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Hydrogen Bonding in 2-Hydroxybenzoyl and 2-Hydroxythiobenzoyl Compounds: Spectroscopic Characterization and Spectroscopic Bond Strength Sequences

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Summary. A survey of IR and NMR spectroscopic data is given for 30 2-hydroxybenzoyl and 2-hydroxy-thiobenzoyl compounds, which are representative for various kinds of (thio)carbonyl groups ($-CY-Cl$, $-CY-O-$, $-CY-S$, $-CY-N\!<$, $-CY-O^-$, $-CY-S^-$; $Y{=}O,S$). The data shall provide a basis for a comparison between corresponding intramolecular O–H··O and O–H··S hydrogen bonds and for the evaluation of systematic dependencies. Correlations between $\tilde{\nu}_{OH}$ frequencies, which are considered as the main characteristic of hydrogen bond strengths, and several other spectroscopic quantities are shown. For O–H··O type associations the bond strength sequence is acid chlorides < tertiary amides < acids ≈ esters < aldehydes < ketones < secondary and primary amides < (thio)-carboxylates, which roughly complies with the sequences obtained for other carbonyl properties, such as oxygen-basicities or $\tilde{\nu}_{CO}$ frequencies; the outstanding position of tertiary amides is known to arise from steric effects. The $\tilde{\nu}_{OH}$ frequencies of O–H··S bonds were found to be rather similar to those of corresponding O–H··O bonds, with the exception of thioacids and thioesters, for which significantly lower frequencies have been obtained.

Keywords. Hydrogen bonding; 2-Hydroxy-benzoyl compounds; 2-Hydroxy-thiobenzoyl compounds; IR spectra; NMR spectra.

Wasserstoffbrückenbindungen in 2-Hydroxy-benzoyl- und 2-Hydroxy-thiobenzoylverbindungen: spektroskopische Charakterisierung und spektroskopische Bindungsstärkesequenzen

Zusammenfassung. Der Artikel enthält eine Zusammenstellung IR- und NMR-spektroskopischer Daten von 30 2-Hydroxy-(thio)benzoylverbindungen, die verschiedenste Arten von (Thio)Carbonylgruppen repräsentieren ($-CY-Cl$, $-CY-O-$, $-CY-S$, $-CY-N\!<$, $-CY-O^-$, $-CY-S^-$; $Y=O,S$). Die Daten sollen als Grundlage für einen Vergleich zwischen einander entsprechenden intramolekularen O–H··O und O–H··S Wasserstoffbrückenbindungen, sowie zur Ermittlung systematischer Zusammenhänge dienen. Korrelationen zwischen $\tilde{\nu}_{OH}$-Frequenzen, die als wesentliches Kriterium zur Charakterisierung der Bindungsstärken herangezogen werden, und verschiedenen anderen spektroskopischen Daten werden gezeigt. Bei den Wasserstoffbrückenbindungen des Typs O–H··O nehmen die Bindungsstärken in der Reihenfolge Säurechloride < tertiäre Amide < Säuren ≈ Ester < Aldehyde <

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Ketone < sekundäre und primäre Amide < (Thio)Carboxylate zu. Dies entspricht in etwa den Sequenzen, die man auch für andere Carbonyleigenschaften erhält, wie etwa den Sauerstoffbasizitäten oder den $\bar{\nu}_{CO}$-Frequenzen. Die auffällige Sonderstellung der tertiären Amide ist auf sterische Effekte zurückzuführen. Die $\bar{\nu}_{OH}$-Frequenzen der O–H··S Wasserstoffbrückenbindungen sind denen der entsprechenden O–H··O Bindungen sehr ähnlich, ausgenommen Thiosäuren und Thioester, für die wesentlich niedrigere Frequenzen gefunden wurden.

Introduction

Whereas there exists an enormous amount of data on X–H··O hydrogen bonds, X–H··S hydrogen bonds are by far less well documented. Evidences for X–H··S hydrogen bonding are known since the early forties [1, 2], but for a long time the proton acceptor capability of sulfur was widely assumed to be only poor [3]. By the time it turned out, however, that, despite the lower electronegativity, sulphur proton acceptors are rather similar to corresponding oxygen proton acceptors. Certain differences have been reported in the literature for the correlation between the $-\Delta H_O$ association enthalpies and the $\Delta\bar{\nu}_{OH}$ frequency shifts, which are most frequently used for a calorimetric and spectroscopic characterisation of hydrogen bond strengths, respectively. From several inter-molecular association studies involving corresponding oxygen and sulfur bases it appeared that the enthalpies are always somewhat larger for the O–H··O than for the O–H··S bonds, while the frequency shifts make only little distinction [4–7].

Within the last few years we have focused attention to intra-molecular hydrogen bonds which exhibit some apparent differences to inter-molecular ones. Two important points may be noted: (*i*) the main geometric features of an intra-molecular bond, X···Y distance and X–H··Y angle, are largely predetermined by the steric requirements and constraints of the system under consideration, while the strength of the interaction primarily affects only the X–H distance; (*ii*) since the corresponding free acids and bases of intramolecular hydrogen bonded systems (usually) do not exist, experimental data of the free species desirable for the evaluation of systematic dependencies can not be determined and investigations are mainly limited to spectroscopic and structural characterisations, to comparisons with data of more or less appropriate reference compounds, and to model calculations. Concerning the latter point some earlier calculations using the *Schroeder–Lippincott* potential function model of the hydrogen bond [8] may be mentioned, which predicted comparable inter-molecular bond strengths (based on potential energies) and frequency shifts for O–H··O and O–H··S, while intra-molecular bonded O–H··S bond strengths and frequency shifts should be larger than those of O–H··O bonds. Some few IR studies on intra-molecular O–H··S bonds available on the literature [9–12] seem to confirm these predictions and the differences between oxygen and sulfur proton acceptors have been qualitatively interpreted to result from the larger lone pair extension of sulfur and from an increased covalent character of the H··S bond [6, 13].

The present study deals with a comparison between intra-moleculary associated carbonyl and thiocarbonyl groups; some 30 2-hydroxy-(thio)benzoyl compounds have been selected that should be representative for the various kinds of (thio)carbonyl groups. Since salicylic acid derivatives establish one of the most popular model systems for studying intra-molecular hydrogen bonds, one might assume that almost everything should already be known about 2-hydroxy-benzoyl compounds. Actually, because of largely varying experimental conditions (solvents, concentrations, solid state sampling techniques) the available literature data were found to be largely insufficient and unsuitable for our intentions. In order to completely and uniformly characterize the hydrogen bonds, basic IR and NMR spectra have been (re)measured for both the oxo-compounds and the thio-compounds, using common experimental standard conditions as far as possible. Additionally, several X-ray structure determinations have been performed and structural data are now available for all solid compounds included in the study. The experimental data should provide a safe basis for a discussion of similarities and differences between intra-molecular O–H··O=C and O–H··S=C bonds.

In the present paper the results of the spectroscopic work are summarized and considered in a mainly phenomenological way. Following a short experimental section, a survey of IR and NMR spectroscopic data is given which includes data of 13 pairs of analogous oxo- and thio-compounds and additional 4 oxo-compounds for which the corresponding thio-compounds are either highly unstable or do not exist at all. Some correlations between $\bar{\nu}_{OH}$ stretching frequencies, which we consider as the main spectroscopic characteristic of hydrogen bond strengths, and other spectroscopic data are shown. Finally, the spectroscopically determined bond strength orders of O–H··O and O–H··S are shown and discussed.

Experimental

The compounds covered in the survey are listed in Table 1, which also gives references to more detailed original work. The compounds are labelled "O" and "S" for O–H··O and O–H··S type association, respectively. The compound numbering roughly corresponds to decreasing $\bar{\nu}_{OH}$ solution frequencies of the oxo-compounds; some minor interchanges have been made to account for chemical similarities. For convenience the compounds are divided into 6 groups: (I) acid chlorides (**1**); (II) tertiary amides (**2–4**); (III) acids and esters (**5–8**); (IV) aldehydes and ketones (**9–10**); (V) primary and secondary amides (**11–13**); (VI) salts (**14–17**). For the preparation and characterization of the majority of the compounds see the references given in Table 1. For **O7**, **O9** and **O10** commercially available samples were purified by distillation.

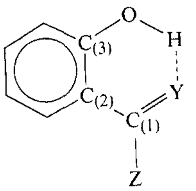
2-Hydroxy-benzoylchloride (**O1**), $C_7H_5ClO_2$, was prepared from salicylic acid and thionylchloride [19] under a nitrogen atmosphere and purified by distillation: m.p. = 17–18 °C; ^{1}H NMR (CCl_4:$CDCl_3$ = 5:1) 6.97 (t), 7.24 (d), 7.32 (dt), 7.82 (dd), 9.63 (OH) ppm; ^{13}C NMR ($CDCl_3$): 117.2, 118.1, 120.3, 133.9, 138.3, 161.6, 173.6 ppm.

O-Methyl-2-hydroxy-thiobenzoate (**S7**), $C_8H_8O_2S$, was prepared from dithiosalicylic acid carboxymethylester and sodium methanolate [20] and purified by liquid chromatography ($CHCl_3$:*n*-heptane = 1:1): orange oil; ^{1}H (CCl_4:$CDCl_3$ = 5:1): 4.28 (s), 6.81 (dt), 7.02 (dd), 7.40 (dt), 7.93 (dd), 11.84 (OH) ppm; ^{13}C NMR ($CDCl_3$): 57.9, 118.8, 119.3, 121.1, 126.9, 135.6, 161.8, 209.8 ppm.

S-Methyl-2-hydroxy-thiobenzoate (**O8**), $C_8H_8O_2S$, was prepared from 2′,6′-dimethylpiperidinium-2-hydroxy-thiobenzoate and methyl iodide [21] and purified by liquid chromatography ($CHCl_3$:*n*-heptane = 1:4): yellow oil; ^{1}H NMR (CCl_4:$CDCl_3$ = 5:1): 2.45 (s), 6.83 (dt), 6.90 (dd), 7.41 (dt), 7.80 (dd), 10.81 (OH) ppm; ^{13}C NMR ($CDCl_3$): 11.5, 118.2, 119.3, 120.1, 128.8, 135.8, 159.3, 197.6 ppm.

Methyl-2-hydroxy-dithiobenzoate (**S8**), $C_8H_8OS_2$, was prepared from dithiosalicylic acid carboxymethylester and methylmercaptane [22] and purified by liquid chromatography ($CHCl_3$:*n*-hexane = 1:9): orange oil; m.p. = 10 °C; ^{1}H NMR ($CDCl_3$): 2.69 (s), 6.92 (dt), 7.07 (dd), 7.42 (dt), 8.13 (dd), 12.15 (OH) ppm; ^{13}C NMR ($CDCl_3$): 19.1, 119.0, 119.9, 126.5, 127.2, 135.0, 158.8, 227.0 ppm.

Table 1. Labelling of compounds and references to original work



	-*Z*	*Y*=O	[Ref.]	*Y*=S	[Ref.]
(I)	-Cl	O1		[a]	
(II)	-$N(CH(CH_3)CH_2)_2CH_2$	O2	[14]	S2	[14]
	-$N(CH_2CH_2)_2CH_2$	O3	[14]	S3	[14]
	-$N(CH_3)_2$	O4	[14]	S4	[14]
(III)	-OH	O5	[14]	[b]	
	-SH	O6	[15]	S6	[14]
	-OCH_3	O7		S7	
	-SCH_3	O8		S8	
(IV)	-H	O9		[a]	
	-CH_3	O10		[a]	
(V)	-$NHNH_2$	O11	[16]	S11	[16]
	-NH_2	O12	[17]	S12	[17]
	-$NHCH_3$	O13	[17]	S13	[17]
(VI)	-$O^- {}^+H_2N(CH(CH_3)CH_2)_2CH_2$	O14	[18]	S14	[18][c]
	-$S^- {}^+H_2N(CH(CH_3)CH_2)_2CH_2$	O15	[18]	S15	[18]
	-$O^- {}^+N(C_2H_5)_4$	O16	[18]	S16	[18][c]
	-$S^- {}^+H(C_2H_5)_4$	O17	[18][d]	S17	[18]

[a] Unstable; [b] does not exist; [c] exists in the solid state only; [d] exists in solution only

Results and Discussion

Data and correlations

Several IR and NMR spectroscopic data are recorded in Table 2 for solutions, which will mainly be considered, and for condensed phase samples. Solution concentrations were about 10^{-2} mol/l for NMR measurements, while IR measurements have been performed at concentrations down to $5 \cdot 10^{-6}$ mol/l. The great majority of data refers to free, non-associated molecules, since changes on dilution have not been observed within the concentration ranges considered. Exceptions are salicylic acid, which remains (partly) inter-molecular associated *via* the carboxyl OH group down to about 10^{-5} mol/l [14], and the ((di)thio)carboxylate salts (group VI), which exhibit appreciable anion-cation association effects (dimethylpiperidinium salts) or solvation effects (tetraethylammonium salts) [18].

In Fig. 1 some correlations between $\bar{\nu}_{OH}$ IR frequencies and other spectroscopic quantities are shown (solution values only). $\bar{\nu}_{OH}$ and/or $\bar{\nu}_{OD}$ frequencies are most frequently and commonly used as reliable and universal spectroscopic criterion for hydrogen bound strengths and often serve even as a synonym for the latter; they are easily available for solids, liquids and solutions, and also available for both,

Table 2. $\bar{\nu}_{OH}$, $\bar{\nu}_{OD}$, $\bar{\nu}_{CO}$ frequencies and $\Delta\bar{\nu}_{CO} = \bar{\nu}(\mathrm{ref}) - \bar{\nu}$ frequency differences (CCl_4 solutions); δ_{OH} proton resonances (CCl_4:$CDCl_3$ = 5:1 solutions), $^{2}\Delta C(D)$ deuterium isotope shifts of C(3) carbon resonances and $\Delta\delta_{CY} = \delta(\mathrm{ref}) - \delta$ differences of C(1) carbon resonances ($CDCl_3$ solutions); $\bar{\nu}_{OH}$ and $\bar{\nu}_{OD}$ condensed phase frequencies (liquids or fluorolube mulls) of 2-hydroxy-(thio)-benzoyl compounds (ref: *ortho*-unsubstituted compounds)

	Solution							Condensed	
	$\bar{\nu}_{OH}$ [cm^{-1}]	$\bar{\nu}_{OD}$ [cm^{-1}]	$\bar{\nu}_{CO}$ [cm^{-1}]	$\Delta\bar{\nu}_{CO}$ [cm^{-1}]	δ_{OH} [ppm]	$^{2}\Delta C(D)$ [ppm]	$\Delta\delta_{CY}$ [ppm]	$\bar{\nu}_{OH}$ [cm^{-1}]	$\bar{\nu}_{OD}$ [cm^{-1}]
O1	3315	[a]	1719	58	9.63	[a]	−5.3	3315	[a]
O2	3250	2410	1625	5	8.95	0.211	0.0	3140[b]	2355[b]
O3	3220	2400	1629	10	9.70	0.191	−0.5	3120[b]	2335[b]
O4	3200	2375	1632	13	9.95	0.200	−0.3	3075[b]	2295[b]
O5	3210	2410	1696	47	10.21	[c]	−4.6	3230	2415
O6	3185	2390	1638	51	10.53	0.215	−5.2	3120	2350
O7	3205	2395	1683	46	10.60	0.177	−3.6	3185	2375
O8	3170	2375	1631	40	10.81	0.208	−4.9	3155	2365
O9	3160	2370	1668	41	11.09	0.230	−4.4	3150	2355
O10	3050	2285	1646	46	12.10	0.250	−7.6	3030	2275
O11	3035	2305	1652	30	11.62	[d]	−2.0	2800	2145
O12	3020	2290	1660	34	11.99	0.255	−3.2	2750	2050
O13	2950	2250	1651	30	12.16	0.264	−2.3	2700	2025
O14	2700	2065	1486[f]	54[f]	15.60[e]	[g]	−3.0	2750	2070
O15	2830	2150	1474	34	13.05	[c]	0.2	2800	2150
O16	2560[h]	1950[h]	1484[fh]	77[fh]	16.03	0.523	−2.1	2450	1875
O17	2630[h]	2000[h]	1475[h]	49[h]	14.12	0.400	−1.2	–	–
S2	3330	2480			7.06	0.135	3.9	3315	2480
S3	3255	2425			7.88	0.176	4.4	3190	2390
S4	3250	2430			8.09	0.183	4.2	3170	2370
S6	2945	2220			12.20	0.311	2.3	2750	2105
S7	3015	2275			11.80	0.261	2.4	2990	2250
S8	3000	2250			11.95	0.300	2.1	2940	2215
S11	3100	2360			10.53	[d]	3.0	2750	2100
S12	2960	2230			11.65	0.313	4.4	2700	2040
S13	3000	2275			11.13	0.283	4.6	2840	2170
S14								2400	1850
S15	2800	2125			12.77	[g]	5.5	2750	2120
S16								2300	1830
S17	2580[h]	1960[h]			13.61	0.446	5.7	2500	1950

[a] Cannot be deuterated directly; [b] intermolecularly associated OH(D) group; [c] broad signal; [d] complex multiplett; [e] in $(CD_3)_2SO$, 130 Hz halfwidth; [f] asymmetric $\bar{\nu}_{CO}$ frequency; [g] too low solubility; [h] in $CDCl_3$

inter- and intra-molecular hydrogen bounds. Basically, $\Delta\bar{\nu}_{OH}$ and/or $\Delta\bar{\nu}_{OD}$ frequency shifts relative to $\bar{\nu}_{OH}$(free) and/or $\bar{\nu}_{OD}$(free) frequencies of the corresponding free acids should be used, which are, however, not available for the intramolecularly associated species under investigation. Instead of referring to frequency shifts relative to more or less arbitrarily chosen alternative reference compounds (*e.g. para*-hydroxy compounds), the absolute values will be used throughout this paper.

$\bar{\nu}_{OH}$ *vs.* $\bar{\nu}_{OD}$ results in the expected almost perfect correlation (Fig. 1a), correlation coefficient of $r = 0.996$ (for liquids and solids: $r = 0.995$), without apparent differences between oxo- and thio-compounds. $\bar{\nu}_{OD}$ frequencies are often more reliable than $\bar{\nu}_{OH}$ ones, since the half widths of $\bar{\nu}_{OD}$ bands are usually distinctly smaller and interferences with other IR bands, *e.g.* $\bar{\nu}_{CH}$ bands, are largely omitted; $\bar{\nu}_{OH}$ versus $\bar{\nu}_{OD}$ correlations may also serve as a valuable check for the correctness and the reliability of assignments.

$\bar{\nu}_{OH}$ *vs.* δ_{OH} (OH proton resonances) gives a reasonably good, although not perfect correlation (Fig. 1b, $r = 0.922$). The enhanced scatter of points in the low frequency and low field range concerns the ((di)thio)acid salts and may partly be due to differing solvents as well as to association and solvation effects, as mentioned above. The correlations seem to be slightly different for O–H··O ($r = 0.966$) and O–H··S ($r = 0.933$) type hydrogen bonds, since at comparable $\bar{\nu}_{OH}$ frequencies the δ_{OH} values for the oxo-compounds are typically slightly larger than those of the thio-compounds, which may be due to different anisotropy effects. On the whole, the

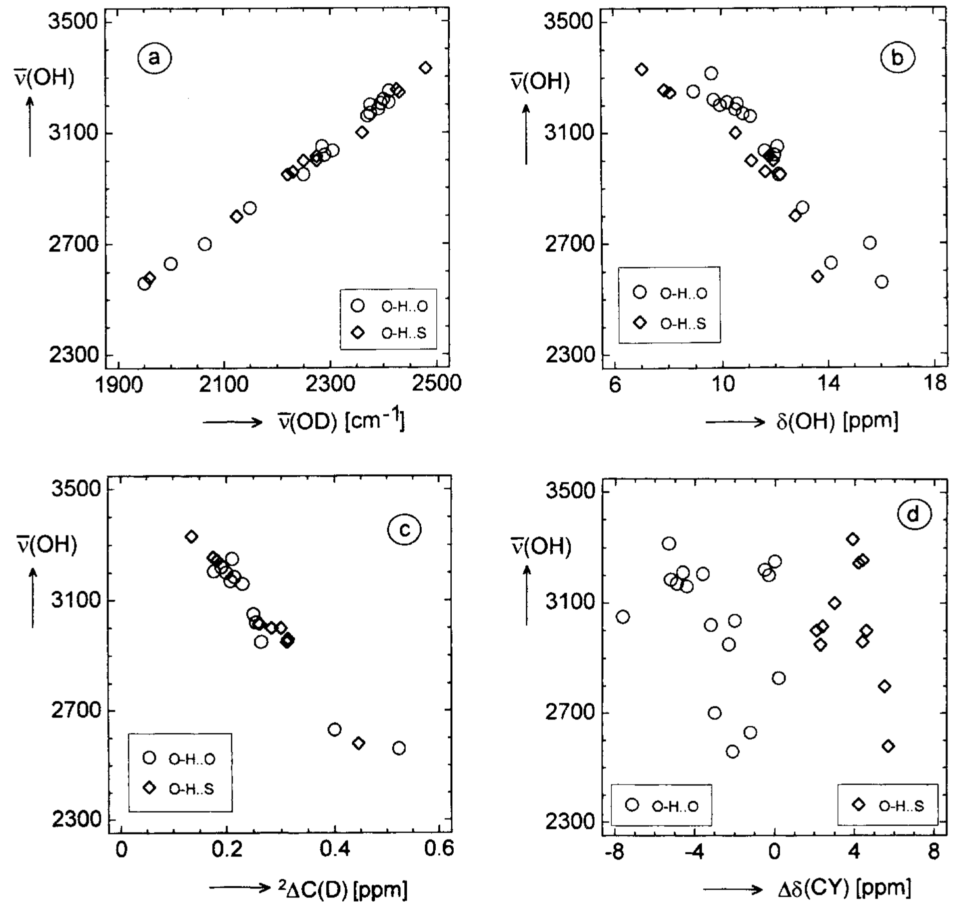


Fig. 1. Correlation of $\bar{\nu}_{OH}$ *vs.* (a) $\bar{\nu}_{OD}$, (b) δ_{OH}, (c) $^{2}\Delta C(D)$, (d) $\Delta\delta_{CY}$ (for abbreviations see text)

hydrogen bond strength sequences based on δ_{OH} proton shifts are, however, largely similar to those based on $\bar{\nu}_{OH}$ frequencies (see below).

$\bar{\nu}_{OH}$ *vs.* $^2\Delta C(D)$ ($=\delta_{C\text{-}OH}-\delta_{C\text{-}OD}$; deuterium isotope shifts of C(3) carbon resonances) yields a fairly good correlation (Fig. 1c) with $r = 0.974$, which, moreover, seems to be largely independent of O–H··O or O–H··S type association (the $\bar{\nu}_{OH}$ *vs.* $^2\Delta C(D)$ correlation for intra-molecular hydrogen bonds will be treated elsewhere in some more detail [23]).

From intermolecular association studies, several other spectroscopic quantities are also known to be indicative of hydrogen bonding effects; when dealing with O–H··O=C bonds, hydrogen bond induced carbonyl frequency shifts, $\Delta\bar{\nu}_{CO} = \bar{\nu}_{CO}(\text{free}) - \bar{\nu}_{CO}$, are a prominent example. Table 2 contains a similar quantity, *i.e.* $\Delta\bar{\nu}_{CO}$ differences between the carbonyl frequency of *ortho*-unsubstituted compounds, which serve as reference compounds, and those of the intra-molecularly associated species. From Table 2 it is obvious, that, although the expected low frequency shifts are obtained throughout, the values are largely scattered without any reasonable quantitative relationship to the hydrogen bond strengths as determined by $\bar{\nu}_{OH}$ frequencies. This finding is, however, not really unexpected, since the observed $\Delta\bar{\nu}_{CO}$ frequency differences are not only caused by the formation of the hydrogen bonds, but also include the backlash of the substituting *ortho*-OH groups on the C=O groups; it clearly shows the problems associated with the evaluation of hydrogen bond induced effects of intra-molecular hydrogen bonds due to the need of choosing more or less appropriate reference compounds (frequency shifts relative to *para*-hydroxy or to *ortho*-methoxy compounds, which could be assumed to be more appropriate reference compounds, yield similar results).

Among the various spectroscopic quantities that have been inspected for systematic dependencies on hydrogen bond effects, another quantity should finally be noted, since it provided a somewhat unexpected result: the differences between the C(1) (thio)carbonyl carbon resonances of the *ortho*-unsubstituted references compounds and of the 2-hydroxy compounds, $\Delta\delta_{CY} = \delta(\text{ref}) - \delta$. Similar to what is observed with $\Delta\bar{\nu}_{CO}$ frequency shifts, as far as the absolute $\Delta\delta_{CY}$ values are concerned there is again no reasonable correlation with $\bar{\nu}_{OH}$ frequencies (Fig. 1d), however, and without sound explanation at the moment, low-field shifts are typically obtained

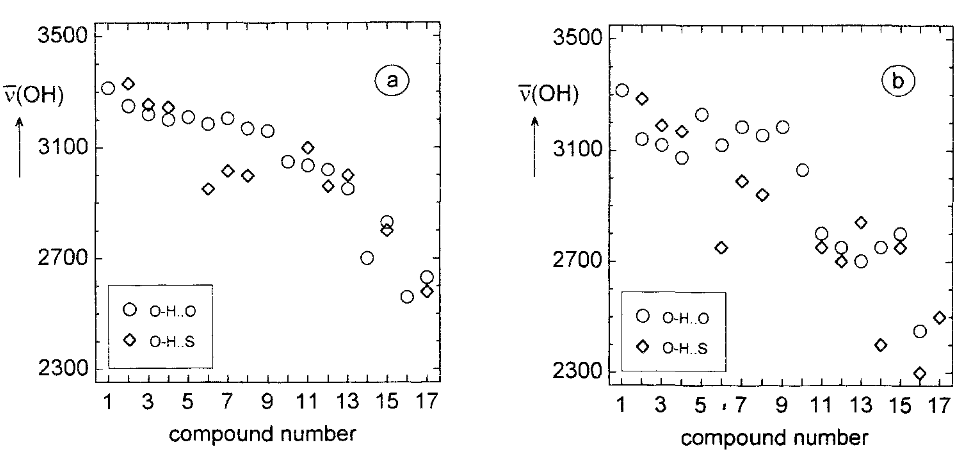


Fig. 2. $\bar{\nu}_{OH}$ (a) solution frequencies and (b) condensed phase frequencies *vs.* compound numbers (see Table 1)

for the oxo-compounds, while high-field shifts are observed for the all the thio-compounds.

O–H··O bond strength sequence

Figure 2a gives a plot of solution $\bar{\nu}_{OH}$ frequencies *vs.* compound numbers and visualizes the spectroscopically determined bond strength sequences of the intra-molecular O–H··O and O–H··S hydrogen bonds (Fig. 2b shows a similar plot for the condensed phase frequencies). The oxo-compounds shall be considered first. Basically, the H-bond capabilities of carbonyl groups should be closely related to several other (more or less well defined) carbonyl properties, such as basicities, proton affinities, stretching frequencies, bond orders, bond polarities, *etc.* Except for $\bar{\nu}_{CO}$ carbonyl frequencies, the available data are rather crude and limited and insufficient for a detailed analysis of a series of distinct compounds. In rough outlines, a generalized sequence can be established at least for O-basicities, esters < acids ≈ aldehydes < ketones < amides < carboxylates [24], which is rather similar to the well known generalized sequence of $\bar{\nu}_{CO}$ frequencies, halides > acids(monomer) ⩾ esters > aldehydes > ketones > amides > carboxylates. In an equally generalized way our hydrogen bond strength sequence reads chlorides < tertiary amides < acids ≈ esters < aldehydes < ketones < secondary and primary amides < (thio)carboxylates, which, with the immediately apparent exception of the tertiary amides, complies reasonably well with the sequences of O-basicities and of $\bar{\nu}_{CO}$ frequencies. The outstanding position of the tertiary amides results from the steric interaction between the *E*-substituent of the nitrogen atom and the *ortho* hydrogen atom of the phenyl ring, which counteracts against planarity between the planes of the amide group and the phenyl ring. While the great majority of 2-hydroxy-benzoyl compounds are planar or at least near planar, which is desirable for effective intra-molecular hydrogen bonding, the tertiary amides exhibit significant deviations from planarity [17] and as a consequence the intra-molecular hydrogen bonds are distinctly longer and weaker than would be the case for (hypothetical) planar compounds.

The correlation between the $\bar{\nu}_{OH}$ solution frequencies of the oxo-compounds and the $\bar{\nu}_{CO}$(ref) carbonyl frequencies of the ortho-unsubstituted reference compounds, which are used to characterize the non-associated carbonyl groups, is explicitly

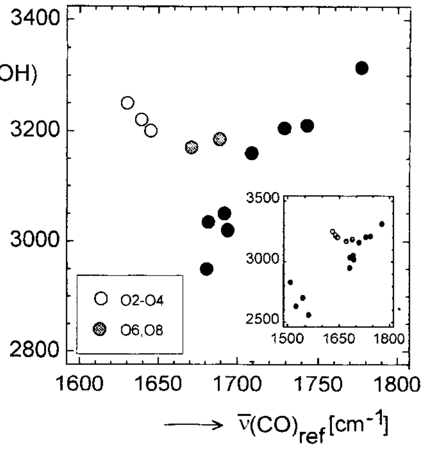


Fig. 3. Correlation of $\bar{\nu}_{OH}$ *vs.* $\bar{\nu}_{CO}$(ref) (ref = *ortho*-unsubstituted compounds)

shown in Fig. 3 (again very similar pictures result if *ortho*-methoxy or *para*-hydroxy compounds are used instead). The insert shows a reasonable, although only rough overall correlation ($r = 0.794$); as expected, the upper and lower limits are established by the acid chloride and by the (thio)carboxylates, respectively. As to the latter, since for carboxylates and thiocarboxylates association and solvation effects may appreciably affect the carboxyl frequencies and since for the carboxylates the higher frequency asymmetric stretching frequencies have somewhat arbitrarily been chosen, the absolute $\bar{\nu}_{CO}$(ref) values given for the salts are of restricted significance.

A cut of the insert, which excludes the less significant data of the (thio)carboxylates, is shown on an enlarged scale and hence in some more detail in Fig. 3. The outstanding position of the tertiary amids, **O2** to **O4**, is evident, but even if they are omitted, the remaining points are widely scattered and a correlation coefficient of only $r = 0.731$ is obtained. Inspection of the origins of the individual points shows that the rather large scatter most likely is brought about mainly by the two thiolo-compounds, **O6** and **O8**; they exhibit $\bar{\nu}_{OH}$ frequencies rather similar to the corresponding ordinary compounds, **O5** and **O7**, but $\bar{\nu}_{CO}$(ref) frequencies that are lower by more than $50\,cm^{-1}$. If **O6** and **O8** are neglected, the correlation coefficient increases to a rather satisfying value of $r = 0.952$. Although there are good reasons for believing that the two thiolo-compounds are somewhat out of turn, we can not give a plausible explanation, as it was the case with the tertiary amides; geometric effects are ruled out, since **O6** and **O8** should belong to the (approximately) planar compounds, as it has been confirmed for **O6** by an X-ray diffraction study [15]. In a previous paper about corresponding –CO–O– and –CO–S– type compounds [25] an explanation has been given for the significant drop of the $\bar{\nu}_{C=O}$ frequency, which results from exchanging –O– by –S–; using simple electronic arguments, the authors qualitatively attributed the frequency lowering to two effects: (*i*) a reduced inductive effect due to the lower electronegativity of sulfur, and (*ii*) a larger contribution of the polar resonance form $-C(O^-)=S^+-$. In view of our results the second effect could not play an important role, since besides lowering the C=O forces constant the increased bond polarity would also be expected to increase the strength of hydrogen bond interaction.

Let us finally consider the results of the condensed phase spectra (Fig. 2b). The exceptional position of the tertiary amides is still enhanced, in that the weak intra-molecular hydrogen bonds become replaced by slightly stronger intermolecular ones [17]. For the remaining oxo-compounds the sequence is not very much different to the solution sequence; expectedly, the $\bar{\nu}_{OH}$ frequencies of the liquids are close to those of the corresponding solutions, while the solids show more or less pronounced low frequency shifts with respect to the solutions. The largest ones concern the amides (group V).

O–H··S versus O–H··O

Because some of the corresponding thio-compounds are missing, our comparison between oxo- and thio- compounds is restricted to 13 compound pairs belonging to groups II, III, V amd VI. A treatment of O–H··S bonds similar to that given for O–H··O bonds, *i.e.* a comparison between $\bar{\nu}_{OH}$ and $\bar{\nu}_{CS}$ frequency sequences, is hardly possible nor would it be meaningful for several reasons. Since the polarities of C=S bonds and hence the intensities of corresponding IR bands are much less than those of C=O bonds and because C=S vibrations are much more stronger coupled with other vibrations than C=O vibrations, reliable assignments are very difficult; moreover, even if $\bar{\nu}_{CS}$ frequencies could have been determined correctly, they are of only limited use for characterizing C=S groups, because of the vibrational coupling effects just noted. We therefore focus on a comparison between corresponding O–H··S and O–H··O bonds.

Figure 2a shows that for the majority of corresponding O–H··S and O–H··O bonds rather similar $\bar{\nu}_{OH}$ frequencies are obtained, but in some instances significant differences are also observed. The tertiary (thio)amides (group II) belong to the first category; the high $\bar{\nu}_{OH}$ frequencies and the corresponding weak hydrogen bond strengths of the thioamides again result from deviations from planarity, which are even more pronounced than those of the amides [17]. Rather similar $\bar{\nu}_{OH}$ frequencies for thio- and oxo-compounds are also obtained for the primary and secondary (thio)amides (group V) and the ((di)thio)salts (group VI), while for the (thio)acids and the (thio)esters (group III) the $\bar{\nu}_{OH}$ frequencies of the thio-compounds are lower by about $200\,\mathrm{cm}^{-1}$ than those of the oxo-compounds. Turning to condensed phase O–H··S hydrogen bonds, there is almost nothing new: the O–H groups of the tertiary amides become intermolecularly associated, as it was the case with the tertiary amides; the $\bar{\nu}_{OH}$ frequencies of the liquids are close to those of the corresponding solutions, while the solids show more or less pronounced frequency shifts with respect to the solutions, the largest ones again concern the thioamides.

Concluding remarks

On summarizing the experimental results, the initial question of the study, *i.e.* O–H··O versus O–H··S hydrogen bonding, can be answered as follows: for the intra-molecular hydrogen bonds of 2-hydroxy-(thio)benzoyl compounds considered in this study the $\Delta\bar{\nu}_{OH}$ frequency shifts and hence the spectroscopically determined strengths of the O–H··S bonds are similar to, or even larger than those of the corresponding O–H··O bonds, which agrees with the predictions of the model calculations [8] and with the results of some few previous literature studies [9–12]. No attempts will be made in the present paper for an interpretation of the experimental findings, neither for the determined hydrogen bond sequences, nor for the observed similarities and differences between oxygen and sulfur proton acceptors. In particular, as far as details are concerned, to our feeling the experimental data do not provide a basis for consistent interpretations or at least a plausible explanation; we hope that additional suitable information can be obtained from model calculations, semiempirical as well as *ab initio*, which are currently in progress.

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