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# *N*-(4-Chlorophenyl)-4-methylpyridin-2-amine

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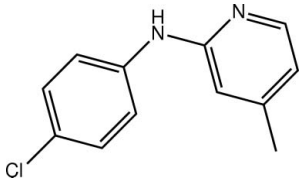
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.002 Å; $R$ factor = 0.042; $wR$ factor = 0.132; data-to-parameter ratio = 17.8.

In the title compound, $C_{12}H_{11}ClN_2$, the dihedral angle between the benzene and pyridyl rings is 48.03 (8)°. Twists are also evident in the molecule, in particular about the $N_a$–$C_b$ (a = amine and b = benzene) bond [C—N—C—C = −144.79 (18)°]. In the crystal, inversion dimers linked by pairs of N—H···N hydrogen bonds result in the formation of eight-membered $\{\cdots NCNH\}_2$ synthons [or $R_2^2(8)$ loops].

## Related literature

For background to the fluorescence properties of compounds related to the title compound, see: Kawai *et al.* (2001); Abdullah (2005).



## Experimental

### *Crystal data*

$C_{12}H_{11}ClN_2$
$M_r$ = 218.68
Monoclinic, $P2_1/n$
$a$ = 15.9335 (15) Å
$b$ = 4.0651 (4) Å
$c$ = 17.0153 (16) Å
$\beta$ = 98.755 (1)°
$V$ = 1089.26 (18) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.32 mm$^{-1}$
$T$ = 293 K
0.30 × 0.30 × 0.20 mm

### *Data collection*

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.776, $T_{max}$ = 0.862
9785 measured reflections
2509 independent reflections
1886 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.030

### *Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.132
$S$ = 1.04
2509 reflections
141 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.22 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.18 e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H2*n*···N1$^{i}$ | 0.86 (1) | 2.19 (1) | 3.029 (2) | 167 (2) |

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5582).

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# supporting information

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## *N*-(4-Chlorophenyl)-4-methylpyridin-2-amine

**Zainal A. Fairuz, Zaharah Aiyub, Zanariah Abdullah, Seik Weng Ng and Edward R. T. Tiekink**

### S1. Comment

The title compound, (I), was investigated in the context of potential fluorescence properties (Kawai *et al.* 2001; Abdullah, 2005). The molecular structure of (I), Fig. 1, shows that the molecule is non-planar as seen in the dihedral angle of 48.03 (8) ° formed between the benzene and pyridyl rings, and in the twists about the central N–C bonds, *i.e.* the C7–N2–C1–N1 and C1–N2–C7–C8 torsion angles are -167.92 (17) and -144.79 (18) °, respectively. The amine-H and pyridine-N atoms are orientated in the same direction, an arrangement that facilitates the formation of N–H···N hydrogen bonds. Thus, centrosymmetrically related molecules are linked *via* N–H···N hydrogen bonds that lead to eight-membered $\{\cdots NCNH\}_2$ synthons, Table 1. The dimeric aggregates stack along the *b* axis, Fig. 2.

### S2. Experimental

2-Chloro-4-methylpyridine (1.0 ml, 1.14 mmol) was added to 4-chloroaniline (1.4543 g, 1.14 mmol) and heated for 2 h. The mixture was cooled and dissolved water (15 ml), extracted with diethyl ether (3 × 10 ml), washed with water (3 × 10 ml), and then dried over anhydrous sodium sulfate. Evaporation of the solvent gave a gray solid. Recrystallization from ethanol yielded colourless blocks of (I).

### S3. Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H 0.93 to 0.96 Å) and were included in the refinement in the riding model approximation, with $U_{iso}$(H) set to 1.2 to 1.5$U_{equiv}$(C). The N-bound H-atom was located in a difference Fourier map, and was refined with a distance restraint of N–H 0.86±0.01 Å; the $U_{iso}$ value was freely refined.

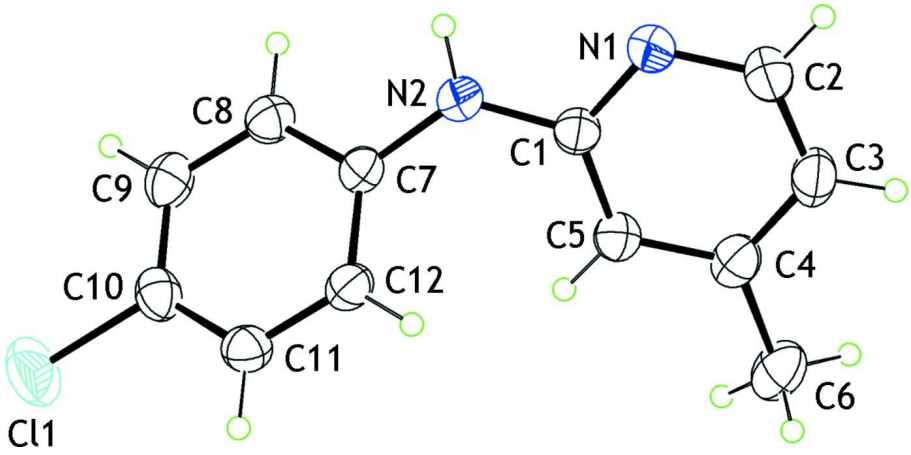


**Figure 1**

The molecular structure of (I) showing displacement ellipsoids at the 35% probability level.

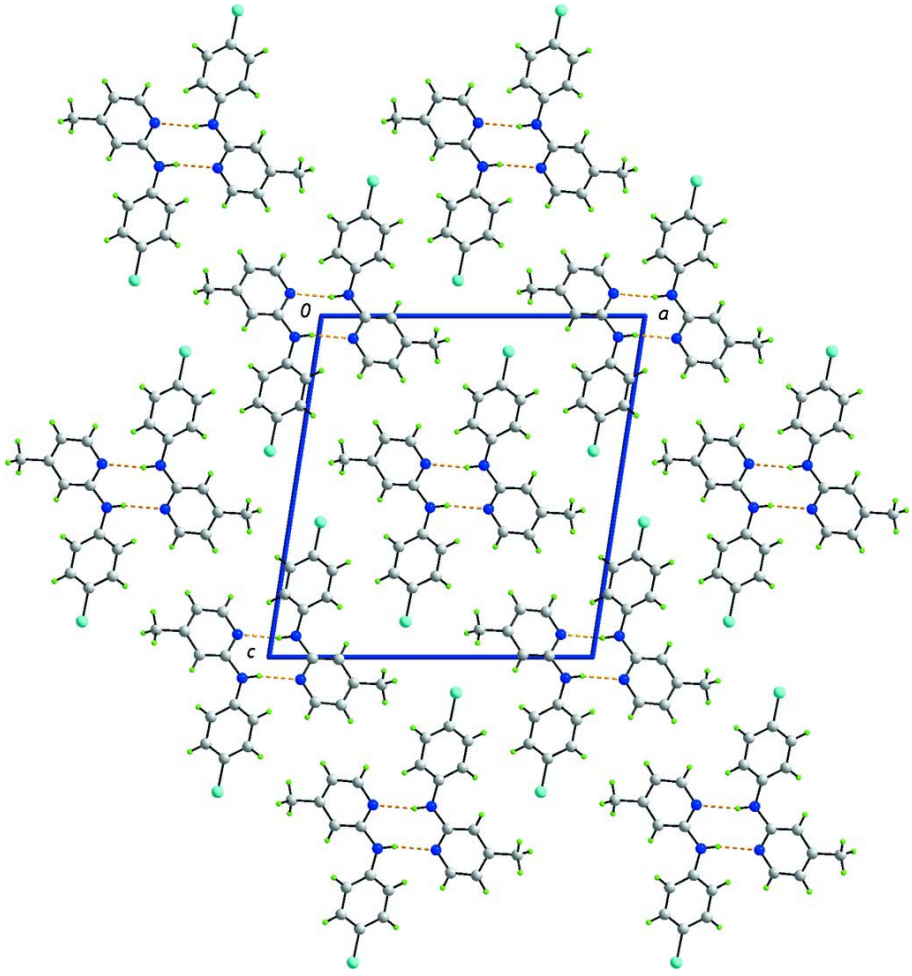


**Figure 2**

Unit-cell contents shown in projection down the *b* axis in (I). The N–H···N hydrogen bonding is shown as orange dashed lines.

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*Crystal data*

$C_{12}H_{11}ClN_2$
$M_r = 218.68$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 15.9335\ (15)$ Å
$b = 4.0651\ (4)$ Å
$c = 17.0153\ (16)$ Å
$\beta = 98.755\ (1)°$
$V = 1089.26\ (18)$ Å$^3$
$Z = 4$

$F(000) = 456$
$D_x = 1.333$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2763 reflections
$\theta = 2.4–25.7°$
$\mu = 0.32$ mm$^{-1}$
$T = 293$ K
Block, colourless
0.30 × 0.30 × 0.20 mm

*Data collection*

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube

Graphite monochromator
$\omega$ scans

Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.776, $T_{max}$ = 0.862
9785 measured reflections
2509 independent reflections
1886 reflections with $I > 2\sigma(I)$

$R_{int}$ = 0.030
$\theta_{max}$ = 27.5°, $\theta_{min}$ = 1.9°
$h$ = −20→19
$k$ = −5→5
$l$ = −22→20

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.132
$S$ = 1.04
2509 reflections
141 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0689P)^2 + 0.1992P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.18 e Å$^{-3}$

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating $R$-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cl1 | 0.59502 (4) | 1.02913 (16) | 0.10424 (3) | 0.0834 (2) |
| N1 | 0.60831 (9) | 0.5290 (4) | 0.56614 (8) | 0.0495 (4) |
| N2 | 0.57324 (9) | 0.6997 (4) | 0.43820 (9) | 0.0552 (4) |
| H2n | 0.5222 (7) | 0.653 (5) | 0.4444 (11) | 0.061 (6)* |
| C1 | 0.63451 (10) | 0.6751 (4) | 0.50365 (9) | 0.0439 (4) |
| C2 | 0.66466 (12) | 0.5088 (5) | 0.63260 (11) | 0.0578 (5) |
| H2 | 0.6472 | 0.4101 | 0.6767 | 0.069* |
| C3 | 0.74612 (12) | 0.6230 (5) | 0.64035 (10) | 0.0570 (5) |
| H3 | 0.7827 | 0.5985 | 0.6881 | 0.068* |
| C4 | 0.77369 (11) | 0.7769 (4) | 0.57556 (10) | 0.0498 (4) |
| C5 | 0.71648 (10) | 0.8019 (4) | 0.50667 (10) | 0.0461 (4) |
| H5 | 0.7323 | 0.9030 | 0.4621 | 0.055* |
| C6 | 0.86175 (12) | 0.9137 (6) | 0.58031 (13) | 0.0661 (5) |
| H6A | 0.8620 | 1.0847 | 0.5414 | 0.099* |
| H6B | 0.8999 | 0.7416 | 0.5701 | 0.099* |
| H6C | 0.8797 | 1.0023 | 0.6325 | 0.099* |
| C7 | 0.58319 (10) | 0.7850 (4) | 0.36041 (9) | 0.0428 (4) |
| C8 | 0.51945 (11) | 0.9664 (4) | 0.31600 (11) | 0.0496 (4) |

| | | | | |
|---|---|---|---|---|
| H8 | 0.4740 | 1.0406 | 0.3396 | 0.059* |
| C9 | 0.52239 (12) | 1.0389 (4) | 0.23723 (11) | 0.0544 (4) |
| H9 | 0.4789 | 1.1588 | 0.2077 | 0.065* |
| C10 | 0.59014 (12) | 0.9323 (4) | 0.20290 (10) | 0.0493 (4) |
| C11 | 0.65418 (11) | 0.7545 (4) | 0.24569 (10) | 0.0481 (4) |
| H11 | 0.6998 | 0.6843 | 0.2219 | 0.058* |
| C12 | 0.65108 (10) | 0.6791 (4) | 0.32428 (10) | 0.0462 (4) |
| H12 | 0.6946 | 0.5570 | 0.3532 | 0.055* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cl1 | 0.1035 (5) | 0.0997 (5) | 0.0472 (3) | −0.0123 (3) | 0.0123 (3) | 0.0172 (3) |
| N1 | 0.0440 (8) | 0.0626 (9) | 0.0425 (8) | 0.0058 (6) | 0.0082 (6) | 0.0026 (6) |
| N2 | 0.0364 (8) | 0.0858 (12) | 0.0428 (8) | −0.0052 (7) | 0.0048 (6) | 0.0083 (7) |
| C1 | 0.0414 (8) | 0.0494 (9) | 0.0409 (8) | 0.0059 (7) | 0.0061 (6) | −0.0034 (7) |
| C2 | 0.0582 (11) | 0.0722 (13) | 0.0430 (9) | 0.0070 (9) | 0.0072 (8) | 0.0058 (8) |
| C3 | 0.0574 (11) | 0.0673 (11) | 0.0424 (9) | 0.0083 (9) | −0.0051 (8) | −0.0042 (8) |
| C4 | 0.0481 (9) | 0.0476 (9) | 0.0515 (10) | 0.0039 (7) | 0.0006 (7) | −0.0127 (7) |
| C5 | 0.0452 (9) | 0.0486 (9) | 0.0439 (9) | −0.0008 (7) | 0.0049 (7) | −0.0019 (7) |
| C6 | 0.0535 (11) | 0.0693 (12) | 0.0705 (13) | −0.0074 (9) | −0.0066 (9) | −0.0119 (10) |
| C7 | 0.0379 (8) | 0.0485 (9) | 0.0409 (8) | −0.0039 (7) | 0.0027 (6) | −0.0004 (7) |
| C8 | 0.0436 (9) | 0.0535 (10) | 0.0512 (10) | 0.0057 (7) | 0.0059 (7) | −0.0012 (7) |
| C9 | 0.0539 (10) | 0.0521 (10) | 0.0541 (10) | 0.0051 (8) | −0.0019 (8) | 0.0089 (8) |
| C10 | 0.0572 (10) | 0.0488 (9) | 0.0411 (8) | −0.0110 (8) | 0.0052 (7) | 0.0025 (7) |
| C11 | 0.0440 (9) | 0.0518 (10) | 0.0495 (9) | −0.0053 (7) | 0.0101 (7) | −0.0027 (7) |
| C12 | 0.0373 (8) | 0.0517 (9) | 0.0486 (9) | 0.0024 (7) | 0.0032 (7) | 0.0034 (7) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cl1—C10 | 1.7376 (18) | C6—H6A | 0.9600 |
| N1—C2 | 1.335 (2) | C6—H6B | 0.9600 |
| N1—C1 | 1.339 (2) | C6—H6C | 0.9600 |
| N2—C1 | 1.368 (2) | C7—C8 | 1.383 (2) |
| N2—C7 | 1.400 (2) | C7—C12 | 1.391 (2) |
| N2—H2n | 0.857 (9) | C8—C9 | 1.380 (2) |
| C1—C5 | 1.398 (2) | C8—H8 | 0.9300 |
| C2—C3 | 1.366 (3) | C9—C10 | 1.373 (3) |
| C2—H2 | 0.9300 | C9—H9 | 0.9300 |
| C3—C4 | 1.396 (3) | C10—C11 | 1.367 (2) |
| C3—H3 | 0.9300 | C11—C12 | 1.380 (2) |
| C4—C5 | 1.375 (2) | C11—H11 | 0.9300 |
| C4—C6 | 1.500 (3) | C12—H12 | 0.9300 |
| C5—H5 | 0.9300 | | |
| | | | |
| C2—N1—C1 | 116.69 (15) | C4—C6—H6C | 109.5 |
| C1—N2—C7 | 128.17 (14) | H6A—C6—H6C | 109.5 |
| C1—N2—H2n | 117.2 (13) | H6B—C6—H6C | 109.5 |

| | | | |
|---|---|---|---|
| C7—N2—H2n | 114.6 (13) | C8—C7—C12 | 118.64 (15) |
| N1—C1—N2 | 114.12 (15) | C8—C7—N2 | 117.97 (15) |
| N1—C1—C5 | 122.47 (15) | C12—C7—N2 | 123.27 (15) |
| N2—C1—C5 | 123.36 (15) | C9—C8—C7 | 120.91 (16) |
| N1—C2—C3 | 124.59 (18) | C9—C8—H8 | 119.5 |
| N1—C2—H2 | 117.7 | C7—C8—H8 | 119.5 |
| C3—C2—H2 | 117.7 | C10—C9—C8 | 119.40 (16) |
| C2—C3—C4 | 119.00 (16) | C10—C9—H9 | 120.3 |
| C2—C3—H3 | 120.5 | C8—C9—H9 | 120.3 |
| C4—C3—H3 | 120.5 | C11—C10—C9 | 120.77 (16) |
| C5—C4—C3 | 117.32 (16) | C11—C10—Cl1 | 119.67 (14) |
| C5—C4—C6 | 120.81 (17) | C9—C10—Cl1 | 119.55 (14) |
| C3—C4—C6 | 121.87 (16) | C10—C11—C12 | 119.99 (16) |
| C4—C5—C1 | 119.92 (16) | C10—C11—H11 | 120.0 |
| C4—C5—H5 | 120.0 | C12—C11—H11 | 120.0 |
| C1—C5—H5 | 120.0 | C11—C12—C7 | 120.28 (15) |
| C4—C6—H6A | 109.5 | C11—C12—H12 | 119.9 |
| C4—C6—H6B | 109.5 | C7—C12—H12 | 119.9 |
| H6A—C6—H6B | 109.5 | | |

| | | | |
|---|---|---|---|
| C2—N1—C1—N2 | −177.70 (15) | C1—N2—C7—C8 | −144.79 (18) |
| C2—N1—C1—C5 | 0.0 (2) | C1—N2—C7—C12 | 39.4 (3) |
| C7—N2—C1—N1 | −167.92 (17) | C12—C7—C8—C9 | 0.6 (3) |
| C7—N2—C1—C5 | 14.4 (3) | N2—C7—C8—C9 | −175.42 (16) |
| C1—N1—C2—C3 | −0.7 (3) | C7—C8—C9—C10 | −0.8 (3) |
| N1—C2—C3—C4 | 1.0 (3) | C8—C9—C10—C11 | 0.3 (3) |
| C2—C3—C4—C5 | −0.6 (3) | C8—C9—C10—Cl1 | −178.88 (14) |
| C2—C3—C4—C6 | 178.85 (18) | C9—C10—C11—C12 | 0.2 (3) |
| C3—C4—C5—C1 | −0.1 (2) | Cl1—C10—C11—C12 | 179.44 (13) |
| C6—C4—C5—C1 | −179.50 (17) | C10—C11—C12—C7 | −0.4 (3) |
| N1—C1—C5—C4 | 0.4 (3) | C8—C7—C12—C11 | −0.1 (2) |
| N2—C1—C5—C4 | 177.85 (16) | N2—C7—C12—C11 | 175.77 (15) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2*n*···N1$^{i}$ | 0.86 (1) | 2.19 (1) | 3.029 (2) | 167 (2) |

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.