

Structural information from OH stretching frequencies—IV. The fixation effect in saturated tertiary alcohols

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Abstract—The OH stretching bands of several tertiary alcohols with a (partly) rigid skeleton have been investigated. It is demonstrated that in CCl_4 the observed OH vibration is related to the distances $\text{OH} \cdots \text{X}$, where X stands for atoms close to OH. The effect of fixation of $\beta\text{-CH}_2$ groups proves to be reducible to changes in the $\text{OH} \cdots \beta\text{-H}$ distances. Evidence is found for the presence of twisted methyl groups in *t*-butanol.

INTRODUCTION

As has been outlined previously [1] fixation is one of the factors entering largely into the ultimately observed OH-stretching band of monohydric alcohols in dilute CCl_4 solution. For instance the difference in wavenumber between *t*-butanol (3616.5) and adamantanol-1 (3606.5) is thought to originate from the fact that the $\beta\text{-CH}_2$ groups in the latter compound are rigidly fixed in the skeleton whereas the $\beta\text{-CH}_3$ groups in the former can (at least to some extent) rotate about the $\text{C}_\alpha\text{-C}_\beta$ axis. For a better understanding of the fixation effect we have studied a series of tertiary alcohols, comparable in (sub)structure except for the fixation of the $\beta\text{-CH}_2$ or $\beta\text{-CH}_3$ group(s).

Calculations with respect to the frequency determining factors of the hydroxyl group revealed [2] that the frequency is hardly affected ($\leq 1 \text{ cm}^{-1}$) by changes of F_{OH} , F_{HOX} and the mass of X because of the isolated character of the OH-stretching vibration. Frequency shifts should therefore be attributed mainly to changes in non-bonding interaction(s).

EXPERIMENTAL

All spectra were run three times in the region 3750–3481 cm^{-1} on a Perkin-Elmer 180 spectrometer equipped with a data magnetic recorder, type 109, set at a wavenumber interval of 1 cm^{-1} . The scanspeed was 55 $\text{cm}^{-1}/\text{min}$ and the resolution better than 2 cm^{-1} .

The alcohols were measured in "infrasil" cells (10 mm) against air, concentration 0.5–1 mg/ml CCl_4 . The purity of the compounds was $\geq 98\%$ (GLC 17.4% diglycerol on teflon or 10% EGSS-X on Chromosorb). Data averaging, correction for blanks, integration, plotting and other calculations were performed on a computer (Cyber 73-28), programs in Fortran IV.

The bandfrequency, ν , the half-bandwidth, $\Delta\nu_{1/2}$, and the α/β ratio were derived from expanded spectra (1 cm^{-1}/mm). They are believed accurate to $\pm 0.5 \text{ cm}^{-1}$, $\pm 1.0 \text{ cm}^{-1}$ and 8–15%, respectively. The equatorial alcohols VIII and IX have been separated from their axial conformers by column chromatography. Aluminumoxide 90 (activity II–III) was the absorbent and pentane and ether the eluents [12].

RESULTS AND DISCUSSION

First we studied the OH-stretching bands of adamantanol-1 and some of its methyl substituted derivatives. In these compounds all $\beta\text{-C}$ -atoms form part of a rigid skeleton, rotation about a $\text{C}_\alpha\text{-C}_\beta$ axis is excluded. Rotation about the C-O axis, though not completely free, will be possible. At ambient temperature it is to be expected therefore that as result of non-bonding short range repulsive forces the favourite OH position will be the one midway between two $\beta\text{-CH}_2$ groups, as indicated in Figs. 1(a and b). On the basis of earlier observations [3] the effect of the substituted methyl groups was thought to be negligible since they are situated far away from the OH. Thus the three rotamers A_q , B_q and C_q will be fully identical and consequently the half-bandwidth will be rather small. The observed data are presented in Table 1. As appears the numbers are practically identical endorsing the foregoing.

Next a second series of compounds was measured, differing in skeleton. The results of these measurements are also displayed in Table 1. The data for the compounds I, V and VI are very much the same but for norbornanol-1 (VII) both the frequency as well as the half-bandwidth deviate clearly. The observed increase must originate from either a change in F_{OH} or/and different non-bonding interaction(s). Regarding the structure of the molecules and the insensitivity of F_{OH} for small alterations in the bond angles of the $\alpha\text{-C}$ -atom [2] the former possibility was ruled out. The non-bonding interactions, containing repulsive and attractive components, can be split up into (i) internal, between the OH group and other atoms of the molecule and (ii) external, between the OH group and atoms of the solvent. As forces of this type are inversely proportional to some power of the distance $\text{OH} \cdots \text{X}$ (X being an atom near to OH) only X-atoms (very) close to the OH group are important. Changes in the molecule in the near vicinity of the OH group will not only affect the internal forces but also the external ones as the accessibility

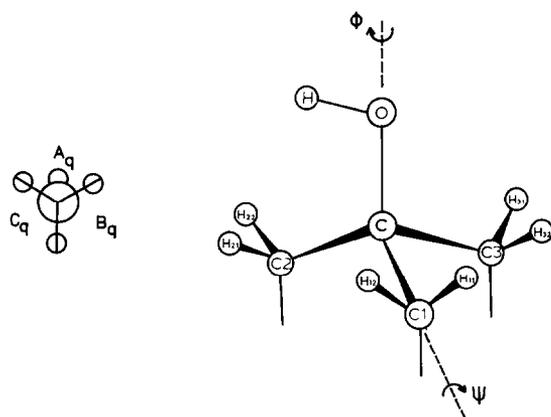


Fig 1 Schematic presentations of a tertiary alcohol (a) Projection in a plane perpendicular to the C—O-axis with the OH group in a position corresponding with rotamer A_q (other possible rotamers B_q and C_q) $\Phi = \beta$ -CH₂ group (b) φ rotation about the C—O-axis with $\varphi = 0^\circ$ for H—O—C—C₁ in a plane, ψ_1 rotation about the C—C₁-axis with $\psi_1 = 0^\circ$ for O—C—C₁—H₁₁ in a plane In adamantanol-1 $\psi_1 = \psi_2 = \psi_3 = 60^\circ$

for solvent molecules will change also In their most pure form the internal forces are found in the gas phase Dissolving brings about external forces which in their turn might influence the molecular structure For CCl₄ the result is always a shift of the OH frequency to lower wavenumbers The better the shielding of the OH group from the solvent molecules the smaller the shift [1]

According to literature [4] the upper part of bicyclo[2 2 2]octanol-1 (V), from OH up to and including the β -CH₂ groups, is practically identical (β -CH₂ groups 0.6° rotated) with adamantanol-1 It was expected that such a small rotation would hardly affect the OH vibration and this is borne out by the observed data (Table 1)

Though there can be some diversion of opinion about the precise structure of norbornanol-1 (VII) it is evident that it will differ appreciably from that of adamantanol-1 CHIANG *et al* [5] and MORINO *et al* [6] have calculated the structure of norbornane and assuming that norbornanol-1 will have a

norbornane-skeleton it follows that two β -CH₂ groups have twisted positions compared to adamantanol-1 and that some angles (valence as well as dihedral) and bond lengths are different (see Table 2) The overall result proves to be that the OH—X distances in this molecule are larger (see Fig 2) with maxima at about 55°, 178° (both 2.52 Å) and 295° (2.96 Å) Assuming that repulsive forces govern the position of the OH group these maxima will give rise to three rotamers ($B_q = C_q$ and A_q) of which the latter is most favoured (see Fig 2) The maxima for adamantanol-1 are found at 60, 180 and 300°, distance 2.43 Å Apparently the increase in distance is attended with a frequency rise of about 10 cm⁻¹ towards 3617.0 cm⁻¹ The half-bandwidth of 15.2 cm⁻¹ indicates the presence of both rotamers (A_q and $B_q = C_q$)

The two six-membered rings in 5-methylbicyclo[3 3 1]nonanol-1 (VI) may in principle be present in boat or chair form PEETERS *et al* [7] and also McEUEEN *et al* [8] and OSINA *et al* [9] have established that the chair form is favoured despite the fact that repulsion of the 3-endo and 7-endo H-atoms gives rise to distortion of the rings The observed data, fairly identical with those of the compounds I and V, indicate in our opinion the presence of an adamantanol-1-like substructure around the OH group and this is only possible if both cyclohexyl skeletons have the chair conformation and if the distortion in the upper part of the molecule is small

Had the structure of *t*-butanol in CCl₄ been (nearly) identical with the upper part of adamantanol-1 the OH absorption frequencies should have been alike Obviously this is not true (see Table 1) and as already noticed before [3] it points in our opinion to the presence of twisted methyl group(s) Undoubtedly an OH group positioned above and in the middle of two methyl groups, the most likely configuration for *t*-butanol, will affect them both equally well In view of the findings for norbornanol we have calculated the OH—H distance upon rotation of a methyl group The results are displayed in Fig 3 In *t*-butanol rotation of two methyl groups is limited due to

Table 1 Parameters of the OH stretching band for several tertiary alcohols Solvent CCl₄, dimensions in cm⁻¹ except for α/β which is dimensionless

Compound	Substituent	ν	$\Delta\nu_{\frac{1}{2}}$	α/β
I adamantanol-1	—	3606.0	13.4	0.8
II adamantanol-1	3-methyl	3606.0	13.3	0.9
III adamantanol-1	4-methyl	3606.5	14.0	0.9
IV adamantanol-1	3,5,7-trimethyl	3607.0	12.5	0.9
V bicyclo[2 2 2]octanol-1	—	3608.5	13.5	1.0
VI bicyclo[3 3 1]nonanol-1	5-methyl	3607.5	13.5	0.9
VII norbornanol-1	—	3617.0	15.2	0.9
VIII cyclohexanol (OH-aq)	1-methyl,4- <i>t</i> -butyl	3610.0	13.2	0.9
IX 5 α -cholestan-3 β -ol (OH-aq)	3 α -methyl	3610.0	13.1	0.9
X tert-butanol	—	3616.0	14.0	1.0

Table 2 Structural data for adamantanol-1 and norbornanol-1
Distances in Å, angles in degrees

Distances	Adamantanol-1	Norbornanol-1
OH	0.956 (a)	0.956 (a)
CO	1.427 (a)	1.427 (a)
CC1=CC3	1.544 (b)	1.556 (d)
CC2	1.544 (b)	1.539 (d)
CH (average)	1.073 (c)	1.115 (d)
angles		
$\angle\text{COH}$	109.47 (e)	109.47 (e)
$\angle\text{C}_1\text{CO} = \angle\text{C}_3\text{CO}$	109.47 (e)	119.2 (d)
$\angle\text{C}_2\text{CO}$	109.47 (e)	109.5 (d)
$\angle\text{CC}_1\text{H}_{11} = \angle\text{CC}_1\text{H}_{12} =$	109.47 (e)	111.1 (d)
$\angle\text{CC}_3\text{H}_{31} = \angle\text{CC}_3\text{H}_{32}$		
$\angle\text{CC}_2\text{H}_{21} = \angle\text{CC}_2\text{H}_{22}$	109.47 (e)	113.2 (d)
$\angle\text{C}_1\text{CC}_2$ (*)	120.0 (e)	115.9 (d)
$\angle\text{C}_1\text{CC}_3$ (*)	120.0 (e)	128.2 (d)
dihedral angles		
$\angle\text{H}_{11}\text{C}_1\text{CO} = \angle\text{H}_{32}\text{C}_3\text{CO}$	60 (e)	34 (d)
$\angle\text{H}_{21}\text{C}_2\text{CO} = \angle\text{H}_{22}\text{C}_2\text{CO}$	60 (e)	61 (d)
$\angle\text{H}_{31}\text{C}_3\text{CO} = \angle\text{H}_{12}\text{C}_1\text{CO}$	60 (e)	87 (d)

(*) Angles in projection in the plane perpendicular to the C—O axis [see Fig 1(b)]

(a) Methanol values [13], (b) Reference [14], (c) Reference [13], (d) Reference [5], (e) tetrahedral valence angles assumed

repulsive forces arising from mutual interaction of their H-atoms and therefore we have calculated also the shortest H—H distance of two symmetrically rotating methyl groups. As appears from Fig 3 β -methyl rotation of about -24° compared to adamantanol-1 ($+24^\circ$ for C_2 , $\psi_1 = 36^\circ$, $\psi_2 = -36^\circ$) results in equal OH—H distances (2.67 Å) for H_{11} and H_{12} . The corresponding shortest H—H distance between the two twisted methyl groups is found to be about 2.12 Å, a value which is unlikely small regarding the Van der Waals radius for a

H-atom (1.1–1.2 Å). A rotation of only $3\text{--}4^\circ$ ($\psi_1 = 56^\circ$, $\psi_2 = -56^\circ$) brings about a situation where the distance H—H between OH and CH_3 is equal to that between the two twisted CH_3 groups (i.e. OH— $\text{H}_{12} = \text{OH—H}_{21} = \text{H}_{21}\text{—H}_{12}$). Supposing that the OH forces the methyl groups to rotate somewhat, the “real” situation might be one in which the methyl groups are twisted more than 4° but less than 24° . Besides there might be small changes in the CCC angles. Consequently the OH—H distance is found somewhere between

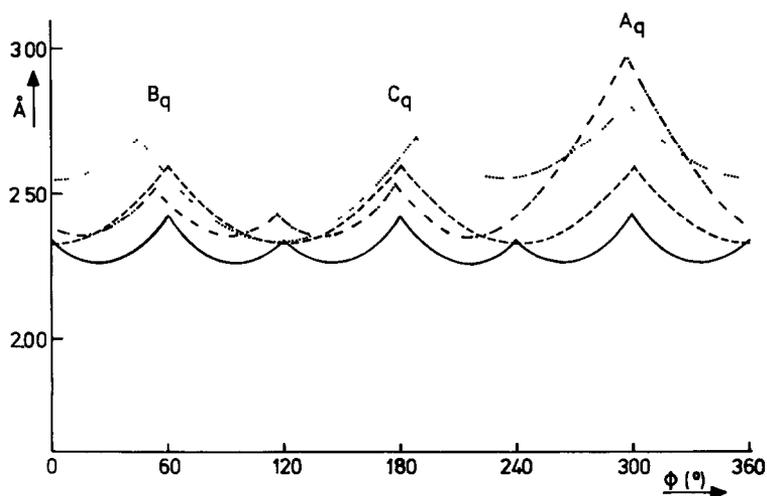
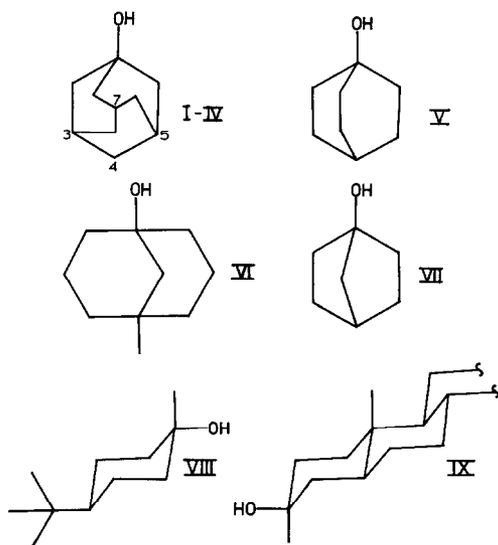


Fig 2 OH...X distances in adamantanol-1 and norbornanol-1 as a function of ϕ_{OH} (rotation about the C—O-axis, X = atom nearest to H) OH...H (—) and OH...C (----) for adamantanol-1 and OH...H (- -) and OH...C (· ·) for norbornanol-1



2.46 and 2.67 Å, but is anyway larger than 2.43 Å, the distance for an adamantanol-like structure and it is this increase in distance that, as for norbornanol, might be responsible for the frequency shift from 3606.5 to 3616.5 cm^{-1} . Regarding the fact that for small molecules the half-bandwidth is somewhat larger due to faster reorientation relaxation as has been set out by DIJKMAN [10], a value of 14.0 cm^{-1} points to just one rotamer.

The experimental data for 1-methyl-4-*t*-butylcyclohexanol (VIII) and 3 α -methyl-5 α -cholestan-3 β -ol (IX) are identical and the molecular structure around the OH group thus very likely

the same. The frequency shift of 35 cm^{-1} compared to adamantanol-1 proves in our opinion that the β -CH₂ groups (and/or the CH₃) have been slightly rotated about the C _{α} -C _{β} -axes. Distortion of the ring in *t*-butylcyclohexanes (with a few degrees) due to axial CH₃-H repulsion has been reported by ALTONA and SUNDARALINGAM [11] on the basis of X-ray analysis. The distortion is said to be asymmetrical. An unaltered skeleton with an OH at C₁ would bring about three different rotamers. Regarding the small half-bandwidth an asymmetrical distortion in the compounds VIII and IX is rather unlikely unless the different rotamers would be very much alike.

In conclusion one might say that for tertiary alcohols in CCl₄ solution the earlier introduced so-called fixation effect is reducible to alterations in the OH...H distance(s) upon fixation of β -C-atoms. The resulting frequency shift can be positive as well as negative. Furthermore it seems that a larger OH...H distance is attended with a higher frequency. Work on secondary and other alcohols is in progress.

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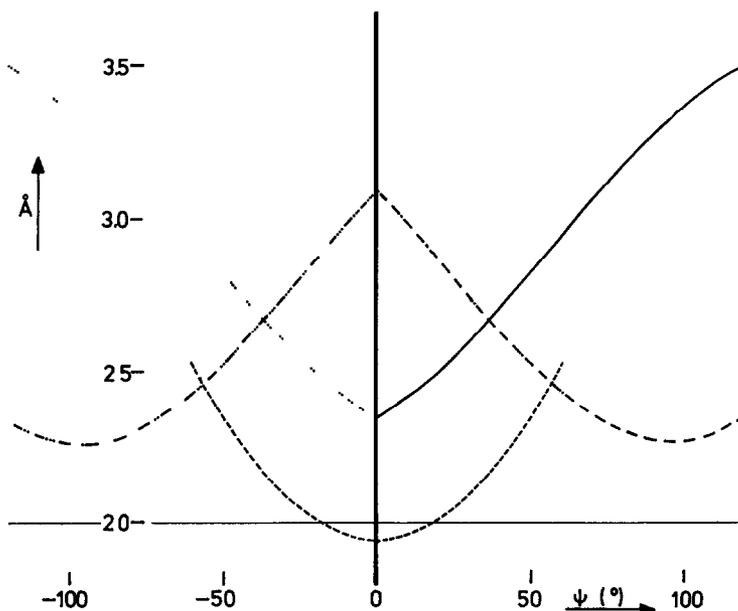


Fig. 3. OH...X distances in *t*-butanol as a function of a simultaneous but opposite rotation of two methyl groups ($\psi_1 = -\psi_2$ and $\varphi_{\text{OH}} = 60^\circ$): OH...H₁₁ (—), OH...H₁₂ (---), OH...H₂₁ (- · -), OH...H₂₂ (· · ·) and H_{12}...H₂₁ (----).}

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