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Abstract

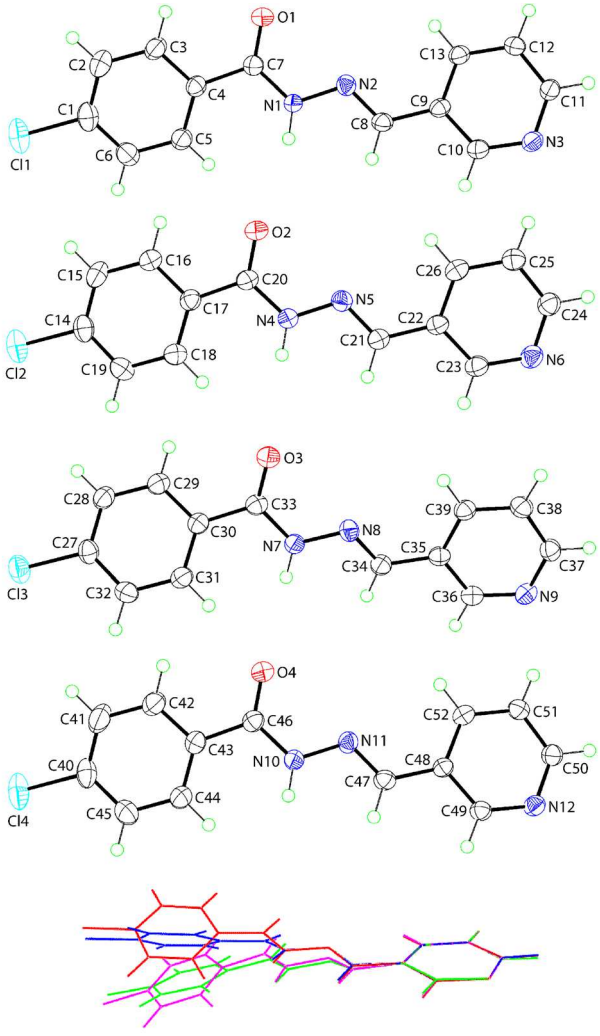
$C_{13}H_{10}ClN_3O$, monoclinic, $P2_1/c$ (no. 14), a = 19.0933(2) Å, b = 23.0910(3) Å, c = 10.6831(2) Å, β = 90.064(1)°, V = 4710.00(12) Å^3, Z = 16, $R_{gt}(F)$ = 0.0411, $wR_{ref}(F^2)$ = 0.1081, T = 160 K.

CCDC no.: 2233777

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of material

Nicotinaldehyde (1.07 g, 0.01 mol) was added to a stirred suspension of 4-chlorobenzohydrazide (1.71 g, 0.01 mol), in ethanol (10 mL), and the mixture was heated under reflux for 1 h. On cooling, the precipitated crude product was filtered, washed with ethanol, dried and recrystallised from ethanol to yield 2.44 g (94%) of the title compound as colourless plates. **Melting point**: 491–493 K (uncorrected). **^{1}H NMR (DMSO-d$_6$, 500.13 MHz)**: d 11.02 (s, 1H, NH), 9.05 (CH=N), 8.99 (s, 1H, Pyridine–H), 8.48–8.62 (m, 2H, Pyridine–H), 7.96 (d, 2H, Ar–H, J = 7.2 Hz) and 7.45–7.59 (m, 2H, Ar–H & 1 Pyridine–H). **^{13}C NMR (DMSO-d$_6$,**



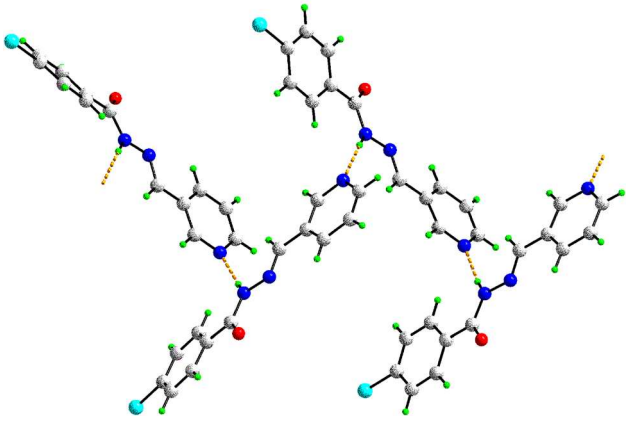


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Table 1: Data collection and handling.

Crystal:	Colourless plate
Size:	0.16 × 0.06 × 0.03 mm
Wavelength:	Cu *K*α radiation (1.54184 Å)
μ:	2.80 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy
θ_{max}, completeness:	74.5°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	49,867, 9505, 0.060
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 8033
$N(param)_{refined}$:	667
Programs:	CrysAlis^{PRO} [1], Shelx [2, 3], WinGX/Ortep [4]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.59359 (4)	1.04498 (3)	0.12812 (9)	0.0508 (2)
O1	0.81695 (11)	0.83009 (9)	0.01032 (17)	0.0418 (5)
N1	0.81780 (10)	0.82111 (9)	0.22192 (19)	0.0253 (4)
H1N	0.8052 (16)	0.8318 (13)	0.299 (3)	0.037 (8)*
N2	0.86948 (9)	0.77919 (8)	0.21536 (19)	0.0258 (4)
N3	1.02511 (10)	0.66183 (9)	0.45775 (19)	0.0284 (4)
C1	0.65304 (13)	0.98756 (11)	0.1273 (3)	0.0357 (6)
C2	0.69210 (13)	0.97746 (12)	0.0217 (3)	0.0370 (6)
H2	0.687848	1.001986	−0.049335	0.044*
C3	0.73779 (13)	0.93090 (12)	0.0205 (2)	0.0340 (6)
H3	0.764485	0.923116	−0.052631	0.041*
C4	0.74516 (11)	0.89532 (10)	0.1249 (2)	0.0258 (5)
C5	0.70582 (12)	0.90698 (11)	0.2315 (2)	0.0298 (5)
H5	0.710965	0.883442	0.303896	0.036*
C6	0.65907 (13)	0.95302 (11)	0.2322 (3)	0.0361 (6)
H6	0.631453	0.960677	0.304244	0.043*
C7	0.79607 (12)	0.84577 (11)	0.1136 (2)	0.0283 (5)
C8	0.88926 (12)	0.75792 (11)	0.3202 (2)	0.0270 (5)
H8	0.867406	0.770135	0.395525	0.032*
C9	0.94552 (11)	0.71479 (10)	0.3244 (2)	0.0245 (5)
C10	0.97166 (12)	0.69866 (11)	0.4408 (2)	0.0283 (5)
H10	0.950236	0.714787	0.513076	0.034*
C11	1.05365 (12)	0.63894 (10)	0.3541 (2)	0.0277 (5)
H11	1.091646	0.612743	0.363559	0.033*
C12	1.03072 (12)	0.65145 (10)	0.2344 (2)	0.0273 (5)
H12	1.052461	0.634029	0.163883	0.033*
C13	0.97570 (12)	0.68966 (10)	0.2188 (2)	0.0267 (5)
H13	0.958728	0.698652	0.137426	0.032*
Cl2	−0.17512 (3)	1.03769 (3)	0.29158 (8)	0.04596 (18)
O2	0.05856 (11)	0.83464 (10)	0.44291 (18)	0.0454 (5)
N4	0.06562 (10)	0.82269 (9)	0.2330 (2)	0.0277 (4)
H4N	0.0517 (16)	0.8318 (14)	0.154 (3)	0.040 (8)*
N5	0.11736 (10)	0.78179 (9)	0.24757 (19)	0.0275 (4)
N6	0.27438 (11)	0.65524 (10)	0.0344 (2)	0.0318 (5)
C14	−0.11112 (12)	0.98401 (11)	0.3011 (3)	0.0332 (5)
C15	−0.08093 (15)	0.97208 (12)	0.4151 (3)	0.0400 (6)
H15	−0.093630	0.993681	0.487274	0.048*
C16	−0.03174 (14)	0.92815 (12)	0.4234 (2)	0.0354 (6)
H16	−0.011138	0.919326	0.502082	0.042*
C17	−0.01203 (12)	0.89665 (10)	0.3175 (2)	0.0274 (5)
C18	−0.04248 (13)	0.91051 (11)	0.2036 (3)	0.0325 (5)
H18	−0.028996	0.889845	0.130590	0.039*
C19	−0.09222 (13)	0.95398 (11)	0.1942 (3)	0.0340 (5)
H19	−0.113015	0.963016	0.115805	0.041*
C20	0.04038 (13)	0.84914 (11)	0.3376 (2)	0.0297 (5)
C21	0.13624 (12)	0.75560 (11)	0.1475 (2)	0.0285 (5)
H21	0.113513	0.763837	0.070352	0.034*
C22	0.19281 (12)	0.71303 (10)	0.1522 (2)	0.0263 (5)
C23	0.21919 (13)	0.69105 (11)	0.0409 (2)	0.0298 (5)
H23	0.196880	0.701990	−0.035024	0.036*
C24	0.30306 (12)	0.63875 (11)	0.1430 (2)	0.0315 (5)
H24	0.342417	0.613616	0.140205	0.038*
C25	0.27879 (13)	0.65615 (11)	0.2595 (2)	0.0305 (5)
H25	0.299722	0.642027	0.334233	0.037*
C26	0.22351 (13)	0.69448 (11)	0.2638 (2)	0.0292 (5)
H26	0.206470	0.708119	0.341979	0.035*
Cl3	0.08214 (3)	1.03786 (3)	0.21099 (8)	0.04106 (16)
O3	0.30269 (10)	0.82449 (9)	0.05898 (17)	0.0381 (4)
N7	0.32103 (10)	0.82356 (9)	0.2694 (2)	0.0271 (4)
H7N	0.3076 (15)	0.8339 (13)	0.348 (3)	0.036 (8)*
N8	0.37216 (10)	0.78150 (9)	0.25922 (19)	0.0275 (4)
N9	0.52135 (10)	0.65395 (9)	0.4889 (2)	0.0296 (4)
C27	0.14266 (12)	0.98153 (10)	0.2002 (3)	0.0305 (5)
C28	0.14180 (14)	0.94615 (11)	0.0960 (3)	0.0340 (5)
H28	0.108069	0.952010	0.031786	0.041*
C29	0.19058 (13)	0.90211 (11)	0.0860 (2)	0.0325 (5)
H29	0.190897	0.878239	0.013623	0.039*
C30	0.23923 (12)	0.89236 (10)	0.1810 (2)	0.0261 (5)
C31	0.23839 (13)	0.92840 (11)	0.2849 (2)	0.0319 (5)
H31	0.270924	0.921952	0.350757	0.038*
C32	0.19099 (13)	0.97365 (12)	0.2943 (3)	0.0345 (5)
H32	0.191854	0.998821	0.364676	0.041*
C33	0.29055 (12)	0.84407 (11)	0.1626 (2)	0.0269 (5)
C34	0.38992 (11)	0.75695 (10)	0.3616 (2)	0.0273 (5)
H34	0.366949	0.766978	0.437392	0.033*
C35	0.44551 (12)	0.71345 (10)	0.3623 (2)	0.0257 (5)
C36	0.46772 (12)	0.69104 (10)	0.4761 (2)	0.0283 (5)
H36	0.443454	0.702664	0.549461	0.034*
C37	0.55412 (12)	0.63711 (11)	0.3841 (2)	0.0301 (5)
H37	0.592423	0.611049	0.391118	0.036*
C38	0.53468 (13)	0.65593 (11)	0.2663 (2)	0.0310 (5)
H38	0.558770	0.642451	0.194224	0.037*
C39	0.47991 (12)	0.69451 (11)	0.2546 (2)	0.0279 (5)
H39	0.465818	0.707992	0.174426	0.033*
Cl4	0.35255 (4)	1.04736 (3)	0.36861 (9)	0.0527 (2)
O4	0.55725 (10)	0.81752 (8)	0.45932 (17)	0.0363 (4)
N10	0.56900 (10)	0.82025 (9)	0.2477 (2)	0.0260 (4)
H10N	0.5583 (17)	0.8348 (14)	0.174 (3)	0.044 (9)*
N11	0.62016 (10)	0.77791 (9)	0.25057 (18)	0.0263 (4)
N12	0.77016 (10)	0.66277 (9)	−0.00942 (19)	0.0281 (4)
C40	0.40712 (13)	0.98701 (11)	0.3610 (3)	0.0374 (6)
C41	0.42203 (19)	0.95691 (13)	0.4692 (3)	0.0533 (9)
H41	0.402978	0.969116	0.546921	0.064*
C42	0.46483 (17)	0.90893 (13)	0.4635 (3)	0.0451 (7)
H42	0.474520	0.887993	0.538090	0.054*

Table 2: (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C43	0.49400 (11)	0.89049 (10)	0.3521 (2)	0.0274 (5)
C44	0.47856 (14)	0.92169 (13)	0.2441 (3)	0.0380 (6)
H44	0.497893	0.909873	0.166278	0.046*
C45	0.43515 (14)	0.96996 (13)	0.2489 (3)	0.0417 (6)
H45	0.424953	0.991047	0.174764	0.050*
C46	0.54228 (12)	0.83948 (11)	0.3585 (2)	0.0279 (5)
C47	0.64068 (12)	0.75953 (10)	0.1438 (2)	0.0279 (5)
H47	0.619606	0.774414	0.069887	0.033*
C48	0.69598 (11)	0.71606 (10)	0.1334 (2)	0.0241 (4)
C49	0.71806 (12)	0.70012 (10)	0.0140 (2)	0.0264 (5)
H49	0.694571	0.716879	–0.055533	0.032*
C50	0.80208 (12)	0.63944 (10)	0.0905 (2)	0.0279 (5)
H50	0.839551	0.613170	0.076552	0.033*
C51	0.78344 (12)	0.65153 (11)	0.2122 (2)	0.0289 (5)
H51	0.807231	0.633411	0.279841	0.035*
C52	0.72991 (12)	0.69020 (11)	0.2350 (2)	0.0274 (5)
H52	0.716338	0.699107	0.318319	0.033*

125.76 MHz): *d* 161.24 (C=O), 152.28, 149.20, 134.54, 129.80, 123.90 (Pyridine–C), 144.66 (CH=N), 138.0, 132.24, 130.08, 127.54 (Ar–C). **Analysis (%)** for $C_{13}H_{10}ClN_3O$ (259.69): C, 58.11 (Calc. 58.06); H, 4.14 (Calc. 4.18); N, 15.64 (Calc. 15.57).

2 Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(C). The N-bound H atoms were located in a difference map and refined freely. The crystal was refined as a two-component twin with the minor component = 0.2253(9).

3 Comment

Hydrazides and their *N*′-arylidene derivatives receive considerable interest for their remarkable biological activities [5, 6]. In addition, carbohydrazide-hydrazone derivatives are utilised as efficient intermediates for the synthesis of several biologically-active heterocyclic compounds [7, 8].

The synthesis and the crystal structure of a new *N*′-arylidene hydrazide derivative (I) are described herein along with an analysis of the molecular packing.

The molecular structures of the four independent molecules comprising the asymmetric-unit of (I) are shown in the upper four images of the figure (50% probability ellipsoids).

While to a first approximation, the molecules are similar to each other, having a strictly planar, central CN_2O residue, are C-connected to a 4-chlorophenyl and to a 3-pyridyl residue via the imine bond, conformational differences are evident as shown in the overlay diagram (the color code for the O1- to O4-containing molecules is red, green, blue and pink, respectively; the images were overlaid so the 3-pyridyl rings are coincident). A small twist is noted about the C8–C9 bond as seen in the value of the N2–C8–C9–C10 torsion angle of 171.5(2)°, suggesting this part of the molecule is relatively planar; the comparable values for the O2- to O4-containing molecules are –171.1(2)°, 174.7(2)° and –176.9(2)°, respectively. A greater twist is seen about the C4–C7 bond, i.e. C5–C4–C7–O1 = 163.5(2)°; the values for the O2- to O4-containing molecules are –170.8(3)°, –159.0(2)° and 174.0(3)°, respectively. These differences manifest in a range of dihedral angles between the terminal rings, i.e. 25.04(11)°, 11.79(12)°, 32.82(12)° and 15.16(12)°, respectively. While the differences in conformation confirm the choice of crystal symmetry, these are unlikely to have any chemical significance.

There are three closely related 3-pyridyl derivatives in the literature, which differ only in the nature of the substitution at the 4-position of the phenyl ring, i.e. with H [9], NMe_2 [10] and NO_2 [11] cf. Cl in (I). For comparison with (I), the values of the dihedral angles between the terminal rings are 47.79(14)°, 5.19(8)° and 28.29(4)°, respectively, highlighting the variability of conformations in this class of compound, at least in the solid-state. The occurrence of a Z' > 1 is not unusual in this class of compounds [12].

A supramolecular chain featuring amide-N–H···N(pyridyl) hydrogen bonds is prominent in the molecular packing, as illustrated in the lower view of the figure. The chains involve all four independent molecules [a representative interaction is H1n···N12^{i} [N1–H1n···N12^{i}: H1n···N12^{i} = 2.16(3) Å, N1···N12^{i} = 3.035(3) Å with angle at H1n = 167(3)° for symmetry operation (i): *x*, 3/2 – *y*, 1/2 + *z*].

Molecules assemble into supramolecular layers in the *ac*-plane. Prominent interactions between the twisted chains along the *a*-axis include pyridyl-C–H···O(carbonyl) [C12–H12···O2^{ii}: H12···O2^{ii} = 2.47 Å, C12···O2^{ii} = 3.176(3) Å with angle at H12 = 131° for (ii): 1 + *x*, 3/2 – *y*, –1/2 + *z*] and pyridyl-C–H···N(imine) [C49–H49···N11^{i}: H49···N11^{i} = 2.51 Å, C49···N11^{i} = 3.415(3) Å with angle at H49 = 158°] interactions. The 4-chlorophenyl rings project alternatively to either side of the layer and these inter-digitate with adjacent layers along the b-axis with close phenyl-C–Cl···π(phenyl, pyridyl) contacts [closest contact: C1–Cl1···Cg(N9-pyridyl)^{iii}: Cl1···Cg(N9-pyridyl)^{iii} = 3.4860(12) Å with angle at Cl1 = 170.47(9)° for (iii): 1 – *x*, 1/2 + *y*, 1/2 – *z*].

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