

The acid adducts hydrazinium 2-hydroxybenzoate–2-hydroxybenzoic acid (1/1) and hydrazinium 3-hydroxy-2-naphthoate–3-hydroxy-2-naphthoic acid (1/1)

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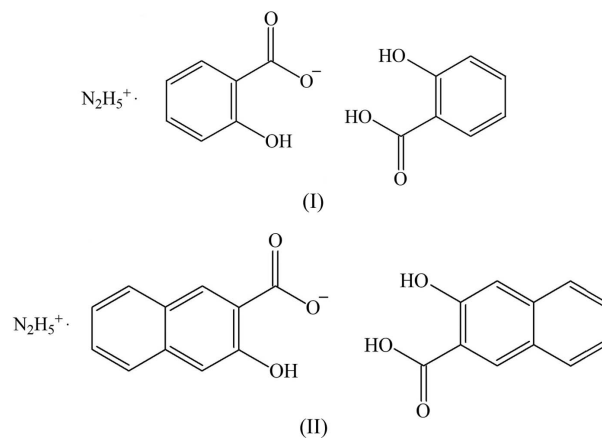
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The title molecular salts, $\text{N}_2\text{H}_5^+ \cdot \text{C}_7\text{H}_5\text{O}_3^- \cdot \text{C}_7\text{H}_6\text{O}_3$ and $\text{N}_2\text{H}_5^+ \cdot \text{C}_{11}\text{H}_7\text{O}_3^- \cdot \text{C}_{11}\text{H}_8\text{O}_3$, are acid adducts containing a hydrazinium cation, one molecule of a deprotonated acid and one molecule of a neutral acid. The two compounds contain essentially identical hydrogen-bond networks between the hydrazinium cation and the acid molecules, which define closely comparable two-dimensional layers in the structures. The planes of the aromatic rings within both structures are approximately parallel and the layers are stacked with comparable intermolecular interactions.

Comment

Acid adducts comprise a combination of an acid and a salt of that acid held together in a single crystal structure stabilized by hydrogen bonds. Structurally characterized examples include 8-hydroxyquinoline salicylate salicylic acid (Jebamony & Thomas Muthiah, 1998), pyridinium 3,5-dinitrosalicylate 3,5-dinitrosalicylic acid (Smith *et al.*, 2003) and tetra-*n*-butylammonium 2,6-dihydroxybenzoate 2,6-dihydroxybenzoic acid (Almeida Paz *et al.*, 2003). Hydrazine, a diacidic base, forms many crystalline salts with carboxylic acids and their structures have been studied (Nilsson *et al.*, 1968; Hady *et al.*, 1969; Thomas, 1973; Thomas & Liminga, 1978; Gajapathy *et al.*, 1983; Chevrier *et al.*, 1987; Fun *et al.*, 1995; Bhogala *et al.*, 2005; Starosta & Leciejewicz, 2008). Amongst hydroxy-substituted aromatic acids, the formation of hydrazinium 2-hydroxybenzoate has been reported (Kuppasamy *et al.*, 1995), although its crystal structure has not been determined. In this paper, we report the crystal structure of the acid adduct hydrazinium 2-hydroxybenzoate–2-hydroxybenzoic acid (1/1), (I), and the closely related adduct hydrazinium 3-hydroxy-2-naphthoate–3-hydroxy-2-naphthoic acid (1/1), (II).

The asymmetric units of (I) and (II) contain one acid anion and one neutral acid molecule linked by hydrogen bonds to the N_2H_5^+ cation (Figs. 1 and 2). After transferring its proton to hydrazine, the deprotonated carboxylate group shows



closely comparable bond lengths: C7–O1 = 1.2507 (13) Å and C7–O2 = 1.2648 (12) Å in (I), and C1–O1 = 1.2465 (14) Å and C1–O2 = 1.2635 (13) Å in (II). The C2–C1–C7–O2 torsion angle in (I) is 19.03 (15)°, while the comparable torsion angle in (II), *viz.* C11–C2–C1–O2, is 21.44 (15)°. Thus, the

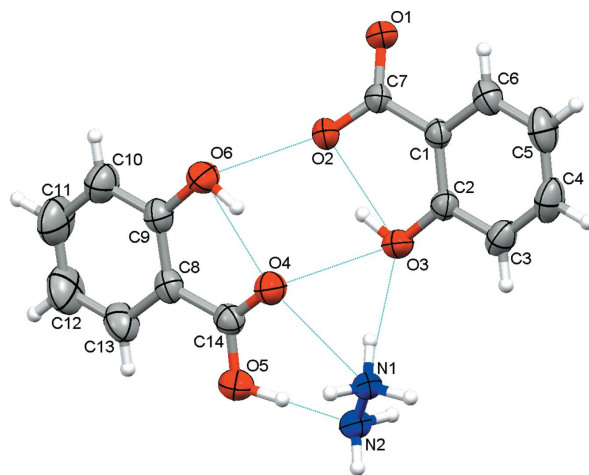


Figure 1
The asymmetric unit of adduct (I), showing 50% probability displacement ellipsoids. Thin dashed lines denote hydrogen bonds.

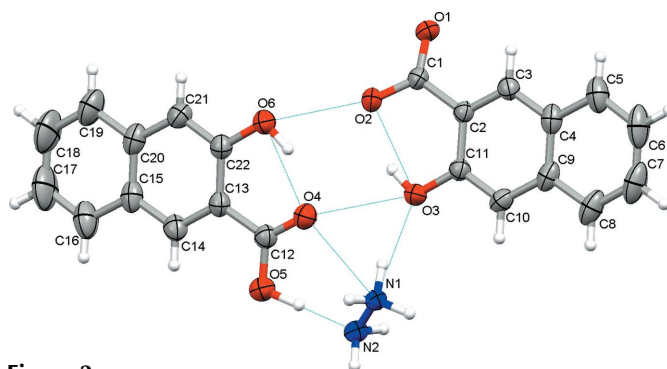


Figure 2
The asymmetric unit of adduct (II), showing 50% probability displacement ellipsoids. Thin dashed lines denote hydrogen bonds.

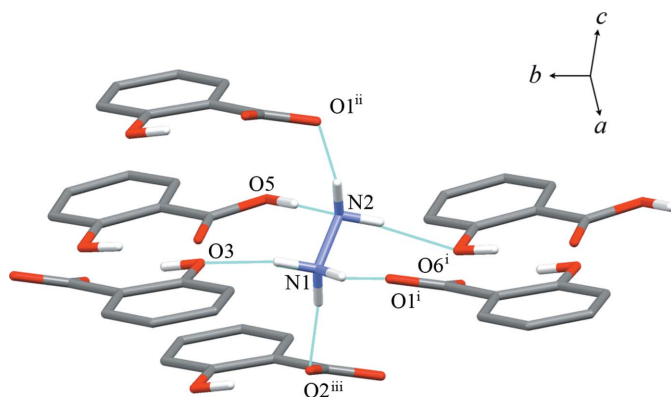


Figure 3
The hydrogen-bonding pattern (thin lines) formed around the hydrazinium cation in (I). The arrangement in (II) is essentially identical. The $N1-H1B \cdots O2^i$ interaction is obscured. Symmetry codes are as in Table 1.

deprotonated carboxylate group is twisted from the plane of the aromatic ring in both structures. By contrast, the protonated carboxyl group remains essentially coplanar with the aromatic ring, as shown by the torsion angles $C13-C8-C14-O5 = 2.06 (17)^\circ$ in (I) and $O5-C12-C13-C14 = 1.52 (16)^\circ$ in (II). For the hydrazinium cation, the $N1-N2$ bond length [$1.4380 (16) \text{ \AA}$ in (I) and $1.4391 (15) \text{ \AA}$ in (II)] is statistically equivalent in the two structures, and in good agreement with the mean value of $1.442 (11) \text{ \AA}$ derived from 49 hydrazinium salts identified in the Cambridge Structural Database (Version 5.32 plus updates; Allen, 2002; see *Supplementary material*).

Hydrogen bonding plays a major role in the construction of acid adducts. The title adducts (I) and (II) contain two types of

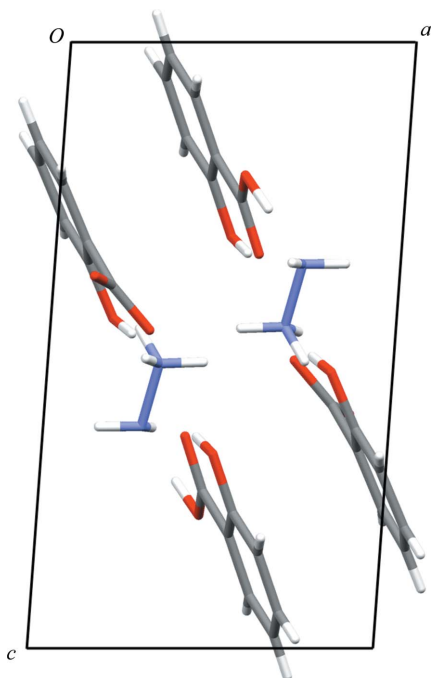


Figure 4
A packing diagram for (I), viewed along the b axis.

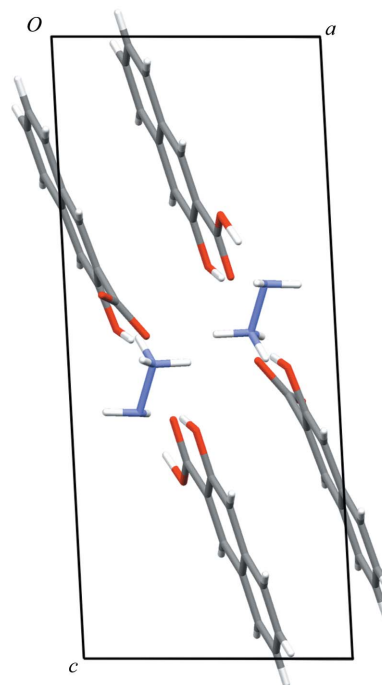


Figure 5
A packing diagram for (II), viewed along the b axis.

intermolecular hydrogen bond (Tables 1 and 2), with $N_2H_5^+$ acting as either a donor or an acceptor (Fig. 3). Intramolecular $O-H \cdots O$ hydrogen bonds are also evident within the acid molecules and anions (Figs. 1 and 2). The hydrogen bonding is essentially identical in the two structures, defining closely comparable two-dimensional layers parallel to the (001) planes (Figs. 4 and 5). In order to highlight the similarity in the (001) planes, adduct (II) is reported using an unconventional nonreduced unit cell. The corresponding reduced cell is: $a = 7.376 (5)$, $b = 7.915 (5)$, $c = 16.778 (5) \text{ \AA}$, $\alpha = 90.752 (5)$, $\beta = 93.037 (5)$ and $\gamma = 100.609 (5)^\circ$. The planes of the aromatic rings within both structures are approximately parallel [interplanar angle = $5.3 (1)^\circ$ in (I) and $3.6 (1)^\circ$ in (II)], and the layers are stacked with closely comparable intermolecular interactions between the aromatic rings [$Cg1 \cdots Cg1^{iv} = 4.86 (1) \text{ \AA}$ in (I) and $4.83 (1) \text{ \AA}$ in (II), where $Cg1$ is the centroid of atoms $C8-C13$ in (I) and atoms $C15-C20$ in (II); symmetry code: (iv) $-x + 1, -y + 2, -z + 2$].

Experimental

Adduct (I) was prepared by dissolving 2-hydroxybenzoic acid (13.8 g, 0.1 mol) in distilled water (50 ml) and then neutralizing this solution with an aqueous solution of hydrazine hydrate (5 ml in 20 ml of water). The clear solution formed at pH 6 was concentrated to half its volume in a water bath at 353 K, then left to evaporate slowly. After 2 d, colourless needles of (I) were filtered off and washed with ethanol. After complete evaporation of the filtrate, the bulk product comprised the simple salt hydrazinium 2-hydroxybenzoate, which has already been reported (Kuppusamy *et al.*, 1995).

Adduct (II) was prepared by dissolving stoichiometric quantities of hydrazine hydrate (99.98% pure; 0.05 ml, 1 mmol) and 3-hydroxy-2-naphthoic acid (0.376 g, 2 mmol) in absolute ethanol (40 ml) at pH 4.

The solution was left to evaporate to dryness and colourless needles of (II) were formed after 3 d. These crystals were recrystallized from ethanol.

Compound (I)

Crystal data

$N_2H_5^+ \cdot C_7H_5O_3^- \cdot C_7H_6O_3$	$\gamma = 101.303 (1)^\circ$
$M_r = 308.29$	$V = 727.33 (4) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.3434 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 7.9884 (2) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$c = 12.7593 (4) \text{ \AA}$	$T = 293 \text{ K}$
$\alpha = 96.497 (2)^\circ$	$0.25 \times 0.20 \times 0.20 \text{ mm}$
$\beta = 92.783 (2)^\circ$	

Data collection

Bruker Kappa APEXII CCD area-detector diffractometer	17523 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2004)	4054 independent reflections
$T_{\min} = 0.973$, $T_{\max} = 0.978$	2980 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.123$	$\Delta\rho_{\max} = 0.24 \text{ e \AA}^{-3}$
$S = 1.03$	$\Delta\rho_{\min} = -0.23 \text{ e \AA}^{-3}$
4053 reflections	
231 parameters	

Compound (II)

Crystal data

$N_2H_5^+ \cdot C_{11}H_7O_3^- \cdot C_{11}H_8O_3$	$\gamma = 100.609 (5)^\circ$
$M_r = 408.40$	$V = 961.2 (9) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.376 (5) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 7.915 (5) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$c = 16.778 (5) \text{ \AA}$	$T = 293 \text{ K}$
$\alpha = 89.248 (5)^\circ$	$0.30 \times 0.25 \times 0.20 \text{ mm}$
$\beta = 86.963 (5)^\circ$	

Data collection

Bruker Kappa APEXII CCD area-detector diffractometer	20463 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2004)	4362 independent reflections
$T_{\min} = 0.970$, $T_{\max} = 0.980$	3408 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.117$	$\Delta\rho_{\max} = 0.27 \text{ e \AA}^{-3}$
$S = 1.03$	$\Delta\rho_{\min} = -0.18 \text{ e \AA}^{-3}$
4362 reflections	
304 parameters	

In both structures, C-bound H atoms were positioned geometrically and allowed to ride during subsequent refinement, with $C-H = 0.93 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The H atoms of the hydrazinium cations were located in difference Fourier maps and refined without restraints with isotropic displacement parameters.

For both compounds, data collection: APEX2 (Bruker, 2004); cell refinement: APEX2 and SAINT (Bruker, 2004); data reduction: SAINT and XPREP (Bruker, 2004); program(s) used to solve structure: SIR92 (Altomare *et al.*, 1993); program(s) used to refine

Table 1

Hydrogen-bond geometry (\AA , $^\circ$) for (I).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O3-H3 \cdots O2$	0.906 (19)	1.736 (18)	2.5747 (11)	152.7 (16)
$O5-H5 \cdots N2$	1.02 (2)	1.67 (2)	2.6840 (14)	177.9 (18)
$O6-H6 \cdots O4$	0.91 (2)	1.71 (2)	2.5579 (12)	153.6 (17)
$N1-H1A \cdots O3$	0.905 (18)	1.963 (17)	2.8335 (13)	161.0 (15)
$N1-H1B \cdots O1^i$	0.971 (18)	1.774 (18)	2.7370 (13)	170.7 (14)
$N1-H1B \cdots O2^i$	0.971 (18)	2.546 (16)	3.1341 (12)	119.0 (11)
$N1-H1C \cdots O2^{iii}$	0.915 (15)	1.911 (15)	2.8219 (14)	173.1 (13)
$N2-H2A \cdots O6^i$	0.891 (17)	2.163 (17)	2.9905 (14)	154.1 (14)
$N2-H2B \cdots O1^{ii}$	0.889 (17)	2.044 (18)	2.9204 (14)	168.1 (14)

Symmetry codes: (i) $x, y-1, z$; (ii) $-x, -y+1, -z+1$; (iii) $-x+1, -y+1, -z+1$.

Table 2

Hydrogen-bond geometry (\AA , $^\circ$) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O3-H3 \cdots O2$	0.844 (18)	1.795 (18)	2.5771 (19)	153.3 (16)
$O5-H5 \cdots N2$	1.03 (2)	1.66 (2)	2.6905 (15)	178.5 (18)
$O6-H6 \cdots O4$	0.894 (19)	1.723 (19)	2.5525 (19)	153.0 (17)
$N1-H1A \cdots O3$	0.917 (15)	1.934 (15)	2.8164 (18)	160.9 (13)
$N1-H1B \cdots O1^i$	0.957 (17)	1.819 (17)	2.7684 (15)	171.1 (14)
$N1-H1B \cdots O2^i$	0.957 (17)	2.496 (16)	3.107 (2)	121.7 (11)
$N1-H1C \cdots O2^{iii}$	0.927 (15)	1.903 (15)	2.824 (2)	172.0 (12)
$N2-H2A \cdots O6^i$	0.896 (15)	2.134 (15)	2.9590 (19)	152.7 (12)
$N2-H2B \cdots O1^{ii}$	0.895 (16)	2.030 (17)	2.916 (2)	170.1 (13)

Symmetry codes: (i) $x, y-1, z$; (ii) $-x, -y+1, -z+1$; (iii) $-x+1, -y+1, -z+1$.

structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997) and Mercury (Macrae *et al.*, 2008); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: B13027). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Almeida Paz, F. A., Soares-Santos, P. C. R., Nogueira, H. I. S., Trindade, T. & Klinowski, J. (2003). *Acta Cryst.* **E59**, o506–o508.
- Altomare, A., Casciarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
- Bhogala, B. R., Vishweshwar, P. & Nangia, A. (2005). *Cryst. Growth Des.* **5**, 1271–1281.
- Bruker (2004). APEX2, SAINT, XPREP and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chevrier, B., Moras, D., Behr, J. P. & Lehn, J. M. (1987). *Acta Cryst.* **C43**, 2134–2137.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Fun, H.-K., Sivakumar, K., Jiang, Y.-Z., Sun, J. & Zhou, Z.-Y. (1995). *Acta Cryst.* **C51**, 2085–2087.
- Gajapathy, D., Govindarajan, S. & Patil, K. C. (1983). *Thermochim. Acta*, **60**, 87–92.
- Hady, S. A., Nahrungbauer, I. & Olovsson, I. (1969). *Acta Chem. Scand.* **23**, 2764–2772.
- Jebamony, J. R. & Thomas Muthiah, P. (1998). *Acta Cryst.* **C54**, 539–540.
- Kuppasamy, K., Sivasankar, B. N. & Govindarajan, S. (1995). *Thermochim. Acta*, **259**, 251–262.

- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Nilsson, A., Liminga, R. & Olovsson, I. (1968). *Acta Chem. Scand.* **22**, 719–731.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Smith, G., Wermuth, U. D., Healy, P. C. & White, J. M. (2003). *Aust J. Chem.* **56**, 707–713.
- Starosta, W. & Leciejewicz, J. (2008). *Open Crystallogr. J.*, **1**, 31–36.
- Thomas, J. O. (1973). *Acta Cryst.* **B29**, 1767–1776.
- Thomas, J. O. & Liminga, R. (1978). *Acta Cryst.* **B34**, 3686–3690.