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Crystal structure and Hirshfeld surface analysis of 2-amino-6-[(1-phenylethyl)amino]-4-(thiophen-2-yl)pyridine-3,5-dicarbonitrile

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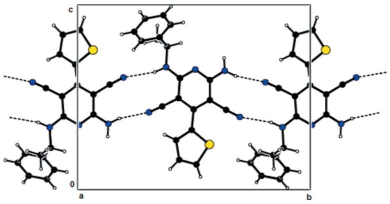
In the title compound, $C_{19}H_{15}N_5S$, the thiophene ring is disordered in a 0.6:0.4 ratio by an approximate 180° rotation of the ring around the C—C bond linking it to the pyridine ring. In the crystal, the molecules are linked by N—H···N hydrogen bonds into dimers with an $R_2^2(12)$ motif, forming chains along the *b*-axis direction. These chains are connected to each other by further N—H···N hydrogen bonds, forming a three-dimensional network. Furthermore, N—H···π and π–π [centroid–centroid separations = 3.899 (8) and 3.7938 (12) Å] interactions also contribute to the crystal cohesion. A Hirshfeld surface analysis indicated that the most important contributions to the surface contacts are from H···H (46.1%), N···H/H···N (20.4%) and C···H/H···C (17.4%) interactions.

1. Chemical context

Diverse C—C, C—N and C—O bond-formation methods play important roles in organic synthesis. The reaction scopes have also been greatly expanded, employing these methods in different fields of chemistry, in both academia and industry (Çelik *et al.*, 2023; Chalkha *et al.*, 2023; Tapera *et al.*, 2022; Gurbanov *et al.*, 2020; Zubkov *et al.*, 2018). The pyridine moiety is a widespread structural motif that can be found in various natural products and pharmacologically active compounds. 3,5-Dicyanopyridines have been reported as intermediates in the synthesis of pyrido[2,3-*d*]pyrimidines, pyridothienotriazines, azabenzanthracenes and pyrimidine *S*-nucleoside derivatives with a broad spectrum of biological activity (Cocco *et al.*, 2005; Zhang *et al.*, 2022; Poustforoosh *et al.*, 2022). The design of new 3,5-dicyanopyridine derivatives is thus of great interest.



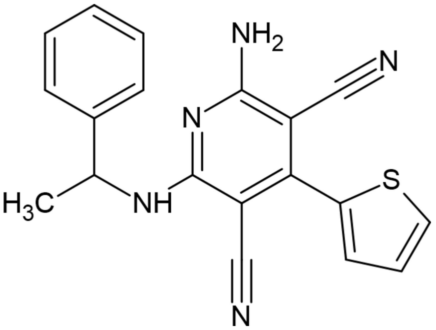


Table 1
Hydrogen-bond geometry (Å, °).

*Cg*4 is the centroid of the C7–C12 ring.

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N2—H2⋯N19$^{\rm i}$	0.91 (3)	2.28 (3)	3.152 (3)	163 (3)
N6—H6*B*⋯N14$^{\rm ii}$	0.89 (3)	2.17 (4)	3.033 (3)	164 (3)
N6—H6*A*⋯*Cg*4$^{\rm iii}$	0.91 (3)	2.62 (4)	3.405 (2)	145 (3)

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

Table 2
Summary of short interatomic contacts (Å) in the title compound.

Contact	Distance	Symmetry operation
H13*A*⋯H6*A*	2.36	$-x, 1-y, z$
H6*B*⋯N14	2.18	$\frac{1}{2}-x, \frac{1}{2}+y, 1-z$
H16⋯N19	2.56	$1-x, 1-y, z$
C17⋯H9	2.86	$-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$
C10⋯C13	3.58	$1+x, y, z$
H12⋯H18*A*	2.31	$x, y, 1+z$
H18⋯H11	2.34	$1-x, 1-y, -1+z$

Continuing our studies of pyridine derivatives exhibiting biological activity, we designed and synthesized a novel 3,5-dicyanopyridine in this series. Thus, in the framework of our ongoing structural studies (Naghiyev *et al.*, 2020, 2021, 2022), we report the crystal structure and Hirshfeld surface analysis of the title compound, 2-amino-6-[(1-phenylethyl)amino]-4-(thiophen-2-yl)pyridine-3,5-dicarbonitrile.

2. Structural commentary

The pyridine ring (N1/C2–C6) of the title compound (Fig. 1) is largely planar [maximum deviation = 0.015 (2) Å for C5]. The thiophene and 1-phenylethan-1-amine groups are linked to the central pyridine ring in an equatorial arrangement. The major and minor parts (S1/C15–C18 and S1*A*/C15*A*–C18*A*) of the disordered thiophene ring make dihedral angles of 44.8 (5) and 48.9 (6)°, respectively, with the pyridine ring. The dihedral angle between the phenyl (C7–C12) and pyridine (N1/C2–C6) rings is 64.42 (11) °.

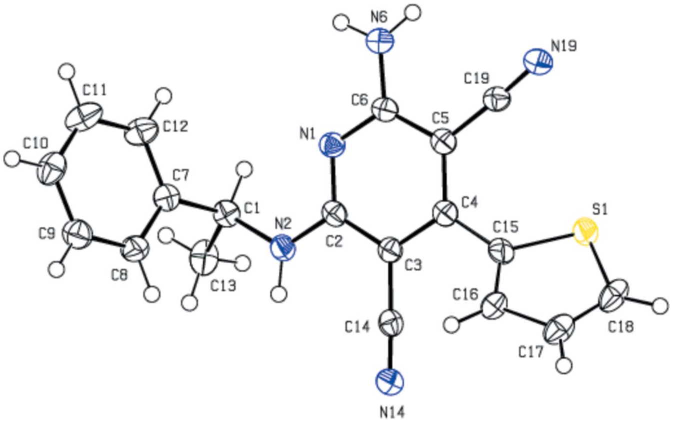


Figure 1
The molecular structure of the title compound, showing the atom labelling and displacement ellipsoids drawn at the 30% probability level. For clarity, the minor disorder component is not shown.

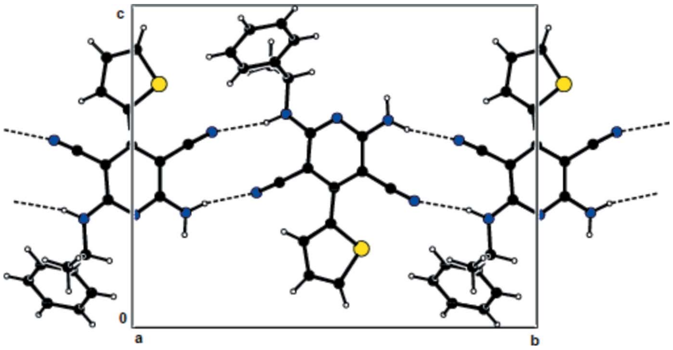


Figure 2
View of the molecular packing along the *a* axis. N—H⋯N hydrogen bonds are shown as dashed lines. For clarity, the minor disorder component is not shown.

3. Supramolecular features and Hirshfeld surface analysis

In the crystal, the molecules are linked by N—H⋯N hydrogen bonds into dimers with an $R_2^2(12)$ motif (Bernstein *et al.*, 1995; Table 1, Fig. 2), forming chains along the *b*-axis direction. These chains are connected to each other by further N—H⋯N hydrogen bonds, forming a three-dimensional network (Tables 1 and 2, Figs. 3 and 4). Furthermore, N—H⋯π and π–π interactions [$Cg1\cdots Cg1^{\rm i}$ = 3.899 (8) Å; slippage = 1.899 Å; $Cg3\cdots Cg3^{\rm ii}$ = 3.7938 (12) Å; slippage =

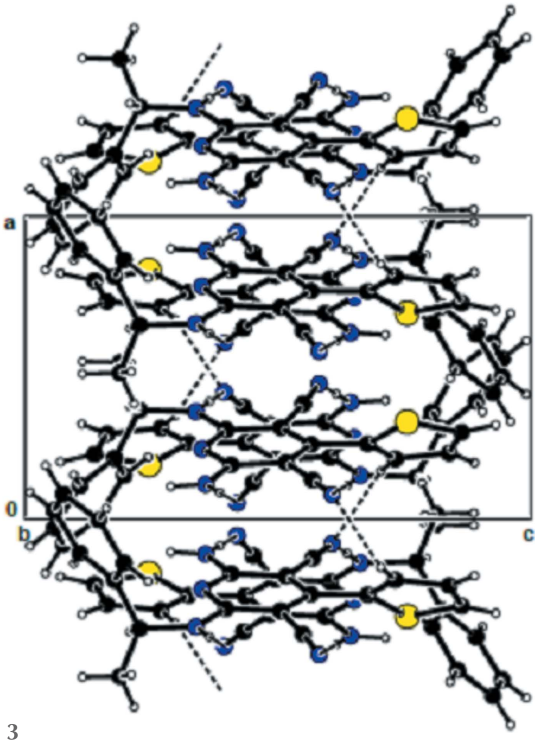


Figure 3
View of the molecular packing along the *b* axis. Hydrogen bonds are shown as dashed lines.

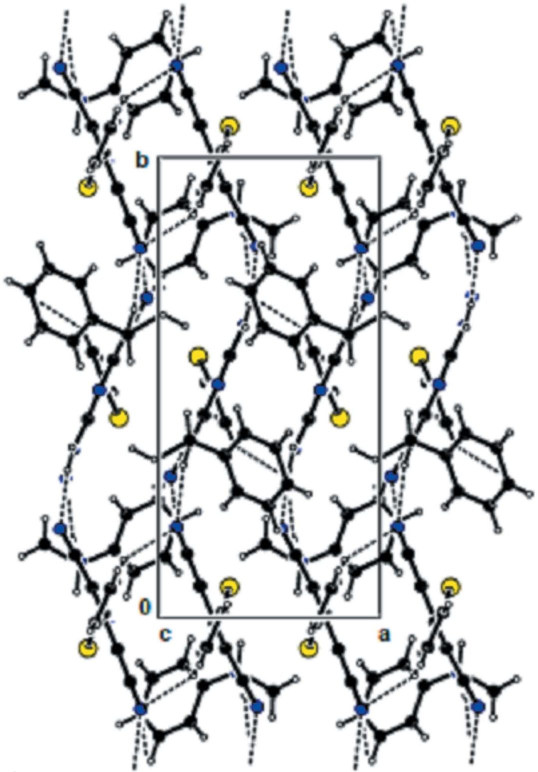


Figure 4
View of the molecular packing along the *c* axis. Hydrogen bonds are shown as dashed lines.

1.383 Å; symmetry codes: (i) $-x, 1 - y, z$; (ii) $1 - x, 1 - y, z$; *Cg*1 and *Cg*3 are the centroids of the major component of the disordered thiophene ring and of the pyridine ring, respectively] also contribute to crystal cohesion (Figs. 5 and 6).

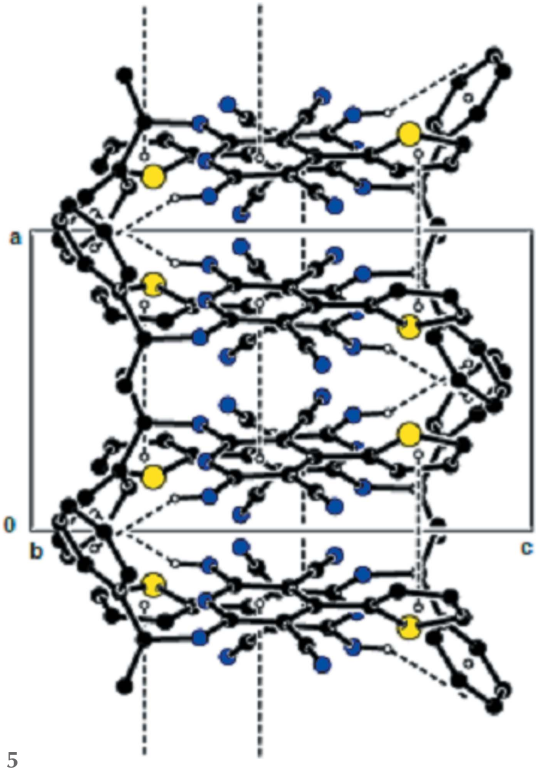


Figure 5
View of the molecular packing along the *b* axis. N—H$\cdots\pi$ interactions and π–π stacking interactions are shown as dashed lines.

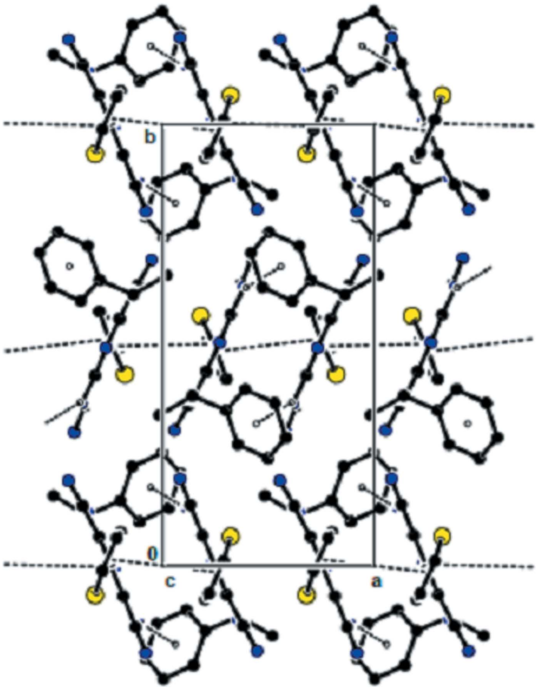


Figure 6
View of the molecular packing along the *c* axis. N—H$\cdots\pi$ interactions and π–π stacking interactions are shown as dashed lines.

Crystal Explorer 17.5 (Spackman *et al.*, 2021) was used to generate Hirshfeld surfaces and two-dimensional fingerprint plots in order to quantify the intermolecular interactions in the crystal. The intermolecular interactions are depicted as red spots, which denotes the N—H$\cdots$N hydrogen bonds, on the Hirshfeld surface mapped over $d_{\rm norm}$ in the range −0.4485 to +1.5784 a.u. (Fig. 7*a*,*b*). Fig. 8 shows the two-dimensional fingerprint plots. The H$\cdots$H contacts comprise 46.1% of the total interactions. Besides this contact, N$\cdots$H/H$\cdots$N (20.4%) and C$\cdots$H/H$\cdots$C (17.4%) interactions make significant

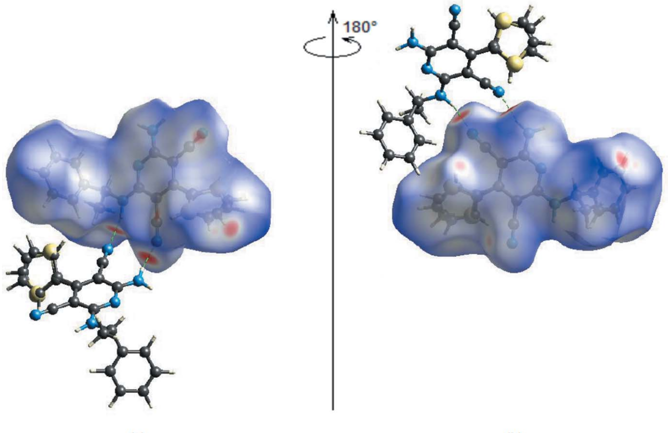


Figure 7
(*a*) Front and (*b*) back sides of the three-dimensional Hirshfeld surface of the title compound mapped over $d_{\rm norm}$, with a fixed colour scale of −0.4485 to +1.5784 a.u. N—H$\cdots$N hydrogen bonds are shown as dashed lines.

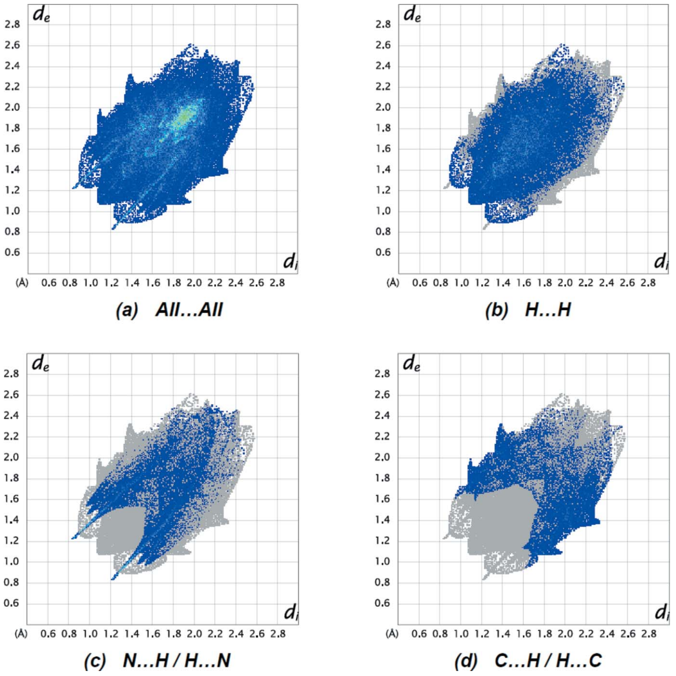


Figure 8
The two-dimensional fingerprint plots of the title compound, showing (*a*) all interactions, and delineated into (*b*) H· · ·H, (*c*) N· · ·H/H· · ·N and (*d*) C· · ·H/H· · ·C interactions. [d_e and d_i represent the distances from a point on the Hirshfeld surface to the nearest atoms outside (external) and inside (internal) the surface, respectively].

contributions to the total Hirshfeld surface. The percentage contributions of the C· · ·C, N· · ·C/C· · ·N, N· · ·N, S· · ·C/C· · ·S, S· · ·H/H· · ·S and S· · ·S contacts are 6.9, 3.8, 2.7, 1.5, 0.6 and 0.6%, respectively.

4. Database survey

The four related compounds found as a result of the search for '2,6-diamino-4-(thiophen-2-yl)pyridine-3,5-dicarbonitrile' in the Cambridge Structure Database (CSD, Version 5.42, update of September 2021; Groom *et al.*, 2016) are MUCLAA (Vu Quoc *et al.*, 2019), WOJCIJ (Vishnupriya *et al.*, 2014*a*), WOPLAQ (Vishnupriya *et al.*, 2014*b*) and DOPWOW (Vishnupriya *et al.*, 2014*c*).

In the crystal of MUCLAA (space group $P2_1/c$), chains running along the *b*-axis direction are formed through N—H· · ·O interactions between the 1,4-dihydropyridine N atom and one of the O atoms of the ester groups. Neighbouring chains are linked by C—H· · ·O and C—H· · ·π interactions. In the crystal of WOJCIJ (space group $P2_1/c$), inversion dimers linked by pairs of N—H· · ·N hydrogen bonds generate $R_2^2(16)$ loops and the dimers are linked by C—H· · ·π and aromatic π–π stacking interactions into a three-dimensional network. In WOPLAQ (space group $P2_1/n$), inversion dimers linked by pairs of N—H· · ·N_c (c = cyanide) hydrogen bonds generate $R_2^2(16)$ loops. In DOPWOW (space group *Pbca*), inversion dimers linked by pairs of N—H· · ·N_n (n = nitrile) hydrogen bonds generate $R_2^2(16)$ loops. Aromatic π–π stacking and very weak C—H· · ·π interactions are also observed.

Table 3
Experimental details.

Crystal data	
Chemical formula	$C_{19}H_{15}N_5S$
M_r	345.42
Crystal system, space group	Orthorhombic, $P2_12_12$
Temperature (K)	100
a, *b*, *c* (Å)	7.89079 (13), 16.4990 (3), 13.1394 (3)
V (Å^3)	1710.62 (6)
Z	4
Radiation type	Cu *Kα*
μ (mm^{-1})	1.77
Crystal size (mm)	0.40 × 0.04 × 0.03
Data collection	
Diffractometer	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Gaussian (*CrysAlis PRO*; Rigaku OD, 2022)
T_{min}, T_{max}	0.532, 0.939
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26907, 3713, 3612
R_{int}	0.044
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.638
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.096, 1.05
No. of reflections	3713
No. of parameters	276
No. of restraints	12
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.15, −0.25
Absolute structure	Refined as an inversion twin
Absolute structure parameter	0.13 (3)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2022), *SHELXT2014/5* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

5. Synthesis and crystallization

To a solution of 2-(thiophen-2-ylmethylene)malononitrile (0.82 g; 5.1 mmol) and malononitrile (0.34 g; 5.2 mmol) in methanol (25 mL), phenylethylamine (0.63 g; 5.2 mmol) was added and the mixture was stirred at room temperature for 48 h. Then 15 mL of methanol were removed from the reaction mixture, which was left overnight. The precipitated crystals were separated by filtration and recrystallized from ethanol/water (1:1) solution (yield 94%; m.p. 460–461 K).

^{1}H NMR (300 MHz, DMSO-d_6, ppm): 1.55 (*d*, 3H, CH_3, $^3J_{H–H}$ = 7 MHz); 5.45 (*k*, 1H, CH—Ar, $^3J_{H–H}$ =7,1 MHz); 7.21–7.88 (*m*, 11H, $5CH_{arom}$ + $3CH_{thienyl}$ + NH_2 + NH); ^{13}C NMR (75 MHz, DMSO-d_6, ppm): 21.69 (CH_3), 50.00 (CH—Ar), 79.77 (=C_{tert}), 80.92 (=C_{tert}), 116.85 (CN), 116.97 (CN), 127.14 ($2CH_{arom}$), 127.22 (CH_{arom}), 128.11 ($CH_{thienyl}$), 128.63 ($2CH_{arom}$), 130.14 ($CH_{thienyl}$), 130.75 ($CH_{thienyl}$), 134.53 (C_{ar}), 144.53 ($C_{thienyl}$), 152.30 (=C_{tert}), 158.70 (N=C_{tert}), 161.38 (=C_{tert}).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The thiophene ring in the title compound was modelled as disordered over two sets of sites related by an approximate rotation of 180° about the C4—C15 bond in a 0.6:0.4 ratio. EADP commands in *SHELXL* were used for the U_{ij} values of equivalent atom pairs (*e.g.*, C16 and C16*A*) and DFIX commands were used to restrain the nearest-neighbour and next-nearest-neighbour bond distances in the two disorder components to be equal with a standard deviation of 0.03 Å. All C-bound H atoms were placed in calculated positions (0.95–1.00 Å) and refined as riding with $U_{iso}(H) = 1.2$ or $1.5U_{eq}(C)$. The N-bound H atoms were located in a difference map and refined with $U_{iso}(H) = 1.2U_{eq}(N)$ [N2—H2 = 0.91 (3) Å, N6—H6*A* = 0.91 (3) Å, N6—H6*B* = 0.89 (3) Å].

Acknowledgements

Authors' contributions are as follows. Conceptualization, ANK and IGM; methodology, ANK, FNN and IGM; investigation, ANK, MA and KAA; writing (original draft), MA and ANK; writing (review and editing of the manuscript), MA and ANK; visualization, MA, ANK and IGM; funding acquisition, VNK, AB and ANK; resources, AB, VNK and KAA; supervision, ANK and MA.

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supporting information

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Crystal structure and Hirshfeld surface analysis of 2-amino-6-[(1-phenylethyl)-amino]-4-(thiophen-2-yl)pyridine-3,5-dicarbonitrile

Farid N. Naghiyev, Victor N. Khrustalev, Khammed A. Asadov, Mehmet Akkurt, Ali N. Khalilov, Ajaya Bhattarai and İbrahim G. Mamedov

Computing details

Data collection: *CrysAlis PRO* 1.171.41.117a (Rigaku OD, 2022); cell refinement: *CrysAlis PRO* 1.171.41.117a (Rigaku OD, 2022); data reduction: *CrysAlis PRO* 1.171.41.117a (Rigaku OD, 2022); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2020).

2-Amino-6-[(1-phenylethyl)amino]-4-(thiophen-2-yl)pyridine-3,5-dicarbonitrile

Crystal data

$C_{19}H_{15}N_5S$	D_x = 1.341 Mg m^{-3}
M_r = 345.42	Cu $K\alpha$ radiation, λ = 1.54184 Å
Orthorhombic, $P2_12_12$	Cell parameters from 17132 reflections
a = 7.89079 (13) Å	θ = 3.4–79.2°
b = 16.4990 (3) Å	μ = 1.77 mm^{-1}
c = 13.1394 (3) Å	T = 100 K
V = 1710.62 (6) Å^3	Needle, colourless
Z = 4	0.40 × 0.04 × 0.03 mm
F(000) = 720	

Data collection

XtaLAB Synergy, Dualflex, HyPix diffractometer	3713 independent reflections
Radiation source: micro-focus sealed X-ray tube	3612 reflections with $I > 2\sigma(I)$
φ and ω scans	R_{int} = 0.044
Absorption correction: gaussian (CrysAlisPro; Rigaku OD, 2022)	$\theta_{\max}$ = 79.7°, $\theta_{\min}$ = 3.4°
$T_{\min}$ = 0.532, $T_{\max}$ = 0.939	$h = -10 \rightarrow 9$
26907 measured reflections	$k = -21 \rightarrow 20$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	Primary atom site location: difference Fourier map
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.036	Hydrogen site location: mixed
$wR(F^2)$ = 0.096	H atoms treated by a mixture of independent and constrained refinement
S = 1.05	
3713 reflections	
276 parameters	
12 restraints	

$w = 1/[\sigma^2(F_o^2) + (0.0507P)^2 + 0.5356P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.15$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}
Absolute structure: Refined as an inversion twin
Absolute structure parameter: 0.13 (3)

Special details

Experimental. CrysAlisPro 1.171.41.123a (Rigaku OD, 2022); Numerical absorption correction based on Gaussian integration over a multifaceted crystal model; Empirical absorption correction using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm.

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

Refinement. Refined as a 2-component inversion twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
S1	0.1793 (3)	0.56636 (9)	0.24471 (14)	0.0306 (3)	0.6
S1A	0.3236 (6)	0.42012 (16)	0.2521 (3)	0.0254 (6)	0.4
N1	0.2686 (2)	0.50614 (12)	0.64994 (15)	0.0250 (4)	
C1	0.1399 (3)	0.38542 (14)	0.77369 (17)	0.0270 (5)	
H1	0.1288	0.4439	0.7928	0.032*	
C2	0.2054 (3)	0.44038 (13)	0.60337 (17)	0.0239 (4)	
N2	0.1451 (2)	0.38039 (12)	0.66239 (15)	0.0263 (4)	
H2	0.112 (4)	0.332 (2)	0.636 (2)	0.032*	
C3	0.1980 (3)	0.43395 (13)	0.49462 (17)	0.0237 (4)	
C4	0.2528 (2)	0.49903 (13)	0.43479 (15)	0.0236 (4)	
C5	0.3127 (3)	0.56866 (13)	0.48450 (17)	0.0244 (4)	
C6	0.3206 (3)	0.56878 (12)	0.59318 (17)	0.0242 (4)	
N6	0.3851 (3)	0.63253 (13)	0.64322 (17)	0.0288 (4)	
H6A	0.392 (4)	0.6297 (19)	0.712 (3)	0.035*	
H6B	0.413 (4)	0.679 (2)	0.615 (2)	0.035*	
C7	0.2992 (3)	0.35278 (14)	0.82352 (17)	0.0255 (4)	
C8	0.3550 (3)	0.27466 (15)	0.80460 (19)	0.0313 (5)	
H8	0.2958	0.2417	0.7571	0.038*	
C9	0.4974 (3)	0.24370 (16)	0.8545 (2)	0.0352 (5)	
H9	0.5354	0.1903	0.8402	0.042*	
C10	0.5827 (3)	0.29053 (17)	0.9245 (2)	0.0352 (5)	
H10	0.6777	0.2691	0.9599	0.042*	
C11	0.5292 (3)	0.3690 (2)	0.9429 (2)	0.0429 (6)	
H11	0.5883	0.4019	0.9904	0.051*	
C12	0.3887 (3)	0.39989 (17)	0.8918 (2)	0.0361 (6)	
H12	0.3540	0.4541	0.9041	0.043*	
C13	−0.0172 (3)	0.34112 (18)	0.8124 (2)	0.0361 (6)	
H13A	−0.1190	0.3670	0.7847	0.054*	
H13B	−0.0203	0.3435	0.8869	0.054*	
H13C	−0.0133	0.2844	0.7904	0.054*	
C14	0.1206 (3)	0.36403 (14)	0.45060 (17)	0.0257 (4)	

N14	0.0540 (3)	0.30718 (12)	0.41871 (16)	0.0310 (4)	
C15	0.251 (3)	0.4906 (6)	0.3229 (3)	0.029 (3)	0.6
C16	0.3006 (16)	0.4236 (4)	0.2681 (5)	0.025 (2)	0.6
H16	0.3422	0.3748	0.2974	0.030*	0.6
C17	0.2816 (10)	0.4371 (4)	0.1618 (5)	0.0346 (15)	0.6
H17	0.3135	0.3981	0.1121	0.042*	0.6
C18	0.2137 (10)	0.5107 (4)	0.1371 (5)	0.0366 (17)	0.6
H18	0.1893	0.5284	0.0698	0.044*	0.6
C15A	0.246 (4)	0.4989 (10)	0.3229 (3)	0.024 (4)	0.4
C16A	0.180 (2)	0.5595 (5)	0.2643 (5)	0.025 (2)	0.4
H16A	0.1294	0.6078	0.2899	0.030*	0.4
C17A	0.1963 (15)	0.5398 (6)	0.1596 (6)	0.029 (2)	0.4
H17A	0.1595	0.5750	0.1069	0.035*	0.4
C18A	0.2696 (14)	0.4661 (7)	0.1404 (6)	0.032 (2)	0.4
H18A	0.2877	0.4439	0.0746	0.038*	0.4
C19	0.3707 (3)	0.63853 (14)	0.43145 (18)	0.0256 (4)	
N19	0.4186 (3)	0.69712 (13)	0.39337 (16)	0.0298 (4)	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0317 (6)	0.0288 (5)	0.0314 (6)	−0.0050 (5)	−0.0049 (7)	0.0067 (5)
S1A	0.0253 (13)	0.0248 (10)	0.0261 (9)	0.0020 (6)	0.0027 (10)	−0.0027 (8)
N1	0.0238 (8)	0.0243 (9)	0.0269 (9)	−0.0001 (7)	−0.0007 (7)	−0.0006 (7)
C1	0.0261 (10)	0.0271 (10)	0.0279 (11)	0.0024 (8)	0.0027 (9)	−0.0004 (8)
C2	0.0183 (9)	0.0223 (9)	0.0311 (11)	0.0022 (8)	0.0001 (8)	0.0025 (8)
N2	0.0276 (9)	0.0248 (9)	0.0266 (9)	−0.0007 (7)	0.0000 (7)	0.0024 (7)
C3	0.0199 (9)	0.0236 (10)	0.0276 (10)	0.0018 (9)	−0.0015 (8)	0.0009 (8)
C4	0.0157 (9)	0.0249 (11)	0.0303 (11)	0.0022 (8)	−0.0005 (7)	0.0013 (9)
C5	0.0190 (9)	0.0246 (10)	0.0298 (10)	0.0012 (9)	0.0002 (8)	0.0012 (8)
C6	0.0190 (9)	0.0221 (10)	0.0314 (11)	0.0014 (8)	−0.0005 (8)	−0.0016 (8)
N6	0.0314 (9)	0.0257 (10)	0.0293 (10)	−0.0028 (8)	−0.0022 (8)	−0.0013 (8)
C7	0.0234 (10)	0.0289 (11)	0.0242 (9)	−0.0018 (8)	0.0052 (8)	0.0007 (8)
C8	0.0296 (11)	0.0290 (11)	0.0355 (12)	−0.0022 (9)	−0.0070 (9)	−0.0009 (9)
C9	0.0301 (11)	0.0311 (12)	0.0443 (13)	0.0014 (10)	−0.0047 (11)	0.0011 (11)
C10	0.0246 (10)	0.0491 (15)	0.0319 (11)	−0.0009 (10)	−0.0018 (9)	0.0025 (11)
C11	0.0339 (13)	0.0532 (16)	0.0415 (14)	−0.0033 (12)	−0.0083 (11)	−0.0148 (13)
C12	0.0335 (12)	0.0384 (14)	0.0364 (12)	0.0008 (10)	−0.0007 (10)	−0.0108 (11)
C13	0.0260 (11)	0.0479 (15)	0.0344 (12)	0.0015 (11)	0.0037 (10)	0.0083 (11)
C14	0.0245 (9)	0.0252 (10)	0.0273 (10)	0.0023 (8)	−0.0004 (8)	0.0028 (9)
N14	0.0334 (10)	0.0264 (10)	0.0331 (10)	−0.0023 (8)	−0.0034 (8)	0.0012 (8)
C15	0.022 (6)	0.027 (4)	0.036 (6)	−0.011 (3)	−0.004 (4)	0.009 (3)
C16	0.023 (3)	0.033 (3)	0.020 (3)	0.0021 (19)	0.003 (2)	−0.0031 (17)
C17	0.027 (3)	0.049 (4)	0.028 (3)	−0.006 (3)	−0.001 (2)	−0.003 (3)
C18	0.029 (3)	0.061 (6)	0.020 (3)	−0.016 (4)	0.001 (3)	0.004 (3)
C15A	0.017 (7)	0.036 (6)	0.020 (6)	0.001 (6)	0.004 (6)	−0.005 (5)
C16A	0.023 (3)	0.033 (3)	0.020 (3)	0.0021 (19)	0.003 (2)	−0.0031 (17)
C17A	0.027 (3)	0.048 (6)	0.012 (4)	0.000 (4)	0.003 (3)	−0.001 (3)

C18A	0.022 (4)	0.053 (8)	0.020 (4)	0.011 (5)	−0.001 (3)	0.005 (5)
C19	0.0224 (9)	0.0251 (10)	0.0293 (10)	0.0005 (8)	−0.0009 (9)	−0.0030 (9)
N19	0.0300 (9)	0.0265 (10)	0.0331 (10)	−0.0034 (8)	0.0004 (8)	−0.0006 (8)

Geometric parameters (Å, º)

S1—C18	1.708 (4)	C8—H8	0.9500
S1—C15	1.713 (4)	C9—C10	1.377 (4)
S1A—C18A	1.707 (4)	C9—H9	0.9500
S1A—C15A	1.711 (4)	C10—C11	1.384 (4)
N1—C6	1.339 (3)	C10—H10	0.9500
N1—C2	1.342 (3)	C11—C12	1.392 (4)
C1—N2	1.465 (3)	C11—H11	0.9500
C1—C7	1.516 (3)	C12—H12	0.9500
C1—C13	1.526 (3)	C13—H13A	0.9800
C1—H1	1.0000	C13—H13B	0.9800
C2—N2	1.344 (3)	C13—H13C	0.9800
C2—C3	1.434 (3)	C14—N14	1.154 (3)
N2—H2	0.91 (3)	C15—C16	1.377 (4)
C3—C4	1.399 (3)	C16—C17	1.423 (4)
C3—C14	1.428 (3)	C16—H16	0.9500
C4—C5	1.404 (3)	C17—C18	1.368 (9)
C4—C15A	1.472 (4)	C17—H17	0.9500
C4—C15	1.477 (3)	C18—H18	0.9500
C5—C19	1.423 (3)	C15A—C16A	1.368 (4)
C5—C6	1.429 (3)	C16A—C17A	1.420 (4)
C6—N6	1.341 (3)	C16A—H16A	0.9500
N6—H6A	0.91 (3)	C17A—C18A	1.369 (13)
N6—H6B	0.89 (3)	C17A—H17A	0.9500
C7—C12	1.382 (3)	C18A—H18A	0.9500
C7—C8	1.384 (3)	C19—N19	1.152 (3)
C8—C9	1.398 (3)		

C18—S1—C15	93.0 (4)	C9—C10—C11	119.5 (2)
C18A—S1A—C15A	92.3 (5)	C9—C10—H10	120.2
C6—N1—C2	118.95 (19)	C11—C10—H10	120.2
N2—C1—C7	112.82 (18)	C10—C11—C12	120.1 (2)
N2—C1—C13	109.13 (19)	C10—C11—H11	119.9
C7—C1—C13	111.07 (19)	C12—C11—H11	119.9
N2—C1—H1	107.9	C7—C12—C11	121.0 (3)
C7—C1—H1	107.9	C7—C12—H12	119.5
C13—C1—H1	107.9	C11—C12—H12	119.5
N1—C2—N2	117.6 (2)	C1—C13—H13A	109.5
N1—C2—C3	122.0 (2)	C1—C13—H13B	109.5
N2—C2—C3	120.4 (2)	H13A—C13—H13B	109.5
C2—N2—C1	122.9 (2)	C1—C13—H13C	109.5
C2—N2—H2	122 (2)	H13A—C13—H13C	109.5
C1—N2—H2	115 (2)	H13B—C13—H13C	109.5

C4—C3—C14	121.65 (19)	N14—C14—C3	177.1 (2)
C4—C3—C2	119.4 (2)	C16—C15—C4	126.3 (4)
C14—C3—C2	118.7 (2)	C16—C15—S1	111.5 (3)
C3—C4—C5	118.08 (19)	C4—C15—S1	122.2 (3)
C3—C4—C15A	123.3 (11)	C15—C16—C17	110.9 (5)
C5—C4—C15A	118.6 (11)	C15—C16—H16	124.5
C3—C4—C15	118.9 (7)	C17—C16—H16	124.5
C5—C4—C15	123.0 (7)	C18—C17—C16	114.4 (6)
C4—C5—C19	122.9 (2)	C18—C17—H17	122.8
C4—C5—C6	118.7 (2)	C16—C17—H17	122.8
C19—C5—C6	118.3 (2)	C17—C18—S1	110.1 (6)
N1—C6—N6	116.7 (2)	C17—C18—H18	125.0
N1—C6—C5	122.8 (2)	S1—C18—H18	125.0
N6—C6—C5	120.5 (2)	C16A—C15A—C4	125.1 (5)
C6—N6—H6A	118 (2)	C16A—C15A—S1A	112.8 (3)
C6—N6—H6B	125 (2)	C4—C15A—S1A	122.1 (4)
H6A—N6—H6B	117 (3)	C15A—C16A—C17A	109.9 (6)
C12—C7—C8	118.5 (2)	C15A—C16A—H16A	125.0
C12—C7—C1	120.3 (2)	C17A—C16A—H16A	125.0
C8—C7—C1	121.1 (2)	C18A—C17A—C16A	115.0 (9)
C7—C8—C9	120.8 (2)	C18A—C17A—H17A	122.5
C7—C8—H8	119.6	C16A—C17A—H17A	122.5
C9—C8—H8	119.6	C17A—C18A—S1A	110.0 (8)
C10—C9—C8	120.1 (2)	C17A—C18A—H18A	125.0
C10—C9—H9	120.0	S1A—C18A—H18A	125.0
C8—C9—H9	120.0	N19—C19—C5	176.4 (2)

C6—N1—C2—N2	−176.22 (19)	C1—C7—C8—C9	−176.9 (2)
C6—N1—C2—C3	2.5 (3)	C7—C8—C9—C10	0.9 (4)
N1—C2—N2—C1	2.4 (3)	C8—C9—C10—C11	−1.7 (4)
C3—C2—N2—C1	−176.30 (19)	C9—C10—C11—C12	0.8 (4)
C7—C1—N2—C2	−90.5 (2)	C8—C7—C12—C11	−1.8 (4)
C13—C1—N2—C2	145.6 (2)	C1—C7—C12—C11	176.0 (2)
N1—C2—C3—C4	−2.2 (3)	C10—C11—C12—C7	1.0 (4)
N2—C2—C3—C4	176.47 (18)	C3—C4—C15—C16	−42 (2)
N1—C2—C3—C14	−176.64 (19)	C5—C4—C15—C16	135.4 (17)
N2—C2—C3—C14	2.0 (3)	C15A—C4—C15—C16	173 (27)
C14—C3—C4—C5	174.0 (2)	C3—C4—C15—S1	136.5 (12)
C2—C3—C4—C5	−0.3 (3)	C5—C4—C15—S1	−46 (2)
C14—C3—C4—C15A	−4.1 (12)	C15A—C4—C15—S1	−8 (23)
C2—C3—C4—C15A	−178.4 (11)	C18—S1—C15—C16	0.1 (16)
C14—C3—C4—C15	−8.0 (9)	C18—S1—C15—C4	−179.0 (17)
C2—C3—C4—C15	177.7 (8)	C4—C15—C16—C17	−179.8 (17)
C3—C4—C5—C19	−179.6 (2)	S1—C15—C16—C17	1 (2)
C15A—C4—C5—C19	−1.4 (11)	C15—C16—C17—C18	−2.2 (17)
C15—C4—C5—C19	2.4 (9)	C16—C17—C18—S1	2.3 (10)
C3—C4—C5—C6	2.2 (3)	C15—S1—C18—C17	−1.3 (10)
C15A—C4—C5—C6	−179.5 (11)	C3—C4—C15A—C16A	130 (2)

C15—C4—C5—C6	−175.7 (8)	C5—C4—C15A—C16A	−48 (4)
C2—N1—C6—N6	−179.01 (19)	C15—C4—C15A—C16A	168 (28)
C2—N1—C6—C5	−0.4 (3)	C3—C4—C15A—S1A	−50 (3)
C4—C5—C6—N1	−2.0 (3)	C5—C4—C15A—S1A	132.2 (18)
C19—C5—C6—N1	179.74 (19)	C15—C4—C15A—S1A	−12 (23)
C4—C5—C6—N6	176.58 (19)	C18A—S1A—C15A—C16A	0 (2)
C19—C5—C6—N6	−1.6 (3)	C18A—S1A—C15A—C4	−180 (2)
N2—C1—C7—C12	126.2 (2)	C4—C15A—C16A—C17A	179 (2)
C13—C1—C7—C12	−110.9 (3)	S1A—C15A—C16A—C17A	−1 (3)
N2—C1—C7—C8	−56.0 (3)	C15A—C16A—C17A—C18A	1 (2)
C13—C1—C7—C8	66.9 (3)	C16A—C17A—C18A—S1A	−1.2 (15)
C12—C7—C8—C9	0.9 (4)	C15A—S1A—C18A—C17A	0.6 (15)

Hydrogen-bond geometry (Å, º)

*Cg*4 is the centroid of the C7–C12 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···N19^{i}	0.91 (3)	2.28 (3)	3.152 (3)	163 (3)
N6—H6*B*···N14^{ii}	0.89 (3)	2.17 (4)	3.033 (3)	164 (3)
N6—H6*A*···*Cg*4^{iii}	0.91 (3)	2.62 (4)	3.405 (2)	145 (3)

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