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Physical Organic Chemistry

Bonding in 1,2,4-Triazoles. Part II.[1] Crystal Structure of 3,4,5-Triamino-1,2,4-triazole Hydrobromide (Guanazine Hydrobromide)

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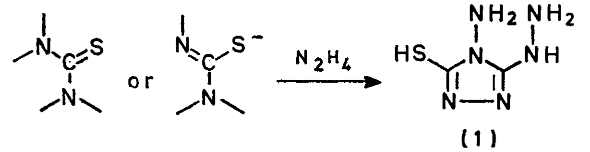
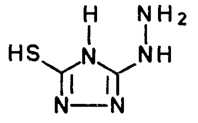
The crystal structure of the title compound was determined from diffractometer data by Patterson and Fourier methods. Crystals are monoclinic, space group *C*2/*c*, with $Z = 8$ in a unit cell of dimensions: $a = 686{\cdot}9(1)$, $b = 1069{\cdot}3(2)$, $c = 1855{\cdot}0(2)$ pm, $\beta = 95{\cdot}66(3)^\circ$. The structure was refined by least-squares to an *R* 0·036 for 915 observed reflections. The molecule is planar. Interatomic distances (each ±0·5 pm): N–N(ring) 140·8, N–N(side-chain) 139·3, C–N(ring) 129·8 and 131·1, and C–N(side-chain) 134·8 and 131·2.

DICKINSON and Jacobsen[2] have found a reliable analytical procedure to detect the thioureido-group (or precursors of such a group) irrespective of the remainder of the molecule, through a reaction with hydrazine to give readily isolable and recognizable 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (1).



(1)

Derivatives of (1) have been found to be important compounds in tests for aldehydes. The structures of (1)[1] and 3-hydrazino-5-mercapto-1,2,4-triazole (2)[3] have interatomic distances which differ from the normal single- and double-bond lengths and also from those found in 1,2,4-triazole itself. The structure of the hydrobromide of 3,4,5-triamino-1,2,4-triazole (3) was undertaken to obtain more information on the nature of the 1,2,4-triazole ring and in particular to observe what effect the sulphur group has in influencing the properties of the triazole ring.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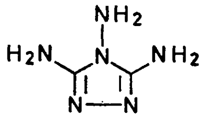
(3)

DISCUSSION

The arrangement of the atoms in the molecule is shown in Figure 1. The interatomic distances for N–N in the triazole ring and the side chain are intermediate between that of 135·0 pm in 1,2,4-triazole[4] and the single-bond value of 147·0 pm.

Results indicate that substitution on C(3) and C(5) has little influence on the bond lengths of the triazole rings except the N(4)–C(5) bond when sulphur replaces the hydrogen atom of 1,2,4-triazole in (1)[1] and (2).[3] There is also a decrease in the aromaticity of the triazole ring for compounds containing a sulphur atom bonded to C(5), *i.e.* the sulphur atom has an effect on the delocalised π orbital system of the triazole ring. Replacement of the hydrogen atoms on C(3) and C(5) in 1,2,4-triazole by other substituents decreases the aromaticity of the triazole ring, this decrease being greatest for (2). The various substituent groups attached to the triazole ring have little effect with this bond length. There is remarkable similarity between the bond lengths obtained for (3) and (1). The results indicate that replacing the amine group on C(3) with the hydrazino-group produces no change in the N(2)–C(3) and C(3)–N(4) bond lengths. The only significant change is in the N(4)–C(5) bond length where replacement of the amine group on C(5) with the sulphur atom produces a lowering of the %

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[1] N. W. Isaacs and C. H. L. Kennard, *J. Chem. Soc.* (*B*), 1971, 1270 is regarded as Part I.

[2] R. G. Dickinson and N. W. Jacobsen, *Analyt. Chem.*, 1969, **41**, 3124.

[3] M. E. Senko and D. H. Templeton, *Acta Cryst.*, 1958, **11**, 808.

[4] P. Goldstein, J. Ladell, and G. Abowitz, *Acta Cryst.*, 1969, *B*, **25**, 135.

double-bond character for this bond. The replacement of substituents appears to affect only the bond lengths in the immediate vicinity of the replacement and is not apparently transmitted over the triazole nucleus. For example, in the case just mentioned, there is little change in the N(1)–N(2) and C(3)–N(4) bond lengths.

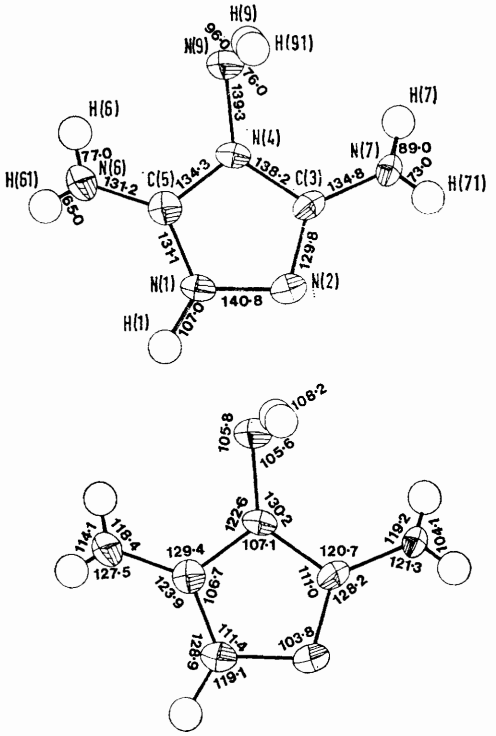
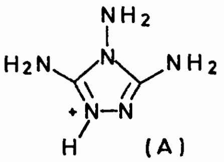
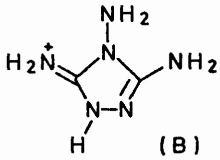
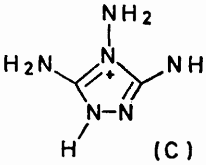


FIGURE 1 Stereochemical arrangement of 3,4,5-triamino-1,2,4-triazole hydrobromide; σ: for bond distances 0·5 pm, for bond angles 0·4°; including hydrogen: distances 5·0 pm, angles 0·8°

In (3), the C(5)–N(6) bond is considerably shorter than the C(3)–N(7) bond. This may be explained by the fact that since the molecule is positively charged, there has been removal of electron density from the H(1)–N(1) bond leaving the hydrogen atom H(1) positively charged. The electron density is then transmitted through the delocalised π orbital system to reside in the C(5)–N(6) bond thus resulting in the formation of a stronger bond. Since the N(9) atom is more basic than the tertiary nitrogen atoms of the triazole ring, the N(4)–N(9) bond is a weaker bond than N(1)–N(2). The bond lengths obtained for the triazole ring in (3) indicate that the molecule can still be considered as having aromatic character but the amount of aromaticity has been decreased from that found in 1,2,4-triazole. In (3), there are two C–N distances within the triazole ring, C(3)–N(4) and N(4)–C(5) joined at a common nitrogen atom N(4) at a mean distance of 136·2 pm, and two external C–N distances, C(3)–N(7) and C(5)–N(6), mean 133·0 pm. These distances indicate that the external C–N bonds have more double-bond character than the internal C–N bonds within the triazole ring. However, these means lie in between the recorded values for pure single (147·0 pm) and double (126·5 pm) bonds. Analysis of double-bond character indicate that it is difficult to describe the structure in terms of any one of the possible canonical forms, but is probably best described by a combination of canonical forms (A) and (B).


(A)


(B)


(C)

Packing of the molecule in the unit cell is shown in Figure 2. The closest distances between the negatively

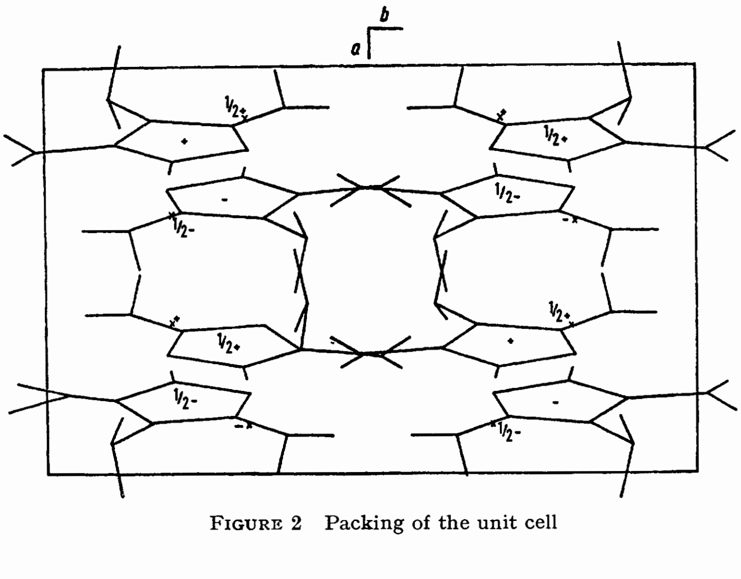


FIGURE 2 Packing of the unit cell

charged bromine atom and the atoms of the triazole ring are: Br ··· H(6) 285·7, Br ··· H(71) 275·7, Br ··· H(7) 267·6, and Br ··· H(1) 223·8 pm, last one being the strongest interaction. This is further evidence for the observation that the positive charge is residing on H(1) and not distributed throughout the molecule as it would be in a resonance structure. This short Br ··· H(1) distance can be partly responsible for the lengthening of the H(1)–N(1) bond by removal of electron density from the bond to reside on the hydrogen atom. The molecule is planar except for atoms H(9) (−28·4), H(91) (20·6), and H(7) (−13·1 pm) which are displaced from the plane.

EXPERIMENTAL

Crystal Data.—$C_2H_7BrN_6$, $M = 195{\cdot}027$. Monoclinic, $a = 686{\cdot}9$ (1), $b = 1069{\cdot}3$ (2), $c = 1855{\cdot}0$ (2) pm, $\beta = 95{\cdot}66°$ (3), $U = 1{\cdot}355$ nm^3, $D_m = 1{\cdot}89$ (by flotation), $Z = 8$, $D_c = 1{\cdot}91$, $F(000) = 768$. Mo-K_α radiation, $\lambda = 71{\cdot}07$ pm; μ(Mo-K_α = 63·47 cm^{-1}. Space group, $C2/c$ (C^6_{2h}, No. 15) or Cc (C^4_s, No. 9).

Counter data, from a crystal mounted about the *b* axis, were used to obtain accurate unit-cell dimensions by a least-squares procedure. A total of 915 out of 1240 independent reflections were observed from a crystal measuring 0·40 × 0·24 × 0·06 mm on a Hilger and Watts computer-controlled four-circle diffractometer by the θ—ω step scan up to θ 26°. Data were collected at a constant scan rate of 0·01° s^{-1} and were considered observed when I was $>2{\cdot}5\sigma(I)$ and scan-width 1·4°. During data collection, a complete sphere of data were collected and $(h,k,l,)$ and $(\bar{h},\bar{k},l)$ were corrected for Lorentz and polarization factors and then averaged. An absorption correction was applied by use of a Gaussian integration method with a grid size of 14 × 24 × 4 with a transmission coefficient of maximum 0·686 and minimum 0·236.

Structure Determination and Refinement.—The position of the bromine atom was found from a Patterson synthesis. A subsequent structure-factor calculation gave R 0·680. By use of refined bromine co-ordinates, a difference Fourier synthesis revealed all the remaining non-hydrogen atom positions. Two cycles of full-matrix isotropic least-squares refinement reduced R to 0·116. Least squares refinement with anisotropic temperature factors lowered R to 0·054 and a difference electron-density map revealed seven hydrogen atom positions. During the refinement, the hydrogen atoms were assigned temperature factors equivalent to the refined isotropic temperature factor of the atom to which they were bonded. A final full-matrix least-squares refinement varying all parameters and with isotropic temperature factors for the hydrogen atoms gave R 0·036 and R' 0·032 $\{R' = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$.

A final difference-Fourier synthesis revealed no prominent features. A weighting scheme using the standard deviations calculated from counting statistics was used during the least-squares refinement. The standard deviation of an observation of unit weight given by $\{[\Sigma w(|F_o| - |F_c|)^2]/(n - m)\}^{\frac{1}{2}}$, where n is the number of observations and m is the number of variables, was 1·14 indicating that the weighting scheme used was adequate. The final atomic parameters are listed in the Table. A list of observed and calculated amplitudes appears in Suppementary Publication No. 20509 (4 pp., 1 microfiche).* The atomic scattering factors used throughout for carbon, nitrogen, bromine were taken from ref. 5, and for hydrogen from ref. 6, and that for bromine corrected for anomalous dispersion.[5] No corrections were made for extinction, since a plot of I_c/I_o *vs.* I_c [7] showed no reflections which were seriously affected by extinction.

(*a*) Atomic positions (fractional co-ordinates) and temperature factors with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	B/Å^2
Br	0·1324(1)	0·1923(1)	0·0993(1)	
C(3)	0·1444(5)	0·7893(3)	0·1260(2)	
C(5)	0·1927(6)	0·6058(4)	0·1775(2)	
N(1)	0·2340(5)	0·6953(3)	0·2250(2)	
N(2)	0·2027(5)	0·8141(3)	0·1932(2)	
N(4)	0·1359(4)	0·6618(3)	0·1141(2)	
N(6)	0·2019(8)	0·4842(4)	0·1864(3)	
N(7)	0·1071(6)	0·8704(4)	0·0707(2)	
N(9)	0·0811(7)	0·5947(4)	0·0510(2)	
H(1)	0·236(7)	0·189(5)	0·218(3)	7·22
H(6)	0·164(6)	0·442(4)	0·154(2)	2·48
H(61	1·234(7)	0·453(5)	0·216(3)	3·24
H(7)	0·008(7)	0·855(4)	0·037(3)	4·73
H(71)	0·100(5)	0·938(4)	0·077(2)	1·28
H(9)	0·447(7)	0·116(5)	0·037(3)	5·31
H(91)	0·144(6)	0·619(4)	0·023(3)	2·90

(*b*) Anisotropic temperature factors (× 10^4) *

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	202(1)	58(1)	16(1)	0(1)	−6(1)	−1(1)
C(3)	153(9)	36(4)	18(1)	−6(4)	−4(3)	−5(2)
C(5)	166(9)	44(4)	15(1)	0(4)	−3(3)	−1(1)
N(1)	251(9)	51(3)	14(1)	0(5)	−10(3)	−3(2)
N(2)	233(9)	45(3)	16(1)	−5(5)	−9(2)	−6(2)
N(4)	164(7)	41(3)	11(1)	−3(4)	−10(2)	−2(1)
N(6)	441(16)	46(4)	16(1)	2(6)	−23(4)	6(2)
N(7)	287(12)	27(3)	18(1)	3(5)	−21(3)	1(1)
N(9)	248(11)	48(4)	13(1)	−12(5)	−3(3)	−3(2)

* In the form exp $-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$.

Calculations.—All computations [8] were made on an IBM 360/44 at the University of Canterbury, Christchurch, New Zealand.

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* For details see Notice to Authors No. 7 in *J. Chem. Soc. A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

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

[6] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[7] G. H. Stout and L. H. Jensen, '*X*-Ray Structure Determination: A Practical Guide,' Macmillan, New York, 1968, p. 411.

[8] IBM 360/44 Programs written by the Canterbury group plus modifications of FORDAP (A. Zalkin and R. J. Dellaca), ORFLS (R. S. Busing, H. A. Levy, and R. J. Dellaca), and ORTEP (C. J. Johnson), used on a CDC 3600 (C.S.I.R.O., Canberra).