Studies on Flavin Derivatives

The Crystal Structure of 5-Acetyl-9-bromo-1,3,7,8,10-pentamethyl-1,5-dihydroisoalloxazine

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The crystal structure of 5-acetyl-9-bromo-1,3,7,8,10-pentamethyl-1,5-dihydroisoalloxazine, $C_{17}H_{19}BrN_4O_3$, has been determined and refined from three-dimensional X-ray film data. The crystals are monoclinic with space group $P2_1/n$. The unit-cell dimensions are $a = 13.259$, $b = 7.361$, $c = 18.320$ Å, $\beta = 91.04°$. A new program system has been used for the evaluation of integrated intensities from an automatic film scanner process.

The atoms of the ring system lie close to two planes intersecting along a line between N(5) and N(10). The dihedral angle is 35°5. A discussion of the structure and its relevance in biological redox processes is given.

The determination of the crystal structure of 5-acetyl-9-bromo-1,3,7,8,10-pentamethyl-1,5-dihydroisoalloxazine, $C_{17}H_{19}BrN_4O_3$, was undertaken as part of a research program on flavin compounds. In the oxidized state the alloxazinium ring system has been shown to be planar.[1] Considering the wide distribution of this ring system in biological energy-conserving redox processes we found it of interest to determine the crystal structure of a flavin in a reduced state.

The structure determination was closely related to the development of a computer program system for an on-line film scanner.[2] The program system[3] has been modified during the data collection on this structure. A separate article on the accuracy of film scanner data will shortly appear elsewhere.[4]

EXPERIMENTAL

Crystals suitable for X-ray data collection were prepared by Dr. L. Marón at this Institute. The substance was synthesized from 5-acetyl-9-bromo-1,3,7,8-tetramethyl-1,5-dihydroalloxazine.[5] By slow evaporation of an ethanol-water solution yellow crystals were obtained which were found to be monoclinic needles elongated in the b direction. (Found: C 50.2; H 4.95; N 13.8. Calc. for $C_{17}H_{19}BrN_4O_3$: C 50.1; H 4.70; N 13.8). Preliminary

rotation and Weissenberg photographs showed systematic absences for $h0l$ with $h+l$ odd and $0k0$ with k odd, which indicates the space group $P2_1/n$. Unit cell dimensions obtained from powder photographs taken in a Guinier-Hägg focusing camera with potassium chloride ($a = 6.2930$ Å) as an internal standard are shown in Table 1.

Table 1. Crystal data.

Lattice constants	$a = 13.259$ (3) Å
	$b = 7.361$ (4) Å
	$c = 18.320$ (6) Å
	$\beta = 91.04°$ (3)
Cell volume	$V = 1787.6$ Å³
Density (X-ray)	$d = 1.51$ g/cm³
Molecules per unit cell	$Z = 4$
Absent reflections	$h0l$ with $h+l = 2n+1$ and
	$0k0$ with $k = 2n+1$
Space group	$P2_1/n$
General position	$\pm[x,y,z;\ x+\frac{1}{2},\frac{1}{2}-y,z+\frac{1}{2}]$

A crystal fragment which measured $0.40 \times 0.26 \times 0.40$ mm³ was selected for the collection of X-ray intensities. This was achieved by means of multiple film pack equi-inclination Weissenberg photographs about the a and b axes. The computer indexing technique applied requires that no β reflections occur. Consequently, Ni-filtered CuK radiation was used. 748 reflections about the a axis and 999 reflections about the b axis were obtained. Absorption corrections ($\mu = 37$ cm⁻¹) and corrections for Lorentz and polarization factors were made. The two sets of data were correlated and placed upon a common scale. The total number of independent reflections was then 1243.

Since it is of interest to compare the separate sets of data a data discrepancy index, R_D, for the 504 structure factors in common was calculated. R_D is defined as

$$R_D = \frac{\sum||F_{OA}| - |F_{OB}||}{\frac{1}{2}(\sum|F_{OA}| + \sum|F_{OB}|)}$$

where F_{OA} and F_{OB} are the observed structure factors from the two sets. The R_D value obtained was 0.102. Considering the large dimensions of the crystal used this was found satisfactory.

DETERMINATION AND REFINEMENT OF THE STRUCTURE

A three-dimensional Patterson synthesis was evaluated. The bromine position was determined from the Harker sections at $u = \frac{1}{2}$ and $v = \frac{1}{2}$ and refined by the method of least-squares. The R index $[R = \sum||kF_o| - |F_c||/\sum|kF_o|]$ for bromine alone was 0.52. The search for other atoms in the structure was pursued by Fourier techniques. By successive F_o and $(F_o - F_c)$ syntheses all the non-hydrogen atoms were found.

Refinement of the structure was carried out with a modified version of the full-matrix least squares program originally written by Gantzel, Sparks and Trueblood (1961).[6] Hughes' weighting scheme [7] was applied with $F_{o,min} = 5.0$ and $h = 4$. The parameters refined were scale factors, atomic coordinates, anisotropic temperature factors for bromine and isotropic temperature factors for the remaining non-hydrogen atoms. The atomic scattering factor curves used for oxygen, nitrogen, and carbon were those given by Freeman[8] and for bromine that by Cromer and Waber [9] corrected for the real part of the anomalous dispersion coefficient. The refinement was terminated when all shifts in

the parameters were less than 5 % of their corresponding standard deviations. The R value obtained was 0.135. A weight analysis obtained in the last cycle is given in Table 2. A list of the observed and calculated structure factors is presented in Table 7.

Table 2. Weight analysis obtained in the final cycle of the least-squares refinement of 5-acetyl-9-bromo-1,3,7,8,10-pentamethyl-1,5-dihydroisoalloxazine. The averages $\overline{w(|F_o|-|F_c|)^2} = \overline{w\varDelta^2}$ are normalized.

Interval $\sin \theta$	Number of independent reflections	$\overline{w\varDelta^2}$	Interval F_{obs}	Number of independent reflections	$\overline{w\varDelta^2}$
0.0 — 0.432	291	2.057	0.0 — 14.0	123	0.892
0.432 — 0.544	245	0.665	14.0 — 17.7	123	0.866
0.544 — 0.623	183	0.662	17.7 — 20.9	123	0.824
0.623 — 0.685	179	0.637	20.9 — 24.2	124	0.842
0.685 — 0.738	101	0.695	24.2 — 28.1	122	0.659
0.738 — 0.784	79	0.699	28.1 — 32.7	123	0.695
0.784 — 0.826	56	0.676	32.7 — 38.4	123	0.517
0.826 — 0.863	37	0.678	38.4 — 47.0	123	0.679
0.863 — 0.898	36	0.689	47.0 — 63.0	123	2.426
0.898 — 0.930	24	0.890	63.0 — 245.5	124	1.593

Table 3. Atomic parameters with their standard deviations.

Atom	x/a	y/b	z/c	B
Br	0.4354 (2)	0.7788 (4)	0.2640 (2)	—
N(1)	0.1261 (11)	0.600 (2)	0.3776 (8)	3.1 (3)
C(2)	0.0363 (14)	0.520 (3)	0.3946 (10)	3.4 (4)
N(3)	0.0459 (11)	0.344 (2)	0.4271 (8)	3.3 (3)
C(4)	0.1367 (13)	0.264 (3)	0.4449 (9)	2.9 (4)
C(4a)	0.2241 (13)	0.372 (3)	0.4367 (9)	2.6 (3)
N(5)	0.3216 (10)	0.304 (2)	0.4578 (8)	2.7 (3)
C(5a)	0.3982 (13)	0.352 (3)	0.4061 (9)	2.4 (3)
C(6)	0.4809 (13)	0.235 (3)	0.3929 (9)	2.9 (4)
C(7)	0.5523 (13)	0.290 (3)	0.3427 (9)	2.9 (4)
C(8)	0.5411 (14)	0.452 (3)	0.3036 (10)	3.3 (4)
C(9)	0.4600 (12)	0.564 (3)	0.3186 (9)	2.4 (3)
C(9a)	0.3855 (12)	0.518 (3)	0.3703 (8)	2.3 (3)
N(10)	0.3030 (11)	0.631 (2)	0.3841 (7)	3.0 (3)
C(10a)	0.2176 (14)	0.536 (3)	0.4009 (9)	2.7 (4)
C(11)	0.1224 (16)	0.769 (3)	0.3308 (12)	4.6 (5)
O(12)	−0.0456 (10)	0.576 (2)	0.3764 (7)	4.4 (3)
C(13)	−0.0500 (16)	0.248 (3)	0.4400 (12)	4.5 (5)
O(14)	0.1350 (10)	0.102 (2)	0.4653 (7)	4.2 (3)
C(15)	0.3455 (13)	0.253 (3)	0.5282 (9)	2.9 (4)
C(15a)	0.2684 (16)	0.279 (3)	0.5865 (11)	4.2 (4)
O(15b)	0.4295 (10)	0.196 (2)	0.5435 (7)	4.5 (3)
C(17)	0.6413 (17)	0.163 (3)	0.3279 (12)	4.8 (5)
C(18)	0.6193 (16)	0.503 (3)	0.2456 (11)	4.0 (4)
C(20)	0.3235 (17)	0.794 (3)	0.4295 (12)	4.6 (5)

For Br the anisotropic temperature factor T obtained was
T = exp[0.0111 h^2 + 0.0137 k^2 + 0.0037 l^2 − 0.0001 hk + 0.0039 hl − 0.0085 kl].

A three-dimensional difference synthesis calculated over the asymmetric part of the unit cell at points 0.2 Å apart showed only small peaks above a slowly varying background. Therefore it does not seem possible to locate the hydrogen atoms in the structure from the intensity data available.

RESULTS AND DISCUSSION

In the following discussion, atoms belonging to different asymmetric units are labelled as follows:

Superscript	Coordinates	Superscript	Coordinates
none	x,y,z	v	$x,y-1,z$
i	$1-x,1-y,1-z$	vi	$x,1+y,z$
ii	$\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$	vii	$\bar{x},\bar{y},1-z$
iii	$\frac{1}{2}-x,y-\frac{1}{2},\frac{1}{4}-z$	viii	$\bar{x},1-y,1-z$
iv	$1\frac{1}{2}-x,y-\frac{1}{2},\frac{1}{4}-z$	ix	$1-x,\bar{y},1-z$

Table 4. Interatomic distances and angles in 5-acetyl-9-bromo-1,3,7,8,10-pentamethyl-1,5-dihydroisoalloxazine with standard deviations.

N(1)	—C(2)	1.37 (3)	N(3)	—C(4)	—C(4a)	116.8 (1.6)
N(1)	—C(11)	1.51 (3)	N(3)	—C(4)	—O(14)	117.3 (1.6)
C(2)	—O(12)	1.20 (3)	O(14)	—C(4)	—C(4a)	125.9 (1.7)
C(2)	—N(3)	1.43 (3)	C(4)	—C(4a)	—C(10a)	119.9 (1.6)
N(3)	—C(13)	1.48 (3)	C(4)	—C(4a)	—N(5)	120.8 (1.6)
N(3)	—C(4)	1.37 (3)	C(10a)	—C(4a)	—N(5)	118.9 (1.5)
C(4)	—O(14)	1.25 (3)	C(4a)	—N(5)	—C(5a)	112.4 (1.3)
C(4)	—C(4a)	1.42 (3)	C(4a)	—N(5)	—C(15)	122.7 (1.4)
C(4a)	—N(5)	1.43 (2)	C(15)	—N(5)	—C(5a)	121.9 (1.4)
N(5)	—C(15)	1.37 (2)	N(5)	—C(15)	—C(15a)	118.9 (1.5)
C(15)	—C(15a)	1.51 (3)	N(5)	—C(15)	—O(15b)	120.3 (1.5)
C(15)	—O(15b)	1.22 (2)	O(15b)	—C(15)	—C(15a)	120.7 (1.6)
N(5)	—C(5a)	1.44 (2)	N(5)	—C(5a)	—C(9a)	116.1 (1.5)
C(5a)	—C(6)	1.42 (3)	N(5)	—C(5a)	—C(6)	121.4 (1.5)
C(6)	—C(7)	1.39 (3)	C(9a)	—C(5a)	—C(6)	122.6 (1.5)
C(7)	—C(17)	1.53 (3)	C(5a)	—C(6)	—C(7)	118.2 (1.6)
C(7)	—C(8)	1.40 (3)	C(6)	—C(7)	—C(17)	118.3 (1.7)
C(8)	—C(18)	1.54 (3)	C(6)	—C(7)	—C(8)	121.4 (1.7)
C(8)	—C(9)	1.39 (3)	C(18)	—C(7)	—C(8)	120.3 (1.6)
C(9)	—Br	1.90 (2)	C(7)	—C(8)	—C(18)	119.5 (1.7)
C(9)	—C(9a)	1.42 (2)	C(7)	—C(8)	—C(9)	118.8 (1.6)
C(9a)	—N(10)	1.40 (2)	C(18)	—C(8)	—C(9)	121.7 (1.7)
N(10)	—C(20)	1.48 (3)	C(8)	—C(9)	—C(9a)	122.5 (1.6)
N(10)	—C(10a)	1.37 (3)	C(8)	—C(9)	—Br	121.2 (1.3)
C(10a)	—N(1)	1.36 (3)	Br	—C(9)	—C(9a)	116.0 (1.2)
C(10a)	—C(4a)	1.37 (3)	C(9)	—C(9a)	—N(10	121.9 (1.5)
C(5a)	—C(9a)	1.39 (3)	C(9)	—C(9a)	—C(5a)	116.4 (1.5)
			C(5a)	—C(9a)	—N(10)	121.7 (1.5)
C(10a)	—N(1)—C(2)	123.3 (1.5)	C(9a)	—N(10)	—C(20)	116.5 (1.4)
C(10a)	—N(1)—C(11)	119.0 (1.5)	C(9a)	—N(10)	—C(10a)	112.7 (1.5)
C(11)	—N(1)—C(2)	117.7 (1.5)	C(20)	—N(10)	—C(10a)	115.6 (1.5)
N(1)	—C(2) —N(3)	114.6 (1.6)	N(10)	—C(10a)—C(4a)	120.7 (1.6)
N(1)	—C(2) —O(12)	124.8 (1.8)	N(10)	—C(10a)—N(1)	119.0 (1.5)
O(12)	—C(2) —N(3)	120.0 (1.7)	C(4a)	—C(10a)—N(1)	120.2 (1.6)
C(2)	—N(3)—C(4)	123.8 (1.5)			
C(2)	—N(3)—C(13)	115.5 (1.5)			
C(13)	—N(3)—C(4)	120.7 (1.6)			

The bond lengths and bond angles uncorrected for thermal motion were computed from coordinates given in Table 3 and are listed in Table 4 (cf. Figs. 1).

The bromine substitution at C(9) causes no significant deviations in distances and angles from usual values in the benzene ring. Furthermore, no alternation
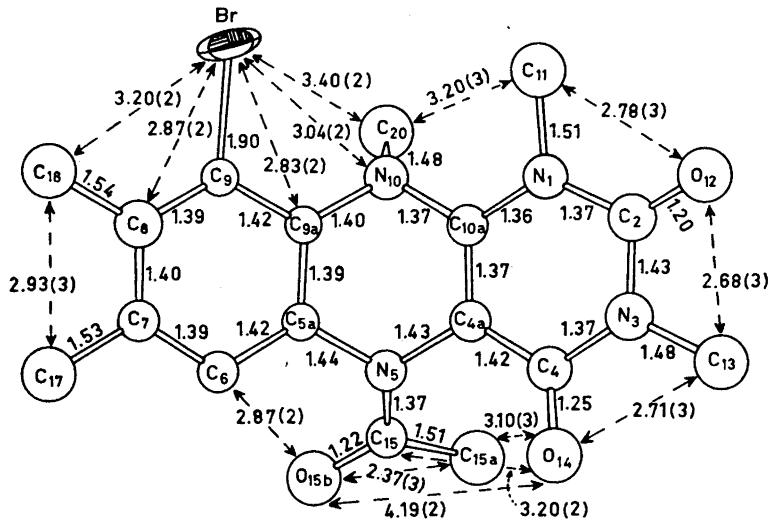
Fig. 1a. Interatomic distances (in Å) in 5-acetyl-9-bromo-1,3,7,8,10-pentamethyl-1,5-dihydroisoalloxazine.
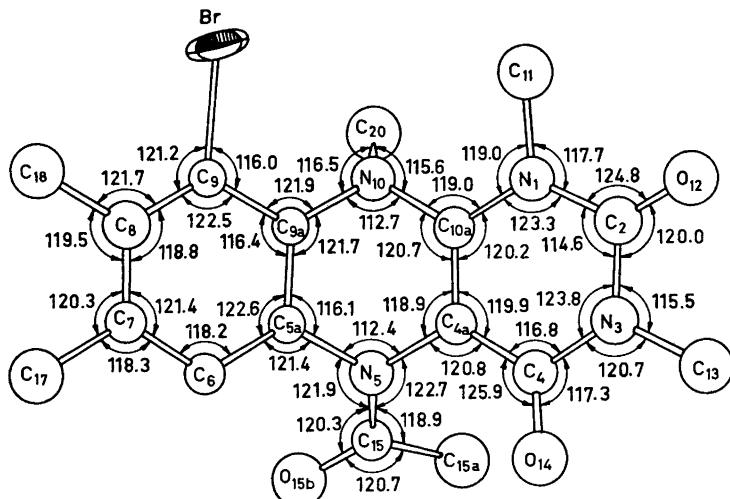
Fig. 1b. Bond angles in 5-acetyl-9-bromo-1,3,7,8,10-pentamethyl-1,5-dihydroiso-alloxazine.

in the single bonds C(7) – C(17), 1.53 Å, and C(8) – C(18), 1.54 Å, are found. The only influences from bromine which may sterically affect the molecule are the contacts Br···C(18) 3.20 Å, Br···C(20) 3.40 Å, and Br···N(10) 3.04 Å. Further information about such interactions will probably be gained from a comparison between this structure and the structure of 5-acetyl-9-bromo-1,3,7,8-tetramethyl-1,5-dihydroalloxazine. A structure determination of this compound has been started at this Institute.

The bond length C(10 a) – C(4 a), 1.37 Å, is in accordance with the generally assumed double bond in reduced flavins for this carbon-carbon contact. It is also notable that the carbon-carbonyl oxygen distances are all, within one standard deviation, equal to the expected double bond distance 1.23 Å.[10]

The small deviations from normal values in carbon-carbon single bonds adjacent to an aromatic ring, 1.53 Å,[10] carbon-carbon single bonds adjacent to a carbon-oxygen double bond, 1.516 Å,[10] aromatic carbon-carbon bonds, 1.395 Å,[10] and carbon-carbonyl oxygen double bonds are not in accordance with the relatively large standard deviations calculated for the bond lengths in the molecule. Furthermore, from the discrepancy index $R_D = 0.102$ (see above) an R value in the range $0.07 - 0.10$ should be expected from a complete anisotropic refinement if no systematic errors were present. It should be noticed that the equations used in the calculations of standard deviations are strictly valid only for random experimental errors. Therefore it might be possible that systematic errors introduced in the integrated intensities by the film scanner technique affects the standard deviations more than the positional parameters. This kind of effect obtained from a systematic error has previously been found and discussed by one of us in a paper about absorption corrections.[11]
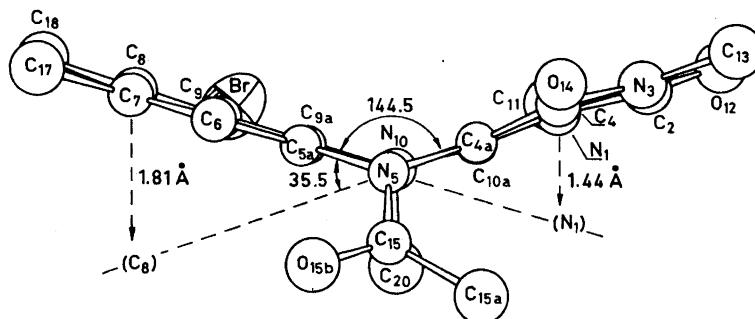
Fig. 2. The structure of 5-acetyl-9-bromo-1,3,7,8,01-pentamethyl-1,5-dihydroiso-alloxazine (rotated 90° from Fig. 1).

The deviations from unity in $\overline{w\varDelta^2}$ for stronger reflections should also be observed (*cf.* Table 2).

The angular shape of the molecule (Fig. 2) is probably due to the reduced state as proposed from spectroscopic data by Dudley, Ehrenberg, Hemmerich and Müller.[12] The atoms of the ring system lie approximately in two planes intersecting along a line between N(5) and N(10). The equations of the least

squares planes through the pyrimidine ring and benzene ring, respectively, are given in Table 5 together with the distances of the atoms from the planes. The dihedral angle between the planes is 35.5°.

Table 5. Least-squares planes.

The planes are described using a vector basis (m,n,p) having $m \| a^*$ $n \| b$ and $p \| c$.

Plane A	$-0.0721\ m + 0.4565\ n + 0.8868\ p = 8.044$
Plane B	$0.5297\ m + 0.4595\ n + 0.7129\ p = 9.222$

The angle between the planes is 35.5°.

Plane A		Plane B	
Atom	Deviation [a]	Atom	Deviation [a]
N(1)	40	N(5)	−9
C(2)	70	C(5a)	0
N(3)	− 2	C(6)	1
C(4)	−88	C(7)	18
C(4a)	40	C(8)	−19
N(5)	41	C(9)	0
N(10)	−37	C(9a)	7
C(10a)	17	N(10)	5
		Br [b]	−157

[a] Deviations are given in 10^{-3} Å.
[b] The bromine atom is not included in the least-squares plane.

The bond angles at N(5) and N(10) (Fig. 1b) indicate some s character for the lone pairs at these atoms. Oxidized flavins show an intense fluorescence with $\lambda_{max} = 530$ nm [13] which may be related to an increasing number and mobility of the π electrons in the planar form of the alloxazinium ring system.
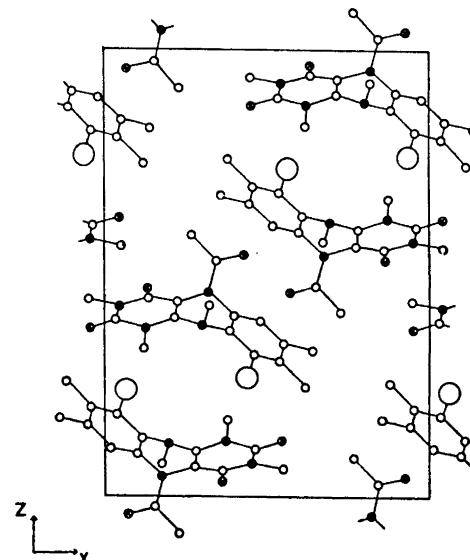
Fig. 3. Projection of the structure along the *b* axis.

The packing of the molecules projected on (010), which is parallel to the needle axis of the crystal, is shown in Fig. 3. As can be seen from this figure the growth in the stacking direction along the needle axis is not due to strong interactions between π clouds in the ring systems.

Table 6. Intermolecular distances shorter than 3.8 Å.

Br	···N(1ii)	3.59 Å
	···C(2ii)	3.43
	···N(3ii)	3.55
	···O(12ii)	3.70
N(1)	···C(13viii)	3.69
C(2)	···N(3viii)	3.61
	···C(13viii)	3.48
N(3)	···N(3viii)	3.74
	···O(12viii)	3.65
C(4)	···O(12viii)	3.70
N(5)	···C(20v)	3.79
C(6)	···O(15bix)	3.58
C(8)	···C(11iii)	3.52
	···C(15ai)	3.76
C(9)	···C(11iii)	3.65
	···O(15bi)	3.39
C(9a)	···O(15bi)	3.58
C(11)	···O(14vi)	3.48
O(12)	···C(13viii)	3.80
	···C(15aviii)	3.22
C(13)	···O(14vii)	3.31
O(14)	···C(20v)	3.44
C(15a)	···C(17ix)	3.80
	···C(18v)	3.75
O(15b)	···C(17iii)	3.68
	···C(20i)	3.30
C(17)	···C(18iv)	3.67

All intermolecular distances less than 3.80 Å are given in Table 6. It is notable that C(15a)···O(12viii), 3.22 Å, represents the closest interaction between the molecules. This distance is significantly shorter than the normal van der Waals distance, 3.40 Å,[14] between methyl carbon and oxygen. Similar shortenings of the van der Waals separation between methyl carbon and oxygen are found in other flavin compounds and is further discussed in the paper about 1,3,10-trimethylisoalloxazinium iodide.[15] A critical discussion of short $C-H\cdots O$ contacts is also given by Donohue.[16]

No hydrogen atoms are available for ordinary hydrogen bondings and therefore the molecules are held together by conventional van der Waals forces. Since no strong intermolecular forces are found in the structure it is probable that an angular shape of the molecule is characteristic also for reduced flavins in solution. Crystallographic studies started at this Institute on other reduced flavins may also give further information on this subject.

The conformation of flavin coenzymes is probably highly relevant to their mode of interaction in stereospecific enzymic reactions. In intact mithochondria for example, the cytochromes and flavoproteins occur in simple

Table 7. Observed and calculated structure factors of 5-acetyl-9-bromo-1,3,7,8,10-pentamethyl-1,5-dihydroisoalloxazine.

H	K	L	Fo	Fc
1	0	-21	21.5	18.5
4	0	-20	11.2	-12.0
2	0	-18	23.0	25.6
4	0	-18	38.4	37.6
6	0	-18	25.7	26.7
3	0	-17	22.0	18.1
7	0	-17	18.6	-22.1
4	0	-16	29.0	-28.6
6	0	-16	40.1	-39.8
1	0	-15	81.1	-65.7
7	0	-15	22.2	22.0
6	0	-14	67.1	55.4
1	0	-13	24.0	20.8
3	0	-13	47.0	41.6
2	0	-12	32.7	-26.2
4	0	-12	24.4	-20.1
6	0	-12	45.4	-40.3
1	0	-11	34.0	-28.3
3	0	-11	39.0	-35.0
5	0	-11	27.6	-21.5
7	0	-11	35.2	30.0
9	0	-11	36.5	33.2
2	0	-10	28.9	21.8
4	0	-10	110.2	90.9
6	0	-10	87.5	71.0
1	0	-9	75.3	55.2
3	0	-9	33.2	30.9
7	0	-9	37.9	-30.9
2	0	-8	69.8	-68.2
4	0	-8	109.1	-73.1
6	0	-8	15.6	-18.0
10	0	-8	25.0	26.3
1	0	-7	108.3	-83.5
3	0	-7	139.2	-101.8
5	0	-7	80.6	-56.6
9	0	-7	44.6	43.0
2	0	-6	70.7	-59.2
4	0	-6	24.1	-12.9
6	0	-6	110.6	79.7
8	0	-6	35.1	35.6
1	0	-5	213.8	154.7
3	0	-5	139.1	116.2
5	0	-5	65.6	52.8
7	0	-5	17.0	10.6
9	0	-5	55.1	-55.4
11	0	-5	64.4	-62.8
2	0	-4	36.4	9.2
4	0	-4	125.3	-85.2
6	0	-4	72.8	-58.1
8	0	-4	28.5	-31.7
10	0	-4	39.2	-36.2
12	0	-4	50.9	52.7
1	0	-3	10.6	13.1
3	0	-3	123.7	-105.7
5	0	-3	146.2	-115.6
7	0	-3	9.4	-6.1
9	0	-3	33.9	32.1
11	0	-3	70.2	71.4
2	0	-2	178.5	-154.1
4	0	-2	39.3	12.3
6	0	-2	97.1	91.9
8	0	-2	31.8	30.7
3	0	-1	65.6	62.5
5	0	-1	72.0	63.9
7	0	-1	4.4	-8.9
9	0	-1	38.8	-34.1
11	0	-1	40.3	42.0
2	0	0	54.6	145.4
4	0	0	64.6	-53.5
6	0	0	53.6	-46.1
8	0	0	56.1	-48.7
10	0	0	49.9	-47.6
12	0	0	40.9	-38.9
1	0	1	27.8	-92.2
3	0	1	121.3	-124.6
5	0	1	24.1	-25.2
7	0	1	21.8	-26.7
11	0	1	40.4	35.8
2	0	2	55.0	-98.8
4	0	2	15.2	-16.3
6	0	2	31.1	31.3
8	0	2	34.2	34.8
12	0	2	23.5	-26.1
1	0	3	63.0	-152.1
3	0	3	34.4	34.9
5	0	3	108.9	114.3
7	0	3	24.8	23.3
11	0	3	33.5	-31.3
0	0	4	28.4	-14.0
2	0	4	59.2	66.2
4	0	4	13.9	-7.9
8	0	4	45.9	-44.8
1	0	5	50.1	42.9
5	0	5	43.5	-42.9
7	0	5	73.5	-69.4
9	0	5	36.3	34.9
0	0	6	245.5	-152.8
4	0	6	44.7	-40.0
6	0	6	29.5	27.6
8	0	6	32.9	31.6
3	0	7	74.4	65.0
5	0	7	90.5	81.8
7	0	7	32.3	32.4
0	0	8	41.6	31.8
2	0	8	147.4	121.3
4	0	8	33.4	32.4
6	0	8	37.5	-42.5
1	0	9	32.7	18.0
0	0	13	80.3	-60.4
2	0	10	75.9	-59.3
6	0	10	24.0	-24.1
1	0	11	43.2	-25.1
7	0	11	41.8	41.5
2	0	12	54.6	44.3
4	0	12	43.7	31.6
1	0	13	37.4	31.9
5	0	13	71.8	-61.1
0	0	14	63.0	-53.0
2	0	14	39.1	-26.9
4	0	14	21.1	-16.0
1	0	15	24.2	-21.9
7	0	15	21.3	21.8
9	0	15	24.1	19.0
0	0	16	14.5	15.5
2	0	16	30.7	22.8
6	0	16	25.4	24.8
4	0	18	19.9	-15.0
1	0	19	27.1	-23.0
4	0	20	15.6	17.3
3	1	-21	13.6	-17.7
6	1	-20	21.6	24.4
1	1	-19	12.2	9.5
3	1	-19	15.6	16.1
5	1	-19	15.1	18.9
3	1	-17	31.0	-29.5
2	1	-16	51.1	-45.1
6	1	-16	19.7	22.3
8	1	-16	30.0	27.4
3	1	-15	20.0	20.9
5	1	-15	48.5	46.0
6	1	-15	20.9	-21.4
7	1	-15	17.5	18.5
1	1	-14	18.6	-18.3
6	1	-14	13.9	-16.6
8	1	-14	18.4	-21.8
1	1	-13	24.6	-25.1
2	1	-13	16.9	-12.1
3	1	-13	58.0	-45.0
5	1	-13	26.4	-25.6
7	1	-13	32.6	-30.9
11	1	-13	24.1	22.6
1	1	-12	16.1	13.1
2	1	-12	79.7	-63.5
3	1	-12	23.1	20.7
4	1	-12	29.4	-24.1
1	1	-11	56.8	-45.6
2	1	-11	41.7	34.2
5	1	-11	64.0	52.7
6	1	-11	10.7	-10.1
7	1	-11	26.0	24.7
2	1	-10	102.5	83.7
4	1	-10	34.5	31.1
5	1	-10	29.0	-27.6
6	1	-10	23.5	-23.6
7	1	-10	29.0	-25.4
8	1	-10	41.5	-39.0
12	1	-10	18.9	-17.6
1	1	-9	15.7	11.3
3	1	-9	27.2	-19.9
5	1	-9	16.6	-16.3
5	1	-9	73.7	-62.2
7	1	-9	31.3	26.3
7	1	-9	25.3	-22.0
13	1	-9	20.0	20.9
1	1	-8	51.4	-40.0
2	1	-8	29.0	-28.6
3	1	-8	41.4	-29.2
4	1	-8	76.6	-62.8
6	1	-8	29.1	-23.1
8	1	-8	45.5	46.0
10	1	-8	49.1	45.7
1	1	-7	56.8	-39.3
2	1	-7	80.2	55.4
3	1	-7	47.8	31.4
4	1	-7	28.0	-19.7
5	1	-7	32.7	30.5
6	1	-7	16.7	-13.1
7	1	-7	90.8	70.5
11	1	-7	20.0	-19.5
1	1	-6	19.6	4.2
2	1	-6	139.3	117.9
3	1	-6	15.5	8.9
4	1	-6	56.0	47.0
5	1	-6	56.9	42.1
6	1	-6	12.1	-10.3
8	1	-6	29.4	-25.8
9	1	-6	18.7	-17.0
10	1	-6	28.7	-29.8
11	1	-6	28.0	-27.8
1	1	-5	210.2	176.4
2	1	-5	34.7	-19.3
3	1	-5	52.1	-41.7
5	1	-5	164.6	-121.6
7	1	-5	60.0	-44.0
9	1	-5	48.3	-46.6
11	1	-5	37.6	-31.9
1	1	-4	78.9	59.4
2	1	-4	140.3	-105.8
4	1	-4	91.9	-74.5
5	1	-4	76.1	52.2
7	1	-4	48.9	31.1
8	1	-4	19.5	16.2
11	1	-4	17.6	-18.0
12	1	-4	19.8	21.3
0	1	-3	77.7	-95.1
1	1	-3	67.1	41.2
2	1	-3	10.9	5.5
3	1	-3	31.1	30.7
5	1	-3	34.5	31.1
6	1	-3	25.9	-18.2
7	1	-3	50.6	42.5
9	1	-3	21.1	25.2
11	1	-3	24.5	-21.8
12	1	-3	19.8	26.1
0	1	-2	16.8	8.6
1	1	-2	49.1	47.1
2	1	-2	62.5	63.7
3	1	-2	17.8	-21.2
4	1	-2	137.1	107.0
5	1	-2	23.0	-21.0
6	1	-2	62.9	53.7
10	1	-2	30.7	-31.7
11	1	-2	24.2	28.5
1	1	-1	92.3	134.8
2	1	-1	6.8	-3.8
3	1	-1	34.0	38.7
4	1	-1	23.5	19.1
5	1	-1	13.7	-13.2
6	1	-1	32.0	-22.6
7	1	-1	73.3	-73.9
9	1	-1	18.8	-22.4
15	1	-1	13.3	12.7
2	1	0	56.5	-77.6
3	1	0	42.1	-41.0
4	1	0	66.8	-79.3
5	1	0	21.5	-21.8
6	1	0	60.5	-60.4
7	1	0	24.5	28.5
12	1	0	23.0	23.4
1	1	1	17.7	-22.9
2	1	1	19.8	24.0
3	1	1	24.8	-15.9
4	1	1	47.9	51.2
5	1	1	17.4	13.9
7	1	1	59.9	64.5
9	1	1	44.5	44.2
11	1	1	21.4	-24.7
1	1	2	57.8	-99.2
2	1	2	89.1	147.5
3	1	2	27.9	-31.9
4	1	2	93.7	114.2
6	1	2	70.1	80.5
7	1	2	28.9	24.5
10	1	2	37.9	-39.6
0	1	3	112.1	-95.1
1	1	3	98.5	173.9
2	1	3	64.8	-88.7
3	1	3	97.4	137.4
4	1	3	24.8	-24.3
5	1	3	44.4	-52.4
6	1	3	25.8	24.8
7	1	3	19.5	-17.2
10	1	3	19.8	18.8
0	1	4	93.9	69.9
1	1	4	19.0	10.6
4	1	4	67.3	-88.0
5	1	4	28.1	-34.4
11	1	4	20.0	-20.0
0	1	5	128.2	-101.3
1	1	5	146.0	-204.6
2	1	5	36.7	37.2
3	1	5	54.7	-68.0
4	1	5	31.0	35.0
5	1	5	12.6	-13.9
6	1	5	34.1	34.4
7	1	5	29.4	32.5
9	1	5	17.0	18.0
11	1	5	30.4	31.8
1	1	6	72.3	77.1
3	1	6	39.0	47.1
4	1	6	21.8	21.5
6	1	6	43.0	45.0
7	1	6	28.7	-32.7
12	1	6	24.5	-24.0
0	1	7	13.8	14.5
2	1	7	26.8	-25.9
3	1	7	26.7	25.1
4	1	7	23.4	-25.1
5	1	7	16.1	19.1
7	1	7	15.7	-15.9
9	1	7	24.2	-26.5
0	1	8	19.7	57.7
2	1	8	34.7	-33.4
3	1	8	40.8	-41.0
4	1	8	38.8	-44.9
6	1	8	37.2	-38.8
9	1	8	21.5	21.3
11	1	8	17.8	18.8
1	1	9	35.0	29.2
2	1	9	114.0	-79.6
1	1	9	24.6	-20.9
2	1	9	24.6	-22.1
3	1	9	24.6	-22.1
5	1	9	18.7	19.6
6	1	9	15.3	-14.8
9	1	9	18.1	18.7
0	1	10	96.4	-77.5
1	1	10	15.1	-1.4
3	1	10	26.5	26.5
4	1	10	34.7	33.2
5	1	10	25.0	24.9
6	1	10	26.8	27.2
8	1	10	16.6	18.4
10	1	10	26.0	26.0
0	1	11	31.5	23.6
1	1	11	61.3	40.9
3	1	11	65.1	46.5
5	1	11	35.8	38.5
7	1	11	21.7	-21.4
0	1	12	25.4	21.8
5	1	12	20.3	-19.6
6	1	12	34.1	-28.7
8	1	12	17.5	-17.7
10	1	12	20.6	23.3
12	1	12	13.0	12.6
0	1	13	36.0	-29.6
1	1	13	24.3	-20.0
3	1	13	68.9	-49.0
0	1	14	43.0	-35.4
1	1	15	21.0	21.3
3	1	15	22.1	14.7
5	1	15	28.1	22.6
0	1	16	27.4	23.7
6	1	16	30.3	-26.4
1	1	17	37.4	-34.5
3	1	17	23.0	-20.1
0	1	18	30.6	-31.7
4	1	18	17.0	18.1
1	1	20	21.6	19.3
0	2	-21	12.4	-14.2
4	2	-20	10.4	13.5
5	2	-20	8.6	-12.5
2	2	-19	10.9	-12.5
2	2	-18	13.5	-14.3
4	2	-18	12.4	-14.7
6	2	-18	9.2	-11.5
1	2	-17	15.0	-17.3
3	2	-17	23.8	-23.0
9	2	-17	11.2	13.7
1	2	-16	9.9	11.9
2	2	-16	17.2	19.6
4	2	-16	16.9	16.5
6	2	-16	20.9	25.5
1	2	-15	66.9	64.8
2	2	-15	33.5	-34.9
3	2	-15	12.9	15.1
7	2	-15	18.0	-20.2
9	2	-15	14.1	-14.4
11	2	-15	14.0	-14.5
2	2	-14	13.4	-14.2
4	2	-14	40.1	-42.3
5	2	-14	16.7	16.9
6	2	-14	10.9	-15.5
7	2	-14	23.2	25.6
1	2	-13	22.0	-21.2
2	2	-13	40.6	-45.1
4	2	-13	29.4	31.2
6	2	-13	19.7	24.6
9	2	-13	37.5	38.8
10	2	-13	17.8	-17.9
1	2	-12	28.8	33.0
2	2	-12	26.1	22.4
4	2	-12	24.2	27.6
6	2	-12	36.7	38.0
7	2	-12	21.5	-22.4
10	2	-12	15.7	-16.6
11	2	-12	10.2	10.0
1	2	-11	74.8	76.5
2	2	-11	15.5	-14.5
3	2	-11	35.8	49.8
4	2	-11	9.6	-12.5
5	2	-11	20.5	-19.9
7	2	-11	37.5	-34.4
8	2	-11	19.2	-17.3
9	2	-11	40.5	-38.4
1	2	-10	74.9	-68.0
3	2	-10	35.8	-35.6
4	2	-10	45.7	-45.0
6	2	-10	47.5	-42.9
9	2	-10	9.2	12.3
10	2	-10	21.6	-21.0
11	2	-10	20.6	18.7
2	2	-9	86.3	-81.7
4	2	-9	26.0	21.7
4	2	-9	47.8	-47.8
5	2	-9	33.0	-34.8
6	2	-9	17.7	17.0
7	2	-9	14.8	12.5
9	2	-9	17.5	19.1
11	2	-9	28.1	27.6
12	2	-9	23.7	-20.0
13	2	-9	9.6	7.3
1	2	-8	21.9	-20.1
2	2	-8	24.7	24.6
3	2	-8	44.9	41.6

Table 7. Continued.

H	K	L	FO	FC
4	2	-8	29.3	29.6
6	2	-8	56.3	51.3
8	2	-8	38.5	39.6
12	2	-8	21.6	-21.1
14	2	-8	11.1	-8.9
1	2	-7	35.7	35.5
3	2	-7	81.5	75.7
4	2	-7	38.4	-35.3
5	2	-7	38.9	41.6
6	2	-7	14.0	-18.4
8	2	-7	17.9	14.2
11	2	-7	11.2	-11.9
1	2	-6	48.0	-41.3
2	2	-6	37.8	33.9
3	2	-6	21.4	-19.4
4	2	-6	8.5	-11.4
5	2	-6	50.4	-43.0
6	2	-6	62.9	-57.7
8	2	-6	35.8	-37.8
9	2	-6	15.7	14.1
14	2	-6	9.4	9.5
1	2	-5	51.7	-47.8
3	2	-5	59.5	-57.1
4	2	-5	8.3	-4.8
5	2	-5	17.9	11.9
6	2	-5	38.4	34.9
7	2	-5	9.2	-6.9
8	2	-5	41.6	34.4
9	2	-5	33.3	29.9
1	2	-4	10.6	15.4
2	2	-4	72.1	-60.9
3	2	-4	48.1	39.8
4	2	-4	43.6	39.2
5	2	-4	28.0	21.1
6	2	-4	43.3	42.3
7	2	-4	22.2	-18.5
8	2	-4	45.8	40.1
9	2	-4	17.7	-15.8
10	2	-4	13.2	14.3
12	2	-4	17.8	-15.6
1	2	-3	76.9	76.8
2	2	-3	23.6	20.4
3	2	-3	120.7	132.5
4	2	-3	7.9	-11.9
5	2	-3	97.5	85.4
6	2	-3	22.7	14.3
7	2	-3	27.7	-26.1
8	2	-3	15.0	14.5
9	2	-3	17.7	-14.0
11	2	-3	27.7	-24.1
13	2	-3	18.1	-14.9
1	2	-2	41.5	-44.0
2	2	-2	65.7	68.8
3	2	-2	50.2	-48.4
4	2	-2	16.7	16.9
5	2	-2	50.0	38.1
6	2	-2	87.0	-81.5
7	2	-2	14.7	11.1
8	2	-2	35.1	-30.8
9	2	-2	11.3	11.1
13	2	-2	10.2	10.3
1	2	-1	83.7	-88.5
3	2	-1	71.0	-71.8
4	2	-1	54.1	-45.4
5	2	-1	83.7	-74.5
6	2	-1	37.5	-27.3
8	2	-1	23.0	22.4
9	2	-1	29.8	25.3
11	2	-1	9.4	8.1
0	2	0	161.7	-173.9
1	2	0	28.2	18.8
2	2	0	45.8	-47.7
3	2	0	14.6	13.6
4	2	0	16.4	18.1
5	2	0	34.8	31.6
6	2	0	22.5	26.3
7	2	0	12.2	12.7
8	2	0	57.6	53.1
10	2	0	27.4	23.8
12	2	0	19.0	-21.6
14	2	0	10.3	-12.4
1	2	1	10.3	-15.1
2	2	1	56.5	56.8
3	2	1	99.4	112.7
4	2	1	34.5	-33.6
6	2	1	91.6	-85.0
7	2	1	23.1	28.9
8	2	1	26.3	-22.1
11	2	1	16.1	-15.4
12	2	1	12.2	14.2
13	2	1	9.4	-11.1
0	2	2	6.5	3.5
1	2	2	30.2	35.5
2	2	2	32.5	34.1
3	2	2	33.6	-36.0
5	2	2	24.1	-27.7
6	2	2	17.3	-18.8
7	2	2	19.5	15.6
8	2	2	16.8	-19.6
10	2	2	10.8	-8.1
12	2	2	12.1	11.4
14	2	2	16.9	15.5
0	2	3	27.2	-34.4
1	2	3	60.4	-55.7

H	K	L	FO	FC
2	2	3	9.1	-6.1
3	2	3	44.9	-48.9
4	2	3	9.4	-3.8
5	2	3	76.0	-71.1
6	2	3	14.9	19.3
7	2	3	10.2	-5.9
8	2	3	18.1	15.4
12	2	3	16.8	16.4
13	2	3	17.9	19.5
14	2	3	8.4	-10.4
0	2	4	103.7	-107.6
1	2	4	28.0	31.8
2	2	4	37.7	-46.4
3	2	4	51.8	-44.6
4	2	4	16.6	-18.6
5	2	4	13.2	-12.3
6	2	4	40.1	33.4
7	2	4	32.7	32.1
8	2	4	47.1	47.8
10	2	4	22.6	21.9
11	2	4	10.8	13.3
12	2	4	16.4	15.4
0	2	5	100.4	101.0
1	2	5	63.7	55.3
2	2	5	26.9	31.5
3	2	5	77.2	81.7
4	2	5	7.1	5.5
5	2	5	54.1	55.7
7	2	5	11.5	12.3
8	2	5	14.1	-17.6
0	2	6	76.5	76.2
1	2	6	10.9	-9.9
2	2	6	67.2	70.6
3	2	6	55.0	-54.1
4	2	6	38.9	45.5
5	2	6	35.6	-33.4
6	2	6	7.9	-7.4
7	2	6	16.9	-15.5
8	2	6	30.9	-31.3
9	2	6	9.9	-11.9
10	2	6	23.1	-22.8
11	2	6	18.0	16.3
0	2	7	24.2	19.2
2	2	7	40.0	-31.6
3	2	7	86.3	-96.6
4	2	7	7.4	14.5
5	2	7	56.5	-55.5
7	2	7	36.4	-34.6
9	2	7	12.2	12.8
10	2	7	16.5	17.9
11	2	7	29.7	28.0
13	2	7	8.0	6.3
0	2	8	14.1	12.0
1	2	8	46.4	-44.6
2	2	8	90.2	-95.9
3	2	8	18.1	16.5
4	2	8	73.6	-76.3
5	2	8	41.7	41.6
6	2	8	9.4	-6.3
7	2	8	12.5	13.4
8	2	8	12.0	13.4
0	2	9	23.3	-22.1
1	2	9	47.2	-46.6
2	2	9	19.6	16.6
3	2	9	15.9	-15.5
4	2	9	49.5	53.4
5	2	9	40.7	38.8
6	2	9	50.2	5.0
7	2	9	12.6	13.8
8	2	9	17.0	-19.9
0	2	10	84.4	76.6
1	2	10	40.2	40.0
2	2	10	60.8	58.1
3	2	10	18.8	20.2
4	2	10	33.3	29.4
5	2	10	16.4	-18.1
7	2	10	26.8	-17.0
10	2	10	16.2	-15.9
11	2	10	23.6	-23.3
12	2	10	9.2	-10.9
0	2	11	47.6	-47.6
1	2	11	12.5	11.9
2	2	11	10.0	-10.5
3	2	11	12.1	-11.5
4	2	11	10.5	-11.1
9	2	11	21.3	-23.6
12	2	11	13.6	10.4
0	2	12	32.1	-34.1
1	2	12	12.3	12.2
2	2	12	34.0	-35.7
4	2	12	14.1	-14.4
6	2	12	12.1	9.5
10	2	12	20.9	22.1
12	2	12	10.7	11.8
0	2	13	12.1	-13.0
1	2	13	24.0	-22.5
2	2	13	12.8	12.2
3	2	13	14.3	15.4
5	2	13	17.8	16.5
4	2	14	16.0	13.0
1	2	14	23.2	21.6
2	2	14	26.0	23.1
4	2	14	11.3	13.8
0	2	15	19.9	21.8

H	K	L	FO	FC
1	2	15	33.9	36.3
2	2	15	11.0	-10.8
3	2	15	10.8	-11.2
1	2	16	14.5	-13.3
2	2	16	9.3	-9.6
3	2	16	9.7	-11.7
4	2	16	15.6	-17.6
5	2	16	13.0	-14.8
1	2	17	8.9	-8.9
3	2	17	15.8	14.9
4	2	17	16.6	17.1
5	2	17	14.9	15.0
7	2	17	16.7	16.0
4	2	18	16.7	16.0
5	2	20	7.6	-10.9
1	3	-20	17.6	-18.4
2	3	-20	14.2	19.6
3	3	-19	15.5	17.1
2	3	-18	13.7	17.0
3	3	-17	19.1	24.4
5	3	-17	19.8	23.4
1	3	-16	22.6	24.6
3	3	-16	28.4	-29.2
5	3	-16	23.0	-25.3
6	3	-16	33.7	-37.2
3	3	-15	22.7	-23.7
5	3	-15	27.9	-25.9
6	3	-15	21.0	24.1
1	3	-14	32.3	29.5
5	3	-14	34.9	35.5
6	3	-14	21.7	23.2
1	3	-13	27.2	25.6
3	3	-13	29.0	-26.5
3	3	-13	43.3	38.4
5	3	-13	30.9	28.6
7	3	-13	43.5	41.2
2	3	-12	50.3	49.6
6	3	-12	41.1	-38.3
4	3	-12	44.8	44.9
3	3	-11	44.5	-42.6
5	3	-11	16.2	-18.7
5	3	-11	53.4	-54.5
7	3	-11	29.8	-31.8
2	3	-10	47.9	-47.4
3	3	-10	47.4	46.3
4	3	-10	29.4	-31.3
5	3	-10	32.9	33.1
6	3	-10	28.6	-8.8
10	3	-10	27.3	24.8
1	3	-9	51.1	-47.0
2	3	-9	33.4	30.7
3	3	-9	39.8	38.8
5	3	-9	36.4	40.4
6	3	-9	18.0	-19.5
7	3	-9	28.9	29.8
8	3	-9	29.8	-24.6
1	3	-8	22.7	-21.2
2	3	-8	76.5	66.0
3	3	-8	17.6	-17.9
4	3	-8	75.1	64.9
5	3	-8	49.7	-49.5
6	3	-8	35.6	-31.0
11	3	-8	19.1	19.6
1	3	-7	50.9	49.1
3	3	-7	49.9	-46.4
4	3	-7	15.0	-12.2
4	3	-7	25.7	-25.7
5	3	-7	39.5	-34.4
7	3	-7	40.8	-34.4
10	3	-7	23.6	21.3
2	3	-6	39.7	-36.7
3	3	-6	94.4	-92.8
4	3	-6	40.4	-37.9
10	3	-6	27.1	21.8
1	3	-5	50.4	-53.6
2	3	-5	22.6	21.2
3	3	-5	18.4	-18.8
6	3	-5	13.3	8.1
7	3	-5	24.4	23.0
9	3	-5	30.6	27.1
1	3	-4	34.2	30.3
2	3	-4	58.2	54.7
3	3	-4	24.6	-24.1
4	3	-4	66.4	65.7
5	3	-4	43.2	-39.3
6	3	-4	50.8	49.7
7	3	-4	58.6	-46.9
1	3	-3	47.1	39.8
2	3	-3	38.4	-37.0
3	3	-3	55.3	10.1
4	3	-3	25.8	-25.9
5	3	-3	13.7	-14.8
6	3	-3	29.7	-28.6
7	3	-3	39.3	-35.8
10	3	-3	30.8	28.7
11	3	-3	22.1	23.1
1	3	-2	61.1	-57.0
3	3	-2	43.1	-43.2
3	3	-2	15.8	10.9
4	3	-2	40.0	-40.2
5	3	-2	27.9	26.5
6	3	-2	24.6	-18.7
1	3	-1	94.9	-98.2
2	3	-1	39.4	38.9

H	K	L	FO	FC
4	3	-1	43.7	39.2
5	3	-1	49.1	44.7
6	3	-1	16.9	20.7
7	3	-1	38.7	39.4
9	3	-1	26.4	22.9
1	3	0	73.4	72.1
3	3	0	28.1	25.2
4	3	0	39.1	40.9
5	3	0	41.1	-41.5
6	3	0	9.5	-8.0
8	3	0	26.1	-21.9
10	3	0	26.8	-22.6
0	3	1	9.1	4.1
1	3	1	56.9	55.6
2	3	1	15.8	16.6
4	3	1	37.0	38.9
5	3	1	55.6	-55.6
4	3	1	14.4	-12.7
6	3	1	28.5	-27.8
7	3	1	32.0	-39.2
9	3	1	28.7	-26.9
0	3	2	37.8	-35.8
1	3	2	43.7	-39.6
2	3	2	82.7	-103.0
3	3	2	12.5	8.8
4	3	2	62.0	-66.1
6	3	2	47.6	-45.4
10	3	2	19.6	20.8
12	3	2	34.7	32.2
0	3	3	45.2	-39.6
1	3	3	35.8	-41.5
2	3	3	13.2	14.3
3	3	3	39.8	-45.5
4	3	3	24.9	25.7
6	3	3	17.2	19.9
7	3	3	23.0	24.1
9	3	3	19.1	22.2
0	3	4	8.7	-9.1
1	3	4	63.8	72.6
3	3	4	48.8	57.7
4	3	4	24.3	24.6
5	3	4	47.1	44.8
6	3	4	23.1	-31.4
7	3	4	20.2	-19.2
0	3	5	59.9	48.5
1	3	5	102.3	102.3
2	3	5	18.1	15.1
3	3	5	20.5	23.9
4	3	5	13.9	-16.3
5	3	5	20.7	-23.3
6	3	5	33.2	-41.7
7	3	5	37.0	-47.2
9	3	5	27.5	-23.6
0	3	6	104.4	94.8
1	3	6	25.7	-25.7
2	3	6	33.4	-32.0
3	3	6	17.4	-19.1
4	3	6	40.8	-41.5
9	3	6	23.3	20.5
0	3	7	16.5	-14.2
1	3	7	74.7	-75.0
3	3	7	23.0	-21.5
5	3	7	19.0	17.3
7	3	7	25.0	24.0
8	3	7	25.4	29.3
0	3	8	9.5	-15.1
1	3	8	18.0	20.9
2	3	8	21.2	20.0
3	3	8	34.0	32.0
6	3	8	39.2	39.7
7	3	8	20.7	18.9
0	3	9	41.9	33.3
1	3	9	32.2	30.9
2	3	9	24.5	20.7
3	3	9	47.6	48.8
9	3	9	22.6	-21.2
11	3	9	18.8	-16.1
1	3	10	27.7	-31.1
3	3	10	30.4	-27.9
4	3	10	37.9	-35.9
5	3	10	22.1	-25.1
7	3	10	21.2	18.1
8	3	10	20.9	-20.8
0	3	11	24.4	-22.5
1	3	11	27.1	-26.5
3	3	11	20.1	-20.8
5	3	11	36.9	-38.0
6	3	11	55.7	95.3
8	3	11	32.4	-30.4
3	3	12	17.3	15.0
6	3	12	36.3	30.4
9	3	12	20.0	-18.6
1	3	13	23.1	25.4
3	3	13	28.3	25.1
5	3	13	18.1	18.4
0	3	14	46.0	46.7
4	3	14	26.4	-26.3
0	3	15	21.1	-20.6
1	3	15	20.3	-18.0
2	3	15	20.7	-21.7
3	3	15	33.1	-33.8
5	3	16	14.8	15.5
2	3	19	13.7	-16.9

Table 7. Continued.

H	K	L	FO	FC		H	K	L	FO	FC		H	K	L	FO	FC		H	K	L	FO	FC
0	3	20	18.5	-20.1		11	4	-1	17.1	-16.3		3	5	-12	33.5	25.2		5	6	-14	18.8	18.6
1	4	-19	20.6	-21.0		0	4	0	89.6	83.6		4	5	-12	33.8	-26.8		4	6	-13	32.5	31.8
2	4	-19	20.5	23.2		1	4	0	82.6	-69.4		5	5	-12	25.6	25.7		6	6	-13	13.2	15.2
4	4	-19	13.1	17.6		2	4	0	63.7	55.8		1	5	-11	38.8	-30.3		1	6	-12	26.6	25.2
2	4	-18	26.7	25.4		3	4	0	45.1	-43.1		2	5	-11	39.7	34.8		4	6	-12	14.5	14.8
4	4	-18	18.5	20.0		6	4	0	20.1	-20.8		4	5	-11	21.4	19.1		7	6	-12	14.8	-22.0
6	4	-18	11.9	13.7		8	4	0	23.8	-18.7		6	5	-11	33.4	-32.1		3	6	-11	18.5	19.2
3	4	-17	18.4	21.1		10	4	0	15.6	-17.6		2	5	-10	31.8	26.8		4	6	-11	32.1	-27.9
4	4	-17	12.3	-18.2		0	4	1	103.2	-90.8		5	5	-10	36.7	-32.1		6	6	-11	23.4	-21.5
7	4	-17	17.8	-18.3		1	4	1	14.2	10.8		1	5	-9	35.1	29.3		1	6	-10	40.1	-34.0
1	4	-16	12.5	-15.4		2	4	1	52.9	-47.4		2	5	-9	36.5	-31.7		3	6	-10	35.5	-28.4
4	4	-16	31.2	-30.7		3	4	1	51.1	-50.7		1	5	-8	27.4	22.0		6	6	-10	16.7	-19.9
6	4	-16	13.7	-16.4		4	4	1	17.6	20.3		2	5	-8	32.4	-28.4		3	6	-9	22.8	-21.2
7	4	-16	11.8	17.1		5	4	1	26.0	-28.9		4	5	-8	39.5	-38.0		4	6	-9	32.7	27.8
3	4	-15	30.7	-29.3		6	4	1	24.0	22.9		7	5	-8	29.1	26.5		6	6	-9	32.5	33.6
9	4	-15	13.0	16.6		8	4	1	25.9	22.8		2	5	-7	51.0	48.3		1	6	-8	46.8	35.1
1	4	-14	34.8	32.5		10	4	1	22.0	19.9		4	5	-7	27.7	19.8		3	6	-8	25.3	25.9
5	4	-14	18.6	-19.0		0	4	2	78.9	-60.6		5	5	-7	64.1	51.5		6	6	-7	28.6	-29.2
6	4	-14	20.6	22.8		2	4	2	42.9	-41.3		7	5	-7	41.2	30.8		1	6	-6	46.9	-40.2
8	4	-14	13.1	14.6		3	4	2	45.3	51.2		1	5	-6	47.4	40.3		3	6	-6	48.2	-35.8
1	4	-13	18.4	18.2		5	4	2	58.9	56.6		4	5	-6	28.5	23.5		4	6	-5	37.5	33.0
2	4	-13	14.3	-16.3		6	4	2	53.5	47.0		5	5	-6	43.4	-41.2		1	6	-4	33.3	29.9
3	4	-13	19.9	22.8		7	4	2	12.6	15.9		7	5	-6	26.1	-25.3		3	6	-4	57.2	50.6
5	4	-13	38.5	34.9		11	4	2	29.3	-23.9		1	5	-5	47.8	43.4		2	6	-3	34.5	29.6
7	4	-13	14.0	-15.3		0	4	3	25.2	-15.7		2	5	-5	72.5	-55.6		3	6	-3	40.6	37.5
9	4	-13	17.7	-16.5		1	4	3	38.2	32.3		4	5	-5	29.0	-26.5		4	6	-3	40.1	33.9
1	4	-12	32.3	-35.5		2	4	3	47.9	41.2		5	5	-5	26.6	-25.1		6	6	-3	40.3	-33.3
2	4	-12	20.2	-19.1		4	4	3	51.4	48.7		6	5	-5	44.3	38.1		2	6	-2	40.0	30.1
4	4	-12	16.3	-19.3		5	4	3	45.7	48.4		7	5	-5	33.5	-27.6		4	6	-2	35.8	-37.2
6	4	-12	44.8	-39.5		11	4	3	14.7	-14.4		1	5	-4	38.3	-33.3		5	6	-2	61.4	-51.3
7	4	-12	21.7	20.1		0	4	4	67.1	61.3		2	5	-4	43.5	-33.7		6	6	-2	54.6	-43.7
1	4	-11	53.8	-47.8		1	4	4	14.5	12.0		3	5	-4	30.6	26.1		7	6	-2	32.8	27.2
3	4	-11	16.2	-18.6		2	4	4	24.2	27.4		5	5	-4	54.7	49.8		2	6	-1	29.4	-31.3
5	4	-11	32.3	24.1		4	4	4	16.1	-22.6		6	5	-4	38.5	-34.2		3	6	-1	44.7	-37.5
4	4	-11	21.7	21.6		5	4	4	31.0	-30.0		7	5	-4	34.2	32.0		6	6	-1	35.1	35.8
11	4	-11	13.8	14.1		6	4	4	22.5	-29.8		1	5	-3	34.7	-34.1		0	6	0	36.1	-31.1
1	4	-10	29.3	24.4		7	4	4	35.5	-34.3		2	5	-3	37.8	37.4		1	6	0	24.3	22.6
4	4	-10	56.8	49.5		0	4	5	62.7	-53.6		4	5	-3	28.6	26.4		3	6	0	20.0	21.5
5	4	-10	30.0	-28.2		1	4	5	14.0	14.9		7	5	-3	38.6	30.4		0	6	1	55.2	45.3
7	4	-10	14.9	-19.6		2	4	5	28.4	-31.5		2	5	-2	30.8	31.5		1	6	1	22.7	21.2
1	4	-9	33.1	30.2		3	4	5	25.6	-23.1		3	5	-2	23.7	19.1		2	6	1	26.8	24.0
3	4	-9	45.7	40.1		5	4	5	10.9	-8.0		6	5	-2	32.5	34.3		4	6	1	28.5	-31.4
4	4	-9	60.7	-58.1		6	4	5	16.4	-17.5		6	5	-2	23.3	26.6		3	6	2	25.9	-28.1
5	4	-9	22.5	22.7		7	4	5	22.1	-28.2		7	5	-2	32.9	-28.5		4	6	2	18.0	28.0
6	4	-9	26.3	-24.7		0	4	6	49.3	-48.1		1	5	-1	20.6	22.4		0	6	2	44.8	-43.5
2	4	-8	27.7	20.4		1	4	6	18.0	-20.9		2	5	-1	47.1	-49.1		1	6	3	19.8	-21.0
4	4	-8	20.9	-19.9		2	4	6	35.7	-39.3		4	5	-1	56.0	-51.4		3	6	3	27.2	-28.4
5	4	-8	22.2	20.5		3	4	6	11.0	9.5		5	5	-1	52.9	-48.2		6	6	3	20.9	28.4
6	4	-8	40.6	-33.9		4	4	6	18.6	23.2		6	5	-1	31.3	-29.6		0	6	4	25.6	-22.1
7	4	-8	19.0	21.0		5	4	6	16.3	-19.9		2	5	0	45.6	-43.3		3	6	4	22.1	23.3
8	4	-8	24.3	-22.3		7	4	6	25.9	27.2		3	5	0	23.2	-19.9		4	6	4	15.3	21.1
9	4	-8	16.1	18.0		8	4	6	17.9	16.4		4	5	0	52.0	-51.2		5	6	4	43.7	39.0
1	4	-7	14.4	-16.8		0	4	7	18.5	17.0		7	5	0	25.5	23.5		6	6	4	11.1	22.0
3	4	-7	53.8	-51.2		2	4	7	45.4	40.7		1	5	1	32.1	-30.0		0	6	5	41.1	36.5
4	4	-7	25.8	19.9		3	4	7	23.3	29.3		2	5	1	30.5	25.3		3	6	5	28.0	25.9
5	4	-7	72.9	-62.0		5	4	7	25.2	28.6		3	5	1	15.3	-13.3		2	6	7	33.7	-33.3
6	4	-7	41.7	32.4		7	4	7	37.3	40.0		4	5	1	32.9	40.8		0	6	9	34.9	33.3
11	4	-7	14.1	15.7		0	4	8	33.7	35.6		6	5	1	48.5	45.8		0	6	10	25.2	21.2
1	4	-6	79.0	67.4		1	4	8	19.0	17.0		0	5	2	32.5	-29.9		7	6	10	14.6	-20.0
2	4	-6	23.4	-16.7		2	4	8	33.3	36.1		1	5	2	34.3	31.9		1	6	12	23.1	-29.9
3	4	-6	34.3	31.8		4	4	8	18.1	24.5		2	5	2	27.7	29.7		0	6	13	18.5	20.8
5	4	-6	34.8	34.2		5	4	8	21.6	-24.4		3	5	2	18.6	13.1		0	6	14	18.0	19.8
6	4	-6	60.0	51.7		6	4	8	18.8	-15.3		4	5	2	38.1	41.8		0	6	16	13.7	-14.7
7	4	-6	26.6	-22.5		7	4	8	23.9	22.8		6	5	2	59.4	49.2		3	7	-12	23.7	-20.2
9	4	-6	32.6	-31.2		0	4	9	31.8	-32.7		7	5	2	24.4	-25.9		7	7	-12	22.6	23.1
5	4	-5	16.5	11.3		1	4	9	19.4	16.9		0	5	3	35.4	31.1		5	7	-10	20.6	26.2
3	4	-5	19.5	21.3		2	4	9	32.9	-35.6		1	5	3	41.5	44.3		2	7	-9	29.8	27.8
4	4	-5	43.3	-38.2		3	4	9	16.9	-14.2		2	5	3	29.2	-28.8		5	7	-8	24.1	-25.3
5	4	-5	30.2	28.7		4	4	9	30.1	-37.1		3	5	3	37.2	37.8		7	7	-8	27.1	-22.1
6	4	-5	36.3	-35.4		5	4	9	52.1	-56.6		4	5	3	49.1	-48.4		2	7	-7	52.4	-42.1
8	4	-5	32.8	-33.9		0	4	10	42.7	-37.8		5	5	3	27.1	-28.7		7	7	-7	30.4	-22.7
9	4	-5	36.5	-32.1		1	4	10	19.7	-18.0		6	5	4	66.7	-62.3		1	7	-6	40.5	-36.0
4	4	-4	33.4	-28.0		2	4	10	44.1	-39.5		3	5	4	40.3	-50.2		3	7	-5	31.2	-23.0
2	4	-4	20.7	19.1		6	4	10	23.2	30.1		4	5	4	22.6	29.4		4	7	-3	23.4	21.7
3	4	-4	60.9	-60.7		7	4	10	19.2	14.8		6	5	4	14.2	-21.4		4	7	-3	23.0	-25.9
4	4	-4	17.1	-18.5		8	4	10	23.0	17.3		0	5	5	43.9	-18.6		3	7	-3	26.8	-23.4
5	4	-4	27.4	-29.6		1	4	11	14.1	-13.2		1	5	5	40.2	-37.1		7	7	-1	19.4	23.1
8	4	-4	25.3	-21.4		2	4	11	24.3	21.8		5	5	6	28.9	30.9		1	7	0	32.4	32.6
11	4	-4	29.4	31.2		3	4	11	25.7	23.6		6	5	6	25.8	30.6		4	7	1	17.3	-24.5
6	4	-3	60.2	-47.0		0	4	12	28.0	28.7		3	5	6	28.7	27.7		1	7	2	32.6	-44.7
1	4	-3	75.9	-69.6		1	4	12	26.8	27.7		5	5	6	15.6	24.4		7	7	2	20.2	-18.0
3	4	-3	27.8	28.9		2	4	12	25.9	29.5		6	5	6	24.9	-27.3		3	7	2	32.6	38.1
5	4	-3	33.8	-32.2		2	4	13	15.1	-17.3		0	5	7	31.8	30.7		4	7	3	16.4	23.7
6	4	-3	35.0	34.1		4	4	13	15.4	-13.7		1	5	7	18.9	26.5		4	7	3	34.2	29.7
9	4	-3	17.9	19.0		5	4	13	20.6	-18.1		3	5	7	18.8	22.6		5	7	5	20.0	-18.4
11	4	-3	21.9	19.6		7	4	13	23.1	-31.1		5	5	7	39.2	-41.7		5	7	7	31.4	-35.2
13	4	-3	17.2	13.6		0	4	14	22.5	-23.9		6	5	7	21.9	-28.1		0	7	7	22.8	-26.6
2	4	-2	43.4	-36.3		1	4	14	21.2	-20.5		3	5	8	32.7	-33.1		1	7	8	44.9	46.8
3	4	-2	56.8	55.5		2	4	14	16.0	-16.3		6	5	8	10.8	-23.9		1	7	8	16.8	19.7
4	4	-2	20.4	18.5		3	4	14	15.0	-15.0		0	5	9	38.6	-36.4		0	7	9	36.5	29.1
5	4	-2	38.8	36.2		4	4	14	20.1	-18.8		0	5	11	29.5	28.2		3	7	10	29.5	-25.1
6	4	-2	24.6	25.8		9	4	15	12.9	16.1		0	5	13	29.7	-24.2		0	7	11	20.7	-21.1
8	4	-2	22.7	22.6		1	4	16	24.5	21.8		0	5	14	24.9	-26.7		0	7	13	22.5	21.7
9	4	-2	16.4	-17.8		6	4	16	16.1	19.2		3	5	14	16.1	19.2		1	8	-6	24.7	23.9
1	4	-1	34.6	29.4		2	5	-16	17.7	-22.1		5	5	17	29.4	-29.0		3	8	-6	24.3	-22.4
2	4	-1	49.4	48.6		3	5	-16	14.2	17.4		0	5	18	10.7	-14.1		4	8	-4	34.3	-27.3
3	4	-1	47.4	41.4		6	5	-15	17.7	-18.2		1	6	-15	22.4	20.9		1	8	-2	22.8	16.4
4	4	-1	27.0	5.8		3	5	-14	28.8	-24.2		2	6	-15	25.3	-22.6		3	8	-2	20.9	25.9
5	4	-1	34.6	31.8		4	5	-14	15.4	20.6		3	6	-15	30.4	23.6		0	8	1	27.1	-28.2
6	4	-1	36.2	-33.7		5	5	-14	18.6	-22.5		4	6	-15	22.6	-22.3		3	8	2	28.8	27.9
7	4	-1	18.9	17.1		7	5	-13	19.9	-21.9		1	6	-14	25.9	-23.8		0	8	3	24.4	27.8
8	4	-1	32.7	-31.2																		

molar ratios to each other. This finding has led to the concept of the respiratory assembly, *i.e.*, an organized macromolecular assembly made up of one molecule of each component in a geometry favorable to their interaction.[17] A conformational change from a planar, oxidized alloxazinium ring system [1] of the magnitude found in the present structure corresponds to a transport of N(1) 1.44 Å out of a plane through the benzene ring or a transport of C(8) 1.81 Å out of a plane through the pyrimidine ring (Fig. 2). Such changes should be of vital importance not only for coenzyme-apoenzyme bindings but also for internal complexing in the coenzymes FAD (flavin-adenine dinucleotide) and FMN (flavin mononucleotide).

In the case of a complete two-electron oxidation followed by a two-electron reduction it might be a 50 % probability for the molecule to return to its initial state. This is because of the occurrence of two isomeric forms obtained from different bending directions through the N(5)···N(10) axis as can be seen from Fig. 3. This might be an argument against non-stereospecific two-electron transfer in some flavoproteins taking part in reversible biological redox processes. However, when the alloxazinium system is bound to a greater unit of an enzyme one of the two reduced isomers may be preferred or even the only one possible to form. It is also possible that for some enzymatic reactions the type of substrate utilized is dependent on which of the two isomeric forms of the reduced flavin that is present. It should, however, be realized that no definite conclusion can be drawn from a model compound of this size in crystalline state.

Summarily the oscillation of the alloxazinium plane at the N(5)···N(10) axis may facilitate electron transfer, hydride ion transfer or detachment processes in different redox enzymes. It may also play an important role in energy conserving mechanisms.

REFERENCES

1. Kierkegaard, P., Leijonmarck, M., Norrestam, R., Torbjörnsson, L. and Werner, P.-E. *Acta Chem. Scand.* **23** (1969) 2197.
2. Abrahamsson, S. *J. Sci. Instr.* **43** (1966) 931.
3. Werner, P. E. *Arkiv Kemi.* **31** (1969) 505.
4. Werner, P. E. *Acta Cryst. To be published.*
5. Univ. Stockholm, Inorg. Chem., DIS No. 32 (1968), p. 13.
6. *IUCr World List of Crystallographic Computer Programs*, 2nd Ed., Cambridge, Mass. 1966, No. 384.
7. Hughes, E. W. *J. Am. Chem. Soc.* **63** (1941) 1737.
8. Freeman, A. J. *Acta Cryst.* **12** (1959) 261.
9. Cromer, D. T. and Waber, J. T. *Acta Cryst.* **18** (1965) 104.

10. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1962.
11. Werner, P. E. *Acta Chem. Scand.* **18** (1964) 1851.
12. Dudley, K. H., Ehrenberg, A., Hemmerich, P. and Müller, F. *Helv. Chim. Acta* **47** (1964) 1354.
13. Radda, G. K. and Dodd, G. H. In Bowen, E. J. *Luminiscence in Chemistry*, Chapter 10, Van Nostrand, London 1968.
14. Pauling, L. *The Nature of the Chemical Bond*, 3rd Ed., Cornell Univ. Press, Ithaca 1960, p. 260.
15. v. Glehn, M., Kierkegaard, P., Norrestam, R., Rönnquist, O. and Werner, P.-E. *To be published*.
16. Donohue, J. In Rich, A. and Davidson, N. *Structural Chemistry and Molecular Biology*, Freeman, San Francisco 1968, p. 443.
17. Lehninger, A. L. *The Mitochondrion*, Benjamin, New York 1965, p. 57.