Monatshefte für Chemie 126, 495–504 (1995)

Monatshefte für Chemie
Chemical Monthly
© Springer-Verlag 1995
Printed in Austria

Hydrogen Bonding in 2-Hydroxybenzoic, 2-Hydroxythiobenzoic, and 2-Hydroxydithiobenzoic Acid. A Structural and Spectroscopic Study[#]

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Summary. X-ray structural data are reported for 2-hydroxythiobenzoic acid ($T = 200\,\mathrm{K}$; $P2_1/a$; $a = 14.903(5)$ Å, $b = 5.203(3)$ Å, $c = 9.114(6)$ Å, $\beta = 92.40(4)°$; $Z = 4$; $R = 0.049$) and 2-hydroxydithiobenzoic acid ($T = 297\,\mathrm{K}$; $P2_1/a$; $a = 14.416(3)$ Å, $b = 13.447(3)$ Å, $c = 3.947(1)$ Å, $\beta = 90.96(2)°$; $Z = 4$; $R = 0.047$). In 2-hydroxythiobenzoic acid, each two molecules form cyclic dimers *via* S–H···O=C hydrogen bonds, analogous to the association pattern of 2-hydroxybenzoic acid. In 2-hydroxydithiobenzoic acid, the molecules are linked to chains by S–H···O(H)-C hydrogen bonds. Solid state IR, and solution IR and NMR spectroscopic data of 2-hydroxybenzoic acid, 2-hydroxythiobenzoic acid, and 2-hydroxydithiobenzoic acid are summarized. The main characteristics of the intramolecularly associated phenolic O–H groups of the three title compounds are $\tilde{\nu}_{OH} = 3230, 3120, 2750\,\mathrm{cm}^{-1}$ for the solids, $\tilde{\nu}_{OH} = 3210, 3185, 2945\,\mathrm{cm}^{-1}$ for solutions (CCl_4), and $\delta_{OH} = 10.21, 10.53, 12.20$ ppm for solutions (CCl_4:$CDCl_3$ = 5:1).

Keywords. Hydrogen bonding; 2-Hydroxy(di(thio))benzoic acid; IR spectra; NMR spectra; X-ray diffraction.

Wasserstoffbrückenbindungen in 2-Hydroxybenzoesäure, 2-Hydroxythiobenzoesäure und 2-Hydroxydithiobenzoesäure. Strukturelle und spectroskopische Untersuchungen

Zusammenfassung. Röntgenstrukturdaten von 2-Hydroxythiobenzoesäure ($T = 200\,\mathrm{K}$; $P2_1/a$; $a = 14.903(5)$ Å, $b = 5.203(3)$ Å, $c = 9.114(6)$ Å, $\beta = 92.40(4)°$; $Z = 4$; $R = 0.049$) und 2-Hydroxydithiobenzoesäure ($T = 297\,\mathrm{K}$; $P2_1/a$; $a = 14.416(3)$ Å, $b = 13.447(3)$ Å, $c = 3.947(1)$ Å, $\beta = 90.96(2)°$; $Z = 4$; $R = 0.047$) werden berichtet. In 2-Hydroxythiobenzoesäure sind jeweils zwei Moleküle über S–H···O=C Wasserstoffbrückenbindungen zu zyklischen Dimeren verbunden, in Analogie zum Assoziationsmuster von 2-Hydroxybenzoesäure. In 2-Hydroxydithiobenzoesäure sind die Moleküle hingegen über S–H···O(H)–C Wasserstoffbrückenbindungen zu Ketten verknüpft. Festkörper-IR-, und Lösungs-IR- und NMR-spektroskopische Daten von 2-Hydroxybenzoesäure, 2-Hydroxythiobenzoesäure und 2-Hydroxydithiobenzoesäure werden gegenübergestellt. Die wesentlichen Charakteristika der intra-

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[#] Dedicated to Prof. *O. Olaj* on the occasion of his 60th birthday

molekular assoziierten phenolischen O–H Gruppen der drei Titelverbindungen sind $\tilde{\nu}_{OH} = 3230, 3120, 2750\,cm^{-1}$ für die Festkörper sowie $\tilde{\nu}_{OH} = 3210, 3185, 2945\,cm^{-1}$ und $\delta_{OH} = 10.21, 10.53, 12.20\,ppm$ für Lösungen (CCl_4 bzw. CCl_4:$CDCl_3$ = 5:1).

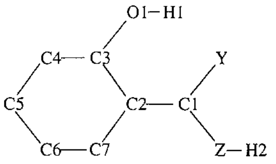
Introduction

Within our studies on intramolecular hydrogen bonds in 2-hydroyxybenzoyl and 2-hydroxythiobenzoyl compounds, the three title compounds have been investigated by IR and NMR spectroscopy and by X-ray diffraction. For 2-hydroxybenzoic acid ("salicylic acid"), structural data are available from an early neutron diffraction study [1] and spectroscopic data have already been published in various papers (cf. Ref. [2, 3]). In contrast, for 2-hydroxydithiobenzoic acid no structural and only a few spectroscopic data have previously been reported [3], and 2-hydroxythiobenzoic acid seems to be almost total unknown. In the present paper we report X-ray structural data of 2-hydroxythiobenzoic acid and of 2-hydroxydithiobenzoic acid as well as solid state IR data and solution IR and NMR data that are of interest for the characterization of the hydrogen bonds. Structural and spectroscopic features of the inter- and intramolecular association patterns of the three title compounds are discussed.

Experimental

Compounds

The compounds are schematically depicted in Scheme 1 along with the numbering of atoms used in this paper.



	1	2	3
Y	O2	O2	S2
Z	O3	S1	S1

Scheme 1

2-Hydroxybenzoic acid (**1**, $C_7H_6O_3$): commercially available product (Aldrich) was used. 2-Hydroxythiobenzoic acid (**2**, $C_7H_6O_2S$): prepared from acetylsalicoyl chloride, KOH and H_2S [4]; white crystals; m.p. = 35–37 °C; ^1H NMR ($CDCl_3$): $\delta = 4.43$ (SH), 6.94 (t), 6.99 (d), 7.50 (dt), 7.70 (dd), 10.73 (OH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 118.3$, 119.6, 129.5, 130.4, 136.8, 159.7, 196.0 ppm. 2-Hydroxydithiobenzoic acid (**3**, $C_7H_6OS_2$; for the preparation see Ref. [3]): orange crystals; m.p. = 49–51 °C; ^1H NMR ($CDCl_3$): $\delta = 5.87$ (SH), 6.90 (t), 7.03 (d), 7.44 (t), 7.92 (d), 12.33 (OH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 119.1$, 120.2, 125.6, 128.0, 137.0, 160.5, 223.1 ppm.

X-ray diffraction

For the X-ray structure determinations of **2** and **3** elongated prismatic crystals of about 0.1 mm diameter and 0.4 mm length were used. As both compounds are distinctly volatile, the crystals were enclosed in thin-walled glass capillaries. All measurements were performed with a Philips PW 1100 four-circle diffractometer using graphite monochromatized Mo$K\alpha$ radiation. Reflection data were measured by Θ-2Θ-scans and corrected for crystal decay (here sublimation of the crystals inside the capillary), and *Lorentz* and polarization effects. Absorption effects were small and ignored. Both structures were solved with direct methods and refined by full-matrix least-squares on F with weights based on counting statistics and corrections for extinction using the program SHELX76 [5]. Anisotropic temperature factors were used for all non-hydrogen atoms. Carbon attached hydrogen atoms were generated in calculated positions and rided with the atoms to which they were bonded (C–H = 0.96 Å). Oxygen- and sulfur-bonded hydrogen atoms were located from difference *Fourier* syntheses and refined without positional constraints. The isotropic temperature factors of the hydrogen atoms were refined for each compound as one variable which was multiplied with the equivalent isotropic temperature factors of the hydrogen carrier atoms.

For 2-hydroxythiobenzoic acid (**2**) at first a room temperature measurement was carried out. Due to sublimation the crystal lost about 31% of its scattering power during the 16 hours of data collection. After successful solution and refinement of the room temperature structure (all data on this part of work are deposited), a second data set was collected at low temperature using a Leybold-Heraeus NCD2 nitrogen gas-stream cooling device. Since cooling to 120 K obviously destroyed the crystals (likely due to a phase transition), a temperature of 200 K was used for data collection. Two failures of the cooling device during data collection decreased the scattering power of the crystal by at most 25% for which corrections *via* the reference reflections were applied. Moreover, two sets of independent reflections were measured. Data reduction and structure refinement were then carried out as described above.

Table 1. Summary of crystal data, data on intensity measurements, and crystal structure refinements

	2	**3**
Formula	$C_7H_6O_2S$	$C_7H_6OS_2$
Temperature [K]	200	297
Space group	$P2_1/a$ (No. 14)	$P2_1/a$ (No. 14)
a [Å]	14.903(5)	14.416(3)
b [Å]	5.203(3)	13.447(3)
c [Å]	9.114(6)	3.947(1)
β [°]	92.40(4)	90.96(2)
V [Å]	706.1(7)	765.0(3)
Z	4	4
ρ_{calc} [gcm^{-3}]	1.450	1.478
μ (Mo$K\alpha$) [cm^{-1}]	3.7	5.9
Θ-scan width [°]	1.2	1.2
Θ-scan rate [°min^{-1}]	2	4
Range of data Θ_{max} [°]	27	25
Range of h, k, l	$\pm h$; $\pm k$; l	$\pm h$; k; l
Measured reflections	3018	1480
Unique non-extinct reflections	1530	1350
Internal consistency (on F_o)	0.038	0.067
Reflections used in refinement	797 [$F_o > 4\sigma(F_o)$]	643 [$F_o > 4\sigma(F_o)$]
Number of refined parameters	98	98
w	$1/[\sigma^2(F_o) + 0.0002F_0^2]$	
R/wR	0.049/0.041	0.047/0.038
S	1.13	1.06
$(\Delta/\sigma)_{max}$	<0.01	<0.01
$(\rho)_{min/max}$ [e Å^{-3}]	−0.29/0.40	−0.22/0.22

For 2-hydroxydithiobenzoic acid (**3**), several orange needles were tested but only one of them with a relatively poor scattering power gave satisfying reflection profiles. During the 13 hours of data collection the crystal lost 34% of its scattering power by sublimation inside a capillary.

Further informations on crystallography, data collection, data reduction, and structure refinement are summarized in Table 1. Atomic coordinates and isotropic temperature factors are given in

Table 2. Atomic coordinates and isotropic temperature factors for 2-hydroxythiobenzoic acid (**2**)

	x/a	y/b	z/c	U_{eq}/U_{iso} [Å^2]
S1	−0.05296(6)	0.7100(3)	0.1919(1)	0.0449(4)
O2	0.0951(2)	0.8277(6)	0.0638(3)	0.042(1)
O1	0.2475(2)	0.5939(7)	0.1004(3)	0.045(1)
C1	0.0627(2)	0.6879(9)	0.1537(4)	0.028(1)
C2	0.1144(2)	0.4831(8)	0.2324(4)	0.028(1)
C3	0.2052(2)	0.4484(9)	0.1985(4)	0.034(1)
C4	0.2542(3)	0.2512(8)	0.2667(4)	0.042(2)
C5	0.2166(3)	0.0974(9)	0.3680(4)	0.045(2)
C6	0.1273(3)	0.1335(9)	0.4065(4)	0.046(2)
C7	0.0785(3)	0.3237(9)	0.3383(4)	0.037(1)
H1	0.211(2)	0.734(8)	0.064(4)	0.057
H2	−0.069(2)	0.910(8)	0.091(4)	0.057
H4	0.3154	0.2232	0.2419	0.053
H5	0.2516	−0.0376	0.4138	0.057
H6	0.1012	0.0266	0.4792	0.057
H7	0.0173	0.3490	0.3640	0.047

Table 3. Atomic coordinates and isotropic temperature factors for 2-hydroxydithiobenzoic acid (**3**)

	x/a	y/b	z/c	U_{eq}/U_{iso} [Å^2]
S1	0.1287(1)	0.5032(1)	0.1542(4)	0.0748(6)
S2	0.2941(1)	0.3863(1)	0.0290(4)	0.0670(6)
O1	0.2591(3)	0.1858(3)	0.2656(11)	0.076(2)
C1	0.1871(3)	0.3909(4)	0.1707(12)	0.048(2)
C2	0.1356(3)	0.3078(3)	0.3060(13)	0.040(2)
C3	0.1715(4)	0.2111(4)	0.3523(14)	0.054(2)
C4	0.1189(4)	0.1353(4)	0.4900(14)	0.068(2)
C5	0.0301(4)	0.1526(5)	0.5871(14)	0.069(3)
C6	−0.0088(4)	0.2464(5)	0.5446(14)	0.060(2)
C7	0.0428(3)	0.3212(4)	0.4129(13)	0.053(2)
H1	0.286(3)	0.242(4)	0.159(14)	0.077
H2	0.186(3)	0.542(3)	0.030(11)	0.079
H4	0.1452	0.0701	0.5171	0.0[illegible]9
H5	−0.0057	0.1000	0.6848	0.070
H6	−0.0718	0.2584	0.6081	0.062
H7	0.0153	0.3860	0.3911	0.052

Table 4. Selected bond distances [Å] and angles [°] for 2-hydroxythiobenzoic acid (**2**) and 2-hydroxydithiobenzoic acid (**3**)

2		**3**	
C1–S1	1.776(3)	C1–S1	1.736(5)
C1–O2	1.211(5)	C1–S2	1.651(5)
C1–C2	1.483(5)	C1–C2	1.448(7)
C2–C3	1.412(5)	C2–C3	1.411(7)
C2–C7	1.396(6)	C2–C7	1.421(7)
C3–C4	1.391(6)	C3–C4	1.387(8)
C4–C5	1.361(6)	C4–C5	1.363(8)
C5–C6	1.403(6)	C5–C6	1.389(9)
C6–C7	1.363(6)	C6–C7	1.359(8)
C3–O1	1.349(5)	C3–O1	1.357(6)
S1–C1–O2	120.8(3)	S1–C1–S2	118.8(3)
S1–C1–C2	116.2(3)	S1–C1–C2	115.5(3)
O2–C1–C2	123.0(3)	S2–C1–C2	125.7(4)
C1–C2–C3	118.0(3)	C1–C2–C3	124.7(4)
C1–C2–C7	123.7(3)	C1–C2–C7	120.2(4)
C3–C2–C7	118.3(4)	C3–C2–C7	115.1(4)
C2–C3–O1	123.6(4)	C2–C3–O1	122.6(5)
C4–C3–O1	117.3(3)	C4–C3–C1	115.6(5)
C2–C3–C4	119.1(4)	C2–C3–C4	121.8(5)
C3–C4–C5	120.9(4)	C3–C4–C5	120.5(5)
C4–C5–C6	120.9(4)	C4–C5–C6	120.0(5)
C5–C6–C7	118.5(4)	C5–C6–C7	119.8(5)
C2–C7–C6	122.3(4)	C2–C7–C6	122.9(5)
S1–H2	1.40(4)	S1–H2	1.11(5)
H2···O2	1.99(4)	H2···O1	2.40(5)
S1···O2	3.390(3)	S1···O1	3.395(4)
S1–H2···O2	175(3)	S1–H2···O1	149(3)
C1–S1–H2	93(1)	C1–S1–H2	93(2)
O1–H1	0.97(4)	O1–H1	0.95(5)
H1···O2	1.79(4)	H1···S2	2.01(5)
O1···O2	2.587(4)	O1···S2	2.900(4)
O1–H1···O2	138(3)	O1–H1···S2	154(5)
C3–O1–H1	112(2)	C3–O1–H1	108(3)
S1–C1–C2–C3	176.2(3)	S1–C1–C2–C3	−177.7(4)
S1–C1–C2–C7	−4.1(5)	S1–C1–C2–C7	0.3(6)
O2–C1–C2–C3	−1.0(6)	S2–C1–C2–C3	3.4(7)
O2–C1–C2–C7	178.7(4)	S2–C1–C2–C7	−178.6(4)

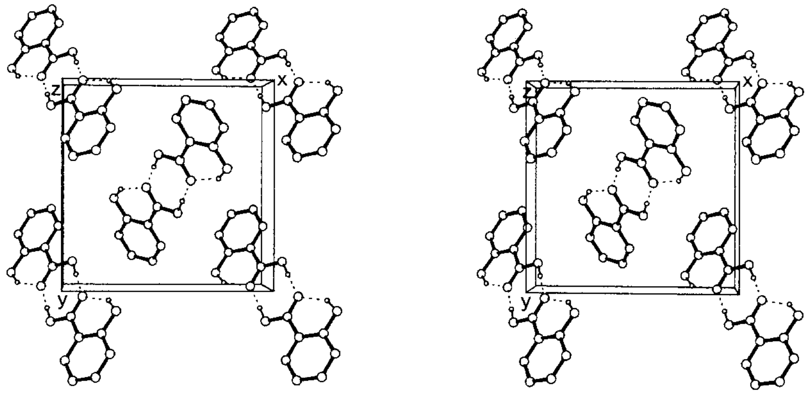


Fig. 1. Stereoview of 2-hydroxybenzoic acid (**1**)

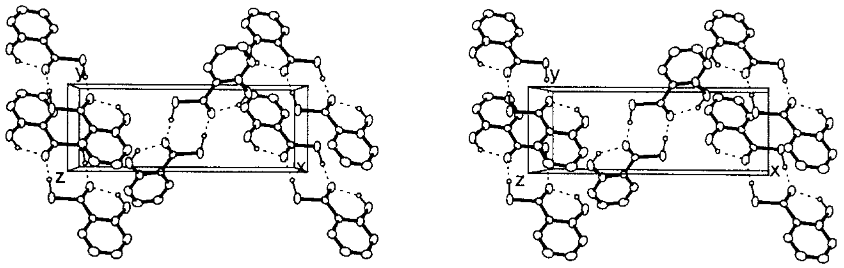


Fig. 2. Stereoview of 2-hydroxythiobenzoic acid (**2**)

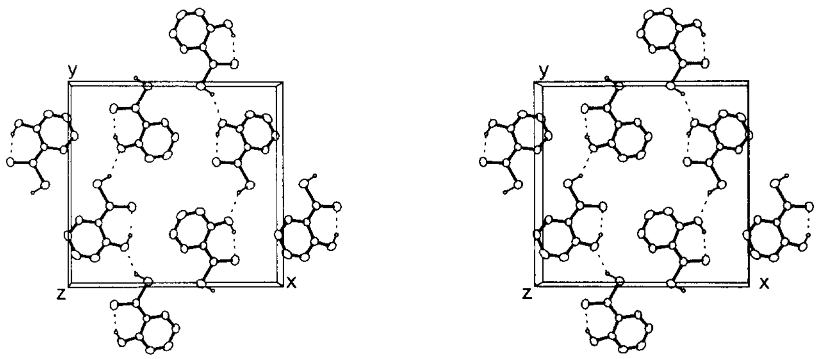


Fig. 3. Stereoview of 2-hydroxydithiobenzoic acid (**3**)

Tables 2 and 3 for **2** and **3** respectively[1]. Selected bond distances and angles are summarized in Table 4. Stereoviews of **1**, **2**, and **3** are shown in Figs. 1, 2, and 3.

Spectroscopy

IR spectra were measured with a Perkin Elmer 1740 FTIR spectrometer for solids (nujol and fluorolube mulls) and solutions (in CCl_4). NMR spectra (in CCl_4:$CDCl_3$ = 5:1) were measured with a Bruker

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[1] Anisotropic thermal parameters, least-squares planes, and structure factor data for **2** (low temperature measurement) and **3** as well as the complete material of the room temperature measurement of **2** are available from the authors upon request.

Table 5. IR stretching frequencies [cm^{-1}] and NMR proton shifts [ppm] of O–H(D) and S–H(D) groups

	1	**2**	**3**
solids			
$\bar{\nu}$(O(1)–H)	3230	3120	2750
$\bar{\nu}$(O(1)–D)	2415	2350	2105
$\bar{\nu}$(O(2)–H/S–H)	2850	2518	2530
$\bar{\nu}$(O(2)–D/S–D)	2235	1834	1840
solutions			
$\bar{\nu}$(O(1)–H)	3210	3185	2945
$\bar{\nu}$(O(1)–D)	2410	2390	2220
$\bar{\nu}$(O(2)–H/S–H)	3528	2586	2569
$\bar{\nu}$(O(2)–D/S–D)	2605	1878	1868
δ(O(1)–$\underline{H}$)	10.21	10.53	12.20
δ(O(2)–$\underline{H}$/S–$\underline{H}$)	10.98	4.47	5.77

AM 400 spectrometer. Some spectroscopic data pertinent for a characterization of the hydrogen bonds are summarized in Table 5.

Results and Discussion

Intermolecular hydrogen bonds

According to the neutron diffraction study of *Bacon* and *Jude* [1], 2-hydroxybenzoic acid (**1**) crystallizes in space group $P2_1/a$ with $a = 11.52$ Å, $b = 11.21$ Å, $c = 4.92$ Å, $\beta = 90.83°$, and a cell content of four molecules. Fig. 4 shows that the acid molecules form hydrogen bonded cyclic dimers with inversion symmetry, a kind of association that is well known from the majority of carboxylic acids. The dimensions of the hydrogen bonds are O(3)–H(2) = 0.99 Å, H(2)···O(2) = 1.650 Å, O(3)···O(2) = 2.636 Å, and O(3)–H(2)···O(2) = 179°. An analogous situation is present in the thioacid **2** (Fig. 5)[2], but the replacement of the carboxylic O–H group by a thiocarboxylic S–H group causes two major structural changes: (i) the hydrogen bond distance in **2** is distinctly larger (S(1)···O(2) = 3.390 Å) than expected from **1** when taking into account the difference between the contact radii of sulfur and oxygen ($\Delta r \approx 0.4$ Å); (ii) the C(1)–S(1)···O(2) angle of 94° in **2** is significantly smaller than the corresponding C(1)–O(3)···O(2) angle in **1** which measures 111°. The latter feature, which results from the higher p-orbital character of sulfur bonding, gives rise to a distinct shear-like shift of the two C(O)–SH groups in comparison to normal C(O)–OH dimers. As a side effect, the packing of the dimers in **1** and in **2**

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[2] To our knowledge, **2** is the first monothiocarboxylic acid for which structural data are now available (no entries could be found in the Cambridge Crystallographic Data Base).

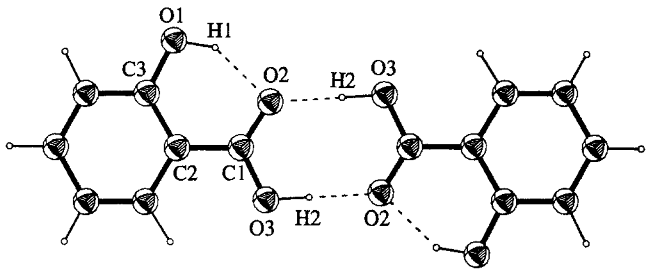

Fig. 4. 2-Hydroxybenzoic acid dimer

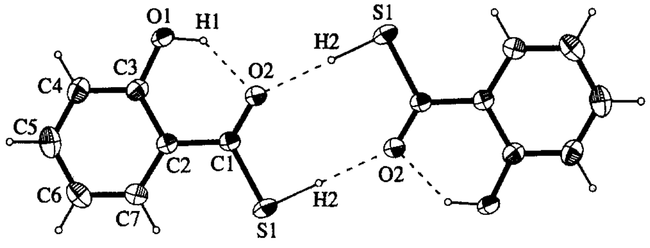

Fig. 5. 2-Hydroxythiobenzoic acid dimer

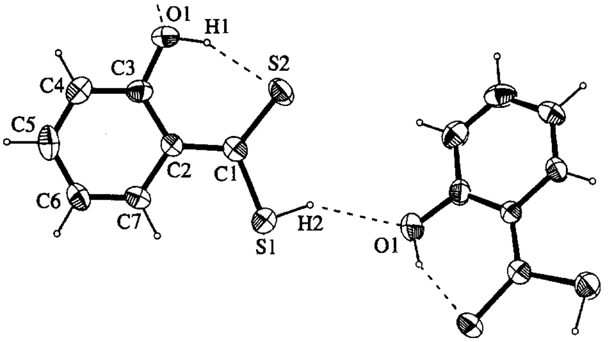

Fig. 6. 2-Hydroxydithiobenzoic acid dimer

is quite different, although both compounds crystallize in the same space group (note also the significantly differing cell dimensions). For the dithioacid **3** one might expect a similar "skew" hydrogen bonded dimer to be present as is observed with the thioacid **2** and also with some dithiophosphinic acids [6][3]. However, in **3** the S(1)–H(2) group is intermolecularly associated with the phenolic O(1) oxygen atom (Fig. 6). Thus, although the lattice symmetry is the same as that of 2-hydroxybenzoic acid (**1**) and the cell dimensions of **1** and **3** are quite similar, very different molecular arrangements and intermolecular hydrogen bond patterns are present in the two compounds.

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[3] The intermolecular association patterns of two CSSH compounds covered in the Cambridge Crystallographic Data Base, 2-iminocyclopentane dithioic acid [7] and dihydrido-*tetrakis*-(dimethylphenylphosphine)-iridium dicyanoacetic acid [8], are unclear.

As is very common for solid carboxylic acids, the strong intermolecular association of **1** is reflected by a broad ν_{OH} IR band with an absorption maximum at about 2850 cm^{-1}, whereas the frequency of the free monomeric ν_{OH} vibration, measured in highly dilute CCl_4 solution (about 10^{-6} *M*), is 3528 cm^{-1}. For the thioacid **2** a solid state $\bar{\nu}_{SH}$ frequency of 2518 cm^{-1} is observed, which raises to 2586 cm^{-1} on dissolution; for the dithioacid **3** the corresponding values are 2530 cm^{-1} and 2569 cm^{-1}, respectively. The relatively small differences between dimeric solid state and monomeric solution $\bar{\nu}_{SH}$ frequencies, when compared with the difference between the corresponding $\bar{\nu}_{OH}$ frequencies of **1**, agree with the well known poor proton donor capability of S–H groups and the corresponding rather weak S–H$\cdots$Y(Y = O, S) hydrogen bonds. Moreover, the differences between the $\bar{\nu}_{SH}$ solid – solution shifts of **2** ($\Delta\bar{\nu} = 68$ cm^{-1}) and **3** ($\Delta\bar{\nu} = 39$ cm^{-1}) can consistently be attributed to the decreased proton acceptor capability of sp^3 oxygens (**3**) when compared with sp^2 oxygens (**2**).

Intramolecular hydrogen bonds

The dimensions of the intramolecular hydrogen bond in 2-hydroxybenzoic acid (**1**) are O(1)–H(1) = 0.96 Å, H(1)$\cdots$O(2) = 1.766 Å, O(3)$\cdots$O(2) = 2.608 Å, and O(3)–H(2)$\cdots$O(2) = 145°. For the analogous O(1)–H(1)$\cdots$O(2) bond of the thioacid **2** the O$\cdots$O hydrogen bond distance is slightly shorter (2.587 Å). Both O$\cdots$O distances are, however, distinctly larger than those of other 2-hydroxybenzoyl compounds, 2.51–2.53 Å for amides [9, 10] and 2.54–2.56 Å for salts [11, 12]. In the dithioacid **3** the intramolecular association is of O–H$\cdots$S type; the O$\cdots$S distance measures 2.90 Å, which is close to the mean value of corresponding distances obtained for other 2-hydroxythiobenzoyl compounds, 2.89–2.94 Å for thioamides [9, 10] and 2.85–2.89 Å for (di)thiosalts [11, 12].

The $\bar{\nu}_{OH}$ IR frequencies of the intramolecular associated phenolic O–H group decrease within the series: **1** (solid/solution: 3230/3210 cm^{-1}) > **2** (3120/3185 cm^{-1}) ≫ **3** (2750/2945 cm^{-1}). This series, which corresponds to increasing hydrogen bond strength, complies with an accordingly increasing series of solution δ_{OH} proton shifts: **1** (10.21 ppm) < **2** (10.53 ppm) ≪ **3** (12.20 ppm). The 110 cm^{-1} difference between the solid state $\bar{\nu}_{OH}$ frequencies of **1** and **2** may reasonably well be mainly attributed to the 0.02 Å difference between the corresponding hydrogen bond distances, whereas the 25 cm^{-1} difference between the corresponding solution IR frequencies seems to be rather insignificant. On the other hand, no obvious and reasonable explanation can be given for the significant differences between the $\bar{\nu}_{OH}$ frequencies of **2** and **3**, 370 cm^{-1} for the solids and 250 cm^{-1} for the solutions. This difference is by far the largest one observed for pairs of corresponding 2-hydroxybenzoyl and 2-hydroxythiobenzoyl compounds, for which in the majority of cases rather similar $\bar{\nu}_{OH}$ frequencies are obtained [13].

Acknowledgement

The study was supported by the *Fonds zur Förderung der Wissenschaftlichen Forschung* under Project No. P6620.

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Received October 17, 1994. Accepted October 24, 1994