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# *N*-Acetyl-4-[(2-hydroxybenzylidene)-amino]benzenesulfonamide monohydrate and *N*-acetyl-4-[(5-bromo-2-hydroxybenzylidene)amino]-benzenesulfonamide monohydrate

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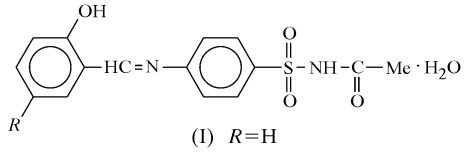
Molecules of the title compounds, $C_{15}H_{14}N_2O_4S\cdot H_2O$ and $C_{15}H_{13}BrN_2O_4S\cdot H_2O$, adopt an *E* configuration about the azomethine C=N double bond. In both molecules, the two benzene rings and the azomethine group are practically coplanar, as a result of intramolecular hydrogen bonds involving the hydroxy O atom and azomethine N atom. The angular disposition of the bonds about the S atom deviates significantly from that of a regular tetrahedron. In the crystal structures, both compounds form two-dimensional layers parallel to the (100) plane.

## Comment

Sulfonamides constitute an important class of antimicrobial agents which exert antibacterial action by inhibiting the enzyme dihydropteroate synthase competitively towards the substrate *p*-aminobenzoate (PAB). This enzyme catalyses the formation of dihydropteroate from PAB and hydroxymethyl-dihydropteridine pyrophosphate (Brown, 1971), so its inhibition leads to bacteriostasis. It is known that *N*-acetyl-4-aminobenzenesulfonamide belongs to the class of sulfonamide drugs with short-term action and it is widely applied in medical practice for the treatment of diseases caused by various coccal infections. The presence of the amino group in this compound leads to condensation with aldehydes and ketones, thus enlarging the number of functional groups and changing its chemical and medicobiological properties. A detailed study of the structural features of inhibitors in relation to their biological activity is an important step towards the deduction of the interaction mechanisms of enzyme inhibition and provides useful knowledge for the design of the most suitable molecules according to the stereo-electronic requirements of the inhibitory interaction. We report here the crystal structures of *N*-acetyl-4-[(2-hydroxybenzylidene)amino]benzenesulfonamide monohydrate, (I), and *N*-acetyl-4-[(5-bromo-2-hydroxybenzylidene)amino]benzenesulfonamide monohydrate, (II), as part of this study.




(I) *R*=H
(II) *R*=Br

The atom-numbering schemes and views of the molecules of (I) and (II) are shown in Figs. 1 and 2, respectively. Both (I) and (II) adopt an *E* configuration about the azomethine C=N double bond, with torsion angles of 180.0 (3) and 179.1 (2)°, respectively. The differences in the bond lengths and angles in (I) and (II) are within three times the combined values of their s.u. values. The S1—C11 distance of 1.760 (3) Å in (I) and (II) is a normal single-bond value and matches well with those observed in other sulfonamides (Singh *et al.*, 1984; Abramenko & Sergienko, 2002). The S—N bond distances in (I) and (II) have a considerable amount of double-bond character. The S—O distances are similar to those found in analogous structures. These distances do not vary significantly in the sulfonamide structures, despite the differing intermolecular interaction patterns observed. The bond lengths and angles in the benzene rings have characteristic values. The angular disposition of the bonds about atom S1 deviates significantly from that of a regular tetrahedron, with the

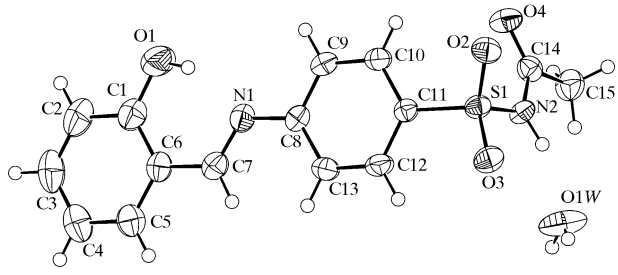



**Figure 1**
A view of (I), including the water molecule, showing the atomic labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles of arbitrary radii.

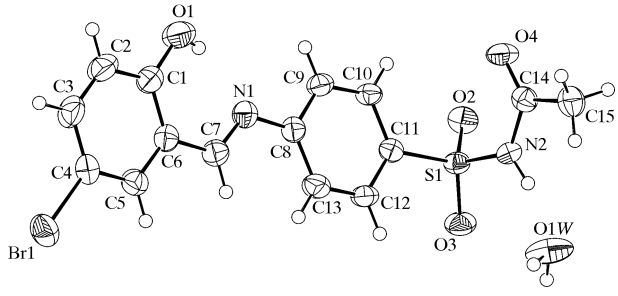



**Figure 2**
A view of (II), including the water molecule, showing the atomic labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles of arbitrary radii.

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largest angle being O2—S1—O3 [120.0 (1)° in (I) and (II)] and the smallest being O3—S1—N2 [104.4 (1) and 104.3 (1)° in (I) and (II), respectively]. These distortions of bond angles may be caused by S1—O2···*Cg* ($\pi$-ring) interactions (Spek, 2003), where *Cg* is the centroid of the C8–C13 aromatic ring at symmetry position ($x$, $y-1$, $z$) in (I) and ($x$, $y+1$, $z$) in (II). The O2···*Cg* and S2···*Cg* separations for (I) are 3.142 and 3.137 Å, respectively, and for (II) are 3.802 and 3.804 Å, respectively, and the angles between the O2—*Cg* vectors and the normals to the C8–C13 benzene rings are 8.3 and 9.06°, respectively, for (I) and (II).

The sulfonamide and acetyl moieties are capable of a variety of conformational states by means of rotations about the S1—N2 and N2—C14 bonds. The dihedral angles describing these conformations are 70.5 (3) and −176.6 (2)° in (I), and 70.9 (2) and −177.1 (1)° in (II). Fig. 3 shows a superimposition of the molecules of (I) and (II), with a weighted r.m.s. deviation of 0.066 Å for atoms N1/C1–C13, illustrating the isostructural nature of these compounds.

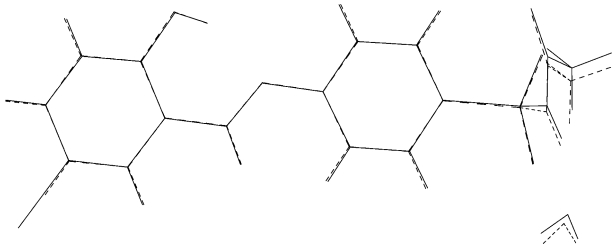

**Figure 3**
A superimposition of the structures of (I) (dashed lines) and (II).

In (I) and (II), in molecules related by a *b* cell translation, short intermolecular contacts of 2.99 and 2.95 Å, respectively, exist between carbonyl atom C14 and sulfonyl atom O2. These molecules are linked by O1*W*—H1*W*···O4, O1*W*—H2*W*···O4 and O1*W*—H2*W*···O2 hydrogen bonds (Tables 2 and 4), which leads to the close approach of atoms O2 and C14 due to rotation of the sulfonamide and acetyl moieties about the S1—N2 and N2—C14 bonds. In the related structures of 2-[4-(acetylaminosulfonyl)phenylcarbamoyl]benzoic acid (phthalylsulfacetamide), (III) (Singh *et al.*, 1984), and *p*-aminobenzenesulfonacetamide, (IV) (Basak & Mazumdar, 1982), where the water molecule is absent in the crystal packing, the O2—S1—N2—C14 and S1—N2—C14—O4 torsion angles are −53.2 and −61.5°, and 6.8 and 7.2°, respectively, whereas in (I) and (II), these angles are −46.0 (3) and −45.8 (2)°, and 4.3 (4) and 3.8 (4)°, respectively. In (III) and (IV), the above-mentioned intermolecular contacts between the carbonyl C and sulfonyl O atoms are 4.69 and 4.39 Å, respectively. A check of the Cambridge Structural Database [Version 5.25 (Allen, 2002) and *ConQuest* (Bruno *et al.*, 2002)] for close contacts between such atoms has been carried out (*R* factor less than 0.075) for compounds containing the benzoylsulfacetamide fragment and in which the given contact ranges from 2.9 to 3.22 Å. Only two such compounds were found,

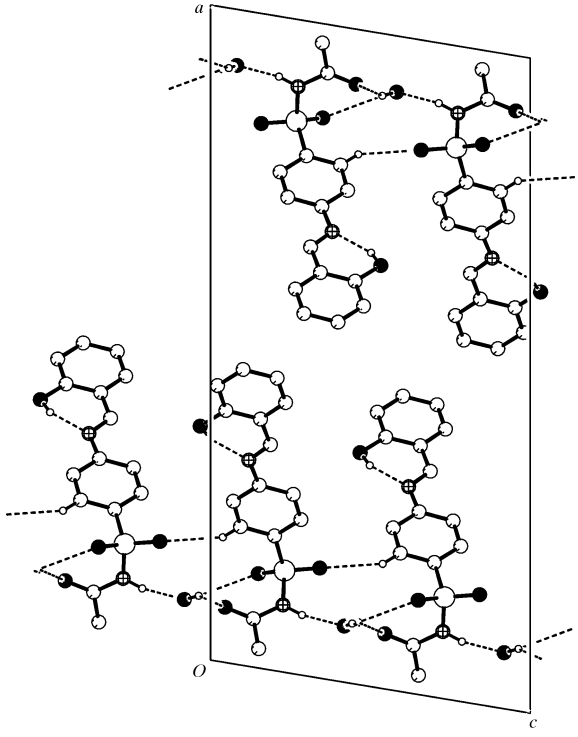


**Figure 4**
Part of the crystal structure of (I), viewed along the *b* axis, showing the formation of the two-dimensional network. H atoms not involved in hydrogen bonding have been omitted for clarity.

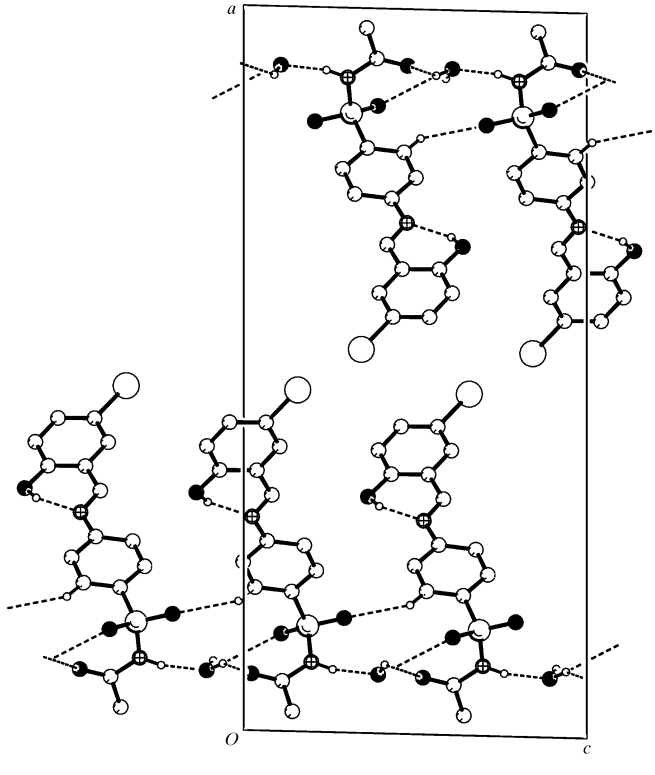


**Figure 5**
A packing diagram for (II), viewed along the *b* axis, showing the formation of the two-dimensional network. H atoms not involved in hydrogen bonding have been omitted for clarity.

namely 2,8-dimethoxy-5,11-di-*p*-tosyl-5,6,11,12-tetrahydrodibenzo[*b*,*f*]diazocine-6,12-dione (Filipenko *et al.* 1988) and the silver salt of *N*-(*p*-aminophenylsulfonyl)acetamide (Ghosh *et al.*, 1990), for which the O···C separations are 3.13 and 3.05 Å, respectively.

In the molecules of (I) and (II), the two benzene rings and the azomethine group are practically coplanar, due to intramolecular O1—H···N1 hydrogen bonds. The deviations of atoms N1/C1–C13 from the best-fit plane through them are between 0.043 and −0.042 Å in (I), and between 0.098 and −0.096 Å in (II). In the structure of (III), where the above-mentioned intramolecular hydrogen bond is absent, the two benzene rings are rotated by 62.1° with respect to one another.

The molecular packings of (I) and (II) are shown in Figs. 4 and 5, viewed down the *b* axis in both cases. Both compounds are arranged in the form of infinite two-dimensional layers parallel to the (100) plane, as a result of N—H···O, C—H···O and O—H···O hydrogen bonds (Tables 2 and 4). Between these layers, there are intermolecular van der Waals interactions. The two structures are essentially isomorphous; the slight lengthening of the *a* cell dimension in bromo compound (II) compared with that in (I) is attributable to the increased size of Br compared with H.

## Experimental

Schiff bases (I) and (II) were prepared by condensation of salicylic acid (1.05 g, 10 mmol) and 5-bromosalicylaldehyde (2.01 g, 10 mmol) with *N*-acetyl-4-aminobenzenesulfonamide (2.14 g, 10 mmol) in boiling ethanol. The products precipitated from the reaction mixtures in yields of 61 and 65%, respectively. Both compounds were recrystallized from alcohol solution.

### Compound (I)

*Crystal data*

$C_{15}H_{14}N_2O_4S\cdot H_2O$
$M_r$ = 336.37
Monoclinic, $P2_1/c$
$a$ = 25.486 (3) Å
$b$ = 4.8964 (13) Å
$c$ = 12.605 (3) Å
$\beta$ = 99.44 (3)°
$V$ = 1551.7 (6) Å$^3$
$Z$ = 4
$D_x$ = 1.440 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 4944 reflections
$\theta$ = 3.3–28.3
$\mu$ = 0.24 mm$^{-1}$
$T$ = 298 K
Prism, yellow
0.26 × 0.13 × 0.11 mm

**Table 1**
Selected geometric parameters (Å, °) for (I).

| | | | |
|---|---|---|---|
| S1—O2 | 1.424 (2) | O4—C14 | 1.223 (3) |
| S1—O3 | 1.431 (2) | N1—C8 | 1.423 (4) |
| S1—N2 | 1.651 (3) | N1—C7 | 1.277 (4) |
| S1—C11 | 1.760 (3) | N2—C14 | 1.376 (3) |
| O1—C1 | 1.354 (5) | | |
| O2—S1—O3 | 120.03 (12) | O1—C1—C6 | 121.6 (3) |
| O2—S1—N2 | 108.32 (13) | N1—C7—C6 | 123.1 (2) |
| O2—S1—C11 | 109.11 (13) | N1—C8—C13 | 124.6 (2) |
| O3—S1—N2 | 104.44 (12) | N1—C8—C9 | 116.8 (2) |
| O3—S1—C11 | 108.81 (13) | S1—C11—C10 | 120.1 (2) |
| N2—S1—C11 | 105.08 (13) | S1—C11—C12 | 119.2 (2) |
| C7—N1—C8 | 122.0 (2) | O4—C14—C15 | 123.2 (3) |
| S1—N2—C14 | 124.81 (19) | N2—C14—C15 | 115.1 (2) |
| O1—C1—C2 | 118.9 (3) | O4—C14—N2 | 121.7 (3) |

*Data collection*

Bruker SMART CCD area-detector diffractometer
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.951, $T_{max}$ = 0.974
11981 measured reflections
2696 independent reflections
1966 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.057
$\theta_{max}$ = 25.0°
$h = -30 \rightarrow 30$
$k = -5 \rightarrow 5$
$l = -14 \rightarrow 14$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.113
$S$ = 1.06
2696 reflections
221 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0529P)^2 + 0.2401P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.008
$\Delta\rho_{max}$ = 0.22 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.30 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H1O···N1 | 0.83 (5) | 1.86 (5) | 2.626 (4) | 152 (4) |
| O1$W$—H1$W$···O2$^{i}$ | 0.84 (4) | 2.51 (4) | 3.054 (3) | 124 (3) |
| O1$W$—H1$W$···O4$^{i}$ | 0.84 (4) | 2.11 (4) | 2.897 (4) | 155 (5) |
| N2—H2$B$···O1$W$ | 0.86 | 1.91 | 2.740 (4) | 161 |
| O1$W$—H2$W$···O4$^{ii}$ | 0.84 (3) | 2.16 (4) | 2.960 (4) | 157 (4) |
| C10—H10$A$···O3$^{iii}$ | 0.93 | 2.49 | 3.188 (3) | 132 |

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

### Compound (II)

*Crystal data*

$C_{15}H_{13}BrN_2O_4S\cdot H_2O$
$M_r$ = 415.26
Monoclinic, $P2_1/c$
$a$ = 26.858 (3) Å
$b$ = 4.855 (2) Å
$c$ = 12.708 (3) Å
$\beta$ = 91.428 (12)°
$V$ = 1656.6 (8) Å$^3$
$Z$ = 4
$D_x$ = 1.665 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 8514 reflections
$\theta$ = 5.6–28.1
$\mu$ = 2.64 mm$^{-1}$
$T$ = 298 K
Prism, yellow
0.24 × 0.23 × 0.11 mm

**Table 3**
Selected geometric parameters (Å, °) for (II).

| | | | |
|---|---|---|---|
| Br1—C4 | 1.901 (3) | O1—C1 | 1.344 (4) |
| S1—O2 | 1.429 (2) | O4—C14 | 1.211 (3) |
| S1—O3 | 1.432 (2) | N1—C7 | 1.277 (4) |
| S1—N2 | 1.649 (2) | N1—C8 | 1.421 (3) |
| S1—C11 | 1.760 (3) | N2—C14 | 1.385 (3) |
| O2—S1—O3 | 119.95 (12) | Br1—C4—C5 | 119.90 (19) |
| O2—S1—N2 | 108.50 (11) | Br1—C4—C3 | 119.9 (2) |
| O2—S1—C11 | 109.03 (12) | N1—C7—C6 | 122.5 (2) |
| O3—S1—N2 | 104.31 (11) | N1—C8—C13 | 124.6 (2) |
| O3—S1—C11 | 108.79 (12) | N1—C8—C9 | 116.8 (2) |
| N2—S1—C11 | 105.25 (11) | S1—C11—C12 | 119.2 (2) |
| C7—N1—C8 | 121.9 (2) | S1—C11—C10 | 120.0 (2) |
| S1—N2—C14 | 124.28 (18) | O4—C14—C15 | 123.2 (3) |
| O1—C1—C6 | 121.9 (3) | N2—C14—C15 | 114.6 (2) |
| O1—C1—C2 | 119.2 (2) | O4—C14—N2 | 122.2 (3) |

*Data collection*

Bruker SMART CCD area-detector diffractometer
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.549, $T_{max}$ = 0.748
13900 measured reflections
2893 independent reflections
2446 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.029
$\theta_{max}$ = 25.0°
$h = -31 \rightarrow 31$
$k = -5 \rightarrow 5$
$l = -15 \rightarrow 15$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.085
$S$ = 1.03
2892 reflections
230 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.6173P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.043
$\Delta\rho_{max}$ = 0.57 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.42 e Å$^{-3}$

**Table 4**
Hydrogen-bond geometry (Å, °) for (II).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H1···N1 | 0.83 (4) | 1.88 (4) | 2.627 (4) | 149 (3) |
| O1*W*—H1*W*···O2$^{i}$ | 0.85 (4) | 2.46 (4) | 3.085 (3) | 130 (4) |
| O1*W*—H1*W*···O4$^{i}$ | 0.85 (4) | 2.13 (5) | 2.889 (4) | 148 (5) |
| N2—H2*B*···O1*W* | 0.86 | 1.92 | 2.749 (3) | 161 |
| O1*W*—H2*W*···O4$^{ii}$ | 0.84 (4) | 2.31 (4) | 2.991 (4) | 138 (4) |
| C10—H10*A*···O3$^{iii}$ | 0.93 | 2.54 | 3.211 (3) | 129 |
| C12—H12*A*···O3 | 0.93 | 2.58 | 2.945 (4) | 104 |

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

Hydroxy H atoms and all water H atoms were found in difference maps at an intermediate stage of the refinement and were refined subject to an O—H restraint of 0.84 (4) Å. All other H atoms were placed in idealized positions, with aromatic C—H = 0.93 Å, methyl C—H = 0.96 Å and N—H = 0.86 Å, and included in the refinement in the riding-model approximation, with $U_{iso}$(H) = $1.2U_{eq}$(C,N).

For both compounds, data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; structure solution: *SHELXS97* (Sheldrick, 1997); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); publication software: *PLATON*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1053). Services for accessing these data are described at the back of the journal.

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