Crystal Structure of 5-Amino-1*H*-1,2,3-triazole-4-carboxamide

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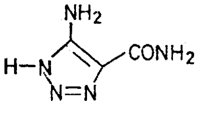
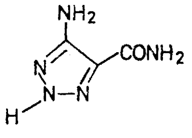
The structure of the title compound has been established by *X*-ray crystallography from diffractometer data. Crystals are monoclinic, space group $P2_1/c$, cell dimensions $a = 4{\cdot}796(5)$, $b = 5{\cdot}049(5)$, $c = 21{\cdot}290(10)$ Å, $\beta = 91{\cdot}43(20)°$, $Z = 4$. The structure was solved by direct methods and refined by least-squares calculations to R 0·053 for 971 independent reflexions. The ring hydrogen is linked to nitrogen N(1), which is in agreement with the short N(2)–N(3) 1·295 Å bond length and with the network of hydrogen bonds formed between the molecules. Analysis of the hydrogen bonding helped to elucidate the observed i.r. spectra.

REACTION of 1-carbamoylacetamidine with tosyl azide in suitable media yielded colourless crystals which were described as 5-amino-1*H*-1,2,3-triazole-4-carboxamide.[1]

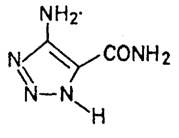
This conclusion (*i.e.* the location of the hydrogen atom on the triazole ring) could not, however, be corroborated unambiguously by i.r. and n.m.r. spectroscopic studies. Without a knowledge of the hydrogen-bond network formed between molecules of the crystal lattice, there was little evidence for the location of the ring hydrogen. Theoretically there are at least three tautomeric possibilities: (I), (II), and (III).



(I)



(II)



(III)

In order to resolve this ambiguity and to give a firm basis to the interpretation of the i.r. spectra, an *X*-ray structure determination of the title compound was performed.

EXPERIMENTAL

Cell dimensions were measured and refined from Weissenberg and Buerger precession photographs by use of Ni-filtered Cu-K_α ($\lambda = 1{\cdot}5418$ Å) radiation.

Crystal Data.—$C_3H_5N_5O$, $M = 127{\cdot}11$. Monoclinic, $a = 4{\cdot}796(5)$, $b = 5{\cdot}049(5)$, $c = 21{\cdot}290(10)$ Å, $\beta = 91{\cdot}43(20)°$, $D_c = 1{\cdot}638$, $Z = 4$, $D_m = 1{\cdot}629$ g cm^{-3} (by flotation). Space group $P2_1/c$ (No. 14) from systematic absences. $\mu(\text{Cu-}K_\alpha) = 11{\cdot}3$ cm^{-1}.

Intensity data were collected on a Stoe semi-automatic two-circle diffractometer. After setting the crystal and the counter in an equi-inclination arrangement, the intensities of each two-dimensional reciprocal layer (up to $\mu_{\text{max.}}$ 50°) were measured automatically but independently. Each reflexion peak was counted over a range of 2·5° for ω with scanning speed of 1° min^{-1} at fixed counter position of $2\theta'$. Background measurements were made at both ends of each peak for 60 s. The positioning of the crystal and the scintillation counter (with Ni filter and pulse-height discriminator) and the reflexion and background measurements were controlled by a Güttinger electronic unit according to setting data computed previously and stored on punched tape. After recording a layer, some reflexions of medium intensity were remeasured to check the stability of the counting system. The mean deviations were comparable to the final residual. The standard deviations of the integrated intensities, corrected for background were calculated from $\sigma(I) = \{I_2 + [T_2/(T_1 + T_3)]^2 . (I_1 + I_3)\}^{1/2}$, where I_2 and T_2 are the total counts and counting time for reflexion peaks, and the other quantities refer to background measurements. Of 971 independent reflexions measured, 46 having $I < 1{\cdot}5\sigma(I)$ were considered unobserved and given an $I_0 = \frac{1}{2}\sigma(I)$. After data reduction an absolute scale factor and overall isotropic temperature factor $\bar{B} = 2{\cdot}07$ Å^2 were determined by Wilson's method. No absorption correction was applied.

Solution and Refinement of the Structure.—The phase problem for 136 reflexions with $E > 1{\cdot}50$ was solved by the program MULTAN.[2] The E map computed from the solution with the best figure of merit revealed all the non-hydrogen atoms.

In the course of refinement it was found that the positions of the oxygen and nitrogen atoms of the carboxamide group had to be interchanged. This was shown clearly by the considerable divergence of the isotropic thermal parameters of the oxygen (B_O 3·21 Å^2) and the nitrogen atoms ($B_N = 1{\cdot}52$ Å^2) from the mean value, $\bar{B}$ 2·14 Å^2.

Full-matrix isotropic and anisotropic refinement reduced R to the final value, 0·053 (R for all reflexions 0·055). The function minimized was $\Sigma w(|F_o| - |F_c|/G)^2$, with the weighting scheme,[3] $w = (4{\cdot}0 + F_o + 0{\cdot}02F_o^2)^{-1}$. All hydrogen atoms were located in a difference-Fourier map at R 0·106, which was then reduced to 0·094. Atomic scattering factors for all atoms were taken from ref. 4. All calculations were performed on an ICL 1903/A computer. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21110 (3 pp.).† Final fractional co-ordinates and anisotropic thermal parameters are given in Tables 1 and 2, hydrogen parameters together with N–H distances in Table 3, and bond distances and angles in Table 4.

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† See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1973, Index issue.

[1] J. Schawartz, M. Hornyák (*née* Hamori), and T. Szüts, *Chem. and Ind.*, 1970, 92.

[2] P. Main, M. M. Woolfson, and G. Germain, MULTAN, A Computer Program for the Automatic Solution of Crystal Structures, Universities of York (England) and Leuven (Belgium), 1971.

[3] D. W. J. Cruickshank, D. E. Pilling, A. Bujosa, F. M. Lovell, and M. R. Truter, in ' Computing Methods and the Phase Problem in *X*-Ray Crystal Analysis,' Pergamon Press, Oxford, 1961.

[4] ' International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

I.r. spectra were obtained for KBr pellets by use of a UR 10 double-beam spectrometer.

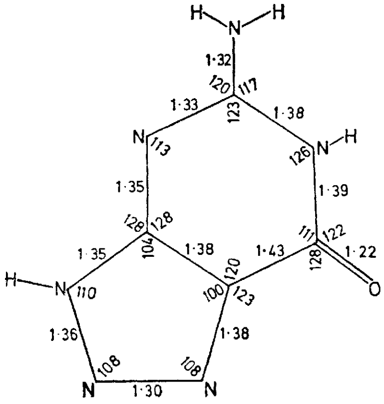

FIGURE 1 Atomic distances (Å) and bond angles (deg.) reported for the structure of 8-azaguanine

TABLE 1

Atomic fractional co-ordinates ($\times 10^4$), with estimated standard deviations in parentheses

	x	y	z
O	4834(4)	−931(4)	1620(1)
N(1)	−1449(5)	4859(5)	1401(1)
N(2)	−2109(5)	4154(5)	800(1)
N(3)	−486(5)	2216(5)	651(1)
N(4)	3495(5)	−1815(5)	610(1)
N(5)	1648(5)	3477(5)	2243(1)
C(1)	1246(5)	1620(6)	1153(1)
C(2)	633(5)	3340(6)	1637(1)
C(3)	3335(5)	−477(6)	1141(1)

TABLE 2

Final thermal parameters * ($\times 10^4$), with their estimated standard deviation in parentheses

	b_{11}	b_{22}	b_{33} †	b_{12}	b_{13}	b_{23}
O	306(8)	394(8)	11	222(14)	−37(3)	−10(3)
N(1)	259(8)	327(9)	12	160(15)	−8(3)	−15(3)
N(2)	283(9)	408(10)	13	257(16)	−29(3)	−23(3)
N(3)	274(8)	396(10)	11	223(16)	−26(3)	−15(3)
N(4)	314(9)	381(10)	11	268(16)	−30(3)	−22(3)
N(5)	370(10)	370(10)	10	70(18)	−17(3)	−9(4)
C(1)	210(9)	339(10)	10	87(17)	−12(3)	−3(4)
C(2)	211(9)	299(10)	11	27(16)	−1(3)	7(3)
C(3)	207(9)	332(10)	10	62(17)	−10(3)	1(4)

* In the form: $T = -[h^2b_{11} + k^2b_{22} + l^2b_{33} + 2(hkb_{12} + hlb_{13} + klb_{23})]$. † All $\sigma < 1$.

DISCUSSION

The molecules are fairly accurately planar (maximum deviation 0·004 Å from the plane given by the equation $0{\cdot}6808X + 0{\cdot}6527Y - 0{\cdot}3324Z = 0{\cdot}0865$, where X,Y,Z are in Å and related to orthogonal axes: a,b,c^*). The endocyclic hydrogen is bound to nitrogen N(1). The N(2)–N(3) bond length (1·295 Å) indicates a strong double bond and the other four bonds of the triazole ring are of multiple-bond character. These facts confirm the structure (I) given by Schawartz *et al.*[1] The

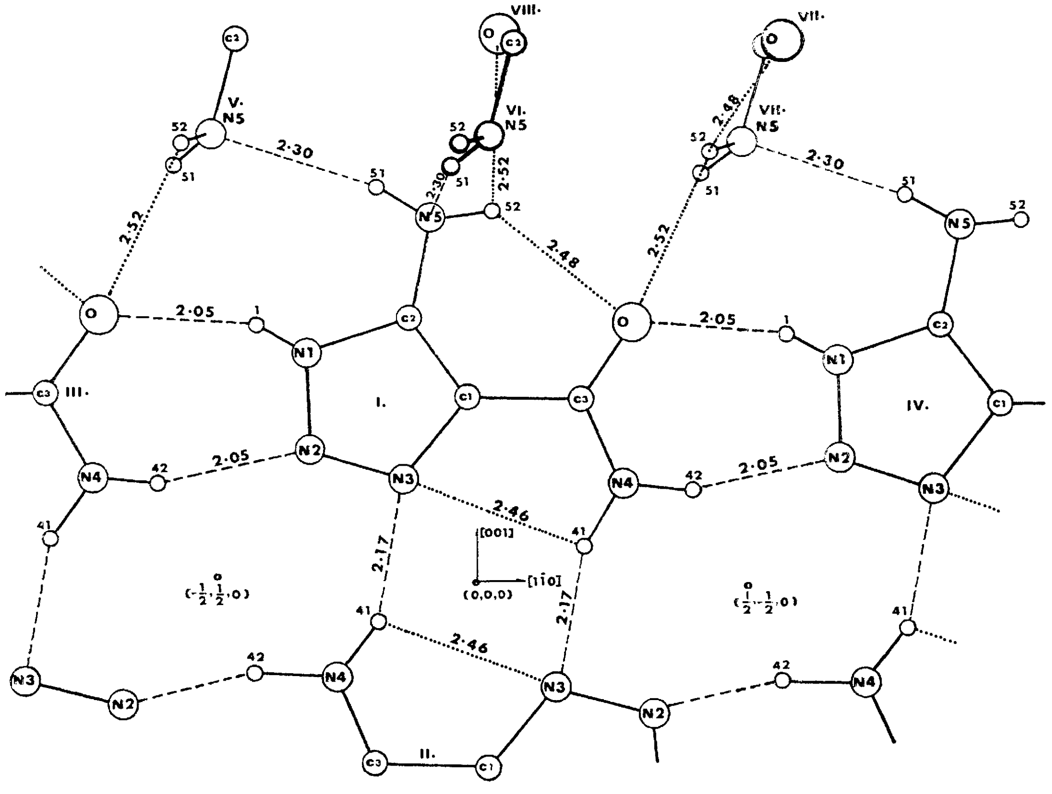

FIGURE 2 Projection of structure along [110], showing an infinite chain of the co-planar dimers maintained by the network of the three strongest hydrogen bonds [Nos. (1), (3), and (4); see Table 5]. The sheets of molecules which lie either in the planes $(11\bar{2})$ or $(\bar{1}12)$ are linked together by two helices formed around the screw axes (Figure 3). Dashed lines indicate strong, and the dotted lines represent weak hydrogen bonds. Equivalent positions are shown by Roman numerals as follows: I x, y, z; II $\bar{x}, \bar{y}, \bar{z}$; III $x - 1, y + 1, z$; IV $x + 1, y - 1, z$; V $\bar{x}, y + \frac{1}{2}, \bar{z} + \frac{1}{2}$; VI $\bar{x}, y - \frac{1}{2}, \bar{z} + \frac{1}{2}$; VII $\bar{x} + 1, y - \frac{1}{2}, \bar{z} + \frac{1}{2}$; VIII $\bar{x} + 1, y + \frac{1}{2}, \bar{z} + \frac{1}{2}$

triazole molecule can be recognized as a part of the 8-azaguanine molecule,[5] which has similar bond distances and angles (Figure 1), if the carboxamide group is turned by 180° around the C(1)–C(3) bond.

TABLE 3

Fractional co-ordinates ($\times 10^3$), isotropic temperature parameters (Å^2), and bond distances (Å) for the hydrogen atoms

	x	y	z	B_i	N–H
H(1)	−230(9)	606(8)	158(2)	2·0(8)	0·83(4)
H(41)	244(9)	−139(9)	26(2)	2·4(9)	0·92(4)
H(42)	485(9)	−311(9)	59(2)	2·8(10)	0·92(5)
H(51)	130(9)	515(9)	245(2)	2·3(8)	0·97(4)
H(52)	337(8)	280(8)	230(2)	3·4(10)	0·90(4)

The molecules are linked together by a complicated three-dimensional network of hydrogen bonds (Figure 2), the effect of which is shown by the rather high density of the crystals. Although this hydrogen bond network had already been inferred from the i.r. spectra, the broad absorption in the region of 3490—2225 cm^{-1} could not permit an unambiguous assignment of the ν(NH) stretching frequencies. Analysis of the non-bonded contacts less than the sum of van der Waals radii indicated four strong and three weak hydrogen bonds (Table 5). Each molecule is a member of a dimeric arrangement maintained by the hydrogen bond [No. (3)] and its symmetry equivalent N(3$^{\mathrm{I}}$) · · · H(41) · · · N(4$^{\mathrm{II}}$). Infinite chains of these dimers are formed by the hydrogen-bond pairs [Nos. (1) and (4)], which together with the molecules lie in both the planes (11$\bar{2}$) and ($\bar{1}$12). These sheets of molecules are cross-linked by two

TABLE 4

Molecular geometry

(*a*) Bond distances (Å)

N(1)–N(2)	1·358(3)	C(2)–N(5)	1·369(3)
N(2)–N(3)	1·295(3)	C(1)–C(3)	1·458(4)
N(3)–C(1)	1·370(3)	C(3)–N(4)	1·321(4)
C(1)–C(2)	1·385(4)	C(3)–O	1·254(3)
C(2)–N(1)	1·346(3)		

(*b*) Bond angles (deg.)

N(1)–N(2)–N(3)	107·6(2)	C(1)–C(3)–N(4)	116·2(2)
N(2)–N(3)–C(1)	109·4(2)	N(4)–C(3)–O	123·9(2)
N(3)–C(1)–C(2)	107·9(2)	C(1)–C(3)–O	119·9(2)
C(1)–C(2)–N(1)	104·4(2)	C(3)–C(1)–C(2)	128·8(2)
C(2)–N(1)–N(2)	110·8(2)	C(1)–C(2)–N(5)	131·0(2)
N(3)–C(1)–C(3)	123·3(2)	N(1)–C(2)–N(5)	124·5(2)
N(2)–N(1)–H(1)	121(3)	H(51)–N(5)–H(52)	116(4)
C(2)–N(1)–H(1)	128(3)	C(3)–N(4)–H(41)	123(3)
C(2)–N(5)–H(51)	115(3)	C(3)–N(4)–H(42)	117(3)
C(2)–N(5)–H(52)	114(3)	H(41)–N(4)–H(42)	120(4)

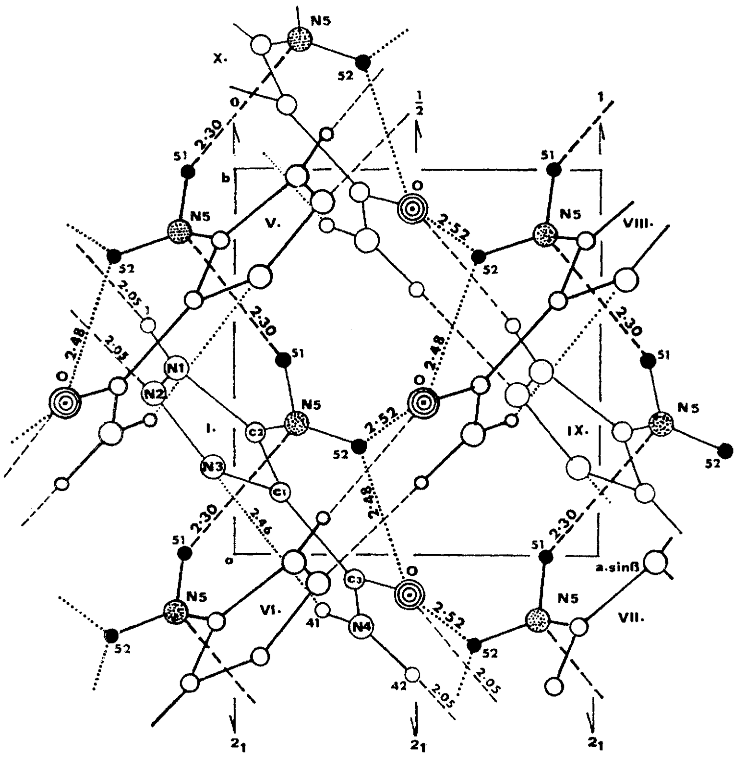

FIGURE 3 Projection of structure along [001]. The nearly perpendicular sheets of molecules are cross-linked on both sides of the dimers [symmetrical parts of the dimers including the hydrogen-bonds, No. (3) are omitted] by two kinds of helix formed by the hydrogen bonds [Nos. (5)—(7)] around the screw axes. Atoms [O, N(5), H(51), and H(52)] of these helices are specially labelled. The helix around the 2_1 screw axis ($\frac{1}{2}$, Y, $\pm\frac{1}{4}$) show clearly that the H(52) atom is really a bifurcated hydrogen. The N(5) atom of sp^3 character takes part in both helices, partly as a donor, partly as an acceptor. Between every pair of N(5) atoms, the co-ordinates of which differ by only $\Delta y = \pm 1$, there is a ten-membered ring [two oxygen, three N(5), two H(51), and three H(52) atoms] built up by the N–H, H · · · N, and H · · · O distances of two adjacent helices. The atoms of reach ring represent four molecules which belong to four different molecular sheets, *e.g.* molecules Nos. I, VII, VIII, and IX. Roman numerals are defined in the caption to Figure 2 except for: IX $x+1, y, z$; X $x, y+1, z$

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[5] J. Sletter, E. Sletter, and L. H. Jensen, *Acta Cryst.*, 1968, **B24**, 1692.

helices of hydrogen bridges (Figure 3). The helix *around* the 2_1 screw axis [0, Y, $\pm 1/4$] is formed by strong hydrogen bonds [No. (5)]. The other helix around the 2_1 screw axis [1/2, Y, $\pm 1/4$] is maintained by two weak hydrogen bonds [Nos. (6) and (7)]. The H(52) atom participates in both weak hydrogen bonds which may thus be regarded as bifurcated hydrogen bonds. On the other hand the H(41) atom which participates in a strong inter- [No. (3)] and a rather weak intra-molecular [No. (2)] hydrogen bond cannot be regarded as a real bifurcated hydrogen in agreement with the conclusion of Jönsson.[6]

TABLE 5

The parameters of hydrogen bonds formed by the molecules

No.*	[x,y,z]	N···X/ Å	H···X/ Å	N–H···X/ deg.
(1)	N(1)–H(1) ··· O^{III}	2·82	2·05	154·7
(2)	N(4)–H(41) ··· N(3^{I})	2·79	2·46	101·4 †
(3)	N(4)–H(41) ··· N(3^{II})	3·02	2·17	154·3
(4)	N(4)–H(42) ··· N(2^{IV})	2·95	2·05	164·3
(5)	N(5)–H(51) ··· N(5^{V})	3·19	2·30	151·3
(6)	N(5)–H(52) ··· O^{I}	3·03	2·48	119·1 †
(7)	N(5)–H(52) ··· O^{VIII}	2·93	2·52	108·1 †

* See text. † Weak. Roman numeral superscripts on the third atom are denoted in the caption to Figure 2.

The hydrogen bonds [Nos. (1), (3), and (4)] give further proofs of location of the endocyclic hydrogen on nitrogen N(1). In these hydrogen bridges nitrogen N(1) is the donor toward an oxygen of an adjacent molecule, while the other two nitrogen atoms [N(2) and N(3)] are acceptors. Even the slightly smaller bond angles at N(2) and N(3) (108 and 109°) with respect to that of 111° at N(1) seem to indicate the effect of the lone pairs of these acceptor atoms.

The oxygen atom is involved in a strong [No. (1)] and two weak hydrogen bonds [Nos. (6) and (7)] which together are presumably responsible for the significantly longer (by 0·03 Å) C–O distance (1·254 Å) (*cf. e.g.* 8-azaguanine, Figure 1). The C–O bond is nearly coplanar with the hydrogen bonds. One of the lone pairs of the oxygen atom is oriented towards the strong [No. (1)] hydrogen bridge while the other bisects the angle between the two weak hydrogen bonds. The three hydrogen bonds formed with the participation of the oxygen as acceptor atom mutually weaken each other. A similar phenomenon can be observed in the hydrogen bonds involving nitrogen N(3).

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[4/816 *Received*, 22*nd April*, 1974]

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[6] P.-G. Jönsson, *Acta Universitatis Upsaliensis*, 1973, No. 253.