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1,5-Diamino-1*H*-1,2,3,4-tetrazole

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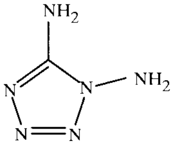
In the title compound, CH_4N_6, the tetrazole ring is planar to within 0.001 (1) Å. The 5-amino group is conjugated with the π-system of the tetrazole ring. In contrast, the N atom of the 1-amino group is sp^3 hybridized and is not conjugated with the π system of the tetrazole ring. All H atoms are localized at the exocyclic N atoms. The molecules are connected by N—H···N hydrogen bonds, forming an infinite three-dimensional framework.

Comment

1,5-Diaminotetrazole, (I), being a simple bifunctional tetrazole derivative with high nitrogen content (84%), is attractive as a gas-generating agent (Gao *et al.*, 1991; Levchik *et al.*, 1993) and a valuable intermediate in the preparation of high-energy materials (Willer & Henry, 1988; Sinditskii & Fogelzang, 1997) and other useful tetrazole-containing compounds (Gaponik & Karavai, 1984; Desenko *et al.*, 1990; Krutikov *et al.*, 1991). However, the structure of (I) has not been investigated. Only a hypothesis about the preferable tautomeric form of (I) (amino–imino tautomerism), based on IR spectroscopy data, has been made (Gaponik & Karavai, 1984; Levchik *et al.*, 1993).



(I)

Our X-ray investigation shows that the tetrazole ring of (I) is planar to within 0.001 (1) Å. All the formal single endocyclic bonds are considerably shorter than those usually found for normal single bonds, but some formal double bonds are longer than the normal double bonds (*International Tables for Crystallography*, 1992, Vol. C). This indicates that the tetrazole ring of (I) reveals a conjugated system of bonds similar to that found in other tetrazole derivatives. On the other hand, significant differences in the endocyclic bond lengths show considerable localization of charge within the ring. In general, the angles and bond distances in the hetero-ring of (I) are consistent with those observed previously for 1-mono- and 1,5-disubstituted tetrazoles.

The exocyclic C5—N6 bond of 1.334 (1) Å is shorter than that of 1.47 Å in ethylenediamine (Ohno *et al.*, 1998), longer than that of 1.29 Å in 1,3-dimethyl-5-iminotetrazoline hydrochloride (Bryden, 1955) and close to the value in *p*-nitroaniline (1.355 Å; Colapietro *et al.*, 1982). The difference between the C5—N1 and C5—N4 bond lengths is rather small. It should be noted that the 5-amino group lies in the tetrazole ring plane; the deviation of the N6 atom from the least-squares tetrazole ring is 0.045 (2) Å. The angles around the N6 atom are close to 120° and have values of 118 (1)° for two C5—N6—H angles and of 119 (1)° for the H—N6—H angle. These data indicate a conjugation between the π systems of the tetrazole ring and the 5-amino group. The results obtained confirm an assumption about the preference of the 5-aminotetrazole form (I) rather than the iminotetrazoline form in the solid (Gaponik & Karavai, 1984).

Similar to the N6 atom, the N5 atom also lies in the tetrazole ring plane. The N1—N5 bond length of 1.383 (1) Å is shorter than that of 1.42 Å in tetramethylhydrazine (Ohno *et al.*, 1998) and similar to that in 2-aminobenzotriazole (1.386 Å; Foces-Foces *et al.*, 1990). The lone electron pair of the N5 atom is not conjugated with the π system of the hetero-ring. This conclusion follows from the H-atom positions of this amino group. The three bond angles around the N5 atom are equal to 107 (1)°; this value being close to a tetrahedral angle indicates that the N5 atom has sp^3 hybridization. It should be noted that the H atoms of the 1-amino group are located on different sides of the tetrazole plane (Fig. 1) and consequently the N5

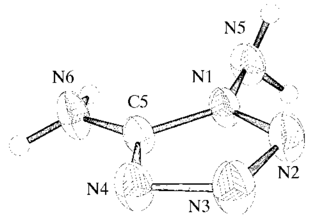


Figure 1
The molecular structure of (I) with the atom-numbering scheme (non-H atom displacement ellipsoids are drawn at the 50% probability level).

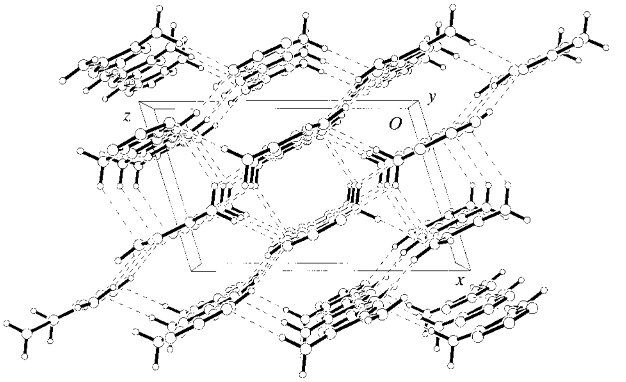


Figure 2
A packing diagram of (I).

lone pair must lie in this plane. These data confirm the conclusions of a theoretical study concerned with the hybridization and conformation of the amino group in *N*-aminoazoles (Foces-Foces *et al.*, 1990), where sp^3 hybridization of amino groups was found to be favoured over sp^2, and the amino lone pair eclipses the ring in monocyclic *N*-aminoazoles, including 1-aminotetrazole.

Inspection of the molecular packing (Fig. 2) reveals that the individual molecules are linked by N—H···N hydrogen bonds, forming an infinite three-dimensional framework.

Experimental

The title compound was prepared according to a previously described method (Gaponik & Karavai, 1984). Trimethylsilyl azide was used as the azidation agent instead of a mixture of sodium azide and ammonium chloride. This increases the yield of (I) from 60 to 80%. Single crystals were grown by slow crystallization from aqueous solution.

Crystal data

CH_4N_6
$M_r = 100.10$
Monoclinic, $P2_1/c$
$a = 6.780$ (1) Å
$b = 6.112$ (1) Å
$c = 10.694$ (2) Å
$\beta = 107.25$ (1)°
$V = 423.2$ (1) Å^3
$Z = 4$

$D_x = 1.571$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 21.0$–23.7°
$\mu = 0.124$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.56 × 0.48 × 0.26 mm

Data collection

Nicolet *R*3*m* four-circle diffractometer
$\omega/2\theta$ scans
1378 measured reflections
1239 independent reflections
1069 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.020$

$\theta_{\rm max} = 30.05$°
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 8$
$l = -15 \rightarrow 14$
3 standard reflections every 100 reflections intensity decay: 3.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.132$
$S = 1.077$
1239 reflections
80 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0884P)^2 + 0.0322P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.26$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.35$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C5	1.345 (1)	N3—N4	1.367 (1)
N1—N2	1.363 (1)	N4—C5	1.327 (1)
N1—N5	1.383 (1)	C5—N6	1.334 (1)
N2—N3	1.279 (1)		
C5—N1—N2	108.84 (8)	C5—N4—N3	105.56 (8)
C5—N1—N5	126.02 (9)	N4—C5—N6	128.17 (8)
N2—N1—N5	125.13 (8)	N4—C5—N1	107.90 (8)
N3—N2—N1	105.79 (8)	N6—C5—N1	123.87 (9)
N2—N3—N4	111.92 (9)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5*A*···N2$^{\rm i}$	0.90 (2)	2.48 (2)	3.063 (1)	123 (1)
N5—H5*A*···N6$^{\rm ii}$	0.90 (2)	2.54 (1)	3.277 (2)	139 (1)
N5—H5*B*···N4$^{\rm iii}$	0.91 (2)	2.26 (2)	3.172 (2)	175 (1)
N6—H6*A*···N4$^{\rm iv}$	0.94 (2)	2.16 (2)	3.074 (1)	162 (1)
N6—H6*B*···N3$^{\rm v}$	0.88 (2)	2.15 (2)	2.982 (2)	157 (2)

Symmetry codes: (i) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $1 - x, -y, 1 - z$; (iii) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (iv) $2 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (v) $x, y - 1, z$.

H-atom positions were found from the ΔF map and all associated parameters were refined freely.

Data collection: *R*3*m Software* (Nicolet, 1980); cell refinement: *R*3*m Software*; data reduction: *R*3*m Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1058). Services for accessing these data are described at the back of the journal.

References

Bryden, J. H. (1955). *Acta Cryst.* **8**, 211–217.
Colapietro, M., Domenicano, A., Marciante, C. & Portalone, G. (1982). *Z. Naturforsch. Teil B*, **37**, 1309–1311.
Desenko, S. M., Orlov, V. D., Gaponik, P. N. & Karavai, V. P. (1990). *Khim. Geterotsikl. Soedin.* pp. 1533–1535. (In Russian.)
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Foces-Foces, C., Cano, F. H., Claramunt, R. M., Sanz, D., Catalan, J., Fabero, F., Fruchier, A. & Elguero, J. (1990). *J. Chem. Soc. Perkin Trans.* 2, pp. 237–244.
Gao, A., Oyumi, Y. & Brill, T. B. (1991). *Combust. Flame*, **83**, 345–352.
Gaponik, P. N. & Karavai, V. P. (1984). *Khim. Geterotsikl. Soedin.* pp. 1683–1686. (In Russian.)
Krutikov, V. I., Kovalenko, A. L. & Sukhanovskay, E. B. (1991). *Zh. Obsch. Khim.* **61**, 257–258. (In Russian.)
Levchik, S. V., Balabanovich, A. I., Ivashkevich, O. A., Lesnikovich, A. I., Gaponik, P. N. & Costa, L. (1993). *Thermochim. Acta*, **225**, 53–65.
Nicolet (1980). *R*3*m Software*. Nicolet XRD Corporation, Cupertino, California, USA.
Ohno, Y., Akutsu, Y., Arai, M., Tamura, M., Matsunaga, T. & Iida, M. (1998). *Acta Cryst.* C**54**, 1160–1162.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Sinditskii, V. P. & Fogelzang, A. E. (1997). *Russ. Khim. Zh.* **4**, 74–80 (In Russian.)
Willer, R. L. & Henry, R. A. (1988). *J. Org. Chem.* **53**, 5371–5374.