The distance (3.52 Å) between the water oxygen atom in compound I and the iodide ion indicates a hydrogen bond O—H···I⁻ in this structure. In compound II two interionic hydrogen bonds N(3)—H···O(14) with a length of 2.88 Å, related by a centre of symmetry are found. In this way, a planar eightmembered ring including the two hydrogen atoms is obtained in this structure. Some O—O, O—N or C—O contacts found in the structures may indicate further hydrogen bonds. However, since reliable hydrogen positions could not be obtained for the present heavy-atom derivatives it is not possible to make any definite conclusions about the occurrence of such bonds.

Full details of these investigations including Pariser-Parr-Pople calculations performed on the cation of compound II and discussions of the structures will shortly be presented elsewhere. Also detailed accounts of structure determinations of two reduced compounds, *viz.* 5-hydro-9-bromo-1,3,7,8,10-pentamethyl-1,5-dihydroalloxazine and 5-acetyl-9-bromo-1,3,7,8,10-pentamethyl-1,5-dihydroalloxazine will be published in the near future. Within the present research program the crystal structures of 9-bromo-3,7,8,10-tetramethylisoalloxazine, 5-acetyl-3,7,8,10-tetramethyl-1,5-dihydroalloxazine and the 1:1 complex of lumiflavin-hydroquinone containing one HCl per molecule have also been worked out and will very soon be reported.

Acknowledgements. These investigations have received financial support from the *Tri-Centennial Fund of the Bank of Sweden* and from the *Swedish Natural Science Research Council.* Permission for the use of the computers CD 3600 and IBM 360/75 was granted by the *Computer Division of the National Swedish Rationalization Agency.*

The authors want to thank Professor Arne Magnéli for all facilities placed at their disposal. They are also indebted to Dr. Franz Müller for the supply of crystals used in the work.

A research fellowship from *Stiftelsen Bengt Lundqvists Minne* to one of us (R.N.) is gratefully acknowledged.

1. Dudley, K. H., Ehrenberg, A., Hemmerich, P. and Müller, F. *Helv. Chim. Acta* **47** (1964) 1354.
2. Slater, E. C., Ed., *Flavins and Flavoproteins*, B. B. A. Library, 8, Elsevier, Amsterdam 1966.

Received August 5, 1969.

Studies on Flavin Derivatives

III.* The Crystal and Molecular Structure of 9-Bromo-5-hydro-1,3,7,8,10-pentamethyl-1,5-dihydroalloxazine

ROLF NORRESTAM, MARIANNE von GLEHN, LARS-OVE HAGMAN and PEDER KIERKEGAARD

Institute of Inorganic and Physical Chemistry University of Stockholm, Stockholm, Sweden

The crystal and molecular structure of 9-bromo-5-hydro-1,3,7,8,10-pentamethyl-1,5-dihydroalloxazine, $C_{15}H_{17}BrN_4O_2$, has been determined by X-ray diffraction methods in order to obtain detailed structural information about a flavin derivative in a reduced state.

The crystalline specimen used was prepared by Maron [2] at this Institute. The crystal structure ($C2/c$, $a=15.680\pm5$ Å, $b=15.440\pm5$ Å, $c=12.845\pm5$ Å, $\beta=103.03\pm0.05°$, $Z=8$) was solved by the heavy-atom method on the basis of 2818 independent, significant reflections registered with Cu$K\alpha$ radiation using a Siemens automatic single-crystal diffractometer. The structure was refined by full-matrix least-squares techniques including anisotropic thermal parameters for the non-hydrogen atoms and isotropic parameters for the hydrogens to a final R value of 0.042.

The dimensions of the molecule are given in Figs. 1—3.

The distances within ring III are in full agreement with those characteristic of a benzene ring system. The distances C(4A)—C(10A), C(2)—O(12) and C(4)—O(14) are of lengths indicating double bond character. The ring skeleton is bent along a line through N(5) and N(10), the ring atoms deviating less than 0.02 Å for the pyrimidine ring and less than 0.45 Å for the benzene ring from two least-squares planes intersecting at an angle of 159°. The results support the conclusions drawn by Dudley, Ehrenberg, Hemmerich, and

* For paper II of this series see Ref. 1.

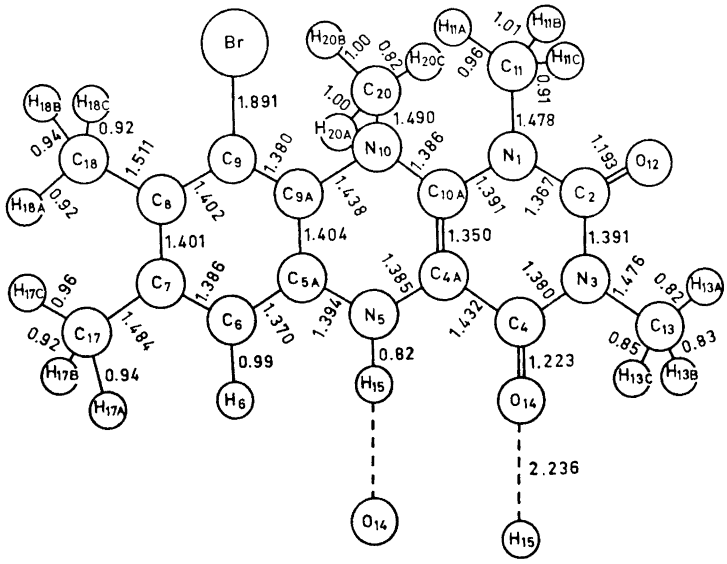

Fig. 1. Bond lengths (in Å) in 9-bromo-5-hydro-1,3,7,8,10-pentamethyl-1,5-dihydroalloxazine. The estimated standard deviations are 0.008 Å for distances between non-hydrogen atoms and 0.07 Å for distances to hydrogens. Two hydrogen bonds forming dimers in the structure have been indicated.

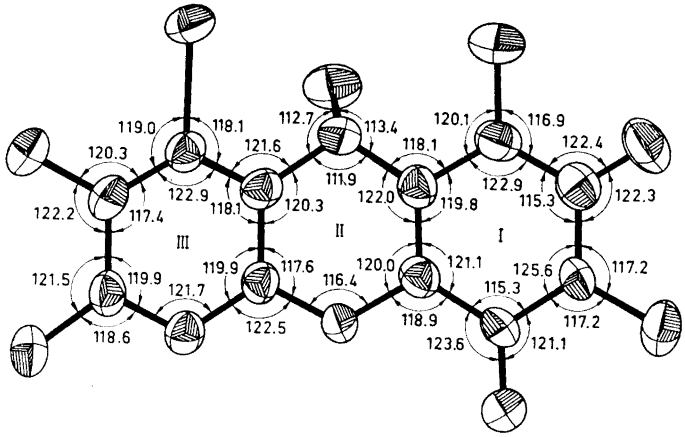

Fig. 2. Bond angles (°) in 9-bromo-5-hydro-1,3,7,8,10-pentamethyl-1,5-dihydroalloxazine. The estimated standard deviations are around 0.5°.

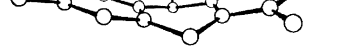

Fig. 3. The structure of 9-bromo-5-hydro-1,3,7,8,10-pentamethyl-1,5-dihydroalloxazine.

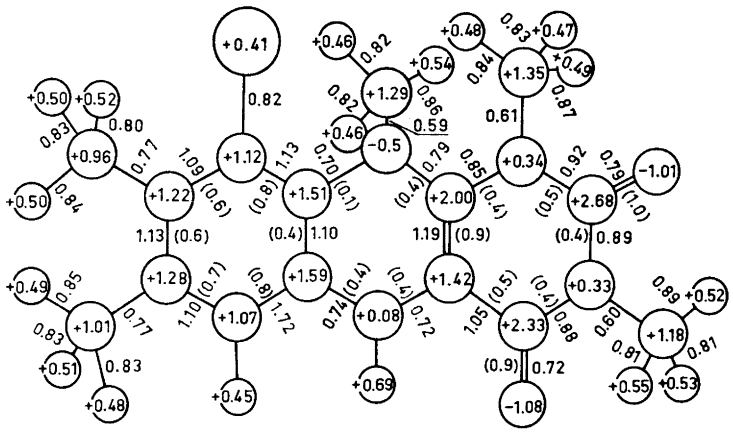

Fig. 4. The net charge distribution (the numbers within the circles), overlap population and approximate π-bond order values (within brackets) calculated for 9-bromo-5-hydro-1,3,7,8,10-pentamethyl-1,5-dihydroalloxazine.

Müller [3] from spectroscopic observations and that reduced flavins adopt the non-planar diketo form.

Symmetry-related molecules form dimers mutually linked by hydrogen bonds N(5)—H(15)···O(14′) as indicated in Fig. 1. The angle at the hydrogen atom is 165°.

Approximate π-bond orders calculated from the correlation functions between bond order and bond distance recently suggested by several authors [4–6] are in reasonable conformity with expected values. The π-bond order values are given (within brackets) in Fig. 4, which also illustrates the charge distribution and overlap population obtained for the observed molecular geometry by extended Hückel calculations [7] performed by using a computer program.[8]

This investigation has received financial support from the *Tri-Centennial Fund of the Bank of Sweden* and from the *Swedish Natural Science Research Council*. Permission for the use of the computer IBM 360/75 was granted by the *Computer Division of the National Swedish Rationalization Agency*.

A research fellowship from the *Stiftelsen Bengt Lundqvists Minne* to one of us (R.N.) is gratefully acknowledged.

1. Kierkegaard, P., Leijonmarck, M., Norrestam, R., Torbjörnsson, L. and Werner, P.-E. *Acta Chem. Scand.* **23** (1969) 2197.
2. Maron, L. In *DIS* No. 32, Univ. Stockholm, Inorg. and Phys. Chem. 1969.
3. Dudley, K. H., Ehrenberg, A., Hemmerich, P. and Müller, P. *Helv. Chim. Acta* **47** (1964) 1354.
4. Roos, B. and Skancke, P. N. *Acta Chem. Scand.* **21** (1967) 233.
5. Fischer-Hjalmars, I. and Sundbom, M. *Acta Chem. Scand.* **22** (1968) 607.
6. Jensen, H. and Skancke, P. N. *Acta Chem. Scand.* **22** (1968) 2899.
7. Hoffman, R. *J. Chem. Phys.* **39** (1963) 1397.
8. Herman, Z. S. and Manne, R. *Research Report No. 224* (1968), Quantum Chemistry Group, Uppsala University, Uppsala.

Received August 5, 1969.