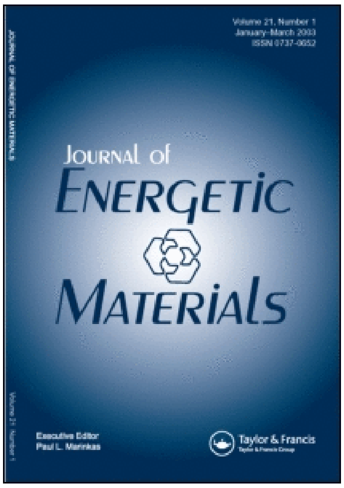

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Synthesis, characterization and explosives properties of 7-(1h -1,2,4-triazol-3-amino)-4,6-dinitrobenzofuroxan (TADNB) and 7-(1h-1,2,3,4-tetrazol-5-amino)-4,6-dinitrobenzofuroxan (TEADNBF)

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SYNTHESIS, CHARACTERIZATION AND EXPLOSIVES PROPERTIES OF 7-(1H -1, 2, 4- TRIAZOL-3- AMINO)-4,6-DINITROBENZOFUROXAN (TADNB) AND 7-(1H -1, 2, 3, 4-TETRAZOL-5-AMINO)-4,6-DINITROBENZOFUROXAN (TeADNBF)

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ABSTRACT

7-(1H -1, 2, 4-triazol-3-amino)-4, 6-dinitrobenzofuroxan(TADNB)and 7-(1H -1, 2, 3, 4-tetrazol-5-amino)-4, 6-dinitrobenzofuroxan(TeADNBF) have been prepared by condensing 7-chloro-4, 6 -dinitro benzofuroxan with 3- amino-1, 2, 4-triazole and 5-amino-1, 2, 3, 4-tetrazole respectively. The compounds have been characterized by spectral data and elemental analysis. Furthermore, some of the explosive properties of these compounds have also been investigated and reported herein.

INTRODUCTION

Explosive performance has been known to depend upon a number of molecular parameters[1]. The basic parameters are density, heat of formation, oxidant balance and nitrogen content. Thus detonation velocity (VOD) and detonation pressure (DP) depend on density and heat of formation and impact sensitivity of energetic materials to a certain extent center around oxidant balance (OB_{100}). Both positive heat of formation and high nitrogen content of energetic materials are very useful for high VOD and DP because nitrogen in

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some extent " the ideal working body" in high temperature process being low molecular weight gas, not dissociating while burning and explosion[2]. It has also been believed that replacement of nitro group by furoxano group can result in the increase of density of explosive molecule and thus velocity of detonation, whereas incorporation of amino group to the explosive molecule can result both in increase of densities and heat resistance as well as decrease in impact sensitivity[3].

In order to utilize the advantages of furoxano and amino groups[4-7], our efforts have been concentrated to synthesize new molecules in this class whose performance are comparable to those of well established thermally stable high explosives.

In the present investigation we report here the synthesis and characterization of two new benzofuroxans viz. TADNBF and TeADNBF and also to some extent their explosive and thermal properties.

EXPERIMENTAL

Melting points were determined on open capillary tubes and are uncorrected. The IR spectra were recorded on Perkin–Elmer Infrared Spectroscopy using KBr matrix. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker 90MHz instrument using DMSO-d_6 as solvent and tetramethylsilane(TMS) as internal standard. Elemental analyses were performed on Carlo-Erba elemental analyser, EA1108. Electron impact mass spectra (EIMS) were recorded on a double focussing JEOL-DS mass spectrometer at 70 eV using direct insertion technique.

Deflagration temperature was determined by heating 0.02 g of sample in a glass tube in Wood's metal bath[8] at a heating rate of 5°C / min. and the temperature at which sample got ignited/ decomposed, was recorded as deflagration temperature. Differential thermal analysis (DTA) was recorded by heating 10 mg of sample at a rate of 10°C/ min. in the presence of static air. The impact sensitivity was determined by Fall Hammer method using 2.0 kg drop weight and friction sensitivity was determined on Julius Peter apparatus by following standard method[9]. The velocity of detonation[10] and detonation pressure[11] were calculated by methods reported in the literature.

Materials:

1, 3-dichloro-2, 4, 6-trinitrobenzene[12] (as prepared from styphnic acid on treatment with pyridine and phosphorus oxychloride) with melting point 129-130°C, 3-amino-1, 2, 4-triazole[13] (prepared by condensing amino guanidine bicarbonate and formic acid) mp. 152-156°C and 5-amino-1, 2, 3, 4-tetrazole[14] (prepared from dicyandiamide on treatment with sodium azide and concentrated hydrochloric acid) with a melting point 202-204°C, were used as starting materials. Sodium azide was obtained commercially from Lancaster. Methyl alcohol and acetic acid, SQ Grade, Qualigens, were used as solvents

Synthesis:

The synthesis of 7-(1H- 1, 2, 4-triazol-3-amino)-4, 6-dinitrobenzofuroxan (TADNBF) and 7-(1H-1, 2, 3, 4-tetrazol-5-amino)-4, 6- dinitrobenzofuroxan (TeADNBF) involve the following steps;

a) Synthesis of dipyridinium styphnate

b) Synthesis of 1, 3-dichloro-2, 4,6-trinitrobenzene

c) Synthesis of 1-azido-3- chloro-2, 4, 6-trinitrobenzene

d) Synthesis of 7- chloro-4, 6-dinitrobenzofuroxan

e) Condensation of 7-chloro-4, 6-dinitrobenzofuroxan with 3-amino-1,2,4-triazole and 5-amino-1, 2,3,4-tetrazole.

The syntheses of dipyridinium styphnate and 1, 3-dichloro-2, 4, 6-trinitrobenzene were carried out using the method reported in the literature[12].

1-Azido-7-chloro-2, 4,6-trinitrobenzene, 1

1, 3-Dichloro-2, 4, 6-trinitrobenzene (styphnyl chloride, 5 g, 17.73 m mole) was transferred into a three-necked round-bottomed flask fitted with a mechanical stirrer and a dropping funnel. To this, 125 ml dimethylformamide (DMF) was added slowly. After the addition of DMF, sodium azide (1.15 g, 17.6 9 m mole) dissolved in 10 ml of distilled water was added drop wise to the reaction flask under stirring at constant temperature, 22°C for 3 hours. The reaction mixture was poured into crushed ice and left overnight for precipitation. The product, thus settled down was filtered, washed thoroughly with distilled water and finally dried at room temperature to afford yield 4.2 g (82%) The compound was recrystallized from methanol and was found to melt at 45- 47°C.

IR (KBr) cm^{-1}: 3085 (Ar-H str.), 2165 ($-N_3$), 1610 (C=C str.),1545 and 1340 (NO_2 asym.and sym.)

^{1}H- NMR (DMSO- d_6 /TMS) δ ppm : 8.5 (s, 1 H, aromatic proton)

Anal Calcd. for $C_6HN_6O_6Cl$ (Mol. Wt. 288) : C, 25.00; H, 0.34; N, 29.17

Found: C, 24.59; H, 0.50; N, 28.85

7-Chloro-4, 6-dinitrobenzofuroxan, 2

1-Azido-3-chloro-2, 4, 6-trinitrobenzene, 1 (5 g, 17.33 m mole) was carefully transferred into a two necked flask fitted with a reflux condenser, and acetic acid (15 ml) was added to it. The reaction mixture was refluxed for two hours over oil bath, which was then cooled at ambient temperature and subsequently poured into crushed ice. The yellow precipitate thus obtained was filtered and washed thoroughly with distilled water till it became acid free. The product was crystallized from methanol, afforded yield, 3.5 g (77%), mp. 110-112° C; DTA, 115° C (endotherm) and 205°C (exotherm).

IR (KBr) cm^{-1} : 3090 (Ar-H str.), 1625 and 1580 (C=C and C=N strs.), 1534 and 1350 (NO_2 asym. and sym. strs.), 810 (C-Cl str.)

^{1}H-NMR(DMSO-d6 /TMS) δ ppm: 8.7 (s, 1H, aromatic proton)

Anal Calcd. for $C_6HN_4O_6Cl$ (Mol. Wt. 260): C, 27.69; H, 0.38; N, 21.53

Found: C, 27.41; H, 0.18; N, 21.36

7-(1H-1, 2, 4-triazol-3- amino)-4, 6-dinitrobenzofuroxan (TADNB), 3

In a three-necked round bottomed flask fitted with a reflux condenser and additional funnel 2 (5.21 g, 20 m mole) was taken and 3-amino-1, 2, 4- triazole (4.2 g, 0.05 mole) was also added along with 100 ml of methanol. The reaction mixture was refluxed for 5 hours, subsequently cooled down to ambient temperature and finally poured into ice cold water. The yellow precipitate thus obtained, was filtered and washed with water to remove excess of 3- amino-1, 2,4-triazole and finally dried to yield 4.5 g (73%). The compound did not melt, however the DTA showed an exotherm at 260° C.

IR (KBr) cm^{-1}: 3388, 3240 (NH- str.), 3138 (Ar-H str.), 2865 (CH str.,triazole ring), 1688 and 1614 (C=C str.), 1530 and 1340 (NO$_2$ asym and sym.), 980 (N-O str.), 866 (penta substituted benzene ring)

^{1}H- NMR (DMSO-d6/TMS) δ ppm: 8.25 (NH bridge proton), 8.92 (Ar-H), 8.6 (CH,triazole), 8.4 (NH, triazole)

^{13}C-NMR(DMSO-d$_6$/TMS)δppm:124.5(s,1C,C$_4$),127.1(s,1C,C$_5$),136.6 (s,1C,C$_6$),145.5(s,1C,C$_7$),148(s,1C,C$_8$),149.6(s,1C,C$_9$),157.1(s,1C,C$_{11}$), 152.4(s,1C,C$_{14}$)

Anal. Calcd. for $C_8H_4N_8O_6$ (Mol. Wt. 308) : C, 31.16; H, 1.29; N, 36.36

Found: C, 31.34; H, 1.09; N, 36.49

7-(1H - 1, 2, 3, 4-tetrazol-5- amino)-4, 6-dinitrobenzofuroxan (TeADNBF), 4

7-chloro-4, 6-dinitrobenzofuroxan (5.21 g, 0.02 mole) and 5-amino-1, 2, 3, 4-tetrazole (5.15 g, 0.05 mole) were carefully transferred into a 250 ml round bottomed flask, followed by immediate addition of methanol (100 ml). The reaction mixture was refluxed for 5 hours, then cooled to ambient temperature, poured into ice-cold water and finally left for overnight to settle down the product. The product was filtered, washed with hot distilled water and dried to yield 4.4 g (71%).The product did not melt, however the DTA was recorded at 124°C (exotherm).

IR (KBr) cm^{-1}: 3446(NH str.), 3088 (Ar-H str., 2164 (-C-N= N-str.), 1586 (C=C and C-N strgs.), 1550 and 1338 (NO2 asym. & sym. strs.), 958 (N-O str.)

^{1}H-NMR (DMSO-d6/TMS) δ ppm: 8.93 (Ar-H), 8.51 (NH, ring proton), 8.35 (NH, bridge-proton).

^{13}CNMR(DMSOd$_6$/TMS)δppm:124.8(s,1C,C$_4$),127.3(s,1C,C$_5$),136.4(s,1C,C$_6$),
146.3(s,1C,C$_7$),148.9(s,1C,C$_8$), 149.8 (s,1C,C$_9$),159.2 (s,1C,C$_{11}$).

Anal. Calcd. for $C_7H_3N_9O_6$ (Mol. Wt. 309) : C, 27.18; H, 0.97; N, 40.77;
Found: C, 26.98; H, 1.05; N, 40.56

RESULTS AND DISCUSSION

The parent compound 7- chloro- 4, 6-dinitrobenzofuroxan, **2** was prepared following the reaction steps as outlined in scheme 1. The dipyridinium styphnate was prepared from styphnic acid on treatment with pyridine, which was then susequently subjected to chlorination, azidation and finally to cyclization reaction to yield **2**. The compound **2**, thus obtained was then condensed with 3-amino-1, 2, 4-triazole and 5-amino-1, 2, 3, 4-tetrazole successively to obtain **3** & **4** with good yield and excellent purity. However, the best yield was obtained when the mixture was heated for 5 hours.

TADNB and TeADNBF are dark orange solids with decomposition temperatures 260°C and 120°C respectively. The compounds have been characterized by spectral data (IR and ^{1}H-NMR) and elemental analysis.

The IR spectra in general of the compounds show strong absorption bands for N-H, -CH (arom.) and asym & sym. stretchings of NO_2 groups. In ^{1}H-NMR, the bridge NH protons and the ring NH protons resonate at δ 8.35-8.25 and δ 8.41-8.51 respectively. The chemical shifts of CH protons of azole ring and the aromatic ring systems display at δ 8.6 and 8.92 respectively. The ^{13}C-NMR spectra correlate well with the structures.

Further attempts were made to record the electron impact mass spectra of compounds **3** and **4** at 70 Ev. However, the molecular ion was not detected due to high molecular weight and low volatility nature of compounds. Chemical ionisation mass spectrum (CIMS) and Fast atom bombardment techniques appear to be more aprropriate for this type of molecules,but we lack this facilities.The EI at 70eV spectrum of **3** showed peaks at m/z 110(base peak), 119,222, 265 and 286, and that of **4** at m/z 291,283,281,240,222,145,143(base peak),131,108,107,97,73 and 69, can be assigned to the expected fragmentation species.

Further, **3** and **4** were also subjected to evaluate the thermal and explosive properties and the data obtained are presented in Table 1. Compound **3** deflagrates at 258°C while the compound **4** at 122°C which are further supported by the DTA thermograms where corresponding exotherms were found at 260 and 124°C respectively. The low thermal stability of the compound **4** may be attributed due to considerable delocalisation of charge as can be depicted by the more number of possible resonating structures in the molecule, causes the destabilizing factor which may promote decomposition at lower temperature through elimination of nitrogen[15]. This may also be rationalized due to electron withdrawing group attached to 5- amino-1, 2, 3, 4-tetrazole unit[8].

The study on explosive properties (Table 1) reveals that compounds are safe towards impact and friction sensitivities. The calculated performance parameters indicate that **4** is more powerful than **3** and its detonation velocity is almost comparable to that of pentaerythritoltetranitrate (PETN) (8300 m/s), a well-known secondary explosive. The experimentally determined high density and insensitivity to impact and friction along with substantially improved high velocity of detonation can be made it attractive molecules for investigation in propellants and explosives formulations.

CONCLUSION

The two new moderately powerful benzofuroxan derivatives have been prepared and characterized satisfactorily. Compound **3** appears more promising over **4** and it may find applications where low thermal stability, high density and high performance are required.

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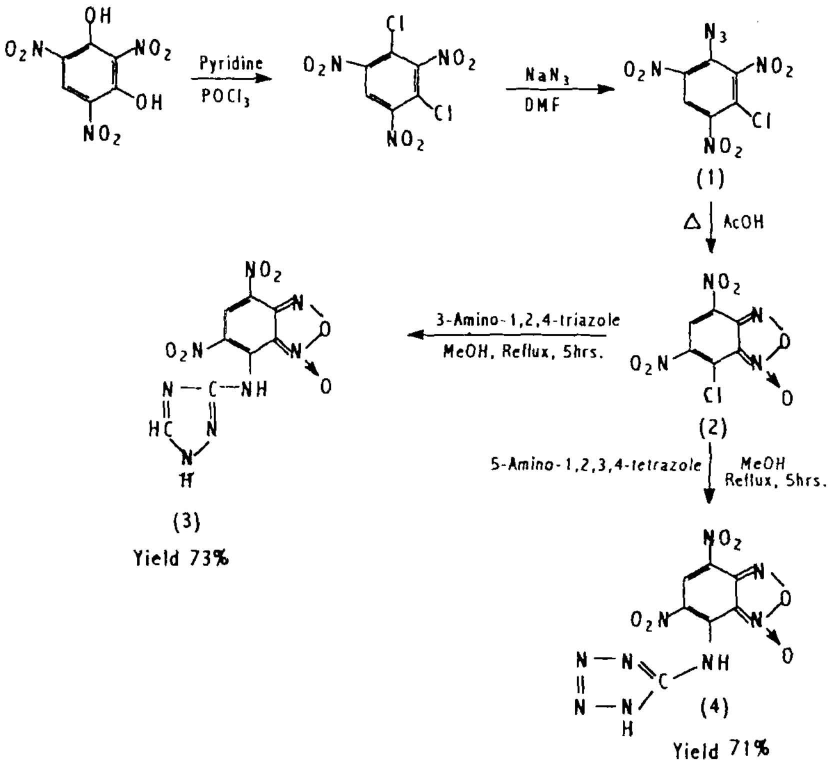
Table 1 : Some data on thermal and explosive properties of TADNB and TeADNBF

Properties	TADNB	TeADNBF
Deflagration Temp.° C	258	122
DTA , ° C	260 (exotherm)	124 (exotherm)
Impact Sensitivity(50% Explo. Ht.) ,cm.	105	76
Friction Sensitivity, kg	36	32.4
Velocity of Detonation, m/s	7791	8400
Detonation Pressure, kbr.	308.05	365.14
Oxygen Balance, %	-62.33	-49.19
Density, g/cc	2.03	2.07

Scheme 1


Pyridine
POCl$_3$
NaN$_3$
DMF
(1)
Δ AcOH
(2)
3-Amino-1,2,4-triazole
MeOH, Reflux, 5hrs.
5-Amino-1,2,3,4-tetrazole
MeOH
Reflux, 5hrs.
(3)
Yield 73%
(4)
Yield 71%