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The Crystal Structure of Riboflavin Hydrobromide Monohydrate

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The crystal structure of riboflavin hydrobromide monohydrate has been determined by a three-dimensional X-ray analysis. The space group is $P\,2_12_12_1$ with four formula units in the unit cell of dimensions $a=18.28$, $b=6.99$ and $c=14.77$ Å. The structural parameters were refined by means of a block-diagonal least-squares method, the final R factor being 0.07. The ribitol does not form a furanose ring but a chain. The protonation of the isoalloxazine ring occurs at the N(1) atom, and the C(4a)-N(10) bond is found to be a double bond. The bromide ion is situated midway between two isoalloxazine rings separated by a period along the b axis.

Riboflavin, in the form of the mono- and dinucleotide, is a prosthetic group of several enzymes concerning biochemical oxidation-reduction. These enzymes act as hydrogen carriers from a substrate to an acceptor molecule, when riboflavin alternatively accepts and releases two hydrogen atoms.

The electronic structure of riboflavin has been investigated in order to elucidate the mechanism of the transfer of the hydrogen atom. Guzzo and Tollin¹⁾ have suggested from the study of EPR spectra that it is reduced into semiquinone by strong acid. On the other hand, Pullman and Pullman have proposed the keto form to the reduced riboflavin from the theoretical calculation.²⁾

The present study has been undertaken to establish the relationship between the structural characteristics of mono-protonated riboflavin and its biological function.

Experimental

The crystals were obtained from 6 N HBr solution of riboflavin. They are yellow rods elongated along the b axis. Unit cell dimensions were determined from the equatorial Weissenberg photographs about the b and c axes, on which the powder pattern of aluminum were superposed for calibration. The crystal data are shown in Table 1.

TABLE 1. CRYSTAL DATA

Unit cell dimensions	$a=18.28\pm0.04$ Å $b=6.99\pm0.02$ $c=14.77\pm0.03$
Absent spectra	$(h00)$; $h=2n+1$ $(0k0)$; $k=2n+1$ $(00l)$; $l=2n+1$
Space group	$P2_12_12_1$
Density	$D_m=1.68$ g/cm³ $D_c=1.67$ g/cm³, when $Z=4$
Molecular weight	475.3
Linear absorption coefficient for Cu$K\alpha$ radiation	30.4
$F(000)$	976

The equi-inclination Weissenberg photographs were taken for layer lines 0 to 5 about the b axis and 0 to 10 about c with Cu$K\alpha$ radiation. The number of independent reflections recorded was 2261, but the intensities of 225 of these were too weak to be measured. The relative intensities were measured visually and the range was 1 to 4000. They were corrected for Lorentz and polarization factors and spot-size factors for the equi-inclination Weissenberg photographs, but the corrections for absorption and secondary extinction were neglected. A rod-shaped crystal having a cross section of 0.5 mm×0.3 mm was used for the b axis photographs. A crystal for the c axis photographs, cut perpendicularly to the b axis, has a dimension of 0.2 mm×0.2 mm× 0.3 mm.

Structure Determination and Refinement

From a three-dimensional Patterson function the bromide ion was easily located at $x=0.205$, $y=0.250$ and $z=0.119$. Fourier synthesis with the phases based on the bromide ion has an additional mirror plane because the y parameter of the heavy atom was a special value. The atoms in the isoalloxazine ring and C(1') in the ribityl group were located near the planes of $y=0.25$, while the as-

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1) A. V. Guzzo and G. Tollin, *Arch. Biochem. Biophys.*, **103**, 231 (1963).

2) B. Pullman and A. Pullman, *Proc. Natl. Acad. Sci. U. S.*, **45**, 136 (1959).

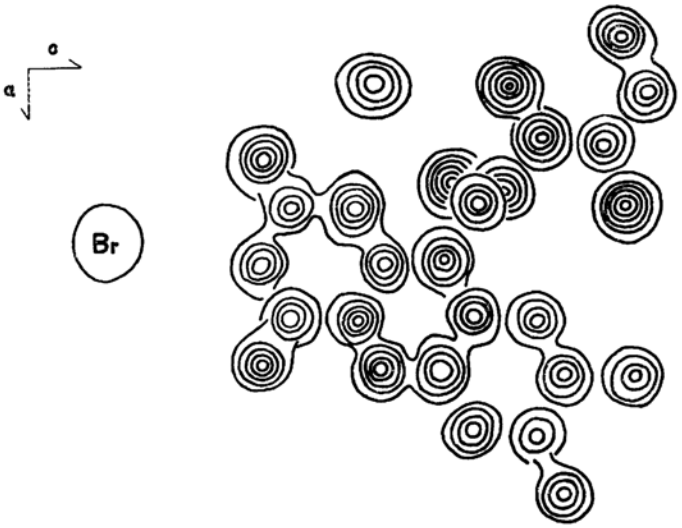

Fig. 1. Composite drawing of the final electron density map viewed along the *b* axis. Contours are drawn at intervals of 2.0 e·Å^{-3}; those for the bromide ion are not drawn. The lowest is 1.5 e·Å^{-3}.

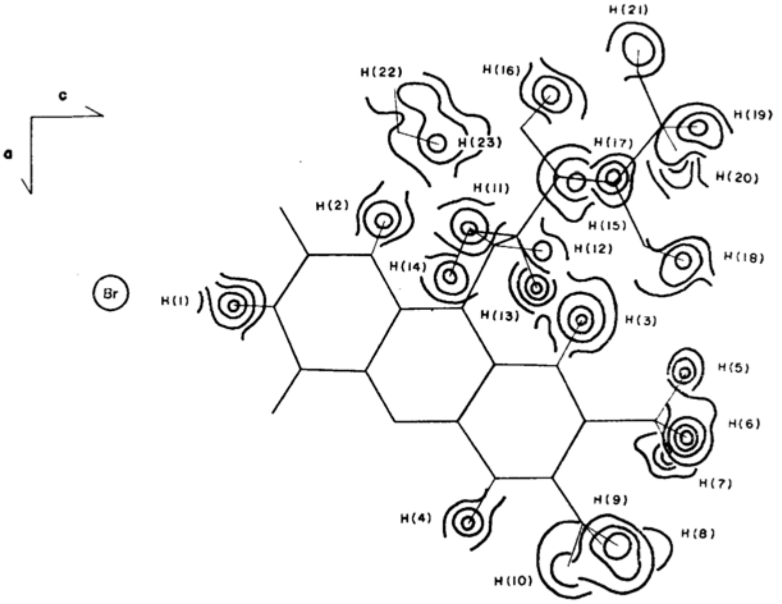

Fig. 2. Location of hydrogen atoms from a three-dimensional difference Fourier map. First contour 0.1 e·Å^{-3}; interval 0.2 e·Å^{-3}.

signment of the peaks to the other light atoms was somewhat puzzling because of the presence of the additional mirror plane. Successive Fourier summations were able to give well resolved peaks for all twenty-nine non-hydrogen atoms.

Atomic positions and anisotropic temperature factors were refined by a block-diagonal least-squares method. A difference Fourier map, calculated after several cycles of least-squares refinement, gave a fair indication of the positions of the hydrogen atoms. Further refinement, including hydrogen atoms, was proceeded with anisotropic temperature factors for all the non-hydrogen atoms and with isotropic ones for hydrogen atoms. Atomic scattering factors were taken from the "International Tables for X-Ray Crystallography." Anomalous scattering effect was corrected for the bromide ion ($\Delta f' = -0.9$, $\Delta f'' = 1.4$). Weighting scheme was as follows;

$$w = 1.0 \quad \text{if } |F_o| > 0$$

$$w = 0.5 \quad \text{if } |F_o| = 0$$

TABLE 2(a). ATOMIC PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	0.2062(1)	0.2367(2)	0.1173(1)	234(3)	1960(26)	365(5)	382(21)	−52(8)	−11(28)
C(2)	0.1642(6)	0.2414(20)	0.3988(9)	212(31)	1705(239)	348(54)	2(190)	−51(70)	162(266)
C(4)	0.2953(6)	0.3106(15)	0.3945(8)	171(29)	939(197)	291(50)	152(144)	113(76)	122(179)
C(5)	0.4261(6)	0.2966(19)	0.6746(9)	179(32)	1111(305)	334(51)	5(170)	105(69)	−344(222)
C(6)	0.4294(6)	0.2904(19)	0.7664(9)	187(32)	1362(288)	337(51)	−16(173)	−2(70)	−5(226)
C(7)	0.3617(6)	0.2770(19)	0.8158(8)	210(33)	1205(249)	279(45)	35(188)	67(66)	−24(225)
C(8)	0.2964(6)	0.2714(17)	0.7740(7)	170(27)	1467(229)	273(42)	−170(197)	33(63)	209(212)
C(4a)	0.2966(6)	0.2916(15)	0.4950(7)	177(29)	979(231)	236(41)	−82(161)	47(65)	97(172)
C(8a)	0.2937(6)	0.2781(15)	0.6795(7)	175(27)	874(198)	232(39)	85(169)	6(62)	−299(178)
C(9a)	0.2287(5)	0.2651(17)	0.5400(8)	181(28)	1026(195)	277(43)	35(153)	7(57)	47(214)
C(10a)	0.3592(5)	0.2911(16)	0.6287(9)	140(27)	709(233)	370(52)	−111(141)	62(67)	174(221)
C(6m)	0.5009(6)	0.3012(24)	0.8182(9)	203(33)	2929(446)	334(55)	−198(214)	88(75)	25(283)
C(7m)	0.3632(6)	0.2697(20)	0.9200(8)	243(35)	1600(255)	293(47)	−268(208)	0(69)	−116(246)
N(1)	0.1659(5)	0.2370(16)	0.4921(6)	197(25)	1481(192)	238(36)	−125(149)	−35(51)	211(183)
N(3)	0.2281(5)	0.2744(15)	0.3533(6)	198(27)	1764(203)	241(36)	99(140)	25(51)	−92(173)
N(9)	0.2278(4)	0.2663(13)	0.6305(6)	142(21)	841(152)	284(37)	227(114)	46(47)	324(177)
N(10)	0.3584(5)	0.3028(14)	0.5360(6)	163(26)	972(230)	229(37)	−214(133)	58(54)	−105(161)
O(2)	0.1081(4)	0.2118(19)	0.3582(6)	206(24)	3889(361)	324(39)	−259(179)	−151(54)	552(234)
O(4)	0.3480(5)	0.3588(14)	0.3498(6)	224(26)	1872(227)	322(37)	−33(139)	167(51)	52(165)
C(1′)	0.1573(5)	0.2585(19)	0.6838(7)	116(24)	1729(220)	257(41)	436(167)	20(54)	−375(228)
C(2′)	0.1439(6)	0.0554(17)	0.7179(8)	135(29)	1411(254)	254(48)	158(152)	5(64)	−156(203)
C(3′)	0.0775(6)	0.0442(17)	0.7774(8)	143(31)	1452(242)	285(49)	3(153)	29(67)	80(203)
C(4′)	0.0844(6)	0.1629(18)	0.8607(9)	194(33)	1696(280)	303(55)	−116(169)	134(72)	4(209)
C(5′)	0.0242(7)	0.1130(21)	0.9305(9)	250(40)	1857(327)	396(64)	25(207)	161(86)	376(263)
O(2′)	0.1347(4)	−0.0664(12)	0.6397(6)	187(23)	1359(173)	311(38)	45(113)	−4(49)	−241(143)
O(3′)	0.0168(4)	0.1002(14)	0.7258(6)	171(25)	2155(231)	277(37)	−6(135)	44(50)	96(173)
O(4′)	0.1545(5)	0.1279(15)	0.9028(6)	204(24)	3052(276)	343(43)	102(150)	−18(56)	−200(193)
O(5′)	−0.0462(4)	0.1137(13)	0.8916(8)	213(26)	1878(207)	588(55)	235(129)	245(70)	−53(217)
OW	0.0149(5)	0.1111(16)	0.5370(7)	240(30)	2700(277)	353(41)	113(161)	−49(61)	92(197)

Anisotropic temperature factors in the expression, $\exp\{-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})\}$, are multiplied by 10^5. The estimated standard deviations given in parentheses refer to the last decimal positions at respective values.

TABLE 2(b). THE FINAL PARAMETERS OF HYDROGEN ATOMS

Atom	**	x	y	y
H(1)	N(3)	0.2173	0.2480	0.2791
H(2)	N(1)	0.1158	0.1801	0.5204
H(3)	C(8)	0.2422	0.2827	0.8004
H(4)	C(5)	0.4729	0.3214	0.6363
H(5)	C(7m)	0.3013	0.2675	0.9622
H(6)	C(7m)	0.3752	0.3626	0.9610
H(7)	C(7m)	0.3992	0.1286	0.9410
H(8)	C(6m)	0.5145	0.1450	0.8551
H(9)	C(6m)	0.5069	0.4366	0.8548
H(10)	C(6m)	0.5324	0.3291	0.7826
H(11)	C(1′)	0.1140	0.3097	0.6552
H(12)	C(1′)	0.1672	0.3218	0.7495

Atom	**	x	y	z
H(13)	C(2′)	0.1886	0.0001	0.7500
H(14)	O(2′)	0.1840	−0.1250	0.6200
H(15)	C(3′)	0.0858	−0.0581	0.7855
H(16)	O(3′)	−0.0216	0.1003	0.7556
H(17)	C(4′)	0.0808	0.2741	0.8508
H(18)	O(4′)	0.1475	0.1694	0.9846
H(19)	C(5′)	0.0439	0.1447	0.9967
H(20)	C(5′)	0.0496	−0.0077	0.9629
H(21)	C(5′)	−0.0652	0.1770	0.8858
H(22)	OW	−0.0285	0.0707	0.5273
H(23)	OW	0.0258	0.0774	0.5868

* The mean value of the e.s.d. of the parameters are $\sigma(x)=0.13$ Å, $\sigma(y)=0.15$ Å and $\sigma(z)=0.14$ Å.

** The heavy atoms bonded to each hydrogen atom.

TABLE 3. OBSERVED AND CALCULATED STRUCTURE FACTORS (×2.5)

K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC
H,L=	0	0	0	0	0	H,L=	1	12	0	36	39	5	23	19	0	58	44	7	23	30	2	0	10	0	26	27	H,L=	7	12
2	918	908	1	0	4	0	71	83	1	121	121	6	36	40	1	234	229	8	0	20	H,L=	5	18	1	30	33	0	10	4
3	0	0	2	42	41	1	20	25	2	60	63	7	29	30	2	91	95	H,L=	5	2	0	0	1	2	26	22	1	48	49
4	311	275	3	24	26	2	76	89	3	91	91	8	19	23	3	130	126	0	173	184	1	25	22	3	41	52	2	0	5
5	0	0	4	32	25	3	22	22	4	37	42	H,L=	3	7	4	108	112	1	388	400	H,L=	6	0	4	0	10	3	17	16
6	189	178	5	0	12	4	46	49	5	58	55	0	91	103	5	101	101	2	150	139	0	286	282	5	30	26	4	5	11
7	0	0	H,L=	0	16	5	23	21	6	14	17	1	118	120	6	20	27	3	182	185	1	270	281	H,L=	6	15	5	14	14
8	58	37	0	36	24	H,L=	1	13	7	52	44	2	134	129	7	59	60	4	15	18	2	31	28	0	66	62	H,L=	7	13
H,L=	0	1	1	0	1	0	36	34	H,L=	2	10	3	107	110	8	17	16	5	108	104	3	161	150	1	16	16	0	21	18
1	102	93	2	76	73	1	23	17	0	77	87	4	96	96	H,L=	4	5	6	30	33	4	49	49	2	16	18	1	26	20
2	89	70	3	21	17	2	0	10	1	62	59	5	61	61	0	279	291	7	31	30	5	129	130	3	38	29	2	0	3
3	94	95	4	58	58	3	0	6	2	59	65	6	62	63	1	47	50	8	43	44	6	31	28	4	0	6	3	0	9
4	182	177	H,L=	0	17	4	50	36	3	0	9	7	18	23	2	174	169	H,L=	5	3	7	82	71	H,L=	6	16	4	0	10
5	22	24	0	0	0	5	0	6	4	30	33	8	31	34	3	49	48	0	59	58	8	13	9	0	0	1	5	15	10
6	113	135	1	68	57	H,L=	1	14	5	47	50	H,L=	3	8	4	92	95	1	103	98	H,L=	6	1	1	47	32	H,L=	7	14
7	37	37	2	28	28	0	137	136	6	0	14		37	37	5	38	40	2	117	111	0	183	197	2	21	17	0	33	32
8	66	73	3	38	39	1	12	18	7	29	19	1	88	87	6	60	62	3	63	61	1	47	53	3	31	25	1	53	49
H,L=	0	2	H,L=	0	18	2	98	106	H,L=	2	11	2	46	44	7	32	35	4	89	92	2	180	165	4	22	27	2	30	35
1	26	12	0	36	32	3	12	19	0	0	5	3	48	45	8	23	18	5	43	47	3	15	16	H,L=	6	17	3	37	28
2	74	62	1	0	3	4	73	72	1	43	48	4	76	79	H,L=	4	6	6	57	61	4	141	133	0	82	66	4	16	20
3	29	38	2	21	18	5	0	12	2	47	53	5	48	49	0	81	88	7	36	40	5	26	23	1	0	3	5	35	33
4	18	21	H,L=	1	0	H,L=	1	15	3	0	11	6	44	32	1	98	102	8	8	21	6	58	59	2	77	66	H,L=	7	15
5	25	22	1	91	70	0	52	51	4	31	36	7	0	7	2	22	25	H,L=	5	4	7	30	31	H,L=	7	0	0	29	32
6	0	1	2	520	512	1	27	22	5	17	20	H,L=	3	9	3	12	15	0	115	110	8	26	7	0	0	0	1	32	26
7	34	32	3	151	158	2	0	6	H,L=	2	12	0	52	66	4	66	62	1	88	87	H,L=	6	2	1	25	17	2	61	55
8	0	17	4	131	121	3	27	17	0	72	71	1	19	23	5	41	50	2	28	25	0	100	102	2	77	76	3	12	12
H,L=	0	3	5	78	87	4	0	8	1	54	55	2	82	78	6	38	34	3	57	59	1	143	137	3	20	15	4	48	49
0	0	0	6	38	45	5	22	20	2	99	98	3	37	41	7	0	16	4	41	40	2	159	154	4	22	20	H,L=	7	16
1	164	154	7	0	29	H,L=	1	16	3	49	42	4	40	37	8	30	28	5	32	40	3	77	78	5	19	15	0	0	10
2	85	82	8	50	41	0	64	66	4	70	70	5	0	13	H,L=	4	7	6	53	56	4	27	28	6	60	56	1	44	43
3	49	42	H,L=	1	1	1	34	31	5	28	29	6	0	10	0	97	98	7	0	9	5	38	39	7	28	27	2	27	28
4	28	18	1	21	4	2	72	70	H,L=	2	13	7	0	9	1	72	68	8	16	15	6	27	25	H,L=	7	1	3	49	47
5	67	69	2	401	372	3	16	14	0	68	74	H,L=	3	10	2	52	55	H,L=	5	5	7	14	19	0	229	262	H,L=	7	17
6	76	86	3	22	31	4	42	41	1	83	78	0	73	74	3	51	47	0	265	235	8	32	28	1	99	90	0	32	23
7	23	22	4	197	192	H,L=	1	17	2	74	75	1	35	38	4	47	50	1	74	73	H,L=	6	3	2	116	106	1	0	12
8	26	22	5	12	22	0	28	25	3	46	49	2	92	94	5	60	63	2	114	111	0	189	196	3	58	55	2	19	16
H,L=	0	4	6	61	70	1	15	13	4	55	56	3	74	78	6	14	23	3	63	56	1	124	121	4	61	68	H,L=	8	0
0	403	457	7	24	27	2	0	2	5	32	31	4	65	69	7	38	37	4	36	22	2	122	123	5	21	17	0	0	8
1	103	97	8	28	36	3	18	20	H,L=	2	14	5	38	39	8	0	6	5	32	29	3	120	122	6	71	73	1	179	176
2	334	334	H,L=	1	2	H,L=	1	18	0	42	40	6	40	39	H,L=	4	8	6	38	42	4	114	111	7	29	26	2	112	105
3	48	40	1	52	53	0	47	42	1	0	10	7	0	11	0	33	37	7	49	45	5	67	74	8	23	22	3	171	161
4	112	111	2	172	158	1	20	18	2	42	41	H,L=	3	11	1	145	151	8	15	16	6	62	62	H,L=	7	2	4	82	85
5	28	34	3	97	94	2	35	35	3	0	12	0	99	110	2	83	85	H,L=	5	6	7	48	56	0	125	126	5	74	73
6	70	66	4	172	185	H,L=	2	0	4	36	36	1	68	67	3	109	113	0	97	104	8	8	18	1	168	157	6	0	6
7	0	2	5	39	35	1	89	82	5	0	8	2	87	83	4	69	69	1	193	194	H,L=	6	4	2	92	91	7	27	25
8	39	33	6	122	110	2	604	537	H,L=	2	15	3	53	50	5	73	80	2	54	54	0	39	37	3	151	152	H,L=	8	1
H,L=	0	5	7	13	19	3	83	77	0	14	16	4	51	48	6	51	41	3	172	174	1	262	253	4	44	45	0	126	134
0	0	0	8	35	25	4	366	342	1	27	25	5	33	36	7	61	55	4	27	23	2	59	56	5	99	107	1	123	116
1	324	328	H,L=	1	3	5	78	77	2	0	9	H,L=	3	12	H,L=	4	9	5	70	76	3	200	211	6	23	26	2	105	98
2	104	107	0	26	23	6	112	103	3	0	14	0	0	8	0	149	161	6	0	8	4	40	42	7	47	41	3	41	44
3	49	47	1	271	275	7	39	47	4	28	18	1	33	29	1	64	58	7	28	30	5	141	152	8	0	12	4	91	94
4	50	56	2	126	114	8	24	41	5	0	5	2	23	27	2	147	139	8	0	12	6	13	21	H,L=	7	3	5	9	17
5	75	83	3	160	151	H,L=	2	1	H,L=	2	16	3	31	31	3	81	86	H,L=	5	7	7	38	49	0	13	20	6	52	56
6	35	37	4	112	113	0	137	63	0	48	45	4	36	44	4	41	48	0	155	153	H,L=	6	5	1	156	151	7	32	31
7	68	66	5	116	119	1	199	201	1	25	22	5	28	26	5	58	65	1	61	55	0	105	119	2	21	17	8	26	22
8	24	27	6	39	39	2	116	123	2	39	39	H,L=	3	13	6	42	29	2	124	122	1	99	98	3	85	79	H,L=	8	2
H,L=	0	6	7	32	30	3	10	16	3	33	32	0	0	10	7	33	28	3	31	32	2	146	148	4	35	37	0	21	15
0	42	39	8	17	19	4	25	30	4	29	30	1	29	27	H,L=	4	10	4	102	102	3	36	37	5	32	38	1	76	77
1	34	43	H,L=	1	4	5	36	45	H,L=	2	17	2	28	29	0	23	27	5	11	18	4	88	97	6	36	34	2	28	27
2	109	103	0	10	16	6	28	41	0	28	2	3	12	22	1	102	95	6	67	57	5	24	30	7	17	23	3	48	48
3	27	33	1	73	70	7	37	46	1	40	33	4	0	7	2	19	18	7	30	28	6	47	44	8	24	28	4	20	13
4	40	30	2	60	56	8	32	35	2	19	18	5	0	5	3	51	52	8	30	29	7	17	19	H,L=	7	4	5	58	63
5	51	54	3	44	40	H,L=	2	2	3	12	33	H,L=	3	14	4	30	31	H,L=	5	8	8	18	21	0	101	86	6	0	8
6	22	22	4	80	81	0	125	118	H,L=	2	18	0	51	56	5	17	24	0	44	45	H,L=	6	6	1	256	242	7	10	17
7	30	26	5	29	37	1	109	103	0	30	27	1	73	65	6	40	41	1	44	41	0	18	15	2	77	73	8	19	16
8	9	18	6	0	13	2	154	149	1	17	16	2	51	59	7	29	31	2	34	33	1	53	59	3	92	86	H,L=	8	3
H,L=	0	7	7	33	32	3	100	98	2	33	34	3	45	41	H,L=	4	11	3	45	45	2	87	86	4	30	35	0	45	100
0	0	0	8	0	9	4	50	50	H,L=	3	0	4	34	35	0	0	7	4	18	23	3	78	78	5	55	62	1	91	93
1	140	139	H,L=	1	5	5	41	35	1	156	146	5	31	30	1	10	8	5	35	32	4	29	33	6	13	16	2	57	54
2	63	70	0	140	136	6	33	28	2	18	25	H,L=	3	15	2	42	43	6	43	39	5	35	41	7	25	27	3	93	89
4	101	98	1	273	267	7	32	32	3	18	18	0	53	49	3	25	29	7	17	16	6	37	37	H,L=	7	5	4	57	57
4	0	12	2	92	82	8	14	26	4	143	195	1	44	46	4	6	18	H,L=	5	9	7	11	17	0	92	96	5	58	62
5	11	16	3	75	82	H,L=	2	3	5	16	14	2	27	23	5	38	42	0	25	23	8	17	14	1	56	58	6	33	35
6	0	2	4	41	32	0	18	20	6	87	104	3	41	40	H,L=	4	12	1	71	72	H,L=	6	7	2	86	89	7	41	41
7	0	3	5	63	71	1	44	45	7	0	1	4	8	15	0	49	55	2	30	35	0	76	86	3	56	49	H,L=	8	4
8	0	4	6	38	40	2	98	94	8	44	35	5	19	19	1	64	69	3	11	16	1	57	57	4	82	85	0	29	31
H,L=	0	8	7	14	23	3	101	96	H,L=	3	1	H,L=	3	16	2	69	67	4	18	26	2	61	53	5	54	50	1	316	315
0	287	301	8	22	17	4	40	34	0	169	175	0	16	18	3	65	62	5	17	19	3	55	56	6	36	33	2	35	41
1	45	34	H,L=	1	6	5	62	65	1	246	227	1	25	30	4	36	34	6	0	11	4	40	36	7	36	35	3	144	141
2	186	175	0	139	146	6	19	19	2	232	213	2	12	19	5	39	41	7	0	19	5	45	52	8	0	11	4	35	41
3	39	51	1	143	129	7	37	35	3	103	100	3	35	30	H,L=	4	13	H,L=	5	10	6	14	23	H,L=	7	6	5	85	100
4	109	104	2	141	137	8	29	31	4	110	115	4	31	31	0	105	105	0	24	23	7	26	19	0	53	56	6	20	19
5	90	97	3	90	91	H,L=	2	4	5	43	50	H,L=	3	17	1	51	45	1	200	201	8	23	3	1	206	209	7	60	[illegible]
6	71	54	4	137	142	0	280	318	6	68	77	0	0	1	2	68	68	2	31	38	H,L=	6	8	2	91	86	H,L=	8	5
7	53	49	5	29	31	1	149	148	7	0	5	1	0	7	3	39	42	3	96	98	0	26	27	3	76	85	0	7	20
H,L=	0	9	6	73	79	2	200	185	8	47	45	2	0	12	4	48	51	4	63	74	1	107	112	4	51	56	1	144	120
0	0	0	7	8	19	3	199	199	H,L=	3	2	3	20	8	5	36	32	5	78	80	2	26	25	5	117	121	2	105	115
1	106	171	8	30	29	4	114	116	0	213	230	H,L=	3	18	H,L=	4	14	6	43	48	3	107	111	6	18	14	3	125	124
2	21	19	H,L=	1	7	5	21	30	1	179	177	0	33	29	0	51	53	7	45	45	4	0	12	7	32	38	4	71	65
3	114	107	0	36	40	6	79	74	2	230	233	1	35	31	1	79	71	H,L=	5	11	5	83	87	H,L=	7	7	5	30	41
4	0	3	1	260	261	7	30	30	3	165	165	2	25	24	2	29	24	0	91	106	6	0	8	0	120	132	6	13	15
5	61	51	2	100	105	8	29	26	4	147	148	H,L=	4	0	3	23	24	1	49	54	7	47	38	1	71	73	7	32	25
6	21	29	3	200	197	H,L=	2	5	5	63	59	0	22	11	4	28	26	2	99	90	H,L=	6	9	2	117	119	8	16	17
7	42	28	4	61	68	0	143	154	6	65	66	1	217	237	5	21	19	3	22	24	0	89	92	3	67	72	H,L=	8	6
H,L=	0	10	5	99	104	1	169	162	7	45	46	2	87	67	H,L=	4	15	4	72	70	1	58	56	4	76	82	0	74	71
0	35	40	6	56	62	2	162	153	8	47	49	3	262	228	0	27	20	5	43	47	2	100	99	5	25	22	1	36	33
1	48	52	7	51	41	3	186	191	H,L=	3	3	4	31	27	1	0	5	H,L=	5	12	3	13	18	6	41	43	2	65	65
2	67	70	8	33	36	4	48	54	0	241	254	5	131	133	2	0	1	0	80	82	4	80	90	7	0	11	3	74	75
3	19	20	H,L=	1	8	5	96	96	1	174	166	6	54	54	3	23	20	1	35	36	5	36	41	H,L=	7	8	4	22	25
4	53	65	0	29	16	6	38	40	2	198	191	7	92	83	4	28	24	2	19	20	6	27	24	0	15	11	5	54	59
5	0	9	1	62	60	7	32	22	3	140	133	8	27	43	5	15	21	3	46	54	7	21	24	1	99	104	6	22	21
6	33	37	2	26	20	8	13	15	4	124	124	H,L=	4	1	H,L=	4	16	4	12	23	H,L=	6	10	2	56	50	7	29	30
7	25	24	3	70	65	H,L=	2	6	5	59	58	0	170	191	0	26	25	5	10	18	0	68	76	3	76	72	H,L=	8	7
H,L=	0	11	4	21	22	0	48	44	6	52	55	1	83	75	1	49	46	H,L=	5	13	1	55	56	4	18	24	0	0	9
0	0	1	5	44	40	1	100	98	7	32	32	2	132	122	2	12	11	0	26	24	2	84	81	5	25	29	1	54	59
1	0	8	6	0	9	2	82	79	8	34	30	3	120	115	3	27	28	1	26	22	3	58	60	6	42	30	2	29	34
2	0	2	7	37	31	3	121	124	H,L=	3	4	4	19	16	4	0	4	2	0	11	4	51	56	7	39	26	3	80	84
3	40	48	H,L=	1	9	4	60	41	0	45	47	5	67	66	H,L=	4	17	3	30	27	5	36	43	H,L=	7	9	4	37	41
4	40	40	0	26	19	5	24	23	1	34	39	6	14	14	0	52	48	4	0	3	6	31	40	0	39	44	5	23	27
5	30	33	1	97	103	6	13	22	2	97	101	7	19	17	1	32	28	5	30	28	7	0	13	1	44	46	6	16	27
H,L=	0	12	2	30	31	7	21	26	3	20	18	8	25	19	2	50	44	H,L=	5	14	H,L=	6	11	2	21	18	7	26	25
0	128	124	3	34	39	8	26	24	4	45	74	H,L=	4	2	H,L=	4	18	0	21	13	0	71	69	3	16	21	H,L=	8	8
1	29	31	4	40	36	H,L=	2	7	5	0	8	0	41	38	0	40	36	1	76	71	1	42	45	4	28	30	0	108	114
2	63	61	5	40	44	0	73	77	6	32	32	1	28	24	1	30	28	2	29	21	2	83	91	5	36	36	1	163	166
3	0	3	6	15	17	1	43	36	7	0	13	2	93	93	H,L=	5	0	3	72	68	3	79	95	6	27	28	2	98	101
4	50	56	7	31	23	2	96	95	8	17	21	3	87	87	0	0	0	4	32	30	4	46	46	7	48	43	3	67	79
5	31	28	H,L=	1	10	3	50	51	H,L=	3	5	4	41	40	1	39	40	5	35	36	5	54	58	H,L=	7	10	4	48	56
H,L=	0	13	0	125	135	4	26	24	0	129	122	5	64	68	2	173	156	H,L=	5	15	H,L=	6	12	0	66	51	5	52	56
0	0	0	1	23	23	5	39	47	1	17	35	6	59	51	3	22	20	0	61	54	0	24	23	1	198	207	6	16	22
1	79	73	2	86	86	6	0	14	2	85	88	7	18	26	4	22	16	1	40	35	1	119	129	2	23	19	7	46	45
2	0	2	3	34	31	7	22	28	3	121	124	8	14	15	5	0	3	2	67	65	2	23	21	3	200	208	H,L=	8	9
3	51	49	4	62	64	8	12	11	4	105	114	H,L=	4	3	6	0	18	3	0	5	3	82	87	4	68	68	0	155	162
4	0	6	5	0	10	H,L=	2	8	5	55	65	0	83	91	7	29	26	4	34	37	4	18	17	5	95	89	1	100	99
5	26	19	6	56	52	0	191	206	6	14	24	1	107	102	8	45	40	H,L=	5	16	5	52	52	6	16	15	2	74	74
H,L=	0	14	7	23	21	1	134	134	7	32	29	2	118	113	H,L=	5	1	0	32	23	H,L=	6	13	7	36	31	3	33	36
0	36	40	H,L=	1	11	2	175	174	8	16	9	3	55	53	0	151	156	1	65	67	0	65	67	H,L=	7	11	4	45	51
1	0	2	0	0	9	3	175	127	H,L=	3	6	4	39	38	1	29	26	2	0	3	1	11	17	0	39	38	5	50	51
2	81	80	1	124	116	4	106	109	0	122	129	5	55	55	2	191	169	3	26	29	2	78	82	1	116	126	6	32	40
3	11	10	2	31	37	5	49	51	1	146	149	6	45	49	3	60	61	4	0	14	3	0	17	2	45	58	7	29	24
4	41	41	3	107	107	6	52	51	2	172	167	7	32	27	4	136	128	H,L=	5	17	4	65	59	3	81	95	H,L=	8	10
5	0	2	4	24	20	7	34	32	3	40	73	8	34	32	5	39	39	0	0	3	5	12	7	4	57	51	0	49	[illegible]
H,L=	0	15	5	62	58	H,L=	2	9	4	71	74	H,L=	4	4	6	52	55	1	0	2	H,L=	6	14	5	56	64	1	57	65

Table 3. (continued)

K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC
2	84	88	1	34	36	6	36	34	6	31	28	3	83	85	1	23	18	H,L=	15	1	6	0	13	H,L=	17	11	0	0	7
3	57	60	2	44	50	H,L=	10	9	H,L=	11	9	4	0	7	2	48	47	0	115	114	H,L=	16	5	0	59	56	1	0	2
4	24	27	3	49	56	0	61	59	0	0	8	5	62	55	3	0	5	1	44	44	0	104	111	1	0	8	2	24	20
5	79	79	4	0	3	1	73	72	1	28	32	6	9	15	4	37	36	2	133	139	1	53	57	2	58	50	3	26	[illegible]
6	28	29	5	23	15	2	100	104	2	10	23	H,L=	12	11	H,L=	13	13	3	35	38	2	63	65	H,L=	17	12	H,L=	19	9
H,L=	8	11	6	25	20	3	84	94	3	44	47	0	21	15	0	54	49	4	69	69	3	32	22	0	15	16	0	30	32
0	73	68	H,L=	9	10	4	54	56	4	57	62	1	0	16	1	23	22	5	0	7	4	24	25	1	28	21	1	18	16
1	144	155	0	88	90	5	80	80	5	31	31	2	0	9	2	32	25	6	37	31	5	12	15	H,L=	18	0	2	23	22
2	132	120	1	102	98	6	23	19	6	43	45	3	7	14	3	12	15	H,L=	15	2	6	27	30	0	52	54	H,L=	19	10
3	90	88	2	16	23	H,L=	10	10	H,L=	11	10	4	0	11	4	24	26	0	45	47	H,L=	16	6	1	39	36	0	27	23
4	66	72	3	58	58	0	33	30	0	102	106	5	0	11	H,L=	13	14	1	112	118	0	0	11	2	25	12	1	32	27
5	53	50	4	33	30	1	42	44	1	38	36	H,L=	12	12	0	74	62	2	72	74	1	65	69	3	69	66	2	20	21
H,L=	8	12	5	56	48	2	58	59	2	61	61	0	76	70	1	0	10	3	83	83	2	31	29	4	0	8	H,L=	[illegible]	[illegible]
0	0	3	6	26	19	3	51	56	3	42	35	1	11	15	2	49	44	4	86	84	3	0	13	5	52	46	0	0	7
1	119	123	H,L=	9	11	4	26	26	4	38	40	2	74	61	H,L=	13	15	5	29	29	4	31	33	H,L=	18	1	1	16	21
2	25	21	0	26	19	5	39	40	5	0	9	3	25	22	0	0	1	6	46	43	5	26	25	0	101	107	H,L=	20	[illegible]
3	106	93	1	124	115	6	0	10	6	36	34	4	46	42	1	36	31	H,L=	15	3	H,L=	16	7	1	51	51	0	59	56
4	9	18	2	13	22	H,L=	10	11	H,L=	11	11	5	15	21	H,L=	14	0	0	62	65	0	108	118	2	86	74	1	81	82
5	52	52	3	60	68	0	62	69	0	0	6	H,L=	12	13	0	274	280	1	32	30	1	0	15	3	37	36	2	57	49
H,L=	8	13	4	54	61	1	53	59	1	103	91	0	0	5	1	129	125	2	45	57	2	100	101	4	66	61	3	60	62
0	76	74	5	30	36	2	0	4	2	29	27	1	51	50	2	162	161	3	43	46	3	36	42	5	27	28	4	17	14
1	38	38	H,L=	9	12	3	35	32	3	51	52	2	23	24	3	17	17	4	34	34	4	47	46	H,L=	18	2	H,L=	20	1
2	79	73	0	82	81	4	10	16	4	0	12	3	45	42	4	114	114	5	55	54	5	40	43	0	21	19	0	28	24
3	28	27	1	90	88	5	0	12	5	32	32	4	0	13	5	26	27	6	22	22	H,L=	16	8	1	20	18	1	37	37
4	32	32	2	34	29	H,L=	10	12	H,L=	11	12	H,L=	12	14	6	57	52	H,L=	15	4	0	34	35	2	0	12	2	16	18
5	14	19	3	57	59	0	59	57	0	36	34	0	34	30	H,L=	14	1	0	0	7	1	42	41	3	0	8	3	33	30
H,L=	8	14	4	42	38	1	63	61	1	0	11	1	0	1	0	89	97	1	29	29	2	45	41	4	10	15	4	26	23
0	50	42	5	40	46	2	70	56	2	50	45	2	28	29	1	49	56	2	0	9	3	46	41	5	0	10	H,L=	20	2
1	0	5	H,L=	9	13	3	58	57	3	33	33	H,L=	12	15	2	122	119	3	0	5	4	28	32	H,L=	18	3	0	35	[illegible]
2	17	15	0	0	4	4	33	32	4	42	35	0	35	33	3	59	56	4	45	47	5	23	21	0	40	35	1	26	24
3	28	15	1	0	7	5	38	36	5	29	30	1	0	6	4	108	105	5	0	4	H,L=	16	9	1	36	34	2	0	[illegible]
4	0	14	2	26	20	H,L=	10	13	H,L=	11	13	H,L=	12	16	5	51	50	6	22	23	0	66	58	2	41	41	3	28	[illegible]
5	19	21	3	19	16	0	48	47	0	0	3	0	35	35	6	46	49	H,L=	15	5	1	26	26	3	25	23	4	10	[illegible]
H,L=	8	15	4	18	23	1	70	68	1	15	10	H,L=	13	0	7	21	26	0	15	18	2	55	53	4	27	17	H,L=	20	3
0	13	5	5	19	17	2	25	22	2	26	17	0	0	0	H,L=	14	2	1	34	38	3	24	19	5	16	15	0	44	37
1	0	6	H,L=	9	14	3	74	69	3	22	23	1	51	54	0	52	52	2	61	51	4	36	39	H,L=	18	4	1	29	31
2	27	6	0	41	46	4	24	22	4	0	14	2	24	30	1	37	40	3	17	19	H,L=	16	10	0	0	3	2	22	16
3	32	22	1	35	28	5	34	37	H,L=	11	14	3	93	94	2	44	47	4	24	27	0	22	20	1	26	22	3	36	35
4	0	11	2	28	28	H,L=	10	14	0	22	15	4	30	34	3	12	21	5	29	28	1	34	28	2	0	9	4	23	25
H,L=	8	16	3	26	24	0	27	28	1	0	5	5	25	28	4	40	42	6	14	14	2	22	19	3	52	48	H,L=	20	4
0	35	33	4	28	26	1	0	10	2	41	39	6	24	20	5	0	9	H,L=	15	6	3	0	7	4	0	9	0	63	[illegible]
1	19	19	H,L=	9	15	2	16	20	3	0	9	H,L=	13	1	6	12	17	0	0	8	4	18	19	5	49	46	1	52	49
2	19	22	0	37	29	3	0	10	4	42	35	0	84	89	H,L=	14	3	1	84	85	H,L=	16	11	H,L=	18	5	2	30	[illegible]
3	0	9	1	69	59	4	18	18	H,L=	11	15	1	51	52	0	0	3	2	44	43	0	0	1	0	75	68	3	40	[illegible]
H,L=	8	17	2	10	34	H,L=	10	15	0	0	2	2	47	44	1	67	69	3	84	75	1	0	5	1	18	17	H,L=	20	[illegible]
0	86	70	3	45	41	0	0	6	1	74	59	3	18	23	2	46	54	4	72	65	2	27	26	2	70	61	0	[illegible]	53
1	0	2	4	27	28	1	0	5	2	50	23	4	42	42	3	65	65	5	25	24	3	26	23	3	[illegible]	11	1	40	4
2	60	60	H,L=	9	16	2	27	14	H,L=	11	16	5	0	6	4	50	57	6	21	20	H,L=	16	12	4	57	57	2	37	[illegible]
H,L=	9	0	0	15	13	3	12	12	0	40	36	6	54	49	5	36	34	H,L=	15	7	0	20	13	5	9	12	3	24	[illegible]
0	0	0	1	54	45	H,L=	10	16	H,L=	12	[illegible]	7	19	19	6	25	24	0	26	21	1	52	46	H,L=	19	6	H,L=	20	6
1	56	51	2	22	19	0	51	42	0	144	152	H,L=	13	2	H,L=	14	4	1	50	55	2	21	21	0	29	24	0	0	[illegible]
2	19	27	3	14	15	1	25	24	1	78	85	0	174	182	0	86	88	2	67	51	3	20	24	1	32	32	1	15	14
3	55	49	H,L=	10	0	2	31	27	2	145	144	1	41	41	1	50	57	3	68	69	H,L=	16	13	2	[illegible]	11	2	0	7
4	0	12	0	81	75	H,L=	11	0	3	30	33	2	110	118	2	82	88	4	30	31	0	66	56	3	34	24	3	22	[illegible]
5	71	79	1	95	89	0	0	0	4	104	107	3	39	42	3	49	52	5	44	41	1	17	19	4	0	7	H,L=	20	7
6	0	8	2	156	151	1	41	46	5	29	35	4	81	81	4	50	51	H,L=	15	8	H,L=	17	0	H,L=	18	7	0	0	[illegible]
7	0	12	3	48	45	2	16	9	6	66	63	5	0	10	5	32	33	0	0	17	0	0	0	0	68	56	1	17	[illegible]
H,L=	9	1	4	103	105	3	61	70	H,L=	12	1	6	66	62	6	31	34	1	70	72	1	51	51	1	14	19	2	0	[illegible]
0	175	173	5	25	24	4	0	1	0	20	20	H,L=	13	3	H,L=	14	5	2	0	3	2	79	83	2	28	31	3	0	[illegible]
1	114	115	6	30	30	5	0	10	1	119	122	0	37	31	0	0	6	3	29	31	3	0	11	3	0	10	H,L=	20	8
2	111	104	7	40	41	6	16	21	2	52	53	1	101	103	1	76	79	4	24	18	4	68	64	4	25	27	0	28	[illegible]
3	85	81	H,L=	10	1	7	21	18	3	74	73	2	55	57	2	50	51	5	20	21	5	35	33	H,L=	18	8	1	25	[illegible]
4	62	66	0	28	32	H,L=	11	1	4	47	50	3	38	37	3	54	55	H,L=	15	9	6	45	56	0	[illegible]	7	2	27	[illegible]
5	59	59	1	108	103	0	14	20	5	74	93	4	19	16	4	73	62	0	0	9	H,L=	17	1	1	37	35	H,L=	20	9
6	37	40	2	65	64	1	136	143	6	46	48	5	39	40	5	60	58	1	0	7	0	33	26	2	11	7	0	14	[illegible]
7	29	35	3	138	140	2	31	35	7	66	67	6	0	8	6	22	16	2	13	18	1	61	58	3	41	39	1	22	[illegible]
H,L=	9	2	4	48	47	3	109	113	H,L=	12	2	7	22	18	H,L=	14	6	3	0	16	2	75	77	H,L=	18	9	H,L=	21	[illegible]
0	72	71	5	59	70	4	37	38	0	50	48	H,L=	13	4	0	0	1	4	0	12	3	0	11	0	52	53	0	0	[illegible]
1	184	174	6	0	14	5	63	66	1	26	26	0	33	29	1	20	20	5	21	26	4	67	64	1	0	17	1	0	[illegible]
2	156	153	7	25	23	6	40	44	2	31	35	1	44	46	2	51	52	H,L=	15	10	5	0	16	2	61	57	2	0	[illegible]
3	86	83	H,L=	10	2	7	0	6	3	29	33	2	40	45	3	53	53	0	45	45	6	35	37	3	22	23	3	23	[illegible]
4	84	85	0	18	22	H,L=	11	2	4	0	2	3	17	17	4	33	35	1	63	55	H,L=	17	2	H,L=	18	10	H,L=	21	1
5	58	64	1	46	46	0	174	188	5	39	47	4	12	20	5	32	29	2	28	24	0	24	25	0	0	6	0	20	21
6	42	44	2	27	24	1	24	22	6	0	9	5	0	7	6	0	11	3	58	49	1	79	90	1	41	25	1	42	41
7	48	49	3	69	72	2	119	118	7	22	33	6	44	41	H,L=	14	7	4	4	10	2	0	7	2	0	3	2	26	[illegible]
8	37	41	4	0	9	3	82	85	H,L=	12	3	7	23	22	0	40	45	5	0	19	3	67	72	3	19	20	3	40	33
H,L=	9	3	5	35	42	4	69	69	0	49	45	H,L=	13	5	1	28	33	H,L=	15	11	4	28	25	H,L=	18	11	H,L=	21	2
0	91	88	6	0	9	5	26	30	1	56	70	0	37	41	2	67	68	0	42	37	5	67	66	0	30	29	0	0	22
1	216	215	7	32	33	6	60	57	2	18	20	1	50	57	3	40	44	1	17	20	H,L=	17	3	1	[illegible]	15	1	18	[illegible]
2	46	42	H,L=	10	3	7	11	18	3	55	60	2	49	49	4	61	63	2	47	41	0	67	64	H,L=	[illegible]	12	2	43	[illegible]
3	165	157	0	106	96	H,L=	11	3	4	49	41	3	42	49	5	27	30	3	53	40	1	17	15	0	11	18	3	16	11
4	34	38	1	101	107	0	26	23	5	50	53	4	19	15	6	35	27	4	29	34	2	[illegible]	55	H,L=	19	0	H,L=	21	3
5	57	61	2	42	33	1	135	139	6	29	27	5	47	44	H,L=	14	8	H,L=	15	12	3	29	24	0	1	0	0	16	[illegible]
6	33	37	3	69	68	2	41	46	7	41	28	6	34	30	0	51	56	0	29	26	4	66	61	1	0	8	1	26	[illegible]
7	27	21	4	0	6	3	96	104	H,L=	12	4	H,L=	13	6	1	29	26	1	25	25	5	12	[illegible]	2	24	21	2	0	4
H,L=	9	4	5	31	33	4	25	28	0	159	171	0	151	165	2	37	33	2	42	34	H,L=	17	4	3	0	13	3	25	[illegible]
0	39	40	6	0	19	5	39	40	1	21	28	1	64	67	3	40	42	3	0	2	0	0	4	4	15	10	H,L=	21	4
1	141	135	7	23	20	6	0	11	2	97	101	2	92	100	4	24	26	H,L=	15	13	1	0	1	5	15	12	0	22	17
2	75	69	H,L=	10	4	7	24	21	3	24	23	3	43	44	5	34	30	0	0	10	2	25	23	H,L=	19	1	1	17	19
3	104	109	0	62	69	H,L=	11	4	4	85	88	4	62	61	H,L=	14	9	1	0	1	3	25	27	0	58	56	2	18	17
4	18	23	1	85	88	0	20	28	5	11	22	5	47	35	0	60	62	2	14	15	4	47	44	1	21	16	3	16	[illegible]
5	53	59	2	137	142	1	0	10	6	66	66	6	68	57	1	72	72	H,L=	15	14	5	15	15	2	41	42	H,L=	21	[illegible]
6	38	39	3	103	114	2	43	45	7	0	10	H,L=	13	7	2	51	56	0	30	29	H,L=	17	5	3	0	10	0	22	21
7	37	44	4	109	117	3	39	44	H,L=	12	5	0	30	35	3	64	59	H,L=	16	0	0	24	21	4	68	65	1	45	39
H,L=	9	5	5	45	53	4	37	38	0	24	27	1	91	108	4	27	28	0	106	104	1	20	20	5	33	11	2	19	[illegible]
0	181	176	6	32	27	5	44	53	1	115	106	2	33	39	5	40	39	1	29	37	2	13	32	H,L=	19	2	3	17	13
1	23	25	7	23	27	6	34	35	2	27	20	3	69	71	H,L=	14	10	2	71	70	3	35	32	0	29	29	H,L=	21	[illegible]
2	119	113	H,L=	10	5	H,L=	11	5	3	76	74	4	12	25	0	31	25	3	75	80	4	25	24	1	66	67	0	0	5
3	116	119	0	57	66	0	42	47	4	19	22	5	39	41	1	0	9	4	31	27	5	17	21	2	20	23	1	48	[illegible]
4	60	64	1	65	73	1	112	114	5	62	67	6	46	40	2	30	31	5	0	4	H,L=	17	6	3	42	41	2	39	[illegible]
5	50	50	2	62	60	2	41	40	6	0	10	H,L=	13	8	3	0	5	6	27	32	0	21	18	4	22	24	H,L=	21	7
6	30	27	3	122	119	3	62	61	7	28	30	0	0	3	4	39	37	H,L=	16	1	1	28	25	5	26	31	0	37	35
7	26	18	4	44	49	4	27	28	H,L=	12	6	1	31	31	5	11	8	0	153	165	2	18	19	H,L=	19	3	1	38	[illegible]
H,L=	9	6	5	53	54	5	36	40	0	52	52	2	16	15	H,L=	14	11	1	64	70	3	66	60	0	37	30	2	35	34
0	159	159	6	22	22	6	26	20	1	19	19	3	0	11	0	0	8	2	146	151	4	29	25	1	24	23	H,L=	22	[illegible]
1	72	66	7	34	31	7	35	31	2	58	56	4	24	30	1	17	22	3	19	26	5	29	26	2	52	51	0	67	[illegible]
2	90	89	H,L=	10	6	H,L=	11	6	3	41	47	5	0	7	2	0	4	4	80	73	H,L=	17	7	3	0	9	1	0	1
3	80	81	0	22	18	0	112	118	4	19	20	6	27	28	3	22	21	5	0	14	0	58	57	4	46	38	2	56	[illegible]
4	61	66	1	20	18	1	23	22	5	19	25	H,L=	13	9	4	0	12	6	24	24	1	0	12	H,L=	19	4	H,L=	22	1
5	43	52	2	40	43	2	129	129	6	0	16	0	41	42	H,L=	14	12	H,L=	16	2	2	67	57	0	0	0	0	0	5
6	46	44	3	11	11	3	34	34	7	18	21	1	29	33	0	48	47	0	29	24	3	12	19	1	14	16	1	20	17
7	37	35	4	36	40	4	86	83	H,L=	12	7	2	36	32	1	27	27	1	22	21	4	55	52	2	30	35	H,L=	22	[illegible]
H,L=	9	7	5	29	34	5	15	22	0	0	6	3	0	10	2	25	24	2	14	17	5	16	22	3	24	17	0	0	[illegible]
0	74	77	6	7	17	6	52	45	1	26	33	4	25	22	3	61	36	3	24	26	H,L=	17	8	H,L=	19	5	1	21	14
1	83	90	7	31	32	7	19	18	2	0	6	5	23	23	4	25	24	4	45	45	0	43	42	0	23	16	2	0	[illegible]
2	42	50	H,L=	10	7	H,L=	11	7	3	17	19	H,L=	13	10	H,L=	14	13	5	14	13	1	40	46	1	11	11	H,L=	22	[illegible]
3	74	77	0	0	1	0	20	11	4	17	18	0	78	77	0	63	57	6	37	42	2	27	23	2	27	27	0	42	[illegible]
4	51	53	1	65	69	1	122	125	5	41	32	1	40	43	1	0	10	H,L=	16	3	3	35	33	3	0	11	1	0	7
5	32	36	2	37	43	2	15	17	6	29	27	2	82	72	2	49	43	0	77	85	4	34	31	4	27	26	2	18	[illegible]
6	34	32	3	41	42	3	57	61	H,L=	12	8	3	38	33	H,L=	14	14	1	26	26	H,L=	17	9	H,L=	19	6	H,L=	22	[illegible]
7	0	13	4	15	18	4	21	28	0	110	115	4	74	68	0	39	34	2	71	76	0	29	25	0	43	37	0	0	[illegible]
H,L=	9	8	5	0	3	5	36	35	1	20	19	5	24	13	1	0	13	3	0	3	1	7	11	1	47	43	1	11	[illegible]
0	17	19	6	0	13	6	0	17	2	78	87	H,L=	13	11	2	56	57	4	31	28	2	26	21	2	34	33	2	20	[illegible]
1	83	79	7	25	19	7	14	17	3	12	13	0	33	30	H,L=	15	0	5	28	28	3	19	16	3	42	37	H,L=	22	5
2	53	54	H,L=	10	8	H,L=	11	8	4	71	67	1	60	62	0	0	0	H,L=	16	4	4	17	18	4	16	18	0	19	[illegible]
3	41	42	0	93	104	0	46	62	5	27	22	2	39	29	1	49	56	0	51	60	H,L=	17	10	H,L=	19	7	1	54	[illegible]
4	19	18	1	44	49	1	25	14	6	38	37	3	52	49	2	46	41	1	67	65	0	27	22	0	44	45	H,L=	22	[illegible]
5	25	26	2	112	118	2	40	44	H,L=	12	9	4	25	27	3	25	31	2	48	52	1	60	51	1	32	33	0	17	[illegible]
6	0	12	3	69	81	3	0	9	0	12	11	5	26	26	4	102	108	3	85	84	2	0	5	2	56	46	1	0	[illegible]
H,L=	9	9	4	85	90	4	37	36	1	91	91	H,L=	13	12	5	64	70	4	16	22	3	30	26	3	26	27			
0	20	15	5	37	35	5	33	35	2	30	34	0	38	36	6	104	102	5	18	23	4	13	3	H,L=	19	8			

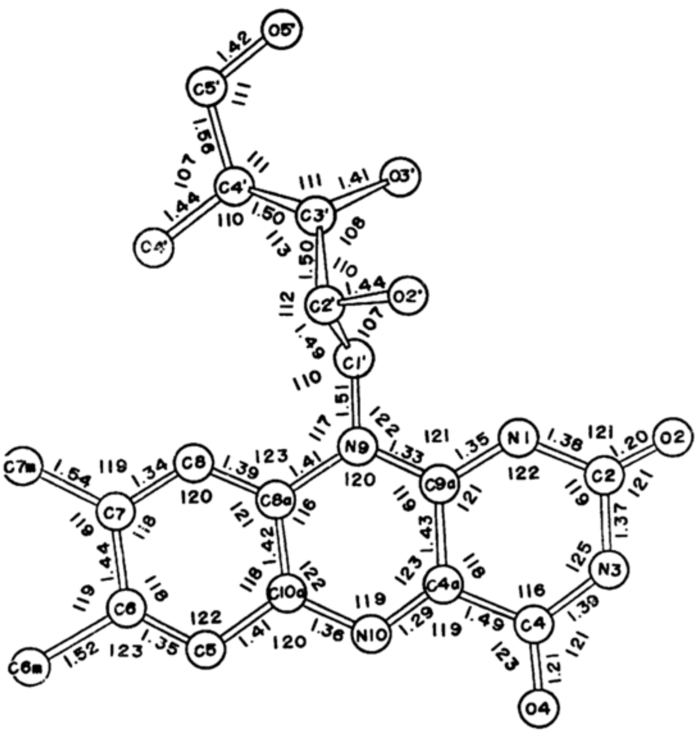

Fig. 3. Bond lengths (Å) and angles (degree).

the R factor was reduced to 0.07 after the refinement. Final atomic parameters are listed in Table 2, and $|F_o|$ and $|F_c|$ are tabulated in Table 3.

Discussion

The bond lengths and angles are shown in Fig. 3. The mean value of the estimated standard deviations for the bond lengths between non-hydrogen atoms except the bromide ion is 0.02 Å and that for the bond angles is 1.0°.

The difference Fourier synthesis (Fig. 2) shows that the addition of proton does not occur at the O(2) atom but at N(1) by hydrogen bromide. This is also supported by the fact that both exocyclic C–O lengths correspond to that of the double bond. The present result agrees with the location of the proton suggested by theoretical calculation,[2,3] and suggests that the pathway 1 in the reduction of riboflavin shown in Fig. 4 is reasonable, contrary to Guzzo and Tollin's expectation.[1]

The C(4)–C(4a) bond in the isoalloxazine ring is 1.49 Å, which corresponds to the single bond length, and the C(4a)–N(10) bond is shorter than the mean value of the other C–N lengths. Therefore, it is presumed that π-electrons are localized at the C(4a)–N(10) bond.

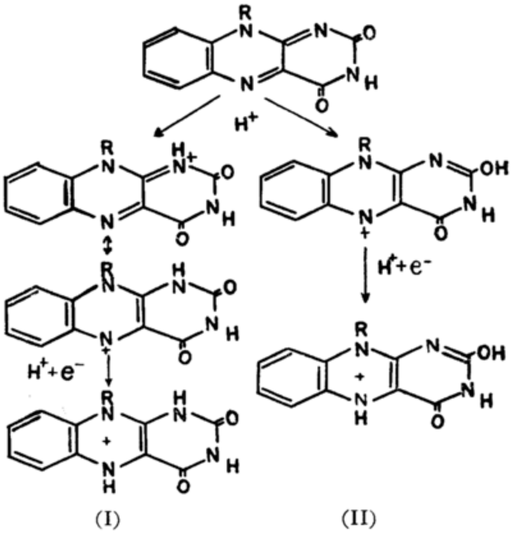

Fig. 4. Alternative pathways for the reduction of isoalloxazine.

On the theoretical calculation of the bond orders in the ring, the Hückel approximation was applied to a system of 16 conjugated π-electrons and 4 mobile electrons due to the hyperconjugation of the two methyl groups, where the Coulomb and exchange integrals were taken from the Ladik's[4]. There are several relations proposed

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[3] B. Grabe, *Biopolymer symposia*, **No. 1**, 289 (1964).

TABLE 4. BOND ORDERS AND BOND LENGTHS

Bond	Bond order	Bond length Theoretical	Bond length Experimental
N(1)—C(2)	1.34	1.38 Å	1.38 Å
N(1)—C(9a)	1.39	1.38	1.35
N(3)—C(2)	1.43	1.36	1.37
N(3)—C(4)	1.45	1.35	1.39
N(9)—C(8a)	1.54	1.33	1.41
N(9)—C(9a)	1.65	1.31	1.33
N(10)—C(4a)	1.70	1.30	1.29
N(10)—C(10a)	1.56	1.33	1.36
C(4a)—C(9a)	1.52	1.42	1.43
C(8a)—C(10a)	1.50	1.42	1.42
C(4)—C(4a)	1.30	1.47	1.49
C(5)—C(6)	1.73	1.38	1.35
C(5)—C(10a)	1.55	1.41	1.41
C(6)—C(7)	1.59	1.40	1.44
C(7)—C(8)	1.72	1.38	1.34
C(8)—C(8a)	1.56	1.41	1.39

for converting the bond order into length.5-10) For C–C bonds, approximately the same values were obtained by all the relations, and the converted bond lengths by, say, Coulson's5) are in good agreement with those observed, as shown in Table 4. On the other hand, the converted C–N lengths show somewhat wider variations with the relations, and agreement between the theoretical and observed lengths is not so good. But if experimental errors are taken into account, significant disagreement is only for N(9)–C(8a). This may suggest that this approximation is not necessarily satisfactory in the present molecule.

The valence angles at the N(1) and N(3) atoms with an extra-annular hydrogen atom are 125° and 122°, respectively, and that at N(10) without hydrogen is 119°. They are consistent with the nitrogen valence angle in heterocyclic compounds discussed by Singh.11) There are some small valence angles at the C(8a) and C(4) atoms which are bonded to the nitrogen atoms with an extra-annular hydrogen atom, whereas slightly large ones are found at the C(4a) and C(10a) atoms bonded to the N(10) atom. These facts have been reported in alloxane,12) anhydrous alloxane,13) anhydrous barbituric acid,14) barbituric acid dihydrate,15) pyridimine,16) and 2-amino-4,6-dichloropyridine.17)

The best planes of the isoalloxazine ring and the six-membered rings are listed in Table 5 together with the deviations of the atoms from them, where the nomenclatures of the rings are as follows:

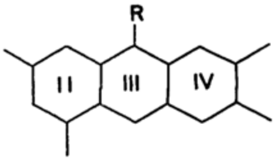

TABLE 5. THE BEST PLANE OF THE RINGS

Atom	Plane I	Plane II	Plane III	Plane IV
N(1)	0.097	−0.014	0.153*	
C(2)	0.119	0.014		
N(3)	0.039	0.019		
C(4)	−0.109	−0.038	−0.100*	
C(4a)	−0.035	0.037	−0.015	
N(10)	−0.020	0.135*	−0.012	−0.033*
C(10a)	0.007		0.025	−0.001
C(5)	0.068		0.073*	0.001
C(6)	0.063			0.001
C(7)	−0.002			0.001
C(8)	−0.062		−0.011*	−0.001
C(8a)	−0.057		−0.016	0.000
N(9)	−0.071	−0.089*	−0.017	0.045*
C(9a)	−0.007	−0.025	0.037	
C(6m)	0.092*			
C(7m)	−0.012*			
O(2)	0.242*			
O(4)	−0.315*			
C(1′)	−0.185*			

Plane I** $0.104X-0.994Y-0.041Z=-1.717$
Plane II $0.175X-0.984Y-0.040Z=-1.375$
Plane III $0.089X-0.995Y-0.033Z=-1.765$
Plane IV $0.053X-0.998Y-0.036Z=-2.010$

Dihedral angles between the planes

Plane I—Plane II	4.1 (degree)
Plane I—Plane III	1.0
Plane I—Plane IV	3.0
Plane II—Plane III	5.0
Plane II—Plane IV	7.1
Plane III—Plane IV	2.1

* Not included in the calculation of the equation of the plane.
** X, Y and Z in the Å unit.

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5) C. A. Coulson, *Proc. Roy. Soc.*, **A169**, 413 (1939).

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and the I represents the isoalloxazine ring. The dihedral angles between the planes are also given in this table. Though the ring IV is strictly planar, the other two rings are puckered; the deviations of the atoms from their best planes are significant. The dihedral angles between the planes indicate that the isoalloxazine ring takes, though slightly, a boat form. However, the isoalloxazine ring in

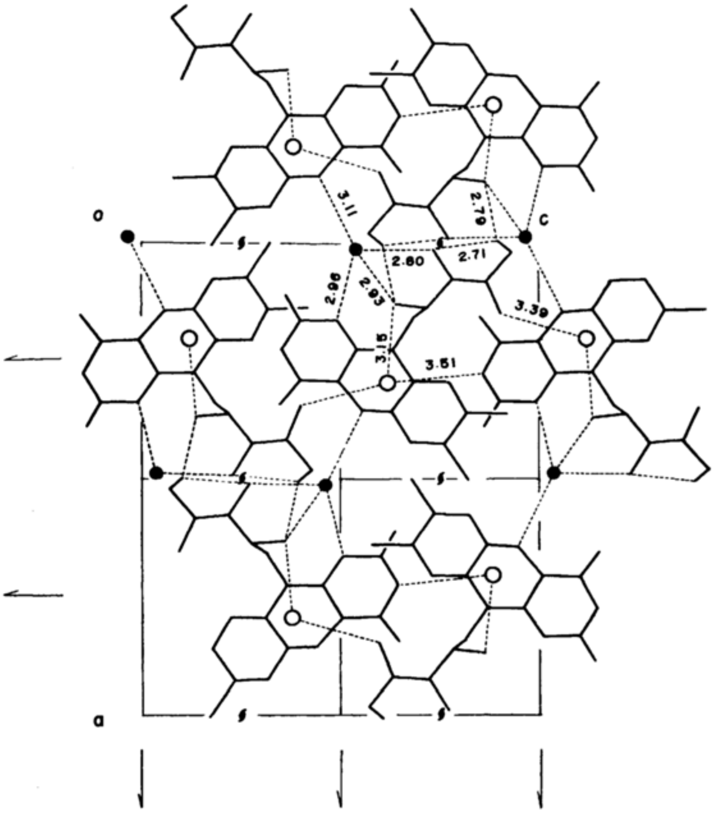

Fig. 5. The packing of the molecules viewed along the *b* axis. The dotted lines show the possible hydrogen bonds.
Medium circle: bromide ion, black circle: water molecule

TABLE 6. LIST OF POSSIBLE HYDROGEN BONDS

X—HY	X—Y	X—H	∠XHY
Br(i)—H(14, v)O(2′, v)	3.15 Å	2.52 Å	151 degree
Br(i)—H(1, i)N(3, i)	3.51	2.40	171
Br(i)—H(18, ii)O(4′, ii)	3.39	2.28	146
OW(i)—H(2, i)N(1, i)	2.96	1.92	162
O(2′, i)—H(23, i)OW(i)	2.93	2.36	130*
O(3′, i)—H(23, i)OW(i)	2.80	2.06	151*
N(10, iii)—H(22, i)OW(i)	3.11	2.43	162
O(5′, i)—H(16, i)O(3′, i)	2.71	2.06	135**
O(2, iv)—H(21, i)O(5′, i)	2.79	2.22	177

Key for molecules
i: x, y, z
ii: $x, y, 1+z$
iii: $-1/2+x, 1/2-y, 1-z$
iv: $-x, 1/2+y, 3/2-z$
v: $1/2-x, -y, -1/2+z$

* May be a bifurcated hydrogen bond
** The intramolecular hydrogen bond

1,3,10-trimethyl isoalloxazine iodide[18] has been reported to be nearly coplanar.

In the ribityl group, the C(1′)–C(2′), C(2′)–C(3′) and C(3′)–C(4′) bonds are a little shorter than the normal C–C length of sp^3 hybridization, whereas the C(4′)–C(5′) does not differ significantly from the normal one. The C–O lengths in this group are between 1.41 Å and 1.44 Å, and their mean value, 1.428 Å, corresponds to the usual single C–O length. The valence angles C–C–C and C–C–O in this group do not differ significantly from their mean value, 107° and 110°, respectively.

TABLE 7. CLOSE INTERMOLECULAR CONTACTS

Atom	Nearest atom	Molecular position	Distance
Br	C(6m)	iii	3.87
O(2)	C(5)	iii	3.35
O(2)	C(6m)	iii	3.26
O(3′)	O(4)	iii	3.29
OW	O(4)	iii	3.48
C(1′)	O(5′)	iv	3.39
Br	C(8a)	v	3.70
Br	C(9a)	v	3.86
Br	C(10a)	v	3.87
Br	N(9)	v	3.71
Br	C(2′)	v	3.72
C(4)	O(4′)	v	3.19
C(4a)	O(4′)	v	3.34
O(2)	C(7)	v	3.50
O(4′)	C(2′)	v	3.48
O(4)	C(3′)	v	3.30
O(4)	O(4′)	v	3.48
Br	C(4a)	vi	3.75
Br	C(8a)	vi	3.50
Br	C(9a)	vi	3.84
Br	C(10a)	vi	3.50
Br	N(9)	vi	3.67
Br	N(10)	vi	3.62
C(2)	C(7m)	vi	3.45
N(3)	C(8)	vi	3.40
O(5′)	C(7m)	vii	3.34

Key for molecules

iii: $-1/2+x,\ 1/2-y,\ 1-z$
iv: $-x,\ 1/2+y,\ 3/2-z$
v: $1/2-x,\ -y,\ -1/2+z$
vi: $1/2-x,\ 1-y,\ -1/2+z$
vii: $-1/2+x,\ 1/2-y,\ 2-z$

This table shows the contacts shorter than 4.0 Å between the bromide ion and the other heavy atom, and those shorter than 3.5 Å in the other cases.

The ribitol does not form a furanose ring but a chain, which has not been found in cases of nucleoside, nucleotide and nucleic acid. The conformation angles defined by Sundarlingam[19] are; $\phi_{C_{2'}-C_{3'}}=62°$ and $\phi_{C_{3'}-C_{4'}}=167°$, whereas they are 34° and −37° in the furanose ring of 5′-AMP.[20]

The molecular packing viewed along the *b* axis is shown in Fig. 5. The hydrogen bonds are shown by the dotted lines, where each figure represents a distance between the non-hydrogen atoms. Table 6 tabulates the X-H distances and X–H–Y angles related to the hydrogen bond. The H(2,i)-OW(i), 1.92 Å, is the normal hydrogen bond. The H(23,i) is located near both 0(2′,i) and 0(3′,i) atoms; the distances are 2.36 Å and 2.06 Å, respectively. Thus, the two contacts, OW-H(23)-0(2′) and OW-H(23)-O(3′), seem to consist a bifurcated hydrogen bond. Another hydrogen atom of water molecule makes *a* weak hydrogen bond with the N(10) atom related by the screw axis along the *a*. This hydrogen bond may suggest the subsequent transfer of the hydrogen atom from the substrate.

The bromide ion contributes to the three hydrogen bonds with the N(3), O(2′) and O(4′) atoms. Though the Br(i)-N(3,i) distance, 3.51 Å, seems a little longer, the Br(i)-H(1,i) is 2.40 Å, which shows that it is a normal hydrogen bond. The bromide ion is situated midway between two isoalloxazine rings separated by a period along the *b* axis, and nearly above the center of the ring III which is indicated to have positive charge from the theoretical calculation of the bond orders.

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