Crystal Structure and Chemical Properties of Bis(*N*-picolinylidene-*N'*-salicyloylhydrazinato)nickel(II)

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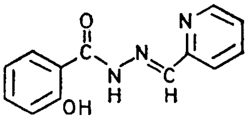
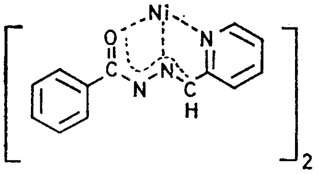
The synthesis, spectral and magnetic properties, and *X*-ray crystal structure of the title complex are described. Crystals are orthorhombic, space group *Aba*2, with unit-cell dimensions: $a = 12{\cdot}61(1)$, $b = 18{\cdot}08(1)$, $c = 10{\cdot}84(1)$ Å, $Z = 4$. The structure was solved from diffractometer data by Patterson and Fourier methods and refined by least-squares techniques to R 3·5% for 1112 independent reflections. It consists of complex molecules in which the nickel atom is octahedrally co-ordinated by two ligand anions related by a two-fold axis. These anions act as terdentate ligands through a hydrazide nitrogen [Ni–N 1·991(3) Å], the pyridine nitrogen [Ni–N 2·132(4) Å], and the hydrazide oxygen [Ni–O 2·086(3) Å].

THE organic molecules containing the ·N:C·C:N· chromophore form an interesting class of ligands which have received attention in metal complex chemistry for their chelating properties.[1] In continuing the research on complexes formed by these ligands, the salicyloylhydrazone of picolinaldehyde (Hsip) has been considered, interest in this molecule being connected with the presence of other donor atoms as well as the nitrogen of the mentioned chromophore. We describe the synthesis and properties of the ligand Hsip (I) and of (II), its nickel(II) complex [Ni(sip)$_2$], in which the ligand is in the deprotonated form. We also describe the results of a crystal structure analysis of the complex which shows that the deprotonated ligand exhibits three chelating points (the oxygen atom of the hydrazide group and the nitrogen atoms of the ·N:C·C:N· chromophore) and a conformation suitable for octahedral co-ordination to the metal.



(I)



(II)

EXPERIMENTAL

Preparation of (I) N-*Picolinylidene*-N'-*salicyloylhydrazine*. —The compound was prepared by heating 1 : 1 molar ratios of salicyl hydrazide and pyridine-2-carbaldehyde under reflux in ethanol for 20 min. The yellow microcrystalline *product* obtained on cooling was recrystallized from hot ethanol, m.p. 220 °C (Found: C, 64·9; H, 4·8; N, 17·4. $C_{13}H_{11}N_3O_2$ requires C, 64·7; H, 4·6; N, 17·4%).

Preparation of (II) *Bis*(N-*picolinylidene*-N'-*salicyloylhydrazinato*)*nickel*(II).—(I) and Ni(AcO)$_2$,4H$_2$O (2 : 1 molar ratio) were heated under reflux in ethanol for 1 h. After 2 days *red-brown crystals* of the compound were obtained by slow evaporation of the solvent at room temperature. There were two types of crystal, monoclinic and orthorhombic, but these gave the same chemical analysis (Found, orthorhombic: C, 57·6; H, 4·2; N, 15·1; Ni,

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[1] L. F. Lindoy and S. E. Livingstone, *Co-ordination Chem. Rev.*, 1967, 2, 173.

10·6; monoclinic: C, 57·8; H, 3·8; N, 15·2; Ni, 10·8. $C_{26}H_{20}N_6NiO_4$ requires C, 57·9; H, 3·7; N, 15·6; Ni, 10·9%) and a very similar i.r. spectrum. It was thus concluded that the compound is dimorphous and the orthorhombic crystals were chosen for the subsequent *X*-ray analysis, since the monoclinic ones were all twinned. Crystals were red-brown bipyramids, elongated along *c*.

Physical Measurements.—The i.r. spectra (4000—250 cm^{-1}; KBr disks) were run on a Perkin-Elmer 457 instrnment. The electronic spectrum (190—850 nm) was recorded for an aqueous solution on a Perkin-Elmer 402 spectrophotometer. Magnetic susceptibility was measured by the Gouy method on a Newport instrument. Crystal data were determined from preliminary Weissenberg and rotation photographs, and accurate unit-cell parameters determined from diffractometer measurements.

TABLE 1

Final fractional atomic co-ordinates ($\times 10^4$ for non-hydrogen atoms and $\times 10^3$ for hydrogen atoms) and temperature factors,* with estimated standard deviations in parentheses

	x/*a*	*y*/*b*	*z*/*c*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0	0	0	1·98(2)	3·20(2)	2·76(2)	0·04(3)	0(0)	0(0)
O(1)	−151(2)	−825(2)	1334(3)	2·26(11)	4·05(13)	3·52(12)	0·33(9)	0·20(10)	0·70(11)
O(2)	2784(2)	−1676(2)	2503(4)	2·49(13)	7·00(18)	6·39(18)	0·15(11)	−0·15(16)	2·36(18)
N(1)	796(3)	576(2)	−1445(3)	3·20(14)	3·23(15)	3·62(17)	−0·15(12)	0·17(14)	−0·09(14)
N(2)	1450(2)	−434(2)	82(4)	2·30(10)	3·25(12)	3·16(14)	0·12(9)	0·33(15)	−0·34(17)
N(3)	1650(2)	−953(2)	964(3)	2·28(13)	4·15(16)	3·67(17)	0·34(12)	0·01(13)	0·46(14)
C(1)	420(4)	1035(3)	−2272(5)	4·21(19)	4·42(21)	4·27(23)	−0·24(18)	−0·29(18)	0·71(20)
C(2)	1023(5)	1311(3)	−3232(5)	6·49(29)	5·09(25)	4·78(27)	−0·22(23)	0·31(23)	1·89(23)
C(3)	2075(4)	1112(3)	−3322(5)	6·80(29)	5·39(26)	4·04(23)	−1·16(22)	1·76(22)	0·37(22)
C(4)	2487(6)	624(2)	−2465(7)	4·23(17)	4·37(18)	5·11(20)	−0·85(27)	1·17(18)	−0·39(31)
C(5)	1830(3)	364(2)	−1545(4)	3·37(16)	3·13(17)	3·44(19)	−0·53(15)	0·47(16)	−0·40(16)
C(6)	2170(3)	−188(2)	−642(4)	2·44(14)	3·95(21)	4·51(21)	0·08(13)	0·69(15)	−0·58(17)
C(7)	738(3)	−1107(2)	1569(4)	2·64(14)	3·24(17)	2·95(16)	0·07(13)	−0·12(14)	−0·37(15)
C(8)	855(3)	−1642(2)	2604(4)	2·64(15)	3·11(17)	3·70(19)	0·13(13)	−0·36(15)	0·02(16)
C(9)	1865(3)	−1888(3)	3037(5)	2·76(16)	4·10(20)	4·35(22)	−0·26(15)	−0·50(16)	0·83(18)
C(10)	1902(4)	−2342(3)	4063(5)	3·41(19)	6·01(29)	5·29(25)	0·33(18)	−0·95(19)	1·56(23)
C(11)	1000(4)	−2592(3)	4643(4)	4·69(21)	4·89(23)	4·21(23)	0·45(19)	−0·19(18)	1·38(19)
C(12)	16(4)	−2392(3)	4190(4)	3·74(16)	4·81(22)	4·32(19)	0·49(19)	0·63(24)	0·64(18)
C(13)	−43(4)	−1918(2)	3197(4)	2·78(14)	4·44(19)	3·82(17)	0·51(19)	−0·03(19)	0·40(16)
				B/Å^2					
H(1)	261(5)	−143(3)	190(5)	8·45(1·44)					
H(2)	−24(3)	116(2)	−211(4)	5·34(1·12)					
H(3)	73(3)	160(2)	−375(4)	5·06(1·07)					
H(4)	243(4)	120(2)	−412(4)	5·30(1·00)					
H(5)	321(3)	42(2)	−242(5)	5·69(1·13)					
H(6)	294(3)	−36(2)	−59(4)	5·61(1·18)					
H(7)	255(4)	−243(2)	439(4)	6·69(1·15)					
H(8)	105(3)	−295(2)	543(4)	4·01(1·03)					
H(9)	−61(3)	−275(2)	459(4)	7·24(1·38)					
H(10)	−71(3)	−182(2)	276(4)	5·26(1·13)					

* Anisotropic thermal parameters are in the form: exp $-0{\cdot}25(h^2\beta_{11}a^{*2} + \ldots + 2kl\beta_{23}b^*c^*)$.

Crystal Data.—[$Ni(C_{13}H_{10}N_3O_2)_2$], $M = 539{\cdot}2$, Orthorhombic, $a = 12{\cdot}61(1)$, $b = 18{\cdot}08(1)$, $c = 10{\cdot}84(1)$ Å, $U = 2471$ Å^3, $D_m = 1{\cdot}50$ g cm^{-3}, $Z = 4$, $D_c = 1{\cdot}47$ g cm^{-3}, $F(000) = 1112$, λ(Mo-K_α) = 0·7107 Å; μ(Mo-K_α) = 8·33 cm^{-1}. Space group *Aba*2 (from the presence of piezoelectric effect and from the crystal structure).

Crystallographic Measurements.—Intensity data were measured on an on-line AED Siemens diffractometer by use of zirconium-filtered Mo radiation. 1735 Independent reflections with $2\theta \leqslant 58°$ were scanned in the θ—2θ mode, a standard check reflection being measured every 20 reflections; 623 reflections having $I < 2\sigma(I)$ were considered unobserved. After Lorentz and polarization corrections, the absolute scale was determined, first by Wilson's method and then by comparison of the observed and calculated structure amplitudes.

Structure Analysis.—The structure was determined by the heavy-atom technique starting from a three-dimensional Patterson calculation, and refined with isotropic and anisotropic least-squares to *R* 0·055. The contributions of the hydrogen atoms, located on a difference map and refined isotropically, improved *R* to 0·035.

Scattering factors used throughout the calculations were those of ref. 2 for non-hydrogen atoms and of ref. 3 for hydrogen atoms. Final positional and thermal parameters with their estimated standard deviations are given in Table 1. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21164 (8 pp., 1 microfiche).*

All calculations were performed on a CDC 6600 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (Bologna), with programs of Immirzi.[4]

RESULTS AND DISCUSSION

I.r. Spectra.—Table 2 lists the main vibrational bands of (I) and (II), with their assignments. The vibrations which are of interest in the spectrum of the free ligand are those of the -CONH- and -OH groups, and of the two aromatic rings.

The i.r. spectrum of (II) differs significantly from that of the unco-ordinated molecule. In particular no ν(N–H) band appears in the 3000 cm^{-1} region, as a consequence of deprotonation of the CONH system.

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[2] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[3] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[4] A. Immirzi, *Ricerca Sci.*, 1967, **37**, 743.

TABLE 2

Selected i.r. bands of (I) and of the orthorhombic phase of (II)

(I)	(II)	Assignment
3240m		ν(N–H)
3040br, w	3060w	ν(C–H)
2940w	2920w	ν(C–H)
2850—2500w	2900—2500w	ν(O–H)
1660sh	1620sh	amide (1), Phenyl
1630vs	1600vs	
1610sh, m	1590sh	Phenyl
1585sh	1560m	
1545s		Amide (2), ν(C:N)
	1510s	ν(C:N)
1495w	1490s	Phenyl
1465m	1468s	Phenyl
1453m	1453sh	Phenyl
1433m		Phenyl
925m	925m	ν(N–N)
855w	865w	

m = medium, br = broad, w = weak, s = strong, sh = shoulder, vs = very strong.

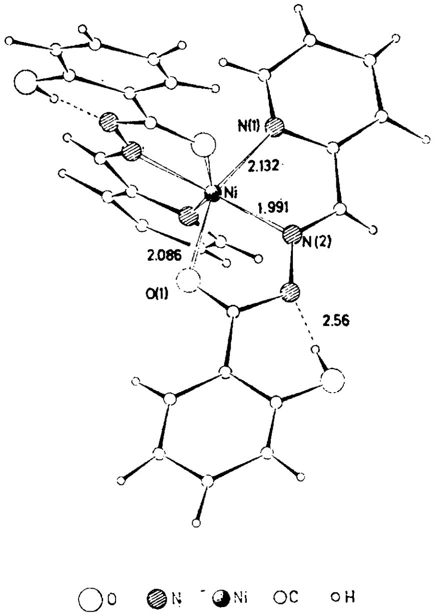

FIGURE 1 Projection of the structure on (001)

The shift of the carbonyl stretching mode to lower frequencies is in accord with co-ordination through oxygen, but the expected shifts of the pyridine bands, indicating co-ordination of the nitrogen atom, is less evident, since the 1600—1400 cm^{-1} region is complicated by the presence of two non-equivalent aromatic rings.

Electronic Spectra.—In the u.v. region there are two intense bands. The first, at 285 nm, can be assigned to a n–π^* transition in the ligand, while that at 377 nm is due to metal–ligand charge transfer. Two bands present in the visible region, at 394 and 850 nm, can be assigned to the $^3T_{1g}\leftarrow{}^3A_{2g}$ and $^3T_{1g}(P)\rightarrow{}^3A_{2g}$ transitions for an octahedral environment.

Magnetic Properties.—The effective magnetic moment (3·03 μ_B) derived from the corrected molar susceptibility χ_M by use of the expression, $\mu_{eff} = 2{\cdot}83\sqrt{\chi_M T}\ \mu_B$, is within the range of the values (3·0—3·3 μ_B) usually found for six-co-ordinated nickel(II) complexes.

X-*Ray Structure*.—Two ligand ions, related by a two-fold axis parallel to [001] through the nickel, are co-ordinated to it in a distorted octahedral environment involving O(1) and N(2) from the hydrazide group and the pyridine nitrogen N(1) (Figure 1). The ligand is therefore terdentate and forms two penta-atomic chelation rings. These rings are planar and lie nearly in the same plane, the dihedral angle they form being only 175·3°. The co-ordination distance involving oxygen (Table 3) is in the middle of the range (1·96—2·32 Å) of accepted values for Ni–O in octahedral Ni^{II} complexes; the Ni–N distances are similarly as expected, that involving the hydrazide N being significantly shorter than that involving the pyridine N. This fact can be explained by assuming that the negative charge due to the loss of the proton, originally bound to N(3), is partially localized on N(2).

The conformation of the ligand anion can best be

TABLE 3

Bond distances (Å) and angles (°)

(*a*) Co-ordination polyhedron			
Ni–O(1)	2·086(3)	Ni–N(1)	2·132(4)
Ni–N(2)	1·991(3)		
O(1)–Ni–N(1)	154·4(1)	O(1)–Ni–N(2)	76·8(1)
N(1)–Ni–N(2)	78·1(2)	O(1)–Ni–N(1^{I})	96·7(2)
O(1)–Ni–N(2^{I})	103·2(2)	N(1)–Ni–N(2^{I})	101·9(2)
O(1)–Ni–O(1^{I})	92·2(2)	N(1)–Ni–N(1^{I})	85·4(2)
N(2)–Ni–N(2^{I})	175·1(2)		
(*b*) Chelation rings and ligand			
N(1)–C(1)	1·311(6)	N(1)–C(5)	1·363(5)
C(1)–C(2)	1·382(7)	C(2)–C(3)	1·378(8)
C(3)–C(4)	1·383(8)	C(4)–C(5)	1·379(8)
C(5)–C(6)	1·462(6)	C(6)–N(2)	1·280(6)
N(2)–N(3)	1·363(5)	N(3)–C(7)	1·353(5)
C(7)–O(1)	1·257(5)	C(7)–C(8)	1·489(6)
C(8)–C(9)	1·428(6)	C(8)–C(13)	1·394(6)
C(9)–O(2)	1·351(5)	C(9)–C(10)	1·383(7)
C(10)–C(11)	1·376(7)	C(11)–C(12)	1·382(7)
C(12)–C(13)	1·378(6)		
Ni–N(1)–C(1)	129·9(3)	Ni–N(1)–C(5)	111·8(3)
C(1)–N(1)–C(5)	118·1(4)	N(1)–C(1)–C(2)	123·0(4)
C(1)–C(2)–C(3)	119·2(5)	C(2)–C(3)–C(4)	118·7(5)
C(3)–C(4)–C(5)	118·6(6)	C(4)–C(5)–N(1)	122·4(4)
C(4)–C(5)–C(6)	122·7(4)	C(6)–C(5)–N(1)	114·8(4)
C(5)–C(6)–N(2)	116·1(4)	C(6)–N(2)–Ni	119·1(3)
C(6)–N(2)–N(3)	122·6(3)	N(3)–N(2)–Ni	118·2(3)
N(2)–N(3)–C(7)	108·9(3)	N(3)–C(7)–O(1)	125·2(4)
N(3)–C(7)–C(8)	114·5(3)	O(1)–C(7)–C(8)	120·3(3)
C(7)–O(1)–Ni	110·4(2)	C(7)–C(8)–C(9)	122·6(4)
C(7)–C(8)–C(13)	120·4(4)	C(9)–C(8)–C(13)	117·4(4)
C(8)–C(9)–O(2)	122·4(4)	C(10)–C(9)–O(2)	119·0(4)
C(8)–C(9)–C(10)	118·6(4)	C(9)–C(10)–C(11)	122·3(4)
C(10)–C(11)–C(12)	119·6(5)	C(11)–C(12)–C(13)	119·3(5)
C(12)–C(13)–C(8)	122·6(4)		
(*c*) Involving H atoms			
O(2)–H(1)	0·82(5)	C(1)–H(2)	0·88(4)
C(2)–H(3)	0·84(4)	C(3)–H(4)	0·99(5)
C(4)–H(5)	0·99(4)	C(6)–H(6)	1·02(4)
C(10)–H(7)	0·91(5)	C(11)–H(8)	1·07(4)
C(12)–H(9)	1·12(5)	C(13)–H(10)	0·97(4)
C(9)–O(2)–H(1)	105(3)	O(2)–H(1)–N(3)	153(3)
N(1)–C(1)–H(2)	112(3)	C(2)–C(1)–H(2)	125(3)
C(1)–C(2)–H(3)	119(3)	C(3)–C(2)–H(3)	122(3)
C(2)–C(3)–H(4)	117(3)	C(4)–C(3)–H(4)	121(3)
C(3)–C(4)–H(5)	128(3)	C(5)–C(4)–H(5)	114(3)
C(5)–C(6)–H(6)	122(2)	N(2)–C(6)–H(6)	122(2)
C(9)–C(10)–H(7)	117(3)	C(11)–C(10)–H(7)	121(3)
C(10)–C(11)–H(8)	121(2)	C(12)–C(11)–H(8)	120(2)
C(11)–C(12)–H(9)	110(2)	C(13)–C(12)–H(9)	129(2)
C(12)–C(13)–H(10)	122(3)	C(8)–C(13)–H(10)	114(3)

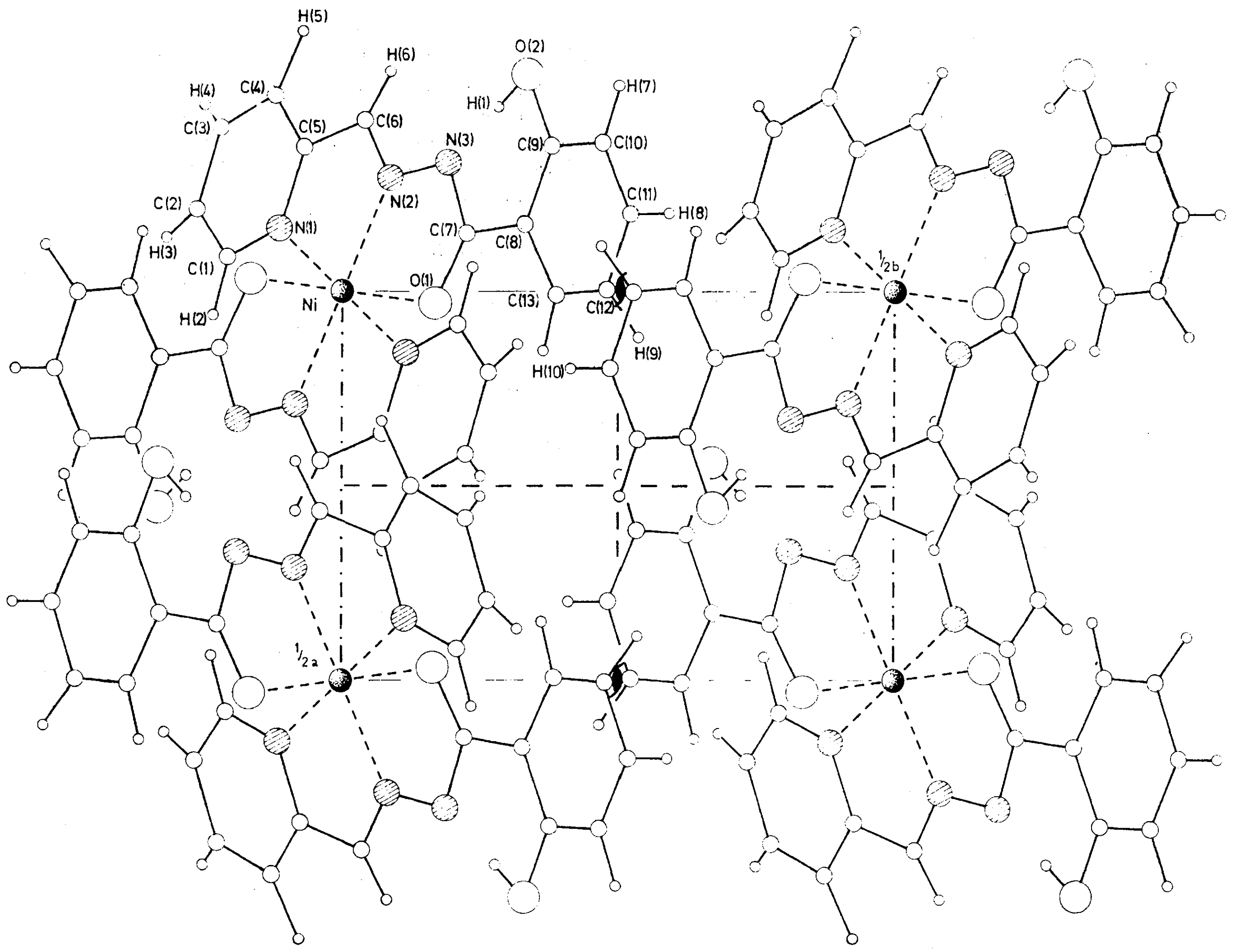

FIGURE 2 Clinographic projection of the structure

described by considering it to consist of three planes (Table 4): (1) the benzene ring, (2) the pyridine ring, and (3) the system C(6),N(2),N(3),C(7),O(1) which bridges the two aromatic moieties. All C–C distances in these two rings are in the range 1·376—1·394 Å, except C(8)–C(9), between the substituted carbon atoms in the benzene ring, which is significantly longer. The two N–C distances in the pyridine ring are significantly different, the longer being that between nitrogen and the substituted carbon atom.

TABLE 4

Deviations (Å) of atoms from planes, in the ligand

Plane (1): N(1), C(1)—(5)
N(1) −0·005, C(1) −0·003, C(2) 0·009, C(3) −0·008, C(4) −0·001, C(5) 0·007
Plane (2): C(8)—(13)
C(8) −0·018, C(9) 0·025, C(10) −0·008, C(11) −0·017, C(12) 0·018, C(13) 0·001
Plane (3): C(6), N(2), N(3), C(7), O(1)
C(6) 0·007, N(2) −0·009, N(3) 0·004, C(7) 0·004, O(1) 0·003

Bond distances and angles in plane (3) indicate sp^2 character for C(6), N(2), and C(7), and π delocalization along the system with a tendency to a localization of the double bonds between C(6) and N(2) (1·280, calc. 1·265 Å) and between C(7) and O(1) (1·257, calc. 1·17 Å). The two distances C(5)–C(6) [1·462(6) Å] and C(7)–C(8) [1·489(6) Å] are as expected for a single bond between two sp^2 hybridized carbon atoms, in agreement with the incomplete coplanarity of the aromatic groups with the central chain.

The hydroxy-group is involved in a strong intramolecular hydrogen bond [O(2)–H(1) · · · N(3) 2·557(5) Å, 152·9°] which is favoured both by the orientation of the hydroxy-group and by the presence of partial negative charge on N(3).

Packing (Figure 2) is determined by normal van der Waals contacts. Those <3·6 Å are listed in Table 5.

TABLE 5

Non-bonded distance (Å) <3·6Å

$O(1) \cdots C(4^{II})$	3·27(1)	$O(1) \cdots C(3^{II})$	3·55(1)
$O(1) \cdots C(11^{III})$	3·56(1)	$O(2) \cdots C(1^{II})$	3·53(1)
$O(2) \cdots C(6^{V})$	3·46(1)	$N(1) \cdots C(11^{IV})$	3·52(1)
$N(3) \cdots C(4^{V})$	3·49(1)		

Roman numerals as subscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I $\bar{x}, \bar{y}, z$
II $\frac{1}{2} + x, \bar{y}, \frac{1}{2} + z$
III $\bar{x}, \frac{1}{2} - y, \frac{1}{2} + z$
IV $x, \frac{1}{2} + y, \frac{1}{2} + z$
V $\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$

[4/1078 *Received*, 3*rd June*, 1974]