Anomalous Broadening of the Hydroxy Stretching Band of Some Intramolecular OH $\cdots$ π Bridged Alcohols in Halogenated Solvents

Tom Visser† and John H. van der Maas*
Laboratory of Analytical Chemistry, University of Utrecht, Croesestraat 77A, 3522 AD Utrecht, The Netherlands

The band parameters of the intramolecular π-bridged OH-stretching vibrations of six unsaturated alcohols with short OH $\cdots$ π distances, dissolved in iso-octane, CCl_4, $CCl_2{=}CCl_2$, CH_3CCl_3, $CHCl{=}CCl_2$, CS_2, $CHCl_3$, $CHBr_3$, or benzene, have been studied. The OH-band of all these compounds appears to be anomalously broadened in the halogen-containing solvents. The factors determining the vibrational bandwidth in solution are discussed and it is suggested that this deviant behaviour originates from a specific interrelated OH $\cdots$ π $\cdots$ solvent interaction.

Within the framework of an extensive study on structural information from OH-stretching vibrations, we have measured, amongst other band parameters, the frequency and the half-bandwidth (HBW) of the i.r. OH-absorption bands of over 500 alcohols in dilute CCl_4 or CS_2 solution.[1–6] The observed band parameters could be adequately related to differences in force constant f_{OH}, intramolecular interactions, and intermolecular OH $\cdots$ solvent interactions.

Initially it was generally accepted that the OH-stretching band of an alcohol dissolved in CS_2 has a lower frequency and a larger HBW than in CCl_4, as a result of stronger OH $\cdots$ solvent interactions. Later Lutz and van der Maas[3,6] demonstrated that shielding of the hydroxy-proton from local solvent interaction decreases the frequency shift $\nu_d[= \nu(CCl_4) - \nu(CS_2)]$ to about 5 cm^{-1}, and the difference in HBW, expressed by $\Delta(HBW)[= HBW(CS_2) - HBW(CCl_4)]$, to 0.

In 1985[5] we observed normal ν_d values for the intramolecular OH $\cdots$ π bridged rotamer(s) of some β-ethynyl alcohols, but an unusual behaviour of Δ(HBW), which appeared to be negative, *i.e.* $HBW(CCl_4) > HBW(CS_2)$. The solvent dependence of HBW is well known and the shape and width of i.r. absorption bands in solution have been subjected to many theoretical and experimental studies[7–20] (for reviews see refs. 7 and 8). A decrease of the vibrational frequency concomitant with a decrease of HBW has not, to the best of our knowledge, been reported in the literature. We have suggested[5] that, for these alcohols, it could have been caused by a smaller inhomogeneous broadening in CS_2 as result of a local ordering of the solvent molecules around the triple bond, due to π(C≡C) $\cdots$ π(C=S) interactions.

Recently we observed negative Δ(HBW) values for some other (unsaturated) alcohols, and therefore decided to study this phenomenon in more detail.

Experimental

Compound (**1**) was synthesized and purified as described by Prey and Pieh.[21] The steroid (**2**) was supplied by Organon Nederland B.V. and compound (**3**) by Professor Martin, University of Illinois. Compound (**4**) was provided by Dr. Tyblewski, ETH Zentrum Zürich, and the alcohols (**5**) and (**6**) by Dr. Klunder, University of Nymegen. The purity of all compounds was >95% (checked by g.l.c.). All solvents were obtained commercially.

The spectra with CCl_4 and CS_2 as solvents were run with a Perkin-Elmer 580B instrument connected to a PE 3600 data station; scanning conditions: mode 6-B-DB, resolution 0.6 cm^{-1}; accuracy: band maximum ±0.6 cm^{-1}, HBW ±0.7 cm^{-1}. All other spectra were run with a Perkin-Elmer 1710 (FT-IR) instrument connected to a PE 3600 data station; scanning conditions; resolution 1 cm^{-1}, 10 scans; accuracy: band maximum ±0.5 cm^{-1}, HBW ±0.7 cm^{-1} (estimated). Solutions in CCl_4, CS_2, and $CCl_2{=}CCl_2$ were studied in 10 mm 'infrasil' cells, and all other solutions in 2 mm CaF_2 cells at ambient temperature.

Results and Discussion

The OH-band parameters of the alcohols which appear to have a smaller half-bandwidth in CS_2 than in CCl_4 [negative Δ(HBW) value] are listed in Table 1 [compounds (**1**)—(**6**)], along with parameters of six alcohols with Δ(HBW) ⩾ 0 for comparison [compounds (**7**)—(**12**)]. These compounds represent the extremes of Δ(HBW) data that have been observed for more than 500 (un)saturated alcohols of various structures.

For the alcohols (**1**)—(**6**) a smooth and highly symmetric band is found (α/β 0.9—1.0), pointing to the presence of just one type of OH rotamer. The frequencies of the band maxima (3 501.5—3 597.0 cm^{-1} in CCl_4) are considerably less than those of the saturated alcohols (**7**)—(**9**), which points to the presence of strong intramolecular OH $\cdots$ π interaction. Therefore the observed OH band of these alcohols has to be assigned to just one, intramolecularly bridged, species. For compound (**4**) this assignment is in agreement with the conclusion of Tyblewski and Bauder.[22]

For compound (**2**) a very small peak is found on the high-frequency side of the band maximum, obviously a minor contribution of (an) 'unbridged' rotamer(s). However as its intensity is very weak and the frequency considerably higher than that of the OH $\cdots$ π bridged component we believe that it does not contribute to the HBW of the main peak.

As can be seen from Table 1 all compounds (**1**)—(**12**) show $\nu_d > 0$. Though (some of) the shifts of compounds (**1**)—(**6**) are smaller than those observed hitherto, the frequency decrease in CS_2 can be attributed as usual[3,8] to a larger OH $\cdots$ solvent interaction. For the same reason one should expect a larger HBW value in CS_2 than in CCl_4 [Δ(HBW) > 0], but it appears that this is only true for compounds (**7**)—(**12**).

To explain the deviant behaviour of the HBW values of (**1**)—(**6**) one can consider either a change of molecular conformation induced by the solvent, or an anomalous band broadening or narrowing effect in (one of) the solvents as result of a specific OH–solvent interaction. In our opinion structural changes can

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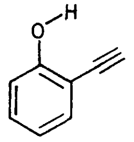
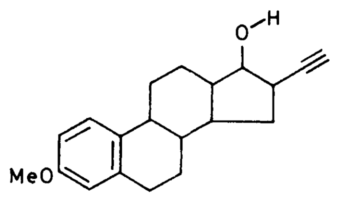
† *Present address:* Laboratory for Organic and Analytical Chemistry, National Institute of Public Health and Environmental Hygiëne, PO Box 1, 3720 BA Bilthoven, The Netherlands.

Table 1. OH-Stretching band parameters for some alcohols dissolved in CCl_4 or CS_2; dimensions cm^{-1} except for α/β, which is dimensionless

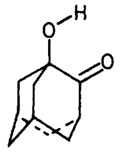
	CCl_4			CS_2				
Compound	ν	HBW	α/β	ν	HBW	α/β	ν_d	Δ(HBW)
(**1**) 2-Ethynylphenol	3 534.5	22.0	0.9	3 523.5	19.5	1.0	11.0	−2.5
(**2**) 16α-Ethynyl-17α-hydroxy-3-methoxyestra-1,3,5(10)-triene	3 555.5	31.0	1.0	3 548.0	23.2	1.1	7.5	−7.8
(**3**) 2-Oxoadamantan-1-ol	3 501.5	41.8	1.0	3 492.7	32.0	1.1	8.8	−9.8
(**4**) Norborna-2,5-dien-7-ol	3 554.5	19.4	0.9	3 545.5	17.6	1.1	9.0	−1.8
(**5**) Tetracyclo[$5.3.0.0^{2,5}.0^{4,8}$]dec-9-en-3-ol (*endo*)	3 597.0	27.2	1.0	3 596.0	19.3	0.8	1.0	−7.9
(**6**) 3-Methyltetracyclo[$5.3.0.0^{2,5}.0^{4,8}$]dec-9-en-3-ol (*endo*)	3 589.0	33.9	1.0	3 589.0	24.6	1.0	0	−9.3
(**7**) Adamantan-1-ol	3 607.0	13.8	1.0	3 596.0	17.5	0.9	11.0	3.7
(**8**) t-Butyl alcohol	3 617.0	16.9	0.9	3 606.5	18.5	0.9	10.5	1.6
(**9**) 2,2,5,5-Tetramethyl-3-t-butylpentan-3-ol	3 629.5	14.3	0.7	3 623.5	16.6	0.6	6.0	2.3
(**10**) Phenol	3 612.5	16.5	0.8	3 593.0	27.8	0.9	19.5	11.3
(**11**) 4-Methyl-2,6-di-t-butylphenol	3 649.5	15.0	0.8	3 643.5	15.4	1.0	6.0	0.4
(**12**) 2-Ethynyladamantan-2-ol	3 609.5	15.3	0.7	3 597.5	21.0	0.6	12.0	5.7



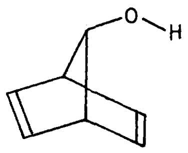
(**1**)



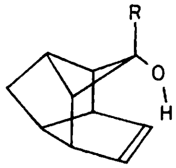
(**2**)



(**3**)

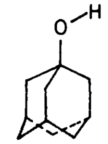


(**4**)



(**5**) R = H

(**6**) R = Me



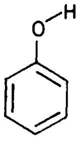
(**7**)

Bu^tOH

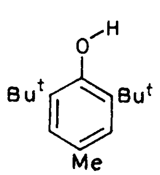
(**8**)

$(Bu^t)_3COH$

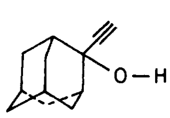
(**9**)



(**10**)



(**11**)



(**12**)

be rejected, as the rigid skeletal structure of the alcohols only allows rotation about the C–O axis, while the observed OH frequencies exclude any position other than the OH ··· π bridged situation. It therefore seemed useful to see which of the factors that determine the half-bandwidth of the i.r. absorption might be responsible for the anomalous behaviour. These factors can be reduced to vibrational and reorientational relaxations, from which (see Dykman[10] and Hawranek and Broda[13]) the latter can be discarded as its effect on the HBW of OH-stretching bands is negligible for alcohols with molecular weights > 100.

Vibrational relaxation depends on four factors, *viz.* (i) the anharmonicity of the vibration, (ii) the localization of the vibration within the molecule, (iii) changes in the environment which affect the OH-oscillator, and (iv) the mobility (freedom of rotation) of the OH in the molecule. Factors (i) and (ii) are solvent-independent and cannot be responsible for the observed phenomenon, while for (iii) and (iv) structural changes in the alcohols (including rotational isomerism) can be ruled out as already mentioned; this leaves only non-bonding effects. In the OH neighbourhood of the alcohols under consideration three types of non-bonding interaction can be distinguished: (*a*) OH ··· solvent, (*b*) OH ··· π, and (*c*) solvent ··· π. The influence of (*a*) and (*b*) on the OH vibration is obvious, as the OH band parameters appear to be solvent-dependent and the hydroxy group is clearly intramolecularly π-bridged. In our opinion interaction (*c*) might influence the OH vibration also, since because of the short distances between the hydroxy group, the unsaturated bond, and the adjacent solvent atom(s)/molecule(s) this interaction will simultaneously affect and be affected by (*a*) and (*b*). The three interactions are thus interdependent.

As we demonstrated earlier,[4] the effect of the interactions on the OH-band parameters depends on both the (electrostatic) properties of the groups involved and their relative positions. The latter must be of particular importance in the origin of an anomalous HBW as the phenomenon is only observed in β-ethynyl alcohols and in compounds (**1**)—(**6**), not in other unsaturated alcohols such as phenols,[3] α-ethynyl alcohols,[4] and benzyl alcohols.[23]

To elucidate the position of the hydroxy group with regard to the unsaturated bond we estimated the distance between the OH proton and the nearest unsaturated atom. The results from measurements on Dreiding models [compounds (**1**)—(**3**)] and molecular mechanics calculations [(**4**)—(**6**)] indicate (i) that the distance is shorter than in the aforementioned α-unsaturated compounds (2.18—2.46 *versus* 2.54 Å), and (ii) that the smaller the OH ··· π distance the smaller the Δ(HBW) value. We therefore conclude that a (very) short OH ··· π distance is essential for the occurence of the anomalous bandwidth phenomenon.

However, the short OH ··· π distance as such does not explain the bandwidth effect, as anomalous band broadening should then have been observed in all solvents. Thus the cause must be related to specific steric and/or electrostatic properties of (one of) the solvent(s) as well. On the one hand the variety in the molecular structure of (**1**)—(**6**) and the shape and size of the CCl_4 and CS_2 molecules seem to exclude different approaching abilities as the origin of the observed HBW effect. On the other

Table 2. OH-Stretching frequencies (cm^{-1}) and HBW values of some alcohols in various solvents

	(2)		**(5)**		**(7)**		**(8)**		**(11)**	
Solvent	ν	HBW	ν	HBW	ν	HBW	ν	HBW	ν	HBW
Iso-octane	3 560.5	17	3 612.0	14	3 612.0	12	3 623.0	15	3 653.5	14
CCl_4	3 555.5	31	3 597.0	27	3 607.0	14	3 617.0	17	3 649.5	15
$CCl_2=CCl_2$	3 554.5	28	3 600.0	21	3 605.5	13	3 616.0	13	3 647.5	12
CH_3CCl_3	3 551.5	33	3 596.0	29	3 601.5	18	3 611.0	19	3 644.0	19
$CHCl=CCl_2$	3 550.5	39	3 589.0	37	3 601.0	18	3 610.0	20	3 644.5	19
CS_2	3 548.0	23	3 596.0	19	3 596.0	17	3 606.5	18	3 643.5	15
$CHCl_3$	3 544.0	55	3 574.0	57	3 597.0	21	3 604.0	24	3 642.5	19
$CHBr_3$	3 538.0	46	3 569.0	47	3 584.0	27	3 595.0	27	3 636.0	24
Benzene	3 548.0	42	3 590.0	26	3 578.5	28	3 587.0	27	3 636.0	24

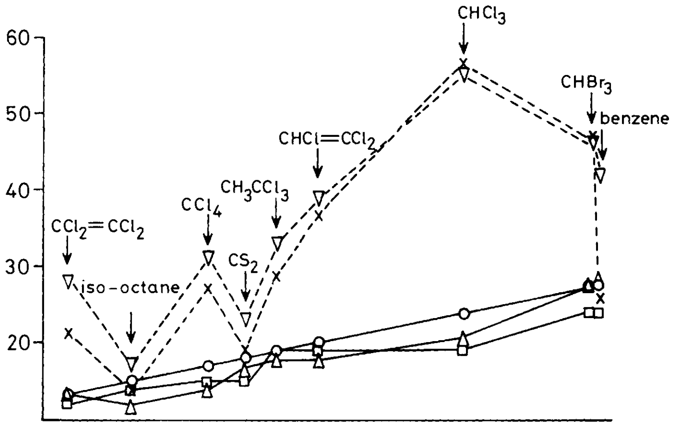


Figure. HBW as a function of solvent (- - - -) for the unsaturated alcohols (**2**) and (**5**), and (——) for the standard compounds (**7**), (**8**), and (**11**)

hand the relatively small ν_d values, in particular for (**5**) and (**6**), could be the result of a difference in approaching ability, as they point to an OH ··· solvent interaction which is either larger than usual in CCl_4 or smaller than usual in CS_2. Nevertheless this endorses the idea that the anomalous behaviour, whether it occurs in just one or in both solvents, emanates from a local interaction in which the hydroxy group, the π-bond, and the adjacent solvent molecule(s)/atom(s) participate.

As can be seen from Table 1, the HBW values of the alcohols (**1**)—(**6**) in CCl_4 are all larger than those of (**7**)—(**12**) whereas in CS_2 solution the HBW values display substantially less scatter. Therefore it seems that the OH band is anomalously affected in CCl_4 and not in CS_2, possibly as a result of a specific π ··· solvent (Cl?) interaction. Should this be the case, other (chlorinated) solvents should affect the OH bandwidth in a similar way. To elucidate this we studied two of the alcohols with negative Δ(HBW) [(**2**) and (**5**)] and three of the reference compounds [(**7**), (**8**), and (**11**)] in the halogenated solvents $CCl_2=CCl_2$, $CHCl=CCl_2$, $CHCl_3$, $CHBr_3$, and CH_3CCl_3, and also in iso-octane (2,2,4-trimethylpentane) and benzene. The observed band parameters are summarized in Table 2. In order to get a clear picture of the effect of solvent on the half-bandwidth, HBW was plotted *versus* solvent, with the assumption of a linear slope for the reference alcohol (**7**) (Figure). The other standard compounds (**8**) and (**11**) show virtually the same slope, whereas the HBW values of (**2**) and (**5**) are considerably larger, in particular in the halogenated solvents.

In our opinion the following conclusions can now be drawn: (i) the negative Δ(HBW) values of (**1**)—(**6**) are the result of anomalous band broadening in CCl_4, (ii) the interaction that causes the broadening has a local character, and (iii) a (very) short intramolecular OH ··· π distance and specific solvent properties are required. As the broadening is by far the largest in the halogenated solvents, we further conclude that the origin lies in properties of Cl and Br which are absent or less present in iso-octane, CS_2, and benzene. One explanation might be the polarizing ability of the halogens, since (see Hawranek *et al.*[13,14] and Hensel *et al.*[20]) the OH bandwidth is, to a certain extent, related to the polarity and the polarizability of the solvent. However neither the dipole moment nor the dielectric constant, nor the molecular and bond polarizabilities of the different solvent molecules, could be correlated with the observed Δ(HBW) values. Thus further study of the precise origin of the band-broadening phenomenon is necessary.

We conclude that alcohols in which the hydroxy group is at a short distance from a π-bond might show an anomalous broadening of the OH stretching band in halogenated solvents. It follows that an increase in the vibrational bandwidth cannot be used as straightforward evidence for a larger solute–solvent interaction.

Acknowledgements

We thank Dr. L. A. van Dijck, Organon Nederland B.V., for supplying the steroid (**2**), Professor J. C. Martin, University of Illinois, for the alcohol (**3**), Dr. M. Tyblewski, ZTH Zentrum Zürich, for compound (**6**), and Dr. A. J. H. Klunder, University of Nijmegen for the products (**5**) and (**6**).

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Received 2nd December 1986; *Paper* 6/2325