114°. Although this latter contact distance represents a rather weak hydrogen bond, it is geometrically feasible.

Since previous interpretations (Yasuda & Okawara, 1965; Clark, O'Brien & Pickard, 1965) of the infrared spectrum of $(CH_3)_3SnNO_3.H_2O$ are not consistent with the structure determined in this study, we suggest that the assignment of the 510 cm^{-1} band to the Sn–C symmetric stretching mode is incorrect, and that it is more likely to be a Sn–O stretch. In the infrared spectrum of anhydrous $(CH_3)_3SnNO_3$ (Clark & O'Brien, 1963; Clark, O'Brien & Pickard, 1965), Clark *et al.* (1965) made a similar suggestion for their previous assignment (1963) of the 520 cm^{-1} band. The shifts to lower frequencies, from 557 to 540 cm^{-1} (asymmetric Sn–C stretch), and from 520 to 510 cm^{-1} (Sn–O stretch), in going from anhydrous $(CH_3)_3SnNO_3$ to $(CH_3)_3SnNO_3.H_2O$, indicate differences in the bonding. An examination of the crystal structure of anhydrous $(CH_3)_3SnNO_3$ is in progress.

We wish to thank the National Research Council of Canada whose financial support made this work possible.

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The Crystal Structure of 1,8-Naphthyridine

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(*Received* 19 *March* 1971)

The crystal structure of 1,8-naphthyridine, $C_8H_6N_2$, has been determined by a symbolic-addition procedure and was refined to an R of 4·8% by block-diagonal least-squares methods. The unit cell is monoclinic, $P2_1/c$, with $a=6{\cdot}170(8)$, $b=10{\cdot}485(6)$, $c=11{\cdot}454(8)$ Å, $\beta=117{\cdot}66(8)°$, and 4 molecules per unit cell. Intensity data were collected on a Picker manually driven 4-circle goniometer using the θ–2θ scan method. The molecule is nonplanar with the two rings twisting in opposite directions about the bridgehead carbon–carbon bond. This results from the repulsion of the lone-pair electrons on the nitrogen atoms, since other naphthyridines are planar as is the 1,8-naphthyridine when it is chelated to a metal atom.

Introduction

Recently, 1,8-naphthyridine complexes of transition metal cations have been prepared (Bodner & Hendricker, 1970). The crystal structure of the tetrakis(1,8-naphthyridine)iron(II) perchlorate complex was subsequently determined and shown to contain a unique eight-coordinate iron(II) ion (Hendricker & Bodner, 1970; Clearfield. Singh & Bernal, 1970; Singh, Clearfield & Bernal, 1971). In this complex the ligands are bonded to the iron arom through the nitrogen lone pairs. The N(1)–C(8*a*)–N(8) outer bridgehead bond angles of the ligands average 111·6°. This small angle is thought to arise from the decreased repulsion of the nitrogen-atom lone pairs on chelation, and the necessity of achieving good overlap between the nitrogen and iron bonding orbitals. Thus, it was of interest to determine the structure of 1,8-naphthyridine to assess the effect of complexation on the molecule. In addition, the effect of the proximity of the nitrogen atoms on the bond distances and angles of the ring system is of interest to organic chemists (Paudler & Kress, 1970), as well as from a theoretical point of view (Longuet-Higgins & Coulson, 1949). In this respect, comparisons can be made with 1,5-naphthyridine and 2,6-naphthyridine, whose structures have been determined previously (Brufani, Duranti & Giacomello, 1959) (Brufani, Fedeli, Giacomello, Riccieri & Vaciago, 1966).

Experimental

Crystals of 1,8-naphthyridine were prepared by the method of Paudler & Kress (1967) and kindly supplied to us by Drs D. G. Hendricker and R. L. Bodner. The crystals are colorless, rectangular prisms with the long direction parallel to the *a* axis. It was necessary to mount the crystals in capillary tubes, since it was found that in air the crystals decomposed when exposed to X-rays. However, inside a capillary tube they were stable in the X-ray beam. Survey Weissenberg and precession photographs exhibited the systematic absences $0k0$ for k odd and $h0l$ for l odd, indicative of space group $P2_1/c$.

All subsequent data were gathered with a Picker manually driven 4-circle diffractometer using filtered Cu $K\alpha$ ($\lambda = 1{\cdot}5418$ Å) radiation. A crystal of approximate dimensions 0·50 × 0·20 × 0·20 mm was mounted with the *a* axis parallel to the φ axis of the goniometer and also parallel to the length of the capillary tube. Accurate unit-cell constants were determined by measurement of the high-angle, axial reflections at a 1·2° take-off angle with narrow slits. Averaging these data gave $a_0 = 6{\cdot}170 \pm 0{\cdot}008$, $b_0 = 10{\cdot}485 \pm 0{\cdot}006$, $c_0 = 11{\cdot}454 \pm 0{\cdot}008$ Å, and $\beta = 117{\cdot}66 \pm 0{\cdot}08°$. The density of the crystals was determined, by flotation in a pentane–carbon tetrachloride mixture, to be $1{\cdot}30 \pm 0{\cdot}02$ g.cm^{-3}, This compares to a density of 1·317 g. cm^3 based on a unit-cell volume of 656·3 Å^3 and $Z = 4$.

Intensity data were measured at a take-off angle of 3·5° using the θ–2θ scan method. The 2θ scan ranges were 1·5° for reflections occurring below 25° in 2θ and 2·0° above 25° 2θ. Reflections up to $2\theta = 130°$ were measured. The scan rate was 1° min^{-1}, and the background was measured separately for each reflection for 10 sec at the beginning and end of each scanning range. The 300 reflection was selected as the standard, and its intensity was recorded every 30 reflections. Fluctuations in intensity of the standard reflection were random with a maximum variation of 2·9%, indicating insignificant deterioration of the crystal. Of the 1116 reflections scanned, 831 were judged to have a significant intensity above background. Lorentz and polarization corrections were applied, but not those for absorption. Since the long dimension of the crystal coincided with the φ axis of the goniometer, the crystal shape approximated that of a cylinder. With the low values of ur ($\mu = 6{\cdot}62$ cm^{-1}), values of the absorption correction factors differ by about 6% in the extreme.

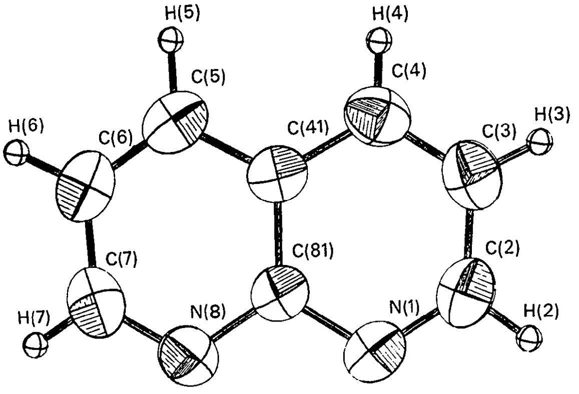

Fig. 1. The 1,8-naphthyridine molecule showing thermal ellipsoids of vibration at the 50% probability level. Hydrogen atoms were given a fictitious value of $B_{\text{iso}} = 0{\cdot}1$ Å^2. The bridgehead carbon atoms labelled C(41) and C(81) are labelled C(4*a*) and C(8*a*), respectively, in the text and subsequent figures.

Structure determination and refinement

The structure was solved by a straightforward application of the $\sum_2$ relationship (Sayre, 1952) in a symbolic-addition procedure (Hauptman & Karle, 1953; Karle & Karle, 1966). The program used was that of Ahmed (1971).

Refinement of the positional and thermal parameters was carried out by the block-diagonal least-squares method (Ahmed, Hall, Pippy & Huber, 1966) on the Ohio University IBM 360/44 computer. The function minimized was $\sum w(|F_o| - |F_c|)^2$ using 4 × 4 blocks for isotropic refinement and 9 × 9 blocks for anisotropic refinement. Two cycles of isotropic refinement, using the carbon-atom scattering factor for all 10 nonhydrogen atoms, reduced the residual, $R_1 = \sum(||F_o| - |F_c||/\sum F_o)$ from 0·439 to 0·287. A Fourier map, at this point, showed two peaks in the 1,8 position distinctly higher than the other eight and they were presumed to be the nitrogen atoms. Next, the thermal parameters for the carbon and nitrogen atoms were allowed to go anisotropic, and in nine cycles R_1 decreased to 0·097. A difference map was calculated and revealed the positions of the hydrogen atoms. These were included in the refinement (with an initial B value of 5), and after five more cycles R_1 reduced to 0·067. The data were found to suffer from extinction effects, and an empirical correction was applied in the form $|F_c| = |F_o|(1 + gI_c)$. The value of g, obtained from a plot of $|F_c|$ against $|F_o|$, was 0·007. Two reflections were found to deviate from the straight-line plot and were, therefore, excluded from the refine-

Table 1. *Positional and thermal parameters* with e.s.d.'s (in parentheses)*

Anisotropic thermal parameters for nonhydrogen atoms in Å² as they appear in

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

Parameters are multiplied by 10^5 for the non-hydrogen atoms

	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
N(1)	32233 (35)	44809 (19)	20527 (19)	3549 (74)	1115 (21)	1056 (20)	−65 (33)	1349 (64)	−413 (65)
C(2)	22507 (48)	53726 (24)	24673 (22)	4600 (100)	1110 (26)	952 (24)	−224 (39)	1541 (84)	−476 (84)
C(3)	−2113 (49)	54424 (24)	21662 (23)	4820 (110)	1089 (26)	1056 (26)	−22 (39)	2297 (92)	−523 (84)
C(4)	−17715 (44)	45503 (24)	13653 (23)	3524 (84)	1221 (27)	1052 (23)	292 (41)	1859 (76)	585 (79)
C(4*a*)	−8798 (38)	35875 (20)	8429 (19)	3099 (72)	947 (21)	836 (21)	349 (36)	1319 (67)	88 (68)
C(5)	−23476 (43)	26478 (24)	−637 (23)	3644 (85)	1162 (26)	1032 (24)	164 (41)	1376 (77)	−620 (79)
C(6)	−12843 (48)	17781 (24)	−5140 (24)	4900 (110)	1012 (27)	1171 (27)	−209 (41)	1972 (92)	−855 (84)
C(7)	12545 (51)	18251 (24)	−371 (26)	5310 (110)	1005 (26)	1399 (30)	−187 (44)	2941 (10)	296 (89)
N(8)	27170 (40)	26795 (10)	7962 (21)	3802 (75)	1021 (21)	1415 (24)	−80 (36)	2281 (73)	298 (66)
C(8*a*)	16610 (40)	35780 (20)	12270 (20)	3121 (71)	869 (20)	873 (20)	227 (34)	1344 (63)	−56 (66)

Table 1 (*cont.*)

Positional parameters are multiplied by 10^4 for hydrogen atoms

	X	Y	Z	B_{iso}
H(2)	3434 (47)	5986 (25)	3009 (26)	3·9 (6)
H(3)	−691 (49)	6103 (26)	2509 (26)	4·0 (6)
H(4)	−3343 (48)	4560 (25)	1181 (26)	3·6 (6)
H(5)	−4125 (50)	2634 (25)	347 (27)	4·0 (6)
H(6)	−2268 (44)	1161 (24)	1172 (24)	4·4 (6)
H(7)	1955 (53)	1270 (28)	392 (29)	5·2 (7)

ment. The extinction correction reduced R_1 to 0·048 in two more cycles. Two additional cycles had no further effect on R_1, and all shifts were below 0·1 of their corresponding estimated standard deviations, except for the y positional parameter for H(7) which was 0·2–0·3 times the e.s.d. value. Therefore, the refinement was considered to be completed. A final difference Fourier was featureless with the largest positive and negative peaks less than 0·15 e.Å^{-3}.

Description of the structure

The final positional parameters and their e.s.d.'s, and the corresponding thermal parameters, are given in Table 1. Table 2 compares observed and calculated structure factors.

The 1,8-naphthyridine molecule showing the thermal ellipsoids of vibration (Johnson, 1965) is given in Fig. 1. Line drawings containing the various bond distances and bond angles together with their e.s.d.'s are reproduced in Figs. 2 and 3.

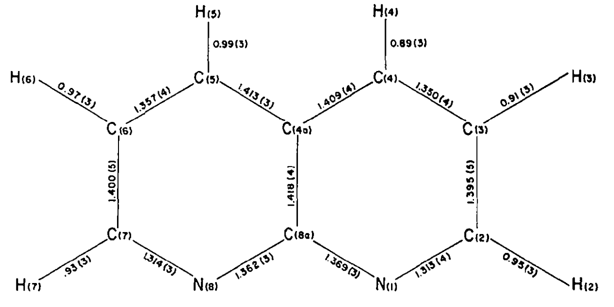
H(5)
H(4)
0.99(3)
0.89(3)
H(6)
0.97(3)
1.357(4)
C(5)
1.413(3)
1.409(4)
C(4)
1.350(4)
0.91(3)
H(3)
C(6)
C(4a)
C(3)
1.400(5)
1.418(4)
1.395(5)
C(7)
C(8a)
C(2)
H(7)
.93(3)
1.314(3)
N(8)
1.362(3)
1.369(3)
N(1)
1.315(4)
0.95(3)
H(2)

Fig. 2. Bond distances in 1,8-naphthyridine including e.s.d.'s in the least significant figures in parentheses.

The most significant feature of the 1,8-naphthyridine molecule is the nonplanarity of the 10-atom ring system. The equation of the least-squares mean plane through the carbon and nitrogen atoms, referred to orthogonal axes ($X'=ax+cz\cos\beta$, $Y'=by$, $Z'=cz\sin\beta$) is:

$$0{\cdot}2310X'+0{\cdot}5859Y'-0{\cdot}7768Z'-1{\cdot}3325=0\,, \quad (1)$$

with $\chi^2=1196{\cdot}8$. Displacements of the atoms from plane (1) are shown in Fig. 4. The e.s.d.'s in these values range from 0·002 to 0·0026 Å. The two nitrogen atoms are displaced from the mean plane in opposite direc-

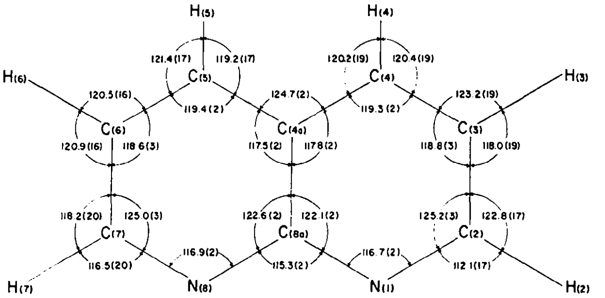
H(5)
H(4)
121.4(17)
119.2(17)
120.2(19)
120.4(19)
H(6)
C(5)
C(4)
H(3)
120.5(16)
124.7(2)
123.2(19)
119.4(2)
119.3(2)
C(6)
C(4a)
C(3)
120.9(16)
118.6(3)
117.5(2)
117.8(2)
118.8(3)
118.0(19)
118.2(20)
125.0(3)
122.6(2)
122.1(2)
125.2(3)
122.8(17)
C(7)
C(8a)
C(2)
116.9(2)
116.7(2)
116.5(20)
115.3(2)
112.1(17)
H(7)
N(8)
N(1)
H(2)

Fig. 3. Bond angles in 1,8-naphthyridine including their e.s.d.'s in parentheses.

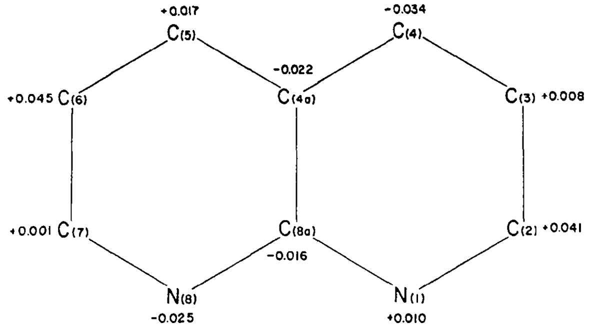
+0.017
C(5)
−0.034
C(4)
−0.022
+0.045 C(6)
C(4a)
C(3) +0.008
+0.001 C(7)
C(8a)
C(2) +0.041
−0.016
N(8)
N(1)
−0.025
+0.010

Fig. 4. Displacements of the ring atoms from the mean plane through all 10 atoms. E.s.d.'s range from 0·002 to 0·0026 Å.

Table 2. *Observed and calculated structure factors* (× 10)

Asterisked values are unobserved.

H	FO	FC
K=	0, L=	0
2	532	-514
3	116	-107
4	12*	-3
5	19	-18
6	12	10
K=	0, L=	2
0	118	173
1	94	-97
2	26	26
3	48	-47
4	44	-42
5	13	-15
K=	0, L=	-2
1	431	456
2	238	-245
3	401	-422
4	81	-71
5	67	-76
6	90	-95
K=	0, L=	4
0	177	179
1	46	-45
2	70	-68
3	100	98
4	91	89
5	10*	-8
K=	0, L=	-4
1	155	156
2	102	109
3	35	37
4	12	11
5	35	30
6	44	-43
7	15	-20
K=	0, L=	6
0	121	-115
1	146	-143
2	23	22
3	13*	-2
4	17	-19
K=	0, L=	-6
1	88	91
2	67	-60
3	117	-117
4	32	-30
5	13*	9
6	21	19
7	11*	1
K=	0, L=	8
0	81	84
1	64	67
2	94	-97
3	88	-93
K=	0, L=	-8
1	12*	0
2	24	-20
3	57	-51
4	43	40
5	141	135
6	47	45
7	25	-26
K=	0, L=	10
0	41	40
1	15	-17
K=	0, L=	-10
1	40	23
2	32	35
3	106	100
4	13*	-5
5	67	-63
6	13	-7
K=	0, L=	-12
1	11*	11
2	22	-20
3	21	-21
4	14	14
5	31	-34
K=	1, L=	0
1	41	-42
2	103	99
3	60	57
4	30	-28
5	31	32
6	23	24
K=	1, L=	1
0	266	-309
1	162	163
2	135	-121
3	127	-117
4	13*	7
5	24	-23
6	16	-18
K=	1, L=	-1
1	209	-318
2	277	291
3	153	140
4	17	-18
5	13*	9
6	12*	-3
K=	1, L=	2
0	340	-384
1	27	21
2	145	140
3	26	24
4	15	7
5	24	25
K=	1, L=	-2
1	131	138
2	152	-170
3	35	31
4	20	20
5	13*	-9
6	18	16
K=	1, L=	3
0	506	504
1	115	-111
2	71	-67
3	12*	4
4	38	-38
3	11*	7
K=	3, L=	6
5	12*	6
K=	1, L=	-3
1	543	561
2	68	-67
3	77	-77
4	32	-33
5	13*	-5
6	48	50
K=	1, L=	4
0	33	-32
1	87	85
2	12	-12
3	117	-113
4	66	-63
5	24	20
K=	1, L=	-4
1	180	183
2	71	-76
3	117	-116
4	11*	17
5	13*	9
6	22	-24
7	10*	-2
K=	1, L=	5
0	11	-14
1	139	138
2	22	-24
3	143	-145
4	50	-53
K=	1, L=	-5
1	54	-60
2	14	15
3	61	-61
4	21	-19
5	13*	-10
6	39	-41
7	11*	-10
K=	1, L=	6
0	142	140
1	125	121
2	71	-72
3	125	-128
4	25	-26
K=	1, L=	-6
1	60	-67
2	145	-141
3	82	-82
4	31	31
5	37	37
6	13*	-6
7	11*	-11
K=	1, L=	7
0	77	75
1	13*	-9
2	13*	9
3	77	79
K=	1, L=	-7
1	59	60
2	132	125
3	127	120
4	34	-32
5	48	-48
6	13*	-11
7	11*	-9
K=	1, L=	8
0	102	99
1	31	26
2	70	-71
3	48	-48
K=	1, L=	-8
1	13	-10
2	72	-69
3	156	-148
4	26	29
5	137	137
6	57	62
7	10*	-8
K=	1, L=	9
0	81	-82
1	23	-24
2	27	31
K=	1, L=	-9
1	38	-38
2	55	-54
3	45	-44
4	13*	-10
5	67	-65
6	42	-42
7	18	19
K=	1, L=	10
0	27	27
1	12*	-5
K=	1, L=	-10
1	40	-38
2	25	-28
3	71	-67
4	35	-33
5	79	78
6	73	77
K=	1, L=	11
0	25	26
K=	1, L=	-11
1	13*	4
2	13*	-6
3	41	-39
4	13*	-6
5	85	83
6	61	62
K=	1, L=	-12
1	20	24
2	26	24
3	12*	-1
4	15	-17
5	11*	7
K=	1, L=	-13
2	35	-32
4	12	13
K=	2, L=	0
0	49	-49
1	18	-18
2	109	108
3	117	109
4	12*	4
5	40	45
6	51	51
K=	2, L=	1
0	275	306
1	30	30
2	186	-186
3	113	-106
4	93	-92
5	51	-52
6	15	11
K=	2, L=	-1
1	13	-17
2	61	65
3	10*	2
4	54	52
5	13*	3
6	28	-25
K=	2, L=	2
1	66	64
2	286	289
3	50	-53
4	86	-84
5	13*	1
K=	2, L=	-2
1	493	-540
2	146	148
3	52	52
4	19	-17
5	13*	-2
6	13*	12
K=	2, L=	3
0	531	521
1	148	139
2	17	-16
3	84	-83
4	34	-33
5	12*	10
K=	2, L=	-3
1	559	-568
2	9	8
3	140	135
4	15	13
5	21	21
6	22	18
K=	2, L=	4
0	8*	0
1	159	153
2	37	-37
3	22	20
4	42	42
5	10*	-11
K=	2, L=	-4
1	269	-286
2	156	152
3	266	283
4	27	23
5	16	-12
6	34	37
7	10*	11
K=	2, L=	5
0	29	-32
1	12	-10
2	12*	-2
3	55	55
4	25	26
K=	2, L=	-5
1	18	-18
2	160	-158
3	17	20
4	156	159
5	100	101
6	46	50
7	10*	6
K=	2, L=	6
0	44	-44
1	81	-77
2	33	35
3	28	29
4	13	-17
K=	2, L=	-6
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6	12*	-4
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3	11*	10
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5	77	77
6	12*	-10
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3	38	-37
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3	29	-29
4	14	-16
K=	10, L=	5
0	36	-39
1	30	-34
K=	10, L=	-5
1	12*	9
2	19	23
3	19	19
4	10*	-5
K=	10, L=	6
0	28	29
K=	10, L=	-6
1	12*	6
2	24	28
3	14	14
K=	10, L=	-7
1	11*	13
2	31	32
3	29	29
K=	11, L=	0
1	16	14
2	15	-14
K=	11, L=	1
0	121	120
1	15	12
2	15	-20
K=	11, L=	-1
1	88	86
2	45	-45
3	54	-53
K=	11, L=	2
0	21	21
1	19	-19
2	17	-14
K=	11, L=	-2
1	31	-28
2	12*	7
3	10*	7
K=	11, L=	3
0	12*	-7
1	11*	-2
K=	11, L=	-3
1	12*	5
2	11*	2
3	19	-19
K=	11, L=	4
0	12	5
1	10*	-1
K=	11, L=	-4
1	13	-16
2	12	-12
3	10*	7
K=	11, L=	5
0	10*	7
K=	11, L=	-5
1	25	26
2	11*	7
K=	12, L=	0
0	36	-33
1	12	-10
K=	12, L=	1
0	34	-36
1	10	-9
K=	12, L=	-1
1	10*	-6
K=	12, L=	2
0	52	51
K=	12, L=	-2
1	31	31
K=	12, L=	-3
1	31	31

tions. This is in accord with the supposition that the lone pairs of electrons on the nitrogen atoms are close enough to repel each other. It is interesting that the positive displacement of N(1) is accompanied by a negative displacement of C(4), and the negative displacement of N(8) is accompanied by a positive displacement of C(5). Thus, the two pyridine moieties twist in opposite directions. The positions of the remaining atoms are, then, such as to make each pyridine ring also nonplanar. The equation of the least-squares mean plane through the six atoms in the ring containing N(1) is:

$$0{\cdot}2203X' + 0{\cdot}5721Y' - 0{\cdot}7900Z' - 1{\cdot}2474 = 0\,, \qquad (2)$$

and $\chi^2 = 109{\cdot}4$. The displacements of the atoms from the mean plane starting with N(1) and going counterclockwise are −0·007, +0·015, −0·001, −0·013, +0·011, and −0·003 Å. The mean plane equation for the other ring is:

$$0{\cdot}2404X' + 0{\cdot}6005Y' - 0{\cdot}7626Z' - 1{\cdot}3784 = 0\,, \qquad (3)$$

with $\chi^2 = 125{\cdot}9$. Again, starting with N(8) and proceeding in a counterclockwise direction the atom displacements are −0·006, +0·015, −0·010, −0·002, +0·014, and −0·010 Å, respectively. The mean-plane equations (2) and (3) are referred to the same orthogonal axes given above. The dihedral angle between the mean planes of the individual pyridine rings is 2·5°.

That the nonplanarity of the 10-membered naphthyridine ring is, indeed, due to the repulsion of the lone pairs of electrons may be inferred from the following indirect structural evidence. The ring systems in 1,5- and 2,6-naphthyridine, where the nitrogen lone pairs are far removed from each other, are planar (Brufani *et al.*, 1959, 1966). Furthermore, the naphthyridine rings in tetrakis-(1,8-naphthyridine)iron(II) perchlorate are also planar. Apparently, the iron–nitrogen bonding in the complex cuts down the repulsion of the electron pairs sufficiently to restore the planarity required by the aromatic-ring system. Furthermore, the structural results reported here are in accord with recent CNDO/2 calculations of dipole moments carried out by Paudler (1971). He found that the dipole moments of 1,5- and 2,6-naphthyridine could be adequately represented by a planar model. However, for 1,8-naphthyridine good agreement was only obtained if the X-ray positional parameters were projected onto a plane. In this instance, the experimental and theoretical dipole moments agree within 0·15 D. Thus, in solution, an averaging process probably takes place.

If it is assumed that the 1,8-naphthyridine molecule is planar, then the molecule would almost possess C_{2v} symmetry with the twofold axis lying along the C(4*a*)–C(8*a*) line of centers. This is seen from the bond angle and bond length (neglecting hydrogen atoms) diagrams of Figs. 2 and 3. C_{2v} symmetry is required by the simple valence bond resonance description of 1,8-naphthyridine similar to that given by Pauling (1960*a*) for naphthalene. In this description, interatomic distances C(2)–C(3), C(4*a*)–C(8*a*), and C(6)–C(7) should be identical. In actuality, the bridgehead bond C(4*a*)–C(8*a*) is significantly longer than the other two. This bond-length difference does not occur in 1,5- or 1,6-naphthyridine, nor does it occur in the 1,8-naphthyridine rings chelated to iron. In all of these cases the rings are planar. Thus, the C(4*a*)–C(8*a*) bond lengthening in the present work must result from the twisting of the rings out of planarity. In all other respects, bond lengths are in qualitative accord with the resonance picture of a 10-membered condensed ring system. According to this picture, the C(3)–C(4) bond and its C_{2v} symmetrically equivalent counterpart should have more double-bond character than the other carbon–carbon bonds and, hence, be shorter. The same applies to the N(1)–C(2) bond length and its symmetrically eqiuvalent counterpart N(8)–C(7).

The mean values of the long and short bond lengths in the three naphthyridines are compared in Table 3. The agreement is quite good, the largest difference being 0·015 Å (between the short carbon–carbon bonds of the 2,6- and 1,8-isomers). This indicates that the π-electron delocalization and participation of the nitrogen lone-pair electrons in the ring bonds are approximately the same in the three isomers.

Table 3. *Mean long and short bond lengths* (Å) *in naphthyridines*

Bond	1,5-isomer*	2,6-isomer†	1,8-isomer‡
Long C–C	1·415	1·410	1·407
Short C–C	1·358	1·369	1·354
Long N–C	1·356	1·361	1·366
Short N–C	1·314	1·314	1·314

* Brufani, Duranti & Giacomello, 1959. $\sigma \simeq 0{\cdot}006$ Å.

† Brufani, Fedeli, Giacomello, Riccieri & Vaciago, 1966. $\sigma \simeq 0{\cdot}006$ Å.

‡ Present work, $\sigma \cong 0{\cdot}004$ Å.

The bond angles in the interior of the rings follow the same pattern in all three isomeric naphthyridines. The smallest bond angle is always the one subtended at the nitrogen atoms. The largest bond angles are, then, those that are subtended at the carbon atoms adjacent to the nitrogen atoms. And finally, bond angles of intermediate value, but less than 120°, are subtended at the remaining carbon atoms. This sequence is correct, except for the 1,5-isomer in which the C(4)–C(4*a*)–C(8*a*) bond angle is slightly smaller (116·7 ± 0·4°) than the C–N–C bond angle (117·9 ± 0·4°). The observed bond angles are qualitatively in accord with expectations (Pauling, 1960*b*).

An interesting trend is noted in the exterior bond angles at the bridgehead atoms. The values are 123·6° for C(4)–C(4*a*)–C(5) in 2,6-naphthyridine; 124·70° for C(4)–C(4*a*)–C(5) in the 1,8-isomer; 120·10° for C(8)–C(8*a*)–N(1) in the 1,5-isomer; 115·3° for N(1)–C(8*a*)–N(8) in the 1,8-isomer. Thus, there is roughly a 4°

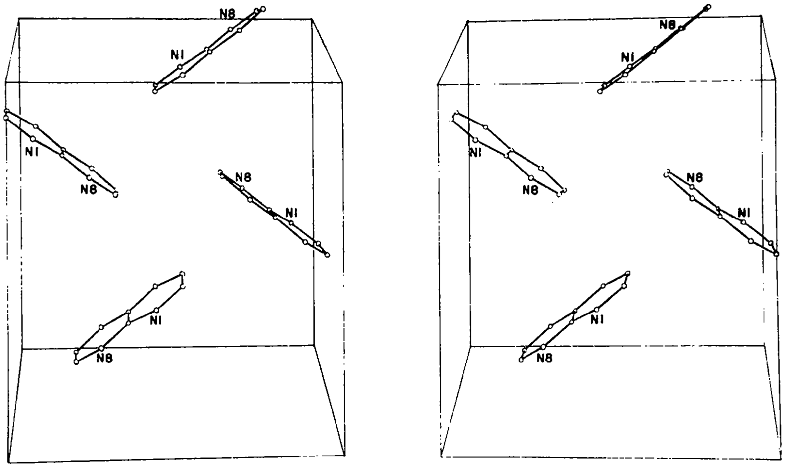

Fig. 5. Stereoscopic view of 1,8-naphthyridine unit cell showing the packing of the symmetry-related molecules.

decrease in the bridgehead angles with each nitrogen atom that participates in the formation of the bond angle.

Finally, there is a significant decrease in the N(1)–C(8*a*)–N(8) bond angle in 1,8-naphthyridine when it is chelated to the iron atom in the tetrakis iron complex. The difference is 3·7°, which is statistically significant based on consideration of the e.s.d.'s. At the same time, the outer bridgehead angle C(4)–C(4*a*)–C(5) increases by 1·4°. These changes apparently arise from the decreased repulsion of the nitrogen lone pairs when they become shared pairs in the complex. A possible secondary contributing factor would involve the deformation required to achieve maximum overlap between the nitrogen and iron bonding orbitals. It may be possible to assess the relative magnitude of the two effects by examining the structures of the other transition metal tetrakis complexes (Mn, Co, Ni, Cu, Zn).

The packing of the molecules in the unit cell is shown in Fig. 5. The nitrogen atoms of each molecule point in opposite directions to those of its two nearest neighbors to minimize the repulsive effects of the nitrogen lone pairs.

The authors thank Dr William W. Paudler, Ohio University Chemistry Department, for helpful discussions during the course of this work.

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