cps, $J_{CH_2-P}=15$ cps), 6.87 s (3 H, OCH$_3$), 8.0 m (2 H, allylic CH$_2$), ca. 8.6 m (ca. 7 H, CH$_3$ and 2 CH$_2$), and 8.92 s (6 H, 2 CH$_3$ at tert. OCH$_3$).

On reaction with crocetindial the mixed Wittig salts (1 and 5) gave lycopene, 1-methoxy-1,2-dihydro-lycopene and 3,4,3′,4′-tetrahydrospirilloxanthin.[5]

Effect of acidic methanol on linalool (4) and geraniol (6). 4 (2 g) and 6 (2 g) in methanol (10 ml) containing conc. H$_2$SO$_4$ (1 drop) were treated separately at room temperature for 20 h. No new products were formed (no allylic rearrangement of 4). 4 (6 g) and 6 (6 g) in methanol (25 ml) containing conc. H$_2$SO$_4$ (2 drops) were refluxed separately for 34 h. A complex mixture of methoxylated and cyclised products was obtained.

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Studies on Flavin Derivatives

VIII.* The Crystal and Molecular Structure of 9-Bromo-3,7,8,10-tetramethylisoalloxazine Monohydrate

MARIANNE von GLEHN, PEDER KIERKEGAARD and ROLF NORRESTAM

Institute of Inorganic and Physical Chemistry, University of Stockholm, Box 6801, S-113 86 Stockholm, Sweden

In connection with studies on flavin derivatives undertaken at this Institute the crystal and molecular structure of 9-bromo-3,7,8,10-tetramethylisoalloxazine monohydrate, $C_{14}H_{13}BrN_4O_2 \cdot H_2O$, has been determined by X-ray diffraction

methods in order to obtain structural information about a flavin derivative in an oxidized, neutral state.

Single crystals suitable for X-ray work were obtained by recrystallization from an acetic acid solution of a specimen prepared by L. Maron[1] at this Institute. The crystal structure ($P2_1/c$, $a=13.047\pm5$ Å, $b=7.053\pm5$ Å, $c=17.957\pm5$ Å, $\beta=120.40\pm5°$, $Z=4$) was solved by the heavy-atom method on the basis of the 1381 independent, most significant reflections registered
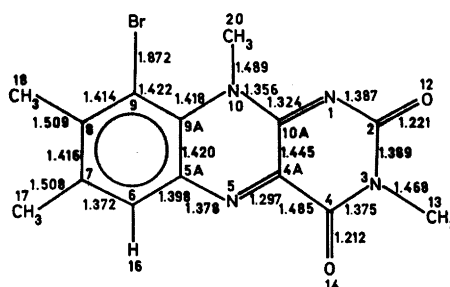

Fig. 1.

with CuKα 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 0.052.

The dimensions of the molecule are given in Fig. 1. The estimated standard deviations are 0.012 Å for distances between non-hydrogen atoms and around 0.25° for the the angles (Fig. 2).

The ring skeleton is essentially planar. The largest deviation of any atom from a least-squares plane through all fourteen non-hydrogen atoms in the three rings is less than 0.1 Å.

The bond lengths within the molecule obtained in the present study are in good agreement with the values for 7,8,10-trimethylisoalloxazine calculated by Grabe[2] using Pariser-Parr-Pople selfconsistent-field molecular orbital method on the π-system of the molecule. The calculated values of distances and π-bond orders and the corresponding observed bond lengths are:
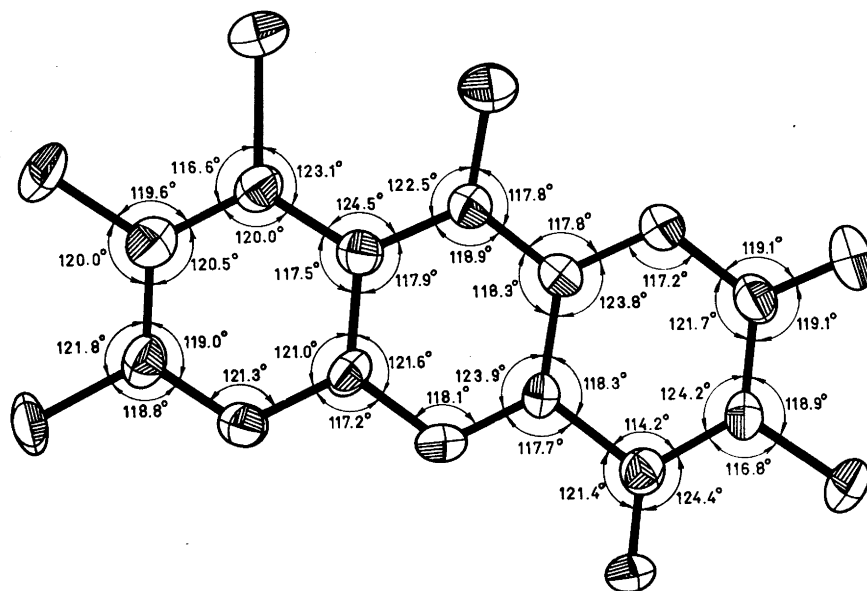
Fig. 2

		obs.	calc.	π-b.o.
N(1)	—C(2)	1.387	1.380	0.43
N(3)	—C(4)	1.375	1.366	0.51
C(4A)	—N(5)	1.297	1.313	0.80
C(5A)	—C(6)	1.398	1.415	0.57
C(7)	—C(8)	1.416	1.409	0.60
C(9)	—C(9A)	1.422	1.411	0.59
C(9A)	—N(10)	1.418	1.382	0.42
C(4A)	—C(10A)	1.445	1.452	0.36
C(2)	—N(3)	1.389	1.381	0.43
C(4)	—C(4A)	1.485	1.466	0.28
N(5)	—C(5A)	1.378	1.376	0.46
C(6)	—C(7)	1.372	1.389	0.71
C(8)	—C(9)	1.414	1.392	0.70
C(9A)	—C(5A)	1.420	1.414	0.57
N(10)	—C(10A)	1.386	1.375	0.46
C(10A)	—N(1)	1.324	1.324	0.75

The present structure investigation thus confirms the planar diketo form of the oxidized, neutral state of flavins. Further studies by means of extended Hückel cal-culations on different geometries of the molecule described in this article are in progress and will be published later.

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