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Synthesis and Characterization of 1,2,4-Butanetrioltrinitrate

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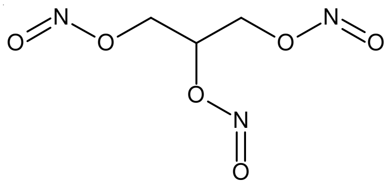
1,2,4-Butanetrioltrinitrate is an energetic plasticizer which is used as a replacement for nitroglycerine. In this paper, 1,2,4-butanetrioltrinitrate is synthesized *via* nitration of 1,2,4-butanetriol.

Key Words: Propellant, Plasticizer, 1,2,4-Butanetrioltrinitrate, Explosive, Nitroglycerine.

INTRODUCTION

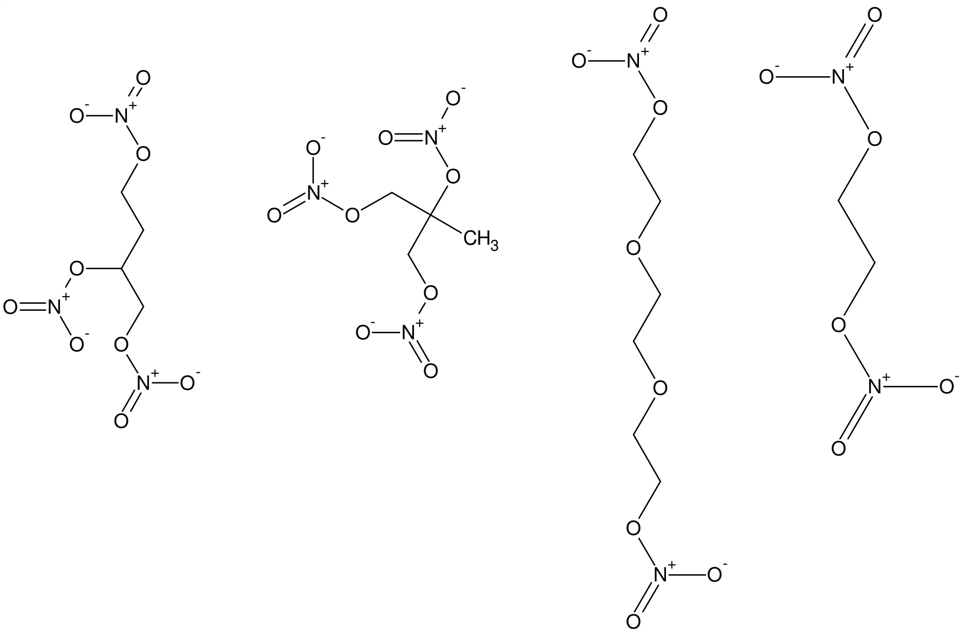
Plasticizers have long been known for their effectiveness in producing flexible plastics for application ranging from the automotive industry to medical and consumer products. The plasticizer industry has grown with the use of plastics worldwide. In recent years, the plasticizer research has been focused on technological challenges including leaching, migrating, evaporating and degradation of plasticizers, each of which eventually lead to deterioration of thermo mechanical properties in plastics.

In explosive and propellant industries, plasticizers are important, the primary plasticizers were inert and they hadn't any energetic bonds, so they caused the explosive and propellants and lost some of mechanical properties. After few years the energetic plasticizers were used as a replacement of inert plasticizers. The primary role of energetic plasticizers in energetic materials formulation is to modify the mechanical properties of the charge to improve safety characteristics. This is achieved by softening of the polymer matrix and making it more flexible. In addition to improving properties such as tensile strength, elongation, toughness and softening point (T_g point), the plasticizer can have secondary roles. These roles include a reduction of mix viscosity to ease processing, modification of oxygen balance and energy content and in the case of propellants, burn rate modification to tailor ballistics. By their own nature, plasticizers are typically oligomeric materials that have number average molecular weights ranging from 200 to 2000. Plasticizers with molecular weights above 2000 tend to be viscous, with properties more akin to the polymer matrix. Those with molecular weight below 200 may be more effective in reducing T_g, but they are highly volatile and tend to migrate out of a formulation readily (exudation)[1]. The first energetic plasticizer for commercial explosives-nitroglycerine (NG) or glyceroltrinitrate - use a high performance nitrate ester having the following structures (Structure 1).



Structure 1: Nitroglycerine

First discovered in 1846, nitroglycerine is a sensitive explosive easily initiated by friction and impact. When heated above 200 °C it will explode, while upon storage it proves unstable[2] at temperatures exceeding 70-80 °C. In addition, nitroglycerine exhibits significant physiological effects, causing dilution of the arteries and severe headaches. Some of the major nitrate ester is use today include 1,2,4-butanetrioltrinitrate (BTTN) or trimethylol ethane trinitrate (MTN or TMETN), triethyleneglycoldinitrate (TEGDN), ethyleneglycoldinitrate (EGDN or nitroglycol) (Structure 2). Being structurally similar to nitroglycerine, they were developed to replace this material; most of these molecules possess some of nitroglycerine's properties without the severe hazards of nitroglycerine[3,4].



BTTN MTN or TMETN TEGDN EGDN

Structure 2: Some of plasticizers

1,2,4-Butanetrioltrinitrate is often used in propellants as a replacement for nitroglycerine. It has a lower density than nitroglycerine, but offers improved stability[5,6]. The energetic plasticizers TMETN and BTTN are used along with the energetic binder GAP to boost performance. A combustion reaction was observed for one formulation in response to thermal threats, fast and slow cook-off[7-9].

They also have a large critical diameter, which helps make them and resistant to sympathetic detonation. These compositions have met MURAT requirements. In one report GAP/TMETN/BTTN/RDX and GAP/TMETN/BTTN/Cl-20 formulations (Table-1) these are reported to give burning type reactions to slow cook-off at 118 and 110 °C, respectively. They also gave satisfactory IM responses to bullet impact[10-12].

TABLE-1
DEVELOPMENTAL FORMULATION [**Ref. 9-14**]

Basic formulation (binder/plasticizer(s) oxidizer/fuel	Specific impulse (s)	Density impulse (s g cm^{-3})	Burn rate (mm/s)
HTPB/AP/Al	264.5	464	9.0(@7mpA)
GAP/AP/Al	–	492	9.9(@7MPa)
GAP/AN/Al	261.5	463	–
GAP/AN/Cl-20/Al	263.7	475	–
GAP/ Cl-20/Al	273.0	521	–
GAP/AND/Al	274.2	491	–
GAP/HNF/Al	272.6	492	–
PolyNIMMO/AP/Al	–	–	9.5(@7MPa)
PGA/TMETN/BTTN/RDX (63 %)	283.5	405	–
GAP/ TMETN/BTTN/RDX (60 %)	242.0	411	14.5(@7MPa)
GAP/ TMETN/BTTN/ Cl-20 (63 %)	252.0	452	20(@7MPA)
HTPB reduced smoke	247.0	421	–

There are number of energetic plasticizers that are available for use (Table-2). Some of which are included in the formulations above. The appropriate choice from among these plasticizers will be determined by a number of factors such as: sufficient plasticization effect, low migration rate, compatibility, processing and hazard properties[15,16].

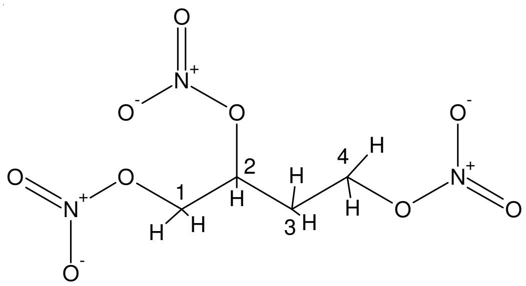
TABLE-2
PLASTICIZER PROPERTIES [**Ref. 17, 18**]

Plasticizers	Density (g cm^{-3})	O_2 Balance	m.p. (ºC)	Drop weight impact (cm)
BTTM	1.52	-16.6	-27	4.7
TMETN	1.46	-34.5	-3	8.8
MEN42	1.4	-	-	-
BuNENA	1.2	-104.0	-27 to -28	-
BDNPA/F	1.39		-15	95.7, 98.4
DGTN	1.52	-18.5	-	-
K10	-	-	-	19.0, 19.6
TEGDN	1.39	-58	-	-
DEGDN	1.38	-40.8	2	-

EXPERIMENTAL

1,2,4-Butanetriol is main reagent for preparing BTTN. It is a multi purpose material. It is colourless, odorless and its molecular weight is 106.12 with 1.010 g/cm^3 density from Acros Chemical Co. It is very hydrophile and highly absorbs water vapour.

Reagent for nitration of 1,2,4-butanetriol is mixture of HNO_3 (98-100 % v/v) and H_2SO_4 (98-100 % v/v) [ratio 2:3, respectively]. For synthesis of BTTN, mixture of acids is settled in ice bath and the temperature of acids mixture must be under -10 ºC. For being all of solution equal (temp. -10 ºC), the solution must be stirred. With a hanging burette, add drop wise 1.5 mole of 1,2,4-butanetriol. Be careful, the temperature of mix mustn't more than 10 ºC. By rate of adding 1,2,4-butanetriol, we can control the temperature of reaction. If temperature of reaction reaches exceed of 15 ºC, the explosion occurs. For safety, the mixture of water and ice must be ready in near of reaction vessel. After termination adding 1,2,4-butanetriol to reaction vessel, for 10 min, the solution must be stirred. Two layers then separated by dropping funnel. The extracted liquid is stored for later separation. The product must be washed by large amount of water (38-48 ºC) for three times. Then must be neutralized by 4 % w/v sodium carbonate solution. Product is kept in desiccator having P_2O_5.



1,2,4-Butantriol trinitrate

RESULTS AND DISCUSSION

After synthesis of 1,2,4-butanetriol trinitrate (BTTN), the analysis of product was run. ^{13}C NMR, ^{1}H NMR, IR, HPLC chromatography, DSC (differential scanning calorimetry) and mass spectrum is done for product (BTTN).

In Fig. 1, the peaks are shown. The interpretation of ^{1}H NMR of BTTN is shown in Table-3. Because of existence a chiral center on carbon 2, the protons attached has seven-fold splitting and this H can't rotate and feel the different environments. In BTTN none of protons of $-CH_2-$ is equal. For establishment of it, we added D_2O in NMR tube (BTTN) and then take a ^{1}H NMR spectrum. The result showed that we guessed right (Figs. 2 and 3).

As seen in Fig. 3, the peaks aren't dislocated, it refer to high purity of product (BTTN). The interpretation of ^{13}C NMR of BTTN is shown in Table-4.

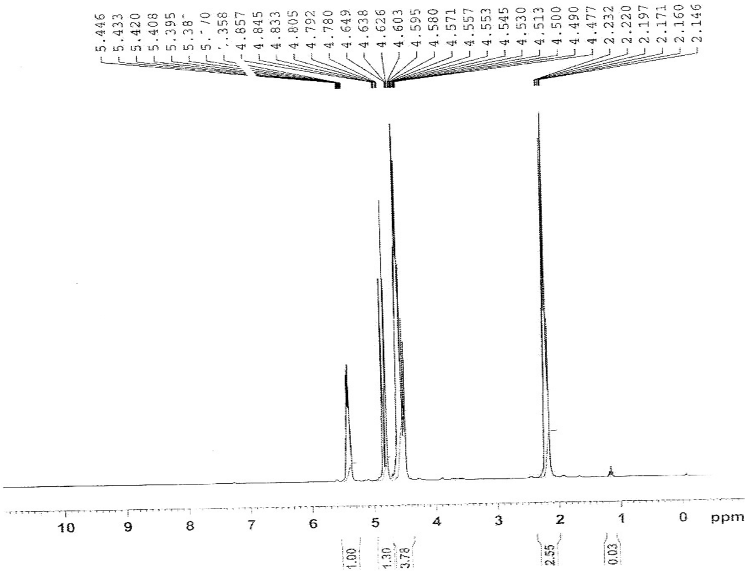


Fig. 1. ^{1}H NMR of BTTN (by Bruker 250 MHz)

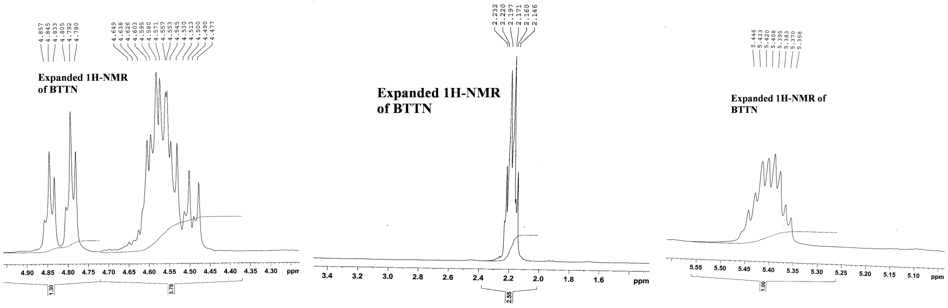


Fig. 2. Expanded ^{1}H NMR of BTTN

TABLE-3
INTERPRETATION OF ^{1}H NMR OF BTTN

Carbon number	Chemical shift for BTTN (ppm)
1, 4	4-48-4.86
2	5.4
3	2.18

TABLE-4
INTERPRETATION OF ^{13}C NMR OF BTTN

Carbon number	Chemical shift for BTTN (ppm)
1	70.95
2	75.98
3	26.73
4	68.18

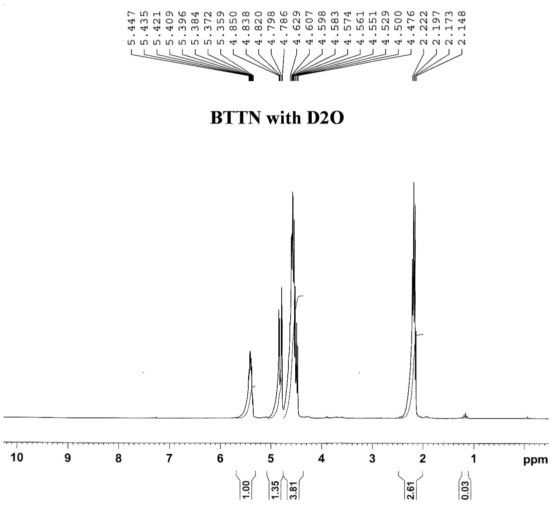


Fig. 3. ^{1}H NMR of BTTN with D_2O

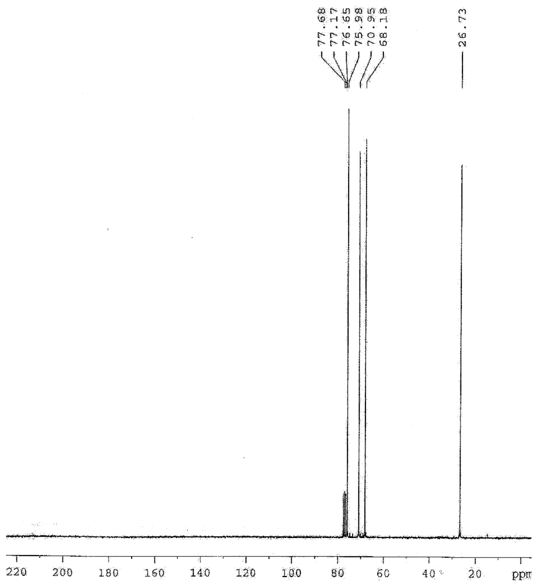


Fig. 4. ^{13}C NMR of BTTN (by Bruker 250 MHz)

As seen in Fig. 4, the absorbing band in 3275 cm^{-1} is related to OH groups in BTTN. It is very small, so the BTTN product hasn't OH grouping its structure. Absorbing in 2900 cm^{-1} is stretching vibration of C-H and absorbing bands in 1629 and 1433 cm^{-1} is related to NO_2 groups. For comparing of BTTN and 1,2,4-butanetriol, the IR spectrum of 1,2,4-butanetriol is shown in Fig. 5. In the spectrum, OH absorbing band is in 3332 cm^{-1} is for hydroxyl groups and 2927 cm^{-1} is related to stretching vibration of C-H and absorbing bands in 1406 is related to bending vibration of C-H and 1059 cm^{-1} is related to bending vibration C-O groups.

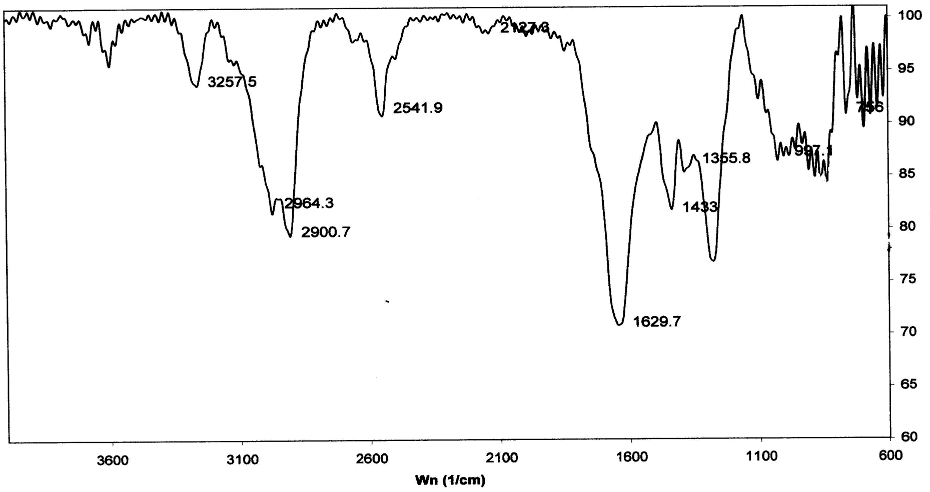


Fig. 4. IR of BTTN

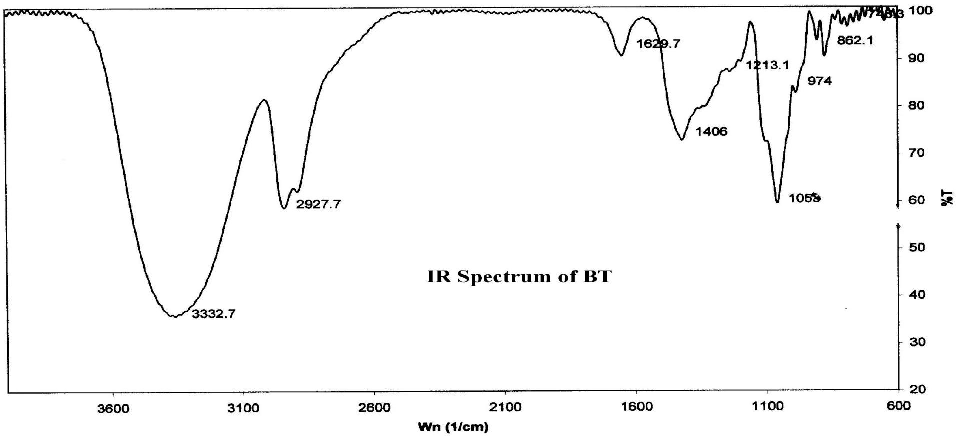


Fig. 5. IR spectrum of 1,2,4-butanetriol

For assay of purity of BTTN and because of lack of analysis information about BTTN, we used HPLC with two known columns. The results show the BTTN is very pure. For determination of heat of formation and boiling point of BTTN, we analyzed BTTN product by DSC (differential scanning calorimetry).

As seen in Fig. 6, the peak 242 is related to M+1 ion molecules. This is the molecular weight of BTTN. In Nitrate esters, the most of bond cleavage is related to C-C in vicinity of ONO_2. The peaks related to NO_2^+ and NO^+ is in 30 and 46. The interpretation of mass spectrum of BTTN is shown in Fig. 6.

The analysis results show that BTTN is highly pure and this reaction is suitable reaction for synthesis of BTTN.

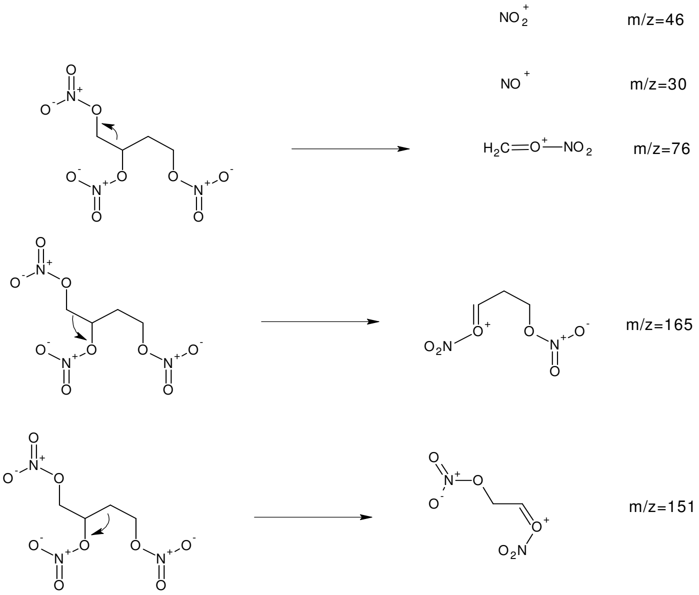


Fig. 6. Mass spectrum of BTTN

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