Bonding in 1,2,4-Triazoles. Part V.† Crystal Structure of 4-Benzylideneamino-5-mercapto-1,2,4-triazole

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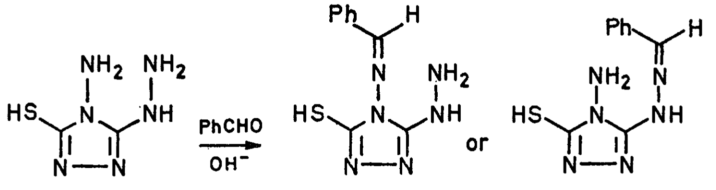
The crystal structure of the title compound (IV) has been determined from three-dimensional diffractometer data by the symbolic addition procedure. Crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions: a = 1084·35(4), b = 447·32(2), c = 2044·14(7) pm, β = 106·25(8)°. The structure was refined by least-squares to R of 0·029 for 1491 observed reflections. The triazole ring is planar with the benzylidene group at an angle of 4° to the triazole ring. Interatomic distances (pm; each ±0·2): C–S 167·3, N–N(ring) 137·0, N–N(side-chain, hydrazino) 139·6, N(2)–C(3) 128·7, C(3)–N(4) 136·7, N(4)–C(5) 138·1, and C(5)–N(1) 134·0.

THE reaction of 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (I) with basic benzaldehyde to form the purple compound, 6-mercapto-3-phenyl-*s*-triazolo[4,3-*b*]-*s*-tetrazine was found to proceed *via* a monobenzylidene intermediate (II) or (III).[1]

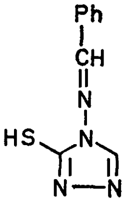


(I) (II) (III)

The compound, 4-benzylideneamino-5-mercapto-1,2,4-triazole (IV), was prepared in order to identify by n.m.r. which related intermediate, (II) or (III), had been formed. The structure of compound (IV) was confirmed by the *X*-ray determination reported here.

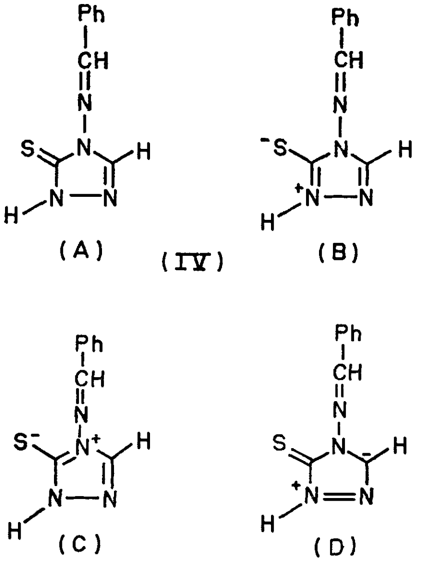
DISCUSSION

The arrangement of the atoms in the molecule is shown in Figure 1. In discussing interatomic distances, both



(IV)

the N–N links, N(1)–N(2) and N(4)–N(9), are longer than in 1,2,4-triazole[2] (135·0 pm) but considerably shorter than the single-bond distance[3] (147·0 pm). The S–C distance (167·3 pm) is shorter than the single S–C bond, (174·6 pm in methanesulphonanilide)[4] but similar to that found in 4-amino-3-(β-benzoylhydrazino)-5-mercapto-1,2,4-triazole[5] (166·8 pm) and 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole[6] (168·1 pm). The C–N bond distances in the triazole ring vary from 128·7 to 138·1 pm. The estimated double-bond character (%) for the following bonds is: C(3)–N(2) 74, C(5)–N(1) 37, C(3)–N(4) 25, and C(5)–N(4) 21. A combination of possible canonical forms (A)—(D), probably best describes the structure. Consequently, C(10)–N(9) (126·9 pm) is a definite double bond. C(10)–C(11) (146·4 pm) is shorter than the normal single-bond (154·0 pm). The atoms of the triazole ring, together with S and N(9), are all planar, the



(A) (IV) (B)

(C) (D)

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† Part IV, R. C. Seccombe, J. V. Tillack, and C. H. L. Kennard, preceding paper.

[1] R. G. Dickinson and N. W. Jacobsen, *Chem. Comm.*, 1970, **24**, 1719.

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

[3] J. H. Bryden, *Acta Cryst.*, 1958, **11**, 31.

[4] H. P. Klug, *Acta Cryst.*, 1968, *B*, **24**, 792.

[5] R. C. Seccombe and C. H. L. Kennard, *J.C.S. Perkin II*, 1973, 4.

[6] N. W. Isaacs and C. H. L. Kennard, *J. Chem. Soc.* (*B*), 1971, 1270.

benzylidene group being bent 4° away from this plane. The molecular packing is shown in Figure 2.

EXPERIMENTAL

Crystal Data.—$C_9H_8N_4S$, $M = 204{\cdot}26$. Monoclinic, $a = 1084{\cdot}35(4)$, $b = 447{\cdot}32(2)$, $c = 2044{\cdot}14(7)$ pm, $\beta = 106{\cdot}25(8)^\circ$, $U = 0{\cdot}9518$ nm^3, $D_m = 1{\cdot}44$ (by flotation), $Z = 4$, $D_c = 1{\cdot}425$, $F(000) = 424$. Cu-K_α radiation, $\lambda = 154{\cdot}18$ pm; μ(Cu-K_α) = 26·14 cm^{-1}. Space group, $P2_1/c$ (C_{2h}^5, No. 14). Unit-cell parameters were refined by least-squares from high-angle reflections. Data were obtained from a crystal measuring 0·1 × 0·2 × 0·2 mm on a Siemens automatic single-crystal diffractometer up to 2θ 86°.[7,8] The integrated intensities were recorded by a θ-2θ scan by use of a five-value method.[9] Scan speed was preset with an upper limit of 0·6 s per step of 0·01°. Nickel attenuators were selected so that the total recorded counts for all reflections were of the same order of magnitude (*i.e. ca.* 10^5 counts min^{-1}). A standard reflection was monitored every 50 reflections and used as a check on crystal and instrument drift. 1591 of the 1812 independent reflections collected were considered observed, having $I > 2{\cdot}5\sigma(I)$. The data were corrected for Lorentz, polarisation and adsorption factors.

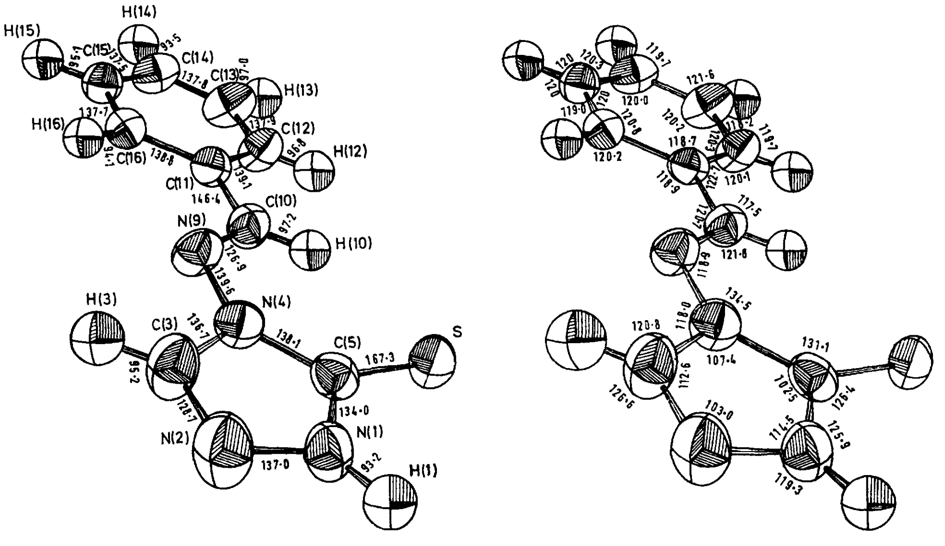

FIGURE 1 Stereochemical arrangement of 4-benzylideneamino-5-mercapto-1,2,4-triazole; σ: for bond distances 0·2 pm, bond angles 0·2°; including hydrogen: distances, 1·7 pm, angles, 1°

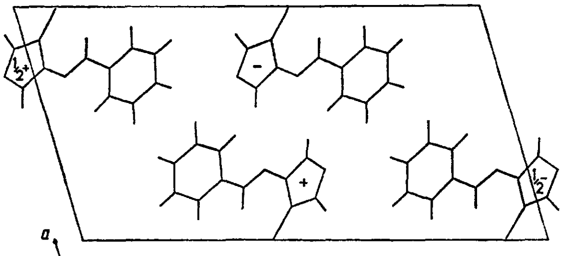

FIGURE 2 Packing of the molecule perpendicular to the *b* axis

Structure Determination.—The structure was determined by the symbolic addition procedure. The largest 206 E values were used to generate Σ_2 relationships. Three origin-defining reflections were selected; $\bar{2}$,1,2, E 3·06; $\bar{1}$,1,4, E 3·69; and $\bar{4}$,3,11, E 3·41. Four other reflections were also chosen, and given symbols, $\bar{3}$,2,6, E 2·93, A; 2,3,11, E 2·87, B; $\bar{3}$,2,7, E 2·94, C; and $\bar{5}$,1,10, E 3·22, D. Signs or symbols were generated for the 206 largest E values by use of the Σ_2 relationship. A set of signs ($A+$, $B+$, $C+$, $D-$) giving the best indication of being the correct set was chosen and an E map computed. This gave all the non-hydrogen atom positions.

Full-matrix least-squares refinement reduced R from an initial value of 0·308 to 0·058. A difference electron-density synthesis revealed the positions of the hydrogen atoms. Further cycles, with anisotropic temperature factors for all the non-hydrogen atoms and isotropic ones for the hydrogen atoms, reduced R to 0·030 and the weighted factor, R', to 0·029 {where $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$}.

Three reflections (2,0,0, $\bar{1}$,1,4, and $\bar{2}$,0,4) were found from a plot of I_c/I_c *vs.* I_c [10] to be seriously affected by extinction and were removed from the final least-squares cycle.

A final difference-Fourier synthesis revealed no prominent features. None of the 206 phases determined by the symbolic addition procedure changed sign during the refinement stages. A weighting scheme using the σ values calculated from counting statistics was used during refinement.

Atomic parameters are listed in the Table. Observed and calculated structure factor amplitudes are listed in Supplementary Publication No. SUP 20506 (5 pp., 1 microfiche).* Atomic scattering factors for carbon and nitrogen were taken

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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).

[7] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1967, **22**, 457.

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[9] U. W. Arndt and B. T. M. Willis, 'Single Crystal Diffractometry,' Cambridge University Press, Cambridge, 1966, pp. 265—267.

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

from ref. 11, for sulphur from ref. 12, and for hydrogen from ref. 13. No corrections for anomalous dispersion were applied.

All computations [14] were made on an IBM 360/50 at the University of New South Wales, Sydney.

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(*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
S	0·00446(4)	1·1839(1)	0·41158(2)	
C(3)	0·3494(2)	1·1517(5)	0·53275(8)	
C(5)	0·1476(1)	1·2024(4)	0·46983(7)	
N(1)	0·1781(1)	1·3751(3)	0·52562(6)	
N(2)	0·3025(1)	1·3461(4)	0·56503(7)	
N(4)	0·2614(1)	1·0549(3)	0·47426(6)	
N(9)	0·3011(1)	0·8443(3)	0·43392(6)	
C(10)	0·2222(2)	0·7601(4)	0·37862(8)	
C(11)	0·2609(1)	0·5454(4)	0·33404(7)	
C(12)	0·3830(2)	0·4204(4)	0·34969(9)	
C(13)	0·4156(2)	0·2269(4)	0·30473(9)	
C(14)	0·3273(2)	0·1558(5)	0·24393(9)	
C(15)	0·2059(2)	0·2761(5)	0·22804(9)	
C(16)	0·1727(2)	0·4686(4)	0·27284(9)	
H(1)	0·122(1)	1·492(4)	0·5412(7)	3·2 †
H(3)	0·434(2)	1·075(4)	0·5450(8)	3·7 †
H(10)	0·136(1)	0·839(4)	0·3636(7)	3·2 †
H(12)	0·445(1)	0·468(4)	0·3925(7)	3·0 †
H(13)	0·502(2)	0·146(4)	0·3170(7)	3·8 †
H(14)	0·349(2)	0·023(4)	0·2140(8)	4·2 †
H(15)	0·146(2)	0·227(4)	0·1863(8)	4·2 †
H(16)	0·089(2)	0·548(4)	0·2616(8)	3·8 †

† Temperature factors fixed in final stages of refinement.

(*b*) Anisotropic temperature factors ($\times 10^4$; for β_{33} and β_{13} $\times 10^5$) *

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	69·0(4)	56·8(3)	220(1)	8·6(9)	78(2)	−29·5(5)
C(3)	77(2)	659(12)	232(5)	21(4)	53(7)	−27(2)
C(5)	73(1)	393(8)	191(4)	−19(3)	148(6)	−2(2)
N(1)	73(1)	536(9)	222(4)	−11(3)	143(5)	−27(2)
N(2)	83(1)	737(11)	234(4)	−1(3)	71(6)	−38(2)
N(4)	75(1)	433(8)	192(3)	2(3)	97(5)	−12(1)
N(9)	85(1)	438(8)	216(4)	14(3)	143(6)	−15(1)
C(10)	78(1)	417(10)	232(4)	7(3)	125(7)	−8(2)
C(11)	78(1)	343(8)	211(4)	−8(3)	149(6)	−2(2)
C(12)	75(2)	424(10)	258(5)	−12(3)	123(7)	−4(2)
C(13)	88(2)	476(11)	332(5)	19(4)	255(8)	3(2)
C(14)	136(2)	517(11)	250(5)	38(4)	277(9)	−12(2)
C(15)	133(2)	590(13)	213(5)	35(5)	68(8)	−22(2)
C(16)	89(2)	520(11)	249(5)	36(4)	75(7)	−10(2)

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

[2/266 *Received, 7th February*, 1972]

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