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RESEARCH ARTICLE

Crystal and Molecular Structure of 5-Amino-1-(2-chloro-ethyl)-1*H*-pyrazole-4-carbonitrile

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Abstract: In the title compound 5-Amino-1-(2-chloro-ethyl)-1*H*-pyrazole-4-carbonitrile (C_6 H_7 Cl N_4), the pyrazole ring is substituted with amino, carbonitrile and the 2-chloro-ethyl groups. The crystal structure is stabilized by intermolecular N-H…N and C-H…Cl interactions, the former interaction results in centrosymmetric dimers corresponding to R^2_2 (12) graph-set motif and the latter interaction forms molecular chains along the crystallographic 'b' axis.

Keywords: Pyrazole derivative, Crystal structure, N-H…N and C-H…Cl weak interactions

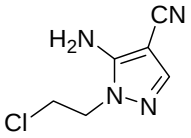
Introduction

Pyrazoles and their derivatives represent one of the most active classes of compounds that are reported to have a wide range of biological activities including antibacterial, fungicidal, herbicidal, and insecticidal activities[1–5], they also possess useful agricultural[6] properties and serve as synthons for other pyrazolo fused bioactive heterocycles[7-8]. It is been shown by the earlier groups that the *N*-unsubstituted pyrazoles in the solid state show several possible N-H…N hydrogen-bonding interactions that's leads to different patterns such as monomer, dimer, trimer, tetramer, hexamer and catemer, wherein both the N atoms of the pyrazoles are involved in the interactions[9-16].

In this context and as a part of our ongoing research on pyrazoles and their crystal structures, herein, we report the crystal and molecular structure of the title compound so that its supramolecular structure could be investigated in terms of possible intermolecular interactions.

Experimental

The compound 5-amino-1-(2-chloro-ethyl)-1*H*-pyrazole-4-carbonitrile was synthesized by two step reaction sequence following the procedure reported earlier[17 -18]. All chemicals were obtained from a commercial source. Solvents were dried and purified with known conventional methods.



Scheme 1. 5-Amino-1-(2-chloro-ethyl)-1*H*-pyrazole-4-carbonitrile

X-ray analysis

Single crystals of the compound were obtained from the solvent DMF. Transparent white plate like crystal was selected for x-ray diffraction analysis. The x-ray diffraction data for the compound ($C_6 H_7 Cl N_4$) was collected on a Bruker Smart CCD Area Detector System, using MoKα (0.71073Å) radiation. Intensity data were collected using a single crystal with dimensions 0.18x0.16x0.16 mm up to a maximum of 26.99° in the ω–ϕ scan mode. The data were reduced using SAINTPLUS[19]. The structure was solved by direct methods using SHELXS97[20] and refined using difference Fourier syntheses using SHELXL97[20]. The positions and anisotropic displacement parameters of all non-hydrogen atoms were included in the full-matrix least-square refinement using SHELXL97[20] and the procedure was carried out for a few cycles until convergence was reached. A total of 9050 reflections were collected, out of which 1712 [R (int) = 0.0240] were independent reflections. The number of reflections satisfying I>2σ (I) criteria were 4013. These were treated as observed. The H atoms were placed at calculated positions in the riding model approximation (C---H 0.93Å), with their temperature factors set to 1.2 times those of the equivalent isotropic temperature factors of the parent atoms. All other non-H atoms were refined anisotropically. The R factor for observed data finally converged to R=0.0529. The maximum and minimum values of residual electron density were 0.422 and -0.554eÅ^{-3}. Molecular diagrams were generated using ORTEP[21]. The mean plane calculation was done using the program PARST[22].

Results and Discussion

Figure 1 shows the ORTEP diagram of the molecule with thermal ellipsoids drawn at 50% probability. Figure 2 and 3 shows the hydrogen bond interactions and crystal packing in the compound. The details of crystal data and refinements are given in Table 1. Table 2 shows the respective hydrogen bond interactions for compound.

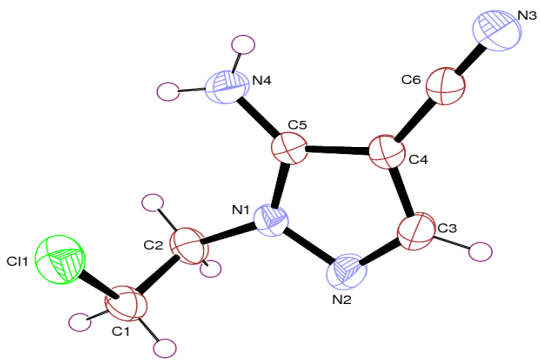


Figure 1. The molecular structure of the compound ($C_6 H_7 Cl N_4$) with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are presented as small spheres of arbitrary radius

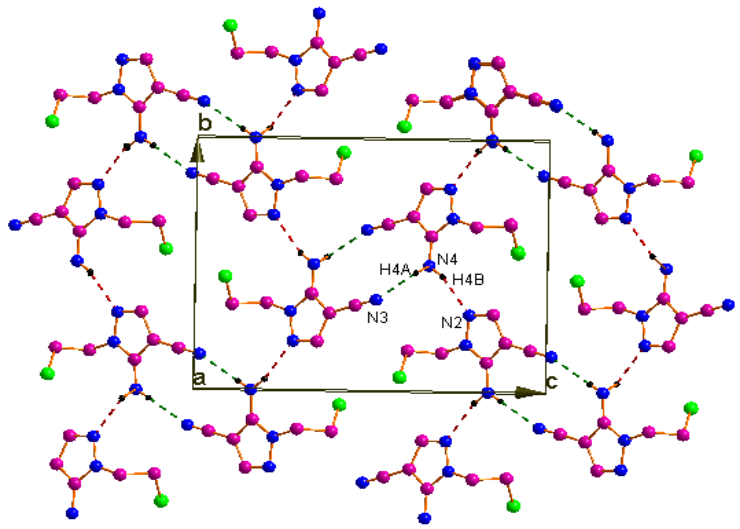


Figure 2. Packing of the molecules in crystal of the compound (C_6 H_7 Cl N_4). Dotted lines indicate, N-H….N intermolecular interaction; the hydrogen's are omitted for clarity

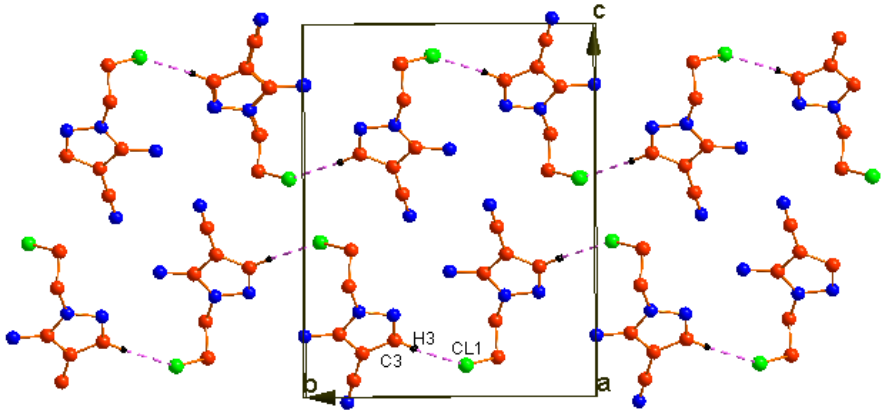


Figure 3. Packing of the molecules in crystal of the compound (C_6 H_7 Cl N_4). Dotted lines indicate, C-H….Cl intermolecular interaction.

In the compound, the pyrazole ring is substituted with amino, carbonitrile and the 2-chloro-ethyl groups. The N(1)-N(2) and C(5)-N(1) bond lengths in the pyrazole ring are shorter{1.375(2)Å and 1.349(1)Å} than the distance characteristics of a single N-N bond (1.45 Å) and C-N(1.45 Å). The *cis* orientation of 2-chloro-ethyl group with respect to the C5-N1 bond is described by the torsion angle C(5)-N(1)-C(2)-C(1) [-107.795(4)°]. The N(1) atom of the pyrazole ring is in the planar trigonal configuration. The molecular structure of the title compound is stabilized by intermolecular N-H…N and C-H…Cl interactions. There are two types of N-H…N intermolecular interactions (Table 1); N4-H4B…N3 hydrogen bond forms centrosymmetric head-to-head dimers about inversion centers corresponding to graph set $R^2_2(12)$ motif[23]. While the N4-H4A…N2 hydrogen bonds generate chains of molecules in a zigzag pattern along the crystallographic 'a' axis. The C-H…Cl intermolecular interaction forms two dimensional molecular chains along the crystallographic 'b' axis.

Table 1. Crystal data and structure refinement of the compound

Empirical formula	$C_6 H_7 Cl N_4$
Formula weight	170.61
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	
a = 4.8215(2)Å	
b = 11.2648(6)Å	
c = 14.5553(7)Å	
β (°) = 95.275(2)	
Volume	787.20(7) Å3
Z,	4
Calculated density ($Mg/m^{3)}$	1.440
Absorption coefficient (mm^{-1})	0.422
F(000)	352
Crystal size	0.18x0.16x0.16 mm
Theta range for data collection	2.29 to 26.99 deg.
Limiting indices	-6<=h<=5, -14<=k<=14, -16<=l<=18
Reflections collected/unique	9050/1712[R(int)=0.0240]
Completeness to theta	26.99 100.0 %
Max. and min. transmission	0.9355 and 0.9278
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1712 / 0 / 106
Goodness-of-fit on F^2	1.200
Final R indices [I> 2sigma (I)]	R1 = 0.0529, wR2 = 0.1386
R indices (all data)	R1 = 0.0553, wR2 = 0.1417
Largest diff. peak and hole ($e.A^{-3}$)	Largest diff. peak and hole ($e.A^{-3}$)

Table 2. Non-bonded interactions and possible hydrogen bonds (Å°) for the compound (*D*-donor; *A*-acceptor; *H*-hydrogen)

D—H· · ·A	D—H	H· · ·A	D· · ·A	D—H· · ·A
N4-H4A ...$N2^{i}$	0.879	2.233	3.083(3)	162
N4-H4A ...$N2^{i}$	0.789	2.254	3.775(2)	171
C3-H3...$Cl1^{ii}$	0.930	2.888	3.775(2)	161

Symmetry code: (i) -x+1,+y+1/2,-z+1/2 (ii) -x,-y+1,-z+1 (iii) -x,+y-1/2,z+1/2

Conclusion

In this paper we are hereby reporting the crystal structure of a pyrazole derivative. Weak interactions and supramolecular assembly, involving several hydrogen bonding interactions of the amino carbonitrile and the 2-chloro ethyl group have been demonstrated. Hydrogen bonds are main non-covalent interactions in the molecule influences the crystal packing.

Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge data centre. The deposition number is CCDC 795601.

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