Bonding in 1,2,4-Triazoles. Part IV.[1] Crystal Structure of the Sodium Salt of 4-Amino-5-mercapto-1,2,4-triazole Trihydrate

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The crystal structure of the title compound 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: $a = 1167{\cdot}9(1)$, $b = 1026{\cdot}4(1)$, $c = 669{\cdot}6(1)$ pm, $\beta = 100{\cdot}84(8)°$. The structure was refined by least squares to R 0·058 for 1178 observed reflections. The triazole ring is planar. Two water molecules are strongly bound to the sodium atom while the third is weakly linked to N(1) in the triazole. Interatomic distances (pm; each ±0·4): C–S 172·4, N–N(ring) 141·2, N–N(side-chain) 141·4, N(2)–C(3) 130·1, C(3)–N(4) 136·4, N(4)–C(5) 139·1, and C(5)–N(1) 131·5.

SOLUTIONS of 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole in 2M-base become pink and eventually purple.[2] When the reported preparation of 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole [3] was repeated in the presence of ethanol, it was found [4] that the purple colour developed more quickly and persisted longer than with the basic triazole solutions. During attempts to determine the source of this purple colour, the sodium salt of 4-amino-5-mercapto-1,2,4-triazole was isolated. The salt does not melt <360 °C, if heated slowly, but does melt between 113—115 °C if heated at a reasonable rate. Because of this unusual property, its crystal structure was determined.

DISCUSSION

The arrangement of the atoms in the molecule is shown in Figure 1.

A common feature of 1,2,4-triazoles [1,5] is for the N–N distances in the triazole ring and in the side-chain to be

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

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

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similar [N(1)–N(2) 141·2, N(4)–N(9) 141·4 pm]. However, they are considerably longer than the distance in 1,2,4-triazole itself (135·0 pm),[6] but less than the single-bond value (147·0 pm). The S–C distance (172·6 pm) is shorter than a single S–C bond, (174·6 pm in methanesulphonanilide [7]) but considerably longer than the distance in 4-amino-3-(β-benzoylhydrazino)-5-mercapto-1,2,4-triazole [5] (166·8 pm) and the S–C double-bond distance (167·9 pm in 6-mercaptopurine monohydrate,[8,9] where the sulphur atom is attached to an aromatic six-membered ring).

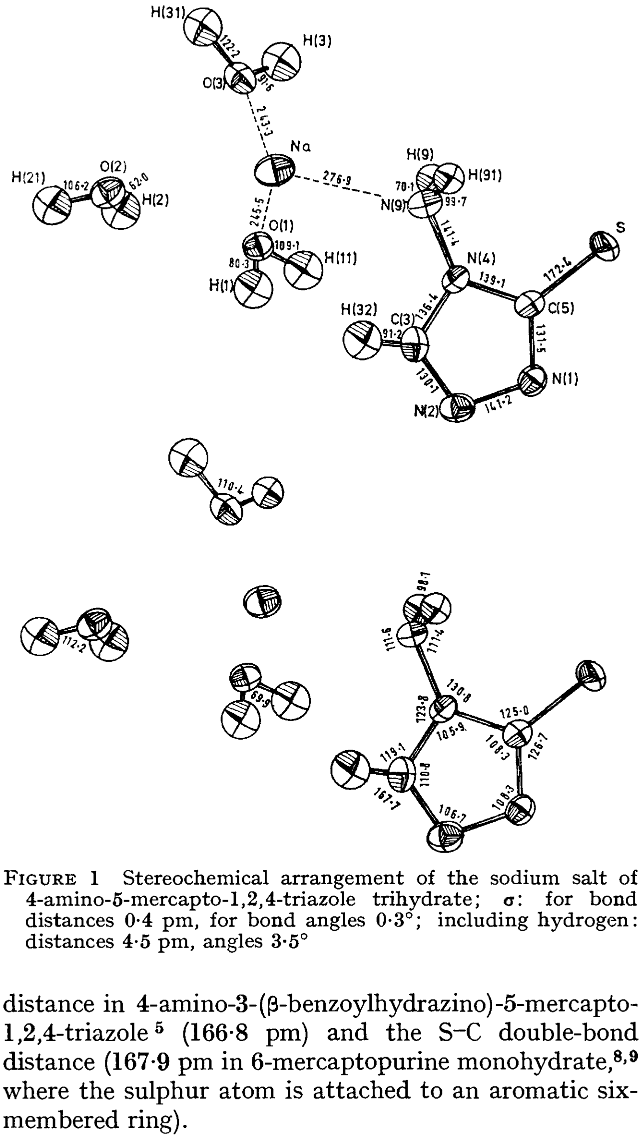
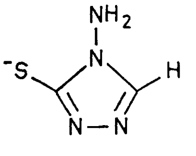
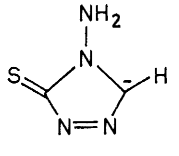


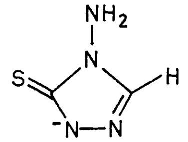
FIGURE 1 Stereochemical arrangement of the sodium salt of 4-amino-5-mercapto-1,2,4-triazole trihydrate; σ: for bond distances 0·4 pm, for bond angles 0·3°; including hydrogen: distances 4·5 pm, angles 3·5°

There are two types of C–N distances within the triazole ring, [C(5)–N(1) and C(3)–N(2), mean 130·8, and C(5)–N(4) and C(3)–N(4), mean 137·8 pm], indicating that the electron density is more confined to residing in a particular bond than distributed over the whole triazole nucleus. The lengthening of some bonds in the triazole ring compared with those in 1,2,4-triazole [6] may be due to the negatively charged sulphur removing electron density from the ring. Form (A) is probably the closest of the possible canonical forms to fit the results.

The sodium atom is surrounded by two of the oxygen atoms from the water molecules, O(1) and O(3), at distances of 245·5 and 243·3 pm while the third oxygen atom, O(2), is at a much longer distance, 363·6 pm. This third water molecule is probably weakly bound to the nitrogen atom N(1) at a distance of 282·4. There are two close intermolecular distances within the unit cell: N(1)–H(11) 186·4, and S–H(31) 213·8 pm. The molecular packing is shown in Figure 2. The atoms of the triazole ring, together with S, N(9), and H(32), are planar.


(A)


(B)


(C)

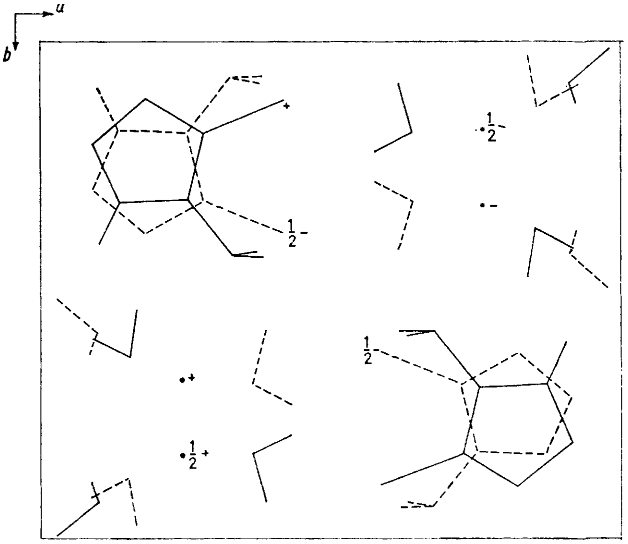


FIGURE 2 Packing of the molecule perpendicular to the c axis

EXPERIMENTAL

Crystal Data.—$C_2H_9N_4NaO_3S$, M = 192·17. Monoclinic, a = 1167·9(1), b = 1026·4(1), c = 669·6(1) pm, β = 100·84(8)°, U = 0·7884 nm^3, D_m = 1·60 (by flotation), Z = 4, D_c = 1·62, $F(000)$ = 400. Cu-K_α radiation λ = 154·18 pm, μ(Cu-K_α) = 39·04 cm^{-1}. Space group $P2_1/c$ (C^5_{2h}, No. 14).

Intensity data for the layers $h0$—$12l$ and $hk0$—8 were collected from two crystals by use of a PDP 8/S controlled

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Supper equi-inclination diffractometer.[10] Intensities were measured by the ω scan method at a rate dependent on peak intensity to give constant counting statistics. After correcting for Lorentz and polarisation factors, the two data sets were scaled together[11,12] to give 1381 independent reflections of which 203 were considered unobserved having $I < 2{\cdot}5\sigma(I)$. No correction was made for absorption.

Structure Determination.—The structure was determined by the symbolic addition procedure. The 88 largest E values were used to generate Σ_2 relationships of the type: $S(h) = S(k) \cdot S(h - k)$, where h and k denote the reflections with Miller indices $h_1k_1l_1$ and $h_2k_2l_2$, and S is the sign of the reflection. Three reflections were assigned phases to fix the origin (1,0,4, E 3·15; $\bar{4}$,10,1, E 2·75; and $\bar{2}$,3,1, E 2·58) and four other reflections were given symbols (2,3,0, E 2·32, A; 5,6,3, E 2·58, B; 1,1,6, E 2·66, C; and 5,5,1, E 3·36 D).

Signs or symbols were generated for the E values by use of Σ_2 relationships and phases assigned to a set of symbols to give the least number of contradictions. All the non-hydrogen atoms were located in the subsequent E map. Full-matrix isotropic least-squares refinement reduced the R from an initial value of 0·386 to 0·088. A difference-Fourier synthesis revealed the positions of the hydrogen atoms, and the least-squares refinement, with anisotropic temperature factors for all non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms reduced R to 0·058 and the weighted factor R' $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ to 0·048. Five reflections (2,0,0, 0,2,0, 1,0,2, 2,0,2, and 0,1,2) were found to be seriously affected by extinction from a plot of I_c/I_o *vs.* I_c[13] and were removed from the final cycle of least-squares refinement. A final difference-Fourier synthesis revealed no prominent features. None of the 88 phases determined by the symbolic addition procedure changed sign during the refinement stages.

A weighting scheme with σ values derived from counting statistics was used in 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 the number of variables was 1·7. The atomic and thermal parameters are listed in the Table. Observed and calculated structure factor amplitudes are listed in Supplementary Publication No. SUP 20505 (6 pp., 1 microfiche).*

The atomic scattering factors used for sodium, oxygen, carbon, and nitrogen were taken from ref. 14, for hydrogen from ref. 15, and for sulphur from ref. 16. No corrections were applied for anomalous dispersion. All computations[17] were made by use of a CDC 3600 computer.

(*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	0·41591(8)	0·1183(1)	0·3839(2)	
Na	0·2391(1)	0·6755(2)	0·4689(2)	
N(1)	0·1789(2)	0·1159(3)	0·4416(5)	
N(2)	0·0857(3)	0·2057(3)	0·4624(5)	
N(4)	0·2503(2)	0·3142(3)	0·4217(5)	
N(9)	0·3244(3)	0·4243(4)	0·4026(6)	
C(3)	0·1318(3)	0·3218(4)	0·4499(6)	
C(5)	0·2771(3)	0·1820(4)	0·4150(5)	
O(1)	0·1492(3)	0·6279(3)	0·1738(5)	
O(2)	0·0922(3)	0·9195(3)	0·2146(5)	
O(3)	0·3618(2)	0·8187(3)	0·2296(1)	
H(1)	0·087(4)	0·594(5)	0·174(7)	4·10
H(11)	0·162(4)	0·529(5)	0·111(7)	3·99
H(2)	0·074(5)	0·876(5)	0·284(8)	3·87
H(21)	0·028(3)	0·998(4)	0·225(7)	3·63
H(3)	0·429(3)	0·770(4)	0·178(6)	3·47
H(31)	0·389(3)	0·924(4)	0·306(6)	3·43
H(32)	0·097(3)	0·402(4)	0·468(6)	3·00
H(9)	0·363(3)	0·421(4)	0·468(7)	2·20
H(91)	0·381(3)	0·424(4)	0·270(6)	2·30

(*b*) Anisotropic temperature factors ($\times 10^4$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	39(1)	51(1)	228(3)	7(1)	−28(1)	3(2)
Na	56(1)	71(2)	149(4)	−11(1)	−9(2)	3(2)
N(1)	45(2)	33(3)	163(9)	−5(3)	−17(4)	−7(5)
N(2)	48(2)	53(4)	157(9)	−8(3)	−17(4)	−8(5)
N(4)	38(2)	36(3)	131(8)	−6(2)	−18(3)	9(5)
N(9)	46(3)	52(4)	203(12)	−10(3)	−28(4)	2(6)
C(3)	49(3)	44(5)	124(10)	10(3)	−17(4)	−6(6)
C(5)	43(3)	45(4)	83(9)	−3(3)	−14(4)	−5(6)
O(1)	54(2)	66(4)	212(9)	−5(2)	−33(4)	−18(4)
O(2)	61(2)	72(5)	158(10)	−7(3)	−11(4)	2(4)
O(3)	40(2)	77(4)	207(9)	5(2)	−15(3)	−4(5)

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

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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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