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Crystal Structures and Hydrogen Bonding Schemes in Four Benzamide Derivatives (2-Hydroxy-benzamide, 2-Hydroxy-thiobenzamide, 2-Hydroxy-N,N-dimethyl-benzamide, and 2-Hydroxy-N,N-dimethyl-thiobenzamide)

Franz Pertlik

Institut für Mineralogie und Kristallographie, Universität Wien, A-1010 Wien, Österreich

Summary. 2-Hydroxy-benzamide, $C_7H_7NO_2$; monoclinic; $I2/a-C_{2h}^6$; $a = 12.901(2)$, $b = 4.982(1)$, $c = 20.987(3)$ Å; $\beta = 91.50(2)°$; $Z = 8$. 2-Hydroxy-thiobenzamide, C_7H_7NOS; monoclinic; $P2_1/n-C_{2h}^5$; $a = 13.508(5)$, $b = 6.780(2)$, $c = 15.878(6)$ Å; $\beta = 93.74(5)°$; $Z = 8$. 2-Hydroxy-N,N-dimethyl-benzamide, $C_9H_{11}NO_2$; orthorhombic; $Pbca-D_{2h}^{15}$; $a = 11.752(2)$, $b = 16.680(3)$, $c = 9.079(2)$ Å; $Z = 8$. 2-Hydroxy-N,N-dimethyl-thiobenzamide, $C_9H_{11}NOS$; monoclinic; $P2_1/c-C_{2h}^5$; $a = 6.983(1)$, $b = 11.652(3)$, $c = 11.704(3)$ Å; $\beta = 100.02(2)°$; $Z = 4$. The crystal structures of these four compounds were determined (respectively refined: 2-hydroxy-benzamide) by single crystal X-ray data. The refinements of the structure parameters by least squares methods yielded in all cases $R < 0.056$. The hydrogen atoms were located by means of difference Fourier summations. The O–H ... O distances are 2.513(1) Å in 2-hydroxy-benzamide (intramolecular) and 2.625(1) Å in 2-hydroxy-N,N-dimethyl-benzamide (intermolecular). The two O–H ... S distances in 2-hydroxy-thiobenzamide are 2.904(2) Å and 2.918(2) Å (intramolceular, two molecules in the asymmetric unit) and 3.228(2) Å in 2-hydroxy-N,N-dimethyl-thiobenzamide (intermolecular). Clear N–H ... O hydrogen bonds with 2.926(1) Å and 3.006(1) Å occur only in the structure of 2-hydroxy-benzamide (intermolecular).

Keywords. 2-Hydroxy-benzamide; 2-Hydroxy-thiobenzamide; 2-Hydroxy-N,N-dimethyl-benzamide; 2-Hydroxy-N,N-dimethyl-thiobenzamide; Molecular structure; Crystal structure; Intramolecular hydrogen bond; Intermolecular hydrogen bond.

Die Kristallstrukturen und Wasserstoffbrücken-Bindungsschemata in vier Benzamid-Derivaten

Zusammenfassung. 2-Hydroxy-benzamid, $C_7H_7NO_2$; monoklin; $I2/a-C_{2h}^6$; $a = 12.901(2)$, $b = 4.982(1)$, $c = 20.987(3)$ Å; $\beta = 91.50(2)°$; $Z = 8$. 2-Hydroxy-thiobenzamid, C_7H_7NOS; monoklin; $P2_1/n-C_{2h}^5$; $a = 13.508(5)$, $b = 6.780(2)$, $c = 15.878(6)$ Å; $\beta = 93.74(5)°$; $Z = 8$. 2-Hydroxy-N,N-dimethyl-benzamid, $C_9H_{11}NO_2$; orthorhombisch; $Pbca-D_{2h}^{15}$; $a = 11.752(2)$, $b = 16.680(3)$, $c = 9.079(2)$ Å; $Z = 8$. 2-Hydroxy-N,N-dimethyl-thiobenzamid, $C_9H_{11}NOS$; monoklin; $P2_1/c-C_{2h}^5$; $a = 6.983(1)$, $b = 11.652(3)$, $c = 11.704(3)$ Å; $\beta = 100.02(2)°$; $Z = 4$. Die Kristallstrukturen dieser vier Verbindungen wurden mittels Röntgen-Einkristalldaten bestimmt (bzw. verfeinert: 2-Hydroxy-benzamid). Die Verfeinerungen der Strukturparameter nach der Methode der kleinsten Quadrate ergab in allen Fällen $R < 0.056$. Die Wasserstoffatome konnten anhand von Differenz-Fourier-Summationen belegt werden. Die O–H ... O-Abstände haben folgende Werte: 2.513(1) Å

in 2-Hydroxy-benzamid (intramolekular) und 2.625 (1) Å in 2-Hydroxy-N,N-dimethyl-benzamid (intermolekular). Die zwei O−H...S-Abstände sind in 2-Hydroxy-thiobenzamid 2.904 (2) Å und 2.918 (2) Å (intramolekular, zwei Moleküle in der asymmetrischen Einheit) und 3.228 (2) Å in 2-Hydroxy-N,N-dimethyl-thiobenzamid (intermolekular). Klar zuzuordnende N−H...O-Wasserstoffbrücken mit 2.926 (1) Å und 3.006 (1) Å treten lediglich in der Struktur des 2-Hydroxy-benzamid auf (intermolekular).

Introduction

The crystal structure determination of the four title compounds by single crystal X-ray techniques were performed to get clear cut information on the conformation of the molecules, as well as on the hydrogen bonding scheme within and between the molecules. In the two compounds, 2-hydroxy-benzamide and 2-hydroxy-thiobenzamide, not only the O−H...O and O−H...S bonds were of interest, but also the possible N−H...O bonds or N−H...S bonds of the NH_2 groups in which the N atom acts as the donor atom.

The crystal structure of the compound 2-hydroxy-benzamide (= salicylamide) was determined by Sasada et al. [1] from single crystal X-ray data, but without determination of the H atom positions.

Experimental

Single crystals of 2-hydroxy-benzamide (Fluka AG, Nr. 84230) and 2-hydroxy-thiobenzamide [2, 3] suitable for X-ray work were obtained from an ethanol-water solution, of 2-hydroxy-N,N-dimethyl-

Table 1. Summary of crystal data and experimental conditions for 2-hydroxy-benzamide (**1**), 2-hydroxy-thiobenzamide (**2**), 2-hydroxy-N,N-dimethyl-benzamide (**3**), and 2-hydroxy-N,N-dimethyl-thiobenzamide (**4**)

	1	**2**	**3**	**4**
a [Å]	12.901(2)	13.508(5)	11.752(2)	6.983(1)
b [Å]	4.982(1)	6.780(2)	16.680(3)	11.652(3)
c [Å]	20.987(3)	15.878(6)	9.079(2)	11.704(3)
β [°]	91.50(2)	93.74(5)	–	100.02(2)
Volume [Å^3]	1348.4	1451.1	1779.8	937.8
ρ_{calc} [g·cm^{-3}]	1.351	1.403	1.233	1.284
Cell content	8 $\{C_7H_7NO_2\}$	8 $\{C_7H_7NOS\}$	8 $\{C_9H_{11}NO_2\}$	4 $\{C_9H_{11}NOS\}$
Space group	$I2/a-C_{2h}^6$	$P2_1/n-C_{2h}^5$	$Pbca-D_{2h}^{15}$	$P2_1/c-C_{2h}^5$
μ (MoKα) [cm^{-1}]	0.62	3.17	0.52	2.50
2θ/ω scan mode with step width in [°]	0.03	0.035	0.03	0.03
Steps/reflection + (α_1, α_2)-splitting	50	60	45	60
Time/step [s]	0.5 to 1.5	0.5 to 1.5	0.5 to 1.5	0.5 to 1.5
Range of data: 2θ max [°]	70	50	60	65
Range of h, k, l	$h, \pm k, \pm l$	$\pm h, k, -l$	$\pm h, k, \pm l$	$\pm h, k, \pm l$
Measured reflections	6167	2885	5681	4061
Unique reflections	2970	2535	2597	3397
R_{int} $[\Sigma \lvert I - \langle I \rangle \rvert / \Sigma I]$	0.052	–	0.048	0.061
Reflections with $F_o > 3\sigma F_o$	1917	1809	1875	2463
Number of variables	119	237	153	153
R and wR; $w = [\sigma(F_o)]^{-2}$	0.056; 0.048	0.052; 0.050	0.053; 0.048	0.046; 0.049
Least-squares shift to error $(\Delta/\sigma)_{max}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$

Table 2. Atomic coordinates and displacement factors: (a) 2-hydroxy-benzamide; (b) molecule 1 and (c) molecule 2 of 2-hydroxy-thiobenzamide; (d) 2-hydroxy-N,N-dimethyl-benzamide; (e) 2-hydroxy-N,N-dimethyl-thiobenzamide

	x/a	y/b	z/c	U_{11}/U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
(a)									
C(1)	0.0793(1)	0.1827(2)	0.3716(1)	0.0342(5)	0.0466(6)	0.0490(7)	−0.0036(4)	0.0057(5)	−0.0021(5)
C(2)	0.1846(1)	0.2282(2)	0.3600(1)	0.0326(5)	0.0385(5)	0.0395(6)	−0.0026(4)	0.0047(4)	−0.0051(4)
C(3)	0.2582(1)	0.0719(2)	0.3928(1)	0.0380(6)	0.0467(6)	0.0483(6)	0.0000(5)	0.0020(5)	−0.0003(5)
C(4)	0.2294(1)	−0.1215(3)	0.4359(1)	0.0555(8)	0.0500(7)	0.0488(7)	0.0026(6)	0.0008(6)	0.0032(5)
C(5)	0.1256(1)	−0.1641(3)	0.4467(1)	0.0654(8)	0.0524(7)	0.0491(7)	−0.0065(6)	0.0118(6)	0.0064(6)
C(6)	0.0508(1)	−0.0141(3)	0.4151(1)	0.0453(7)	0.0622(8)	0.0596(8)	−0.0106(6)	0.0137(6)	0.0043(6)
C(7)	0.2126(1)	0.4399(2)	0.3137(1)	0.0316(5)	0.0379(5)	0.0413(5)	−0.0021(4)	0.0045(4)	−0.0043(4)
N(1)	0.3119(1)	0.4811(2)	0.3007(1)	0.0325(4)	0.0473(5)	0.0535(6)	−0.0018(4)	0.0070(4)	0.0042(5)
O(1)	0.1432(1)	0.5802(2)	0.2871(1)	0.0359(4)	0.0501(5)	0.0595(5)	0.0013(3)	0.0040(4)	0.0098(4)
O(2)	0.0030(1)	0.3250(2)	0.3418(1)	0.0306(4)	0.0697(6)	0.0807(7)	−0.0037(4)	0.0034(4)	0.0189(5)
H(3)	0.3325(11)	0.1005(28)	0.3861(7)	0.0575(39)					
H(4)	0.2792(12)	−0.2361(31)	0.4565(7)	0.0634(43)					
H(5)	0.1041(13)	−0.3034(30)	0.4747(7)	0.0655(43)					
H(6)	−0.0254(14)	−0.0446(31)	0.4210(7)	0.0750(47)					
H(1n)	0.3259(12)	0.6207(29)	0.2733(7)	0.0622(42)					
H(2n)	0.3634(11)	0.3718(27)	0.3159(7)	0.0525(38)					
H(1)	0.0349(15)	0.4578(34)	0.3174(8)	0.0834(52)					
(b)									
C(11)	0.6084(3)	0.5525(5)	0.7252(2)	0.0461(25)	0.0485(23)	0.0495(22)	−0.0035(19)	0.0095(18)	−0.0025(19)
C(21)	0.6293(3)	0.3588(5)	0.7486(2)	0.0458(25)	0.0419(20)	0.0364(18)	−0.0001(19)	0.0082(17)	0.0016(17)
C(31)	0.6467(3)	0.2252(6)	0.6836(2)	0.0707(31)	0.0488(23)	0.0441(22)	0.0111(22)	0.0090(20)	−0.0018(19)
C(41)	0.6398(4)	0.2805(7)	0.6001(3)	0.0967(39)	0.0740(30)	0.0385(22)	0.0204(28)	0.0158(22)	−0.0033(22)
C(51)	0.6150(3)	0.4683(7)	0.5792(2)	0.0766(33)	0.0820(33)	0.0401(22)	0.0036(27)	0.0088(21)	0.0111(23)
C(61)	0.5996(3)	0.6053(6)	0.6402(2)	0.0723(31)	0.0524(24)	0.0474(22)	0.0038(23)	0.0041(20)	0.0139(21)
C(71)	0.6340(3)	0.2884(5)	0.8375(2)	0.0478(25)	0.0383(20)	0.0401(20)	0.0012(18)	0.0067(17)	−0.0043(17)

Table 2 (continued)

	x/a	y/b	z/c	U_{11}/U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	0.6263(2)	0.0984(4)	0.8498(2)	0.0836(26)	0.0416(18)	0.0363(16)	0.0005(18)	0.0023(16)	0.0057(14)
S(1)	0.6496(1)	0.4397(1)	0.9214(1)	0.1029(10)	0.0494(6)	0.0377(5)	−0.0158(6)	0.0052(5)	−0.0060(5)
O(1)	0.5928(2)	0.7007(4)	0.7815(2)	0.0968(23)	0.0382(14)	0.0537(17)	0.0050(15)	0.0046(15)	−0.0003(13)
H(11)	0.6312(23)	0.0468(48)	0.8982(19)	0.0380(101)					
H(21)	0.6046(30)	0.0005(64)	0.8079(26)	0.1121(151)					
H(31)	0.6656(20)	0.0886(40)	0.6955(16)	0.0345(80)					
H(41)	0.6492(29)	0.1682(58)	0.5655(23)	0.0993(143)					
H(51)	0.6065(27)	0.5192(60)	0.5225(23)	0.0931(135)					
H(61)	0.5842(21)	0.7406(41)	0.6295(16)	0.0384(85)					
H(1)	0.6100(25)	0.6358(52)	0.8306(20)	0.0725(114)					
(c)									
C(12)	0.3808(3)	0.2294(5)	0.7584(2)	0.0483(26)	0.0460(22)	0.0389(20)	−0.0043(19)	0.0018(17)	0.0006(17)
C(22)	0.3757(3)	0.0321(5)	0.7840(2)	0.0467(24)	0.0419(20)	0.0340(18)	−0.0023(19)	0.0038(16)	−0.0030(17)
C(32)	0.3609(3)	−0.1109(6)	0.7219(2)	0.0725(30)	0.0524(23)	0.0410(21)	−0.0071(23)	0.0011(20)	−0.0030(20)
C(42)	0.3536(4)	−0.0648(7)	0.6368(2)	0.1007(40)	0.0687(30)	0.0418(23)	−0.0167(28)	−0.0024(23)	−0.0126(23)
C(52)	0.3597(4)	0.1302(7)	0.6130(2)	0.0865(35)	0.0887(34)	0.0342(21)	−0.0121(29)	−0.0052(21)	0.0098(25)
C(62)	0.3735(3)	0.2747(6)	0.6711(2)	0.0694(32)	0.0535(25)	0.0523(24)	−0.0076(23)	0.0026(22)	0.0137(21)
C(72)	0.3839(3)	−0.0282(5)	0.8744(2)	0.0494(26)	0.0374(20)	0.0407(20)	−0.0015(18)	0.0051(17)	0.0021(17)
N(2)	0.4050(3)	−0.2135(4)	0.8908(2)	0.0939(28)	0.0421(18)	0.0391(17)	0.0053(19)	0.0129(17)	0.0008(15)
S(2)	0.3652(1)	0.1276(2)	0.9547(1)	0.1096(10)	0.0485(6)	0.0377(5)	0.0166(7)	0.0116(5)	−0.0025(5)
O(2)	0.3956(2)	0.3840(4)	0.8110(2)	0.0945(23)	0.0404(15)	0.0518(16)	−0.0082(15)	0.0086(15)	0.0004(14)
H(12)	0.4064(25)	−0.2500(48)	0.9454(20)	0.0660(111)					
H(22)	0.4143(33)	−0.3208(64)	0.8399(27)	0.1184(164)					
H(32)	0.3521(19)	−0.2453(36)	0.7344(15)	0.0284(76)					
H(42)	0.3349(25)	−0.1633(50)	0.5968(20)	0.0689(114)					
H(52)	0.3418(27)	0.1639(52)	0.5566(22)	0.0772(118)					
H(62)	0.3732(22)	0.4140(44)	0.6551(17)	0.0483(92)					
H(2)	0.3913(30)	0.3307(61)	0.8721(24)	0.0904(148)					

Table 2 (continued)

	x/a	y/b	z/c	U_{11}/U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
(d)									
C(1)	0.8710(1)	0.8765(1)	0.5871(2)	0.0648(8)	0.0443(8)	0.0499(8)	0.0029(6)	0.0037(6)	0.0047(7)
C(2)	0.7596(1)	0.8778(1)	0.5363(1)	0.0462(7)	0.0391(6)	0.0446(7)	0.0015(6)	0.0049(6)	0.0028(6)
C(3)	0.7263(2)	0.8229(1)	0.4289(2)	0.0615(10)	0.0482(8)	0.0585(9)	−0.0017(7)	0.0026(8)	−0.0052(8)
C(4)	0.8031(2)	0.7689(1)	0.3705(2)	0.0888(15)	0.0493(10)	0.0678(11)	0.0038(9)	0.0086(11)	−0.0128(9)
C(5)	0.9132(2)	0.7684(1)	0.4207(2)	0.0790(13)	0.0486(10)	0.0726(12)	0.0175(8)	0.0213(10)	0.0027(9)
C(6)	0.9483(1)	0.8212(1)	0.5282(2)	0.0508(9)	0.0576(10)	0.0692(10)	0.0150(7)	0.0125(8)	0.0155(9)
C(7)	0.6710(1)	0.9302(1)	0.6048(1)	0.0383(7)	0.0461(8)	0.0430(7)	0.0007(6)	−0.0056(6)	−0.0037(7)
C(8)	0.5890(2)	1.0604(1)	0.6530(2)	0.0660(12)	0.0539(10)	0.0774(14)	0.0184(8)	−0.0023(10)	−0.0089(11)
C(9)	0.7667(2)	1.0506(1)	0.5077(3)	0.0735(12)	0.0531(10)	0.0802(13)	0.0005(9)	0.0093(11)	0.0171(10)
N(1)	0.6766(1)	1.0093(1)	0.5880(1)	0.0532(7)	0.0428(7)	0.0527(7)	0.0058(5)	−0.0011(6)	−0.0020(6)
O(1)	0.5926(1)	0.8971(1)	0.6733(1)	0.0496(6)	0.0553(6)	0.0773(7)	−0.0031(5)	0.0165(6)	−0.0060(6)
O(2)	0.8988(1)	0.9288(1)	0.6953(1)	0.0503(7)	0.0734(7)	0.0711(7)	0.0125(6)	−0.0165(6)	−0.0142(6)
H(81)	0.5864(20)	1.1063(16)	0.6075(31)	0.1290(101)					
H(82)	0.5144(27)	1.0396(15)	0.6394(32)	0.1421(101)					
H(83)	0.5722(27)	1.0577(17)	0.7612(42)	0.1619(111)					
H(91)	0.7407(21)	1.0882(15)	0.4448(26)	0.1170(88)					
H(92)	0.8118(22)	1.0825(16)	0.5740(28)	0.1248(97)					
H(93)	0.8276(24)	1.0142(18)	0.4658(31)	0.1356(94)					
H(3)	0.6442(15)	0.8238(8)	0.3909(18)	0.0587(44)					
H(4)	0.7758(16)	0.7334(12)	0.2958(21)	0.0852(60)					
H(5)	0.9691(16)	0.7320(11)	0.3816(21)	0.0800(54)					
H(6)	1.0274(18)	0.8210(9)	0.5639(19)	0.0734(51)					
H(1)	0.9678(18)	0.9184(10)	0.7349(21)	0.0804(56)					
(e)									
C(1)	0.8102(2)	0.2740(1)	0.3972(1)	0.0425(27)	0.0400(8)	0.0335(7)	0.0001(6)	0.0054(6)	−0.0018(6)
C(2)	0.8250(2)	0.3534(1)	0.3094(1)	0.0400(7)	0.0351(7)	0.0321(7)	−0.0007(6)	0.0054(6)	−0.0032(6)

Table 2 (continued)

	x/a	y/b	z/c	U_{11}/U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(3)	0.9925(3)	0.3531(2)	0.2600(2)	0.0483(8)	0.0557(11)	0.0442(9)	−0.0010(8)	0.0139(7)	0.0004(8)
C(4)	1.1411(3)	0.2768(2)	0.2957(2)	0.0440(9)	0.0777(14)	0.0602(11)	0.0068(9)	0.0160(8)	−0.0086(11)
C(5)	1.1224(3)	0.1959(2)	0.3799(2)	0.0497(9)	0.0600(12)	0.0614(12)	0.0168(9)	0.0000(9)	−0.0087(10)
C(6)	0.9583(3)	0.1949(2)	0.4304(2)	0.0581(2)	0.0442(9)	0.0438(9)	0.0082(8)	0.0019(8)	0.0031(8)
C(7)	0.6590(2)	0.4301(1)	0.2627(1)	0.0414(7)	0.0325(7)	0.0326(7)	−0.0019(6)	0.0080(6)	0.0024(6)
C(8)	0.7296(3)	0.5456(2)	0.4407(2)	0.0680(12)	0.0565(12)	0.0507(11)	0.0023(10)	−0.0031(10)	−0.0202(10)
C(9)	0.4446(3)	0.5878(2)	0.2891(2)	0.0654(12)	0.0465(10)	0.0550(11)	0.0186(9)	0.0090(9)	0.0003(9)
N(1)	0.6120(2)	0.5137(1)	0.3295(1)	0.0507(7)	0.0369(7)	0.0370(7)	0.0043(6)	0.0048(6)	−0.0037(5)
S(1)	0.5383(1)	0.4094(1)	0.1275(1)	0.0639(3)	0.0522(3)	0.0319(2)	0.0107(2)	−0.0010(2)	−0.0031(2)
O(1)	0.6466(2)	0.2781(1)	0.4458(1)	0.0560(7)	0.0530(7)	0.0511(7)	0.0068(6)	0.0221(6)	0.0144(6)
H(81)	0.8151(39)	0.4886(24)	0.4717(24)	0.1148(88)					
H(82)	0.8332(43)	0.6011(25)	0.4254(27)	0.1353(107)					
H(83)	0.6597(44)	0.5870(26)	0.4913(26)	0.1379(111)					
H(91)	0.3261(36)	0.5510(22)	0.2618(21)	0.0873(78)					
H(92)	0.4546(41)	0.6274(25)	0.2170(26)	0.1189(102)					
H(93)	0.4067(42)	0.6325(29)	0.3477(28)	0.1270(108)					
H(3)	1.0062(26)	0.4089(15)	0.1988(16)	0.0494(48)					
H(4)	1.2527(26)	0.2819(18)	0.2661(16)	0.0635(55)					
H(5)	1.2299(26)	0.1408(17)	0.4037(16)	0.0625(55)					
H(6)	0.9435(23)	0.1392(16)	0.4858(15)	0.0534(50)					
H(1)	0.6408(35)	0.2228(22)	0.4934(22)	0.0885(80)					

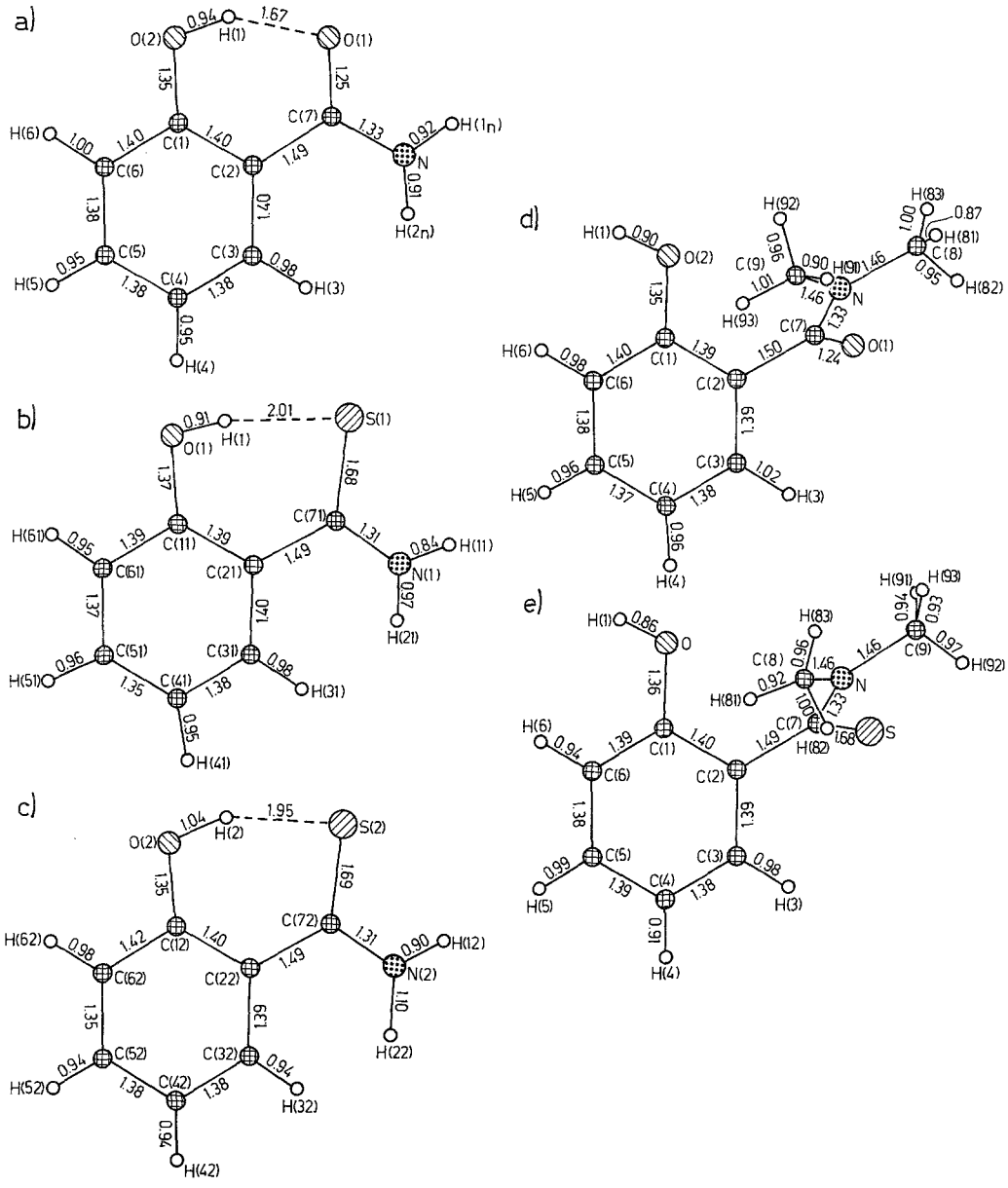


Fig. 1. The five molecules of the four different amides in projections onto the plane C(2) − C(4) C(6) with interatomic distances in Å. The e.s.d.'s for the distances between C, N, O and S atoms are < 0.01 Å, for the N−H and O−H distances < 0.05 Å. The numbering scheme used in text and tables corresponds with the scheme drawn in this figure. The intramolecular hydrogen bonds are given as broken lines: **a** 2-hydroxy-benzamide; **b** molecule 1 and **c** molecule 2 of 2-hydroxy-thiobenzamide, **d** 2-hydroxy-N,N-dimethyl-benzamide; **e** 2-hydroxy-N,N-dimethyl-thiobenzamide

benzamide [4] from a chloroforme-hexane solution and of 2-hydroxy-N,N-dimethyl-thiobenzamide [5] from a benzene-hexane solution. In all four cases cut crystal chips (cubes) of approximately 0.027 mm^3 were used for preliminary X-ray work by oscillation and Weissenberg-film methods. These investigations yielded the lattice constants, Laue symmetry and extinction rules. Further the "quality" of the crystals to be investigated were proved by these methods. The intensities of three-dimensional

X-ray data for structure determinations were collected on an automatic four-circle diffractometer. The crystals of all four compounds are stable at room temperature and atmospheric conditions. The compounds 2-hydroxy-thiobenzamide and 2-hydroxy-N,N-dimethyl-thiobenzamide decompose slowly, when exposured to X-ray radiation. Therefore in both cases only one set of unique X-ray data could be measured without greater intensity damage.

Table 1 presents crystal data for the four title compounds and experimental conditions for their structure determinations. In all four cases the collected intensities were corrected for Lorentz and polarization effects. Especially for 2-hydroxy-benzamide the atomic coordinates given by Sasada et al. [1] were used in a starting set of refinement of these coordinates, for the other three compounds the positions of the nonhydrogen atoms were determined by direct methods. The atomic coordinates of all atoms in consideration, of the anisotropic displacement factors for the atoms C, N, O, and S as well as isotropic ones for the hydrogen atoms were refined by least-squares techniques. Complex scattering functions for neutral atoms were taken from [6].

In Table 2 the atomic coordinates and anisotropic displacement factors (hydrogen atoms isotropic) of the form

$$\exp\left(-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} h_i h_j a_i^* a_j^*\right)$$

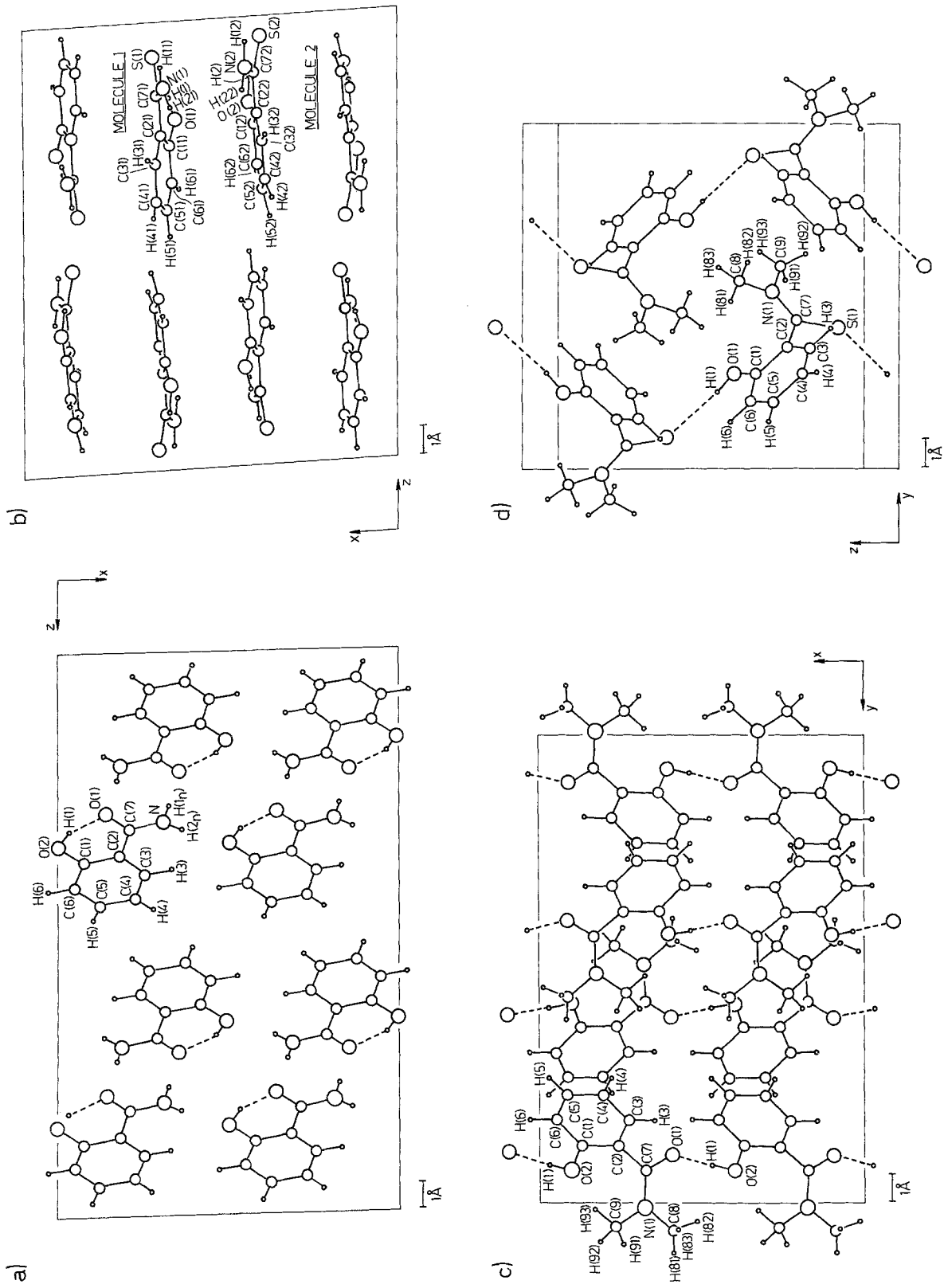
are compiled.

The e.s.d.'s are given in parentheses. Lists of structure factors have been deposited at the "Institut für Mineralogie und Kristallographie" of the University of Vienna, Austria.

Table 3. Distances (Å) within the different hydrogen-bonding systems and angles (°) at the hydrogen atom. The e.s.d.'s are given in parentheses: (a) Donor-hydrogen; (b) donor-acceptor; (c) acceptor-hydrogen; (d) angle donor-hydrogen-acceptor

2-Hydroxy-benzamide			*2-Hydroxy-N,N-dimethyl-benzamide*		
(a)	O(2)–H(1)	0.94(2)	(a)	O(2)–H(1)	0.90(2)
(b)	O(2)–O(1)	2.513(1)	(b)	O(2)–O(1)	2.625(1)
(c)	O(1)–H(1)	1.67(2)	(c)	O(1)–H(1)	1.72(2)
(d)	O(2)–H(1)–O(1)	148.4(2)	(d)	O(2)–H(1)–O(1)	174.4(10)
2-Hydroxy-thiobenzamide			*2-Hydroxy-N,N-dimethyl-thiobenzamide*		
(a)	O(1)–H(1)	0.91(3)	(a)	O–H(1)	0.86(3)
(b)	O(1)–S(1)	2.904(2)	(b)	O–S	3.228(2)
(c)	S(1)–H(1)	2.01(3)	(c)	S–H(1)	2.40(2)
(d)	O(1)–H(1)–S(1)	167.0(10)	(d)	O–H(1)–S	164.2(10)
(a)	O(2)–H(2)	1.04(3)			
(b)	O(2)–S(2)	2.918(2)			
(c)	S(2)–H(2)	1.954(3)			
(d)	O(2)–H(2)–S(2)	153.8(5)			

Fig. 2. Stacking of the molecules in different projections. The hydrogen bonds are drawn as broken lines. The notation of the different atoms is in correspondence with Table 2: **a** 2-hydroxy-benzamide; **b** 2-hydroxy-thiobenzamide; **c** 2-hydroxy-N,N-dimethyl-benzamide; **d** 2-hydroxy-N,N-dimethyl-thiobenzamide


a)
b)
c)
d)
MOLECULE 1
MOLECULE 2
1Å

Results and Discussion

Figure 1 gives the bond lengths within each molecule of the four title compounds and the intramolecular hydrogen bond distances in 2-hydroxy-benzamide and 2-hydroxy-thiobenzamide. Interatomic distances and angles of the hydrogen-bonding systems are given in Table 3, some selected torsional angles are summarized in Table 4. The interatomic distances as well as the bond angles between the non-hydrogen atoms are in accordance with crystal chemical experience: related literature, interatomic distances and bond angles of salicylamide derivates were compiled by Etter et al. [7]. The values of the C–H and O–H distances are, as usual, somewhat short in comparison with results from neutron diffraction structure determinations [8]. Responsible for this shortening is the delocalization of the binding electrons between carbon, oxygen and hydrogen, respectively.

The molecules of the two amids with unsubstituted NH_2 groups are more or less planar and the hydrogen bonds of the hydroxy groups are built up within the same molecule with O resp. S atom as acceptors. Further in 2-hydroxy-benzamide there are two N–H ... O bonds to a neighbouring molecule [N–H(1n) ... O(1) = 2.926(1) Å and N–H(2n) ... O(2) = 3.006(1) Å]. In 2-hydroxy-thiobenzamide one intermolecular N–H ... S distance from each one molecule can be interpreted as a hydrogen bond [N(1) – H(11) ... S(2) = 3.458(3) Å and N(2) – H(12) ... S(1) = 3.474(3) Å]. For the atoms H(21) and H(22) no atom neighbours within the range up to 3.6 Å from the central N atom and with a plausible orientation to form a N–H ... S or O bond were found.

This hydrogen bonding scheme shows that in the amides with unsubstituted NH_2 groups (in both cases) the molecules are connected to endless chains by N–H ... O and N–H ... S bonds, respectively. In the amides with substituted NH_2 groups the molecules are also combined to chains in one direction, but contrary to the compounds with unsubstituted NH_2 groups, by hydrogen bonds of the type O–H ... O and O–H ... S, respectively. In the other two directions the molecules are combined by van der Waals forces in all four compounds (cf. Fig. 2).

Table 4. Selected torsional angles (°) with e.s.d.'s in parentheses

2-Hydroxy-benzamide		*2-Hydroxy-N,N-dimethyl-benzamide*	
O(2)–C(1)–C(2)–C(7)	0.2(1)	O(2)–C(1)–C(2)–C(7)	4.4(1)
C(1)–C(2)–C(7)–O(1)	2.1(1)	C(1)–C(2)–C(7)–N	69.7(1)
C(3)–C(2)–C(7)–N	2.0(1)	C(2)–C(7)–N–C(8)	179.1(1)
		C(2)–C(7)–N–C(9)	1.3(1)
		C(3)–C(2)–C(7)–O(1)	61.3(1)
2-Hydroxy-thiobenzamide		*2-Hydroxy-N,N-dimethyl-thiobenzamide*	
O(1)–C(11)–C(21)–C(71)	2.0(3)	O–C(1)–C(2)–C(7)	6.4(1)
C(11)–C(21)–C(71)–S(1)	19.3(2)	C(1)–C(2)–C(7)–N	70.4(1)
C(31)–C(21)–C(71)–N(1)	18.9(3)	C(2)–C(7)–N–C(8)	8.7(1)
		C(2)–C(7)–N–C(9)	177.2(1)
O(2)–C(12)–C(22)–C(72)	1.6(4)	C(3)–C(2)–C(7)–S	64.9(1)
C(12)–C(22)–C(72)–S(2)	19.3(2)		
C(32)–C(22)–C(72)–N(2)	18.9(3)		

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