THE INFLUENCE OF HYDROGEN BONDING UPON THE FREQUENCY AND INTENSITY OF THE OD IN-PLANE DEFORMATION VIBRATION OF·SOME PHENOLS AND ALCOHOLS

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Abstract—The shifts upon hydrogen bonding were determined for the OD in-plane deformation band of some phenols and alcohols. The bonding took place either between molecules of the same species or with dioxane or pyridine as proton acceptors. The ratio $\frac{\Delta\delta\,OD}{\Delta\nu\,OD}$ is near 0,5 for weak hydrogen bonds (alcohols to dioxane), between 0,2 and 0,4 for medium-strong bonds (self-association of alcohols and phenols, or phenols to dioxane), and about 0,1 for strong bonds (phenols to pyridine). No shift of the δ OD band occurs with sterically hindered phenols, although the shift of the stretching band indicates rather strong hydrogen bonding.

Integrated absorption intensities were determined for the δ OD bands of some free and associated phenols and alcohols, respectively. There is practically no change of integrated absorption upon hydrogen bonding.

Spectroscopic investigations of hydrogen bonding have been directed mainly towards the changes affecting the $X-H$ stretching vibration bands and very few quantitative data exist on the shift of the deformation bands[1,2,3]. Similarly, very little work has been done on intensity changes of the deformation bands upon hydrogen bonding[4,5]. Data of the first mentioned kind are necessary if we want to develop models of the hydrogen bond beyond the present stage of one-dimensional ones. Intensity data are very important because of their relationship to the bond polar properties, and especially so are the intensities of the deformation bands because they are related directly to the dipole moment. However, there are many difficulties in obtaining such data. The main one is that bands corresponding to a pure deformation vibration of the hydroxyl group can be found only in the spectra of very simple molecules, e.g. metal hydroxydes, acid salts of some mineral acids, etc. This kind of compounds being insoluble in appropriate solvents it is practically impossible to measure their absorption intensities and to vary the hydrogen bond strength by taking different proton acceptors. Favourable solubilities are encountered with organic hydroxylic compounds, but here the OH in-plane

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vibration is usually coupled to other vibrations[6,7,8] and the degree of coupling varies with the strength of the hydrogen bond.

This difficulty can be avoided to some extent by taking the deuterated analogs in which the coupling is usually much reduced and even negligible. Of course the work with deuterated compounds is rather cumbersome, but the difficulties are more of a technical character.

The purpose of this paper is to report on some experimental work concerning both the shifts and the intensity changes upon hydrogen bonding of the bands due to the in-plane deformation of the OD group of some phenols and alcohols. The number of compounds for which integrated absorption could be determined is small because it is difficult to find cases in which there is no heavy overlap with other bands. We shall not discuss the results presently as we feel that more data should be accumulated before doing so. Nevertheless, we hope that even these data might be useful in current theoretical work on hydrogen bonding.

EXPERIMENTAL

The substances used were good commercial samples. Their purity was checked before use. Deuterated phenols were prepared either by recrystallisation from D_2O or by shaking them with D_2O and subsequent drying over P_2O_5. Deuterated alcohols were prepared by the decomposition of the magnesium alcoholates with D_2O. The solvent (CS_2) as well as dioxane and pyridine were dried by repeated distillation over appropriate drying agents in a special still. The spectra were recorded with a Perkin–Elmer Mod. 21 spectrophotometer equipped with a NaCl prism. The spectral slit-width was about 5 cm^{-1} at 900 cm^{-1}. Cells with amalgamated spacers were used for the samples and a variable path cell for the compensation of solvent absorption. The thicknesses of the sample cells were measured by the method of interference fringes.

The areas of absorption bands were obtained by graphical integration of the redrawn absorption curves. Overlapping bands were graphically resolved before integration. The actual concentrations of the associated and monomeric deuterated species were obtained by measuring the peak extinctions at the corresponding stretching vibration frequency.

RESULTS

The observed shifts of the δ OD bands are collected in Table 1. They are related to the shifts of the corresponding stretching vibration bands and the ratios $\dfrac{\Delta \delta \text{OD}}{\Delta \nu \text{OD}}$ are listed in the last column of the Table. Figure 1 illustrates the dependence of this ratio upon the shift of the stretching band, the latter being taken as a measure of the strength of the hydrogen bond. Although it does not appear possible to lay a curve unequivocally through the experimental

Table 1—OD Stretching and Bending Frequencies and their Shifts upon Hydrogen Bonding

Compound	*	ν_{OD} [cm^{-1}]	$\Delta\nu_{OD}$	δ_{OD} [cm^{-1}]	$\Delta\delta_{OD}$	$\dfrac{\Delta\delta OD}{\Delta\nu OD}$
Phenol	1	2660	—	918	—	—
	2	2530	130	974	56	0·43
	3	2480	180	990	72	0·40
	4	2200	460	1000	82	0·18
o-Cresol	1	2660	—	917	—	—
	2	2530	130	968	51	0·39
	3	2530	130	975	58	0·45
p-Cresol	1	2660	—	914	—	—
	3	2475	185	970	56	0·32
	4	2320	340	1000	86	0·25
m-Chlorophenol	1	2660	—	935	—	—
	2	2475	185	982	47	0·25
	3	2480	180	980	45	0·25
	4	2160	500	995	60	0·12
p-Chlorophenol	1	2650	—	916	—	—·
	2	2480	170	980	64	0·38
	3	2470	180	980	64	0·36
	4	2100	550	1005	89	0·16
p-Nitrophenol	1	2650	—	922	—	—
	2	2420	230	983	61	0·26
	3	2480	170	970	48	0·28
	4	2170	480	1010	88	0·18
β—Naphtol	1	2660	—	930	—	—
	2	2470	190	974	44	0·23
	3	2410	250	1000	70	0·28
Methanol	1	2700	—	867	—	—
	2	2610	90	915	48	0·53
	3	2490	210	940	73	0·35
	4	2500	200	940	73	0·37
Ethanol	1	2680	—	890	—	—
	2	2600	80	928	38	0·48
	3	2490	190	948	58	0·31
	4	2490	190	942	52	0·27

* 1. Dilute solution in carbon disulphide.
2. Solution in carbon disulfide with dioxane added 1 : 5 volume ratio.
3. Pure compound at room temperature (solid or liquid).
4. Solution in carbon disulfide with pyridine added 1 : 10 volume ratio.

points it may be noted that the ratio assumes values of about 0·5 for weak hydrogen bonds such as formed between alcohols and dioxane, and varies between 0·2 and 0·4 for bonds of intermediate strength as existing between alike alcohol and phenol molecules or between phenols and dioxane or alcohols and pyridine respectively. The ratio approaches 0·1 for the strong bonds between phenols and pyridine. These results are in agreement with those of Tarte[3].
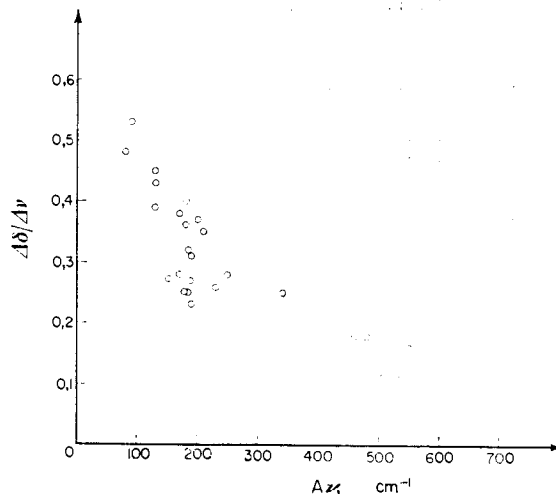

FIG. 1. The dependence of the ratio $\dfrac{\varDelta\delta\,OD}{\varDelta\nu\,OD}$ upon the hydrogen bond strength as expressed by the shift of the νOD band. Numerical data refer to Table 1.

Not included in the Table are the sterically hindered phenols (2,4,6-tribromphenol; 2,6-diisopropylphenol; 2,6-diisobutylphenol; pentachlorophenol and pentamethylphenol) and triphenylcarbinol. It is well-known that these compounds do not undergo self-association through hydrogen bonding, but we have observed shifts of several hundred wave numbers of the stretching vibration band if pyridine or even dioxane were added to the solutions of these phenols in carbon disulfide. However, no shift of the δOH or δOD bands exceeding a few wave numbers has been observed in such conditions. The δOD band of triphenylcarbinol shifts 34 cm^{-1} upon addition of pyridine but this is less than half of the shift exhibited by the corresponding band of ethanol or methanol.

The apparent integrated absorption intensities are collected in Table 2. The differences between the values for the free and bonded species, respectively, are small and divergent. No high accuracy can be claimed for these results in view of the experimental difficulties. The actual concentrations of the deuterated species, both free and hydrogen bonded, had to be determined spectrophotometrically. Some uncertainties arise also from the wings of the

TABLE 2—Frequencies, Apparent Intensities and Half Band Widths of OD in Plane Deformation Bands

Compounds	ν [cm^{-1}]	$\Delta\nu^{1}/_{2}$ [cm^{-1}]	d [cm]	C [mol/1]	Molar ratio to proton acceptor	$\frac{1}{cd}\int \ln\frac{T_0}{T}\,d\nu$ [mol^{-1} 1 cm^{-2}] $\times 10^3$
Phenol	918	14	0·0517	0·034	—	7·24
	974	47	0·0517	0·071	Dioxane 1 : 15	7·27
o-Cresol	917	14	0·0517	0·036	—	5·50
	975	40	0·0517	0·068	Dioxane 1 : 15	5·77
p-Chloro-phenol	916	—	0·0517	0·031	—	8·69
	980	59	0·0517	0·066	Dioxane 1 : 15	8·56
Penta-chloro-phenol	1283	10	0·0104	0·10	—	10·38
	1280	27	0·0104	0·10	Dioxane 1 : 20	13·40
	1196	13	0·0104	0·10	—	13·85
	1194	41	0·0104	0·10	Dioxane 1 : 20	18·27
Methanol	867	24	0·0545	0·151	—	2·405
	940	56	0·0545	0·151	Pyridine 1 : 10	2·435

There is another, smaller, peak at 935 cm^{-1} connected with the OD vibration which has not been integrated.

bands which were usually overlapped by other bands. The small differences between the values of the free and bonded OD group deformation band intensities should not be given much significance. Hence, it may be concluded that hydrogen bonding of the type investigated here does not influence the intensities of the deformation bands to a measurable extent. The case of pentachlorophenol seems to be an exception to the above conclusion. Since there are only two bands in the spectrum of this compound which are due to vibrations involving the deformation of the COH angle[9], the apparent absorption intensities of both bands were determined. A net increase upon hydrogen bonding to dioxane is observed.

Table 2 contains also the apparent half-band widths. It is noted that the width increases on hydrogen bonding but not to such an extent as in the case of the stretching vibration bands[1].

Acknowledgements

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DISCUSSION

G. C. Pimentel. These results are in accord with our studies of the deformation of water. The intensity of the bending mode of water decreased by a factor near 0·7, small change in intensity, as observed by Hadži *et al*. Our studies of chloroform in strong bases (e. g., triethylamine) suggest that $\Delta\delta$ increases as $\Delta\nu$ increases, in contrast to the results just presented. The curve of $\Delta\delta/\Delta\nu$ *vs.* $\Delta\nu$ given by Hadži suggests that $\Delta\nu$ continues to increase whereas $\Delta\delta$ is more nearly independent of hydrogen bond strength.

P. Tarte. Les résultats du Prof. Hadži sur la variation du rapport $\dfrac{\Delta\delta\,OH}{\Delta\nu\,OH}$ en fonction de la longueur du pont hydrogène sont très intéressants, car ils montrent que l'effet que nous avions observé en phase solide [Tarte, *Spectrochim. Acta* **13**, 107 (1958)] existe aussi en solution: il s'agirait donc peut-être d'une propriété générale de la liaison hydrogène.

En ce qui concerne les mérites relatifs des études en phase solide ou en solution, on peut remarquer que chaque méthode a des avantages et des inconvenients: en solution, on évite les effets secondaires qui peuvent exister dans l'état solide, mais les ponts hydrogène n'ont pas une longueur déterminée, ce qui provoque un élargissement supplementaire des bandes. En phase solide par contre, les ponts hydrogène ont une longueur bien déterminée, qu'on peut déterminer par rayons X, et les bandes peuvent — dans certains cas du moins — être notablement plus fines.

D. Hadži. Il y a encore une difficulté avec les cristaux: la distance $O \ldots\ldots O_n$ peut être prise comme mesure de la force de la liaison hydrogène que dans le cas que le proton soit sur la ligne joignante les oxygènes. Malheureusement nous ne sommes pas sûrs de ceci sauf en cas des déterminations de la position du proton par diffractions des neutrons.

S. Califano. I should like to ask Prof. Hadži about the coupling of the δ (OH) with the phenyl ring vibrations. As consequence of this coupling one has to get a spreading out of the intensity variation due to the OH def. mode over all the bands of the phenol ring of the same symmetry class, the amount of intensity participation depending upon the percentage of normal coordinate mixing.

D. Hadži. This problem is being investigated in our laboratory. I have mentioned the example of pentachlorophenol in the spectrum of which are two bands connected with the δ OH vibration. Both bands show an increase of intensity upon hydrogen bonding. On the other hand, the band near 1430 cm^{-1} in the spectrum of benzoic acid which is associated mainly with the δ OH vibration nearly disappears upon bonding to pyridine whereas the band near 1360 cm^{-1} (mainly C—O stretching) strongly increases. There is clearly a redistribution of intensities upon bonding to pyridine.

J. Lecomte. Il est assez intéressant de remarquer que les acides hydroxamiques d'après les mesures de Hadži *et coll.*, ne présentent pas de couplages de vibration

δ[OH, ν (N=N) etc.], contrairement aux résultats actuels sur les autres substances de la présente communication. Des éclaircissements pourraient s'obtenir par la considération de cristaux, de manière à déterminer la direction exacte des vibrations, ainsi qu'on l'a fait pour les amides. On peut alors, suivant les précédents du Prof. Mizushima, trouver la proportion de chaque vibration contribuant à une bande d'absorption.

D. Hadži. Nous sommes en train de faire des mesures dans le genre indiqué par M. Lecomte. En particulier, il s'agit du resorcinole (étude du dichroisme) et de l'acide formique (calcul du changement de la repartition de l'énergie potentielle parmi les vibrations normales sous l'influence de la dimérization).