Structural information from OH-stretching vibrations—XIV. The influence of local interactions on the OH-stretching frequency in alcohols with an α-triple bond

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Abstract—The effect on the OH-stretching vibration of changes in the π-character of alcohols with an α-triple bond has been studied by means of the i.r. absorption band. It is demonstrated that in the investigated alcohols the OH . . . π interaction causes an increase of the OH-frequency as a result of the position of the OH-group with respect to that of the triple bond. Changes in the charge on the triple bond are reflected in the frequency: the larger the negative charge the higher the OH-frequency. Compared to saturated tertiary alcohols the accessibility of the hydroxyl for solvent molecules and hence the OH . . . solvent interaction is increased due to the absence of two (shielding) β-H-atoms. It turns out that the raising of the frequency caused by the triple bond is overruled by the lowering effect of the solvent.

INTRODUCTION

Earlier we reported on the interaction of the hydroxyl with a triple bond in tertiary α-ethynyl alcohols dissolved in CCl_4 [1]. As we demonstrated, the OH in these compounds is only present in a position next to the triple bond due to attractive and/or repulsive OH . . . π forces. In that position the OH-stretching frequency is found to be decreased 2–5 cm^{-1} compared to the corresponding rotamer in the α-methyl analogue.

A study on the OH in α-ethynyl and α-methyl steroids [2] revealed that substitution of the ethynyl proton by a methyl group is attended by a frequency increase of 2.5 cm^{-1}. In order to widen the insight into the factors determining the OH-stretching frequency of α-ethynyl compounds it seemed useful to study that effect in more detail. As one expects to find larger frequency shifts for more polar substituents we have looked for that type of molecule in particular.

EXPERIMENTAL

Spectra

The spectra were run on a Perkin–Elmer 580B connected to a PE3600 data station. Scanning condition: mode 6-B-DB, resolution 0.6 cm^{-1}, data interval 0.5 cm^{-1}, region 3725–3481 cm^{-1}. Accuracy bandmaximum 0.5 cm^{-1}, HBW ± 0.7 cm^{-1}, α/β-ratio 8–15 %. The alcohols in CCl_4 and CS_2 solution were measured in "infrasil" cells (10 mm) against dried air and a concentration of 0.5–1.0 mg/ml solvent. Gas-phase spectra were recorded with 10 cm KBr cells against dried air; vapour pressure at ambient temperature.

Compounds

Tert. butanol was obtained commercially. Compounds II–IV, IX and X were synthesized according to the literature [3] by the reaction of the corresponding ketones with propynyllithium and ethynyllithium respectively in hexane/THF solution. The steroids V, VI and XI were a gift from Organon Nederland B. V. Sample XII was synthesized by Dr. H. WESTMIJZE, Laboratory of Organic Chemistry,

University of Utrecht and the alcohols I, VII, VIII and XIII–XX were supplied by Professor L. BRANDSMA from the same laboratory. The purity of all compounds was ≥ 95 % (GLC checked).

RESULTS AND DISCUSSION

First we studied the α-propynyl compounds I–VI in order to establish the variancy of the OH-stretching frequency on substituting the ethynyl proton by a methyl group. As expected both the HBW and the α/β-value of all observed bands (Table 1) point to just one type of rotamer which we assign according to earlier work [1, 2] to an OH positioned next to the triple bond i.e. the B-rotamer or B(= C) (Fig. 1). Comparing the data of these α-propynyl compounds with those of the corresponding α-ethynyl analogues (VII XII) reveals that the frequency increase of the former appears to be fairly constant, viz. 2.5–3.5 cm^{-1}.

Next we studied the 2-ethynyl 2-propanol derivatives XIII–XX (Table 2) to find out whether other types of substituents give rise to different shifts. As in the case of the compounds I–XII the observed HBW- and α/β-values prove that the bands are monorotameric,
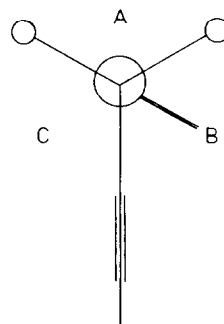

Fig. 1. Preferential OH–rotamer for the α-ethynylalcohol derivatives as listed in Tables 1 and 2.

Table 1. OH-Stretching band parameters for some tertiary α-ethynyl- and α-propynyl alcohols dissolved in CCl₄. Dimensions in cm⁻¹ except for α/β which is dimensionless

Compound	Substituent at	-Propynyl				-Ethynyl				
		No.	ν	HBW	α/β	No.	ν	HBW	α/β	Δν
Propanol-2	2	I	3613.5	14.4	0.8	VII	3611.0	14.6	0.8	2.5
Cyclopentanol	1	II	3612.5	14.0	0.9	VIII	3609.5	17.8	0.8	3.0
Cyclohexanol	1 3,3,5,5-tetramethyl	III	3610.0	14.7	0.6	IX	3606.5	14.5	0.8	3.5
Cyclohexanol	1 3,3,5-trimethyl	IV	3613.0	14.4	0.6	X	3609.5	15.1	0.7	3.5
Estratriene	17α 3β-methoxy, 17β-ol	V	3616.0	14.8	0.7	XI	3613.5	15.4	0.6	2.5
Estratriene	17β 3β-methoxy,17α-ol	VI	3615.0	14.7	0.7	XII	3612.5	15.9	0.7	2.5

obviously the B(= C)-position. The observed OH-frequencies vary between 3613.5 and 3607.5 cm⁻¹. As the skeletal structure in the OH-surroundings is identical for all compounds the observed frequency differences must be the result of one of the following effects:

(i) non-bonding OH . . . substituent interaction, but as the shortest possible internuclear distance between the OH-proton and the substituent is ≥ 3.9 Å such effect is highly improbable and rejected therefore.

(ii) an (inductive) through-bond effect on f_{OH}, but this is not very likely either as the distance is (too) large. According to BRUTAN and FADEEV [4] such effects are known to fall off very rapidly on increasing distance. This is endorsed by the results of LAURENCE and BERTHELOT [5] who measured practically identical OH-frequencies for various meta- and para-substituted benzyl alcohols (also alcohols with an α-π-system).

(iii) changes in the π-system which affect the OH . . . π interactions, i.e. the proton . . . π attraction and/or oxygen–lone-pair . . . π repulsion.

Were there no nuclear . . . nuclear repulsive forces the OH should be positioned right above the C–C≡C axis (dihedral angle 0°). In that position the direction of the OH . . . π attraction is almost perpendicular to the direction of the OH-vibration (Fig. 2) and as the influence on the vibration is proportional to the cosine of the angle φ between the directions of the interaction and the vibration it follows that the OH-frequency will be hardly influenced by changes in the OH . . . π interaction then. We have observed frequency differences up to 6 cm⁻¹ for the various ethynyl substituents so the OH must be positioned between the C–C≡C and one of the C–CH₃ groups (dihedral angle between 0 and 120°). It confirms the presence of nuclear–nuclear repulsions at these distances. This is in agreement with the results of both HIROTA [6] who measured a dihedral angle of 59 ± 3° for 1-propyn-3-ol, and BENDAZOLLI et al. [7] who calculated 54° for the same compound attributing the barrier to nuclear- and Coulomb-repulsions.

Changes in the dihedral angle are attended not only with changes in φ but also in the distance OH . . . π, consequently changing the OH . . . π interaction. A
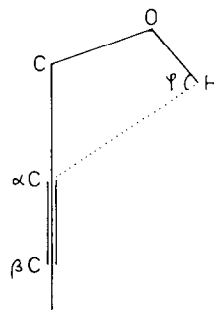

Fig. 2. Angle φ between the direction of the OH-vibration and the H . . . α–C ≡ attraction at dihedral angle 0°.

Table 2. OH-Stretching band parameters and v_d-values for some tertiary 3-methyl-1-butyn-3-ol derivatives dissolved in CCl_4. Dimensions in cm^{-1} except for α/β which is dimensionless

No.	Compound	v	HBW	α/β	v_d
	$(CH_3)_2C(OH)-C \equiv C-$				
VII	–H	3611.0	14.6	0.8	12.5
I	–CH_3	3613.5	14.4	0.8	12.0
XIII	–C_4H_9	3613.5	14.0	0.9	12.0
XIV	–$C(CH_3)_3$	3612.0	16.0	0.9	
XV	–CH_2-O-CH_3	3611.5	15.5	1.0	13.5
XVI	–$CH_2-S-C_2H_5$	3611.0	15.1	0.7	12.0
XVII	–$C-C(CH_3)_2OH$	3612.0	15.3	0.6	14.0
XVIII	–$C \equiv C-C(CH_3)_2OH$	3607.5	14.0	0.9	13.0
XIX	–Cl	3609.5	14.5	0.8	12.5
XX	–C_6H_5	3610.5	14.8	0.8	13.5

dihedral angle between 0 and 120° leads up to φ-values between 84 and 30° and thus to $\cos \varphi$ between $+0.10$ and $+0.87$, while the OH ... π distance varies between 2.3 and 2.9 Å. The positive sign of $\cos \varphi$ implies that, irrespective of the precise value of the dihedral angle, the OH ... π attraction causes a shortening of the OH-bond and thus an increase of the OH-frequency.

Referring to the extended work of ARMAND and ARNAUD [8,9] on α-ethenyl alcohols, electron donating substituents will induce a negative charge on the triple bond sp-atoms thus increasing the OH-proton ... π attraction. Consequently substitution of the ethynyl proton by electron-donating groups should give rise to an increase of the OH-frequency whereas for electron-drawing substituents the opposite effect should be observed. Indeed as can be seen from Table 2 the frequencies which are significantly higher than the ethynyl compound VII correspond to alcohols with electron-donating subsituents [10] whereas the decreased frequencies belong to either an electron-accepting group or a structural element giving rise to conjugation.

As appeared from our earlier work [1] in CCl_4-solution the α-ethynyl alcohols show a lower OH-frequency than the saturated α-methyl analogues. It follows that this must be the result of either a different through-bond (α-methyl vs α-ethynyl) effect and/or an increased OH ... solvent interaction. To get an insight into this matter one should have the gas phase frequencies at hand. The volatility at ambient temperature allows measurement of the compounds I, VII and

XIX. Compared with the vapour phase value of the α-methyl analogue of these compounds, i.e. tert. butanol, the frequencies of the (substituted) ethynyl compounds are higher (Table 3) once more confirming the increasing effect of a triple bond in the α-position. Moreover the frequencies show the same order as in CCl_4, solution which endorses the effect of the ethynyl-substituents on the π-character.

Besides it can be concluded now that the larger frequency decrease of the ethynyl compounds on going over from the gas phase to solution ($35 \, cm^{-1}$) compared to the shift of the tert. butanol frequency ($27 \, cm^{-1}$) must be the result of a larger OH ... solvent interaction. For additional information about this phenomenon we measured the compounds in CS_2 in order to obtain the v_d-values of the OH-bands since, as we have set out elsewhere [11], these values are related to the amount of shielding of the OH from solvent-interactions by its local environment. It appears (Table 2) that the observed solvent shifts of $12.0-14.0 \, cm^{-1}$ are, on average, $1-2 \, cm^{-1}$ larger than those of similar α-methyl rotamers, thus pointing to a larger OH ... solvent interaction. This must be the result of a decreased shielding of the OH, i.e. a more "open" position due to the absence of the protons of the substituted methyl group.

Summarizing we conclude that in the investigated tertiary alcohols with a triple bond in the α-position the OH-stretching frequency is influenced by the OH-proton ... π attraction. The effect is frequency-increasing while its magnitude depends on (i) the distance OH ... π, (ii) the angle φ between the

Table 3. OH-Stretching frequencies for some tertiary alcohols in the gasphase and dissolved in CCl_4

Compound		v_{gas}	v_{CCl_4}	Δ
Propanol-2	2-methyl	3643.0	3616.0	27.0
1-Butyn-3-ol	3-methyl	3646.5	3611.0	35.5
2-Pentyn-4-ol	4-methyl	3648.5	3613.5	35.0
1-Butyn-3-ol	3-methyl, 1-chloro	3646.0	3609.5	36.5

directions of the OH-vibration and the OH . . . π attraction and (iii) the charge on the α- (and β-) sp-atoms. In CCl_4 solution the OH . . . solvent interaction causes a frequency decrease of about 35 cm^{-1} which is approximately 8 cm^{-1} larger than in the corresponding α-CH$_3$ alcohol due to absence of two (shielding) β-H-atoms.

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