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Short Note

3-(4-Amino-1,2,5-oxadiazol-3-yl)-4-(4-nitro-1,2,5-oxadiazol-3-yl)-1,2,5-oxadiazole

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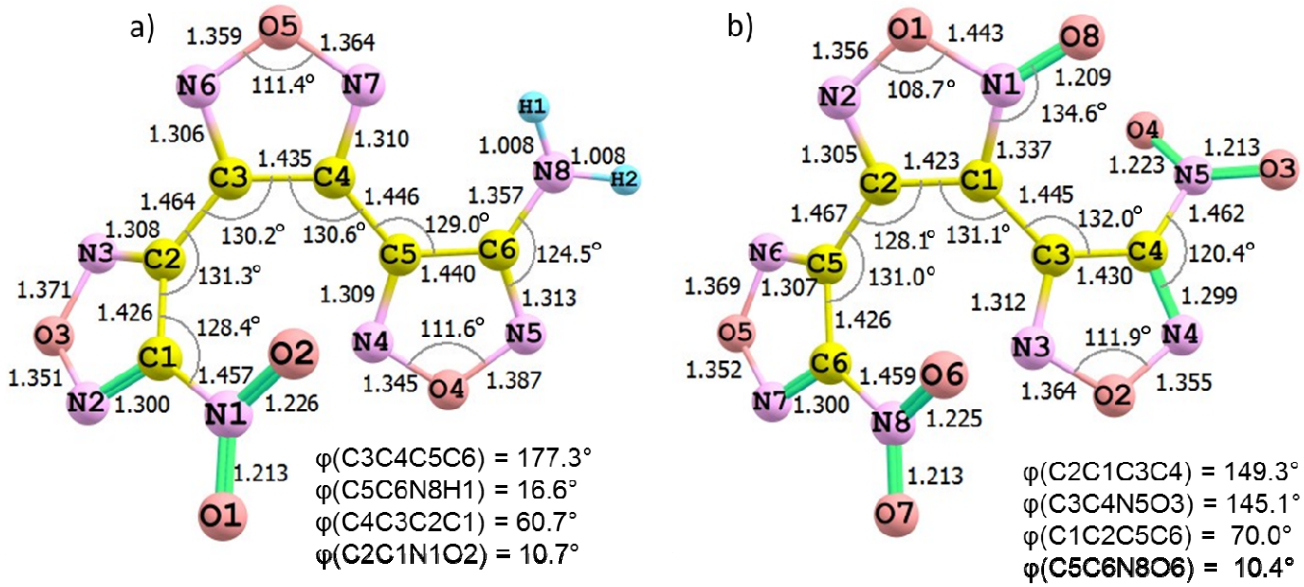
Abstract: The title compound 3-(4-amino-1,2,5-oxadiazol-3-yl)-4-(4-nitro-1,2,5-oxadiazol-3-yl)-1,2,5-oxadiazole (ANFF-1) was synthesized by: (**1**) by reaction of 3,4-bis(4-nitro-1,2,5-oxadiazol-3-yl)-1,2,5-oxadiazole (BNFF-1) with gaseous ammonia in toluene and (**2**) by partial oxidation of 3,4-bis(4-amino-1,2,5-oxadiazol-3-yl)-1,2,5-oxadiazole (BAFF-1) with 35% H_2O_2 in concentrated H_2SO_4.

Keywords: high explosives; heterocyclic energetic materials

Introduction

The relatively high density (1.782 g/mL) together with low melting point (100 °C) makes ANFF-1 (Figure 1a) very attractive as a secondary explosive, oxidizer and melt-castable explosive [1]. It is structurally similar to another heterocyclic energetic compound, 3,4-bis(4-nitro-1,2,5-oxadiazol-3-yl)-1,2,5-oxadiazole-1-oxide (BNFF, Figure 1b) [2–7] and may serve as an alternative to BNFF in some weapon applications. In this short note, we report two synthetic methods that were developed for the synthesis of ANFF-1.

Figure 1. Geometry structures of (**a**) ANFF-1 and (**b**) BNFF molecules were obtained from Density Functional Theory modeling in the B3LYP/6-31+G(2df,p) approximation. The bond distances are shown in Å.



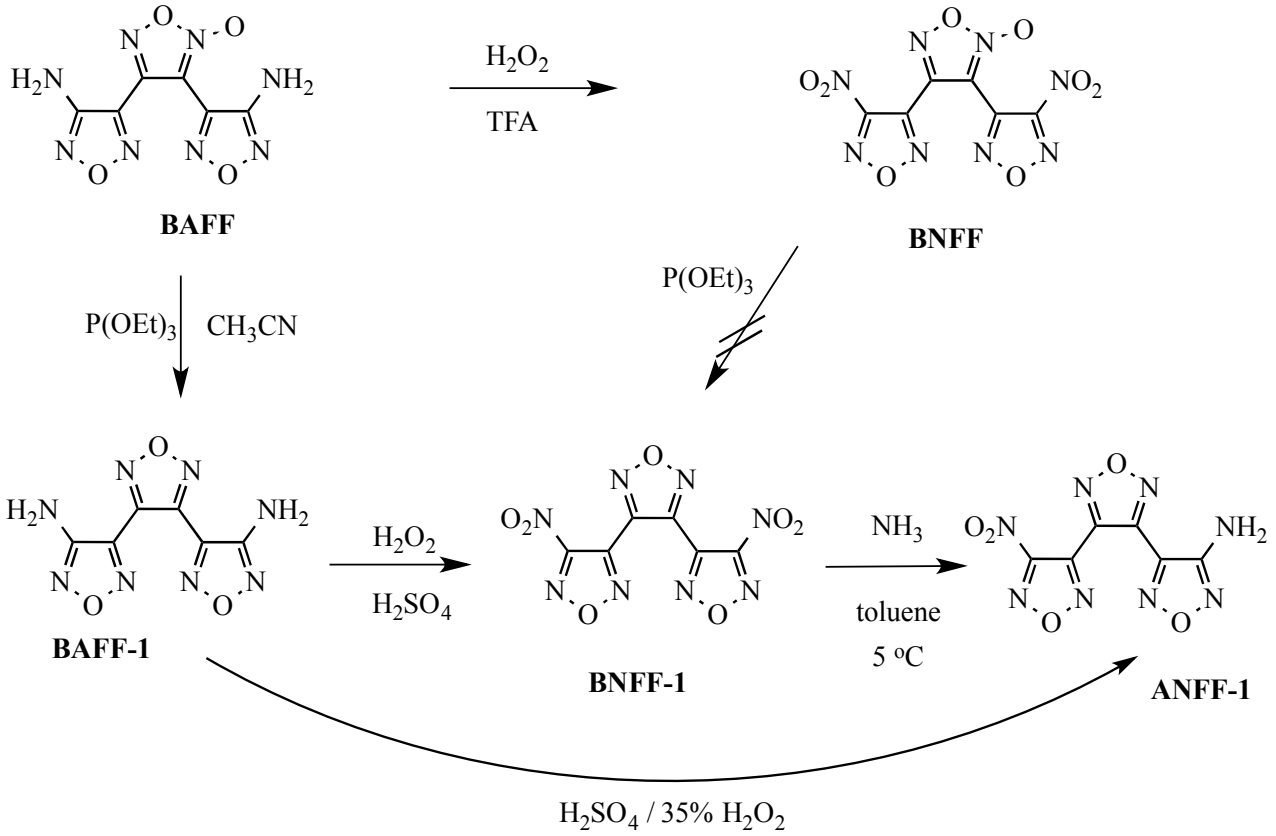
Experimental (Scheme 1)

The first method involved allowing BNFF-1 to react with gaseous ammonia in toluene at 0–5 °C. With stirring, BNFF-1 (5 g) was dissolved in toluene (100 mL) in a 250 mL round-bottomed flask equipped with a stir bar, thermometer and gas bubbler. The mixture was cooled to <5 °C and anhydrous ammonia was bubbled in for 10 min to yield a saturated solution. The mixture was stirred 1 h at <5 °C, filtered to remove insoluble $NaNO_2$ and the solvent was removed to yield a light yellow solid. Purification by flash column chromatography (CH_2Cl_2, SiO_2) yielded 1.4 g of ANFF-1 as a white powder. Recrystallization from $CHCl_3$ yielded white needles; m.p. 100 °C; ^{1}H-NMR (DMSO-d_6) δ 6.72 (s, 2H); ^{13}C-NMR (DMSO-d_6) δ 160.05, 155.2, 144.25, 140.92, 139.23, 135.70 ppm; ^{14}N-NMR (DMSO-d_6) δ 1139 (-NH_2) ppm.

The method of choice for the synthesis of ANFF-1 involves the partial oxidation of BAFF-1 with 35% H_2O_2 in concentrated H_2SO_4. Into a 300 mL 3-necked round-bottomed flask equipped with a thermometer, stir bar, and addition funnel was placed concentrated (96% sulfuric acid (200 mL) and 3,4-bis(4-amino-1,2,5-oxadiazol-3-yl)-1,2,5-oxadiazole (BAFF-1, 20 g, 84 mmol). The mixture is stirred until a solution is realized. With stirring, the solution is cooled to <10 °C with an ice water bath and 35% hydrogen peroxide (20–30 mL, 8 fold molar excess of H_2O_2, ~530 mmol) is added dropwise at <20 °C. The mixture turns a blue-green color after an hour BNFF-1 forms as a light blue-green precipitate. The mixture is stirred at 18–23 °C for 3 h. The reaction mixture is filtered through a glass fritted Buchner funnel to remove the insoluble BNFF-1 into 2 liters of ice water, resulting in precipitation of ANFF-1 as a white solid. The precipitate (ANFF-1) is collected by suction filtration, washed with water and allowed to air dry to yield 10.5 g (45%) of a white solid. Recrystallization from $CHCl_3$ (insoluble BAFF-1 is removed by gravity filtration) yields ANFF-1 as white needles; m.p. 100 °C; ^{1}H-NMR (DMSO-d_6) δ 6.72 (s, 2H); ^{13}C-NMR (DMSO-d_6) δ 160.05, 155.2, 144.25, 140.92, 139.23,

135.70 ppm; ^{14}N-NMR (DMSO-d_6) δ 1139 (-NH_2) ppm. The resulting material with particles sizes of 0.64 × 0.57 × 0.43 mm^3 exhibited friction sensitivity of 0/10@36 kg (BAM Friction) and impact sensitivity measured with drop hammer tests was larger than 177 cm (2.5 kg weight). The two samples had the same particle size and sensitivity since both were recrystallized from $CHCl_3$ prior to performing small-scale safety tests.

Scheme 1. Synthesis of ANFF-1.



Thermal stability of ANFF-1was recently explored and analyzed in great detail [8,9].

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Author Contributions

All authors equally contributed to preparation of this manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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