Stable hemiaminals containing a triazole ring

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General Remarks. All reactions were performed using commercially available reagents. All solvents were purchased from either POCh or Aldrich chemical companies and were used without further purification. NMR spectra were recorded on BRUKER-500 spectrometer. Infrared spectra were recorded KBr pellets on a Bruker IFS66 FT-IR spectrometer. Elemental analyses were carried out at the Microanalytical Laboratory of this university.

X-ray crystal structure analysis. All measurements were performed on a Kuma KM4CCD κ-axis diffractometer [1] with graphite monochromated MoKα radiation (λ = 0.71073 Å) at 100 K (**1**-**7**), 230 K (**2a**), and 295 K (**4a**) using an Oxford Cryosystem adapter [2]. Data collection: CrysAlis CCD [3]; data reduction: CrysAlis RED; program(s) used to solve structure: SHELXS97 [4]; program(s) used to refine structure: SHELXL97 [4]; software used to prepare material for publication: SHELXL97 and molecular graphics: DIAMOND [5].

Syntheses

(2-nitrophenyl)(4H-1,2,4-triazole-4-ylamino)methanol (**1**). Acetonitrilic solution (20 ml) of 2-nitrobenzaldehyde (5 mM) was added to an acetonitrilic solution (20 ml) of 4-amino-1,2,4-triazole (5 mM). The reaction mixture after complete dissolution was stirred for 15 minutes at room temperature (20 ˚C). The title compound crystallized directly from the acetonitrilic solution. Upon standing 3h at the room temperature, the solution deposited yellow crystals. The crystals were filtered off, washed with a small amount of acetonitrile and diethyl ether then dried in the air to afford (2-nitrophenyl)(4H-1,2,4-triazol-4-ylamino)methanol – (0.89g, 76%) m.p. 123-124 ˚C. Calculated: C 45.96, H 3.82, N 29.78%; found: C 46.13, H 3.60, N 30.06%. MS: (m/z) 236.1$[M]^+$.

^{1}H NMR (500 MHz, DMSO): δ 8.25 (s, 2H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 4.6 Hz, 1H), 6.05 – 5.93 (m, 1H).

^{13}C NMR (125 MHz, DMSO): δ 79.4, 124.1, 128.0, 129.7, 132.8, 133.0, 143.4, 148.3

IR (KBr, cm^{-1}): 3445sh, 3194sh, 3089sh, 2996m, 2850m, 1557m, 1515vs, 1441w, 1338vs, 1254w, 1191s, 1067vs, 1039vs, 980m, 953w, 879m, 860s, 788s, 717vs, 639vs.

(3-nitrophenyl)(4H-1,2,4-triazole-4-ylamino)methanol (**2**). Acetonitrilic solution (20 ml) of 3-nitrobenzaldehyde (5 mM) was added to an acetonitrilic solution (20 ml) of 4-amino-1,2,4-triazole (5 mM). The reaction mixture after complete dissolution was stirred for 15 minutes at room temperature (20 ˚C). The title compound crystallized directly from the acetonitrilic solution. Upon standing 2 days at the room temperature, the solution deposited yellow crystals (plates). The crystals were filtered off, washed with a small amount of acetonitrile and diethyl ether then dried in the air to afford (3-nitrophenyl)(4H-1,2,4-triazol-4-ylamino)methanol – (0.91g, 78%) m.p. 141-143 ˚C. Calculated: C 45.96, H 3.82, N 29.78%; found: C 45.86, H 3.78, N 29.91%. MS: (m/z) 236.1$[M]^+$.

^{1}H NMR (500 MHz, DMSO) δ 8.43 (s, 2H), 8.34 (s, 1H), 8.20 (d, *J* = 8.1 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.68 (t, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 6.7 Hz, 1H), 6.92 (s, 1H), 5.67 (d, *J* = 6.6 Hz, 1H).

^{13}C NMR (125 MHz, DMSO): δ 82.5, 121.4, 123.0, 129.7, 133.4, 142.2, 143.9, 147.6

IR (KBr, cm^{-1}): 3429sh, 3206sh, 3117sh, 2937sh, 2856sh, 2736sh, 1582w, 1520vs, 1481m, 1423w, 1353vs, 1309m, 1202m, 1096m, 1070vs, 1056vs, 979m, 953m, 927m, 882s, 759m, 729s, 674s, 636sh, 587sh.

(*N*-(3-nitrobenzylidene)-4*H*-1,2,4-triazole-4-amine) (**2a**). Ethanolic solution (20 ml) of 3-nitrobenzaldehyde (2 mM) was added to an ethanolic solution (20 ml) of 4-amino-1,2,4-triazole (2 mM). 3 drops of hydrochloric acid were added after complete dissolution and then the reaction mixture was stirred for 4 h at room temperature (20 ˚C). The title compound crystallized directly from the ethanolic solution. Upon standing 2 weeks at the room temperature, the solution deposited colorless crystals (needles). The crystals were filtered off, washed with a small amount of ethanol and diethyl ether then dried in the air to afford (*N*-(3-nitrobenzylidene)-4*H*-1,2,4-triazole-4-amine) – (0.35 g, 54%) m.p. 240-241 ˚C. Calculated: C 49.76, H 3.23, N 32.26%; found: C 49.58, H 3.15, N 32.25%. MS: (m/z) 218.1 $[M]^+$.

^{1}H NMR (500 MHz, DMSO) δ 9.32 (s, 1H), 9.28 (d, *J* = 0.4 Hz, 2H), 8.64 (s, 1H), 8.43 (dd, *J* = 8.2, 2.2 Hz, 1H), 8.27 (d, *J* = 7.8 Hz, 1H), 7.88 (t, *J* = 8.0 Hz, 1H).

^{13}C NMR (125 MHz, DMSO): δ 122.5, 126.4, 130.9, 133.8, 134.1, 139.0, 148.2, 156.0.

IR (KBr, cm^{-1}): 3440sh, 3139m, 3085sh, 3058sh, 1611m, 1578w, 1524vs, 1470m, 1360vs, 1330m, 1287m, 1219m, 1168s, 1110w, 1081w, 1061vs, 978m, 929w, 870w, 848m, 807m, 736s, 679s, 621s, 596m.

(4-nitrophenyl)(4H-1,2,4-triazole-4-ylamino)methanol (**3**). Similarly to other hemiaminals acetonitrilic solution (20 ml) of 4-amino-1,2,4-triazole (5 mM) was added to an acetonitrilic solution (20 ml) of 4-nitrobenzaldehyde (5 mM). The reaction mixture after complete dissolution was stirred for 20 minutes at room temperature (20 ˚C). The title compound crystallized directly from the acetonitrilic solution. Upon standing 4 days at the room

temperature, the solution deposited yellow crystals (needles). The crystals were filtered off, washed with a small amount of acetonitrile and diethyl ether then dried in the air to afford (4-nitrophenyl)(4H-1,2,4-triazol-4-ylamino)methanol – (0.81g, 69%) m.p. 145-147 ˚C. Calculated: C 45.96, H 3.82, N 29.78%; found: C 46.28, H 3.50 , N 30.02%. MS: (m/z) 236.1$[M]^+$.

^{1}H NMR (500 MHz, DMSO) δ 8.41 (s, 2H), 8.24 (d, *J* = 8.7 Hz, 2H), 7.76 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 6.6 Hz, 1H), 6.90 (d, *J* = 5.4 Hz, 1H), 5.65 (t, *J* = 6.0 Hz, 1H).

^{13}C NMR (125 MHz, DMSO): δ 82.6, 123.2, 128.0, 143.9, 147.15, 147.24.

IR (KBr, cm^{-1}): 3423sh, 3166sh, 3089sh, 2983sh, 2858sh, 2769sh, 1607m, 1569m, 1515vs, 1417w, 1349vs, 1291m, 1214w, 1199w, 1168m, 1107m, 1070s, 1050vs, 990m, 949s, 856vs, 755s, 739s, 688s, 630vs.

(2,4-dinitrophenyl)(4H-1,2,4-triazole-4-ylamino)methanol (**4**). Acetonitrilic solution (20 ml) of 4-amino-1,2,4-triazole (5 mM) was added to an acetonitrilic solution (20 ml) of 2,4-dinitrobenzaldehyde (5 mM). The reaction mixture after complete dissolution was stirred for 30 minutes at room temperature (20 ˚C). The title compound crystallized directly from the acetonitrilic solution. Upon standing 2h at the room temperature, the solution deposited yellow crystals. The crystals were filtered off, washed with a small amount of acetonitrile and diethyl ether then dried in the air to afford (2,4-dinitrophenyl)(4H-1,2,4-triazol-4-ylamino)methanol – (1.17g, 84%) m.p. 122-123 ˚C. Calculated: C 38.57, H 2.85, N 30.00%; found: C 38.93, H 2.66, N 30.12%. MS: (m/z) 281.1 $[M]^+$.

^{1}H NMR (500 MHz, DMSO) δ 8.73 (d, *J* = 2.3 Hz, 1H), 8.54 (dd, *J* = 8.6, 2.3 Hz, 1H), 8.27 (s, 2H), 8.04 (d, *J* = 8.6 Hz, 1H), 7.64 (d, *J* = 7.1 Hz, 1H), 7.39 (d, *J* = 5.5 Hz, 1H), 6.12 – 6.01 (m, 1H).

^{13}C NMR (125 MHz, DMSO): δ 79.1, 119.7, 127.1, 129.9, 139.3, 143.4, 147.5, 148.1.

IR (KBr, cm^{-1}): 3432sh, 3299sh, 3120sh, 2888sh, 2755sh, 1607s, 1532vs, 1496s, 1348vs, 1253w, 1189s, 1148m, 1078s, 1056vs, 978m, 908w803m, 716s, 632s, 569m.

(*N*-(2,4-dinitrobenzylidene)-4*H*-1,2,4-triazole-4-amine) (**4a**). Ethanolic solution (20 ml) of 4-amino-1,2,4-triazole (3 mM) was added to an ethanolic solution (20 ml) of 2,4-dinitrobenzaldehyde (3 mM). 3 drops of hydrochloric acid were added after complete dissolution and then the reaction mixture was stirred for 4 h at room temperature (20 ˚C). The title compound crystallized directly from the solution to afford (*N*-(2,4-dinitrobenzylidene)-4*H*-1,2,4-triazole-4-amine) (0.47g, 60%) m.p. 182-184 ˚C. Upon standing 2 weeks at the room temperature, the solution deposited colorless crystals (needles). Calculated: C 41.22, H 2.29, N 32.06%; found: C41.24, H 2.15, N 32.04%. MS: (m/z) 263.1 $[M]^+$.

^{1}H NMR (500 MHz, DMSO) δ 9.42 (s, 1H), 9.26 (s, 2H), 8.87 (d, *J* = 2.3 Hz, 1H), 8.70 (dd, *J* = 8.6, 2.3 Hz, 1H), 8.30 (d, *J* = 8.6 Hz, 1H).

^{13}C NMR (125 MHz, DMSO): δ 120.4, 128.3, 131.1, 131.8, 139.1, 148.5, 148.8, 152.4.

IR (KBr, cm^{-1}): 3446sh, 3098sh, 3038sh, 1611m, 1593m, 1529vs, 1459s, 1344vs, 1219w, 1208w, 1197w, 1170m, 1157m, 1050s, 920m, 855m, 832m, 771m, 740m, 711m, 676w, 614m, 515w.

(2-chloro-6-nitrophenyl)(4H-1,2,4-triazole-4-ylamino)methanol (**5**). Acetonitrilic solution (20 ml) of 4-amino-1,2,4-triazole (5 mM) was added to an acetonitrilic solution (20 ml) of 2-chloro-6-nitrobenzaldehyde (5 mM). The reaction mixture after complete dissolution was stirred for 20 minutes at room temperature (20 ˚C). The title compound crystallized directly from the acetonitrilic solution. Upon standing 3 days at the room temperature, the solution deposited yellow crystals (plates). The crystals were filtered off, washed with a small amount of acetonitrile and diethyl ether then dried in the air to afford (2-chloro-6-nitrophenyl)(4H-1,2,4-triazole-4-ylamino)methanol – (0.93g, 69%) m.p. 148-150 ˚C. Calculated: C 40.08, H 2.96, N 25.98%; found: C 40.39, H 2.83, N 26.19%. MS: (m/z) 270.0 $[M]^+$.

^{1}H NMR (500 MHz, DMSO) δ 8.28 (s, 2H), 8.03 (d, *J* = 8.6 Hz, 1H), 7.78 (d, *J* = 2.3 Hz, 1H), 7.72 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.53 (d, *J* = 7.3 Hz, 1H), 7.24 (d, *J* = 5.5 Hz, 1H), 6.07 – 5.91 (m, 1H).

^{13}C NMR (125 MHz, DMSO): δ 82.0, 122.7, 130.0, 130.8, 132.9, 133.6, 143.7, 150.6

IR (KBr, cm^{-1}): 3429sh, 3316sh, 3140sh, 3107sh, 2890sh, 2760sh, 1594w, 1530vs, 1442m, 1369s, 1295w, 1272w, 1215w, 1192m, 1087m, 1056s, 979m, 908w, 873m, 802m, 765m, 722m, 631s, 583w, 474w.

(4-chloro-3-nitrophenyl)(4H-1,2,4-triazole-4-ylamino)methanol (**6** and **7**). Acetonitrilic (**6**) or methanolic (**7**) solution (20 ml) of 4-amino-1,2,4-triazole (5 mM) was added to an acetonitrilic or methanolic solution (20 ml), respectively, of 4-chloro-3-nitrobenzaldehyde (5 mM). The reaction mixture after complete dissolution was stirred for 15 minutes at room temperature (20 ˚C). Upon standing 2 weeks at the room temperature, the solution deposited yellow crystals (needles). The crystals were filtered off, washed with a small amount of acetonitrile and diethyl ether then dried in the air to afford (4-chloro-3-nitrophenyl)(4H-1,2,4-triazole-4-ylamino)methanol – (0.85g, 63%) m.p. 133-134 ˚C. Calculated: C 40.08, H 2.96, N 25.98%; found: C 40.14, H 2.88, N 26.06%. MS: (m/z) 270.0 $[M]^+$.

^{1}H NMR (500 MHz, DMSO) δ 8.44 (s, 2H), 8.13 (s, 1H), 7.80 (s, 2H), 7.49 (d, *J* = 6.6 Hz, 1H), 6.98 (d, *J* = 5.5 Hz, 1H), 5.63 (t, *J* = 6.0 Hz, 1H).

^{13}C NMR (125 MHz, DMSO): δ 81.9, 123.7, 124.5, 131.4, 132.1, 141.0, 143.8, 147.1.

IR (KBr, cm^{-1}): 3141sh, 3085sh, 2979sh, 2868sh, 1693w, 1606m, 1528vs, 1476m, 1449w, 1393m, 1346vs, 1321s, 1285m, 1204w, 1177w, 1124w, 1066vs, 986m, 946s, 893m, 860s, 822m, 754m, 671m, 923vs, 555m.

X-Ray crystallography

Table a. Crystal data, data collection and structure refinement parameters for hemiaminals 1-5.

	(**1**)	(**2**)	(**3**)	(**4**)	(**5**)
Crystal					
Empirical formula	$C_9H_9N_5O_3$	$C_9H_9N_5O_3$	$C_9H_9N_5O_3$	$C_9H_8N_6O_5$	$C_9H_8N_5O_3Cl$
Molecular weight (g mol^{-1})	235.21	235.21	235.21	280.21	269.65
Crystal system., space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, Cc	Orthorhombic, $Pccn$	Monoclinic, $P2_1/c$
a (Å)	11.591(4)	12.316(4)	6.948(3)	14.202(4)	12.882(4)
b (Å)	10.437(4)	10.616(3)	20.546(6)	14.267(4)	8.440(3)
c (Å)	8.892(3)	7.863(3)	7.362(2)	11.223(3)	21.129(7)
β (°)	105.27(2)°	92.39(3)°	93.56(3)°		100.04(3)°
V (Å^3)	1037.7(6)	1027.2(6)	1048.9(7)	2274(1)	2262(1)
Z	4	4	4	8	8
D_{calc} (g cm^{-3})	1.506	1.521	1.489	1.637	1.584
μ (mm^{-1})	0.117	0.119	0.116	0.137	0.347
F(000)	488	488	488	1152	1104
Crystal description	Yellow plates	Yellow plates	Yellow needels	Yellow plates	Yellow plates
Diffractometer	Kuma KM4CCD	Kuma KM4CCD	Xcalibur PX with Onyx CCD	Kuma KM4CCD	Kuma KM4CCD
radiation, λ (Å)	MoK_α, 0.71073	MoK_α, 0.71073	MoK_α, 0.71073	MoK_α, 0.71073	MoK_α, 0.71073
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)
θ range for data collection (°)	3.24 – 30.00	3.23 – 30.00	4.84 – 31.99	3.63 – 29.50	2.90 – 30.00
Range of *hkl*	$-16 \le h \le 16$	$-17 \le h \le 17$	$-9 \le h \le 10$	$-19 \le h \le 19$	$-17 \le h \le 16$
	$-11 \le k \le 14$	$-14 \le k \le 14$	$-30 \le k \le 25$	$-19 \le k \le 19$	$-9 \le k \le 11$
	$-12 \le l \le 11$	$-11 \le l \le 9$	$-10 \le l \le 10$	$-11 \le l \le 15$	$-29 \le l \le 29$
Measured reflections	13472	15102	6722	26651	25378
Observed reflections ($I > 2\sigma(I)$)	2995	2988	1791	3151	6273
R_{int}	0.0976	0.0527	0.0210	0.0548	0.1096
Refinement					
Refinement on	F^2	F^2	F^2	F^2	F^2
R ($F_o^2 > 2\sigma(F_o^2)$)	$R1 = 0.0689$	$R1 = 0.0482$	$R1 = 0.0328$	$R1 = 0.0481$	$R1 = 0.0789$
	$wR2 = 0.1450$	$wR2 = 0.1232$	$wR2 = 0.0870$	$wR2 = 0.1141$	$wR2 = 0.1660$
S	1.188	1.099	1.057	1.161	1.052

Table b. Crystal data, data collection and structure refinement parameters for hemiaminals 6, 7 and Schiff bases 2a and 4a.

	(**6**)	(**7**)	(**2a**)	(**4a**)
Crystal				
Empirical formula	$C_9H_8N_5O_3Cl$	$C_9H_8N_5O_3Cl$	$C_9H_7N_5O_2$	$C_9H_6N_6O_4$
Molecular weight (g mol^{-1})	269.65	269.65	217.20	262.20
Crystal system., space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
a (Å)	7.143(2)	12.386(4)	3.870(2)	16.286(5)
b (Å)	21.329(6)	10.764(3)	10.917(4)	7.007(2)
c (Å)	7.429(2)	8.407(3)	23.019(7)	19.746(6)
β (^{o})	94.31(3)º	93.08(2) º	94.18(3)º	91.24(3)º
V (Å^3)	1128.6(5)	1119.2(6)	969.7(7)	2253(1)
Z	4	4	4	8
D_{calc} (g cm^{-3})	1.587	1.600	1.487	1.546
μ (mm^{-1})	0.348	0.351	0.112	0.126
F(000)	552	552	488	1072
Crystal description	Yellow needels	Yellow plates	Colorless needels	Colorless needels
Diffractometer	Kuma KM4CCD	Kuma KM4CCD	Kuma KM4CCD	Kuma KM4CCD
radiation, λ (Å)	MoK_α, 0.71073	MoK_α, 0.71073	MoK_α, 0.71073	MoK_α, 0.71073
T (K)	100(2)	100(2)	230(2)	295(2)
θ range for data collection (^{o})	3.35– 28.64	3.08– 25.06	3.25– 28.77	3.08– 28.75
Range of *hkl*	$-9 \le h \le 9$	$-14 \le h \le 14$	$-5 \le h \le 5$	$-21 \le h \le 21$
	$-27 \le k \le 27$	$-12 \le k \le 12$	$-14 \le k \le 14$	$-6 \le k \le 9$
	$-9 \le l \le 8$	$-9 \le l \le 10$	$-27 \le l \le 30$	$-26 \le l \le 25$
Measured reflections	7678	11195	8490	31807
Observed reflections ($I > 2\sigma(I)$)	2699	1985	2367	5577
R_{int}	0.0195	0.0259	0.0296	0.0578
Refinement				
Refinement on	F^2	F^2	F^2	F^2
R ($F_o^2 > 2\sigma(F_o^2)$)	$R1 = 0.0350$	$R1 = 0.0286$	$R1 = 0.0422$	$R1 = 0.0488$
	$wR2 = 0.0954$	$wR2 = 0.0755$	$wR2 = 0.1053$	$wR2 = 0.1307$
S	1.103	1.052	0.966	0.952

1: Crystal structure of (2-nitrophenyl)(4H-1,2,4-triazole-4-ylamino)methanol.

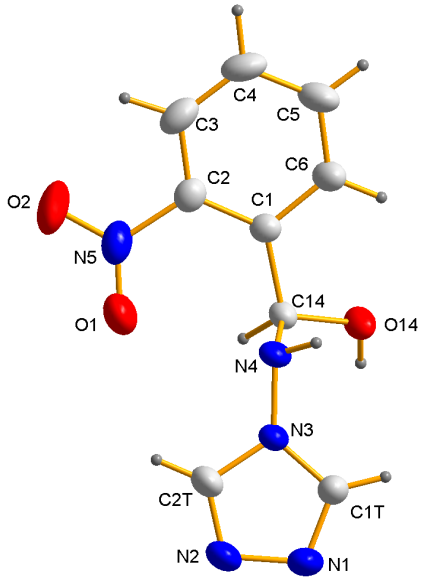

Figure 1 Crystal structure and labeling for (2-nitrophenyl)(4H-1,2,4-triazole-4-ylamino)methanol (**1**). Displacement ellipsoids are shown at the 50% probability level.

Table 1 Summary of selected bond lengths and angles [Å, °] for **1**.

Bond lengths [Å]		Selected angles [°]	
N(4)-N(3)	1.412(2)	N(3)-N(4)-C(14)	111.8(2)
N(4)-C(14)	1.469(2)	O(14)-C(14)-N(4)	112.3(2)
O(14)-C(14)	1.408(2)	O(14)-C(14)-C(1)	109.7(2)
N(3)-C(1T)	1.350(2)	N(4)-C(14)-C(1)	105.3(2)
N(3)-C(2T)	1.349(2)	C(14)-N(4)-N(3)-C(1T)	79.3(2)
C(14)-C(1)	1.525(2)	C(14)-N(4)-N(3)-C(2T)	-101.7(2)
O(1)-N(5)	1.216(2)	N(3)-N(4)-C(14)-O(14)	-72.9(2)
C(1)-C(6)	1.392(3)	N(3)-N(4)-C(14)-C(1)	167.9(2)
C(1)-C(2)	1.400(3)	C(6)-C(1)-C(14)-N(4)	100.4(2)
C(2)-C(3)	1.384(3)		
C(2)-N(5)	1.477(3)		
N(2)-C(2T)	1.297(3)		
N(2)-N(1)	1.388(2)		
N(1)-C(1T)	1.305(2)		
N(5)-O(2)	1.225(2)		
C(6)-C(5)	1.383(3)		
C(4)-C(3)	1.371(3)		
C(4)-C(5)	1.374(3)		

Table 2 Intermolecular hydrogen-bonds and short contacts geometry (Å, °) for **1**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
N(4)–H(40)...N(1)^{i}	0.86(2)	2.26(2)	3.112(2)	169(2)
O(14)–H(41)...N(2)^{ii}	0.92(2)	1.89(3)	2.794(2)	170(3)
C(1T)–H(1T)...O(14)^{iii}	0.91(2)	2.30(2)	3.205(3)	174(2)
C(14)–H(14)...O(2)^{iv}	0.99(2)	2.50(3)	3.533(3)	158(2)

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

2: Crystal structure of (3-nitrophenyl)(4H-1,2,4-triazole-4-ylamino)methanol.

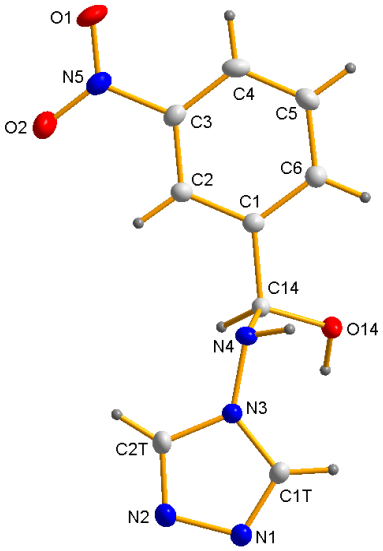

Figure 2 Crystal structure and labeling for (3-nitrophenyl)(4H-1,2,4-triazole-4-ylamino)methanol (**2**). Displacement ellipsoids are shown at the 50% probability level.

Table 3 Summary of selected bond lengths and angles [Å, °] for **2**.

Bond lengths [Å]		Selected angles [°]	
N(4)-N(3)	1.416(2)	N(3)-N(4)-C(14)	110.2(1)
N(4)-C(14)	1.478(2)	O(14)-C(14)-N(4)	112.6(1)
O(14)-C(14)	1.400(2)	O(14)-C(14)-C(1)	110.7(1)
N(3)-C(1T)	1.363(2)	N(4)-C(14)-C(1)	107.3(1)
N(3)-C(2T)	1.355(2)	C(14)-N(4)-N(3)-C(1T)	80.6(2)
C(14)-C(1)	1.517(2)	C(14)-N(4)-N(3)-C(2T)	-96.3(1)
O(1)-N(5)	1.235(2)	N(3)-N(4)-C(14)-O(14)	-73.9(1)
C(1)-C(6)	1.393(2)	N(3)-N(4)-C(14)-C(1)	164.1(1)
C(1)-C(2)	1.393(2)	C(6)-C(1)-C(14)-N(4)	100.1(1)
C(2)-C(3)	1.387(2)		
C(3)-N(5)	1.467(2)		
N(2)-C(2T)	1.312(2)		
N(2)-N(1)	1.393(2)		
N(1)-C(1T)	1.311(2)		
N(5)-O(2)	1.231(2)		
C(6)-C(5)	1.397(2)		
C(4)-C(3)	1.388(2)		
C(4)-C(5)	1.386(2)		

Table 4 Intermolecular hydrogen-bonds and short contacts geometry (Å, °) for **2**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
N(4)–H(40)...N(1)^{i}	0.92(2)	2.29(2)	3.194(2)	167(2)
O(14)–H(41)...N(2)^{ii}	0.92(2)	1.78(2)	2.706(2)	176(2)
C(1T)–H(1T)...O(14)^{iii}	0.95	2.12	3.069(2)	178
C(2T)–H(2T)...O(2)^{iv}	0.95	2.53	3.453(2)	165
C(14)–H(14)...O(2)^{v}	1.00	2.43	3.405(2)	166

Symmetry codes: (i) 1-x, -1/2-y, 1/2-z; (ii) x, 5/2-y, -1/2+z; (iii) 1-x, 2-y, -z; (iv) 2-x, 2-y, 1-z; (v) 2-x, 1/2+y, 1/2-z.

2a: Crystal structure of *N*-(3-nitrobenzylidene)-4*H*-1,2,4-triazole-4-amine.

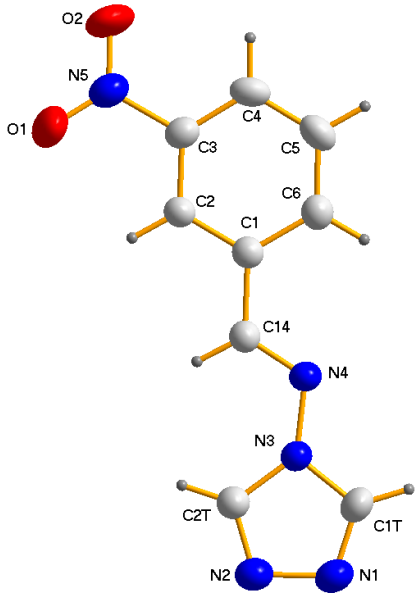

Figure 3 Crystal structure and labeling for (*N*-(3-nitrobenzylidene)-4*H*-1,2,4-triazole-4-amine) (**2a**). Displacement ellipsoids are shown at the 50% probability level.

Table 5 Summary of selected bond lengths and angles [Å, °] for **2a**.

Bond lengths [Å]		Selected angles [°]	
O(1)-N(5)	1.206(2)	N(3)-N(4)-C(14)	116.8(1)
O(2)-N(5)	1.212(2)	N(4)-C(14)-C(1)	121.1(1)
N(1)-C(1T)	1.296(2)	C(14)-N(4)-N(3)-C(1T)	176.3(1)
N(1)-N(2)	1.394(2)	C(14)-N(4)-N(3)-C(2T)	-5.2(2)
N(2)-C(2T)	1.297(2)	N(3)-N(4)-C(14)-C(1)	178.7(1)
N(3)-C(1T)	1.351(2)	C(6)-C(1)-C(14)-N(4)	3.8(2)
N(3)-C(2T)	1.364(2)		
N(3)-N(4)	1.392(2)		
N(4)-C(14)	1.265(2)		
N(5)-C(3)	1.469(2)		
C(1)-C(2)	1.379(2)		
C(1)-C(6)	1.395(2)		
C(1)-C(14)	1.462(2)		
C(2)-C(3)	1.375(2)		
C(3)-C(4)	1.378(2)		
C(4)-C(5)	1.374(2)		
C(5)-C(6)	1.380(2)		

Table 6 Intermolecular short contacts geometry (Å, °) for **2a**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
C(1T)–H(1T)...O(1)^{i}	0.94	2.38	3.201(2)	146
C(4)–H(4)...O(2)^{ii}	0.94	2.41	3.317(2)	162
C(2T)–H(2T)...N(1)^{iii}	0.94	2.46	3.387(2)	168
C(2)–H(2)...N(2)^{iii}	0.94	2.44	3.320(2)	156

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

3: Crystal structure of (4-nitrophenyl)(4H-1,2,4-triazole-4-ylamino)methanol.

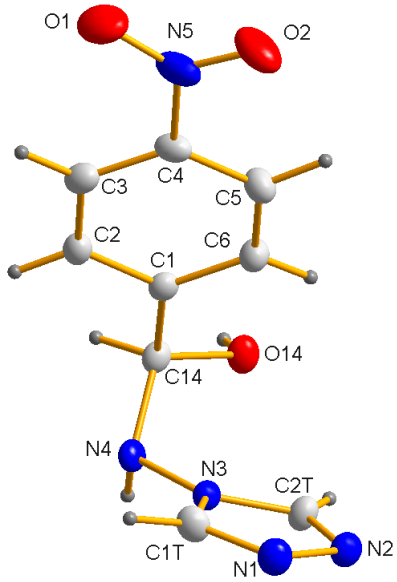

Figure 4 Crystal structure and labeling for (4-nitrophenyl)(4H-1,2,4-triazole-4-ylamino)methanol (**3**). Displacement ellipsoids are shown at the 50% probability level.

Table 7 Summary of selected bond lengths and angles [Å, °] for **3**.

Bond lengths [Å]		Selected angles [°]	
N(4)-N(3)	1.411(2)	N(3)-N(4)-C(14)	111.9(1)
N(4)-C(14)	1.467(2)	O(14)-C(14)-N(4)	112.7(1)
O(14)-C(14)	1.406(2)	O(14)-C(14)-C(1)	110.6(1)
N(3)-C(1T)	1.353(2)	N(4)-C(14)-C(1)	110.8(1)
N(3)-C(2T)	1.366(2)	C(14)-N(4)-N(3)-C(1T)	120.3(2)
C(14)-C(1)	1.515(2)	C(14)-N(4)-N(3)-C(2T)	-59.3(2)
O(1)-N(5)	1.221(2)	N(3)-N(4)-C(14)-O(14)	60.1(1)
C(1)-C(6)	1.393(2)	N(3)-N(4)-C(14)-C(1)	-64.3(2)
C(1)-C(2)	1.403(2)	C(6)-C(1)-C(14)-N(4)	104.1(1)
C(2)-C(3)	1.382(2)		
C(4)-N(5)	1.470(2)		
N(2)-C(2T)	1.311(2)		
N(2)-N(1)	1.388(2)		
N(1)-C(1T)	1.308(2)		
N(5)-O(2)	1.231(2)		
C(6)-C(5)	1.390(2)		
C(4)-C(3)	1.385(2)		
C(4)-C(5)	1.384(2)		

Table 8 Intermolecular hydrogen-bonds and short contacts geometry (Å, °) for **3**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
N(4)–H(40)...N(2)^{i}	0.88(2)	2.09(2)	2.967(2)	173(2)
O(14)–H(41)...N(1)^{ii}	0.86(3)	1.90(3)	2.751(2)	171(3)
C(2)–H(2)...O(2)^{iii}	0.95	2.60	3.265(2)	128
C(2T)–H(2T)...O(1)^{iv}	0.95	2.50	3.193(2)	130

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

4:Crystal structure of (2,4-dinitrophenyl)(4H-1,2,4-triazole-4-ylamino)methanol.

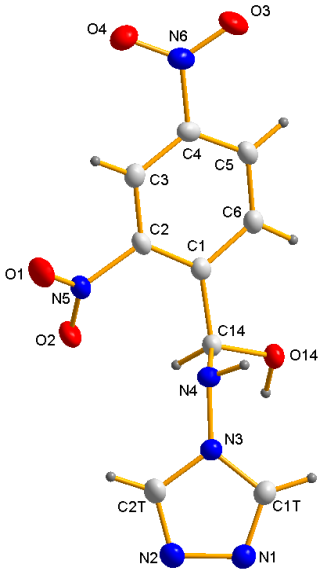

Figure 5 Crystal structure and labeling for (2,4-dinitrophenyl)(4H-1,2,4-triazole-4-ylamino)methanol (**4**). Displacement ellipsoids are shown at the 50% probability level.

Table 9 Summary of selected bond lengths and angles [Å, °] for **4**.

Bond lengths [Å]		Selected angles [°]	
N(4)-N(3)	1.412(2)	N(3)-N(4)-C(14)	111.2(1)
N(4)-C(14)	1.483(2)	O(14)-C(14)-N(4)	113.9(1)
O(14)-C(14)	1.401(2)	O(14)-C(14)-C(1)	110.9(1)
N(3)-C(1T)	1.351(2)	N(4)-C(14)-C(1)	103.8(1)
N(3)-C(2T)	1.357(2)	C(14)-N(4)-N(3)-C(1T)	79.9(2)
C(14)-C(1)	1.520(2)	C(14)-N(4)-N(3)-C(2T)	-94.7(2)
O(1)-N(5)	1.224(2)	N(3)-N(4)-C(14)-O(14)	-65.4(2)
C(1)-C(6)	1.390(2)	N(3)-N(4)-C(14)-C(1)	174.0(1)
C(1)-C(2)	1.401(2)	C(6)-C(1)-C(14)-N(4)	113.5(2)
C(2)-C(3)	1.383(2)		
C(2)-N(5)	1.476(2)		
N(2)-C(2T)	1.305(2)		
N(2)-N(1)	1.398(2)		
N(1)-C(1T)	1.306(2)		
N(5)-O(2)	1.225(2)		
C(6)-C(5)	1.391(2)		
C(4)-C(3)	1.378(2)		
C(4)-C(5)	1.378(2)		
N(6)-C(4)	1.476(2)		
N(6)-O(4)	1.222(2)		
N(6)-O(3)	1.228(2)		

Table 10 Intermolecular hydrogen-bonds and short contacts geometry (Å, °) for **4**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
N(4)-H(40)...O(1)^{i}	0.84(2)	2.66(2)	3.421(2)	151(2)
O(14)-H(41)...N(1)^{ii}	0.94(2)	1.81(2)	2.744(2)	168(2)
C(2T)-H(2T)...O(14)^{iii}	0.91(2)	2.42(2)	3.288(2)	162(2)
C(1T)-H(1T)...O(2)^{i}	0.95(2)	2.58(2)	3.226(2)	126(2)

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

4a: Crystal structure of *N*-(2,4-dinitrobenzylidene)-4*H*-1,2,4-triazole-4-amine.

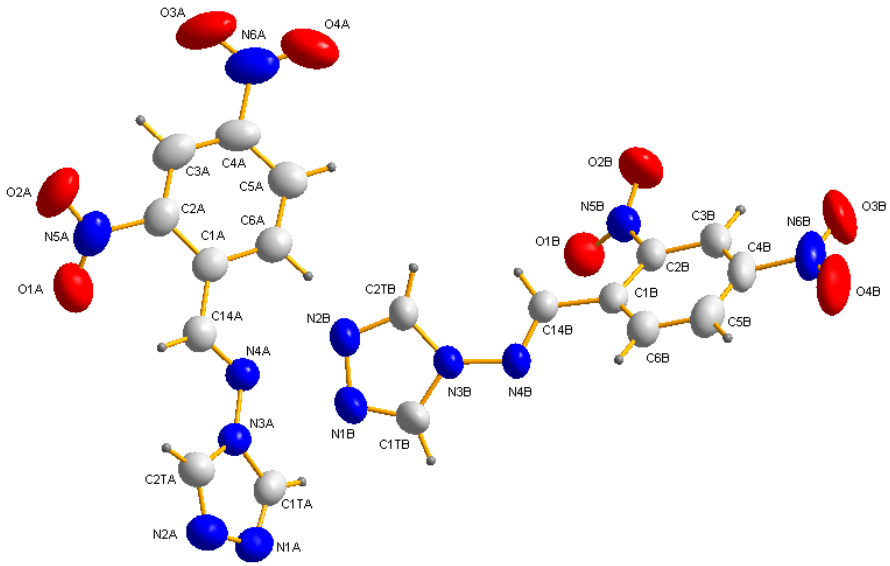

Figure 6 Crystal structure and labeling for (*N*-(2,4-dinitrobenzylidene)-4*H*-1,2,4-triazole-4-amine) (**4a**). Displacement ellipsoids are shown at the 50% probability level.

Table 11 Summary of selected bond lengths and angles [Å, °] for molecules A and B for **4a**.

Bond lengths [Å] for A and B			Selected angles [°] for A and B		
	A	B		A	B
N(3)-C(1T)	1.356(2)	1.343(3)	N(3)-N(4)-C(14)	117.7(2)	114.9(2)
N(3)-C(2T)	1.349(3)	1.357(3)	N(4)-C(14)-C(1)	117.1(2)	119.2(2)
N(3)-N(4)	1.383(2)	1.398(2)	C(14)-N(4)-N(3)-C(1T)	165.3(2)	162.1(2)
N(4)-C(14)	1.258(2)	1.267(2)	C(14)-N(4)-N(3)-C(2T)	-15.3(3)	-20.9(3)
N(2)-C(2T)	1.299(3)	1.295(3)	N(3)-N(4)-C(14)-C(1)	177.2(2)	174.0(2)
N(2)-N(1)	1.396(3)	1.384(2)	C(6)-C(1)-C(14)-N(4)	-20.8(3)	-32.2(3)
N(5)-O(1)	1.222(3)	1.217(2)			
N(5)-O(2)	1.219(3)	1.217(2)			
N(5)-C(2)	1.474(3)	1.464(3)			
C(14)-C(1)	1.469(3)	1.465(3)			
C(2)-C(3)	1.377(3)	1.383(3)			
C(2)-C(1)	1.392(3)	1.390(3)			
C(1)-C(6)	1.396(3)	1.390(3)			
C(6)-C(5)	1.377(3)	1.375(3)			
C(4)-C(3)	1.372(3)	1.363(3)			
C(4)-C(5)	1.369(3)	1.374(3)			
C(4)-N(6)	1.471(3)	1.483(3)			
N(1)-C(1T)	1.296(3)	1.294(3)			
N(6)-O(3)	1.122(3)	1.199(3)			
N(6)-O(4)	1.227(3)	1.223(3)			

Table 12 Intermolecular short contacts geometry (Å, °) for **4a**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
C(1TB)–H(1TB)...O(2B)^{i}	0.93	2.47	3.174(3)	132
C(2TA)–H(2TA)...N(2B)^{ii}	0.93	2.59	3.410(3)	148
C(14A)–H(14A)...N(2B)^{ii}	0.93	2.51	3.185(3)	130
C(2TB)–H(2TB)...N(2A)^{iii}	0.93	2.45	3.351(3)	164
C(14B)–H(14B)...N(1A)^{iii}	0.93	2.47	3.310(3)	151

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

5: Crystal structure of (2-chloro-6-nitrophenyl)(4H-1,2,4-triazole-4-ylamino)methanol.

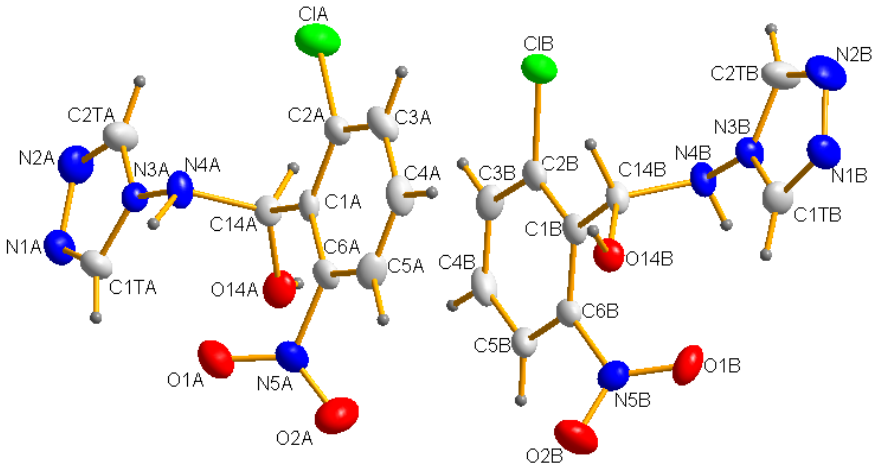

Figure 7 Crystal structure and labeling for (2-chloro-6-nitrophenyl)(4H-1,2,4-triazole-4-ylamino)methanol (**5**). Displacement ellipsoids are shown at the 50% probability level.

Table 13 Summary of selected bond lengths and angles [Å, °] for molecules A and B for **5**.

Bond lengths [Å] for A and B			Selected angles [°] for A and B		
	A	B		A	B
N(4)-N(3)	1.412(4)	1.417(4)	N(3)-N(4)-C(14)	111.2(3)	110.8(3)
N(4)-C(14)	1.479(5)	1.472(5)	O(14)-C(14)-N(4)	113.3(3)	114.9(3)
O(14)-C(14)	1.404(5)	1.405(5)	O(14)-C(14)-C(1)	111.5(3)	110.3(3)
N(3)-C(1T)	1.348(5)	1.352(5)	N(4)-C(14)-C(1)	106.4(3)	105.9(3)
N(3)-C(2T)	1.351(6)	1.357(5)	C(14)-N(4)-N(3)-C(1T)	89.0(5)	73.0(5)
C(14)-C(1)	1.525(5)	1.529(5)	C(14)-N(4)-N(3)-C(2T)	-92.1(5)	-112.4(4)
N(1)-C(1T)	1.294(5)	1.305(5)	N(3)-N(4)-C(14)-O(14)	-54.0(5)	-55.6(5)
C(1)-C(6)	1.392(6)	1.395(5)	N(3)-N(4)-C(14)-C(1)	-176.8(3)	-177.6(3)
C(1)-C(2)	1.390(5)	1.396(6)	C(6)-C(1)-C(14)-N(4)	100.4(4)	92.8(4)
C(2)-C(3)	1.388(6)	1.383(5)			
C(6)-N(5)	1.485(5)	1.477(5)			
N(2)-C(2T)	1.302(5)	1.313(5)			
N(2)-N(1)	1.390(5)	1.384(5)			
N(5)-O(1)	1.246(4)	1.233(4)			
N(5)-O(2)	1.196(5)	1.211(4)			
C(6)-C(5)	1.391(5)	1.383(5)			
C(4)-C(3)	1.388(6)	1.386(5)			
C(4)-C(5)	1.365(6)	1.377(6)			
Cl-C(2)	1.730(5)	1.747(4)			

Table 14 Intermolecular hydrogen-bonds and short contacts geometry (Å, °) for **5**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
O(14A)–H(41A)...N(1B)^{i}	0.84	1.89	2.720(4)	168
O(14B)–H(41B)...N(1A)^{ii}	0.84	1.94	2.757(4)	165
C(1TA)–H(1TA)...O(1A)^{iii}	0.95	2.41	3.341(6)	167
C(1TB)–H(1TB)...O(2A)^{iv}	0.95	2.57	3.242(6)	128
C(1TB)–H(1TB)...O(2B)^{iv}	0.95	2.56	3.423(5)	111
C(4A)–H(4A)...N(1A)^{ii}	0.95	2.57	3.423(5)	150
C(4B)–H(4B)...O(2A)^{v}	0.95	2.57	3.307(5)	134

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

6: Crystal structure of (4-chloro-3-nitrophenyl)(4H-1,2,4-triazole-4-ylamino)methanol.

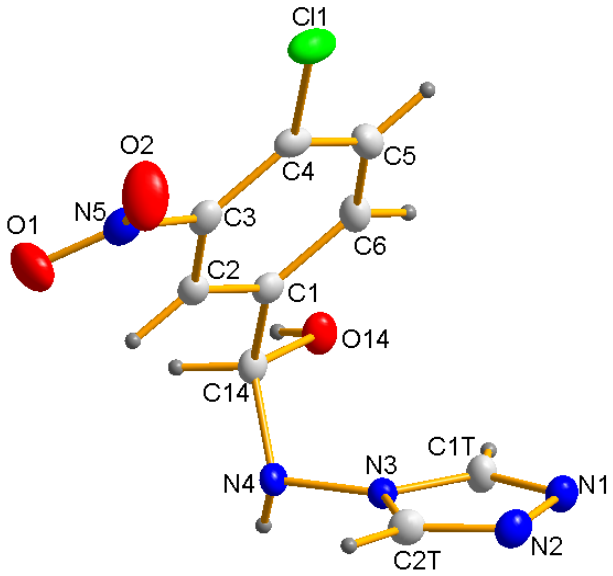

Figure 8 Crystal structure and labeling for (4-chloro-3-nitrophenyl)(4H-1,2,4-triazole-4-ylamino)methanol (**6**). Displacement ellipsoids are shown at the 50% probability level.

Table 15 Summary of selected bond lengths and angles [Å, °] for **6**.

Bond lengths [Å]		Selected angles [°]	
N(4)-N(3)	1.412(2)	N(3)-N(4)-C(14)	112.0(1)
N(4)-C(14)	1.468(2)	O(14)-C(14)-N(4)	113.2(1)
O(14)-C(14)	1.408(2)	O(14)-C(14)-C(1)	110.2(1)
N(3)-C(1T)	1.356(2)	N(4)-C(14)-C(1)	109.6(1)
N(3)-C(2T)	1.348(2)	C(14)-N(4)-N(3)-C(1T)	-56.7(2)
C(14)-C(1)	1.513(2)	C(14)-N(4)-N(3)-C(2T)	120.6(1)
O(1)-N(5)	1.230(2)	N(3)-N(4)-C(14)-O(14)	63.0(1)
C(1)-C(6)	1.392(2)	N(3)-N(4)-C(14)-C(1)	-60.5(1)
C(1)-C(2)	1.385(2)	C(6)-C(1)-C(14)-N(4)	111.9(1)
C(2)-C(3)	1.390(2)		
C(3)-N(5)	1.468(2)		
N(2)-C(2T)	1.304(2)		
N(2)-N(1)	1.388(2)		
N(1)-C(1T)	1.308(2)		
N(5)-O(2)	1.214(2)		
C(6)-C(5)	1.389(2)		
C(4)-C(3)	1.396(2)		
C(4)-C(5)	1.384(2)		
Cl(1)-C(4)	1.728(2)		

Table 16 Intermolecular hydrogen-bonds and short contacts geometry (Å, °) for **6**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
N(4)–H(40)...N(1)^{i}	0.85(2)	2.11(2)	2.952(2)	173(2)
O(14)–H(41)...N(2)^{ii}	0.81(2)	1.99(2)	2.800(2)	175(2)
C(6)–H(6)...N(1)^{iii}	0.95(2)	2.54(2)	3.446(2)	159(2)
C(14)–H(14)...O(1)^{iv}	0.96(2)	2.43(2)	3.345(2)	160(2)

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

7: Crystal structure of (4-chloro-3-nitrophenyl)(4H-1,2,4-triazole-4-ylamino)methanol.

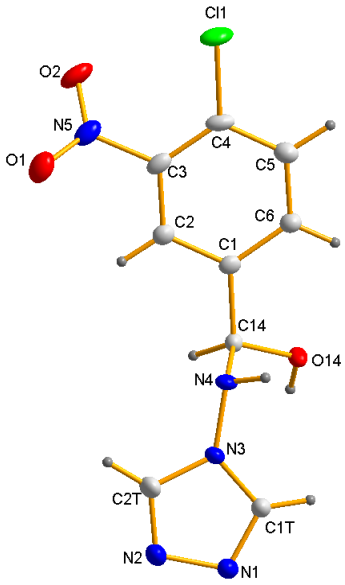

Figure 9 Crystal structure and labeling for (4-chloro-3-nitrophenyl)(4H-1,2,4-triazole-4-ylamino)methanol (**7**). Displacement ellipsoids are shown at the 50% probability level.

Table 17 Summary of selected bond lengths and angles [Å, °] for **7**.

Bond lengths [Å]		Selected angles [°]	
N(4)-N(3)	1.416(2)	N(3)-N(4)-C(14)	111.4(1)
N(4)-C(14)	1.474(2)	O(14)-C(14)-N(4)	113.0(1)
O(14)-C(14)	1.401(2)	O(14)-C(14)-C(1)	110.3(1)
N(3)-C(1T)	1.360(2)	N(4)-C(14)-C(1)	106.0(1)
N(3)-C(2T)	1.352(2)	C(14)-N(4)-N(3)-C(1T)	77.9(2)
C(14)-C(1)	1.514(2)	C(14)-N(4)-N(3)-C(2T)	-102.0(2)
O(1)-N(5)	1.226(2)	N(3)-N(4)-C(14)-O(14)	-70.9(2)
C(1)-C(6)	1.389(2)	N(3)-N(4)-C(14)-C(1)	168.2(2)
C(1)-C(2)	1.393(2)	C(6)-C(1)-C(14)-N(4)	100.7(2)
C(2)-C(3)	1.383(2)		
C(3)-N(5)	1.465(2)		
N(2)-C(2T)	1.305(2)		
N(2)-N(1)	1.394(2)		
N(1)-C(1T)	1.309(2)		
N(5)-O(2)	1.229(2)		
C(6)-C(5)	1.387(2)		
C(4)-C(3)	1.389(2)		
C(4)-C(5)	1.384(2)		
Cl(1)-C(4)	1.730(2)		

Table 18 Intermolecular hydrogen-bonds and short contacts geometry (Å, °) for **7**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
N(4)–H(40)...N(1)^{i}	0.87(2)	2.37(2)	3.214(2)	166(2)
O(14)–H(41)...N(2)^{ii}	0.87(2)	1.85(2)	2.725(2)	174(2)
C(1T)–H(1T)...O(14)^{iii}	0.95(2)	2.16(2)	3.106(2)	175(2)
C(14)–H(14)...O(2)^{iv}	0.96(2)	2.41(2)	3.332(2)	160(2)

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

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