Table 2. *Important bond lengths* (Å) *and angles* (°) *with e.s.d.'s*

Compound (I)

C(6)–C(7)	1·549 (8)	C(25)–C(35)	1·542 (9)
C(6)–C(13)	1·532 (8)	C(35)–O(2)	1·188 (7)
C(6)–C(19)	1·554 (8)	C(35)–O(1)	1·324 (8)
N(5)–H(5)	0·996 (68)	O(1)–C(36)	1·469 (8)
C(6)–N(5)	1·493 (8)	C(27)–O(4)	1·194 (7)
C(25)–N(5)	1·450 (7)	C(27)–O(3)	1·292 (7)
C(25)–C(26)	1·543 (8)	O(3)–C(28)	1·458 (8)
C(25)–N(5)–H(5)	106·2 (37)	C(26)–C(25)–N(5)	110·0 (5)
C(6)–N(5)–C(25)	116·8 (5)	C(35)–C(25)–N(5)	112·6 (5)
C(6)–N(5)–H(5)	111·9 (36)	C(35)–C(25)–C(26)	109·2 (5)

Compound (II)

	Molecule *A*	Molecule *B*
C(19)–C(1)	1·507 (19)	1·551 (14)
C(19)–C(7)	1·598 (14)	1·586 (12)
C(19)–C(13)	1·545 (15)	1·525 (17)
C(19)–N(20)	1·447 (12)	1·458 (12)
C(21)–N(20)	1·458 (14)	1·463 (12)
H(20)–N(20)	0·842 (124)	0·677 (90)
C(21)–C(22)	1·507 (17)	1·501 (17)
C(21)–C(32)	1·532 (18)	1·518 (17)
C(22)–O(23)	1·193 (15)	1·202 (13)
C(22)–O(24)	1·342 (11)	1·299 (11)
O(24)–C(25)	1·460 (14)	1·458 (15)
C(19)–N(20)–C(21)	116·6 (8)	118·3 (8)
H(20)–N(20)–C(19)	106·5 (81)	107·5 (92)
H(20)–N(20)–C(21)	105·1 (75)	133·0 (90)
N(20)–C(21)–C(22)	114·5 (10)	114·9 (9)
N(20)–C(21)–C(32)	108·1 (9)	107·9 (8)
C(22)–C(21)–C(32)	106·6 (11)	108·9 (10)

values are given in Table 1. Important bond lengths and angles are listed in Table 2.*

The structure of (I) clearly demonstrates that the α-benzyl ester group approaches the bulky trityl moiety, whereas the β-ester is pointing away. This can explain the difficulty in the alkaline hydrolysis of the α-benzyl ester of this compound. Moreover, the bonds observed between the N—H and the two carbonyl groups [H(5)···O(2) = 2·393 (75), H(5)···O(4) = 2·436 (75) Å] show a weak interaction between the two ester chains and the bulky N-terminal trityl group.

The low precision of the refinement of (II) is due to the poor quality of the crystals and to large thermal vibration of the phenyl rings (two independent molecules with 70 non-H atoms in the asymmetric unit). We have refined the structure with the phenyl rings constrained to be regular hexagons. Also, we have tried to include two different orientations of the rings and refined occupation factors, without obtaining better convergence. In the final $\Delta\rho$ map we were able to localize the positions of H(20*A*) and H(20*B*). The two molecules of the asymmetric unit are interconnected by two hydrogen bonds involving, as in compound (I), the N-terminal N—H moiety and the ester carbonyl group [H(20*A*)···O(23*B*) = 2·383 (115), H(20*B*)···O(23*A*) = 2·728 (140) Å].

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, a complete list of bond lengths and angles, torsion angles and equations of planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43427 (65 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of 1,3,4-Thiadiazole-2,5-diamine

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Abstract. $C_2H_4N_4S$, $M_r = 116{\cdot}1$, monoclinic, $P2_1/n$, $a = 11{\cdot}099\ (2)$, $b = 10{\cdot}328\ (3)$, $c = 8{\cdot}971\ (2)$ Å, $\beta = 112{\cdot}58\ (1)°$, $V = 949{\cdot}6\ (4)$ Å^3, $Z = 8$, $D_m = 1{\cdot}65$ (by flotation), $D_x = 1{\cdot}63$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}322$ mm^{-1}, $F(000) = 480$, $T = 293$ K, final $R = 0{\cdot}029$ for 1436 significant reflections. The asymmetric unit contains two crystallographically unique molecules which are essentially planar. Both molecules have almost complete C_{2v} symmetry and are linked by N(amino)—H···N(ring) hydrogen bonds in the crystal.

Introduction. Recently we reported the formation of heterocyclic ring compounds by the reactions between substituted thioureas and iron(II or III) chloride

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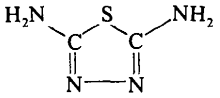
(Senda & Maruha, 1985*a*,*b*; Senda, Matsuoka & Maruha, 1986). We present here the structure of 1,3,4-thiadiazole-2,5-diamine, which was obtained from dithiobiurea, $[H_2NC(=S)NH-]_2$ (dtbu), and $FeCl_2.4H_2O$.



Experimental. An ethanol solution of $FeCl_2.4H_2O$ and a suspension of dtbu in ethanol mixed and refluxed at about 330 K for 5 h. Dark violet iron complex filtered off. Violet-brown crystals formed in the filtrate after standing for two weeks.

Space group $P2_1/n$, systematic absences $0k0$, k odd; $h0l$, $h+l$ odd. Crystal: 0·38 × 0·24 × 0·22 mm. Rigaku AFC-4 four-circle diffractometer, graphite-monochromated Mo $K\alpha$. Cell parameters refined by least-squares method on the basis of 2θ values of 25 reflections ($30{\cdot}0 < 2\theta < 38{\cdot}4°$). Intensity measurement performed to $2\theta = 50°$ (h −13→13, k −12→0, l 0→10), $\theta/2\theta$ scan technique, scan speed 4° min^{-1} (θ). Three standard reflections showed no significant variation, $0{\cdot}989 < |F_o|/|F_o|_{\rm initial} < 1{\cdot}014$. 1653 independent reflections, 217 reflections with $|F_o| < 3\sigma|F_o|$ considered unobserved. Lorentz–polarization correction, no absorption correction. Structure solved by direct methods with *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). All 14 non-H atoms located from *E* map and refined by block-diagonal least-squares method on *F* with anisotropic thermal parameters using *UNICS* program system (Sakurai, 1967). Eight H atoms obtained from ΔF synthesis and included in the refinement isotropically. Final $R = 0{\cdot}029$ and $wR = 0{\cdot}025$ for 1436 observed reflections, $w = 1/(\sigma^2|F_o| + 0{\cdot}01428|F_o| - 0{\cdot}00024|F_o|^2)$, $S = 0{\cdot}61$. $(\Delta/\sigma)_{\rm max} = 0{\cdot}23$ for non-H atoms and 0·88 for H atoms. Max. and min. height in final ΔF synthesis $\pm 0{\cdot}18$ e Å^{-3}. Scattering factors for non-H atoms from *International Tables for X-ray Crystallography* (1974) and for H atoms from Stewart, Davidson & Simpson (1965). All calculations performed on a FACOM M-360AP computer.

Discussion. Final atomic coordinates are given in Table 1, and bond distances and angles in Table 2.* The crystal structure is shown in Fig. 1 together with the atom numbering.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for non*-H *atoms*

	x	y	z	B_{eq}*
Molecule *A*				
S	0·31924 (4)	0·12381 (4)	0·41039 (4)	3·45
N(1)	0·3593 (1)	0·0419 (1)	0·1631 (1)	3·81
N(2)	0·4733 (1)	0·1089 (1)	0·2588 (1)	4·05
N(3)	0·1593 (1)	−0·0255 (1)	0·1658 (1)	3·79
N(4)	0·5614 (1)	0·2248 (2)	0·5010 (2)	4·61
C(1)	0·2727 (1)	0·0401 (1)	0·2274 (2)	2·89
C(2)	0·4664 (1)	0·1558 (1)	0·3893 (2)	3·08
Molecule *B*				
S	0·36993 (4)	0·37187 (4)	0·95548 (4)	3·32
N(1)	0·3931 (1)	0·4099 (1)	0·6851 (1)	3·56
N(2)	0·4833 (1)	0·3130 (1)	0·7630 (1)	3·55
N(3)	0·2353 (1)	0·5438 (1)	0·7206 (2)	4·48
N(4)	0·5596 (1)	0·1930 (1)	1·0016 (1)	4·32
C(1)	0·3267 (1)	0·4491 (1)	0·7684 (2)	3·05
C(2)	0·4824 (1)	0·2827 (1)	0·9033 (2)	2·90

* Hamilton (1959).

Table 2. *Bond distances* (Å) *and angles* (°) *for non*-H *atoms and possible hydrogen bonds*

	Molecule *A*	Molecule *B*
S–C(1)	1·749 (1)	1·751 (1)
S–C(2)	1·746 (2)	1·753 (2)
C(1)–N(1)	1·297 (2)	1·299 (2)
C(2)–N(2)	1·296 (2)	1·301 (2)
N(1)–N(2)	1·408 (2)	1·398 (2)
C(1)–N(3)	1·347 (2)	1·355 (2)
C(2)–N(4)	1·346 (2)	1·339 (2)
C(1)–S–C(2)	86·76 (7)	86·81 (7)
S–C(1)–N(1)	114·0 (1)	113·7 (1)
S–C(2)–N(2)	114·1 (1)	113·8 (1)
C(1)–N(1)–N(2)	112·5 (1)	113·0 (1)
C(2)–N(2)–N(1)	112·6 (1)	112·7 (1)
S–C(1)–N(3)	121·8 (1)	121·9 (1)
S–C(2)–N(4)	121·2 (1)	122·0 (1)
N(1)–C(1)–N(3)	124·1 (1)	124·4 (1)
N(2)–C(2)–N(4)	124·6 (2)	124·2 (1)

Possible hydrogen bonds

	$X\cdots Y$	H$\cdots Y$	$\angle X$–H$\cdots Y$
N(*A*4)–H(N*A*4)1$\cdots$N(*B*2)	2·945 (2) Å	2·14 (2) Å	164 (2)°
N(*B*4)–H(N*B*4)1$\cdots$N(*A*2$^{\rm i}$)	2·949 (2)	2·15 (2)	162 (2)

Symmetry codes: none x, y, z; (i) $x, y, 1 + z$.

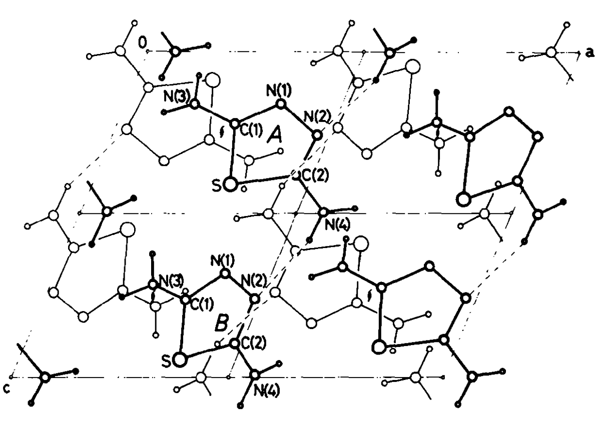


Fig. 1. Crystal structure projected along **b**. Hydrogen bonds are indicated by broken lines.

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* Lists of structure factors, anisotropic thermal parameters, atomic parameters for H atoms, bond distances and angles involving H atoms, torsion angles and deviations from the least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43411 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The asymmetric unit contains two crystallographically unique molecules *A* and *B* (Fig. 1). These independent molecules are alternately arranged parallel to the $(10\bar{1})$ plane and are linked by hydrogen bonds between one of the cyclic N atoms and a neighbouring amino H atom (Fig. 1 and Table 2). Both molecules exhibit almost complete C_{2v} symmetry. Recently we reported the structure of 2,5-diamino-3*H*-1,3,4-thiadiazolinium chloride monohydrate (Senda, Matsuoka & Maruha, 1986), in which the cation no longer possesses C_{2v} symmetry because an H atom is attached to one of the two endocyclic N atoms. The distances and angles in *A* and *B* are almost equal to each other (Table 2), and are in good agreement with those in unsubstituted 1,3,4-thiadiazole (Markov & Stolevik, 1970; la Cour, 1974). Four cyclic C—N bond distances suggest localized double bonding (Senda, Matsuoka & Maruha, 1986; Mathew & Palenik, 1974). The exocyclic C—N bond lengths indicate partial double-bond character. The C—S bond distances (1·746–1·753 Å) are somewhat shorter than the value of 1·77 Å for a C(sp^2)—S single bond (Mathew & Palenik, 1974). The N—N distance (mean 1·403 Å) is comparable to the normal single-bond distance (1·40 Å: Sutton, 1965). All N—H distances lie in the range 0·76–0·87 Å. The five-membered rings of the molecules are planar: the maximum deviation from the least-squares plane is 0·009 Å for C(*A*1). Exocyclic N(4) atoms also lie in these planes, but the deviations of N(3) atoms, especially of the *A* molecule, are large: 0·102 Å for the *A* and 0·021 Å for the *B* molecule.

The intermolecular contacts N(*A*1)···N($B4^{ii}$) 3·147 (2) [(ii) $1-x$, $-y$, $1-z$], N(*B*1)···N($A3^{iii}$) 3·047 (2) [(iii) $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$] and N(*B*3)···N($A1^{iii}$) 3·190 (2) Å are close to the sum of the van der Waals radii.

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Structure of *cyclo*(-L-Methionyl-L-prolyl-)

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Abstract. $C_{10}H_{16}N_2O_2S$, $M_r = 228·3$, orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 9·816$ (3), $b = 11·129$ (5), $c = 10·105$ (5) Å, $V = 1103·9$ Å^3, $D_x = 1·373$, D_m(by flotation) $= 1·372$ g cm^{-3}, λ(Mo $K\alpha$) $= 0·7107$ Å, $\mu = 2·29$ cm^{-1}, $F(000) = 488$, room temperature, $R = 0·056$ for 926 observed reflections. The diketopiperazine has a boat conformation with the methionyl chain in the pseudo-equatorial position. The torsional