

## Structural information from OH stretching frequencies—V. On the presence of different rotamers in substituted tertiary cyclohexanol compounds

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**Abstract**—The presence of different hydroxyl rotamers in a number of saturated acquatorial and axial tertiary cyclohexanols has been studied by means of the i.r. spectra of the OH stretching band. Band resolving experiments indicate that an OH positioned over a cyclohexylring contributes appreciably to the overall band. Frequencies have been assigned and the existence of some kind of non-bonding lone-pair effect has been established. Evidence has been found for a special type of rotamer in t,t,t-perhydrophenalen-9-ol.

### INTRODUCTION

The symmetry and/or doublet character of OH stretching bands of saturated alcohols in apolar solvents has been noticed first by PICCOLINI and WINSTEIN [1] in 1959. Several investigators have looked into this matter since [2–10] and have attributed the phenomenon to conformational heterogeneity. Nowadays it is known that the OH stretching band may contain contributions of possible skeletal conformers and rotamers.

OKI and IWAMURA [4] were the first who assigned frequencies to rotational isomers in aliphatic alcohols. In 1968 JORIS *et al.* [5] have assigned the rotamers in a number of cyclohexanol compounds, their key assumption being that the OH frequency is primarily determined by the type of rotamer and not by any other structural feature. They did not take into account frequency and bandshape determining effects such as fixation, shielding, substitution, nor solute–solvent interactions. As we know now [9, 11] these effects can have considerable influence on the final OH band and consequently on the assignment of frequencies to rotamers.

A study into more detail seemed to be useful for a better understanding of the presence of rotamers and their contribution to the overall OH-band.

The compounds to be investigated should have well-known and fixed skeletal structures to preclude the presence of different conformers. Therefore certain cyclohexyl compounds have been chosen, all with rings in the chair form. In order to prevent the compounds from possible axial/equatorial equilibrium and chair/boat inversion a tertiary butylgroup was used as a skeletal anchor [16]. At this stage primary and secondary alcohols have not been investigated as the presence of (an)  $\alpha$ -H atom(s) would unnecessarily enlarge the number of unknown effects.

If tertiary alcohols as defined above give rise to more than one absorption maximum in the OH-stretching region (or to a clearly deviating asym-

metry number) then apart from fortuitous circumstances different rotamers must be present.

From calculations and measurements [17] on the rotational barrier of the OH group about the C—O axis it is known that in saturated primary and secondary alcohols the height varies from 1.7 to 8.4 kJ/mol (=0.4–2 kcal/mol). The barrier for tertiary alcohols have not been reported but it is unlikely that completely free rotation will occur at ambient temperature.

### EXPERIMENTAL

**Compounds.** The 1-adamantyl derivatives XVIII and XIX have been prepared by reaction of 1-adamantyl-MgBr with the ketones. The Grignard reagent has been prepared from 1-adamantylbromide in anhydrous diethyl-ether according to the literature [12]. After the ketones were added dropwise the reaction mixtures were refluxed for 1 h and stored overnight at ambient temperature. Then the mixtures were poured into a separatory funnel containing a solution of  $\text{NH}_4\text{Cl}$  in (ice)water. The ether fractions were dried over  $\text{MgSO}_4$  and the alcohols were purified by column-chromatography. Aluminumoxide 90 (activity II–III) was the absorbent and hexane and ether the eluents.

The methyl- and *tert*-butyl-derivatives, XIV, XV, XVI, XVII were synthesized by condensation of the corresponding alkyl-lithium reagents with the appropriate ketones. The Li-compounds and the ketones were commercially obtained. The compounds VIII and IX were prepared according to the literature [13].

$^1\text{H}$ NMR investigations have pointed out that for the compounds XIV and XVII the favourable position for the OH group is the axial one [14]. Spectra: Scanning conditions and preparation techniques were as reported in [15]. The alcohols I, XI and X have also been measured in  $\text{CS}_2$ ; conditions as for  $\text{CCl}_4$ . Additionally the compounds I, VI, VIII–XI and XIII–XIX have been run on a Perkin–Elmer 580B connected to a Perkin–Elmer data station (CDS). Scanning conditions: Mode 6-B-DB, resolution  $0.6\text{ cm}^{-1}$ , data interval  $0.5\text{ cm}^{-1}$ , region  $3725\text{--}3481\text{ cm}^{-1}$ . Purity of the compounds  $\geq 90\%$ .

Band resolving proceeded by means of the CDS on the basis that the overall band is composed of two (or three) adamantanol-1-like peaks differing in intensity and in frequency. The difference band,  $S_{\text{obs}} - S_{\text{comp}}$ , has been used as a criterion for the correctness of the splitting.

## RESULTS AND DISCUSSION

## The equatorial rotamer

The OH stretching bandparameters of adamantanol-1 and some of its methyl substituted derivatives have been reported [15] earlier. No doubt the favourite OH position for this type of compounds is the one midway between two  $\beta$ -CH<sub>2</sub> groups thus resulting in only one equatorial rotamer,  $A_q$  (Fig. 1); the corresponding parameters are  $\nu = 3606\text{--}3607\text{ cm}^{-1}$ ,  $\Delta\nu_{\frac{1}{2}} = 12.2\text{--}14.0\text{ cm}^{-1}$  and  $\alpha/\beta = 0.9$  (See Table 1). Significant deviations from these halfbandwidths (=HBW) and  $\alpha/\beta$  ratios indicate the presence of at least a second type of rotamer; small changes may be due to differences in intra- and intermolecular interaction.

The agreement of the (HBW and  $\alpha/\beta$ ) data for the single rotameric adamantanol-1 derivatives (I–IV) with the compounds V–VII does not guarantee that only one rotamer is present as peaks may coincide accidentally because of different solute-solvent interaction. Measurements in the gasphase might provide a decisive answer with respect to the presence of rotamers but so far it has not been possible to obtain a useful gasspectrum at ambient

temperature. The frequencies of V, VI and VII have been shifted to higher wavenumbers due to the non-fixed  $C_\alpha\text{--}C_\beta$  axis [15]. Because of this higher frequency we conclude that the OH is positioned next to the methyl group,  $B_q$ , though  $A_q$  cannot be excluded (Fig. 1).

## THE AXIAL ROTAMER

Three fixed  $C_\alpha\text{--}C_\beta$  axes

First we studied the decalol compounds VIII and IX in which two or three types of rotamers might be present:  $A_x$ ,  $B_x$  and  $C_x$  (See Fig. 1). Would for *trans*-decalol the rotamer equilibrium be statistically determined the ratio should be 2:1 ( $A_x = B_x$ ). The band parameters as well as the bandshape for this compound clearly indicate the presence of two peaks. Band resolving with two adamantanol-1-like peaks brings about frequencies of 3624.0 and 3612.0  $\text{cm}^{-1}$  (See Fig. 2). For three reasons the low frequency is assigned to rotamer  $C_x$ :

- (i) the position of the OH for this rotamer resembles that for the  $A_q$ -one in adamantanol-1 with a frequency of 3606.0  $\text{cm}^{-1}$ ;
- (ii) the peak has the lowest intensity of the two;
- (iii) measurements in CS<sub>2</sub> followed by bandsplitting showed a difference in the lowering of the frequencies of the two rotamers. The high frequency is shifted by about 8  $\text{cm}^{-1}$  from 3624.0 to 3616.5 and the low one by about 11  $\text{cm}^{-1}$  from 3612.0 to 3600.5  $\text{cm}^{-1}$ . The latter agrees well with the shift for adamantanol-1 from 3606.0 to 3594.5  $\text{cm}^{-1}$  (CS<sub>2</sub>).

Consequently the other peak must be attributed to the  $A_x$  rotamer. This assignment fully agrees with that of JORIS *et al.* [5]. The skeletal structure of c,c,t-perhydrophenalen-9-ol (X) is to a large extent identical to that of *trans*-decalol (Fig. 1). The band of this compound X although similar to that of IX shows two maxima, viz. at 3624.7 and 3608.6  $\text{cm}^{-1}$  (see Fig. 2). Doubtless the splitting of the band arises from the fact that the low frequency component,  $C_x$ , has shifted somewhat to a lower wavenumber. We assume that this shift is due to changes in the environment of the OH group in the  $C_x$  position; the local structure has become more adamantanol-1-like. The frequencies in CS<sub>2</sub> confirm the assignment: 3617.5 (shift 7  $\text{cm}^{-1}$ ) and 3596.5 (shift 12  $\text{cm}^{-1}$ ) respectively. The two peaks in the band of compound X offer the possibility to determine approximately the HBW of each of them as the left wing of the  $A_x$ -peak is roughly free from a contribution of the  $B_x$ -one and the opposite holds for the right wing of  $B_x$ . A value of approximately 14  $\text{cm}^{-1}$  is found for both peaks that way. Evidently a different surroundings of the OH group is not necessarily accompanied by a different HBW.

Next we have examined the band of *cis*-decalol. At least two peaks should be present but band

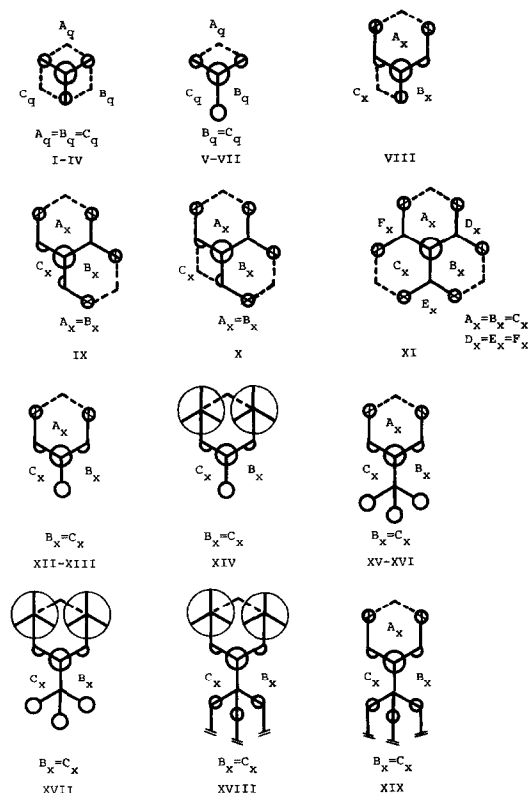


Fig. 1. Possible rotamers for the compounds as listed in Table 1. —○ non-fixed  $\beta$ -CH<sub>3</sub>-group; —⊖ fixed CH<sub>2</sub>-group; —⊖ fixed CH-group; ⊗ axial positioned H-atom; ⊕ OH-group; ⊕ axial positioned CH<sub>3</sub>-group; A, B, C rotamer positions between two  $\beta$ -C-atoms; D, E, F rotamer positions over a  $C_\alpha\text{--}C_\beta$ -axis; q, x subscript pointing to an aequatorial or axial OH group respectively.

Table 1. OH-stretching band parameters for some tertiary alcohols dissolved in  $\text{CCl}_4$ . Dimensions in  $\text{cm}^{-1}$  except for  $\alpha/\beta$  which is dimensionless

NUMBER	COMPOUND		$\nu$	$\Delta\nu_{\frac{1}{2}}$	$\alpha/\beta$
I	Adamantanol-1		3606.0	13.1	0.9
II	Adamantanol-1	3-methyl	3606.0	13.2	0.9
III	Adamantanol-1	4-methyl	3606.5	14.0	0.9
IV	Adamantanol-1	3,5,7-trimethyl	3607.0	12.2	0.9
V	5 $\alpha$ -Cholestan-3 $\beta$ -ol	3 $\alpha$ -methyl	3610.0	13.0	0.9
VI	Cyclohexanol (eq)	1-methyl, 4- <i>tert</i> -butyl	3610.0	13.2	0.9
VII	Cyclohexanol (eq)	1,3,3,5-tetramethyl	3609.2	14.5	0.9
VIII	Decalol-9 (cis)		3608.1	18.1	1.4
IX	Decalol-9 (trans)		3623.5	23.4	0.4
X	Perhydrophenalen-9-ol (cis, cis, trans)		3624.7	14 *	
			3608.6	14 *	
XI	Perhydrophenalen-9-ol (trans, trans, trans)		3611.6		
			3600.0		
XII	5 $\alpha$ -Cholestan-3 $\alpha$ -ol	3 $\beta$ -methyl	3615.0	16.2	1.0
XIII	Cyclohexanol (ax)	1-methyl, 4- <i>tert</i> -butyl	3614.3	17.0	1.1
XIV	Cyclohexanol (ax)	1,3,3,5,5-pentamethyl	3610.5	14.2	1.0
XV	Cyclohexanol (ax)	1- <i>tert</i> -butyl	3624.0	15.2	0.9
XVI	Cyclohexanol (ax)	1,4-di- <i>tert</i> -butyl	3624.0	15.8	0.9
XVII	Cyclohexanol (ax)	1- <i>tert</i> -butyl, 3,3,5,5-tetramethyl	3620.0	12.2	1.1
XVIII	Cyclohexanol (ax)	1-(1-adamantyl), 3,3,5,5-tetramethyl	3617.6	12.5	1.0
XIX	Cyclohexanol (ax)	1-(1-adamantyl), 4- <i>tert</i> -butyl	3620.8	17.2	0.9

separation revealed that a correct fit could only be obtained with three peaks, differing in frequency as well as in intensity. Maxima are found at 3621.5, 3610.0 and  $3606.0\text{ cm}^{-1}$  (see Fig. 2). Bearing in mind what has been said about *trans*-decalol and c,c,t-perhydrophenalen-9-ol we would like to assign the highest frequency to the  $A_x$ -rotamer where the OH is positioned over the ring and the lowest frequency to the  $C_x$ -one with the OH above the downwards-oriented cyclohexylring. This leaves

$3610.0\text{ cm}^{-1}$  for the the  $B_x$ -rotamer. The above-made assignment differs from that of JORIS *et al.* [5]; they only considered two rotamers. From the intensities it appears that the position of the OH over the ring is less favourable. In this series of polycyclic compounds we have finally studied t,t,t-perhydrophenalen-9-ol (XI). In view of the symmetric structure one would expect to find one rotamer of the  $A_x$ -type (Fig. 1) with an absorption band in the region  $3621\text{--}3625\text{ cm}^{-1}$ , a HBW of

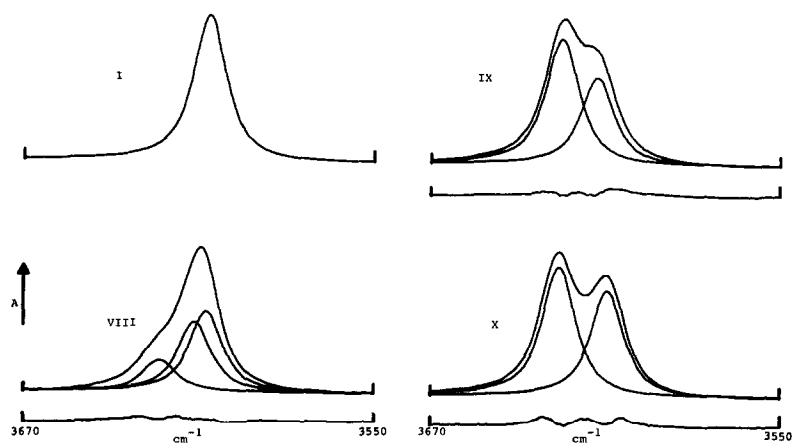


Fig. 2. The observed OH absorption band,  $S_{\text{obs}}$ , the peaks of the contributing rotamers,  $S_{\text{rot}}$ , as obtained by band resolving and underneath, the difference band  $S_{\text{obs}} - S_{\text{comp}}$ , where  $S_{\text{comp}} = \sum S_{\text{rot}}$ . Absorbance (A) for  $S_{\text{obs}}$  from 0.00 to 0.50. I Adamantanol-1; VIII *cis*-decalol; IX *trans*-decalol; X c,c,t-perhydrophenalen-9-ol.

12–14  $\text{cm}^{-1}$  and an  $\alpha/\beta$  ratio of 0.9. Surprisingly the OH-band proves to be split with maxima at 3511.5 and 3600  $\text{cm}^{-1}$  (Fig. 3). Considering that (i) compounds with just one type of rotamer never have given rise to more than one peak in  $\text{CCl}_4$  and (ii) there are two peaks in  $\text{CS}_2$  as well, we conclude that at least two rotamers must be present in this molecule. We assume that the second rotamer is the one with the OH above a  $\text{C}_\alpha\text{—C}_\beta$  axis ( $D_x$ , Fig. 1). The distance to the axial H-atoms,  $d(\text{OH} \dots \text{H})$ , is the same for both rotamers,  $A_x$  and  $D_x$ , and it is these short distances which are highly responsible for the possible positions and the corresponding probabilities. The distance to the  $\alpha$ -C-atoms,  $d(\text{OH} \dots \text{C})$ , is larger for  $A_x$  than for  $D_x$ . No doubt this will have some influence on the interaction(s) but not too much on the probabilities as  $d(\text{OH} \dots \text{H}) \ll d(\text{OH} \dots \text{C})$ . Splitting the band into its two components brings about an intensity ratio  $I_A/I_B$ , of approximately 0.9 and assuming equal extinction coefficients for both rotamers, an  $A_x/D_x$  ratio close to 1. The assumption seems reasonable in view of the small limits between which the coefficients for saturated tertiary alcohols are found (band areas roughly between 9 and 13  $\text{km/mol}$ ). The  $A_x/D_x$  ratio fits into the above-stated reasoning and so does the presence of two peaks. They indicate that the intramolecular interaction(s) for  $A_x$  and  $D_x$  have to be different as for reasons of symmetry the interaction with the solvent will be essentially the same.

In *trans*-decalol as well as in *c,c,t*-perhydrophenalen-9-ol the OH-group can have a position equal to the  $D_x$ -one in *t,t,t*-perhydrophenalen-9-ol, but we believe this situation to be unstable compared to the adjacent  $A_x$  (or  $B_x$ ) one where one of the lone pairs is situated between two  $\beta$ -C-atoms ( $C_c$ ).

#### Two fixed $\text{C}_\alpha\text{—C}_\beta$ axes and one $\alpha$ -alkyl substituent

From this type of tertiary alcohols we have

studied the axial cyclohexanol derivatives with a methyl-, *tert*-butyl- and 1-adamantyl-group. In all these compounds the  $\alpha$ -substituent can, though not completely free, rotate about the  $\text{C}_\alpha\text{—C}_\beta$  axis.

1-Methyl,4-*tert*-butylcyclohexanol (XIII) has two different rotamers, viz.  $A_x$  and  $B_x$  ( $=C_x$ ). Both, the HBW as well as the  $\alpha/\beta$  ratio indicate that the OH-band is composed of two peaks. Band resolving leads to frequencies of 3612.0 and 3618.5  $\text{cm}^{-1}$  (see Fig. 3). On the basis of the assignment for the decalols we would like to attribute the highest frequency to  $A_x$  and the lowest one to  $B_x$ . This is confirmed by the data to compound XIV, where two axial 3,5-methyl-groups prevent the position of the OH over the ring. In this compound the band is found at a low frequency and the HBW is small. From the intensities of  $A_x$  and  $B_x$  in XIII it follows that the former contributes considerably. That the frequencies of both  $B_x$ -rotamers, 3610.5 and 3612.0  $\text{cm}^{-1}$ , are slightly different is in our opinion due to changes in the skeleton forced by the methylgroups at the 3,5-positions. The OH-band of compound XII, 3 $\beta$ -methyl-5 $\alpha$ -cholestan-3 $\alpha$ -ol, in which cyclohexanol forms part of a larger skeleton is fairly identical with that of XIII, indicating once more that the OH group is only influenced by the local structure.

On going over from a methyl to a *tert*-butyl substituent we expected a frequency raise as the OH-group becomes more shielded in the  $B_x$  position (Fig. 1). The data of compound XVII confirm our expectation. For reasons set out above the  $A_x$  position is absent in this molecule thus leaving just one type of rotamer  $B_x$  ( $=C_x$ ); the HBW is small and the frequency increased compared to the methyl analogon. The shift is +10  $\text{cm}^{-1}$ . In the compounds XV and XVI two rotamers,  $A_x$  and  $B_x$ , might be present. The bands are fully identical and the HBW values of 15.2 and 15.8  $\text{cm}^{-1}$ , about 3  $\text{cm}^{-1}$  larger than for XVII, indicate the presence of two rotamers. Band resolving leads to peaks with

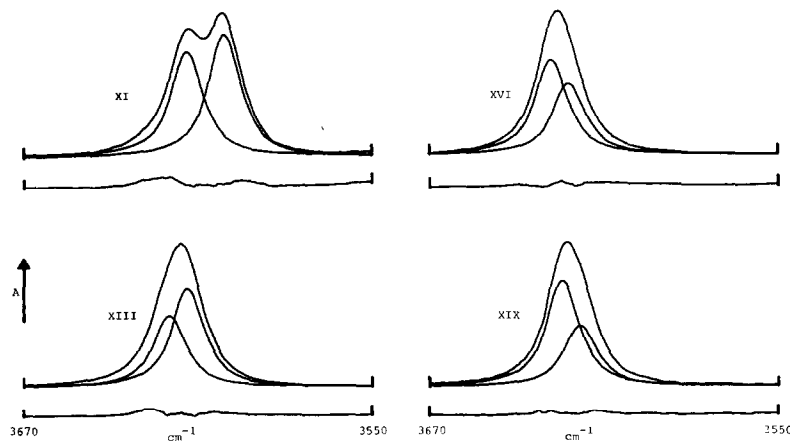


Fig. 3. The observed OH absorption band,  $S_{\text{obs}}$ , the peaks of the contributing rotamers,  $S_{\text{rot}}$ , as obtained by band resolving and underneath, the difference band  $S_{\text{obs}} - S_{\text{comp}}$ , where  $S_{\text{comp}} = \sum S_{\text{rot}}$ . Absorbance (A) for  $S_{\text{obs}}$  from 0.00 to 0.50. XI *t,t,t*-perhydrophenalen-9-ol; XIII 1-methyl,4-*tert*-butylcyclohexanol; XVI 1,4-di-*tert*-butylcyclohexanol; XIX 1-(1-adamantyl),4-*tert*-butylcyclohexanol.

frequencies at 3626.0 and 3620.0  $\text{cm}^{-1}$  (Fig. 3); the latter agrees best with the estimated value of 3612.0 (XIII) + 10  $\text{cm}^{-1}$  (shift) and is assigned to  $B_x$  therefore. The value for the  $A_x$ -type indicates that this rotamer is sensitive to the change in substituent.

Finally we studied the 1-adamantyl substituents XVIII and XIX, the main difference with the *tert*-butylgroup being the fixed character of the skeleton including the  $\beta$ -methylenegroups. Comparing the data of XVII and XVIII reveals that the HBW's are the same (one rotamer:  $B_x$ ) but that the frequencies differ by as much as 2.4  $\text{cm}^{-1}$  (less shielding in XVIII). Splitting the observed band of XIX into two peaks results in maxima at 3616.5 (estimated 3620.0 - 2.4 = 3617.6) and 3622.5  $\text{cm}^{-1}$  (Fig. 3) corresponding with  $B_x$  and  $A_x$ , respectively. Reviewing the foregoing tends to some general conclusions in regard to the OH-stretching vibration in  $\text{CCl}_4$ .

1. The frequency of an OH group is highly dependent on the local molecular structure in the OH environment. By consequence the within-one-molecule existing rotamers may have different frequencies. As the finally observed absorption band is composed of the (in frequency as well as in intensity) contributing rotamers no simple rule can be given beforehand for the OH band of tertiary alcohols.

2. The frequencies of the  $B_x$ -rotamers in the compounds XVII and XVIII compared to that of XIV, demonstrate once more the raising effect of shielding.

3. From the intensities of the  $A_x$ -rotamers in the compounds XIII, XV, XVI and XIX it follows that the position of the OH group over the cyclohexyl ring contributes appreciably. Furthermore it seems that the rigidity of the skeleton influences the extent in which this type of rotamer is present (cf. the intensities of  $A_x$  in VIII and XIII in Figs. 2 and 3).

4. As appears from the frequencies of the  $A_x$  and  $B_x$  rotamers in XVI and XIX the OH vibration is not only dependent on the position of its hydrogen atom but also on that of the oxygen lone pairs in the molecule. Hard figures regarding the separate contribution cannot be given yet as it is difficult to

establish changes in the molecular structure which only affect either the lone pair(s) or the hydrogen atom. Intermolecular *trans* lone pair interaction with  $\alpha$ -CH bonds (bonding interaction) have been reported earlier [18] for primary and secondary alcohols. In tertiary alcohols  $\alpha$ -CH bonds do not exist and consequently the lone pair effect must be of a different (non-bonding) type.

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