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Synthesis and Characterization of BNFF Analogues

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Even though novel candidates for high energetic materials have been synthesized continuously, higher performance and thermal stability are gradually becoming major concerns for practical high energetic materials. Moreover, to improve high energetic material's safety and survivability for military or industrial explosives and propellants, it is required that high energetic materials must be insensitive and be capable of withstanding unwanted stimuli such as heat, frictions, impact and shocks.[1]

Generally, nitro and amino 1,2,5-oxadiazoles (furazan) and 1,2,5-oxadiazole-2-oxide (furoxan) compounds have been considered as potent explosives and propellants. They have high nitrogen contents, high energy density and good oxygen balance.[2] Despite of such advantages, many of simple furazan and furoxan containing compounds could not be applied for high energetic materials due to their poor thermal stability, impact sensitivity and nucleophilic substitution of nitro groups.[3] But among the such furazan and furoxan derivatives, bis(nitrofurazano)furoxan (BNFF, **4**) contains nitrofurazan and furoxan ring and shows relatively increased crystal density compared to other simple furazan derivatives. BNFF exhibits high density, high detonation velocity and detonation pressure, which is comparable to HMX.[4] Furthermore, its low melting point (110 °C) and relatively high thermal stability make BNFF easy to cast and process.

From commercially available malononitrile, bis(aminofurazano)furoxan (BAFF, **2**) and bisaminofurazanodioxadiazine (BAFOZ, **3**) were selectively synthesized *via* 1,3-dipolar cycloaddition of nitrile oxide **1**, a key intermediate, depending on the reaction conditions. Both diamino compound **2** and **3** were oxidized to give BNFF(**4**) and bisnitrofurazanodioxadiazine (BNFOZ, **5**) in moderate yield (Scheme 1).[5,6]

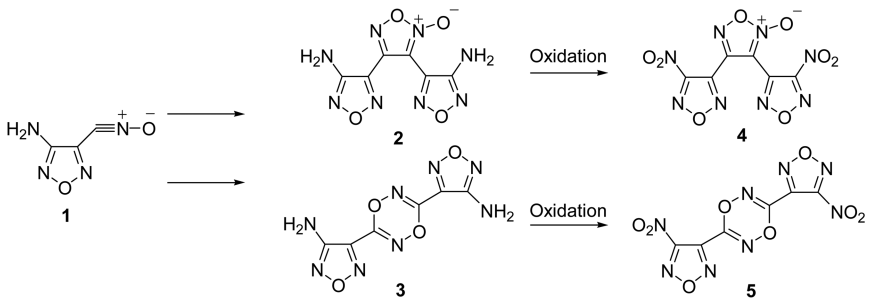
BNFOZ exhibited relatively low thermal stability and high volatility compared to BNFF.[6] Later, we found that the dioxadiazine ring was significantly more unstable than furoxan under various reaction conditions such as oxidation and reduction. In the present study, we have focused on the synthesis of BNFF analogues to understand the characteristics of furazan and furoxan rings and improve their explosive performance.

Results and Discussion

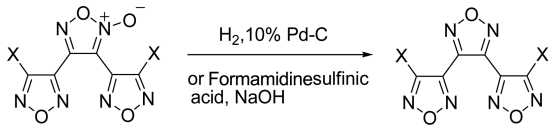
At first, we had examined the partial oxidation of BAFF to prepare 3-(aminofurazano)-4-(nitrofurazano)furoxan (ANFF, **8**), the mono-amino substituted analogue of BNFF. Despite of various oxidative conditions, which hydrogen peroxide was mainly used as an oxidant, ANFF was not prepared, but BNFF was given as a major compound. Mild oxidation conditions had just resulted in the lowering yield of BNFF and lower reaction temperature afforded somewhat polymeric materials which were hard to interpret on TLC analysis.

Therefore, we had changed our approaches from the partial oxidation of BAFF to the partial reduction of BNFF. There were numerous methods for selective reduction of aromatic and aliphatic nitro compounds including catalytic hydrogenation,[7] sodium borohydride/catalyst,[8] hydrazine/catalyst,[9] and metals such as iron, tin or zinc in the presence of an acid.[10]

Among the conditions, we examined the possibility of selective reduction through simple catalytic hydrogenation with palladium on activated carbon. The reduction resulted in the complex mixture of products which were difficult to



Scheme 1. A Synthesis of BNFF(**4**) and BNFOZ(**5**).



Scheme 2. A Synthesis of BAFF^R(**6**) and BNFF^R(**7**).

identify.

However, BNFF was treated with H_2/Pd-C in shorter reaction time, bis(nitrofurazano)furazan (BNFF^R, **7**), its deoxygenated product, was given in moderate yield. BNFF^R showed a loss of the asymmetry in its ^{13}C NMR spectroscopy and was more unstable compared to BNFF. It decomposed slowly even under 0 °C in nitrogen atmosphere. In the same manner, BAFF was also reduced to afford bis(aminofurazano)furazan (BAFF^R, **6**) which showed same loss of the asymmetry in ^1H NMR and ^{13}C NMR spectroscopy compared to BAFF. The reaction of BAFF proceeded faster even in milder condition and resulted in higher yield than that of BNFF. From these two cases of BNFF^R and BAFF^R, it seemed that deoxygenation reaction of furoxan moiety underwent preferentially to the nitro group under catalytic hydrogenation conditions.

In general, furoxan compounds were reduced to give the corresponding dioxime or resulted in mass, because of extensive decomposition, under catalytic hydrogenation.[11] The N-oxide moiety of furoxan and other heteroaromatic N-oxides were readily converted to the corresponding deoxygenated compounds by various reducing agents such as trialkyl phosphite, zinc/ammonium formate, and triphenyl phosphine.[12,13]

To confirm the deoxygenation of the furoxan comprised of nitro groups, other method was examined. Following Balicki's procedure, BNFF was treated with formamidinesulfinic acid to give BNFF^R (Scheme 2).[13] Formamidinesulfinic acid also exhibited good selectivity between nitro group and N-oxide in BNFF.

Because BNFF^R was slightly decomposed during reactions, direct oxidations of BAFF^R to BNFF^R were also considered. When BAFF^R was treated with TFAA/60% H_2O_2/H_2SO_4 or ammonium persulfate/60% H_2O_2/H_2SO_4, the same reaction condition of BAFF oxidation, BNFF^R was not given.[5,6] It seemed that the lower stability of furazan compared to furoxan, made BAFF^R readily decomposed under strong acidic and oxidative conditions.

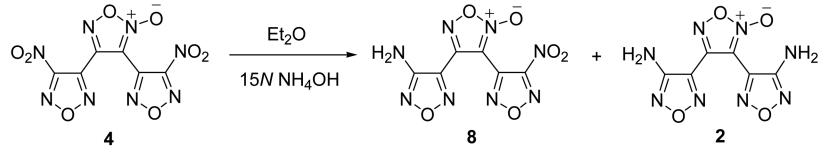
Secondly, we examined the selective reduction of nitro groups *via* hydrogen transfer reactions. In the reaction with triethylamine/formic acid or ammonium formate in the presence of Pd-C, nitro groups were converted to amino ones,[14] or pyridine N-oxide derivatives were to the corresponding piperidines.[15] Without a solvent, BNFF was somewhat decomposed even below 0 °C and too many spots appeared on TLC. However, a nitro group of furazan was readily substituted by methoxy group in the presence of methanol as a solvent. With non nucleophilic solvents such as THF and *t*-butyl alcohol, the reaction gave too many compounds. In the reaction of BNFF with MeOH and a base like Et_3N, BNFF disappeared and the corresponding methoxy substituted compound was given within 20 min, along with a few unknown compounds. Due to liability of nitro groups and low stability of furazano-furoxan heteroarmatic ring system, hydrogen transfer reductions were again improper for selective reduction of nitro in BNFF.

As we observed, during hydrogen transfer reactions, displacement of furazano-nitro group to methoxy group underwent fairy mildly and selectively without neither deoxygenation of furoxan's N-oxide nor decomposition of furazano-furoxan heteroarmatic ring system.

In the previous reports, nitro groups were readily substituted by other nuclophiles such as amines, hydroxyls and so on.[16] Therefore, we focused on the substitution reaction, instead of selective reduction in order to prepare an amino-nitro furazano-furoxan from dinitro one. Thus, a solution of BNFF(**4**) in diethyl ether was treated with 15 N ammonium hydroxide. After stirred for 1 h at rt, the reaction mixture was extracted with diethyl ether. The corresponding mono-substituted compound was obtained as a major one, along with a very small amount of the disubstituted one, BAFF(**2**), like methoxy nucleophile. As one nitro was substituted faster than another one in the reaction, one mono substituted compound was given as a major one. The characteristic peak (δ 102.4) of furoxan's N-oxide moiety was found in ^{13}C NMR spectroscopy and the amino peak (δ 6.24) in ^1H NMR spectroscopy. However, the position of amino group was not disclosed by NMR analysis. When the reaction might be affected by steric hindrance, 4-(aminofurazano)-3-(nitrofurazano)furoxan (ANFF, **8**) was selectively obtained (Scheme 3).

As shown in Figure 1, DSC curve for ANFF showed that an endothermic peak began at 104.4 °C with summit peak at 106.8 °C and major exothermic peak at 245.5 °C. The curve exhibited similar pattern compared to those of BNFF. As shown in DSC curve for BNFF^R, an endothermic summit peak was at 136.0 °C and major exothermic peak at 173.0 °C. Decomposition point of BNFF^R was significantly lower than BNFF and ANFF. As a result, it was certain that furoxan structure had higher thermal stability than furazan one.

To evaluate explosive property of a certain compound, density is usually very important factor. As shown in



Scheme 3. A Synthesis of ANFF(**8**).

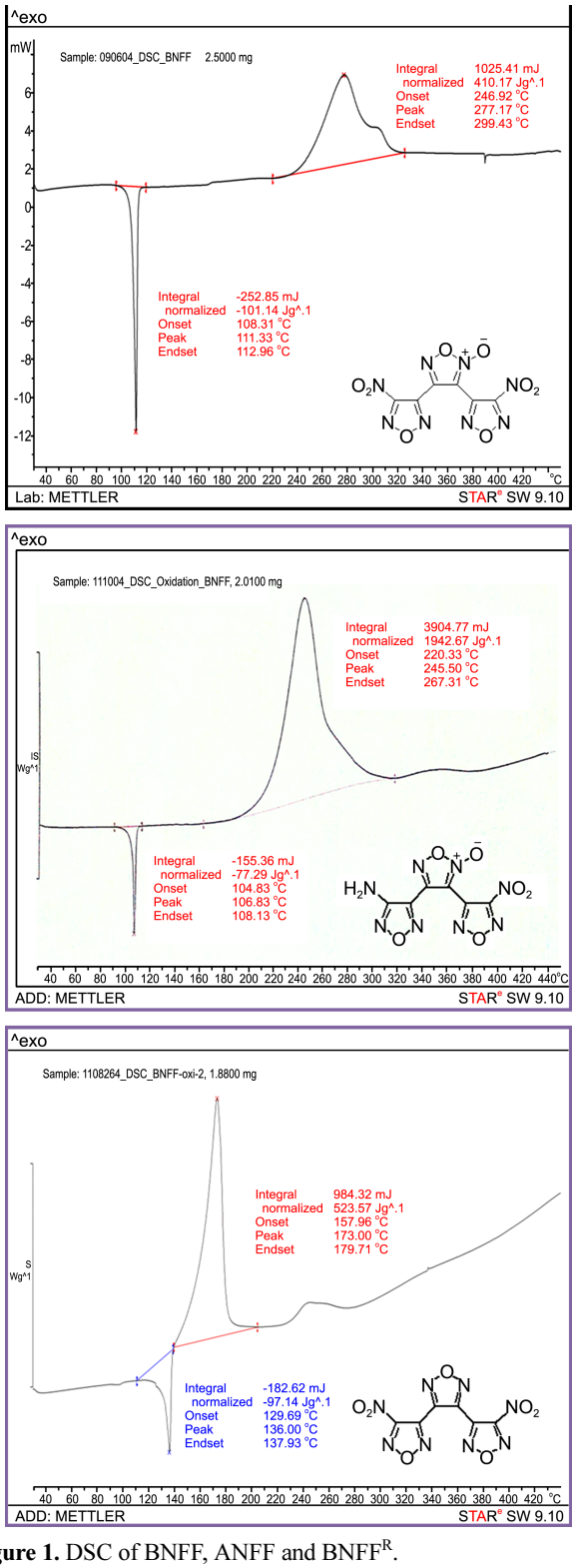


Figure 1. DSC of BNFF, ANFF and BNFF^R.

Table 1, the density of dinitro compound was higher than amino-nitro or diamino compound among BNFF analogues.

In conclusion, the derivatives of BNFF were synthesized *via* catalytic hydrogenation and substitution. Because BNFF's furoxan heteroaromatic ring system was vulnerable to reductive conditions, synthesis of ANFF was very difficult *via* selective reduction of BNFF. Without reduction of the nitro group, BNFF was selectively deoxygenated to give BNFF^R under catalytic hydrogenations. ANFF, our first target was synthesized *via* simple amino substitution. BAFF^R was hardly converted to BNFF^R, because the furazanofurazan ring system was vulnerable to oxidative conditions. On the basis of the thermal properties of DSC, ANFF has similar thermal stability, compared to BNFF, while BNFF^R showed significant thermal unstability and lower decomposition temperature than BNFF. In terms of calculated density, BNFF was highest among BNFF analogues. It was certain that furoxan structure was preferred to furazan one for explosive performance.

Experimental Section

General. ^{1}H/^{13}C NMR spectra were recorded on Unitynova 400 instrument. Melting points were performed on recrystallized solids and recorded on a SRS Optimelt or electrothermal 9100 melting point apparatus and were uncorrected.

Caution: Furazan and furoxan derivatives are suspected explosives. Should be treated with appropriate precaution.

Bis(nitrofurazano)furazan (BNFF^R, 7). To a solution of BNFF (0.3 g, 1.0 mmol) in methanol (10 mL) was added 10% Pd/C (0.06 g). After being stirred for 30 min under hydrogen atmosphere, the suspension was filtered through Celites and washed with diethyl ether. The resulting filtrate was concentrated *in vacuo* to give a crude product as a brown liquid. The crude was purified using flash silica gel chromatography (THF/DCM = 5:18) to give a white solid (0.138 g, 48.6%). mp 160-162 °C (melt); IR (KBr) 2360, 2340, 1579, 1547, 1384, 1357, 1196 cm^{-1}; ^{13}C NMR (Acetone-d_6, 100 MHz) δ 160.8, 141.8, 139.5; ESI-MS (pos.): 320.16 ([M+Na]$^+$, $C_6N_8O_7^+$; calc. 296.02.

Bis(aminofurazano)furazan (BAFF^R, 6). Compound **6** was prepared as a white solid (0.142 g, 60.7%) from BAFF (0.25 g, 1.0 mmol). mp 178-180 °C (melt); IR (KBr) 3458, 3351, 1643, 1609, 1533, 1264, 974 cm^{-1}; ^{1}H NMR (acetone-d_6, 400 MHz) δ 8.44; ^{13}C NMR (acetone-d_6, 100 MHz) δ 155.6, 142.4, 140.1; ESI-MS (pos.): 237.93 ([M+2H]$^{2+}$, $C_6H_4N_8O_3^+$; calc. 236.04).

3-(Aminofurazano)-4-(nitrofurazano)furoxan (ANFF, 8). To a solution of BNFF (0.3 g, 1.0 mmol) in diethyl ether

Table 1. Crystal densities of BNFF analogues[17,a]

	BAFF	BNFF	BAFF^R	BNFF^R	ANFF
Pred. ρ (crystal)	1.765	1.900	1.623(1.620)^b	1.760	1.728(1.711)^b
Exp.	1.795	1.937			
Error	0.03	0.037			

^{a}The density was calculated by B3LYP/6-31G. ^{b}The value represented the density of two optimized structures.

(15 mL) was added dropwise 15 N ammonium hydroxide (9 mL). The reaction mixture was vigorously stirred at ambient temperature. After being stirred for 1 h, the reaction mixture was extracted three times with diethyl ether. The organic layer was washed with distilled water, dried with $MgSO_4$ and concentrated *in vacuo* to give a crude product as a pale yellow liquid. The crude product was purified using flash silica gel chromatography (ethyl acetate/*n*-hexane = 1:9) to give a white solid (0.081 g, 30.1%). mp 100-102 °C (melt); IR (KBr) 3471, 3341, 1637, 1560, 1509, 1289, 966 cm^{-1}; ^1H NMR (acetone-d_6, 400 MHz) δ 6.24; ^{13}C NMR (acetone-d_6, 100 MHz) δ 161.0, 156.0, 147.1, 138.3, 137.0, 102.4; ESI-MS (pos.): 305.14 ($[M+Na]^+$, $C_6H_2N_8O_6^+$; calc. 282.01).

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