

Studies on Flavin Derivatives

The Crystal Structure of 5-Diethyl-3,7,8,10-tetramethyl-1,5-dihydroisoalloxazine Trihydrate

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The crystal structure of 5-diethyl-3,7,8,10-tetramethyl-1,5-dihydroisoalloxazine trihydrate, $C_{18}H_{24}N_4O_2 \cdot 3H_2O$, has been determined and refined from three-dimensional X-ray film data. The crystals are orthorhombic with space group *Pccn*. The unit cell dimensions are $a = 10.578$, $b = 20.68$, and $c = 18.46$ Å.

The molecule forms a zwitterion, and the atoms of the ring system lie close to two planes intersecting along a line between N(5) and N(10). The dihedral angle between the planes is 8.9° . Discussions are given of systematic and statistical errors in the film scanner technique used for the data collection, and of the structure.

The determination of the structure of 5-diethyl-3,7,8,10-tetramethyl-1,5-dihydroisoalloxazine trihydrate, $C_{18}H_{24}N_4O_2 \cdot 3H_2O$, was undertaken as part of a series of structure determinations of flavin compounds. The primary aim of the present study has been to examine the molecular conformation and bonding system in a quaternary leucoflavin. The molecule has a canonical form, in which a formal negative charge at N(1) and a formal positive charge at N(5) (*cf.* Fig. 1) constitute a zwitterion.

EXPERIMENTAL

The studies were carried out on yellow single crystals selected from material kindly provided by P. Hemmerich, University of Konstanz.

Preliminary rotation and Weissenberg photographs indicated orthorhombic symmetry. Systematic absences for $0kl$ and $h0l$ reflections with l odd and for $hk0$ reflections with $h+k$ odd indicated the space group to be *Pccn*. The 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 given in Table 1.

Two crystals, A: $0.035 \times 0.128 \times 0.544$ mm³, and B: $0.080 \times 0.192 \times 0.272$ mm³, were used for the collection of X-ray diffraction data. Multiple-film (three) equi-inclination

Table 1. Crystal data.

Lattice constants ¹	$a = 10.578(5) \text{ \AA}$ $b = 20.68 (2) \text{ \AA}$ $c = 18.46 (2) \text{ \AA}$
Cell volume	$V = 4038.2 \text{ \AA}^3$
Density (X-Ray)	$d = 1.259 \text{ g/cm}^3$
Analysis	C 56.7; H 7.6; N 14.6 % Calc. for $C_{18}N_4H_{24}O_3 \cdot 3H_2O$ C 56.5; H 7.9; N 14.7; O 20.9 %
Molecules per unit cell	$Z = 8$
Absent reflections	$0kl$ with $l = 2n + 1$ $h0l$ with $l = 2n + 1$ and $hk0$ with $h + k = 2n + 1$
Space group	$Pccn$
General position	$\pm [x, y, z; \frac{1}{2} - x, \frac{1}{2} - y, z; \bar{x}, \frac{1}{2} + y, \frac{1}{2} - z; \frac{1}{2} + x, \bar{y}, \frac{1}{2} - z]$

Weissenberg photographs were taken with $CuK\alpha$ radiation and Ilford Industrial G X-ray film. The films were developed in Ilford Phenisol X-ray developer for 4 min at 22–23°C, and fixed 30 min in $Na_2S_2O_5$.

1485 independent values of $I(hkl)$ were measured by an automatic SAAB film scanner² on-line to an IBM 1800 process controller. Integrated intensities for all spots with a relative optical density D' ($=^{10}\log(\text{background transmission/peak transmission})$) in the range $0.07 < D' < 1.4$ were calculated.³ The cross section of the light beam used was $60 \mu\text{m} \times 90 \mu\text{m}$, and about 80 % of the integrated spots contained 40–100 individual density readings (*i.e.* spot size = 0.20–0.50 mm^2).

The layers $0kl - 6kl$ (crystal A) and $h0l - h9l$ (crystal B) were correlated by the method of Monahan, Schiffer and Schiffer⁴ after corrections for Lorentz and polarisation effects. No corrections for absorption ($\mu = 7.5 \text{ cm}^{-1}$) were made.

Mutual agreement factors defined as $R_M = \sum(|F_{ikl}| - |F_{hjl}|) / 0.5 \sum(|F_{ikl}| + |F_{hjl}|)$, where ikl and hjl denote overlaps, *i.e.* equivalent reflections from different crystals, were calculated (see Table 2). R_M for all 465 overlaps between reflections from the two crystals was 0.069. The R_M -values 0.113 and 0.126 for the $h0l$ and $h1l$ layers indicate somewhat larger errors in these layers than in the others. They were therefore excluded and the remaining layers were rescaled. The recalculated R_M -values obtained are shown in Table 3. The final total R_M for 390 overlaps from the two crystals A and B was 0.058, and the number of independent reflections was then 1439.

Table 2. Number of overlaps and mutual agreement factors,

$$R_M = \sum(|F_{ikl}| - |F_{hjl}|) / 0.5 \sum(|F_{ikl}| + |F_{hjl}|),$$

between structure factors obtained from different rotation axes (a and b).

		$h =$								
		0	1	2	3	4	5	6		
$k =$	0	5	5	4	2	5	4	4	$R_M =$	
	1		11	9	7	10	3	6		0.113
	2	14	12	14	7	8	9	10		0.081
	3		14	15	12	13	8	10		0.050
	4	7	14	11	7	7	7	6		0.052
	5		9	9	8	9	4	2		0.052
	6	7	11	9	8	4	7	2		0.046
	7		6	7	8	6	2	5		0.052
	8	4	10	6	7	4	2	3		0.076
	9		6	5	6	5	2	2		0.041
$R_M =$		0.050	0.080	0.062	0.067	0.078	0.077	0.062		

Table 3. Number of overlaps and mutual agreement factors,

$$R_M = \sum | |F_{ikh}| - |F_{hjl}| | / 0.5 \sum (|F_{ikh}| + |F_{hjl}|),$$

between structure factors obtained from different rotation axes (*a* and *b*). The data sets F_{hol} and F_{hkl} excluded.

		<i>h</i> =							
		0	1	2	3	4	5	6	
<i>k</i> =	2	14	12	14	7	8	9	10	$R_M = 0.081$
	3		14	15	12	13	8	10	0.050
	4	7	14	11	7	7	7	6	0.049
	5		9	9	8	9	4	2	0.051
	6	7	11	9	8	4	7	2	0.047
	7		6	7	8	6	2	5	0.050
	8	4	10	6	7	4	2	3	0.073
	9		6	5	6	5	2	2	0.040
		$R_M =$	0.050	0.071	0.045	0.054	0.064	0.065	0.091

DETERMINATION AND REFINEMENT OF THE STRUCTURE

Attempts to solve the structure by molecular packing technique were unsuccessful, although it was later found that the indicated position and orientation of the isoalloxazine ring system were rather accurately deduced. The structure was solved by direct methods.

A set of 75 signs for $E > 1.5$ was determined by the Sayre equation.⁵ 151 more signs were generated, using the Hauptman-Karle sigma two relationship.⁶ This was accomplished by the program MAGIC, written by R. B. K. Dewar and A. L. Stone at the University of Chicago, and modified by R. Karlsson, University of Stockholm, for the computer IBM 360/75. An E-map computed with these 226 terms revealed 20 non-hydrogen atoms in the asymmetric unit. By four successive F_o -syntheses all the non-hydrogen atoms were found.

Initial least-squares refinement was carried out with a block-diagonal matrix program (SFLS, written by S. Åsbrink, University of Stockholm, and C.-I. Brändén, University of Uppsala, modified by B. G. Brandt at this Institute). A full-matrix program (LALS, originally written by Gantzel, Sparks and Trueblood,⁷ and modified by R. Liminga, J.-O. Lundgren and C.-I. Brändén, University of Uppsala) was used in later stages. The scattering factor curves used for oxygen, carbon, and nitrogen were those given by Freeman,⁸ and for hydrogen that of Stewart, Davidson and Simpson.⁹ The least-squares programs used minimize the function $\sum w(|F_o| - |F_c|)^2$. Anisotropic refinement of all non-hydrogen atoms gave an R ($= \sum (|kF_o| - |F_c|) / \sum |kF_o|$) of 0.146. For eight atoms, positive-definite temperature factors were not obtained. In view of the low R_M -value, 0.058, this was not considered satisfactory.

The result initiated a search for systematic errors in the data collection technique used. The average film factor was 2.27 ± 0.05 , far from the value 2.9 given by Morimoto and Uyeda¹⁰ for Ilford Industrial G film. Small but significant slopes in film factors plotted as a function of intensity were also noted.¹¹ Through use of wedges from different crystals (*i.e.* different spot sizes) it was found that correct intensities, regardless of spot size, were obtained if

the relative optical densities D' ($=^{10}\log$ (background transmission/spot transmission)), used in the spot integration procedure,³ were corrected by the formula $D_{\text{corr}} = D'(1 + 0.5 D')$. Interestingly, this is identical to the equation proposed by Mammi, Bardi and Bezzi,¹² who claim that X-ray film is non-linear even below optical density 1.0. It cannot be excluded, however, that the equation partly compensates for a hardware error in the photomultiplier. The equation also explains why the use of uncorrected D' -values have relatively little influence on integrated intensities measured from precession photographs and integrated Weissenberg photographs. In these cases, large differences in integrated intensities can be measured from relatively small differences in optical densities. It may also be mentioned that the equation has been successfully used in the structure determination of 5-acetyl-9-bromo-1,3,7,8-tetra-methyl-1,5-dihydroisalloxazine.¹³

In order to refine the present structure and to prove the statement that the high R -value 0.146 and the physically impossible temperature factors were caused by systematic rather than statistical errors, the following technique was used.

It was assumed that a single function, $I_{\text{corr}} = f(I_{\text{obs}})$, applicable to all films, exists. This should be approximately true because of the relatively small differences in spot size for these crystals (see above). Then, using the average measured film factor 2.27 and a corrected film factor 2.7, one may write $2.7f(I_{\text{obs}}) = f(2.27 I_{\text{obs}})$. This should hold for any I_{obs} . Hence

$$2.7f(2.27^{n-1} I_{\text{obs}}) = f(2.27^n I_{\text{obs}})$$

Iterations with $n=1$ to 9, beginning with I_{corr} set equal to I_{obs} for the smallest measured I_{obs} , were performed to cover the complete range of observed intensities. The I_{obs} were approximated as F_o^2 . Thus, no explicit expression for the function $f(I_{\text{obs}})$ was introduced. Because of the unequal intervals determined for the function, all intensities (F_o^2) were rescaled by the use of Lagrange interpolation.¹⁴

The refinement of the structure was continued with use of the rescaled F_o -values and variation of the same 244 parameters as before. The least-squares refinement was continued three cycles. At this stage, the shifts in all parameters were lower than one-fourth of the corresponding standard deviations. The reliability index, based on 1418 observed reflections having non-zero weights, was 0.119. Furthermore, all temperature factors were positive-definite. Hence the systematic error can be pinpointed.

The weights were calculated according to the expression suggested by Cruickshank¹⁵

$$w = (a + F_o + cF_o^2)^{-1}$$

with $a = 2F_o^{\text{min}}$ and $c = 2/F_o^{\text{max}}$. The approximate values $F_o^{\text{min}} = 10$ and $F_o^{\text{max}} = 200$ were used. The weight analysis obtained in the final cycle is given in Table 4.

During refinement, the H atom coordinates (*cf.* Table 5), calculated from a model, were kept constant with an isotropic over all temperature factor of 3.0 \AA^2 . The model was derived from an early difference synthesis and from ordinary stereochemical considerations.

Table 4. Weight analysis obtained in the final cycle of the least-squares refinement of 5-diethyl-3,7,8,10-tetramethyl-1,5-dihydroisalloxazine trihydrate. The averages $w(|F_o| - |F_c|)^2 = w\Delta^2$ are normalized.

Interval sin θ	Number of independent reflections	$\overline{w\Delta^2}$	Interval F_{obs}	Number of independent reflections	$\overline{w\Delta^2}$
0.0 - 0.450	364	1.33	0.0 - 8.0	133	0.94
0.450 - 0.567	305	0.92	8.0 - 10.8	142	0.93
0.567 - 0.649	226	0.61	10.8 - 13.7	138	0.81
0.649 - 0.715	173	1.09	13.7 - 17.5	144	0.72
0.715 - 0.770	126	1.11	17.5 - 22.0	143	0.59
0.770 - 0.818	83	0.97	22.0 - 27.1	144	0.57
0.818 - 0.861	49	0.69	27.1 - 32.2	143	1.30
0.861 - 0.901	39	0.89	32.2 - 39.5	143	1.08
0.901 - 0.937	33	0.68	39.5 - 53.0	143	1.42
0.937 - 0.970	19	0.87	53.0 - 145.4	144	1.64

The final positional and thermal parameters are given in Tables 6 and 7. Observed (rescaled) and calculated structure factors are listed in Table 8.

It should be noted that systematic errors of the kind discussed above have small influence on the phase determination when isomorphous substitution

Table 5. Fractional coordinates ($\times 10^4$) for hydrogen atoms.

Atom	Bonded to	x/a	y/b	z/c
H(1)	C(6)	2300	5810	350
H(2)	C(9)	50	7270	1930
H(3)	C(13)	2160	3800	3950
H(4)	C(13)	3180	4203	4448
H(5)	C(13)	3599	3888	3636
H(6)	C(15a)	2508	4446	1430
H(7)	C(15a)	2296	4912	748
H(8)	C(15b)	222	4900	1771
H(9)	C(15b)	494	4253	1267
H(10)	C(15b)	248	4906	866
H(11)	C(15c)	4400	5137	1792
H(12)	C(15c)	4111	5559	1071
H(13)	C(15d)	3666	6444	2054
H(14)	C(15d)	4770	6020	2470
H(15)	C(15d)	5049	6354	1674
H(16)	C(17)	1200	7250	-400
H(17)	C(17)	452	6579	-617
H(18)	C(17)	2084	6626	-625
H(19)	C(18)	9137	7790	957
H(20)	C(18)	330	7986	437
H(21)	C(18)	-750	7485	136
H(22)	C(20)	760	7260	2850
H(23)	C(20)	1068	6859	3618
H(24)	C(20)	-330	6767	3184

is used. This is of particular interest in protein crystallographic work. The use of this film scanner technique on precession photographs also reduces systematic as well as statistical errors, as discussed in a previous paper by one of us.¹¹

Table 6. Fractional atomic coordinates ($\times 10^4$) for non-hydrogen atoms with e.s.d.'s as calculated from the least-squares refinement in parentheses.

Atom	x/a	y/b	z/c
N(1)	1412 (9)	5691 (4)	3654 (4)
C(2)	1824 (11)	5147 (5)	3956 (5)
N(3)	2480 (9)	4684 (4)	3568 (4)
C(4)	2733 (11)	4745 (5)	2822 (5)
C(4a)	2217 (10)	5319 (4)	2512 (4)
N(5)	2466 (10)	5431 (4)	1731 (4)
C(5a)	1796 (11)	6014 (4)	1452 (5)
C(6)	1831 (11)	6129 (5)	707 (5)
C(7)	1227 (11)	6661 (5)	412 (5)
C(8)	501 (12)	7071 (5)	872 (6)
C(9)	536 (12)	696 (4)	1601 (6)
C(9a)	1174 (10)	6439 (4)	1901 (5)
N(10)	1180 (8)	6346 (3)	2669 (4)
C(10a)	1616 (10)	5779 (4)	2935 (5)
O(12)	1638 (8)	5046 (4)	4630 (4)
C(13)	2952 (11)	4096 (5)	3940 (6)
O(14)	3361 (8)	4328 (3)	2519 (4)
C(15a)	2083 (14)	4848 (5)	1268 (5)
C(15b)	700 (18)	4715 (6)	1296 (7)
C(15c)	3899 (15)	5534 (6)	1598 (7)
C(15d)	4396 (14)	6130 (6)	1985 (7)
C(17)	1254 (14)	6758 (6)	-416 (6)
C(18)	-233 (14)	7626 (6)	572 (7)
C(20)	620 (13)	6838 (5)	3139 (6)
O(1k)	2030 (10)	3138 (5)	2279 (6)
O(2k)	2318 (10)	3183 (4)	761 (5)
O(3k)	4337 (8)	3968 (4)	344 (4)

RESULTS AND DISCUSSION OF THE STRUCTURE

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

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

A perspective view of the molecule, showing the atom numbering, is given in Fig. 1.

Table 7. Thermal parameters. The β values refer to the temperature factor $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})10^{-6}]$. R(i), i=1,3, are the r.m.s. components of thermal displacement (in Å) along the principal axes of the ellipsoid of thermal vibration (calculated with the program ORTEP²⁶).

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R(1)	R(2)	R(3)
N(1)	659	171	150	281	36	28	0.036	0.039	0.084
C(2)	439	192	174	217	250	-29	0.030	0.045	0.072
N(3)	571	156	155	348	53	131	0.025	0.043	0.080
C(4)	477	213	149	136	32	87	0.035	0.047	0.070
C(4a)	462	130	94	286	108	71	0.026	0.031	0.072
N(5)	371	149	154	88	160	31	0.036	0.037	0.064
C(5a)	391	121	175	46	35	39	0.034	0.042	0.063
C(6)	533	171	186	-48	152	70	0.036	0.046	0.074
C(7)	537	168	168	-204	-137	95	0.034	0.042	0.076
C(8)	747	161	257	110	-50	79	0.031	0.046	0.092
C(9)	658	127	273	105	-309	72	0.032	0.049	0.085
C(9a)	279	146	170	-18	-32	-12	0.038	0.041	0.053
N(10)	616	105	176	242	-87	-40	0.028	0.042	0.081
C(10a)	294	161	140	146	-92	57	0.030	0.042	0.058
O(12)	1012	265	163	212	114	6	0.040	0.050	0.102
C(13)	691	201	295	567	-50	176	0.020	0.057	0.091
O(14)	860	226	238	550	362	55	0.033	0.046	0.100
C(15a)	942	153	205	69	25	-50	0.038	0.046	0.097
C(15b)	1281	240	487	-280	-119	-118	0.045	0.071	0.114
C(15c)	698	284	402	102	447	267	0.042	0.060	0.092
C(15d)	711	319	470	-92	-241	251	0.050	0.069	0.088
C(17)	1405	276	201	-31	-245	176	0.037	0.057	0.119
C(18)	1632	273	398	577	-1093	120	0.023	0.061	0.137
C(20)	1341	145	302	504	139	-139	0.026	0.057	0.118
O(k1)	1501	382	585	104	251	-92	0.061	0.076	0.123
O(k2)	1193	330	477	-96	-209	6	0.057	0.068	0.110
O(k3)	861	243	417	-115	-247	-168	0.044	0.066	0.095

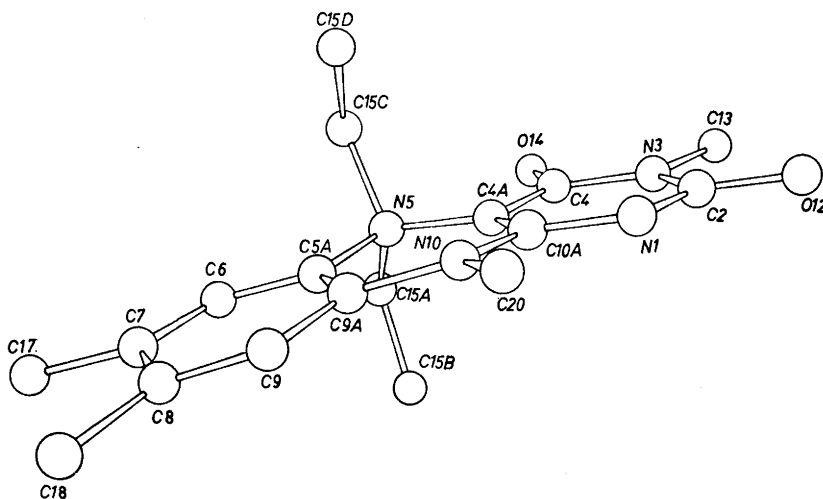


Fig. 1. Perspective view of the molecule, showing the atom numbering.

Table 8. Continued.

H	K	L	KFOB	FCAL	H	K	L	KFOR	FCAL	H	K	L	KFOR	FCAL	H	K	L	KFOB	FCAL
1	17	16	7.29	11.02	2	6	4	45.10	43.84	2	13	10	9.21	8.73	3	6	2	7.91	7.79
1	3	17	18.07	22.82	2	7	4	115.26	127.87	2	14	10	6.05	11.76	3	7	2	79.18	78.22
1	10	17	9.87	15.14	2	8	4	67.10	67.52	2	15	10	18.74	13.47	3	8	2	35.41	31.86
1	12	17	15.35	17.15	2	9	4	64.54	53.92	* 2	16	10	46.11	10.93	3	9	2	20.70	15.92
1	14	17	6.46	9.32	2	10	4	15.27	15.66	2	1	11	35.67	29.18	3	10	2	17.40	13.89
1	0	18	32.64	36.95	2	11	4	10.61	6.98	2	2	11	11.10	12.46	3	11	2	34.13	31.81
1	2	18	30.93	34.74	2	12	4	13.76	12.17	2	3	11	62.00	55.87	3	12	2	40.59	36.65
1	4	18	25.31	27.27	2	13	4	17.19	17.60	2	4	11	28.48	25.94	3	13	2	48.86	45.74
1	6	18	13.64	16.98	2	14	4	27.02	25.98	2	5	11	20.22	13.93	3	14	2	33.18	30.31
1	7	18	7.67	12.01	2	16	4	9.05	14.30	2	6	11	10.37	13.20	3	16	2	21.41	20.22
1	8	18	7.29	7.95	2	18	4	12.13	14.02	2	8	11	17.37	14.86	3	18	2	15.94	17.68
1	10	18	12.31	14.07	2	22	4	7.88	8.27	2	9	11	45.31	37.58	3	23	2	12.76	14.78
1	12	18	6.06	8.15	2	1	5	36.30	31.72	2	10	11	36.17	34.99	3	2	3	15.06	12.31
1	13	18	5.23	7.49	2	2	5	19.16	20.67	2	12	11	40.38	39.81	3	3	3	23.63	23.06
* 1	14	18	6.09	0.74	2	3	5	3.46	5.79	2	13	11	56.42	46.47	3	4	3	26.94	28.63
1	15	18	5.72	7.27	2	4	5	24.22	24.25	2	14	11	28.71	32.45	3	5	3	17.45	19.12
1	2	19	6.43	7.25	2	5	5	56.31	55.40	2	15	11	21.43	26.77	3	6	3	16.19	17.91
1	11	19	6.68	10.01	2	6	5	4.19	4.32	2	16	11	40.09	45.17	3	7	3	74.97	82.89
1	12	19	5.27	5.50	2	7	5	90.85	94.18	2	21	11	5.05	8.16	3	8	3	32.04	28.07
1	14	19	5.07	7.28	2	8	5	48.23	41.52	2	0	12	10.10	12.11	3	9	3	50.61	49.57
1	7	20	6.84	12.81	2	9	5	24.21	26.96	2	1	12	27.38	23.08	3	11	3	30.77	25.69
1	9	20	5.74	6.59	2	10	5	7.65	7.07	* 2	2	12	5.01	0.35	3	12	3	41.37	34.30
1	11	20	9.94	13.22	2	11	5	27.82	24.96	2	3	12	30.98	24.58	3	13	3	12.20	7.50
1	12	20	6.13	9.08	* 2	12	5	4.99	0.17	2	4	12	26.43	23.44	3	14	3	25.34	25.62
1	9	21	4.08	7.73	2	14	5	36.67	32.97	2	5	12	16.43	14.56	3	15	3	9.85	10.69
1	0	22	10.59	12.52	2	22	5	8.83	9.81	2	6	12	28.57	23.78	3	16	3	29.57	24.55
1	2	22	5.47	6.53	2	23	5	19.22	21.01	2	8	12	34.70	10.48	3	17	3	12.24	15.33
1	4	22	6.43	5.06	2	24	5	4.76	4.45	2	9	12	62.98	41.17	3	22	3	10.81	11.79
1	5	22	6.37	12.13	2	0	6	114.74	110.41	2	10	12	34.91	32.27	3	0	4	33.40	23.65
1	7	22	3.40	4.21	2	1	6	45.82	42.48	2	11	12	34.86	32.85	3	1	4	8.20	9.15
1	2	23	3.21	2.76	2	2	6	22.13	17.34	2	12	12	16.65	19.26	3	2	4	5.56	4.81
2	4	23	44.54	68.22	2	3	6	16.22	12.73	2	13	12	28.93	32.45	3	3	4	36.58	39.76
2	6	23	74.93	74.93	2	4	6	42.34	42.67	2	15	12	13.03	17.78	3	4	4	24.56	24.18
2	8	23	40.62	47.12	2	6	6	51.23	45.90	2	21	12	4.45	8.59	3	5	4	76.39	75.61
2	10	23	9.13	5.70	2	7	6	18.67	13.84	2	1	13	40.61	38.90	3	6	4	42.74	33.38
2	12	23	17.19	13.65	2	8	6	39.19	36.24	2	2	13	26.86	26.66	3	7	4	16.47	16.68
2	14	23	31.05	33.91	2	9	6	65.83	62.22	2	4	13	14.92	7.76	3	8	4	24.42	25.11
2	16	23	21.13	23.25	2	10	6	66.91	44.16	2	4	13	26.79	26.46	3	9	4	16.12	29.88
2	5	1	65.03	89.42	2	11	6	19.00	13.70	2	5	13	55.54	47.82	3	10	4	21.48	15.42
2	6	1	76.48	83.21	2	12	6	34.67	31.49	2	6	13	17.21	19.33	3	11	4	14.18	17.83
2	7	1	45.55	52.11	2	14	6	16.34	17.37	2	7	13	56.55	52.02	3	12	4	13.11	12.11
2	8	1	42.59	45.68	2	16	6	22.66	22.44	2	8	13	42.57	30.38	3	2	4	8.33	13.65
2	9	1	25.60	25.04	2	18	6	7.82	14.51	2	9	13	21.98	21.33	3	4	4	6.63	9.43
2	10	1	31.84	31.84	2	10	6	9.16	15.52	2	10	13	12.72	14.17	3	2	5	13.17	21.16
2	11	1	12.85	14.89	2	20	6	15.39	14.82	2	11	13	7.83	12.74	3	3	5	20.88	18.30
2	12	1	17.39	15.30	2	21	6	12.65	13.16	2	12	13	34.75	35.70	3	4	5	33.68	34.51
2	15	1	23.72	23.18	2	24	6	12.27	14.01	2	13	13	16.57	18.44	3	5	5	48.17	54.33
2	16	1	48.50	43.41	2	1	7	7.54	7.74	2	20	13	6.41	8.41	3	6	5	36.81	30.76
2	17	1	29.75	25.63	2	2	7	9.34	14.46	2	0	14	15.50	15.70	3	7	5	20.56	13.72
2	18	1	35.94	32.10	2	3	7	5.89	4.06	2	1	14	10.25	8.66	3	8	5	46.73	36.13
2	19	1	31.15	29.88	2	4	7	21.20	26.52	2	2	14	23.34	18.47	3	9	5	21.51	18.48
2	21	1	7.35	10.07	2	5	7	6.40	6.21	2	3	14	27.93	24.19	3	10	5	36.71	30.67
2	0	2	46.90	106.24	2	6	7	26.21	27.88	2	4	14	26.75	25.70	3	11	5	11.91	10.02
2	1	2	65.31	57.94	2	7	7	6.16	42.98	2	5	14	16.32	18.33	3	12	5	34.77	28.38
2	2	2	44.37	40.97	2	8	7	30.33	23.54	2	7	14	16.33	19.85	3	13	5	19.72	18.10
2	3	2	124.21	162.73	2	9	7	32.54	32.65	2	9	14	23.26	24.82	3	14	5	20.21	19.86
2	4	2	88.49	70.88	2	10	7	14.54	8.71	2	10	14	12.13	16.49	3	15	5	8.27	8.49
2	5	2	39.57	41.79	2	11	7	26.24	21.48	2	11	14	7.82	10.24	3	0	6	23.32	19.53
2	6	2	53.26	56.31	2	12	7	38.49	27.65	2	12	14	14.65	18.76	3	1	6	25.77	25.69
2	7	2	28.74	25.11	2	13	7	47.66	39.76	2	20	14	4.64	7.30	3	2	6	27.25	23.28
2	8	2	44.17	37.64	2	15	7	15.22	16.37	2	3	15	16.34	13.12	3	4	6	57.96	56.60
2	9	2	51.21	48.22	2	20	7	14.24	21.61	2	5	15	32.26	28.41	3	5	6	36.52	35.46
2	10	2	63.41	41.68	2	0	8	104.75	94.42	2	6	15	21.43	22.59	3	6	6	23.14	22.84
2	11	2	15.69	20.64	2	1	8	51.59	47.15	2	7	15	60.69	42.38	3	7	6	21.08	13.56
2	12	2	24.12	24.12	2	2	8	13.28	15.17	2	10	15	28.71	31.81	3	8	6	46.91	42.57
2	13	2	26.40	23.50	2	3	8	31.92	30.84	2	11	15	7.66	10.82	3	9	6	29.76	26.65
2	14	2	24.61	21.95	2	4	8	36.78	32.57	2	9	16	11.86	16.49	3	10	6	11.83	12.16
2	15	2	16.04	14.97	2	5	8	7.79	6.11	2	11	16	12.51	15.70	3	12	6	18.37	16.22
2	16	2	31.74	33.83	2	6	8	7.25	3.30	2	12	16	10.76	13.98	3	14	6	16.88	18.05
2	17	2	53.42	47.18	2	7	8	32.61	29.53	2	13	16	6.77	11.73	3	16	6	20.83	25.04
2	18	2	35.31	20.46	2	8	8	28.84	10.17	2	2	17	12.99	16.00	3	22	6	15.26	15.90
2	21	2	31.77	22.69	2	9	8	7.29	11.47	2	4	17	7.79	14.60	3	1	7	30.52	25.29
2	23	2	6.11	5.57	2	10	8	13.63	16.38	2	5	17	7.75	15.35	3	2	7	46.32	38.45
2	25	2	6.59	8.71	2	11	8	25.38	18.72	2	11	17	9.22	9.20	3	3	7	34.13	33.27
2	1	3	11.33	92.40	2	12	8	6.41	7.71	2	15	17	3.99	7.32	3	4	7	64.81	66.59
2	2	3	111.67	156.09	2	15	8	7.74	11.96	* 2	16	17	4.51	0.41	3	5	7	29.37	30.84
2	3	3	97.70</																

Table 8. Continued.

M	K	L	KFOB	FCAL	H	K	L	KFOB	FCAL	H	K	L	KFOB	FCAL	H	K	L	KFOB	FCAL
3	7	9	7.32	7.54	4	5	2	84.18	94.27	4	0	10	23.76	24.03	5	15	2	46.98	44.37
3	10	9	28.91	25.45	4	6	2	72.94	70.99	4	1	10	34.17	26.00	5	16	2	29.99	26.34
3	11	9	16.43	14.65	4	7	2	62.21	51.36	4	1	10	33.62	23.00	5	17	2	12.97	17.77
3	12	9	21.26	15.95	4	8	2	11.79	8.29	4	4	10	31.43	26.05	5	19	2	8.41	12.73
3	0	10	30.54	30.26	4	9	2	14.53	10.90	4	5	10	12.98	12.13	5	1	3	59.81	56.23
3	2	10	39.25	34.70	4	10	2	22.38	25.49	4	7	10	12.79	0.54	5	2	3	28.44	32.85
3	3	10	23.88	22.61	4	11	2	24.07	26.77	4	8	10	17.90	19.48	5	3	3	4.03	3.03
3	4	10	25.40	17.11	4	14	2	66.68	59.24	4	10	10	10.74	13.07	5	4	3	18.76	18.95
3	7	10	43.81	42.61	4	16	2	34.40	30.80	4	12	10	19.36	20.36	5	4	3	35.85	39.58
3	11	10	21.29	20.10	4	18	2	11.68	14.71	4	16	10	20.72	19.58	5	6	3	42.74	42.76
3	14	10	80.07	58.71	4	19	2	10.77	11.91	4	17	10	29.31	26.59	5	7	3	7.86	11.30
3	16	10	23.37	24.96	4	21	2	14.63	12.76	4	18	10	32.72	30.23	5	8	3	8.29	10.49
3	1	11	91.98	10.83	4	1	3	65.37	72.27	4	1	11	25.75	23.28	5	10	3	13.99	12.30
3	2	11	8.33	9.77	4	2	3	35.65	34.27	4	2	11	12.70	10.83	5	11	3	19.58	19.37
3	3	11	22.72	21.21	4	3	3	52.49	49.36	4	5	11	16.15	12.19	5	14	3	42.74	42.76
3	4	11	7.17	11.64	4	4	3	31.50	33.70	4	7	11	15.22	13.55	5	17	3	19.52	21.16
3	5	11	36.57	28.14	4	5	3	29.55	27.06	4	10	11	12.35	11.97	5	0	4	27.70	29.55
3	6	11	13.93	13.07	4	6	3	41.21	40.33	4	11	11	15.79	18.08	5	1	4	10.41	9.12
3	7	11	15.78	14.44	4	7	3	52.91	52.16	4	13	11	12.70	10.83	5	2	4	17.77	18.47
3	10	11	14.29	17.71	4	9	3	26.54	24.82	4	15	11	15.72	32.99	5	2	4	5.34	5.21
3	13	11	12.63	17.65	4	10	3	22.43	20.32	4	18	11	23.16	21.79	5	4	4	49.03	47.13
3	14	11	10.53	11.35	4	11	3	25.76	19.53	4	0	12	55.74	57.40	5	5	4	77.62	77.62
3	15	11	31.47	30.47	4	12	3	30.52	24.37	4	1	12	9.67	12.08	5	6	4	72.11	71.55
3	16	11	25.40	25.33	4	13	3	11.61	10.35	4	3	12	12.53	10.70	5	6	4	25.73	24.34
3	0	12	35.32	29.95	4	16	3	43.18	44.63	4	5	12	13.77	11.07	5	7	4	11.48	6.50
3	2	12	23.31	23.76	4	17	3	41.60	34.38	4	6	12	24.16	24.94	5	7	4	16.22	11.93
3	3	12	31.41	24.35	4	18	3	13.74	12.42	4	8	12	34.83	30.26	5	10	4	42.56	40.11
3	4	12	60.91	56.35	4	23	3	15.05	11.15	4	9	12	45.81	42.36	5	11	4	8.49	5.31
3	5	12	25.82	21.07	4	0	4	46.95	65.64	4	12	12	11.69	11.99	5	12	4	9.94	12.27
3	6	12	22.82	16.50	4	1	4	11.53	8.88	4	15	12	18.72	17.07	5	14	4	14.03	16.07
3	7	12	38.99	30.15	4	3	4	31.59	34.09	4	1	13	13.17	12.83	5	7	4	36.72	31.85
3	8	12	35.11	30.10	4	4	4	19.97	18.31	4	2	13	15.61	15.04	5	3	5	22.69	21.59
3	9	12	46.73	43.09	4	5	4	27.79	23.08	4	3	13	39.72	31.89	5	4	5	36.16	33.10
3	12	12	17.17	21.07	4	6	4	92.05	44.94	4	4	13	85.23	49.70	5	5	5	34.15	29.90
3	13	12	15.41	19.33	4	7	4	56.41	53.60	4	6	13	44.17	36.11	5	6	5	18.92	17.60
3	14	12	26.75	26.68	4	8	4	22.36	23.53	4	4	13	44.17	36.11	5	6	5	18.92	17.60
3	1	13	16.83	15.62	4	11	4	20.19	16.65	4	7	13	44.40	38.34	5	7	5	8.77	6.05
3	2	13	20.32	16.12	4	12	4	11.98	0.07	4	8	13	15.26	5.11	5	11	5	12.71	15.42
3	3	13	43.56	43.56	4	13	4	12.11	7.90	4	10	13	18.61	17.38	5	13	5	25.55	23.59
3	8	13	67.81	39.10	4	14	4	11.22	9.77	4	11	13	19.54	18.38	5	16	5	27.73	26.65
3	9	13	34.92	31.07	4	21	4	11.04	12.99	4	14	13	20.68	27.66	5	19	5	10.49	14.06
3	11	13	16.31	19.48	4	22	4	8.87	9.65	4	15	13	20.69	19.51	5	0	6	41.83	45.82
3	17	13	7.44	8.48	4	23	4	14.61	17.44	4	0	14	24.72	21.16	5	1	6	23.71	21.14
3	3	14	35.52	30.47	4	1	5	27.71	27.94	4	4	14	11.50	8.64	5	2	6	34.44	32.27
3	4	14	35.56	33.17	4	2	5	37.22	36.17	4	6	14	15.68	11.00	5	3	6	43.39	39.69
3	5	14	50.57	49.91	4	4	5	26.07	23.09	4	6	14	50.12	47.25	5	4	6	27.08	26.00
3	6	14	8.03	7.66	4	5	5	57.29	53.31	4	9	14	29.48	25.22	5	4	6	24.16	21.94
3	7	14	40.58	40.61	4	6	5	26.19	21.72	4	11	14	14.46	16.72	5	6	6	74.16	70.07
3	8	14	23.79	23.20	4	7	5	38.46	37.20	4	12	14	24.13	17.43	5	7	6	8.96	11.59
3	9	14	35.66	30.06	4	9	5	32.07	29.73	4	13	14	10.78	8.04	5	8	6	23.54	21.17
3	10	14	15.42	17.37	4	10	5	10.48	8.64	4	2	15	26.45	22.78	5	9	6	7.84	5.12
3	11	14	36.57	34.63	4	11	5	36.21	34.40	4	3	15	26.49	23.18	5	10	6	34.07	34.74
3	1	15	21.72	16.33	4	13	5	49.63	39.34	4	5	15	39.35	39.44	5	11	6	15.37	16.19
3	3	15	10.43	10.50	4	0	6	27.22	19.16	4	7	15	18.55	18.58	5	13	6	17.44	17.60
3	5	15	45.69	26.52	4	1	6	12.15	4.24	4	0	15	15.62	17.60	5	14	6	9.62	11.72
3	6	15	17.13	19.20	4	2	6	36.79	33.54	4	10	15	16.40	14.93	5	15	6	29.62	24.27
3	7	15	44.04	43.02	4	3	6	13.43	15.33	4	12	15	39.32	34.19	5	16	6	4.37	10.95
3	9	15	45.88	46.12	4	5	6	25.76	29.40	4	4	16	12.33	12.93	5	2	7	22.78	21.28
3	12	15	8.81	12.43	4	6	6	17.45	10.59	4	5	16	20.49	19.15	5	3	7	32.34	31.81
3	0	16	9.40	15.34	4	7	6	26.97	29.38	4	6	16	11.51	9.96	5	4	7	22.91	21.92
3	5	16	23.84	24.72	4	8	6	21.07	16.82	4	9	16	10.35	14.13	5	5	7	15.46	12.24
3	6	16	9.37	15.47	4	9	6	9.36	11.02	4	11	16	10.28	12.92	5	7	7	18.59	16.58
3	7	16	24.94	28.35	4	10	6	26.07	29.15	4	13	16	13.40	2.65	5	8	7	7.83	5.49
3	10	16	15.37	15.92	4	11	6	24.96	19.34	4	14	16	9.20	10.94	5	13	7	32.58	30.44
3	12	16	28.05	22.38	4	12	6	31.17	23.59	4	5	17	13.72	13.68	5	14	7	33.20	30.33
3	16	16	5.23	4.17	4	1	7	55.37	53.76	4	0	18	15.89	16.09	5	18	7	9.01	12.08
3	1	17	15.97	14.64	4	2	7	19.70	15.27	4	4	18	10.28	5.68	5	0	8	13.54	13.08
3	2	17	21.93	24.48	4	3	7	18.72	15.82	4	12	18	8.40	6.12	5	2	8	26.02	24.27
3	3	17	16.12	14.36	4	5	7	89.95	82.97	4	1	19	12.18	14.90	5	3	8	15.08	15.86
3	10	17	8.30	10.75	4	6	7	55.14	46.02	4	3	19	9.86	11.01	5	4	8	23.14	20.86
3	12	17	13.72	13.14	4	7	7	34.36	32.18	4	9	19	12.78	12.94	5	5	8	15.07	18.88
3	14	17	18.59	19.45	4	9	7	36.14	32.57	5	3	0	74.71	83.02	5	7	8	22.34	18.29
3	0	18	50.27	47.22	4	10	7	13.81	12.91	5	0	19	48.68	15.76	5	8	8	7.49	10.64
3	2	19	11.26	13.79	4	13	7	31.32	23.27	5	7	0	18.84	13.41	5	10	8	18.37	17.68
3	4	19	15.65	16.81	4	14	7	24.13	19.93	5	9	0	48.84	47.56	5	11	8	31.81	34.78
4	6	0	30.87	33.81	4	18	7	22.61	22.44	5	13	0	67.64	68.96	5	20	8		

Table 8. Continued.

H	K	L	KFOB	FCAL	H	K	L	KFOB	FCAL	H	K	L	KFOB	FCAL	H	K	L	KFOB	FCAL
5	0	12	24.55	25.38	6	17	1	9.82	11.85	6	10	6	21.05	18.96	6	13	11	15.44	17.64
5	1	12	41.66	40.25	6	18	1	14.71	15.67	6	12	6	9.58	12.98	6	15	11	16.47	15.45
5	2	12	39.61	39.17	6	0	2	29.52	22.06	6	15	6	9.45	12.10	6	3	12	12.40	16.16
5	3	12	48.17	46.02	6	2	2	36.07	32.72	6	1	7	24.96	26.68	6	4	12	24.30	27.23
5	4	12	30.71	30.46	6	3	2	30.93	26.14	6	2	7	35.75	36.03	6	7	12	26.20	24.93
5	5	12	53.32	48.90	6	4	2	48.99	52.69	6	3	7	18.00	12.51	6	9	12	15.70	16.29
5	6	12	11.40	14.88	6	5	2	60.01	59.01	6	5	7	28.95	27.25	6	2	13	55.41	51.76
5	7	12	44.17	42.58	6	6	2	69.17	59.05	6	6	7	25.28	25.90	6	3	13	19.72	14.19
5	8	12	28.10	26.53	6	7	2	57.42	53.34	6	7	7	31.66	27.94	6	5	13	25.76	26.30
5	10	12	10.62	11.98	6	8	2	59.14	50.70	6	8	7	11.91	12.03	6	7	13	11.99	10.46
5	14	12	27.72	25.04	6	9	2	26.88	30.11	6	9	7	17.67	14.77	6	8	13	8.94	10.58
5	1	13	41.19	36.47	6	10	2	11.21	11.44	6	10	7	29.86	32.19	6	9	13	11.48	13.45
5	3	13	24.07	24.53	6	12	2	32.41	35.70	6	11	7	6.69	5.90	6	13	13	7.76	10.59
5	4	13	10.36	10.42	6	13	2	16.07	14.24	6	12	7	8.85	13.65	6	3	14	14.67	14.40
5	6	13	33.05	31.67	6	14	2	18.46	18.34	6	15	7	10.71	12.10	6	4	14	49.05	44.49
5	7	13	33.19	30.13	6	15	2	21.46	18.40	6	0	8	27.40	30.31	6	5	14	12.40	14.51
5	0	14	9.66	10.69	6	17	2	12.24	11.85	6	1	8	6.26	8.69	6	6	14	36.45	35.48
5	1	14	18.98	18.20	6	11	3	39.55	29.38	6	3	8	6.85	7.46	6	7	14	9.79	12.40
5	3	14	41.52	41.11	6	2	3	19.33	10.09	6	4	8	16.58	17.01	6	11	14	13.82	11.49
5	5	14	60.53	59.72	6	3	3	16.96	16.45	6	5	8	8.70	10.27	6	5	15	10.56	12.73
5	6	14	13.97	16.85	6	5	3	19.06	18.02	6	6	8	13.08	12.29	6	7	15	7.64	7.79
5	7	14	21.66	26.10	6	6	3	31.72	33.57	6	7	8	40.31	42.07	6	8	15	6.51	5.98
5	12	14	13.20	14.20	6	7	3	37.34	36.82	6	8	8	40.76	37.39	6	10	15	19.30	19.14
5	15	14	9.92	7.70	6	8	3	6.99	2.15	6	9	8	13.24	14.47	6	6	16	17.58	19.47
5	3	15	15.09	16.24	6	0	3	39.84	35.86	6	11	8	7.34	4.14	6	8	16	8.62	9.37
5	5	15	17.80	17.71	6	10	3	37.54	36.08	6	13	8	22.39	22.78	6	5	19	11.34	0.41
5	7	15	15.48	16.13	6	11	3	16.53	20.79	6	15	8	11.35	15.07	6	6	18	8.71	13.22
5	9	15	12.34	9.69	6	12	3	27.57	28.56	6	16	8	14.50	17.34	6	7	18	5.77	8.86
5	10	15	9.02	6.90	6	14	3	28.04	27.15	6	1	9	17.19	12.31	6	2	19	5.74	7.76
5	11	15	21.81	19.17	6	5	16	17.31	17.31	6	3	9	35.50	32.02	6	9	19	8.17	19.36
5	3	16	26.39	29.48	6	19	3	8.04	7.64	6	4	9	28.40	26.42	7	10	2	33.13	40.12
5	4	16	27.64	16.31	6	0	4	24.01	29.03	6	6	9	32.93	28.29	7	13	2	29.82	39.17
5	5	16	9.47	13.58	6	1	4	48.34	46.21	6	7	9	12.95	14.37	7	1	3	40.19	44.45
5	6	16	18.66	19.51	6	2	4	16.66	17.46	6	10	9	16.95	18.18	7	2	3	34.67	33.71
5	7	16	11.52	14.81	6	3	4	63.98	60.63	6	12	10	31.17	35.50	7	6	3	33.11	32.46
5	3	16	15.15	19.03	6	4	4	49.46	44.59	6	13	9	9.00	12.12	7	7	3	21.53	17.51
5	8	17	8.34	10.72	6	5	4	27.62	28.68	6	15	9	11.12	12.38	7	8	3	53.07	49.30
6	2	0	10.89	18.58	6	6	4	10.50	14.63	6	17	9	18.50	17.06	7	12	3	15.39	16.55
6	4	0	12.44	17.57	6	7	4	6.24	7.15	6	19	9	13.05	5.43	7	1	4	48.21	46.69
6	6	0	51.89	52.07	6	8	4	42.81	36.61	6	10	10	14.15	14.01	7	6	4	26.51	28.41
6	8	0	23.01	24.28	6	10	4	25.65	23.49	6	4	10	17.89	15.86	7	10	4	28.11	26.42
6	10	0	31.85	34.95	6	14	4	9.82	9.79	6	5	10	6.34	11.27	7	4	5	46.99	45.61
6	16	0	33.33	28.70	6	15	4	12.35	11.92	6	6	10	17.79	17.02	8	2	2	32.13	41.49
6	18	0	24.28	21.65	6	1	5	22.70	21.24	6	8	10	9.14	12.54	8	7	2	54.31	55.02
6	3	1	15.35	15.91	6	2	5	17.24	17.35	6	10	10	6.95	8.27	8	8	2	31.76	36.44
6	4	1	31.61	38.45	6	4	5	37.31	37.47	6	12	10	7.50	12.48	8	0	2	57.45	67.56
6	5	1	81.69	90.50	6	6	5	4.80	2.04	6	13	10	12.25	15.80	8	1	2	33.30	31.47
6	6	1	4.48	5.73	6	7	5	29.69	26.33	6	14	10	11.96	11.43	8	12	3	22.55	27.22
6	7	1	29.97	33.12	6	8	5	6.63	5.47	6	19	10	5.14	18.91	8	6	4	34.52	23.69
6	8	1	54.67	57.12	6	9	5	13.48	15.73	6	1	11	49.76	42.86	8	7	4	36.74	36.39
6	9	1	10.76	11.95	6	12	5	6.62	9.14	6	2	11	22.73	19.77	8	1	7	32.45	38.08
6	10	1	18.84	17.01	6	14	5	10.32	13.39	6	3	11	9.59	9.86	9	2	3	25.75	25.87
6	11	1	23.77	22.70	6	0	6	58.75	51.57	6	4	11	31.11	31.36	9	10	3	24.19	23.37
6	12	1	23.16	21.22	6	2	6	48.12	43.75	6	5	11	7.64	8.76	9	12	3	44.50	54.95
6	13	1	48.04	44.15	6	3	6	15.90	14.69	6	6	11	35.27	33.44	10	1	3	21.22	23.14
6	14	1	44.32	41.85	6	4	6	12.73	11.81	6	7	11	19.29	18.16	11	8	3	15.90	22.55
6	15	1	19.98	18.00	6	6	6	12.72	15.54	6	8	11	9.37	8.98	11	10	3	12.08	19.30
6	16	1	31.10	7.14	6	8	6	22.46	22.89	6	12	11	20.09	23.61					

The bond lengths are given in Table 9, and the angles are listed in Table 10. No attempts have been made to correct bond lengths for the effects of thermal motion, although the pattern of the thermal ellipsoids is plausible (*cf.* Table 7). Because of the different sources of error discussed above, the e.s.d.'s as calculated from the least-squares refinement might well be multiplied by a factor of two to give a range of 0.02 to 0.03 Å for the bonds and 1.4° to 2.0° for the angles. The highest e.s.d.'s were obtained for the bonds of the ethyl groups.

The observed bond length variations in the benzene group are reasonable, and their mean value, 1.389 Å, agrees well with 1.394 Å given by Sutton¹⁶ for aromatic C—C bonds. The two N(5)—C_{sp}³ bonds have an average length of 1.54 Å. This average may be compared with the value 1.52 ± 0.03 Å, quoted by Hamilton, Hamor, Robertson and Sim¹⁷ as characteristic for the N⁺—C_{sp}³ bond length in a number of alkaloids. The bonds N(5)—C(4a), 1.48 Å, and N(5)—C(5a), 1.49 Å, are in agreement with the carbon-nitrogen single bond distance 1.475 Å, given by Cox and Jeffrey.¹⁸ From the bond angle C(2)—N(1)—C(10a), 118.2, it may be concluded that no extra-annular hydrogen is attached to N(1).¹⁹ Also the bond lengths N(1)—C(2), 1.33 Å, and C(2)—O(12),

Table 9. Bond lengths and their calculated e.s.d.'s.

	Distance	e.s.d.
N(1)–C(2)	1.329 Å	0.012 Å
N(1)–C(10a)	1.357	0.010
C(2)–N(3)	1.378	0.012
C(2)–O(12)	1.277	0.011
N(3)–C(4)	1.409	0.011
N(3)–C(13)	1.487	0.012
C(4)–C(4a)	1.427	0.013
C(4)–O(14)	1.224	0.012
C(4a)–N(5)	1.484	0.010
C(4a)–C(10a)	1.384	0.012
N(5)–C(5a)	1.491	0.011
N(5)–C(15a)	1.533	0.012
N(5)–C(15c)	1.551	0.018
C(5a)–C(6)	1.395	0.012
C(5a)–C(9a)	1.375	0.012
C(6)–C(7)	1.385	0.013
C(7)–C(8)	1.425	0.014
C(7)–C(17)	1.542	0.013
C(8)–C(9)	1.365	0.013
C(8)–C(18)	1.492	0.016
C(9)–C(9a)	1.389	0.013
C(9a)–N(10)	1.431	0.010
N(10)–C(10a)	1.353	0.011
N(10)–C(20)	1.463	0.012
C(15a)–C(15b)	1.490	0.024
C(15c)–C(15d)	1.518	0.017

1.28 Å, may be attributed to a negative charge at N(1). Thus, the crystal structure confirms the zwitterion character of the molecule.

The bond lengths C(4a)–C(10a), 1.38 Å, and C(4)–C(4a), 1.43 Å, may be compared with the corresponding bond lengths 1.37 Å and 1.42 Å, respectively, found in 5-acetyl-9-bromo-1,3,7,8,10-pentamethyl-1,5-dihydroisoalloxazine.²⁰ These bonds tend to be significantly lengthened in oxidized flavins.^{21–23} Thus, in reduced flavins, π -electrons seem to be localized also in the bond C(4)–C(4a).

The isoalloxazine ring system is basically planar. Two least-squares planes through the pyrimidine and benzene parts of the molecule and distances of atoms from these planes are given in Table 11. The dihedral angle between the planes is 8.9° in spite of the tetrahedral hybridization at N(5) (*cf.* Fig. 2). This feature is not found in other reduced flavin structures. Thus, for example, the corresponding angle in 5-acetyl-9-bromo-1,3,7,8,10-pentamethyl-1,5-dihydroisoalloxazine²⁰ is 35.5°, while the angle calculated from the coordinates given by Tanaka *et al.*²¹ for (the oxidized) riboflavin hydrobromide is 4.1°.

It is notable that the largest deviations from the ideal tetrahedral angle 109.47° at N(5) are found in the angles C(15a)–N(5)–C(15c), 106.1°, and C(4a)–N(5)–C(5a), 112.2°. These deviations cannot be caused by overcrowding at C(15a) and C(15c), respectively. Furthermore, the intramolecular distances C(15a)···O(14) 2.89 Å, C(15a)···C(4) 2.96 Å, and C(15c)···C(6) 3.00 Å

Table 10. Bond angles and their calculated e.s.d.'s.

	Angle	e.s.d.
C(2)–N(1)–C(10a)	118.2°	0.8°
N(1)–C(2)–N(3)	122.1	0.8
N(1)–C(2)–O(12)	119.8	0.9
N(3)–C(2)–O(12)	118.1	0.8
C(2)–N(3)–C(4)	123.0	0.8
C(2)–N(3)–C(13)	119.8	0.8
C(4)–N(3)–C(13)	117.3	0.8
N(3)–C(4)–C(4a)	113.0	0.8
N(3)–C(4)–O(14)	119.3	0.9
C(4a)–C(4)–O(14)	127.7	0.8
C(4)–C(4a)–N(5)	116.8	0.8
C(4)–C(4a)–C(10a)	121.5	0.8
N(5)–C(4a)–C(10a)	121.5	0.8
C(4a)–N(5)–C(5a)	112.2	0.7
C(4a)–N(5)–C(15a)	111.9	0.7
C(4a)–N(5)–C(15c)	110.4	0.8
C(5a)–N(5)–C(15a)	108.5	0.8
C(5a)–N(5)–C(15c)	107.4	0.8
C(15a)–N(5)–C(15c)	106.1	0.9
N(5)–C(5a)–C(6)	117.7	0.8
N(5)–C(5a)–C(9a)	122.4	0.8
C(6)–C(5a)–C(9a)	119.9	0.8
C(5a)–C(6)–C(7)	120.7	0.9
C(6)–C(7)–C(8)	119.1	0.8
C(6)–C(7)–C(17)	119.0	0.9
C(8)–C(7)–C(17)	121.6	0.9
C(7)–C(8)–C(9)	118.3	0.9
C(7)–C(8)–C(18)	121.1	0.9
C(9)–C(8)–C(18)	120.5	1.0
C(8)–C(9)–C(9a)	122.4	0.9
C(5a)–C(9a)–C(9)	119.3	0.8
C(5a)–C(9a)–N(10)	120.6	0.8
C(9)–C(9a)–N(10)	120.1	0.8
C(9a)–N(10)–C(10a)	118.6	0.7
C(9a)–N(10)–C(20)	119.5	0.7
C(10a)–N(10)–C(20)	121.7	0.7
N(1)–C(10a)–C(4a)	122.1	0.8
N(1)–C(10a)–N(10)	114.7	0.8
C(4a)–C(10a)–N(10)	123.2	0.8
N(5)–C(15a)–C(15b)	112.7	1.0
N(5)–C(15c)–C(15d)	112.1	1.0

do not indicate any considerable overlap. This gives rise to the biochemically interesting question as to whether a two-protonated flavin at N(5) may have the same small deviation from planarity as found in the present structure.

The possible hydrogen bonds are listed in Table 12. As can be seen from Fig. 3, they link the molecules together in all directions. The crystal water oxygen atoms O(k1), O(k1) (i), O(k2) (i), and O(k2) form a square with an edge of 2.82 Å. It follows from the oxygen positions and from the space group *Pccn* that four protons should be statistically distributed within this square.

Table 11. Least-squares planes. The planes are described in terms of a vector basis $m|a, n|b$ and $p|c$.

Plane I: $0.8697 m + 0.4493 n + 0.2044 p = 7.968$.

Plane II: $0.8303 m + 0.5493 n + 0.0940 p = 8.672$.

The angle between the planes is 8.9° .

Atom	Plane I Deviation ^a	Atom	Plane II Deviation ^a
N(1)	- 2	N(5)	- 35
C(2)	- 15	C(5a)	- 10
N(3)	15	C(6)	21
C(4)	21	C(7)	45
C(4a)	- 37	C(8)	- 48
N(5)	1	C(9)	- 14
N(10)	21	C(9a)	4
C(10a)	4	N(10)	37
Atoms not included in the least-squares plane		Atoms not included in the least-squares plane	
O(12)	24	C(15a)	- 1115
C(13)	42	C(15c)	1317
O(14)	96	C(17)	1771
C(15a)	- 1069	C(18)	- 113
C(15c)	1364	C(20)	187
C(20)	141		

^a Deviations are given in 10^{-3} Å.

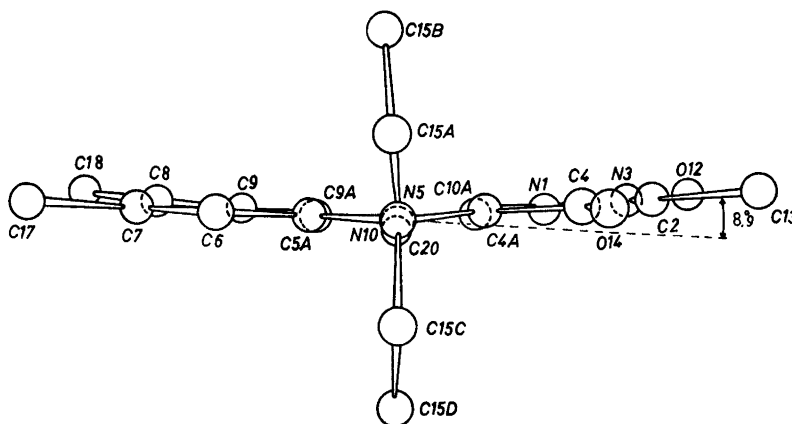


Fig. 2. Perspective view of the molecule, showing the angle between the calculated least-squares planes (cf. Table 11).

Table 12. Possible hydrogen bonds.

O(k1)···O(k1)(i)	2.82 Å
O(k1)···O(k2)	2.82
O(k1)···O(14)	2.87
O(k2)···O(k2)(i)	2.85
O(k2)···O(k3)	2.79
O(k3)···N(1)(iii)	2.99
O(k3)···O(12)(iv)	2.79

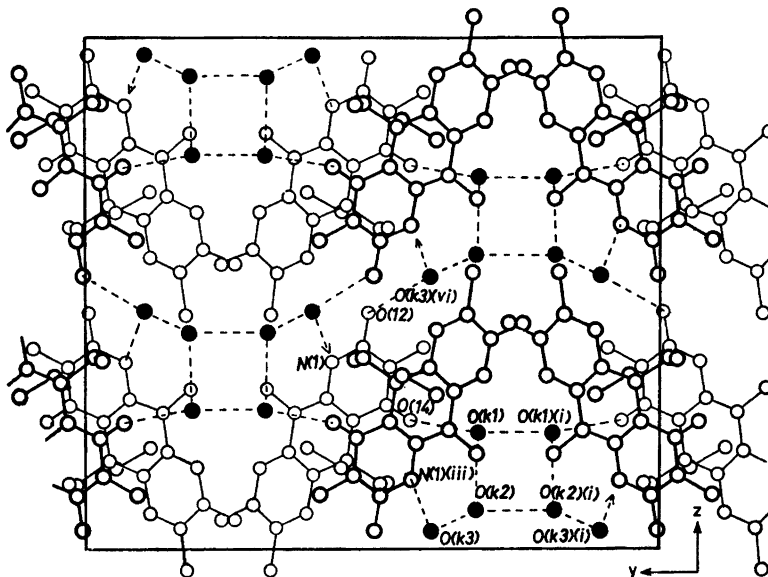


Fig. 3. Projection of the structure along the a axis. Filled circles denote crystal water oxygen. Arrows indicate atoms in unit cells above or below the unit cell drawn in the figure.

Table 13. Intermolecular distances less than 3.8 Å between non-hydrogen atoms. Crystal water not included.

N(1)···C(15c)(v)	3.70 Å
N(1)···C(17)(ii)	3.73
C(2)···C(15c)(v)	3.55
N(3)···C(15b)(iii)	3.63
C(4)···C(15b)(v)	3.71
C(6)···O(12)(vi)	3.40
C(8)···C(13)(iii)	3.64
C(9)···C(13)(iii)	3.64
C(9a)···O(14)(iii)	3.54
N(10)···O(14)(iii)	3.31
C(10a)···O(14)(iii)	3.55
O(12)···O(12)(vii)	3.73
O(12)···C(15a)(vi)	3.34
O(14)···C(20)(iii)	3.61
C(15d)···C(18)(viii)	3.77

The intermolecular distances given in Table 13 do not show any unusually short contacts. However, the distance from C(18) to the crystal water oxygen O(k3) (ix), 3.28 Å, is significantly shorter than the normal van der Waals separation, 3.40 Å, between methyl carbon and oxygen.²⁴ A critical discussion of short C—H···O contacts was recently given by Donohue.²⁵

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