Spectrochimica Acta, Vol. 39A, No. 3, pp. 241–244, 1983
Printed in Great Britain.

0584–8539/83/030241–04$03.00/0

Structural information from OH stretching frequencies—XI. The orientation of the hydroxyl group in tertiary α-ethynyl alcohols

T. Visser and J. H. Van der Maas

Laboratory for Analytical Chemistry, University of Utrecht, Croesestraat 77A, 3522 AD Utrecht, The Netherlands

(*Received* 21 *July* 1982)

Abstract—The presence of different OH-rotamers in 11 tertiary α-ethynyl alcohols dissolved in CCl_4 has been studied by means of the i.r. absorption band. In all compounds the hydroxyl appears to be present only in a position next to the triple bond. It is demonstrated that this phenomenon arises from OH . . . π interactions. The existence of OH . . . π hydrogen bonding could not unambiguously be established. Like in saturated compounds the orientation of the OH proves to be influenced by β- and γ-CH_3 groups.

INTRODUCTION

The phenomenon of intramolecular interactions between a hydroxyl group and π-systems has been subject to numerous studies. Most of the work in this field concerns interactions with double bonds, especially aromatic rings; less attention is paid to triple bonds. The interaction is generally described as some type of hydrogen bonding, the origin being attractive forces between the OH-proton and the unsaturated linkage. Some authors suggest involvements of other effects. Abraham and Bakke[1] concluded that in benzyl alcohol intramolecular hydrogen bonding in the generally accepted sense of the word is absent, Baker and Dyall[2] attributed the preference for the hydrogen bonded conformers in benzyl and naphthylbicycloheptanols to strong repulsive forces between the oxygen-lone-pair orbitals and the aromatic π-orbitals. According to Zushi, Uzawa and Kodama *et al.* [3–5] attractive CH . . . π interactions also play an important role in the occurrence of hydrogen bonded conformers in β-phenyl-alkanols.

From our work on OH-stretching bands [6] we already know that the distribution of the hydroxyl over its possible rotamers in saturated alcohols, is influenced by the presence/absence of alkyl groups in its local environment. Following that study it seems useful to investigate whether these effects are transferable to unsaturated alcohols. Besides it might widen the insight into the effect(s) which form the basis of OH . . . π interactions. The cylinder-symmetrical triple bond is better suited for a study on this subject than the less symmetrical double bond. Investigations concerning this type of compounds appear to be limited to a few [7–13]. Moll[7] and Von R. Schleijer[8] reported the distribution of the OH over the free and the bonded conformer/rotamer to be influenced by the distance OH-triple bond; the smaller the distance the larger the contribution of the bonded conformer/rotamer, and the lower its frequency. These authors, as well as Nyquist[9], Bendazolli *et al.*[10] and Hirota[11], have established the absence of the non-bonded (*trans*) rotamer in 1-propyn-3-ol while Lutz and Van der Maas[13] have observed the same phenomenon in some secondary α-ethynyl alcohols. A study on tertiary ethynyl alcohols would offer the possibility on the one hand to reduce the number of conformational isomers, on the other hand to investigate the influence of various alkyl substituents. In view of the preceding studies on saturated tertiary alcohols [6, 13–19] the choice of the α-ethynyl analogues seems to be a logical step.

EXPERIMENTAL

Compounds

Compounds **I** and **V** were synthesized according to the literature [21] by the reaction of the corresponding ketones with ethynyl-lithium in hexane/THF solution. The alcohols **II–IV**, **VIII**, **IX** and **XI** were prepared by the condensation of the ketones and ethynyl-lithium in liquid ammonia. The compounds **VI**, **VII** and **X** were a gift from Professor L. Brandsma, University of Utrecht.

Spectra

The alcohols were measured in CCl_4 in Infrasil cells (10 mm) against air, concentration 0.5–1.0 mg/ml. Purity > 95% (GLC checked). The spectra were run on a Perkin–Elmer 580B connected to a Perkin–Elmer data station. The scanning conditions were: mode 6-B-DB, resolution 0.6 cm^{-1}, data interval 0.5 cm^{-1}, region 3725–3481 cm^{-1}. Accuracy: band frequency ± 0.5 cm^{-1}, HBW ± 1.0 cm^{-1}, α/β-ratio 8–15%.

RESULTS AND DISCUSSION

In order to avoid the presence of (skeletal) conformational isomers we first studied the α-ethynyl (cyclic) alcohols **I–V** which have a fixed skeletal structure (Fig. 1). Although the observed OH stretching band for each of these compounds appears to be slightly asymmetric (α/β-value 0.7–0.8) the small HBW (14.4–15.4 cm^{-1}) suggests the presence of just one type of rotamer.

In compound **I** the two axial (3, 5-) methyl groups prevent position A [15] and thus the observed band at 3606.5 cm^{-1} has to be assigned to rotamer B = C. As

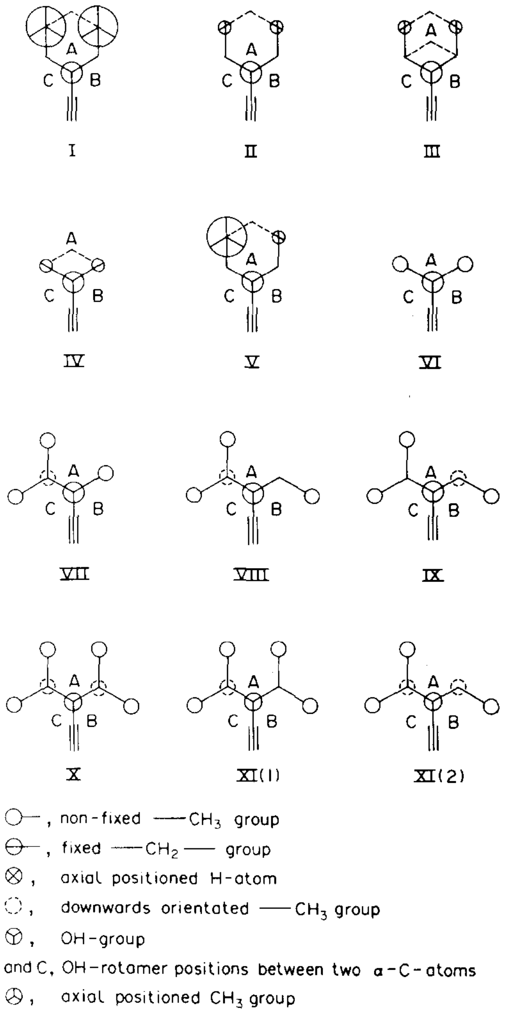

Fig. 1. Possible OH-rotamers for the α-ethynyl compounds listed in Table 1.

can be seen from Table 1 its frequency is 4 cm^{-1} lower than the one of the saturated α-methyl analogue. Apparently the effect of the triple bond for this rotamer is a frequency decrease.

We then studied the compounds **II** and **III** with frequencies at 3610.0 and 3608.5 cm^{-1}, respectively. An assignment to the A-rotamer is rejected since it is unlikely that the frequency of this rotamer would decrease by as much as 10–14 cm^{-1} on going over from α-CH_3 to an α-ethynyl group. An assignment to the B(C) rotamers agrees well; the frequencies are almost identical with that of compound **I** and so are the differences with respect to the saturated α-methyl analogues (3.0 cm^{-1} for both). Besides, as the two OH-bands do not show a shoulder at the high frequency side it follows that the B(C) rotamer is the only one present. The preference for the B(C) position must be the result of OH . . . π interaction, i.e. proton . . . π attraction and/or oxygen-lone-pair . . . π repulsion. For these investigated α-ethynyl compounds both interactions (if present) tend to the same situation: a position of the proton next to the triple bond. Such a position is reported also for the crystalline 2-ethynyl-adamantanol-2 (compound **III**) by LIN *et al.* [20].

In compound **IV** the OH-surroundings in the A-position resemble that in adamantanol-1 (frequency 3606.0 cm^{-1}) and in the B(C)-position that in **I**–**III** (frequencies 3606.5–3610.0 cm^{-1}). The observed data point to the presence of one (or two coinciding) peak(s). As we do not have data for the A-rotamer its presence in this molecule cannot be ascertained. However, in view of the absence of A in **II** and **III** we would like to attribute the observed frequency of 3607.5 cm^{-1} to the B(C)-rotamer. The decrease of 2.5 cm^{-1} compared to the saturated α-methyl analogue agrees well with this reasoning.

We can now summarize the results for the OH-band of the α-ethynyl compounds **I**–**IV** as follows: (i) frequency 2.5–4.0 cm^{-1} lower compared to the α-methyl analogue, (ii) HBW 14.4–15.5 cm^{-1} and (iii) α/β-value 0.7–0.8. Besides the A-rotamer is absent as it seems.

We then synthesized and measured compound **V**. Both the HBW (15.1 cm^{-1}) and the α/β-value (0.7) resemble those of **I**–**IV** pointing to just one type of rotamer. As the axial γ-methyl group prevents position A [18] an assignment to B = C seems to be obvious. However, as LUTZ and VAN DER MAAS reported [18, 19]

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

	Compound			α-Ethynyl		α-Methyl	
			ν	HBW	α/β	ν_1	ν_2
1	cyclohexanol (ax)	3, 3, 5, 5-tetramethyl	3606.5	14.5	0.8		3610.5
II	cyclohexanol (ax)	4-*tert*-butyl	3610.0	15.4	0.8	3620.0	3613.0
III	adamantanol-2		3608.5	15.3	0.7	3632.5	3611.5
IV	cyclohexanol (eq)	4-*tert*-butyl	3607.5	14.4	0.7		3610.0
V	cyclohexanol (ax)	3, 3, 5e-trimethyl	3609.5	15.1	0.7	3616.5	3610.0
VI	propanol-2		3611.0	14.6	0.8		3616.0
VII	butanol-2	3, 3-dimethyl	3618.5	13.4	0.7		3623.5
VIII	pentanol-3	2, 2-dimethyl	3623.5	13.5	0.8		
IX	pentanol-3	2, 4-dimethyl	3623.5	14.9	0.8		
X	pentanol-3	2, 2, 4, 4-tetramethyl	3628.5	11.7	0.7	3633.0	3625.0
XI	pentanol-3	2, 2, 4-trimethyl	3628.0	15.1	0.7		

for the α-methyl analogue B ≠ C due to strong repulsive forces between the axial γ-methyl group and the oxygen-lone-pairs. This repulsion is thought to initialize a clockwise distortion of the OH around the C–O axis resulting in different positions and thus different frequencies. In the α-ethynyl compound the two other effects which are involved in the orientation of the hydroxyl: (i) OH . . . π attraction and (ii) oxygen-lone-pair . . . π repulsion also tend to a rotation of the OH, clockwise for the B-rotamer, but anti-clockwise for the C. The total effect of both the α-methyl and the α-ethynyl group on the position of the OH cannot be predicted as neither the strength of the interactions relative to each other, nor the precise relation between the position of the hydroxyl and its frequency, are known. Compared to the α-methyl analogue the difference between the B- and the C-rotamer might therefore increase, probably favouring the absence of one of them or decrease possibly leading to B = C. The frequency differences of 0.5 and 7.0 cm^{-1} do not bring a decisive answer any nearer. Yet, the influence of the triple bond on the frequency of the OH is evident.

In order to see whether the observed effects also occur in molecules with non-fixed C–C axes we studied the compounds **VI–XI**. In 3-methyl-1-butyn-3-ol (**VI**) two types of rotamers can be distinguished, namely A and B(C). The data of the observed band, however, point to the presence of only one and as the frequency of 3611.0 cm^{-1} is in close agreement with those already attributed to B(C) in **I–IV** we assign the band accordingly. The frequency difference of 5.0 cm^{-1} compared to the corresponding α-methyl derivative endorses the correctness of the assignment.

In compound **VII** three different OH-positions can be distinguished, namely A, B and C. As can be seen from Table 1 both the HBW (13.4 cm^{-1}) and the α/β-value (0.8) point to the presence of just one peak at 3618.5 cm^{-1}. An assignment to rotamer B is rejected as its frequency should have been like those of B(C) in **I–IV**, i.e. 3606.5–3611.0 cm^{-1}. Its absence proves that next to OH . . . π also OH . . . β-CH_3 interactions play a role in the orientation of the hydroxyl in this molecule. The latter type of interaction has been established earlier [18]. The absence of B implies that both oxygen-lone-pair . . . β-CH_3 attraction and OH-proton . . . β-CH_3 repulsion can be left out of the question which leaves oxygen-lone-pair . . . β-CH_3 repulsion and OH-proton . . . β-CH_3 attraction. Both effects, if present, cause equal probabilities for the A and the C-position. For the following reasons we would like to assign the observed band to the C-rotamer:

(a) compared to the C(= A) rotamer of the α-methyl analogue the frequency decrease falls within the usual range (2–5 cm^{-1});
(b) compared to **VI** the shielding effect [22] of the adjacent β-methyl shows the normal increase of 7–12 cm^{-1};
(c) so far the A-rotamer has not been observed in the investigated ethynyl compounds.

The number of different types of rotamers in compound **VIII** depends on the orientation(s) of the ethyl group. Regarding repulsive forces between the methyl groups of the ethyl and the *tert*-butyl the former will likely be present in a position as indicated in Fig. 1. The observed HBW (13.5 cm^{-1}) and the α/β-value (0.8) point to the presence of just one peak. Would oxygen-lone-pair . . . β-CH_3 repulsion be completely absent then B (**VIII**) = C (**VIII**) = C (**VII**). However, as the frequencies (and thus the OH-positions) of **VII** and **VIII** are different, it follows that such repulsion is clearly present resulting in B ≠ C for **VIII**. Whether the peak is to be assigned to B or C cannot be decided straightforward from the observed data. However some preference for the C-rotamer might be derived from the fact that in that position the third orientated β-methyl group reinforces the clockwise rotation of the OH (compared to **VII**) thus explaining the frequency difference.

Additionally we studied compound **IX**. Mutual steric interactions between both *iso*propyl groups will lead to a conformer as presented in Fig. 1 with the *gauche* orientated β-methyls as in **VIII**. Consequently one should find identical frequencies for both compounds as is the case.

Next we synthesized and measured 3-ethynyl-2,2,4,4-tetramethyl pentanol-3 (**X**). As can be seen from Table 1 one single band is observed at 3628.5 cm^{-1} with a very small HBW (11.7 cm^{-1}). Occasionally we have measured such small HBWs before [15, 16] and without exception it concerned compounds with bulky groups in the vicinity of the OH. Undoubtedly the steric interaction in this molecule between both *tert*-butyl groups will give rise to an asymmetric orientation of these groups with respect to the C–O axis which may lead to A ≠ B ≠ C. However, as the hydroxyl will be involved in this orientation too, we suppose that the final result will be identical (mirrored) positions for the OH whether in B or in C thus reducing the number of different rotamers to two [A and B(C)]. Regarding the results of the preceding compounds an assignment of the observed band to B(C) seems obvious, but the observed OH-frequency difference with the B(C) of the α-methyl analogue would be positive (+3.5 cm^{-1}) then. As it is reasonable to suppose that substitution of the α-CH_3 by an α-ethynyl does not appreciably influence the orientation of the *tert*-butyl groups, we considered that the saturated compound could have been erroneously assigned. Thereupon we measured the α-methyl compound in CS_2 in order to be able to use the ν_d-values for further evidence [17]. The ν_d of 2.5 cm^{-1} for the 3625.0 cm^{-1} peak clearly points to the (shielded) A-rotamer and the 10.5 cm^{-1} for the 3633.0 cm^{-1} band to the more open B(C) structure. So we conclude that the assignment for the α-methyl derivative has to be reversed. Now the band of **X** appears to be 4.5 cm^{-1}

lower than the B(C) one of the saturated analogue which corroborates the assignment to B(C).

Finally we studied 3-ethynyl-2,2,4-trimethylpentanol-3 (**XI**). In principle the *iso*propyl group in this molecule may be present in three different orientations but very likely, one of them will be absent due to the large repulsive forces between the CH_3s of the *tert*-butyl and the *iso*propyl. This leaves, with equal probabilities, the two conformers **XI**(1) and **XI**(2) as shown in Fig. 1. The oxygen-lone-pair . . . β-CH_3 repulsion will favour position C of **XI**(2), a situation as in **IX**, possibly even resulting in the absence of **XI**(1). Comparing the data of **XI** and **IX** reveals that the HBWs are practically identical whereas the frequencies differ, likely due to somewhat different β-CH_3 orientations. It should be noted however that the observed data do not allow to exclude the presence of **XI**(1).

CONCLUSIONS

In the investigated α-ethynyl alcohols the orientation of the hydroxyl appears to be determined by two types of interaction: (i) with the triple bond, leading to the absence of rotamer A and (ii) with neighbouring alkyl groups favouring B or C. The absence of A proves that the OH . . . π interaction must be rather strong while the frequency decrease of 2–5 cm^{-1} indicates that the influence on the OH-vibration is small. This can be explained by assuming that the interaction predominantly originates from oxygen-lone-pair . . . π repulsions rather than OH-proton . . . π attractions (hydrogen bonding). On the other hand one should consider that the influence on the OH-frequency will depend on the position of the π-system with respect to the direction of the OH-stretching-vibration.

The presence of repulsive forces between the oxygen-lone-pair(s) and β-methyl groups has been incontrovertibly established. The absence of A-type rotamers proves that these forces are weaker than the OH . . . π ones.

Acknowledgement—The authors are very much indebted to Professor L. BRANDSMA and co-workers for supplying the alcohols **VI**, **VII** and **X** and for their hospitality and support in the preparation of the other samples. The cooperation of Mr. A. E. VAN DIJK in preparing and purifying several of the alcohols is gratefully acknowledged.

REFERENCES

[1] R. J. ABRAHAM and J. M. BAKKE, *Tetrahedron* **34**, 2947 (1978).
[2] R. BAKER and L. K. DYALL, *J. Chem. Soc.* **13**, 1952 (1971).
[3] S. ZUSHI, Y. KODAMA, Y. FUKUDA, K. NISHIHATA, M. NISHIO, M. HIROTA and J. UZAWA, *Bull. Chem. Soc. Japan* **54**, 2113 (1981).
[4] J. UZAWA, S. ZUSHI, Y. KODAMA, Y. FUKUDA, K. NISHIHATA, K. UMEMURA, M. NISHIO and M. HIROTA, *Bull. Chem. Soc. Japan* **53**, 3623 (1980).
[5] Y. KODAMA, K. NISHIHATA, S. ZUSHI, M. NISHIO, J. UZAWA, K. SAKAMOTO and H. IWAMURA, *Bull. Chem. Soc. Japan* **52**, 2661 (1979).
[6] E. T. G. LUTZ and J. H. VAN DER MAAS, *Spectrochim. Acta* **37A**, 693 (1981).
[7] F. MOLL, *Arch. Pharm. Beil.* **299**, 429 (1966).
[8] P. VON R. SCHLEIJER, D. S. TRIFAN and R. BACSKAI, *J. Am. Chem. Soc.* **80**, 6691 (1958).
[9] R. A. NYQUIST, *Spectrochim. Acta* **27A**, 2513 (1971).
[10] G. L. BENDAZOLLI, F. BERNARDI and D. PALMIERI, *J. Chem. Soc. Faraday* II **69**, 579 (1973).
[11] E. HIROTA, *J. Mol. Spec.* **26**, 335 (1968).
[12] G. A. CROWDER and E. W. LOYLA, *J. Mol. Struct.* **62**, 297 (1980).
[13] E. T. G. LUTZ and J. H. VAN DER MAAS, *Spectrochim. Acta* **34A**, 915 (1978).
[14] E. T. G. LUTZ and J. H. VAN DER MAAS, *Spectrochim. Acta* **36A**, 177 (1980).
[15] E. T. G. LUTZ and J. H. VAN DER MAAS, *Spectrochim. Acta* **36A**, 805 (1980).
[16] E. T. G. LUTZ and J. H. VAN DER MAAS, *Spectrochim. Acta* **37A**, 129 (1981).
[17] T. VISSER and J. H. VAN DER MAAS, *Spectrochim. Acta* **38A**, 293 (1982).
[18] E. T. G. LUTZ and J. H. VAN DER MAAS, *Spectrochim. Acta* **38A**, 743 (1982).
[19] J. H. VAN DER MAAS and E. T. G. LUTZ, *Spectrochim. Acta* **38A**, 927 (1982).
[20] S. Y. LIN, Y. OKAYA, D. M. CHIOU and W. J. LE NOBLE, *Acta Cryst.* **B38**, 1669 (1982).
[21] L. BRANDSMA and H. D. VERKRUYSSE, *Synthesis of Acetylenes, Allenes and Cumulenes.* Elsevier, Amsterdam (1981).
[22] J. H. VAN DER MAAS and E. T. G. LUTZ, *Spectrochim. Acta* **30A**, 2005 (1974).