

2-Amino-5-methyl-1,3,4-thiadiazole and 2-amino-5-ethyl-1,3,4-thiadiazole

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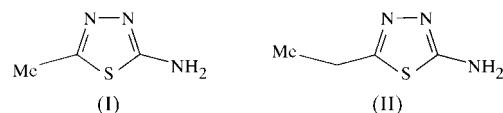
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The structures of 2-amino-5-methyl-1,3,4-thiadiazole, $C_3H_5N_3S$, and 2-amino-5-ethyl-1,3,4-thiadiazole, $C_4H_7N_3S$, have been determined for comparison with unsubstituted 2-amino-1,3,4-thiadiazole. Despite their different space groups ($P2_1/n$ and $Pbca$, respectively), the packing modes of the methyl and ethyl derivatives are similar, with comparable three-dimensional hydrogen-bonding associations. This is in contrast to the hydrogen-bonding network in 2-amino-1,3,4-thiadiazole, which is one-dimensional and has denser packing. It is shown that both packing forms are different polymorphs of a specific subunit of each array.

Comment

In terms of hydrogen-bonding potential, 2-amino-1,3,4-thiadiazole has two donor elements, the 2-amino H atoms, and two acceptors, N3 and N4 of the thiadiazole ring. The structure of this compound is known (Khusenov *et al.*, 1997) and shows a hydrogen-bonding network comprising two associated molecules linked *via* N—H...N interactions, graph set $R_2^2(8)$, which in turn associate with another molecular pair *via* N—H...N hydrogen bonds, graph set $R_4^4(10)$. The overall pattern produces a flat ribbon array (see supplementary figure). In this network, the 5-position does not appear to affect the overall lattice packing, so it was postulated as to whether or not substitution at this point would influence the parent hydrogen-bonding network. The structures of several 5-substituted analogues are known, yet of the small substituents, such as NH_2 (Senda & Maruha, 1987), SH (Downie *et al.*, 1972) and SO_2NH_2 (Pedregosa *et al.*, 1993), each is itself involved in hydrogen-bonding interactions, thus significantly altering the resultant arrays. Similarly, in the structures of the HBr (Antolini *et al.*, 1993) and HCl-hydrate salts of 2-amino-5-methyl-1,3,4-thiadiazole (Pilz *et al.*, 1998), the halides are involved in the hydrogen-bonding network. Larger substituents, such as those containing phenyl rings (Foresti *et al.*, 1985; Molina *et al.*, 1988; Leung *et al.*, 1992; Anders *et al.*, 1999), affect the molecular packing by their very size. Thus, the structures of 2-amino-1,3,4-thiadiazoles with simple non-hydrogen-bonding substituents, namely, 2-amino-5-methyl-

1,3,4-thiadiazole, (I), and 2-amino-5-ethyl-1,3,4-thiadiazole, (II), have been investigated to elucidate the influence of these substituents on the molecular packing observed in the parent thiadiazole.



Interestingly, crystals of (I) (Fig. 1) and (II) (Fig. 2) could not be obtained from simple organic solvent solutions, yet crystals of both compounds abounded when attempts were made to form adducts of these materials with aromatic carboxylic acids, such as those used by Lynch *et al.* (1998, 1999). For (I) and (II), the specific crystals used for data collection were separated as unreacted starting materials following the attempted formation of cocrystals of (I) with 2-aminobenzoic acid, and of (II) with *N*-methylpyrrole-2-carboxylic acid. The only successfully characterized cocrystal of either (I) or (II) was that of (II) with indole-2-carboxylic acid (see supplementary figure), yet the inherent disorder in this structure, even in data collected at 150 K, yields an *R*

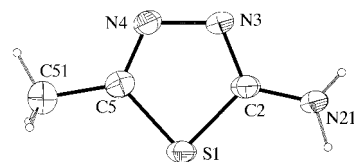


Figure 1

The molecular configuration and atomic numbering scheme for (I), showing 50% probability displacement ellipsoids. H atoms are drawn as small spheres of arbitrary radii.

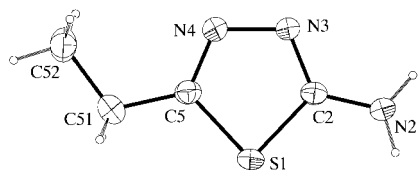


Figure 2

The molecular configuration and atomic numbering scheme for (II), showing 50% probability displacement ellipsoids. H atoms are drawn as small spheres of arbitrary radii.

value of 0.11. As expected for these types of complexes, the carboxylate groups associate across the N3/N21 sites, thus creating $R_2^2(8)$ graph-set dimers.

An overview of the data for (I) and (II) shows that they crystallize in monoclinic and orthorhombic space groups, respectively, yet the resultant molecular packing is quite similar. Figs. 3 and 4 display the packing for both molecules, while hydrogen-bonding geometries are listed in Tables 1 and 2, respectively. Short contact distances not listed in the tables, yet worthy of note, are for (I), $S1 \cdots S1(2-x, -y, 1-z)$ 3.628 (2) Å, and for (II), $S1 \cdots N4(\frac{1}{2}-x, y-\frac{1}{2}, z)$ 3.517 (2) Å.

Figs. 3 and 4 show an interesting three-dimensional hydrogen-bonded polymeric network that essentially consists

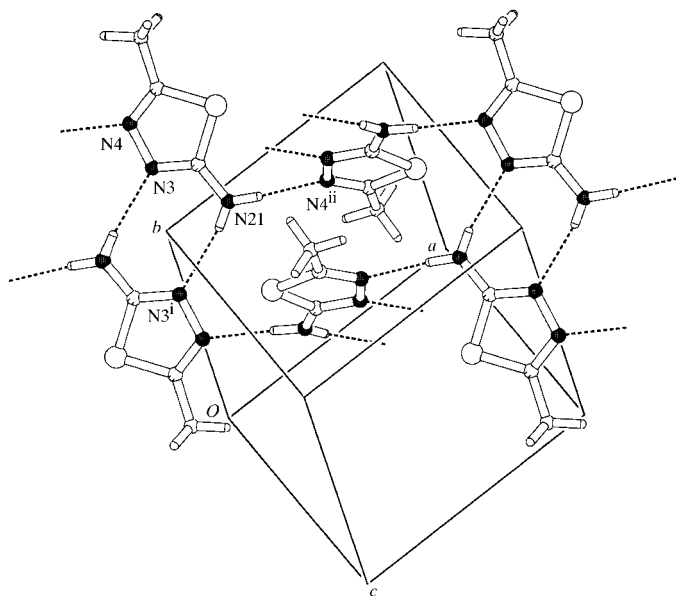


Figure 3
The molecular packing for (I). Hydrogen bonds are indicated by dotted lines [symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$].

of repeating ring systems made up of six associated molecules [graph set $R_6^6(20)$]. As expected, both (I) and (II) form dimers *via* the $N21-H \cdots N3$ interaction, but the main difference in packing between these two and the parent 2-amino-1,3,4-thiadiazole arises *via* the $N21-H \cdots N4$ interaction. In 2-amino-1,3,4-thiadiazole, the dimers formed by the $N21-H \cdots N3$ interaction form further dimers (*via* the $N21-H \cdots N4$ interaction) with similarly associated molecules. In (I) and (II), the $N21-H \cdots N4$ interactions from one molecular pair

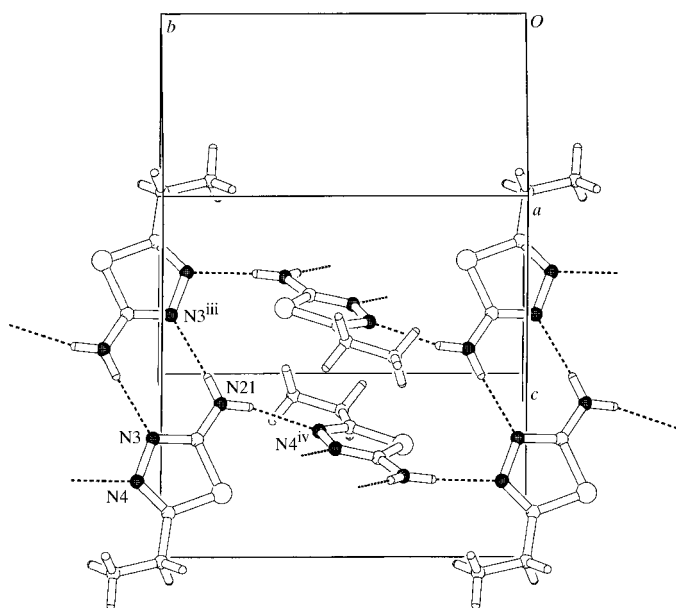


Figure 4
The molecular packing for (II). Hydrogen bonds are indicated by dotted lines [symmetry codes: (iii) $1 - x, -y, -z$; (iv) $\frac{1}{2} - x, \frac{1}{2} + y, z$].

then link different sets of dimers. These hydrogen-bonding networks [*i.e.* those of (I) and (II) *versus* that of the parent] are essentially two different arrangements of the same dimer association, but the packing in the parent (see supplementary figure) is more dense ($\rho = 1.609 \text{ Mg m}^{-3}$) than that shown in Figs. 3 and 4 ($\rho = 1.416$ and 1.418 Mg m^{-3} , respectively). It would now be interesting to elucidate the structures of both 5-propyl- and 5-halo-substituted 2-amino-1,3,4-thiadiazoles to determine what effect, if any, these substituents have on the overall hydrogen-bonding networks, and to determine if other packing forms are possible.

Experimental

Crystals of (I) and (II) were separated as unreacted starting materials following the total evaporation of ethanol solutions containing equimolar amounts (2 mmol) of (I) with 2-aminobenzoic acid, and of (II) with *N*-methylpyrrole-2-carboxylic acid.

Compound (I)

Crystal data

$C_3H_5N_3S$
 $M_r = 115.16$
Monoclinic, $P2_1/n$
 $a = 8.5116$ (17) Å
 $b = 6.5690$ (13) Å
 $c = 10.243$ (2) Å
 $\beta = 109.36$ (3)°
 $V = 540.34$ (18) Å³
 $Z = 4$

$D_x = 1.416 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 9981 reflections
 $\theta = 2.9\text{--}30.5^\circ$
 $\mu = 0.47 \text{ mm}^{-1}$
 $T = 150$ (2) K
Block, colourless
 $0.25 \times 0.15 \times 0.10 \text{ mm}$

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans
Absorption correction: multi-scan (SORTAV; Blessing, 1995)
 $T_{\min} = 0.893, T_{\max} = 0.955$
7274 measured reflections

1235 independent reflections
982 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.055$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -11 \rightarrow 11$
 $k = -7 \rightarrow 8$
 $l = -13 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.105$
 $S = 0.82$
1235 reflections
73 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0755P)^2 + 0.3034P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.25 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N21-H21 \cdots N3^i$	0.77 (3)	2.20 (3)	2.954 (2)	169 (2)
$N21-H22 \cdots N4^{ii}$	0.90 (2)	2.03 (2)	2.933 (3)	174 (2)

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

Compound (II)

Crystal data

C₄H₇N₃S
M_r = 129.19
 Orthorhombic, *Pbca*
a = 7.2752 (3) Å
b = 10.7294 (4) Å
c = 15.4991 (7) Å
V = 1209.84 (9) Å³
Z = 8
D_x = 1.418 Mg m⁻³

Mo *Kα* radiation
 Cell parameters from 6797
 reflections
 $\theta = 2.9\text{--}45.3^\circ$
 $\mu = 0.42\text{ mm}^{-1}$
T = 150 (2) K
 Block, colourless
 0.35 × 0.18 × 0.07 mm

Data collection

Nonius KappaCCD area-detector
 diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SORTAV; Blessing, 1995)
T_{min} = 0.866, *T_{max}* = 0.971
 7813 measured reflections

1385 independent reflections
 1125 reflections with *I* > 2σ(*I*)
R_{int} = 0.041
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -9 \rightarrow 8$
 $k = -12 \rightarrow 13$
 $l = -19 \rightarrow 20$

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.036
wR (*F*²) = 0.092
S = 1.05
 1385 reflections
 82 parameters
 H atoms treated by a mixture of
 independent and constrained
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 0.4846P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.26\text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.33\text{ e \AA}^{-3}$

Table 2

Hydrogen-bonding geometry (Å, °) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N21—H21...N3 ⁱⁱⁱ	0.86 (2)	2.12 (2)	2.983 (2)	175 (2)
N21—H22...N4 ^{iv}	0.85 (2)	2.17 (2)	3.012 (2)	167 (2)

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

The 5-methyl and 5-ethyl H atoms were included in the refinement at calculated positions and refined as riding models, with C—H = 0.98 (CH₃) or 0.99 Å (CH₂). The 2-amino H atoms were located from difference syntheses and refined freely. Two packing diagrams, of the parent 2-amino-1,3,4-thiadiazole and of the cocrystal of (II) with indole-2-carboxylic acid, are available as supplementary figures.

For both compounds, data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Nonius, 1998); cell refinement: *DENZO* 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: *PLUTON94* (Spek, 1994) and *PLATON97* (Spek, 1997); 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: GG1069). Additional figures are also available. Services for accessing these data are described at the back of the journal.

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