

Table 2. Selected geometric parameters (Å, °)

S—C(7)	1.697 (2)	N(3)—C(4)	1.368 (3)
S—C(10)	1.713 (3)	C(7)—C(8)	1.438 (3)
O(2)—C(2)	1.214 (2)	C(7)—C(6)	1.441 (3)
O(4)—C(4)	1.215 (2)	C(8)—C(9)	1.376 (4)
N(1)—C(5)	1.398 (2)	C(9)—C(10)	1.368 (4)
N(1)—C(2)	1.362 (3)	C(6)—C(5)	1.344 (3)
N(3)—C(2)	1.385 (2)	C(5)—C(4)	1.479 (3)
C(7)—S—C(10)	92.1 (1)	N(1)—C(5)—C(6)	131.1 (2)
C(5)—N(1)—C(2)	110.5 (2)	N(1)—C(5)—C(4)	105.5 (2)
C(2)—N(3)—C(4)	111.6 (2)	C(6)—C(5)—C(4)	123.3 (2)
S—C(7)—C(8)	109.9 (2)	O(2)—C(2)—N(1)	126.6 (2)
S—C(7)—C(6)	125.0 (1)	O(2)—C(2)—N(3)	126.3 (2)
C(8)—C(7)—C(6)	124.8 (2)	N(1)—C(2)—N(3)	107.1 (2)
C(7)—C(8)—C(9)	112.6 (2)	O(4)—C(4)—N(3)	126.7 (2)
C(8)—C(9)—C(10)	112.4 (2)	O(4)—C(4)—C(5)	128.2 (2)
S—C(10)—C(9)	112.5 (2)	N(3)—C(4)—C(5)	105.1 (2)
C(7)—C(6)—C(5)	129.7 (2)		

Table 3. Hydrogen-bonding geometry (Å, °)

D—H...A	H...A	D...A	D—H...A
N(1)—H(1)...O(4 ⁱ)	2.17 (2)	2.924 (2)	159 (2)
N(3)—H(3)...O(2 ⁱⁱ)	1.96 (3)	2.826 (2)	165 (2)

Symmetry codes: (i) $1 + x, y, z$; (ii) $x - \frac{1}{2}, -\frac{1}{2} - y, z$.

Part of the molecule is disordered. The thiophene ring exists in two different orientations which are related to each other by an approximate 180° rotation about the C(6)—C(7) bond. The major isomer is shown in Fig. 1. The disorder became obvious from observations made during the course of refinement of a model consisting of only the major isomer. At the anisotropic stage the difference electron density map contained two large peaks near atom C(8) of 0.88 and $1.0 e \text{ \AA}^{-3}$. The C(7)—C(8) bond was too long at 1.493 (6) Å for a double bond. In comparison the C(9)—C(10) bond length was 1.334 (9) Å. The S—C bond lengths were slightly short at 1.694 (5) and 1.684 (6) Å. An ORTEPII (Johnson, 1976) drawing showed a smaller than expected displacement ellipsoid for C(8) and a larger than expected one for S; the ellipsoids for C(9) and C(10) were elongated. The *R* factor for the final model converged at the rather high value of 0.072.

Many of these observations had been made earlier for the thiophene derivatives of 3,3'-dithienyl and β-thiophenic acid (Visser, Heeres, Wolters & Vos, 1968). In both of these cases, inclusion in the model of a second orientation of the thiophene ring improved the results considerably.

The disorder in this structure was modeled as follows; initially, the S and C(8) atoms were treated as composite atoms, *i.e.* the S site was occupied by both atoms S and C(8') with their occupancy factors totaling 1.0. Likewise, the C(8) site was occupied by atoms C(8) and S' with their occupancy factors totaling 1.0. The occupancy factor for C(8) was constrained to be equal to that of S, so that only the occupancy factor for S was allowed to refine and it converged at 0.804 (3). This model decreased the *R* factor, cleaned up the difference electron density map and improved the *B* values for the thiophene ring. However, the bond lengths for the thiophene ring still appeared as described above. So, a second orientation of the thiophene ring was included in the model; its coordinates were obtained by rotating the original ring by 180° about the C(6)—C(7) bond. This second orientation is referred to as the 'rotated' ring and its occupancy factor was fixed at 0.20, while the 'original' ring had its occupancy factor fixed at 0.80. The 'original' ring and the 'rotated' ring were refined in alternate cycles. Atoms S', C(8'), C(9') and C(10')

of the 'rotated' ring were kept isotropic. H atoms were added to both orientations of the thiophene ring and to atom C(6) at calculated positions [C—H = 0.98 Å and $B(H) = 1.2B_{eq}(C)$], and were fixed. The two H atoms bonded to atoms N(1) and N(3) were refined isotropically.

The inclusion of the 'rotated' ring in the model improved the geometry of the 'original' thiophene ring. However, the metrical parameters for the rotated ring are not very good.

Data reduction was carried out using TEXSAN (Molecular Structure Corporation, 1987). The structure was solved by the direct-methods program MITHRIL (Gilmore, 1984). Full-matrix least-squares refinements also used TEXSAN.

We thank the National Institutes of Health for financial support of this research.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including H-atom geometry, least-squares-planes data and geometry for the disordered thiophene ring have been deposited with the IUCr (Reference: BK1050). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Lumiflavinium (7,8,10-Trimethyl-isoalloxazinium) Nitrate

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(Received 24 June 1994; accepted 7 December 1994)

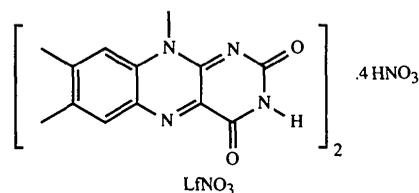
Abstract

The crystal and molecular structure of lumiflavine in its protonated form (lumiflavinium nitrate, $2C_{13}H_{12}N_4O_2 \cdot$

4HNO₃) is reported in order to examine the possibility of hydrogen bonding around the isoalloxazine ring. This structure was solved by direct methods and refined by least-squares calculations to a final $R = 0.054$. There are two molecules of lumiflavine (numbered 100 and 200) and four nitrate ions in the asymmetric unit. The molecules of oxidized lumiflavine are flat and the atoms on the three rings are coplanar to within 0.71 (11) Å. The N1 atom of the isoalloxazine ring is protonated and the molecules are held together by a network of hydrogen bonds *via* the nitrate ions. The structure of protonated lumiflavinium is compared with other flavin compounds.

Comment

The possible occurrence of hydrogen bonding in flavo-proteins seems to contribute to the conformation of the whole enzyme molecule and at the same time to the electronic structure of the coenzyme moiety (Ghisla & Massey, 1989; Nishimoto, Fukunaga & Yagi, 1986). This work is part of a general study on the precise effect of hydrogen bonding on the molecular structure of the isoalloxazine nucleus of flavins in flavoproteins. The structure of the title compound is described, the data are compared with other flavin derivatives and the forces responsible for crystal cohesion analyzed. This paper follows the description of the molecular structure of oxidized lumiflavine hydrochloride hydrate (Wouters *et al.*, 1994). Lumiflavine, 7,8,10-trimethylisoalloxazine (C₁₃H₁₂N₄O₂), was prepared according to a reported procedure (Yoneda, Sakuma, Ichiba & Shinomura, 1976) and crystals of oxidized lumiflavinium nitrate were obtained by slow evaporation of the compound in nitric acid at room temperature. A drawing of the molecular



structure of lumiflavinium nitrate (LfNO₃) is shown in Fig. 1. Distances and bond angles are listed in Table 2. Fig. 2 is a stereoscopic packing illustration.

N1 is the site of protonation of the isoalloxazine ring in riboflavin hydrobromide hydrate (Tanaka, Ashida, Sasada & Kakudo, 1969), in 10-methylisoalloxazine hydrobromide dihydrate (Trus & Fritchie, 1969), in oxidized lumiflavine hydrochloride hydrate (Wouters *et al.*, 1994) and also in the present structure of 7,8,10-trimethylisoalloxazinium nitrate. Monoprotonation at N1 is in agreement with an energy stabilization of 89 kJ mol⁻¹ for N1-protonated lumiflavine *versus* the N5-protonated form, as deduced by *ab initio* RHF-SCF-

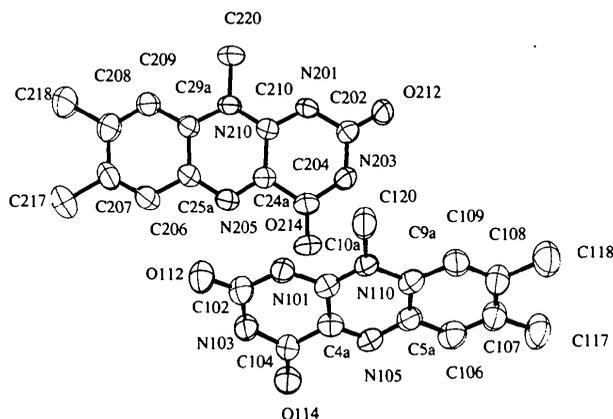


Fig. 1. Molecular structure and conformation of lumiflavinium nitrate. Non-H atoms are represented by displacement ellipsoids at the 50% probability level. The atomic numbering scheme used in this report is shown.

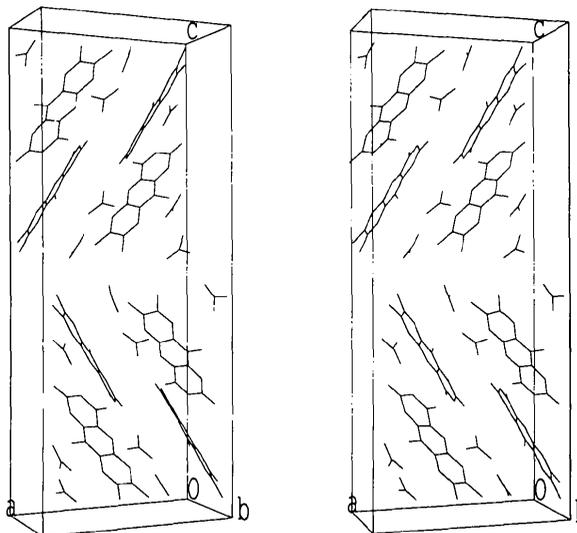


Fig. 2. Stereoview of the crystal packing and molecular conformation of lumiflavinium nitrate.

LCAO calculations (Wouters, Perpète, Dory & Durant, 1992).

The comparison between LfNO₃, lumiflavine (Lf; Abe & Kyogoku, 1987), 3-methyllumiflavine (MLf; Norrestam & Stensland, 1972), lumiflavine hydrochloride hydrate (LfHCl; Wouters *et al.*, 1994) and 1,3,9-trimethylalloxazine (TMAl; Ertan & Koziol, 1993) is based on the examination of selected bond lengths and endocyclic bond angles (Table 3). In the protonated forms of the isoalloxazine ring (LfNO₃ and LfHCl), stabilization of the resulting positive charge is achieved by electronic delocalization from N10 to N1 through C10a, as indicated by an increase of the N1—C10a and a decrease of the N10—C10a bond lengths in these compounds. The double-bond character of C4a—C10a is also increased upon protonation of N1 (decrease of this

bond length in LfNO₃ and LfHCl). The same structural implications are observed upon introduction of a methyl group at N1 (TMAlI). As a consequence, the electronic structure of protonated isoalloxazine rings approaches that of alloxazines. Methyl substitution generally lengthens adjacent bond distances (Ertan & Koziol, 1993) and this is well illustrated in Table 3 for the C2—N3 and N3—C4 bonds in MLf and TMAlI (methyl substitution of N3) which are longer than in the structures of LfNO₃ or Lf. Substitution also influences endocyclic valence angles in the flavin rings: upon substitution of N1 (by a proton or a methyl group), the C10a—N1—C2 angle is increased in comparison with the values for molecules that are not substituted at the N1 atom. Also at N10, the valence angle is larger in Lf, LfNO₃, LfHCl and MLf than in TMAlI.

The two lumiflavinium ions (100 and 200) are nearly planar as shown by the least-squares planes (Table 4). These molecules are flat and the 14 atoms of the tricyclic isoalloxazine ring coplanar to within 0.066 (12) and 0.050 (12) Å for molecules 100 and 200, respectively. The largest deviation from the plane is observed for the methyl C118 atom [−0.142 (14) Å] and the carbonyl O214 atom [0.096 (9) Å]. This conformation is similar in the crystal structures of several isoalloxazine rings but the crystal packing is different. The packing formation in LfNO₃ is strongly influenced by the presence of hydrogen bonding (Table 5). N3—H and the protonated N1 atom participate in this bonding as hydrogen donors. Of the three possible hydrogen-bond receptor sites at the protonated isoalloxazine ring, O12, O14 and N5, only O12 is actually involved in the bonding scheme for LfNO₃. From this observation, one could conclude that O12 is the most basic site in protonated flavins, in contrast with what has been proposed elsewhere (Trus & Fritchie, 1969) and with what is observed in LfHCl. Indeed, in the structure of oxidized lumiflavine hydrochloride hydrate both N5 and O14 are involved in a (bifurcated) hydrogen bond with a water molecule [water...O14 2.795 (5), water...N5 3.057 (6) Å]. This makes it difficult to predict protonation sites on the isoalloxazine ring system.

Experimental

Crystal data

2C₁₃H₁₂N₄O₂·4HNO₃

M_r = 764.5

Orthorhombic

*Pna*2₁

a = 14.0100 (10) Å

b = 7.1040 (10) Å

c = 34.086 (2) Å

V = 3392.5 (6) Å³

Z = 4

D_x = 1.493 Mg m^{−3}

Cu *K*α radiation

λ = 1.5418 Å

Cell parameters from 25 reflections

θ = 40–50°

μ = 1.05 mm^{−1}

T = 295 K

Prism

0.2 × 0.2 × 0.2 mm

Yellow

Data collection

Enraf–Nonius CAD-4

diffractometer

ω/2θ scans

Absorption correction:

ψ scans

*T*_{min} = 0.87, *T*_{max} = 0.99

4804 measured reflections

3397 independent reflections

2499 observed reflections

[*I* > 2σ(*I*)]

*R*_{int} = 0.008

θ_{max} = 72°

h = 0 → 17

k = 0 → 8

l = −31 → 42

3 standard reflections

frequency: 60 min

intensity decay: 0.04%

Refinement

Refinement on *F*

R = 0.054

wR = 0.052

S = 2.05

2499 reflections

486 parameters

*U*_{iso} refined for H atoms

Unit weights applied

(Δ/σ)_{max} = 0.122

Δρ_{max} = 0.27 e Å^{−3}

Δρ_{min} = −0.23 e Å^{−3}

Extinction correction: none

Atomic scattering factors

from *International Tables for Crystallography* (1992),

Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^* \cdot \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
O112	−0.0788 (5)	0.3300 (11)	0.2131 (4)	0.066 (3)
O114	0.0948 (5)	−0.1769 (9)	0.2486 (4)	0.061 (3)
N101	0.0075 (6)	0.3539 (11)	0.2693 (5)	0.049 (3)
N103	0.0129 (6)	0.0823 (11)	0.2296 (4)	0.052 (3)
N105	0.1645 (6)	0.0109 (11)	0.3143 (4)	0.048 (3)
N110	0.0935 (6)	0.3724 (11)	0.3275 (4)	0.048 (3)
C4a	0.1027 (7)	0.0912 (14)	0.2905 (5)	0.048 (3)
C5a	0.1926 (7)	0.1093 (14)	0.3458 (5)	0.052 (3)
C9a	0.1568 (7)	0.2910 (14)	0.3548 (5)	0.052 (3)
C10a	0.0678 (7)	0.2767 (13)	0.2961 (5)	0.045 (3)
C102	−0.0213 (7)	0.2607 (15)	0.2357 (5)	0.054 (3)
C104	0.0721 (7)	−0.0150 (15)	0.2554 (5)	0.049 (3)
C106	0.2587 (8)	0.0258 (17)	0.3726 (5)	0.063 (4)
C107	0.2863 (8)	0.1162 (18)	0.4057 (5)	0.067 (4)
C108	0.2472 (9)	0.2951 (18)	0.4146 (5)	0.066 (4)
C109	0.1832 (8)	0.3810 (16)	0.3895 (5)	0.060 (4)
C117	0.3616 (10)	0.028 (2)	0.4321 (5)	0.085 (5)
C118	0.2722 (10)	0.395 (2)	0.4521 (6)	0.089 (5)
C120	0.0551 (10)	0.5639 (15)	0.3343 (5)	0.080 (5)
O212	0.3889 (6)	0.8339 (11)	0.2754 (4)	0.067 (3)
O214	0.2180 (5)	0.3237 (9)	0.2399 (4)	0.063 (3)
N201	0.3026 (6)	0.8554 (10)	0.2194 (4)	0.049 (3)
N203	0.2984 (6)	0.5847 (12)	0.2588 (4)	0.050 (3)
N205	0.1503 (6)	0.5095 (11)	0.1745 (5)	0.051 (3)
N210	0.2168 (6)	0.8716 (10)	0.1605 (4)	0.046 (3)
C24a	0.2094 (7)	0.5904 (13)	0.1980 (5)	0.044 (3)
C25a	0.1218 (7)	0.6039 (14)	0.1424 (5)	0.049 (3)
C29a	0.1549 (7)	0.7911 (13)	0.1338 (5)	0.046 (3)
C202	0.3347 (7)	0.7614 (14)	0.2530 (5)	0.051 (3)
C204	0.2408 (7)	0.4854 (14)	0.2333 (5)	0.051 (3)
C206	0.0568 (8)	0.5222 (16)	0.1161 (5)	0.062 (4)
C207	0.0275 (8)	0.6079 (18)	0.0832 (5)	0.065 (4)
C208	0.0624 (8)	0.7922 (17)	0.0749 (5)	0.062 (4)
C209	0.1256 (7)	0.8787 (15)	0.0994 (5)	0.054 (3)
C210	0.2448 (7)	0.7769 (13)	0.1928 (5)	0.044 (3)
C217	−0.0443 (10)	0.514 (2)	0.0560 (6)	0.098 (6)
C218	0.0283 (10)	0.893 (2)	0.0379 (5)	0.085 (5)
C220	0.2558 (10)	1.0637 (15)	0.1528 (5)	0.074 (5)

Table 2. Selected geometric parameters (Å, °)

				LfHCl		Molecule 1		Molecule 2	
O112—C102	1.219 (17)	O212—C202	1.194 (17)	N01	C02	1.395	1.386		
O114—C104	1.216 (13)	O214—C204	1.213 (12)	N01	C10a	1.361	1.359		
N101—C10a	1.360 (19)	N201—C202	1.400 (19)	N03	C02	1.362	1.382		
N101—C102	1.38 (2)	N201—C210	1.337 (17)	N03	C04	1.369	1.365		
N103—C102	1.371 (13)	N203—C202	1.369 (13)	C4a	C04	1.489	1.483		
N103—C104	1.392 (17)	N203—C204	1.380 (17)	N05	C4a	1.313	1.305		
N105—C4a	1.317 (17)	N205—C24a	1.287 (18)	N05	C5a	1.363	1.356		
N105—C5a	1.340 (19)	N205—C25a	1.34 (2)	N10	C10a	1.341	1.329		
N110—C9a	1.410 (17)	N210—C29a	1.381 (17)	C4a	C10a	1.412	1.422		
N110—C10a	1.318 (19)	N210—C210	1.349 (19)						
N110—C120	1.481 (14)	N210—C220	1.493 (14)						
C4a—C10a	1.418 (14)	C24a—C204	1.48 (2)			Lf	MLf	TMAI	
C4a—C104	1.48 (2)	C24a—C210	1.426 (13)	N01	C02	1.366	1.368	1.373	
C5a—C9a	1.418 (15)	C25a—C29a	1.439 (14)	N01	C10a	1.309	1.303	1.391	
C5a—C106	1.430 (19)	C25a—C206	1.403 (19)	N03	C02	1.394	1.410	1.398	
C9a—C109	1.39 (2)	C29a—C209	1.39 (2)	N03	C04	1.352	1.362	1.382	
C106—C107	1.35 (2)	C206—C207	1.34 (2)	C4a	C04	1.506	1.483	1.474	
C107—C108	1.417 (18)	C207—C208	1.426 (18)	N05	C4a	1.296	1.300	1.313	
C107—C117	1.52 (2)	C207—C217	1.52 (2)	N05	C5a	1.378	1.372	1.358	
C108—C109	1.38 (2)	C208—C209	1.363 (19)	N10	C10a	1.371	1.360	1.304	
C108—C118	1.50 (2)	C208—C218	1.53 (2)	C4a	C10a	1.447	1.446	1.430	
C10a—N101—C102	123.0 (9)	C202—N201—C210	123.4 (9)						
C102—N103—C104	124.8 (12)	C202—N203—C204	126.5 (13)						
C4a—N105—C5a	117.4 (9)	C24a—N205—C25a	118.3 (10)	LfNO ₃					
C9a—N110—C10a	119.8 (9)	C29a—N210—C210	120.9 (9)	C10a	N01	C02	123.3	123.6	
C9a—N110—C120	120.1 (12)	C29a—N210—C220	119.5 (12)	N01	C02	N03	117.5	116.2	
C10a—N110—C120	120.1 (11)	C210—N210—C220	119.5 (11)	C02	N03	C04	124.8	126.3	
N105—C4a—C10a	123.1 (13)	N205—C24a—C204	118.1 (10)	C9a	N10	C10a	119.8	121.0	
N105—C4a—C104	117.9 (10)	N205—C24a—C210	124.1 (14)	N10	C10a	C4a	119.8	117.9	
C10a—C4a—C104	118.9 (12)	C204—C24a—C210	117.7 (12)	C4a	N05	C5a	117.6	118.4	
N105—C5a—C9a	123.0 (12)	N205—C25a—C29a	122.1 (12)						
N105—C5a—C106	119.1 (10)	N205—C25a—C206	120.4 (10)	LfHCl					
C9a—C5a—C106	117.9 (13)	C29a—C25a—C206	117.5 (13)	C10a	N01	C02	122.8	123.3	
N110—C9a—C5a	116.9 (13)	N210—C29a—C25a	116.8 (13)	N01	C02	N03	117.0	116.2	
N110—C9a—C109	122.6 (10)	N210—C29a—C209	123.8 (9)	C02	N03	C04	126.4	126.8	
C5a—C9a—C109	120.5 (12)	C25a—C29a—C209	119.4 (12)	C9a	N10	C10a	119.2	120.0	
N101—C10a—N110	120.5 (9)	O212—C202—N201	121.5 (10)	N10	C10a	C4a	119.2	119.0	
N101—C10a—C4a	119.9 (13)	O212—C202—N203	122.7 (14)	C4a	N05	C5a	116.9	117.8	
N110—C10a—C4a	119.6 (12)	N201—C202—N203	115.9 (11)						
O112—C102—N101	121.5 (10)	O214—C204—N203	121.4 (14)						
O112—C102—N103	120.6 (13)	O214—C204—C24a	123.3 (13)						
N101—C102—N103	117.8 (12)	N203—C204—C24a	115.3 (9)						
O114—C104—N103	120.3 (14)	C25a—C206—C207	123.0 (11)			Lf	MLf	TMAI	
O114—C104—C4a	124.2 (13)	C206—C207—C208	118.6 (13)	C10a	N01	C02	118.1	118.8	123.0
N103—C104—C4a	115.5 (9)	C206—C207—C217	120.9 (12)	N01	C02	N03	120.2	120.5	117.3
C5a—C106—C107	121.4 (11)	C208—C207—C217	120.5 (14)	C02	N03	C04	126.5	124.1	125.6
C106—C107—C108	119.6 (13)	C207—C208—C209	121.0 (14)	C9a	N10	C10a	120.6	121.1	116.7
C106—C107—C117	119.7 (12)	C207—C208—C218	119.2 (12)	N10	C10a	C4a	116.0	116.8	122.7
C108—C107—C117	120.7 (14)	C209—C208—C218	119.8 (12)	C4a	N05	C5a	117.1	117.2	117.3
C107—C108—C109	121.0 (14)	C29a—C209—C208	120.5 (11)						
C107—C108—C118	121.0 (13)	N201—C210—N210	121.4 (9)						
C109—C108—C118	118.0 (12)	N201—C210—C24a	120.9 (13)						
C9a—C109—C108	119.7 (11)	N210—C210—C24a	117.6 (12)						

Table 3. Selected bond lengths and angles in LfNO₃, LfHCl, Lf, MLf and TMAI

The maximum e.s.d.'s are 0.019, 0.006, 0.004 and 0.004 Å and 1.2, 0.9, 0.2 and 0.2° for LfNO₃, LfHCl, MLf and TMAI, respectively. No values are reported for Lf, but they are estimated to be about 0.04 Å and 2.0°.

LfNO ₃		Molecule 1	Molecule 2
N01	C02	1.380	1.400
N01	C10a	1.360	1.337
N03	C02	1.371	1.369
N03	C04	1.392	1.380
C4a	C04	1.480	1.480
N05	C4a	1.317	1.287
N05	C5a	1.340	1.340
N10	C10a	1.318	1.349
C4a	C10a	1.418	1.426

Table 4. Deviations from least-squares planes (Å)

The planes are given by the equation $PX + QY + RZ = S$ with $P = 10.779$ (16), $Q = 2.805$ (17), $R = -17.11$ (4), $S = -3.561$ (14) for molecule 100 and $P = 10.883$ (16), $Q = -2.685$ (17), $R = -17.17$ (4), $S = -2.731$ (14) for molecule 200. All the atoms of the isoalloxazine ring were included in the calculation of these least-squares planes.

N101	0.029 (9)	N201	-0.034 (9)
C102	0.031 (10)	C202	-0.016 (10)
N103	0.010 (9)	N203	-0.029 (9)
C104	-0.069 (10)	C204	0.047 (10)
C4a	-0.040 (10)	C24a	0.035 (10)
C105	-0.006 (9)	C205	0.008 (9)
C5a	0.029 (10)	C25a	-0.004 (11)
C106	0.054 (12)	C206	-0.044 (12)
C107	0.032 (12)	C207	-0.022 (13)
C108	-0.038 (12)	C208	0.002 (11)
C109	-0.055 (12)	C209	0.038 (12)
C9a	0.006 (10)	C29a	0.004 (10)
N110	0.014 (9)	N210	0.014 (9)
C10a	0.011 (10)	C210	0.003 (10)

Table 5. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	D...A	D—H...A
N101—H101...O212 ⁱ	0.883 (8)	2.784 (10)	163.7
N103—H103...O311 ⁱⁱ	1.122 (12)	2.781 (16)	161.6
N201—H201...O112 ⁱⁱⁱ	0.855 (8)	2.794 (10)	169.0
N203—H203...O22	1.060 (12)	2.782 (16)	162.2

Symmetry codes: (i) $x - \frac{1}{2}, \frac{3}{2} - y, z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z$; (iii) $\frac{1}{2} + x, \frac{3}{2} - y, z$.

Since crystals of lumiflavinium nitrate degrade rapidly, the crystal selected for X-ray intensity data collection was sealed in a capillary with mother liquor to prevent degradation. Corrections for background, decay, Lorentz and polarization factors, and absorption effects, were included in the data reduction. The structure was solved by direct methods with the program *SIR92* (Altomare, Casciarano, Giacovazzo & Guagliardi, 1994), and resulted in reliable positions for all the non-H atoms. The initial model was refined with *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Two H atoms could not be located; they belong to two HNO₃ moieties. *PLATON* (Spek, 1990) was used for the generation of the Crystallographic Information File and geometry analysis.

Data collection: CAD-4 *EXPRESS*. Cell refinement: CAD-4 *EXPRESS*. Data reduction: *NRCVAX*.

JW thanks the National Foundation for Scientific Research (FNRS Belgium) for his Research Assistant position. The authors acknowledge IBM Belgium and the Facultes Notre Dame de la Paix for the use of the Namur Scientific Computing Facilities. They are also indebted to Synthelabo Recherche (centre de Rueil-Paris) for preparing lumiflavine.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DU1097). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). **C51**, 1227–1229

(E)-4-Nitrobenzaldehyde Phenylhydrazone

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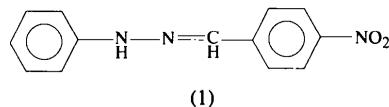
(Received 22 August 1994; accepted 2 November 1994)

Abstract

The title compound, C₁₃H₁₁N₃O₂, is found to be in the *E* conformation and the crystal structure is stabilized by intermolecular N—H...O hydrogen bonds. The dihedral angle between the planes of the phenyl and nitrophenyl rings is 15.55 (9)°.

Comment

In recent years the need to discover organic materials with large quadratic non-linear coefficients, for application in optical signal processing, has been recognized (Chemla & Zyss, 1987). The crystal structure determination of the title compound (1) forms part of our work on the discovery and properties of



non-linear optical organic materials. This compound shows nearly half the second harmonic generating capacity of urea (Mini, 1991). The N—O distances in the nitro group are asymmetrical [N16—O17 1.233 (4) and N16—O18 1.219 (4) Å]. The C6—N7 distance, 1.382 (4) Å, is well below the single-bond distance indicating electron delocalization over the region of the molecule [*cf.* other phenylhydrazone derivatives (Wiley & Drew, 1985) that have different substituents at C9]. The nitro group is tilted by 7.4 (2)° with respect to the plane of the phenyl ring. The structural conformation of the molecule is the *E* isomer, the most common conformation for benzaldehyde derivatives. Presumably, this conformation minimizes steric hindrance between the bulky phenyl and anilino groups lying across the C—N double bond [C9=N8 1.290 (4) Å]. The packing of the molecules in the unit cell is governed by N—H...O hydrogen bonds between N7 and O18 ($-x - 1/2, -y - 1, z + 1/2$) [N7—H7 1.02 (4), N7...O18 3.018 (4), H7...O18 2.00 (4) Å and N7—H7...O18 169 (3)°]. Vickery, Wiley & Drew