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3,5-Diamino-4*H*-1,2,4-triazol-1-ium 4-nitrobenzoate dihydrate

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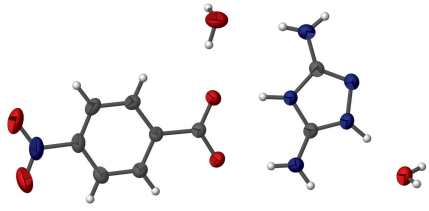
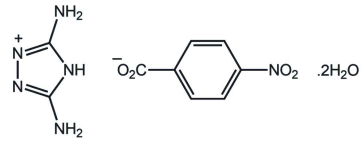
Structural data: full structural data are available from iucrdata.iucr.org

The crystal of the title salt hydrate, $C_2H_6N_5^+\cdot C_7H_4NO_4^-\cdot 2H_2O$, is built up from a 3,5-diamino-4*H*-1,2,4-triazol-1-ium cation linked to a 4-nitrobenzoate anion and to two water molecules through strong hydrogen bonds. The triazolyl ring is virtually planar, with the maximum deviation from the mean plane being 0.003 (1) Å. Small twists are noted in the anion with the dihedral angles between the ring and carboxylate and nitro groups being 7.82 (13) and 9.10 (15)°, respectively. In the crystal, molecules are linked by N—H···O, N—H···N, O—H···O and C—H···O interactions, forming layers parallel to $(\bar{1}01)$. The sheets are linked by O—H···O hydrogen bonds and π–π interactions between triazole and benzene rings [inter-centroid separation = 3.4967 (8) Å] to form a three-dimensional structure.

3D view



Chemical scheme



Structure description

Guanazole (3,5-diamino-1,2,4-triazole) derivatives, attract an interest and are actively studied as ligands in the synthesis of *d*-metal complexes (Aznar *et al.*, 2006), precursors of condensed *N*-heterocyclic systems (Fernandes *et al.*, 2015), corrosion inhibitors (El Issami *et al.*, 2007; Kuznetsov & Kazansky, 2008), biologically active compounds with a wide range efficiency (Chohan *et al.*, 2010) and as high-energy compounds (Kofman, 2002). The present work report the synthesis and crystal structure of the title compound (Fig. 1).

The asymmetric unit comprises a 3,5-diamino-4*H*-1,2,4-triazol-1-ium cation, a 4-nitrobenzoate anion and two water molecules The maximum deviation from the mean plane of the triazolyl ring is 0.003 (1) Å. Small twists are noted in the anion with the dihedral angles between the ring and carboxylate and nitro groups being 7.82 (13) and

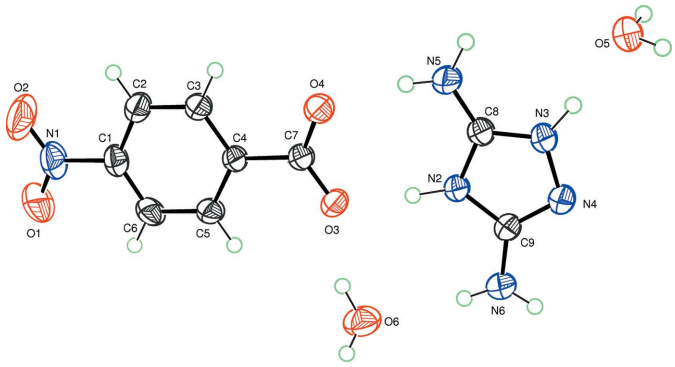


Figure 1
Plot of the constituents of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

9.10 (15)°, respectively. A similar structure has been reported previously (Ren *et al.*, 2013) isolated from the reaction of 3,5-dinitrobenzoic acid and 3,5-diamino-1,2,4-triazole.

In the crystal, the cations and anions are interconnected and are connected to the water molecules by N—H···O, N—H···N and O—H···O strong hydrogen bonds to form sheets parallel to ($\bar{1}$01); C—H···O interactions are also noted. In addition, the layers are linked by O—H···O hydrogen bonds and π–π interactions between triazolyl and benzoate rings [inter-centroid distance = 3.4967 (8) Å], forming a three-dimensional network as shown in Fig. 2 and Table 1.

Synthesis and crystallization

A mixture of 3,5-diamino-1,2,4 triazole (0.50 g; 5 mmol), 4-nitrobenzoyl chloride (0.92 g; 5 mmol) in ethanol-water solution (30 ml) was heated at reflux for 12 h. The completion of the reaction was confirmed by TLC. The solvent was removed by evaporation and the residue was recrystallized from ethanol solution to afford the title salt as colourless crystals.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

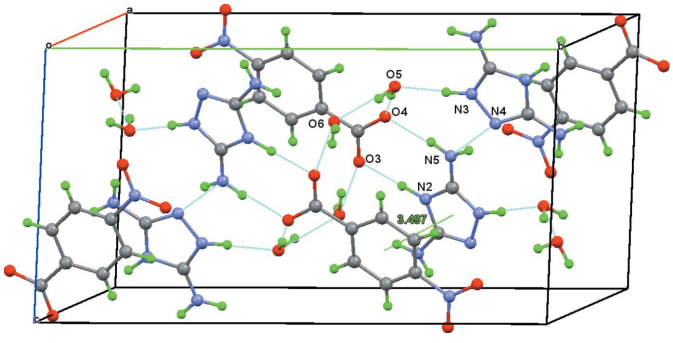


Figure 2
Partial crystal packing for the title compound, showing molecules linked by N—H···O and O—H···O hydrogen bonds and by π–π interactions, forming a three-dimensional network.

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2*N*···O3	0.97	1.76	2.7221 (14)	176
N3—H3*N*···O5	0.94	1.86	2.8021 (16)	176
N5—H5*B*···O4	0.87	1.93	2.7871 (17)	170
N6—H6*A*···O6	0.85	2.34	3.1866 (19)	174
N6—H6*B*···O5^{i}	0.85	2.29	3.1318 (17)	170
N5—H5*A*···N4^{ii}	0.90	2.06	2.9224 (17)	159
O5—H5*AO*···O6^{iii}	0.88	1.95	2.8156 (18)	166
O5—H5*BO*···O4^{i}	0.87	1.92	2.7868 (16)	176
O6—H6*AO*···O3	0.92	1.87	2.7363 (15)	157
O6—H6*BO*···O4^{iv}	0.92	2.24	3.0419 (19)	146
C6—H6···O2^{v}	0.93	2.45	3.333 (2)	160

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_2H_6N_5^+\cdot C_7H_4NO_4^-\cdot 2H_2O$
M_r	302.26
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	296
a, b, c (Å)	7.2050 (2), 19.8831 (6), 9.7676 (3)
β (°)	105.691 (1)
V (Å^3)	1347.14 (7)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.13
Crystal size (mm)	0.37 × 0.32 × 0.27
Data collection	
Diffractometer	Bruker X8 *APEX*
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.645, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	24987, 3487, 2811
R_{int}	0.028
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.676
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.133, 1.05
No. of reflections	3487
No. of parameters	190
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.34, −0.23

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *SHELXTL2014* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008) and *publCIF* (Westrip, 2010).

Acknowledgements

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full crystallographic data

IUCrData (2017). **2**, x170159 [https://doi.org/10.1107/S2414314617001596]

3,5-Diamino-4*H*-1,2,4-triazol-1-ium 4-nitrobenzoate dihydrate

Sanae Lahmidi, El Mokhtar Essassi, Mohammed Benchidmi, Mohamed Saadi and Lahcen El Ammari

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Crystal data

$C_2H_6N_5^+·C_7H_4NO_4^-·2H_2O$
M_r = 302.26
Monoclinic, $P2_1/n$
a = 7.2050 (2) Å
b = 19.8831 (6) Å
c = 9.7676 (3) Å
β = 105.691 (1)°
V = 1347.14 (7) Å^3
Z = 4
$F(000)$ = 632
D_x = 1.490 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3487 reflections
θ = 2.4–28.7°
μ = 0.13 mm^{-1}
T = 296 K
Block, colourless
0.37 × 0.32 × 0.27 mm

Data collection

Bruker X8 APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.645, T_{max} = 0.746
24987 measured reflections
3487 independent reflections
2811 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 28.7°, θ_{min} = 2.4°
h = −9→9
k = −26→26
l = −13→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.133
S = 1.05
3487 reflections
190 parameters
0 restraints
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.068P)^2 + 0.370P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

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}
C1	0.5653 (2)	0.65186 (7)	0.88659 (15)	0.0402 (3)
C2	0.6168 (2)	0.58783 (7)	0.93513 (15)	0.0436 (3)
H2	0.6969	0.5804	1.0259	0.052*
C3	0.5457 (2)	0.53473 (7)	0.84470 (14)	0.0395 (3)
H3	0.5783	0.4909	0.8752	0.047*
C4	0.42631 (18)	0.54581 (6)	0.70904 (13)	0.0313 (3)
C5	0.3781 (2)	0.61125 (6)	0.66323 (15)	0.0378 (3)
H5	0.2987	0.6190	0.5723	0.045*
C6	0.4482 (2)	0.66517 (7)	0.75320 (17)	0.0424 (3)
H6	0.4166	0.7092	0.7237	0.051*
C7	0.34457 (19)	0.48612 (6)	0.61666 (14)	0.0349 (3)
C8	0.1939 (2)	0.32045 (6)	0.39199 (14)	0.0370 (3)
C9	0.02010 (18)	0.37170 (7)	0.20317 (14)	0.0350 (3)
N1	0.6422 (2)	0.70814 (7)	0.98345 (16)	0.0554 (4)
N2	0.12815 (16)	0.38183 (5)	0.34091 (12)	0.0352 (2)
H2N	0.1630	0.4232	0.3935	0.042*
N3	0.12583 (18)	0.27665 (6)	0.28955 (13)	0.0419 (3)
H3N	0.1470	0.2300	0.2980	0.050*
N4	0.01422 (18)	0.30828 (6)	0.16723 (13)	0.0415 (3)
N5	0.3061 (2)	0.30868 (6)	0.52092 (14)	0.0546 (4)
H5A	0.3503	0.2672	0.5476	0.066*
H5B	0.3371	0.3434	0.5763	0.066*
N6	−0.0649 (2)	0.42254 (7)	0.11816 (14)	0.0478 (3)
H6A	−0.0507	0.4620	0.1533	0.057*
H6B	−0.1362	0.4100	0.0385	0.057*
O1	0.6188 (2)	0.76516 (6)	0.93599 (18)	0.0773 (4)
O2	0.7257 (3)	0.69499 (8)	1.10651 (16)	0.0888 (5)
O3	0.24541 (16)	0.49644 (5)	0.49201 (11)	0.0478 (3)
O4	0.37626 (18)	0.42890 (5)	0.67293 (12)	0.0518 (3)
O5	0.20562 (17)	0.13888 (5)	0.32618 (12)	0.0516 (3)
H5AO	0.3003	0.1230	0.2943	0.077*
H5BO	0.1041	0.1162	0.2822	0.077*
O6	0.01665 (19)	0.56608 (6)	0.26751 (13)	0.0589 (3)
H6AO	0.0886	0.5529	0.3562	0.088*
H6BO	−0.0927	0.5865	0.2780	0.088*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0440 (7)	0.0333 (6)	0.0431 (7)	−0.0053 (5)	0.0115 (6)	−0.0109 (5)
C2	0.0512 (8)	0.0400 (7)	0.0337 (7)	−0.0024 (6)	0.0014 (6)	−0.0045 (5)
C3	0.0489 (8)	0.0293 (6)	0.0352 (6)	0.0010 (5)	0.0025 (6)	0.0009 (5)
C4	0.0340 (6)	0.0265 (5)	0.0316 (6)	−0.0020 (4)	0.0059 (5)	−0.0007 (4)
C5	0.0413 (7)	0.0289 (6)	0.0384 (7)	0.0011 (5)	0.0028 (5)	0.0032 (5)
C6	0.0482 (8)	0.0251 (6)	0.0516 (8)	0.0019 (5)	0.0098 (6)	0.0001 (5)

C7	0.0377 (6)	0.0275 (6)	0.0352 (6)	−0.0012 (5)	0.0024 (5)	−0.0006 (5)
C8	0.0405 (7)	0.0269 (6)	0.0384 (7)	−0.0021 (5)	0.0017 (5)	−0.0006 (5)
C9	0.0320 (6)	0.0342 (6)	0.0352 (6)	−0.0006 (5)	0.0026 (5)	−0.0027 (5)
N1	0.0634 (9)	0.0411 (7)	0.0603 (9)	−0.0095 (6)	0.0143 (7)	−0.0194 (6)
N2	0.0386 (6)	0.0265 (5)	0.0345 (6)	0.0001 (4)	−0.0004 (4)	−0.0021 (4)
N3	0.0489 (7)	0.0265 (5)	0.0426 (6)	−0.0020 (5)	−0.0006 (5)	−0.0032 (4)
N4	0.0441 (6)	0.0338 (6)	0.0387 (6)	−0.0017 (5)	−0.0021 (5)	−0.0041 (5)
N5	0.0730 (9)	0.0319 (6)	0.0425 (7)	0.0040 (6)	−0.0126 (6)	0.0009 (5)
N6	0.0533 (7)	0.0404 (6)	0.0399 (6)	0.0080 (5)	−0.0045 (5)	0.0004 (5)
O1	0.0944 (11)	0.0375 (6)	0.0920 (10)	−0.0042 (6)	0.0115 (8)	−0.0217 (7)
O2	0.1303 (14)	0.0664 (9)	0.0536 (8)	−0.0222 (9)	−0.0027 (8)	−0.0234 (7)
O3	0.0591 (6)	0.0337 (5)	0.0373 (5)	0.0006 (4)	−0.0096 (5)	−0.0014 (4)
O4	0.0699 (7)	0.0267 (5)	0.0455 (6)	−0.0028 (4)	−0.0074 (5)	0.0024 (4)
O5	0.0571 (7)	0.0361 (5)	0.0538 (6)	−0.0023 (5)	0.0018 (5)	−0.0070 (4)
O6	0.0613 (7)	0.0595 (7)	0.0495 (6)	0.0077 (6)	0.0041 (5)	0.0136 (5)

Geometric parameters (Å, º)

C1—C6	1.373 (2)	C9—N4	1.3065 (17)
C1—C2	1.374 (2)	C9—N6	1.3459 (18)
C1—N1	1.4734 (18)	C9—N2	1.3748 (16)
C2—C3	1.3831 (19)	N1—O1	1.219 (2)
C2—H2	0.9300	N1—O2	1.218 (2)
C3—C4	1.3884 (18)	N2—H2N	0.9671
C3—H3	0.9300	N3—N4	1.3964 (17)
C4—C5	1.3891 (17)	N3—H3N	0.9397
C4—C7	1.5107 (17)	N5—H5A	0.8975
C5—C6	1.3918 (19)	N5—H5B	0.8689
C5—H5	0.9300	N6—H6A	0.8520
C6—H6	0.9300	N6—H6B	0.8459
C7—O3	1.2508 (16)	O5—H5AO	0.8816
C7—O4	1.2573 (16)	O5—H5BO	0.8682
C8—N3	1.3170 (17)	O6—H6AO	0.9193
C8—N5	1.3203 (18)	O6—H6BO	0.9165
C8—N2	1.3548 (16)		
C6—C1—C2	123.04 (13)	N5—C8—N2	125.02 (12)
C6—C1—N1	119.40 (13)	N4—C9—N6	125.65 (12)
C2—C1—N1	117.56 (13)	N4—C9—N2	111.90 (12)
C1—C2—C3	117.91 (13)	N6—C9—N2	122.44 (12)
C1—C2—H2	121.0	O1—N1—O2	123.74 (15)
C3—C2—H2	121.0	O1—N1—C1	118.22 (15)
C2—C3—C4	121.01 (13)	O2—N1—C1	118.04 (14)
C2—C3—H3	119.5	C8—N2—C9	106.10 (10)
C4—C3—H3	119.5	C8—N2—H2N	123.8
C3—C4—C5	119.51 (11)	C9—N2—H2N	129.9
C3—C4—C7	119.09 (11)	C8—N3—N4	111.24 (11)
C5—C4—C7	121.35 (11)	C8—N3—H3N	124.5

C4—C5—C6	120.10 (12)	N4—N3—H3N	124.2
C4—C5—H5	119.9	C9—N4—N3	103.62 (11)
C6—C5—H5	119.9	C8—N5—H5A	121.2
C1—C6—C5	118.42 (12)	C8—N5—H5B	116.2
C1—C6—H6	120.8	H5A—N5—H5B	122.6
C5—C6—H6	120.8	C9—N6—H6A	117.3
O3—C7—O4	124.21 (12)	C9—N6—H6B	114.1
O3—C7—C4	118.71 (11)	H6A—N6—H6B	128.3
O4—C7—C4	117.03 (11)	H5AO—O5—H5BO	105.6
N3—C8—N5	127.85 (13)	H6AO—O6—H6BO	107.7
N3—C8—N2	107.13 (11)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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O6—H6*BO*···O4^{iv}	0.92	2.24	3.0419 (19)	146
C6—H6···O2^{v}	0.93	2.45	3.333 (2)	160

Symmetry codes: (i) $x-1/2, -y+1/2, z-1/2$; (ii) $x+1/2, -y+1/2, z+1/2$; (iii) $-x+1/2, y-1/2, -z+1/2$; (iv) $-x, -y+1, -z+1$; (v) $x-1/2, -y+3/2, z-1/2$.