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6-Chloro-3-chloromethylene-7-methyl-1,2,4-triazolo[4,3-*b*]pyridazine

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.064
wR factor = 0.114
Data-to-parameter ratio = 19.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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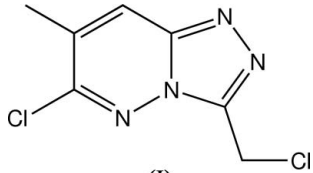
The title compound, $C_7H_6Cl_2N_4$, forms a layered structure stabilized by short C—H···N and Cl···Cl contacts.

Comment

Azolopyridazines are important as synthetic intermediates and as pharmaceutical hypotensive (Katrusiak *et al.*, 2001), anti-convulsant (Moreau *et al.*, 1998), and sedative (Rubat *et al.*, 1990) agents.



(I)

The title compound, (I), has been synthesized from 3-chloro-6-hydrazino-4-methylpyridazine and α-chloroacetic acid. It forms part of a series of azolopyridazine derivatives prepared for pharmaceutical evaluation aimed at obtaining new hypertensive drugs (Katrusiak *et al.*, 2005). The purpose of this study was to confirm the molecular structure of (I), the configuration of the chloromethyl substituent, and to identify the association in the crystalline state.

The structure of (I) (Fig. 1) is the first report of a 7-methylazolopyridazine molecule substituted by chloromethyl at the C3 position. The azolopyridazine system is essentially planar; the planes through the pyridazine and triazole rings are inclined by 1.4 (2)°. The only significant non-H distortion of the molecular planarity is seen in the position of atom Cl1; the N2—C3—C10—Cl1 and N4—C3—C10—Cl1 torsion angles are 105.4 (3) and −74.9 (3)°, respectively. Practically the same conformation was reproduced by *PM3* and *AM1* calculations (104.4 and −74.7°, and 104.3 and −74.6°,

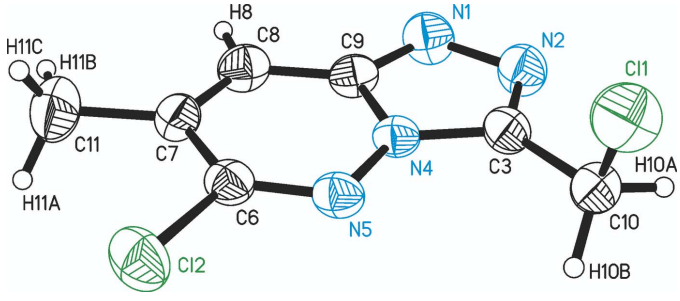


Figure 1
Atom numbering scheme for (I), with displacement ellipsoids drawn at the 50% probability level.

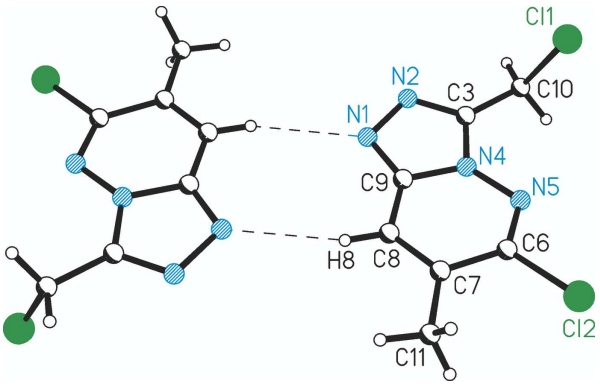


Figure 2
The centrosymmetric dimer of molecules linked *via* C8—H···N1 interactions (dashed lines).

respectively), indicating that this configuration is dictated by steric effects rather than crystal packing.

The pyridazine CH group is located on the same side of the molecule as N1, which is a potential H-acceptor in hydrogen bonding. In the crystal structure, the molecules form two short C8—H8–N1^{i} contacts about a centre of symmetry, as shown in Fig. 2 [symmetry code (i): $2-x$, $2-y$, $-z$]. This contact is characterized by an H8···N1^{i} distance of 2.50 (3) Å, a C8···N1^{i} distance of 3.390 (3) Å, and an angle of 166 (1)° at H8. According to the *PM3* and *AM1* calculations, H8 is positively charged (0.14 and 0.07 e, respectively) and N1 carries a residual negative charge (−0.05 and −0.04 e, respectively). On the opposite side of the molecule, two Cl atoms interact with the Cl atoms of the neighbouring molecules, as illustrated in Fig. 3. Each Cl atom forms two short

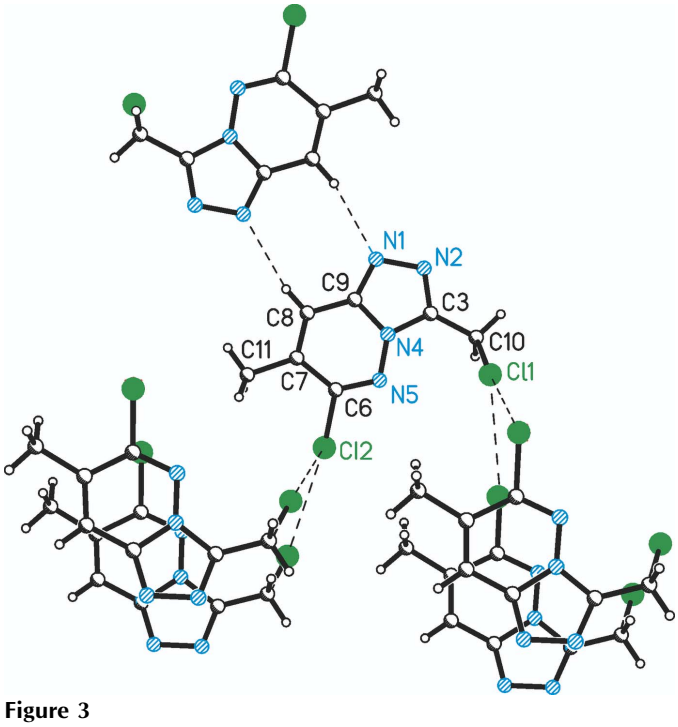


Figure 3
Molecules of (I) interacting *via* Cl···Cl contacts (dashed lines).

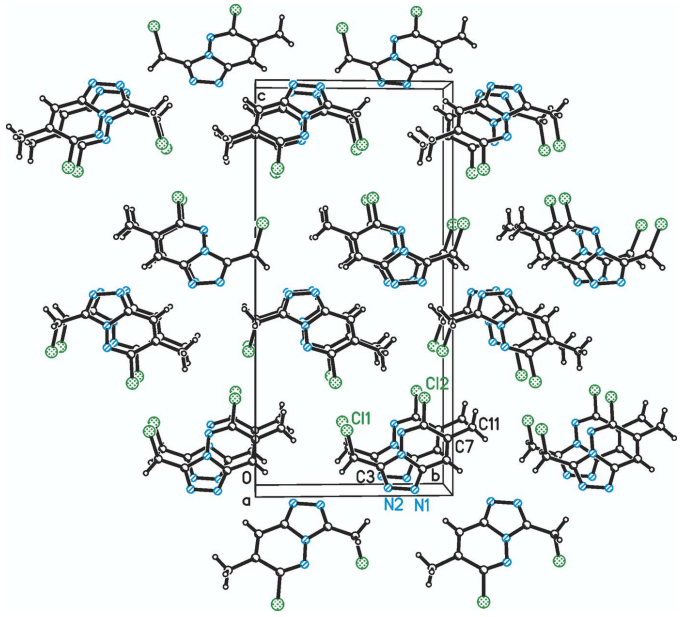


Figure 4
Molecular packing in (I), shown as an autostereographic projection (Katrusiak, 2001).

contacts with other Cl atoms and so each molecule forms four such contacts. The parameters associated with these contacts are Cl1···Cl2^{ii} = 3.467 (1) Å [symmetry code (ii): $\frac{1}{2}-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$] and Cl1···Cl2^{iii} = 3.495 (1) Å [symmetry code (iii): $\frac{3}{2}-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$]. Sheets connected by these Cl···Cl interactions extend parallel to (001), as shown in Fig. 4. The molecules of adjacent sheets interact along [001] by the CH···N contacts, as detailed above.

The crystal structure of (I) can exemplify the role of intermolecular interactions for molecular arrangement of very many biologically and technologically important substances. However, the energetics and contribution of specific interactions to the molecular association and crystal cohesion can be controversial. For example, and relevant to the present report, the Cl···Cl interactions are sometimes described as main contributors, comparable to hydrogen bonds, for intermolecular association (Legon, 1999; Metrangolo & Resnati, 2001). Another explanation of the existence of short Cl···Cl contacts was postulated by Grineva & Zorky (1998; 2000). Here, the contacts involving Cl atoms are least favourable, and therefore the Cl···Cl contacts formed are termed the 'chlorophobic' effect. Recently, high-pressure studies of chlorinated simple alkanes have been carried out to resolve this controversy (Bujak *et al.*, 2004; Podsiadło *et al.*, 2005). However, further systematic theoretical and experimental studies are still needed to resolve this issue. In the present study, the PM3 and AM1 calculations showed the Cl atoms have opposite net atomic charges: Cl1 −0.09 and −0.05 e, and Cl2 0.06 and 0.16 e, respectively. Thus, in the structure of (I) consistently all CH···N and Cl···Cl interactions involve atoms with opposite net atomic charges, an observation which confirms the contribution of electrostatic attraction to the crystal's cohesion forces.

Experimental

Compound (I) was obtained by refluxing 3-chloro-6-hydrazino-4-methylpyridazine (0.16 g, 0.01 mol) and α-chloroacetic acid (0.09 g, 0.01 mol) for 3 h. After cooling, the reaction mixture was poured into water and extracted with CH_2Cl_2. The extract was dried over $MgSO_4$ and evaporated to dryness. The residue was recrystallized from ethanol solution [yield 82%; m.p. (uncorrected) = 356 K].

Crystal data

$C_7H_6Cl_2N_4$
M_r = 217.06
Monoclinic, $P2_1/n$
a = 4.2640 (9) Å
b = 10.144 (2) Å
c = 21.308 (4) Å
β = 91.47 (3)°
V = 921.3 (3) Å^3
Z = 4
D_x = 1.565 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2037 reflections
θ = 2.2–29.9°
μ = 0.66 mm^{-1}
T = 293 (2) K
Prism, colourless
0.27 × 0.23 × 0.16 mm

Data collection

Kuma KM-4-CCD diffractometer
ω scans
Absorption correction: none
8015 measured reflections
2392 independent reflections
1500 reflections with $I > 2\sigma(I)$
R_{int} = 0.060
θ_{max} = 29.9°
$h = -4 \rightarrow 5$
$k = -13 \rightarrow 12$
$l = -24 \rightarrow 28$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.114
S = 1.10
2392 reflections
125 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.038P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Methylene and methyl H atoms were constrained to their ideal geometries with C—H = 0.96 or 0.97 Å, respectively, and with U(H) = 1.3U_{eq}(C). H8 was refined freely; C8—H = 0.91 (3) Å.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: Stereochemical Workstation Operation Manual (Siemens, 1989); software used to prepare material for publication: *SHELXL97*.

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