Structural information from OH stretching frequencies monohydric saturated alcohols

J. H. van der Maas and E. T. G. Lutz

Laboratory for Analytical Chemistry, University of Utrecht,
Croesestraat 77A, The Netherlands

Abstract—Infrared data have been recorded of the hydroxyl stretching band for about 70 monohydric saturated alcohols in dilute carbon tetrachloride solution. The wavenumber maximum, the half-bandwidth and the band pattern could be related to the structure of the molecules. Not only primary, secondary and tertiary alcohols can be distinguished but also β-branched and cyclic ones. Four effects seem to be connected with the OH stretching band; viz. substitution and fixation both lowering the frequency, and rotation and shielding both enhancing it. For identification purposes a table correlating structure, wavenumber and half-bandwidth is presented.

INTRODUCTION

WITHIN the framework of a comprehensive infrared frequency structure correlation investigation in our laboratory several functional groups are studied. The aim of the work is the development of reliable identification procedures based on logic yes/no decisions leading to the structure of the unknown compound or at least to part of its structure. Next to the methyl [1, 2] and the carbonyl [3] the OH group has been chosen as: (a) it is a very common group in organic compounds, (b) its stretching frequency is sensitive to (minor) variations in the structure of a molecule and (c) in a spectrum the stretching band is easily found.

However it had to be expected that correlating band and structure would be hampered as result of the tendency of the OH group to form hydrogen bridges and the possibility to rotate about the C–O axis; different conformers and rotamers might thus form part of the observed band. Though band resolution might be helpful here it only is if one knows before hand how many bands are present and of what type.

The parameters that can be used to characterize a band are the wavenumber value of the absorption maximum, ν, the apparent halfbandwidth, $\Delta\nu_{1/2}$, the asymmetry number, α/β, and eventually the overall bandpattern (see Fig. 1).

The OH stretching vibration in the first and second overtone region as well as in the fundamental region has been the object of numerous investigations [4–24],

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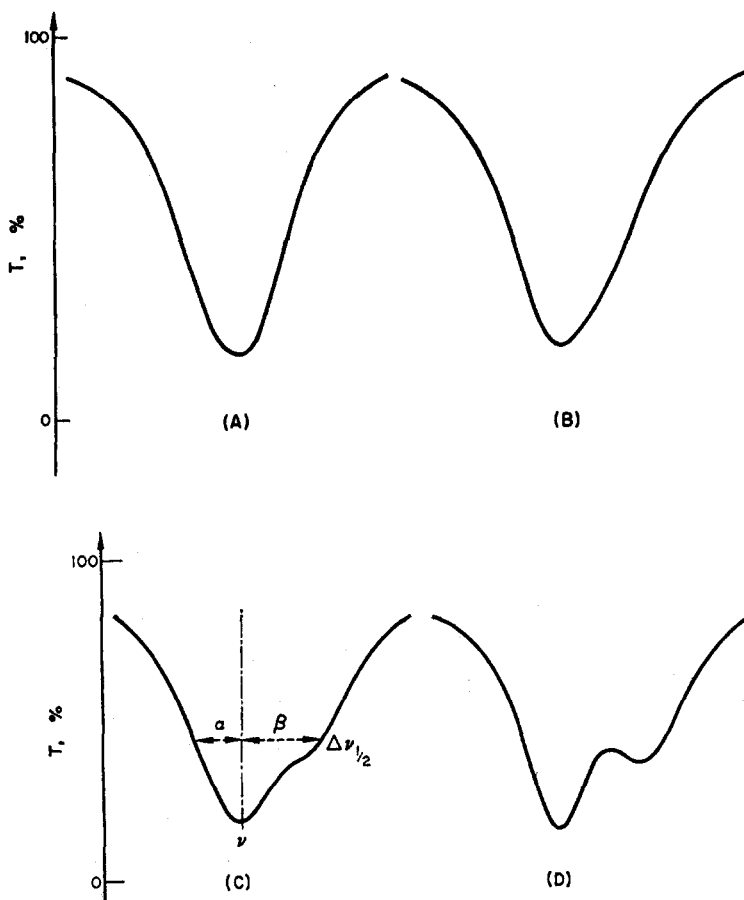[13] R. PICCOLINI and S. WINSTEIN, *Tetrahedron Lett.* 4 (1959).

Fig. 1. Typical patterns of the OH stretching band.

the formation of a hydrogen-bridge being most favorite. Occasionally the band-frequency, the bandshape and the halfbandwidth have been studied and related to the molecular structure [16, 17]. Provided the OH compound is adequately diluted in an inert solvent such as CCl_4 one can observe an OH stretching band free from intermolecular bridges.

It appears that the OH band can be (Fig. 1): (a) totally symmetric; a few cases

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only, (b) asymmetric, (c) asymmetric with a shoulder, (d) a doublet; sometime well split.

Several causes have been suggested to explain the observed pattern such as:

(i) *Fermi resonance*

According to FLYNN *et al.* [4] the asymmetry in an OH band is due to the presence of a second band caused by Fermi resonance with a combination band of the α–CH_2 group in an alcohol. However since almost all alcohols including the secondary and tertiary ones without that group do show asymmetric bands this explanation seems to be very unlikely as has been pointed out by DALTON *et al.* [5] and FRUWERT *et al.* [6].

(ii) *Interaction of electrons*

SAIER *et al.* [7], WEINMAN [8–10] and FRUWERT *et al.* [11] suggested oxygen lone pair interaction with a hydrogen atom at the γ–C atom. This explanation is highly doubtful as compounds without a γ–H atom (Table 1, nr 8) do not behave significantly different. KRUEGER *et al.* [12] assumed that the lone pair p electrons of the oxygen atom would interact with the 1s electron of an α–H atom when in trans position to each other giving rise to an increase of ν_{OH}. As the authors state their explanation is essentially not different from a rotational concept.

(iii) *Rotational isomerism*

This has been mentioned first by PICCOLINI and WINSTEIN [13] and was supported later on by OKI and IWAMURA [14], ARNAUD and ARMAND [15, 19], DALTON *et al.* [5], AARON *et al.* [16, 17], EDDY *et al.* [18] and DITTER and LUCK [20] to explain the asymmetry of the OH band and its variation in frequency. At ambient temperature the rotation of the OH group about the C–O axis can be either "free" or (partly) hindered thus leading to a few energetically favourable conformers.

In order to obtain reliable frequency structure correlations we have measured the OH stretching band of about 70 monohydric saturated alcohols. The results may be used as well to get a decisive answer about the factors determining the shape of the OH band.

<div align="center">EXPERIMENTAL</div>

Spectra were recorded on either a Perkin–Elmer 257 equipped with a wavenumber marker or a 421 spectrometer. Wavenumber calibration was by CH_4 and NH_3 gas. Band positions are believed accurate to $\pm 1 \cdot 5$/cm and $\Delta\nu_{1/2} \pm 1$/cm. Scanningtime was 100 and 10/cm per minute respectively. Resolution was better than 2/cm. Double beam operation was employed using "infrasil" cells of 2, 10 or 50 mm. Concentrations were about 1 μl/ml CCl_4 or 1 mg/ml; i.e. about 0·01 M. Intermolecular association was precluded that way as the spectra did show. For band resolution a curve resolver (310, Du Pont de Nemours, Inc.) was used. The purity of the compounds was at least 98%; checked by G.L.C., melting point or other physical methods.

<div align="center">RESULTS AND DISCUSSION</div>

The asymmetry of the OH band arises most probably from different molecular conformations as we have seen before. Band deconvolution is an obvious method then to obtain practical knowledge about the different conformers and their relative populations, however it involves certain assumptions with respect to the number of absorption maxima and the corresponding intensities. Assuming that two bands

(conformers) are present only graphical separation has been done by DALTON et al. [5], KRUEGER et al. [12, 21], SAIER et al. [7], ARMAND and ARNAUD [19], AARON et al. [17], WEINMAN [8, 9] and FRUWERT et al. [11]. As some of the authors point out the results depend to a large extent on the assumption made before.

For a number of bands we have carried out graphical separation by means of a curve resolver. From this it appeared that the results for three and more bands are not unique whereas for two bands they are of limited value only.

To get some idea about what happens when (Lorentzian) bands are superimposed we have calculated and plotted the overall curve for two peaks with fixed intensity ratio's at varying distance from each other. In a few cases the same has been done for three bands. The results were invaluable for a better understanding of the observed OH band patterns.

In Table 1, 2 and 3 the ν and $\Delta\nu_{1/2}$ values for the primary, secondary and tertiary

Table 1.
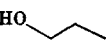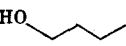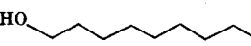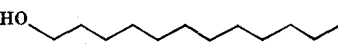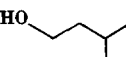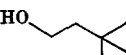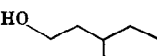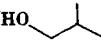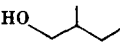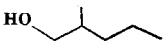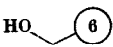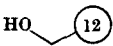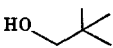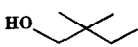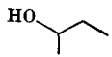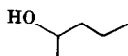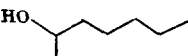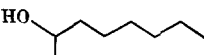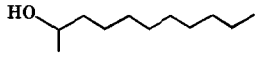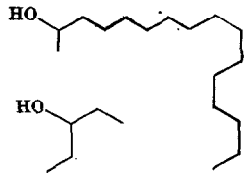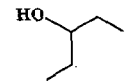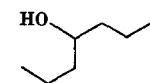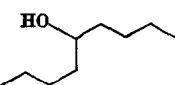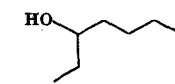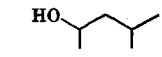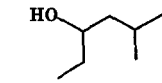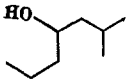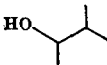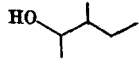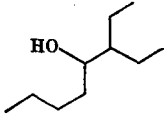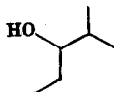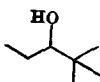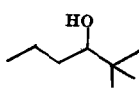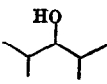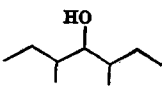
nr	compound		ν	$\Delta\nu_{1/2}$
1	methanol	HO	3643·7	21
2	ethanol	HO	3634·8	26
3	propanol-1	HO	3638·5	26
4	butanol-1	HO	3638·8	26
5	nonanol-1	HO	3637·6	24
6	dodecanol-1	HO	3638·2	24·5
7	3 methylbutanol-1	HO	3638·6	25
8	3,3 dimethylbutanol-1	HO	3636·8	25
9	3 methylpentanol-1	HO	3636·4	25·5
10	2 methylpropanol-1	HO	3640·4	24
11	2 methylbutanol-1	HO	3640·1	22
12	2 methylpentanol-1	HO	3639·4	22
13	cyclohexylmethanol	HO (6)	3640·0	22
14	cyclododecylmethanol	HO (12)	3638·9	24
15	2,2 dimethylpropanol-1	HO	3641·7	20
16	2,2 dimethylbutanol-1	HO	3641·7	20
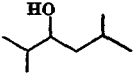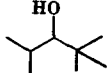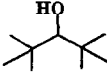
Table 2a.

nr	compound		ν	$\Delta\nu_{1/2}$
17	propanol-2		3626·1	22
18	butanol-2		3627·0	25
19	pentanol-2		3626·3	23
20	heptanol-2		3626·3	23
21	octanol-2		3627·4	22
22	undecanol-2		3626·7	23
23	hexadecanol-2		3626·0	22
24	pentanol-3		3631·1	27·5
25	heptanol-4		3632·8	26
26	nonanol-5		3632·9	28
27	heptanol-3		3630·4	26
28	4 methylpentanol-2		3628·5	24
29	5 methylhexanol-3		3630·0	25·5

(Table 2a. *Cont.*)

nr	compound		ν		$\Delta\nu_{1/2}$
30	2 methylheptanol-4		3630·0		29·5
31	3 methylbutanol-2		3630·5		26
32	3 methylpentanol-2		3629·4		27
33	3 ethyloctanol-4		3631·5		31
34	2 methylpentanol-3		3636·6		30·5
35	3,3 dimethylbutanol-2		3634·8		21
36	2,2 dimethylpentanol-3		3641·7	3616·3	15*
37	2,2 dimethylhexanol-3		3641·1	3617·0	16*
38	2,4 dimethylpentanol-3		3641·5	3614·0	19*
39	3,5 dimethylheptanol-4		3640·4	3615·0	20*

(Table 2a. *Cont.*)

nr	compound		ν		$\Delta\nu_{1/2}$
40	dicyclohexylmethanol		3641·5	3615·0	18*
41	2,5 dimethylhexanol-3		3634·7		33
42	2,2,4 trimethylpentanol-3		3642·8	3624	25*
43	2,2,4,4 tetramethylpentanol-3		3651·7	3624·6	17*

* $\Delta\nu_{1/2}$ for the band at the highest wavenumber; the second band is included to some extent.

Table 2b.

nr	compound		ν	$\Delta\nu_{1/2}$
44	cyclobutanol	HO—④	3626·7	25
45	cyclopentanol	HO—⑤	3625·5	17
46	cyclohexanol	HO—⑥	3623·9	19·5
47	cycloheptanol	HO—⑦	3621·7	16
48	cyclooctanol	HO—⑧	3621·4	17
49	cyclododecanol	HO—⑫	3625·7	20

(Table 2b *Cont.*)
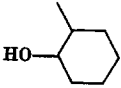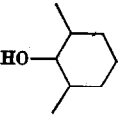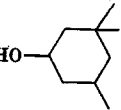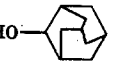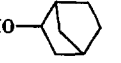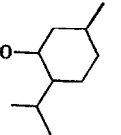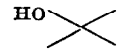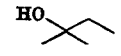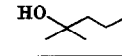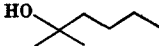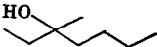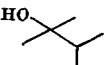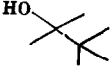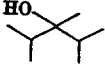
nr	compound		ν	$\Delta\nu_{1/2}$
50	2 methylcyclohexanol		3631·0	24
51	2,6 dimethylcyclohexanol		3636·1	28·5
52	3,3,5 trimethylcyclohexanol		3626·9	19·5
53	adamantanol-2		3622·5	16·5
54	norborneol		3621·1	21
55	menthol		3626·8	31

Table 3a.

nr	compound		ν	$\Delta\nu_{1/2}$
56	tert. butanol		3617·0	14
57	2 methylbutanol-2		3616·9	20
58	2 methylpentanol-2		3616·9	18

(Table 3a. *Cont.*)
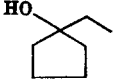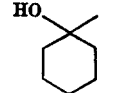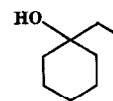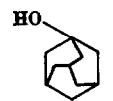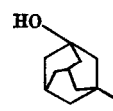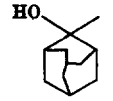
nr	compound		ν	$\Delta\nu_{1/2}$
59	2 methylhexanol-2		3617·0	19
60	3 methylpentanol-3		3618·1	21
61	4 methylheptanol-4		3617·1	19
62	3 ethylpentanol-3		3621·6	20
63	3 methylheptanol-3		3617·1	20·5
64	2,4 dimethylheptanol-4		3615·3	21
65	2,3 dimethylbutanol-2		3622·1	22
66	2,3,3 trimethylbutanol-2		3624·6	15
67	2,3,4 trimethylpentanol-3		3627·6 3613·5	29

alcohols are summarized. On inspection of these tables, the corresponding band-patterns and the molecular structure four more or less independent effects do show up, viz. (A) substitution, (B) shielding, (C) fixation and (D) rotation. We will discuss these effects subsequently hereunder.

A. *Substitution effect*

Though a straightforward comparison of the ν-values should be rejected as in general the observed bandmaximum is the result of composed bands it is unquestionable that the frequencies of the alcohols decrease on going from primary to secondary

Table 3b.

nr	compound		ν	$\Delta\nu_{1/2}$
68	1 ethylcyclopentanol		3617·6	23
69	1 methylcyclohexanol		3612·7	19
70	1 ethylcyclohexanol		3615·0	23·5
71	adamantanol-1		3606·4	14
72	3 methyladamantanol-1		3605·8	15·5
73	2 methyladamantanol-2		3611·7	19·5

and tertiary compounds. Replacing an α-H atom by a methyl group causes a decrease of about 9/cm (see Table 4). According to OKI and IWAMURA [14] and DALTON *et al.* [5] the different ν-values arise from the three different conformers, OH between two H atoms (1), between a H and a C atom (2) and between two C atoms (3), and their relative populations and not from any substitution ($=$inductive) effect. For a reasonable interpretation of the ν_{OH} data Dalton *et al.* had to suppose (i) that each skew alkyl group causes an appreciable decrease in the OH frequency and (ii) that a staggered group has a smaller effect whose sign depends on the size of the group.

From vibrational calculations [28] we know that a distinct change in ν_{OH} requires a distinct change in the O . . . H force constant. Alkylgroups in skew and staggered positions can only count for small changes of a few wavenumbers. Mainly for that reason we prefer the concept of a substitution effect though the result might essentially be the same.

[25] W. WELTNER JR and K. S. SPITZER, *J. Am. Chem. Soc.* **73**, 2606 (1951).
[26] G. M. BARROW, *J. Chem. Phys.* **20**, 1739 (1952).
[27] S. KONDO and E. HIROTA, *J. Mol. Spectrosc.* **34**, 97 (1970).
[28] Internal report.

Substitution of a β–H atom by an alkyl group is attended by an increase in the frequency whereas replacement of a γ–H atom by a methyl group proves to have little or no effect (Tables 5 and 6). To us the former is no real substitution effect but the outcome of shielding of the OH group (q.v.B.).

Table 4. The effect of replacement of an α-H atom by a methyl group. The average value for the substitution is about $-9/cm$

nr	compound	ν	nr	compound	ν	nr	compound	ν
1	methanol	3643·7 −8·9	10	2 methyl propanol-1	3640·4 −9·9	15	2, 2 dimethyl propanol-1	3641·7 −6·9
2	ethanol	3634·8 −8·7	31	3 methyl butanol-2	3630·5 −8·4	35	3, 3 dimethyl butanol-2	3634·8 −10·2
17	i-propanol	3626·1 −9·1	65	2, 3 dimethyl butanol-2	3622·1	66	2, 3, 3 trimethyl butanol-2	3624·6
56	t-butanol	3617·0						

Table 5. The effect of replacement of a β-H atom by a methyl group

nr	compound	ν	nr	compound	ν	nr	compound	ν
4	butanol-1	3638·8	24	pentanol-3	3631·1	60	3 methyl pentanol-3	3618·1
11	2 methyl-	3640·1	34	2 methyl-	3636·6			
16	2, 2 dimethyl-	3641·7	38	2,4 dimethyl-	3641·5 3614·0	67	2,3,4 trimethyl-	3627·6 3613·5
			42	2,2,4 tri- methyl-	3642·8 3624			
			43	2,2,4,4 tetra methyl-	3651·7 3624·6			

Table 6. The effect of replacement of a γ-H atom by a methyl group

nr	compound	ν	nr	compound	ν
4	butanol-1	3638·8	7	3 methylbutanol-1	3638·6
			8	3,3 dimethylbutanol-1	3636·8
			9	3 methylpentanol-1	3636·4
19	pentanol-2	3626·3	28	4 methylpentanol-2	3628·5
25	heptanol-4	3632·8	29	5 methylhexanol-3	3630·0
			30	2 methylheptanol-4	3630·0
61	4 methylheptanol-4	3617·1	64	2,4 dimethylheptanol-4	3615·3

B. *Shielding effect*

From table 1 it appears that the ν-values increase upon branching (or substitution) at the β–C atom. The same proves to be valid for the secondary and tertiary alcohols as can be seen from Table 5. As we thought it very unlikely that β–substitution would influence the OH force constant through the bonds as much as that we inspected the possibility of external interaction. Molecular models with and without methyl substitution at the β–C atom revealed that in the former case the OH group is more encompassed, shielded from external influences. One could say that the "free" space around the OH group is diminished; part of the interaction with CCl_4, or more

precisely with its Cl atoms is changed into one with a CH_3 (or CH_2) group. We assume that the OH—Cl interaction is of the hydrogen bonding type lowering the frequency to some extent. This is supported by the ν-values (see Table 7) in isooctane (a compact molecule with five methyl and one methylene group on the outside) which are all higher than in CCl_4 but not each as much. The effect might as well be called steric. It is about $+3$–$5/cm$ for an adjacent (=shielding) methyl or methylene group.

Table 7. The effect of the solvent on the ν-value. The variation of Δ clearly indicates that the effect is related to the structure of the alcohol

nr	compound	CCl_4	Isooctane	Δ
1	methanol	3643·7	3651·9	8·2
2	ethanol	3634·8	3642·7	7·9
17	isopropanol	3626·1	3633·9	7·8
56	tert. butanol	3617·0	3622·6	5·6
38	2,4 dimethylpentanol-3	3641·5	3646·7	5·2
		3614·0	3619·2	

C. *Fixation effect*

From the ν-values of the cyclic compounds 45–49 it can be concluded that ring-strain is not affecting the OH stretching vibration. However comparing the frequency of adamantanol-1 with corresponding open chain compounds such as tert. butanol (see Table 8) let see a difference of about $10/cm$. Though we believe, on inspection of all ring compounds, that the observed effect is generally valid it cannot be proved unambigously as most of the noncyclic molecules will be present as different rotational isomers thus making a direct comparison of the ν-values a rather difficult affair. But the fact that the ring compounds are found at the low (frequency) side for the secondary as well as for the tertiary alcohols can hardly be accidental. It is thought that the real cause of the decrease in the fixation of the β–C group, i.e. the rotation about the C–C axis is blocked.

Table 8. The effect of fixation of the three β-C atoms

nr	compound	ν-value	fixed axes	remarks
56	tert. butanol	3617·0	non	
69	1 methylcyclohexanol	3612·7	2	
73	2 methyladamantanol-2	3611·7	2	
70	1 ethylcyclohexanol	3615·0	2	shielding
71	adamantanol-1	3606·4	3	

D. *Rotational effect*

The rotational barrier for the OH group is calculated to be $0·9$ kcal/mole for methanol, WELTNER and SPITZER [25], less than $1·2$ kcal/mole for ethanol, BARROW [26], 1–2 kcal/mole for isopropanol, KONDO and HIROTA [27], FRUWERT et al. [11], and $0·4$ kcal/mole for a long chain alcohol, LUCK and DITTER [24]. Though rotation about the C–O axis is strictly speaking not free it is clear that the barrier is easily overcome at room temperature. Besides rotation about the C–C axis somewhere in

Table 9. ν and $\Delta\nu$ values of compounds with a well
defined skeletal structure

nr	compound	ν-value	$\Delta\nu_{1/2}$
1	methanol	3643·7	21
45	cyclopentanol	3625·5	17
53	adamantanol-2	3622·5	16·5
71	adamantanol-1	3606·4	14
72	3 methyladamantanol-1	3605·8	15·5
56	tert. butanol	3617·0	14

Table 10. ν and $\Delta\nu_{1/2}$ data of compounds clearly
present in at least two structures; either a mixture
of isomers or a mixture of different conformations of
the skeleton. "True" value $\Delta\nu_{1/2}$: 17/cm

nr	compound	ν-value	$\Delta\nu_{1/2}$
44	cyclobutanol	3626·7	25
54	norborneol	3621·1	21
46	cyclohexanol	3623·9	19·5
50	2 methylcyclohexanol	3631·0	24
51	2,6 dimethylcyclohexanol	3636·1	28·5

the skeleton is also possible. Hence alcohols in solution can be present in many different conformations. But as appears from the rather constant ν–values for the alcohols 3, 4, 5 and 6 either the skeleton is always present in the same favourable conformation or different orientations about the C–C axes have no effect on the OH frequency.

Introduction of CH_2 and CH_3 groups in the close vicinity of the OH group, branching at the β–C atom, certainly will produce higher barriers thus restraining rotation. We inspected the half band width of the alcohols to see whether it could be used as a source of information about the rotational possibilities of the OH group and so about its molecular environment. Two conclusions can be drawn from the available data:

(a) the "true" $\Delta\nu_{1/2}$ for primary, secondary and tertiary alcohols is estimated to be 21, 17 and 14, 5/cm resp., the apparent value being the result of the complex character of the OH band. The data are derived from the compounds in Table 9 which are highly symmetric with a rather rigid structure. Higher values for $\Delta\nu_{1/2}$ clearly point to more than one rotational isomer (see Table 10). In a few cases (36–40, 42, 43 and 67; see also Table 11) band splitting is observed. At least

Table 11. Examples of β-substituted compounds with a split OH
stretching band. 36 and 43 are well split whereas 42 can be composed
of 36 + 43 and hence is not well split

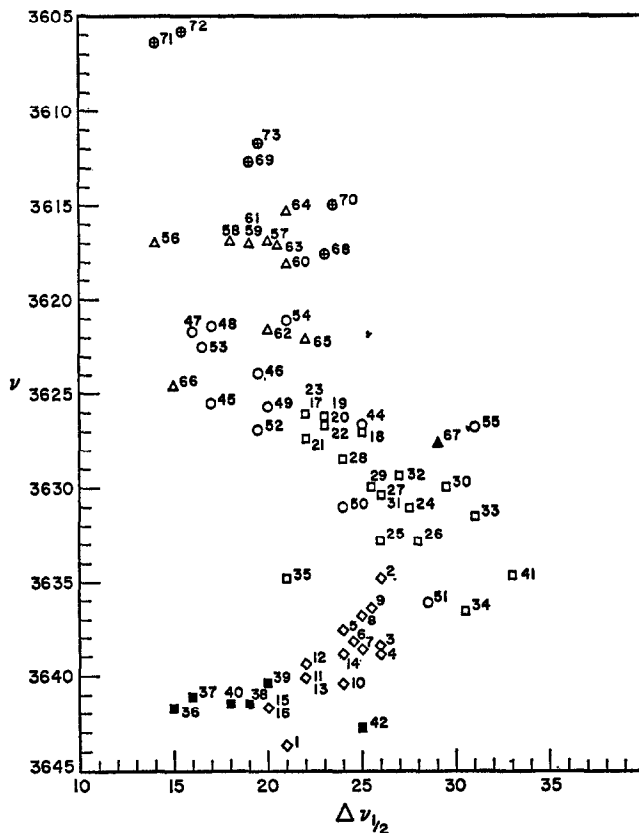| nr	compound				
36	2,2 dimethylpentanol-3		3641·7		3616·3
43	2,2,4,4 tetramethylpentanol-3	3651·7		3624·6	
42	2,2,4 trimethylpentanol-3		3642·8	3624	

Fig. 2. Frequency-halfbandwidth-structure correlation table. The numbers refer to the structures of the compounds in the tables 1, 2 and 3. (Not included is compound 43.) ◇ primary, □ secondary, △ tertiary, ○ cyclic and ⊕ tertiary (bi) cyclic alcohols. Split bands are marked fully black; only the strongest band is given.

four C atoms must be attached to the β–C atoms. Obviously branching as such is limiting the number of different conformers to a few only. Provided the difference in frequency between the remaining individual conformers is sufficiently large splitting of the band will be observed.

(b) the highest $\Delta\nu_{1/2}$ value is found for compounds of which (i) the OH group can rotate "freely" (e.g. primary alcohols) and (ii) the skeleton exists in different conformations (e.g. 46). The value is lowered when rotation is limited (e.g. 15), however this does not necessarily mean that the observed $\Delta\nu_{1/2}$ will be smaller as the presence of different rotamers can bring about the opposite (e.g. 33). Assuming that the half band width and the ε for the different conformers are identical it is possible to get a rough idea about the ratio in which they occur if the band is resolved in its individual components.

Correlation table

Figure 2 contains the ν and $\Delta\nu_{1/2}$ data of the recorded alcohols except those with identical values and structure. When from an unknown monohydric saturated

alcohol the frequency and the halfbandwidth are measured it is possible to tell (i) whether it is a primary, secondary or tertiary one, (ii) whether it is β-branched and to what extent and (iii) whether it is (bi)cyclic. Simply take the number(s) of the compound(s) with (nearly) identical data and look for them in the Tables 1–3 to find the corresponding structural units. When more than one compound is found a final conclusion may be reached considering the earlier mentioned effects.