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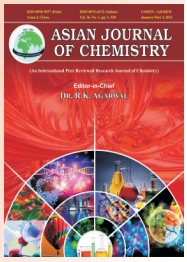

Synthesis and Structural Characterization of N-Amino Compounds

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Seven N-amino compounds were successfully synthesized *via* N-amination reaction. The structures of target compounds and intermediates were characterized by ^{1}H NMR, ^{13}C NMR, IR, elementary analysis, MS and X-ray single-crystal diffraction analysis. The single crystals of 3,5-diamino-1,2,4-triazole and 3,5-dinitro-1,2,4-triazole were obtained. Crystal data of 3,5-diamino-1,2,4-triazole: $C_2H_5N_5$, M_r = 99.11, Monoclinic, P2(1)/c, a = 10.652(4), b = 4.3411(14), c = 10.822(4) Å, α = 90(4), β = 118.714(4), γ = 90°, V = 0.4389(2) nm^3, Z = 4, Dc = 1.500 g cm^{-3}, μ = 0.113 mm^{-1}, F(000) = 208, R = 0.0354 and wR = 0.0936. Crystal data of 3,5-dinitro-1,2,4-triazole: $C_2H_3N_5O_5$, M_r = 177.09, Orthorhombic, P2(1)2(1)2(1), a = 4.937(3), b = 9.344(5), c = 140447(7) Å, α = 90, β = 90, γ = 90°, V = 0.6665(6) nm^3, Z = 4, Dc = 1.765 g cm^{-3}, μ = 0.171 mm^{-1}, F(000) = 360, R = 0.0555 and wR = 0.1772.

Keywords: N-amination reaction, N-amino compounds, Synthesis, Characterization, Crystal structure.

INTRODUCTION

Nitrogen-rich heterocyclic-based compounds have most often been utilized in energetic compounds due to their higher positive heats of formation, density and oxygen balance than those of their carbocyclic analogues[1]. Nitrogen-rich compounds form a unique class of energetic materials whose energy is derived from their high heats of formation directly attributable to the large number of inherently energetic C-N, N-N, C=N and N=N bonds[2]. Smaller amounts of hydrogen and carbon contribute to a better oxygen balance than normally is found with their carbocyclic analogues, a higher percentage of their decomposition products will be N_2[1,2]. Pyrazole, triazole, tetrazole, tetrazine, furazan and furoxan derivatives are interesting high energy materials due to their highly positive heats of formation, high nitrogen content and good thermal stability deriving from their aromaticity[3-7].

Recently, the combination of an azo group with high-nitrogen heteroaromatic rings has been extensively studied because the azo linkage not only desensitizes but also dramatically increases the heats of formation of high-nitrogen compounds, such as 3,3'-azo*bis*(6-amino-1,2,4,5-tetrazine)[8], 4,4'-azo*bis*-1,2,4-triazole[9], 1,1'-azo*bis*(3-nitro-1,2,4,5-tetrazole)[10], 1,1'-azo*bis*-1,2,3-triazole[3], 4,4',6,6'-*tetra*(azido)azo-1,3,5-triazine[11], 1,1'-azo*bis*(tetrazole)[5]. Most of the above compounds were synthesized using the N-amino compounds as raw materials. N-amination reaction is a effective method for obtaining N-amino compounds using imino compounds as starting materials[12].

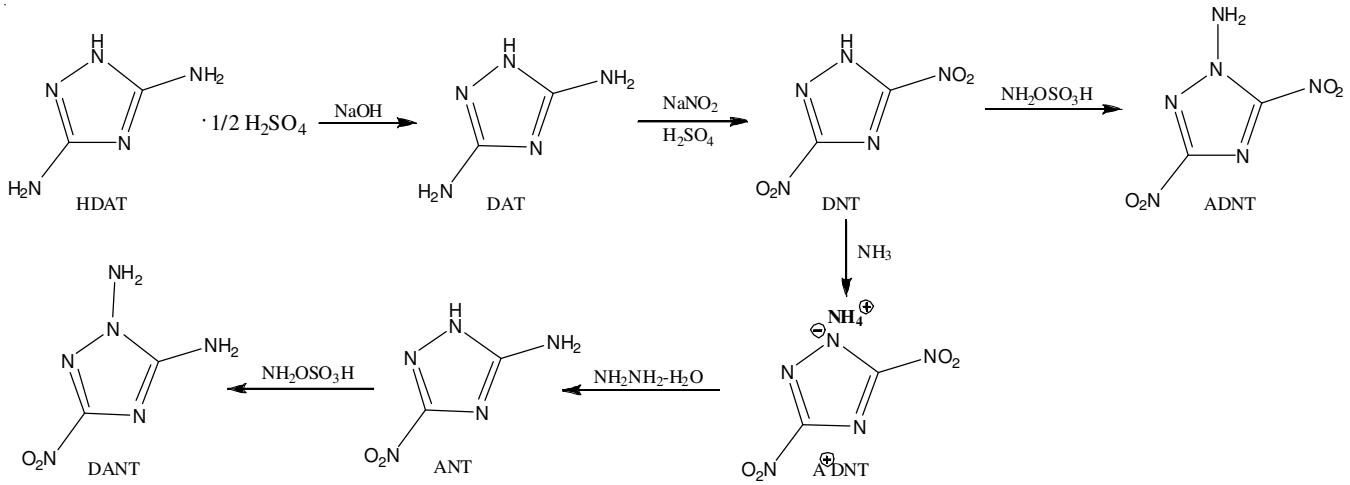
In this paper, seven N-amino compounds were synthesized using imino compounds as starting materials *via* N-amination reaction. The structures of target compounds were characterized by IR, ^{1}H NMR, ^{13}C NMR, elemental analysis and MS. Two single crystals of 3,5-diamino-1,2,4-triazole (DAT) and 3,5-dinitro-1,2,4-triazole (DNT·H_2O) were grown and their crystal structure were characterized by single-crystal X-ray diffraction analysis[13,14].

EXPERIMENTAL

All reagents were purchased from commercial sources and used without further purification. ^{1}H NMR and ^{13}C NMR were obtained in DMSO-d_6 on a Bruker AV 500 NMR spectrometer. Infrared spectra were obtained from KBr pellets on a Nicolet NEXUS870 Infrared spectrometer in the range of 400-4000 cm^{-1}. Elemental analyses (C, H and N) were performed on a VARI-El-3 elemental analyzer. Differential scanning calorimetry (DSC) was carried out in a platinum sample container using a Shimadzu DSC-60, the 1.0-1.5 mg sample was heated at a rate of 10 °C/min. The data of single crystal were collected on a Bruker SMART APEXII CCD X-ray diffractometer.

General procedure: Synthesis of DANT and ADNT: 1,5-diamino-3-nitro-1,2,4-triazole (DANT) and 1-amino-3,5-dinitro-1,2,4-triazole (ADNT) were synthesized by the method outlined in **Scheme-I**.

3,5-Diamino-1,2,4-triazole sulfate (DAT·1/2H_2SO_4) (32 g, 0.216 mol) was transferred into a three-necked round bottom



Scheme-I: Synthetic route for ADNT and DANT

flask fitted with a mechanical stirrer and a dropping funnel and then 274.5 mL of water was added. The solution was cooled to 15 °C after the solid was dissolved. Solid sodium hydroxide (8.72 g, 0.218 mol) was added to the reaction flask. After the sodium hydroxide was added completely, the reaction mixture was heated up to 40 °C and stirred for another 1.5 h. The water was removed under reduced pressure and then 500 mL of methanol was added to solid, the methanol mixture was heated up to 70 °C and stirred for another 2 h. The insoluble solid was filtered, the methanol was removed under reduced pressure and 12.6 g white solid of 3,5-diamino-1,2,4-triazole (DAT) was obtained with a yield of 58.9 %. ^{1}H NMR(DMSO-d_6, 500 MHz), δ : 5.227 (s, 4H, NH_2), 10.810 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 125 MHz), δ: 158.45; IR (KBr, ν_{max}, cm^{-1}), 3398, 3310 (-NH_2), 3235 (-NH); Anal. calcd for $C_2H_5N_5$: C 24.24, N 70.67, H 5.09; found C 24.11, N 70.61, H 5.13; MS (*m/z*): 99 [M$^+$].

To a solution of 54.2 g (0.786 mol) of sodium nitrite in 63.3 mL water at -10 to -5 °C, we added a solution of 8 g (0.081 mol) of DAT in 169.5 mL 1.2 mol/L sulfuric acid for 1.5 h, the reaction mixture was heated up to 60 °C and stirred for another 1 h, then cooled the reaction mixture to room temperature. 26.9 mL 6 mol/L sulfuric acid and 4.7 g (0.048 mol) aminosulfuric acid were added to reaction system and stirred for another 0.5 h, extracted with 90 × 5 mL of ether, dried with magnesium sulfate and the solvent was removed under reduced pressure and 7.89 g yellow oil 3,5-dinitro-1,2,4-triazole (DNT) was obtained with a yield of 61.4 %. ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 6.424 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 125 MHz), δ: 162.56; IR (KBr, ν_{max}, cm^{-1}), 3224 (-NH-), 1659, 1382 (-NO_2); Anal. calcd for $C_2H_3N_5O_5$: C 13.57, N 39.55, H 1.71; found C 13.73, N 38.91, H 2.13; MS (*m/z*): 159 [M$^+$].

3,5-Dinitro-1,2,4-triazole (DNT) (1 g, 6.289 mmol) was transferred into a three-necked round bottom flask, then 22 mL of water and sodium hydroxide (1.38 g, 34.6 mmol) were added. The reaction mixture was heated up to 50 °C and then a solution of hydroxylamino-*O*-sulfuric acid (2.13 g, 18.87 mmol) in 5 mL of water was added for 10 min. The pH was kept at 8-9 by the addition of 30 % sodium hydroxide solution. The reaction solution was stirred at 50 °C for another 4 h, extracted with 30 × 5 mL of ether, dried with magnesium sulfate and the solvent was removed under reduced pressure and 0.053 g yellow solid 1-amino-3,5-dinitro-1,2,4-triazole (ADNT) was obtained with a yield of 4.9 %. ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 6.369 (s, 1H, NH), 6.833 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 125 MHz), δ: 155.31, 155.92; IR (KBr, ν_{max}, cm^{-1}), 3424, 3340, 3297, 3229 (-NH_2), 1671 (C=N), 1520, 1313 (-NO_2); Anal. calcd for $C_2H_2N_6O_4$: C 13.80, N 48.28, H 1.16; found C 13.96, N 48.01, H 1.22; MS (*m/z*): 174 [M$^+$].

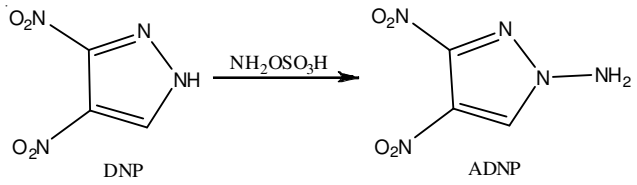
To a solution of 135.6 g (1.965 mol) of sodium nitrite in 158.2 mL of water at -10 to -5 °C, we added a solution of 20 g (0.202 mol) of DAT in 423.7 mL 1.2 mol/L sulfuric acid for 1.5 h. The reaction mixture was heated up to 60 °C and stirred for another 1 h, then cooled the reaction mixture to room temperature. 67.2 mL 6 mol/L sulfuric acid and 11.85 g (0.121 mol) aminosulfuric acid were added to reaction system and stirred for another 0.5 h, extracted with 322.5 × 3 mL of tri-octylamine and 265.5 mL toluene, dried with magnesium sulfate overnight. The magnesium sulfate was filtered and the filtrate reacted with excess ammonia to obtain the yellow solid, dried in vacuum to give 25.1 g of 3,5-dinitro-1,2,4-triazole ammonium (A$^{\oplus}$ DNT).

3,5-Dinitro-1,2,4-triazole ammonium (25.1g, 0.143 mol) was transferred into a three-necked round bottom flask, then 65 mL 80 % of hydrazine hydrate was added. The reaction mixture was heated up to 80 °C and stirred for another 2 h, cooled to room temperature, adjusted to pH 1-2 by 36 % HCl. The solid product was filtered, washed with cold water and dried in vacuum to give 14 g yellow solid 3-amino-5-nitro-1,2,4-triazole (ANT) with a yield of 76.1 %. m.p.: 234.6-235.9 °C. ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 6.817 (s, 2H, NH_2), 13.158 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 125 MHz), δ: 157.43, 160.90; IR (KBr, ν_{max}, cm^{-1}), 3453, 3330 (-NH_2), 3272 (-NH-), 1519, 1313 (-NO_2); Anal. calcd for $C_2H_5N_5O_3$: C 16.33, N 47.62, H 3.43; found C 16.69, N 48.94, H 3.27; MS (*m/z*): 129 [M$^+$].

To a solution of 1.5 g (11.6 mmol) of ANT in 28 mL of water at room temperature, we added sodium hydroxide (2.8 g, 69.8 mmol), the reaction mixture was heated up to 50 °C, then a solution of hydroxylamino-*O*-sulfuric acid (3.94 g, 34.88 mmol) in 7 mL of water was added. The reaction mixture

was stirred for another 4 h, cooled the reaction mixture to room temperature, extracted with 40 × 5 mL of ethyl acetate, dried with magnesium sulfate. The magnesium sulfate was filtered and the solvent was removed under reduced pressure and 0.69 g yellow solid 1,5-diamino-3-nitro-1,2,4-triazole (DANT) was obtained with a yield of 41.2 %. ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 6.425 (s, 2H, NH_2), 6.889 (s, 2H, NH_2); ^{13}C NMR (DMSO-d_6, 125 MHz), δ: 155.29, 155.89; IR (KBr, ν_{max}, cm^{-1}), 3426, 3338, 3228 (-NH_2), 1670 (C=N), 1519, 1313 (-NO_2); Anal. calcd for $C_2H_4N_6O_2$:C 16.67, N 58.32, H 2.80; found C 16.37, N 58.46, H 2.91; MS (*m/z*): 144 [M^+].

Synthesis of ADNP: 1-Amino-3,4-dinitropyrazole (ADNP) was synthesized by the method outlined in **Scheme-II**.



Scheme-II: Synthetic route for ADNP

To a solution of 1 g (6.33 mmol) of 3,4-dinitropyrazole (DNP) and 1.35 g (12.68 mmol) of sodium carbonate in 25 mL of water at 70-75 °C, we added a solution of 2.15 g (18.99 mmol) of hydroxylamino-*O*-sulfuric acid in 10.8 mL of water for 15 min. The pH was kept at 8-9 by the addition of sodium bicarbonate. The mixture was kept at 70-75 °C for 1.5 h, cooled the reaction mixture to room temperature, extracted with 35 × 5 mL of ether, dried with magnesium sulfate. The magnesium sulfate was filtered and the solvent was removed under reduced pressure and 0.16 g brown solid 1-amino-3,4-dinitropyrazole (ADNP) was obtained with a yield of 14.6 %. ^{1}H NMR(DMSO-d_6, 500 MHz), δ: 6.110 (s, 2H, NH_2), 7.768 (s, 1H, CH); ^{13}C NMR (DMSO-d_6, 125 MHz), δ: 115.97, 131.26, 144.81; IR (KBr, ν_{max}, cm^{-1}), 3498, 3452, 3368 (-NH_2), 3239 (=CH), 1546, 1322 (-NO_2); Anal. calcd. for $C_3H_3N_5O_4$: C 20.82, N 40.46, H 1.75; found C 20.37, N 39.26, H 1.92; MS (*m/z*): 173 [M^+].

Synthesis of ADNPP and DADNP: 1-Amino-3,6-dinitropyrazolo[4,3-c]pyrazole(ADNPP) and 1,4-diamino-3,6-dinitropyrazolo[4,3-c] pyrazole (DADNP) were synthesized by the method outlined in **Scheme-III**.

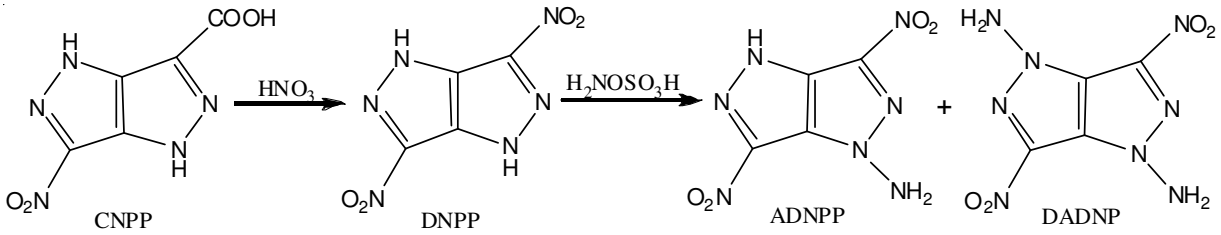
The concentrated nitric acid (1100 mL) was transferred into a three-necked round bottom flask fitted with a mechanical stirrer, then 6-dinitropyrazolo[4,3-c]pyrazole-3-carboxylic acid (CNPP) (190 g , 0.96 mo1) was added by portion wise addition under the cold water condition. The reaction mixture was heated up to 45 °C and stirred for another 6 h. The reaction mixture was poured into ice water, the yellow solid product was filtered, washed with cold water and dried in vacuum to give 137.1 g of 3,6-dinitropyrazolo[4,3-c] pyrazole (DNPP) with a yield of 72.3 %. ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 15.058 (s, 2H, 2NH); ^{13}C NMR (DMSO-d_6, 125 MHz), δ: 131.58, 137.89; IR (KBr, ν_{max}, cm^{-1}), 3266 (-NH-), 1548, 1521, 1373, 1348 (-NO_2); Anal. Calcd for $C_4H_2N_6O_4$: C 24.24, N 42.42, H 1.01; found C 24.38, N 42.71, H 1.16; MS (*m/z*): 198 [M^+].

To a solution of 4 g (0.0202 mol) of 3,6-dinitropyrazolo[4,3-c]pyrazole (DNPP) and 6.42 g (0.0605 mol) of sodium carbonate in 85 mL of water at 70-75 °C, we added a solution of 9.14 g (0.0808 mol) of hydroxylamino-*O*-sulfuric acid in 32 mL of water for 20 min. The pH was kept at 8-9 by the addition of sodium bicarbonate. The mixture was kept at 70-75 °C for 2 h and was then cooled to 15-20 °C. The precipitate was filtered off, washed with cold water and dried to give 0.57 g brown solid 1,4-diamino-3,6-dinitro pyrazolo[4,3-c]pyrazole (DADNP) with a yield of 12.4 %. ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 7.221(s, 4H, -2NH_2); ^{13}C NMR (DMSO-d_6, 125 MHz), δ: 128.49, 131.94; IR (KBr, ν_{max}, cm^{-1}), 3319, 3272 (-NH_2), 1532, 1395 (-NO_2); Anal. calcd for $C_4H_4N_8O_4$: C 21.05, N 49.12, H 1.75; found (%): C 21.09, N 48.57, H 1.98; MS (*m/z*): 228 [M^+].

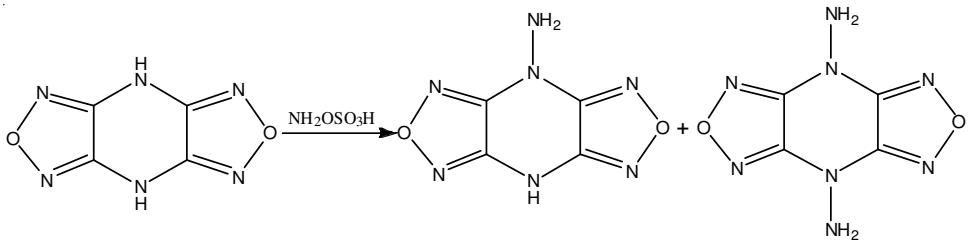
During the neutralization of the above alkaline filtrate solution with hydrochloric acid, the monosubstitition product of DNPP was separated. It was washed with cold water and dried to give 0.71 g brown 1-amino-3,6-dinitropyrazolo[4,3-c]pyrazole (ADNPP) with a yield of 16.5 %. ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 7.268 (s, 2H, NH_2), 15.091 (s, 1H, NH); ^{13}C NMR (DMSO-δ_6, 125 MHz), δ: 111.31 (s), 129.66 (s), 138.37 (s), 144.56 (s); IR (KBr, ν_{max}, cm^{-1}), 3513, 3318 (-NH_2), 3169 (-NH), 1626 (C=N), 1529, 1392, 1357 (-NO_2), 1239, 1172, 1033 (pyrazole ring); Anal. Calcd for $C_4H_3N_7O_4$: C 22.54, H 1.42, N 46.01; found C 22.47, H 1.51, N 46.09; MS (*m/z*): 213 [M^+].

Synthesis of ADFP and DADFP: 4-Aminodifurazano[3,4-b,e]pyrazine (ADFP) and 4,8-diaminodifurazano[3,4-b,e]pyrazine (DADFP) were synthesized by the method outlined in **Scheme-IV**.

To a solution of 0.5 g (0.003 mol) of 4,8-dihydrodifurazano[3,4-b,e]pyrazine (DFP) and 0.75 g (0.007 mol) of sodium carbonate in 14.5 mL of water at 70-75 °C, we added a solution of 1.02 g (0.008 mol) of hydroxylamino-*O*-sulfuric acid in 5.2 mL of water for 10 min. The pH was kept at 8-9 by the addition of sodium bicarbonate. The mixture was kept at 70-75 °C for 1.5 h and was then cooled to 15-20 °C. The precipitate was filtered off, washed with water and acetone and dried to give 0.04 g offwhite solid 4,8-diamino-difurazano[3,4-



Scheme-III: Synthetic route for ADNPP and DADNP



Scheme-IV: Synthetic route for ADNPP and DADNP

b,e]pyrazine (DADFP) with a yield of 6.8 %. m.p.: 282.3-283.8 °C. ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 5.788 (s, 4H, -2NH$_2$); ^{13}C NMR (DMSO-d_6, 125 MHz), δ: 149.93; IR (KBr, ν_{max}, cm^{-1}), 3312, 3246 (-NH$_2$), 1666 (C=N), 1613, 1443, 1021 (furazan ring); Anal. calcd for $C_4H_4N_8O_2$: C 24.50, N 57.13, H 2.06; found (%): C 24.41, N 57.23, H 2.01; MS (*m/z*): 180 [M-NH$_2$]$^-$.

During the neutralization of the above alkaline filtrate solution with hydrochloric acid, the monosubstitition product of DFP was separated. It was washed with water and dried to give 0.153 g white solid 4-aminodifurazano[3,4-b,e]pyrazine (ADFP) with a yield of 28.1 %. m.p.: 217.8-219.4 °C. ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 5.751 (s, 2H, -NH$_2$), 11.913 (s, 1H, -NH); ^{13}C NMR (DMSO-d_6, 125 MHz), δ: 146.89, 150.22; IR (KBr, ν_{max}, cm^{-1}), 3325 (-NH$_2$), 3283 (-NH), 1654 (C=N), 1618, 1445, 1003 (furazan ring); Anal. Calcd for $C_4H_3N_7O_2$: C 26.53, N 54.14, H 1.67; found C 26.38, N 54.21, H 1.76; MS (*m/z*): 180 [M-H]$^-$.

Structural determination of DAT: Single crystals of DAT suitable for X-ray diffraction studies were grown by allowing ethanol to slowly diffuse into a saturated solution of DAT for five days at room temperature.

A colorless single crystal with dimensions of 0.21 mm × 0.23 mm × 0.15 mm was chosen for X-ray diffraction analysis and the data were collected on a Bruker SMART APEXII CCD X-ray diffractometer with a MoK$_\alpha$ radiation (λ = 0.71073 Å) by using a ϕ-ω scan mode at 296(2) K. In the range of 3.77 ≤ θ ≤ 28.37°, a total of 2513 reflections were collected including 1068 unique ones (Rint = 0.0236), of which 1068 were observed with I > 2σ(I). The structure was solved by direct methods using SHELXS program of the SHELXL-97 package and refined with SHELXL package[13,14]. The final refinement was performed by full-matrix least-squares method with anisotropic thermal parameters on F^2 for the non-hydrogen atoms. The hydrogen atoms were located from Fourier difference maps. The final R = 0.0354, wR = 0.0936, S = 1.005, (Δρ)max = 0.163 and (Δρ)min = -0.215 e/Å^3.

Structural determination of DNT: Single crystals of DNT suitable for X-ray diffraction studies were grown by allowing water to slowly diffuse into a saturated solution of DNT for ten days at room temperature.

A yellow single crystal with dimensions of 0.20 × 0.18 × 0.23 was chosen for X-ray diffraction analysis and the data were collected on a Bruker SMART APEXII CCD X-ray diffractometer with a MoK$_\alpha$ radiation (λ = 0.71073 Å) by using a ϕ-ω scan mode at 296(2) K. In the range of 2.82 ≤ θ ≤ 28.33°, a total of 3144 reflections were collected including 1483 unique ones (Rint = 0.0276), of which 1483 were observed with I > 2σ(I). The structure was solved by direct methods using SHELXS program of the SHELXL-97 package and refined with SHELXL package[13,14]. The final refinement was performed by full-matrix least-squares method with anisotropic thermal parameters on F^2 for the non-hydrogen atoms. The hydrogen atoms were located from Fourier difference maps. The final R = 0.0555, wR = 0.1772, S = 1.166, (Δρ)max = 0.345 and (Δρ)min =-0.397 e/Å^3.

RESULTS AND DISCUSSION

Crystal structure of DAT: The selected bond lengths and bond angles, selected torsion angles and hydrogen bonds are given in Tables 1-3, respectively. A displacement ellipsoid plot with atomic numbering scheme and a perspective view of the crystal in a unit cell are shown in Figs. 1 and 2, respectively.

It can be seen from Fig. 1 that the molecular structure of DAT is composed of one 1,2,4-triazole ring and two amino groups to C(1) and C(2), respectively. Because of the Van Der Waals repulsion between those substituents contacted to C(1) and C(2), The torsion angles, which are N(4)-C(2)-N(3)-C(1) (-175.19(9)), N(4)-C(2)-N(1)-N(2) (175.13(9)), N(5)-C(1)-N(3)-C(2) (-176.20(10)), N(5)-C(1)-N(2)-N(1) (176.17(10)), C(2)-N(1)-N(2)-C(1) (0.06(11)), N(1)-C(2)-N(3)-C(1) (0.19(11)), in Table-2 indicate that all non-hydrogen atoms are amost in one plane. Moreover, the final three-dimensional networks (Fig. 2) are formed by classical intermolecular

TABLE-1
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°)

Bond	Dist.	Bond	Dist.	Bond	Dist.
C(1)-N(2)	1.3356(13)	C(1)-N(3)	1.3350(13)	C(1)-N(5)	1.3515(14)
C(2)-N(1)	1.3215(13)	C(2)-N(3)	1.3581(13)	C(2)-N(4)	1.3740(13)
N(1)-N(2)	1.3914(12)				
Angle	(°)	Angle	(°)	Angle	(°)
N(2)-C(1)-N(3)	110.42(9)	N(2)-C(1)-N(5)	124.19(10)	N(3)-C(1)-N(5)	125.27(9)
N(1)-C(2)-N(3)	115.66(9)	N(1)-C(2)-N(4)	123.00(9)	N(3)-C(2)-N(4)	121.17(9)
C(2)-N(1)-N(2)	101.57(8)	C(1)-N(2)-N(1)	109.58(9)	C(1)-N(3)-C(2)	102.77(8)

TABLE-2
SELECTED TORSION ANGLES (°)

Angle	(°)	Angle	(°)	Angle	(°)
N(3)-C(2)-N(1)-N(2)	-0.16(11)	N(4)-C(2)-N(1)-N(2)	175.13(9)	N(3)-C(1)-N(2)-N(1)	0.05(12)
N(5)-C(1)-N(2)-N(1)	176.17(10)	C(2)-N(1)-N(2)-C(1)	0.06(11)	N(2)-C(1)-N(3)-C(2)	-0.14(11)
N(5)-C(1)-N(3)-C(2)	-176.20(10)	N(1)-C(2)-N(3)-C(1)	0.19(11)	N(4)-C(2)-N(3)-C(1)	-175.19(9)

TABLE-3
HYDROGEN BONDS

D-H...A	d(D-H)	d(H...A)	d(D...A)	< (DHA)°	Symmetry code
N(2)-H(1)...N(1)	0.850(16)	2.154(16)	2.9534(13)	156.7(13)	-x, y + 1/2, -z + 3/2
N(4)-H(2)...N(5)	0.873(16)	2.489(16)	3.2200(17)	141.7(13)	x, -y-1/2, z + 1/2
N(4)-H(3)...N(1)	0.872(18)	2.301(18)	3.1046(16)	153.1(14)	-x, -y, -z + 2
N(5)-H(4)...N(4)	0.864(18)	2.347(18)	3.1424(16)	153.2(14)	x, -y + 1/2, z-1/2
N(5)-H(5)...N(3)	0.903(19)	2.107(19)	2.9976(15)	169.0(15)	-x + 1, -y, -z + 2

hydrogen bonds N(2)-H(1)...N(1) (-x, y + 1/2, -z + 3/2), N(4)-H(2)...N(5) (x, -y-1/2, z + 1/2), N(4)-H(3)...N(1) (-x, -y, -z + 2), N(5)-H(4)...N(4) (x, -y + 1/2, z-1/2), N(5)-H(5)...N(3) (-x + 1, -y, -z + 2) (Table-3), which further stabilize the solid structure of compound DAT.

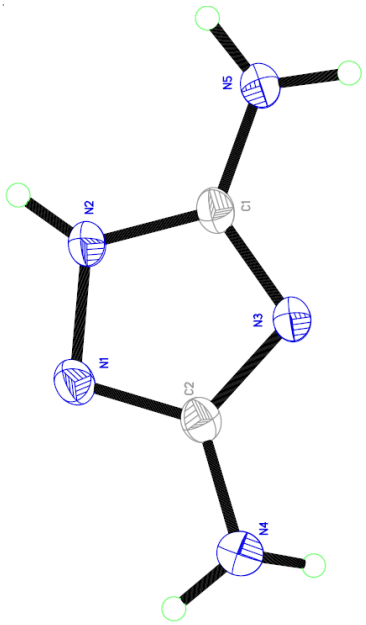


Fig. 1. Crystal structure of DAT

Crystal structure of DNT: The selected bond lengths and bond angles, selected torsion angles and hydrogen bonds are given in Tables 4-6, respectively. A displacement ellipsoid plot with atomic numbering scheme and a perspective view of the crystal in a unit cell are shown in Figs. 3 and 4, respectively.

It can be seen from Fig. 1 that the molecular structure of DNT is composed of one 1,2,4-triazole ring and two nitro groups to C(1) and C(2), respectively. Because of the van der Waals repulsion between those substituents contacted to C(1) and C(2), The torsion angles, which are O(2)-N(4)-C(1)-N(3) (177.7(2)), N(1)-N(2)-C(1)-N(3) (-0.2(3)), N(2)-N(1)-C(2)-N(5) (178.71(19)), O(4)-N(5)-C(2)-N(1) (0.6(3)), N(1)-N(2)-C(1)-N(4) (-179.3(2)), O(4)-N(5)-C(2)-N(3) (179.2(2)), O(2)-N(4)-C(1)-N(2) (-3.3(3)), O(3)-N(5)-C(2)-N(3) (-1.7(4)), in Table-5 indicate that all non-hydrogen atoms are amost in one plane. In addition, there are intermolecular O(5)-H(1)...O(3)

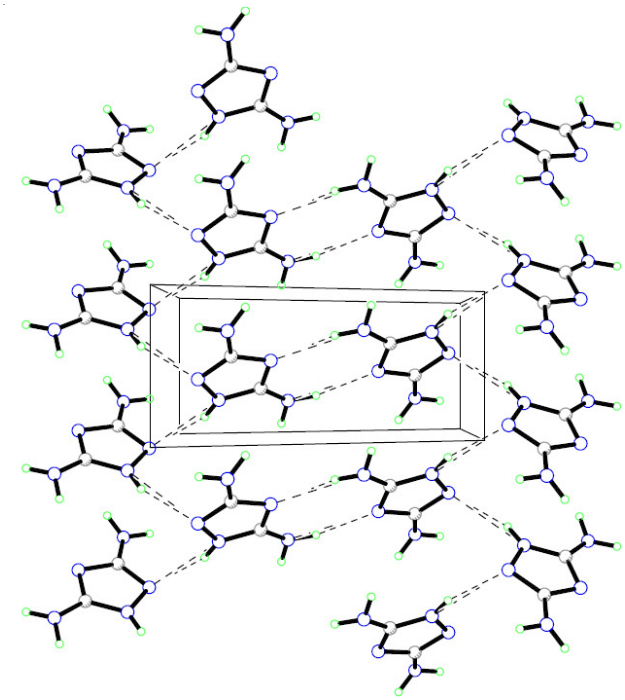


Fig. 2. Packing structure of DAT in a unit cell

(x + 1, y, z), O(5)-H(1)...N(5) (x + 1, y, z), N(2)-H(3)...O(5) (-x + 3/2, -y + 1, z + 1/2) hydrogen bonds between DNT and water, which further stabilize the structure. The corresponding lengths and angles of hydrogen bonds are listed in Table-6.

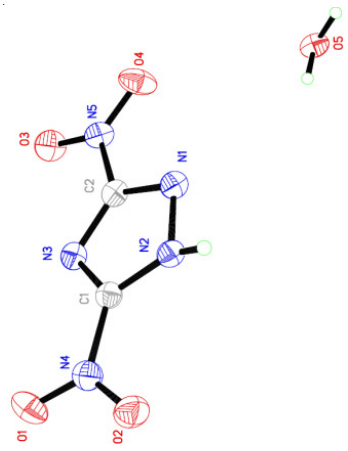


Fig. 3. Crystal structure of DNT

TABLE-4
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°)

Bond	Dist.	Bond	Dist.	Bond	Dist.
N(1)-C(2)	1.326(3)	N(1)-N(2)	1.329(3)	N(3)-C(2)	1.317(4)
N(3)-C(2)	1.317(4)	N(2)-C(1)	1.335(3)	N(5)-O(4)	1.208(3)
N(5)-O(3)	1.223(3)	N(5)-C(2)	1.454(3)	N(4)-O(1)	1.222(3)
N(4)-O(2)	1.231(3)	N(4)-C(1)	1.428(4)		
Angle	(°)	Angle	(°)	Angle	(°)
C(2)-N(1)-N(2)	101.1(2)	C(2)-N(3)-C(1)	99.6(2)	N(1)-N(2)-C(1)	108.8(19)
O(4)-N(5)-O(3)	124.5(2)	O(4)-N(5)-C(2)	117.9(2)	O(3)-N(5)-C(2)	117.6(2)
O(1)-N(4)-O(2)	123.3(3)	O(1)-N(4)-C(1)	118.8(2)	O(2)-N(4)-C(1)	117.9(2)
N(3)-C(1)-N(2)	112.3(2)	N(3)-C(1)-N(4)	126.0(2)	N(2)-C(1)-N(4)	121.7(2)
N(3)-C(2)-N(1)	118.1(2)	N(3)-C(2)-N(5)	122.5(2)	N(1)-C(2)-N(5)	119.4(2)

TABLE-5
SELECTED TORSION ANGLES (°)

Angle	(°)	Angle	(°)	Angle	(°)
C(2)-N(1)-N(2)-C(1)	0.1(2)	C(2)-N(3)-C(1)-N(2)	0.1(3)	C(2)-N(3)-C(1)-N(4)	179.2(2)
N(1)-N(2)-C(1)-N(3)	-0.2(3)	N(1)-N(2)-C(1)-N(4)	-179.3(2)	O(1)-N(4)-C(1)-N(3)	-1.4(4)
O(2)-N(4)-C(1)-N(3)	177.7(2)	O(1)-N(4)-C(1)-N(2)	177.6(2)	O(2)-N(4)-C(1)-N(2)	-3.3(3)
C(1)-N(3)-C(2)-N(1)	-0.1(3)	C(1)-N(3)-C(2)-N(5)	-178.8(2)	N(2)-N(1)-C(2)-N(3)	0.0(3)
N(2)-N(1)-C(2)-N(5)	178.71(19)	O(4)-N(5)-C(2)-N(3)	179.2(2)	O(3)-N(5)-C(2)-N(3)	-1.7(4)
O(4)-N(5)-C(2)-N(1)	0.6(3)	O(3)-N(5)-C(2)-N(1)	179.6(2)		

TABLE-6
HYDROGEN BONDS

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)°	Symmetry code
O(5)-H(1)...O(3)	1.01(3)	2.04(3)	3.042(3)	169(3)	x + 1, y, z
O(5)-H(1)...N(5)	1.01(3)	2.69(4)	3.557(3)	144(3)	x + 1, y, z
N(2)-H(3)...O(5)	0.75(6)	2.03(6)	2.685(3)	145(6)	-x + 3/2, -y + 1, z + 1/2

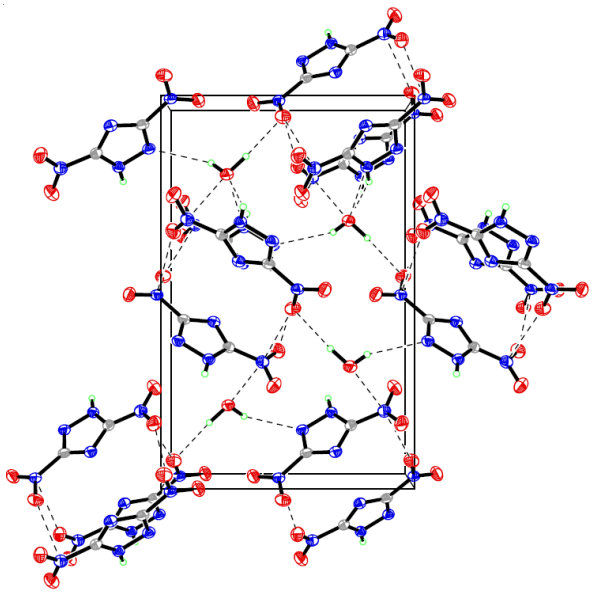


Fig. 4. Packing structure of DNT in a unit cell

Conclusion

In summary, seven N-amino compounds were synthesized using imino compounds as start materials and hydroxylamino-O-sulfuric acid as amination reagent as N-amination reaction. The structures of target compounds and intermediates were characterized. Two single crystals of 3,5-diamino-1,2,4-triazole (DAT) and 3,5-dinitro-1,2,4-triazole (DNT·H_2O) were grown and their crystal structure were characterized by single-crystal X-ray diffraction analysis.

Supplementary data: Crystallographic data for the structural analysis have been deposited in the Cambridge Data Center (CCDC), CCDC number of 3,5-diamino-1,2,4-triazole (DAT): 920604 for $C_2H_5N_5$, CCDC number of 3,5-dinitro-1,2,4-triazole (DNT·H_2O): 920605 for $C_2H_3N_5O_5$.

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