

and N(9) are also displaced from the plane toward the atoms to which they are hydrogen bonded.

Packing of the molecules

The 8-azaguanine molecules pack on top of one another as in crystals of other purine and pyrimidine compounds. This tendency of 'stacking', which is also found for certain purine derivatives in solution (Broom, Schweizer & Ts'o, 1967), is supposed to be mainly due to London dispersion forces (Hanlon, 1966). The interplanar distance in 8-azaguanine is fairly short (3.25 Å) and Macintyre has interpreted this as due to formation of a charge-transfer self-complex, responsible for the anticarcinogenic activity of the compound. However, in light of the fact that most natural occurring derivatives stack together in a similar way, a more probable explanation of the anticarcinogenic action of 8-azaguanine involves the ability of N(8) to participate in hydrogen bonding.

The molecules are held together in a tight network of hydrogen bonds as shown in Fig. 1. In one configuration the water molecule, O(101) (ii), provides protons to form hydrogen bonds to O(6) (ii) and to the other water molecule, O(102) (i), which in turn provides a proton for a hydrogen bond to N(8) (iii). The other proton on O(102) does not participate in any hydrogen bond and seems to alternate between the two positions

H(102) and H(105) [Fig. 2(b)]. It is interesting to note that the disordered water molecule permits the maximum number of hydrogen bonds to form.

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Crystal Structure of 2-Mercapto-6-methyl-purine Monohydrate*

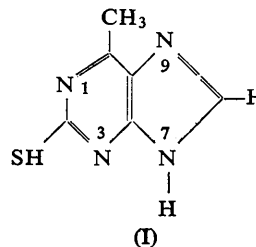
BY R. SRINIVASAN AND R. CHANDRASEKHARAN†

Centre of Advanced Study in Physics, University of Madras, Madras 25, India

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$C_6H_4N_4S \cdot H_2O$ crystallizes in space group $P2_1/a$ with $a=8.72$, $b=27.60$, $c=4.26$ Å, $\beta=93.75$, $Z=4$. The three nearest neighbours of the oxygen atom are N(7), N(9) and S distant 2.81, 2.81 and 3.26 Å respectively and belonging to three different purine molecules, and the intermolecular distance $N(7) \cdots S$ is 3.37 Å. The structure determination is not accurate enough to indicate which of the two atoms N(7) or N(9) is protonated or to draw definite conclusions regarding the hydrogen bonding system.

The application of a computer program using direct methods to the solution of the crystal structure of a purine derivative was briefly reported earlier (Cochran, Srinivasan & Tollin, 1963). The compound, which had the chemical formula $C_6H_4N_4S$, was found to be 2-mercapto-6-methyl purine (I) as revealed by the projection on which the direct method was applied.



* Contribution No. 256 from the Centre of Advanced Study in Physics, University of Madras.

† Present address: Department of Biophysics, University of Chicago, Chicago, Illinois 60637, U.S.A.

Although the projection was well resolved, the positions of hydrogen atoms were not located and consequently no conclusions could be drawn as to whether

the nitrogen N(9) or N(7) was protonated. The three-dimensional structure has since been established by making use of the zero and first layer data. Since it is not proposed to continue this work the three-dimensional trial structure of this compound is briefly reported in this note.

The crystallographic data of the compound are: system, monoclinic; $a=8.72$, $b=21.60$, $c=4.26$ Å, $\beta=93.75^\circ$; formula unit $C_6H_6N_4S \cdot H_2O$ and four formula units in the unit cell. The systematic absences were $0k0$ reflexions with k odd and $h0l$ reflexions with h odd, and hence the space group is $P2_1/a$.

Intensity data for the $hk0$ and $hk1$ reflexions were collected by the usual Weissenberg multiple-film techniques and a total of 320 reflexions were measured visually by using a standard set of spots. Absorption corrections were made.

The molecular features were clearly discernible in the well-resolved c -axis electron density projection calculated by the direct method of Cochran, Srinivasan & Tollin (1963). A three-dimensional model was constructed which had satisfactory stereochemical features. The model was subjected to three cycles of full-matrix least-squares refinement with the program of Busing, Martin & Levy (1962) on a CDC 3600 computer. The reflexions were treated with unit weight and the scale factors for the two layers, the atomic coordinates, and individual isotropic thermal parameters were refined. The atomic scattering factors were adopted from *International Tables for X-ray Crystallography* (1962). The final R value was 0.15.

The atomic coordinates and thermal parameters are given in Table 1. A view of the structure projected

along the c axis is shown in Fig. 1. The standard deviations for the positional parameters are high. The mean values of these for the x and y coordinates are C 0.025, N 0.019, O 0.018 and S 0.007 Å, while for the z coordinates they are 0.08, 0.06, 0.05 and 0.02 Å.

Table 1. Atomic coordinates (fractional) and isotropic thermal parameters

	x	y	z	B
N(1)	0.3915	0.0707	0.7524	1.08 Å ²
C(2)	0.4945	0.1113	0.8453	1.69
N(3)	0.4874	0.1742	0.7591	1.51
C(4)	0.3745	0.1903	0.6145	1.75
C(5)	0.2706	0.1503	0.4737	1.67
C(6)	0.2791	0.0871	0.5732	2.08
N(7)	0.3390	0.2500	0.4962	0.98
C(8)	0.2182	0.2435	0.2333	1.99
N(9)	0.1703	0.1836	0.2356	1.24
C(10)	0.1725	0.0365	0.4109	2.00
S	0.6339	0.0822	1.1007	1.55
O	0.4376	0.3595	0.8041	2.71

The rather large standard deviations in the positional parameters do not warrant a detailed discussion of the intra- and intermolecular features. However, the following main features of intermolecular packing arrangement may be mentioned. The water oxygen (O) has three nearest neighbours. The distances involved are $N(7) \cdots O = 2.81$ Å, $S \cdots O = 3.26$ Å, and $N(9) \cdots O = 2.81$ Å. Also the distance of N(1) from sulphur is 3.37 Å. While the above four distances are the important ones to be reckoned with, in the discussion of the hydrogen bond system in the structure, it is not possible, with the present accuracy of the data, to de-

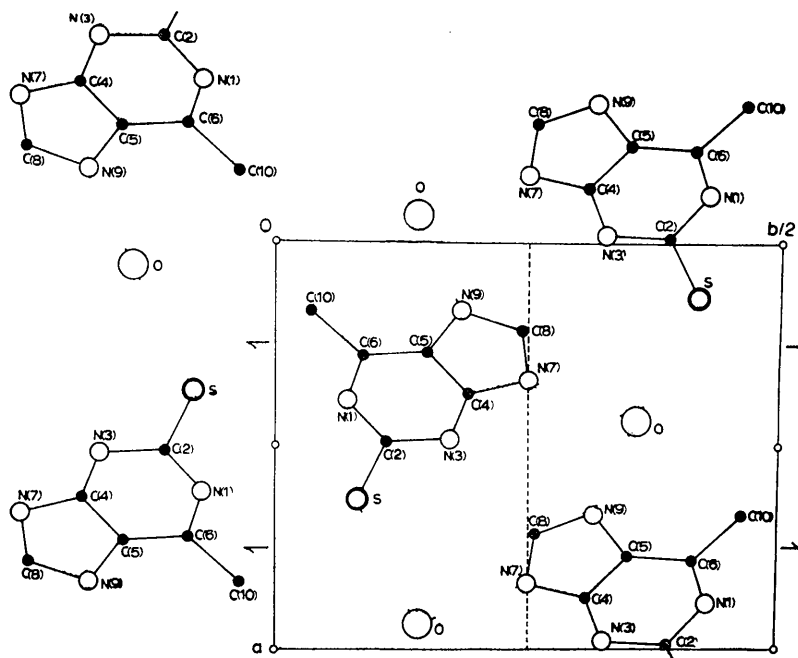


Fig. 1. A view of the structure projected down the c axis

cide the exact type. For instance, N(7) or N(9) could be protonated and this would decide whether the hydrogen bond involving the water oxygen atom is $\text{OH}\cdots\text{N}(7)$ or $\text{OH}\cdots\text{N}(9)$. However, the distance $\text{O}\cdots\text{S}=3.26 \text{ \AA}$ is favourable for a good hydrogen bond of the type $\text{OH}\cdots\text{S}$ which agrees with the mean value of 3.28 \AA for such a bond reported by Srinivasan & Chacko (1967). Although there is a possibility that the sulphur exists as an SH group it seems likely that it exists in the thion form, a feature reported in the similar structure of 6-mercaptapurine monohydrate (Brown, 1967) where, as a consequence, N(1) is protonated. This is also in broad agreement with the observation of Srinivasan & Chacko (1967) that there is a high tendency for the sulphur atom to take part in a hydrogen bond as an acceptor rather than as a donor. Also from the point of view of hydrogen bond angles, the $\text{OH}\cdots\text{S}$ and $\text{OH}\cdots\text{N}(9)$ appear favourable. While these features broadly point to the system of four bonds $\text{OH}\cdots\text{S}$, $\text{OH}\cdots\text{N}(9)$, $\text{N}(7)\text{H}\cdots\text{O}$ and $\text{N}(1)\text{H}\cdots\text{S}$ as more probable no definite conclusion could be drawn regarding this from the present data. These require clarification only by a detailed accurate analysis of the structure.

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