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2-Amino-5-trifluoromethyl-1,3,4-thiadiazole and a redetermination of 2-amino-1,3,4-thiadiazole, both at 120 K: chains of edge-fused $R_2^2(8)$ and $R_4^4(10)$ rings, and sheets of $R_2^2(8)$ and $R_6^6(20)$ rings

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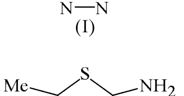
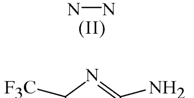
Molecules of 2-amino-5-trifluoromethyl-1,3,4-thiadiazole, $C_3H_2F_3N_3S$, are linked by two independent N—H···N hydrogen bonds into sheets of alternating $R_2^2(8)$ and $R_6^6(20)$ rings, while the molecules of the unsubstituted 2-amino-1,3,4-thiadiazole, $C_2H_3N_3S$, are linked, again by two independent N—H···N hydrogen bonds, but into chains of edge-fused $R_2^2(8)$ and $R_4^4(10)$ rings.

Comment

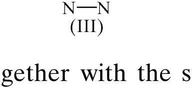
The structure of 2-amino-1,3,4-thiadiazole, (I), was reported several years ago (Khusenov *et al.*, 1997). The use of room-temperature diffraction data gave a final *R* value of 0.079, but no H-atom coordinates were reported, so that it is not possible fully to analyse the supramolecular aggregation. We have now reinvestigated this compound using diffraction data collected at 120 K, together with the substituted analogue 2-amino-5-trifluoromethyl-1,3,4-thiadiazole, (II), which is itself closely related to both 2-amino-5-methyl-1,3,4-thiadiazole, (III) (Lynch, 2001), and 5-amino-3-trifluoromethyl-1*H*-1,2,4-triazole, (IV) (Borbulevych *et al.*, 1998; Boechat *et al.*, 2004).



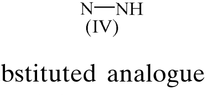
(I)



(II)



(III)



(IV)

Within the molecules of (I) and (II) (Figs. 1 and 2), the corresponding bond distances (Table 1) are fairly similar, and they show no real evidence for aromatic type π-electron delocalization. In particular, the C—S distances are all much longer than such bonds in thiophenes (Allen *et al.*, 1987). In each of (I) and (II), the C—S—C angle is less than 90°, with compensatory larger angles elsewhere in the rings (Table 1).

In each of (I) and (II), the amino groups act as double donors in N—H···N hydrogen bonds (Tables 2 and 3). However, in (I), the resulting supramolecular structure is one-dimensional, while in (II) it is two-dimensional. In compound (I), amino atom N2 in the molecule at (x, y, z) acts as hydrogen-bond donor, *via* atoms H21 and H22, respectively, to atoms N3 at $(1-x, 1-y, 1-z)$ and atom N4 at $(x, y, -1+z)$. Propagation by inversion and translation of these two interactions generates a chain of edge-fused rings running parallel to the [001] direction, with $R_2^2(8)$ (Bernstein *et al.*, 1995) rings centred at $(\frac{1}{2}, \frac{1}{2}, n+\frac{1}{2})$ (n = zero or integer) and $R_4^4(10)$ rings centred at $(\frac{1}{2}, \frac{1}{2}, n)$ (n = zero or integer) (Fig. 3).

The molecules of compound (II) are also linked into centrosymmetric $R_2^2(8)$ dimers (Fig. 4) by paired N—H···N hydrogen bonds (Table 3), exactly the same as those in compound (I). However, the further linking of these dimers generates a (100) sheet, rather than an [001] chain. Amino atoms N2 in the molecules at (x, y, z) and $(1-x, 1-y, 1-z)$, components of the $R_2^2(8)$ dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, act as hydrogen-bond donors, *via* atom H21, to ring atoms N4 in the molecules at $(x, \frac{1}{2}-y, \frac{1}{2}+z)$ and $(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$, respectively, which are components of the $R_2^2(8)$ dimers centred at $(\frac{1}{2}, 0, 1)$ and $(\frac{1}{2}, 1, 0)$, respectively. Similarly, atoms N4 in the molecules at (x, y, z) and $(1-x, 1-y, 1-z)$ accept hydrogen bonds from atom N2 in the molecules at $(x, \frac{1}{2}-y,$

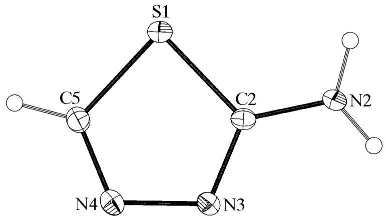


Figure 1
The molecule of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

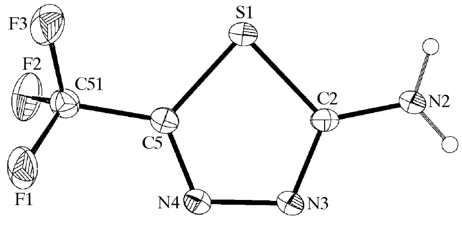


Figure 2
The molecule of compound (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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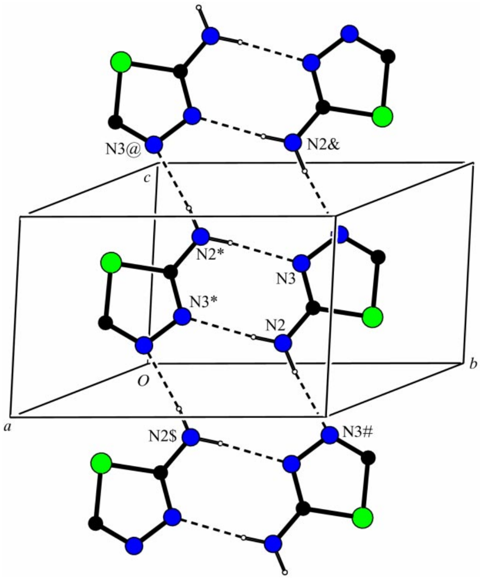

Figure 3
Part of the crystal structure of compound (I), showing the formation of an [001] chain of edge-fused $R_2^2(8)$ and $R_4^4(10)$ rings. For the sake of clarity, the H atom bonded to atom C5 has been omitted. Atoms marked with an asterisk (*), a hash (#), a dollar sign ($), an ampersand (&) or an 'at' sign (@) are at the symmetry positions $(1 - x, 1 - y, 1 - z)$, $(x, y, -1 + z)$, $(1 - x, 1 - y, -z)$, $(x, y, 1 + z)$ and $(1 - x, 1 - y, 2 - z)$, respectively.

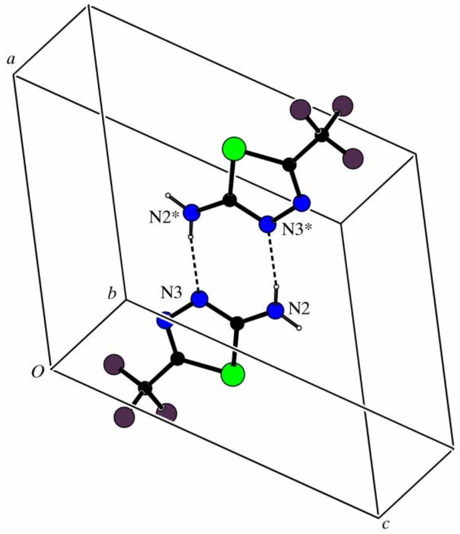

Figure 4
Part of the crystal structure of compound (II), showing the formation of a centrosymmetric $R_2^2(8)$ dimer. Atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, 1 - z)$.

$-\frac{1}{2} + z)$ and $(1 - x, \frac{1}{2} + y, \frac{3}{2} - z)$, respectively, which are themselves components of the dimers centred at $(\frac{1}{2}, 0, 0)$ and $(\frac{1}{2}, 1, 1)$. Propagation of these two hydrogen bonds then generates a (100) sheet in the form of a (6,3)-net (Batten & Robson, 1998) built from alternating $R_2^2(8)$ and $R_6^6(20)$ rings (Fig. 5).

Thus, the modes of supramolecular aggregation in (I) and (II) are entirely different from one another. In addition, they differ from that in the related triazole, compound (IV), where only two of the three available N—H bonds participate in the aggregation to form a $C(4)C(5)[R_2^2(7)]$ chain of rings (Boechat *et al.*, 2004). However, compounds (II) and (III) are nearly isostructural, when due account is taken of the space-group settings employed, $P2_1/c$ for compound (II) reported here and $P2_1/n$ for (III) reported by Lynch (2001). Both compounds form sheets of alternating $R_2^2(8)$ and $R_6^6(20)$ rings, so that the description of the supramolecular aggregation in (III) as three-dimensional (Lynch, 2001) is, in fact, incorrect.

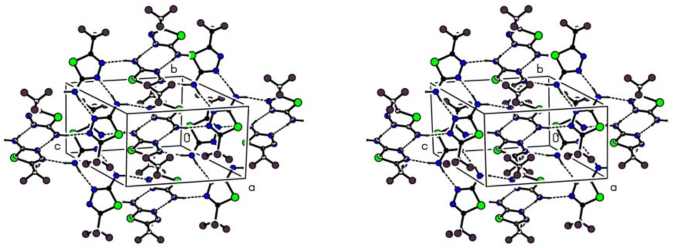

Figure 5
A stereoview of part of the crystal structure of compound (II), showing the formation of a (100) sheet of alternating $R_2^2(8)$ and $R_6^6(20)$ rings.

Experimental

To a mixture of equimolar quantities (75 mmol of each) of the thiosemicarbazide $H_2NCSNHNH_2$ and the appropriate carboxylic acid RCO_2H (R = H or CF_3), sulfuric acid (49 mmol) was added dropwise at ambient temperature. The reaction mixtures were then heated at 373 K for 7–10 h with stirring, cooled, poured onto ice–water and rendered alkaline with aqueous sodium hydroxide solution. The resulting solid products were collected by filtration, washed with water, dried and recrystallized from ethanol, to yield crystals of compounds (I) and (II) suitable for single-crystal X-ray diffraction. Analysis for (I): 10 h reaction, 74% yield, m.p. 464–465 K; ^{1}H NMR (MeOD): δ 7.06 (*s*, 1H), 8.54 (*s*, 2H, NH_2); ^{13}C NMR (MeOD): δ 144.8 (C1), 171.2 (C2); IR (KBr, ν, cm^{-1}): 3286 and 3091 (N—H), 1618 (C═N), 1509 (NH_2), 1021 (C═S). Analysis for (II): 7 h reaction, 85% yield, m.p. 489–491 K; ^{1}H NMR (MeOD): δ 7.71 (*s*, NH_2); ^{13}C NMR (MeOD: δ 121.1 (*q*, CF_3, J = 269 Hz), 146.8 (*q*, C2, J = 38 Hz), 173.8 (C1); ^{19}F NMR (MeOD): δ −61.45 (CF_3); IR (KBr, ν, cm^{-1}): 3303 and 3127 (N—H), 1640 (C═N), 1519 (NH_2), 1075 (C═S), 1193 and 745 (CF_3).

Table 1
Selected geometric parameters (Å, °) for compounds (I) and (II).

	(I)	(II)
S1—C2	1.745 (2)	1.749 (2)
C2—N3	1.323 (2)	1.328 (3)
N3—N4	1.390 (2)	1.378 (3)
N4—C5	1.293 (3)	1.291 (3)
C5—S1	1.735 (2)	1.727 (2)
C2—N2	1.345 (3)	1.325 (3)
C5—C51		1.494 (4)
C5—S1—C2	86.59 (10)	86.31 (11)
S1—C2—N3	113.86 (15)	113.56 (18)
C2—N3—N4	111.73 (16)	111.81 (19)
N3—N4—C5	113.04 (16)	113.03 (19)
N4—C5—S1	114.78 (16)	115.29 (19)
S1—C2—N2	121.89 (14)	122.35 (17)
N3—C2—N2	124.25 (19)	124.1 (2)

Compound (I)

Crystal data

$C_2H_3N_3S$
$M_r = 101.13$
Monoclinic, $P2_1/n$
$a = 5.5718$ (5) Å
$b = 13.4573$ (17) Å
$c = 5.7875$ (5) Å
$\beta = 109.984$ (6)°
$V = 407.83$ (7) Å^3
$Z = 4$
$D_x = 1.647$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 936 reflections
$\theta = 3.0$–27.6°
$\mu = 0.60$ mm^{-1}
$T = 120$ (2) K
Needle, colourless
0.15 × 0.04 × 0.02 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.919$, $T_{\max} = 0.988$
6842 measured reflections

936 independent reflections
736 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.096$
$\theta_{\max} = 27.6°$
$h = -7 \rightarrow 7$
$k = -17 \rightarrow 17$
$l = -6 \rightarrow 7$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.102$
$S = 1.08$
936 reflections
59 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.056P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.39$ e Å^{-3}
$\Delta\rho_{\min} = -0.38$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H21···N3$^{\rm i}$	0.87	2.13	2.999 (3)	175
N2—H22···N4$^{\rm ii}$	0.89	2.08	2.969 (2)	172

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

Compound (II)

Crystal data

$C_3H_2F_3N_3S$
$M_r = 169.14$
Monoclinic, $P2_1/c$
$a = 9.1082$ (12) Å
$b = 6.9373$ (10) Å
$c = 10.8048$ (14) Å
$\beta = 116.656$ (9)°
$V = 610.15$ (14) Å^3
$Z = 4$
$D_x = 1.841$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 1386 reflections
$\theta = 3.6$–27.5°
$\mu = 0.51$ mm^{-1}
$T = 120$ (2) K
Plate, colourless
0.32 × 0.24 × 0.06 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.853$, $T_{\max} = 0.970$
6231 measured reflections

1386 independent reflections
1093 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.044$
$\theta_{\max} = 27.5°$
$h = -11 \rightarrow 11$
$k = -9 \rightarrow 9$
$l = -14 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.113$
$S = 1.10$
1386 reflections
91 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0491P)^2 + 0.4024P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.33$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ e Å^{-3}

Table 3
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H21···N3$^{\rm i}$	0.84	2.16	2.985 (3)	171
N2—H22···N4$^{\rm ii}$	0.87	2.10	2.959 (3)	169

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

The space groups $P2_1/n$ and $P2_1/c$ for compounds (I) and (II), respectively, were uniquely assigned from the systematic absences. All H atoms were located in difference maps. The coordinates of the H atom bonded to carbon in compound (I) were freely refined, giving a C—H distance of 0.95 (3) Å. H atoms bonded to nitrogen were allowed to ride at the positions found from the difference maps, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm N})$; the resulting N—H distances were in the range 0.84–0.89 Å. In (II), the anisotropic displacement parameters for the F atoms suggest that there may be some libration of the CF_3 group about the C5—C51 bond.

For both compounds, data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *WinGX* (Farrugia, 1999) and *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *OSCAIL* (McArdle, 2003) and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1892). Services for accessing these data are described at the back of the journal.

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