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5-Amino-3-anilino-*N*-(chlorophenyl)-1*H*-pyrazole-4-carboxamide ethanol solvate

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Key indicators

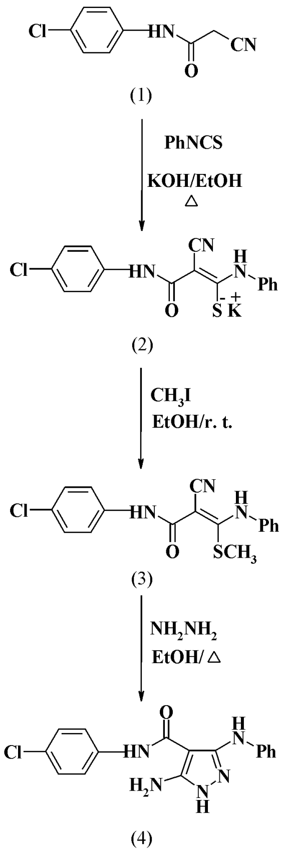
Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.003 Å
R factor = 0.035
wR factor = 0.083
Data-to-parameter ratio = 12.2

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

In the title compound, $C_{16}H_{14}ClN_5O{\cdot}C_2H_6O$, the main residue is approximately planar except for the aniline group. Classical intramolecular hydrogen bonds are observed from the amino N atom to the carbonyl O atom and from the carboxamide N atom to the aniline N atom. Four further hydrogen bonds connect the residues to form layers parallel to (101).

Comment

During the course of our studies directed toward exploring the synthetic potential of ketene dithioacetals for new classes of novel antimetabolites (Elgemeie *et al.*, 1997, 1999, 2000), we have recently reported various successful approaches for the synthesis of mercaptopurine and thioguanine analogues by the reaction of ketene dithioacetals with diazoles containing amino and active methylene functions (Elgemeie *et al.*, 1998, 2001, 2002).



In an extension of this work, the present paper describes a novel synthesis of a 5-aminopyrazole by the reaction of a ketene *N*,*S*-acetal with an amine. The cyanoacetanilide derivative (1) reacted with phenyl isothiocyanate in KOH–EtOH to give the corresponding stable potassium salt, (2). The latter, on alkylation with methyl iodide in ethanol, afforded the novel ketene *N,S*-acetal (3). Reaction of compound (3) with hydrazine in refluxing ethanol gave the corresponding 5-aminopyrazole derivative (4). The structure (4) was supported by its mass (m/z = 327), which agrees with the empirical formula. In order to establish unambiguously the structure and stereospecifity of the product (4), its crystal structure was determined.

The X-ray analysis (Fig. 1) confirms the exclusive presence of the pyrazole form (4) in the solid state. The compound crystallizes with one molecule of ethanol, which is well ordered. Bond lengths and angles may be regarded as normal. Apart from the aniline group, the molecule is approximately planar (r.m.s. deviation of all other non-H atoms: 0.102 Å), a form supported by the intramolecular hydrogen bonds from N3 to O1 and from N5 to N4 (and perhaps also from C17 to O1). The aniline group makes an interplanar angle of 81.55 (3)° to the main plane.

The ethanol molecule is hydrogen bonded to atom N2. This hydrogen bond, together with three classical intermolecular hydrogen bonds, combine to form layers of residues parallel to (101) (Table 2 and Fig. 2). The potential hydrogen-bond donor N3—H031 is, however, not involved in hydrogen bonding. The layers are linked by a Cl$\cdots$Cl interaction: Cl$\cdots$Cl^{v} = 3.6286 (11) Å, with C15—Cl$\cdots$Cl^{v} = 101.82 (7)° [symmetry code: (v) $-x, 2-y, 1-z$].

Experimental

A mixture of ketene *N,S*-acetal (3) (0.01 mol) and hydrazine (0.01 mol) was refluxed in ethanol for 30 min. The solid product was collected and recrystallized from ethanol in 78% yield (m.p. 388 K) and contained crystals suitable for X-ray analysis.

Crystal data

$C_{16}H_{14}ClN_5O\cdot C_2H_6O$
M_r = 373.84
Monoclinic, $P2_1/n$
a = 10.6757 (10) Å
b = 7.7798 (9) Å
c = 21.919 (2) Å
β = 99.14 (1)°
V = 1797.3 (3) Å^3
Z = 4

D_x = 1.382 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 63 reflections
θ = 4.5–12.5°
μ = 0.24 mm^{-1}
T = 173 (2) K
Tablet, colourless
0.4 × 0.4 × 0.3 mm

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
4927 measured reflections
3167 independent reflections
2349 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.022

$\theta_{\rm max}$ = 25.0°
$h = -12 \rightarrow 12$
$k = -9 \rightarrow 4$
$l = 0 \rightarrow 25$
3 standard reflections every 247 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.083
S = 0.93
3167 reflections
260 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.001
$\Delta\rho_{\rm max}$ = 0.19 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.27 e Å^{-3}

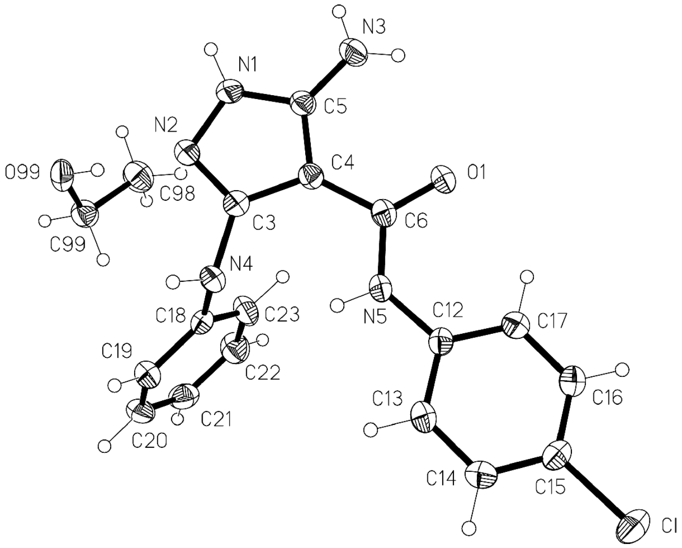


Figure 1
The formula unit of compound (4) in the crystal. Displacement ellipsoids are drawn at the 50% probability level. H-atom radii are arbitrary.

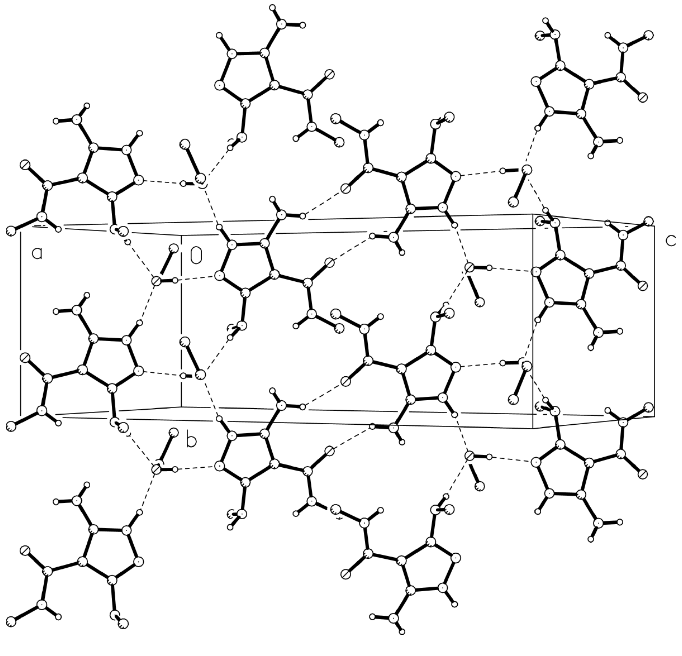


Figure 2
Packing diagram of compound (4), with the view direction perpendicular to (101). For clarity, phenyl rings are represented only by their *ipso* C atoms, and H atoms not involved in hydrogen bonding have been omitted. Dashed lines represent hydrogen bonds.

Table 1
Selected geometric parameters (Å, °).

N1—N2	1.378 (2)		
C5—N1—N2	112.53 (15)	C3—N2—N1	104.24 (14)
N4—C3—C4—C5	175.67 (16)	C6—N5—C12—C17	−8.0 (3)
N4—C3—C4—C6	−1.0 (3)	N5—C12—C17—C16	179.20 (16)
C5—C4—C6—N5	−177.41 (15)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H032···O1	0.87 (2)	2.41 (2)	2.914 (2)	117.4 (18)
N5—H05···N4	0.83 (2)	2.26 (2)	2.955 (2)	142.0 (18)
N1—H01···O99^{i}	0.92 (2)	1.90 (2)	2.801 (2)	165.6 (17)
N3—H032···O1^{ii}	0.87 (2)	2.22 (2)	2.950 (2)	142 (2)
N4—H04···O99^{iii}	0.876 (19)	2.30 (2)	3.163 (2)	170.7 (17)
O99—H099···N2	0.83 (2)	1.96 (2)	2.7928 (19)	176 (2)
C17—H17···O1	0.95	2.28	2.884 (2)	121
C21—H21···O1^{iv}	0.95	2.56	3.494 (2)	167

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

H atoms attached to N or O atoms were refined freely. Methyl H atoms were identified in a difference synthesis, idealized and refined as a rigid group (C—H = 0.98 Å and H—C—H = 109.5°) allowed to rotate but not tip. Other H atoms were included using a riding model with fixed C—H bond lengths (aromatic = 0.95 Å and methylene = 0.99 Å); $U_{\rm iso}$(H) values were fixed at $1.2U_{\rm eq}$ of the parent C atom.

Data collection: *XSCANS* (Fait, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

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References

Elgemeie, G. H., El-Ezbawy, S. R. & El-Aziz, H. A. (2001). *Synth. Commun.* **31**, 2453–2458.

Elgemeie, G. H., Elghandour, A. H., Ali, H. A. & Abdel-Azzez, H. M. (1999). *J. Chem. Res.* (*S*), pp. 6–7.

Elgemeie, G. H., Elghandour, A. H., Ali, H. A. & Hussein, A. M. (2002). *Synth. Commun.* **32**, 2245–2253.

Elgemeie, G. H., Elghandour, A. H., Elzanate, A. M. & Ahmed, S. A. (1997). *J. Chem. Soc. Perkin Trans.* 1, pp. 3285–3289.

Elgemeie, G. H., Elghandour, A. H., Elzanate, A. M. & Ahmed, S. A. (1998). *J. Chem. Res.* (*S*), pp. 162–163.

Elgemeie, G. H., Elghandour, A. H., Elzanate, A. M. & Masoud, W. A. (2000). *Phosphorus Sulfur Silicon*, **163**, 91–97.

Fait, J. (1991). *XSCANS*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Siemens (1994). *XP*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.