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N-[(*E*)-Quinolin-2-ylmethylidene]-1,2,4-triazol-4-amine hemihydrate

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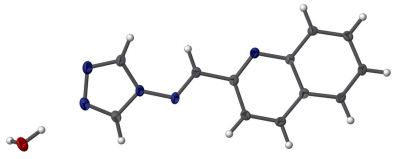
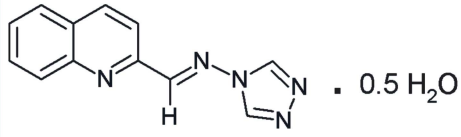
The title hemihydrate, $C_{12}H_9N_5\cdot0.5H_2O$, was isolated from the condensation reaction of quinoline-2-carbaldehyde with 4-amino-4*H*-1,2,4-triazole. The Schiff base molecule adopts an *E* configuration about the C=N bond and is approximately planar, with a dihedral angle between the quinoline ring system and the 1,2,4-triazole ring of 12.2 (1)°. In the crystal, one water molecule bridges two Schiff base molecules *via* O—H···N hydrogen bonds. The Schiff base molecules are interconnected by π–π stacking interactions [centroid-centroid distances of 3.7486 (7) and 3.9003 (7) Å] into columns along [1$\bar{1}$0].

3D view



Chemical scheme



Structure description

Schiff bases containing a heterocyclic 1,2,4-triazole moiety have been investigated for their bioactivities and pharmaceutical applications (Bhalgat *et al.*, 2014; Saadaoui *et al.*, 2019; Zhang *et al.*, 2019; Akin *et al.*, 2019). Recently, the structures of Schiff bases obtained from 3-amino-1*H*-1,2,4-triazole have been reported in detail (Kołodziej *et al.*, 2019). In the present work, we report the crystal structure of a new Schiff base, namely *N*-[(*E*)-quinolin-2-ylmethylidene]-1,2,4-triazol-4-amine hemihydrate.

Fig. 1 illustrates the molecular structure of the title compound with the atomic numbering. The bond lengths and angles are within the expected range and normal values. In particular, C3—C4, C3—N4 and N3—N4 bond lengths are 1.475 (2), 1.279 (2) and 1.387 (2) Å, respectively, confirming its Schiff base structure. The title compound as a whole is a conjugated system with two aromatic fragments (quinoline and triazole) linked by the azomethine C3=N4 double bond and is approximately planar, adopting an *E* configuration. The azomethine (N4/C3/H3) fragment is twisted by 7.36 (9)° with respect

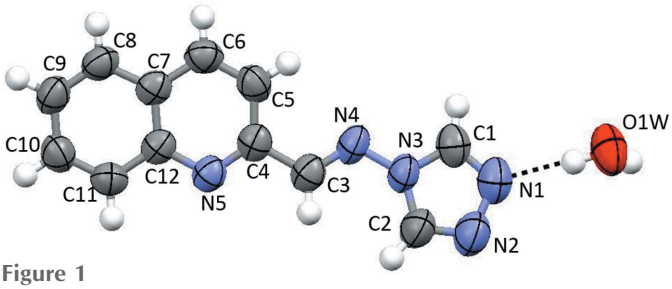


Figure 1
The molecular structure of the title compound, showing the atom-labelling scheme and 50% probability displacement ellipsoids.

to the quinoline ring system, and the dihedral angle between the quinoline ring system and the 1,2,4-triazole ring is 12.2 (1)°.

In the crystal, the O atom of water molecule lies on a twofold rotation axis and also close to the plane of the adjacent quinoline ring system, deviating by 0.157 Å. As a result, the water molecule forms a symmetric system of O—H···N hydrogen bonds (Table 1) with two Schiff base molecules (Fig. 2); the hydrogen bonds link the water molecule with the 1,2,4-triazole rings. The Schiff base molecules are stacked, forming molecular columns along [1$\bar{1}$0] (Fig. 3) by π–π stacking interactions with centroid–centroid distances of 3.7486 (7) Å between the C1/N1/N2/C2/N3 and C7–C12 rings, and 3.9003 (7) Å between the C1/N1/N2/C2/N3 and N5/C4–C7/C12 rings.

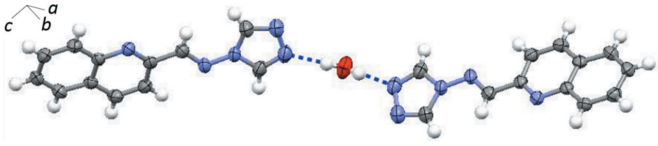


Figure 2
A partial packing diagram of the title compound, showing two Schiff base molecules linked by two identical intermolecular O—H···N hydrogen bonds.

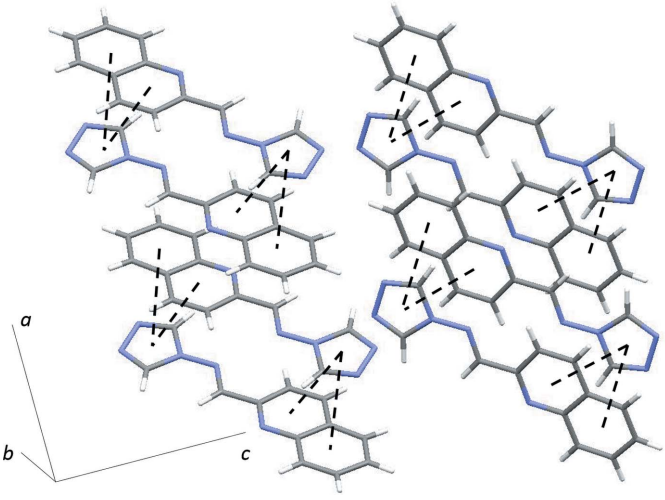


Figure 3
A partial packing diagram of the title compound, showing a molecular column formed by π–π stacking interactions.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1W···N1	0.914 (18)	1.939 (18)	2.8422 (11)	169.3 (17)

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{12}H_9N_5{\cdot}0.5H_2O$
M_r	232.25
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	100
a, b, c (Å)	13.7212 (12), 7.5047 (6), 21.1686 (18)
β (°)	100.524 (2)
V (Å^3)	2143.1 (3)
Z	8
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.79
Crystal size (mm)	0.36 × 0.26 × 0.17
Data collection	
Diffractometer	Bruker D8 Venture
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.626, 0.754
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	36175, 2200, 2142
R_{int}	0.036
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.090, 1.09
No. of reflections	2200
No. of parameters	164
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.22, −0.23

Computer programs: *APEX3* (Bruker, 2014), *SAINT* (Bruker, 2014), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *SHELXTL* (Sheldrick, 2008).

Synthesis and crystallization

A solution of quinoline-2-carbaldehyde (1.00 g, 6.0 mmol) was mixed with an equimolar solution of 4-amino-4*H*-1,2,4-triazole (0.54 g, 6.0 mmol) in a mixture of absolute ethanol and chloroform (1:1) (20 ml). Glacial acetic acid (2 drops) was added into the reaction mixture, followed by heating at 351 K for 6 h for complete conversion to the product (as confirmed by TLC analysis). The mixture was then kept in an ambient environment for two weeks. The crude product obtained was recrystallized from ethyl acetate solution, giving clear brown crystals (yield 55%) suitable for X-ray analysis. Presumably the water molecule of crystallization was absorbed from the atmosphere or as a by product during the synthesis. Analysis: $C_{12}H_9N_5$ (%): C 64.56, H 4.06, N 31.37; found (%): C 64.74, H 4.34, N 30.67; ^{1}H NMR (DMSO-d_6): δ 9.35 (*s*, 2H, H-1,2), 9.27 (*s*, 1H, CH═N, H-3), 8.56 (*d*, 1H, H-5. J = 8.12 Hz 1H), 8.17 (*d*, 1H, H-6. J = 8.12 Hz), 8.12 (*m*, 2H, H-8,11), 7.89 (*t*, 1H, H-10, J = 6.8 Hz), 7.75 (*t*, 1H, H-9, J = 6.8 Hz). ^{13}C NMR (DMSO-d_6): δ 157.55 (CH═N, C3), 152.17 (C1,2), 147.83, 139.79, 137.98, 131.12, 129.63, 128.92, 128.68, 118.36. IR (KBr, cm^{-1}): 3103

(Aryl C—H), 1597 (C═N), 1051 (N—N), 957 (C═S). EI—MS calculated for $C_{12}H_9N_5$ $[M]^+$: 223.24, Found: 223. m.p. 487–489 K.

The title compound was also synthesized using a green synthesis method. A solution of 4-amino-4*H*-1,2,4-triazole (0.11 g, 1.3 mmol) in 5 ml of distilled water was added to quinoline-2-carbaldehyde (0.20 g, 1.3 mmol) in 5 ml of distilled water. The resulting mixture was then stirred at room temperature for 1 h while the reaction progress was monitored by TLC. The clear light-brown crude product formed quantitatively after 1 h and was vacuum filtered, dried and recrystallized from ethyl acetate solution to give clear dark-brown crystals with 60% yield. The recrystallized compound from the conventional synthesis method and that from the green method were confirmed to be identical as given by the similar data from FTIR, TLC, MS, and melting-point measurements.

Refinement

Crystal data, data collection and structure refinement details of the title compound are summarized in Table 2.

Acknowledgements

We are thankful to the Chemical Sciences, Faculty of Science, Universiti Brunei Darussalam for supporting this research work. We also thank the National University of Singapore for the data collection and analysis of the single-crystal X-ray diffraction and the analytical data. We also thank Tennessee State University for collecting the NMR spectroscopic data.

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full crystallographic data

IUCrData (2020). **5**, x200134 [https://doi.org/10.1107/S2414314620001340]

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_N_-[(_E_)-Quinolin-2-ylmethylidene]-1,2,4-triazol-4-amine hemihydrate

Crystal data

$C_{12}H_9N_5{\cdot}0.5H_2O$
M_r = 232.25
Monoclinic, $C2/c$
a = 13.7212 (12) Å
b = 7.5047 (6) Å
c = 21.1686 (18) Å
β = 100.524 (2)°
V = 2143.1 (3) Å^3
Z = 8
$F(000)$ = 968
D_x = 1.440 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 9219 reflections
θ = 4.3–74.4°
μ = 0.79 mm^{-1}
T = 100 K
Block, brown
0.36 × 0.26 × 0.17 mm

Data collection

Bruker D8 Venture diffractometer
Radiation source: Sealed Microfocus Source
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2014)
T_{min} = 0.626, T_{max} = 0.754
36175 measured reflections
2200 independent reflections
2142 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 74.5°, θ_{min} = 4.3°
h = −17→17
k = −9→9
l = −25→26

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.090
S = 1.09
2200 reflections
164 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0426P)^2 + 1.6998P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Extinction correction: SHELXL2014 (Sheldrick, 2015*b*), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0104 (4)

Special details

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.14712 (7)	0.46460 (13)	0.69779 (5)	0.0216 (2)
N2	0.22716 (7)	0.56151 (14)	0.73141 (5)	0.0234 (2)
N3	0.24350 (6)	0.54032 (12)	0.63061 (4)	0.0168 (2)
N4	0.27388 (7)	0.54247 (12)	0.57163 (4)	0.0172 (2)
N5	0.46063 (6)	0.73766 (12)	0.50056 (4)	0.0156 (2)
C1	0.15910 (8)	0.45416 (15)	0.63833 (5)	0.0188 (2)
H1	0.1152	0.3949	0.6050	0.023*
C2	0.28338 (8)	0.60519 (16)	0.69030 (5)	0.0207 (3)
H2	0.3430	0.6720	0.7003	0.025*
C3	0.35238 (8)	0.62997 (14)	0.56723 (5)	0.0164 (2)
H3	0.3880	0.6932	0.6030	0.020*
C4	0.38588 (7)	0.62967 (14)	0.50486 (5)	0.0155 (2)
C5	0.33874 (8)	0.51790 (15)	0.45428 (5)	0.0176 (2)
H5	0.2856	0.4423	0.4602	0.021*
C6	0.37095 (8)	0.52081 (14)	0.39711 (5)	0.0173 (2)
H6	0.3398	0.4485	0.3624	0.021*
C7	0.45134 (7)	0.63285 (14)	0.38995 (5)	0.0150 (2)
C8	0.49101 (8)	0.63959 (14)	0.33287 (5)	0.0176 (2)
H8	0.4652	0.5636	0.2979	0.021*
C9	0.56649 (8)	0.75496 (15)	0.32765 (5)	0.0181 (2)
H9	0.5923	0.7598	0.2890	0.022*
C10	0.60599 (8)	0.86659 (15)	0.37961 (5)	0.0181 (2)
H10	0.6571	0.9485	0.3751	0.022*
C11	0.57180 (8)	0.85879 (14)	0.43664 (5)	0.0167 (2)
H11	0.6008	0.9319	0.4717	0.020*
C12	0.49343 (7)	0.74173 (13)	0.44309 (5)	0.0145 (2)
O1W	0.0000	0.27774 (16)	0.7500	0.0257 (3)
H1W	0.0437 (13)	0.351 (3)	0.7347 (9)	0.053 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0192 (5)	0.0245 (5)	0.0230 (5)	0.0016 (4)	0.0086 (4)	0.0027 (4)
N2	0.0225 (5)	0.0295 (5)	0.0201 (5)	0.0004 (4)	0.0087 (4)	0.0000 (4)
N3	0.0151 (4)	0.0211 (5)	0.0154 (4)	0.0012 (3)	0.0059 (3)	0.0007 (3)
N4	0.0163 (4)	0.0227 (5)	0.0138 (4)	0.0030 (3)	0.0056 (3)	0.0015 (3)
N5	0.0146 (4)	0.0177 (4)	0.0147 (4)	0.0019 (3)	0.0031 (3)	0.0003 (3)
C1	0.0155 (5)	0.0203 (5)	0.0218 (5)	0.0016 (4)	0.0062 (4)	0.0021 (4)
C2	0.0194 (5)	0.0269 (6)	0.0167 (5)	−0.0003 (4)	0.0060 (4)	−0.0016 (4)
C3	0.0153 (5)	0.0184 (5)	0.0155 (5)	0.0026 (4)	0.0033 (4)	0.0007 (4)
C4	0.0133 (5)	0.0181 (5)	0.0150 (5)	0.0035 (4)	0.0024 (4)	0.0022 (4)
C5	0.0136 (5)	0.0209 (5)	0.0178 (5)	−0.0017 (4)	0.0018 (4)	0.0024 (4)
C6	0.0164 (5)	0.0190 (5)	0.0153 (5)	−0.0005 (4)	−0.0001 (4)	−0.0002 (4)
C7	0.0144 (5)	0.0165 (5)	0.0135 (5)	0.0022 (4)	0.0008 (4)	0.0018 (4)
C8	0.0193 (5)	0.0205 (5)	0.0125 (5)	0.0000 (4)	0.0015 (4)	−0.0002 (4)

C9	0.0174 (5)	0.0241 (6)	0.0132 (5)	0.0009 (4)	0.0037 (4)	0.0022 (4)
C10	0.0149 (5)	0.0210 (6)	0.0182 (5)	−0.0021 (4)	0.0027 (4)	0.0021 (4)
C11	0.0160 (5)	0.0184 (5)	0.0153 (5)	−0.0010 (4)	0.0012 (4)	−0.0009 (4)
C12	0.0136 (5)	0.0164 (5)	0.0132 (5)	0.0032 (4)	0.0020 (4)	0.0010 (4)
O1W	0.0228 (6)	0.0227 (6)	0.0356 (7)	0.000	0.0153 (5)	0.000

Geometric parameters (Å, º)

N1—C1	1.3011 (14)	C5—H5	0.9500
N1—N2	1.3985 (14)	C6—C7	1.4169 (15)
N2—C2	1.3057 (14)	C6—H6	0.9500
N3—C1	1.3621 (14)	C7—C8	1.4140 (14)
N3—C2	1.3714 (14)	C7—C12	1.4245 (14)
N3—N4	1.3866 (12)	C8—C9	1.3698 (15)
N4—C3	1.2793 (14)	C8—H8	0.9500
N5—C4	1.3233 (14)	C9—C10	1.4099 (15)
N5—C12	1.3724 (13)	C9—H9	0.9500
C1—H1	0.9500	C10—C11	1.3739 (14)
C2—H2	0.9500	C10—H10	0.9500
C3—C4	1.4752 (14)	C11—C12	1.4143 (14)
C3—H3	0.9500	C11—H11	0.9500
C4—C5	1.4196 (15)	O1W—H1W	0.914 (18)
C5—C6	1.3623 (15)		
C1—N1—N2	107.30 (9)	C5—C6—C7	119.32 (10)
C2—N2—N1	107.22 (9)	C5—C6—H6	120.3
C1—N3—C2	105.24 (9)	C7—C6—H6	120.3
C1—N3—N4	121.04 (9)	C8—C7—C6	122.77 (9)
C2—N3—N4	133.67 (9)	C8—C7—C12	119.37 (9)
C3—N4—N3	117.85 (9)	C6—C7—C12	117.86 (9)
C4—N5—C12	117.27 (9)	C9—C8—C7	120.42 (10)
N1—C1—N3	110.36 (10)	C9—C8—H8	119.8
N1—C1—H1	124.8	C7—C8—H8	119.8
N3—C1—H1	124.8	C8—C9—C10	120.08 (10)
N2—C2—N3	109.88 (10)	C8—C9—H9	120.0
N2—C2—H2	125.1	C10—C9—H9	120.0
N3—C2—H2	125.1	C11—C10—C9	121.06 (10)
N4—C3—C4	117.94 (9)	C11—C10—H10	119.5
N4—C3—H3	121.0	C9—C10—H10	119.5
C4—C3—H3	121.0	C10—C11—C12	119.93 (10)
N5—C4—C5	124.21 (10)	C10—C11—H11	120.0
N5—C4—C3	115.64 (9)	C12—C11—H11	120.0
C5—C4—C3	120.16 (9)	N5—C12—C11	118.53 (9)
C6—C5—C4	118.91 (10)	N5—C12—C7	122.41 (9)
C6—C5—H5	120.5	C11—C12—C7	119.06 (9)
C4—C5—H5	120.5		
C1—N1—N2—C2	0.18 (12)	C4—C5—C6—C7	0.96 (15)

C1—N3—N4—C3	178.11 (10)	C5—C6—C7—C8	178.09 (10)
C2—N3—N4—C3	−4.93 (17)	C5—C6—C7—C12	−1.59 (15)
N2—N1—C1—N3	−0.19 (12)	C6—C7—C8—C9	177.65 (10)
C2—N3—C1—N1	0.12 (12)	C12—C7—C8—C9	−2.68 (15)
N4—N3—C1—N1	177.84 (9)	C7—C8—C9—C10	0.74 (16)
N1—N2—C2—N3	−0.11 (13)	C8—C9—C10—C11	1.74 (16)
C1—N3—C2—N2	0.00 (13)	C9—C10—C11—C12	−2.19 (16)
N4—N3—C2—N2	−177.30 (10)	C4—N5—C12—C11	178.64 (9)
N3—N4—C3—C4	178.88 (8)	C4—N5—C12—C7	−1.26 (14)
C12—N5—C4—C5	0.58 (15)	C10—C11—C12—N5	−179.70 (9)
C12—N5—C4—C3	−179.61 (8)	C10—C11—C12—C7	0.21 (15)
N4—C3—C4—N5	172.73 (9)	C8—C7—C12—N5	−177.90 (9)
N4—C3—C4—C5	−7.45 (15)	C6—C7—C12—N5	1.78 (15)
N5—C4—C5—C6	−0.45 (16)	C8—C7—C12—C11	2.20 (15)
C3—C4—C5—C6	179.75 (9)	C6—C7—C12—C11	−178.12 (9)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*···N1	0.914 (18)	1.939 (18)	2.8422 (11)	169.3 (17)