The total effect of this arrangement is to produce a three-dimensional network of hydrogen bonds throughout the crystal. With the exception of O(4), O(9) and O(10), every oxygen is the acceptor of a hydrogen bond; every hydrogen associated with an oxygen atom is also involved in a hydrogen bond.

Sodium coordination

The coordination around sodium is unusual in that each sodium ion exhibits a different coordination number. Distances between sodium ion and oxygen range from 2·276(3) to 2·493(2) Å. The coordination of Na(1) may best be described as a distorted tetrahedron; Na(2) coordination is a distorted tetragonal pyramid; while Na(3) coordination is that of a distorted octahedron. Bond distances and angles between sodium and its nearest neighbors are summarized in Table 8. Two slightly longer distances of 2·816(2) and 2·759(3) Å are observed between Na(2) and oxygen; the next closest distance between sodium ion and oxygen is 3·183 (2) Å.

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The Crystal Structure of a Flavin Molecular Complex: 10-Propylisoalloxazine–Bis(naphthalene-2,3-diol)

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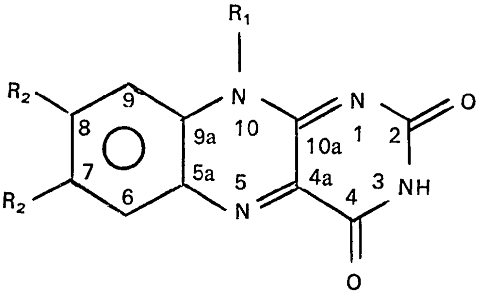
The crystal structure of the orange molecular complex 10-propylisoalloxazine–bis(naphthalene-2,3-diol), a possible model for enzymic flavin–substrate interactions, has monoclinic symmetry and space group $A2/a$. There are eight formula groups, $C_{13}H_{12}N_4O_2.2C_{10}H_8O_2$, in the unit cell having constants $a=26{\cdot}69$ (3), $b=7{\cdot}246$ (8), $c=29{\cdot}20$ (4) Å, and $\beta=102{\cdot}51$ (3)°. The calculated density is 1·39 g cm^{-3}; the measured value is 1·40 g cm^{-3}. The final R index, based on 869 statistically observed, counter-measured reflections, is 4·0 %. Half the naphthalene-2,3-diol molecules alternate with the isoalloxazines in a ···DADA··· type stack running parallel to **b**; the remainder lie between stacks and are hydrogen bonded to N(1) and O(2) of the flavins. Intermolecular spacings within the stacks are 3·38 and 3·46 Å, the shorter involving a naphthalenediol interaction with the pyrimidinoid and pyrazinoid rings of the flavin and the longer with the phenylene and pyrazinoid rings. Flavins are base-paired by N(3)H(3)··· O(2) hydrogen bonds across C_2 axes, and O(4) of each flavin is also hydrogen bonded to a hydroxyl group of a stacked naphthalenediol molecule. Both naphthalenediol molecules exhibit internal OH···O hydrogen bonding.

Introduction

Isoalloxazine or flavin (I) is an essential component of electron-transfer processes in many biological systems. It is found in nature as a prosthetic group in the form of riboflavin 5′-phosphate, FMN, or the pyrophosphate, FAD, produced by linking FMN with adenosine 5′-phosphate. When the flavin prosthetic group alternately accepts and releases one or two reducing equivalents, the flavoenzyme acts as an electron carrier from a substrate to an acceptor.



(I)

Riboflavin: R_1 = D-ribityl
R_2 = methyl
Isoalloxazine: $R_1 = R_2$ = hydrogen

It has been suggested (Szent-Gyorgyi, 1960) that charge-transfer bonding between the flavin and its substrate may be an initial step in the enzymic reaction. Various complexes of flavins with different hydroxylated benzenes and naphthalenes, prepared from both acidic and neutral solutions, have been reported (Fleischman & Tollin, 1965*a*, *b*, *c*; Ray, Guzzo & Tollin, 1965; Langhoff & Fritchie, 1970; Bear, Waters & Waters, 1970). The acidic complexes, presumably containing N[1]*-protonated flavins, are generally more intensely colored and therefore more characteristic of charge-transfer complexes. Because of the low basicity of flavins, however, which accept an additional proton only in very acidic solutions, with $pH \leq 0$, it is expected that the study of neutral complexes would provide more significant insight into the behavior of flavins in biological reactions. We have prepared complexes of several electronically similar but sterically somewhat different flavins with the common donor naphthalene-2,3-diol. One of these, containing lumiflavin (or 7,8,10-trimethylisoalloxazine) and yellow in color, has been described (Wells, Trus, Johnston, Marsh & Fritchie, 1974). A neutral complex of orange color, 10-propylisoalloxazine–bis(naphthalene-2,3-diol), was chosen for this study. It has already been described in part (Kuo, Dunn & Fritchie, 1970).

Experimental data

10-Propylisoalloxazine was synthesized by a method similar to that described by Guzzo & Tollin (1963). The crude product was recrystallized from hot formic acid. Orange crystals of the molecular complex 10-propylisoalloxazine–bis(naphthalene-2,3-diol), $C_{13}H_{12}N_4O_2.2C_{10}H_8O_2$, were grown by cooling and evaporation of an aqueous solution nearly saturated in both components. All crystals were small and most were twinned. One small, untwinned acicular crystal was mounted on its long axis for data collection. Zero and upper-layer Weissenberg and precession photographs showed that the crystal belongs to the monoclinic system and was mounted on **b**. Systematic absence of reflections in the classes hkl, $k+l \neq 2n$, and $0k0$, $k \neq 2n$ led to assignment of $A2/a$ as most probable space group. The structure determination has confirmed this choice.

Preliminary lattice constants determined from the films were refined by least-squares calculations, by the use of 2θ measurements made with a Picker diffractometer. The refined unit-cell constants are $a = 26{\cdot}69$ (3), $b = 7{\cdot}246$ (8), $c = 29{\cdot}20$ (4) Å and $\beta = 102{\cdot}51$ (3)°. The density was determined to be $1{\cdot}40$ g cm^{-3} by flotation methods in a carbon tetrachloride–hexane mixture; the calculated value was $1{\cdot}39$ g cm^{-3} with eight formula units per cell.

Intensity data were measured on a four-circle punched-card Picker diffractometer with Ni-filtered Cu $K\alpha$ radiation. All the independent reflections with 2θ up to 90° were scanned in the 2θ mode at a rate of 1° min^{-1}, with a scan range of 2°. A 20 s background count was recorded on either side of the scan range. Several standards measured every few hours to check any variation in the crystal or instrument remained essentially constant throughout the run. The structure amplitudes, $|F_o|$, and their standard deviations, σ_F, were derived by application of the Lorentz–polarization (LP) factor. The values of σ_F were chosen to be the greater of $\sigma_I/2|F_o|$LP or $p|F_o|$, where LP is the Lorentz–polarization correction, σ_I is the standard deviation of each reflection estimated from counting statistics alone, according to the formula below, and p was set equal to $0{\cdot}025$. The uncertainty in each intensity due to counting statistics was formulated as $\sigma_I = [C + (t_C/2t_B)^2(B_1 + B_2)]^{1/2}$, where t_C and t_B are time in seconds for the integrated scan and for each background respectively, C is the net count, and B_1 and B_2 are the background counts. 869 reflections fit the criterion $|F_o| \geq 2\sigma_F$ and were classified as observable. The approximately 1300 remaining, 'unobserved' reflections were omitted from all calculations. No corrections for absorption or extinction were made.

Solution and refinement

The structure was solved by a combination of Patterson and Fourier techniques. The 14-atom anthracene-like core of the flavin was located by use of multiple superposition of peaks in the Patterson function from this approximately centrosymmetric fragment (Patterson, 1939). Several closely related locations for the bulk of the nearly parallel naphthalenediol molecule were found at the same time and a first Fourier map, phased by the 14-atom group, hinted at the correct position for the naphthalenediol. Hydrogen-bonding

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* Brackets refer to the standard chemical numbering scheme for flavins, illustrated in (I); parentheses refer to that illustrated in Fig. 1.

and packing considerations permitted assignment of all non-hydrogen atoms in these two molecules except for the β and γ carbon atoms of the propyl side chain. A second Fourier map led to location of the remaining naphthalenediol molecule, and a third, phased on 41 atoms, revealed the last two heavy atoms. An isotropic refinement, effected by the method of least squares (Hughes, 1941), and including structure-factor contributions from all hydrogen atoms after their location in difference maps, converged at $R=9{\cdot}1\%$. Despite the relatively low number of reflections, difference maps indicated that anisotropic refinement was warranted, and the Hamilton R-factor ratio test (Hamilton, 1964) confirms the validity of this choice. An ellipsoidal heavy-atom refinement, during which all except hydroxyl hydrogen atoms were periodically idealized in position, converged at $R=4{\cdot}0\%$, for an R-factor ratio of 2·3. The ratio test gives $\mathscr{R}_{0\cdot005}=1{\cdot}17$. Isotropic temperature factors of 4 Å^2 were used for all hydrogen atoms except 52–54, which were given the value 5 Å^2.

Atomic form factors corrected for real and imaginary components of anomalous dispersion were obtained from Ibers and Templeton's tabulations (*International Tables for X-ray Crystallography*, 1968). Computations were performed on the Tulane Computer Laboratory IBM 7044 computer. Major computing programs used were *BLSA* (a local version of *UCLALS* 1 by Gantzel, Sparks & Trueblood, 1961, unpublished); *FOUR* (Fritchie, 1962, unpublished); *GSET*4 (Prewitt, 1964); and *ORTEP* (Johnson, 1965). The final positional parameters appear in Table 1 and the thermal parameters in Table 2.*

Table 1. *Positional parameters*

Figures in parentheses are standard deviations estimated from the least-squares matrices.

	x	y	z
N(1)	0·20042 (17)	−0·1632 (7)	0·09641 (17)
C(2)	0·21821 (21)	−0·2199 (10)	0·05843 (21)
N(3)	0·18329 (18)	−0·2436 (8)	0·01449 (16)
C(4)	0·13188 (24)	−0·2212 (10)	0·00693 (21)
N(5)	0·06446 (18)	−0·1372 (7)	0·04532 (18)
C(6)	−0·00377 (24)	−0·0464 (11)	0·08149 (24)
C(7)	−0·02438 (23)	0·0122 (11)	0·11683 (26)
C(8)	0·01120 (23)	0·0461 (11)	0·15947 (25)
C(9)	0·06404 (22)	0·0214 (10)	0·01645 (22)
N(10)	0·13441 (17)	−0·0653 (7)	0·12937 (16)
C(11)	0·15083 (22)	−0·1312 (9)	0·09231 (20)
C(12)	0·11362 (22)	−0·1652 (9)	0·04844 (21)
C(13)	0·04784 (22)	−0·0772 (9)	0·08367 (22)
C(14)	0·08247 (22)	−0·0394 (9)	0·12647 (21)
O(15)	0·26379 (14)	−0·2500 (7)	0·05990 (14)
O(16)	0·10392 (15)	−0·2511 (7)	0·03102 (14)
C(17)	0·17278 (23)	−0·0223 (11)	0·17297 (23)
C(18)	0·18308 (26)	−0·1817 (10)	0·20768 (23)
C(19)	0·22063 (30)	−0·1366 (12)	0·25171 (26)
C(20)	0·02991 (24)	−0·5737 (10)	0·07363 (25)
C(21)	0·06265 (24)	−0·5285 (10)	0·11767 (23)
C(22)	0·11328 (20)	−0·5521 (10)	0·12385 (25)
C(23)	0·13423 (24)	−0·6178 (10)	0·08848 (25)
C(24)	0·18722 (26)	−0·6434 (11)	0·09223 (27)
C(25)	0·20890 (24)	−0·7069 (12)	0·05826 (27)
C(26)	0·17696 (25)	−0·7471 (12)	0·01441 (26)
C(27)	0·12511 (25)	−0·7246 (11)	0·00819 (23)
C(28)	0·10323 (23)	−0·6610 (9)	0·04451 (23)
C(29)	0·04996 (24)	−0·6398 (11)	0·03908 (24)
O(30)	−0·02084 (15)	−0·5432 (7)	0·07316 (15)
O(31)	0·04092 (16)	−0·4626 (7)	0·15251 (15)
C(32)	0·36682 (26)	−0·0989 (12)	0·21451 (24)
C(33)	0·33214 (26)	−0·0894 (11)	0·17047 (26)
C(34)	0·33276 (29)	0·0549 (11)	0·14275 (26)
C(35)	0·36685 (26)	0·2038 (11)	0·15721 (23)
C(36)	0·36727 (31)	0·3586 (13)	0·12870 (28)
C(37)	0·40031 (35)	0·5020 (14)	0·14362 (30)
C(38)	0·43189 (30)	0·4896 (14)	0·18629 (32)
C(39)	0·43395 (29)	0·3432 (14)	0·21558 (29)
C(40)	0·40044 (27)	0·1946 (12)	0·20150 (25)
C(41)	0·40026 (25)	0·0385 (12)	0·22914 (25)
O(42)	0·36467 (20)	−0·2525 (8)	0·24244 (17)
O(43)	0·30184 (20)	−0·2440 (8)	0·16108 (18)
H(44)	−0·0269	−0·0661	0·0524
H(45)	−0·0607	0·0243	0·1137
H(46)	−0·0006	0·0911	0·1855
H(47)	0·0876	0·0453	0·1933
H(48)	0·1598	0·0730	0·1885
H(49)	0·2038	0·0109	0·1653
H(50)	0·1965	−0·2777	0·1930
H(51)	0·1522	−0·2168	0·2159
H(52)	0·2353	−0·2745	0·2698
H(53)	0·2048	−0·0406	0·2707
H(54)	0·2582	−0·0769	0·2397
H(55)	0·1355	−0·5241	0·1531
H(56)	0·2093	−0·6145	0·1214
H(57)	0·2451	−0·7250	0·0632
H(58)	0·1915	−0·7876	−0·0105
H(59)	0·1035	−0·7512	−0·0215
H(60)	0·0276	−0·6765	0·0110
H(61)	0·1972	−0·2806	−0·0114
H(62)	0·3103	0·0575	0·1126
H(63)	0·3437	0·3636	0·0988
H(64)	0·4003	0·6053	0·1241
H(65)	0·4545	0·5853	0·1969
H(66)	0·4576	0·3412	0·2458
H(67)	0·4264	0·0623	0·2577
H(68)	−0·0475	−0·6250	0·0437
H(69)	0·0050	−0·4931	0·1472
H(70)	0·3430	−0·3500	0·2240
H(71)	0·2760	−0·2130	0·1310

Description

Half the naphthalenediol molecules (molecules of the type labelled *A* in Fig. 1) are interleaved with the flavin molecules to form π-complex stacks running parallel to **b**. The remainder (molecules labeled *B*) fall into channels between the columns and are hydrogen bonded to them. Hydrogen bonds between stacks create a bilayer-like structure broadly similar to that often postulated for biological membranes, with layers running parallel to (001). This structure is illustrated in Fig. 2. A generally similar, bilayer structure is found in lumiflavin–bis(naphthalene-2,3-diol) (Wells *et al.*, 1974).

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* Observed and final calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30417 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The 10-propylisoalloxazine molecules are hydrogen bonded across C_2 axes into base pairs, with N(3)H(61) as donor (N[3]H[3] in standard flavin notation) and O(15) (O[2]) as acceptor. Hydrogen-bonding details are given in Figs. 1 and 2. A cyclical hydrogen-bonding pattern of the two-molecule, mutual donor–acceptor type in which N[3]H[3] and O[2] are involved is known in one other structure, a riboflavin–5′-deoxy-5′-bromoadenosine complex (Voet & Rich, 1971) in which N[3] and N[7]H_2 of the adenosine serve as acceptor and donor respectively. Three crystals have shown such cyclical patterns involving N[3]H[3] as donor but O(12) (O[4]) as acceptor: 10-methylisoalloxazine (Wang & Fritchie (1973), who mistakenly describe the donor in this structure as O[4]), riboflavin hydroquinone di(hydrobromide) (Bear, Waters & Waters, 1970), and lumiflavin–bis(naphthalene-2,3-diol) (Wells *et al.*, 1974). In the first two of these latter complexes, flavins are base paired across centers of symmetry; in the third, an –OH group from a dihydroxynaphthalene molecule serves both as acceptor from N[3]H[3] and as donor to O[4].

As anticipated (Langhoff & Fritchie, 1970), the primary chelate site C(4)O(16)–N(5) contains an –OH dipole, hydrogen bonded in this case to O(16). The secondary site, consisting of N(1)–O(15) or N[1]–O[2] (Trus, Wells, Johnston, Fritchie & March, 1971; Fritchie, 1972; Wade & Fritchie, 1973), also contains an –OH dipole, apparently forming a bifurcated bond to both N[1] and O[2].

Like most oxidized flavins (Wang & Fritchie, 1973, and references therein), the 10-propylisoalloxazine molecule in this structure is almost but not quite planar. Unlike most others, which generally display a folding on the order of 2–3° along N(5)–N(10), occasionally accompanied by a small twist along the longitudinal molecular axes, the flavin in this structure reveals a longitudinal twist as the major distortion.

Table 2. *Anisotropic thermal parameters*

The temperature factor is exp $[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$. Figures in parentheses are standard deviations estimated from the least-squares equations.

	$10^5\beta_{11}$	$10^4\beta_{22}$	$10^5\beta_{33}$	$10^4\beta_{12}$	$10^5\beta_{13}$	$10^4\beta_{23}$
N(1)	50 (10)	182 (15)	103 (10)	5 (6)	83 (15)	−5 (6)
C(2)	79 (13)	164 (19)	107 (13)	14 (8)	68 (20)	15 (8)
N(3)	123 (10)	213 (15)	48 (9)	−4 (7)	49 (15)	−15 (7)
C(4)	163 (14)	121 (18)	85 (12)	−11 (9)	75 (21)	−3 (8)
N(5)	101 (10)	113 (14)	121 (10)	10 (6)	137 (15)	3 (6)
C(6)	109 (13)	252 (23)	163 (15)	16 (10)	95 (23)	−2 (10)
C(7)	90 (13)	251 (23)	109 (15)	5 (10)	91 (22)	−11 (10)
C(8)	125 (13)	241 (23)	156 (13)	15 (9)	194 (21)	7 (9)
C(9)	102 (13)	192 (20)	85 (13)	2 (9)	4 (21)	−1 (8)
N(10)	100 (10)	181 (15)	39 (9)	−12 (7)	25 (15)	−3 (6)
C(11)	107 (12)	152 (18)	22 (11)	−5 (8)	105 (18)	−3 (7)
C(12)	108 (14)	150 (18)	53 (11)	−8 (8)	91 (19)	−5 (8)
C(13)	106 (13)	99 (17)	102 (12)	9 (8)	133 (20)	−3 (8)
C(14)	100 (12)	173 (19)	60 (12)	−6 (9)	51 (19)	−32 (8)
O(15)	61 (8)	341 (15)	117 (8)	22 (6)	81 (13)	−5 (6)
O(16)	90 (8)	316 (14)	85 (8)	−12 (7)	−3 (13)	−12 (6)
C(17)	115 (14)	256 (23)	85 (13)	−4 (9)	11 (22)	0 (9)
C(18)	213 (16)	193 (21)	95 (13)	4 (10)	75 (23)	−18 (9)
C(19)	318 (20)	320 (26)	113 (14)	52 (12)	−102 (30)	−30 (11)
C(20)	104 (14)	156 (20)	171 (14)	2 (9)	−15 (23)	30 (9)
C(21)	176 (14)	137 (19)	130 (14)	−3 (9)	99 (33)	9 (9)
C(22)	177 (15)	193 (21)	123 (14)	−27 (10)	−34 (23)	−4 (9)
C(23)	90 (14)	126 (19)	194 (15)	−89 (9)	−54 (23)	16 (9)
C(24)	143 (15)	235 (24)	241 (16)	−13 (10)	107 (24)	42 (10)
C(25)	72 (14)	333 (26)	353 (19)	47 (10)	176 (25)	97 (12)
C(26)	204 (17)	313 (25)	264 (16)	45 (11)	271 (25)	62 (12)
C(27)	140 (13)	258 (23)	100 (13)	3 (10)	94 (21)	−12 (9)
C(28)	104 (13)	170 (19)	104 (12)	−8 (9)	93 (20)	−15 (8)
C(29)	128 (15)	236 (22)	131 (13)	6 (9)	−3 (23)	−25 (9)
C(30)	143 (9)	236 (14)	119 (9)	2 (6)	−12 (14)	−26 (6)
C(31)	145 (9)	250 (15)	161 (10)	−15 (6)	60 (15)	−24 (6)
C(32)	141 (13)	356 (25)	98 (13)	10 (10)	25 (23)	15 (10)
C(33)	138 (15)	239 (22)	161 (14)	−21 (10)	−109 (14)	24 (10)
C(34)	270 (17)	273 (23)	125 (14)	−17 (12)	−70 (27)	58 (10)
C(35)	243 (16)	290 (25)	92 (14)	0 (11)	164 (23)	10 (10)
C(36)	293 (17)	405 (30)	198 (17)	−33 (13)	112 (29)	0 (12)
C(37)	515 (24)	391 (31)	241 (19)	−27 (15)	335 (34)	65 (13)
C(38)	305 (18)	461 (33)	360 (20)	−101 (13)	406 (24)	−104 (13)
C(39)	189 (17)	499 (34)	274 (19)	0 (13)	85 (29)	−82 (13)
C(40)	207 (16)	392 (27)	118 (13)	−23 (11)	171 (23)	−53 (10)
C(41)	106 (14)	431 (28)	100 (14)	23 (11)	−41 (23)	−22 (11)
O(42)	305 (12)	392 (18)	162 (10)	1 (8)	−59 (18)	75 (7)
O(43)	334 (13)	331 (17)	222 (10)	−64 (8)	−34 (19)	85 (7)

Table 3, presenting a series of least-squares planes, demonstrates this twist. It also reveals that the benzene ring is essentially planar, whereas the pyrimidine ring is not.

Table 3. *Least-squares planes*

Planes are described by the equation $Am+Bn+Cp=D$, where A, B, and C are direction cosines and m, n, and p are atomic coordinates in an orthonormal coordinate system, **M,N,P**, having $\mathbf{M}\|\mathbf{b}\times\mathbf{c}^*$, $\mathbf{N}\|\mathbf{b}$, and $\mathbf{P}\|\mathbf{c}^*$. Displacements in parentheses indicate atoms given zero weight; for all others, the atomic number was used as the weight.

Plane	*A*	*B*	*C*	*D*(Å)
I	0·1645	0·9471	−0·2754	−1·040
II	0·1669	0·9555	−0·2433	−1·001
III	0·1565	0·9461	−0·02837	−1·080
IV	0·1559	0·9369	−0·3131	−4·498
V	0·7944	−0·4417	−0·4168	4·461

Displacements

(*a*) 10-Propylisoalloxazine

	Plane I	Plane II	Plane III
N(1)	−0·057 Å	−0·006 Å	
C(2)	−0·030	−0·016	
N(3)	0·044	0·016	
C(4)	0·039	0·002	
N(5)	−0·021	(−0·023)	(−0·003) Å
C(6)	−0·020		0·006
C(7)	−0·022		0·001
C(8)	−0·012		−0·005
C(9)	0·005		0·001
N(10)	0·032	(−0·114)	(0·020)
C(11)	−0·019	0·027	
C(12)	−0·026	−0·023	
C(13)	−0·024		−0·009
C(14)	0·007		0·006
O(15)	−0·050	(−0·033)	
O(16)	0·048	(−0·026)	
C(17)	0·108		
C(18)	(−1·249)		

(*b*) Naphthalenediol *A*

	Plane IV		Plane IV
C(20)	−0·002 Å	C(26)	0·019 Å
C(21)	0·004	C(27)	0·018
C(22)	−0·006	C(28)	−0·001
C(23)	−0·014	C(29)	−0·025
C(24)	−0·005	O(30)	−0·001
C(25)	−0·009	O(31)	0·017

(*c*) Naphthalenediol *B*

	Plane V		Plane V
C(32)	0·009 Å	C(38)	−0·018 Å
C(33)	−0·013	C(39)	−0·001
C(34)	0·007	C(40)	0·002
C(35)	0·009	C(41)	0·031
C(36)	0·004	O(42)	−0·017
C(37)	−0·006	O(43)	−0·002

The intermolecular π overlap is shown in Fig. 3. The least-squares plane of the flavin is inclined at an angle of 2·3° to that of the stacked naphthalenediol. There is significant overlap of the flavin with two translationally related naphthalenediol molecules, with separations of approximately 3·38 Å to the upper molecule and 3·46 Å to the lower. In accord with previous observations (Wells *et al.*, 1974), the shorter intermolecular separation involves the pyrimidine ring of the flavin to a greater extent than the phenylene ring. In

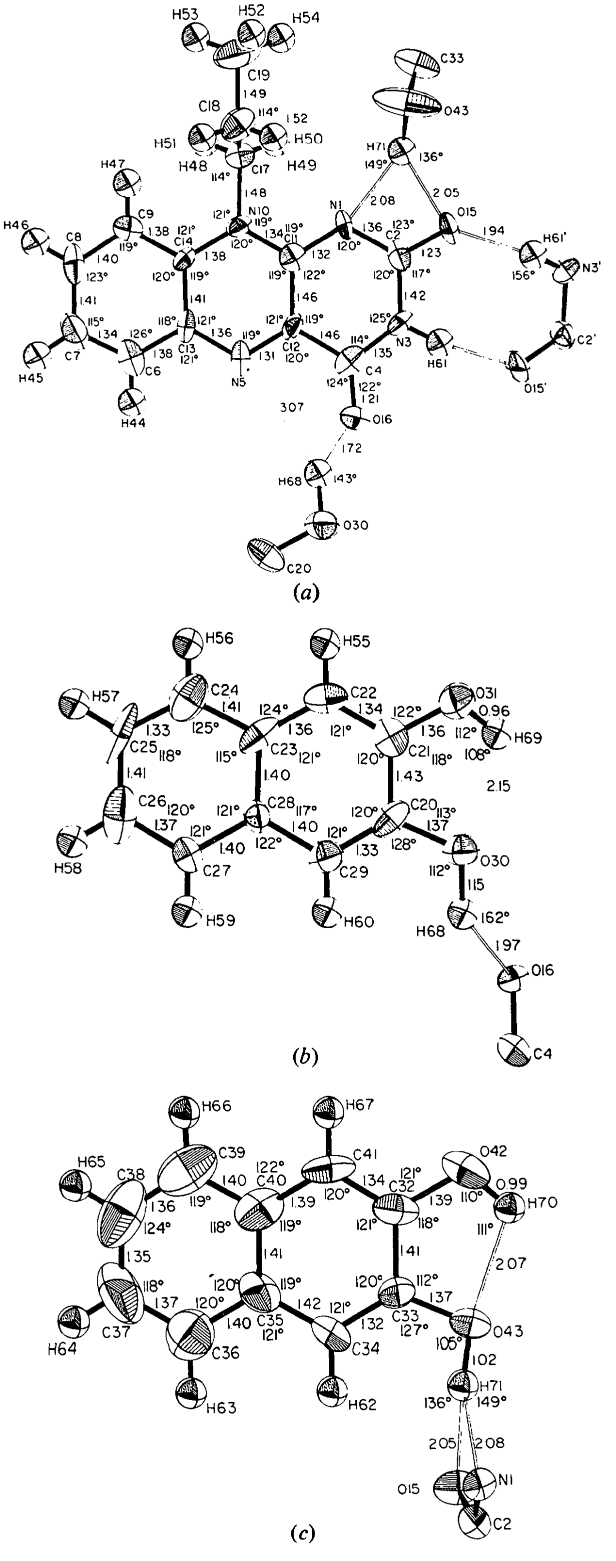

Fig. 1. Numbering system, bond distances and bond angles. Standard deviations in bonds and angles not involving hydrogen are about 0·016 Å and 1·0° respectively. (*a*) 10-Propylisoalloxazine. (*b*) The π-complexed naphthalenediol, molecule *A*. (*c*) Naphthalenediol *B*.

this structure, an additional factor contributing to the greater separation from the lower naphthalenediol is the larger number of almost direct flavin–naphthalenediol atomic superpositions (6 *versus* 3).

In agreement with the orange color of this complex and the yellow color of lumiflavin–bis(naphthalene-2,3-diol) (Wells *et al.*, 1974), at least one significantly smaller interplanar spacing is found in this structure (3·38 and 3·46 Å *versus* 3·46 and 3·48 Å in the latter). In addition, although in both structures the flavin is sandwiched between two translationally related naphthalene-2,3-diol molecules and in both structures the long axes of diol and flavin molecules are nearly parallel, the relative polar senses of the long molecular axes are reversed. In the lumiflavin complex, the two –OH groups point toward the pyrimidine ring; in this structure they point toward the phenylene ring.

Standard deviations in bonds not involving hydrogen are calculated to be approximately 0·01 Å. The root-mean-square difference of a bond in the 10-propylisoalloxazine molecule from the corresponding 'ideal' value (Wang & Fritchie, 1973) is 0·016 Å. Similar r.m.s. differences for the two naphthalenediol molecules are 0·016 and 0·017 Å (Fritchie & Johnston, 1974). Some underestimation of error by the usual formulas is common; if one assumes an underestimation of about 60% in this structure, bond lengths in both the flavin and the naphthalene-2,3-diol molecules are normal. The movement of internally hydrogen-bonded atoms O(30) and O(43) toward the donor –OH groups which was noted earlier (Wells *et al.*, 1974) is also seen here. In this structure, the two pertinent C–C–O angles are 112° and 113°; in the earlier paper, values of 115° and 115° were found.

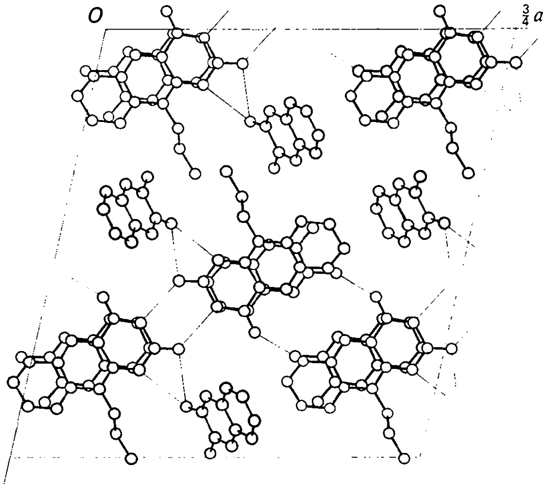

Fig. 2. (010) projection. Hydrogen atoms are omitted for clarity. The light lines are hydrogen bonds. Intramolecular hydrogen bonds in the naphthalene-2,3-diol molecules are not shown.

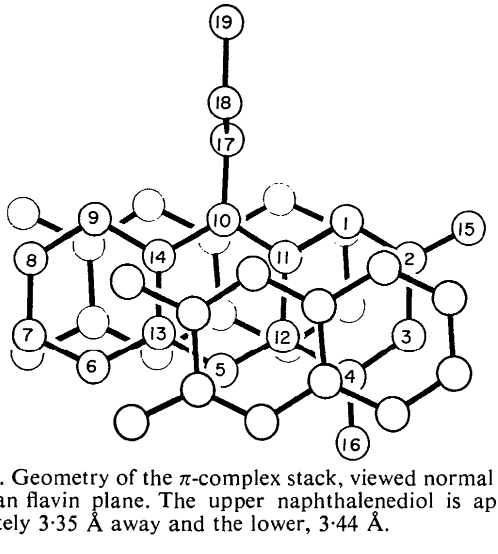

Fig. 3. Geometry of the π-complex stack, viewed normal to the mean flavin plane. The upper naphthalenediol is approximately 3·35 Å away and the lower, 3·44 Å.

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