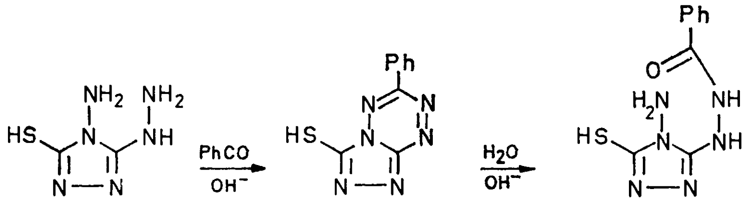
Bonding in 1,2,4-Triazoles. Part III.[1] Crystal Structure of 4-Amino-3-(β-benzoylhydrazino)-5-mercapto-1,2,4-triazole

By **R. C. Seccombe** and **C. H. L. Kennard**,* Department of Chemistry, University of Queensland, Brisbane Queensland 4067, Australia

The crystal structure of the title compound (II), has been determined from three-dimensional diffractometer data by the symbolic addition procedure. Crystals are monoclinic, space group *C*2/*c*, with $Z = 8$ in a unit cell of dimensions: $a = 1812{\cdot}5(9)$, $b = 606{\cdot}9(2)$, $c = 2063{\cdot}8(9)$ pm, $\beta = 104{\cdot}875(8)°$. The structure was refined by least squares to *R* 0·049 for 960 observed reflections. The triazole ring is planar. Interatomic distances (pm) (each ±0·3) C–S 166·8, N–N(ring) 139·0, side-chain N–N(hydrazino) 138·3, side-chain N–N(amino) 139·9, N(2)–C(3) 131·7, C(3)–N(4) 134·5, N(4)–C(5) 136·8, C(5)–N(1) 133·3.

THE classical qualitative tests for aldehydes with 2,4-dinitrophenylhydrazine, Fehling's solution, and Tollen's and Schiff's reagents are non-specific. In a new test,[2] 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole condenses with the formyl group of the aldehyde to form an unstable, oxygen-labile intermediate, 1,2,3,4-tetrahydro-6-mercapto-3-substituted-*s*-triazolo[4,3-*b*]-*s*-tetrazine. At the liquid–air interface, the intermediate is rapidly oxidised in 1 min by aerial oxygen to a purple 6-mercapto-3-substituted-*s*-triazolo[4,3-*b*]-*s*-tetrazine. Dependent on the nature of the 3-substituted group derived from the aldehyde moiety, the colours produced range from magenta (R = aliphatic) to purple (R = aromatic) and purple-brown (R = aliphatic and aromatic substituents with additional functional groups).



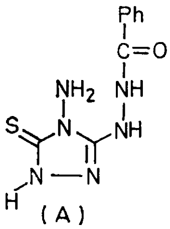
(I) (II)

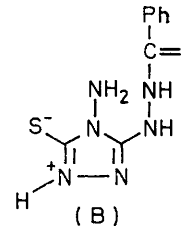
If benzaldehyde is used in the reaction, a purple compound (I) is formed. If compound (I) is then allowed to react with water in basic solution, a compound, 4-amino-3-(β-benzoylhydrazino)-5-mercapto-1,2,4-triazole, (II) is obtained, whose structure was determined.

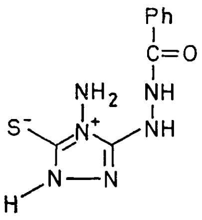
DISCUSSION

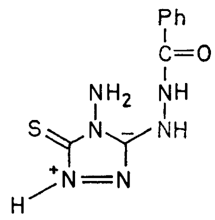
The arrangement of the atoms in the molecule is shown in Figure 1. The N–N distance in the triazole ring (139·0 pm) and the side-chain (hydrazino 138·3, amino 139·9 pm) is similar to that in 3,4,5-triamino-1,2,4-triazole[1] (ring 140·8, amino 139·3 pm) and in 1,2,4-triazole[3] (ring 135·0 pm). It is less than the single-bond value (147·0 pm). The S–C distance (166·8 pm) is considerably shorter than the single S–C bond, for example in methanesulphonanilide[4] (174·6 pm) and longer than the partial triple-bond value of 156 pm observed in carbonyl sulphide.[5]

There are two types of C–N distances. Within the triazole ring C(5)–N(1) and C(3)–N(2) bonds (mean 132·5 pm) are shorter than C(5)–N(4) and C(3)–N(4) (mean 135·7 pm). The latter distance is very close to that for the two external C–N bonds [(C(3)–N(7) and N(8)–C(10), mean 135·3 pm)]. The results indicate a considerable amount of conjugation within the molecule and it is difficult to describe the structure in terms of any one of the possible canonical forms (A)—(D).


(A)


(B)


(C)


(D)

The triazole ring including S and N(9) is planar with N(7) and N(8) being only slightly displaced (by +11·4 and −24·5 pm).

Packing of the molecule in the unit cell is shown in

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[1] Part II, R. C. Seccombe and C. H. L. Kennard, preceding paper.

[2] R. G. Dickinson and N. W. Jacobsen, *Chem. Comm.*, 1970, 1719.

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Figure 2. The closest O · · · H intermolecular interaction is between H(9) and O (227·0 pm).

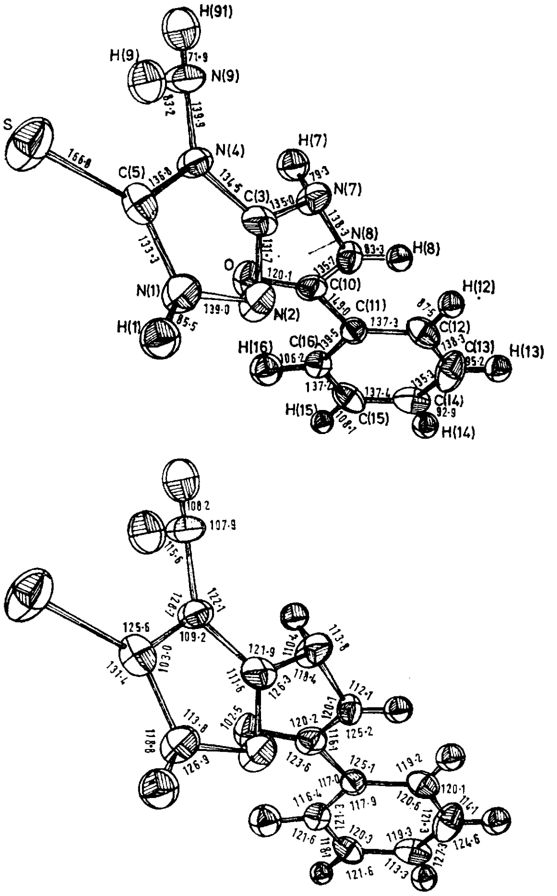

FIGURE 1 Stereochemical arrangement of 4-amino-3-(β-benzoylhydrazino)-5-mercapto-1,2,4-triazole; σ: for bond distances 0·3 pm, for bond angles 0·3°; including hydrogen: distances 0·7 pm, angles 0·9°

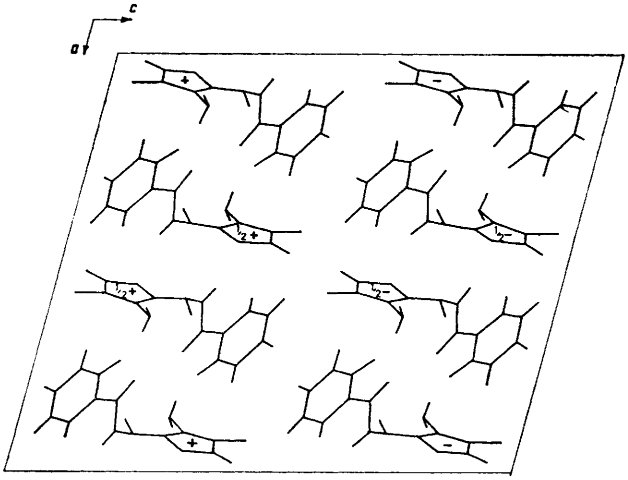

FIGURE 2. The packing of the molecule in the unit cell

EXPERIMENTAL

Crystal Data.—$C_9H_{10}N_6OS$, $M = 250·28$. Monoclinic, $a = 1812·5(9)$, $b = 606·9(2)$, $c = 2063·8(9)$ pm, $\beta = 104·875(8)°$, $U = 2·194$ nm^3, $Z = 8$, $D_c = 1·51$, $F(000) = 1040$. Mo-K_α radiation, $\lambda = 71·07$ pm, μ(Mo-K_α) $= 2·874$ cm^{-1}. Space group $C2/c$ (C^6_{2h}, No. 15) or Cc (C^4_s, No. 9); $C2/c$ was used.

Cell parameters were obtained by a least-squares procedure from 12 reflections measured on a Picker four-circle diffractometer. Intensity data were collected with Zr filtered Mo-K_α radiation by the 2θ—ω scanning mode on a crystal 0·35 × 0·25 × 0·05 mm. Reflections were scanned at a constant rate of 1° min^{-1} and the background measured with a stationary counter for 20 s on either side of the peak. The angular range scanned for each reflection was 1·4°. Of the 1750 reflections collected up to 2θ 47°, 960 had $I > 3\sigma(I)$ and were classed as observed. Intensities were corrected for Lorentz and polarisation factors. No absorption correction was made.

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

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*/Å^2
S	0·4278(1)	1·7896(3)	0·4590(1)	
C(3)	0·4199(4)	1·4665(10)	0·2983(3)	
C(5)	0·4305(3)	1·6082(11)	0·3989(3)	
N(1)	0·4549(3)	1·4004(9)	0·4019(2)	
N(2)	0·4503(3)	1·3066(9)	0·3397(2)	
N(4)	0·4069(3)	1·6471(8)	0·3314(2)	
N(7)	0·4068(3)	1·4638(9)	0·2307(2)	
N(8)	0·4002(3)	1·2625(9)	0·1986(2)	
N(9)	0·3749(3)	1·8391(8)	0·2983(3)	
O	0·2820(3)	1·2120(9)	0·2079(2)	
C(10)	0·3325(4)	0·1528(10)	0·1840(3)	
C(11)	0·3269(4)	0·9578(11)	0·1393(3)	
C(12)	0·3778(4)	0·9063(12)	0·1027(3)	
C(13)	0·3680(4)	0·7185(15)	0·0632(3)	
C(14)	0·3098(5)	0·5781(14)	0·0579(3)	
C(15)	0·2551(4)	0·6331(12)	0·0958(3)	
C(16)	0·2645(4)	0·8175(12)	0·1345(3)	
H(1)	0·477(3)	1·346(10)	0·440(3)	2·19
H(7)	0·374(3)	1·549(11)	0·214(3)	1·90
H(8)	0·435(3)	1·241(10)	0·180(3)	1·71
H(91)	0·398(3)	1·955(12)	0·311(3)	2·53
H(9)	0·337(4)	1·850(14)	0·302(4)	2·95
H(12)	0·414(3)	1·001(10)	0·101(2)	2·20
H(13)	0·406(4)	0·698(12)	0·040(3)	2·44
H(14)	0·298(5)	0·449(17)	0·037(5)	2·20
H(15)	0·208(3)	0·525(10)	0·095(3)	2·06
H(16)	0·232(4)	0·844(14)	0·169(4)	3·14

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

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	29(1)	191(5)	11(1)	32(2)	1(1)	−8(1)
C(3)	10(2)	132(19)	16(2)	−10(5)	2(1)	1(5)
C(5)	14(3)	173(19)	9(2)	−7(6)	1(1)	−2(4)
N(1)	23(2)	152(16)	9(1)	16(5)	2(1)	1(4)
N(2)	20(3)	154(16)	14(1)	15(5)	4(1)	−4(4)
N(4)	17(2)	97(16)	12(1)	5(4)	3(1)	0(3)
N(7)	29(3)	161(17)	11(1)	8(5)	4(1)	−7(4)
N(8)	19(2)	166(18)	13(1)	2(5)	7(1)	−8(4)
N(9)	27(2)	85(16)	16(1)	−2(4)	4(2)	1(4)
O	21(2)	239(16)	25(1)	14(5)	12(1)	−2(4)
C(10)	22(3)	159(21)	12(2)	13(6)	2(2)	10(4)
C(11)	12(3)	174(21)	14(2)	7(5)	3(2)	16(5)
C(12)	26(3)	183(21)	18(2)	−20(7)	5(2)	−1(5)
C(13)	30(3)	299(28)	18(2)	15(8)	9(2)	−21(6)
C(14)	35(3)	162(26)	20(2)	−26(7)	−3(2)	2(6)
C(15)	23(3)	226(25)	19(2)	−22(7)	4(2)	4(6)
C(16)	20(3)	196(21)	17(2)	−1(6)	2(2)	2(5)

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

Structure Determination.—A trial structure was obtained by use of the symbolic addition, phase-determining procedure. The largest 200 E values were used to generate Σ_2 relationships of the type $S(h) = S(k)$. $S(h\text{-}k)$, where h and k

denote the reflections with Miller indices $h_1k_1l_1$ and $h_2k_2l_2$ and S refers to the sign of the reflection. Reflections 8,4,3, (E 2·63) and $9,1,\bar{1}$ (E 2·28) were used to select the origin. In addition to these two origin-defining reflections, four other reflections were chosen as starting phases for the symbolic addition procedure by use of the Σ_2 relationships. They were: $1,3,\bar{4}$ (E 2·64), $8,2,\overline{16}$ (E 3·45), $6,6,\bar{5}$ (E 2·64), and $3,3,\overline{14}$ (E 2·76) and were given the symbols A, B, C, and D respectively. Of the 200 reflections used, 198 reflections were assigned a phase. The symbols A—D were then given all possible combinations of plus and minus. The set ($A+$, $B-$, $C+$, $D+$) which gave the least number of contradictions for the sign of the reflections was used to calculate an E map which then revealed all the non-hydrogen atom positions. The initial R of 0·666, was reduced after six cycles of full-matrix least-squares refinement to 0·074. A difference electron-density synthesis indicated the positions of all the hydrogen atoms.

Three reflections (2,2,1, 1,1,5, and $1,1,\bar{3}$) were found to be seriously affected by extinction from a plot of I_c/I_o *vs.* I_c[6] and were removed from the final cycle of least squares. This gave R 0·049 and the weighted residual R' 0·056 $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$. A final difference-Fourier synthesis revealed no unaccounted electron density. Unit weights were used in the least-squares refinement.

Of the 198 reflections whose phase was determined by the symbolic addition procedure, only one (3,1,4) changed sign during subsequent refinement.

The final atomic parameters are listed in the Table. Observed and calculated structure amplitudes are listed in Supplementary Publication No. SUP 20507 (5 pp., 1 microfiche) * Atomic scattering factors for carbon, nitrogen, and oxygen were taken from ref. 7, for sulphur from ref. 8 and for hydrogen from ref. 9. No corrections were made for anomalous dispersion.

The structure was determined, refined, and bond distances calculated with local versions of standard programmes.[10]

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* See note about Supplementary Publications in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

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