The Crystal Structure of Riboflavin Hydrobromide Monohydrate

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Riboflavin, in the form of the mono- and dinucleotides, acts as the prosthetic group of several enzymes involved in the biological oxidation-reduction reactions. These enzymes serve as bridges over which hydrogen atoms can pass between two other molecules, and riboflavin alternately accepts and releases two hydrogen atoms, being reversibly transformed to leucoriboflavin because of its intermediate redox potential. The present investigation has been undertaken in order to elucidate the structural characteristics of monoprotonated riboflavin.

Riboflavin hydrobromide monohydrate crystallizes in an orthorhombic unit cell with dimensions ; $a=18.24$ Å, $b=6.96$ Å, $c=14.76$ Å. The space group is $P2_12_12_1$. The three-dimensional intensities of 2267 reflections were measured visually from Weissenberg photographs taken about the b and c axes with Cu$K\alpha$ radiation. The structure was solved by the heavy atom method. The positional and thermal parameters of each atom were refined by the block-diagonal least-squares method. The R factor at the present stage is 0.09. Intramolecular bond distances and angles are shown in Fig. 1.

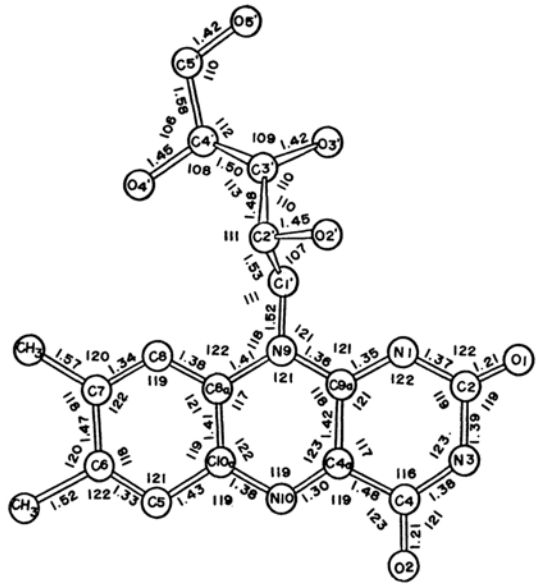

Fig. 1. Bond distances and angles.
The standard deviation of the distance is about 0.02 Å and that of the angle is about 1.5°.

Isoalloxazine ring, having itself a hydrogen atom at N(3), may be protonated at either N(1) or N(10) by addition of hydrogen bromide. The bond angle at N(10) is smaller than those at other three nitrogen atoms. Singh's discussion on the bond angles at nitrogen atoms[1] suggests that the hydrogen atom is not bonded to N(10) but to N(1). This is confirmed by the difference Fourier synthesis ; a peak of height of 0.7 e/Å^3 could be reasonably assigned as the hydrogen atom bonded to N(1). This result agrees with the location of the proton suggested by the theoretical calculation made by Pullman.[2]

Ribitol does not form a furanose ring but a chain, which has not been found in cases of nucleotides composing nucleic acids.

A detailed account of this work will be presented in the near future.

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1) C. Singh, *Acta Cryst.*, **19**, 861 (1965).

2) B. Pullman and A. Pullman, *Proc. Natl. Acad. Sci. U.S.*, **45**, 137 (1959).