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N-(4-Chlorophenyl)ethanimidamide

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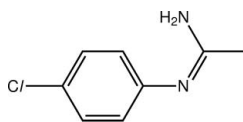
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Key indicators: single-crystal X-ray study; $T = 120$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.047; wR factor = 0.150; data-to-parameter ratio = 18.0.

A twisted conformation is found in the title compound, $\text{C}_8\text{H}_9\text{ClN}_2$, with the ethanimidamide residue being twisted substantially to the benzene ring [dihedral angle = $66.54(14)^\circ$]. The conformation about the $\text{C}=\text{N}$ double bond [$1.299(3)$ Å] is *Z*. A two-dimensional array with a zigzag topology is formed in the crystal structure via $\text{N}-\text{H}\cdots\text{N}$ and $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen-bonding interactions.

Related literature

For background to the synthesis of *N*-(*p*-chlorophenyl)-acetamide and related *N*-arylacetamidines used as reagents in the formation of anti-leishmanial compounds, see: Shearer *et al.* (1997); Rousselet *et al.* (1993); Patai (1975). For background to leishmaniasis, see: Ouellette *et al.* (2004); Croft *et al.* (2006); Ferreira *et al.* (2007); World Health Organization (2010).



Experimental

Crystal data

$\text{C}_8\text{H}_9\text{ClN}_2$
 $M_r = 168.62$
Orthorhombic, *Pbca*
 $a = 9.6460(9)$ Å

$b = 9.0192(4)$ Å
 $c = 19.3281(5)$ Å
 $V = 1681.53(18)$ Å³
 $Z = 8$

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Mo $K\alpha$ radiation
 $\mu = 0.39$ mm⁻¹

$T = 120$ K
 $0.35 \times 0.20 \times 0.10$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 2007)
 $T_{\min} = 0.792$, $T_{\max} = 1.000$

14006 measured reflections
1924 independent reflections
1185 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.081$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.150$
 $S = 1.05$
1924 reflections
107 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.34$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.33$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N2}-\text{H1n}\cdots\text{N1}^{\text{i}}$	0.88 (3)	2.08 (3)	2.965 (3)	176 (3)
$\text{N2}-\text{H2n}\cdots\text{Cl}^{\text{ii}}$	0.80 (3)	2.83 (3)	3.464 (2)	138 (3)

Symmetry codes: (i) $x - \frac{1}{2}, y, -z + \frac{3}{2}$; (ii) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$.

Data collection: COLLECT (Hooft, 1998); cell refinement: DENZO (Otwinowski & Minor, 1997) and COLLECT; data reduction: DENZO and COLLECT; 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: HG2664).

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supporting information

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S1. Comment

N-(*p*-Chlorophenyl)acetamidine and related *N*-arylacetamidines (Shearer *et al.* 1997; Rousselet *et al.* 1993; Patai, 1975) were synthesized for use as reagents in the formation of 5-(difluoromethyl)-2-methyl-1-(substituted-phenyl)-1*H*-imidazoles, which are active anti-leishmanial compounds (Ferreira *et al.*, 2007). Leishmaniasis is caused by several species of protozoan parasites transmitted by the bite of the female phlebotomine sand fly. This neglected disease is currently prevalent in four continents, being endemic in 88 countries, 72 of which are developing countries, threatening 350 millions worldwide (World Health Organization, 2010). The treatment of Leishmaniasis, currently, is dependent on old and highly toxic drugs (Croft *et al.*, 2006). In addition, the development of clinical resistance and the increase of co-infections leishmaniasis AIDS, in some countries is causing further worries. Thus, the development of new, efficient, and safe drugs for the treatment of this disease is imperative (Ouellette *et al.*, 2004; Croft *et al.*, 2006; Ferreira *et al.*, 2007). This contribution describes the synthesis and crystallographic characterisation of an *N*-(*p*-chlorophenyl)acetamidine derivative, (I).

The molecular structure of (I), Fig. 1, is twisted about the C1–N1 bond as seen in the value of the C2–C1–N1–C7 torsion angle of $-118.6(2)^\circ$; the dihedral angle formed between the benzene ring and ethanimidamide residue is $66.54(14)^\circ$. The molecule has approximate mirror symmetry with the non-hydrogen atoms of the ethanimidamide lying on the putative plane and the benzene ring being bisected by the plane. The conformation about the C7=N1 double bond [$1.299(3) \text{ \AA}$] is *Z*.

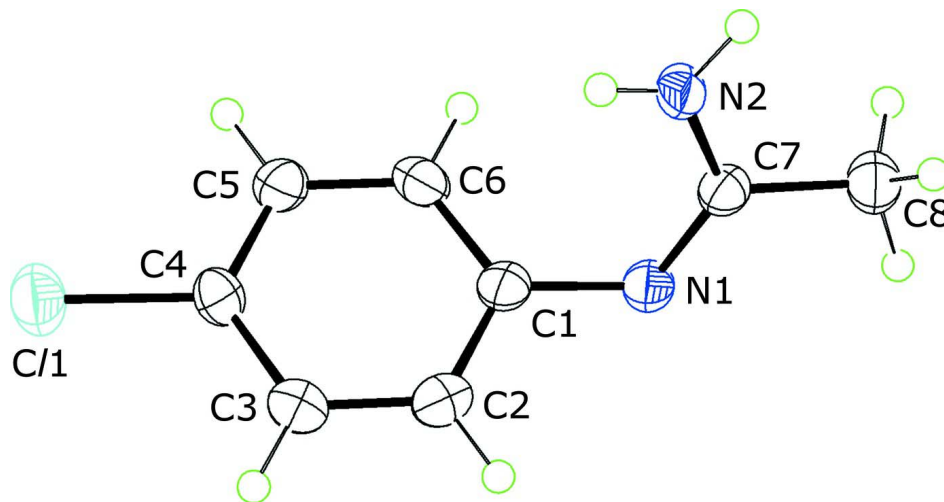
The crystal packing is dominated by N–H⋯N and N–H⋯Cl hydrogen bonding interactions, Table 1. These lead to the formation of 22-membered $\{\cdots\text{HNH}\cdots\text{ClC}_4\text{NCNH}\cdots\text{ClC}_4\text{N}\cdots\text{HNHCN}\}_2$ synthons that are connected into supramolecular arrays in the *ac* plane, Fig. 2; these have a zig-zag topology.

S2. Experimental

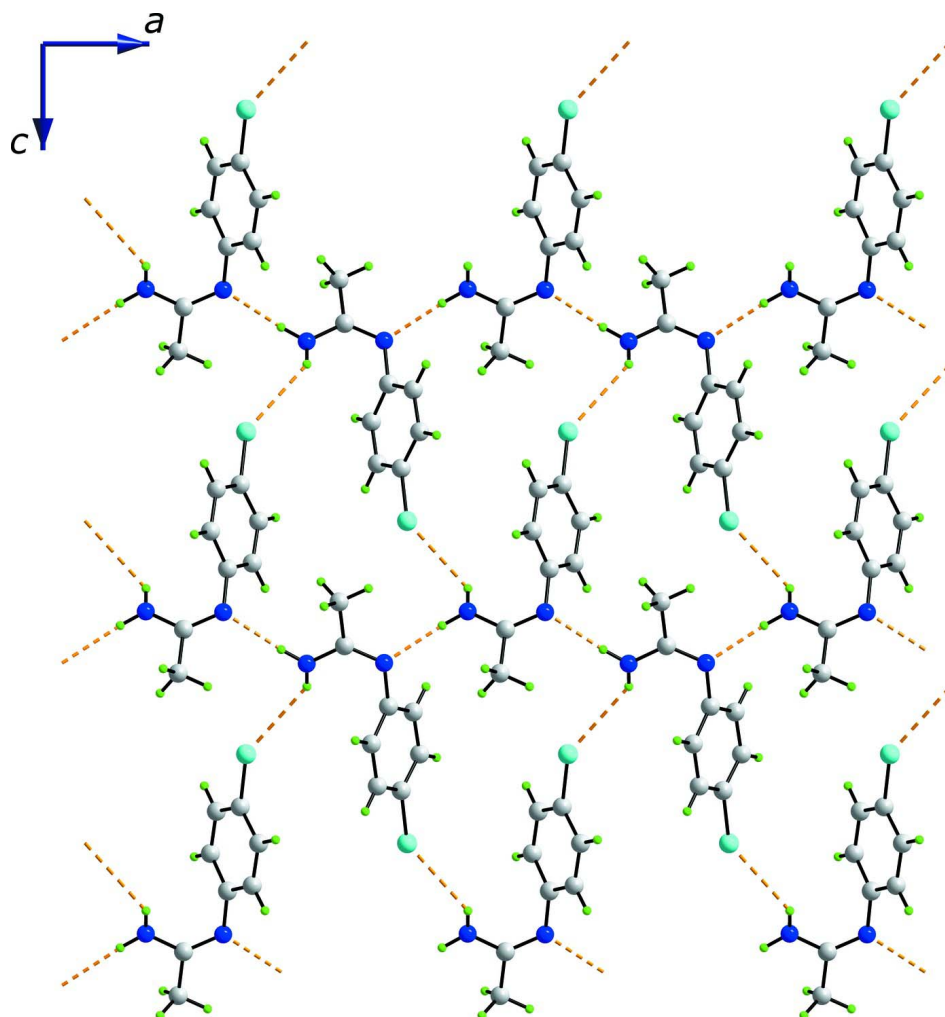
To a stirred solution of *p*-chloroaniline (10.75 mmol) in acetonitrile (40 ml) was bubbled hydrogen chloride. A precipitate was formed immediately. The resulting suspension was refluxed and became homogeneous. Upon complete reaction, as shown by TLC, the mixture was rotary evaporated and the residue partitioned between CH₂Cl₂ and saturated aqueous NaHCO₃. The aqueous layer was washed (3 times) with CH₂Cl₂, and the combined organic layers were dried over sodium sulfate, filtered, and the filtrate concentrated under reduced pressure to yield a white solid; yield 96%, m.p. 389–390 K. The sample used in the X-ray study was slowly grown from an ethanol solution of (I). IR (KBr, cm⁻¹): 3451, 3295, 3079, 1640, 1586, 1482. ¹H NMR (500 MHz, CDCl₃): δ 1.99 (*s*, 3H, CH₃); 4.53 (*br s*, 2H, 2); 6.77 (*d*, 2H, *J* = 8.0 Hz); 7.24 (*d*, 2H, *J* = 8.0 Hz) p.p.m. ¹³C NMR (125 MHz, CDCl₃): δ 21.59 (CH₃); 122.5 121.1; 128.6; 144.6; 155.3 (H₂N—C=N) p.p.m. EI—MS (*m/z*): 168 (M⁺, 68%); 153 (M⁺-15, 38%); 127 (M⁺-41, 100%); 111 (M⁺-57, 54%); 75 (M⁺-93, 42%).

S3. Refinement

The C-bound H atoms were geometrically placed ($C-H = 0.95-0.98 \text{ \AA}$) and refined as riding with $U_{iso}(H) = 1.2-1.5U_{eq}(C)$. The positions of the N-H atoms were refined with $U_{iso}(H) = 1.2U_{eq}(N)$.

**Figure 1**

The molecular structure of (I) showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level.

**Figure 2**

A view of a supramolecular array in (I) in the *ac* plane. The N–H···N and N–H···Cl hydrogen bonding interactions are shown as orange dashed lines. Colour code: Cl, cyan; N, blue; C, grey; and H, green.

N-(4-Chlorophenyl)ethanimidamide

Crystal data

$C_8H_9ClN_2$

$M_r = 168.62$

Orthorhombic, *Pbca*

Hall symbol: $-P\ 2ac\ 2ab$

$a = 9.6460\ (9)\ \text{\AA}$

$b = 9.0192\ (4)\ \text{\AA}$

$c = 19.3281\ (5)\ \text{\AA}$

$V = 1681.53\ (18)\ \text{\AA}^3$

$Z = 8$

$F(000) = 704$

$D_x = 1.332\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2182 reflections

$\theta = 2.9\text{--}27.5^\circ$

$\mu = 0.39\ \text{mm}^{-1}$

$T = 120\ \text{K}$

Block, colourless

$0.35 \times 0.20 \times 0.10\ \text{mm}$

Data collection

Nonius KappaCCD area-detector diffractometer	$T_{\min} = 0.792$, $T_{\max} = 1.000$
Radiation source: Enraf Nonius FR591 rotating anode	14006 measured reflections
10 cm confocal mirrors monochromator	1924 independent reflections
Detector resolution: 9.091 pixels mm ⁻¹	1185 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.081$
Absorption correction: multi-scan (SADABS; Sheldrick, 2007)	$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.0^\circ$
	$h = -11 \rightarrow 12$
	$k = -11 \rightarrow 9$
	$l = -25 \rightarrow 21$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.047$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.150$	$w = 1/[\sigma^2(F_o^2) + (0.081P)^2]$
$S = 1.05$	where $P = (F_o^2 + 2F_c^2)/3$
1924 reflections	$(\Delta/\sigma)_{\max} = 0.001$
107 parameters	$\Delta\rho_{\max} = 0.34 \text{ e } \text{\AA}^{-3}$
0 restraints	$\Delta\rho_{\min} = -0.33 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.43525 (8)	0.20450 (7)	0.43084 (3)	0.0430 (3)
N1	0.36389 (19)	0.4659 (2)	0.71058 (10)	0.0308 (5)
N2	0.1234 (2)	0.4244 (2)	0.70948 (11)	0.0305 (5)
H1N	0.044 (3)	0.438 (3)	0.7313 (13)	0.037*
H2N	0.124 (3)	0.379 (3)	0.6740 (14)	0.037*
C1	0.3774 (2)	0.4032 (3)	0.64327 (12)	0.0274 (6)
C2	0.4543 (2)	0.2746 (3)	0.63454 (14)	0.0316 (6)
H2	0.4938	0.2272	0.6738	0.038*
C3	0.4741 (3)	0.2144 (3)	0.56933 (13)	0.0317 (6)
H3	0.5266	0.1260	0.5638	0.038*
C4	0.4169 (2)	0.2837 (3)	0.51261 (13)	0.0286 (6)
C5	0.3428 (3)	0.4144 (3)	0.51965 (12)	0.0342 (6)
H5	0.3054	0.4627	0.4802	0.041*
C6	0.3243 (3)	0.4736 (3)	0.58491 (13)	0.0348 (6)
H6	0.2745	0.5638	0.5901	0.042*

C7	0.2408 (2)	0.4770 (3)	0.73731 (13)	0.0269 (6)
C8	0.2239 (3)	0.5538 (3)	0.80540 (14)	0.0367 (6)
H8A	0.3153	0.5706	0.8261	0.055*
H8B	0.1680	0.4919	0.8364	0.055*
H8C	0.1774	0.6492	0.7983	0.055*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0537 (5)	0.0446 (5)	0.0307 (4)	0.0051 (3)	0.0060 (3)	-0.0034 (3)
N1	0.0210 (11)	0.0449 (13)	0.0264 (12)	-0.0010 (9)	-0.0007 (9)	-0.0032 (9)
N2	0.0205 (11)	0.0461 (14)	0.0248 (12)	-0.0033 (9)	0.0019 (9)	-0.0061 (10)
C1	0.0171 (11)	0.0372 (14)	0.0280 (14)	-0.0036 (10)	-0.0002 (10)	0.0003 (11)
C2	0.0286 (13)	0.0340 (14)	0.0321 (15)	-0.0010 (11)	-0.0040 (11)	0.0052 (11)
C3	0.0297 (13)	0.0288 (13)	0.0367 (16)	0.0031 (10)	0.0014 (11)	0.0001 (11)
C4	0.0284 (13)	0.0306 (15)	0.0266 (14)	-0.0016 (10)	0.0072 (10)	0.0012 (10)
C5	0.0327 (14)	0.0437 (16)	0.0263 (14)	0.0074 (11)	0.0018 (11)	0.0068 (11)
C6	0.0296 (14)	0.0403 (15)	0.0345 (15)	0.0119 (11)	0.0047 (12)	0.0019 (11)
C7	0.0233 (12)	0.0329 (13)	0.0246 (14)	-0.0026 (10)	-0.0006 (10)	0.0029 (10)
C8	0.0281 (13)	0.0512 (16)	0.0307 (14)	-0.0059 (12)	0.0014 (11)	-0.0066 (12)

Geometric parameters (Å, °)

C11—C4	1.743 (3)	C3—C4	1.377 (4)
N1—C7	1.299 (3)	C3—H3	0.9500
N1—C1	1.425 (3)	C4—C5	1.385 (3)
N2—C7	1.340 (3)	C5—C6	1.381 (3)
N2—H1N	0.89 (3)	C5—H5	0.9500
N2—H2N	0.80 (3)	C6—H6	0.9500
C1—C2	1.387 (3)	C7—C8	1.496 (4)
C1—C6	1.393 (3)	C8—H8A	0.9800
C2—C3	1.386 (4)	C8—H8B	0.9800
C2—H2	0.9500	C8—H8C	0.9800
C7—N1—C1	118.52 (19)	C6—C5—C4	119.1 (2)
C7—N2—H1N	119.4 (17)	C6—C5—H5	120.5
C7—N2—H2N	121 (2)	C4—C5—H5	120.5
H1N—N2—H2N	119 (3)	C5—C6—C1	121.0 (2)
C2—C1—C6	118.7 (2)	C5—C6—H6	119.5
C2—C1—N1	119.5 (2)	C1—C6—H6	119.5
C6—C1—N1	121.6 (2)	N1—C7—N2	125.8 (2)
C3—C2—C1	120.8 (2)	N1—C7—C8	119.0 (2)
C3—C2—H2	119.6	N2—C7—C8	115.2 (2)
C1—C2—H2	119.6	C7—C8—H8A	109.5
C4—C3—C2	119.4 (2)	C7—C8—H8B	109.5
C4—C3—H3	120.3	H8A—C8—H8B	109.5
C2—C3—H3	120.3	C7—C8—H8C	109.5
C3—C4—C5	121.0 (2)	H8A—C8—H8C	109.5

C3—C4—C11	119.65 (19)	H8B—C8—H8C	109.5
C5—C4—C11	119.4 (2)		

Hydrogen-bond geometry (Å, °)

<i>D—H</i> ⋯ <i>A</i>	<i>D—H</i>	<i>H</i> ⋯ <i>A</i>	<i>D</i> ⋯ <i>A</i>	<i>D—H</i> ⋯ <i>A</i>
N2—H1n⋯N1 ⁱ	0.88 (3)	2.08 (3)	2.965 (3)	176 (3)
N2—H2n⋯C11 ⁱⁱ	0.80 (3)	2.83 (3)	3.464 (2)	138 (3)

Symmetry codes: (i) $x-1/2, y, -z+3/2$; (ii) $x-1/2, -y+1/2, -z+1$.