Table 2. *Best least-squares planes*

Deviations of atoms from the planes (Å)

Plane	C(1)	N(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)†	χ^2
1(*A* + *B*)	0·005	0·010	0·005	0·017	−0·008	−0·014	0·001	0·012	0·005	−0·001	−0·018	54·54
2(*A*)	0·001	0·005	0·003	0·008					0·005	−0·008	−0·002	14·12
3(*B*)					0·003	−0·004	0·000	0·003	−0·003	0·001		3·04
	C(11)†	C(12)	C(13)	C(14)	C(15)	C(16)	C(17)					
4(*C*)	0·037	0·003	0·003	0·001	−0·005	0·005	0·001					3·12
5	O(1)	C(18)	O(2)	O(3)								
	0·000	0·002	0·000	0·000								0·20

Equations to the planes [x,y,z are orthogonal coordinates (in Å), z is along z^*]

1 $-0{\cdot}6923x - 0{\cdot}5483y - 0{\cdot}4691z + 1{\cdot}6778 = 0$
2 $-0{\cdot}6957x - 0{\cdot}5484y - 0{\cdot}4641z + 1{\cdot}6675 = 0$
3 $-0{\cdot}6879x - 0{\cdot}5484y - 0{\cdot}4755z + 1{\cdot}6829 = 0$
4 $0{\cdot}7960x - 0{\cdot}1816y - 0{\cdot}5775z + 4{\cdot}1053 = 0$
5 $0{\cdot}3614x + 0{\cdot}5689y - 0{\cdot}7387z + 2{\cdot}4856 = 0$

Angles between the planes

1 to 4	100·4°
2 to 3	0·8

† Excluded from the calculation.

A projection of the structure along **b**, illustrating the packing of the molecules, is shown in Fig. 3.

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1-(2-Pyridyl)-5-methylimidazole

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Abstract. $C_9H_9N_3$, triclinic, $P\bar{1}$, $a = 7{\cdot}271$ (2), $b = 6{\cdot}533$ (2), $c = 9{\cdot}685$ (3) Å, $\alpha = 114{\cdot}12$ (3), $\beta = 100{\cdot}93$ (2), $\gamma = 93{\cdot}42$ (3)° ($\lambda = 1{\cdot}5418$ Å), $U = 407{\cdot}5$ Å^3, $Z = 2$, $D_x = 1{\cdot}30$, $D_m = 1{\cdot}30$ g cm^{-3}. The structure was solved by direct methods, and least-squares refinement gave $R = 0{\cdot}047$ for 1068 unique significant reflections whose intensities were measured by counter diffractometry. The analysis identified the molecule as the title compound. The 5-methyl substituent is co-

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planar with the imidazole-ring plane, and that plane is inclined to the plane of the pyridine ring by 37° with the torsion angles C(2)–N(1)–C(2′)–N(1′) and C(5)–N(1)–C(2′)–C(3′) being respectively −31 and −43°.

Introduction. In the course of an investigation of the mode of coordination of substituted 1-(2-pyridyl)- and 1-(2-picolyl)-imidazoles and first-row transition-metal ions (Sundberg, Yilmaz & Mente, 1977) it was noted that when 1-(2-pyridyl)- and 1-(2-picolyl)-4,5-dimethylimidazole were titrated against Co^{2+} ion the signal from one of the two methyl groups moved upfield. Signals from all other imidazole ring protons and methyl groups moved downfield with respect to tetramethylsilane (TMS) with increasing metal-ion concentration. To determine which of the two methyl groups was associated with this negative coordination shift, 1-(2-pyridyl)-4-methylimidazole and 1-(2-pyridyl)-5-methylimidazole were prepared together and separated by chromatography. A tentative assignment of the isomers was made on the basis of relative polarity in chromatography. The isomer having the less hindered imidazole-3 nitrogen, 1-(2-pyridyl)-5-methylimidazole, was taken to be the less readily eluted component of the mixture. Differentiation between 4- and 5-substituents on imidazole rings is difficult by purely spectroscopic means (Matthews & Rapoport, 1973) and the application of recommended techniques failed to provide an unambiguous confirmation of the tentative assignment. In order to make the structural assignment conclusively, and thereby identify the methyl group exhibiting an upfield shift, a single-crystal X-ray analysis of the less readily eluted component was undertaken.

For the analysis, a well formed colorless prism obtained by recrystallization from ether–hexane was cut to a cube 0·5 mm on a side. Precession photographs, taken with Mo $K\alpha$ radiation, indicated that the crystal belonged to the triclinic system, and the distribution of intensity as a function of scattering angle for the complete diffraction pattern indicated the centrosymmetric space group $P\bar{1}$. With $Z = 2$, no molecular symmetry is implied. Intensity measurements were made by automatic single-crystal diffractometry for a hemisphere of reciprocal space ($2\theta \leq 120°$). The θ–2θ scan method was used with monochromatic (HOG) Cu $K\alpha$ radiation, scintillation counting, and pulse-height analysis. Scattered intensity significantly above background $[I > 3\sigma(I)]$ was measured at 1068 of the 1142 independent reciprocal-lattice points surveyed. Periodic monitoring of two reference reflections showed a 2·5% r.m.s. deviation around their mean intensities with no systematic trends. Structure amplitudes and normalized structure amplitudes were derived in the usual ways. No absorption corrections were made (μr = 0·3–0·5).

The structure was solved routinely by the use of the program *MULTAN* (Germain, Main & Woolfson, 1971) with the 200 $E(hkl) > 1·45$. Refinement of the parameters was by block-diagonal least-squares treatment (3 × 3, 6 × 6 blocks) minimizing the function $\Sigma\, w(F_o - kF_c)^2$ with a Hughes (1941) weighting scheme

Table 1. *Heavy-atom positional parameters* ($\times 10^4$) *and their standard deviations*

E.s.d.'s in parentheses are applicable to the least significant figures given.

	x	*y*	*z*
N(1)	3794 (2)	3706 (3)	2421 (2)
C(2)	3151 (3)	1422 (3)	1725 (3)
N(3)	1912 (3)	870 (3)	2377 (2)
C(4)	1759 (3)	2892 (3)	3562 (3)
C(5)	2873 (3)	4668 (3)	3624 (2)
C(*M*5)	3142 (3)	7114 (4)	4687 (3)
N(1′)	6643 (2)	3398 (3)	1676 (2)
C(2′)	5339 (3)	4735 (3)	2091 (2)
C(3′)	5408 (3)	6894 (3)	2171 (2)
C(4′)	6998 (4)	7770 (4)	1892 (3)
C(5′)	8397 (3)	6464 (4)	1498 (3)
C(6′)	8155 (3)	4297 (4)	1380 (3)

Table 2. *Positional parameters* ($\times 10^3$) *and isotropic thermal parameters for the hydrogen atoms*

	x	*y*	*z*	*B* (Å^2)
H(2)	358 (3)	33 (3)	76 (2)	4·6 (5)
H(4)	97 (3)	298 (3)	427 (2)	5·3 (5)
H(*M*5*a*)	258 (3)	732 (4)	558 (3)	6·3 (6)
H(*M*5*b*)	452 (2)	784 (3)	507 (2)	4·2 (5)
H(*M*5*c*)	257 (3)	800 (3)	421 (2)	4·9 (5)
H(6′)	903 (3)	320 (3)	98 (3)	5·3 (5)
H(5′)	953 (3)	702 (4)	131 (3)	6·5 (6)
H(4′)	705 (3)	926 (4)	197 (2)	5·4 (5)
H(3′)	439 (3)	776 (3)	244 (2)	4·8 (5)

Table 3. *Selected bond lengths* (Å) *and angles* (°) *with their e.s.d.'s*

N(1)–C(2)	1·369 (2)	N(1′)–C(2′)	1·334 (2)
N(1)–C(5)	1·396 (2)	N(1′)–C(6′)	1·348 (2)
N(1)–C(2′)	1·427 (2)	C(2′)–C(3′)	1·378 (2)
C(2)–N(3)	1·305 (2)	C(3′)–C(4′)	1·379 (3)
N(3)–C(4)	1·379 (2)	C(4′)–C(5′)	1·376 (3)
C(4)–C(5)	1·348 (2)	C(5′)–C(6′)	1·371 (3)
C(5)–C(*M*5)	1·482 (2)	C(3′)–H(3′)	0·97 (2)
C(*M*5)–H(*M*5*a*)	0·99 (2)	C(4′)–H(4′)	0·94 (2)
C(*M*5)–H(*M*5*b*)	1·01 (2)	C(5′)–H(5′)	0·96 (2)
C(*M*5)–H(*M*5*c*)	0·95 (2)	C(6′)–H(6′)	1·00 (2)
C(2)–H(2)	1·03 (2)	C(4)–H(4)	0·96 (2)
N(1)–C(2)–N(3)	112·0 (2)	N(1′)–C(2′)–C(3′)	124·6 (2)
N(1)–C(5)–C(4)	104·4 (2)	N(1′)–C(6′)–C(5′)	123·4 (2)
C(2)–N(3)–C(4)	104·6 (2)	C(2′)–C(3′)–C(4′)	117·2 (2)
N(3)–C(4)–C(5)	112·2 (2)	C(3′)–C(4′)–C(5′)	119·8 (2)
C(2)–N(1)–C(5)	106·8 (2)	C(4′)–C(5′)–C(6′)	118·5 (2)
C(4)–C(5)–C(*M*5)	130·5 (2)	C(2′)–N(1′)–C(6′)	116·3 (2)
N(1)–C(5)–C(*M*5)	125·2 (2)	C(3′)–C(2′)–N(1)	121·7 (2)
C(5)–N(1)–C(2′)	128·6 (2)	N(1′)–C(2′)–N(1)	113·7 (2)
C(2)–N(1)–C(2′)	123·9 (2)		

adopted. H atoms were found from difference electron-density maps calculated in the ring planes and normal to the C(5)—C(*M*5) bond. Anisotropic thermal parameters were assumed for N and C, isotropic *B* values for H, and positional and thermal parameters for all atoms were refined. At convergence $[\Delta(p) < 0\cdot1\sigma(p)]$ the conventional weighted and unweighted residuals were 0·055 and 0·047.* Final atomic parameters are given in Tabes 1 and 2, and selected bond lengths and angles in Table 3.

Scattering functions were for the neutral atoms (Hanson, Herman, Lea & Skillman, 1964; Stewart, Davidson & Simpson, 1965). With the exception of *ORTEP* (Johnson, 1976) and *MULTAN*, for which use was made of a CDC 6400 computer, all calculations were carried out with programs written in this laboratory for the XDS Sigma 2 computer.

Discussion. The identification of this isomer as 1-(2-pyridyl)-5-methylimidazole (Fig. 1) establishes that it is the 4-methyl substituent in these potential ligands which is associated with the upfield chemical-shift behavior observed on titration against Co^{2+}. The crystal structure of a typical complex, dichlorobis[1-(2-pyridylmethyl)-4,5-dimethylimidazole]cobalt(II), has been determined and further details of the spectral properties provided (Sundberg *et al.*, 1977).

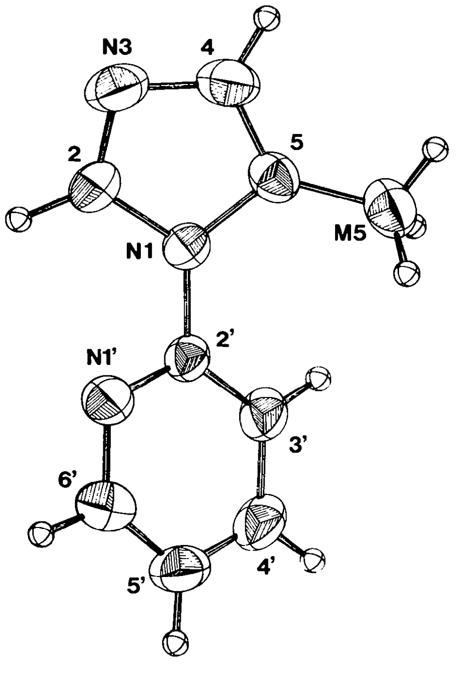

Fig. 1. View of the molecular structure (*ORTEP*) showing the numbering scheme adopted.-(Hydrogen atoms are numbered to correspond to the atom of attachment.) Thermal ellipsoids for the C and N atoms are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary radius.

In the title compound, the atoms of the imidazole ring and the 5-methyl C atom are exactly coplanar, the equation* of the least-squares mean plane through the six atoms being $0\cdot6372X - 0\cdot4445Y + 0\cdot6296Z = 2\cdot0552$.

The mean and maximum deviations of the ring atoms from this plane are 0·002 and 0·005 Å, respectively, and C(2'), the atom of attachment on the pyridine ring, is 0·19 Å from the plane. The equation of the least-squares mean plane through the six atoms of the pyridine ring is $0\cdot2541X - 0\cdot0668Y + 0\cdot9649Z = 2\cdot4065$, and the ring shows slight, but significant, puckering. With N(1') and C(4') in the plane, C(2') and C(5') are below the plane by 0·02 and 0·01 Å, respectively, whereas C(3') and C(6') are displaced by the respective amounts above the plane. N(1), the atom of attachment of the imidazole ring, is 0·06 Å below the plane.

These two planes are inclined to one another at 37°, with the torsion angles C(2)–N(1)–C(2')–N(1') and C(5)–N(1)–C(2')–C(3') being respectively −31 and −43°. This is attributable to the need to minimize steric interactions between H(3') and the C(5) methyl-group protons. These interactions are reflected in the asymmetry of the exocyclic valence angles at N(1) (128·6 *vs* 123·9°) and C(2') (121·7 *vs* 113·7°). The intramolecular contacts H(3')···H(*M*5*c*) and H(3')···H(*M*5*b*) are respectively 2·32 and 2·51 Å, and H(4)···H(*M*5*a*) is 2·67 Å. This conformation, despite the obvious strain involved, is clearly preferred over that which would place the N(1') lone pair in contact with the methyl group.

Bond distances in the pyridine ring agree well with one another (mean C–C, 1·376 Å; mean C–N, 1·341 Å) and with distances found in other 2-substituted pyridines (Chao, Schempp & Rosenstein, 1975). Bond distances in the imidazole ring, though these are very sensitive to substitution patterns, are comparable with those found in related compounds (Hsu & Craven, 1974; Guggenberger, 1975).

There are short intermolecular N···H–C contacts: N(3)···H(5') 2·66 Å, and N(1)'···H(2) 2·58 Å; both involving H atoms on C atoms adjacent to N, and presumably reflecting strong dipolar interactions (Carey, Smith, Maher & Bryan, 1977). Other intermolecular contacts correspond to normal van der Waals separations.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32905 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

* *X*, *Y*, and *Z* in the equations are in Å with respect to an orthogonal axial system having its origin coincident with that of the cell axial system. The matrix relating the cell coordinates to the orthogonal coordinates is:

$$\begin{matrix} 7\cdot27150 & 0\cdot00000 & 0\cdot00000 \\ 0\cdot38970 & 6\cdot52147 & 0\cdot00000 \\ 1\cdot83634 & 4\cdot07449 & 8\cdot59196. \end{matrix}$$

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p-Fluorobenzonitrile

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Abstract. FC_6H_4CN, triclinic, $P\bar{1}$ (No. 2), a = 6·559 (2), b = 12·191 (3), c = 3·869 (1) Å, α = 96·18 (2), β = 97·23 (2), γ = 90·30 (3)°, Z = 2, molecular volume 152·5 Å^3, D_o = 1·32 (flotation in aqueous KI solution), D_c = 1·319 g cm^{-3}. Least-squares refinement of diffractometer data (1364 independent reflections, including those with zero intensity) converged at a conventional R value of 0·084; for the 971 reflections with $I > 2\sigma(I)$, R = 0·063. The molecule has $mm2$ symmetry within experimental error; the bond lengths and angles are normal. The packing of the molecules closely resembles that in crystalline terephthalonitrile.

Introduction. As part of a study of intermolecular donor–acceptor interactions in crystals we are determining the structures of a variety of halobenzonitriles. When the halogen is Cl, Br or I, we expect to find a nitrile–halogen, donor–acceptor contact that is closer than the contact distance that would be predicted from the usual van der Waals radii. *p*-Iodobenzonitrile (Schlemper & Britton, 1965) and *p*-bromobenzonitrile (Britton, Konnert & Lam, 1977) are examples of such a situation. When the halogen is F we would not expect such a contact since the F atom in a molecule is not an electron acceptor. We have determined the crystal structure of *p*-fluorobenzonitrile to see what, if any, unusual features occur in the packing.

p-Fluorobenzonitrile, from Aldrich Chemical Co., Inc., was sublimed to provide suitable crystals. A thick needle, elongated along **c**, was cut to an equant shape approximately 1 mm on each edge and sealed in epoxy cement to prevent loss of the crystal by sublimation (the melting point is 34 °C). Data were collected at room temperature with a four-circle Hilger & Watts automatic diffractometer using Zr-filtered Mo $K\alpha$ radiation (λ = 0·7107 Å). The cell dimensions were determined from the least-squares fit of 13 crystallographically independent planes. Intensity data were collected for 3406 reflections comprising the complete

Table 1. *Positional parameters* (× 10^4)

	x	y	z
C(1)	2539 (2)	3383 (1)	2380 (3)
C(2)	4232 (2)	2757 (1)	1672 (4)
C(3)	4194 (3)	1643 (1)	1871 (5)
C(4)	2465 (3)	1171 (1)	2775 (4)
C(5)	777 (3)	1761 (1)	3487 (5)
C(6)	808 (2)	2878 (1)	3295 (4)
C(7)	2568 (2)	4554 (1)	2161 (4)
N	2583 (2)	5482 (1)	1981 (4)
F	2445 (2)	64 (1)	2975 (4)
H(2)	5391 (27)	3140 (14)	1152 (39)
H(3)	5272 (29)	1184 (13)	1349 (40)
H(5)	−453 (34)	1379 (16)	3909 (48)
H(6)	−300 (27)	3304 (14)	3747 (37)