 10^{-3}M) and (8b) (5.728 × 10^{-3}M). In CCl_4; 20 mm cells

equatorial epimer (11f) (Figure 2 and Table 1). In contrast, A_{OH} for (11f) in the absence of hydrogen bond formation is of almost the same order as A_{OH} for the free ν_{OH} of the saturated alcohols. It should be pointed out, however, that even in this morphinane system, the result for the γ-hydroxy-substituted compound (11b) is different from that for the β-hydroxy derivative (10b). The hydrogen-bonded ν_{OH} of (10b) shows a shift lower than that for (11b) and its A_{OH} value, 0.48, is about half that, 1.01, for (11b). This fact may indicate that the spatial circumstances of the β-hydroxy group and the methoxyphenyl moiety in the 15α-ol are similar to those of the OH $\cdots$ π system in the b-structures (4b)—(8b). The hydrogen-bonded ν_{OH} of (9b) shifts to lower wavenumber, but its A_{OH} is small.

TABLE 1

I.r. spectral data of OH stretching bands

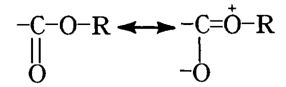
Compound	Alcohol	ν_{OH}/cm^{-1}	$\Delta\nu_{OH}$ [a]/cm^{-1}	ε/mol^{-1} dm^3 cm^{-1}	$\Delta\nu_{1/2}$/cm^{-1}	$10^{-4}A_{OH}$ [b]/mol^{-1} dm^3 cm^{-2}
(1)	*exo*-Norbornan-2-ol	3 623		56.7	18.0	0.37
(2)	*endo*-Norbornan-2-ol	3 625		48.9	26.4	0.47
(3)	Norbornan-7-ol	3 630		62.0	23.5	0.53
π-Electron						
(4f)	*exo*-Benzobicyclo[2.2.2]octen-2-ol	3 622		57.1	26.9	0.55
(4b)	*endo*-Benzobicyclo[2.2.2]octen-2-ol	3 619		17.1	21.4	0.13
		3 585	37	40.4	19.0	0.28
						(0.40)
(5f)	*exo*-Benzonorbornen-2-ol	3 624		77.9	20.1	0.57
(5b)	*endo*-Benzonorbornen-2-ol	3 619		10.3	22.8	0.08
		3 578	46	65.0	19.4	0.46
						(0.53)
(6f)	*anti*-2,3-Dimethylenenorbornan-7-ol	3 630		107.5	16.7	0.65
(6b)	*syn*-2,3-Dimethylenenorbornan-7-ol	3 627		22.4	23.5	0.19
		3 582	48	40.1	18.2	0.26
						(0.37)
(7f)	*anti*-Benzonorbornen-9-ol	3 632		73.1	23.8	0.63
(7b)	*syn*-Benzonorbornen-9-ol	3 619		8.2	20.4	0.06
		3 575	57	60.0	18.7	0.41
						(0.46)
(8f)	*anti*-Norbornen-7-ol	3 632		69.3	26.5	0.66
(8b)	*syn*-Norbornen-7-ol	3 628		6.5	30.6	0.07
		3 575	57	40.0	21.8	0.32
						(0.35)
(9b)	Dibenzonorbornadien-11-ol	3 562		61.4	19.0	0.44
(10b)	3-Methoxy-*N*-methylmorphinan-15α-ol	3 632		5.0	20.4	0.04
		3 573		63.8	18.9	0.44
						(0.48)
(11f)	3-Methoxy-*N*-methylmorphinan-6β-ol	3 623		56.2	16.7	0.34
						(0.44)
		3 608		14.7	18.0	0.10
(11b)	3-Methoxy-*N*-methylmorphinan-6α-ol	3 589	34	105.5	26.5	1.01
Epoxy						
(12f)	2α,5-Epoxy-5α-cholestan-3β-ol	3 635		79.7	21.8	0.63
						(0.70)
		3 617		19.2	10.5	0.07
(12b)	2α,5-Epoxy-5α-cholestan-3α-ol	3 621		9.2	22.1	0.07
		3 589	46	55.9	21.7	0.43
						(0.49)
Epithio						
(13f)	2α,5-Epithio-5α-cholestan-3β-ol	3 624		75.9	27.1	0.74
(13b)	2α,5-Epithio-5α-cholestan-3α-ol	3 618		9.6	30.6	0.11
		3 551	73	22.3	40.0	0.32
						(0.41)

[a] $\Delta\nu_{OH}$ = Free ν_{OH} (f-structure) − H-bonded ν_{OH} (b-structure). [b] A_{OH} Values given in parentheses were estimated by extrapolation to 100% formation of the hydrogen bond.

Data obtained for (12) and (13) which contain *n*-electrons in the epoxy and epithio groups are similar to the above (Table 1, Figure 3). The A_{OH} of free ν_{OH} of the f-structures are 0.70 for (12) and 0.74 for (13); they are *ca.* 1.6 times greater than those for the saturated alcohols. Further, the A_{OH} values of hydrogen-bonded ν_{OH} of the b-structures are smaller than those of the corresponding f-structures.

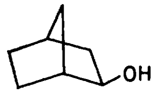
In order to explain the large A_{OH} of the free ν_{OH} and small A_{OH} of the hydrogen-bonded ν_{OH} observed for compounds (4)—(8), (12), and (13), we suggest an important contribution by the interaction between the π- or *n*-electrons and the sp^3 carbon atom bearing the hydroxy groups.

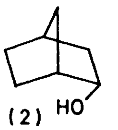
(b) *Carbonyl and* C–O *Stretching Bands in Acetates.*—The i.r. spectra of acetate (14), with a π-system, and (15) and (16), with *n*-systems, are presented in Figure 4. The spectral data are in Table 2. In all compounds, the $\nu_{C=O}$ values of the f-structures shift to higher wavenumbers than those of the b-structures and, in contrast, the ν_{C-O} values to lower wavenumbers. The shifts to higher wavenumbers, except in the case of (16), are accompanied by a decrease in the integrated intensities for $\nu_{C=O}$ and the shifts to lower wavenumbers by an increase in those for ν_{C-O}. The general class of saturated acetates, R–OAc, is known to have $\nu_{C=O}$ at *ca.* 1 735 cm^{-1} in carbon tetrachloride and ν_{C-O} at *ca.* 1 240 cm [38-40] and the wavenumber of $\nu_{C=O}$ is affected by resonance in the acetoxy group.* Compounds (14f)—(16f) have higher $\nu_{C=O}$ and lower ν_{C-O} values than those of the saturated acetates. Also, *exo*-2-acetoxybenzobicyclo[2.1.1]hexene shows a high $\nu_{C=O}$ at 1 745 and a low ν_{C-O} at 1 231 cm^{-1}.[41] The $\nu_{C=O}$ of phenyl acetate at 1 768 cm^{-1} and ν_{C-O} at 1 212 and 1 196 cm^{-1} are in the same category. The shifts of $\nu_{C=O}$ to high values and those of ν_{C-O} to low values were intensively studied by Jones and Sandrofy [38] using steroid acetates. The most important factor for these shifts is considered to be resonance, as in equation (1),[38,40,42] which would be suppressed, if R is replaced by an αβ-unsaturated group,



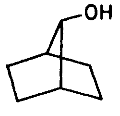
$$-\underset{\underset{\displaystyle O}{\|}}{C}-O-R \longleftrightarrow -\underset{\underset{\displaystyle -O}{|}}{C}=\overset{+}{O}-R \qquad (1)$$

due to the contribution of resonance as in equation (2). The resonance in equation (2) increases the double-bond character of C=O and decreases that of C–O.[38-40]


(1)

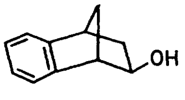


(2)

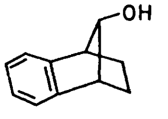


(3)

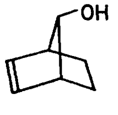
$10^{-4}A_{OH}$ 0·37 0·47 0·53



(5f)

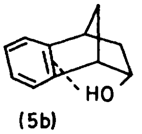


(7f)

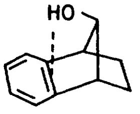


(8f)

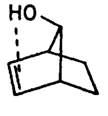
$10^{-4}A_{OH}$ 0·57 0·63 0·66



(5b)

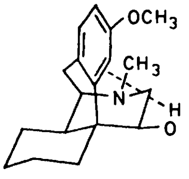


(7b)

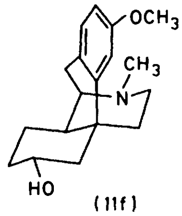


(8b)

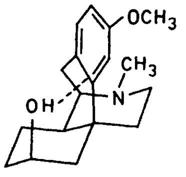
$10^{-4}A_{OH}$ 0.53 0.46 0.35



(10b)



(11f)



(11b)

$10^{-4}A_{OH}$ 0.48 0.44 1.01

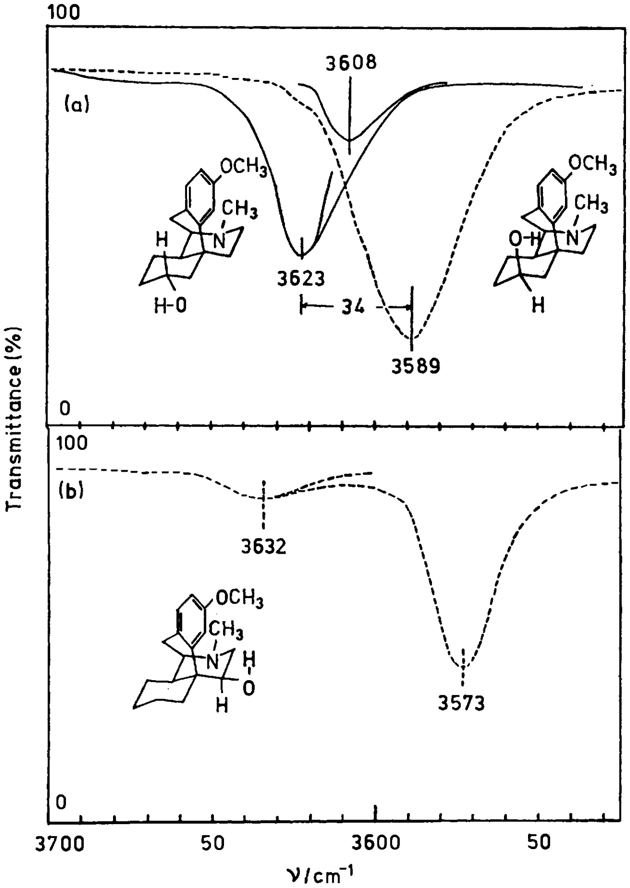


FIGURE 2 I.r. spectra of (a) 6β- and 6α-hydroxy-3-methoxy-*N*-methylmorphinane (11f) (1.085×10^{-3}M) and (11b) (1.113×10^{-3}M) and (b) 3-methoxy-*N*-methylmorphinan-15α-ol (10b) (1.075×10^{-3}M). In CCl_4; 50 mm cells

TABLE 2

I.r. spectral data of C=O and C–O stretching bands

Compound	Acetate	$\nu_{C=O}$/cm^{-1}	$10^{-4}A$/mol^{-1} dm^3 cm^{-2}	ν_{O-O-C}/cm^{-1}	$10^{-4}A$/mol^{-1} dm^3 cm^{-2}
(14f)	*anti*-7-Acetoxynorbornene	1 742	2.29	1 238	3.37
(14b)	*syn*-7-Acetoxynorbornene	1 739	2.51	1 247	3.33
(15f)	3β-Acetoxy-2α,5-epoxy-5α-cholestane	1 749	0.73	1 222	0.56
		1 741	1.67	1 241	3.90
(15b)	3α-Acetoxy-2α,5-epoxy-5α-cholestane	1 737	2.52	1 242	2.48
				1 254	0.72
(16f)	3β-Acetoxy-2α,5-epithio-5α-cholestane	1 747	1.75	1 238	3.53
		1 732	0.81		
(16b)	3α-Acetoxy-2α,5-epithio-5α-cholestane	1 738	2.49	1 242	2.96

Compounds (14b)—(16b) show $\nu_{C=O}$ at slightly higher wavenumbers and ν_{C-O} at significantly higher wavenumbers compared with the corresponding values for the general class of saturated acetates.

As suggested above, the interaction between π- or

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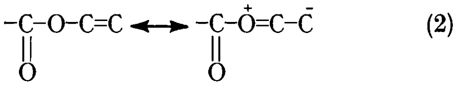
* Because the C–O stretching mode is usually strongly coupled with other vibration modes, its character is less reliable than that of the C=O stretching mode.

n-electrons and the sp^3 carbon atom bearing the acetoxy group is considered to be an important factor for the spectral features of the f-structures. The results from the b-structures can be explained by electron–electron repulsion which exists between the π- or *n*-electrons and the lone pair electrons of the ester oxygen atom.



$$-\underset{\underset{O}{\|}}{C}-O-C=C \longleftrightarrow -\underset{\underset{O}{\|}}{C}-\overset{+}{O}=C-\overset{-}{C} \qquad (2)$$

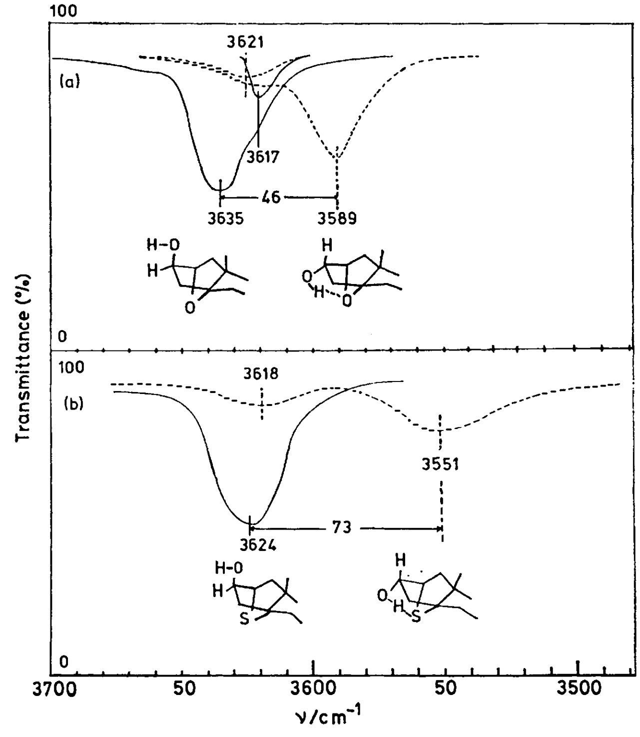
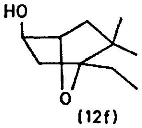
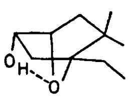
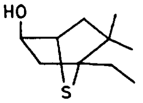


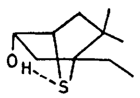
FIGURE 3 I.r. spectra of (a) 3β- and 3α-hydroxy-2α,5-epoxy-5α-cholestane (12f) (1.656×10^{-3}M) and (12b) (1.636×10^{-3}M) and (b) 3β- and 3α-hydroxy-2α,5-epithio-5α-cholestane (13f) (1.911×10^{-3}M) and (13b) (1.820×10^{-3}M). In CCl_4; 20 mm cells

(c) *Correlation between* A_{OH} *and* $\nu_{C=O}$ *for f-Structures.*—The integrated intensity is proportional to the quantity $(\delta\mu/\delta Q)$,[2] where μ is the molecular dipole moment and Q is the normal co-ordinate.[3] A free ν_{OH} band virtually corresponds to the OH stretching mode.[12] Enhancement









	(12f)	(12b)	(13f)	(13b)
$10^{-4}A_{OH}$	0.70	0.49	0.74	0.41

of A_{OH} of the free ν_{OH} indicates in an approximate sense polarization in an OH band. For example, because of resonance between the benzene ring and one of the lone pair electrons of the oxygen atom in the hydroxy group, A_{OH} of free ν_{OH} (3 612 cm^{-1}) of phenol is 1.15 which is 2.6 times greater than A_{OH} for the saturated alcohols. The $\nu_{C=O}$ at 1 768 cm^{-1} of phenyl acetate shifts to a wavenumber 33 cm^{-1} higher than that of the saturated acetate; this is considered to be due to resonance as mentioned in the last paragraph. A linear correlation, shown in Figure 5, is obtained by plotting A_{OH} of the free ν_{OH} for the saturated alcohols, (8f), (12f), and (13f) and phenol against $\nu_{C=O}$ for the saturated acetates (14f)—(16f) and phenyl acetate. The circle for the

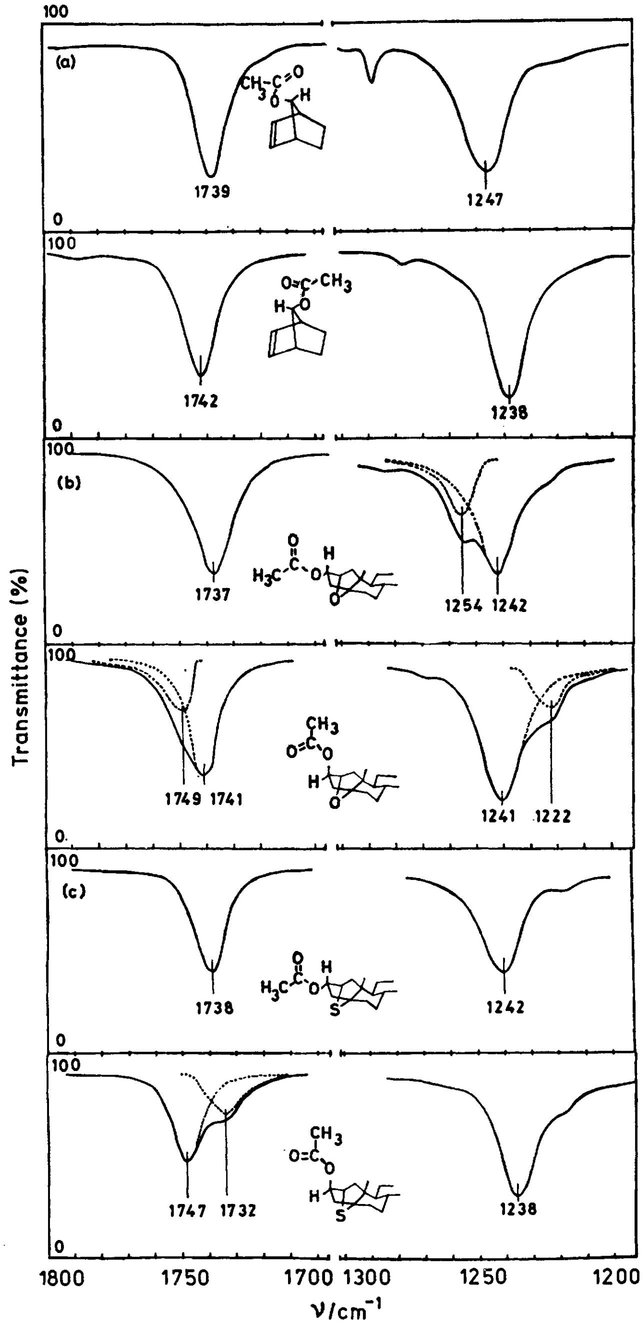


FIGURE 4 I.r. spectra of (a) *anti*- and *syn*-7-acetoxynorbornene (14f) (8.430×10^{-3}M) and (14b) (8.723×10^{-3}M); (b) 3β- and 3α-acetoxy-2α,5-epoxy-5α-cholestane, (15f) (8.177×10^{-3}M) and (15b) (8.698×10^{-3}M); (c) 3β- and 3α-acetoxy-2α,5-epithio-5α-cholestane (16f) (6.161×10^{-3}M) and (16b) (6.255×10^{-3}M). In CCl_4; 1 mm cells

saturated alcohols and acetates and that for phenol and phenyl acetate are located at both terminals of the line, and the circles for (8f) and (14f), (12f) and (15f), and (13f) and (16f) are located in between with increasing A_{OH} values in the order epithio > epoxy ≃ etheno. Note that this order does not agree with the electronegativity order.

In summary, the present study provides the following significant results. (a) the A_{OH} values of free ν_{OH} bands in f-structures are greater than those in saturated alcohols and also the A_{OH} values of hydrogen-bonded ν_{OH} bands in b-structures. (b) Wavenumbers of $\nu_{C=O}$ of acetates with f-structures are high. (c) A linear correlation exists between A_{OH} of alcohols and $\nu_{C=O}$ of acetates. We rationalize all these results by assuming an interaction between the π- or n-electrons and the sp^3-hybridized carbon atom bearing the functional groups. The inconsistency of the observed order of the effectiveness of the electrons (Figure 5) with that of the electronegativity and the structural features of the molecules suggest that the through-space interaction is more important than through-bond interaction. This through-space interaction causes a decrease in the dipole moment induced in OH · · · π or OH · · · n intramolecular hydrogen bonds.† With the decrease, the A_{OH} values of the hydrogen-bonded ν_{OH} in b-structures do not increase.

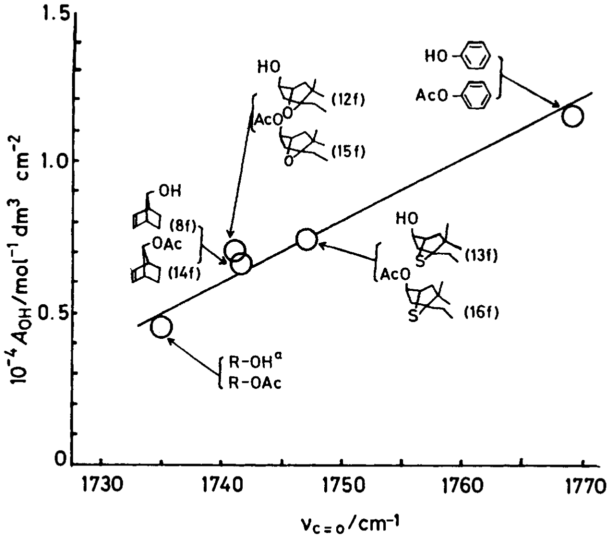


FIGURE 5 Correlation between A_{OH} of free ν_{OH} for alcohols and $\nu_{C=O}$ for acetates. ^{a} See text

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† Similarly, salicylaldehyde has a small A_{OH} despite the very strong intramolecular hydrogen bonding. This is explained by large delocalization of the OH bond electrons through the hydrogen bond system.[12]

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