Table 3. *Inter- and intramolecular hydrogen-bonding geometry* (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N(2)—H(N2)···S	0.88 (3)	2.68 (3)	2.630 (2)	77 (2)
N(3)—H(N3*B*)···S	0.87 (4)	2.68 (3)	2.654 (2)	79 (2)
N(3)—H(N3*B*)···N	0.97 (3)	2.25 (3)	2.618 (3)	101 (2)
N(2)—H(N2)···O(*W*)	0.88 (3)	2.03 (3)	2.890 (3)	167 (2)
N(3)—H(N3*B*)···S[i]	0.87 (4)	2.55 (4)	3.393 (22)	163 (2)

Symmetry code: (i) $1 - x, -y, -z$.

Data were corrected for Lorentz–polarization effects. The structure was solved using *SHELXS*86 (Sheldrick, 1985). All the H atoms were located from difference Fourier maps. Full-matrix least-squares refinement with anisotropic displacement parameters for non-H and isotropic for H atoms was performed using the *NRCVAX* crystal structure system (Larson, Lee, Le Page, Webster, Charland, Gabe & White, 1990).

The authors wish to thank Dr N. C. Shivaprakash, ISU, X-RD laboratory, IISc, Bangalore, India, for the data. One of the authors, MKK, thanks Professor J. Shashidharaprasad, Department of Postgraduate Studies in Physics, Manasagangothri, Mysore, India, for providing the computational facilities.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1072). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). **C51**, 333–336

4-Amino-*N*-(2-pyrimidinyl)-benzenesulfonamide

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(*Received* 9 *March* 1993; *accepted* 17 *December* 1993)

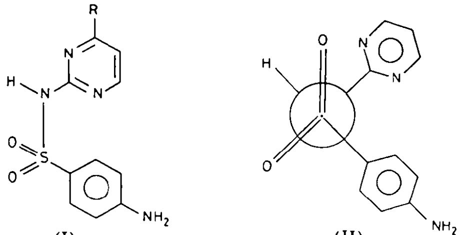
Abstract

The structure of the title compound, $C_{10}H_{10}N_4O_2S$, has been determined. The two six-membered rings are planar and folded towards each other making an acute angle of 74.9 (2)°. The molecules are linked by intermolecular N—H···O and N—H···N bonds.

Comment

4-Amino-*N*-(2-pyrimidinyl)benzenesulfonamide, (I), (R = H) is one of the most important 'sulpha' drugs and is useful in the treatment of bacterial infections and extraluminal urinary-tract infections (Aurthur Osol, 1990); its higher homologue (R = CH_3), known as sulphamerazine, has been used in combination with other antibiotics (Aurthur Osol, 1990). Crystal structure studies of sulfonamides have revealed the nature of their intermolecular hydrogen bonding (O'Connell & Maslen, 1967), their interaction with protic solvents (Rambaud, Maury, Pauvert, Audran, Lasserre, Berge & Declercq, 1985) and their binding with specific proteins (Acharya, Kuchela & Kartha, 1982). The crystal structure of sulphadiazine (I) (R = H) has been reported (Ihn, Kim & Koo, 1975) and interesting variations of its solid-state conformation have been found in its silver and zinc complexes (Cook & Turner, 1975; Brown, Cook &

Sengier, 1985). In the light of the above observations, crystal structure analysis of the title compound, (I) (R = H), has been undertaken.



(I) (II)

The C(4)—N(1) bonds [1.386 (8) Å] are quite large compared to those of sulphamerazine [1.363 (12) Å], but similar to the C—NH_2 distance [1.385 (26) Å] of β-sulfanilamide (O'Connell & Maslen, 1967) and agree with the value of 1.402 (2) Å in α-sulfanilamide (O'Connor & Maslen, 1965), having trigonal hybridization. However, this bond length is significantly longer than the C—NH_2 distance of 1.316 (7) Å in 1,3,5-trinitrobenzene (Cady & Larson, 1965) which shows sp^3 hybridization of the N atom.

Abrahams (1955) calculated the S—C single-bond distance to be 1.82 Å, which is close to the sum of the covalent radii for S and C atoms (Pauling, 1960). In the present study, C(1)—S(1) is 1.736 (5) Å, which is close to the bond length of 1.750 (18) Å given by O'Connell & Maslen (1967), and appears to have π-bond character. Furthermore, the observed bond length of S(1)—N(2) [1.643 (5) Å] indicates a sufficient degree of double-bond character, which is also observed in N'-(4,6-dimethyl-2-pyrimidinyl)sulfanilamide methanol solvate (Rambaud, Maury, Pauvert Audran, Lasserre, Berge & Declercq, 1985).

The sulfonamide group is approximately tetrahedral, the large deviation of the angle O(1)—S(1)—O(2) [119.5 (3)°] from the ideal tetrahedral configuration results from the type of non-bonded interactions described by Bartel (1962). Further examination of the contact distances, O(1)···O(2) = 2.481 (7), O(1)···N(2) = 2.511 (6) and O(2)···N(2) = 2.398 (6) Å, resulting from non-bonded interactions indicates that the tetrahedron is distorted in a manner consistent with minimum hindrance (O'Connell & Maslen, 1967).

The bonds S(1)—O(1) [1.432 (5) Å] and S(1)—O(2) [1.440 (5) Å] are almost equal in length to those of 1.430 (6) and 1.441 (6) Å, respectively, in sulphamerazine (Acharya, Kuchela & Kartha, 1982). The bond lengths and angles of the *para*-aminobenzene are comparable with those of other sulfonamides (O'Connell & Maslen, 1967). The C—N distances within the pyrimidine ring, C(7)—N(3) = 1.338 (7) and C(7)—N(4) = 1.337 (7) Å, are comparable with the average ring distance in N-atom heterocycles [1.339 (5) Å (Sutton, 1965)].

In the structure of sulphadiazine (Ihn, Kim & Koo, 1975) both O atoms of the sulfonamide group enter into intermolecular hydrogen bonding with H atoms of the amino group; the same is observed in the title compound [N(1)—H(N1A)···O(1) = 2.994 (6) and N(1)—H(N1B)···O(2) = 2.971 (5) Å]. The present structure also shows intermolecular hydrogen bonding between the pyrimidine atom N(3) with the sulfonamide N(2) [N(2)—H(N2)···N(3) = 2.941 (8) Å], whereas in the structure of sulphadiazine (Ihn, Kim & Koo, 1975) the amino N atom forms N—H···N hydrogen bonds between molecules related by a centre of symmetry.

Sulphadiazine molecules can exist in different conformations as a result of rotation across C(1)—S(1), S(1)—N(2) and N(2)—C(7). The three dihedral angles describing these conformations are C(1)—S(1)—N(2)—C(7) = − 78.6 (3), S(1)—N(2)—C(7)—N(4) = 17.2 (2) and C(2)—C(1)—S(1)—N(2) = 120.0 (4) or C(6)—C(1)—S(1)—N(2) = − 62. (3)°. This indicates that the molecule adopts a *gauche* conformation, (II), when viewed along the S—N axis. The molecular packing viewed down the c axis is shown in Fig. 2. The molecules are held by hydrogen bonds, the details of which are given in Table 3.

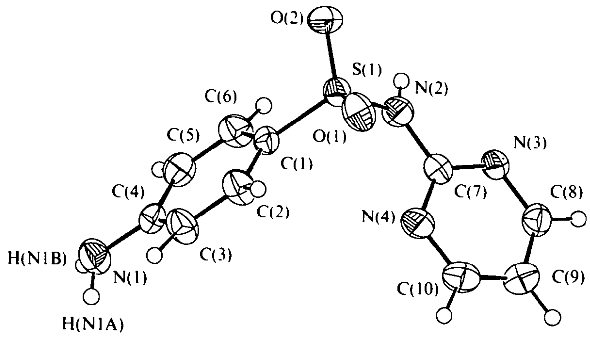


Fig. 1. *PLATON* (Spek, 1990) plot of the title compound. Displacement ellipsoids are shown at the 50% probability level.

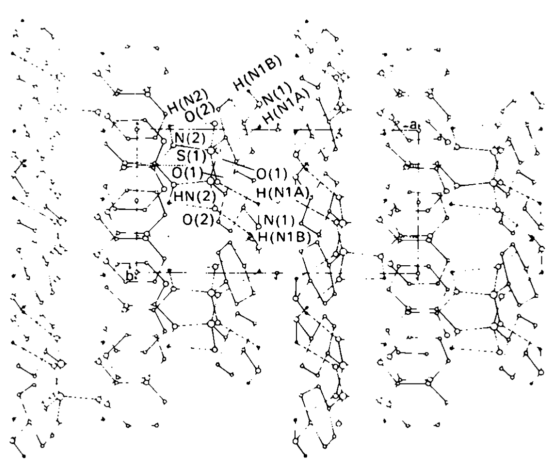


Fig. 2. The molecular packing viewed down the c axis.

Experimental

Crystal data

$C_{10}H_{10}N_4O_2S$
$M_r = 250.28$
Monoclinic
$P2_1/c$
$a = 13.613$ (5) Å
$b = 5.919$ (9) Å
$c = 14.988$ (2) Å
$\beta = 114.563$ (10)°
$V = 1098.3$ (4) Å^3
$Z = 4$
$D_x = 1.514$ Mg m^{-3}
$D_m = 1.509$ Mg m^{-3}
D_m measured by flotation in KI solution

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 20$–$25°$
$\mu = 2.56$ mm^{-1}
$T = 300$ K
Needle
1.1 × 0.3 × 0.1 mm
Pale yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3698 measured reflections
3698 independent reflections
1686 observed reflections [$I \geq 2.5\sigma(I)$]

$\theta_{max} = 65°$
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 6$
$l = -17 \rightarrow 17$
3 standard reflections monitored every 100 reflections
intensity decay: no specific variation

Refinement

Refinement on F
$R = 0.064$
$wR = 0.086$
$S = 2.78$
1686 reflections
194 parameters
All H-atom parameters refined
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{max} = 0.349$
$\Delta\rho_{max} = 0.55$ e Å^{-3}
$\Delta\rho_{min} = -0.60$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (1/3)\Sigma_i\Sigma_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
S(1)	0.2648 (1)	0.1331 (3)	0.5580 (1)	2.72 (6)
N(1)	0.4350 (4)	−0.1176 (10)	0.2681 (4)	3.9 (3)
N(2)	0.1328 (4)	0.1130 (9)	0.5008 (4)	3.12 (23)
N(3)	−0.0402 (4)	0.2422 (9)	0.4202 (3)	2.72 (22)
N(4)	0.1050 (4)	0.4208 (9)	0.3968 (4)	3.34 (24)
O(1)	0.2938 (3)	0.3625 (8)	0.5877 (3)	3.82 (22)
O(2)	0.2898 (3)	−0.0407 (9)	0.6314 (3)	4.02 (23)
C(1)	0.3139 (4)	0.0589 (10)	0.4720 (4)	2.5 (3)
C(2)	0.3746 (5)	0.2154 (11)	0.4471 (5)	3.4 (3)
C(3)	0.4141 (5)	0.1554 (11)	0.3785 (5)	3.5 (3)
C(4)	0.3945 (4)	−0.0567 (11)	0.3357 (4)	3.0 (3)
C(5)	0.3360 (5)	−0.2133 (11)	0.3635 (4)	3.3 (3)
C(6)	0.2962 (5)	−0.1572 (11)	0.4319 (5)	3.3 (3)
C(7)	0.0636 (4)	0.2661 (10)	0.4365 (4)	2.7 (3)
C(8)	−0.1094 (5)	0.3926 (11)	0.3596 (4)	3.2 (3)
C(9)	−0.0762 (5)	0.5614 (12)	0.3154 (5)	3.6 (3)
C(10)	0.0319 (5)	0.5661 (11)	0.3365 (5)	3.7 (3)

Table 2. *Selected geometric parameters* (Å, °)

S(1)—N(2)	1.643 (5)	C(1)—C(6)	1.391 (9)
S(1)—O(1)	1.432 (5)	C(2)—C(3)	1.391 (8)
S(1)—O(2)	1.440 (5)	S(1)—C(1)	1.736 (5)
C(3)—C(4)	1.385 (9)	N(1)—C(4)	1.386 (8)
C(4)—C(5)	1.395 (9)	C(5)—C(6)	1.385 (9)
N(2)—C(7)	1.372 (8)	C(8)—C(9)	1.375 (9)
N(3)—C(7)	1.338 (7)	N(3)—C(8)	1.339 (8)
C(9)—C(10)	1.370 (9)	N(4)—C(7)	1.337 (7)
N(4)—C(10)	1.342 (8)	C(1)—C(2)	1.392 (8)
N(2)—S(1)—O(1)	109.4 (3)	N(2)—S(1)—O(2)	101.9 (3)
N(2)—S(1)—C(1)	105.6 (3)	N(1)—C(4)—C(3)	121.1 (6)
N(1)—C(4)—C(5)	119.7 (6)	O(1)—S(1)—O(2)	119.5 (3)
C(3)—C(4)—C(5)	119.2 (5)	O(1)—S(1)—C(1)	109.2 (3)
C(4)—C(5)—C(6)	120.7 (6)	O(2)—S(1)—C(1)	110.1 (3)
C(1)—C(6)—C(5)	119.3 (5)	N(2)—C(7)—N(3)	115.0 (5)
N(2)—C(7)—N(4)	118.2 (5)	S(1)—N(2)—C(7)	126.9 (4)
N(3)—C(7)—N(4)	126.8 (5)	N(3)—C(8)—C(9)	122.0 (5)
C(7)—N(3)—C(8)	116.5 (5)	C(7)—N(4)—C(10)	114.0 (5)
C(8)—C(9)—C(10)	116.1 (6)	S(1)—C(1)—C(2)	119.0 (5)
S(1)—C(1)—C(6)	120.2 (4)	C(2)—C(1)—C(6)	120.8 (5)
N(4)—C(10)—C(9)	124.6 (6)	C(1)—C(2)—C(3)	119.0 (6)
C(2)—C(3)—C(4)	121.0 (6)		

Table 3. *Hydrogen-bonding geometry* (Å, °)

D	H	*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N(2)	H(N2)	O(2)	0.73 (8)	2.24 (7)	2.40 (1)	93 (2)
N(1)	H(N1*A*)	O(1^{i})	0.91 (9)	2.50 (7)	2.99 (1)	115 (2)
N(1)	H(N1*B*)	O(2^{ii})	1.01 (7)	2.00 (7)	2.97 (1)	162 (4)
N(2)	H(N2)	N(3^{iii})	0.73 (8)	2.23 (9)	2.94 (1)	166 (4)

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

Data were corrected for Lorentz–polarization effects. The structure was solved using *SHELXS*86 (Sheldrick, 1985). All H atoms were located from difference Fourier maps and refined by full-matrix least-squares techniques, with anisotropic displacement parameters for non-H atoms and isotropic for H atoms, using the *NRCVAX* crystal structure system (Larson, Lee, Le Page, Webster, Charland, Gabe & White, 1990).

The authors wish to thank Dr N. C. Shivaprakash, ISU, X-RD Laboratory, IISc, Bangalore, India, for the data. One of the authors, MKK, thanks Professor J. Shashidharaprasad, Department of Postgraduate Studies in Physics, Manasagangothri, Mysore, India, for providing the computational facilities.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: CR1071). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 336–339

N-Acetylglycyl-L-alaninamide and *N*-Acetyl-L-alanyl-L-alaninamide †

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(*Received* 30 *May* 1994; *accepted* 19 *July* 1994)

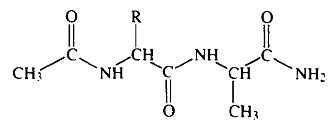
Abstract

The main conformations of *N*-acetylglycyl-L-alaninamide (NAGAA), $C_7H_{13}N_3O_3$, and *N*-acetyl-L-alanyl-L-alaninamide (NAA$_2$A), $C_8H_{15}N_3O_3$, occur in the *F* and *E* regions, respectively, of the φ, ψ map, according to the classification of Zimmerman, Pottle, Némethy & Scheraga [*Macromolecules* (1977), **10**, 1–9]. In both structures, the packing is governed by intermolecular hydrogen bonds which involve all the donor groups. In the NAGAA crystal, each molecule shares eight hydrogen bonds with eight nearest molecules, thus forming a three-dimensional network of hydrogen bonds. The methyl groups lie at van der Waals distances in channels which grow parallel to *b* and around the screw axis. In NAA$_2$A, screw-related molecules are joined by three hydrogen bonds and form ribbons which extend parallel to the *bc* plane, alternately at $x = 0$ and 0.5. A fourth hydrogen bond connects the ribbons along the direction of the *a* axis.

† The authors dedicate this paper to the memory of Professor George Némethy, who spent some periods of his activities in Naples during recent years.

Comment

N-Acetyl peptidoamides are useful model compounds for the investigation of peptide interactions and the preferred conformations in polypeptide chains. As part of our continuing studies concerning crystallographic determinations (Puliti, Mattia & Lilley, 1993, and references therein), as well as some thermodynamic parameters connected with phase transitions, whose trends have been discussed on the basis of crystallographic results (Barone, Giancola, Lilley, Mattia & Puliti, 1992), we present here the crystal structures of *N*-acetylglycyl-L-alaninamide (NAGAA) and *N*-acetyl-L-alanyl-L-alaninamide (NAA$_2$A).



NAGAA R = H
NAA$_2$A R = CH_3

Perspective views of the NAGAA and NAA$_2$A molecules are shown in Figs. 1(*a*) and 1(*b*), respectively. For each molecule, the peptide linkage between the residues displays close to the ideal *trans* form.

In NAGAA, the φ_1 and ψ_1 torsion angles are rather similar to those of φ_2 and ψ_2 (see Table 2) and fall in the *F* region of the Zimmerman map (Zimmerman, Pottle, Némethy & Scheraga, 1977). Although this region does

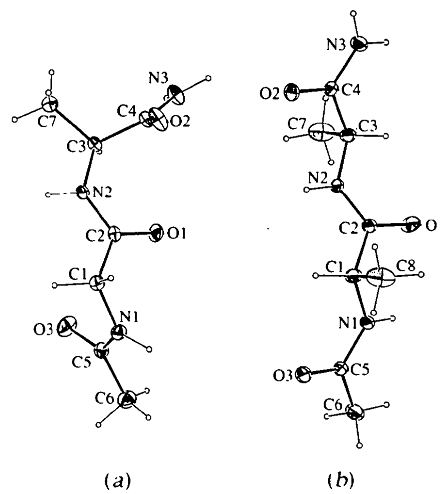


Fig. 1. Perspective views of the molecules with the atomic labelling schemes for non-H atoms: (*a*) NAGAA and (*b*) NAA$_2$A. Displacement ellipsoids are shown at the 30% probability level.

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