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5-Formylsalicylic acid and 5-(benzimidazolium-2-yl)salicylate

Yu-Bing Lu, Ping Yang, Wen-Na Huang, Yan-Na Yang and Jian-Zhong Wu*

School of Chemistry and Environment, South China Normal University, Guangzhou 510006, People's Republic of China
Correspondence e-mail: wujzh@scnu.edu.cn

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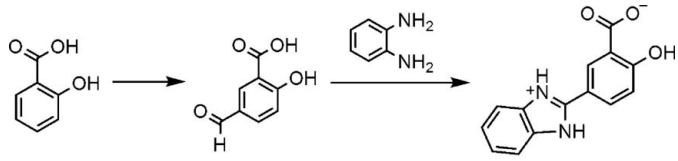
Both title compounds are derivatives of salicylic acid. 5-Formylsalicylic acid (systematic name: 5-formyl-2-hydroxybenzoic acid), $C_8H_6O_4$, possesses three good hydrogen-bond donors and/or acceptors coplanar with their attached benzene ring and abides very well by Etter's hydrogen-bond rules. Intermolecular O—H···O and some weak C—H···O hydrogen bonds link the molecules into a planar sheet. Reaction of this acid and *o*-phenylenediamine in refluxing ethanol produced in high yield the new zwitterionic compound 5-(benzimidazolium-2-yl)salicylate [systematic name: 5-(1*H*-benzimidazol-3-ium-2-yl)-2-hydroxybenzoate], $C_{14}H_{10}N_2O_3$. Each imidazolium N—H group and its adjacent salicyl C—H group chelate one carboxylate O atom *via* hydrogen bonds, forming seven-membered rings. As a result of steric hindrance, the planes of the molecules within these pairs of hydrogen-bonded molecules are inclined to one another by ∼74°. There are also π–π stacking interactions between the parallel planes of the imidazole ring and the benzene ring of the salicyl component of the adjacent molecule on one side and the benzimidazolium component of the molecule on the other side.

Comment

Salicylic acid is a plant hormone and widely used in organic synthesis (Hayat & Ahmad, 2007). This acid and many of its derivatives have medical applications, such as in anti-inflammatory treatments, easing aches and pains and reducing fevers. Formylation leads to separation of 3- and 5-formylsalicylic acids (Duff & Bills, 1932, 1934). The formyl group can then be used to react with various amines, which normally afford Schiff bases. The reaction of 5-formylsalicylic acid has received much less attention than that of 3-formylsalicylic acid. The crystal structure of 5-formylsalicylic acid, (I), has not been reported previously, although a cocrystal containing deprotonated (I), namely 2-aminopyridinium 5-formylsalicylate, has been published (Li *et al.*, 2006).

A unique type of salicylic acid derivative, the benzimidazolylsalicylic acids, was designed to combine both chemotherapeutic benzimidazole and salicylic acid moieties. These compounds have antimicrobial, cytotoxic and anthelmintic potential and were synthesized by interaction of 5,6-dimethyl- or 6-nitrobenzimidazoles with diazotized 5-aminosalicylic acid in the presence of cupric chloride (Dahiya & Pathak, 2007). The reported multi-step reaction is somewhat complicated. We found that when (I) is reacted with *o*-phenylenediamine in refluxing ethanol, the zwitterionic form of a benzimidazolylsalicylic acid, namely 5-(benzimidazolium-2-yl)salicylate, (II), could be obtained immediately in high yield. The imidazole ring in the new compound, (II), was formed through a one-step condensation between the formyl group of (I) and *o*-phenylenediamine, much more convenient than the method mentioned above (Dahiya & Pathak, 2007). Such an imidazole ring-enclosure approach involving aldehydes and aromatic *ortho*-diamines has occasionally been utilized (Bindra & Elix, 1969; da Silva *et al.*, 2010). However, in the case of 3-formylsalicylic acid, its reaction with *o*-phenylenediamine yielded a salen-type double Schiff base instead of an imidazolyl compound (Cheng & Liu, 2000; Lalehzari *et al.*, 2008).



(I) (II)

It is also notable that when (I) and *o*-phenylenediamine were mixed in refluxing syrupy phosphoric acid, which has a much higher boiling point than ethanol, it was the carboxyl not the aldehyde group of (I) that participated in the formation of imidazolyl ring closure, with the product being 2-(2-hydroxyphenyl)benzimidazole (Tong *et al.*, 2005).

In the crystal structure of (I), the parent benzene ring and the three attached O-containing functional groups are almost exactly coplanar (Fig. 1). The interaction of the molecules can be analysed using the graph-set theory for hydrogen-bond

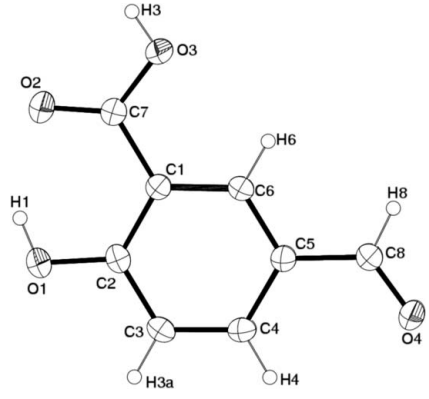


Figure 1
The molecule of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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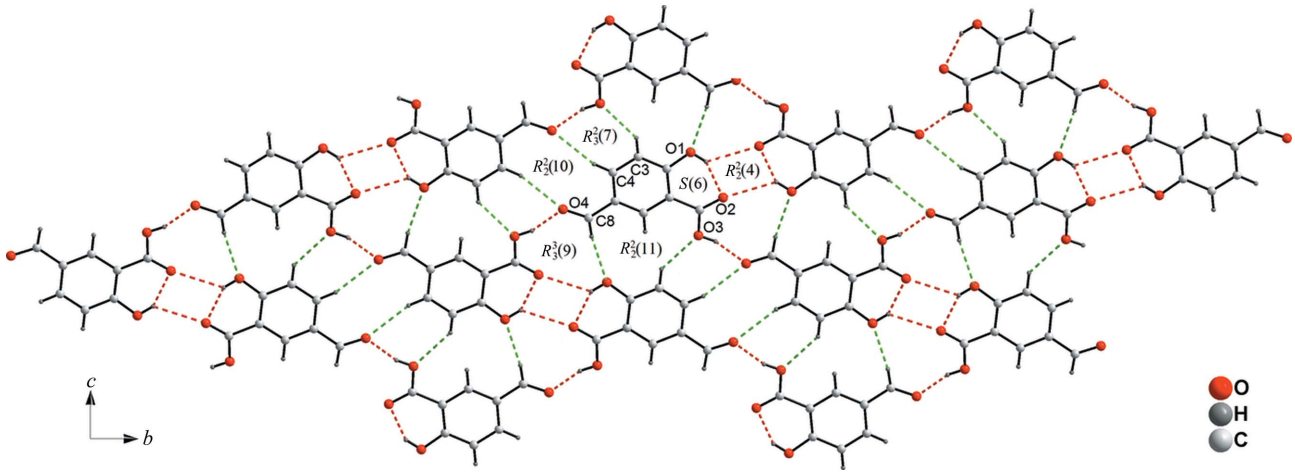

Figure 2
The planar sheet of molecules of (I) connected *via* O—H···O and C—H···O hydrogen bonds (dashed lines; red and green, respectively, in the electronic version of the paper). The hydrogen-bond patterns are shown by graph-set analysis.

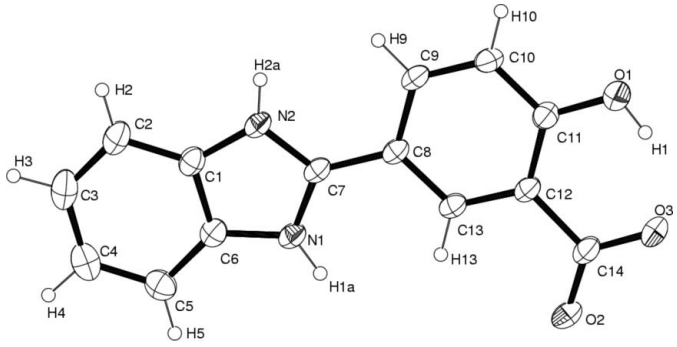

Figure 3
The zwitterionic molecule of (II), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

patterns of organic compounds, developed by Etter (1990). Some hydrogen-bond rules have been proposed, including one that all good hydrogen-bond donors and acceptors are used in hydrogen bonding, whereas less acidic H atoms may be used in hydrogen bonding when there are extra hydrogen-bond acceptors available after all the more acidic H atoms have found an acceptor. These rules apply very well in the case of (I). The hydroxy, carboxyl and formyl groups are all good hydrogen-bond donors and/or acceptors. The hydroxy group as hydrogen-bond donor and the C=O part of the carboxyl group as hydrogen-bond acceptor form both intra- and intermolecular O—H···O hydrogen bonds (Fig. 2 and Table 1), and their hydrogen-bond patterns can be encoded as $S(6)$ and $R_2^2(4)$, respectively (Etter, 1990). The resulting dimers are connected through intermolecular hydrogen bonding between the carboxyl donor and the formyl acceptor, leading to the formation of an infinite two-dimensional planar network parallel with the $(10\bar{2})$ plane. Some of the less acidic C—H groups also participate in intermolecular C—H···O hydrogen bonds, which are quite weak as the corresponding H···O distances are fairly long (Table 1), but which still agree with the description of C—H···O hydrogen bonds (Steiner, 2003).

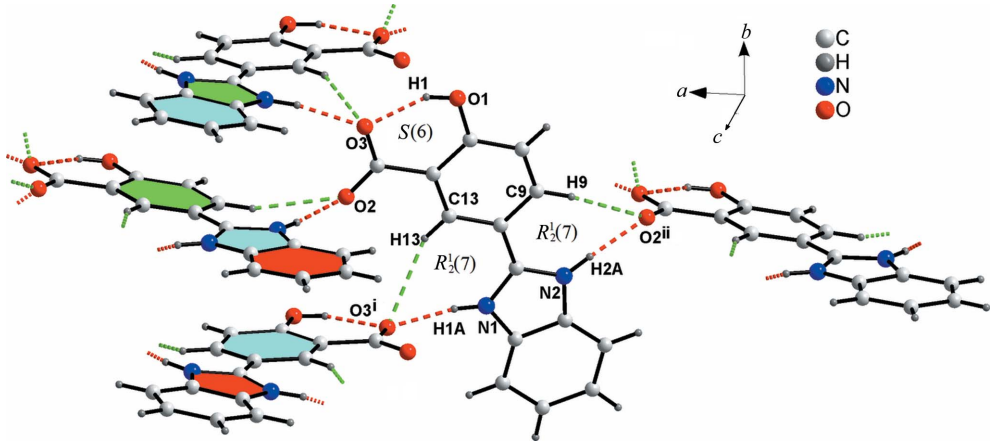

Figure 4
Interactions between the molecules of (II), including O—H···O, N—H···O (dashed lines; red in the electronic version of the paper) and C—H···O (dashed lines; green) hydrogen bonds, and π–π stacking interactions (stacking pairs of rings are highlighted with the same shading). [Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x-\frac{1}{2}, y, -z+\frac{1}{2}$.]

Thus, a series of hydrogen-bond patterns is formed, including $R_3^3(9)$, $R_2^2(11)$, $R_3^3(7)$ and $R_2^2(10)$ (Fig. 2). Through these conventional and unconventional hydrogen bonds, one molecule of (I) is connected to six adjacent molecules in the same plane. These planar sheets are separated evenly by 3.406 Å, as there is a weak interaction between adjacent parallel phenyl rings [centroid–centroid distance = 3.7763 (2) Å].

Compound (II) is the zwitterionic form of 5-(benzimidazol-2-yl)salicylic acid, in which the carboxyl group is deprotonated and an imidazole N atom is protonated, as shown in Fig. 3. The carboxylate and hydroxy groups are coplanar with their attached benzene ring, whereas the benzimidazolium moiety is slightly twisted from the salicyl moiety by 7.60 (4)°. Graph-set analysis is also applicable for the hydrogen bonding in (II). As shown in Fig. 4 and Table 2, the hydroxy and carboxylate groups form an intramolecular $S(6)$ hydrogen-bond pattern, similar to (I). Intermolecular N—H···O hydrogen bonds connect each molecule to four neighbouring molecules and form a two-dimensional network parallel to the (001) plane. Nonclassical C—H···O hydrogen bonds also play an important role in the crystal packing. It is quite interesting that each of the two carboxylate O atoms is chelated by an N—H group and an adjacent salicyl C—H group, forming a seven-membered $R_2^1(7)$ ring. Due to steric requirements, these chelate rings mean that each pair of hydrogen-bonded molecules is not coplanar but the planes of the constituent molecules are inclined by an angle of ∼74°. The three molecules on the same side of their connected molecule (Fig. 4) are aligned almost parallel and staggered. They are stabilized by two kinds of π–π stacking interactions between the imidazole ring and the benzene ring of the salicyl component of the adjacent molecule on one side and the benzimidazolium component of the molecule on the other side, as evident from the centroid–centroid distances: Cg(C1/C6/C7/N1/N2)···Cg(C8–C13)^{i} = 3.5742 (8) Å and Cg(C1/C6/C7/N1/N2)···Cg(C1–C6)^{ii} = 3.6978 (8) Å [symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, z$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, z$].

Experimental

Compound (I) was prepared according to well established procedures (Duff & Bills, 1932, 1934). Single crystals (m.p. 453 K, with decomposition) were obtained by vapour diffusion of diethyl ether into an ethanol solution. Analysis calculated for $C_8H_6O_4$: C 57.84, H 3.64%; found: C 57.72, H 3.75%. For the preparation of compound (II), a solution of *o*-phenylenediamine (1.08 g, 0.01 mol) in ethanol (20 ml) was added to a solution of (I) (1.66 g, 0.01 mol) in ethanol (20 ml). The mixture was refluxed for 6 h. The flaxen solid product was filtered off, washed and recrystallized from ethanol (yield 2.14 g, 84%). Single crystals (m.p. 433–435 K) were obtained by vapour diffusion of diethyl ether into an ethanol solution. Analysis calculated for $C_{14}H_{10}N_2O_3$: C 66.14, H 3.96, N 11.02%; found: C 65.97, H 3.94, N 11.14%.

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O4^{i}	0.82	1.80	2.5848 (15)	161
O1—H1···O2^{ii}	0.82	2.54	3.0988 (16)	127
O1—H1···O2	0.82	1.94	2.6528 (15)	145
C3—H3A···O3^{iii}	0.93	2.63	3.4315 (18)	144
C4—H4···O4^{iv}	0.93	2.68	3.5641 (18)	158
C8—H8···O1^{v}	0.93	2.75	3.6576 (18)	165

Symmetry codes: (i) $-x+2, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+1, -y+1, -z$; (iii) $x-1, -y+\frac{3}{2}, z-\frac{1}{2}$; (iv) $-x+1, -y+2, -z$; (v) $x+1, -y+\frac{3}{2}, z+\frac{1}{2}$.

Compound (I)

Crystal data

$C_8H_6O_4$
M_r = 166.13
Monoclinic, $P2_1/c$
a = 3.7762 (3) Å
b = 16.3219 (11) Å
c = 11.6334 (8) Å
β = 91.525 (5)°
V = 716.77 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.13 mm^{-1}
T = 298 K
0.50 × 0.30 × 0.20 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.956, T_{max} = 0.975
9607 measured reflections
1708 independent reflections
1202 reflections with $I > 2\sigma(I)$
R_{int} = 0.043

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.123
S = 1.03
1699 reflections
111 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Compound (II)

Crystal data

$C_{14}H_{10}N_2O_3$
M_r = 254.24
Orthorhombic, *Pbca*
a = 16.2033 (4) Å
b = 8.1005 (2) Å
c = 18.8425 (5) Å
V = 2473.17 (11) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 298 K
0.35 × 0.30 × 0.20 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.966, T_{max} = 0.981
23379 measured reflections
2949 independent reflections
2007 reflections with $I > 2\sigma(I)$
R_{int} = 0.040

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.104
S = 1.05
2949 reflections
174 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O3^{i}	0.86	1.86	2.7102 (13)	170
N2—H2A···O2^{ii}	0.86	1.81	2.6544 (14)	165
O1—H1···O3	0.82	1.82	2.5482 (14)	147
C9—H9···O2^{ii}	0.93	2.58	3.4303 (16)	151
C13—H13···O3^{i}	0.93	2.60	3.4749 (17)	156

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x-\frac{1}{2}, y, -z+\frac{1}{2}$.

H atoms attached to C or N atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H = 0.93 Å and N—H = 0.86 Å, and with $U_{iso}(H) = 1.2U_{eq}$(C or N). H atoms bound to O atoms were determined from difference Fourier maps and treated in the riding-model approximation, with O—H = 0.82 Å and $U_{iso}(H) = 1.5U_{eq}(O)$.

For both compounds, data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3389). Services for accessing these data are described at the back of the journal.

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