Cette description est la même quelle que soit la direction **x**, **y** ou **z** envisagée pour les axes 2_1. La succession des sites est toujours Cu Li Cu Li .... Cette disposition des sites laisse de grandes lacunes pour le passage des chaînes phosphorées.

L'empilement des oxygènes peut être considéré comme la déformation d'un empilement compact ABAB, si on le projette sur le plan (111). L'enchaînement des sites de cations présente alors une pseudo-symétrie ternaire d'axe [111].

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The Crystal Structure of the 1:1 Molecular Complex between Lumiflavinium Chloride and Hydroquinone

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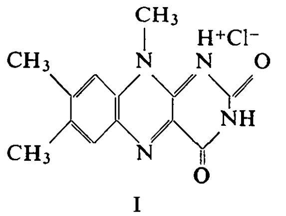
Crystals of the 1:1 molecular complex between lumiflavinium chloride and hydroquinone are monoclinic, space group $P2_1/c$ with $a=24{\cdot}15$, $b=12{\cdot}52$, $c=12{\cdot}39$ Å, $\beta=93{\cdot}74°$. There are two complexes per asymmetric unit, related by a pseudo-translation $(\frac{1}{2},0,\frac{1}{2})$, causing the reflexions with $h+l$ odd to be weak. The structure was solved by direct methods. The problem of determining the phases of the weak odd reflexions was solved by expressing each structure factor as a linear function of the atomic displacement parameters due to the pseudo-translation. The complexes crystallize as isolated units, held together by hydrogen bonds. Within each complex, the angle between the molecular planes is 5·6° and the average perpendicular separation is 3·49 Å.

Introduction

The investigation of the complex between lumiflavinium chloride (I) and hydroquinone was undertaken because complexes of this kind have been suggested by Tollin (1965) as possible models with bondings similar to those present in coenzyme–protein complexes. Tollin pointed out the existence of a donor-acceptor π–π complex in acid solutions, and made spectroscopic, e.s.r. and conductivity measurements on crystals, both with and without hydroquinone.



I

The crystal structure of the related complex with HBr instead of HCl has been determined at this Institute (Tillberg & Norrestam, 1972). The complex between riboflavin, hydroquinone and HBr has been investigated by Bear, Waters & Waters (1970).

Experimental

Crystals of the complex were kindly supplied by Dr Göran Eriksson of the Institute of Biophysics, University of Stockholm. They are dark green, fairly regular prisms, frequently twinned. Oscillation and Weissenberg photographs were taken along all three axes for the zero and first layers with Ni-filtered Cu $K\alpha$ radiation for preliminary examination of the space group and cell constants. Accurate cell constants were determined on a Siemens four-circle diffractometer.

The crystal data are: monoclinic, space group $P2_1/c$, $a=24{\cdot}15\,(2)$, $b=12{\cdot}52\,(1)$, $c=12{\cdot}39\,(1)$ Å, $\beta=93{\cdot}74°\,(5)$, $Z=8$, $U=3738$ Å^3, $F(000)=1680$, $D_m=1{\cdot}419$ g.cm^{-3} (flotation in xylene and carbon tetrachloride), $D_c=1{\cdot}421$ g.cm^{-3}, $\mu(\text{Cu }K\alpha)=21$ cm^{-1}.

6329 independent intensities were collected by using two crystals of approximate dimensions $0{\cdot}12\times0{\cdot}22\times0{\cdot}30$ mm and $0{\cdot}10\times0{\cdot}10\times0{\cdot}19$ mm, Ni-filtered Cu $K\alpha$ radiation and the θ–2θ scan technique. The scan interval was 1·60° for all reflexions, in steps of 0·01° with a maximum step time of 0·6 sec. The intensities of three, quite strong reference reflexions 040, 004 and 460 were checked approximately every 150 reflexions. The first crystal slowly decomposed in the X-ray beam but no changes in intensity were detected with the second. The first crystal was used to collect data in the sinθ interval of 0·7–0·9. When data collection on the first crystal was discontinued, the intensity of the three test reflexions had decreased by 20·0, 21·3 and 20·5% respectively.

The second crystal was used to collect data in the sin θ interval of 0·0–0·7. Data from the first crystal was corrected for decomposition, which was assumed to be linear with time between successive reference measurements. The data were corrected for the Lp factor and for absorption.

It was found that reflexions with $h+l$ odd were weak and that they contributed only 9% to the total intensity sum. The symmetric and antisymmetric parts of the structure were obtained in two separate refinements using the even and odd reflexions respectively.

Solution and refinement of the symmetric part

The structure was solved by the method of symbolic addition for a *B*-centred cell. An *E* map based on 400 *E*'s, all of which had correct signs, revealed all non-hydrogen atoms, and the weakness of the odd reflexions was explained. Four oxygen atoms attached to the benzene ring of the hydroquinone molecule appeared with half weight. The second hydroquinone molecule in the asymmetric unit is rotated almost 60° around the C_6 axis of the benzene ring and translated nearly

Table 2. *Isotropic temperature factors, final coordinates* ($\times 10^3$) *and displacement parameters* ($\times 10^4$) *for the hydrogen atoms*

The estimated standard deviations for $x,y,z,\mathrm{d}x,\mathrm{d}y,\mathrm{d}z$ are 1, 3, 3, 0·7, 1·5, 1·5 ($\times 10^3$) respectively and for B 1·8 Å^2. The primed atoms belong to the hydroquinone molecule. The atoms are numbered according to those to which they are attached.

	x	y	z	dx	dy	dz	B(Å^2)
H(1)	501	245	256	21	22	39	8·7
H(3)	570	57	505	14	24	23	9·2
H(6)	425	475	722	−2	15	7	7·6
H(9)	376	535	322	18	−4	2	6·6
H(15*a*)	312	641	675	−2	10	−22	9·1
H(15*b*)	362	612	769	−2	−5	−18	10·0
H(15*c*)	362	720	671	−15	0	11	9·5
H(16*a*)	341	750	479	−10	−28	−12	9·3
H(16*b*)	324	684	365	−18	−18	−24	9·8
H(16*c*)	290	663	482	3	0	−27	9·2
H(17*a*)	416	276	241	17	−15	29	6·9
H(17*b*)	380	387	251	14	5	19	6·8
H(17*c*)	444	420	221	13	−15	19	9·5
H(3′)	283	377	676	−5	−19	−24	6·3
H(6′)	250	379	295	19	−63	−29	8·2
H(1′)	314	248	366				1·7
H(2′)	336	246	574				0·2
H(4′)	218	513	613				4·2
H(5′)	191	505	387				1·3

Table 1. *Isotropic temperature factors and final coordinates* ($\times 10^5$)

For double atoms, the average coordinates and displacement parameters ($\times 10^5$) are given. Standard deviations are given in parentheses for the last significant digit. The primed atoms belong to the hydroquinone molecule. The primed oxygen atoms are numbered according to the carbon atoms to which they are attached.

	x	y	z	dx	dy	dz	B(Å)
C(1)	40171 (4)	09062 (7)	45365 (9)	214 (2)	61 (4)	872 (5)	3·90
N(1)	50332 (12)	23069 (22)	33989 (19)	332 (7)	148 (13)	326 (10)	2·86
C(2)	53831 (11)	14780 (21)	37183 (19)	315 (8)	202 (16)	376 (14)	3·96
N(3)	54736 (13)	13121 (27)	48049 (23)	224 (6)	101 (12)	392 (11)	2·96
C(4)	52486 (11)	18947 (26)	55918 (26)	171 (7)	150 (14)	312 (12)	2·43
C(4*a*)	49039 (12)	28142 (24)	52234 (22)	183 (6)	125 (13)	249 (12)	2·00
N(5)	46979 (10)	34232 (21)	59472 (19)	118 (6)	80 (12)	226 (10)	2·26
C(5*a*)	43616 (12)	42379 (25)	55910 (23)	114 (6)	53 (13)	158 (12)	1·80
C(6)	41423 (14)	49312 (29)	63524 (27)	6 (7)	−12 (15)	75 (14)	2·60
C(7)	37864 (13)	57367 (28)	60294 (28)	−12 (7)	−38 (15)	−7 (15)	3·01
C(8)	36547 (13)	59029 (26)	49064 (26)	103 (7)	−4 (14)	−16 (14)	2·10
C(9)	38612 (14)	52299 (26)	41443 (26)	207 (7)	32 (14)	62 (14)	2·71
C(9*a*)	42078 (12)	43843 (23)	44795 (23)	184 (7)	63 (13)	137 (12)	2·75
N(10)	44099 (10)	36629 (19)	37504 (18)	252 (6)	65 (11)	189 (10)	2·06
C(10*a*)	47824 (12)	29374 (23)	40955 (22)	239 (7)	114 (13)	241 (12)	1·58
C(15)	35233 (17)	64178 (32)	68601 (35)	−123 (8)	−112 (18)	−129 (17)	5·10
C(16)	32779 (17)	67926 (31)	45126 (25)	81 (9)	−79 (17)	175 (18)	4·36
C(17)	41766 (13)	36311 (23)	26097 (20)	241 (9)	−49 (16)	190 (14)	4·36
O(18)	56054 (11)	09474 (21)	30604 (17)	405 (7)	187 (13)	421 (10)	5·58
O(19)	53329 (11)	16698 (21)	65422 (17)	145 (5)	110 (11)	324 (9)	4·00
C(1′)	29223 (14)	30803 (28)	42277 (30)	319 (8)	−180 (16)	−127 (16)	3·73
C(2′)	30307 (15)	30816 (31)	53353 (29)	116 (8)	102 (16)	−56 (16)	3·47
C(3′)	27598 (17)	37871 (31)	59665 (31)	−68 (8)	102 (17)	−372 (16)	3·73
C(4′)	23737 (16)	44944 (33)	55069 (31)	−78 (8)	−165 (17)	−766 (18)	3·83
C(5′)	22635 (16)	44866 (33)	43895 (35)	95 (9)	−462 (18)	−849 (18)	4·35
C(6′)	25363 (16)	37861 (33)	37598 (35)	312 (9)	−441 (18)	−482 (17)	4·54
O(2′)	34079 (25)	24185 (50)	58714 (50)				4·40
O(5′)	18864 (25)	50919 (50)	37756 (50)				4·74
O(1′)	81162 (25)	24127 (50)	85591 (50)				5·55
O(4′)	71522 (25)	52117 (50)	12897 (50)				5·16

$\frac{1}{2}$ in the x and z directions (Fig. 1) with respect to the first molecule.

The structure was first refined isotropically (R= 0·20) and then anisotropically. Hughes's weighting scheme with $w=1/(F_{\text{obs}})^2$ was applied with absolute $F_{\text{min}}=4$. A subsequent difference Fourier map showed all hydrogen atoms on the flavin molecule and two of the hydrogen atoms which were not obscured by the oxygen atoms in the hydroquinone molecule. No trace of the hydroxyl hydrogens was found. A final refinement, using the 3029 observed even reflexions with $\sigma(I)/(I)$ less than 0·40 and with isotropic hydrogen atoms, yielded $R=0{\cdot}058$. Final parameters are listed in Tables 1, 2, and 3.

Solution and refinement of the antisymmetric part

The structure factor expression for atoms related by the pseudo-translation (double atoms) takes a different form if $h+l$ is even or odd (g or u). It can be expressed in terms of the average positions and the displacements, denoted r_j and Δr_j respectively. For simplicity, the formulae for the spacegroup $P\bar{1}$ are shown, the temperature factor term having been omitted.

$$F_g=4\sum_j f_j \cos(2\pi h r_j)\cos(2\pi h \Delta r_j) +2\sum_k f_k \cos(2\pi h r_k) \quad (1)$$

$$F_u=-4\sum_j f_j \sin(2\pi h r_j)\sin(2\pi h \Delta r_j) +2\sum_k f_k \cos(2\pi h r_k) \quad (2)$$

where j is summed over all double atoms and k over all single atoms.

As the displacements are very small (less than 0·14 Å) F_u is approximately linear in Δr. If r and enough signs of F_u are known, Δr can be directly calculated. The signs calculated from the positions of the four single oxygen atoms sufficed to solve the phase problem.

A second successful method of solution was based on the fact that signs could be determined rather well by the use of only the biggest term in equation (2), *i.e.* the one which has the largest value of $f.\Delta p$, where Δp is any component of Δr, in this case the z component for the chloride ion. The author has also successfully applied the method to the known structure of hydroquinone (Maartman-Moe, 1966).

The anisotropic temperature factors obtained from the even reflexions are corrected for the displacement effect in the following way: the factor $\cos[2\pi(h\Delta r)]$ in equation (1) can be included in the temperature factor expression with negligible error, as can be seen from the series development:

$$\exp(-\sum_i\sum_j \beta_{ij}h_ih_j)=1-\sum_i\sum_j \beta_{ij}h_ih_j+\ldots \quad (3)$$

Table 3. *Anisotropic thermal parameters for the nonhydrogen atoms* ($\times 10^5$)

The temperature factor expression used is

$\exp(-h^2\beta_{11}-k^2\beta_{22}-l^2\beta_{33}-hk\beta_{12}-hl\beta_{13}-kl\beta_{23})$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	150 (2)	448 (7)	1052 (11)	50 (6)	42 (7)	194 (13)
N(1)	229 (7)	537 (23)	284 (17)	230 (20)	180 (18)	105 (31)
C(2)	232 (9)	543 (28)	387 (24)	220 (26)	214 (26)	49 (43)
N(3)	170 (6)	533 (22)	370 (19)	202 (18)	99 (17)	25 (32)
C(4)	129 (6)	521 (25)	313 (19)	91 (21)	34 (22)	−30 (36)
C(4*a*)	111 (7)	419 (26)	304 (27)	14 (20)	59 (20)	−93 (40)
N(5)	122 (5)	529 (21)	364 (17)	66 (16)	6 (15)	−167 (30)
C(5*a*)	102 (7)	404 (25)	386 (19)	16 (21)	27 (21)	−139 (38)
C(6)	130 (6)	568 (27)	488 (25)	90 (21)	3 (20)	−339 (42)
C(7)	115 (6)	502 (27)	652 (28)	30 (20)	61 (21)	−390 (43)
C(8)	122 (6)	374 (27)	647 (27)	34 (21)	66 (22)	15 (37)
C(9)	140 (6)	436 (25)	507 (25)	47 (20)	97 (21)	155 (38)
C(9*a*)	113 (5)	319 (26)	420 (29)	−25 (20)	99 (22)	−30 (41)
N(10)	153 (6)	418 (23)	303 (20)	35 (21)	80 (18)	101 (30)
C(10*a*)	137 (8)	333 (29)	312 (30)	8 (25)	109 (25)	76 (42)
C(15)	182 (8)	772 (36)	826 (35)	276 (29)	49 (28)	−585 (58)
C(16)	209 (9)	547 (30)	930 (38)	254 (27)	100 (30)	142 (54)
C(17)	246 (9)	652 (31)	309 (22)	214 (28)	−55 (23)	138 (41)
O(18)	427 (9)	928 (31)	446 (23)	791 (29)	366 (24)	68 (39)
O(19)	222 (6)	828 (23)	318 (16)	421 (19)	−3 (16)	−17 (30)
C(1′)	151 (7)	522 (25)	718 (32)	−47 (21)	32 (26)	67 (45)
C(2′)	137 (6)	506 (28)	718 (28)	−46 (18)	−31 (27)	127 (51)
C(3′)	166 (7)	661 (30)	658 (40)	−53 (19)	−72 (29)	96 (48)
C(4′)	170 (7)	596 (28)	778 (35)	−17 (20)	−10 (25)	−5 (50)
C(5′)	154 (8)	631 (33)	924 (40)	20 (26)	−61 (29)	267 (61)
C(6′)	191 (7)	671 (29)	664 (30)	6 (23)	−37 (26)	127 (55)
O(1′)	265 (7)	940 (28)	743 (31)	270 (21)	22 (20)	−22 (42)
O(2′)	197 (7)	721 (30)	810 (24)	170 (23)	−133 (24)	194 (47)
O(4′)	255 (7)	910 (27)	1083 (33)	207 (23)	−56 (21)	−377 (42)
O(5′)	209 (7)	933 (29)	952 (30)	345 (23)	0 (24)	504 (45)

$$\cos(2\pi h\Delta r) = 1 - 2\pi^2(h\Delta r)^2 + \ldots \qquad (4)$$

It is seen that the term $2\pi^2(\Delta x)^2$ is included in β_{11}, $4\pi^2\Delta x\Delta y$ is included in β_{12} *etc.* If the second term in equation (4) is called ε^2 the error in neglecting subsequent terms will be less than $\varepsilon^4/12$.

The displacement parameters for all atoms including hydrogen, were refined by a least-squares method based upon equation (2). Since the differences between the thermal parameters of atoms related by pseudo-translation have been found to be negligible, these atoms were assigned the same thermal parameters. A difference map showed four hydrogen atoms attached to the hydroquinone ring. These atoms overlap with the oxygen atoms (within 0·1–0·2 Å) in the symmetric part of the structure. Thus, the values obtained for these hydrogen atoms are not very reliable.

The thermal parameters were corrected for the displacement effect, and a final refinement of the displacements, the positions and thermal parameters for the four hydrogen and oxygen atoms reduced the R value to 0·12. The refinement was based on 2650 odd reflexions having $\sigma(I)/(I)$ less than 0·40. All reflexions were given unit weight and the scale factor determined for the even reflexions was held constant. The largest peak in the final difference map, computed from all

Table 4. *Bond distances and angles for the lumiflavin molecules*

I refers to data calculated from the average coordinates; *A* and *B* refer to the first and second molecules in the asymmetric unit. In the last column the differences between equivalent bonds lengths are given (× 10³ Å). The e.s.d.'s are 0·004 Å and 0·3° for the bonds in molecule I. The corresponding e.s.d.'s, when a hydrogen atom is included in the bonds, are 0·04 Å and 1·8°. The e.s.d.'s for bond length differences in the last column are 0·003 Å. The corresponding e.s.d.'s are 0·03 when a hydrogen atom is included in the bond.

Angles

	I	*A*	*B*
C(10*a*)–N(1)—C(2)	123·4°	123·7°	123·2°
N(1)—C(2)—O(18)	120·8	121·1	120·5
N(1)—C(2)—N(3)	116·9	117·1	116·8
O(18)—C(2)—N(3)	122·2	121·8	122·7
C(2)—N(3)—C(4)	124·4	124·9	125·9
N(3)—C(4)—C(4*a*)	116·1	116·4	115·8
N(3)—C(4)—O(19)	121·4	120·8	122·1
O(19)—C(4)—C(4*a*)	122·4	122·8	122·1
C(4)—C(4*a*)–C(10*a*)	117·8	117·8	117·8
C(4)—C(4*a*)–N(5)	118·5	118·5	118·5
C(10*a*)–C(4*a*)–N(5)	123·5	123·6	123·4
C(4*a*)—N(5)—C(5*a*)	117·6	117·5	117·7
N(5)—C(5*a*)–C(9*a*)	121·8	121·8	121·8
N(5)—C(5*a*)–C(6)	119·2	119·4	118·9
C(9*a*)—C(5*a*)–C(6)	119·0	118·8	119·3
C(5*a*)—C(6)—C(7)	120·9	121·1	120·7
C(6)—C(7)—C(15)	120·1	120·4	119·9
C(6)—C(7)—C(8)	119·4	119·2	119·5
C(15)—C(7)—C(8)	120·5	120·4	120·6
C(7)—C(8)—C(16)	121·3	121·5	121·0
C(7)—C(8)—C(9)	120·8	120·7	120·9
C(16)—C(8)—C(9)	117·9	117·8	118·1
C(8)—C(9)—C(9*a*)	119·7	119·8	119·5
C(9)—C(9*a*)–N(10)	121·9	122·0	121·8
C(9)—C(9*a*)–C(5*a*)	120·1	120·2	120·1

	I	*A*	*B*
N(10)—C(9*a*)—C(5*a*)	117·9°	117·8°	118·0°
C(9*a*)—N(10)—C(17)	120·5	120·3	120·8
C(9*a*)—N(10)—C(10*a*)	119·6	119·8	119·4
C(17)—N(10)—C(10*a*)	119·6	119·6	119·6
N(10)—C(10*a*)–N(1)	121·3	121·6	120·9
N(10)—C(10*a*)–C(4*a*)	118·9	118·9	119·0
N(1)—C(10*a*)–C(4*a*)	119·8	119·5	120·1
C(10*a*)–N(1)—H(1)	122·5	120·5	124·4
H(1)—N(1)—C(1)	113·8	115·7	111·9
C(2)—N(3)—H(3)	118·0	117·3	118·9
H(3)—N(3)—C(4)	116·3	118·0	119·3
C(5*a*)—C(6)—H(6)	116·3	117·8	116·8
H(6)—C(6)—C(7)	122·6	121·1	122·4
H(15*a*)–C(15)—C(7)	111·6	113·2	110·3
H(15*b*)–C(15)—C(7)	111·5	110·2	112·7
H(15*c*)–C(15)—C(7)	107·9	109·2	106·6
H(16*a*)–C(16)—C(8)	112·0	112·4	111·7
H(16*b*)–C(16)—C(8)	111·9	111·7	112·2
H(16*c*)–C(16)—C(8)	105·8	106·3	105·0
H(9)—C(9)—C(8)	122·3	121·0	123·4
H(9)—C(9)—C(9*a*)	118·0	117·8	118·2
H(17*a*)–C(17)—N(9)	104·1	104·2	104·0
H(17*b*)–C(17)—N(9)	114·5	114·1	114·9
H(17*c*)–C(17)—N(9)	102·6	102·9	102·3

Distances

	I	*A*	*B*	*B–A*
N(1)—C(2)	1·380 Å	1·374 Å	1·386 Å	– 12 Å
C(2)—O(18)	1·205	1·213	1·197	16
C(2)—N(3)	1·366	1·368	1·364	2
N(3)—C(4)	1·359	1·361	1·354	7
C(4)—O(19)	1·215	1·217	1·213	4
C(4)—C(4*a*)	1·475	1·474	1·477	– 3
C(4*a*)–C(10*a*)	1·418	1·417	1·419	– 2
C(4*a*)–N(5)	1·301	1·302	1·299	3
N(5)—C(5*a*)	1·359	1·360	1·359	1
C(5*a*)–C(9*a*)	1·415	1·414	1·416	– 2
C(5*a*)–C(6)	1·410	1·409	1·412	– 3
C(6)—C(7)	1·368	1·371	1·365	– 6
C(7)—C(15)	1·509	1·505	1·512	– 7
C(7)—C(8)	1·422	1·420	1·425	– 5
C(8)—C(16)	1·500	1·502	1·498	– 4
C(8)—C(9)	1·383	1·384	1·382	2
C(9)—C(9*a*)	1·396	1·392	1·400	– 8

	I	*A*	*B*	*B–A*
C(9*a*)—N(10)	1·388 Å	1·390 Å	1·387 Å	3 Å
N(10)—C(17)	1·488	1·489	1·487	2
N(10)—C(10*a*)	1·329	1·325	1·334	– 9
C(10*a*)–N(1)	1·343	1·345	1·342	3
H(1)—N(1)	1·047	1·041	1·055	– 14
H(3)—N(3)	1·012	0·981	1·041	– 60
H(6)—C(6)	1·109	1·022	1·033	– 11
H(15*a*)–C(15)	0·969	0·944	0·994	– 50
H(15*b*)–C(15)	1·106	1·102	1·110	– 8
H(15*c*)–C(15)	1·106	1·043	1·029	14
H(16*a*)–C(16)	0·989	0·956	1·022	– 66
H(16*b*)–C(16)	1·063	1·069	1·055	14
H(16*c*)–C(16)	1·035	1·039	1·030	9
H(9)—C(9)	1·164	1·162	1·166	– 4
H(17*a*)–C(17)	1·117	1·130	1·107	23
H(17*b*)–C(17)	0·963	0·989	0·937	52
H(17*c*)–C(17)	1·097	1·071	1·123	– 52

even and odd reflexions had a height of 0·3 e.Å^{-3}. The final displacements are listed in Tables 1 and 2.

Description and discussion of the structure

As can be seen from Tables 4 and 5, the differences between bond distances and angles for the two independent molecules in the asymmetric unit are quite small. The greatest difference is 0·016 Å, which is equal to 4σ. The discrepancy between equivalent bond distances is, however, much less than that calculated from the displacement parameters. This is explained by the fact that the two complexes in the asymmetric unit are slightly rotated relative to each other about the translation vector and slightly tilted from parallelism. It is noteworthy that the positions of the hydroquinone benzene rings relative to their complexed flavinium ions are nearly identical, despite the different positions of the hydroquinone oxygen atoms (Fig. 1).

Table 5. *Bond distances and angles for the hydroquinone molecules*

The e.s.d.'s are 0·005 Å for bonds and 0·5° for angles for the non-hydrogen atoms.

Angles	*A*	*B*
C(6′)–C(1′)–C(2′)	119·3°	120·0°
O(1′)–C(1′)–C(6′)	–	117·9
O(1′)–C(1′)–C(2′)	–	122·2
C(1′)–C(2′)–C(3′)	120·4	119·6
O(2′)–C(2′)–C(1′)	121·8	–
O(2′)–C(2′)–C(3′)	117·8	–
C(2′)–C(3′)–C(4′)	120·3	121·0
C(3′)–C(4′)–C(5′)	119·0	119·0
O(4′)–C(4′)–C(3′)	–	118·1
O(4′)–C(4′)–C(5′)	–	122·8
C(4′)–C(5′)–C(6′)	120·0	120·3
O(5′)–C(5′)–C(4′)	121·0	–
O(5′)–C(5′)–C(6′)	118·9	–
C(5′)–C(6′)–C(1′)	120·7	120·2
H(1′)–C(1′)–C(2′)	126·4	–
H(1′)–C(1′)–C(6′)	114·0	–
H(2′)–C(2′)–C(1′)	–	121·0
H(2′)–C(2′)–C(3′)	–	119·3
H(3′)–C(3′)–C(2′)	116·2	123·6
H(3′)–C(3′)–C(4′)	123·2	115·4
H(4′)–C(4′)–C(3′)	110·1	–
H(4′)–C(4′)–C(5′)	130·5	–
H(5′)–C(5′)–C(4′)	–	134·0
H(5′)–C(5′)–C(6′)	–	105·5
H(6′)–C(6′)–C(5′)	121·0	125·9
H(6′)–C(6′)–C(1′)	118·3	113·4
Distances	*A*	*B*
C(1′)–O(1′)	–	1·344 Å
C(1′)–C(2′)	1·384 Å	1·379
C(2′)–O(2′)	1·365	–
C(2′)–C(3′)	1·374	1·375
C(3′)–C(4′)	1·381	1·385
C(4′)–O(4′)	–	1·381
C(4′)–C(5′)	1·400	1·389
C(5′)–O(5′)	1·373	–
C(5′)–C(6′)	1·370	1·374
C(6′)–C(1′)	1·382	1·388
H(1′)–C(1′)	1·11	–
H(2′)–C(2′)	–	1·22
H(3′)–C(3′)	1·01	0·97
H(4′)–C(4′)	1·29	–
H(5′)–C(5′)	–	1·25
H(6′)–C(6′)	0·98	1·03

The molecules are connected by an extensive network of hydrogen bonds. Fig. 2 shows a flat non-staggered sheet of molecules forming a herringbone pattern. As the molecules are almost perpendicular to the *ab* plane, they are drawn as straight lines. The chloride ion and the centres of the molecules lie at about the same z value, $z=0·0$. The next sheet of molecules, at $z=0·5$, is generated by the pseudo-translation $\frac{1}{2}a+\frac{1}{2}c$. The sheets are connected by hydrogen bonds between the lumiflavinium ions via the atoms H(1) and O(19) (see Fig. 3 for atomic labeling).

Thus chains of flavin molecules cross at right angles the molecular sheet described above. The chloride ions link, by hydrogen bonding, the flavin and the hydroquinone molecules. Unfortunately, the hydrogen atoms could not be located but the Cl–O distances (Table 6) indicate hydrogen bonding. Fig. 1 shows the two hydroquinone molecules superimposed on the least-squares plane of the flavin molecule. It is seen that bonds equally related to the flavin molecule are more similar than bonds equally related to the hydroxyl groups. In the crystal structure of hydroquinone (Maartman-Moe 1966) the centre of the hydroquinone molecule coincides with the centre of symmetry.

From the distances and angles (Fig. 1 and Table 5), molecular centrosymmetry of the hydroquinone molecule may be recognised. Some large deviations from the least-squares plane of the hydroquinone ring occur for the oxygen atoms (Table 7). The deviations are about 0·03 Å, which is 10 to 30 times larger than the deviations for the carbon atoms.

The oxygen atoms O(2′) and O(5′) in molecule *A* both lie on the side of the plane away from the flavin ring. The distance from the centre of the hydroquinone ring to the flavin plane is 3·498 Å (3·484 Å for molecule *B*). The distance between adjacent flavin planes

Table 6. *Distances and angles involving hydrogen bonds*

Values in parentheses refer to molecule *B*.

Cl––H(3)	2·16 (2·11 Å)	N(1)–H(1)	1·04 (1·05) Å
Cl––N(3)	3·18 (3·13)	N(1)–O(19)	2·74 (2·80)
H(3)–N(3)	0·98 (1·04)	H(1)–O(19)	1·86 (1·91)
Cl––H(3)–N(3)	166·0 (164·2)°	N(1)–H(1)–O(19)	140·8 (140·2)°
Cl–(O2′)	3·054 Å	O(2′)–Cl–O(4′)	83·5°
Cl–(O5′)	3·087	O(1′)–Cl–O(5′)	87·6
Cl–O(1′)	3·080	O(2′)–Cl–H(3)	128·0
Cl–O(4′)	3·169	O(4′)–Cl–H(3)	95·1

Table 7. *Distances* ($\times 10^3$ Å) *from the least-squares planes*

Atoms after the blank line in each subcolumn are not included in the plane calculation

	I*A*	I*B*
N(1)	47	42
C(2)	44	46
N(3)	−18	8
C(4)	−56	−52
C(4*a*)	32	26
N(5)	46	39
C(5*a*)	65	55
C(6)	107	112
C(7)	76	83
C(8)	63	47
C(9)	9	−15
C(9*a*)	−17	−29
N(10)	−128	−131
C(10*a*)	−98	−8
C(15)	20	41
C(16)	59	53
O(18)	117	117
O(19)	−148	−151
C(17)	−522	−476
C(1′)	−3438	−3468
C(2′)	−3330	−3354
C(3′)	−3375	−3366
C(4′)	−3543	−3500
C(5′)	−3666	−3615
C(6′)	−3607	−3603
O(2′)	−3200	
O(5′)	−3854	
O(1′)		−3490
O(4′)		−3476

	II*A*	II*B*
C(5*a*)	13	8
C(6)	8	8
C(7)	−21	−17
C(8)	14	11
C(9)	7	4
C(9*a*)	−20	−14

	III*A*	III*B*
N(1)	−23	−27
C(2)	−7	−9
N(3)	−4	15
C(4)	5	5
C(4*a*)	71	68
C(10*a*)	−38	−32
O(18)	27	20
O(19)	−30	−39
H(1)	32	86
H(3)	−86	−58

	IV*A*	IV*B*
C(1′)	2	1
C(2′)	−5	−1
C(3′)	33	1
C(4′)	2	−1
C(5′)	−4	1
C(6′)	2	−1
O(2′)	−42	
O(5′)	−24	
O(1′)		−29
O(4′)		31

(centrosymmetrically related) is 3·72 Å. To make the flavin and hydroquinone planes parallel, the hydroquinone plane would have to turn 5·6° about an axis parallel to the flavin plane and passing approximately through the atoms C(1′) and C(4′). C(2′) would then approach the flavin plane. Moreover the hydroquinone and lumiflavin ring do not coincide in projection (Fig. 1). One ring must first be translated 0·9 Å along the C(6)–C(8) direction and rotated 8° in the plane. The angle between the flavin plane and the axis connecting the centres of the benzene rings is 49·3°.

One may ask to what extent the geometrical features mentioned above are the effects either of a charge transfer interaction or of the ionic distribution and hydrogen-bonding system. In the two other complexes, the corresponding hydrobromide (Tillberg & Norrestam, 1972) and riboflavinium–hydroquinone–hydrobromide (Bear *et al.*, 1970), the intermolecular distances are shorter (about 3·30 Å). In contrast to the present structure, there is an infinite stacking of the molecules with charge transfer interactions, such that the hydroquinone molecule is sandwiched between the benzene ring and pyrimidine ring of the flavin ion. In the lumiflavin hydrobromide structure, the flavin and the hydroquinone planes are tilted 4° from parallelism about an axis perpendicular (instead of parallel) to the oxygen–oxygen line. The orientation of the hydroquinone molecule is the same as that in complex *B* in the present structure. A computer plot of the lumiflavinium ion with atomic labeling is shown in Fig. 3. The ion is protonated at N(1). Bond distances and angles, all near 120°, are listed in Table 4. Least-squares calculations indicate that the ion is distorted around its long

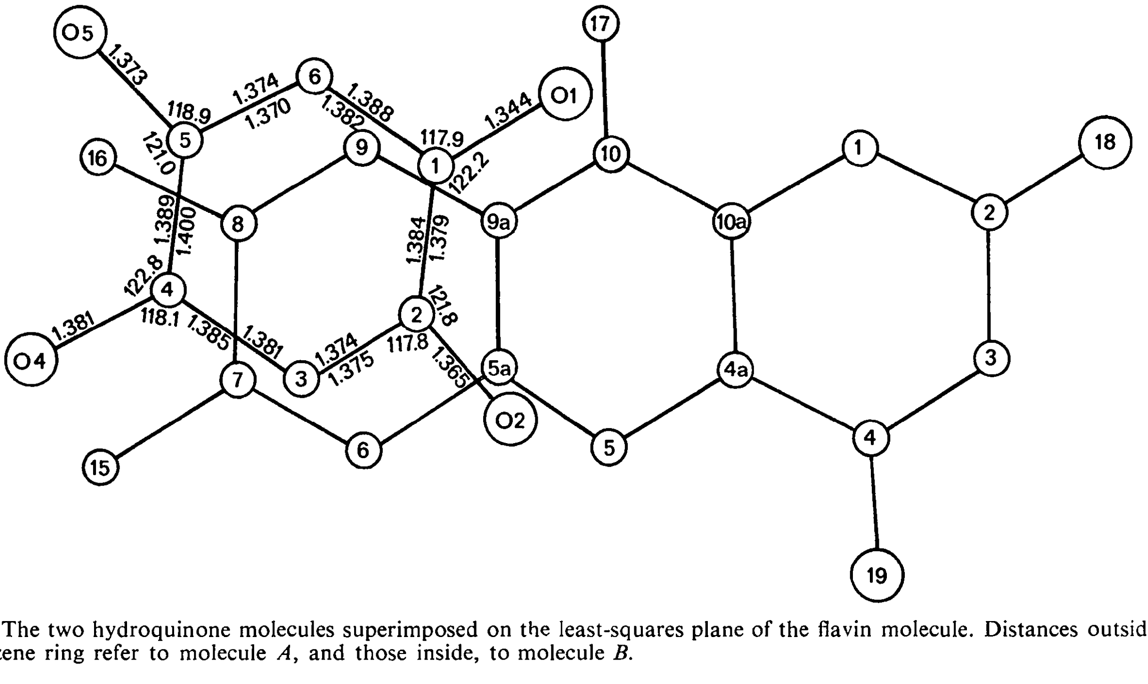


Fig. 1. The two hydroquinone molecules superimposed on the least-squares plane of the flavin molecule. Distances outside the benzene ring refer to molecule *A*, and those inside, to molecule *B*.

Table 8. *Computer programs used in this paper*

SIP. Generation of steering papertape for Siemens AED.	R. Norrestam. Stockholm, Sweden.
SIMSA. Interpretation of output papertape for Siemens AED.	R. Norrestam. Stockholm, Sweden.
*DATAP*2. Lp- and absorption corrections.	P. Coppens, L. Leiserowitz & D. Rabinovich. Rehovoth Israel.
FAME and *MAGIC*. Wilson plot, calculation of *E* values and symbolic addition.	R. B. K. Dewar & A. L. Stone. Chicago, U.S.A.
DRF. Fourier summations and structure factor calculations.	A. Zalkin. Berkeley, U.S.A.
LALS. Full-matrix least-squares refinement of positional and thermal parameters and scale factors.	P. K. Gantzel, R. A. Sparks & K. N. Trueblood. Los Angeles, U.S.A.
DISTAN. Calculation of interatomic distances and bond angles with estimated standard deviations.	A. Zalkin. Berkeley, U.S.A.
ORTEP. Thermal-ellipsoid plot.	C. K. Johnson. Oak Ridge, U.S.A.

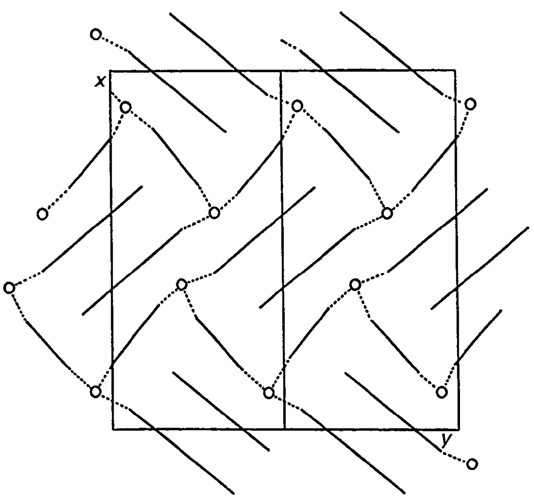


Fig. 2. One sheet of the molecular packing in the *xy* projection shown in two unit cells. The long full lines and the short full lines represent the lumiflavin and the hydroquinone molecules respectively. The dashed lines are hydrogen bonds and the circles chloride ions.

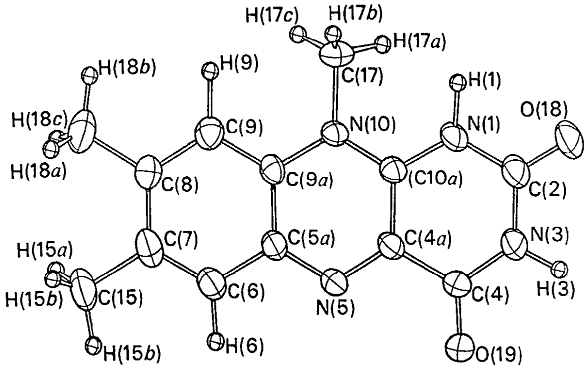


Fig. 3. An *ORTEP* plot of the flavinium ion.

axis. Separate calculations for the pyrimidine ring indicate a significant buckling (Table 7). The bond distances agree rather well with those found in the bromide and in the 10-methylisoalloxazin-HBr dihydrate (Fritchie, Trus & Charles, 1969). Data for the riboflavin complex have not yet been published.

Atomic scattering factors for C, N, O and Cl^- were calculated from the analytical constants given by Cromer (1968) for Hartree–Fock wave functions and those for H were taken from *International Tables for X-ray Crystallography* (1962).

The observed and calculated structure factors can be obtained from the author on request. Some of the computer programs used in this paper are listed in Table 8. All the programs used are written in Fortran IV and modified for the IBM 3600/75.

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