

Microwave assisted facile synthesis of {1/1,3-bis/1,3,5-tris-[(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene]} using bismuth nitrate pentahydrate as an eco-friendly nitrating agent

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Abstract

1-(2-Nitroxyethylnitramino)-2,4,6-trinitrobenzene (3a), 1,3-bis(2-nitroxyethyl nitramino)-2,4,6-trinitrobenzene (3b) and 1,3,5-tris(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene (3c) were prepared by the nitration of 1-(2-hydroxyethylamino)-2,4,6-trinitrobenzene (2a) 1,3-bis(2-hydroxyethylamino)-2,4,6-trinitrobenzene (2b) and 1,3,5-tris(2-hydroxyethylamino)-2,4,6-trinitrobenzene (2c) using bismuth nitrate pentahydrate (eco-friendly nitrating agent) in tetrahydrofuran adsorbed on silica gel under microwave irradiation, respectively. Key intermediate compounds viz., 2a, 2b and 2c were synthesized by condensing picryl chloride, styphnyl chloride and 1,3,5-trichloro-2,4,6-trinitrobenzene with ethanol amine, respectively, based on the lines of the reported method. The synthesized compounds were characterized based on their physical constant, infrared (IR) spectroscopy and ¹H nuclear magnetic resonance (NMR) spectroscopy. The spectroscopic data obtained indicated the formation of nitrate esters (3a–3c). The nitration methodology adopted in the present study is of relevance in the context of green chemistry. The target compounds (3a–3c) synthesized using eco-friendly approach are of interest from the point of high energy materials (HEMs). © 2007 Elsevier B.V. All rights reserved.

Keywords: Bismuth nitrate pentahydrate; Eco-friendly nitration; Microwave irradiation; High energy materials; Hazardous materials

1. Introduction

Search is on in many research institutes to develop less hazardous, inexpensive and environment friendly nitrating agent. The nitrated products find broad spectrum of applications in the area of high energy materials, pharmaceuticals and fertilizers. A series of nitrated products, namely 2,4,6-trinitrotoluene (TNT), 2,4,6-trinitrohexahydro triazine (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), hexanitrohexaazaisowurtzitane (CL-20) trinitroazetidine (TNAZ), dinitrodifurazano piperazine (DNDFP), trinitrotriaminobenzene (TATB), nitrotriazolone (NTO), tetraoxa explosive (TEX),

octanitrocubane (ONC), ammonium dinitramide (ADN), hydrazinium nitroformate (HNF) are key high energy materials (HEMs). Different nitrating agents have been used for the synthesis of these HEMs. The selection of a nitrating agent for a particular nitration reaction is mainly dependent on the type of substrate molecule being nitrated. Most commonly used nitrating agent is the mixture of concentrated nitric acid and sulphuric acid. Conventionally used nitrating agents pose serious threat of pollution thereby necessitating efficient and costly effluent treatment. In view of these reasons chemists and technologists are looking for the environment friendly or environment compatible methods for the synthesis of HEMs. Apart from pollution, the other problems associated with the use of conventional nitrating agent is that, if the substrate molecule is deactivated due to presence of strong electron withdrawing groups such as NO₂, C=O and SO₂ (attached to nitrogen or carbon or oxygen) the conventional nitration fails. Even if the nitration of deactivated substrates is carried out under harsher conditions using

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conventional nitrating agents, the yields/of purity of the end product/s are poor. Another reason for the failure of nitration is that, certain substrate molecules or their intermediates are unstable in acidic media.

The recent trend in overcoming these drawbacks is to use certain novel catalytic materials, based on metal oxides, zeolites inorganic metal triflates [1] in association with conventional nitrating systems. However, the information available on the use of conventional nitrating agent in presence of novel catalytic materials is scanty. Olah et al. [2] have recently reviewed nitration chemistry with strong emphasis on nitronium salt. The best known salts, nitronium tetrafluoroborate (NO_2BF_4) and nitronium hexafluorophosphate (NO_2PF_6) are effective nitrating agents for deactivated substrate molecules. Suzuki et al. [3,4] have been able to nitrate selectively certain aromatics using $\text{N}_2\text{O}_4/\text{O}_3/\text{O}_2$ mixtures. It is also reported that $(\text{CF}_3\text{CO})_2\text{O}/\text{HNO}_3$ can be used for selective nitration of certain deactivated substrates. However, this system is not recommended as its use results in explosion.

This calls for the synthesis of high energy materials (HEMs) using alternate/new nitrating agents. The use of bismuth(III) derivatives as catalysts in organic synthesis has increased considerably. This new interest in bismuth is easily justified by its user-friendly ecological behavior [5]. The catalytic properties of bismuth(III) compounds have been investigated during the past few years. Montmorillonite impregnated with $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ has been reported as an excellent nitrating reagent for aromatic nitration's in high yield [6]. Aromatic nitro compounds represent versatile intermediates for a wide range of industrial products, like pharmaceuticals, dyestuffs and explosives [7–9]. Bismuth(III) compounds have received particular attention as low toxicity reagents and catalysts for various organic transformations [10,11]. High speed microwave synthesis has also attracted a considerable amount of attention in recent years [12]. A large number of review articles [13,14] and several books provide extensive coverage of the subject.

Nitrate esters are widely reported as potential explosive and rocket propellant ingredients due to the presence of O–NO₂ bond [15]. This class of compounds included a variety of materials such as pentaerythritol tetra nitrate (PETN), nitro cellulose

(NC), and nitro glycerin (NG), which are used extensively for gun and rocket propellants [16]. The reported thermal stability of aromatic nitrate esters is in par with the cyclotrimethylene trinitramine (RDX) [17]. Aromatic nitrate esters possess better oxygen balance than aromatic nitro compounds and thus are more energetic as explosives and propellants ingredients. In addition to high energy properties, some nitrate esters also possess significant promising biological activities [18].

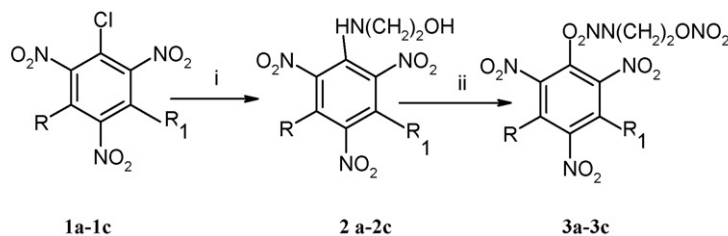
The preparation of nitrate esters from alcohols, alkenes, amines or organic halides and sulfonates by the use of various nitrating reagents including acetyl nitrate, acridinium nitrate, benzyl trimethylammonium nitrate, bromonium nitrate, dinitrogen tetroxide, dinitrogen pentoxide, mercury(I) and mercury(II) chlorides, nitric acid, *N*-nitrocollidinium tetrafluoroborate, silver nitrate, tetra (*n*-butyl)ammonium nitrate, thallium(III) nitrate, thionyl chloride nitrate and thionyl nitrate has been recently reported [19]. The reported methods require the acidic conditions, expensive reagents, toxic and corrosive chemicals and/or elaborate safety precautions and moreover some are not suitable for large-scale preparations [19]. Researchers from High Energy Materials Research Laboratory, Pune, India, recently reported [20–22] the synthesis of nitrate esters as possible high energy materials using conventional nitrating agent.

In view of the above observations and our continued research and development activities [23] in the area of high energy materials, we report here the eco-friendly synthesis of nitrate esters (3a–3c) using bismuth nitrate pentahydrate as a nitrating agent (Scheme 1). Synthesis of nitrate esters was achieved by the use of bismuth nitrate pentahydrate in THF adsorbed on silica gel, under microwave irradiation [24,25].

2. Experimental

2.1. Materials and methods

The starting materials used in the present study are of laboratory grade, were purchased from commercial sources and were used directly without purification. Silica gel (60–120 mesh) supplied by S.D. Fine Chem. Ltd., Mumbai, India, was acti-



Reaction conditions: i) Ethanolamine, MeOH ii) $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ THF, silica gel, MW

	1a	1b	1c	2a	2b	2c	3a	3b	3c
R	H	H	Cl	H	H	$\text{HN}(\text{CH}_2)_2\text{OH}$	H	H	$\text{O}_2\text{NN}(\text{CH}_2)_2\text{-ONO}_2$
R1	H	Cl	Cl	H	$\text{HN}(\text{CH}_2)_2\text{OH}$	$\text{HN}(\text{CH}_2)_2\text{OH}$	H	$\text{O}_2\text{NN}(\text{CH}_2)_2\text{-ONO}_2$	$\text{O}_2\text{NN}(\text{CH}_2)_2\text{-ONO}_2$

Scheme 1. Synthesis scheme of nitrate esters (3a–3c).

vated by microwave irradiation for 10 min before its use for the reactions. Key precursors such as picryl chloride, styphnyl chloride and 2,4,6-trichlorotrinitrobenzene were obtained from High Energy Materials Research Laboratory, Pune, and were further utilized. After ascertaining the purity of these precursors, further experimental work was undertaken. The precursors (2a–2c) used in the present work was synthesized based on the lines of the reported method [20]. The synthesized compounds were characterized by their spectroscopic properties and physical constant. Infrared spectra of the compounds were recorded (KBr pellets) on Shimadzu FT-IR-8400 Spectrophotometer. ^1H nuclear magnetic resonance (NMR) spectra were recorded on Varian Mercury Spectrometer at 300 MHz in deuterated chloroform (CDCl_3) using tetramethyl silane as internal standard. A Kenstar (OM 99181C, 2350W) microwave oven with facility to change the power level used to carry out the reactions. Differential scanning calorimetry (DSC) studies were undertaken on a Perkins-Elmer DSC-7 instrument at the heating rate of $10^\circ\text{C}/\text{min}$ in nitrogen atmosphere.

Caution: Title compounds 3b and 3c have been reported [20] to be impact insensitive ($h_{50\%}$) up to 60 and 32 cm, respectively, and friction insensitive up to 19 and 12 kg, respectively [20]. Therefore, adequate care must be exercised during the synthesis or handling of these materials in accordance with the energetic materials safety regulations.

2.2. Synthesis of 1-(2-hydroxyethylamino)-2,4,6-trinitrobenzene (2a)

A solution of ethanolamine (3.05 g, 2 m) in methanol (30 ml) was prepared and added drop wise over a period of 40 min with continuous stirring at ambient temperature (30°C) to a solution of picryl chloride (2.47 g, 1 m) in methanol (20 ml). Stirring was continued for another 3 h until the completion of reaction. The reaction mixture was poured into ice-cold water; the product obtained was filtered, washed with ice-cold water and dried. The crude product was further re-crystallized from methanol to afford the corresponding ethanolamine condensed derivative (2a). Yield, 2.30 g (93%); melting point, $109\text{--}110^\circ\text{C}$.

Similarly, compounds 1,3-bis(2-hydroxyethylamino)-2,4,6-trinitrobenzene (2b) and 1,3,5-tris(2-hydroxyethylamino)-2,4,6-trinitrobenzene (2c) were prepared adopting the above procedure. (2b) Yield, 14 g (84%); melting point, $199\text{--}200^\circ\text{C}$. (2c) Yield, 2.30 g (80%); melting point, $200\text{--}202^\circ\text{C}$.

2.3. Synthesis of 1-(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene (3a)

Ethanolamine condensed derivative (2a) (1.35 g, 0.5 m) was dissolved in suspension of bismuth nitrate pentahydrate (4.85 g, 1 m) in tetrahydrofuran (10 ml) adsorbed on silica gel (5 g). The reaction mixture was irradiated under microwave at 30 W power with interval of 1–2 min. The completion of the reaction was monitored by thin layer chromatography. Finally the reaction mixture was poured into cold methanol and the obtained crude product was filtered, washed with cold water and dried. The

crude product was re-crystallized from methanol to afford nitrate ester (3a). Yield, 1.50 g (83%); melting point, $127\text{--}128^\circ\text{C}$.

Similarly, compounds 1,3-bis(2-nitroxyethyl nitramino)-2,4,6-trinitrobenzene (3b) and 1,3,5-tris(2-nitroxyethyl nitramino)-2,4,6-trinitrobenzene (3c) were prepared adopting the above procedure. (3b) Yield, 4.30 g (84%); melting point, $122\text{--}123^\circ\text{C}$. (3c) Yield, 4.60 g (80%); melting point, $150\text{--}151^\circ\text{C}$.

3. Results and discussion

3.1. Infrared spectral studies

The compound 2a showed the IR stretching frequencies (cm^{-1}) at 3580 (OH), 3248 (NH), 3030 (Ar-CH), 2830–2835 (CH), 1590 (C=C), 1530 and 1340 (NO_2). The presence of an additional band at 1640 cm^{-1} and the absence of bands at 3580 and 3248 cm^{-1} (which corresponded to –OH and –NH functional groups), in compound 3a indicated the conversion of –OH and –NH functional groups into corresponding – ONO_2 and – NNO_2 functional groups, respectively.

The compound 2b displayed the IR stretching frequencies (cm^{-1}) at 3590 (OH), 3250 (NH), 3030 (Ar-CH), 2830–2835 (CH), 1612 (C=C), 1632 and 1340 (NO_2). The conversion of compound 2b to 3b was confirmed from the IR spectroscopy. The title compound 3b showed the presence of an additional band at 1640 cm^{-1} . The absence of bands at 3590 and 3250 cm^{-1} , corresponding to –OH and –NH groups, respectively, in the case of compound 2b indicated complete conversion of –OH and –NH groups to corresponding – O-NO_2 and – N-NO_2 groups (Table 1).

The compound 2c showed the IR stretching frequencies at 3610 and 3250 cm^{-1} due to OH and NH groups, respectively, at 3050 and 2830 cm^{-1} due to Ar-CH and CH stretching frequencies, respectively. The stretching frequencies due to C=C and NO_2 were displayed at 1588 and 1535, 1420 cm^{-1} , respectively. The formation of compound 3c was confirmed from its IR spectrum. It is clear from Table 1 that in the case of compound 3c, absence of bands at 3610 and 3250 cm^{-1} , which correspond to –OH and –NH groups, respectively, and presence of additional band at 1640 cm^{-1} indicate complete conversion of –NH and –OH groups to corresponding – N-NO_2 and – O-NO_2 groups. The IR spectral data of the title compounds obtained in the present study is in close agreement with the reported data for the conventionally nitrated products [20].

3.2. ^1H NMR spectral studies

The formation of the compounds 3a, 3b and 3c were further confirmed from their cm^{-1} spectra. NMR spectral data obtained on the title compounds 2a–2c and 3a–3c is given in Table 1. It is very clear from Table 1 that, the title compound 2a showed the ^1H NMR signals at δ 9.12 (1H, s, –NH), 8.79 (2H, s, Ar-H), 4.90 (2H, s, –OH), 3.80 (2H, t, $\text{CH}_2\text{-OH}$) and 3.18 (2H, t, HN-CH_2). In the case of compound 3a, protons of – CH_2 groups attached to – O-NO_2 group appeared at δ 4.60 ppm, while the protons of – CH_2 groups attached to – N-NO_2 group resonated

Table 1
Characterization data of compounds 2a, 2b and 2c and 3a, 3b and 3c

Compound	Yield (%)	mp (°C) [lit. mp]	Time (min)	Spectral data	
				FT-IR (ν , cm^{-1})	^1H NMR (δ)
2a	95	109–110 [108–110]	30	3580 (OH), 3248 (NH), 3030 (Ar-CH), 2835 (CH), 1590 (C=C), 1340, 1530 (NO_2)	9.12 (1H, s, -NH), 8.79 (2H, s, Ar-H), 4.90 (2H, s, -OH), 3.80 (2H, t, CH_2 -OH), 3.18 (2H, t, HN- CH_2)
2b	90	199–200 [199–201]	40	3590 (OH), 3250 (NH), 3050 (Ar-CH), 2835 (CH), 1594 (C=C), 1632, 1341 (ONO_2), 1612 (C=C)	9.10 (1H, bs, NH), 8.96 (2H, s, Ar-H), 3.62 (2H, t, CH_2 - ONO_2), 3.43 (2H, t, $\text{O}_2\text{N-CH}_2$), 4.93 (2H, s, -OH)
2c	80	200–202 [200–205]	45	3610 (OH), 3250 (NH), 3050 (Ar-CH), 2830 (CH), 1588 (C=C), 1535, 1420 (NO_2)	9.43 (2H, t, NH), 5.12 (2H, s, -OH) 3.73 (4H, t, CH_2 -OH), 3.22 (4H, t, HN- CH_2)
3a	84	127–128 [127–129]	5	3050 (Ar-CH), 1640 (ONO_2), 1580 (C=C), 1556, 1420 (NO_2)	9.10 (1H, s, Ar-H), 4.60 (2H, t, H_2ONO_2), 4.42 (2H, t, $\text{O}_2\text{N-CH}_2$)
3b	91	122–123 [121–123]	8	3030 (Ar-CH), 2950 (CH), 1640 (O-NO_2), 1610 (C=C), 1320, 1540 (NO_2)	9.34 (1H, s, Ar-H), 3.73 (4H, t, H_2ONO_2), 3.54 (4H, t, $\text{O}_2\text{N-CH}_2$)
3c	82	150–151 [149–151]	10	2940 (CH), 1640 (ONO_2), 1590 (C=C), 1520, 1310 (NO_2)	3.76 (6H, t, CH_2 - NO_2), 3.59 (6H, t, $\text{O}_2\text{N-CH}_2$)

at δ 4.42 ppm. The aromatic protons appeared to resonate at 9.10 ppm. The absence of protons of -OH and -NH groups indicated full conversion of these protons to corresponding - NO_2 groups.

The title compound 2b resonated proton signals at δ 9.10 (1H, bs, NH), 8.96 (2H, s, Ar-H), 3.62 (2H, t, CH_2 - ONO_2), 3.43 (2H, t, $\text{O}_2\text{N-CH}_2$) and 4.93 (2H, s, -OH). The formation of the nitrate ester (3b) was confirmed from its NMR spectrum. The proton magnetic resonance spectrum of 3b revealed the presence of signals at δ 9.34 (1H, s, Ar-H), 3.73 (4H, t, H_2ONO_2) and 3.54 (4H, t, $\text{O}_2\text{N-CH}_2$). The absence of protons due to NH and OH in the NMR spectrum of 3b indicated its formation (Table 1).

In the case of compound 2c, protons of - CH_2 groups attached to -OH and -NH groups appeared at δ 3.73 and 3.22 ppm, respectively. The aromatic proton appeared at δ 8.80 ppm while that of -NH proton resonated at δ 9.43 ppm. The hydroxyl protons of - CH_2OH appeared at δ 5.12 ppm. In the case of compound 3c, protons of - CH_2 groups attached to - O-NO_2 and - N-NO_2 appeared at δ 3.76 and 3.59 ppm, respectively. The aromatic proton resonated at δ 9.3 ppm. The absence of protons of -OH and -NH groups indicated full conversion of these protons to corresponding - NO_2 groups. The NMR spectral data obtained for the title compounds (2a–2c) and (3a–3c) is in close agreement with the reported data [20].

The nitrate ester compounds synthesized in the present investigation are interesting from the point of their energetic materials properties.

3.3. Thermal analysis

Some of the selected precursors used in the present study were subjected for thermal analysis. The DSC thermogram of 1-(2-hydroxyethylamino)-2,4,6-trinitrobenzene (2a) (Fig. 1) showed an endothermic peak with peak maxima (T_{max}) at 159.83 °C ($\Delta = +90.484$ J/g) followed by an exothermic decomposition at 236.67 °C ($\Delta = -1580.457$ J/g). The DSC profile

of 1,3-bis(2-hydroxyethylamino)-2,4,6-trinitrobenzene (Fig. 2) displayed an initial endotherm with peak maxima (T_{max}) at 100.57 °C ($\Delta = +64.278$ J/g) followed by an exothermic decomposition at 245.00 °C ($\Delta = -342.446$ J/g). The DSC thermogram of 1,3,5-tris(2-hydroxyethylamino)-2,4,6-trinitrobenzene (2c) (Fig. 3) showed a minor endothermic peak at 165 °C followed by an exothermic peak at 209 °C (T_{max} , $\Delta H = -854.594$ J/g). The reported [20] differential thermal analysis (DTA) data indicated the exothermic peak temperature for 2a, 2b and 2c at 275, 238 and 199 °C, respectively. The DSC data reported in the present study may be more accurate and nearly close to the reported differential thermal analysis (DTA) data [20]. The thermal analysis data indicated the energetic nature of the precursor compounds. The thermal analysis results reported in the paper warrants the further detailed investigations.

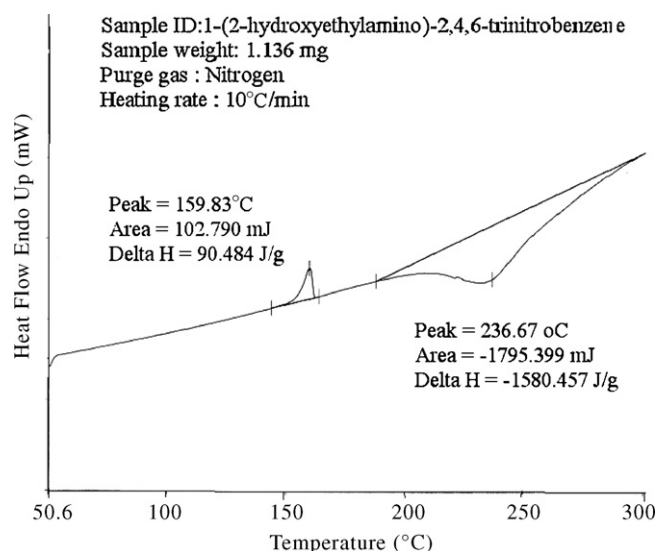


Fig. 1. DSC thermogram of 1-(2-hydroxyethylamino)-2,4,6-trinitrobenzene (2a).

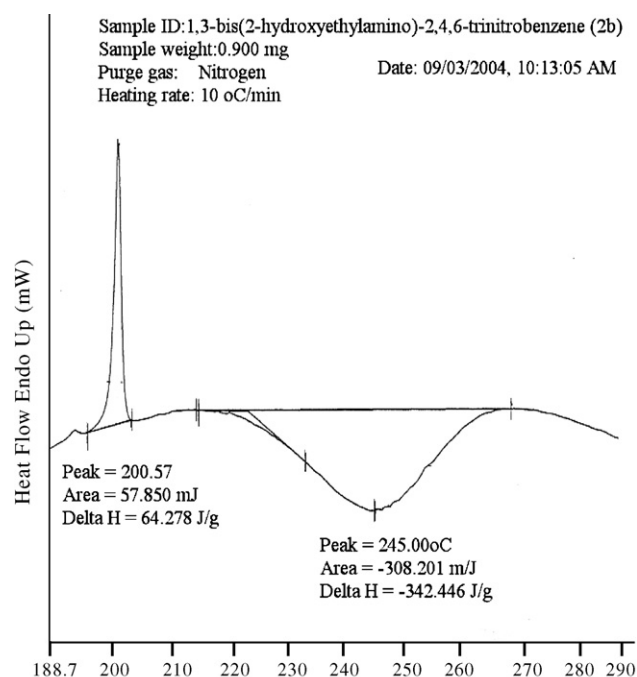


Fig. 2. DSC profile of 1,3-bis(2-hydroxyethylamino)-2,4,6-trinitrobenzene (2b).

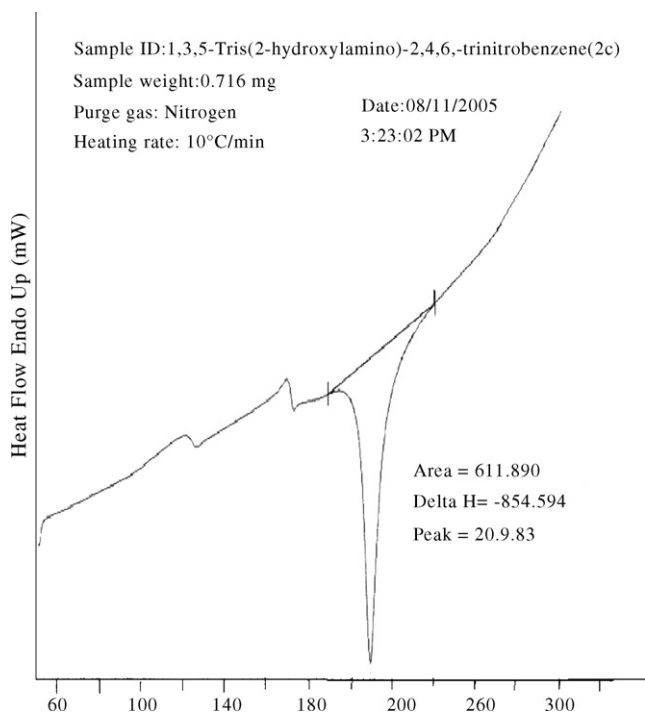


Fig. 3. DSC profile of 1,3,5-tris(2-hydroxyethylamino)-2,4,6-trinitrobenzene (2c).

4. Conclusion

The present study demonstrated the microwave assisted synthesis of 1-(2-nitroxyethylnitramino)-2,4,6 trinitrobenzene (3a), 1,3-bis(2-nitroxyethylnitramino)-2,4,6 trinitrobenzene (3b) and 1,3,5-tris(2-nitroxyethylnitramino)-2,4,6 trinitrobenzene

(3c) by the nitration of 1-(2-hydroxyethylamino)-2,4,6-trinitrobenzene (2a), 1,3-bis(2-hydroxyethylamino)-2,4,6-trinitrobenzene (2b) and 1,3,5-tris(2-hydroxyethylamino)-2,4,6-trinitrobenzene (2c) using eco-friendly nitrating agent bismuth nitrate pentahydrate. The synthesized compounds have been characterized using IR and NMR spectral studies. Thermolysis studies on the precursors (2a, 2b and 2c) suggested the energetic nature of the compounds. The present work warrants the further in-depth investigations on the utilization of bismuth nitrate pentahydrate for the synthesis of nitrate esters as potential HEMs at pilot plant scale. The present work is a step forward in reducing environment pollution. The nitration method used in the present study is of particular interest for the high energy materials researchers, scientists and technologists.

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References

- [1] K. Wilson, J.H. Clark, Solid acids and their use as environmentally friendly catalyst in organic synthesis, *Pure Appl. Chem.* 72 (2000) 1313–1319.
- [2] G.A. Olah, P. Ramaih, G.K. Suryaprakash, Electrophilic nitration of alkanes with nitronium hexafluorophosphate, *Proc. Natl. Acad. Sci. U.S.A.* 94 (1997) 11783–11785.
- [3] H. Suzuki, T. Murashima, K. Shimizu, K. Tsukamoto, Ozone-mediated nitration of arenes with nitrogen dioxide: change-over of the orienting influences of alkyl, alkoxy and halogen substituent groups from meta to ortho-para dominance, *J. Chem. Soc. Chem. Commun.* 1 (1994) 1367–1369.
- [4] H. Suzuki, S. Yonezawa, T. Mori, K. Maeda, Unusual isomer distribution of dinitrobenzenes and nitrophenols formed as side products during the ozone-mediated nitration of benzene with nitrogen dioxide. Further evidence for the alternative mechanism of electrophilic nitration of arenes, *J. Chem. Soc., Perkin Trans. 2* (1995) 41–44.
- [5] S. Patai, Z. Rappoport, in: S. Patai (Ed.), *Organic Arsenic, Antimony and Bismuth Compounds Series*, in: S. Patai, Z. Rappoport (Eds.), *The Chemistry of Functional Groups: A Series of Advanced Treatises*, 13 July 2004 (Print ISBN 9780471930440, Online ISBN 9780470023471, doi:10.1002/0470023473, Copyright © 1994 John Wiley & Sons Ltd.).
- [6] S. Samajdar, F.F. Becker, B.K. Banik, Surface mediated highly efficient regioselective nitration of aromatic compounds by bismuth nitrate, *Tetrahedron Lett.* 41 (2000) 8017–8020.
- [7] G.A. Olah, R. Malhorta, S.C. Narang, *Nitration Methods and Mechanisms*, VCH, New York, 1989.
- [8] H. Zollinger, *Color Chemistry: Properties and Applications of Organic Dyes*, second ed., John Wiley, New York, 1991.
- [9] R. Meyer, J. Kholer, A. Homburg, *Explosives*, fifth ed., John Wiley, New York, 2002.
- [10] N.M. Leonard, L.C. Wieland, R.S. Mohan, Applications of bismuth(III) compounds in organic synthesis, *Tetrahedron* 58 (2002) 8373–8397.
- [11] H. Suzuki, T. Ikegami, Y. Matano, Bismuth in organic transformations, *Synthesis* 3 (1997) 249–267.
- [12] D. Adam, Microwave chemistry: out of the kitchen, *Nature* 421 (2003) 571–572.
- [13] B.L. Hayes, *Microwave Synthesis: Chemistry at the Speed of Light*, CEM Publishing, Matthews, NC, 2002.

- [14] A. Loupy, *Microwaves in Organic Synthesis*, Wiley-VCH, Weinheim, 2002.
- [15] W.B. Sudweeks, R.D. Larsen, R.D. Balli Reigels, *Handbook of Industrial Chemistry*, eighth ed., VNR, New York, 1983.
- [16] T. Urbanski, *Chemistry and Technology of Explosives*, vol. 2, Pergamon, Oxford, 1964.
- [17] E. Sitzman Michael, High melting aromatic nitrate esters: ethnaol amine condensed derivatives of polynitroaromatic compounds, *Propellants, Explos. Pyrotech.* 19 (1994) 249–254.
- [18] G.R.J. Thatcher, B.M. Bennett, J.N. Reynolds, R.J. Boegman, K. Jhamandas, Nitrate esters and methods of making same, United States Patent 6,677,374, Application number 108513, Filing date 03/29/2002, Publication date 01/13/2004, <http://www.freepatentsonline.com/6677374.html>.
- [19] J.R. Hwu, K.A. Vyas, H.V. Patel, C.H. Lin, J.C. Yang, Practical methods for the preparation of nitrate esters, *Synthesis* 5 (1994) 471–473.
- [20] J.P. Agrawal, R.N. Surve, S.H. Sonawane, Some aromatic nitrate esters: synthesis, structural aspects, thermal and explosive properties, *J. Hazard. Mater. A* 77 (2000) 11–31.
- [21] S.H. Sonawane, Mehilal, R.N. Surve, J.P. Agrawal, Synthesis, characterization and explosive properties of some aromatic nitrate esters, in: *Poster Presentation*, vol. 54. 29th International Annual ICT Conference Poster Program, July 2, 1998.
- [22] J.P. Agrawal, R.D. Hodgson, *Organic Chemistry of Explosives*, Chapter 3—Synthetic Routes to Nitrate Esters, vol. 2, John Wiley & Sons Ltd., 2007 (Copyright © 2007, pp. 87–123).
- [23] D.M. Badgajar, M.B. Talawar, S.N. Asthana, P.P. Mahulikar, Environmentally benign synthesis of aromatic nitro compounds using silica supported inorganic nitrates, *J. Sci. Ind. Res.* 66 (3) (2007) 250–251.
- [24] D.H. More, D.G. Hundiwale, U.R. Kapadi, P.P. Mahulikar, Microwave assisted solvent free synthesis of *O*-alkylation and acylation of thymol and geraniol using fly ash as solid support, *J. Sci. Ind. Res.* 65 (2006) 817–820.
- [25] H.P. Narkhede, U.B. More, D.S. Dalal, D.H. More, P.P. Mahulikar, Fly-ash-supported synthesis of 2-mercaptobenzothiazole derivatives under microwave irradiation, *Synth. Commun.* 37 (4) (2007) 573–577.