Monatshefte für Chemie 121, 809 – 820 (1990)

Monatshefte für Chemie
Chemical Monthly

O – H ... O (S) Hydrogen Bonds in 2-Hydroxy(thio)benzamides. Survey of Spectroscopic and Structural Data

Erich Steinwender and **Werner Mikenda***

Institut für Organische Chemie, Universität Wien, A-1090 Wien, Austria

Summary. From a survey of spectroscopic and structural data of six corresponding 2-hydroxybenzamides and 2-hydroxythiobenzamides (amide, N-methylamide, N,N-dimethylamide, piperidide, morpholide, 2,6-dimethylpiperidide) remarkable similarities between O (N) – H ... O and O (N) – H ... S hydrogen-bonds are obtained, concerning both, hydrogen-bond patterns and hydrogen-bond strengths. In dilute solution the OH groups of all compounds are intramolecularly associated to the (thio)carbonyl O (S) atoms with distinctly larger hydrogen-bond strengths for primary and secondary amides [$\bar{\nu}$ (O – H) = 2 950 – 3 020 cm^{-1}, δ (OH) = 12.16 – 11.99 ppm] and thioamides [$\bar{\nu}$ (O – H) = 2 960 – 3 000 cm^{-1}, δ (OH) = 11.65 – 11.13 ppm], than for tertiary amides [$\bar{\nu}$ (O – H) = 3 200 – 3 250 cm^{-1}, δ (OH) = 9.95 – 8.95 ppm] and thioamides [$\bar{\nu}$ (O – H) = 3 245 – 3 330 cm^{-1}, δ (OH) = 8.09 – 7.06 ppm]. In the solid state, the OH groups of the primary and secondary (thio)amides are also engaged in rather strong intramolecular O – H ... O = C [O ... O = 2.51 Å, $\bar{\nu}$ (O – H) = 2 700 – 2 750 cm^{-1}] and O – H ... S = C [O ... S = 2.90 – 2.94 Å, $\bar{\nu}$ (O – H) = 2 700 – 2 840 cm^{-1}] hydrogen-bonds; the *trans*-NH groups of the primary (thio)amides and the NH groups of the secondary (thio)amides connect the molecules to N – H ... O – H [N ... O = 2.93 – 3.10 Å, $\bar{\nu}$ (N – H) = 3 319 – 3 407 cm^{-1}] hydrogen-bonded chains; the remaining *cis*-NH groups of the primary (thio)amides give rise to eight-membered cyclic dimers via N – H ... O = C [N ... O = 2.93 Å, $\bar{\nu}$ (N – H) = 3 226 cm^{-1}] and N – H ... S = C [N ... S = 3.46 – 3.47 Å, $\bar{\nu}$ (N – H) = 3 233 – 3 277 cm^{-1}] hydrogen-bonds. Contrary, the OH groups of the tertiary (thio)amides are intermolecular associated in the solid state and link the molecules to O – H ... O = C [O ... O = 2.63 – 2.75 Å, $\bar{\nu}$ (O – H) = 3 075 – 3 135 cm^{-1}] and O – H ... S = C [O ... S = 3.18 – 3.26 Å, $\bar{\nu}$ (O – H) = 3 130 – 3 190 cm^{-1}] hydrogen-bonded chains.

Keywords. 2-Hydroxybenzamides; 2-Hydroxythiobenzamides; Hydrogen bonds; Hydrogen-bond geometries; Ir spectra.

O – H ... O (S)-Wasserstoffbrückenbindungen in 2-Hydroxy(thio)benzamiden. Ein Überblick über spektroskopische und strukturelle Daten

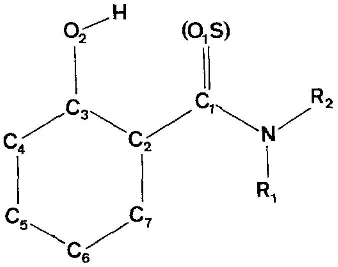
Zusammenfassung. Aus einer Zusammenstellung von spektroskopischen und strukturellen Daten von sechs entsprechenden 2-Hydroxybenzamiden und 2-Hydroxythiobenzamiden (Amid, N-Methylamid, N,N-Dimethylamid, Piperidid, Morpholid, 2,6-Dimethylpiperidid) ergeben sich bemerkenswerte Analogien zwischen O (N)-H ... O und O (N) – H ... S H-Brücken, die sowohl die H-Brücken-Muster als auch die H-Brücken-Stärken betreffen. In verdünnter Lösung sind die OH-Gruppen aller Verbindungen intramolekular mit den O (S)-Atomen der (Thio)Carbonylgruppen assoziiert, wobei die H-Brücken bei den primären und sekundären Amiden [$\bar{\nu}$ (O – H) = 2 950 – 3 020 cm^{-1}, δ (OH) =

12.16 – 11.99 ppm] und Thioamiden [$\bar{\nu}$(O–H) = 2960 – 3060 cm^{-1}, δ(OH) = 11.65 – 11.13 ppm] deutlich stärker sind, als bei den tertiären Amiden [$\bar{\nu}$(O–H) = 3200 – 3250 cm^{-1}, δ(OH) = 9.95 – 8.95 ppm] und Thioamiden [$\bar{\nu}$(O–H) = 3245 – 3330 cm^{-1}, δ(OH) = 8.09 – 7.06 ppm]. Im Festkörper weisen die primären und sekundären (Thio)Amide ebenfalls sehr starke intramolekulare O–H...O=C [O...O = 2.51 Å, $\bar{\nu}$(O–H) = 2700 – 2750 cm^{-1}] und O–H...S=C [O...S = 2.90 – 2.94 Å, $\bar{\nu}$(O–H) = 2700 – 2840 cm^{-1}] H-Brücken auf; die *trans*-NH-Gruppen der primären (Thio)Amide und die NH-Gruppen der sekundären (Thio)Amide verknüpfen die Moleküle über N–H...O–H H-Brücken [N...O = 2.93 – 3.10 Å, $\bar{\nu}$(N–H) = 3318 – 3407 cm^{-1}] zu Ketten; die verbleibenden *cis*-NH-Gruppen der primären (Thio)Amide bilden zyklische, über N–H...O=C [N...O = 2.93 Å, $\bar{\nu}$(N–H) = 3226 cm^{-1}] und N–H...S=C [N...S = 3.46 – 3.47 Å, $\bar{\nu}$(N–H) = 3233 – 3277 cm^{-1}] H-Brücken gebundene, 8-Ring-Dimere. Im Gegensatz dazu sind die OH-Gruppen der tertiären (Thio)Amide im Festkörper intermolekular assoziiert und verknüpfen die Moleküle über O–H...O=C [O...O = 2.63 – 2.75 Å, $\bar{\nu}$(O–H) = 3075 – 3135 cm^{-1}] und O–H...S=C [O...S = 3.18 – 3.26 Å, $\bar{\nu}$(O–H) = 3130 – 3190 cm^{-1}] H-Brücken zu Ketten.

Introduction

The great majority of (thio)benzoyl compounds exhibit an approximately planar molecular structure which is energetically favoured by resonance stabilization between the aromatic ring and the (thio)carbonyl group. In 2-hydroxy(thio)benzoyl compounds such a planar structure is highly advantageous for the formation of a strong intramolecular O – H... O = C(S = C) hydrogen-bond which is a main characteristic of the compounds of this type. Therefore, corresponding 2-hydroxybenzoyl and 2-hydroxythiobenzoyl type compounds build up a model system which is particularly useful for an investigation of analogous intramolecular O – H... O and O – H... S hydrogen-bonds.

In a first preliminary paper [1] about corresponding O – H... O and O – H... S hydrogen-bonds we have reported spectroscopic data of 4 pairs of N,N-disubstituted



compound	$N{<}^{R_2}_{R_1}$	references	
		ir/nmr	X-ray
(1O)(1S)	$N{<}^{H}_{H}$	this work	3,3
(2O)(2S)	$N{<}^{CH_3}_{H}$	this work	4,4
(3O)(3S)	$N{<}^{CH_3}_{CH_3}$	1	3,3
(4O)(4S)	$N{<}^{CH_2-CH_2}_{CH_2-CH_2}{>}CH2$	1	5,6
(5O)(5S)	$N{<}^{CH_2-CH_2}_{CH_2-CH_2}{>}O$	1	5,7
(6O)(6S)	$N{<}^{CH(CH_3)-CH_2}_{CH(CH_3)-CH_2}{>}CH2$	1	-

Scheme 1. Numbering of atoms, compounds included in the survey and references to original work

2-hydroxy(thio)benzamides. Tertiary (thio)benzamides are known to exhibit large deviations from the usually preferred approximately planar conformation (cf. Ref. [2]) which results from the steric hindrance between the N-substituents and the *ortho* protons of the phenyl rings. As a consequence, in N,N-disubstituted 2-hydroxy(thio)benzamides, when compared with other approximately planar 2-hydroxy(thio)benzoyl compounds, the intramolecular O . . . O (S) distance is largely increased and the formation of the intramolecular O – H . . . O = C(S = C) hydrogen-bond is strongly disfavoured.

Besides reporting some supplementary data, it is the main scope of the present paper to survey the spectroscopic and structural data of corresponding 2-hydroxybenzamides and 2-hydroxythiobenzamides as far as available (Scheme 1). The data provide a basis for a comprehensive discussion concerning the intra- and intermolecular associations of the OH and NH groups in dilute solution and in the solid state, paying particular attention to a comparison between corresponding oxo- and thiocompounds.

Experimental and Results

Commercially available 2-hydroxybenzamide (**1 O**) was recrystallized from ethanol/water. N-methyl-2-hydroxybenzamide (**2 O**) and 2-hydroxythiobenzamide (**1 S**) were prepared according to Ref. [8] and Ref. [9], respectively. N-methyl-2-hydroxythiobenzamide (**2 S**) was prepared by a Willgerodt-Kindler reaction in analogy to Ref. [10] and recrystallized from benzene (m.p. = 69 – 72 °C; uv in cyclohexane: λ_{max}[nm](log ε) = 385 (2.88), 330 (3.71) and 290 (3.96); ^{1}H nmr in 5 CCl_4 : 1 $CDCl_3$: δ [ppm] = 3.32 (d, 3 H), 6.80 (t, 1 H), 7.00 (d, 1 H), 7.30 (m, 2 H) 7.60 (broad, NH), 11.13 (s, OH)).

Table 1. Proton shifts, δ in ppm (relative to *TMS*; ~ 10^{-3} mol/l in 5 CCl_4: 1 $CDCl_3$), and stretching frequencies, $\bar{\nu}$(*X*-H) in cm^{-1} [$\bar{\nu}$(*X*-D) values are given in parentheses] (liquid: ~ $5 \cdot 10^{-4}$ mol/l in CCl_4; solid: in fluorolube), for OH (D) and NH (D) groups of 2-hydroxbenzamide (**1 O**) and 2-hydroxythiobenzamide[a] (**1 S**) at 300 K

	$C_6H_4(OH)-CO-NH_2$		$C_6H_4(OH)-CS-NH_2$	
	Liquid	Solid	Liquid	Solid
δ (OH)	11.99		11.65	
$\bar{\nu}$ (O – H)	3 020 (2 290)	2 750 (2 050)	2 960 (2 230)	2 700 (1 985 + 2 100)
δ (NH_2)[b]	6.05		7.10	
$\bar{\nu}_s$ (NH_2)	3 425 (2 499)	3 189 (2 358)	3 391 (2 471)	3 178 + 3 204 (2 363 + 2 386)
$\bar{\nu}_{as}$ (NH_2)	3 544 (2 651)	3 397 (2 546)	3 506 (2 631)	3 392 + 3 406 (2 545 + 2 555[d])
$\bar{\nu}$ (*cis*-NH)[c]	3 464 (2 559)	3 226 (2 386)	3 443 (2 543)	3 233 + 3 277 (2 400 + 2 431)
$\bar{\nu}$ (*trans*-NH)[c]	3 503 (2 586)	3 378 (2 500)	3 443 (2 543)	3 380 + 3 385[d] (2 498)

[a] For previously reported spectroscopic data see Ref. [11]

[b] Broad

[c] From isotopically dilute samples

[d] Shoulder

Table 2. Proton shifts, δ in ppm (relative to *TMS*; ~ 10^{-3} mol/l in 5 CCl_4 : 1 $CDCl_3$), and stretching frequencies, $\bar{\nu}$ (*X*-H) in cm^{-1} [$\bar{\nu}$ (*X*-D) values are given in parentheses] (liquid: ~ $5 \cdot 10^{-4}$ mol/l in CCl_4; solid: in fluorolube), for OH (D) and NH (D) groups of N-methyl-2-hydroxybenzamide (**2 O**) and N-methyl-2-hydroxythiobenzamide[a] (**2 S**) at 300 K

	$C_6H_4(OH)-CO-NHCH_3$		$C_6H_4(OH)-CS-NHCH_3$	
	Liquid	Solid	Liquid	Solid
δ (OH)	12.16		11.13	
$\bar{\nu}$ (O−H)	2 950 (2 250)	2 700 (2 025)	3 000 (2 275)	2 840 (2 170)
δ (NH)[b]	6.15		7.60	
$\bar{\nu}$ (N−H)	3 484 (2 577)	3 407 (2 530)	3 434 (2 529)	3 319 (2 458)

[a] For previously reported spectroscopic data see Ref. [12]

[b] Broad

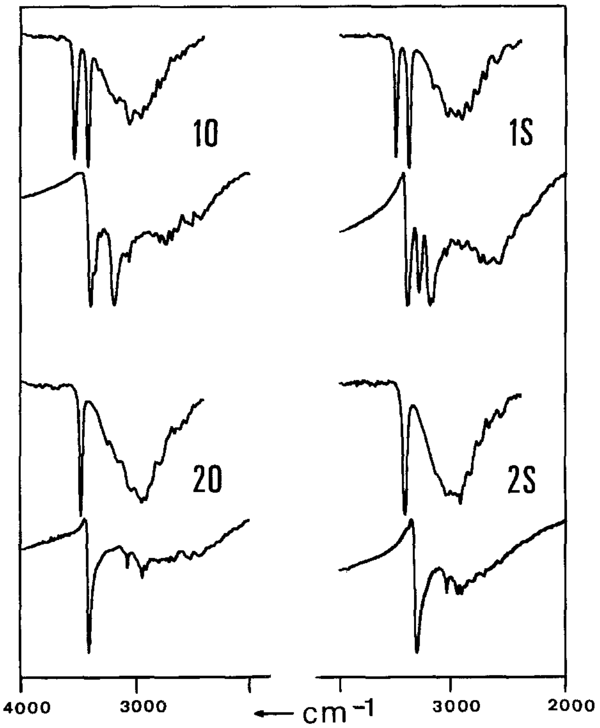


Fig. 1. Ir spectra of 2-hydroxybenzamide (**1 O**), 2-hydroxythiobenzamide (**1 S**), N-methyl-2-hydroxybenzamide (**2 O**) and N-methyl-2-hydroxythiobenzamide(**2 S**) at 300 K (upper spectrum: dilute CCl_4 solution; lower spectrum: fluorolube mull)

For the spectroscopic equipment see Ref. [1]. The more recent ir spectra have been measured with a Perkin-Elmer 1740 spectrometer. Spectroscopic data which are of main interest for a characterization of hydrogen-bonds are given in Table 1 for 2-hydroxy(thio)benzamide (**1 O**) (**1 S**) and in Table 2 for N-methyl-2-hydroxy(thio)benzamide (**2 O**) (**2 S**). Additionally, the 4 000 to 2 000 frequency ranges of ir solution and solid state spectra are shown in Fig. 1. As is usually the case with strongly hydrogen-bonded OH (D) groups the low O − H and O − D stretching frequencies listed in Tables 1 and 2 could only be estimated with some uncertainties from the centers of gravity of the broad and highly strucured stretching bands.

The O−D stretching band of deuterated samples are usually smaller and less structured than the corresponding O−H bands and the O−D frequencies may, therefore, be more reliable than the O−H frequencies.

Discussion

Solutions

In Fig. 2 the O−H stretching frequencies and the proton shifts obtained for the OH groups of 6 pairs of 2-hydroxy(thio)-benzamides (Scheme 1) in dilute solutions are summarized in a correlation plot. As can be shown by dilution studies, the OH groups are intramolecular associated with the O(S) atoms of the (thio)carbonyl groups in either of the 12 compounds. Both, the stretching frequencies and the proton shifts, are commonly used for a characterization of hydrogen-bond strengths. However, since the proton shifts strongly depend on the chemical nature of the proton acceptors, only the O−H frequencies (or frequency shifts) can serve as a common measure for O−H...O and O−H...S hydrogen bonds. The compounds included in the plot may reasonably well be devided into two groups: (1) the primary and secondary 2-hydroxy(thio)benzamides which are characterized by low frequency O−H stretching bands in the ir spectra, corresponding low field proton resonances in the nmr spectra and hence rather strong O−H...O(S) hydrogen-bonds, and (2) the tertiary 2-hydroxy(thio)benzamides which are characterized by much more higher frequency O−H bands, corresponding much more smaller proton shifts and hence significantly weaker O−H...O(S) hydrogen-bonds. The O−H frequency shifts relative to the $\bar{\nu}$(O−H) frequencies of the free OH groups, which should actually be used for a characterization of hydrogen-bond strengths instead of the simple O−H frequencies, cannot be determined unambiguously, because the $\bar{\nu}$(O−H) frequencies of the individual compounds are not available. If $\bar{\nu}_0(\mathrm{O-H}) = 3610\,\mathrm{cm}^{-1}$ of free phenolic OH groups is taken as an approximate and common reference, $\Delta\bar{\nu}(\mathrm{O-H})$ shifts of 590−660 (610−650) cm^{-1} and 360−410 (280−365) cm^{-1} are obtained for group 1 and group 2 compounds, respectively. Since the spectroscopic data of group 1 compounds excellently comply with the data obtained for the OH groups of the great majority of other 2-hydroxy(thio)benzoyl compounds [13], it can be claimed that these compounds exhibit the expected approximately planar structure. On the other hand, as already noted above, the weakness of the O−H...O(S) hydrogen-bonds in group 2 compounds is a special feature of N,N-disubstituted 2-hydroxy(thio)benzamides and results from the large deviations from the planar structure which are characteristic of tertiary (thio)benzamides.

The O−H frequency versus proton shift correlations of Fig. 2 are certainly rather satisfying. Not unexpected the correlations obtained for the oxo- and the thiocompounds are slightly different, which may mainly be ascribed to different anisotropy effects of carbonyl and thiocarbonyl groups. Moreover, the O−H frequencies of group 2 compounds are on average larger by about 50 cm^{-1} for thio- than for oxocompounds. Another minor difference between benzamides and thiobenzamides concerns the sequence of hydrogen-bond strengths in (**1 O**) (**1 S**) and (**2 O**) (**2 S**). According to the spectroscopic data the O−H...O interaction is slightly stronger in the secondary amide (**2 O**), than in the primary amide (**1 O**), which

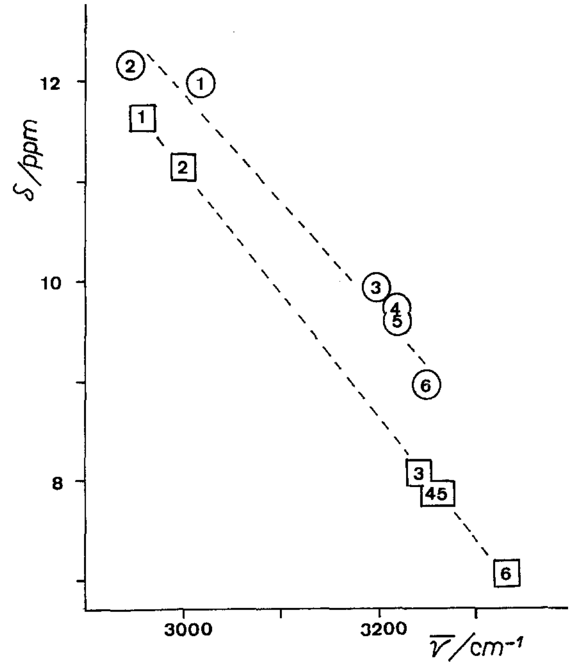


Fig. 2. Stretching frequency versus proton shift correlation for OH groups of 2-hydroxybenzamides (○) and 2-hydroxythiobenzamides (□) in dilute solution. The compound numbers are those of Scheme 1

agrees with expectation, since the basicity, and hence also the hydrogen-bond capability, increases from primary to secondary amides. On the other hand and without obvious reason, the sequence of hydrogen-bond strengths is found to be reversed for the O – H... S hydrogen-bonds in the two corresponding thioamides (**1** S) and (**2** S).

In the ir spectra of group 1 compounds, besides the broad O – H stretching bands rather narrow high frequency bands due to free NH groups are observed. As a consequence of the partial double bond character of the C – N bond and the resulting hindered rotation, secondary (thio)amides can exist in two rotameric isomers, with the N – H stretching frequencies of *Z*-isomers being slightly larger than those of corresponding *E*-isomers [14]. The *E*-isomers are known to be present in larger extents only in exceptional cases [14] and in secondary (thio)benzamides the *E*-configuration is additionally disfavoured by steric hindrance effects, analogous to those of tertiary (thio)benzamides. The *Z*-isomers should, therefore, by far be predominant and in agreement with expectation only a single rather high frequency N – H stretching band due to the *Z*-isomer is observed in the ir spectra of both, (**2** O) and (**2** S). Similar to the differences between the NH groups of *Z*- and *E*-isomers of secondary (thio)amides, the two NH groups of primary (thio)amides should also be slightly different. Basically, when dealing with vibrational spectra of NH_2 groups the possible differences between the NH oscillators are obscured by intramolecular coupling effects, they can, however, be directly observed in the spectra of NHD species obtained from partly deuterated samples. For 2-hydroxybenzamide (**1** O) two uncoupled N – H frequencies are actually observed that differ by 39 cm^{-1} (Table 1) which is very close to the 31 cm^{-1} difference obtained for *ortho*-unsubstituted benzamide. On the other hand, similar differences between the two NH groups are not observed for the corresponding thioanalogues. In the spectra of both, 2-hydroxythiobenzamide (**1** S) and thiobenzamide, the symmetric and asymmetric NH_2 stretching bands degenerate to only one uncoupled N − H band on isotopic dilution, which however, as should be noted, also applies to thioacetamide [15].

Solids

Structural data of 5 pairs of 2-hydroxy(thio)benzamides [no X-ray data are available for (**6 O**) (**6 S**)] are summarized in Table 3 (selected intramolecular bond distances and angles). Except for the torsion angles around the $C_{(1)} - C_{(2)}$ bond, Table 3 shows no significant and systematic differences, neither between different oxocompounds and between different thiocompounds, nor between corresponding oxo- and thiocompounds. In particular the angles within the (thio)amide moieties are very close to the ideal value of 120° in all compounds. In the secondary (thio)amides the amide groups exhibit the expected *Z*-configuration with the NH groups being *trans* with respect to the (thio)carbonyl groups. Geometric data of the intra- and intermolecular hydrogen-bonds in the ten compounds are summarized in Table 4. With one exception the hydrogen positions have also been refined, however, since the O − H and N − H distances reported in the original papers differ by more than 0.25 Å, the directly related H . . . O and H . . . S distances are almost useless. The X-ray values have, therefore, been corrected [16] by adopting the X − H distances to reasonable values (1.00 Å for NH groups; 1.00 and 0.95 Å for intramolecular and intermolecular associated OH groups, respectively) and recalculating $H \ldots Y_{cor}$ distances. At least for approximately linear hydrogen-bonds these normalized $H \ldots Y_{cor}$ distances may reasonably well be used alternatively to the X . . . Y distances.

In the four group 1 compounds the hydroxyl protons form the characteristic intramolecular hydrogen-bonded six-membered rings, with very short $O_{(2)} \ldots O_{(1)}$ (2.51 Å) and O . . . S (2.90–2.94 Å) distances, respectively. Accordingly, broad and highly structured low frequency O − H stretching bands (2 700–2 840 cm^{-1}) are observed in the ir spectra with rather similar frequencies for all four compounds. The dihedral angles between the planes of the phenyl rings and the (thio)amide groups are almost zero for the oxo- and about 20° for the thiocompounds. When compared with corresponding data of *ortho*-unsubstituted (thio)benzamides (e.g. 25° for benzamide [17], 14° for N-methyl-benzamide [18], 38° for isonicotinethioamide [19]) the dihedral angles are significantly reduced in the 2-hydroxy(thio)benzamides, which certainly results from the intramolecular O − H . . . O (S) hydrogen-bonds which additionally favour a planar structure.

As expected from general structural chemistry principles [20], the NH groups of all group 1 compounds are also engaged in hydrogen-bonds, even though they are partly very weak. In both, N-methyl-2-hydroxybenzamide (**2 O**) and N-methyl-2-hydroxythiobenzamide (**2 S**), the NH group donates its proton to an hydroxyl oxygen of a neighboring molecule giving rise to intermolecular $N - H \ldots O_{(2)}$ bonded chains. The hydrogen-bond arrangements are somewhat different for (**2 O**) and (**2 S**), since the molecules are related by translation in the first, but by a twofold screw axis in the second compound. In the oxocompound the hydrogen-bond distances are somewhat shorter (N . . . O = 2.98 Å, $H \ldots O_{cor} = 2.06$ Å) than in the thiocompound (N . . . O = 3.10 Å, $H \ldots O_{cor} = 2.17$ Å), the latter being only slightly less than the sum of the van-der-Waals radii which establish an ultimate upper

Table 3. Selected bond distances (in Å) and angles of 2-hydroxy(thio)benzamides

Compound	$C_6H_4(OH)-CO-Z$						$C_6H_4(OH)-CS-Z$					
	C_3-O_2	C_1-O_1	C_1-N	O_1C_1N	$O_1C_1C_2$	$O_1C_1C_2C_3$	C_3-O	C_1-S	C_1-N	SC_1N	SC_1C_2	$SC_1C_2C_3$
(1)	1.35	1.25	1.33	120	120	2	1.37	1.68	1.31	119	123	−19
							1.35	1.69	1.31	119	123	−19
(2)	1.35	1.24	1.32	121	121	0	1.36	1.68	1.32	121	124	±26[a]
(3)	1.35	1.24	1.33	122	118	±112[b]	1.36	1.68	1.33	122	119	±110[b]
(4)	1.37	1.24	1.34	122	118	±105[b]	1.36	1.68	1.32	124	118	±108[b]
(5)	1.36	1.25	1.34	121	120	114	1.37	1.70	1.33	122	118	115
	1.36	1.24	1.34	121	120	108	1.40	1.67	1.35	122	120	110

[a] Different enantiomers within different chains

[b] Alternating enantiomers within the chains

Table 4. Hydrogen-bond geometries (distances in Å) and frequency shifts (in cm^{-1}) of 2-hydroxy(thio)benzamides

Compound	$C_6H_4(OH)-CO-Z$	X-H	H... Y^a	$X ... Y$	XHY	$\Delta\bar{\nu}^b$	$6H_4(OH)-CS-Z$	X-H	H... Y^a	$X ... Y$	XHY	$\Delta\bar{\nu}^b$
Intramolecular hydrogen bonds:												
(1)	$O_2-H...O_1$	0.94	1.67 (1.61)	2.51	148	860	$O_2-H...S$	0.91	2.01 (1.92)	2.90	167	910
							$O'_2-H...S'$	1.04	1.95 (1.99)	2.92	154	910
(2)	$O_2-H...O_1$	0.88	1.67 (1.55)	2.51	161	910	$O_2-H...S$	0.81	2.20 (2.04)	2.94	150	770
Intermolecular hydrogen bonds												
(1)	$N-H...O_1$	0.92	2.00 (1.93)	2.93	179	238	$N-H...S'$	0.84	2.62 (2.46)	3.46	176	210
							$N'-H...S$	0.90	2.63 (2.54)	3.47	157	166
	$N-H...O_2$	0.91	2.11 (2.02)	3.01	168	125	$N-H...O$	0.97	2.08 (2.06)	2.93	145	63
							$N'-H...O'$	1.10	2.07 (2.15)	3.01	142	58
(2)	$N-H...O_2$	0.82	2.22 (2.06)	2.98	153	77	$N-H...O$	0.91	2.25 (2.17)	3.10	154	105
(3)	$O_2-H...O_1$	0.90	1.72 (1.68)	2.63	174	535	$O_2-H...S$	0.86	2.40 (2.31)	3.23	164	440
(4)	$O_2-H...O_1$	0.88	1.77 (1.70)	2.65	174	490^c	$O_2-H...S$	0.83	2.43 (2.34)	3.26	170	420
(5)	$O_2...O'_1$	0.91	1.86 (1.82)	2.75	168	490^d	$O_2-H...S'^e$			3.20		470
	$O'_2-H...O_1$	0.96	1.74 (1.75)	2.69	170	525	$O'_2-H...S^e$			3.18		480

---

[a] Corrected H... Y_{cor} distances (see text) are given in parentheses

[b] Frequency shifts $\Delta\bar{\nu}(O-H)$ relative to $\bar{\nu}_o(O-H) \sim 3610\ cm^{-1}$ of phenolic OH groups in dilute solution, $\Delta\bar{\nu}(N-H)$ relative to corresponding $\bar{\nu}_0(N-H)$ in solution (see text)

[c] Mean value of two submaxima

[d] Shoulder (band splitting is evident from the O−D spectra)

[e] Hydrogen position not refined

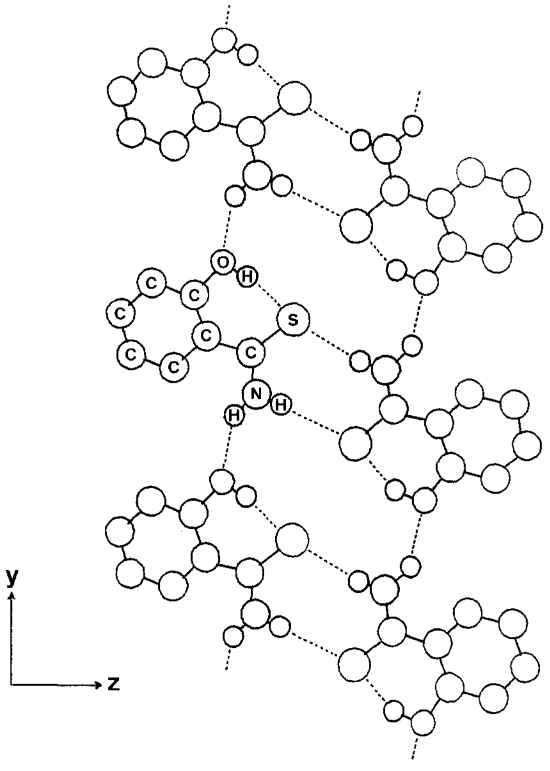


Fig. 3. Hydrogen-bond pattern of 2-hydroxythiobenzamide (aromatic hydrogens have been omitted)

limit for the existence of hydrogen-bonds from a geometrical point of view. High frequency N − H stretching bands are observed in the spectra of both compounds with frequency shifts relative to the $\bar{\nu}$(N − H) frequencies in solution of $\Delta\bar{\nu}$(N − H) = 77 and 105 cm^{-1} for (**2 O**) and (**2 S**), respectively.

Very similar to the secondary (thio)amides, in the primary (thio)amides the *trans* NH group is intermolecular associated to an $O_{(2)}$ hydroxyl oxygen atom [N...O = 3.01 Å and H...O_{cor} = 2.02 Å for (**1 O**), N...O = 2.93 + 3.01 Å and H...O_{cor} = 2.06 + 2.15 Å for (**1 S**)] linking the molecules to extended N − H...$O_{(2)}$ hydrogen-bonded chains. In both compounds the hydrogen-bonded molecules are related by translation. Additionally, the *cis* NH group donates the proton to a (thio)carbonyl group of a neighboring molecule, which on the other hand donates its *cis* NH-proton to the (thio)carbonyl group of the first molecule [N...O = 2.93 Å and H...O_{cor} = 1.93 Å for (**1 O**), N...S = 3.46 + 3.47 Å and H...O_{cor} = 2.46 + 2.54 Å for (**1 S**)] hence giving rise to closed eight-membered N − H...$O_{(1)}$(S) hydrogen-bonded dimers. The hydrogen-bond pattern of the thio-compound is depicted in Fig. 3 (cf. Ref. [21] for the oxocompound). The solid state ir spectra are in agreement with the structural data: besides the broad and low frequency O − H band, two rather narrow high frequency bands due to the weak N − H...$O_{(2)}$ and the moderately strong N − H...$O_{(1)}$(S) intermolecular hydrogen-bonds are observed. Moreover, the small splittings of the N − H stretching bands in the spectrum of (**1 S**), which become better apparent in the low temperature spectrum than in the room temperature spectrum of Fig. 1, agree with the existence of two different molecules in the asymmetric unit. The $\Delta\bar{\nu}$ (N − H) frequency shifts, that can be evaluated from the differences between solution and solid state spectra of isotopically dilute NHD oscillators, amount to 125 and 238 cm^{-1} for the oxo-, and to 58 + 63 and 166 + 210 cm^{-1} for the thiocompound. Comparing these values with those of (**2 O**) (**2 S**) the higher frequency lines of (**1 O**) and (**1 S**) should be due to the $N-H...O_{(2)}$ group, while the lower frequency lines may be assigned to the $N-H...O_{(1)}(S)$ group. Although there is a reasonable overall correspondence abetween $\Delta\bar{\nu}$ (N − H) frequency shifts and hydrogen-bond distances (for a frequency versus distance correlation for N − H...O hydrogen-bonds see Ref. [22]), a more detailed inspection of Table 4 reveals some obvious inconsistencies. In particular this applies to the $N-H...O_{(2)}$ bonds in (**2 S**) and (**1 S**), which are distinctly weaker in the latter compound despite the distinctly shorter distances. Significant deviations from the commonly accepted inverse correlation between frequency shifts and distances are, however, not really unfamiliar and have been discussed for N − H...O bonds in some detail in Ref. [18].

As to the tertiary 2-hydroxy(thio)benzamides, the consequences that arise from the steric hindrance and the resulting deviations from planar conformations are still more pronounced in the solid state than in the solutions. While these compounds were found to form rather weak, but nevertheless intramolecular $O-H...O_{(1)}(S)$ hydrogen-bonds in solutions, the characteristic intramolecular association of the OH group is replaced by intermolecular association in the solids. In all 6 N,N-disubstituted 2-hydroxy(thio)benzamides listed in Table 4 the phenolic OH groups form medium strong, approximately linear intermolecular $O-H...O_{(1)}(S)$ hydrogen-bonds [O...O = 2.63–2.75 Å and $H...O_{cor}$ = 1.68 − 1.82 Å for (**3 − 5 O**), O...S = 3.18 − 3.26 Å and $H...S_{cor}$ = 2.31–2.34 Å for [**3–5 S**], which connect the molecules to extended chains. The hydrogen-bonded molecules are related by a glide in (**3 O**) (**3 S**) and (**4 O**) and (**4 S**) and by a pseudo twofold screw axis in (**5 O**) (**5 S**). The existence of medium strong hydrogen-bonds is well confirmed by the O − H frequencies in the solid state ir spectra, the O − H stretching frequencies being smaller by about 70 cm^{-1} for $O-H...O_{(1)}$ (3 075–3 120 cm^{-1}) than for O − H...S (3 130–3 190 cm^{-1}) hydrogen-bonds. For the dihedral angles between the planes of the phenyl rings and the (thio)amide moieties values of approximately 70° are obtained with no essential differences between oxo- and thiocompounds. Comparisons show, that the distorsions around the $C_{(1)}$–$C_{(2)}$ bonds are larger for 2-hydroxy- than for *ortho*-unsubstituted compounds (e.g. 46° for N,N-dimethyl-4-bromo-benzamide [23], 47° for benzoylmorpholine [24], 63° for N,N-dimethyl-thiobenzamide [25], 65° for thiobenzoylmorpholine [26]), which most probably results from the steric requirements of the intermolecular $O-H...O_{(1)}(S)$ hydrogen-bonds.

Conclusion

On summarizing it should be emphasized that the inspection of spectroscopic and structural data of corresponding 2-hydroxybenzamides and 2-hydroxythiobenzamides revealed remarkable similarities between corresponding oxo- and thiocompounds with respect to hydrogen-bond patterns and hydrogen-bond strengths. Analogies concern (i) the intramolecular O − H...O (S) hydrogen-bonds in solution; (ii) the intramolecular O − H...O (S) hydrogen-bonds of primary and secondary (thio)amides, and the intermolecular O − H...O (S) hydrogen-bonds of tertiary (thio)amides in the solid state; (iii) the N−H...O(S) hydrogen-bonds and hence the total hydrogen-bond patterns of primary and secondary (thio)amides in the solid state.

Acknowledgement

We thank Prof. F. Pertlik for providing X-ray data prior to publication. Financial support by the Fonds zur Förderung der Wissenschaftlichen Forschung under Proj. No. 6620 kindly acknowledged.

References

[1] Derkosch J., Mikenda W., Steinwender E. (1987) Spectrochim. Acta **43 A**: 823
[2] Fong C. W., Grant H. G. (1981) Aust. J. Chem. **34**: 957
[3] Pertlik F. (1990) Monatsh. Chem. **121**: 129
[4] Pertlik F. (to be published)
[5] Pertlik F. (1987) Monatsh. Chem. **118**: 1349
[6] Van Roey P., Kerr K. A. (1981) Acta Cryst. **B37**: 1679
[7] Kerr K. A., Van Roey P. (1979) Acta Cryst. **B35**: 2727
[8] Kondo M. (1972) Bull. Chem. Soc. Japan **45**: 2710
[9] Shome S. C., Mazumdar M. (1969) Anal. Chim. Acta **46**: 155
[10] Berg U. (1976) Acta Chem. Scand. **B30**: 695
[11] Banerjee K., Raychaudaury S. (1982) Bull. Chem. Soc. Japan **55**: 3621
[12] Kondo M. (1979) Bull. Chem. Soc. Japan **52**: 521
[13] Steinwender E., Mikenda W. (to be published)
[14] Walter W. (1970) Z. Chem. **10**: 371
[15] Ginzburg I. M., Bessonova N. N. (1975) Zh. Obshch. Khim. **45**: 622
[16] Taylor R., Kennard O. (1983) Acta Cryst. **B39**: 133
[17] Blake C. C. F., Small R. W. H. (1972) Acta Cryst. **B28**: 2201
[18] Leiserowitz L., Tuval M. (1978) Acta Cryst. **B34**: 1230
[19] Colleter J. C., Gadret M. (1967) Bull. Soc. Chim. France **9**: 3463
[20] Etter M. C. (1982) J. Am. Chem. Soc. **104**: 1095
[21] Etter M. C., Urbanczyk-Lipkowska Z., Ameli T. M., Panunto T. W. (1988) J. Cryst. Spectrosc. Res. **18**: 491
[22] Lautie A., Froment F., Novak A. (1976) Spectrosc. Lett. **9**: 289
[23] Shibaev R. P., Atovmyan L. O. (1968) Zh. Strukt. Khim. **9**: 90
[24] Arte E., Feneau-Dupont J., Declercq J. P., Germain G., Van Meersche M. (1977) Cryst. Struct. Comm. **6**: 767
[25] Walter W., Harto S., Voss J. (1976) Acta Cryst. **B32**: 2876
[26] Kerr K. A., Van Roey P. (1979) Acta Cryst. **B35**: 2344

Received February 20, 1990. Accepted April 24, 1990