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Structural information from OH stretching frequencies—IX. The influence of γ-alkyl substituents on the different OH rotamers in saturated axial cyclohexanols

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Abstract—The sensitivity of the OH-vibration in saturated axial cyclohexanols for γ-alkyl substituents has been studied. It appears that axial γ-substituents considerably influence both, the frequency and the presence of the rotamers. Besides the OH-vibration proves to be sensitive to the type of α-alkyl substituent. At least two types of intramolecular interaction affect the OH-frequency: (i) repulsive lone pair . . . β- and γ-alkyl interaction and (ii) β-methyl . . . axial β–H interaction.

INTRODUCTION

We have previously reported on the presence of different OH-rotamers in cyclohexanol and adamantanol-2 derivatives [1–4]. We demonstrated that the occurrence of the different rotamers is related to the presence and the orientation of α- and β-alkylgroups [4] and that the stretching frequency of each rotamer is highly dependent on the molecular structure in the OH environment [2].

The aim of this work is to obtain information about the sensitivity of the frequency of the different OH rotamers in axial cyclohexanols for γ-alkyl substituents in equatorial as well as in axial position. In consequence of rotation about the C–O axis the number of possible OH-rotamers is three, viz. A_x, B_x and C_x (Fig. 1). As these rotamers might be affected differently by the nature of the α-substituent we investigated next to methyl also ethyl and *tert*-butyl derivatives.

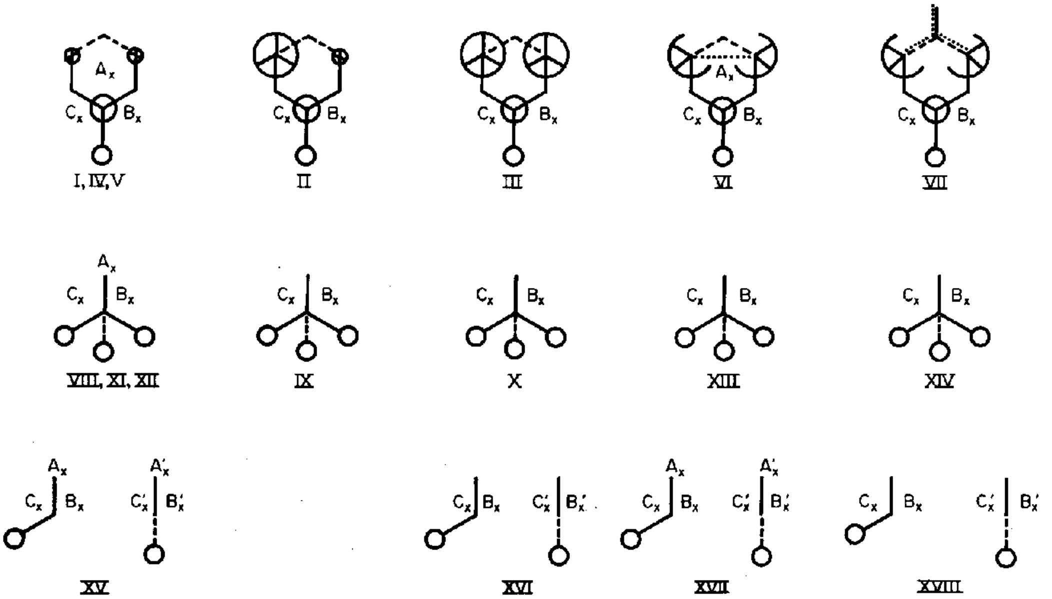
EXPERIMENTAL

Compounds

The synthesis of the compounds **I**, **III**, **VIII**, **X** and **XVI** has been described previously [2, 3, 6]. The methyl and *tert*-butyl derivatives **II**, **IV–VII**, **IX** and **XI–XIV** were prepared by condensation of the alkyllithium reagents and the ketones.

Reaction of the magnesium Grignard reagent of ethyliodide with the appropriate ketones in anhydrous diethylether produced the alcohols **XV**, **XVII** and **XVIII**. The alcohols were all purified by column chromatography (Silica gel 60 with hexane/ether as eluent).

Tricyclo[5.3.1.$0^{3,8}$]undecanone-5 and bicyclo[3.2.1]octanone-3 were a gift from Professor LAMATY. The ketones



I, IV, V II III VI VII
VIII, XI, XII IX X XIII XIV
XV XVI XVII XVIII

Fig. 1. Possible OH-rotamers for the compounds listed in Table 1. ⊘, OH-group; O—, CH_3-group; ⊗, axial H-atom, ⊖, axial CH_2-group; ⊘, axial CH_3-group; A, B, C, different rotamer positions and *x*, subscript pointing to an axial OH-group.

4-*tert*-butyl, 3,5-dimethyl, 3,3,5-trimethyl and 3,3,5,5-tetramethyl cyclohexanone were obtained commercially.

3-*tert*-Butyl cyclohexanol was a gift from Dr Peters. The analogous ketone was prepared by oxidizing the alcohol with chromic acid[7].

Spectra

The spectra have been run on a Perkin–Elmer 580B connected to a data station. Scanning conditions: mode 6-B-DB, resolution 0.6 cm^{-1}, data interval 0.5 cm^{-1}, region 3725–4381 cm^{-1}, Infrasil cells (10 mm), concentration 0.5 mg/ml CCl_4. The accuracies were: band frequency ± 0.5 cm^{-1} and α/β-ratio 8–15%.

Some of the compounds have been remeasured; the band parameters might therefore be slightly different from those reported before. Band-splitting experiments proceeded by means of the data station on the basis of adamantanol-1-like peaks differing only in intensity and frequency. In the compounds **XVII** and **XVIII** the OH-band of 5-*tert*-butyl tricyclo[5.3.1.$0^{3,8}$]undecanol-5, **XIV**, has been taken as a standard for splitting procedures, the

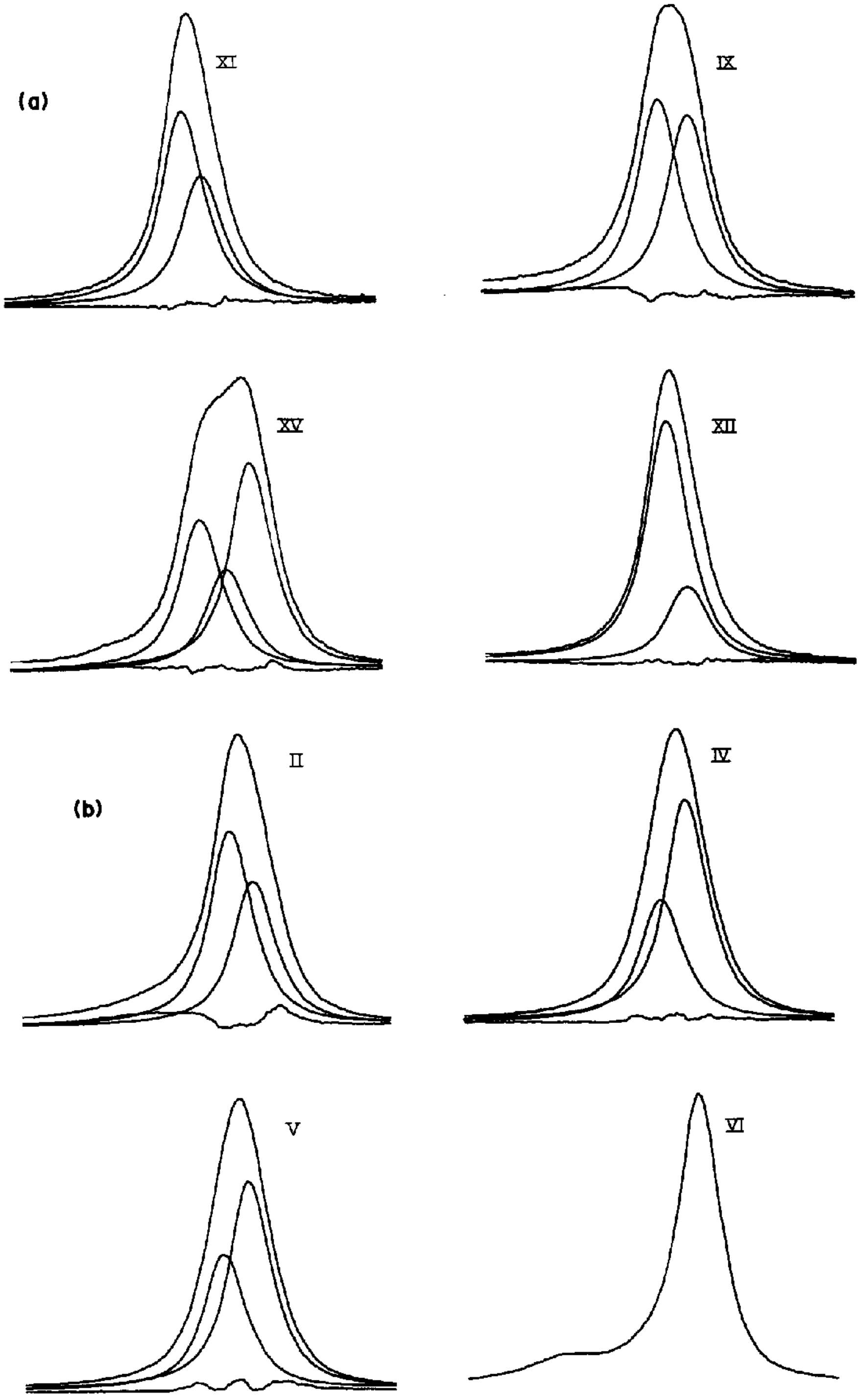


Fig. 2(a) and (b).

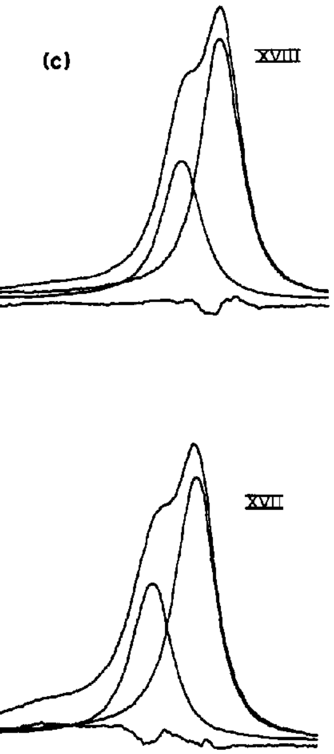


Fig. 2(c).

Fig. 2. The observed OH-absorption bands, S_{obs}, for some of the compounds listed in Table 1; absorption from 0.0 to 1.0. Where bandsplitting has been applied the contributing components, S_i, and the difference band $S_{obs} - S_{tot}$, are displayed underneath the observed band.

Table 1. OH-stretching band parameters for some tertiary cyclohexanols dissolved in CCl_4. Dimensions in cm^{-1} except for α/β which is dimensionless

NUMBER	COMPOUND	ν	$\Delta\nu_{\frac{1}{2}}$	α/β	ν-rotamers		
I	cyclohexanol(ax) 1-methyl,4-*tert*-butyl	3614.5	18.1	1.1	3620.0	3613.0	3613.0
II	" " 1,3,3,5-tetramethyl	3614.5	17.9	0.7		3610.5	3616.5
III	" " 1,3,3,5,5-pentamethyl	3610.5	14.6	0.9		3610.5	3610.5
IV	" " 1-methyl,3-*tert*-butyl	3614.0	17.5	1.3	3620.0	3613.0	3613.0
V	" " 1e,3e,5e-trimethyl	3615.0	17.9	1.0	3620.0	3613.0	3613.0
VI	bicyclo[3.2.1]octanol-3 3-methyl	3610.5	13.9	1.0	~3643	3610.5	3610.5
VII	tricyclo[5.3.1.$0^{3,8}$]undecanol-5 5-methyl	3606.5	13.6	1.1		3606.5	3606.5
VIII	cyclohexanol(ax) 1,4-di*tert*-butyl	3624.0	16.8	0.7	3625.0	3618.0	3618.0
IX	" " 1-*tert*-butyl,3,5,5-trimethyl	3623.0	19.0	1.0		3619.0	3627.0
X	" " 1-*tert*-butyl,3,3,5,5-tetramethyl	3620.0	12.2	1.1		3620.0	3620.0
XI	" " 1,3-di*tert*-butyl	3623.5	15.7	0.9	3625.5	3620.5	3620.5
XII	" " 1-*tert*-butyl,3e,5e-dimethyl	3624.0	15.6	0.8	3625.0	3619.5	3619.5
XIII	bicyclo[3.2.1]octanol-3 3-*tert*-butyl	3621.5	13.4	1.1		3621.5	3621.5
XIV	tricyclo[5.3.1.$0^{3,8}$]undecanol-5 5-*tert*-butyl	3616.5	12.5	0.9		3616.5	3616.5
XV	cyclohexanol(ax) 1-ethyl,4-*tert*-butyl	3611.0	25.4	1.7	3622.5	3608.5	3615.5
XVI	" " 1-ethyl,3,3,5,5-tetramethyl	3606.5	20.7	1.9		3605.0	3615.5
XVII	bicyclo[3.2.1]octanol-3 3-ethyl	3607.5	22.2	2.2	~3640	3606.5	3618.0
XVIII	tricyclo[5.3.1.$0^{3,8}$]undecanol-5 5-ethyl	3602.0	20.8	2.4		3602.0	3612.5

final result being better that way. A study on the factors influencing the OH-bandshape is under consideration. The difference between the observed band and the composed one has been used as a criterion for the correctness of the splitting. The accuracy was ±1 cm^{-1} not including small peaks for which it might be larger.

RESULTS AND DISCUSSION

We studied the OH-stretching vibration of 18 saturated axial tertiary alcohols in CCl_4 solution. The observed bands of the compounds that have not been previously published are displayed in Fig. 2; included are the separate bands derived from bandsplitting. The data of the overall bands and the frequencies of the separate rotamers are listed in Table 1. First we will assign the frequencies to the OH-rotamers of the compounds that have not been studied before. Next the frequencies are discussed in reference to the different γ-substituents.

OH ROTAMERS AND FREQUENCY ASSIGNMENT

Bandsplitting revealed that the OH-band of the compounds **IV** and **V** proves to be composed of two peaks at 3620.0 and 3613.0 cm^{-1}. The assignment to A_x and B_x ($= C_x$) follows easily in view of the frequencies reported earlier[2] for the comparable compound **I**. The small HBW value for **VII** points to the presence of just one type of rotamer. It follows that here too like in **III**[2] the position of the OH over the ring is prohibited as a result of strong sterical hindrance and that the frequency of 3606.5 cm^{-1} is to be assigned to $B_x(= C_x)$ therefore. The ν_d-values—the frequency differences between measurements in CCl_4 and CS_2—of 12.0 and 11.5 cm^{-1} for **III** and **VII**, respectively corroborate the correctness of the assignment as these values fully agree with those reported by VISSER and VAN DER MAAS[5] for B_x-rotamers in these type of molecules. The ν_d values for A_x-rotamers are in the range 4.5–8.0 cm^{-1}.

For **VI** we expected similar results, however, the observed band shows a small but distinct shoulder at the high frequency side (Fig. 2). We would like to attribute the sharp band at 3610.5 cm^{-1} to $B_x(= C_x)$ and the minor absorption to the A_x-rotamer despite the sterical interaction of the OH in this position. The ν_d values of the rotamers of this compound, 11.5 and about 3 cm^{-1}, support the assignment.

In principle for compound **II** one could think of three rotamers of which A_x will absorb at the highest frequency because of the axial γ-methyl group. As appears the observed OH-band can be successfully split into two peaks with frequencies at 3616.5 and 3610.5 cm^{-1} whereas there is not the slightest evidence for a peak at higher frequencies. Would A_x be present then one expects its absorption maximum between 3635 and 3650 cm^{-1} (cf. the A_x rotamer in compound **VI**). Therefore we conclude that A_x is absent and that $B_x \neq C_x$. Additionally this compound has been measured in CS_2 and again the observed band can be split into two peaks at 3605.0 and 3598.5 cm^{-1}. The ν_d values, 11.5 and 12.0 cm^{-1}, confirm that the peaks are to be assigned to B_x and C_x, the shifts being too large for an A_x-rotamer. Which frequency belongs to which rotamer cannot be decided at this stage. The frequency assignment of **XI** and **XII** follows easily from that of compound **VIII**[2], with $B_x(= C_x)$ at 3625.0 and A_x at 3618.0 cm^{-1}, as the rotamers absorb at almost the same wavenumbers: 3625.5 and 3625.0 cm^{-1} to $B_x(= C_x)$ and 3620.5 and 3619.5 cm^{-1} to A_x.

The frequencies of the OH-band of the *tert*-butyl compounds **X**, **XIII** and **XIV** are assigned to the $B_x(= C_x)$-rotamer for reasons already set out for the methyl analogues.

Bandsplitting of the composed band of **IX** brings about two peaks at 3627.0 and 3619.0 cm^{-1} (Fig. 2), which we attribute to B_x and C_x, in agreement with the assignment of **II**.

Based on earlier observations[2] we expected two different orientations of the ethyl group, *trans* and *gauche* (Fig. 3), in the ethyl substituted derivatives. The number of possible rotamers in compound **XV** will be five then, viz. A_x, A_x', $B_x = C_x$, B_x' and C_x'. Since a good fit is obtained when the OH-band is split into three peaks at 3622.5, 3615.5 and 3608.5 cm^{-1} we believe that $A_x \cong A_x'$ and $B_x \cong B_x'$. We would like to assign the highest frequency to A_x and in view of the data for the methyl derivative, **I**, no doubt the 3608.5 peak belongs to B_x and the 3615.5 one to C_x as the frequency of the latter rotamer should be raised due to the β-methyl group (shielding effect).

The maxima of the two peaks of **XVI** derived from bandsplitting have been assigned earlier[3]. For the compounds **XVII** and **XVIII** we propose a likewise assignment. The bandshapes are very much alike except for a minor contribution at the high frequency side in the latter, to be ascribed to the A_x-rotamer. The frequencies 3613.5 and 3618.5 cm^{-1} are assigned to C_x and the lower frequencies 3602.5 and 3607.5 cm^{-1} to B_x ($\cong B_x' = C_x'$).

OH ROTAMERS AND FREQUENCY SENSITIVITY

α-Methyl compounds

The absorption maxima of the separate rotamers within this series of compounds (Table 1) have been studied using those of the rotamers of 1-

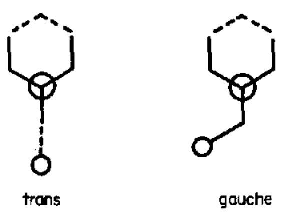


Fig. 3. Possible conformers for the α-ethyl substituted cyclohexanols. T, the ethyl group *trans* with respect to the C–O axis; G, the ethyl group *gauche*.

methyl,4-*tert*-butyl cyclohexanol(ax), **I**, as a starting point. Equatorial γ-substituents (**IV**, **V**) prove to have no effect, neither on the frequency of the A_x nor on that of the B_x and C_x rotamers. It follows that these substituents do not influence the OH surroundings considerably. From the compounds **III** and **VII** with two axial γ-alkyl substituents we conclude that (i) the A_x rotamer is prohibited and (ii) the frequency of the $B_x(=C_x)$ rotamer is shifted to lower wavenumbers. The A_x rotamer is also absent in **II**, with only one γ-methyl group. Evidently this group prevents the OH position over the ring and additionally gives rise to different frequencies for the rotamers B_x and C_x. In our opinion the latter phenomenon is the result of an interaction of the axial γ-methyl with the lone pair(s) of the oxygen atom thus directing the OH into different positions.

The data of 3-methyl bicyclo[3.2.1]octanol-3 (**VI**) demonstrate that all three rotamers are present. Apparently the two axial γ-methylenes in this compound and those in **VII** are differently positioned with respect to the OH. FOURNIER and WAEGELL[8] have studied the energies of the possible conformers and rotamers of **VI** and they have found the methyl group to be preferentially in the equatorial position; the energies of the A_x and $B_x(=C_x)$ rotamer have been calculated to be 130.2 and 123.5 kJ/mol respectively. Assuming a Boltzmann distribution this data leads to a contribution of 3% for the A_x rotamer which is in agreement with the observations.

From the absence of A_x in **III** and the identical B_x-frequency with respect to **VI** we conclude that the energy difference between the A_x and B_x rotamer will be larger than 6.7 kJ/mol.

So far we have found that a γ-alkyl substituent in equatorial position has no effect whereas in axial position it does influence (1) the presence of the A_x-rotamer and (2) the frequency of all rotamers. As these observations might depend on the type of α-substituent we pursued our study with some α-*tert*-butyl and α-ethyl derivatives.

α-tert-*Butyl compounds*

Comparing the frequencies of the rotamers of the α-*tert*-butyl compounds (Table 1) with those of 1,4-di*tert*-butyl cyclohexanol(ax), **VIII**, reveals that: (i) equatorial γ-alkyl substitution does not influence the OH vibration and (ii) axial γ-alkyl substitution not only prevents the presence of the A_x rotamer but also affects the frequency of the B_x and C_x rotamers.

As no extra bands appear compared with the α-methyl analogues we conclude that the α-*tert*-butylgroup demonstrates a similar "symmetrical" behaviour. In Table 3 the frequency difference for the corresponding rotamers, A_x B_x and C_x, in the α-methyl and α-*tert*-butyl substituted cyclohexanols have been listed for the various compounds.

Beforehand one should expect a frequency difference of 7–10 cm^{-1} for the B_x, C_x due to the presence of the shielding effect of the β-methyl group[4] and no effect at all for the A_x as the OH-surroundings seems to be the same in both type of compounds.

It appears that the rotamers B_x and C_x show a frequency increase of 5.0–11.0 cm^{-1}. For the A_x a shift of about 5 cm^{-1} is observed (Table 3) very likely the result of an interaction between the downwards orientated β-methyl of the *tert*-butyl and the axial β–H atoms of the ring (see Fig. 4). This assumption is supported by the observed frequency difference of the A_x-rotamers in 2-isopropyl- and 2-*tert*-butyl adamantanol-2[3] (3625–3640 and 3640–3660 cm^{-1}, respectively) which undoubtedly points to skeletal influence as the lone pair interaction will be the same in both compounds. However the influence of lone pair . . . β-CH_3 interaction cannot be excluded decisively within this series of alcohols. In our opinion the repulsive interaction is such that it even makes itself felt in the OH-surroundings. We believe that this interaction is also responsible for the absence of the A_x-rotamer in compound **XIII** as compared to the A_x in **III** the sterical hindrance will have been increased. Regarding its effect on A_x one should not be surprised to find also influence on the B_x- and C_x-rotamers. From the data in Table 3 it can be concluded that compounds with an axial γ-alkyl substituent show larger shifts (8.5–11.0 cm^{-1}) than the non-axially substituted compounds (5.0–7.5 cm^{-1}).

We suggest that not only the interaction with the

Table 2. OH-stretching band parameters for some tertiary cyclohexanols dissolved in CS_2

Compound	overall band			Δν for the rotamers			
number	ν	$\Delta\nu_{\frac{1}{2}}$	α/β	A_x	B_x	$B_x = C_x$	C_x
II	3601.0	20.6	1.0		3605.0*		3598.0*
III	3599.0	17.6	0.8			3599.0	
VI	3599.0	15.5	1.1	3640*		3599.0*	
VII	3595.0	16.3	1.1			3595.0	
IX	3611.5	23.5	1.4		3619.5*		3610.5*

*Maximum derived after bandsplitting.

Table 3. The frequency difference, $\Delta\nu$, between the corresponding A_x, B_x and C_x-rotamers of the α-methyl and α-*tert*-butyl compounds

Compounds		$\Delta\nu$ for the rotamers A_x	B_x	$B_x = C_x$	C_x
VII	XIV			10.0	
VI	XIII	Inacc.		11.0	
III	X			9.5	
II	IX		8.5		10.5
I	VIII	5.0		5.0	
IV	XI	5.5		7.5	
V	XII	5.0		6.5	

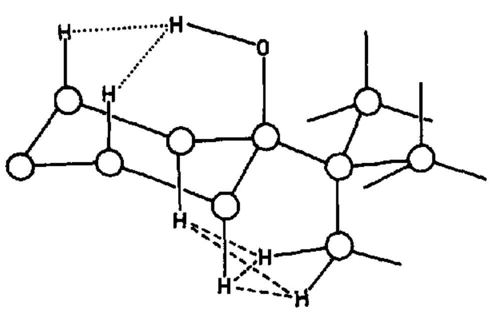


Fig. 4. The interaction between the downwards orientated β-methyl and the axial β-H atoms of the cyclohexylring (– – –) thus affecting the OH... γ-H interaction (· · ·).

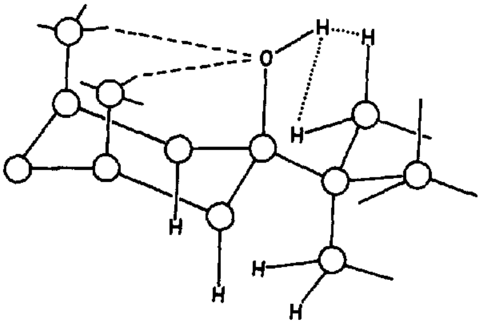


Fig. 5. The interaction of the axial γ-alkylsubstituents with the oxygen atom (– – –) thus affecting the OH... β-CH_3 interaction (· · ·).

Table 4. The frequency difference, $\Delta\nu$, between the corresponding A_x, B_x and C_x-rotamers of the α-methyl and α-ethyl compounds

Compounds		$\Delta\nu$ for the rotamers A_x	B_x	C_x
I	XV	+2.5	-4.5	+2.5
III	XVI		-5.5	+5.0
VI	XVII	Inacc.	-4.0	+7.5
VII	XVIII		-4.5	+6.0

β-methyl but also that of the axial γ-alkyl substituent(s) with the (lone pair of the) oxygen are involved (see Fig. 5).

α-*Ethyl compounds*

As follows from the assignment section the number of rotamers with clearly different frequencies in this type of compound is three or two (Fig. 1). This is because the OH in the A_x position behaves similar to that in the A_x' and furthermore $B_x \cong B_x' = C_x'$. It should be pointed out however that regarding the bandsplitting procedure minor frequency differences (1–2 cm^{-1}) cannot be excluded.

In Table 4 the frequency differences for the rotamers, A_x, B_x and C_x, with respect to the corresponding α-methyl ones are presented. The frequency lowering of the B_x-rotamers might be ascribed to (i) the interaction of the downwards orientated β-methyl with the axial β-H atoms of the ring and/or (ii) lone pair . . . β-methyl interaction thus giving rise to a different orientation of the OH-group with respect to the α-methylene group.

For the C_x-rotamers a frequency increase of 2.5–7.5 cm^{-1} is observed. Due to β-methyl shielding a frequency raise was to be expected. Obviously the compounds with an axial γ-alkyl show larger shifts (5.0–7.5 cm^{-1}) than the non-axially substituted compound XV (2.5 cm^{-1}). The C_x-rotamer is only present in the *gauche* conformer of each molecule where β-methyl... axial β-H interaction is absent. As the lone pair interactions in the α-ethyl series as well as in the α-methyl one are identical for rotamer C_x, we

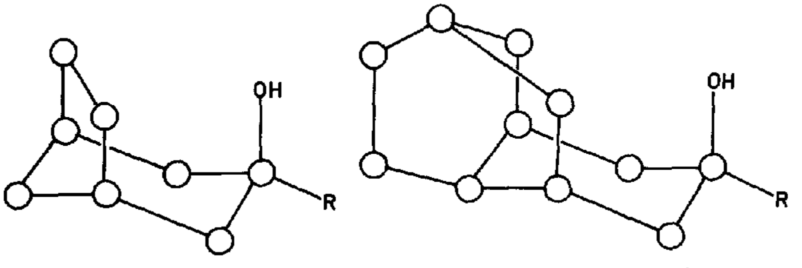


Fig. 6. The skeletal structures of bicyclo[3.2.1]octanol(ax) and tricyclo[5.3.1.0^{3,8}]undecanol(ax).

conclude that the frequency increase within "one pair" (e.g. **VII** and **XVIII**) is to be fully ascribed to OH . . . β-CH_3 interaction (shielding) whereas the mutual difference between the pairs has to be attributed to interaction of the axial γ-alkyl substituents with the (lone pair of the) oxygen.

As there is no evidence for a significant difference in the frequencies of A_x and A_x' in **XV** it follows that the observed difference of 2.5 cm^{-1} for this rotamer in **I** and **XV** (Table 4) in our opinion is due to β-CH_3 . . . lone pair interaction (G-conformer) and β-CH_3 . . . axial β-H interaction (T-conformer).

The frequency difference is small and detailed information regarding the ratio of the conformers T/G is absent; therefore conclusive evidence cannot be obtained from this data.

CONCLUSIONS

Reviewing the foregoing tends to some general conclusions in regard to the OH-stretching vibration of axial cyclohexanols in CCl_4:

(1) The OH-frequency is sensitive for the following intramolecular interactions (Figs. 4 and 5)

(i) repulsive lone pair . . . β- and γ-methyl(ene) and/or

(ii) β-methyl . . . axial β-H atom(s).

(2) Equatorial γ-alkyl substitution does not affect the OH-vibration.

(3) Axial γ-alkyl substitution reduces the presence of the A_x-rotamer considerably and influences the frequency of all rotamers.

(4) Variation of α-substituents influences the frequency of all rotamers.

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