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Diethyl 2-aminothiazole-4,5-dicarboxylate hemihydrate

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The structure of the title compound, $C_9H_{12}N_2O_4S\cdot 0.5H_2O$, comprises two thiazole molecules and one water molecule in the asymmetric unit. The two thiazoles associate *via* N—H···N hydrogen-bonding interactions to form $R_2^2(8)$ graph-set dimers, while the other NH groups and water molecules construct a hydrogen-bonding network that involves three of the four ethyl ester carbonyl O atoms.

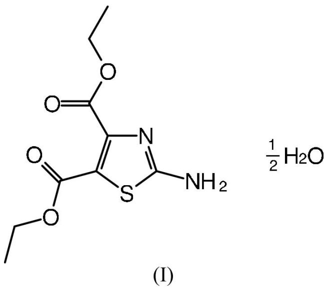
Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
R factor = 0.046
wR factor = 0.122
Data-to-parameter ratio = 17.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The title compound (I) was prepared as part of an ongoing investigation into the synthesis and structural properties of 2-aminothiazole derivatives.



(I)

As a part of that study, we have been examining the hydrogen-bonding networks of 2-aminothiazoles with ethyl ester substituents at the 5-position. The addition of two hydrogen-bond acceptors to the existing hydrogen-bond acceptors in 2-aminothiazole has led to some interesting

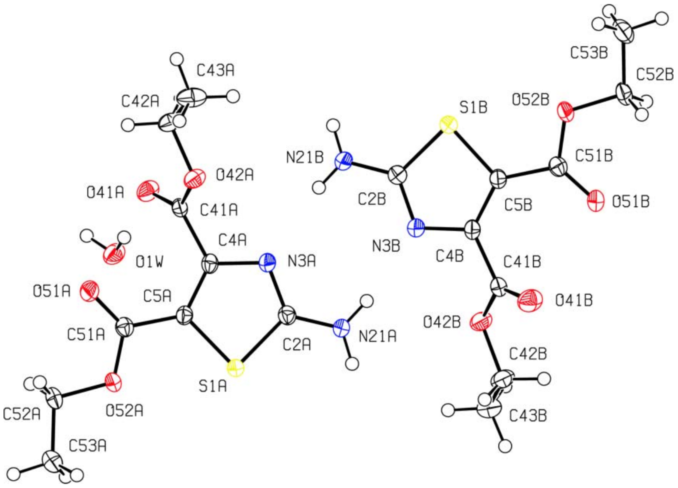


Figure 1
The structure of the asymmetric unit of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as spheres of arbitrary radii.

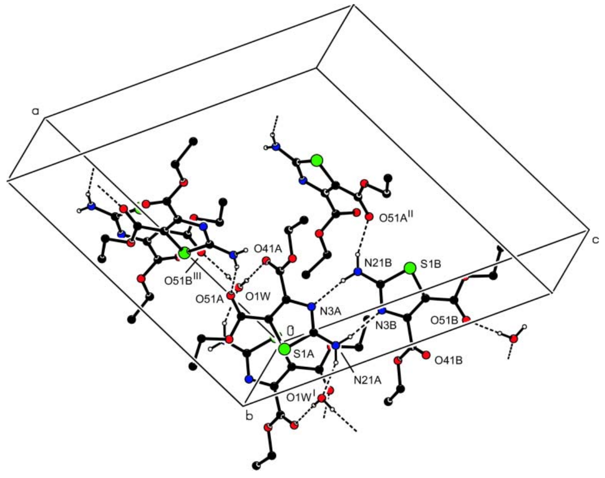


Figure 2

Partial packing diagram for (I). Hydrogen-bonding interactions are shown as dotted lines. H atoms not involved in the hydrogen-bonding network have been omitted for clarity. [Symmetry codes: (i) $-x, -y, -z$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x + \frac{1}{2}, -y - \frac{1}{2}, z - \frac{1}{2}$.]

packing arrangements. For the three previous structures that contain a primary 2-amino group, *viz.* ethyl 2-amino-4-phenyl-1,3-thiazole-5-carboxylate (Lynch & McClenaghan, 2000), ethyl 2-amino-4-*tert*-butyl-1,3-thiazole-5-carboxylate (Lynch & McClenaghan, 2004) and ethyl 2-amino-4-isopropyl-1,3-thiazole-5-carboxylate (Kennedy *et al.*, 2004), all molecules pack with one NH group interacting with an adjacent thiazole N atom, to form an $R_2^2(8)$ graph-set (Etter, 1990) dimer, while the other NH group associates with the ethyl ester carbonyl O atom. In the other four known thiazoles with ethyl ester substituents at the 5-position and substituted 2-amino N atoms, two have tertiary amino groups, *viz.* ethyl 2-(5-ethoxycarbonyl-2-(pyrrol-1yl)thiazol-4yl-2-iminoethanoate (Brickute *et al.*, 2002) and ethyl 4-phenyl-2-(pyrrolyl)-1,3-thiazole-5-carboxylate (Lynch & McClenaghan, 2002*b*), and the other two both contain competing carbonyl O atoms with which the single NH groups associate, *viz.* ethyl 2-[*N*-(*t*-butoxycarbonyl)-L-alanylamino]-4-methyl-1,3-thiazole-5-carboxylate (Singh *et al.*, 2000) and ethyl 4-*tert*-butyl-2-(3-phenylureido)-1,3-thiazole-5-carboxylate (Lynch & McClenaghan, 2002*a*). All five structures containing at least one NH group show that an amino group prefers to interact with a carbonyl O atom, whether from the ester group or from another group in the molecule. With this in mind we decided to examine a 2-aminothiazole analogue with two ethyl ester substituents to see which substituted position would be preferred by the NH groups in the hydrogen-bonding network.

The asymmetric unit of (I) comprises two thiazole molecules; these are connected in a three-dimensional hydrogen-bonding network. The addition of the second ethyl ester and thus the increase in hydrogen-bond acceptor atoms leads to the incorporation of a water molecule to satisfy the hydrogen-bonding requirements of the packing network (Desiraju, 1991). Similarly to the three previous structures where the 2-amino group was unsubstituted, the two thiazole molecules in (I) associate *via* N—H$\cdots$N interactions and form $R_2^2(8)$ graph-set dimers (Fig. 1). The hydrogen-bonding geometry is listed in Table 1. The second NH group on each thiazole molecule individually associates with different hydrogen-bond acceptor sites; on molecule *A*, the second NH group hydrogen-bonds to the water O atom, while the second NH group on molecule *B* hydrogen-bonds to the 5-substituted ester carbonyl O atom, on an adjacent molecule A. In turn, the water H atoms are donors to the 4-substituted ester carbonyl O atom on an adjacent molecule *A* and the equivalent 5-substituted O atom to molecule *B*; thus three of the four ester carbonyl O atoms are involved in the hydrogen-bonding network (Fig. 2). Separation distances of O41*B* (the remaining carbonyl O atom) of 3.208 (2) Å to C52*A*$(-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$ and 3.365 (2) Å to C43*B*$(-\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$ indicate C—H$\cdots$O interactions.

Experimental

The title compound was obtained from Key Organics Ltd and crystals were grown from an ethanol solution.

Crystal data

$C_9H_{12}N_2O_4S\cdot0.5H_2O$
$M_r = 253.28$
Monoclinic, $P2_1/n$
$a = 16.7835$ (4) Å
$b = 8.4580$ (2) Å
$c = 18.0373$ (5) Å
$\beta = 111.653$ (1)°
$V = 2379.8$ (1) Å^3
$Z = 8$

$D_x = 1.414$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 5676 reflections
$\theta = 2.9$–27.5°
$\mu = 0.28$ mm^{-1}
$T = 120$ (2) K
Prism, colourless
0.18 × 0.15 × 0.07 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.952$, $T_{\max} = 0.981$
28267 measured reflections
5447 independent reflections

4260 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.051$
$\theta_{\max} = 27.5°$
$h = -21 \rightarrow 21$
$k = -10 \rightarrow 10$
$l = -23 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.122$
$S = 1.09$
5447 reflections
309 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0594P)^2 + 0.8191P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.56$ e Å^{-3}
$\Delta\rho_{\min} = -0.66$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0145 (11)

Table 1

Hydrogen-bond geometry (Å, °).

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
N21A—H21A$\cdots$N3B	0.88	2.13	2.979 (2)	161
N21A—H22A$\cdots$O1W^{i}	0.88	1.97	2.805 (2)	158
N21B—H21B$\cdots$N3A	0.88	2.16	3.005 (2)	160
N21B—H22B$\cdots$O51A^{ii}	0.88	2.05	2.890 (2)	160
O1W—H1W$\cdots$O41A	0.83 (3)	2.02 (3)	2.853 (2)	175 (2)
O1W—H2W$\cdots$O51B^{iii}	0.84 (3)	1.97 (3)	2.808 (2)	175 (2)

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

All H atoms, except the two water H atoms, were included in the refinement at calculated positions, in the riding-model approximation, with C—H distances of 0.98 (CH_3 H atoms) and 0.99 Å (CH_2 H atoms) and an N—H distance of 0.88 Å. The two water H atoms were located in Fourier syntheses and positional parameters were refined. The isotropic displacement parameters for all H atoms were set equal to 1.25U_{eq} of the carrier atom.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON97* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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