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DOUBLET CHARACTER OF O-H ABSORPTION IN SATURATED ALCOHOLS*

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CONSIDERABLE attention has been directed recently to the doublet character of the O-H stretching absorption of monomeric unsaturated alcohols.[1] The two absorption bands can be ascribed to different species containing free and π-hydrogen bonded hydroxyl groups, respectively. It seems to be not as well recognized, however, that doublet O-H absorption can be displayed by saturated alcohols as well.[2] For example, this was observed in the second overtone region for several primary alcohols by Badger,[2a] and by Tuomikoski and Toivonen[2b] for ethanol, borneol and the epimeric fenchols.

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[*] Research sponsored by the Office of Ordnance Research, U.S. Army.

[**] National Science Foundation Predoctoral Fellow, 1958-1959.

[1a] I. M. Goldman and R. O. Crisler, J. Org. Chem. **23**, 751 (1958);

[b] P. Schleyer, D. S. Trifan and R. Bacskai, J. Amer. Chem. Soc. **80**, 6691 (1958) and references cited therein; D. S. Trifan, R. Bacskai, P. Schleyer and C. Wintner, Abstracts 135th Meeting of American Chemical Society, p. 98-O. April 5-10, 1959, Boston, Mass.

[2a] R. M. Badger and S. H. Bauer, J. Chem. Phys. **4**, 711 (1936);

[b] P. Tuomikoski, Suomen Kemistilehti **23B**, 44 (1950) and references cited therein; P. Tuomikoski, E. Pulkkinen, P. Hirsjärvi and N. J. Toivonen, Ibid. **23B**, 53 (1950).

In the present work, some seventy saturated alcohols were investigated conveniently in dilute solution in carbon tetrachloride, using 10 cm matched quartz cells on the Cary Model 14 spectrophotometer in the first overtone 1.4μ region, where the separation between component bands is relatively large and bands associated with strong intermolecular hydrogen bonds are absent.

Most of the compounds exhibited hydroxyl absorption of the general type illustrated in Fig. 1, the component bands being separated graphically and the relative intensities of absorption (relative areas, $\underline{B}_1/\underline{B}_2$) approximated without correction for the band wings. Some examples are summarized in Table 1. In representative cases, e.g., 2-propanol, 3-pentanol and 3-phenylpropanol-1, it was demonstrated that the relative band intensities were independent of concentration from that commonly employed, 0.01-0.02 M, down to 0.001 M. Deuterated 2-propanol-d exhibited an absorption doublet similar to that of 2-propanol in the corresponding 1.9μ region. With ethanol, 2-butanol, 2-pentanol, 3-pentanol and t-butyl alcohol, it was observed that the O-H absorption pattern in the second overtone 0.9μ region was analogous to that at 1.4μ.

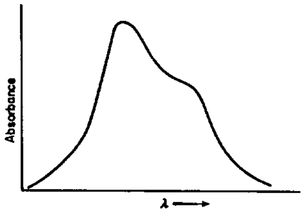


FIG. 1. Schematic illustration of O-H absorption band.

TABLE 1. Infrared absorption of some alcohols (ca. 0.01 M) in CCl_4 solution in the first overtone

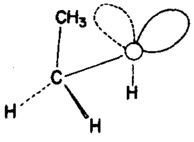
Compound	λ-max, Å					
	1[a]	2[b]	3[a]	B_1/B_2	B_1/B_3	, cm^{-1}
CH_3OH	14042	—	—	—	—	—
CH_3CH_2OH	14081	14130	—	7.92	—	24.5
$(CH_3)_2CHOH$	14110	14179	—	7.56	—	33
$(CH_3)_3COH$	14157	—	—	—	—	—
$(CH_3)_2CHOD$	18996	19082	—	1.85	—	23
F_3CCH_2OH	14068[b]	14132[a]	—	0.135	—	32
$CH_3CH_2CH(OH)CH_3$	14110	14194	—	5.64	—	42
$CH_3(CH_2)_2CH(OH)CH_3$	14110	14190	—	5.84	—	40
$(C_2H_5)_2CHOH$	14100	14204	—	5.86	—	52
$ClCH_2CH_2OH$	14083	14140	14227	9.16	0.462	28.5,72
$C_6H_5CH_2CH_2OH$	14080	14130	14209	1.41	0.934	24, 64.5

[a] ± 2 Å

[b] ± 5 Å

The most obvious cause of the splitting observed for the saturated alcohols[2a] is conformational heterogeneity. In the series, MeOH, EtOH, i-PrOH and t-BuOH, this depends solely on rotation about the C-O bond and is thus absent in the symmetrical members of the series, MeOH and t-BuOH. With EtOH and i-PrOH, two conformations are expected, these being illustrated for EtOH, Correspondingly, MeOH and t-BuOH show singlet O-H absorption, while EtOH and i-PrOH display a doublet (Table 1).

Trifluoroethanol displays doublet absorption analogous to that of ethanol except for a reversal of relative band intensities (Table 1).



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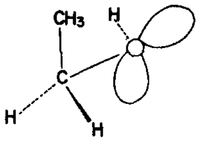

gauche

Other primary alcohols, e.g., 1-propanol, isobutyl alcohol, 1-octanol and neopentyl alcohol, are analogous to ethanol, $\Delta\nu$ being ca. 25 cm^{-1}. Secondary alcohols in general show doublet absorption as does 2-propanol, but the $\Delta\nu$ is quite variable, the largest value so far observed being the 52 cm^{-1} displayed by 3-pentanol (Table 1).

It is not yet clear just when the possibility of conformational heterogeneity can be expected to lead to doublet O-H absorption. For example, in the series, $(CH_3)_2C(OH)R$, singlet absorption is observed for R=ET, just as for Me, but a doublet is present for R=i-Pr. Also, methylcyclobutylcarbinol shows singlet absorption, even though methylisopropylcarbinol shows a doublet. Finally, cyclopentanol shows a single band, whereas cyclohexanol and cyclodecanol display doublet absorption. Further, it is not clear whether conformational heterogeneity of saturated alcohols will lead to still greater multiplicity of O-H absorption bands, since no clear case of this has been observed.

The indications are that there will be sufficient regularity of behavior of alicyclic and bicyclic alcohols to make the doublet character of the O-H absorption useful for diagnosis of configuration and conformation.

Thus in cyclohexanols which are relatively homogeneous with respect to the conformational disposition of the oxygen atom[3], those with an *equatorial* hydroxyl group, e.g., *trans*-2-methylcyclohexanol, *trans*-4-t-butylcyclohexanol, 3β-cholestanol and menthol, show doublet O-H absorption. On the other hand, those with an *axial* hydroxyl group, e.g., *cis*-2-cyclohexylcyclohexanol, neomenthol and *cis*-4-t-butylcyclohexanol, exhibit a single absorption band. With bicyclic compounds, those closely related to *exo*-2-norborneol (I, II[4], III[5], IV[5], V[6], VI[5], VII[6]) all show only single bands. Similarly, 7-norborneol (VIII) exhibits a single O-H absorption. However, those compounds related to *endo*-2-norborneol (IX, X[5], XI[5], XII[6], XIII[6], XIV[6]) all exhibit doublets.

There are, however, limitations to the above generalizations, in that increased steric congestion in the *axial*-cyclohexanols can convert the singlet to a doublet, e.g., in *cis*-2-t-butylcyclohexanol. Similarly, vicinal methyl substitution on *exo*-2-norborneol induces doublet character in the O-H absorption, e.g., in *exo*-camphenilol[6] (XV). The behavior of the epimeric bicyclo[3.2.0.]heptan-2-ols[7] (XVI and XVII) may be considered analogous, the *trans*-epimer XVI showing singlet, the *cis*-epimer XVII exhibiting doublet absorption. Distortion of the *exo*-2-norborneol structure can also convert singlet to doublet absorption, as in the case of the half-cage alcohol[5] XVIII.

With alcohols in which intramolecular hydrogen bonding is possible,

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[3] S. Winstein, and N. J. Holness, *J. Amer. Chem. Soc.* **77**, 3054 (1955).

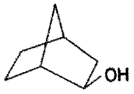
[4] S. B. Soloway, *J. Amer. Chem. Soc.* **74**, 1027 (1952).

[5] S. Winstein, *Experientia Supplementum II* 137 (1955).

[6] S. Winstein, Abstracts 15th Nat. Org. Chem. Symposium of American Chemical Society, p. 29. June 17-20, 1957, Rochester, N.Y.

[7] S. Winstein, F. Gadient, E. T. Stafford and P. E. Klinedinst, Jr., *J. Amer. Chem. Soc.* **80**, 5895 (1958).

three components to the monomeric O–H absorption are often observed.[8] An example is ethylene chlorohydrin[9] (Table 1), two of the bands being analogous



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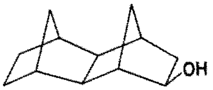

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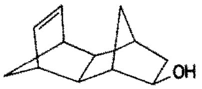

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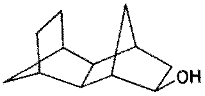

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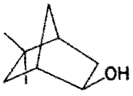

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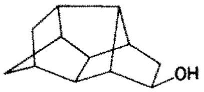

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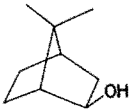

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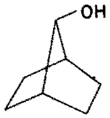

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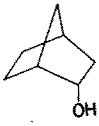

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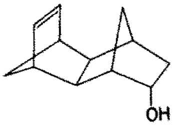

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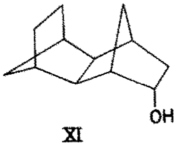

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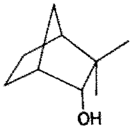

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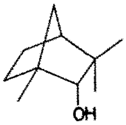

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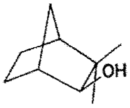

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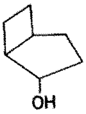

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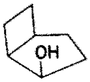

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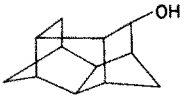

XVIII

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[8] R. Piccolini and J. Sonnenberg, unpublished work.

[9] L. R. Zumwalt and R. M. Badger, J. Amer. Chem. Soc. 62, 305 (1940).

to those of ethanol and the third at higher wavelength being due to those of the conformations which are _gauche_ with respect to rotation about both the C–C and C–O bonds which have _syn_ chlorine and hydroxyl hydrogen atoms for hydrogen bonding. The case of 2-phenylethanol[8] is quite analogous (Table 1).

The demonstration that doublet character of the O–H absorption is quite general for saturated alcohols has obvious implications for the interpretation of the spectra of unsaturated alcohols,[8] e.g., benzyl alcohol[1b,10] or allyl alcohol,[1b] which show doublet absorption, since neither of the two bands need necessarily be associated with an attractive hydrogen bonding interaction. Other criteria for intramolecular hydrogen bonding, besides doublet character of the O–H absorption, must be employed.[8]

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[10] J. J. Fox and A. E. Martin, _Trans. Faraday Soc._ **36**, 897 (1940).