Bond lengths and valence angles of the heterocycle are in the range of values found in pyridine rings (Van Havere, Lenstra, Geise, Van den Berg & Benschop, 1982) with N—C values of 1·32 (1) and 1·35 (1) Å. The exocyclic C—N bond of 1·43 (1) Å compares well with the corresponding value of 1·42 (1) Å in the molecule of salampy. The C—CH$_3$ distances in the substituted pyridine have values of 1·49 (1) and 1·50 (1) Å in agreement with the sp^2–sp^3 character of this bond.

The phenyl ring in saladimpy is planar [$\chi^2 = \sum(\Delta/\sigma)^2 = 0.2$] as for salampy, and the exocyclic C(7) lies in this plane [deviation 0·006 (7) Å]. The pyridine ring is also planar ($\chi^2 = 5.0$). The maximum deviation from the plane corresponds to C(9) at −0·008 (6) Å. The two substituents omitted from the calculations of the least-squares plane are out of it by 0·015 (9) and 0·027 (8) Å respectively. The hydrogen-bonded ring C(1),C(2),C(7),O,N(1) deviates markedly from planarity with $\chi^2 = 39.4$ ($\chi^2 = 12.0$ for salampy). The mean planes of the phenyl ring and the hydrogen-bonded ring are coplanar [dihedral angle 1·0 (9)°], while the pyridine ring and the phenyl ring form an angle of 5·4 (9)°. This angle for salampy is 9·4 (9)°.

The tilting and folding of the molecule are revealed by the calculated torsion angles C(9)—C(8)—N(1)—C(7) = 171·5 (6), N(2)—C(8)—N(1)—C(7) = −8·1 (9) and C(1)—C(7)—N(1)—C(8) = −179·6 (6)°. The first two values indicate a rotation of the pyridine ring about the N(1)—C(8) bond by approximately 8° with respect to the rest of the molecule. The last value measures the folding of the molecule about the N(1)—C(7) bond, which is not significant in this case. The molecule of salampy is tilted by approximately 12° about N(1)—C(8) and folded by 178·0 (8)°. The crystal packing is effected only by van der Waals forces.

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Low-Temperature (163 K) Structure of 1,8-Naphthyridine, C$_8$H$_6$N$_2$

BY P. DAPPORTO, C. A. GHILARDI, C. MEALLI, A. ORLANDINI AND S. PACINOTTI

Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR, Via F. D. Guerrazzi 27, 50132 Firenze, Italy

Abstract. $M_r = 130.15$, monoclinic, $P2_1/c$, $a = 6.135$ (6), $b = 10.407$ (8), $c = 11.258$ (9) Å, $\beta = 117.76$ (4)°, $V = 636.1$ (10) Å^3, $Z = 4$, $D_x = 1.359$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.79$ cm^{-1}, $F(000) = 272$, $T = 163$ K. The crystal structure of 1,8-naphthyridine has been re-examined at low temperature (163 K) with the hope of obtaining more reliable information about the observed distortions of the molecule from planarity. A deformation density map has been calculated by opportunely selecting the Fourier coefficients. Full-matrix least-squares refinement converged at R and R_w of 0.049 and 0.053, respectively, for 1275 observed reflections [$I \geq 3\sigma(I)$]. The non-equivalence of the two condensed rings in

terms of out-of-plane displacements rules out the hypothesis that the 1,8-naphthyridine distorts only on account of an inner electronic repulsion between nitrogen lone pairs. The examination of the contact distances between adjacent molecules in the crystal lattice shows that the environment about the two nitrogen atoms is not equivalent.

Introduction. This laboratory has been interested for a long time in the coordination chemistry of the molecule 1,8-naphthyridine (NN) (Gatteschi, Mealli & Sacconi, 1973; Sacconi, Mealli & Gatteschi, 1974; Gatteschi, Mealli & Sacconi, 1976; Mealli & Sacconi, 1977). As did other authors, we noticed that the geometry of the ligand NN in most cases is not rigorously planar. The displacements of single atoms from the condensed-ring plane can be as large as 0·045 Å (Clearfield, Sims & Singh, 1972). The hypothesis that there is an electronic repulsion between the nitrogen lone pairs is widely accepted. This is based on the fact that the largest deviations from planarity are found in the unco-ordinated NN molecule itself. When NN is co-ordinated, the repulsion between the lone pairs should be reduced thus leading to an increased planarity of the ring. Enwall & Emerson (1979) argued that, if this is true, a correlation should be found between the mode of coordination and the degree of distortion of NN; actually this is not the case and in some complexes the deviations are of the same order as those found in the structure of the uncoordinated molecule. The data of the latter structure collected at room temperature seem accurate enough to establish that the deformation from planarity is real. On the other hand, the geometry must be known with a high degree of certainty if a reasonable dissertation on the true origin of the distortion is to be made.

We have therefore collected and elaborated a set of X-ray data at 163 K with the aim of obtaining precise structural details on NN, hopefully including a view of the nitrogen lone pairs from a calculated electron density map.

Part of this work has already been presented (Dapporto, Ghilardi, Mealli, Orlandini & Zanobini, 1980).

Experimental. White parallelepiped crystal, 0·10 × 0·20 × 0·60 mm, delimited by the (100), (010) and (001) and their centrosymmetric faces, Philips PW 1100 automatic four-circle diffractometer, Leybold–Hereaeus cryostat (liquid nitrogen), graphite monochromated Mo $K\alpha$ radiation, unit-cell parameters from least-squares fit of 25 reflections with $11\cdot0 \le 2\theta \le 36\cdot4°$. There is no phase transition on cooling, the volume changes from 656·3 (11) Å^3 at room temperature to 636·1 (10) Å^3 at 163 K, while the values of the calculated density are 1·317 and

Table 1. *Positional* ($\times 10^4$) *and thermal* (Å$^2 \times 10^3$) *parameters*

	x	y	z	U_{eq} or U
N(1)	3228 (2)	4512 (1)	2064 (1)	24 (1)
N(8)	2755 (3)	2680 (1)	806 (1)	27 (1)
C(2)	2250 (3)	5416 (2)	2479 (2)	25 (1)
C(3)	−265 (3)	5471 (2)	2164 (2)	27 (1)
C(4)	−1826 (3)	4553 (2)	1354 (2)	25 (1)
C(5)	−2363 (3)	2626 (2)	−75 (2)	24 (1)
C(6)	−1284 (4)	1745 (2)	−524 (2)	27 (1)
C(7)	1288 (3)	1810 (2)	−40 (2)	30 (1)
C(41)	−889 (3)	3584 (2)	836 (1)	19 (1)
C(81)	1680 (3)	3586 (2)	1237 (2)	20 (1)
H(2)	3313 (40)	6065 (21)	3024 (21)	32 (6)
H(3)	−863 (43)	6157 (23)	2533 (22)	41 (6)
H(4)	−3581 (41)	4547 (21)	1143 (21)	34 (6)
H(5)	−4137 (40)	2603 (21)	−334 (21)	38 (6)
H(6)	−2165 (39)	1117 (20)	−1149 (20)	28 (5)
H(7)	2060 (39)	1212 (20)	−322 (20)	28 (5)

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

1·359 g cm^{-3} at room and low temperature, respectively. Reflections collected within $2\theta \le 70°$, ω–2θ scan, variable scan range equal to $A + B\tan\theta$ (Alexander & Smith, 1964), $A = 0\cdot8°$ and $B = 0\cdot69$, scan speed $0\cdot05°s^{-1}$ in θ, background measurements taken on each side of the peak for a time equal to half the scan time. 3 standard reflections ($1\overline{3}5$, 222, $\overline{2}58$) recorded every 100 min, slow loss of intensity, reaching 7% by the end and intensities were rescaled. 2 symmetry-related sets of intensity data (hkl and $h\overline{k}l$) collected to improve the accuracy of the experiment, $-9 \le h \le 8$, $-15 \le k \le 15$, $0 \le l \le 16$, standard deviations of intensities calculated (Corfield, Doedens & Ibers, 1967) using 0·03 for instability factor p, intensities corrected for Lorentz–polarization and absorption, transmission factors 0·99–0·98, 2 symmetry-related sets averaged, $R_{int} = 0\cdot035$; 1460 reflections measured, 1275 independent having $I \ge 3\sigma(I)$ considered observed and used in the calculations, scattering factors for non-hydrogen atoms in the neutral state from *International Tables for X-ray Crystallography* (1974), for hydrogen atoms from Stewart, Davidson & Simpson (1965), anomalous dispersion corrections, real and imaginary parts, applied in the F_c calculations (*International Tables for X-ray Crystallography*, 1974), all calculations performed using *SHELX*76 (Sheldrick, 1976) and locally written programs on a SEL 32/70 computer installed in our Institute; refinement of structure using final parameters of room-temperature structure, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/\sigma^2(F_o)$, all non-hydrogen atoms anisotropic, hydrogen atoms introduced in calculated positions and fully refined, isotropic extinction, g refined to $0\cdot013 \times 10^{-4}$ $[F_{corr} = F(1 - gI_{corr})]$, rigid-body thermal-motion correction applied, but unnecessary, effect of this correction resulting within one e.s.d.; final $R = 0\cdot049$ and $R_w = 0\cdot053$, $S = 1\cdot26$, max. $\Delta/\sigma = 0\cdot05$. Data of the subset consisting of 769 reflections with

Table 2. *Bond distances* (Å), *bond angles* (°) *and displacements from the least-squares plane* (Å) *through all the non-hydrogen atoms*

	Low temperature	Room temperature*
N(1)–C(2)	1·314 (2)	1·313 (4)
C(2)–C(3)	1·414 (3)	1·395 (5)
C(3)–C(4)	1·360 (3)	1·350 (5)
C(4)–C(41)	1·415 (2)	1·409 (4)
C(41)–C(81)	1·423 (2)	1·418 (4)
C(41)–C(5)	1·414 (2)	1·413 (3)
C(5)–C(6)	1·359 (3)	1·357 (4)
C(6)–C(7)	1·410 (3)	1·400 (5)
C(7)–N(8)	1·319 (2)	1·314 (3)
N(8)–C(81)	1·364 (2)	1·362 (3)
C(81)–N(1)	1·368 (2)	1·369 (3)
C(2)–N(1)–C(81)	117·3 (1)	116·7 (2)
N(1)–C(2)–C(3)	124·5 (2)	125·2 (3)
C(2)–C(3)–C(4)	119·0 (2)	118·8 (3)
C(3)–C(4)–C(41)	118·9 (2)	119·3 (2)
C(4)–C(41)–C(81)	118·1 (2)	117·8 (2)
C(81)–C(41)–C(5)	118·1 (1)	117·5 (2)
C(4)–C(41)–C(5)	123·8 (2)	124·7 (2)
C(41)–C(5)–C(6)	119·2 (2)	119·4 (2)
C(5)–C(6)–C(7)	118·3 (2)	118·6 (3)
C(6)–C(7)–N(8)	125·2 (2)	125·0 (3)
C(7)–N(8)–C(81)	116·8 (1)	116·9 (2)
N(8)–C(81)–C(41)	122·2 (1)	122·6 (2)
C(41)–C(81)–N(1)	122·2 (1)	122·1 (2)
N(1)–C(81)–N(8)	115·6 (1)	115·3 (2)
N(1)	0·008 (2)	0·010
C(2)	0·043 (2)	0·041
C(3)	0·007 (2)	0·008
C(4)	−0·036 (2)	−0·034
C(41)	−0·022 (2)	−0·022
C(81)	−0·023 (2)	−0·016
C(5)	0·014 (2)	0·017
C(6)	0·039 (2)	0·045
C(7)	0·001 (2)	0·001
N(8)	−0·031 (2)	−0·025

* Clearfield *et al.* (1972); e.s.d. range for the displacements is 0·0020–0·0026 Å.

$\sin\theta/\lambda \le 0.595$ Å^{-1} were used in calculation of deformation density maps, computed with the coefficients $\Delta F = F_o - F_{c,\text{high order}}$. Structure model used in the calculation of $F_{c,\text{high order}}$ consists of N, C and H parameters obtained from refinement performed using F_o having $\sin\theta/\lambda \ge 0.481$ Å^{-1} (781 reflections). Scale factor was refined using subset of data with $\sin\theta/\lambda \le 0.595$ Å^{-1} and high-order structure model. Table 1 lists atomic parameters.*

Discussion. The present low-temperature investigation of NN confirms the results already reported by Clearfield *et al.* (1972) about the structural parameters and the displacements of the single atoms out of the ring plane. However, the somewhat lower

standard deviations and the fact that a reasonable map of the residual electron density could be calculated verify the reality of the out-of-plane deformation. In effect, this point deserves additional comments. Table 2 shows selected geometrical parameters of NN obtained from this study and that at room temperature. The calculated electron density map is shown in Fig. 1. The prominent peaks correspond to electron accumulation in the middle of the bonds (height in the range 0·2–0·6 e Å^{-3}) and in the region external to the condensed rings near the nitrogen atoms. The latter peaks at *ca* 0·7 Å from the nitrogen atoms have electron densities of about 0·3 e Å^{-3} and can be identified with the chemist's useful construct of lone pairs in spite of their relatively low charge density. We would like to comment on the directionality of these lone pairs since the peaks seem to converge toward each other. There is also a trend for the lone pairs to be displaced out of the ring plane in a direction opposite to that of the corresponding nitrogen atom. However, the broadness and the weakness of the peaks do not allow us to emphasize these results. On the other hand, the displacements of the non-hydrogen atoms from the NN least-squares plane are reliable. By taking these into account the C_{2v} symmetry of the planar molecule is completely lost. The symmetry descends directly to C_1, neither the mirror plane nor the twofold axis being saved. The observation already made (Clearfield, Sims & Singh, 1972; Enwall & Emerson, 1979) that the two nitrogen atoms are displaced in opposite directions holds qualitatively but the absolute displacement of N(8) is four times that of N(1). This is sufficient to rule out the deformation of the ring as due *only* to inner electronic repulsion between the nitrogen lone pairs. Whatever the electronic origin of the distortion, the equivalence of the two condensed rings should be preserved.
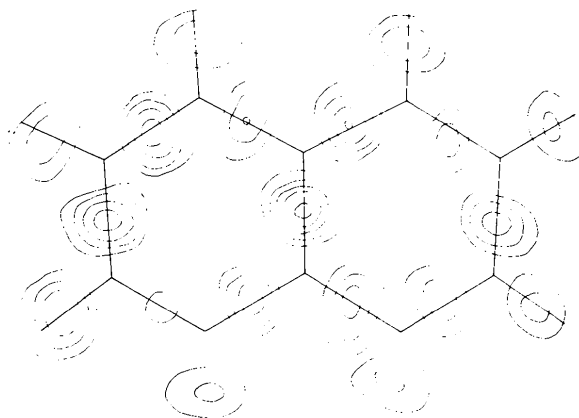

Fig. 1. Deformation density map. Contour lines are drawn at each 0·1 e Å^{-3} starting from 0·12 e Å^{-3}.

On the other hand, packing effects seem to be operative for the loss of the C_{2v} symmetry. Thus, we suggest that the crystal packing forces are mainly responsible for distortion from planarity. No contact between adjacent molecules is much shorter than the sum of the van der Waals radii; however, as already emphasized (Kitaigorodskii, 1973; Murray-Rust, 1978), long contacts with specific directional properties can play an important role. Fig. 2 shows the surroundings of an NN molecule. These are clearly asymmetric with respect to the two condensed rings and possibly this is where the asymmetry of the out-of-plane deformations comes from. It is noteworthy that there are no contacts shorter than 2·9 Å about the H(3) and H(7) atoms nor about the C(3) and C(7) atoms bonded to them. All of these atoms practically lie in the least-squares plane. On the other hand, atoms C(2), C(4), C(5) and C(6) and the hydrogen atoms linked to them are most involved in short contacts with the nitrogen atoms.

Focusing our attention at N(1) and N(8), we see (Fig. 2) that the former atom has two contacts of 2·68 (2) and 2·61 (3) Å, respectively, with H(6^i) and H(4^{ii}) of two different molecules, approaching from opposite sides. On the other hand, there are three hydrogen atoms at distances in the range 2·72 (2)– 2·86 (2) Å from N(8). Two of these, H(4^{ii}) and H(5^{ii}), lie on one side of the reference molecule, while the third one H(2^{iii}) is on the opposite side (all the displacements from the NN plane are of the order of 1·30–1·50 Å). The H(4^{ii}) hydrogen atom is almost symmetrically bridging between N(1) and N(8) atoms. The N(8) atom, which is more affected by out-of-plane deformation [−0·031 (2) Å], is displaced towards H(2^{iii}). If the interactions between the nitrogen lone pairs and the hydrogen atoms are regarded as closed-shell repulsions, the combined repulsive action of H(4^{ii}) and H(5^{ii}) over N(8) prevails over that of H(2^{iii}). By using similar arguments the small displacement [0·008 (2) Å] of N(1) in the direction of the bridging H(4^{ii}) atom indicates that the action of the latter is weaker than that of the H(6^i) atom which lies on the opposite side.
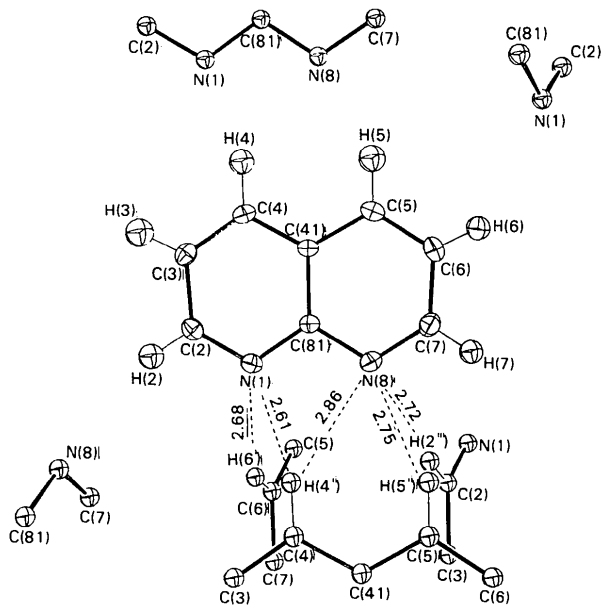

Fig. 2. Diagram showing the reference molecule [ORTEP (Johnson, 1965) drawing with 50% probability ellipsoids] and molecular fragments involved in selected intermolecular contacts. Symmetry code: none x, y, z; (i) $1+x, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $1+x, y, z$; (iii) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$. (Distances in Å.)

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