organic papers

2-Amino-5-(4-chlorophenyl)-1-methylimidazole

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The asymmetric unit of the title compound, $C_{10}H_{10}ClN_3$, contains four independent molecules, two of which are related by a pseudo-inversion centre. Intermolecular N—H···N and N—H···Cl interactions are present in the crystal.

Comment

According to the Cambridge Structural Database (Allen & Kennard, 1993) and to the best of our knowledge, the X-ray structure of the title compound, (I), has not been determined previously. The present analysis showed that four independent molecules are present in the asymmetric unit (molecules *A*, *B*, *C* and *D*). The planar phenyl ring (C6—C11) is twisted about the C5—C6 bond with respect to the planar imidazole moiety (N1—C5) by 22.8 (1), 29.8 (1), 28.9 (1) and 29.3 (1)° for molecules *A–D*, respectively. The main structural features of these four molecules are essentially identical, as shown in Table 1.
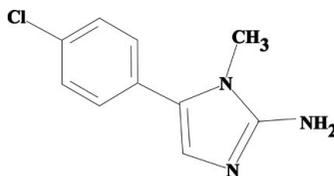
(I)

There are four endocyclic C—N bonds of the imidazole ring and one exocyclic C—N bond involving an amino group. As might be expected, the shortest C—N bond is the endocyclic C2=N3 double bond [mean 1.319 (3) Å], whereas the other C—N bond lengths follow the order C2—N1 [mean 1.359 (3)] < C2—N13 [mean 1.367 (3)] < C4—N3 [mean 1.377 (3)] < C5—N1 [mean 1.402 (3) Å]. A reason why the C2—N1 and C2—N13 single bonds are shorter than the other C—N bonds is the possibility of conjugation between the lone pairs of atoms N1 and N13 and the C2=N3 double bond.

Although amino–imino tautomerism is possible for α-aminoheterocycles, X-ray data confirm the amine form of the present structure.

A system of intermolecular N—H···N and N—H···Cl contacts is formed in the crystal (Table 2). The hydrogen bonds N13*C*—H10*C*···N3*C*[iii] (molecule *C*) and N13*D*—H10*D*···N3*D*[iv] (molecule *D*) [symmetry codes: (iii) $1-x$, $1-y$, $1-z$; (iv) $1-x$, $2-y$, $2-z$] link molecules *C* or *D* in the crystal into centrosymmetric dimers, whereas molecules *A* and *B* are linked by similar N—H···N bonds to form a pseudocentrosymmetric dimer (Fig. 1). Moreover, molecules *C* and *D* form endless chains, as shown in Fig. 2 and Table 2. Molecules
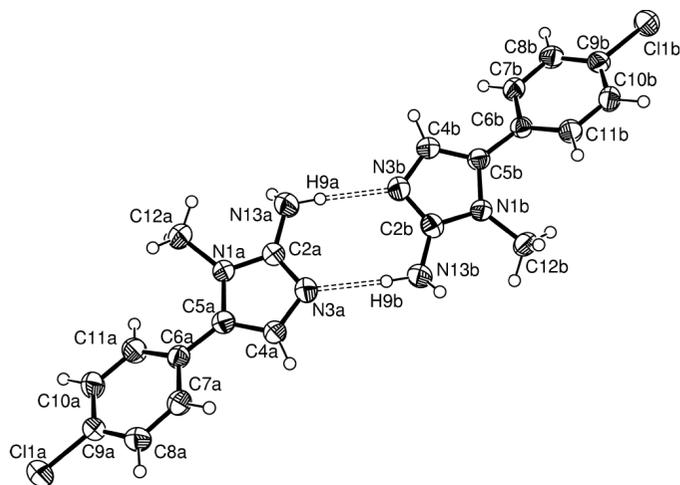
Figure 1
View of the pseudocentrosymmetric dimer of molecules A and B with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

A and B display similar packing, forming endless chains with long H···Cl contacts, as shown in Table 2.

Experimental

The title compound was prepared according to the procedure of Babaev & Belykh (2001). A single crystal of (I) was obtained while attempting to perform alkylation of the title compound with ethyl bromide. In a single experiment, 0.2 g of 2-amino-1-methyl-5-(4–chlorophenyl)imidazole was refluxed with excess EtBr in 10 ml MeCN for 3 h. After cooling the reaction mixture, the precipitated crystals were of the unchanged aminoimidazole.

Crystal data

$C_{10}H_{10}ClN_3$	$Z = 8$
$M_r = 207.66$	$D_x = 1.401$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.552$ (5) Å	Cell parameters from 25
$b = 12.833$ (5) Å	reflections
$c = 15.432$ (11) Å	$\theta = 16.0–17.0°$
$\alpha = 95.53$ (2)°	$\mu = 0.35$ mm^{-1}
$\beta = 106.57$ (2)°	$T = 293$ (2) K
$\gamma = 97.02$ (2)°	Prism, colourless
$V = 1969.0$ (18) Å^3	$0.3 \times 0.3 \times 0.3$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{max} = 27.0°$
ω scans	$h = -13 \rightarrow 12$
Absorption correction: none	$k = -16 \rightarrow 16$
8918 measured reflections	$l = 0 \rightarrow 19$
8591 independent reflections	2 standard reflections
5153 reflections with $I > 2\sigma(I)$	every 200 reflections
$R_{int} = 0.017$	frequency: 120 min
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.051$	$+ 0.5308P]$
$wR(F^2) = 0.133$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} = 0.047$
8591 reflections	$\Delta\rho_{max} = 0.27$ e Å^{-3}
666 parameters	$\Delta\rho_{min} = -0.41$ e Å^{-3}
All H-atom parameters refined	

Table 1
Selected geometric parameters (Å, °).

Cl1A—C9A	1.740 (3)	Cl1C—C9C	1.740 (2)
N1A—C2A	1.360 (3)	N1C—C2C	1.356 (3)
N1A—C5A	1.400 (3)	N1C—C5C	1.404 (3)
N1A—C12A	1.461 (3)	N1C—C12C	1.455 (3)
C2A—N3A	1.323 (3)	C2C—N3C	1.316 (3)
C2A—N13A	1.367 (3)	C2C—N13C	1.366 (3)
N3A—C4A	1.375 (3)	N3C—C4C	1.382 (3)
C4A—C5A	1.360 (3)	C4C—C5C	1.358 (3)
C5A—C6A	1.447 (3)	C5C—C6C	1.454 (3)
C6A—C11A	1.398 (3)	C6C—C11C	1.396 (3)
C6A—C7A	1.398 (3)	C6C—C7C	1.407 (3)
C7A—C8A	1.373 (4)	C7C—C8C	1.375 (4)
C8A—C9A	1.374 (4)	C8C—C9C	1.375 (4)
C9A—C10A	1.374 (4)	C9C—C10C	1.388 (3)
C10A—C11A	1.384 (4)	C10C—C11C	1.380 (3)
Cl1B—C9B	1.737 (3)	Cl1D—C9D	1.738 (2)
N1B—C2B	1.360 (3)	N1D—C2D	1.359 (3)
N1B—C5B	1.402 (3)	N1D—C5D	1.402 (3)
N1B—C12B	1.450 (3)	N1D—C12D	1.454 (3)
C2B—N3B	1.319 (3)	C2D—N3D	1.317 (3)
C2B—N13B	1.371 (3)	C2D—N13D	1.365 (3)
N3B—C4B	1.376 (3)	N3D—C4D	1.376 (3)
C4B—C5B	1.363 (3)	C4D—C5D	1.360 (3)
C5B—C6B	1.457 (3)	C5D—C6D	1.457 (3)
C6B—C11B	1.395 (3)	C6D—C11D	1.397 (3)
C6B—C7B	1.399 (3)	C6D—C7D	1.401 (3)
C7B—C8B	1.378 (4)	C7D—C8D	1.373 (3)
C8B—C9B	1.379 (4)	C8D—C9D	1.380 (4)
C9B—C10B	1.384 (4)	C9D—C10D	1.384 (3)
C10B—C11B	1.383 (4)	C10D—C11D	1.380 (4)
C2A—N1A—C5A	107.06 (19)	C2C—N1C—C5C	106.64 (19)
C2A—N1A—C12A	122.8 (2)	C2C—N1C—C12C	123.5 (2)
C5A—N1A—C12A	128.7 (2)	C5C—N1C—C12C	128.4 (2)
N3A—C2A—N1A	112.2 (2)	N3C—C2C—N1C	112.7 (2)
N3A—C2A—N13A	125.0 (2)	N3C—C2C—N13C	124.5 (2)
N1A—C2A—N13A	122.7 (2)	N1C—C2C—N13C	122.8 (2)
C2A—N3A—C4A	104.3 (2)	C2C—N3C—C4C	104.3 (2)
C5A—C4A—N3A	112.4 (2)	C5C—C4C—N3C	111.9 (2)
C4A—C5A—N1A	104.1 (2)	C4C—C5C—N1C	104.4 (2)
C4A—C5A—C6A	129.6 (2)	C4C—C5C—C6C	129.6 (2)
N1A—C5A—C6A	126.2 (2)	N1C—C5C—C6C	125.5 (2)
C11A—C6A—C7A	116.0 (2)	C11C—C6C—C7C	117.1 (2)
C11A—C6A—C5A	124.2 (2)	C11C—C6C—C5C	123.7 (2)
C7A—C6A—C5A	119.7 (2)	C7C—C6C—C5C	119.1 (2)
C8A—C7A—C6A	122.7 (2)	C8C—C7C—C6C	121.6 (2)
C7A—C8A—C9A	119.2 (2)	C7C—C8C—C9C	119.6 (2)
C10A—C9A—C8A	120.8 (2)	C8C—C9C—C10C	120.8 (2)
C10A—C9A—Cl1A	118.8 (2)	C8C—C9C—Cl1C	120.09 (19)
C8A—C9A—Cl1A	120.4 (2)	C10C—C9C—Cl1C	119.14 (19)
C9A—C10A—C11A	119.2 (2)	C11C—C10C—C9C	119.2 (2)
C10A—C11A—C6A	122.1 (2)	C10C—C11C—C6C	121.7 (2)
C2B—N1B—C5B	106.56 (19)	C2D—N1D—C5D	106.24 (19)
C2B—N1B—C12B	124.0 (2)	C2D—N1D—C12D	123.7 (2)
C5B—N1B—C12B	129.3 (2)	C5D—N1D—C12D	127.9 (2)
N3B—C2B—N1B	112.7 (2)	N3D—C2D—N1D	112.8 (2)
N3B—C2B—N13B	124.9 (2)	N3D—C2D—N13D	124.9 (2)
N1B—C2B—N13B	122.3 (2)	N1D—C2D—N13D	122.2 (2)
C2B—N3B—C4B	104.3 (2)	C2D—N3D—C4D	104.4 (2)
C5B—C4B—N3B	112.0 (2)	C5D—C4D—N3D	111.8 (2)
C4B—C5B—N1B	104.4 (2)	C4D—C5D—N1D	104.8 (2)
C4B—C5B—C6B	129.5 (2)	C4D—C5D—C6D	129.4 (2)
N1B—C5B—C6B	126.0 (2)	N1D—C5D—C6D	125.4 (2)
C11B—C6B—C7B	117.0 (2)	C11D—C6D—C7D	117.2 (2)
C11B—C6B—C5B	123.9 (2)	C11D—C6D—C5D	123.2 (2)
C7B—C6B—C5B	119.1 (2)	C7D—C6D—C5D	119.5 (2)
C8B—C7B—C6B	122.0 (2)	C8D—C7D—C6D	121.8 (2)
C7B—C8B—C9B	119.2 (2)	C7D—C8D—C9D	119.4 (2)
C8B—C9B—C10B	120.8 (2)	C8D—C9D—C10D	120.6 (2)
C8B—C9B—Cl1B	120.02 (19)	C8D—C9D—Cl1D	119.71 (19)
C10B—C9B—Cl1B	119.2 (2)	C10D—C9D—Cl1D	119.7 (2)
C11B—C10B—C9B	119.2 (2)	C11D—C10D—C9D	119.4 (2)
C10B—C11B—C6B	121.8 (2)	C10D—C11D—C6D	121.5 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
N13C—H10C···N3C[i]	0.85 (3)	2.11 (3)	2.955 (3)	173 (3)
N13D—H10D···N3D[ii]	0.85 (3)	2.11 (3)	2.949 (3)	175 (3)
N13A—H9A···N3B[iii]	0.89 (3)	2.09 (3)	2.979 (4)	176 (2)
N13B—H9B···N3A[iv]	0.89 (3)	2.11 (3)	2.998 (3)	176 (3)
N13C—H9C···Cl1C[iii]	0.81 (4)	2.90 (4)	3.646 (3)	154 (3)
N13D—H9D···Cl1D[iii]	0.82 (3)	2.91 (4)	3.650 (3)	152 (3)
N13A—H10A···Cl1A[iii]	0.78 (3)	3.21 (3)	3.696 (3)	122 (3)
N13B—H10B···Cl1B[iv]	0.82 (3)	3.11 (3)	3.729 (3)	134 (3)

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

All H atoms were refined isotropically; the C—H distances were in the range 0.78 (3)–1.04 (3) Å.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *WinGX*98 (Farrugia, 1998) and *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1998) and *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97.
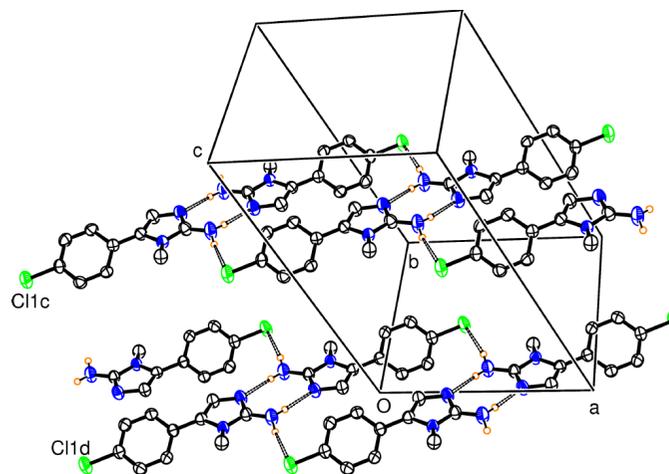
Figure 2
Part of the structure showing the formation of endless chains involving N—H···Cl hydrogen bonds. For the sake of clarity, H atoms not participating in the hydrogen bonding have been omitted, and no labels have been shown apart from those of the Cl atoms to differentiate the two chains formed by molecules *C* and *D*.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
Babaev, E. V. & Belykh, E. N. (2001). Unpublished work.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Farrugia, L. J. (1998). *ORTEP*-3 for Windows and *WinGX*98. University of Glasgow, Scotland.
Harms, K. & Wocadlo, S. (1995). *XCAD*4. University of Marburg, Germany.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.