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THE MOLECULAR STRUCTURE OF 3-METHYL-6-AMINO-1,2,4-TRIAZIN-5(2H)-ONE MONOHYDRATE

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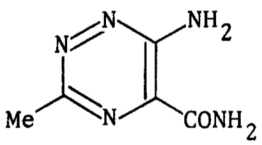
The molecular structure of the title compound has been studied by using three-dimensional X-ray counter data. The molecule is unusual in the point that the non-ionic canonical structure contributes scarcely to the resonance in it.

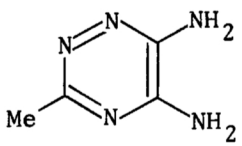
It has recently been found that the Hofmann reaction of 3-methyl-6-amino-1,2,4-triazine-5-carboxamide (1) with sodium hypobromite affords not the normal product, 3-methyl-5,6-diamino-1,2,4-triazine (2), but two other products (3 and 4) having the formulae, $C_4H_6N_4O \cdot H_2O$ and $C_4H_6N_4O$, respectively.[1] In order to determine unambiguously the molecular structures of these unusual products, we have undertaken X-ray crystallographic analyses of them. The present paper outlines the structure determination of 3.

The compound, 3, crystallizes in the monoclinic space group, $P2_1/c$, with four formula units in a unit cell with the dimensions of a = 6.953(3), b = 12.811(4), c = 7.351(3) Å, and β = 94.90(5)°. Diffraction data were collected from a crystal with dimensions of about 0.1 × 0.2 × 0.5 mm^3, on an automatic, four-circle diffractometer using Cu Kα radiation monochromatized with a LiF crystal. The intensity measurement was made by the θ-2θ continuous scan technique at a scan rate of about 0.5°(θ)/min. The intensities thus obtained were corrected for the usual Lorentz and polarization factors, but not for the absorption or the extinction effect. In the range of 2θ-values up to 140°, 1179 structure factor magnitudes above σ(F) were selected for the subsequent structure analysis and refinement.

The structure was solved by the symbolic addition procedure using 209 E-values above 1.30. Approximate positions of all non-hydrogen atoms were obtained from an E-map based on 172 phases. These atomic coordinates were refined by the block-diagonal-matrix least-squares method, first with isotropic and then with anisotropic thermal parameters. A difference Fourier map yielded the locations of all eight hydrogen atoms. Further least-squares refinement including these hydrogen atoms with isotropic temperature factors reduced an R-value to 4.5%. Thus, it has been established that 3 is the monohydrate of 3-methyl-6-amino-1,2,4-triazin-5(2H)-one as shown in Fig. 1.



1



2

As will be seen in Fig. 2, all the observed bond distances are normal, and can be well reproduced by superposing the five canonical structures shown in Fig. 3. The relative weights of these structures were calculated by using Pauling's relation between bond orders and distances[2] and assuming that the C-C, C=C, C-N, C=N, C-O, C=O, N-N, and N=N distances are 1.54, 1.33, 1.47, 1.24, 1.45, 1.20, 1.46, and 1.22 Å respectively.[3,4] It has been reported that the contributions of the non-ionic canonical structures for thymine monohydrate[3] and isocytosine[5] are in the range of 30-35%. Hence, it is surprising that, as in the case of meso-ionic compounds, the non-ionic structure contributes scarcely to the resonance in 3. In the crystalline state, the ionic structures may be much stabilized by the hydrogen bonding and other crystalline fields acting on the molecule. Further details are now under investigation.

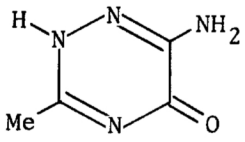


Fig. 1

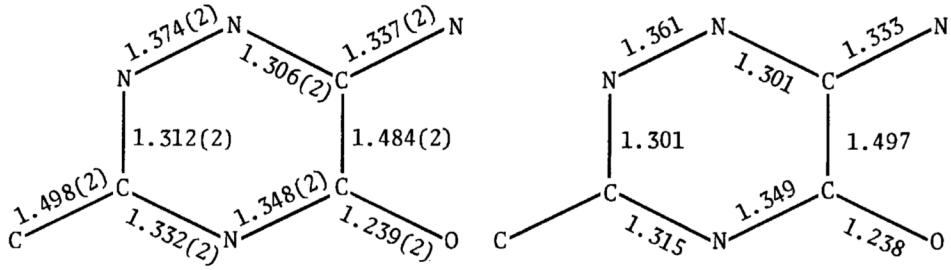
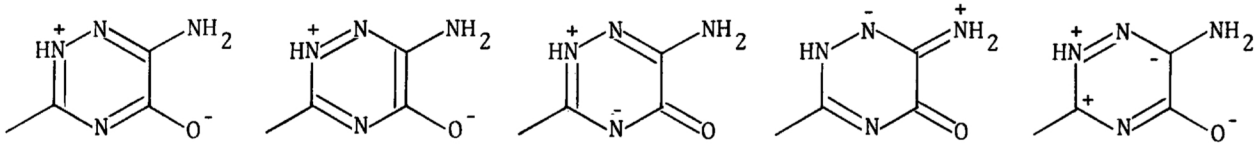


Fig. 2. The observed (left) and theoretically-calculated (right) bond distances (Å).



16% 8% 32% 33% 11%

Fig. 3. The canonical structures for 3.

References

1) The details will be reported elsewhere.
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