INTRODUCTION

Nowadays, nitrogen-riched heterocyclic compounds have been considered as potential energetic materials due to their high heats of formation and highly endothermic in nature\textsuperscript{1-3}.

Hydroxynitrofurazan (3) is a useful building block in the synthesis of oxyfurazanyl modified energetic materials\textsuperscript{4}. And some symmetrical and unsymmetrical difurazanyl ether derivatives have been developed as highly energetic materials having good explosive performance\textsuperscript{5}. Normally, these compounds were found to be quite dense and have high thermal stability and performance as insensitive high explosives (IHEs). The symmetrical and unsymmetrical difurazanyl ethers could be prepared by SN\textsubscript{2} reaction from hydroxynitrofurazan in which nitro group was as a leaving group\textsuperscript{5,6}.

Picryl groups (2,4,6-trinitrophenyl-) and triazine are also important building blocks in energetic materials. In this study, novel unsymmetrical nitrofurazanyl picryl ether derivatives and nitrofurazane triazine ether derivative were synthesized \textit{via} Williamson reaction (Scheme-I). Three novel unsymmetrical nitrofurazanyl ethers were synthesized \textit{via} Williamson reaction. Some properties of the product, such as density, heat of formation, oxygen balance, detonation pressures and detonation velocities were calculated.

**Key Words:** Unsymmetrical nitrofurazanyl ethers, Hydroxynitrofurazan, Properties.

SYNTHESIS OF UNSYMMETRICAL NITROFURAZANYL ETHERS

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\textbf{Scheme-I} Synthesis of unsymmetrical nitrofurazanyl ethers

**EXPERIMENTAL**

3,4-Diaminofurazan (1) was synthesized followed in literature\textsuperscript{7}. 3,4-Dinitrofurazan (2) was prepared by oxidation of 3,4-diaminofurazan in H\textsubscript{2}SO\textsubscript{4}/H\textsubscript{2}O\textsubscript{2} system\textsuperscript{8}. 3,4-Dinitrofurazan (2) was transformed to 3-hydroxy-4-nitrofurazan (3) with weak base K\textsubscript{2}CO\textsubscript{3} in dry acetonitrile\textsuperscript{9}.

**Compound 2.** Yellow liquid, 62 % yield. (KBr, \textit{v}\textsubscript{max}, cm\textsuperscript{-1}): 1576, 1541, 1452, 1353, 1139, 1031, 842, 806; \textsuperscript{13}C NMR (125 MHz, DMSO-\textit{d}\textsubscript{6}) \textdelta 153.9.

**Compound 3.** Yellow liquid, 72 % yield. (KBr, \textit{v}\textsubscript{max}, cm\textsuperscript{-1}): 3569-3200, 1615, 1548, 1448, 1382, 1206, 1030; \textsuperscript{13}C NMR (125 MHz, DMSO-\textit{d}\textsubscript{6}) \textdelta 153.84, 158.57.

3-Nitro-4-(2,4,6-trinitrophenoxy)furazan (5): To a solution of compound 4 (0.65 g, 4.25 mmol) suspended in 50 mL acetonitrile, 1-chloro-2,4,6-trinitrobenzene (0.94 g, 3.80 mmol) was added. The reaction mixture was stirred at 81-82 ºC for 14-15 h and poured into ice overnight. The filtered aqueous solution was concentrated in vacuum. Then the product was dipped by acetone three times and concentrated in vacuum. Saturated aqueous NaCl solution was added to the crude product and extracted three times with acetonitrile. The combined extracts were then washed with saturated aqueous NaCl solution, dried,
filtered and evaporated in vacuum to dryness. Recrystallization from acetonitrile (3:1) afforded product 5 (0.40 g, 31%). (KBr, νmax, cm⁻¹): 3613, 3543, 3092, 1635, 1615, 1561, 1515, 1494, 1429, 1373, 1344, 1282, 1085; ¹H NMR (500 MHz, CDCl₃) δ 8.735; ¹³C NMR (125 MHz, CDCl₃) δ 163.09, 142.88, 127.97, 127.16, 126.55, 124.015. Anal. calcd. for C₁₅H₁₀O₅N₆: C, 50.41; H, 2.69; N, 31.13. Found: C, 49.99; H, 2.63; N, 31.08.

The reactions were monitored by HPLC. For 2-chloro-1,3,5-trinitrobenzene, the reaction was more faster that it transformed completely in 2 h. when 4 reacted with 2,4,6-trichloro-1,3,5-triazine at 3-5 °C, the starting material consumed completely in 7.5 h.

For the synthesis of salt 4, sodium methoxide should be excess more than 100 % (in molar ratio). The yield of salt 4 was low as about 30-45 % when sodium methoxide was equal to 3. The unreacted sodium methoxide was concomitant with salt 4 and could produce methyloxyl derived polynitrobenzene. However these byproducts could be easily separated by filtered from the reaction mixture aqueous solution.

The estimated densities of compounds 5, 6 and 7 were calculated using atom/molecular group volume additivity methods[10,11]. The heats of formation of compounds 5, 6 and 7 are computed using the method of isodesmic reactions[12]. The enthalpy of reaction (ΔHr°) is obtained by combining the MP2(full)/6-311++G** energy difference for the reaction, the scaled zero-point energies (B3LYP/6-31+G**) and other thermal factors. Thus, the heat of formation being investigated can be readily extracted. The expected detonation pressures (P) and detonation velocities (D) were calculated using the semiempirical equations suggested by Kamlet et al.[13,15] and Zhang.[16] All these data were listed in Table-1.

The geometric optimization (Fig. 1) and total atom charge (Table-2) of compound 5 were carried out by using B3LYP functional with 6-31+G** basis set. The O9 atom carries the largest negative charge in the structure. Compound 5 was decomposed at O9 atom when it was heated. TGA result (Fig. 2) of 5 shows two steps of mass loss, in which the first mass loss process is attributed to the formation of picric acid derived from the cleavage of O9-C2.
TABLE-2
TOTAL ATOM CHARGE DISTRIBUTION OF COMPOUND 5

<table>
<thead>
<tr>
<th>Atom</th>
<th>Charge</th>
<th>Atom</th>
<th>Charge</th>
<th>Atom</th>
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<tr>
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<tr>
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</tr>
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<td>-0.54</td>
<td>O18</td>
<td>-0.28</td>
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</table>

Fig. 2. TGA curve of compound 5

Conclusion

In conclusion, we reported here the synthesis of nitrofurazanyl polynitrobenzene ethers and nitrofurazanyl triazine ether derivatives. A series of unsymmetrical furazanyl ethers could be prepared by this method. Further studies of other nitrogen-riched heterocyclic nitrofurazanyl ethers are in progress in our laboratory.

REFERENCES